THE THEORETICAL STUDY OF MULTIPHOTON IONIZATION OF ATOM BY MULTIPLE LASER BEAMS

A THESIS SUBMITTED TO THE

CENTRAL DEPARTMENT OF PHYSICS

INSTITUTE OF SCIENCE AND TECHNOLOGY

TRIBHUVAN UNIVERSITY

NEPAL

FOR THE AWARD Of

DOCTOR Of PHILOSOPHY

IN PHYSICS

BY

Mrs. NILAM SHRESTHA PRADHAN

APRIL 2014 AD

RECOMMENDATION

This is to recommend that **Mrs. Nilam Shrestha Pradhan,** has carried out research entitled "**The theoretical study of Multiphoton Ionization of atom by multiple laser beams**" for the award of **Doctor of Philosophy (Ph.D.)**, in **Physics** under our supervision. To our knowledge this work has not been submitted previously for any other degree.

She has fulfilled all the requirements laid down by the Institute of Science and Technology (IOST), Tribhuvan University, Kirtipur for the submission of thesis for the award of Ph.D. degree.

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APRIL 2014

LETTER OF APPROVAL

On the recommendation of Prof. Dr. Lok Narayan Jha and Prof . Dr. Jeevan Jyoti Nakarmi, this Ph.D. thesis submitted by Mrs. Nilam Shrestha Pradhan entitled "**The theoretical study of Multiphoton Ionization of atom by multiple laser beams**" is forwarded by Central Department Research Committee (CDRC) to Dean the, IOST, TU.

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Prof. Dr. Binil Aryal
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If we knew what we were doing, it would not be research

- Albert Einstein

To my dearest family,

DECLARATION

Thesis entitled "**The theoretical study of Multiphoton Ionization of atom by multiple laser beams**" which is being submitted to the Central Department of Physics, Institute of Science and Technology (IOST), is a research work carried out by me under the supervision of Prof. Dr. Lok Narayan Jha, Central Department of Physics, Tribhuvan University and co supervised by Prof. Dr. Jeevan Jyoti Nakarmi, Central Department of Physics, TU. This research is original and has not been submitted earlier in part or full in this or any other to any university, here or elsewhere, for the award of any degree.

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ACKNOWLEDGEMENTS

First and foremost my supervisor Prof. Dr. Jeevan Jyoti Nakarmi deserves a deep appreciation for his support and encouragement. He has relentlessly managed time to discuss an array of problems that I had, and has suggested intriguing new research opportunities on numerous occasions. My heartfelt thanks to my supervisor Prof. Dr. Lok Narayan Jha, head of department, Central Department of Physics, Tribhuvan University, Kirtipur, for providing me necessary facility to carry out research. Everybody in central department of physics, Tribhuvan University deserves collective gratitude for countless interesting lunches, seminars and fruitful discussion. I have had several wonderful discussions with Prof. Sitaram Bhyahut that resulted on improving my understanding and knowledge of atomic physics. I am also thankful to Prof. Shankar Prashad Shrestha for his effort in collecting papers and Prof. Gunter Gross, University of Hannover, Germany, for his book support. I would like to express my gratitude to Prof. Devendra Raj Mishra for his prolific remarks about two-photon ionization of hydrogen atom. Very special thanks to my dear friends Mrs. Gauri Shrestha, Mrs. Neema Pradhan and Dr. Sanju Shrestha for building conducive background, distinctive support and creating friendly atmosphere.

I would like to thank Prof. Ramesh Babu Thayyullathil, who acted more as supervisor and mentor, for his amicable guidance, encouragement, generosity and exceptional wisdom. His enthusiasm towards quantum physics has great impact on my life-time decision to devote six precious months in theoretical physics at Cochin University of Science and Technology (CUSAT), India, which resulted in strengthening and broadening my knowledge, furthering a career that involves the frontier of scientific research. No words could express the depth of my appreciation for him. While staying in Kochi, South India, I also had a pleasure of meeting a lot of wonderful people who contributed in making a memorable and enthralling environment. Amongst the notable, I would like to thank my roommate Ms. Bhayva and colleagues: Vivek, Priyesh, Shaju, Nijo, Sanish, Tharanath and of course Ms. Sethulaxmi (for wonderful trip to Kanyakumari away from tenacious work schedule). Particularly I am grateful to Prof. M. R. Anantharaman, Head of Department of Physics, for providing me with the necessary means and facilities to carry my research. The time I spent at Kochi was extraordinarily rewarding - both academically and personally. I am also very much grateful for the computational program that was developed by Dr. Radhakrishanan, Department of Theoretical Physics, University of Madras, Chhenai. Which constitute an essential part of the

means of production necessary for the research and preparation of this thesis.

It is my pleasure to acknowledge 3rd International Union of Pure and Applied Physics (IUPAP), International Conference on Women in Physics (ICWIP) 2008, Seoul, South Korea, National Science Council, Taiwan and 4th IUPAP, ICWIP 2011, Stellenbosch, South Africa, for the awarding grants to attend the conference and present the paper. INSA - NAST bilateral exchange program is sincerely thankful for funding my research at CUSAT, Kerala, India (April-October, 2010). I also acknowledge partial financial support provided by the University Grant Commission (UGC), Kathmandu to pursue my doctoral research work.

At last, but not the least, I sincerely thank my brother, Mr. Udaya Shrestha (USA) for his unconditional support, love and encouragement, my sweet sister Mrs. Meenu Hada for loving concern and respect and recognition for my achievement, and my lovely sons Nischal and Nischit Pradhan for their confidence, understanding and assistant in computer support. Finally I thank my better half Mr. Lokendra P. N. Pradhan for his patience, conviction and perseverance with all my ♥!.

ABSTRACT

Multiphoton processes occur and are important for many aspects of matter-radiation interaction that include the efficient ionization of atoms and molecules, and more generally atomic transition mechanism, system-environment couplings, and dissipative quantum dynamics, laser physics, optical parametric processes and interferometry. A single review can not account for all aspects such an enormously vast subject. Here we concentrate our attention on atomic transition due to presence of multiple beams in non-linear media.

The interference of the amplitudes of atomic transition from an initial state $|g\rangle$ to the given final state $|f\rangle$ is one of the major consequences of the validity of quantum mechanics. In the case of radiative transitions, new possibilities for the illustration and investigation of this phenomenon are created in the simultaneous interaction of an atom with the fundamental frequency of laser.

The time dependent Schrodinger equation (TDSE) for non relativistic, semi-classical in dipole approximation, based under the framework of high order perturbation theory is solved by using Dalgarno-Lewis technique. We have evaluated multiphoton ionization of ground state hydrogen atom due to the simultaneous interaction with multiple laser beams of the same frequencies, direction of propagation but different polarization. We could able to separate the radial and angular part of transition amplitudes and obtain the analytical expression for the various multiphoton transition rates as a function of polarization, phase shift, intensities and frequency of the incident photon. In this formulation we can use any number of incident beams with arbitrary polarization. Based on our analytical expression, we have shown numerical results the change in angular distribution of ejected photo- electrons by varying intensity, phase, and polarization of different beams. The results illustrate the influence of laser frequency on angular distribution of ejected electron by varying phases and polarization on the differential ionization cross-section of the MPI.

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LIST OF ACRONYMS AND ABBREVIATIONS

ATI	Above Threshold Ionization
a.u.	Atomic Units
2ph	Two Photon Ionization
3ph	Three Photon Ionization
2C2PI	Two Color Two Photon Ionization
B3LYP	Becke Three parameter, LEE- Yang parr
COLTRIMS	Cold Target Recoil Ion Momentum Spectroscopy
DIC	Differential Ionization Cross-section
DFT	Density Functional Theory
DL	Dalgarno-Lewis
DOS	Density of States
EOM-CCSD	Equation Of Motion- Couple Cluster Single Double
HHG	High Harmonic Generation
IP	Ionization Potential
KFR	Keldysh-Faisal-Riess
LOPT	Lowest Order Perturbation
MI	Multiple Ionization
MPI	Multiphoton Ionization
OBI	Over the Barrier Ionization
PSD	2D Positive Sensitive Detectors
QC	Quantum and Classical
R2PI	Resonance Two Photon Ionization
REMPI	Resonance Enhance Multiphoton Ionization
SAE	Single Active Electron
SPI	Single Photon Ionization
TDDFT	Time Dependent Density Functional Theory
TDPT	Time Dependent Perturbation Theory
TDSE	Time Dependent Schrodinger Equation
TI	Tunnel Ionization
TOF	3D Time of Flight
TOFMS	Time of Flight Mass Spectrometry
WKB	Wentzel-Kramers-Brillouin
XUV	Extremely High Ultra Violet

CHAPTER 1

INTRODUCTION

Historical background

The history begins from 1905, when Albert Einstein described light as the electromagnetic wave from the Maxwell's laws. First it has been predicted theoretically at the middle of 1920. Schrödinger and Dirac developed the first order perturbation theory and applied it to one-photon absorption processes. Moreover, Dirac also discussed the applications for the second order perturbation theory. He applied the second order perturbation theory to the electron scattering which is a two photon process.

In 1931, Geopart-Mayer noticed that the second order theory is able to describe other different theories from the scattering process of two photon absorption. Because of the lack of a proper intense monochromatic light source such a experiment could not be imagined. Furthermore it became clear after Geopart-Mayer's work that high order perturbation theory reveals Multiphoton process.

The advent of powerful laser in the early 1960 and its capability to create breakdown in gases has sparked a strong interest both from experimental as well as theoretical side. For example, the measurement of two-photon ionization in alkali and alkaline atoms have confirmed the theoretical predictions on total cross-sections and electronic angular distributions (Delone and Krainov, 1999). Different methods for evaluating two photon transition amplitudes in hydrogen like atoms are compared with improved method of direct summation (Miladen and Marko, 2000). The multiphoton spectroscopy of alkaline outer shells contributed to their identification of excited states. While laser technology has raised intensity higher and higher the new unexpected high

field phenomena were discovered. They include Above Threshold Ionization (ATI), High Harmonic Generation (HHG) and Multiple Ionization(MI)(Lin et al., 2004).

Interpretation of the wave function(Ψ)

A quantity with which quantum mechanics is concerned is the wave function $\Psi(r, t)$ of the body. Each photon is associated with a wave $\Psi(r, t)$, called probability amplitude or simply amplitude, whose modulus squared gives the probability of finding the particle in given state. Here, t is the parameter representing the time, and r represents the co-ordinates of the system. The function $\Psi(r, t)$ must be continuous, single valued and square integrable. While $\Psi(r, t)$ itself has no physical interpretation, the square of its absolute magnitude

$$|\Psi(r, t)|^2 = e^{(+iEt/\mathrm{k})}\Psi^*(r) \times e^{(-iEt/\mathrm{k})}\Psi(r) = |\Psi(r)|^2 \qquad (1.1)$$

evaluated at a particular place at a particular time is proportional to the probability $P(r, t)$ of finding the system between r and $r + dr$ at that time t. Again we see that the wave function itself is not a meaningful quantity-introducing the factor $e^{(-iEt/\mathrm{k})}$ has given us an apparent time dependence in a time - independent problem, the wave function is merely a means to calculate other quantities that do have meaning, such as the probability density. This probability density describes the **electron density** in this region of space. The linear momentum, angular momentum, and the energy of the body are other quantities that can be established from Ψ. The integral of $|\Psi|^2$ taken over all space must have some finite value, because the body must be somewhere in space. The integral can not be either 0 or ∞. Thus $|\Psi|^2$ can not be negative or complex. Therefore the only remaining possibility is for the integral to have finite value of the wave function should describe a real body. Instead of taking $|\Psi|^2$ as being proportional to the probability P. It is convenient to take it as equal to probability density P. If $|\Psi|^2$ is to equal P, then it must be true that

$$\int_{-\infty}^{\infty} |\Psi|^2 \, dV = 1 \qquad (1.2)$$

Because, the body must be somewhere at all time, i.e.

$$\int_{-\infty}^{\infty} P \, dV = 1$$

A wave function that satisfies equation (1.2) is said to be normalized. Every wave function that is acceptable can be normalized by multiplying by a suitable constant. The wave function must satisfy other condition besides being normalizing, Ψ must be singled value, since P can have only one value at a particular place and time, it must further be continuous. Consideration of momentum requires that the partial derivatives ($\partial\Psi/\partial r$) of wave function along three coordinate's axes must be finite, continuous, and single valued. It is only when all these conditions are satisfied that the wave function can give results which are physically meaningful (Beiser, 2001). Here, from above calculations, the probability density P is given as:

$$P_n(t) = |C_n(t)|^2$$

By definition, it can take value 0 or 1, and it follows that $0 = |C_n(t)|^2 = 1$ for all values of n. This inequality need not hold if n is one of a continuum of eigenstates. Since $|C_n(t)|^2$ is then not probability but a probability density. In this case the integral of $|C_n(t)|^2$ over any part of the continuum is a probability (namely the probability that the system may be found with quantum numbers lying within this part of the continuum). The value of every such integral must lie between 0 and 1 though the probability density can have arbitrary +ve values.

Mechanism of multiphoton ionization

In his famous discovery of the photoelectric effect, Albert Einstein reasoned that photons might ionize an atom only if they had an energy greater than a particular threshold energy corresponding to the ionization energy of the atom. In 1929, Maria Göppert-Mayer predicted theoretically that an atom might absorb two or more photons simultaneously, thus allowing an electron to transition to states unreachable by single photon absorption. An atom absorbing multiple photons simultaneously might be ionized by photons with energies less than the threshold energy of which Einstein spoke. Because any observable effect of this phenomenon could not be possible without a very intense beam of radiation, his prediction could not be investigated in detail until the construction of the first laser in 1960. At the sufficiently high photon flux densities, however, there is an increasing probability for simultaneous absorption of two or even more photons by the atom and hence the process is called Multiphoton Ionization. If the total energy of these n absorbed photons is greater than ionization potential (I.P) energy of atom, the atom A is ionized by light field, whose single

photon energy $k\omega$ is much less than ionization energy.

$$A + nk\omega = A^{+} + e^{-} \tag{1.3}$$

In the case of free atom, as is well known, a free electron i. e. not subjected to the field of atom or an ion, cannot absorbs the photons from the laser field because of the condition imposed by law of conservation of momentum (between residual ion and photoelectron). In the phenomenon called the inverse bremsstrahlung, an electron generated from the multiphoton ionization of the atom and subjected to the nearby atoms or ions absorbs photons from laser radiation.

$$E_{\text{excess energy}} = nk\omega - I.P$$

Types of external radiation field

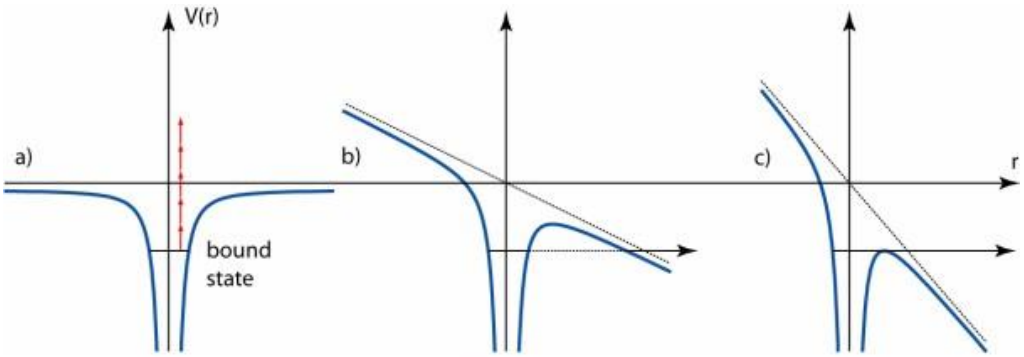
- Weak field - In the early days studies concentrated on the very low intensities continuous wave lasers. In this case electromagnetic field of laser has an enormous number of cycles so that the photon picture is appropriate. The first systematic and correlated calculation of non resonant lowest order perturbation (LOPT) ionization for H_2 have recently been performed (Awasthi, 2009).

- Strong field at low intensities (Moderate range) about $10^{9} - 10^{12}$ W/cm^2, at which MPI is possible, the light field represents only a small perturbation of the atomic system and the transition of an electron from the ground state to the continuum can be reasonably described by the common perturbative approach in terms of time dependent perturbation theory, which is governed by time dependent Schrodinger equation (TDSE).

- Strong field at high intensities ($I \cong 10^{10} - 10^{16}$ W/cm^2), the atomic structure becomes more strongly affected i. e. the interaction of light with atom is so strong that normal perturbative approaches breakdown, however as long as ionization processes can be at least phenologically described by absorption of n photons by discrete bound state, they are subsumed under the label MPI.

- Strong field at extremely high intensities (Super intense) ($I \cong 10^{17} - 10^{20}$ W/cm^2) - the electric field strength of light field becomes comparable in magnitude to the field the outer electrons experience in the atomic potential. The

potential well is strongly deformed by the laser's external field and non perturbative process emerge like HHG, TI, and Over the barrier ionization (OBI), which can not be described by perturbation (Perturbative treatment is not valid) and other approaches are necessary. Hence, at sufficiently high field strength, a finite potential barrier is created, through which electron can tunnel out. If the field frequency is low compared to the classical frequency of the bound electron's motion, the ionization probability is greatly enhanced by this process, which is called tunneling or tunnel ionization (TI)(Martin, 2008). While tunneling is a purely quantum mechanical process, the following electron propagation in the continuum is described. Expressions are obtained for probability of ionization of atoms and solid in strong electromagnetic field (Keldysh, 1965; Corkum et al., 1999; Corkum, 1993).



(a) multi-photon-ionization at intensities up to 10^{14} W/cm²
(b) tunnel-ionization at an intermediate intensity range up to 10^{15} W/cm².
(c) over-barrier-ionization.

Figure 1.1: Ionization Mechanism in presence of strong field,(a) MPI (b)TI (c)OBI (Martin, 2008)

Classification of ionization

Basically two regimes of multiphoton ionization are commonly distinguished. Both regimes are distinguished by Keldysh in (1964), parameter (γ) which relates the time scales of atomic motion and laser field. An atom is exposed to a linear polarized laser field $E(t) = E_0 sin(\omega t)$ where E_0 is the field amplitude and ω is the laser frequency. The electron tunnels through the Coulomb barrier and releases into the continuum with zero velocity at time $t = t_i$, where t_i is the tunneling time for which the electron is able to return into the ion core. Assume that the only force experienced by the electron

is the force from the electric field $F(t) = -eE(t)$, where the e is the elementary charge and show that the position of electron as the function of time $t \geq t_i$ is given by

$$x(t) = \frac{eE_0}{m\omega^2}[sin(\omega t) - sin(\omega t_i) - \omega(t - t_i)cos(\omega t_i)] \quad (1.4)$$

Where m is the electron mass. If the electron is instead released in laser field of arbitrary polarization, then experienced force is then proportional to the electric field

$$E(t) = \sqrt{\frac{E_0}{1+\alpha^2}}[cos(\omega t)\ \mathbf{e}_x + \alpha sin(\omega t)\ \mathbf{e}_y] \quad (1.5)$$

where α gives the polarization state of laser light; $\alpha = 0$ corresponds to linear polarization, and $\alpha = \pm 1$ to a circular polarization. The work of Keldysh introduced the adiabacity parameter to distinguish the relevant ionization processes. It is expressed in SI unit as

$$\gamma = \frac{\omega_{laser}}{\omega_{tunnel}}$$

where ω_{laser} is the angular frequency of optical field and ω_{tunnel} is the tunneling rate through the barrier at the peak of optical field (Sheehy, 1996). In terms of ionization potential (Schultze, 2008),

$$\gamma = \sqrt{\frac{I_p}{2U_p}}$$

Where, U_p is the ponderomotive energy, denotes the mean energy transferred to an electron in its oscillatory motion caused by the electromagnetic laser field. It is the cycle averaged kinetic energy of free electron oscillating in an electric field of intensity I:

$$U_p = \frac{e^2E^2}{4m\omega^2} \text{in SI units}$$

,

$$U_p = \frac{I_p}{4\omega^2} \text{ in atomic units}$$

In electron volt, it becomes $U_p \sim 10^{-14}$ I (W/cm ^{2}) $\lambda^2(\mu$ m), Where ω is the laser field frequency, E is the amplitude of electric field. Since the ponderomotive energy scales with the inverse square root ω^{-2} of the photon energy, the rescattering ionization, the above-threshold ionization and the higher harmonic generation all vanish at higher photon energies and not exceedingly large intensities. The contribution of tunneling ionization also decreases because the Keldysh parameter increases with increasing photon energy. The Kelydsh parameter ascertains the ionization processes (Jinghua and Yaguo, 2011):

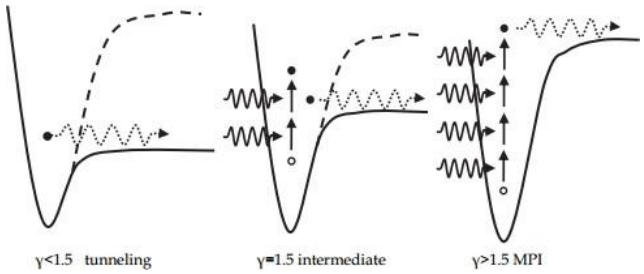


Figure 1.2: Systematic of photo ionization for different Keldysh parameter (Jinghua and Yaguo, 2011).

1. If Keldysh parameter is less than 1.5 - the process is Tunnel Ionization (TI)- here the photon energy is much smaller (high intensity, low frequency) than the ionization potential and the peak electric field strength of laser approaching the atomic electric field strength then the electron will have significant probability of tunneling the potential barrier. After tunneling the electron will appear in the continuum with zero kinetic energy, thereafter will be accelerated by external field of laser (Wickenhauser, 2006). At very high intensities the radiation field deforms the ionic potential so strongly that bound electrons can tunnel through the remaining potential barrier in a process called tunneling ionization.

2. If Keldysh parameter is greater than 1.5 (where intensity is low, or high frequency)- here electromagnetic field becomes of the same magnitude as the Coulomb field (5.1×10^9V/cm), corresponding intensity $I = \frac{1}{2} c\varepsilon_o E^2 \approx 3 \times 10^{16}$ W/cm^2 which binds a $1s$ electron in a hydrogen atom, three highly non linear phenomena can happen (Steinman, 2007).

- Electrons initially in a ground state absorbs large number of photons (MPI), if many more than the minimum number photons required for ionization, thus being ionized with a high kinetic energy. This process is called Above threshold ionization (ATI) (Karule et al., 2010) first observed by Agostini in 1979 (Karule, 1988; Corcum et al., 1989; Takashi and Gabrila, 2006).

- Not only one, but many electrons can be emitted from the atom. They can be emitted one at a time in a sequential process or simultaneously a mechanism called direct or non sequential. The removal of a large number of electrons from the many electron atom and the production of multiply charged ion is called

multiple ionization (MI). This effect was first observed in 1982 by L. Huiltter et al (Mainfray and Manus, 1980).

- Finally efficient photon emission in the extreme ultraviolet (XUV) range in the form of high order harmonics of the fundamental (linearly-polarized) laser field can occur. This is called High Harmonic Generation (HHG) first time observed in 1987.

Possible transition

Multiphoton processes include both transition accompanied by real (sequential) absorption or emission of many photons and transition accompanied by virtual (simultaneous) absorption or emission of several photons or combination of these. In particular, such processes of virtual absorption and emission are responsible for an ac Stark shift of considered atomic levels (Fedorov, 1997). When the frequency of impinging photon is equal to the Bohr frequency of the atomic transition, the atom absorbs it. Energy is conserved during such transition and the process is called real absorption. If the energy can be conserved during transition, the interaction is described by virtual absorption and remission of photons by the atoms (Cohen-Toannoudji , 2004). In the real transition, photons disappears, this is absorption. In the virtual transition, during very short time, photons are absorbed and they do not propagate i. e. anomalous dispersion. For the real transition, there is finite life time of atomic ground state. In virtual transition, there is a shift of ground state energy level. When the resonance condition is met at one or more of the intermediate states, an increase in the multiphoton absorption signal is observed due to resonance enhancement. There are two types of transition (Fox , 2006):

- Resonance or REMPI - If the light frequency corresponds to the natural frequency of atom i. e. $\Delta E = 0$, the magnitude of dipole oscillation will be large and the interaction between light with atom will be strong. However the ionization rate becomes finite value, because of damping terms arising from the coupling of the resonant state with the ground state and the continuum (Mainfray and Manus, 1991) i. e. due to sum runs over all intermediate electronic states. The situation represents via real intermediate states. Multiphoton transition can be classified as simultaneous (virtual intermediate), sequential if absorption proceeds via a real intermediate state (resonance enhanced), or combination of these (Rajini, 1989). When resonance condition is met at one or more of

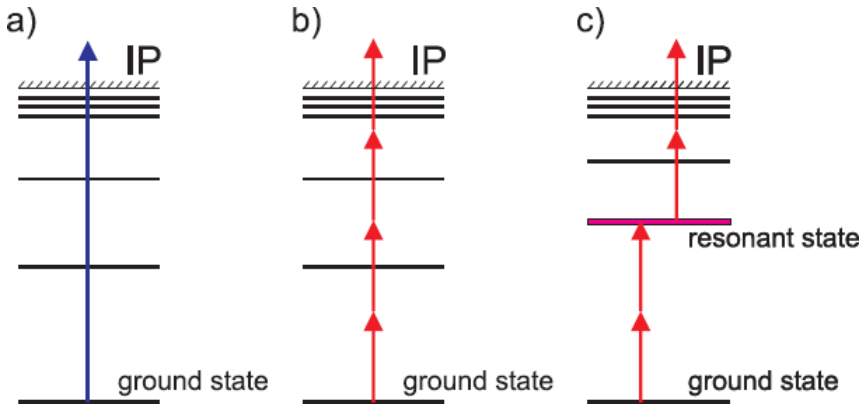


Figure 1.3: SPI in panel (a), Non resonant MPI in (b), and Resonance enhanced MPI in (c) (Steinmann, 2007).

intermediate states, an increase in multiphoton absorption is observed due to resonance enhancement. The required condition, of REMPI to be occurred is, when the energy of m-photons match with one of the intermediate state in the infinite sum and the remaining $N - m$ photons can cause the electron to reach the continuum state, but it is possible to have resonance enhance two photons ionization (Faisal, 1986).

- Non-Resonance MPI - If the light frequency is far away from the natural frequency of the atom, the magnitude of driven oscillations will be small and light-atom interaction will be small. Since the interaction between the light- atom will be very much stronger in the case of Resonant, it is a good approximation to ignore the off resonant.

Alkali atoms

The alkali atoms are Li, Na, Rb and Cs. Their common feature being that they have one electron (so called valence electron) moving around a center of force determined by the charge of the nucleus and all of the other electrons belonging to the atom and forming a spherically symmetric shell. The net charge that the outer electron feels still is practically $Z = 1$, but the force although central, is not a pure Coulomb force (Lambropoulos and Petrosyan, 2007). Being most similar to Hydrogen atom,

so called 'hydrogen like or Hydrogenic atom'. Hydrogenic atoms are atoms that only have one electron orbiting around the nucleus, even though the nucleus may have more than one proton and one or more neutrons. In this case, the electron has the same orbital as the hydrogen atom, except that they are scaled by a factor of $1/Z$. Where, Z is the atomic number of the atom, i.e. the number of protons in the nucleus. The increased number of positively charged protons shrinks the size of the orbital. Thus, the same graphs for hydrogen above apply to hydrogenic atoms, except that instead of expressing the radius in units of a_0, the radius is expressed in units of $\frac{a_0}{Z}$. Correspondingly, the values have to be renormalized by a factor of $(\frac{Z}{a_0})^{3/2}$. So a He^+ atom has orbital that are the same shape but half the size of the corresponding hydrogen orbital and a Li^{+2} atom has orbital that are the same shape but one third the size of the corresponding hydrogen orbital. In our work, we consider the simplest one electron atom and coupling with the external radiation, which results the transitions between the atomic energy levels accompanied by photon absorption. The one electron atom consists of single electron of mass m_e bound to the central force potential $V(r)$, $r = \mathbf{r}$ being the distance of electron from the origin of potential, which makes the system spherically symmetric. We need not to be concerned with the translational motion of the nucleus in space, but only the motion of electron with respect to the nucleus which being much heavier than electron will be taken as fixed in space origin of the system of co-ordinates. Given the spherical symmetry of the system, it is most convenient to use spherical coordinates (r, ϑ, φ). The Hamiltonian of the system being the sum of kinetic energy and potential energy given as

$$H = \frac{p^2}{2m_e} + V(r)$$

For the spacial case of Hydrogen like atom, the potential is due to point charge and has $V(r) \propto r^{-1}$ (Lambropoulos and Petrosyan, 2007).

Photoelectron angular distribution

Photoelectron angular distributions generally contain more information about the dynamics of a process than its total probability. They are simply measured, in the case of linearly polarized light by rotating the laser polarization in the plane perpendicular to the light polarization. Experiment was done for four photon in Cesium atom by inserting a half-wave plate between Glan prism and focussing lens (Petite et al., 1984). Differential cross-section of multiphoton ionization of hydrogen atom by circularly

polarized radiation depend on the angle ϑ determining the direction of the electron ejection, simply by,

$$\frac{d\sigma^K}{d\Omega} \sim \sin^{2K}\vartheta$$

Here, K is the number of photon absorbed and ϑ is the angle between the direction of propagation of the emitted electron and the direction of direction of propagation of electromagnetic radiation. Thus, angular distribution does not depend on the radiation frequency for circularly polarized light, but in the case of linearly polarized light, the angular dependence is proportional to $P_l^2(\cos\vartheta)$, where P_l is a Legendre Polynomial corresponding to the value of the orbital quantum number l of the final state. Here, ϑ is the angle between the direction of propagation of the ejected electron and the vector of electric field strength in the electromagnetic wave. All Legendre polynomials have at $\vartheta = 0^o$ and $\vartheta = 180^o$, so that in general the angular distributions have two maxima at those angles and an oscillatory dependence between them. The degree of the Legendre polynomial $P_l(\cos\vartheta)$ is equal to l; hence according to Dixit (Delone and Krainov, 1999)

$$\frac{d\sigma^K}{d\Omega} = A_0 + A_1\cos^2\vartheta + A_2\cos^4\vartheta + \cdots + A_K\cos^{2K}\vartheta \tag{1.6}$$

Where the coefficients A_i are determined vis K-photon matrix element. It is seen that the higher the value of K, more the oscillation appear in the angular distribution between 0^o and 180^o. Due to parity conservation law of Legendre polynomial in the final wave function, it follows that in above Eq. (1.6)

$$\frac{d\sigma^K}{d\Omega} = B_0 + B_1P_2(\cos\vartheta) + B_2P_4(\cos\vartheta) + \cdots + B_KP_{2K}(\cos\vartheta)$$

These angular distributions are dependent on the radiation frequency since the coefficient A_i(orB_i), thus cross-section for linear polarization generally depend on the radiation frequency (Delone and Krainov, 1999). The angular distribution in multiphoton ionization have first been calculated by Zernik in (1964) for the special case of two-photon ionization of $2s$ metastable state of hydrogen. Tully in (1968) and Lambroupoulos and Berry in (1973) pointed out that angular distribution measurements in resonant two-photon ionization may be used to observe relaxation of coherence in the intermediate state. The angular distribution of photoelectrons in multiphoton ionization was first experimentally observed by Einstein in (1974) when ionizing titanium atoms in a resonant two-photon process. In subsequent experiments on sodium, cesium, strontium, neon, and barium, the influence of resonant intermediate states on

the angular distribution was studied. Experiments observing photo electron angular distributions in non resonant multiphoton ionization were performed on Xe and Na (Chin and Lambroupoulos, 1984). Angular distribution of ejected electron depends on pulse duration and provides insight into the role of electron correlations in the two-electron photoemission process (Imre et al., 2006). Electron angular distribution produced in resonance enhanced two photon ionization of H_2^+ molecular ion using ultra-short laser pulse have been theoretically reported (Selstø et al., 2006).

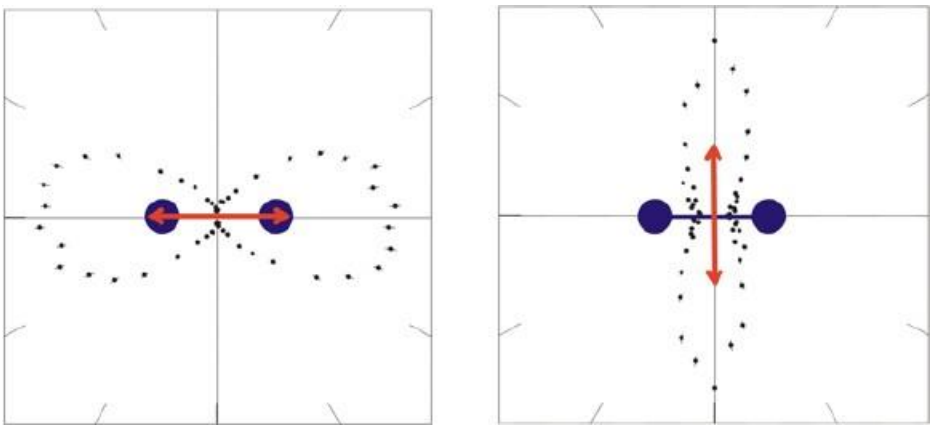


Figure 1.4: Double ionization of H_2 with linearly polarized photons (left: horizontally polarized, right: vertically polarized photon; polarization vector in red and molecular axis in blue.)(Goethe-Universität)

Light polarization effect

Polarization describes the orientation of electric field vector when the electromagnetic wave is propagating in space. The theoretical explanation on the polarization dependence of multiphoton ionization by Lambropoulos (Lambropoulos, 1972) shown that, total cross-section of two-and three-photon ionization of one-electron atom depend on the polarization of incident light. Expressions are derived for the ratio of the cross-section for circularly polarized to that for linearly polarized light and their maximum values are obtained. Polarization dependence are best understood by the relation connecting the cross-section of linear and circular polarization. For this purpose, the ratio of K-photon atomic ionization cross-sections by the fields of circular and linear polarization with the sane mean intensity and frequency is used. In the case of linear polarized field the orbital quantum number can either increase or decrease by unity

when photon is absorbed, according to selection rules. Hence, for example, a hydrogen atom in a p-state can be excited both to s-state and to d-states. If we assume that in case of linear polarization only an increase of orbital momentum is possible, then K-photon matrix elements of absorption of circularly and linearly polarized radiation differ from each other only in the Clebsh-Gorden coefficients. Thus the ratio of cross-sections for K-photon ionization in circularly and linearly polarized fields can be derived in general form for any atomic structure. The famous factorial formula derived by Klarsfed and Maquet is given by

$$w_c / w_l = R = (2K - 1)!!/K! \tag{1.7}$$

where, w_c and w_l are the ionization rates for the K-photon process in circular and linear polarized field respectively. The factorial formula is correct at $K \leq 3$, but even in this case small frequency ranges exist where the ionization cross-section foe circularly and linearly polarized radiation vanishes due to interference of channels with different principle quantum numbers of intermediate states. There are no experimental data on the polarization dependence of MPI cross-section for hydrogen atom available. The factorial formula hold for any atoms with arbitrary number of valence electrons in the single particle approximation. Thus for the alkali atoms, the single-particle approximation is correct and that the atomic structure is nearly hydrogen like (Delone and Krainov, 1999).

Objective of study

The most fundamental phenomena in nature are also the most desirable to be thoroughly understood since they are the basis for the advanced scientific theories and concepts serving as indications for the future research direction. Continuous development of new experimental tools and technique requires continuous reconsideration of the well known phenomena bringing them to the next level of understanding.

One of the recent developments in molecular spectroscopy has been the ability to observe transition where more than one photon is absorbed simultaneously. A spectrum of these multiphoton transitions often displays quite different information from normal single photon spectrum because of altered selection rules and transition intensities. Entirely new states and vibration are seen in multiphoton spectra that provide a much more complete understanding of excited state structure. Atoms,

molecules and ions are the basic building blocks of all complete structures in the universe and understanding of their structure and dynamics of their interaction is of fundamental relevance not only in physics, but also in chemistry, biology, medicine, astronomy and material science and scientific treatment of many systems on physical quantum level is becoming of increasing importance. However, atom changes its properties when immersed in an external electromagnetic field. There has been a tremendous progress in both the theoretical description and experimental determination and verification of the properties of stationary quantum systems i.e. atoms, ions and molecules in terms of their energy levels and wave functions.

More than a hundred years have passed since Einstein published his explanation of the photo effect and established the concept of an ionization threshold. At that time single-photon ionization was the only experimentally achievable process. Sixty years later advancement of laser technology provided the possibility of atomic ionization via the absorption of multiple photons. The possibility of multiphoton ionization (MPI) led to a generalization of EinsteinŠs concept of a threshold photon energy required for the photo effect.

Since the study of the MPI reflects both the characteristics of the laser pulse and the properties of the atom perturbed by multiple laser beams, it thus constitutes a favorable method for studying the response of atom in the presence of multiple beams. The most striking feature of multiphoton ionization spectroscopy is the fact, it has a non-linear response to the photon density and the selection rules are complementary with that of one-photon spectroscopy. Furthermore, with presence of multiple beams, The interference of the amplitudes of atomic transition from an initial state $|g\rangle$ to the given final state $|f\rangle$ is one of the major consequences of the validity of quantum mechanics i.e this leads to signals which are dependent on relative phase between the different beams.

Thus the objective of our research is to study the structure and dynamics of atoms by interacting with multiple laser beams. As a system absorbs or emits radiation, it undergoes transition from one state to another. In the case of radiative transitions, new possibilities for the illustration and investigation of this phenomenon are created in the simultaneous interaction of an atom with the fundamental frequency (ω) of a laser beam.

In a sense the familiar nonlinearity of an N-photon process through the N^{th} power of the intensity in perturbation theory has been superseded by a much more complex behavior involving all orders. We analyze via perturbative calculation of multiphoton ionization of atomic hydrogen initially in ground state caused by interaction with an electromagnets field consisting of superposition of two and three monochromatic fields (multiple laser beams) with the same frequency, same direction of propagation but different polarization using variation of Dalgarno and Lewis method. That displays many of the typical characteristics of how atoms interact with photons by changing, phase, intensity and polarization of incident beams. Our goal is to obtain the multiphoton transition amplitudes by solving the Time Dependent Schrodinger equation (TDSE). This method provides an expansion of exact electron wave function in powers of the field strength amplitude in a closed form solutions for evaluating transition amplitudes.

Since we know, the perturbation theory is valid (when the radiation field strength is less than the atomic field strength) for intensity of light up to I = 10^{13} W/cm^2 i. e. (~ 10^{16} W/cm^2)), for the treatment of multiphoton ionization processes, the evaluation of higher order perturbation matrix elements become important. Among different methods for its evaluation of transition amplitudes, Dalgarno and Lewis method (DL) has its own merits. The idea of DL method is to define an auxiliary operator such that the evaluation of intermediate sum is not needed. The basic idea is to recast the problem of summing over the intermediate states to a problem of solving a system of inhomogeneous differential equations. By doing this we can overcome the problem of infinite summation coming in the perturbative treatment for higher processes. The integral representation of solutions to these equations for two- and three-photon transitions is obtained and its analytical properties are studied by varying intensity, phase and polarization of different beams. Detailed mathematical derivation is shown in chapter 3 and chapter 4.

Interaction of electromagnetic radiation with matter

The interaction between light and matter has only been investigated in the perturbative regime since the advent of spectroscopy. In the perturbative regime, the electric field applied is very small compared to the atomic fields and the electronic

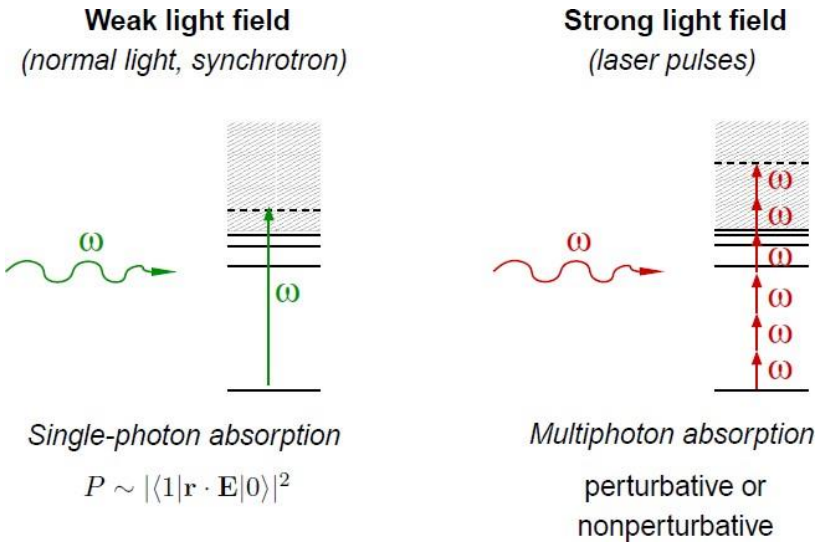


Figure 1.5: Laser - Matter Interaction(Peter and Gerry, 2005)

wave function is distorted very slightly in a time-dependent manner due to the oscillations in the electric field. In conventional perturbation theoretical approaches, this "perturbation" is expanded in a power series and the effect of each term in the expansion is investigated. The perturbation, if small enough, leads to a rapid decrease in the effects of the higher terms in the power series. However, if the perturbing field is, however, comparable to the internal fields, then the higher terms contribute to the final state and are therefore non-negligible. Perturbation theory then does not satisfactorily explain the observed phenomenon and recourse has to be taken to full fledged calculations of the effects of the electric field on the atomic and molecular wave functions. Given that the field-free atomic or molecular Hamiltonian itself is not exactly solvable, the problem of solving the full Hamiltonian taking the field into consideration is intractable. Approximate techniques have therefore been developed to solve the Schrodinger equation, which is successful in explaining in general some qualitative and quantitative features of intense light-field-matter interaction.

Atoms certainly belong to the most frequently studied quantum systems. They consist of a heavy nucleus and one or many light electrons. Since the nucleus carries a positive electric charge, it attracts electrons which reside nearby to the nucleus. The positive

and negative charges of the nucleus and electrons compensate and the atom normally looks like a neutral particle. However, atom changes its properties when immersed in an external electromagnetic field.

$$H(r, t) = \frac{1}{2m}(\mathbf{p} - e\mathbf{A})^2 - e\Phi(r, t) + V(r) \tag{1.8}$$

$$H(r, t) = \frac{1}{2m}\mathbf{p}^2 - \frac{e}{2m}[\mathbf{A}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A}] - \frac{e^2}{2m}\mathbf{A}^2 - e\Phi(r, t) + V(r) + \frac{e^2}{4\pi\epsilon^o r}$$

Where $\mathbf{p}$ is the electron momentum, $-e$ is the electronic charge, V is the static electric potential, detail of this conversion to quantum mechanical operators are explained in Appendix $A.2$. $\mathbf{A}$ and Φ are the vector and scalar potential for the electromagnetic field respectively. We have $\mathbf{A}$ and Φ, invariant under the following gauge transformations. Gauge transformations are introduced from the fact that although $\mathbf{E}$ and $\mathbf{B}$ are directly measurable physical quantities, the potential $\mathbf{A}$ and Φ are secondary quantities that have physical meaning only through ($\mathbf{B} = \nabla\times\mathbf{A}$) and $\mathbf{E} = -\nabla\Phi - \frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}$ Thus, we transform A and Φ into new potential $\mathbf{A'}$ and Φ' by the gauge transformations. where,

$$\Phi'(r, t) = \Phi(r, t) - \frac{\partial}{\partial t}\chi(r, t)$$

$$\mathbf{A'}(r, t) = \mathbf{A}(r, t) + \nabla\chi(r, t)$$

where, χ is the scalar function that generates this transformation. Thus magnetic and electric field of vector potential becomes,

$$\mathbf{B} = \nabla \times A' \text{and, } \mathbf{E} = -\nabla\Phi' - \frac{1}{c}\frac{\partial A'}{\partial t}$$

Since the system is non-relativistic $v \ll c$, the magnetic contribution is much smaller than the electric contribution to the interaction (Chandra, 2000). Introducing the unitary transformation such as, $\Psi'(r, t) = R\Psi(r, t)$, By substituting the values of A' and Φ' we get the same terms. Hence, the physical quantities $\mathbf{B}$ and $\mathbf{E}$ are invariants under the gauge transformation (Mizushima, 1970), then we have the Schrodinger equation transformed as

$$H_g\,\Psi'(r, t) = i\hbar\frac{\partial}{\partial t}\Psi'(r, t)$$

Where, the gauge transformed Hamiltonian H_g is defined as (Gerery and Night, 2005)

$$H_g = RHR^* + i\hbar\frac{\partial}{\partial t}RR^*$$

We can choose the operator as $R = e^{-ie\chi(r,t)/\hbar}$. Then the gauge transformed Hamiltonian has the form

$$H_g = \frac{1}{2m}[\mathbf{p} + e\mathbf{A} + \nabla\chi]^2 + e\frac{\partial}{\partial t}\chi + V(r)$$

Now we choose the Coulomb gauge where, $\nabla \cdot \mathbf{A}' = 0, \Phi' = 0$. In this gauge the field is completely described by the vector potential $\mathbf{A}$ and it satisfies the wave equation

$$\nabla^2 \mathbf{A} - \frac{1}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2} = 0$$

The solution of the wave equation has the form

$$\mathbf{A}(r, t) = |A_o|\,\varepsilon(e^{i(k\cdot r-\omega t+\alpha)} + e^{-i(k\cdot r-\omega t+\alpha)})$$

Where, ε is the polarization vector, for linearly polarized, it is taken as $\varepsilon \cdot \varepsilon = 1$, for transverse wave $k \cdot \varepsilon = 0$

$$\mathbf{A} = |A_o|\,(e^{i(k\cdot r-\omega t+\alpha)} + e^{-i(k\cdot r-\omega t+\alpha)})$$

and, $|A_o| = A_o e^{i\alpha}$ is the amplitude of the plane wave, k is the wave vector and ω is the angular frequency of the given wave, and α is arbitrary (real) phase constant. If the size of the atomic system is small compared to the wavelength of radiation field ($\lambda \quad r$) over the extend of the atom can be neglected and we can take $e^{-ik\cdot r} \sim 1$. This is called dipole approximation. Now by choosing the gauge function $\chi(r, t) = -\frac{1}{c}\mathbf{A} \cdot r$ we get

$$\nabla\chi(r, t) = -\mathbf{A}(t)$$
$$\frac{\partial}{\partial t}\chi(r, t) = -r \cdot \frac{1}{c}\frac{\partial}{\partial t}\mathbf{A} = -r \cdot \mathbf{E}$$

With this the transformed Hamiltonian will take the form

$$H_g = \frac{\mathbf{p}^2}{2m} + V(r) + er \cdot E$$

Where, the operator $-er$ is called dipole operator d. From now on we denote the transformed Hamiltonian as H.

The goal of this chapter is to introduce the concept of transition amplitudes, which is essential for the quantum description of interaction between atoms and photons. The transition amplitudes associated with a physical process is the evolution - operator

matrix element between initial and final states of the process under study (belong to the discrete or to the continuous spectrum of H_0). For the calculation of these amplitudes, we have used perturbation theory, which is based on splitting of the total Hamiltonian H into unperturbed part H_0 and the coupling part V. We seek to obtain new insight atomic processes and to test advanced theoretical treatment by achieving new levels of completeness in the description of the distribution of moments or internal states of the products and their correlation. An atom is originally in a given stationary state, i.e. ground state, it is then perturbed by passing charged particles (800nm Ti: Sapphire laser of frequency ($\omega = 0.057au$)), by a light wave or in some other way. After the particle has passed, or irradiated the atom for a certain time, the atom may have made a transition to one of the other stationary states. An atom and the radiation field form two quantum-mechanical systems with interaction energy H (Hamiltonian). This interaction is regarded as a perturbation. The perturbation theory proves to be valid for intensity up to $I = 10^{13}$ W cm $^{-2}$. It was found that at moderate intensity of direct multiphoton ionization as well as Above threshold ionization (ATI) are satisfactorily explained by perturbation theory. It will cause transitions of the unperturbed system (atom + radiation) in general consisting (i) transition of the atom from one quantum state to another, and (ii) of an emission or absorption of light quanta (Heitler, 1957).

Dynamical variables that relate to the motion of the particles can be represented by a linear operator. The operator may be simply a multiplication operator such as r for the position, or it may be a differential operator such as $-i\hbar\nabla$ for the momentum. With the each operator can be associated an eigenfunction corresponding to an eigenvalue. The values of energy E_n for which Schrodinger's steady-state equation can be solved are called eigenvalues and corresponding wave functions Ψ_n are called eigenfunctions. Perturbation of the eigenfunction and their eigenvalues were determined for such cases where the system was subjected to perturbation upon the space-co-ordinates. However there are physical situations where the Hamiltonian depends on time. Such situation arises when a system is subjected to readjustment in its states to other energy state.

The interaction of time independent electromagnetic field on atom changes the state of atomic energy levels, splits spectroscopic lines and even ionizes the atom. The manifold of mentioned phenomena enormously increases if one studies the influence of time dependent electromagnetic field on atom. There are two reasons for this

to increase. Firstly a conventional source of time dependent field (i.e. a source of electromagnetic waves) creates a much shorter field than sources of constant are able to produce. Secondly, time dependent fields bring into play different mechanisms of studied phenomena. Hence, it is necessary to study the effect of time dependent perturbation. In nuclear physics, especially in nuclear scattering, nuclear reaction and nuclear disintegrations, high harmonic generation, photo dissociation and multiphoton ionization, we require to find the outcome of perturbation in time. Hamiltonian function in this problem is time dependent the appropriate equation for evaluation of specific problems would be the time dependent Schrodinger equation. The evolution of the wave function Ψ with time is governed by the time dependent Schrodinger Equation given as

$$i\hbar\frac{\partial\Psi(r,t)}{\partial t} = H(r,t)\Psi(r,t)$$

Where r will denote set of coordinate variables of all particles in the systems. If the system contains particular spin, Ψ will be a multi component wave function with the appropriate number of components and H the Hamiltonian, in general be a function of the relevant spin matrices as well as r and p. For simplicity we consider spin less case, initially.

Quantum mechanical treatment of radiation

The idea of probability amplitude plays a central role in the quantum description of the time evolution of a physical process (Cloude, 1991). The system under study is prepared at an instant t in the given state $|\psi(t)\rangle$. The probability amplitude of finding it, at another instant is t', in the state $|\psi(t')\rangle$. The quantum mechanical treatment of this problem is done by expressing the wave function in the 'interaction picture' i. e.,

$$\varphi(t) = e^{iH_0t/\hbar}\psi(t)$$

where $\psi(t)$ is the state vector in the Schrodinger picture. Substituting this in the TDSE, $\varphi(t)$ should satisfy

$$i\hbar\frac{\partial}{\partial t}\varphi(t) = e^{iH_0t/\hbar}H'e^{-iH_0t/\hbar}\varphi(t) = H'_I\varphi(t)$$

where, H'_I is the interaction picture representation of H'. After performing integration

$$|\varphi(t)\rangle = |\varphi(t_0)\rangle + -\frac{i}{\hbar}\int_{t_0}^{t} dt' H'_I(t')|\varphi(t')\rangle$$

Now we define unitary operator $U(t, t')$, which takes a state from time $t = t'$ to a state at time t i. e. $|\varphi(t)\rangle = U(t, t')|\varphi(t')\rangle$. The time evolution operator $U(t, t')$ obeys Schrodinger equation

$$i\hbar\frac{\delta}{\delta t}U(t, t') = [H_0 + H_{int}(t)]\,U(t, t')$$

where H_{int} is the system-field interaction. The solution can be written as:

$$U(t, t') = U_0(t, t') - \frac{i}{\hbar}\int_{t'}^{t} U(t, t'')H_{int}(t'')U_0(t'', t')dt''$$

Then equation becomes

$$U(t, t_1) = 1 - \frac{i}{\hbar}\int_{t_1}^{t} dt_1' H_I(t_1')U(t_1', t_1)$$

This leads to final Dyson expansion

$$U(t, t') = 1 + \sum_{n=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_1}^{t} dt_1 \int_{t_1}^{t_1'} dt_2 \cdots \int_{t_1}^{t_{n-1}'} dt_n' H_I'(t_1')\cdots H_I'(t_n')$$

The n^{th} order term has the form

$$U^n(t, t') = \left(-\frac{i}{\hbar}\right)^n \int_{t_1}^{t} dt_1 \int_{t_1}^{t_1'} dt_2 \cdots \int_{t_1}^{t_{n-1}'} dt_n' H_I'(t_1')\cdots H_I'(t_n')$$

Suppose the system is in the initial state $|g\rangle$ at time $t = -\infty$. The probability of finding the state in the final state $|f\rangle$ at a time $t = \infty$ can be obtained by

$$U_{fg}(t, -t) = \langle|U(t, -t)|g\rangle$$

by taking the limit $t \to +\infty$, $|g\rangle$ and $|f\rangle$ are the eigen states of the unperturbed part of the Hamiltonian. We have the interaction Hamiltonian in the length form as

$$H_I' = e^{iH_0t/\hbar}[d \cdot \mathbf{E}]e^{-iH_0t/\hbar}$$

where $\mathbf{E} = \frac{1}{2}(E_0^* e^{i\omega t} + E_0 e^{-i\omega t})$ is the electric field strength. With this, H_I' will take the new form

$$H_I' = e^{iH_0t/\hbar}\frac{1}{2}\left(d \cdot E_0^* e^{i\omega t} + d \cdot E_0 e^{-i\omega t}\right)e^{-iH_0t/\hbar}$$

Therefore the one photon transition becomes

$$U_{fg}^{(1)} = -\frac{i}{\hbar}\int_{t_1}^{t} dt_1' \left[e^{i(\omega_0+\omega)t_1'}(d\cdot\mathbf{E})_{fg} + e^{i(\omega_0-\omega)t_1'}(d\cdot\mathbf{E})_{fg} \right]$$

Where, $\omega_{fg} = E_f - E_g/\hbar$ and $(d\cdot\mathbf{E})_{fg} = \langle f|d\cdot\mathbf{E}|g\rangle$. In order to perform the integration we assume that the integration will take place only over the length of the pulse, which is in fact the longer than the dimension of the atomic system. This will make the integration limits $t_1 \to -\infty$ and $t \to \infty$ and finally using the definition of delta function, the transition amplitude becomes

$$U_{fg}^{(1)}(\infty, -\infty) = -\frac{2\pi i}{\hbar}\left[\frac{(d\cdot\mathbf{E})_{fg}}{2}\delta(\omega_0 + \omega) + \frac{(d\cdot\mathbf{E})_{fg}}{2}\delta(\omega_0 - \omega)\right]$$

Transition rate is therefore proportional to the modulus square of transition amplitude. Here the first term corresponds to emission and second term corresponds to absorption. For the two photon (second order) process have the form

$$U_{fg}^{(2)}(t, t_1) = -\frac{i}{\hbar}^2 \sum_m \int_{t_1}^{t} dt_1' e^{i(\omega_{fm}-\omega)t_1'} \left[\frac{(d\cdot\mathbf{E}^*)_{fm}}{2} + \frac{(d\cdot\mathbf{E})_{fm}}{2}\right] \times \int_{t_1}^{t_1'} dt_2' e^{i(\omega_{mg}-\omega)t_2'} \left[\frac{(d\cdot\mathbf{E}^*)_{mg}}{2} + \frac{(d\cdot\mathbf{E})_{mg}}{2}\right]$$

where, $\omega_{mg} = \omega_m - \omega_g$ and $\omega_{fm} = \omega_f - \omega_m$ After integration

$$U_{fg}^{(2)}(-\infty, \infty) = -\frac{\pi i}{2\hbar^2}\sum_m \Big[\delta(\omega_0 + 2\omega)\frac{(d\cdot\mathbf{E})_{fm}(d\cdot\mathbf{E})_{mg}}{\omega_{mg} + \omega} + \delta(\omega_0 - 2\omega)\frac{(d\cdot\mathbf{E})_{fm}(d\cdot\mathbf{E})_{mg}}{\omega_{mg} - \omega} + \delta(\omega_0)|\mathbf{E}|^2\left[\frac{(d\cdot\mathbf{E})_{fm}(d\cdot\mathbf{E})_{mg}}{\omega_{mg} + \omega} + \frac{(d\cdot\mathbf{E})_{fm}(d\cdot\mathbf{E})_{mg}}{\omega_{mg} - \omega}\right]\Big] \quad (1.9)$$

The first two terms corresponds to two-photon absorption and emission respectively and the last terms corresponds to ac-Sark shifts.

Thus, in order to find the second order transition amplitude we have to evaluate the expression inside the bracket of Eq. (1.9) which is in general very difficult. The main problem arises due to n^{th} infinite summation coming in the expression and also due to the resonance cases where the denominator become zero. In the next chapter three, we apply Dalgarno-Lewis method for the evaluation of these kind of Matrix

elements. We wish to solve Schrodinger equation

$$i\frac{d}{dt}|\psi(t)\rangle = (H_o + H(t))|\psi(t)\rangle$$

Now let us switch to interaction picture defined by

$$|\psi_I(t)\rangle = e^{iH_o t}|\psi_S(t)\rangle$$

$$i\frac{d}{dt}|\psi_I(t)\rangle = H_I(t)|\psi_I(t)\rangle$$

where,

$$H_I(t) = e^{iH_0 t}H_S(t)e^{-iH_0 t}$$

Note $H_I(t)$ is time dependent even if $H_S(t)$ is time independent (unless H commutes with H_0). Note also that $H_I(t)$ at one time generally does not commute with $H_I(t)$ at another time. Finally note that if, for some time interval, $H_S(t)$ vanishes then $|\psi_I(t)\rangle$ does not evolve during that time interval. That is essentially the point of working in the "interaction picture". To express the evolution in interaction picture using starting time t_0 at which initial co-ordinates are specified, it is convenient to write

$$\psi_I(t)\rangle = e^{iH_0 t}|\psi_S(t)\rangle$$

$$= e^{iH_0 t}U_S(t, t_0)|\psi_S(t_0)\rangle$$

$$= e^{iH_0 t}U_S(t, t_0)e^{-iH_0 t}|\psi_I(t_0)\rangle$$

Here, $U_S(t, t_0)$ is the Schrodinger picture evolution operator equal to

$$exp(-iH(t - t_0))$$

When the hamiltonian is time dependent

$$i\frac{d}{dt}U_S(t, t_0) = H(t)U_S(t, t_0)$$

Thus, we have

$$|\psi_I(t)\rangle = U_I(t, t_0)|\psi_I(t_0)\rangle$$

where,

$$U_I(t, t_0) = e^{iH_0 t}U_S(t, t_0)e^{-iH_0 t_0}$$

We have,

$$i\frac{d}{dt}U_I(t,t_0) = e^{iH_0t}[-H_0 + H_S(t)]U_S(t,t_0)e^{-iH_0t_0}$$
$$= [e^{iH_0t}H_S(t)e^{-iH_0t}]e^{iH_0t}U_S(t,t_0)e^{-iH_0t_0}$$

Thus,

$$i\frac{d}{dt}U_I(t,t_0) = H_I(t)U(t,t_0)$$

with the initial condition

$$U_I(t_0,t_0) = 1$$

Atomic units

To simply the notation considerably, we will almost exclusively use atomic units (a.u.). They are defined as

$$\mathrm{k} = m = e = a_0 = 1a.u.$$

Detailed of this system of units are noted in Appendix. In some formulae respective quantities are written down explicitly, to give familiar combinations of quantities that are less irritating for a quick check of units (Grossmann, 2008).

Selection rule

The condition under which the matrix element $\langle nlm|\hat{\epsilon}\cdot\hat{r}|n'l'm'\rangle$ do not vanish are referred to as selection rules. For linearly polarized light, it is customary to take the polarization (unit) vector of the radiation $\hat{\epsilon}$ as the z-axis, in which case $\hat{\epsilon}\cdot\hat{r} = z$ and the matrix element is $\langle nlm|z|n'l'm'\rangle$. Mathematically, these rules follow from the properties of the spherical harmonics, since the polarization vectors can also be expressed in terms of spherical harmonics. Physically, they are due to the fact that the photon, in the dipole approximation, has one unit of angular momentum which must be accommodated - absorbed or emitted - between the atomic states; hence the condition $l - l' = \pm 1$ which also follows from $\langle nlm|\hat{\epsilon}\cdot\hat{r}|n'l'm'\rangle = \int d^3r\, \Psi^*_{nlm}(\hat{\epsilon}\cdot\hat{r})\Psi_{n'l'm'}$. When the atomic states are described in the angular momentum basis $|ls;jm\rangle$, the selection rules for m are identical to those for m_l. The selection rules for l remain the same, while the rule for j in a matrix element of the type $\langle nls;jm|\hat{\epsilon}\cdot\hat{r}|n'l's';j'm'\rangle$ is $j - j' = 0, \pm 1$, with the restriction that $j = j' = 0$ is forbidden.

The transition probability in multiphoton ionization(MPI) is quite different than single-photon ionization (SPI). Transitions that are "forbidden" in SPI can be allowed by MPI and vice versa. The selection rules are best predicted for SPI and MPI by solving the vector in $\langle nlm|\hat{\epsilon}\cdot\vec{r}|n'l'm'\rangle$ and matrix element for two or three-photon respectively. The parity rule follows by odd parity of dipole operator. In a non linear, two and three photon absorptions occurs between the states of same parity, while in the single photon absorption states involved are opposite parity. When a single photon collides with a ground state atom, the atom can absorb the photon via electronic transitions to energy levels higher than the ground state by $E = k\omega$. Flowing out of the mathematics of quantum mechanical wave functions, selection rules govern these transitions such that the change in angular momentum in single photon transitions is $\delta l = +1, -1$. Thus, an electron in a ground state s-state may transition by one photon only to a higher p-state. When an atom absorbs two photons simultaneously, the electron will change angular momentum by $\delta l = +2, 0,$ or -2, since each photon has angular momentum of $+1$ or -1. This allows an s-state electron to transition to another s-state or to a d-state: states out-of-reach by single photon absorption. If a third photon interacts with the atom soon after the two-photon process, the third photon may ionize the atom. An s-state electron may not transition to a p-state by two photon absorption. When absorbing multiple photons simultaneously, an atom will proceed to an intermediate state corresponding to a characteristic eigenstate or to a 'virtual state'. These virtual states are not eigenstate; they correspond to no specific n or l state. Instead, they are merely superpositions of waves. No population of electrons transitions to the virtual state. The lifetime of a virtual state is short, relative to eigenstate. Actually, the closer the virtual state is to an actual eigenstate, the longer the lifetime of the virtual state. If the photons corresponding eigenstate energies are incident on the atom, the effect of two-photon absorption will be enhanced.

The absorption cross will be non zero only if the selection rule regarding the electronic and rotational transition are obeyed. These selection rule are obtained by considering the symmetry properties of above mentioned wave functions. The relative intensities of these transitions are governed by the overlap of the upper and lower state vibrational wave functions. The value of overlap integral determines the magnitude of the transition probability. The intensity of transition is proportional to $|M|^{(N)}$ as long as other selection rules are respected (Rajini, 1989). This will be explained in detail in chapters 3 and 4.

CHAPTER 2

LITERATURE REVIEW and METHODOLOGY

Literature review

Keldysh in 1963 − 1964 published a paper (Keldysh, 1965) on the theory of atoms in strong laser field. He coined a parameter γ known as adiabaticity parameter now known as Keldysh parameter (quantitative indicator) that separates the regimes of MPI and Tunnel Ionization. It was concluded that If γ 1, the process is MPI and γ 1 is the tunnel ionization. From 1960s to till the early 1980s, only the condition γ 1 was satisfied in all experiment using long (ns to sub ns) pulses. From 1996 − 1997, Delone et al's work contribute to coherence effect, pulse laser effect leading to ATI and HHG (Mikhail, 1997).

Today, the development of intense and powerful tunable (terawatt) laser has revolutionized optical spectroscopy and led to the discovery of many distinctly new non linear optical phenomena (Klepper et al., 1997). One of them is Multiphoton Ionization (MPI) of atoms and molecules (Xi, 1995) or negative ion (Dimitrovski, 2005). Compared to atoms, molecules offer additional degrees of freedom. One is the internuclear distance; other is the angle of alignment of the molecular axis with respect to the direction of polarization of the laser. MPI of molecules by using synchrotron radiation and pulsed dye laser are studied by V. Mickoy (Mickoy et al., 1986). Analysis focuses on two aspects of the ionization of molecules in intense laser field are, the great influence of field on concomitant transitions between vibrational states and other is, the dependence of certain ionization process on the alignment of molecules with respect to the acting forces (Requate, 2007).

In the case of -ve ion the process of promotion of the outer electron to continuum (ionization), which is called detachment, has occurred. Results have shown existence of bound states of the electron in -ve ion as initial state. Ionization probability increases as increase of laser pulse reported from the various plots (Dimitrovski, 2005). Non-linear optics is a field in physics with long history that studies the non linear interaction of intense light with matter. Optical phenomena are called non linear when the material response to an applied optical field depends on the field strength in a non linear fashion (Dimitrovski, 2005). The transformation of significant amount of the energy of the laser pulse into nonlinear electromagnetic pulses may turn out to be an important channel for the absorption of a relativistically strong laser pulse. The interaction of relativistically strong laser pulse and matter depends critically on ratio of pulse carrier frequency (ν) to the Langmuir frequency ν_p (Kenichi and Katsumi , 2002).

Depending on light (laser) frequency and intensity, it can result in the ejection of two valence shell electron from a variety of mechanism, following the absorption of a single high energy photon (Bulanov and Naumova , 1994). Single ionization in such strong fields has been intensely studied for many years now. The experimental observable are the ionization rates as function of laser intensity and wavelength, the electron energy and angular distribution as well as emission of high harmonic light using SAE (single active electron) model (Bottcher et al., 2007). Multiphoton double ionization was discovered in mid 1970s and investigated by several groups. Double ionization means removal of two electrons by many orders of magnitude (Dörner et al., 2001). ATI provides a new controllable heating mechanism for plasmas. It will be practically important at low densities where other heating mechanisms are ineffective (Yudin and Ivanov, 2001).

Results are presented on generation of high-harmonics through the scattering of relativistic electrons from high intensity laser light. The characteristic signature of this processes are found to be the emission of even-order harmonics, linear dependence on the electron density, significant amount of harmonics with circular polarization and small optical extent of the source (Umstadlter, 2003). Angle resolved photoelectron spectra of atoms by XUV (extremely high ultra violet) attosecond (10^{-18}) second pulses in the presence of a circularly polarized laser field are calculated to examine their dependence on the duration and the chirp parameter of the attosecond pulses

using a genetic algorithm (Banerjee et al., 2003). Multiphoton ionization of any atoms have been investigated with femtosecond (10^{-15}) second laser field and ionization rates in the interaction (laser-matter) are calculated experimentally by combination of TOF (3d time of flight) and PSD (2d position sensitive detectors). By using perturbative treatment based on the central field approximation, MPI probabilities are calculated in two-three and four photon ionization of cesium and potassium at double Nd glass laser frequency and also performed some calculation for hydrogen (Aymar and Crance, 1981). By the use of approximate wave function (Ritz Variational method), based on the time independent perturbation theory, two-electron atom are worked out and program of greatly increasing the accuracy in the calculation of many properties of atomic system is envisaged (Schwartz, 1959).

Multiphoton ionization of I and Ag are determined experimentally by using a modified form of Time of Flight Mass Spectrometry (TOFMS), known as charge reversal apparatus with a femtosecond laser pulse (Bredy et al., 2004). TOF mass spectroscopy is one of the very common experimental tools for studying the structure of atomic and molecular system, for studying dynamical processes such as photo ionization, photo dissociation, photo association etc, it can provide essential diagnostics for scattering experiments (Doo et al., 1997).

Based on numerical calculation, elastic and inelastic scattering of electrons by ions in intense laser field showed that in elastic collisions, the cross-section is close to Rutherford cross-sections calculated from drift velocity. In inelastic collisions at drift velocities lower than the oscillator velocity are determined by a small fraction of the electron, called the representative electron (Yoon et al., 1999). Titanium doped sapphire or Ti-Sapphire is most common laser system for micro-matching. Micro-matching is a process by which pulse from a femtosecond laser are used to induce micro meter sized structure on the surface or in the bulk of solid materials (Weckenbrock et al., 2004). Recently two photon double ionization and ATI of Helium were experimentally observed with the Ti-sapphire 27^{th} harmonic pulses (Cerent and Mazur, 2007).

Femto second laser pulse can ionize any atom. The mechanism is described by field ionization. Ionizing atomic gases produce the shortest wavelength coherent XUV radiation. The radiation can reach 1000 KeV photon energy or it can be concentrated into short pulses with duration as short as 250 attosecond (Barna et

al., 2006). Multiphoton ionization of Xenon and Argon at wavelength of 800 nm and 400 nm at intensities 10^{13} to 10^{14} W/cm^2 have shown that eight photons required for Xenon and ten photons are required for Argon to ionize (Bhardwaj et al., 2007). Multiphoton ionization of hydrogen atom in strong field using renormalization method based on Hamiltonian with two degree of freedom has been calculated theoretically using renormalization and empirical rules together in order to obtain very accurate information on the stability of the system (Lang et al.).

Multiphoton ionization of clusters of immiscible liquids was studied experimentally by using R2PI (Resonance two photon ionization) time of flight spectroscopy instrument. Among the clues provided by data are the frequency shifts of the transitions, their Vander-Waals structures, the fragmentation of photo ionized clusters and the complexation-induced origin intensity (Chandre and Uzer, 2002). Investigations have revealed that sufficiently intense interaction with clusters can lead to multiple ionization of event. Experiments from TOFMS have reported that the interaction of intense fields with Vander-Waal's and hydrogen bonded clusters were, the first to measure the large values of kinetic energy release in such highly charged clusters (Xe20+, Kr18+, O5+) and provide the first direct observations for the mass to charge ratio of atomic ions ejected from clusters with charge states of large magnitude (Garrett and Zwier, 1992). The two photon ionization of Cs atoms in the range 460 − 540 nm have been studied experimentally and found the generalized cross-section $(9 \pm 5) \times 10^{-52}$ cm^4 second exhibits a deep minimum at 480nm (Morellec et al., 1980). Multiphoton ionization rate using TDDFT showed that, they may affect the transfer scheme of diatomic molecules (Na_2) with ultra short pulse (ns) through the concept of light induced potentials (Snyder, 1996).

Multiphoton ionization of Hydrogen molecule has been studied by Lars Bojer Madsen by using non perturbative Floquet method which is related to wave-packet method. This method is applicable to the description of dynamics arising from periodic interaction potential (Bojer, 1998). In case of molecule the intermolecular distance (R) is an extra parameter. The report has shown a series of peaks and troughs occur in ionization rate with R. Knowing the ionization rate as a function of R, the theory can be used for predicting the energy spectra of the fragment ions and vice versa. The motion of electron under influence of the field is treated as classical particle ionized at a particular phase of the laser field, and the electron-ion interaction is considered if the newly ionized electron returns to the ion (Nikura and Corkum,

2006). Multiphoton ionization in polyatomic molecules with strong field has shown that, ionization depends on properties such as molecular geometry and bonding, the path length of delocalized electrons and/or ionization potentials as well as on basic laser parameters such as wavelength and intensity (Lezius et al., 2002). K-Photon ionization cross-sections can also be calculated by the method of Dalgarno-Lewis in the first non vanishing order of perturbation theory (Aymar and Crance, 1981). This method is described in detail in our next chapter. Calculation based on this method were carried out by Gontier and Trahin for $2 \leq K \leq 8$ (Gontier and Trahin, 1971). The results are in good agreement with calculation by the method of Sturmian expansion of a Green' function.

Absorption of photons by electrons above the ionization threshold can take place one and two step processes. Diagnostic method based on intensity and pressure dependencies and on the magnitude and the angular distribution of probabilities are proposed (Gontier et al., 1980). The two photon transition rate for hydrogen atom is evaluated with the choice of gauges ($\vec{E} \cdot \vec{x}$ and $\vec{A} \cdot \vec{p}$) interactions including the continuum (Bassani et al., 1977). Choosing a gauge for the interaction of an electron with a laser radiation field (i.e., $\mathbf{rF}$ or, $p\mathbf{A}/c + \mathbf{A}^2/2c^2$) must also be considered in calculating cross-sections of multiphoton ionization of hydrogen atom, as for other atoms (Quattropani et al., 1982). They found that the contribution in multiphoton matrix elements from the bound spectrum is quite different in the first and second gauges. Multiphoton ionization cross-sections have also been calculated variationally (Gao and Starace, 1988, 1989). They found the 7-photon ionization cross-section of the ground state of hydrogen atom by linearly polarized radiation, only the final continuum state with maximum orbital quantum number ($l = 7$) was considered. Dalgarno method is also used (Crance and Aymar, 1979) for three-photon 16 p resonant ionization of Cs I. By using partial-closure approximation (Bassi, 2000) transition probabilities for two-photon for hydrogen and helium atom are also calculated. The Keldysh-Faisal-Riess (KFR) theory which completely neglects the effect of the atomic potential on the final state scattering wave function is shown to be equivalent to the plane wave Born approximation for the photoelectric effect. This equivalent is gauge invariant and emphasize the need to treat the atomic potential more carefully in order to predict genuine multiphoton transitions (Unnikrishan, 1991). Three-photon ionization rates for rare gas atoms and alkali atoms (except Li) have been calculated (Barry and Albert, 1966; Barry, 1967).

Methodology

The theoretical problem that describe the interaction of atom with laser field consists in solving the Time Dependent Schrodinger Equation (TDSE). This is one of the approximation method. Approximation methods offer, in general powerful economical prescriptions for determining reliable results for the system that can not be solved exactly. A number of methods have been proposed to solve this problem. Two of them are, the numerical solution of TDSE and the semiclassical strong field approximation. We have concentrated our effort on solving the problem of Hydrogen atom or more generally single-active electron atom in multiple laser beam. We treat non-relativistic motion of electron and nuclei quantum mechanically and the external radiation field classically i. e. the system becomes semi-classical. For the quantum mechanical treatment of emission of an atom, we replaced the classical dipole moment $p = er$ with the expectation value or dipole matrix element such as

$$\langle D_{fg} \rangle_r = e \int \Psi_f^* r \Psi_g d\tau$$

with Ψ_f and Ψ_g being the eigenfunction of the states E_f, E_g and the integral over the all volume element $d\tau$ delivers the quantum mechanical average of the co-ordinates r of the radiating electron for the transition $E_g \rightarrow E_f$. This will help to clarify the fundamental assumption of our discussion and to introduce the basic theoretical approximation. All the theoretical studies (Transition probability and cross-sections) on MPI are done within the Time dependent Perturbation theory (TDPT) governed by TDSE, which requires a calculation of perturbative sums over the whole spectrum of intermediate states of the atom. These sums are calculated by different techniques. We have chosen by using *Dalgarno-Lewis method*, which convert the summation into the solving of relevant inhomogeneous differential equation. One can distinguish between perturbative and non-perturbative approximation methods. Non perturbative methods do not accept any assumption about the strength of external and internal fields acting upon or in the atom. Absence of such assumption makes non-perturbative methods are general than perturbative methods. However, the non perturbative methods require much larger computational effort. We will consider only the perturbative approach to deal with the equation. Perturbation of the eigen function and their eigenvalues were determined for such cases where the system was subjected to perturbation upon the space-co-ordinates. However there are physical situations where the Hamiltonian depends on time. Such situation

arises when a system is subjected to readjustment in its states to other energy state, i.e. the transitions between atomic levels accompanied by the emission or absorption of radiation, by the interaction between atoms and the electromagnetic field (Gasiorowicz, 2000).

The interaction of time independent electromagnetic field on atom, changes the position of atomic energy levels, splits spectroscopic lines and even ionizes the atom. The manifold of mentioned phenomena enormously increases if one studies the influence of time dependent electromagnetic field on atom. There are two reasons for this to increase. Firstly a conventional source of time dependent field (i.e. a source of electromagnetic waves) creates a much shorter field than sources of constant are able to produce. Secondly, time dependent fields bring into play different mechanisms of studied phenomena. Hence it is necessary to study the effect of time dependent perturbation. In nuclear physics, especially in nuclear scattering, nuclear reaction and nuclear disintegrations, high harmonic generation, photo dissociation and multiphoton ionization, we require to find the outcome of perturbation in time. We shall discuss the theory of time dependent perturbation, which is the basis of understanding quantum optics, in two stages:

- In the first stage we shall present that is generally known as Semiclassical Theory in which the electromagnetic field is regarded as classical field and atomic states are treated quantum mechanically. Almost all optical experiments made before the advent of lasers can best be explained on the basis of appropriate semiclassical models and concept.

- In the second stage we develop the 'complete' theory in which both the atoms and the field are treated quantum mechanically.

It must be mentioned here that the theory in either form, is an approximate theory and is based on the assumption that the perturbation is small. Approximation methods are great importance in discussing the application of quantum theory to specific systems such as the atomic and molecular etc. The theory appears to describe the interaction of radiation with matter precisely. This method of evaluation was first developed by Dirac and is also known as Dirac's theory of radiation. Since the Hamiltonian function in this problem is time dependent the appropriate equation for evaluation of specific problems would be the time dependent Schrodinger equation. The evolution of the wave function Ψ with time is governed by the time dependent Schrodinger Equation

given as

$$i\mathrm{k}\frac{\delta\Psi(\mathbf{r}, t)}{\delta t} = H\Psi(\mathbf{r}, t)$$

The Hamiltonian in dipole approximation (λ *systemsize*)

$$H(t) = H_0 + E(t) \cdot \sum_j r_j$$

with $E(t)$ electric field. This is called Length Gauge. Alternatively

$$H(t) = H_0 + A(t) \cdot \sum_j [p_j + \frac{A(t)}{2}]$$

with $A(t) = -\int_{\infty}^{t} \mathbf{E}(t')dt'$, This is called velocity gauge. The velocity gauge wave function $\Psi'(t)$ is related to length gauge wave function $\Psi(t)$ by $\Psi'(t) = e^{-iA(t)\cdot\sum_j r_j}\Psi(t)$. Here $\mathbf{r}$ will denote set of coordinates variables of all particles in the systems. If the system contains particular spin, Ψ will be a multicomponent wave function with the appropriate number of components and H the Hamiltonian, in general be a function of the relevant spin matrices as well as $\mathbf{r}$ and $\mathbf{p}$. For simplicity we consider spin less case initially.

Perturbation theory

Quantum mechanical system may be exposed to perturbation including electric field, magnetic field or, electromagnetic radiation. Due to such perturbation, the quantum system considered here is stimulated and as a consequence changes its state. This change of state may include changes in the shape of wave function, state energies and occupation probability of states. In the perturbative regime, the electric field applied is very small compared to the atomic fields and the electronic wave function is distorted very slightly in a time-dependent manner due to the oscillations in the electric field. In conventional perturbation theoretical approaches, this "perturbation" is expanded in a power series and the effect of each term in the expansion is investigated. The perturbation, if small enough, leads to a rapid decrease in the effects of the higher terms in the power series. However, if the perturbing field is, however, comparable to the internal fields, then the higher terms contribute to the final state and are therefore non-negligible. Perturbation theory then does not satisfactorily explain the observed phenomenon and non-perturbative techniques (Borbèly, 2008) have been developed to solve the Schrodinger equation (Moore, 2005). The perturbation theory is one of the

most important methods for obtaining the approximate solution to the Schrodinger's equation. The new Hamiltonian due to perturbation becomes:

$$H = H_0 + \lambda H'$$

Lowest order perturbation theory (LOPT) and need of higher order perturbation

If the perturbation is neglected ($\lambda = 0$), one obtains the unperturbed Schrodinger equation with original eigenvalues and eigen function. Since the system is described by the Hamiltonian H has experience only a small perturbation ($\lambda \neq 0$), when compared to unperturbed system. This LOPT is the simplest form of the approach, consists in calculating the rate of an a N -photon transition by using the N^{th}-order perturbation theory of the atom-field interaction.

$$\Gamma^{(N)} = \sigma^{(N)} \left(\frac{I}{\mathrm{k}\omega} \right)^{N}$$

Where the symbols have their usual meanings. An advantage of LOPT, is that it introduces well defined approximation (the ordinary, linear optical properties of material), and can systematically improved on. The absorption of photons in the weak field case is restricted to the absorption of a single photon. In the intense field regime, the photon flux is so large as to make it possible for atoms and molecules to absorb more than a single photon to make transitions. As the laser intensity increases, this theory becomes inappropriate, because there are large number of atomic states coupled in the process, and therefore higher order perturbation theory is needed(e.g. non-linear optical processes such as high harmonic generation and multiphoton). This theory predicts that the log-log plot of the ionization rate (or ionization probability) versus the intensity of the laser field is straight line, with slope the multiplicity of the process (n^{th}-order). An alternative approaches to perturbation theory have been suggested by several authors, they lie in the class of the usually called non-perturbative (Brandi et al., 1982).

Time dependent Schrodinger equation (TDSE)

At low and moderate field intensities the TDSE is a well known approximation for single photon and multiphoton processes and even for the Above threshold ionization (ATI) (Mainfray and Manus, 1991) and From the point of view of modern quantum

mechanics, the properties of free atom and the atom in the external field can be explained solving Schrodinger time dependent equation as:

$$i\hbar\frac{\partial\Psi(r,t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 - i\hbar\frac{e}{2m}(\mathbf{A}\cdot\nabla + \nabla\cdot\mathbf{A}) + \frac{e^2}{2m}\mathbf{A}^2 - \frac{e^2}{4\pi\epsilon_o r}\Psi(r,t)$$

or,

$$i\hbar\frac{\partial\Psi(r,t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_o r} - i\hbar\frac{e}{m}\mathbf{A}\cdot\nabla + \frac{e^2}{2m}\mathbf{A}^2\Psi(r,t)$$

Hydrogenic Hamiltonian is

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_o r}$$

and, the interaction Hamiltonian is

$$H_{int}(t) = H^J(t) = -i\hbar\frac{e}{m}\mathbf{A}\cdot\nabla + \frac{e^2}{2m}\mathbf{A}^2 \approx -i\hbar\frac{e}{m}\mathbf{A}\cdot\nabla$$

The perturbation theory assumes that Hamiltonian Operator H can be separated into two parts;

$$H = H_0 + H^J(t)$$

here, $H^J(t)$ is a small correction to the unperturbed operator Hamiltonian H_0. The unperturbed Hamiltonian is time independent.

If interaction Hamiltonian is independent of time such as

$$H = H_0 + V(r)$$

This form of Hamiltonian H for a system of particles, is said to be time independent, which interact with another can not be derived from the general principles of quantum mechanics alone. It is obtained by adding to the Hamiltonian of non-interacting particles a certain functions V(r) of their coordinates. The first term can be regarded as the quantum mechanical operator of the kinetic energy and the second part as that of the potential energy of the particle in an external field, both are time independent. Although both time dependent as well as time independent fields can ionize the atom, ionization method differ significantly. In the case of time independent perturbation the ionization takes place due to a tunnel effect, while an electromagnetic wave transmitting a certain amount of its energy. This energy can excite or even release the atomic electron(s) (Landau and Lifshitz, 1965).

We now turn to detail study of perturbations depending on time. Consider Time dependent Schrodinger equation:

$$H(r, t)\Psi(r, t) = E\Psi(r, t)$$

The solution will be

$$\Psi(r, t) = C_0 e^{(-iEt/\hbar}\psi(r) \qquad (2.1)$$

Here, Hamiltonian H and total energy E both are energy operators; yet while H depends on space coordinates as well as time coordinate. E depends on time coordinate only. The Schrodinger equations shown above are valid for non relativistic material particles (which requires dependence of the energy on momentum, $E = (p^2/2m)$. Some more quantum and classical relation are given in appendix $A.2$. Ψ is the wave function describing the atom when the energy is E. In order to obtain Ψ one can use separation variable method, where Ψ is expressed as the product of two functions, one involving the space co-ordinates (r) while the other involving the time co-ordinate alone: $\Psi(r, t) = \psi(r)u(t)$ Where, $\psi(r)$ is independent of time and $u(t)$ is independent of position coordinates (r). With this assumption, the Schrodinger wave equation becomes,

$$-\frac{\hbar^2}{2m}\nabla^2 + V(r) \quad \psi(r)u(t) = i\hbar\frac{\partial}{\partial t}\Psi(r)u(t)$$

For hydrogen atom , the potential energy V is independent of time. Dividing both sides by the product $\Psi(r)u(t)$,

$$\frac{1}{\psi(r)u(t)} \quad -\frac{\hbar^2}{2m}\nabla^2 + V(r) \quad \psi(r)u(t) = \frac{1}{\psi(r)u(t)} i\hbar\frac{\partial}{\partial t}\Psi(r)u(t)$$

$$\text{or,} \frac{1}{\psi(r)} \quad -\frac{\hbar^2}{2m}\nabla^2 + V(r) \quad \psi(r) = \frac{1}{u(t)} i\hbar\frac{\partial}{\partial t}u(t)$$

L.H.S is independent of time and R.H.S is independent of position coordinates. This is possible only when both sides are separately equal to a constant. Let this constant be E. Hence, we separate the equation into two equations one space dependent and other time dependent.

$$\frac{1}{\psi(r)}\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(r) = E$$

and

$$\frac{1}{u(t)} i\hbar\frac{\partial}{\partial t}u(t) = E$$

Rewriting the time dependent part in the form

$$\frac{\partial u(t)}{u(t)} = -\frac{i}{\hbar} E \partial t$$

which on integration gives

$$log_e u(t) = -\frac{i}{\hbar} Et$$

$$or, u(t) = e^{-\frac{i}{\hbar} Et}$$

Comparing this equation with that for a plane wave ($e^{i\omega t}$) where, $\omega = 2\pi\upsilon = 2\pi E/h = E/\hbar$, we see that the dimension of E must be that of the energy. Thus, E is the energy of the particle which is described by this solution of Schrodinger equation. If V is constant in time, each of the energy eigenstate is separably a solution of the time-dependent Scrounger equation (with different values of energy E if the solutions are degenerate). Explicitly, the n^{th} energy eigenfunction can be written following Eq. (2.1) above.

$$\Psi_n(r, t) = \psi_n(r) \exp(-iE_n t/\hbar)$$

where E_n is the n^{th} energy eigenvalue, and we presume that the ψ_n (and consequently the Ψ_n) are normalized. This function is a solution of the time-dependent Schrodinger equation. Because of the linear superposition defined above, any sum of such solution is also a solution (David, 2008). Suppose that we had expanded the original solution at time $t = 0$ in energy eigenfunction , i. e.,

$$\psi(r) = \sum_n C_n \psi_n(r) \qquad (2.2)$$

where,the C_n are the expansion coefficients (the C_n are simply fixed complex numbers). We know that any spatial function $\psi(r)$ can be expanded this way because the set of eigenfunctions $\psi_n(r)$ is believed to be complete for describing any spatial solution. We can now write a corresponding time-dependent function

$$\Psi(r, t) = \sum_n C_n \Psi_n(r, t) = \sum_n C_n \psi_n(r) u_n(t)$$

where, $u_n(t) = e^{-\frac{i}{\hbar} E_n t}$

$$\Psi(r, t) = \sum_n C_n \psi_n(r) e^{-\frac{i}{\hbar} E_n t} \qquad (2.3)$$

We know that this function is a solution to the time-dependent Schrodinger equation because it is constructed from a linear combination of solutions to equation. At

$t = 0$, it correctly gives the known spatial form of the solution. Hence Eq. (2.3) is the solution to the time-dependent Schrodinger equation with initial condition

$$\Psi(r, 0) = \psi(r) = \sum_n C_n \psi_n(r)$$

For the case where the potential V does not vary in time. In other words, if we have a solution $\psi_n(r)$ of the TISE, with corresponding eigenenergy E_n, then multiplying by the factor $e^{-\frac{i}{\hbar}E_n t}$ will give us a solution of the time dependent Schrodinger equation. Here, the sum over n means a summation over the discrete part of the set and integration over its continuous part. Where, C_n the expansion coefficients or arbitrary constants are the independent of time This can be determined from the wave function Ψ at some particular time say at $t = 0$, thus,

$$C_n = \int_{-a}^{+a} \psi_n^*(r)\psi(r, t = 0)dr$$

If the atom is isolated, the probability that the atom is in state a or state b is respectively given by

$$C_a^* C_a = |C_a|^2 \text{ and, } C_b^* C_b = |C_b|^2$$

For bound system, the various allowed values of energy E are called the characteristics or proper or eigenvalues. Corresponding to each eigenvalue, there appears a function Ψ as the solution of the wave equation. Thus Ψ is known as eigenfunction. The probability of finding the system in any particular state is given simply by the square of the modulus of the corresponding amplitude of the state i. e. C_n (Loud, 1991). [The coefficient $C_n(t)$, depending on time, is called fourier transform. It describes how the amplitudes of the waves vary with time. The Fourier transform specifies the wave group as completely as wave function (Ψ). Consider any continuous periodic function.

$$\psi(r) = \sum_{-\infty}^{\infty} C_n e^{+inr}$$

This function Ψ is completely determined by its famous coefficient C_n. Knowing the value of all the C_n is equivalent to determining $\psi(r)$.]

Time dependent perturbation theory

This method is sometimes called the method of variation of constants. Let us assume the Schrodinger time dependent equation

$$i\hbar\frac{\partial\Psi(r,t)}{\partial t} = H\Psi(r,t)$$

When a system is subjected to the external radiation field, that is passing of particle or light wave the above situation is changed. The system may undergo a transition from one stationary state to another under the action of these external factors. Such external factors appear in quantum mechanics in the form of an interaction potential which must be added to the unperturbed Hamiltonian H_0. Suppose an atom is in the n^{th} stationary state defined by the eigenfunction Φ_n and eigenvalue E_n and at a time $t = 0$, we switch on any extra perturbing potential. The atom is no longer in a quantum state, since Φ_n and E_n are not an eigenfunction and an eigenvalue of the new potential. By applying Schrodinger equation to the atom in the new potential distribution, we can find how the wave function Ψ changes from initial time $t = 0$ to a new function at a later time. Since the Hamiltonian depends on time. Such situation arises, readjustment in its states to other energy state. Due to external radiation the Hamiltonian of the system is perturbed and can be expressed as:

$$H = H_0 + H^{I}(t) \tag{2.4}$$

here, H_0 is unperturbed Hamiltonian also known as field free atomic Hamiltonian and $H^{I}(t)$ is small perturbation on H_0 also known as time dependent interaction (atom + field) hamiltonian. Its functional form depends upon the nature of the forces. However $H^{I}(t)$ depends on the time and has the effect of causing transition between eigenstate of H_0 that would be stationary in the absence of $H^{I}(t)$see the equation (2.4). Now the TDSE with new time dependent Hamiltonian becomes:

$$i\hbar\frac{\partial\Psi(r,t)}{\partial t} = H(r,t)\Psi(r,t)$$

Following, the usual techniques of quantum mechanics, we assume the solution of this equation to be a linear superposition of the basic wave functions $\Psi_1(r,t)$, $\Psi_2(r,t)\cdots$ etc, The coefficients $C_n(t)$ are now time dependent. The general solution of TDSE becomes:

$$\Psi(r,t) = \sum_n C_n(t)\Phi_n(r)e^{-\frac{i}{\hbar}E_n t}$$

Where, $\Phi_n(r)$ are the eigenfunctions of the Hamiltonian and $C_n(t)$ are determined by $\Psi(r, 0)$. Rewriting the equations,

$$i\hbar\frac{\partial\Psi(r,t)}{\partial t} = H_o\Psi(r,t) + H'(t)\Psi(r,t)$$

Or,

$$i\hbar\frac{\partial}{\partial t}\sum_n C_n(t)\Phi_n(r)e^{-\frac{i}{\hbar}E_n t} = H_o\sum_n C_n(t)\Phi_n(r)e^{-\frac{i}{\hbar}E_n t} + H'(t)\sum_n C_n(t)\Phi_n(r)e^{-\frac{i}{\hbar}E_n t}$$

Or,

$$i\hbar\sum_n C_n(t)\Phi_n(r)\left(\frac{-i}{\hbar}\right)E_n e^{-\frac{i}{\hbar}E_n t} + i\hbar\sum_n \frac{\partial C_n t)}{\partial t}\Phi_n(r)e^{-\frac{i}{\hbar}E_n t}$$
$$= H_o\sum_n C_n\Phi_n(r)e^{-\frac{i}{\hbar}E_n t} + H'(t)\sum_n C_n(t)\Phi_n(r)e^{-\frac{i}{\hbar}E_n t}$$

The L. H. S. of first term and R. H. S. of the first term are canceled, because they are equal to the time independent Schrodinger equation ($H_0\Phi_n = E_n\Phi_n$).

$$i\hbar\sum_n \frac{\partial C_n(t)}{\partial t}\Phi_n\sum_{-E\ t}\frac{i}{\hbar}(r)e \quad = H(t)\ {}_n(t)\Phi_n(r)e^{-\frac{i}{\hbar}E_n t}$$
$$C$$

Multiplying by Φ^*_m and integrating both sides

$$i\hbar\sum_n \frac{\partial C_n(t)}{\partial t}e^{-\frac{i}{\hbar}E_n t}\int \Phi^*_m\Phi_n d\tau = \sum_n C_n(t)e^{-\frac{i}{\hbar}E_n t}\int H'(t)\Phi^*_m\Phi_n d\tau$$

Where, $d\tau$ is the integral over the volume space.

$$\frac{dC_n(t)}{dt}e^{-\frac{i}{\hbar}E_n t}\int \Phi^*_m\Phi_n dV = (i\hbar)^{-1}\sum_n C_n(t)e^{-\frac{i}{\hbar}E_n t}\int \Phi^*_m H'(t)\Phi_n dV$$

Using the orthonormality of Φ^*_m,

$$\langle\Phi^*_m|\Phi_n\rangle = \int \Phi^*_m\Phi_n d\tau = \delta_{mn}$$

Where, δ_{mn} is the Kroneckor delta symbol defined as

$$\delta_{mn} = 0 \text{ for, } m \neq n$$

$$\delta_{mn} = 1 \text{ for, } m = n$$

We can write above equation in the form:

$$\frac{dC_m(t)}{dt} e^{-\frac{i}{\hbar} E_m t} = (i\hbar)^{-1} \sum_n C_n(t) e^{-\frac{i}{\hbar} E_n t} H^J_{mn}$$

where,

$$H^J_{mn} = \int \psi^*_m H^J \psi_n d\tau = \langle \psi^*_m | H^J(t) | \psi_n \rangle$$

This is called a matrix element of the Hamiltonian H^J. We have assumed that the system is in a state n when the perturbation was switched on at $t = 0$. If the perturbation is off at $t = t^J$, the probability of the system in state is m, which is $|C_m(t)|^2$. Where, ω_{mn} is Bohr angular frequency given as $\omega_{mn} = \frac{E_m - E_n}{\hbar}$ If, $H^J(t) = 0$, then, $C_m(t)$ would be constants. The expansion coefficients $C_m(t)$ must satisfy a set of equations.

$$\dot{C}_m(t) = (i\hbar)^{-1} \sum_n C_n(t) e^{i\omega_{mn} t} H^J_{mn} \tag{2.5}$$

Expanding C's as power series in λ, where λ is a parameter, used to distinguish between various orders of perturbation calculation.

$$C_n = C_n^{(0)} + \lambda C_n^{(1)} + \lambda^2 C_n^{(2)} + \cdots$$

This is continuous analytical function of λ and for λ between zero and one. Now the equation becomes,

$$\dot{C}_m(t) = (i\hbar)^{-1} \sum_n \left(C_n^{(0)} + \lambda C_n^{(1)} + \lambda^2 C_n^{(2)} + \cdots \right) e^{i\omega_{mn} t} H^J_{mn} \tag{2.6}$$

Equating the coefficients of corresponding power of λ. Equating coefficients of λ^0

$$i\hbar \dot{C}_m = 0$$

Equating coefficients of λ^1,

$$i\hbar \dot{C}_m^{(1)} = \sum_n C_n^{(0)} H^J_{mn} e^{i\omega_{mn} t}$$

and in general

$$\dot{C}_m^{(s+1)} = (i\hbar)^{-1} \sum_n C_n^{(s)}(t) e^{i\omega_{mn} t} H^1_{mn} \tag{2.7}$$

The superscript (s) on $C_m(t)$ represents order of the perturbation having the value $s = 0, 1, 2, 3, \cdots\cdots\cdots$.

For zeroth order calculation, we have $\dot{C}_m^{(0)} = 0$ and $C_m^{(0)}$ = constant in time. As an initial condition at $t = 0$, we take the system to be in particular state ψ_k, so that $\Psi(0) = \psi_k$ For convenience without loss of generality, we may put $C_n^{(0)} = \int \psi_n^* \psi_k dV = \delta_{nk}$ accordingly as the initial state k is one of the discrete or continuous set. Sometimes the initial state is specified in the distant past, in that case,

$$\lim_{t_0 \to -\infty} C_n(t_0) = \delta_{nk}$$

Since departures from these values at later times will depend on λ.

First order perturbation

For first order calculation, this yields the differential equation (for $m \neq k$)

$$\dot{C}_m^{(1)}(t) = (i\mathrm{k})^{-1} \langle \psi_m^* \left| \mathrm{H}^{\mathrm{J}}(t) \right| \psi_k \rangle e^{i(E_m - E_k)t/\mathrm{k}}$$

upon integration over t

$$C_m^{(1)}(t) = (i\mathrm{k})^{-1} \int_0^t dt^{\mathrm{J}} e^{i(E_m - E_k)t^{\mathrm{J}}/\mathrm{k}} \langle \Phi_m \left| \mathrm{H}^{\mathrm{J}}(t^{\mathrm{J}}) \right| \Phi_k \rangle$$

$$C_m^{(1)}(t) = (i\mathrm{k})^{-1} \int_0^t dt^{\mathrm{J}} e^{i\omega_{mk}t^{\mathrm{J}}} \langle \psi_m \left| \mathrm{H}^{\mathrm{J}}(t^{\mathrm{J}}) \right| \psi_k \rangle \qquad (2.8)$$

Where,

$$\omega_{mk} = \frac{E_m - E_k}{\mathrm{k}}$$

Single-photon ionization

If, $s = 0$, $\lambda = 1$ from equations Eq. (2.7) and Eq. (2.8) when a light quantum or **a single photon** is emitted or absorbed. These transitions occur directly, without any intermediate states, or one intermediate state. The transition probabilities are then given by the matrix element of $\mathrm{H}^{\mathrm{J}}(t)$ for the direct transition from the initial to the final state. Thus,

$$C_m^{(1)} = (i\mathrm{k})^{-1} \int_0^t dt^{\mathrm{J}} e^{i(E_m - E_k)t^{\mathrm{J}}/\mathrm{k}} \langle \Phi_m^* \left| \mathrm{H}^{\mathrm{J}}(t) \right| \Phi_k \rangle$$

The probability that a later time t, the state $\Psi(t)$ is an eigenstate of H_0 with energy E_n, then Φ_n according to the expansion postulate

$$P^{(N)} = |\langle \psi_n \mid \Psi(t) \rangle|^2 = \cdot C_n^{(N)}(t) \cdot^2 \tag{2.9}$$

This is the probability (that is the particle in one state or another) at time t under influence of the perturbation, here the atom is in the stationary state n and N is the order of perturbation.

Perturbation constant in time

Consider a perturbation that is constant in time and that it operates only during the time 0 to t.

$$C_m^{(1)} = (i\mathrm{k})^{-1} \int_0^t e^{i\omega_{mk}t'} \mathrm{H}'_{mk} dt' \tag{2.10}$$

Where, $C_n^{(0)} = 1$ and H'_{mk} comes out from integration sign. Thus,

$$C_m^{(1)} = (i\mathrm{k})^{-1} \mathrm{H}'_{mk} \left[\frac{e^{i\omega_{mn}t'}}{i\omega_{mk}} \right]_0^t$$

$$C_m^{(1)} = \frac{\mathrm{H}'_{mk}}{\mathrm{k}} \left[\frac{1 - e^{i\omega_{mk}t}}{\omega_{mk}} \right] = \frac{\mathrm{H}'_{mk}}{\mathrm{k}} \left[\frac{1 - e^{i\omega_{mk}t}}{\omega_{mk}} \right] \tag{2.11}$$

Transition probability

It is the probability of transition of the particle from the initial state as k^{th} state to final state as m^{th} can be determined as,

$$\cdot \quad \cdot \text{Probability } (P_m^{(1)}) = C^2$$

$$(t) \qquad = \cdot C_m^{(1)*} \times C_m^{(1)} \cdot$$

$$= \frac{|\mathrm{H}_{mk'}|^2}{(\mathrm{k}\omega_{mk})_2^2} \left[1 - e^{i\omega_{mk}t} \right] \left[1 - e^{-i\omega_{mk}t} \right]$$

$$= \frac{|\mathrm{H}_{mk}|}{(\mathrm{k}\omega_{mk})^2} \left[1 - e^{i\omega_{mk}t} - e^{-i\omega_{mk}t} + 1 \right]$$

$$= \frac{|\mathrm{H}'_{mk}|^2}{(\mathrm{k}\omega_{mk})^2} \left[2 - \frac{2}{2} (e^{i\omega_{mk}t} + e^{-i\omega_{mk}t} \right]$$

$$= \frac{|\mathrm{H}'_{mk}|^2}{(\mathrm{k}\omega_{mk})_2^2} (2 - 2\cos\omega_{mk}t)$$

$$= \frac{|\mathrm{H}'_{mk}|^2}{(\mathrm{k}\omega_{mk})^2} \left[4\sin^2 \frac{\omega_{mk}t}{2} \right]$$

Constant transition rate or Fermi golden rule

It is the probability per unit time also known as transition rate. Applying equation Eq. (2.9) into a system, whose energy levels are very closely spaced. We consider a situation, where (i) there is large number of states m within the energy interval ΔE. and (ii) ΔE is yet small enough that the variation of $|H^{I}_{mk}|$ with m within this interval is negligible. Under this condition the total transition probability to all states is given by the mean square amplitude of the disturbances.

$$\Gamma = \frac{\overline{P}}{t} = \frac{\sum_m \cdot \overline{C_m^{(1)}(t)\cdot}^2}{t} = \frac{\overline{1}}{t}\frac{|H^{I}_{mk}|^2}{k^2}\sum_m 4\overline{\frac{\sin^2\frac{\omega_{mk}t}{2}}{\omega_{mk}^2}}$$

We have assumed so far that the transition frequency ω_{mk} is a well defined quantity. In practice, however, there is always some uncertainty in the value of ω_{mk}. Even in an idealized experiment with perfect frequency resolution, there is always an uncertainty in the intrinsic value of the spectral line width owing to the spontaneous emission. This uncertainty can be accounted for integrating the expression over the range $\Delta\omega$ and representing in terms of energy ΔE. Since appreciable contributions to the sum come only from within the interval ΔE, when there is a broad band of energies, then $|H^{I}_{mk}|$ is practically constant. Density of states (DOS) is defined by

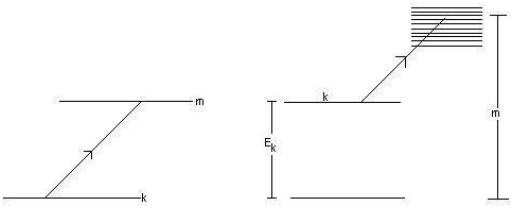


Figure 2.1: Number of states in final continuum states(Andrei, 2007)

$(\rho\ (E))\ \overline{m}\ \frac{\text{no of states}}{\text{enery interval}\,\Delta E}$ Here we have chosen k and m for the initial and final continuum states instead of g and f. Since E_k is fixed, we have $\Delta E_m = k(\omega_m - \omega_k) = k\Delta\omega_{mk}$. Or,

$$\text{no of states} = \text{DOS} \cdot \Delta E$$

To gain the probability $P(t)$ i. e. to find the system in any one of the continuum states at time t, we have to change sum over all relevant $|C_m(t)|^2$ into an integral. Thus,

$$\sum_m \cdot C_m^{(1)}(t) \cdot^2 = \sum_n = \int \rho(E_m) dE_m = \rho(E_m) \int dE_m$$

$$\sum_m \cdot C_m^{(1)}(t) \cdot^2 = \frac{|H'_{mk}|^2}{\hbar} \rho(E_m) \int \frac{4 \sin^2 \frac{\omega_{mk} t}{2}}{\omega_{mk}^2} d\omega_{mk}$$

Since, $d\omega_{mk} = \hbar^{-1} d(E_m - E_k) = \hbar^{-1} dE_m$. And $\rho(E_m)$ represents the number of final states with an energy between E_m and $E_m + dE_m$. The energy of final states $E_m = E_n + \hbar\omega$, known as energy density, or density of states. As the integrand is practically zero outside ΔE, Just for simplicity, taking the limits of integration as ($-\infty$ to $+\infty$). With this, integral can be written as

$$\int \frac{4 \sin^2 \omega_{mk} t/2}{\omega_{mk}^2} d\omega_{mk} = 2\pi t$$

Let, $\frac{\omega_{mk} t}{2} = x$ Then, $\omega_{mk} = \frac{2x}{t}$, $d\omega_{mk} = \frac{2dx}{t}$ Here,

$$\int_{-\infty}^{\infty} 4 \frac{\sin^2 x}{\frac{4}{t^2} x^2} \frac{2}{t} dx = 2t \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx = 2\pi t$$

$$\sum_m \cdot C_m^{(1)}(t) \cdot^2 = \frac{2\pi}{\hbar} t \, |H'_{mk}|^2 \rho(E_m)$$

This expression is directly proportional to t. Thus transition probability per unit time is defined as

$$\Gamma = \frac{1}{t} \sum_m \cdot C_m^{(1)}(t) \cdot^2 = \frac{2\pi}{\hbar} |H'_{mk}|^2 \rho(E_m) \qquad (2.12)$$

This is important result of time dependent perturbation theory (Mathews and Venkatesan, 1976), and also called the **Fermi's golden rule**. The transition rate depends next to $\rho(E_m)$ also on the square of the matrix element H'_{mk}. Almost all calculations of intensities of spectral lines, and many cross-sections for various processes are based on the use of this rule.

Ionization rate of Hydrogen atom:

We now calculate the probability of ionization of a hydrogen atom initially in its ground state, when it is placed in a harmonically time varying electric field. The

perturbation $H' = 2eE_0 r \cos \omega t$ Fermi-Golden rule for the transition rate,

$$\Gamma_{fg} = \frac{2\pi}{\hbar} |\langle f|H'|g\rangle|^2 \, \delta(E_f - E_g - \hbar\omega)$$

Taking the incoming wave to be an electromagnetic field having vector potential as:

$$\vec{A}(\vec{r}, t) = \vec{A}_0 \cos(\vec{k} \cdot \vec{r} - \omega t)$$

Hence the interaction Hamiltonian is given by replacing the electron kinetic energy term such as: $(p^2/2m)$ with $(\vec{p} + \frac{e}{c}\vec{A})^2/2m$ the relevant new term after neglecting higher order terms is

$$\frac{1}{2m}\left(\frac{e}{c}(\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p})\right)$$

Because under the coulomb gauge transformation, and $\vec{A} \cdot \vec{p} = \vec{p} \cdot \vec{A}$ Hence,

$$H' = \frac{e}{mc} \cos(\vec{k} \cdot \vec{r} - \omega t)\vec{A}_0 \cdot \vec{p} = H_0 e^{-i\omega t} + (H_0)^* e^{i\omega t} \; \varepsilon \cdot \vec{p}$$

It can also be written in terms of the atom's dipole moment er. Thus the matrix interaction Hamiltonian becomes

$$H'_{fg}(t) = \langle f|H'|g\rangle = \frac{e}{2mc}\tilde{A}_0 e^{-i\omega t}\varepsilon . i m\omega \, |\tilde{r}_{fg}| = \frac{ie\omega}{2mc}\tilde{A}_0 e^{-i\omega t}\varepsilon \cdot |\tilde{r}_{fg}|$$

Density of states: We make assumption that for the case of continuum of final state is the plane wave state, $|\vec{k}_f\rangle \propto e^{i\vec{k}_f \cdot \vec{r}}$ which has to be confined into a box of side L and use the boundary conditions. The normalized plane wave state becomes:

$$|\vec{k}\rangle = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} = \frac{1}{L^{3/2}} e^{i\vec{k}\cdot\vec{r}}$$

Suppose these states are very closely distributed, both in momentum space (k-space) and energy. Considering one dimensional case of a particle and using the boundary conditions $\Psi = 0$ at $x = 0$ and $\Psi = 0$ at $x = L$, $e^{ik\cdot L} = 1$ and $kL = 2n\pi$, where n is an integer or, $k = 2n\pi/L$. The density of states $\rho(E)$ in energy space is

$$\rho(E) = \frac{L}{2\pi}\frac{m}{\hbar^2 k}$$

For the density of states by multiplying $4\pi k^2$, since the states in the energy range lie between two close concentric spheres in k-space

$$\rho(k)\Delta k = \left(\frac{L}{2\pi}\right)^3 4\pi k^2 \Delta k$$

In terms of energy is, it gives

$$\rho(E)\Delta E = 4\pi k^2 \left(\frac{L}{2\pi}\right)^3 \frac{m}{\hbar^2 k} \Delta E$$

The ejected electron is detected by such an apparatus, which is restricted to a solid angle $d\Omega$, and then 4π are replaced by $d\Omega$.

Matrix element for hydrogen atom

The ground state wave function for hydrogen is

$$|g\rangle = |\psi_g\rangle = |100\rangle = \sqrt{\frac{1}{\pi a_0^3}}\, e^{-r/a_0} \tag{2.13}$$

and the final state wave function such as

$$|f\rangle = |\psi_f\rangle = e^{-ik_f r}$$

Here, the interaction Hamiltonian matrix for the hydrogen atom is

$$H_{fg} = \langle f|H|g\rangle = \left[\frac{1}{L^3}\right]^{3/2} \frac{e}{2mc} \sqrt{\frac{1}{\pi a_0^3}} \int d^3 r\, e^{-ik_f \cdot r} A_0 \cdot (-i\hbar\nabla)\, e^{-r/a_0}$$

Integrating by parts gives the gradient operator acting on the plane wave states, solving the integration, and using Fermi-Golden Rule:

$$\Gamma_{fg} = \frac{2\pi}{\hbar} |\langle f| H' |g\rangle|^2 \delta(E_f - E_g - \hbar\omega)$$

$$= \frac{2\pi}{\hbar} (1/L)^3 \left(\frac{e}{2mc}\right)^2 \frac{8\pi/a_0}{(a_0^{-2} + k_f^2)^2} \sqrt{\frac{1}{\pi a_0^3}}\, A_0 \cdot p_f\, \delta(E_f - E_g - \hbar\omega)$$

Here δ - function measures the density of possible outgoing states. The ejected electrons are measured by a sensitive detector to some small solid angle $d\Omega$. Hence density

of states in energy for outgoing solid angle $d\Omega$ is:

$$\rho(k, d\Omega) = (L/2\pi)^3 k(m/\hbar^2)d\Omega$$

Hence,

$$\Gamma_{fg} = \frac{2\pi}{\hbar}|\langle f|H'|g\rangle|^2 \delta(E_f - E_g - \hbar\omega)$$
$$= \frac{2\pi}{\hbar}\cdot(1/L)^{3/2}\left(\frac{e}{2mc}\right)\left(\frac{1}{\pi a_0^3}\right)^{1/2}(\vec{A}_0\cdot\hat{p}_f)\left(\frac{8\pi/a_0}{(a_0^{-2}+k_f^2)^2}\right)^2\cdot(L/2\pi)^3 k_f(m/\hbar^2)d\Omega \quad (2.14)$$

Here, $(\vec{A}_0\cdot\hat{p}_f)^2 = A_0^2 p_f^2\cos^2\theta$ ejection is most likely to be parallel to the electric field. The total ionization rate is given by the integrating the rate over all angles, and on the unit sphere $\overline{\cos^2\theta} = \overline{z^2} = 1/3$, thus,

$$(\vec{A}_0\cdot\hat{p}_f)^2 d\Omega = 4\pi A_0^2 p_f^2/3$$

The total ionization rate is:

$$\Gamma_{fg} = \frac{2\pi}{\hbar}\cdot(1/L)^{3/2}\left(\frac{e}{2mc}\right)\left(\frac{1}{\pi a_0^3}\right)^{1/2}\left(\frac{8\pi/a_0}{(a_0^{-2}+k_f^2)^2}\right)^2\cdot\times$$
$$\frac{4\pi}{3}A_0^2 p_f^2(L/2\pi)^3 k_f(m/\hbar^2)$$

$$\Gamma_{fg} = \frac{16e^2A_0^2p_f^3}{3mc^2\hbar^4a_0^5(a_0^{-2}+(p_f/\hbar)^2)^4}$$

Ionization cross-section:

The area of the disc equivalent to one atom is the ionization cross-section. Since during ionization an atom takes energy of $\hbar\omega$ from the incident beam, the rate of energy absorption is just $\hbar\omega\,\Gamma_{i-f}$, hence,

$$\hbar\omega\Gamma_{fg} = cE_\rho(\omega)\times \text{ Cross-section}(\sigma(\omega))$$

Energy density is given by ,

$$E_\rho(\omega) = \frac{1}{8\pi}\left(\cdot\overline{E}\cdot^2 + \cdot\overline{B}\cdot^2\right) = \frac{1}{8\pi}\,2\frac{\omega^2}{c^2}\overline{A_0^2\sin^2(k\cdot r-\omega t)}$$

Averaging over $\sin^2(k \cdot r - \omega t)$, gives the energy absorption density,

$$\langle E_\rho(\omega)\rangle = \frac{A_0^2\omega^2}{8\pi c^2}$$

This gives,

$$\frac{A_0^2\omega^2\sigma}{8\pi c} = k\omega\Gamma_{fg}$$

$$\sigma(\omega) = \frac{8\pi c k\omega\Gamma_{fg}}{A_0^2\omega^2}$$

$$= \frac{8\pi c k\omega}{A_0^2\omega^2} \times$$

$$\frac{2\pi}{k} \cdot \frac{1}{(1/L)^{3/2}} \cdot \left(\frac{e}{2mc}\right)^2 \cdot \frac{1}{\pi a_0^3} \cdot \frac{8\pi/a_0}{(a_0^{-2} + k_f^2)^2} \cdot \frac{4\pi}{3} A^2 p^2 (L/2\pi)^3 k (m/k^2)$$

On simplifying, we get (Shrestha, 2008):

$$\sigma(\omega) = \frac{128}{\omega}\left(\frac{e^2}{a_0^3 k^3}\right)\left(\frac{\pi p_f^3}{3mc}\right)\frac{1}{\left(a_0^{-2} + (p_f/k)^2\right)^4}$$

Various methods

The calculation of the transition amplitudes and transition probabilities of three-photon transition in Hydrogen atom involves a summation over discrete and continuum states. Different methods can be employed to evaluate this sum exactly. They are roughly divided into two classes such as perturbative and non-perturbative (Shih-I, 1986). We summarize few of the available and widely used methods for analyzing various multiphoton processes.

Green's function method

An alternative to Dalgarno method for performing the infinite summations, is to introduce the Green's functions associated with the Hamiltonian. The Green's function method replaces the summation over the complete atomic spectrum by the calculation of relevant Green's function. The relevant Green function for hydrogen atom is the Coulomb Green's function which can be obtained analytically in many form (Leplanche et al., 1976). This has been done when the atomic wave functions are known analytically, as in the case of Hydrogen atom (Chin and Lambroupoulos, 1984). For the Hamiltonian with the complete basis of discrete states $|\alpha\rangle$ with energy E_α, and

the continuum states $|c\rangle$ with energyE_c, the Green function $G(E, r, r')$ may be defined as

$$G(E, r, r') = \sum_{\alpha} \frac{\langle r|\alpha\rangle\langle\alpha|r'\rangle}{E - E_\alpha} + \int dc \frac{\langle r|c\rangle\langle c|r'\rangle}{E - E_c}$$

Mark Edwards presented a technique for calculating MPI Green function by using Wentzel- Kramers - Brillouin (WKB)approximation (Edwards, 1992).

Floquet theory

It is fully non perturbative approach for studying laser matter interaction, first used by J. H. Shirely in 1965. It permits the TDSE for an atomic system interacting with a periodical laser field to be reduced to an infinite set of time-independent coupled equations, in which the atom-field coupling is treated in a completely non-perturbative way. The Hamiltonian is then periodic,

$$H(t + T) = H(t)$$

with a period $T = 2\pi/\omega$. P V Likhatov (Likhatov and Telnov, 2009) presented *ab initio* time dependent non Hermitian Floquet for the calculation of MPI rates of hydrogen molecular ions subjected to intense linearly polarized monochromatic laser field with wavelength of 800nm. Recent progresses in theoretical investigation using non perturbative have been used to study light matter interaction at high intensity (Stancalie et al., 2010).

Pseudostate summation technique

Pseudostates summation is an accurate powerful method for carrying out the second-order sums common in atomic theoretical calculations. It is one of the efficient technique in which, the intermediate state of conventional second-order perturbation theory are replaced by the finite set of pseudostates and the energy denominator are replaced by expectation values of the unperturbed Hamiltonian with respect to those pseudostates (Drachman et al., 1990). Thus, it does not require sums over large numbers of discrete states and difficult integration over continuum states. The infinite summation over the complete set of unperturbed atomic states (intermediate states) are replaced by finite set of pseudostates, which are expanded in terms of basis which is discrete and complete (Kundiliya et al., 2001) (Kundiliya et al., 2001).

$$\varphi_j = e^{-ar} r^{l+j} Y_{lm}(\vartheta, \varphi)$$

and

$$j = 1, 2, \cdots N$$

where, a is the basis parameter, l is the angular momentum and N is the size of the basis. The target Hamiltonian is diagonalized in the basis and N pseudostates are obtained. They are

$$|n\rangle = \Psi_n = \sum_j \frac{C(n,j)\varphi_j}{r}$$

These psedostates have the normalization $\langle n|n'\rangle = \delta_{nn'}$ and the psedoenergies are given by

$$\langle n|H_0|n'\rangle = E_{n'}\delta_{nn'}$$

Two-photon transitions from the ground state (and the metastable $2s$ state) to the Rydberg states of atomic hydrogen are studied and calculated the transition amplitudes as a function of the frequency of one of the incident photons using the efficient pseudostate summation technique (Joshi, 2007). As the basis functions taken are of the simple form one can solve the integrals involved analytically to evaluate transition amplitudes. Recently used to calculate the molecular polarizabilities (Jones, 2010).

Coulomb-Volkov method (CV)

This is fully non-perturbative method for the studying the ionization of atoms or molecules by strong laser pulses. The long range coulomb potential in the presence of intense field has a significant influence on the final state of the ionization processes. In CV semiclassical Schrodinger equation (in length gauge), the dipole interaction potential is replaced by the dipole interaction energy as obtained as

$$i\frac{\delta}{\delta t}\Phi^v(r,t) = \left(\frac{\hat{p}^2}{2} - \frac{Z}{r} + F(t).r(t)\right)\Phi^v(r,t)$$

Where, the laser field $F(t)$ is defined below and $r(t)$ is the electron trajectory,

$$r(t) = r_0 + (t - t_0)p + (\alpha(t) - \alpha(t_0))$$

Where $\alpha(t) = \frac{1}{c}\int dt' A(t')$ is the quiver radius and r_0 is the initial position at $t = t_0$. Equation can be readily integrated to obtain the desired semiclassical CV wave function (Thomas, 2008).

$$\Phi_v^{\pm}(r,t) = e^{-\frac{1}{2}p^2t - i\varphi_c(t)}e^{\left(\frac{\pi Z}{2p}\right)}\Gamma(1 \mp iZ/p)e^{ip.r}F(\pm iZ/p, 1, \pm i(pr \mp p.r))$$

where, $\varphi_c(t) = \int_{t_0}^{t} (F(t') \cdot r(t'))dt'$ and

$$\Phi_v^{\pm}(r, t) = e^{-\frac{1}{2}p^2 t - i\varphi_c(t)} e^{(ip.r \mp i\frac{z}{p})ln(pr \mp p.r)}$$

The Coulomb effect on photo-ionization of Hydrogen atom in intense laser field with linearly and circularly polarized light is studied by representing the final continuum state by Coulomb Volkov state (Jingtao, 2007). The ionization of atoms and molecules by high harmonics laser pulses which are generated through Coulomb Volkov treatment (Duchateau et al., 2002) (Duchateau et al., 2000). A simple analytical approximation exists for the wave function of an unbound electron interacting both with strong circularly polarized laser field and an atomic Coulomb potential. This wave function is Volkov state with the first order Coulomb correction. The total photo-ionization rate in the strong field approximation grows more for linear than circular polarization due to coulomb correction (Bauer, 1997). The interference effect in the double differential of ionization cross-section of hydrogen atom are studied theoretically. The non-perturbative model Volkov and numerical solution of TDSE are developed for the ionization of atomic system by intense ultra short laser pulse and are applied with success to study the ionization by fast charged particle impact (Borbèly et al., 2009) later proved by numerically and experimentally (Sælen et al., 2010).

TDDFT method

Density functional theory (DFT), as first introduced by Hohenberg and Kohn (1964) and Kohn and Sham (1965), describes a system of interacting particles in terms of density. The theory is based on existence of exact mapping between densities and external potentials and leads to the density of interacting system being obtained from the density of auxiliary system of non-interacting particles moving in an effective local single-particle potential i. e. the particle interaction are treated in an averaged over-manner. A time dependent formalism of DFT (TDDFT) was provided by Runge and Gross (1984) (Taylor and Dundas, 1999), who showed that the time dependent density could be obtained from the response of non-interacting particles to the time dependent local effective potential.

$$V_s(r, t) = v(r, t) + \int dr' \frac{n(r', t)}{|r - r'|} + v_{xc}(r, t)$$

In this expression the first terms on the right hand side represent respectively, $v(r, t)$ = external potential, $\int dr' \frac{n(r',t)}{|r-r'|}$ = Hartree potential and $v_{xc}(r, t)$ = local exchange-correlation potential. Expanding the total wave function of the N-particle system as a Slater determinant of single-electron orbital $\phi_j(r, t)$, results in the density, $n(r, t)$, being given as:

$$n(r, t) = \sum_{j=1}^{N} |\phi_j(r, t)|^2$$

Both the variational-perturbation and configuration approaches to the physics of many-electron systems aim to include the correlation effects which are absent in the Hartree-Fock approximation. An alternative approach including correction effects is the density functional theory in which the electron number plays the central role rather than the many-electron wave function (Bransden and Joachain , 2003). Using a time dependent density functional theory (TDDFT) for many electrons. TDDFT with optimized potential and self interaction correction is given by:

$$i\frac{d}{dt}\Psi_{i\sigma}(r, t) = H(r, t)\frac{d\Psi_{i\sigma}(r, t)}{dt} = -\frac{1}{2}\nabla^2 + V_{eff,\sigma(r,t)} \quad \Psi_{i\sigma}(r, t)$$

Where, $i = 1, 2, 3, \cdots N_\sigma$ and $V_{eff,\sigma}(r, t)$ is the time dependent effective potential (Marques and Gross, 2004). MPI of rare gas atoms (He, Ne and Ar) in intense laser fields by means of self interaction free time dependent density functional theory (TDDFT) recently developed (Xiao-Min and Shih-I, 2001).

Experimental method

From the given figure (2.2) schematically depicts an experimental set up for studying atom in strong laser beams. The most crucial element is the short-pulse laser. The laser pulses used are often in femtosecond range, the shortest are well below 10 fs. Focussed intensities are needed to get into strong field regime are order of $10^{12} - 10^{14}$ W/cm^2. In last decade Ti-Sapphire laser became the most favorite tool. It operates at 800nm in near-infrared and provides very short pulse duration with high laser intensity at high repetition rate. An intense laser beam is focussed into an atomic gas jet and out going electrons are detected by an electron spectrometer, which record their momentum.

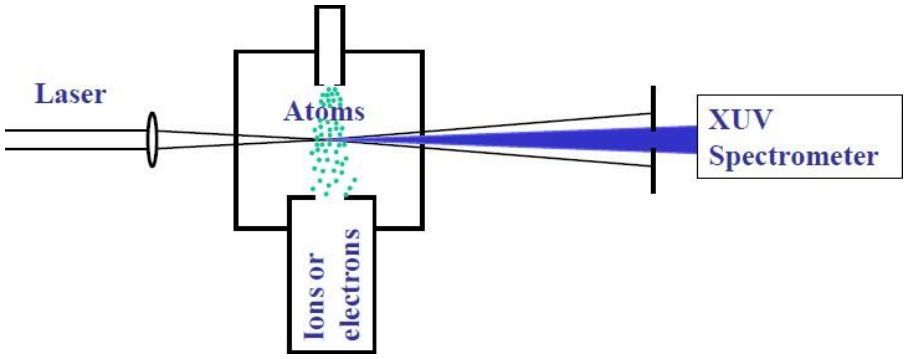


Figure 2.2: Principle of an experimental set up (Lewenstein and Huiller , 2008)

The three photon excitation of Xenon and Carbon monoxide was monitored by detecting the florescence decay in vacuum ultraviolet (Faisal et al., 1977). The first experimental evidence of destructive inference effects in multiphoton ionization shows a Cs atomic beam crossed with linearly polarized dye laser beam whose intensity reaches $20\ \mathrm{GW/cm^2}$ in $460 - 540$nm wavelength range (Morellec et al., 1980). The experimental study of femtosecond time-resolved molecular multiphoton ionization was done by T. Baumert. Femtosecond pump-probe techniques are combined with time-of-flight spectroscopy to measure transient ionization spectra of Na_2 in a molecular-beam experiment (Baumert et al., 1991). In strong Laser field all atoms have high probability to become singly or even multiply ionized. These ionization processes can be studied in great detail by imaging the momenta of resulting ions and electrons with COLTRIMS (Cold Target Recoil Ion Momentum Spectroscopy (Rolf, 2005)) (Dörner et al., 2001) (Constants, 1996). Multiphoton ionization and dissociation in diazirine have been studied experimentally via $304 - 325$ nm two-photon absorption and theoretically by using the EOM-CCSD and B3LYP methods (Fedorov et al., 2009). The experimental effects on the intermediate state of polarization and photo fragment angular distribution in REMPI of molecule (HCl)by two photon transition have been investigated (Chichinin et al., 2006). Recently MPI of Ar atoms with high intensity short laser pulse are observed and found distinct resonance structures in both ionization channels

(Zhang, 2010). The two color, two-photon ionization (2C2PI) of Ar atoms using femtosecond pulses of infrared laser radiation in the combination with its extreme-ultra violet harmonic shown that the intensities of photoelectron lines resulting from the absorption of photons from both fields strongly depend on the respective phases of fields and on the atomic quantities such as asymmetry parameter. These phases, which are notoriously difficult to measure can be estimated by changing the polarization state of laser radiation (O'Keeffe et al., 2004). The effect of interference stabilization is shown to exist in a system of two atomic levels coupled by a strong two color laser field, the two frequencies of which are close to a two photon Raman-type resonance between the chosen levels with open channels of one-photon ionization from both of them (Fedorov, 2003).

Dalgarno-Lewis method (DL) (1955)

This is the one on which we mainly concentrate for the calculation of transition amplitudes.

A. Dalgarno and J. T. Lewis provide an elegant method to obtain exact results for various orders in perturbation theory, while avoiding infinite sums which arise in each order (Dalgarno and Lewis, 1956). DL method was originally introduced for the evaluation of long range forces between atoms by perturbation theory and which enabled the exact results to be obtained for various orders in perturbation theory, and which replaced the infinite sums that arise in each order by the solution of differential equations. Later on it was modified by Schwartz (Schwartz, 1959) for various orders in higher perturbation theory.

In this method, the goal is to find the perturbed ground state Ψ^1, which is assumed to be related to the ground state in the form $\Psi^{(1)} = F\Psi$, where F is the scalar function of of the variables that occur in Hamiltonian, and then use of $E^{(2)} = \langle\Psi|H^{I}|\Psi^{(1)}\rangle - E^{(1)}\langle\Psi|\Psi^{(1)}\rangle = \langle\Psi|H^{I}|\Psi^{(1)}\rangle$ (the first-order energy correction $E^{(1)} = 0$) to compute the second-order energy correction ($E^{(2)}$). H^{I} being the perturbing Hamiltonian and Ψ is the ground state wave function for the hydrogen atom (Noureddine, 2005). The first-order equation in perturbations theory is given as.

$$(H_0 - E_0)\Psi^{(1)} + (H^{I} - E^{(1)})\Psi = 0$$

Setting $\Psi^{(1)} = F\Psi$ and defining a reduced potential by $V^{I} = H^{I} - E^{(1)} = H^{I} -$

$\langle\Psi|H'|\Psi^{(1)}\rangle$, then the first-order perturbation equation, it can be written as

$$[H_0, F]\Psi + V'\Psi = 0$$

Where $H_0 = -\frac{k^2}{2m}\nabla^2 + u(r)$ is the free Hamiltonian for the H-atom and $u(r) = \frac{e^2}{4\pi\varepsilon}\frac{1}{r}$ is the Coulombic potential. Because $u(r)$ and F commute, then we can show that the F is the solution of inhomogeneous differential equations.

In our calculation, we have assumed two auxiliary dimensionless operator F_j for two photon and G_{jk} for three photon, which enables us to perform the summation over the whole spectrum exactly. This operator are determined by a certain inhomogeneous differential equation which depend functionally on the initial wave function of the atom. We define F_j such as

$$\begin{aligned}(\hat{\epsilon}_j \cdot \hat{r})|g\rangle &= [F_j H_0 - H_0 F_j + \omega F_j]|g\rangle \\ (\hat{\epsilon}_j \cdot \hat{r})\psi &= (F_j H_0 - H_0 F_j + \omega F_j)\psi \\ &= \frac{\nabla^2 F_j}{2}\psi + \nabla F_j \cdot \nabla\psi + \omega F_j \psi\end{aligned} \tag{2.15}$$

Similarly for three photon ionization, it is expressed as:

$$\begin{aligned}(\hat{\epsilon}_k \cdot \hat{r})F_j|g\rangle &= [G_{jk}H_0 - H_0 G_{jk} + 2\omega G_{jk}]\,|g\rangle \\ (\hat{\epsilon}_k \cdot \hat{r})F_j\psi &= \frac{\nabla^2 G_{jk}}{2}\psi + \nabla G_{jk} \cdot \nabla\psi + 2\omega G_{jk}\psi\end{aligned} \tag{2.16}$$

Where, $(\hat{\epsilon}_j \cdot \hat{r})$ is the interaction part of Hamiltonian, ψ is the ground state wave function and H_0 is the unperturbed Hamiltonian for the system under consideration, which is given in atomic units as

$$\begin{aligned}H_0 &= -\frac{\nabla^2}{2} - \frac{1}{r} \\ H_0|g\rangle &= -\frac{1}{2}|g\rangle\end{aligned} \tag{2.17}$$

Thus the idea is to include the contribution from the infinite summation over the intermediate state coming in the higher order perturbation matrix element. This can be done by defining a set of $N-1$ operators F_n with $n = 1, 2, \cdots N-1$ such as

$$(\hat{\epsilon}_k \cdot \hat{r})F_{n-1}|g\rangle = (F_n H_0 - H_0 F_n + n\omega F_n)|g\rangle$$

Here the appearance of $(N-1)^{th}$ order transition amplitude as inhomogeneous term for the determination of the N^{th} order transition amplitude is a general feature of this method (Delone and Krainov, 1999). Thus instead of finding the contribution from the summing over all the intermediate states it is enough to find an analytical expression for F_n. Its detail application is given in chapter three and four.

The method is used as perturbation and determining energy levels of diatomic molecular ion (Bailey, 1965) as sum rule (Pyykko, 1967). The Dalgarno and Lewis summation technique as used in the Rayleigh and Schrodinger perturbation theory is examined. It is shown that this technique forms an independent perturbation theory and can be used to deal with both bound- and continuum-state problems (Nandi, 1996). Efficient and accurate method for the calculation of multiphoton ionization process (Chang and Poe, 1976). Three- photon ionization of Cs I initially excited in state 6p near the resonance have been studied by Dalgarno Lewis method (Crance and Aymar, 1979).

CHAPTER 3

Two-Photon Ionization

Interaction hamiltonian for multiple beams

When two or more electromagnetic fields of different frequencies (or same) are physically superposed, the linear superposition equation implies that the fields readjust themselves into a new mean frequency whose common amplitude undulates at half their difference frequency (Dong-Ik and Chandrashekhar, 2003). The multiphoton ionization of Hydrogen atom for two and three photon processes are studied by using two and three color beams (Aurelia, 1992; Bivona et al., 2008; Potvliege and Smith, 1991). MPI of two and three color beams of same frequency but different polarization have been studied (Fifirig and Stroe, 2002). Calculation of differential and total ionization cross-section by two radiation field with different properties have been reported (Bivona et al., 1991). Ionization rates, angular distributions, and above-threshold-ionization spectra for a hydrogen atom in a strong, two-color laser field is calculated. The two lasers are first- and second-harmonic fields with the same intensity and a constant relative phase difference between them. In all cases, they found that the total ponderomotive shift of the ionization limit is the sum of the shifts for the two individual fields (Kenneth and Kenneth, 1992). Perturbative calculation are done by Coherence superposition of three harmonics. Numerical results reveal a strong dependence of ionization rate on the relative phases of harmonic with respect ro the fundamental (Fifirig, 2000, 2001; Fifirig et al., 2000). The atomic photo-effect due to a monochromatic radiation of low intensity, in the presence of another intense monochromatic field (the laser) is also studied by M. Fifirig (Fifirig, 2003). Multiphoton resonant ionization of hydrogen atom exposing to two color laser pulses are studied, it finds that ionization probability shows several resonance peaks and is also much larger than the linear superpositions of probabilities by applying

two laser separately (Wang and Fang, 2008).

We consider a ground state hydrogen atom (IP = 0.5 a. u.) interacting with multiple beams (n_b) taken as superposition of fundamental frequency ω. From now we consider atomic units, for detail see appendix (1).

$$H(1s) + \sum_{n_b} N\nu(\hat{\epsilon}_j) = H^+ + e^-(E_k, \mathrm{k}k)$$

where, E_k the energy of ejected electron with momentum $\mathrm{k}k$ and N is the number of photons absorbed.

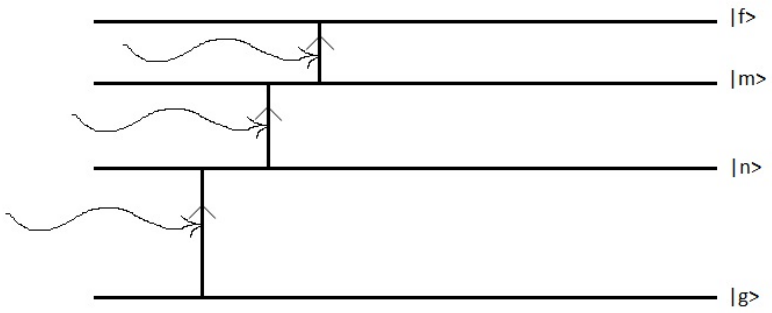


Figure 3.1: MPI due to multiple beams

Single-photon ionization

The electron is released by the absorption of single photon from multiple beams i.e they might be from one color-one photon (1P1C), two color-one photon (1P2C), and three color-one photon(1P3C). We need to calculate first-order perturbation. The expansion coefficient starting from the most general term as:

$$\dot{C}_f^{(s+1)} = \frac{1}{i}\sum_g C_g^{(s)} \langle f | H | g \rangle e^{i\omega_{fg} t} \tag{3.1}$$

Where the interaction Hamiltonian H^I is expressed as:

$$H^I = \sum_j \hat{\epsilon}_j \cdot \hbar E_{oj} e^{-i\omega_j t}$$

and the laser frequency ω_j represents different for different beams. For first perturbation, $s = 0$, and we suppose the first state is $|n\rangle$ as final state and initial state as ground state $|g\rangle$ such as:

$$\begin{aligned} \dot{C}_n^{(1)} &= \frac{1}{i} \sum_m C_g^{(0)} \sum_j \langle n | H_j | g \rangle e^{i(\omega_{nn} - \omega_j)t} \\ C_g^{(0)} &= \delta_{ng} = 1 \\ \dot{C}_n^{(1)} &= \frac{1}{i} \sum_j \langle n | H_j | g \rangle e^{i(\omega_{ng} - \omega_j)t} \end{aligned} \tag{3.2}$$

The interaction Hamiltonian $H^I(t)$, let us say (just for simplicity), H_j if the beams have same frequencies, but different polarization is in form as:

$$\begin{aligned} H^I(t) &= \sum_{j=1to3} \hat{\epsilon}_j \cdot \hbar E_{0j} e^{i(\omega t + \delta_j)} \\ &= \hat{\epsilon}_j \cdot \hbar E_{0j} e^{i(\omega t + \delta_j)} + \hat{\epsilon}_k \cdot \hbar E_{0k} e^{i(\omega t + \delta_k)} \\ &\quad + \hat{\epsilon}_l \cdot \hbar E_{0l} e^{i(\omega t + \delta_l)} \end{aligned}$$

Assuming, $H_j = \hat{\epsilon}_j \cdot \hbar E_{0j}$ for $j^{th} = 1, 2,$ or 3 beams having same frequency, but different polarization (δ_j) and intensity E_{0j} , similarly for $H_k = \hat{\epsilon}_k \cdot \hbar E_{0k}$ and $H_l = \hat{\epsilon}_l \cdot \hbar E_{0l}$ have the same meaning with different beams of k^{th} and l^{th} respectively.

Thus from (3.2), we have

$$\frac{\partial C_n^{(1)}(t)}{\partial t} = \frac{1}{i} \sum_{n_b=1}^{3} \langle n | H^I(t) | g \rangle e^{i(\omega_{ng} - \omega_j)t}$$

If the beams are particularly 1, 2 and 3, of their respective frequencies and polarization, the equation becomes:

$$\frac{\partial C_n^{(1)}(t)}{\partial t} = \frac{1}{i} \left[\langle n | H_1 | g \rangle e^{i(\omega_{ng} - \omega_1)t} + \langle n | H_2 | g \rangle e^{i(\omega_{ng} - \omega_2)t} + \langle n | H_3 | g \rangle e^{i(\omega_{ng} - \omega_3)t} \right] \tag{3.3}$$

Integrating limit from 0 to t,

$$C_n^{(1)}(t) = \langle n|H_1|g\rangle \frac{1 - e^{i(\omega_{ng}-\omega_1)t}}{(\omega_{ng} - \omega_1)} + \langle n|H_2|g\rangle \frac{1 - e^{i(\omega_{ng}-\omega_2)t}}{(\omega_{ng} - \omega_2)} + \langle n|H_3|g\rangle \frac{1 - e^{i(\omega_{ng}-\omega_3)t}}{(\omega_{ng} - \omega_3)} \quad (3.4)$$

For the beams *j, k,* and *l*, of same frequencies, but different polarization, the firs-order perturbation theory becomes:

$$\frac{\partial C_n^{(1)}(t)}{\partial t} = \frac{1}{i}\langle n|H_j|g\rangle e^{i(\omega_{ng}-\omega)t} + \langle n|H_k|g\rangle e^{i(\omega_{ng}-\omega)t} + \langle n|H_l|g\rangle e^{i(\omega_{ng}-\omega)t}$$

Integrating limit from 0 to t

$$C_n^{(1)}(t) = \langle n|H_j|g\rangle \frac{1 - e^{i(\omega_{ng}-\omega)t}}{(\omega_{ng} - \omega)} + \langle n|H_k|g\rangle \frac{1 - e^{i(\omega_{ng}-\omega)t}}{(\omega_{ng} - \omega)} + \langle n|H_l|g\rangle \frac{1 - e^{i(\omega_{ng}-\omega)t}}{(\omega_{ng} - \omega)}$$

Here, E_{0j} is the amplitude of the electromagnetic field along the direction of the polarization vector $\hat{\epsilon}_j$. Similarly for k^{th} and l^{th} beams, we can have E_{0k} and E_{0l} are the amplitudes along the direction $\hat{\epsilon}_k$ and $\hat{\epsilon}_l$.

Therefore we can write, in general single-photon ionization for multiple beams as:

$$C_f^{(1)}(t) = -i \int_0^t dt' H_{fg}^{J}(t') e^{i\omega_{fg}t'} C_g^{(0)}$$

Thus we know that $H_{f\,g}^{J}$, the interaction Hamiltonian consists of both intensity and matrix part (transition from ground state to the final state). Let us say a new symbol $D_{fg}^{(1)}$ as transition amplitude containing both the intensity and the matrix part. Thus the transition amplitude for the one-photon ionization is :

$$D_{fg}^{(1)} = -\sum_{j=1}^{n_b} \sqrt{\frac{I_j}{\bar{I}}}\, e^{i\delta_j} M_j^{(1)}$$

where, $I_j = E_{0j}^2$ is the intensity of the j^{th} beams, $\bar{I}$, is the mean intensities of multiple beams, and $M_j^{(1)}$ is the matrix element given as

$$M_j^{(1)} = \langle f|\hat{\epsilon}_j \cdot \vec{r}|g\rangle$$

This is the simplest form matrix element of known initial and final state wave function

of hydrogen atom. We have evaluated this integration for one-photon ionization for linearly polarized light of frequency ω assuming final wave as plane wave in chapter 2. This shows probability dependence linearly on intensity (I_j) with phase $e^{i\delta_j}$ for the multiple beams of polarization $\hat{\epsilon}_j$.

Two-photon processes(2PP)

In the two-photon absorption, the two-photons simultaneously transfer their energy to the atom for their transition. In the case when laser radiation contains two fields with polarization vector*j* and *k*, the final continuum of energy $E = E_1 + 2k\omega$.Similar situation occur in the case of three beams of same frequency with polarization vectors*j*, *k* and *l*. The same final state is reached quantum interference of six different routes. We thus need to evaluate second order perturbation. Here we assume second state as $|m\rangle$ as final state and initial state is the same as in single-photon processes.

Beams having different frequencies and different polarization, the second-order perturbation theory is expressed as:

$$\dot{C}_m^{(2)} = \frac{1}{i}\sum_n C_n^{(1)}\langle m|H'|n\rangle e^{i\omega_{mn}t} \tag{3.5}$$

$$\dot{C}_m^{(2)} = \frac{1}{i}\sum_n C_n^{(1)}\sum_k \langle m|H_k|n\rangle e^{i(\omega_{mn}-\omega_k)t} \tag{3.6}$$

$$= -\frac{1}{i}\sum_{n\ j}\sum \langle n|H_j|g\rangle \frac{e^{i(\omega_{ng}-\omega_j)t}-1}{(\omega_{ng}-\omega_j)}\sum_k \langle m|H_k|n\rangle e^{i(\omega_{mn}-\omega_k)t}$$

$$= -\frac{1}{i}\sum_{j,k}\sum_n \langle m|H_k|n\rangle\langle n|H_j|g\rangle \frac{e^{i(\omega_{ng}+\omega_{mn}-\omega_k-\omega_j)t}-e^{i(\omega_{mn}-\omega_k)t}}{(\omega_{ng}-\omega_j)}$$

On integrating, the expression becomes as:

$$C_m^{(2)} = \sum_{j,k}\sum_n \langle m|H_k|n\rangle\langle n|H_j|g\rangle \frac{1-e^{i(\omega_{ng}+\omega_{mn}-\omega_k-\omega_j)t}}{(\omega_{ng}-\omega_j)(\omega_{mn}+\omega_{ng}-\omega_j-\omega_k)} \tag{3.7}$$

For the same frequency, but different polarization:

$$\dot{C}_m^{(2)} = E_{0k}\frac{1}{i}\sum_n C_n^{(1)}(t)\sum_k \langle m|\hat{\epsilon}_k\cdot\hat{r}|n\rangle e^{i(\omega_{mn}-\omega)t} \tag{3.8}$$

$$= -E_{0j}E_{0k}\frac{1}{i}\sum_n\sum_j \langle n|\hat{\epsilon}_j\cdot\hat{r}|g\rangle \frac{e^{i(\omega_{ng}-\omega)t}-1}{(\omega_{ng}-\omega)}\sum_k \langle m|\hat{\epsilon}_k\cdot\hat{r}|n\rangle e^{i(\omega_{mn}-\omega)t} \tag{3.9}$$

$$= -E_{0j}E_{0k}\frac{1}{i}\sum_{j,k}\sum_n \langle m|\hat{\epsilon}_k\cdot\hat{r}|n\rangle\langle n|\hat{\epsilon}_j\cdot\hat{r}|g\rangle \frac{e^{i(\omega_{ng}+\omega_{mn}-2\omega)t}-e^{i(\omega_{mn}-\omega)t}}{(\omega_{ng}-\omega)}$$

By integrating:

$$C_m^{(2)} = E_{0j}E_{0k}\sum_{j,k}\sum_n \langle m|\hat{\epsilon}_k\cdot\hat{r}|n\rangle\langle n|\hat{\epsilon}_j\cdot\hat{r}|g\rangle \frac{1-e^{i(\omega_{ng}+\omega_{mn}-2\omega)t}}{(\omega_{ng}-\omega)(\omega_{mn}+\omega_{ng}-2\omega)}$$

$$C_m^{(2)} = -E_{0j}E_{0k}\sum_{j,k}\sum_n \langle m|\hat{\epsilon}_k\cdot\hat{r}|n\rangle\langle n|\hat{\epsilon}_j\cdot\hat{r}|g\rangle \frac{e^{i(\omega_{ng}+\omega_{mn}-2\omega)t}-1}{(\omega_{mn}+\omega_{ng}-2\omega)}\times\frac{1}{(\omega_{ng}-\omega)}$$

$$C_m^{(2)} = -E_{0j}E_{0k}\sum_{j,k}\sum_n \langle m|\hat{\epsilon}_k\cdot\hat{r}|n\rangle\langle n|(\hat{\epsilon}_j\cdot\hat{r})|g\rangle \delta(\omega_{ng}+\omega_{mn}-2\omega)\times\frac{1}{(\omega_{ng}-\omega)}$$

$$C_m^{(2)} = -E_{0j}E_{0k}\sum_{j,k}\sum_n \langle m|\hat{\epsilon}_k\cdot\hat{r}|n\rangle\langle n|\hat{\epsilon}_j\cdot\hat{r}|g\rangle \delta(\omega_{mg}-2\omega)\times\frac{1}{(\omega_{ng}-\omega)} \tag{3.10}$$

Since atoms are small compared to the wavelength of light, the amplitudes of electric field will not vary significantly over the dimensions of atom. We can therefore take them constants out from the calculation of integrals (Mark, 2006). We have retained only those terms in which the denominators approaches zero. Here we can see that a resonance occurs at $\omega_{mg} = 2\omega$ corresponding to the two photon transition for the identical laser frequency ω, from the ground state $|g\rangle$ to the final state $|m\rangle$ through one intermediate state $|n\rangle$. Thus, the matrix element $D^{(2)}_{mg}$

$$D^{(2)}_{mg} = \sum_{j,k}\frac{\mathbf{r}_j\mathbf{r}_k}{I}e^{-i(\delta_j+\delta_k)}M_{jk} \tag{3.11}$$

where

$$M^{(2)}_{mg} = \sum_{j,k}\sum_n \frac{\langle m|\hat{\epsilon}_k\cdot\hat{r}|n\rangle\langle n|\hat{\epsilon}_j\cdot\hat{r}|g\rangle}{(\omega_{ng}-\omega)} \tag{3.12}$$

The infinite intermediate sum includes both discrete and continuum states. We there-

fore can express the transition amplitude for two-photon processes as:

$$D_{mg}^{(2)} = \sum_{j,k}^{n_b} \sqrt{\frac{I_j I_k}{\bar{I}^2}} \; e^{-i(\delta_j+\delta_k)} M_{mg}^{(2)} \tag{3.13}$$

Thus, the matrix element $M_{mg}^{(2)}$ of (3.13) for two-photon ionization is our main concern to evaluate. Once we know the matrix element, we can expressed the transition amplitude as given in Eq. (3.13) and hence the ionization rate, cross-section etc. For the particular beams of 1, 2 and 3 of their respective frequencies and polarization, the second-order perturbation theory is expressed as:

$$\begin{aligned}
\frac{\partial C_m^{(2)}(t)}{\partial t} &= \frac{1}{i\hbar}\Big[\sum_n \langle m|H_1|n\rangle\langle n|H_1|g\rangle \; \frac{1-e^{i(\omega_{ng}-\omega_1)t}}{(\omega_{ng}-\omega_1)} \; e^{i(\omega_{mn}-\omega_1)t} \\
&+ \sum_n \langle m|H_2|n\rangle\langle n|H_1|g\rangle \; \frac{1-e^{i(\omega_{ng}-\omega_1)t}}{(\omega_{ng}-\omega_1)} \; e^{i(\omega_{mn}-\omega_2)t} \\
&+ \sum_n \langle m|H_3|n\rangle\langle n|H_1|g\rangle \; \frac{1-e^{i(\omega_{ng}-\omega_1)t}}{(\omega_{ng}-\omega_1)} \; e^{i(\omega_{mn}-\omega_3)t} \\
&+ \sum_n \langle m|H_2|n\rangle\langle n|H_2|g\rangle \; \frac{1-e^{i(\omega_{ng}-\omega_2)t}}{(\omega_{ng}-\omega_2)} \; e^{i(\omega_{mn}-\omega_2)t} \\
&+ \sum_n \langle m|H_1|n\rangle\langle n|H_2|g\rangle \; \frac{1-e^{i(\omega_{ng}-\omega_2)t}}{(\omega_{ng}-\omega_2)} \; e^{i(\omega_{mn}-\omega_1)t} \\
&+ \sum_n \langle m|H_3|n\rangle\langle n|H_2|g\rangle \; \frac{1-e^{i(\omega_{ng}-\omega_2)t}}{(\omega_{ng}-\omega_2)} \; e^{i(\omega_{mn}-\omega_3)t} \\
&+ \sum_n \langle m|H_3|n\rangle\langle n|H_3|g\rangle \; \frac{1-e^{i(\omega_{ng}-\omega_3)t}}{(\omega_{ng}-\omega_3)} \; e^{i(\omega_{mn}-\omega_3)t} \\
&+ \sum_n \langle m|H_1|n\rangle\langle n|H_3|g\rangle \; \frac{1-e^{i(\omega_{ng}-\omega_1)t}}{(\omega_{ng}-\omega_1)} \; e^{i(\omega_{mn}-\omega_1)t} \\
&+ \sum_n \langle m|H_2|n\rangle\langle n|H_3|g\rangle \; \frac{1-e^{i(\omega_{ng}-\omega_3)t}}{(\omega_{ng}-\omega_3)} \; e^{i(\omega_{mn}-\omega_2)t}
\end{aligned} \tag{3.14}$$

Integrating limit from 0 to t,

$$C_m^{(2)}(t) = \sum_n \langle m|H_1|n\rangle\langle n|H_1|g\rangle \frac{1 - e^{i(\omega_{mn}-\omega_{ng}-2\omega_1)t}}{(\omega_{mn}-\omega_{ng}-2\omega_1)(\omega_{ng}-\omega_1)}$$
$$+ \sum_n \langle m|H_2|n\rangle\langle n|H_1|g\rangle \frac{1 - e^{i(\omega_{mn}-\omega_{ng}-\omega_1-\omega_2)t}}{(\omega_{mn}-\omega_{ng}-\omega_1-\omega_2)(\omega_{ng}-\omega_1)}$$
$$+ \sum_n \langle m|H_3|n\rangle\langle n|H_1|g\rangle \frac{1 - e^{i(\omega_{mn}-\omega_{ng}-\omega_1-\omega_3)t}}{(\omega_{mn}-\omega_{ng}-\omega_1-\omega_3)(\omega_{ng}-\omega_1)}$$
$$+ \sum_n \langle m|H_2|n\rangle\langle n|H_2|g\rangle \frac{1 - e^{i(\omega_{mn}-\omega_{ng}-2\omega_2)t}}{(\omega_{mn}-\omega_{ng}-2\omega_2)(\omega_{ng}-\omega_2)}$$
$$+ \sum_n \langle m|H_1|n\rangle\langle n|H_2|g\rangle \frac{1 - e^{i(\omega_{mn}-\omega_{ng}-\omega_1-\omega_2)t}}{(\omega_{mn}-\omega_{ng}-\omega_1-\omega_2)(\omega_{ni}-\omega_2)}$$
$$+ \sum_n \langle m|H_3|n\rangle\langle n|H_2|g\rangle \frac{1 - e^{i(\omega_{mn}-\omega_{ng}-\omega_2-\omega_3)t}}{(\omega_{mn}-\omega_{ng}-\omega_2-\omega_3)(\omega_{ng}-\omega_2)}$$
$$+ \sum_n \langle m|H_3|n\rangle\langle n|H_3|g\rangle \frac{1 - e^{i(\omega_{mn}-\omega_{ng}-2\omega_3)t}}{(\omega_{mn}-\omega_{ng}-2\omega_3)(\omega_{ng}-\omega_3)}$$
$$+ \sum_n \langle m|H_1|n\rangle\langle n|H_3|g\rangle \frac{1 - e^{i(\omega_{mn}-\omega_{ng}-\omega_1-\omega_3)t}}{(\omega_{mn}-\omega_{ng}-\omega_1-\omega_3)(\omega_{ng}-\omega_3)}$$
$$+ \sum_n \langle m|H_2|n\rangle\langle n|H_3|g\rangle \frac{1 - e^{i(\omega_{mn}-\omega_{ng}-\omega_2-\omega_3)t}}{(\omega_{mn}-\omega_{ng}-\omega_2-\omega_3)(\omega_{ng}-\omega_3)}$$

Where, H_1, H_2, and H_3 are the interaction hamiltonian for 1, 2 and 3rd beams with frequencies ω_1, ω_2, and ω_3 respectively. Thus, for different frequencies, matrix element becomes:

$$M_{mg}^{(2)} = \sum_{j,k}\sum_n \frac{\langle m|H_k|n\rangle\langle n|H_j|g\rangle}{(\omega_{ng} - \omega_j)} \tag{3.15}$$

$$M_{mg}^{(2)} = \sum_n \frac{\langle m|H_k|n\rangle\langle n|H_j|g\rangle}{(\omega_{ng} - \omega_j)} + \sum_n \frac{\langle m|H_k|n\rangle\langle n|H_j|g\rangle}{(\omega_{ng} - \omega_k)} \tag{3.16}$$

Calculation of second order matrix element

We thus need to calculate the matrix element of H^{I} between the pair of atomic states. The result given (3.12) allows us to evaluate the matrix element for the particular transition if the initial and final state wave function are known.

Dalgarno-Lewis(DL) method

Now we will apply Dalgarno-Lewis's principle, the idea of DL method is to define an auxiliary operator such that the evaluation of intermediate sum is not needed. Here let us define an operator F_j , then from (2.15) we have

$$\hat{\epsilon}_j \cdot \vec{r}|g\rangle = (H_0F_j - F_jH_0)\,|g\rangle - \omega F_j|g\rangle$$

Taking scalar product of bra vector n

$$\begin{aligned} \langle n|\hat{\epsilon}_j \cdot \vec{r}|g\rangle &= -\langle n|F_jH_0 - H_0F_j|g\rangle - \omega\langle n|F_j|g\rangle \\ &= -(E_g - E_n + \omega)\langle n|F_j|g\rangle \\ &= (E_n - E_g - \omega)\langle n|F_j|g\rangle \\ &= (\omega_{ng} - \omega)\langle n|F_j|g\rangle \end{aligned} \tag{3.17}$$

Using (3.12) in (3.17) and after canceling the denominator (3.12) becomes:

$$M^{(2)}_{mg} = \sum_{j,k}\sum_{n} \langle m|\hat{\epsilon}_k \cdot \vec{r}|n\rangle\langle n|F_j|g\rangle \tag{3.18}$$

Now using the and Closure relation $\sum_n |n\rangle\langle n| = I$, Thus the transition matrix element of (3.12) is reduced to

$$M^{(2)}_{mg} = \langle m|\hat{\epsilon}_k \cdot \vec{r}F_j|g\rangle \tag{3.19}$$

Hence the difficulties associated with the infinite summation is reduced to the problem of finding the appropriate expression for the operator F_j. Since $M^{(2)}_{mg}$ is a function of ω, we have to keep the important fact in our mind that, any analytical expression for the unknown operator F_j should display all the analytical properties present in the second order matrix element given in Eq.(3.12).

Expression for differential equation

In order to find the analytical form of F_j, we have to start its defining equations (2.15), it is also clear that the form of F_j depends on the initial state $|g\rangle$. Sice we are considering transforms from the ground sate to the final state, which is given from Eq. (2.13) for a. u. such as $|g\rangle = e^{-r}/\sqrt{\pi}$. With these assumptions the defining

equations (2.15) for F_j becomes

$$\begin{aligned}
\hat{\epsilon}_j \cdot \hat{r}|g\rangle &= -[F_j H_0 - H_0 F_j + \omega F_j]g\rangle \qquad (3.20)\\
\hat{\epsilon}_j \cdot \hat{r}\psi &= -(F_j H_0 - H_0 F_j + \omega F_j)\psi \\
&= -\left(F_j\left[-\frac{\nabla^2}{2} - \frac{1}{r}\right] - \left[-\frac{\nabla^2}{2} - \frac{1}{r}\right]F_j\right)\psi + \omega F_j\psi \\
&= -\left(-F_j\frac{\nabla^2}{2}\psi + \frac{\nabla^2}{2}(F_j\psi)\right) + \omega F_j\psi \\
&= -\left(-F_j\frac{\nabla^2}{2}\psi + \frac{1}{2}\left(\psi\nabla^2 F_j + F_j\nabla^2\psi + 2\nabla F_j\cdot\nabla\psi\right)\right) + \omega F_j\psi \qquad (3.21)\\
&= -\left(\frac{\nabla^2 F_j}{2}\psi + \nabla F_j\cdot\nabla\psi\right) + \omega F_j\psi
\end{aligned}$$

Thus,

$$\hat{\epsilon}_j \cdot \hat{r}|g\rangle = -\frac{\nabla^2 F_j}{2}\psi - \nabla F_j\cdot\nabla\psi - \omega F_j\psi \qquad (3.22)$$

In hydrogen atom, the electron potential is the well known spherically symmetric coulomb potential, owing to the spherically symmetric of $V(r) = -\frac{1}{r}$, it is very convenient to solve TDSE in Spherical coordinates (David, 2002), where the position vector

$$\hat{r} = r\hat{r} = (r\sin\vartheta\cos\varphi, r\sin\vartheta\sin\varphi, r\cos\vartheta,)$$

$$\nabla = \hat{r}\frac{\partial}{\partial r} + \frac{1}{r}\hat{\vartheta}\frac{\partial}{\partial\vartheta} + \hat{\varphi}\frac{1}{\sin\vartheta}\frac{\partial}{\partial\varphi}$$

and Laplacian

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}$$

and the orbital angular momentum $L = \hat{r}\times(-i\hbar\nabla)$, which is independent of r. Here, ϑ is the angle between r and arbitrarily chosen z axis(so called polar angle), and φ is angle between the x axis and the projection of r upon xy plane, so called azimuthal angle. Here, $\nabla\psi = -\nabla(e^{-r}) = -\psi\hat{r}$ By inspection we can see that the operator F_j has the angular dependence given by Legendre polynomial $P_l(\hat{k}\cdot\hat{r})$ and unknown radial function $f(r)$.

Let,

$$F_j = (\hat{\epsilon}_j\cdot\hat{r})f(\omega, r) \qquad (3.23)$$

Polarization dependance

Here, the polarization vector $\hat{\epsilon}_j$ these vectors are normalized such as $\hat{\epsilon}_j^* \cdot \hat{\epsilon}_j$ beam of radiations are parallel and along z direction, polarization is in the $x - y$ plane and for elliptical polarization

$$\hat{\epsilon}_j = \hat{e}_x \cos(\zeta_j/2) + i\hat{e}_y \sin(\zeta_j/2)$$

here $\hat{e}_x$ and $\hat{e}_y$represent the unit polarization vector along the direction x and y axis of the co-ordinate system, which are chosen semi-major and semi-minor axes of the ellipse described by the radiation. The ellipticity angle ζ_j takes the values $-\pi/2 \geq \zeta \geq \pi/2$ the values $\zeta = 0$ corresponds to linear $\zeta = \pm\pi/2$ corresponds to circular polarization. The angle ζ_j determines the helicity $h = \sin\zeta$ of the field ($h > 0$ and $h < 0$ represent the left and respectively right elliptically polarized light) (Fifirig, 2001).

Now from Eq. (3.22)

$$\begin{aligned}
\hat{\epsilon}_j \cdot \hat{\pi}\psi &= -\frac{1}{2} f\nabla^2\hat{\epsilon}\cdot\hat{\pi} + \hat{\epsilon}_j \cdot \hat{\pi}\nabla^2 f + 2\nabla\hat{\epsilon}_j \cdot \hat{\pi}\cdot\nabla f \\
&\quad - [f\nabla\hat{\epsilon}_j \cdot \hat{\pi} + \hat{\epsilon}\cdot\hat{\pi}\nabla f]\cdot\nabla\psi - \omega\hat{\epsilon}_j \cdot \hat{\pi} f\psi \\
&= -\frac{1}{2}\left[\hat{\epsilon}_j \cdot \hat{\pi}\nabla^2 f + 2\nabla\hat{\epsilon}_j \cdot \hat{\pi}\nabla f\right]\psi - f\left[\nabla\hat{\epsilon}_j \cdot \hat{\pi}\nabla\right. \\
&\quad - \hat{\epsilon}_j \cdot \hat{\pi}\nabla f\cdot\nabla\psi - \omega\hat{\epsilon}_j \cdot \hat{\pi} f\psi \\
&= -\frac{1}{2}\left[\hat{\epsilon}_j \cdot \hat{\pi}\nabla^2 f + 2\nabla\hat{\epsilon}_j \cdot \hat{\pi}\nabla f\right]\psi - f\left[\nabla\hat{\epsilon}_j \cdot \hat{\pi}(-\hat{r}\psi)\right. \\
&\quad - \hat{\epsilon}_j \cdot \hat{\pi}\nabla f\cdot(-\hat{r}\psi) - \hat{\epsilon}_j \cdot \hat{\pi}\omega f\psi \\
&= -\frac{1}{2}\left[\hat{\epsilon}_j \cdot \hat{\pi}\nabla^2 f + 2\nabla\hat{\epsilon}_j \cdot \hat{\pi}\nabla f\right]\psi + f\nabla\hat{\epsilon}_j \cdot \hat{\pi}\hat{r}\psi \\
&\quad + \hat{\epsilon}_j \cdot \hat{\pi}\frac{\partial f}{\partial r}\psi - \hat{\epsilon}_j \cdot \hat{\pi}\omega f\psi \\
&= -\hat{\epsilon}_j \cdot \hat{\pi}\frac{\nabla^2 f}{2}\psi - \nabla\hat{\epsilon}_j \cdot \hat{\pi}\hat{r}\frac{\partial f}{\partial r}\psi \\
&\quad + f\nabla\hat{\epsilon}_j \cdot \hat{\pi}\hat{r}\psi + \hat{\epsilon}_j \cdot \hat{\pi}\frac{\partial}{\partial r}\psi - \hat{\epsilon}_j \cdot \hat{\pi}\omega f\psi
\end{aligned}$$

Now the equation becomes

$$\hat{\epsilon}_j \cdot \hat{\pi}\psi = -\frac{\nabla^2}{2}\hat{\epsilon}_j \cdot \hat{\pi} f\psi + \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\pi} f\nabla^2\psi - \omega\hat{\epsilon}_j \cdot \hat{\pi} f\psi$$

With a little bit of algebra, we can show that the radial differential equation satisfied by $f(r)$ as

$$\begin{aligned} -r(\hat{\epsilon}_j \cdot \hat{r}) &= r\hat{\epsilon}_j \cdot \hat{r}\left(\frac{f''}{2} + \frac{1}{r}f'\right) + \hat{\epsilon}_j \cdot \hat{r}f' - \hat{\epsilon}_j \cdot \hat{r}f \\ &\quad - r\hat{\epsilon}_j \cdot \hat{r}f' + r\omega\hat{\epsilon}_j \cdot \hat{r}f \\ -r &= r\frac{f''}{2} + (2-r)f' + (r\omega - 1)f \end{aligned} \tag{3.24}$$

Thus the differential equation for the unknown radial function f is

$$rf'' + (4 - 2r)f' + (2\omega r - 2)f = -2r \tag{3.25}$$

For the different frequency, we obtained the same result as(Radhakrishnan and Thayyullathil, 2004):

$$rf'' + (4 - 2r)f' + (2\omega r - 2)f = 2r \tag{3.26}$$

Two photon ionization rate and cross-section

The differential ionization rate at particular angle is expressed (Fifirig and Stroe, 2002) as

$$\frac{d\Gamma^{(2)}}{d\Omega} \propto \left(\frac{\bar{I}}{I_0}\right)^2 |M_{mg}^{(2)}|^2$$

For laser beams of radiation of different frequencies ω_j and ω_k, the transition rate becomes (Thayyullathil and Prasanna, 1994)

$$\Gamma_{mg}^{(2)} \propto |M_{mg}^{(2)}|^2 \delta(\omega_j + \omega_k - E_{mg})$$

where, I_0 is the atomic unit for radiation intensity. The differential ionization cross-section for two photon-ionization has the expression (Fifirig, 2001)

$$\frac{d\sigma^{(2)}}{d\Omega} = \left(\frac{\alpha}{4\pi}\right)^2 \left(\frac{\bar{I}}{I_0}\right)^2 |D_{mg}^{(2)}|^2 a_0^2 \omega k_f \tag{3.27}$$

where, k_f = momentum of ejected electron, α the fine structure constant, $\bar{I}$

$$\bar{I} = \sum_{j=1}^{2} I_j$$

is the mean intensity of radiation beams, and the D_{fg} is transition amplitude from initial ground state $|g\rangle$ to final continuum state $|m\rangle$.

The wave function of Hydrogen like atom for the bound states (Bethe and Salpeter, 1957)

$$\psi_{nlm} = R_{nl}(r)P_{lm}(\vartheta)e^{im\varphi}\frac{1}{\sqrt{2\pi}} \tag{3.28}$$

As we know there are two kinds of atomic states, bound and free. In bound states, when $E < 0$, the motion of electron is finite and energies are usually negative, as said to be discrete, so called discrete atomic levels, that can be calculated by using the (3.28). Whereas in the free state the motion of electron is unlimited in space, but it does not mean that electron has to be absolutely free from any interaction. However, when $E > 0$ the electron energies lies above $n = \infty$ level. Since the wave function are finite at $r = \infty$ (i.e. is bounded by 1), there is now no need to truncate the series. As the result, the state of electron can assume all positive energies, hence the name **continuum state** (Hill and Chi, 2007). Where, $E = 0$ is associated with threshold energy or the threshold of continuum spectrum. The free electron energy is continuous i. e. in the continuum, the atomic electron can have any positive energy E, $0 \leq E \leq \infty$, thus in continuum the principle quantum number is replaced by continuously changing electron energy $E(k)$, $E(k) \geq 0$ and corresponding atomic wave function can be normalized by dirac delta function (Mikhail, 1997). Thus far, we have focussed on bound states which corresponds to solution to the radial equation as final state wave function.

$$|\psi_f\rangle = 4\pi \sum_{lm} (i)^l R_{k_f l}(r) Y_{lm}(\hat{r}) Y^*_{lm}(\hat{k}) \tag{3.29}$$

where Y_{lm} are the well known spherical harmonics and the radial part of Hydrogen atom wave function for an attractive Coulomb potential can be taken as (Messaih, 1962):

$$R_{k}(r) = e^{\frac{\pi\nu}{2}}\frac{\Gamma(l+1-i\nu)}{\Gamma(2l+2)}(2rk)^l e^{ikr} F\,(l+1-i\nu,\, 2l+2,\, -2ikr) \tag{3.30}$$

and $\nu = \frac{1}{k}$ with the ground state wave function

$$|\psi_g\rangle = \frac{e^{-r}}{\sqrt{\pi}}$$

We have

$$M_{fg}^{(2)} = E_{0k}\langle f|\hat{\epsilon}_k \cdot \hbar F_j|g\rangle \tag{3.31}$$

where,

$$F_j = E_{0j}\hat{\epsilon}_j \cdot \hbar f_j$$

Discrete states can be calculated as transition from the initial state as a ground state $|\psi_g\rangle$ with quantum number n, l, m to the final state as *discrete state* $|\psi_f\rangle$ with quantum numbers n^J, l^J, m^J for $rE_{0k}\hat{\epsilon}_k \cdot \hat{r}$ is given as

$$M_{fg}^{(2)} = E_{0k} \int \psi^*_{n^J l^J m^J} \hat{\epsilon}_k \cdot \hbar F_j \psi_{nlm} d\tau$$

Where, M_{fg}, is the transition amplitude for the multiple beams of electric field strength $E^J s$. We have calculated amplitudes for continuum states for the multiple beams having same frequencies, same direction but different polarization, Thus the equation becomes:

$$M_{fg}^{(2)} = E_{0k} \int \psi_f \hat{\epsilon}_k \cdot \hbar F_j \psi_g d\tau \tag{3.32}$$

The **transition amplitude** for two photon ionization is

$$|M_{fg}^{(2)}|^2 = |E_{0j}E_{0k}|^2 \left| \int \psi_f \hat{\epsilon}_k \cdot \hbar \hat{\epsilon}_j \cdot \hbar f \psi_g d\tau \right|^2 \tag{3.33}$$

Here we have used the method of Laplace transform (Ince, 1956) for the solution of differential equations (3.25). Let us define the functions as (Thayyullathil and Prasanna, 1994), (Thayyullathil et al., 2003) and (Radhakrishnan and Thayyullathil, 2004)

$$\Phi(p, q, \lambda, t, r) = \int_{\lambda}^{t} e^{-r(s-1)} K(p, q, \lambda, s) ds, \tag{3.34a}$$

where,

$$K(p, q, \lambda, s) = \left(\frac{1-\lambda}{1+\lambda}\right)^{\frac{1}{\lambda}} (s+\lambda)^{p+\frac{1}{\lambda}} (s-\lambda)^{q-\frac{1}{\lambda}}. \tag{3.34b}$$

Here p and q are real numbers and λ's are in general complex ($\lambda_1 = \sqrt{(1-2\omega)}$). Finally we have the forms of the radial functions $f(r)$, $g_0(r)$ and $g_2(r)$

$$f(r) = \frac{1}{\omega} - \frac{1}{2\omega^3}\Phi(1, 1, \lambda_1, 1, r) \tag{3.35}$$

Evaluation of angular part of matrix element

From now we have used the symbols old j = new i, old k = new j and old l = new k, to avoid confusion with the orbital angular momentum l. Consider two photons simultaneously absorbed from two beams (i^{th} and j^{th}) with different polarizations $\hat{\epsilon}_i$ and $\hat{\epsilon}_j$ and for the simplicity same frequency. For the evaluation of angular parts involving various polarization vectors $\hat{\epsilon}$s ejected momentum vectors k_f we have to use standard integrals involving integrals of Legendre polynomials. Assuming that the atom make a transition from initial state as a ground state $|g\rangle$ to the final state $|m\rangle$ by absorbing two photons.

The corresponding second order matrix element from (3.19) with F_i such as:

$$F_i = E_{0i}(\hat{\epsilon}_i \cdot \hat{r})f(r)$$

becomes:

$$M_{fg}^{(2)} = E_{0j}E_{0i}\langle f|(\hat{\epsilon}_j \cdot \hat{r})(\hat{\epsilon}_i \cdot \hat{r})f_i|g\rangle \tag{3.36}$$

Two-photon selection rule

Selection rule for a two photon processes can be seen directly from the expression for the second order matrix element given in (3.12) which will be non zero only for $l = 0$ and $l = 2$, thus the only final states accessible by two photon transition from initial s states are s and d states. Thus, from (3.29), (3.30) and (3.36) the matrix element becomes:

$$M_{fg}^{(2)} = E_{0i}E_{0j}\int 4\pi \sum_{lm} (i)^l R_{k_f l}(r) Y_{lm}^*(\hat{r}) Y_{lm}(\hat{k})(\hat{\epsilon}_j \cdot \hat{r})(\hat{\epsilon}_i \cdot \hat{r}) f_i \psi_g d\tau \tag{3.37}$$

We have From spherical addition theorem (Devananthan, 2002)

$$P_l(\hat{k} \cdot \hat{r}) = \frac{4\pi}{2l+1} \sum_{lm} Y_{lm}(\hat{k}) Y_{lm}^*(\hat{r})$$

Or,

$$\sum_{lm} Y_{lm}(\hat{k}) Y_{lm}^*(\hat{r}) = \frac{2l+1}{4\pi} P_l(\hat{k} \cdot \hat{r})$$

Where, P_l is the Lengendre polynomial of order l .
Now (3.37) becomes

$$M_{fg}^{(2)} = 4\pi \frac{2l+1}{4\pi} E_{0i} E_{0j} \int (i)^l R_{k_f l}(r) P_l(\hat{k}\cdot\hat{r}) \hat{\epsilon}_j \cdot \hat{r} \hat{\epsilon}_i \cdot \hat{r} f_i \psi_g d\tau \qquad (3.38)$$

The angular separation of the function can be performed in terms of the spherical harmonics using the orthogonality property of the Legendre Polynomials. For higher order $l \geq 2$ we have the recursion relation satisfied by Legendre Polynomials as

$$P_l(x) = \frac{2l-1}{l} x P_{l-1}(x) - \frac{l-1}{l} P_{l-2}(x) \qquad (3.39)$$

For, $x = (\hat{k}\cdot\hat{r})$, we have the given integrals involving Legendre polynomials

$$\int P_l(\hat{k}\cdot\hat{r}) d\Omega = \begin{cases} 4\pi & \text{if } l = 0 \\ 0 & \text{if } l \neq 0 \end{cases}$$

Similarly

$$\int P_l(\hat{k}\cdot\hat{r}) \hat{\epsilon}_i \cdot \hat{r} d\Omega = \begin{cases} \int \hat{k}\cdot\hat{r}\hat{\epsilon}\cdot\hat{r} d\Omega = \frac{4\pi}{3} \hat{k}\cdot\hat{\epsilon} & \text{if } l = 1 \\ 0 & \text{if } l \neq 1 \end{cases}_i$$

Now for $l = 2$ and $l = 0$

$$\int P_l(\hat{k}\cdot\hat{r}) \hat{\epsilon}_i \cdot \hat{r} \hat{\epsilon}_j \cdot \hat{r} d\Omega = 0 \quad \text{if} \quad l \neq 2 \quad \text{or} \quad 0 \qquad (3.40)$$

$$\int P_0(\hat{k}\cdot\hat{r}) \hat{\epsilon}_i \cdot \hat{r} \hat{\epsilon}_j \cdot \hat{r} d\Omega = \frac{4\pi}{3} \hat{\epsilon}_i \cdot \hat{\epsilon}_j \quad \text{for} \quad l = 0 \qquad (3.41)$$

For $l = 2$

$$\int P_2(\hat{k}\cdot\hat{r}) \hat{\epsilon}_i \cdot \hat{r} \hat{\epsilon}_j \cdot \hat{r} d\Omega = \int \left[\frac{1}{2} 3(\hat{k}\cdot\hat{r})^2 - 1 \right] \hat{\epsilon}_i \cdot \hat{r} \hat{\epsilon}_j \cdot \hat{r} d\Omega$$
$$= \frac{3}{2} \frac{4\pi}{15} \left[(\hat{k}\cdot\hat{\epsilon}_i)\hat{k}\cdot\hat{\epsilon}_j + \hat{k}\cdot\hat{\epsilon}_j \hat{k}\cdot\hat{\epsilon}_i + \hat{k}\cdot\hat{k}\hat{\epsilon}_i\cdot\hat{\epsilon}_j \right] - \frac{1}{2} \frac{4\pi}{3} \hat{\epsilon}_i \cdot \hat{\epsilon}_j \qquad (3.42)$$

For $l = 0$, i.e., s-orbital

Separating radial and angular part

$$M_{fg}^{(2)} = E_{0i} E_{0j} \int r^4 R_{k0}(r) f_i \psi_g dr \int P_0(\hat{k}\cdot\hat{r}) \hat{\epsilon}_i \cdot \hat{r} \hat{\epsilon}_j \cdot \hat{r} d\Omega \qquad (3.43)$$

After performing the angular integration

$$M_{fg}^{(2)} = \frac{4\pi}{3} E_{0i} E_{0j} \int r^4 R_{k0}(r) f_f e^{-r} dr \, \hat{\epsilon}_i \cdot \hat{\epsilon}_j \tag{3.44}$$

Hence, final equation for $l = 0$ is

$$M_{fg}^{(2)} = \frac{4\pi}{3} E_{0i} E_{0j} \hat{\epsilon}_i \cdot \hat{\epsilon}_j \int r^4 R_{k0}(r) f_f e^{-r} dr \tag{3.45}$$

Thus the s-orbital do not have angular momentum, the wave function must be entirely radially i.e., completely spherically symmetric.

For $l = 2$, i.e., d-orbital

$$M_{fg}^{(2)} = 4\pi (i)^2 E_{0i} E_{0j} \frac{5}{4\pi} \int r^4 R_{k2}(r) f_i \psi_g dr \int P_2(\hat{k} \cdot \hat{r}) \hat{\epsilon}_i \cdot \hat{r} \hat{\epsilon}_j \cdot \hat{r} d\Omega \tag{3.46}$$

$$M_{fg}^{(2)} = (-5) E_{0i} E_{0j} \int r^4 R_{k2}(r) f_i \psi_g dr \int \frac{1}{2}(3(\hat{k} \cdot \hat{r})^2 - 1) \hat{\epsilon}_i \cdot \hat{r} \hat{\epsilon}_j \cdot \hat{r} d\Omega \tag{3.47}$$

From "(3.42) and (3.47)" after performing angular integration

$$M_{fg}^{(2)} = (-5) E_{0i} E_{0j} \int r^4 R_{k2}(r) f_i \psi_g dr \times \frac{3}{2} \frac{4\pi}{15} \left[\hat{k} \cdot \hat{\epsilon}_i \hat{k} \cdot \hat{\epsilon}_j + \hat{k} \cdot \hat{\epsilon}_j \hat{k} \cdot \hat{\epsilon}_i + \hat{k} \cdot \hat{k} \hat{\epsilon}_i \cdot \hat{\epsilon}_j \right] - \frac{1}{2} \frac{4\pi}{3} \hat{\epsilon}_i \cdot \hat{\epsilon}_j \tag{3.48}$$

Hence the final equation for two photon processes for $l = 2$

$$M_{fg}^{(2)} = (-5) E_{0i} E_{0j} \times \frac{3}{2} \frac{4\pi}{15} \left[\hat{k} \cdot \hat{\epsilon}_i \hat{k} \cdot \hat{\epsilon}_j + \hat{k} \cdot \hat{\epsilon}_j \hat{k} \cdot \hat{\epsilon}_i + \hat{k} \cdot \hat{k} \hat{\epsilon}_i \cdot \hat{\epsilon}_j \right] - \frac{1}{2} \frac{4\pi}{3} \hat{\epsilon}_i \cdot \hat{\epsilon}_j \times \int r^4 R_{k2}(r) f_i \psi_g dr \tag{3.49}$$

Therefore the second-order transition matrix element is evaluated, and hence we can calculate the ionization cross-section.

CHAPTER 4

THREE-PHOTON IONIZATION

Three-photon processes (3PP)

In 3PP, where three photons with frequency ω are simultaneously are absorbed in one event and make a transition from initial state $|g\rangle$ to and excited state $|f\rangle$ allowed by three photon selection rules (John, 2000). We have used third-order perturbation theory for studying these effect and this is an extension of the discussion in the previous chapter. We need to modify third order perturbation theory such as:

$$\dot{C}_f^{(3)} = \frac{1}{i}\sum_m C_m^{(2)}\langle f|H|m\rangle e^{i\omega_{fm}t} \tag{4.1}$$

$$= E_{0l}\frac{1}{i}\sum_{m}\sum_{l} C_m^{(2)}\langle f|\hat{\epsilon}_l\cdot\vec{r}|m\rangle e^{i(\omega_{fm}-\omega)t} \tag{4.2}$$

$$\dot{C}_f^{(3)} = E_{0j}E_{0k}E_{0l}\sum_{j,k,l}\sum_{m,n}\langle f|\hat{\epsilon}_l\cdot\vec{r}|m\rangle\langle m|\hat{\epsilon}_k\cdot\vec{r}|n\rangle\langle n|\hat{\epsilon}_j\cdot\vec{r}|g\rangle\times$$

$$\frac{1-e^{i(\omega_{ng}+\omega_{mn}-2\omega)t}}{(\omega_{ng}-\omega)(\omega_{mn}+\omega_{ng}-2\omega)}\; e^{i(\omega_{fm}-\omega)t}$$

$$\dot{C}_f^{(3)} = E_{0j}E_{0k}E_{0l}\sum_{j,k,l}\sum_{m,n}\langle f|\hat{\epsilon}_l\cdot\vec{r}|m\rangle\langle m|\hat{\epsilon}_k\cdot\vec{r}|n\rangle\langle n|\hat{\epsilon}_j\cdot\vec{r}|g\rangle\times$$

$$\frac{e^{i(\omega_{fm}-\omega)t}-e^{i(\omega_{fm}+\omega_{mn}+\omega_{ng}-3\omega)t}}{(\omega_{ng}-\omega)(\omega_{mn}+\omega_{ng}-2\omega)}$$

Third order matrix element

We have from third order perturbation theory, the expansion coefficient as:

$$\frac{\partial C_f^{(3)}(t)}{\partial t} = \sum_m C_m^{(2)}(t) \times \Big\{ \langle f|H_1|m\rangle e^{i(\omega_{fm}-\omega_1)t} + \langle f|H_2|m\rangle e^{i(\omega_{fm}-\omega_2)t} + \langle f|H_3|m\rangle e^{i(\omega_{fm}-\omega_3)t} \Big\} \tag{4.3}$$

By integrating

$$C_f^{(3)} = E_{0j}E_{0k}E_{0l} \sum_{j,k,l\,m,n} \langle f|\hat{\epsilon}_l \cdot \hat{r}|m\rangle\langle m|\hat{\epsilon}_k \cdot \hat{r}|n\rangle\langle n|\hat{\epsilon}_j \cdot \hat{r}|\rangle \times \frac{1 - e^{i(\omega_{fm}+\omega_{ng}+\omega_{mn}-3\omega)t}}{(\omega_{ng} - \omega)(\omega_{mn} + \omega_{ng} - \omega_j - \omega_k)((\omega_{fm} + \omega_{mn} + \omega_{ng} - 3\omega)} \tag{4.4}$$

Where we have retained only those terms in which the denominators approaches zero. Here we can see that a resonance occurs at $\omega_{fm} + \omega_{mn} + \omega_{ng} = \omega_{fg} = 3\omega$ corresponding to three photon transition from the ground state $|g\rangle$ to the final state $|f\rangle$ through two intermediate states $|n\rangle$ and $|m\rangle$ processes. Hence by dropping the antiresonance term, the matrix elements in dipole approximation for three-photon process has the form:

$$M_{fg}^{(3)} = \sum_{j,k,l\,m,n} \frac{\langle f|\hat{\epsilon}_l \cdot \hat{r}|m\rangle\langle m|\hat{\epsilon}_k \cdot \hat{r}|n\rangle\langle n|\hat{\epsilon}_j \cdot \hat{r}|g\rangle}{(\omega_{ng} - \omega)(\omega_{mg} - 2\omega)} \tag{4.5}$$

For different laser frequency It can be expressed as (Thayyullathil et al., 2003):

$$M_{fg}^{(3)} = \sum_{i,j,k\,m,n} \frac{\langle f|\hat{\epsilon}_k \cdot \hat{r}|m\rangle\langle m|\hat{\epsilon}_j \cdot \hat{r}|n\rangle\langle n|\hat{\epsilon}_i \cdot \hat{r}|g\rangle}{(\omega_{ng} - \omega_i)(\omega_{mg} - \omega_i - \omega_j)} \tag{4.6}$$

We can also evaluate for particularly three different laser frequencies of 1, 2 and 3 such as:

$$M_{fg}^{(3)} = \sum_m \sum_n \frac{\langle f \mid H_1 \mid m\rangle\langle m \mid H_1 \mid n\rangle\langle n \mid H_1 \mid g\rangle}{(\omega_{mg} - 2\omega_1)(\omega_{ng} - \omega_1)} \delta(\omega_{fg} - 3\omega_1) \tag{4.7}$$

$$+ \sum_m \sum_n \frac{\langle f \mid H_2 \mid m\rangle\langle m \mid H_1 \mid n\rangle\langle n \mid H_1 \mid g\rangle}{(\omega_{mg} - 2\omega_1)(\omega_{ng} - \omega_1)} \delta(\omega_{fg} - 2\omega_1 - \omega_2)$$

$$+ \sum_m \sum_n \frac{\langle f \mid H_3 \mid m\rangle\langle m \mid H_1 \mid n\rangle\langle n \mid H_1 \mid g\rangle}{(\omega_{mg} - 2\omega_1)(\omega_{ng} - \omega_1)} \delta(\omega_{fg} - 2\omega_1 - \omega_3)$$

$$+ \sum_m \sum_n \frac{\langle f \mid H_1 \mid m\rangle\langle m \mid H_2 \mid n\rangle\langle n \mid H_1 \mid g\rangle}{(\omega_{mg} - \omega_1 - \omega_2)(\omega_{ng} - \omega_1)} \delta(\omega_{fg} - 2\omega_1 - \omega_2)$$

$$+ \sum_m \sum_n \frac{\langle f \mid H_3 \mid m\rangle\langle m \mid H_2 \mid n\rangle\langle n \mid H_1 \mid g\rangle}{(\omega_{mg} - \omega_1 - \omega_2)(\omega_{ng} - \omega_1)} \delta(\omega_{fg} - \omega_1 - \omega_2 - \omega_3)$$

$$+ \sum_m \sum_n \frac{\langle f \mid H_2 \mid m\rangle\langle m \mid H_2 \mid n\rangle\langle n \mid H_1 \mid g\rangle}{(\omega_{mg} - \omega_1 - \omega_2)(\omega_{ng} - \omega_1)} \delta(\omega_{fg} - 2\omega_2 - \omega_1)$$

$$+ \sum_m \sum_n \frac{\langle f \mid H_1 \mid m\rangle\langle m \mid H_3 \mid n\rangle\langle n \mid H_2 \mid g\rangle}{(\omega_{mg} - \omega_2 - \omega_3)(\omega_{ng} - \omega_2)} \delta(\omega_{fg} - \omega_1 - \omega_2 - \omega_3)$$

$$+ \sum_m \sum_n \frac{\langle f \mid H_3 \mid m\rangle\langle m \mid H_3 \mid n\rangle\langle n \mid H_3 \mid g\rangle}{(\omega_{mg} - 2\omega_3)(\omega_{ng} - \omega_3)} \delta(\omega_{fg} - 3\omega_3)$$

$$+ \sum_m \sum_n \frac{\langle f \mid H_1 \mid m\rangle\langle m \mid H_1 \mid n\rangle\langle n \mid H_3 \mid g\rangle}{(\omega_{mg} - \omega_1 - \omega_3)(\omega_{ng} - \omega_2)} \delta(\omega_{fg} - 2\omega_1 - \omega_3)$$

$$+ \sum_m \sum_n \frac{\langle f \mid H_2 \mid m\rangle\langle m \mid H_1 \mid n\rangle\langle n \mid H_3 \mid g\rangle}{(\omega_{mg} - \omega_1 - \omega_3)(\omega_{ng} - \omega_3)} \delta(\omega_{fg} - \omega_1 - \omega_2 - \omega_3)$$

$$+ \sum_m \sum_n \frac{\langle f \mid H_1 \mid m\rangle\langle m \mid H_3 \mid n\rangle\langle n \mid H_2 \mid g\rangle}{(\omega_{mg} - \omega_2 - \omega_3)(\omega_{ng} - \omega_2)} \delta(\omega_{fg} - \omega_1 - \omega_2 - \omega_3)$$

$$+ \sum_m \sum_n \frac{\langle f \mid H_3 \mid m\rangle\langle m \mid H_1 \mid n\rangle\langle n \mid H_3 \mid g\rangle}{(\omega_{mg} - \omega_1 - \omega_3)(\omega_{ng} - \omega_3)} \delta(\omega_{fg} - \omega_1 - 2\omega_3)$$

$$+ \sum_m \sum_n \frac{\langle f \mid H_1 \mid m\rangle\langle m \mid H_3 \mid n\rangle\langle n \mid H_1 \mid g\rangle}{(\omega_{mg} - \omega_1 - \omega_3)(\omega_{ng} - \omega_1)} \delta(\omega_{fg} - 2\omega_1 - \omega_3)$$

contd.

$$
\begin{aligned}
&+\sum_m\sum_n \frac{\langle f\mid H_3\mid m\rangle\langle m\mid H_3\mid n\rangle\langle n\mid H_1\mid g\rangle}{(\omega_{mg}-\omega_1-\omega_3)(\omega_{ng}-\omega_1)}\delta(\omega_{fg}-2\omega_3-\omega_1)\\
&+\sum_m\sum_n \frac{\langle f\mid H_3\mid m\rangle\langle m\mid H_1\mid n\rangle\langle n\mid H_2\mid g\rangle}{(\omega_{mg}-\omega_1-\omega_2)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-\omega_1-\omega_2-\omega_3)\\
&+\sum_m\sum_n \frac{\langle f\mid H_1\mid m\rangle\langle m\mid H_3\mid n\rangle\langle n\mid H_2\mid g\rangle}{(\omega_{mg}-\omega_2-\omega_3)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-\omega_1-\omega_2-\omega_3)\\
&+\sum_m\sum_n \frac{\langle f\mid H_3\mid m\rangle\langle m\mid H_3\mid n\rangle\langle n\mid H_2\mid g\rangle}{(\omega_{mg}-\omega_2-\omega_3)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-\omega_2-2\omega_3)\\
&+\sum_m\sum_n \frac{\langle f\mid H_1\mid m\rangle\langle m\mid H_3\mid n\rangle\langle n\mid H_3\mid g\rangle}{(\omega_{mg}-2\omega_3)(\omega_{ni}-\omega_3)}\delta(\omega_{fg}-\omega_1-2\omega_3)\\
&+\sum_m\sum_n \frac{\langle f\mid H_2\mid m\rangle\langle m\mid H_3\mid n\rangle\langle n\mid H_3\mid g\rangle}{(\omega_{mg}-2\omega_3)(\omega_{ng}-\omega_3)}\delta(\omega_{fg}-\omega_2-2\omega_3)\\
&+\sum_m\sum_n \frac{\langle f\mid H_1\mid m\rangle\langle m\mid H_2\mid n\rangle\langle n\mid H_3\mid g\rangle}{(\omega_{mg}-\omega_2-\omega_3)(\omega_{ni}-\omega_3)}\delta(\omega_{fg}-\omega_1-\omega_2-\omega_3)\\
&+\sum_m\sum_n \frac{\langle f\mid H_2\mid m\rangle\langle m\mid H_2\mid n\rangle\langle n\mid H_3\mid g\rangle}{(\omega_{mg}-\omega_2-\omega_3)(\omega_{ni}-\omega_3)}\delta(\omega_{fg}-2\omega_2-\omega_3)\\
&+\sum_m\sum_n \frac{\langle f\mid H_3\mid m\rangle\langle m\mid H_2\mid n\rangle\langle n\mid H_3\mid g\rangle}{(\omega_{mg}-\omega_2-\omega_3)(\omega_{ni}-\omega_3)}\delta(\omega_{fg}-\omega_2-2\omega_3)\\
&+\sum_m\sum_n \frac{\langle f\mid H_2\mid m\rangle\langle m\mid H_3\mid n\rangle\langle n\mid H_1\mid g\rangle}{(\omega_{mg}-\omega_1-\omega_3)(\omega_{ni}-\omega_1)}\delta(\omega_{fg}-\omega_1-\omega_2-\omega_3)\\
&+\sum_m\sum_n \frac{\langle f\mid H_2\mid m\rangle\langle m\mid H_2\mid n\rangle\langle n\mid H_2\mid g\rangle}{(\omega_{mg}-2\omega_2)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-3\omega_2)\\
&+\sum_m\sum_n \frac{\langle f\mid H_3\mid m\rangle\langle m\mid H_2\mid n\rangle\langle n\mid H_2\mid g\rangle}{(\omega_{mg}-2\omega_2)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-2\omega_2-\omega_3)\\
&+\sum_m\sum_n \frac{\langle f\mid H_1\mid m\rangle\langle m\mid H_1\mid n\rangle\langle n\mid H_2\mid g\rangle}{(\omega_{mg}-\omega_1-\omega_2)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-2\omega_1-\omega_2)\\
&+\sum_m\sum_n \frac{\langle f\mid H_2\mid m\rangle\langle m\mid H_1\mid n\rangle\langle n\mid H_2\mid g\rangle}{(\omega_{mg}-\omega_1-\omega_2)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-2\omega_2-\omega_1)
\end{aligned}
$$

Where, symbols have their own meaning. Thus, as usual we will write $D_{fg}^{(3)}$ for the transition amplitude containing both the intensity part and matrix part. Hence the transition amplitude for three-photon processes becomes:

$$D_{fg}^{(3)} = \sum_{j,k,l}^{n_b} \frac{\mathbf{r}\sqrt{I_j I_k I_l}}{\bar{I}^3}\; e^{-i(\delta_j+\delta_k+\delta_l)} M_{lkj}$$

Where, $M_{fg}^{(3)} = M_{lkj}$ for same frequency, but different polarization is expressed as:

$$M_{fg}^{(3)} = \sum_{j,k,l\,m,n} \sum \frac{\langle f|\hat{\epsilon}_l \cdot \vec{r}|m\rangle\langle m|\hat{\epsilon}_k \cdot \vec{r}|n\rangle\langle n|\hat{\epsilon}_j \cdot \vec{r}|g\rangle}{(\omega_{ng} - \omega)(\omega_{mg} - 2\omega)} \tag{4.8}$$

Dalgarno-Lewis method

Since the transition matrix element for three-photon (4.8) includes two intermediate sums. Now we have to define one more axillary operator G_{jk} (in addition to first operator F_j) in such a way that

$$\hat{\epsilon}_j \cdot \vec{r}|g\rangle = (H_0F_j - F_jH_0)\,|g\rangle - \omega F_j|g\rangle \tag{4.9a}$$

$$\hat{\epsilon}_k \cdot \vec{r}F_j|g\rangle = (H_0G_{jk} - G_{jk}H_0)\,|g\rangle - 2\omega G_{jk}|g\rangle \tag{4.9b}$$

Now proceeding in a similar manner as in the previous chapter, the operator F_j can be used to remove one of the energy denominator. Then with the use of closure relation one of the infinite summation can be eliminated. This is done by taking the scalar product of Eq. (4.9a) with $|n\rangle$ to obtain

$$\begin{aligned}\langle n|\hat{\epsilon}_j \cdot \vec{r}|g\rangle &= \langle n|\,(H_0F_j - F_jH_0)\,|g\rangle - \omega F_j|g\rangle \\ &= (E_n - E_g - \omega)\langle n|F_j|g\rangle\end{aligned} \tag{4.10}$$

Substituting the above relation in Eq.(4.8), we can write

$$M_{fg}^{(3)} = \sum_{j,k,l\,m,n} \sum \frac{(E_n - E_g - \omega)\langle f|\hat{\epsilon}_l \cdot \vec{r}|m\rangle\langle m|\hat{\epsilon}_k \cdot \vec{r}|n\rangle\langle n|\hat{\epsilon}_j \cdot \vec{r}|g\rangle}{(E_n - E_g - \omega)(E_m - E_g - 2\omega)} \tag{4.11}$$

Canceling out one of the energy denominator, the expression in Eq.(4.11) becomes

$$M_{fg}^{(3)} = \sum_{j,k,l\,m,n} \sum \frac{\langle f|\hat{\epsilon}_l \cdot \vec{r}|m\rangle\langle m|\hat{\epsilon}_k \cdot \vec{r}F_j|g\rangle}{(E_m - E_g - 2\omega)} \tag{4.12}$$

Similarly by taking scalar product of bra vector m to Eq. (4.9b)

$$\begin{aligned}\langle m|\hat{\epsilon}_k \cdot \vec{r}F_j|g\rangle &= \langle m|H_0G_{jk} - G_{jk}H_0|g\rangle - 2\omega)\langle m|G_{jk}|g\rangle \\ &= (E_m - E_g - 2\omega\langle m|G_{jk}|g\rangle \\ &= (E_m - E_g - 2\omega)\langle m|G_{jk}|g\rangle \\ &= (\omega_{mg} - 2\omega)\langle m|G_{jk}|g\rangle\end{aligned} \tag{4.13}$$

Thus,

$$\langle m|\hat{\epsilon}_j \cdot \hat{r} F_k|g\rangle = (\omega_{mg} - 2\omega)\langle m|G_{jk}|g\rangle$$

Now using the above relation in Eq.(4.12), we can cancel the remaining energy denominator because $\omega_{mg} = E_m - E_g$, finally using the closure relation $\sum_m |m\rangle\langle m| = \hat{I}$, This removes the infinite sum over the intermediate states and becomes the simple form as

$$M_{fg}^{(3)} = \langle f|\hat{\epsilon}_l \cdot \hat{r} G_{jk}|g\rangle \tag{4.14}$$

Thus the problem of finding an analytic expression for the transition matrix element is reduced to a problem of finding operator G_{jk}. We have already seen that the operator F_j is used to calculate matrix element for various two-photon process and it appears as the inhomogeneous term for the determination of G_{jk} in the Eq. (4.9b). As we have done earlier taking the initial state as the ground state of hydrogen atom, from the definition of G_{jk} we have

$$(\hat{\epsilon}_k \cdot \hat{r})F_j\psi = \frac{\nabla^2 G_{jk}}{2}\psi + \nabla G_{jk} \cdot \nabla\psi + 2\omega G_{jk}\psi$$

Like in two-photon process, here our goal is to find an analytical expression for G_{jk}.

Differential equation for G_{jk}

In order to find the analytical form of G_{jk}, we can start from its defining equations such as:

$$\hat{\epsilon}_k \cdot \hat{r} F_j|g\rangle = [H_0 G_{jk} - G_{jk} H_0 - 2\omega G_{jk}]\,|g\rangle \tag{4.15}$$

The RHS of equation (4.15) has the expression as:

$$(H_0 G_{jk} - G_{jk} H_0 - 2\omega G_{jk})\psi = \left[-\frac{1}{2}\nabla^2 - \frac{1}{r}\right] G_{jk} - G_{jk}\left[-\frac{1}{2}\nabla^2 - \frac{1}{r}\right] + 2\omega G_{jk}\psi \tag{4.16}$$

Again we are considering the case of atomic hydrogen, where the unperturbed part of Hamiltonian is

$$H_0 = -\frac{1}{2}\nabla^2 - \frac{1}{r}$$

and the ground state of hydrogen atom, we have $|g\rangle = \frac{e^{-r}}{\sqrt{\pi}} = \psi$. Using this and after simplification, the equation (4.16) becomes:

$$\hat{\epsilon}_k \cdot \hat{r} F_j \psi = -\frac{\nabla^2 G_{jk}}{2}\psi - \nabla G_{jk} \cdot \nabla\psi - 2\omega G_{jk}\psi \tag{4.17}$$

The appearance of the radial and angular part of the unknown operator G_{jk} can be done by separating as

$$G_{jk} = \frac{3}{2}\hat{\epsilon_j} \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon_k} r^2 \; g_2 + \hat{\epsilon_j} \cdot \hat{\epsilon_k} g_0 \tag{4.18}$$

where the unknown radial functions g_0 is for $l = 0$ and g_2 is for $l = 2$ hence, Or, in simple form as

$$G_{jk} = \frac{r^2}{2} Q_{jk} g_2(r) + q_{jk} g_0(r) \tag{4.19}$$

where $Q_{jk} = (\hat{\epsilon}_j \cdot \hat{r})(\hat{\epsilon}_k \cdot \hat{r}) - 3(\hat{\epsilon}_j \cdot \hat{\epsilon}_k)$ and $q_{jk} = (\hat{\epsilon}_j \cdot \hat{\epsilon}_k)$. This enable us to write the equation satisfied by G_{jk} as

$$\nabla^2 G_{jk} - 2\hat{r} \cdot \nabla G_{jk} + 4\omega G_{jk} = -\frac{2}{3}\overline{r}^2 (Q_{jk} + q_{jk}) f$$

Thus, substituting the forms of G_{jk}, we can simplify such as,

$$\nabla G_{jk} = \nabla \left[\frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r_2 \; g_2 + \hat{\epsilon_j} \cdot \hat{\epsilon_k} g_0\right] \tag{4.20}$$

Or,

$$\begin{aligned}
\nabla G_{jk} = {} & \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot r \nabla g_2 + \frac{3}{2} g_2 \nabla \hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} + g_0 \nabla \hat{\epsilon}_j \cdot \hat{\epsilon}_k + \hat{\epsilon}_j \cdot \hat{\epsilon}_k \nabla g_0 \\
& - \frac{1}{2}\nabla \hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 g_2 \\
= {} & \frac{3}{2}[\hat{\epsilon_j} \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}] \nabla g_2 + \frac{3}{2} g_2 \nabla [\hat{\epsilon_j} \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}] - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon_k} \nabla (r_2 g_2) \\
& - \frac{r^2}{2} g_2 [\nabla \hat{\epsilon}_j \cdot \hat{\epsilon}_k] + g_0 [\nabla \hat{\epsilon}_j \cdot \hat{\epsilon}_k] + \hat{\epsilon}_j \cdot \hat{\epsilon}_k \nabla g_0
\end{aligned}$$

$$\nabla G_{jk} = \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}\ \nabla g_2 + \frac{3}{2} g_2 \nabla [\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}] - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k g_2 \nabla r^2$$

$$- \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2\ \nabla g_2 + \hat{\epsilon}_j \cdot \hat{\epsilon}_k \nabla g_0$$

$$= \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}\ \nabla g_2 + \frac{3}{2} g_2 [\hat{\epsilon}_j \cdot \hat{r}\nabla \hat{\epsilon}_k \cdot \hat{r}] + g_2 [\hat{\epsilon}_k \cdot \hat{r}\nabla \hat{\epsilon}_j \cdot \hat{r}]$$

$$- r [3\hat{r}\hat{\epsilon}_j \cdot \hat{\epsilon}_k] g_2 - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2\ \nabla g_2 + [\hat{\epsilon}_j \cdot \hat{\epsilon}_k] \nabla g_0$$

And

$$\nabla G_{jk} \cdot \nabla \psi = \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}\ \nabla g_2 + \frac{3}{2} g_2 [\hat{\epsilon}_j \cdot \hat{r}\nabla \hat{\epsilon}_k \cdot \hat{r} + \hat{\epsilon}_k \cdot \hat{r}\nabla \hat{\epsilon}_j \cdot \hat{r}]$$

$$- r \times [3\hat{r}\hat{\epsilon}_j \cdot \hat{\epsilon}_k] g_2 - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2\ \partial g_2 + [\hat{\epsilon}_j \cdot \hat{\epsilon}_k] \nabla g_0\ (-\hat{r}\psi)$$

$$= \frac{3}{2}\hat{r}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}\frac{\partial g_2}{\partial r} + \frac{3}{2} g_2 [\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k] + \frac{3}{2} g_2 [(\hat{\epsilon}_k \cdot \hat{r}\hat{\epsilon}_j] \tag{4.21}$$

$$- 3 \times r\hat{r}\hat{\epsilon}_j \cdot \hat{\epsilon}_k g_2 - \frac{1}{2}\hat{r}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 \frac{\partial g_2}{\partial r} + \hat{r}\hat{\epsilon}_j \cdot \hat{\epsilon}_k \frac{\partial g_0}{\partial r}\ (-\hat{r}\psi)$$

$$= \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}\frac{\partial g_2}{\partial r} + 3 g_2 \frac{\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}}{r} - 3r\hat{\epsilon}_j \cdot \hat{\epsilon}_k g_2$$

$$- \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 \frac{\partial g_2}{\partial r} + \hat{\epsilon}_j \cdot \hat{\epsilon}_k \frac{\partial g_0}{\partial r}\ (-\psi)$$

Now for $\nabla^2 G_{jk}$

$$\nabla_2 G_{jk} = \nabla^2 \left[\frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r_2\ g_2 + \hat{\epsilon}_j \cdot \hat{\epsilon}_k g_0\right] \tag{4.22}$$

Or,

$$\nabla^2 G_{jk} = \frac{3}{2}\nabla^2 [\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} g_2] - \frac{1}{2}\nabla^2\ \hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 g_2 + \nabla^2 [\hat{\epsilon}_j \cdot \hat{\epsilon}_k g_0]$$

$$= \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}\nabla^2 g_2 + 3\nabla [\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}] \nabla g_2$$

$$+ \frac{3}{2} g_2\ \hat{\epsilon}_j \cdot \hat{r}\nabla^2 \hat{\epsilon}_k \cdot \hat{r} + 2\nabla \hat{\epsilon}_j \cdot \hat{r}\nabla \hat{\epsilon}_k \cdot \hat{r} + \hat{\epsilon}_k \cdot \hat{r}\nabla^2 \hat{\epsilon}_j \cdot \hat{r}$$

$$- \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k\ \nabla^2 (r^2 g_2) - \frac{1}{2} r^2 g_2 \nabla^2 \hat{\epsilon}_j \cdot \hat{\epsilon}_k - \frac{1}{2}\ 2\nabla \hat{\epsilon}_j \cdot \hat{\epsilon}_k\ \nabla (r^2 g_2)$$

$$+\ \hat{\epsilon}_j \cdot \hat{\epsilon}_k \nabla^2 g_0 + \nabla g_0 \nabla \hat{\epsilon}_j \cdot \hat{\epsilon}_k$$

$$\nabla^2 G_{jk} = \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}\nabla^2 g_2 + 3\left[\hat{\epsilon}_j \cdot \hat{r}\nabla\hat{\epsilon}_k \cdot \hat{r} + \hat{\epsilon}_k \cdot \hat{r}\nabla\hat{\epsilon}_j \cdot \hat{r}\right]\nabla g_2$$
$$+ 3g_2\hat{\epsilon}_j \cdot \hat{\epsilon}_k - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k\, r^2 \nabla^2 g_2 + g_2\nabla^2 r^2 + 2\nabla r^2 \nabla g_2$$
$$+ \hat{\epsilon}_j \cdot \hat{\epsilon}_k \nabla^2 g_0 + \nabla g_0 \nabla\hat{\epsilon}_j \cdot \hat{\epsilon}_k$$
$$= \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}\nabla^2 g_2 + 3\left[\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k + \hat{\epsilon}_k \cdot \hat{r}\hat{\epsilon}_j\right]\nabla g_2 + 3g_2\hat{\epsilon}_j \cdot \hat{\epsilon}_k$$
$$- \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 \nabla^2 g_2 - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k g_2 6 - 2r\hat{r}\hat{\epsilon}_j \cdot \hat{\epsilon}_k \nabla g_2$$
$$+ \hat{\epsilon}_j \cdot \hat{\epsilon}_k \nabla^2 g_0 + \nabla g_0 \nabla\hat{\epsilon}_j \cdot \hat{\epsilon}_k$$
$$= \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}\nabla^2 g_2 + 3\left[2\frac{\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}}{r}\frac{\partial g_2}{\partial r}\right]$$
$$+ 3g_2\hat{\epsilon}_j \cdot \hat{\epsilon}_k - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r_2 \nabla_2 g_2$$
$$- 3\hat{\epsilon}_j \cdot \hat{\epsilon}_k g_2 - 2r\hat{\epsilon}_j \cdot \hat{\epsilon}_k \frac{\partial g_2}{\partial r} + \hat{\epsilon}_j \cdot \hat{\epsilon}_k \nabla^2 g_0$$

$$\nabla^2 G_{jk} = \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 \nabla^2 g_2 + \frac{2}{r}g_2^{\prime}$$
$$+ 6\frac{\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}}{r} - 2r\hat{\epsilon}_j \cdot \hat{\epsilon}_k \frac{\partial g_2}{\partial r} + \hat{\epsilon}_j \cdot \hat{\epsilon}_k \nabla^2 g_0$$

$$\nabla^2 G_{jk} = \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 g_2^{\prime\prime} + \frac{2}{r}g_2^{\prime}$$
$$+ 6\frac{\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}}{r} - 2r\hat{\epsilon}_j \cdot \hat{\epsilon}_k g_2^{\prime} + \hat{\epsilon}_j \cdot \hat{\epsilon}_k g_0^{\prime\prime} + \frac{2}{r}g_0^{\prime}$$
$$= \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 g_2^{\prime\prime}$$
$$+ \frac{2}{r} \times \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 + 6\frac{\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}}{r} - 2r\hat{\epsilon}_j \cdot \hat{\epsilon}_k g_2^{\prime}$$
$$+ \hat{\epsilon}_j \cdot \hat{\epsilon}_k g_0^{\prime\prime} + \frac{2}{r}g_0^{\prime}$$
$$= \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 g_2^{\prime\prime}$$
$$+ \frac{2}{r}\left[\frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 + \frac{4}{r}\left[\frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2\right] g_2^{\prime}\right]$$
$$+ \hat{\epsilon}_j \cdot \hat{\epsilon}_k g_0^{\prime\prime} + \frac{2}{r}g_0^{\prime}$$
$$= \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 g_2^{\prime\prime} + \frac{6}{r}\left[\frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2\right] g_2^{\prime}$$
$$+ \hat{\epsilon}_j \cdot \hat{\epsilon}_k g_0^{\prime\prime} + \frac{2}{r}g_0^{\prime}$$

Thus, the final equation for $\nabla^2 G_{jk}$ becomes:

$$\nabla^2 G_{jk} = \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 \quad g_2'' + \frac{6}{r} g_2' + \hat{\epsilon}_j \cdot \hat{\epsilon}_k \quad g_0'' + \frac{2}{r} g_0' \tag{4.23}$$

Now from equations "(4.15) (4.21) and (4.23)" the required equation for $r^2 \hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} f \psi$ has the expression

$$\begin{aligned} r^2 \hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} f \psi = \frac{1}{2} \Bigg(& \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 \quad g_2'' + \frac{6}{r} g_2' + \hat{\epsilon}_j \cdot \hat{\epsilon}_k \quad g_0'' + \frac{2}{r} g_0' \Bigg) \psi \\ & + \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} \frac{\partial g_2}{\partial r} + 3 g_2' \frac{\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}}{r} - r \hat{\epsilon}_j \cdot \hat{\epsilon}_k g_2 - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 \frac{\partial g_2}{\partial r} \\ & + \hat{\epsilon}_j \cdot \hat{\epsilon}_k \frac{\partial g_0}{\partial r} (-\psi) \\ & + 2\omega \quad \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 \quad g_2' + \hat{\epsilon}_j \cdot \hat{\epsilon}_k g_0' \quad \psi \end{aligned} \tag{4.24}$$

$$\begin{aligned} r^2 \hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} f = \frac{1}{2} \Bigg(& \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 \quad g_2'' + \frac{6}{r} g_2' + \hat{\epsilon}_j \cdot \hat{\epsilon}_k \quad g_0'' + \frac{2}{r} g_0' \Bigg) \\ & + \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} g_2' + 3 g_2 \frac{\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}}{r} - r \hat{\epsilon}_j \cdot \hat{\epsilon}_k g_2 - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 g_2' \\ & + \hat{\epsilon}_j \cdot \hat{\epsilon}_k g_0' \quad (-1) \\ & + 2\omega \quad \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 \quad g_2' + \hat{\epsilon}_j \cdot \hat{\epsilon}_k g_0 \\ = \frac{1}{2} \Bigg(& \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 \quad g_2'' + \frac{6}{r} g_2' + \hat{\epsilon}_j \cdot \hat{\epsilon}_k \quad g_0'' + \frac{2}{r} g_0' \Bigg) \\ & + \Bigg(\frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 \quad g_2' + \frac{2}{r} \frac{3}{2}\hat{\epsilon}_j \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 \quad g_2 \Bigg) \\ & + \hat{\epsilon}_j \cdot \hat{\epsilon}_k g_0' \quad (-1) \\ & + 2\omega \quad \frac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2 \quad g_2 + \hat{\epsilon}_j \cdot \hat{\epsilon}_k g_0 \end{aligned}$$

$$
\begin{aligned}
r^2\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r}f
&= \frac{1}{2}\Big[\frac{3}{2}\hat{\epsilon}_j \cdot \hat{n}\hat{\epsilon}_k \cdot \hat{n} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k\, r^2\Big]\, g_2^{JJ} + \frac{6}{r} g_2^J \\
&\quad + \Big[\frac{3}{2}\hat{\epsilon}_j \cdot \hat{n}\hat{\epsilon}_k \cdot \hat{n} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k\, r^2\Big]\, g_2^J \\
&\quad + \Big[\frac{3}{2}\hat{\epsilon}_j \cdot \hat{n}\hat{\epsilon}_k \cdot \hat{n} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k\, r^2\Big]\, \Big(\frac{2}{r} + 2\omega\Big)\, g_2 + \hat{\epsilon}_j \cdot \hat{\epsilon}_k\, g_0^J \quad (-1) \\
&\quad + \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k\, g^{JJ} + \frac{2}{r} g^J + 2\omega \hat{\epsilon}_j \cdot \hat{\epsilon}_k\, g^J \\
&= \frac{1}{2}\Big[\frac{3}{2}\hat{\epsilon}_j \cdot \hat{n}\hat{\epsilon}_k \cdot \hat{n} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2\Big]\, g_2^{JJ} + \frac{3}{r^2} g^J \\
&\quad + \Big[\frac{3}{2}\hat{\epsilon}_j \cdot \hat{n}\hat{\epsilon}_k \cdot \hat{n} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2\Big]\, g_2^J \\
&\quad + \Big[\frac{3}{2}\hat{\epsilon}_j \cdot \hat{n}\hat{\epsilon}_k \cdot \hat{n} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2\Big]\, \Big(\frac{2}{r} + 2\omega\Big)\, g_2 + \hat{\epsilon}_j \cdot \hat{\epsilon}_k\, g_0^J \quad (-1) \\
&\quad + \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k\, g^{JJ} + \frac{2}{r} g^J + 2\omega \hat{\epsilon}_j \cdot \hat{\epsilon}_k\, g^J \\
&= \frac{1}{2}\Big[\frac{3}{2}\hat{\epsilon}_j \cdot \hat{n}\hat{\epsilon}_k \cdot \hat{n} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2\Big]\, g_2^{JJ} \\
&\quad + \Big[\frac{3}{2}\hat{\epsilon}_j \cdot \hat{n}\hat{\epsilon}_k \cdot \hat{n} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2\Big]\, \Big(\frac{3}{r} - 1\Big) g_2^J \\
&\quad - \Big[\frac{3}{2}\hat{\epsilon}_j \cdot \hat{n}\hat{\epsilon}_k \cdot \hat{n} - \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k r^2\Big]\, \Big(\frac{2}{r} + 2\omega\Big)\, g_2 \\
&\quad + \frac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k\, g^{JJ} + \frac{2}{r} g^J + 2\omega \hat{\epsilon}_j \cdot \hat{\epsilon}_k\, g_0 - \hat{\epsilon}_j \cdot \hat{\epsilon}_k\, g_0^J
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{1}{2}\left[\frac{3}{2}\hat{\epsilon}_j\cdot\hat{n}\hat{\epsilon}_k\cdot\hat{n} - \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right] r^2\, g_2'' + \left[\frac{3}{2}\hat{\epsilon}_j\cdot\hat{n}\hat{\epsilon}_k\cdot\hat{n} - \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right] r^2 \left(\frac{3}{r} - 1\right) g_2' \\
&\quad - \left[\frac{3}{2}\hat{\epsilon}_j\cdot\hat{n}\hat{\epsilon}_k\cdot\hat{n} - \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right] r^2 \left(\frac{2}{r} + 2\omega\right) g_2 \\
&\quad + \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k g_0'' + \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k \frac{2}{r} g_0' + 2\omega\hat{\epsilon}_j\cdot\hat{\epsilon}_k g_0 - \hat{\epsilon}_j\cdot\hat{\epsilon}_k g_0' \\
&= \frac{1}{2}\left[\frac{3}{2}\hat{\epsilon}_j\cdot\hat{n}\hat{\epsilon}_k\cdot\hat{n} - \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right] r^2\, g_2'' + \left[\frac{3}{2}\hat{\epsilon}_j\cdot\hat{n}\hat{\epsilon}_k\cdot\hat{n} - \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right] r^2 \left(\frac{3}{r} - 1\right) g_2' \\
&\quad - \left[\frac{3}{2}\hat{\epsilon}_j\cdot\hat{n}\hat{\epsilon}_k\cdot\hat{n} - \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right] r^2 \left(\frac{2}{r} + 2\omega\right) g_2 \\
&\quad + \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k g_0'' + \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k\left(\frac{2}{r} - 2\right) g_0' + 2\omega\hat{\epsilon}_j\cdot\hat{\epsilon}_k g_0 \\
&= \left[\frac{3}{2}\hat{\epsilon}_j\cdot\hat{n}\hat{\epsilon}_k\cdot\hat{n} - \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right] r^2 \left[\frac{1}{2} g_2'' + \left(\frac{3}{r} - 1\right) g_2' + \left(2\omega - \frac{2}{r}\right) g_2\right] \\
&\quad + \frac{1}{2}(\hat{\epsilon}_j\cdot\hat{\epsilon}_k) g_0'' + \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k\left(\frac{2}{r} - 2\right) g_0' + 2\omega\hat{\epsilon}_j\cdot\hat{\epsilon}_k g_0 \\
&\qquad = \left[\frac{3}{2}\hat{\epsilon}_j\cdot\hat{n}\hat{\epsilon}_k\cdot\hat{n} - \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right] r^2 \left[\frac{1}{2} g_2'' + \left(\frac{3}{r} - 1\right) g_2' + \left(2\omega - \frac{2}{r}\right) g_2\right] \\
&\qquad\quad + \hat{\epsilon}_j\cdot\hat{\epsilon}_k \left[\frac{g_0''}{2} + \left(\frac{1}{r} - 1\right) g_0' + 2\omega g_0\right] \\
&\qquad = \frac{1}{2}\left[\frac{3}{2}\hat{\epsilon}_j\cdot\hat{n}\hat{\epsilon}_k\cdot\hat{n} - \frac{1}{2}(\hat{\epsilon}_j\cdot\hat{\epsilon}_k)\right] r^2 \left[g_2'' + \left(\frac{6}{r} - 2\right) g_2' + \left(4\omega - \frac{4}{r}\right) g_2\right] \\
&\qquad\quad + \hat{\epsilon}_j\cdot\hat{\epsilon}_k \left[g_0'' + \left(\frac{2}{r} - 2\right) g_0' + 4\omega g_0\right]
\end{aligned}
$$

Thus the final equation becomes:

$$
\begin{aligned}
2r^2\hat{\epsilon}_j\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}f = {} & \left[\frac{3}{2}\hat{\epsilon}_j\cdot\hat{n}\hat{\epsilon}_k\cdot\hat{n} - \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right] r^2 \times \\
& \left[g_2'' + \left(\frac{6}{r} - 2\right) g_2' + \left(4\omega - \frac{4}{r}\right) g_2\right] + \hat{\epsilon}_j\cdot\hat{\epsilon}_k \left[g_0'' + \left(\frac{2}{r} - 2\right) g_0' + 4\omega g_0\right]
\end{aligned}
\tag{4.25}
$$

After changing RHS of equation (4.25) of vec r ($\hat{n}$) into hat r ($\hat{r}$), the equation has the form

$$
\begin{aligned}
2r^2\hat{\epsilon}_j\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}f_j = r^2 & \left[\frac{3}{2}\hat{\epsilon}_j\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r} - \frac{1}{2}\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right] g_2'' + \left(\frac{6}{r} - 2\right) g_2' + \left(4\omega - \frac{4}{r}\right) g_2 \\
& + \hat{\epsilon}_j\cdot\hat{\epsilon}_k\left[g_0'' + \left(\frac{2}{r} - 2\right) g_0' + 4\omega g_0\right]
\end{aligned}
\tag{4.26}
$$

As we know, a vector has components of which each one is associated with one co-ordinate axis (i. e. A_x, A_y and A_z of the $\vec{A}$ are associated with x, y and z axes respectively) and they transform some particular way, when we change from one coordinate system to another. Here changing cartesian to spherical as $\hat{\epsilon}\cdot\hat{r} = \hat{\epsilon}_x x + \hat{\epsilon}_y y + \hat{\epsilon}_z z = \sum_{\mu=0,\pm1} \epsilon^*_\mu (\hat{r})_\mu$. Thus,we have,

$$\int \hat{\epsilon_j}\cdot\hat{r}\hat{\epsilon_k}\cdot\hat{r}d\Omega = \sum_{ln} (\hat{\epsilon}_j)_l (\hat{\epsilon}_k)_n \int \hat{r_l}\hat{r_n}d\Omega = \frac{4\pi}{3}(\hat{\epsilon_j})_l\cdot(\hat{\epsilon_k})_n\delta_{ln}$$

$$\int \hat{\epsilon}_j\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}d\Omega = \frac{4\pi}{3}\hat{\epsilon}_j\cdot\hat{\epsilon}_k$$

and

$$\int \hat{\epsilon}_j\cdot\hat{\epsilon}_k d\Omega = 4\pi\hat{\epsilon}_j\cdot\hat{\epsilon}_k$$

Now equation (4.26) becomes

$$2r^2\frac{4\pi}{3}\hat{\epsilon_j}\cdot\hat{\epsilon_k}f = r^2\left[\frac{3}{2}\times\frac{4\pi}{3}\hat{\epsilon_j}\cdot\hat{\epsilon_k} - \frac{1}{2}\times 4\pi\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right]g_2'' + \left(\frac{6}{r} - 2\right)g_2' + \left(4\omega - \frac{4}{r^2}\right)g_2$$
$$+ 4\pi(\hat{\epsilon_j}\cdot\hat{\epsilon_k})\left[g_0'' + \left(\frac{2}{r} - 2\right)g_0' + 4\omega g_0\right] \quad (4.27)$$

Here, From the RHS of (4.27), g_2 terms becomes zero and the remanning terms are the differential equation of g_0

$$2r^2\frac{4\pi}{3}\hat{\epsilon_j}\cdot\hat{\epsilon_k}f = 4\pi\hat{\epsilon}_j\cdot\hat{\epsilon_k}\left[g_0'' + \left(\frac{2}{r} - 2\right)g_0' + 4\omega g_0\right] \quad (4.28)$$

$$\frac{2}{3}r^2 f = \left[g_0'' + \left(\frac{2}{r} - 2\right)g_0' + 4\omega g_0\right] \quad (4.29)$$

Thus the required differential equation for g_0 is

$$\frac{2}{3}r^3 f = r g_0'' + (2 - 2r)g_0' + 4\omega r g_0 \quad (4.30)$$

The differential equation for g_2 is obtained from (4.27) and (4.29)

$$2r^2\frac{4\pi}{3}\hat{\epsilon_j}\cdot\hat{\epsilon_k}f = r^2\left[\frac{3}{2}\times\frac{4\pi}{3}\hat{\epsilon_j}\cdot\hat{\epsilon_k} - \frac{1}{2}\times 4\pi\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right]g_2'' + \left(\frac{6}{r}-2\right)g_2' + \left(4\omega - \frac{4}{r}\right)g_2 + 4\pi\hat{\epsilon}_j\cdot\hat{\epsilon}_k\frac{2}{3}r^2 f \tag{4.31}$$

$$2\times\frac{4\pi}{3}\hat{\epsilon}_j\cdot\hat{\epsilon}_k - \frac{2}{3}\times 4\pi\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right)r^2 f = r^2\left[\frac{3}{2}\times\frac{4\pi}{3}\hat{\epsilon}_j\cdot\hat{\epsilon}_k - \frac{1}{2}\times 4\pi\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right]\times g_2'' + \left(\frac{6}{r}-2\right)g_2' + \left(4\omega - \frac{4}{r}\right)g_2 \tag{4.32}$$

Or,

$$\frac{4}{3}\left[\frac{3}{2}\times\frac{4\pi}{3}\hat{\epsilon}_j\cdot\hat{\epsilon}_k - \frac{1}{2}\times 4\pi\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right]r^2 f = r^2\left[\frac{3}{2}\times\frac{4\pi}{3}\hat{\epsilon}_j\cdot\hat{\epsilon}_k - \frac{1}{2}\times 4\pi\hat{\epsilon}_j\cdot\hat{\epsilon}_k\right]\times g_2'' + \left(\frac{6}{r}-2\right)g_2' + \left(4\omega - \frac{4}{r}\right)g_2 \tag{4.33}$$

Hence, integrating over the angular coordinates enable us to get the differential equation satisfied by the radial terms $g_0(r)$ and $g_2(r)$ as

$$\frac{4}{3}f = g_2'' + \left(\frac{6}{r}-2\right)g_2' + \left(4\omega - \frac{4}{r}\right)g_2 \tag{4.34}$$

$$\frac{4}{3}rf = rg_2'' + (6-2r)g_2' + (4\omega r - 4)g_2 \tag{4.35}$$

Or,

$$rg_0'' + (2-2r)g_0' + 4r\omega g_o = 2\frac{r^3}{3}f \tag{4.36a}$$

$$rg_2'' + (6-2r)g_2' + g_2(4\omega r - 4) = \frac{4}{3}rf \tag{4.36b}$$

We also have the following differential equations for the beams having different frequencies, and different polarization (Radhakrishnan and Thayyullathil, 2004).

$$rf'' + (4-2r)f' + (2\omega r - 2)f = -2r \tag{4.37a}$$

$$rg_0'' + (2-2r)g_0' + 4\omega r g_o = \frac{2}{3}r^3 f \tag{4.37b}$$

$$rg_2'' + (6-2r)g_2' + g_2(4\omega r - 4) = \frac{4}{3}rf \tag{4.37c}$$

Multiphoton ionization rate and cross-section

The ionization rate for three-photon will be obtained using

$$\frac{d\Gamma^{(3)}}{d\Omega} \propto \left(\frac{\bar{I}}{I_0}\right)^3 |M_{fg}^{(3)}|^2$$

where,

$$\bar{I} = \sum_{j=1}^{3} I_j$$

is the total intensity of radiation beams.

And **the differential scattering cross-section** is given as

$$\frac{d\sigma^{(3)}}{d\Omega} = \left(\frac{\alpha}{2\pi}\right)^3 \left(\frac{I}{2I_0}\right)^2 |M_{fg}^{(3)}|^2 \alpha_0^2 \omega k_f \tag{4.38}$$

Here, the transition amplitude of three photon ionization

$$|M_{fg}^{(3)}|^2 = |\langle f|E_{0l}(\hat{\epsilon}_l \cdot \hat{r})G_{jk}|g\rangle|^2$$

The matrix element from ground state quantum numbers n, l and m to the final state quantum numbers n', l' and m' will be

$$M_{fg}^{(3)} = E_{0l} \int r\psi^*_{n'l'm'}(\hat{\epsilon}_l \cdot \hat{r})G_{jk}\psi_{nlm}d\tau \tag{4.39}$$

$$\begin{aligned} G_{jk} &= r^2 E_{0j}E_{0k}\left[\tfrac{3}{2}\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} - \tfrac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k\right] g_2 + E_{0j}E_{0k}(\hat{\epsilon}_j \cdot \hat{\epsilon}_k)\, g_0 \\ &= E_{0j}E_{0k}\left[r^2 \tfrac{3}{2}(\hat{\epsilon}_j \cdot \hat{r})(\hat{\epsilon}_k \cdot \hat{r}) - \tfrac{1}{2}\hat{\epsilon}_j \cdot \hat{\epsilon}_k\right] g_2 + \hat{\epsilon}_j \cdot \hat{\epsilon}_k\, g_0 \end{aligned} \tag{4.40}$$

Finally using the value of $f(r)$, $g_0(r)$ and $g_2(r)$ as,

$$f(r) = \frac{1}{\omega} - \frac{1}{2\omega^3}\Phi(1, 1, \lambda_1, 1, r) \tag{4.41}$$

$$g_2(r) = \frac{1}{3\omega^2} - \frac{1}{3\omega^4}\Phi(1, 1, \lambda_1, 1, r) + \frac{2}{3\omega^4}\int_{\lambda_1}^{1} dt \frac{K(1, 1, \lambda_1, t)t}{K(3, 3, \lambda_2, t)}\Phi(2, 2, \lambda_2, t, r) \tag{4.42}$$

where $\lambda_1 = \sqrt{(1-2\omega)}$ and $\lambda_2 = \sqrt{1-4\omega}$

$$g_0(r) = \frac{2}{3\omega^2}\left[\frac{r^2}{4} + \frac{1}{4\omega^2}(1-2\lambda_1) - \frac{3}{8\omega}\right] - \frac{1}{3\lambda_1\omega^4}\Phi(0,0,\lambda_2,1,r)$$

$$\left[-\frac{1}{6\omega^4}\left\{r^2 + \frac{\lambda_1}{\omega}r - \frac{1}{\omega}\left(1+\frac{1}{\lambda_1}\right)\right\}\Phi(1,1,\lambda_1,1,r)\right.$$

$$\left. -\frac{1}{3\omega}\left[1+\frac{1}{\lambda_1}\int_{\lambda_1}^{1} dt\, K(1,1,\lambda_1,t)\times\left\{\omega(1+\lambda_1) - \omega\, t + \lambda_1(t+\lambda_1)^2\right\}\Phi(0,0,\lambda_2,t,r)\right.\right] \tag{4.43}$$

Angular part of the matrix element

From now we have used the symbols old j = new i, old k= new j and old l = new k, just to make clear from the orbital angular momentum l. Assuming that the atom make a transition from initial state as a ground state $|g\rangle$ to the final state $|f\rangle$ by absorbing three photons.

Three photon selection rule

The matrix element (4.8) will be non zero only when, $l = 0$ and $l = 2$ for to two photon process and $l = 1$ and $l = 3$ corresponds to three photon process.
By performing the same as done in privious chapter 3, the matrix element becomes

$$M^{(3)}_{fg} = \langle f|\ \hat{\epsilon}_k \cdot \hat{r}\left[\frac{3}{2}\hat{\epsilon}_i \cdot \hat{r}\,\hat{\epsilon}_j \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_i \cdot \hat{\epsilon}_j r^2\right] g_2 + \hat{\epsilon}_i \cdot \hat{\epsilon}_j\, g_0\ |g\rangle \tag{4.44}$$

Or,

$$M^{(3)}_{fg} = E_{0k}\int 4\pi \sum_{lm} (i)^l \times$$

$$R_{kl}(r)Y^*_{lm}(\hat{r})Y_{lm}(\hat{k})(\hat{\epsilon}_k \cdot \hat{r})\ E_{0i}E_{0j}\left[\frac{3}{2}\hat{\epsilon}_i \cdot \hat{r}\epsilon_j \cdot \hat{r} - \frac{1}{2}\hat{\epsilon}_i \cdot \hat{\epsilon}_j r^2\ g_2\right. \tag{4.45}$$

$$\left. + E_{0i}E_{0j}\hat{\epsilon}_i \cdot \hat{\epsilon}_j g_0\right]\psi_g d\tau$$

Using spherical addition theorem

$$M_{fg}^{(3)} = E_{0i}E_{0j}E_{0k}\int 4\pi\frac{2l+1}{4\pi}P_l(\hat{k}\cdot\hat{r})(i)^l R_{kl}(r)\hat{\epsilon}_k\cdot\hat{\pi}\times \left(\frac{3}{2}\hat{\epsilon}_i\cdot\hat{\pi}\epsilon_j\cdot\hat{\pi} - \frac{1}{2}\hat{\epsilon}_i\cdot\hat{\epsilon}_j r^2\right) g_2 + \hat{\epsilon}_i\cdot\hat{\epsilon}_j g_0 \psi_g d\tau \quad (4.46)$$

For $l = 1$, i.e., p - orbital

Separating angular and radial part

$$M_{fg}^{(3)} = 3(i)E_{0i}E_{0j}E_{0k}\int R_{k1}(r)r^2\psi_g dr \int P_1(\hat{k}\cdot\hat{r})\hat{\epsilon}_k\cdot\hat{\epsilon}\times \left(\frac{3}{2}\hat{\epsilon}_i\cdot\hat{\epsilon}\epsilon_j\cdot\hat{\epsilon} - \frac{1}{2}\hat{\epsilon}_i\cdot\hat{\epsilon}_j r^2 g_2 + \hat{\epsilon}_i\cdot\hat{\epsilon}_j g_0\right)d\Omega$$

$$= 3(i)E_{0i}E_{0j}E_{0k}\int R_{k1}(r)r^2\psi_g dr \int P_1(\hat{k}\cdot\hat{r})\hat{\epsilon}_k\cdot\hat{\epsilon}\left(\frac{3}{2}\hat{\epsilon}_i\cdot\hat{\epsilon}\epsilon_j\cdot\hat{\epsilon} - \frac{1}{2}\hat{\epsilon}_i\cdot\hat{\epsilon}_j r^2 g_2\right)d\Omega$$
$$+ 3(i)E_{0i}E_{0j}E_{0k}\int R_{k1}(r)r^2\psi_g dr \int P_1(\hat{k}\cdot\hat{r})\hat{\epsilon}_k\cdot\hat{\epsilon}\hat{\epsilon}_i\cdot\hat{\epsilon}_j g_0 d\Omega$$

$$= 3(i)E_{0i}E_{0j}E_{0k}\int R_{k1}(r)r^5\psi_g dr \int P_1(\hat{k}\cdot\hat{r})\hat{\epsilon}_k\cdot\hat{r}\left(\frac{3}{2}\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{r} - \frac{1}{2}\hat{\epsilon}_i\cdot\hat{\epsilon}_j g_2\right)d\Omega$$
$$+ 3(i)E_{0i}E_{0j}E_{0k}\int R_{k1}(r)r^3\psi_g dr \int P_1(\hat{k}\cdot\hat{r})\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{\epsilon}_j g_0 d\Omega$$

$$= 3(i)E_{0i}E_{0j}E_{0k}\int R_{k1}(r)r^5 g_2\psi_g dr \left(\frac{3}{2}\int P_1(\hat{k}\cdot\hat{r})\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{r}\epsilon_j\cdot\hat{r}d\Omega - \frac{1}{2}\int P_1(\hat{k}\cdot\hat{r})\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{\epsilon}_j d\Omega\right)$$
$$+ 3(i)E_{0i}E_{0j}E_{0k}\int R_{k1}(r)g_0 r^3\psi_g dr \int P_1(\hat{k}\cdot\hat{r})\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{\epsilon}_j d\Omega$$

$$= 3(i)E_{0i}E_{0j}E_{0k}\int R_{k1}(r)r^5 g_2 e^{-r}dr \left(\frac{3}{2}\int \hat{k}\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{r}d\Omega - \frac{1}{2}\hat{\epsilon}_i\cdot\hat{\epsilon}_j\int \hat{k}\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}d\Omega\right)$$
$$+ 3(i)E_{0i}E_{0j}E_{0k}\hat{\epsilon}_j\cdot\hat{\epsilon}_i\int R_{k1}(r)g_0 r^3 e^{-r}dr \int \hat{k}\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r})d\Omega$$

$$= 3(i)E_{0i}E_{0j}E_{0k}\int R_{k1}(r)r^5 g_2 e^{-r}dr\times \left(\frac{3}{2}\int \hat{k}\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{r}d\Omega - \frac{1}{2}(\hat{\epsilon}_i\cdot\hat{\epsilon}_j)\frac{4\pi}{3}\hat{k}\cdot\hat{\epsilon}_k\right)$$
$$+ 3(i)E_{0i}E_{0j}E_{0k}\hat{\epsilon}_j\cdot\hat{\epsilon}_i\int R_{k1}(r)g_0 r^3 e^{-r}dr\frac{4\pi}{3}\hat{k}\cdot\hat{\epsilon}_k$$

Thus the final equation for $M_{fg}^{(3)}$

$$
\begin{aligned}
M_{fg}^{(3)} = {} & 3(i)E_{0i}E_{0j}E_{0k} \int R_{k1}(r)r^5 g_2 e^{-r} dr \times \\
& \frac{4\pi}{15} \Big[\hat{k}\cdot\hat{\epsilon}_i \hat{k}\cdot\hat{\epsilon}_j \hat{k}\cdot\hat{\epsilon}_k + \hat{k}\cdot\hat{\epsilon}_j \hat{k}\cdot\hat{\epsilon}_i \hat{k}\cdot\hat{\epsilon}_k + \hat{k}\cdot\hat{\epsilon}_k \hat{k}\cdot\hat{\epsilon}_j \hat{k}\cdot\hat{\epsilon}_i \Big] \\
& - \frac{4\pi}{9} \hat{\epsilon}_i\cdot\hat{\epsilon}_j \hat{k}\cdot\hat{\epsilon}_k \Big] \\
& + 4\pi(i)E_{0i}E_{0j}E_{0k} \hat{k}\cdot\hat{\epsilon}_i \hat{k}\cdot\hat{\epsilon}_j \hat{k}\cdot\hat{\epsilon}_k \int R_{k1}(r) g_0 r^3 e^{-r} dr
\end{aligned}
\tag{4.47}
$$

For $l = 3$, i.e., f - orbital

Separating angular and radial part

$$
\begin{aligned}
M_{fg}^{(3)} &= 4\pi\frac{7}{4\pi}(-i)E_{0i}E_{0j}E_{0k}\int R_{k3}(r)r^2\psi_g dr\int P_3(\hat{k}\cdot\hat{r})\hat{\epsilon}_k\cdot\hat{n}\times \\
&\quad \frac{3}{2}\hat{\epsilon}_i\cdot\hat{n}\hat{\epsilon}_j\cdot\hat{n} - \frac{1}{2}\hat{\epsilon}_i\cdot\hat{\epsilon}_j\Big)g_2 + \hat{\epsilon}_i\cdot\hat{\epsilon}_j g_0\Big)d\Omega \\
&= 7(-i)E_{0i}E_{0j}E_{0k}\int R_{k3}(r)r^2\psi_g dr\int P_3(\hat{k}\cdot\hat{r})\hat{\epsilon}_k\cdot\hat{n}\times \\
&\quad \frac{3}{2}\hat{\epsilon}_i\cdot\hat{n}\hat{\epsilon}_j\cdot\hat{n} - \frac{1}{2}\hat{\epsilon}_i\cdot\hat{\epsilon}_j\Big)g_2 + \hat{\epsilon}_i\cdot\hat{\epsilon}_j g_0\Big)d\Omega \\
&= 7(-i)E_{0i}E_{0j}E_{0k}\int R_{k3}(r)r^5e^{-r}dr\int P_3(\hat{k}\cdot\hat{r})\hat{\epsilon}_k\cdot\hat{r}\Big(\frac{3}{2}\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{r} - \frac{1}{2}\hat{\epsilon}_i\cdot\hat{\epsilon}_j\Big)g_2 d\Omega \\
&\quad + 3(-i)E_{0i}E_{0j}E_{0k}\int R_{k3}(r)r^3e^{-r}dr\int P_3(\hat{k}\cdot\hat{r})\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{\epsilon}_j g_0 d\Omega \\
&= 7(-i)E_{0i}E_{0j}E_{0k}\int R_{k3}(r)r^5 g_2 e^{-r}dr\times \\
&\quad \int\Big(\frac{1}{2}\Big[5(\hat{k}\cdot\hat{r})^3 - 3(\hat{k}\cdot\hat{r})\Big]\frac{3}{2}\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{r}d\Omega \\
&\quad - \int\frac{1}{2}\Big[5(\hat{k}\cdot\hat{r})^3 - 3(\hat{k}\cdot\hat{r})\Big]\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{\epsilon}_j d\Omega \\
&\quad + 3(-i)E_{0i}E_{0j}E_{0k}\int R_{k3}(r)g_0 r^3 e^{-r}dr\int\frac{1}{2}\Big[5(\hat{k}\cdot\hat{r})^3 - 3\hat{k}\cdot\hat{r}\Big]\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\epsilon_{\hat{j}}d\Omega \\
&= 7(-i)E_{0i}E_{0j}E_{0k}\int R_{k3}(r)r^5 g_2 e^{-r}dr\times \\
&\quad \int\frac{15}{4}(\hat{k}\cdot\hat{r})^3\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}d\Omega - \frac{9}{4}\int\hat{k}\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}d\Omega \\
&\quad - \int\frac{5}{4}(\hat{k}\cdot\hat{r})^3\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{\epsilon}_k d\Omega + \frac{3}{4}\int\hat{k}\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{\epsilon}_k d\Omega \\
&\quad + 3(-i)E_{0i}E_{0j}E_{0k}\int R_{k3}(r)g_0 r^3 e^{-r}dr\int\frac{5}{2}(\hat{k}\cdot\hat{r})^3\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\epsilon_{\hat{j}}d\Omega \\
&\quad - \int\frac{3}{2}\hat{k}\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{\epsilon}_j d\Omega
\end{aligned}
\tag{4.48}
$$

The angular part of first integral is

$$I_1 = \int_{\hbar} (\hat{k}\cdot\hat{r})^3 \hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{r}\epsilon_k\cdot\hat{r}d\Omega = \frac{4\pi}{21}\times$$
$$(\hat{k}_1\cdot\hat{\epsilon}_i)(\hat{k}_2\cdot\hat{\epsilon}_j)(\hat{k}_3\cdot\hat{\epsilon}_k) + (\hat{k}_1\cdot\hat{\epsilon}_j)(\hat{k}_2\cdot\hat{\epsilon}_i)(\hat{k}_3\cdot\hat{\epsilon}_k) + (\hat{k}_1\cdot\hat{\epsilon}_k)(\hat{k}_2\cdot\hat{\epsilon}_i)(\hat{k}_3\cdot\hat{\epsilon}_j)$$
$$+ (\hat{k}_2\cdot\hat{\epsilon}_i)(\hat{k}_1\cdot\hat{\epsilon}_j)(\hat{k}_3\cdot\hat{\epsilon}_k) + (\hat{k}_2\cdot\hat{\epsilon}_j)(\hat{k}_1\cdot\hat{\epsilon}_i)(\hat{k}_3\cdot\hat{\epsilon}_k) + (\hat{k}_2\cdot\hat{\epsilon}_k)(\hat{k}_1\cdot\hat{\epsilon}_i)(\hat{k}_3\cdot\hat{\epsilon}_j)$$
$$+ (\hat{k}_3\cdot\hat{\epsilon}_i)(\hat{k}_2\cdot\hat{\epsilon}_j)(\hat{k}_3\cdot\hat{\epsilon}_k) + (\hat{k}_3\cdot\hat{\epsilon}_j)(\hat{k}_2\cdot\hat{\epsilon}_k)(\hat{k}_1\cdot\hat{\epsilon}_i) + (\hat{k}_3\cdot\hat{\epsilon}_k)(\hat{k}_2\cdot\hat{\epsilon}_i)(\hat{k}_1\cdot\hat{\epsilon}_j)$$
$$+ (\hat{k}_1\cdot\hat{\epsilon}_i)(\hat{k}_3\cdot\hat{\epsilon}_j)(\hat{k}_2\cdot\hat{\epsilon}_k) + (\hat{k}_1\cdot\hat{\epsilon}_j)(\hat{k}_3\cdot\hat{\epsilon}_i)(\hat{k}_2\cdot\hat{\epsilon}_k) + (\hat{k}_1\cdot\hat{\epsilon}_k)(\hat{k}_2\cdot\hat{\epsilon}_j)(\hat{k}_3\cdot\hat{\epsilon}_i)$$
$$+ (\hat{k}_2\cdot\hat{\epsilon}_i)(\hat{k}_1\cdot\hat{\epsilon}_k)(\hat{k}_3\cdot\hat{\epsilon}_j) + (\hat{k}_2\cdot\hat{\epsilon}_j)(\hat{k}_1\cdot\hat{\epsilon}_k)(\hat{k}_3\cdot\hat{\epsilon}_i) + (\hat{k}_2\cdot\hat{\epsilon}_k)(\hat{k}_1\cdot\hat{\epsilon}_j)(\hat{k}_3\cdot\hat{\epsilon}_i)$$
$$+ (\hat{k}_3\cdot\hat{\epsilon}_i)(\hat{k}_2\cdot\hat{\epsilon}_k)(\hat{k}_1\cdot\hat{\epsilon}_j) + (\hat{k}_3\cdot\hat{\epsilon}_j)(\hat{k}_2\cdot\hat{\epsilon}_i)(\hat{k}_1\cdot\hat{\epsilon}_k) + (\hat{k}_3\cdot\hat{\epsilon}_k)(\hat{k}_2\cdot\hat{\epsilon}_j)(\hat{k}_1\cdot\hat{\epsilon}_i)\Big]_{\mathbf{i}} \quad (4.49)$$

The angular part of second integral is

$$I_2 = \int_{\hbar} \hat{k}\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}d\Omega$$
$$= \frac{4\pi}{15}\Big[\hat{k}\cdot\hat{\epsilon}_i\,\hat{k}\cdot\hat{\epsilon}_j\,\hat{k}\cdot\hat{\epsilon}_k + \hat{k}\cdot\hat{\epsilon}_j\,\hat{k}\cdot\hat{\epsilon}_i\,\hat{k}\cdot\hat{\epsilon}_k + \hat{k}\cdot\hat{\epsilon}_k\,\hat{k}\cdot\hat{\epsilon}_j\,\hat{k}\cdot\hat{\epsilon}_i\Big]_{\mathbf{i}} \quad (4.50)$$

The third part is

$$I_3 = \int_{\hbar} (\hat{k}\cdot\hat{r})^3 \hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{\epsilon}_k d\Omega \quad (4.51)$$
$$= \hat{\epsilon}_j\cdot\hat{\epsilon}_k \int_{\hbar} (\hat{k}\cdot\hat{r})^3 \hat{\epsilon}_i\cdot\hat{r}d\Omega$$
$$= \frac{4\pi}{3}\Big[(\hat{\epsilon}_j\cdot\hat{\epsilon}_k)(\hat{k}\cdot\hat{\epsilon}_i)(\hat{k}_1\cdot\hat{k}_2)(\hat{k}_3\cdot\hat{k}_1) + (\hat{k}_2\cdot\hat{\epsilon}_i)(\hat{k}_1\cdot\hat{k}_3) + (\hat{k}_3\cdot\hat{\epsilon}_i)(\hat{k}_1\cdot\hat{k}_2)\Big]_{\mathbf{i}}$$

the fourth part of integral is

$$I_4 = \int_{\hbar} \hat{k}\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{\epsilon}_k d\Omega \quad (4.52)$$
$$= \hat{\epsilon_j}\cdot\hat{\epsilon_k}\int_{\hbar} \hat{k}\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{r}d\Omega$$
$$= \frac{4\pi}{3}(\hat{\epsilon_j}\cdot\hat{\epsilon}_k)(\hat{k}\cdot\hat{\epsilon}_i)$$
$$= \frac{4\pi}{3}\hat{k}\cdot\hat{\epsilon}_i\,\hat{\epsilon}_j\cdot\hat{\epsilon}_k$$

The fifth part of integral is

$$I_5 = \int_{\hbar} (\hat{k}\cdot\hat{r})^3 \hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{\epsilon}_k d\Omega \quad (4.53)$$

The solution is the same as that of (4.49)

The sixth part of integral is

$$I_6 = \int \hat{k}\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{\epsilon}_j d\Omega = \hat{\epsilon}_i\cdot\hat{\epsilon}_j \int \hat{k}\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}d\Omega = \frac{4\pi}{3}\hat{\epsilon}_i\cdot\hat{\epsilon}_j\hat{k}\cdot\hat{\epsilon}_k \qquad (4.54)$$

Thus, different location have different probabilities of finding the particle, which is given as usual notations

$$|\psi|^2 = |R_{nl}|^2|Y_{l,m_l}|^2$$

Where, $0 \le l < n$ and $-l < m_l < +l$, m_l has $(2l+1)$ states. For each set of three quantum numbers, there is specific wave function or orbital with unique shape. Thus, by substituting the values of (4.49), (4.50), (4.51), (4.52), (4.53) and (4.54) to the (5.4) and by manipulation, the transition amplitudes can be evaluated and hence the rate and cross-section are determined.

In simple notation

To make the program convenient, we have modified the symbol in simple form.

Angular integrals

Consider, three photons are simultaneously absorbed from three beams (j_1, j_2 and j_3) with different polarizations ($\hat{\epsilon}_{j_1}$, $\hat{\epsilon}_{j_2}$ and $\hat{\epsilon}_{j_3}$) and same frequency. We have the transition matrix element has the form

$$M^{(3)}_{j_1j_2j_3} = \langle f|\hat{\epsilon}_{j_1}\cdot\hat{r}G_{j_2j_3}|g\rangle \qquad (4.55)$$

$$M_{j_1j_2j_3} = \sum_l (-i)^l \frac{(2l+1)}{\sqrt{\pi}} \int e_{-r} R_{kl} \frac{r^3}{2} g_2\hat{\epsilon}_{j_1}\cdot\hat{r}Q_{j_2j_3} + rg_0(\hat{\epsilon}_{j_1}\cdot\hat{r})q_{j_2j_3}]P_l(\hat{k}\cdot\hat{r})d^3r$$

For evaluating the angular integrals involving Legendre polynomials let us consider the given equations

$$\int P_1(\hat{k}\cdot r)(\hat{\epsilon}_k\cdot\hat{r})(\hat{\epsilon}_i\cdot\hat{\epsilon}_k)d\Omega$$

$$= \frac{4\pi}{3}\hat{k}\cdot\hat{\epsilon}_k\hat{\epsilon}_i\cdot\hat{\epsilon}_j \int P_1(\hat{k}\cdot r)(\hat{\epsilon}_i\cdot\hat{r})(\hat{\epsilon}_j\cdot\hat{r})(\hat{\epsilon}_k\cdot\hat{r})d\Omega$$

$$= \frac{4\pi}{15}\left[\hat{k}\cdot\hat{\epsilon}_i\hat{\epsilon}_j\cdot\hat{\epsilon}_k + \hat{k}\cdot\hat{\epsilon}_j\hat{\epsilon}_i\cdot\hat{\epsilon}_k + \hat{k}\cdot\hat{\epsilon}_k\hat{\epsilon}_i\cdot\hat{\epsilon}_j\right]$$

$$\int P_1(\hat{k}\cdot r)(\hat{\epsilon}_k\cdot\hat{r})\frac{1}{2}\left[3(\hat{\epsilon}_i\cdot\hat{r})(\hat{\epsilon}_j\cdot\hat{r}) - (\hat{\epsilon}_i\cdot\hat{\epsilon}_j)\right]d\Omega$$

$$= \frac{4\pi}{15}\left[3\hat{k}\cdot\hat{\epsilon}_i\hat{\epsilon}_j\cdot\hat{\epsilon}_k + 3\hat{k}\cdot\hat{\epsilon}_i\hat{\epsilon}_j\cdot\hat{\epsilon}_k - 2\hat{k}\cdot\hat{\epsilon}_k\hat{\epsilon}_i\cdot\hat{\epsilon}_j\right] \quad (4.56a)$$

$$\int P_3(\hat{k}\cdot\hat{r})(\hat{\epsilon}_i\cdot\hat{r})(\hat{\epsilon}_j\cdot\hat{r})(\hat{\epsilon}_k\cdot\hat{r})d\Omega$$

$$= \frac{12\pi}{105}\left[5\hat{k}\cdot\hat{\epsilon}_i\hat{k}\cdot\hat{\epsilon}_j\hat{k}\cdot\hat{\epsilon}_k - \hat{k}\cdot\hat{\epsilon}_i\hat{\epsilon}_j\cdot\hat{\epsilon}_k - \hat{k}\cdot\hat{\epsilon}_j\hat{\epsilon}_i\cdot\hat{\epsilon}_k - \hat{k}\cdot\hat{\epsilon}_k\hat{\epsilon}_i\cdot\hat{\epsilon}_j\cdots\right] \quad (4.56b)$$

With the standard algebra including the integrals of Legendre polynomial we have the final form of the three photon matrix element as

$$M_{j_1j_2j_3} = -i4\sqrt{\pi}\int drR^*_{k1}\left[r^3g_0 - \frac{r^5}{2}g_2\right]e^{-r}\hat{k}\cdot\hat{\epsilon}_{j_1}\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3}$$
$$-i\sqrt{\frac{\pi}{5}}\int drR^*_{k1}r^5g_2e^{-r}\left[\hat{k}\cdot\hat{\epsilon}_{j_1}\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_2}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_3}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_2}\right]$$
$$-i\sqrt{\frac{3}{10}}\pi\int drR^*_{k3}r^5g_2e^{-r}\times$$
$$\left[5\hat{k}\cdot\hat{\epsilon}_{j_1}\hat{k}\cdot\hat{\epsilon}_{j_2}\hat{k}\cdot\hat{\epsilon}_{j_3} - \hat{k}\cdot\hat{\epsilon}_{j_1}\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3} - \hat{k}\cdot\hat{\epsilon}_{j_2}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_3} - \hat{k}\cdot\hat{\epsilon}_{j_3}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_2}\right]$$

We have to identity for a general vector $T_{j_1j_2j_3}$ symmetric in j_1, j_2 and j_3 we have

$$\sum_{j_1j_2j_3} T_{j_1j_2j_3} = \frac{1}{3}\sum_{j_1j_2j_3}\left[\hat{k}\cdot\hat{\epsilon}_{j_1}\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_2}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_3}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_2}\right]$$

And with the new notation the angular integrals are given by

$$\Theta^{(1)}_{j_1j_2j_3} = \hat{k}\cdot\hat{\epsilon}_{j_1}\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_2}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_3}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_2}$$

and

$$\Theta^{(3)}_{j_1j_2j_3} = 5(\hat{k}\cdot\hat{\epsilon}_{j_1})(\hat{k}\cdot\hat{\epsilon}_{j_2})(\hat{k}\cdot\hat{\epsilon}_{j_3}) - \Theta^{(1)}_{j_1j_2j_3}$$

Thus the final form of $M_{j_1j_2j_3}$ is

$$M_{j_1j_2j_3} = \Theta^{(1)}_{j_1j_2j_3} \times -i\frac{4\sqrt{\pi}}{15}\int drR^*_{k1}\ 5r^3g_0 + 2r^5g_2\ e^{-r} + \Theta^{(3)}_{j_1j_2j_3} \times i\frac{\sqrt{6}}{5\sqrt{\pi}}\int drR^*_{k3} r^5 g_2 e^{-r} \tag{4.57}$$

Radial integrals

let us define the radial integrals as

$$M^{(1)} = \frac{4\sqrt{\pi}}{15}(-i)\int drR^*_{k1}\ 5r^3g_0 + 2r^5g_2\ e^{-r} \tag{4.58}$$

$$M^{(3)} = \frac{6\sqrt{\pi}}{5}(i)\int drR^*_{k3} r^5 g_2 e^{-r} \tag{4.59}$$

with these definition we have the $M_{j_1j_2j_3}$ as

$$M_{j_1j_2j_3} = M^{(1)}\Theta^{(1)}_{j_1j_2j_3} + M^{(3)}\Theta^{(3)}_{j_1j_2j_3} \tag{4.60}$$

Evaluation of the radial integrals in $M^{(1)}$ and $M^{(3)}$ can be done using the integrals involving confluent hypergeometric functions. For that let us use the final state wave function as

$$R_{kl}(r) = e^{\frac{\pi\nu}{2}}\frac{\Gamma(l+1-i\nu)}{\Gamma(2l+2)}(2rk_f)^l e^{ik_f r}F(l+1-i\nu, 2l+2, -2ik_f r) \tag{4.61}$$

we can obtain the the above integrals in terms of standard functions involving confluent hypergeometric functions.

Asymmetries in multiphoton ionization

Total ionization rate for three photon transition is given by

$$\Gamma^{(3)} = \left(\frac{I}{I_0}\right)^3 |M^{(3)}|^2$$

where

$$M^{(3)} = \sum_{j_1 j_2 j_3} \sqrt{\frac{I_{j1} I_{j2} I_{j3}}{I^3}} e^{-i(\delta_{j_1}+\delta_{j_2}+\delta_{j_3})} \quad M^{(1)} \Theta^{(1)}_{j_1 j_2 j_3} + M^{(3)} \Theta^{(3)}_{j_1 j_2 j_3}$$

here the radial integrals are given by

$$M^{(1)} = -i \frac{4}{15} \sqrt{\pi} \int e^{-r} R^*_{k1} \left[5r^3 g_0 + 2r^5 g_2 \right] dr$$

and

$$M^{(3)} = i \frac{6}{5} \sqrt{\pi} \int e^{-r} R^*_{k3} r^5 g_2 \, dr$$

differential scattering cross section is given by

$$\frac{d\sigma^{(3)}}{d\Omega} = \left(\frac{\alpha}{4\pi} \right) \left(\frac{I}{I_0} \right)^2 |M^{(3)}_{fg}|^2 a_0^2 \omega k \tag{4.62}$$

Polarization dependance

The polarization vector $\hat{\epsilon}_j$ these vectors are normalized such as $\hat{\epsilon}_j^* \cdot \hat{\epsilon}_j$ beam of radiations are parallel and along z direction, polarization is in the x-y plane and for elliptical polarization

$$\hat{\epsilon}_j = \hat{e}_x \cos(\zeta_j/2) + i\hat{e}_y \sin(\zeta_j/2)$$

here $\hat{e}_x$ represents the unit polarization vector along the direction x axis the ellipticity angle ζ_j takes the values $-\pi/2 \geq \zeta \geq \pi/2$ the values $\zeta = 0$ corresponds to linear $\zeta = \pm\pi/2$ corresponds to circular polarization.

The polarization dependance can be well studied by using the functions $\Theta^{(1)}_{j_1 j_2 j_3}$ and $\Theta^{(3)}_{j_1 j_2 j_3}$.

CHAPTER 5

Results and Discussions

Analytical results

Two-photon ionization

We consider the ground states hydrogen atom is subjected to an electromagnetic field of frequency ω, composed of two or three beams of different polarization states. In the case when the laser radiation contains two beams with polarization vectors ϵ_i, ϵ_j, the final continuum of energy $E = E_1 + 2k\omega$, (where E_1 is the ground state energy) can be reached by quantum interference of three different routes. For three beams, the same final continuum state is reached now by quantum interference of six different routes as given in Eq.(3.14), with polarization vectors ϵ_i, ϵ_j and ϵ_k. Each two photon pathways involves the same l, final states ($l = 0$, $l = 2$). Within the second order perturbation theory and in the length gauge, the transition amplitude possible for two photon ionization, are,

$l = 0$, **i.e., s-orbital**

$$M_{fg}^{(2)} = \frac{4\pi}{3} E_{0i} E_{0j} \hat{\epsilon_i} \cdot \hat{\epsilon_j} \int r^4 R_{k0}(r) f_i e^{-r} dr \tag{5.1}$$

$l = 2$, **i.e., d-orbital**

$$M_{fg}^{(2)} = \left(-5\right) E_{0i} E_{0j} \times \frac{3}{2}\frac{4\pi}{15} \left[\hat{k} \cdot \hat{\epsilon}_i \hat{k} \cdot \hat{\epsilon}_j + \hat{k} \cdot \hat{\epsilon}_i \hat{k} \cdot \hat{\epsilon}_j + \hat{k} \cdot \hat{k} \hat{\epsilon}_i \cdot \hat{\epsilon}_j \right] - \frac{1}{2}\frac{4\pi}{3} \hat{\epsilon}_i \cdot \hat{\epsilon}_j \times \int r^4 R_{k2}(r) f_i \psi_g dr \tag{5.2}$$

The Eq.(5.1) and Eq. (5.2) of $M_{fg}^{(2)}$, which are discussed in chapter three, will be used to evaluate the transition rate and differential cross-section of the two photon ionization process under different conditions concerning the polarization, phase and ejected photoelectrons.

Three-photon ionization

Similarly, for three photon, the ground states hydrogen atom is subjected to an electromagnetic field of frequency ω, composed of two or three beams of different polarization states. In the case when the laser radiation contains two beams with polarization vectors ϵ_i, ϵ_j, the final continuum of energy $E = E_1 + 3k\omega$, (where E_1 is the ground state energy) can be reached by quantum interference of six different routes. For three beams, the same final continuum state is reached now by quantum interference of nine different routes, with polarization vectors ϵ_i, ϵ_j and ϵ_k. Each three photon pathways involves the same l, final states ($l = 1$, $l = 3$). Within the third order perturbation theory and in the length gauge, the transition amplitude possible for three photon ionization, are,

For $l = 1$, i.e., p - orbital

$$M_{fg}^{(3)} = 3(i)E_{0i}E_{0j}E_{0k}\int R_{k1}(r)r^5 g_2 e^{-r}dr \times \left\{\frac{4\pi}{15}\left[\hat{k}\cdot\hat{\epsilon}_i\,\hat{k}\cdot\hat{\epsilon}_j\,\hat{k}\cdot\hat{\epsilon}_k + \hat{k}\cdot\hat{\epsilon}_j\,\hat{k}\cdot\hat{\epsilon}_i\,\hat{k}\cdot\hat{\epsilon}_k + \hat{k}\cdot\hat{\epsilon}_k\,\hat{k}\cdot\hat{\epsilon}_j\,\hat{k}\cdot\hat{\epsilon}_i\right]\right\} - \frac{4\pi}{9}\hat{\epsilon}_i\cdot\hat{\epsilon}_j\,\hat{k}\cdot\hat{\epsilon}_k + 4\pi(i)E_{0i}E_{0j}E_{0k}\hat{k}\cdot\hat{\epsilon}_i\hat{k}\cdot\hat{\epsilon}_j\hat{k}\cdot\hat{\epsilon}_k\int R_{k1}(r)g_0 r^3 e^{-r}dr \quad (5.3)$$

For $l = 3$, i.e., f - orbital

$$M_{fg}^{(3)} = 7(-i)E_{0i}E_{0j}E_{0k}\int R_{k3}(r)r^5 g_2 e^{-r}dr \times$$
$$\left\{\int \frac{15}{4}(\hat{k}\cdot\hat{r})^3\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}d\Omega - \frac{9}{4}\int \hat{k}\cdot\hat{r}\hat{\epsilon}_i\hat{r}\hat{\epsilon}_j\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}d\Omega\right.$$
$$-\int \frac{5}{2}(\hat{k}\cdot\hat{r})^3\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{\epsilon}_k d\Omega + \frac{3}{2}\int \hat{k}\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{\epsilon}_k d\Omega \qquad (5.4)$$
$$+3(-i)E_{0i}E_{0j}E_{0k}\int R_{k3}(r)g_0 r^3 e^{-r}dr\left[\frac{5}{2}\int(\hat{k}\cdot\hat{r})^3\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\hat{\epsilon}_j d\Omega\right.$$
$$\left.\left.-\frac{3}{2}\int \hat{k}\cdot\hat{r}\hat{\epsilon}_k\cdot\hat{r}\hat{\epsilon}_i\cdot\hat{\epsilon}_j d\Omega\right]\right\}$$

Now onwards, we have used $j_1j_2j_3$ for the beams symbols instead of ijk

$$M_{j_1j_2j_3} = -i4\sqrt{\pi}\int drR_{k1}^*\left[r^3 g_0 - \frac{r^5}{2}g_2\right]e^{-r}\hat{k}\cdot\hat{\epsilon}_{j_1}\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3}$$
$$-i\frac{\sqrt{\pi}}{5}\int drR_{k1}^* r^5 g_2 e^{-r}\left[\hat{k}\cdot\hat{\epsilon}_{j_1}\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_2}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_3}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_2}\right]$$
$$-i\frac{3\sqrt{\pi}}{10}\int drR_{k3}^* r^5 g_2 e^{-r}\times \qquad (5.5)$$
$$\left[5\hat{k}\cdot\hat{\epsilon}_{j_1}\hat{k}\cdot\hat{\epsilon}_{j_2}\hat{k}\cdot\hat{\epsilon}_{j_3} - \hat{k}\cdot\hat{\epsilon}_{j_1}\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3} - \hat{k}\cdot\hat{\epsilon}_{j_2}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_3} - \hat{k}\cdot\hat{\epsilon}_{j_3}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_2}\right]$$

for a general vector $T_{j_1j_2j_3}$, which is symmetric in j_1, j_2 and j_3 we have,

$$\sum_{j_1j_2j_3} T_{j_1j_2j_3} = \frac{1}{3}\sum_{j_1j_2j_3}\hat{k}\cdot\hat{\epsilon}_{j_1}\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_2}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_3}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_2}$$

Now it is the time for defining few functions which has the entire ϑ, φ and polarization dependence. Therefore let

$$\Theta_{j_1j_2j_3}^{(1)} = \hat{k}\cdot\hat{\epsilon}_{j_1}\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_2}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_3}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_2}$$

Here, $\hat{k}(\vartheta, \phi) = (\sin\vartheta\cos\phi, \sin\vartheta\sin\phi, \cos\phi)$,

$\hat{\epsilon}_{j_i} = (\cos\zeta/2\cdot\hat{\epsilon}_x + i\sin\zeta/2\cdot\hat{\epsilon}_y)$, and $\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3} = \cos^2\zeta/2 - \sin^2\zeta/2$

$$\hat{k}\cdot\hat{\epsilon}_{j_1}(\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3}) = \hat{k}(\vartheta,\phi)\cdot(\cos\zeta/2\cdot\hat{\epsilon}_x + i\sin\zeta/2\cdot\hat{\epsilon}_y)(\cos^2\zeta/2 - \sin^2\zeta/2)$$
$$= (\cos\zeta/2\sin\vartheta\cos\phi + i\sin\zeta/2\sin\vartheta\sin\phi)(\cos^2\zeta/2 - \sin^2\zeta/2)$$

$$M_{j_1j_2j_3} = M^{(1)}\Theta^{(1)}_{j_1j_2j_3} + M^{(3)}\Theta^{(3)}_{j_1j_2j_3}. \tag{5.6}$$

Differential ionization cross-section and angular distribution

The differential ionization cross-section is obtained by evaluating electric dipole matrix element for the transition from ground state to the final continuum state. The continuum state is as superposition of an incoming spherical and outgoing plane wave and can be expand in Legendre polynomials, which in turn can be expand in products of spherical harmonics. The spherical harmonics contains Θ, Φ, ϕ and ϑ, which describe electron wave vector k and the radius vector r respectively. The angular distribution of the photoelectron is then proportional to the absolute value of the square of electric dipole matrix element. Differential scattering cross section for N-photon ionization is given by

$$\frac{d\sigma^{(N)}}{d\Omega} = \frac{\alpha}{2\pi}\left(\frac{1}{2I_0}\right)^{(N-1)} |M^{(N)}_{fg}|^{(N)} \alpha_0^2 \omega k \tag{5.7}$$

here the energy is given in units of e^2/a_0 (atomic units), α is the fine structure constant, $a_0 = 5.2917 \times 10^{-9}$ is the first Bohr radius, $I_0 = 7.019 \times 10^{16}$ W/cm^2 is the atomic unit of the field strength intensity. $M^{(N)}_{fg}$ refers to the N^{th} order transition amplitude corresponding to a transition from the ground state $|g\rangle$ to a final continuum state $|f\rangle$ and k is the momentum of the ejected electron and its magnitude for an N-photon process is given by $k = \sqrt{2N\omega - 1.}$

Numerical results

We have used mathematica software program, which provides a range of tools with atomic systems. The symbolic tools include orthogonal polynomials-Legendre, Laguerre, Clebsch-Gorden coefficients while graphical capabilities cover the polar plots, spherical plots in two or three dimensions and animation. These are applied for the manipulation of all the integrals obtained in our final expressions and visualization of

atomic orbital. The spherical harmonic $Y_l^m(\vartheta, \varphi)$ are the eigenfunction of Laplacian operator(which is the quantum mechanical angular momentum operator). They are important in many theoretical and practical applications, particularly in computing atomic orbital electronic configuration. The electronic orbital presented here represent a volume of space within which an electron would have a certain probability of being based on particular energy states and atoms. For example, as simplicity lowest energy state hydrogen atom, the electrons are most likely to be found within a sphere around a nucleus of an atom. In a higher energy state, the shape becomes lobes and rings, due to the interaction of the quantum effects between different atomic states. These shapes continue on infinitely getting ever more lobes or rings on them. The shape of the orbital depend upon many factors. The most important are the quantum number with the particular energy states (n, l, m). Although, the $l = 0$, and $m = 0$ orbital looks like simple sphere, regardless of the n values, this is not actually the case. For $n \geq 4$, $l = 0$, $m = 0$ orbital showing that, it is really a concentric sphere The atomic orbital model thus predicts line spectra, which are observed experimentally.

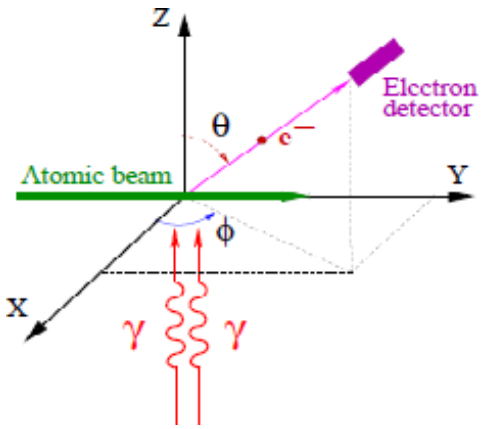


Figure 5.1: Geometry accepted in theoretical consideration of the angular distribution (Koval, 2004)

Two-photon symmetry

We have plotted differential scattering cross-section of two photon ionization produced by an electromagnetic field containing, single, two and three beams with varying phase difference propagating along the same direction taken as z axis of coordinates system. We have used polar angle $\vartheta = \pi/2$ and wavelength of the photon $\lambda = 12 \times 10^{-8} m$ for most of the polar plots, otherwise the wavelength changes are shown. The angular distribution represented here, as polar diagrams, is calculated in the $x - y$ plane, in which all two laser beams are vibrating. Polar plot can provide a complete view of atomic orbital.

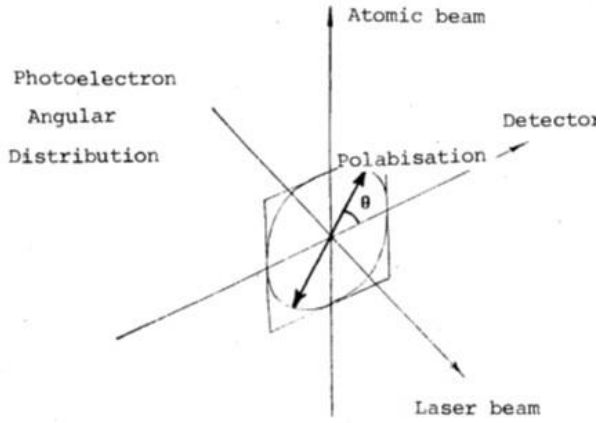


Figure 5.2: Measurement geometry of angular distribution (Ding et al , 1989)

Differential scattering cross section for 2-photon ionization is given

$$\frac{d\sigma^{(2)}}{d\Omega} = \frac{\alpha}{2\pi} \frac{I}{2I_0}^{(2-1)} |M_{fg}^{(2)}|^{(2)} \alpha_0^2 \omega k \tag{5.8}$$

Here, the energy is given in units of e^2/a_0 (atomic units). α is the fine structure constant, $a_0 = 5.2917 \times 10^{-9}$ is the first Bohr radius, I is the field strength intensity of the radiation field, $I_0 = 7.019 \times 10^{16} \mathrm{W/cm^2}$ is the atomic unit of the field strength intensity. In all the graphs, the plotted quantity is $I^{-1} \frac{d\sigma^{(2)}}{d\Omega}$ multiplied by those constants. The arbitrary beams j_1 and j_2 which are numbered as single, two, three and four or many, beams for two photon.

For a transition to the final state with $I = 0$ The expression for the matrix

element corresponding to a $\Delta l = 0$ transition is

$$M_{j_1 j_2} = \frac{4\pi}{3}(\hat{\epsilon}_{j_1} \cdot \hat{\epsilon}_{j_2}) \int r^4 R_{k0}(r) f(r) e^{-r} dr \tag{5.9}$$

For a transition to a the final state with $l = 2$

$$M_{j_1 j_2} = 2\pi \left[\hat{k} \cdot \hat{\epsilon}_{j_1} \hat{k} \cdot \hat{\epsilon}_{j_2} \int + \hat{k} \cdot \hat{\epsilon}_{j_1} \hat{k} \cdot \hat{\epsilon}_{j_2} + \hat{k} \cdot \hat{k} \hat{\epsilon}_{j_1} \cdot \hat{\epsilon}_{j_2} \right] \tag{5.10}$$

$$- \frac{2\pi}{15} (\hat{\epsilon}_{j_1} \cdot \hat{\epsilon}_{j_2}) \int r^4 R_{k2}(r) f(r) e^{-r} dr \tag{5.11}$$

Let's define Θ for angular part, and their superscript are represented for $l = 0$ and $l = 2$, the allowed transition, then above expression becomes

$$\Theta^{(0)}_{j_1 j_2} = \frac{4\pi}{3}(\hat{\epsilon}_{j_1} \cdot \hat{\epsilon}_{j_2}) \tag{5.12}$$

$$\Theta^{(2)}_{j_1 j_2} = 2\pi \left[\hat{k} \cdot \hat{\epsilon}_{j_1} \hat{k} \cdot \hat{\epsilon}_{j_2} + \hat{k} \cdot \hat{\epsilon}_{j_1} \hat{k} \cdot \epsilon_{j_2} + \hat{k} \cdot \hat{k} \hat{\epsilon}_{j_1} \cdot \hat{\epsilon}_{j_2} \right] \tag{5.13}$$

$$- \frac{2\pi}{15} (\hat{\epsilon}_{j_1} \cdot \hat{\epsilon}_{j_2})$$

With these definition we have the transition amplitudes $M_{j_1 j_2}$ as

$$M_{j_1 j_2} = M^{(0)} \Theta^{(0)}_{j1j2} + M^{(2)} \Theta^{(2)}_{j1j2}, \tag{5.14}$$

Where,

$$M^{(0)} = 8\frac{\sqrt{\pi}}{3} \int r^4 R^*_{k0}(r) f(r) e^{-r} dr \tag{5.15}$$

$$M^{(2)} = \frac{16\sqrt{\pi}}{3} \int r^4 R^*_{k2}(r) f(r) e^{-r} dr \tag{5.16}$$

The radial parts of integrals are done in (Radhakrishnan and Thayyullathil, 2004). We have discussed only the angular parts (angular distribution in terms of polar plots) with phase dependance and polarization dependance.

When we include two or three incident beams with different states of polarization and phase difference, the energy conservation can be achieved by quantum interference of various routes, so we have to sum all the possible configuration.

$$M_{j_1 j_2} = \sum e^{i(\delta_{j_1}+\delta_{j_2})}[m20\Theta^{(0)}_{j_1 j_2} + m10\Theta^{(2)}_{j_1 j_2}]$$

Polar plots for multiphoton and multiple beams

Phase Dependance of Two photon

Two photon, two beams

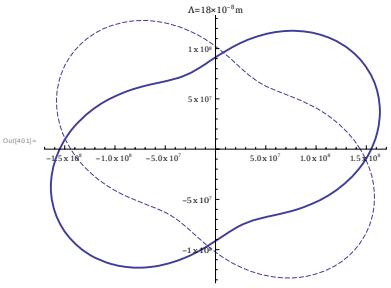


Figure 5.3: Polar plots of differential cross-section of two-photon ionization with two beams, dashed line $\delta_1 = \pi/2$, $\delta_1 = 0$ and thick line $\delta_1 = -\pi/2$, $\delta_1 = 0$ For $\zeta_1 = \pi/2$ and $\zeta_2 = 0$

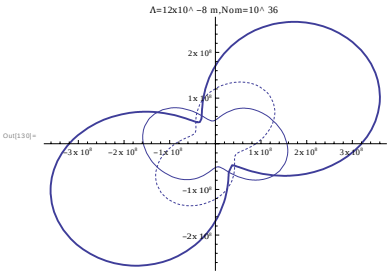


Figure 5.4: Polar plots of differential cross-section of two-photon ionization with two beams, dashed line $\delta_1 = -\pi/4$, $\delta_2 = \pi/4$, thick line $\delta_1 = 0$, $\delta_2 = 0$, thin line $\delta_1 = \pi/4$, $\delta_2 = -\pi/4$ For $\zeta_1 = \pi/2$ and $\zeta_2 = 0$

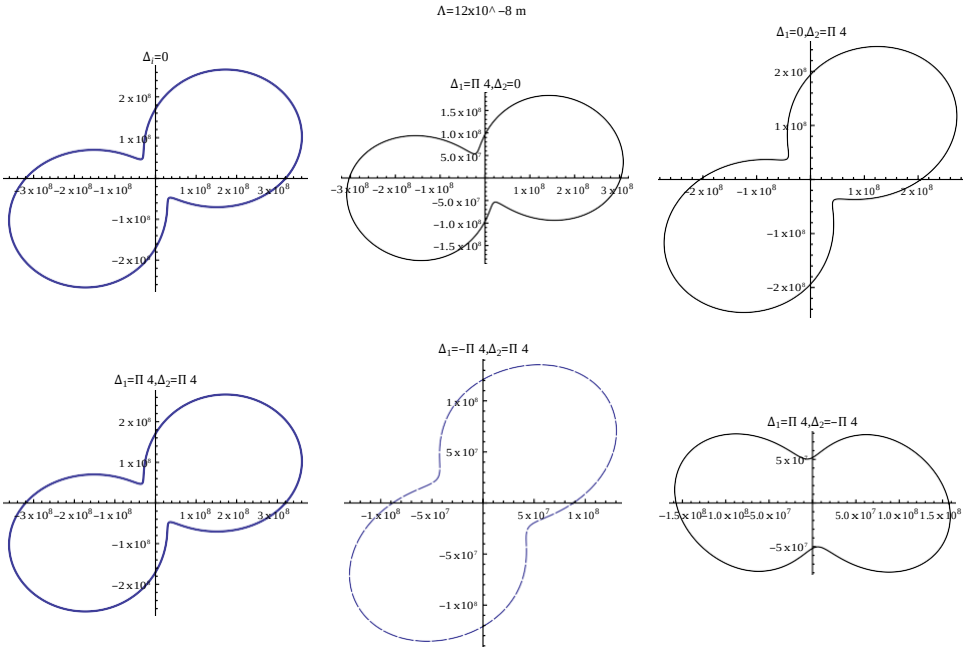


Figure 5.5: Polar plots of differential cross-section of two-photon ionization with two beams with changing phases, for $\zeta_1 = \pi/2,\ \zeta_2 = 0$

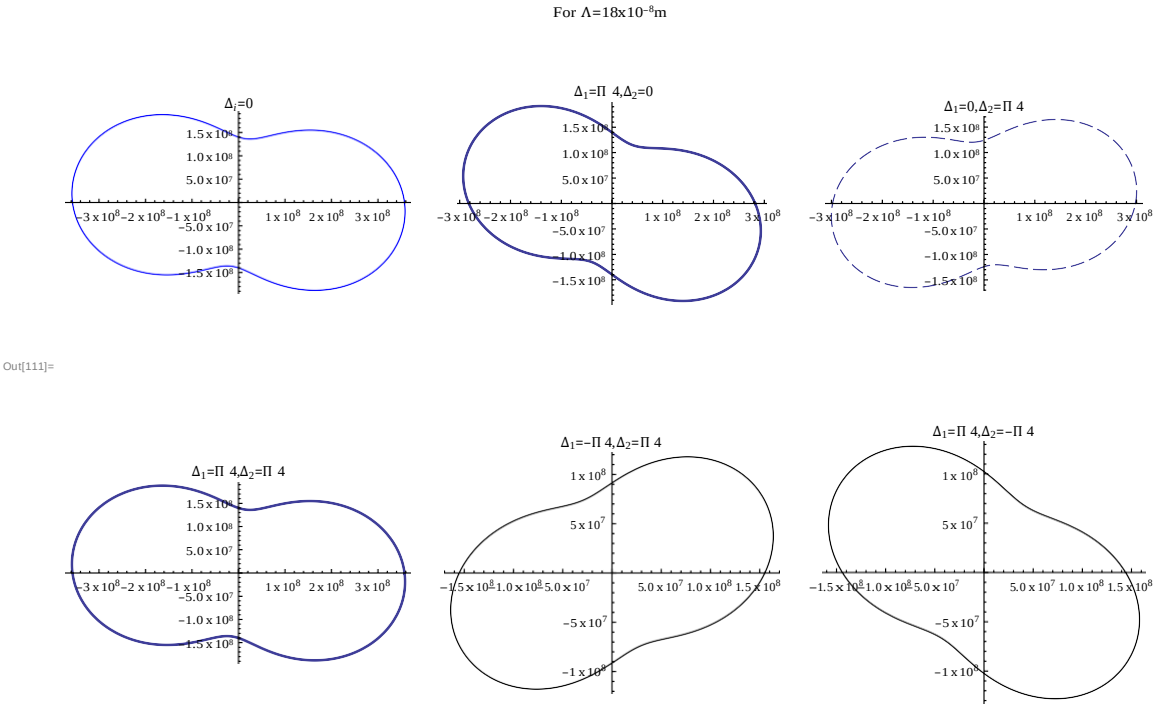


Figure 5.6: Polar plots of two photon ionization for $\lambda = 18 \times 10^{-8} m$ and Norm = 10^{36} by changing phases

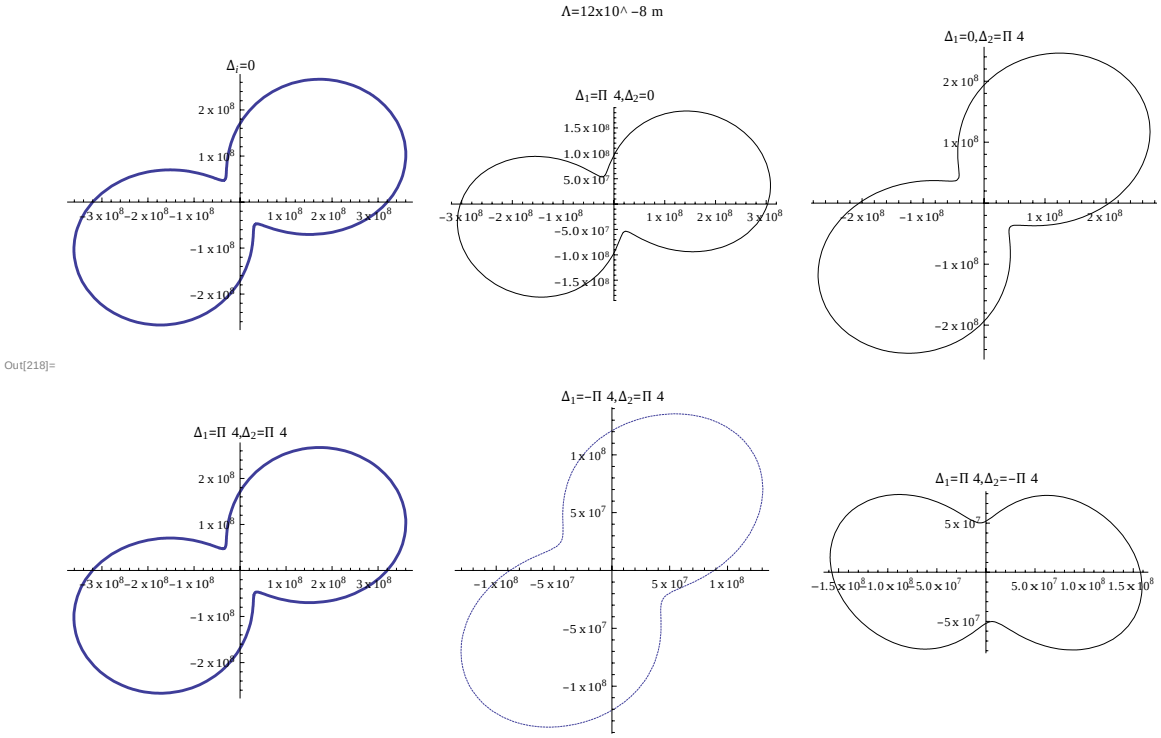


Figure 5.7: Polar plots of two photon ionization for $\lambda = 12 \times 10^{-8} m$ and Norm = 10^{36} by changing phases

Changing the normalization, increases the magnitude

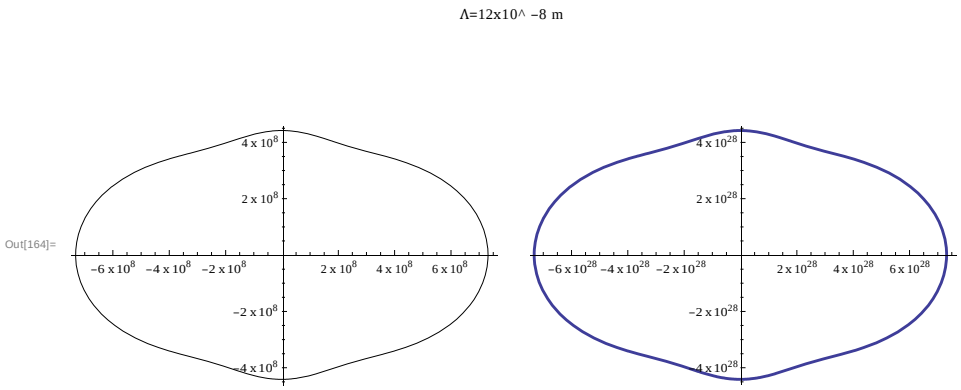


Figure 5.8: Polar plots of differential cross-section of two-photon ionization with two beams first with norm 10^{36} and second figure with norm 10^{56}

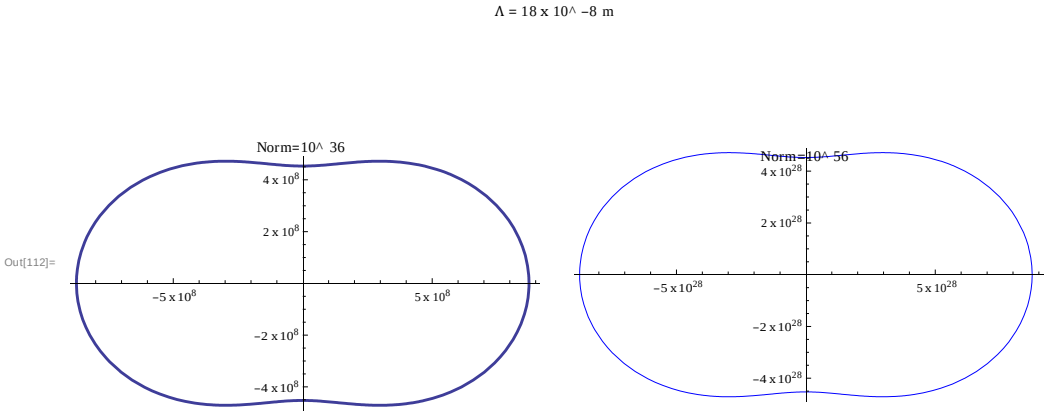


Figure 5.9: Polar plots of differential cross-section of two-photon ionization with two beams first with norm 10^{36} and second figure with norm 10^{56}

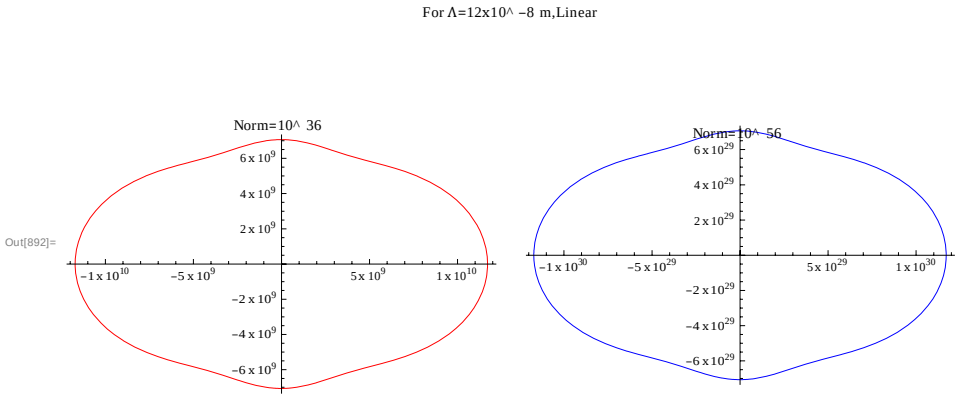


Figure 5.10: By changing normalization for Two photon-four beams

Two photon, three beams

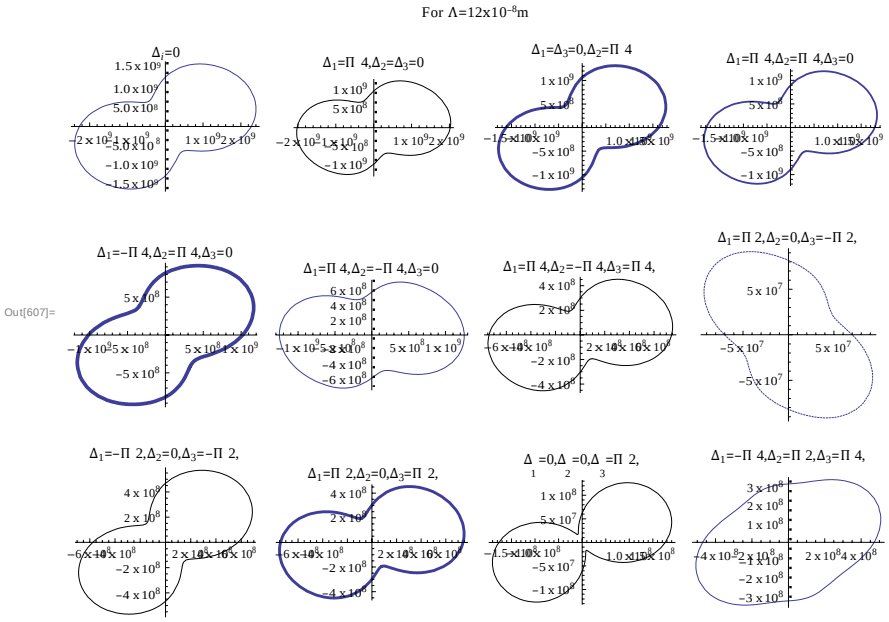
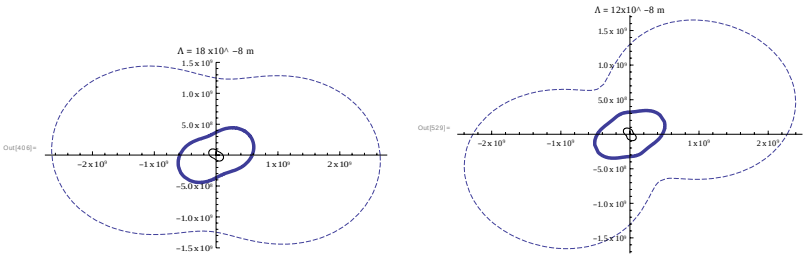


Figure 5.11: Changing phases for three beams with $\lambda = 12 \times 10^{-8} m$ and Norm = 10^{36}



(a) Wavelength $\lambda = 18 \times 10^{-8} m$ (b) Wavelength $\lambda = 12 \times 10^{-8} m$

Figure 5.12: Dashed line $\delta_i = 0$, Thin line $\delta_1 = \pi/2$, $\delta_2 = 0$, $\delta_3 = -\pi/2$ and Thick line for $\delta_1 = -\pi/4$, $\delta_2 = \pi/2$, $\delta_3 = \pi/4$

Figure 5.13: Changing phases for two photos three beams with $\lambda = 18 \times 10^{-8} m$ and Norm = 10^{56}

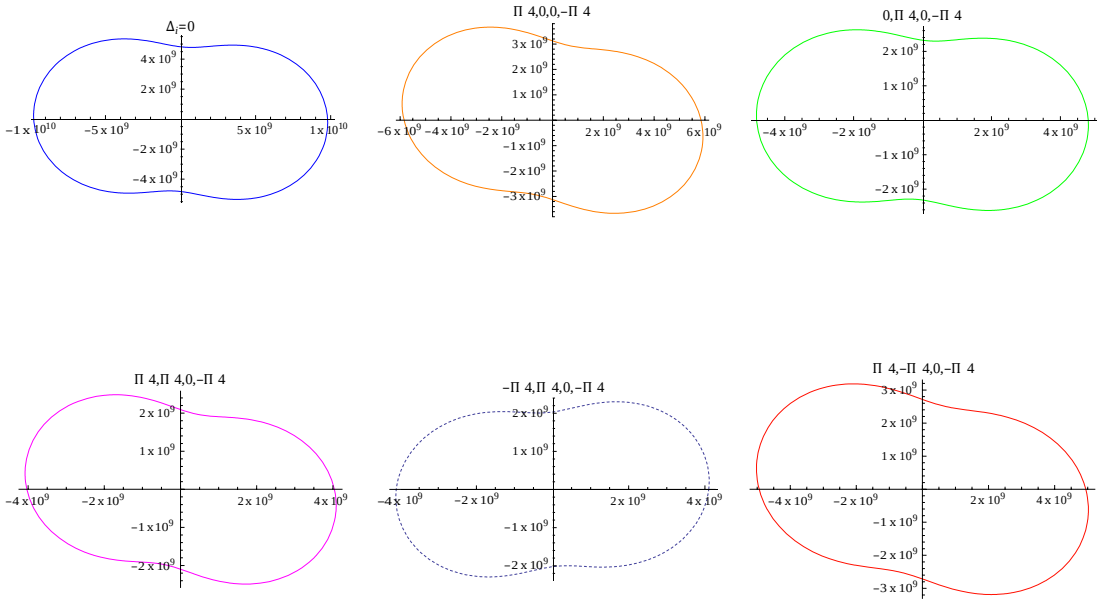


Figure 5.14: Changing phases for two photos three beams with $\lambda = 18 \times 10^{-8} m$ and Norm = 10^{36}

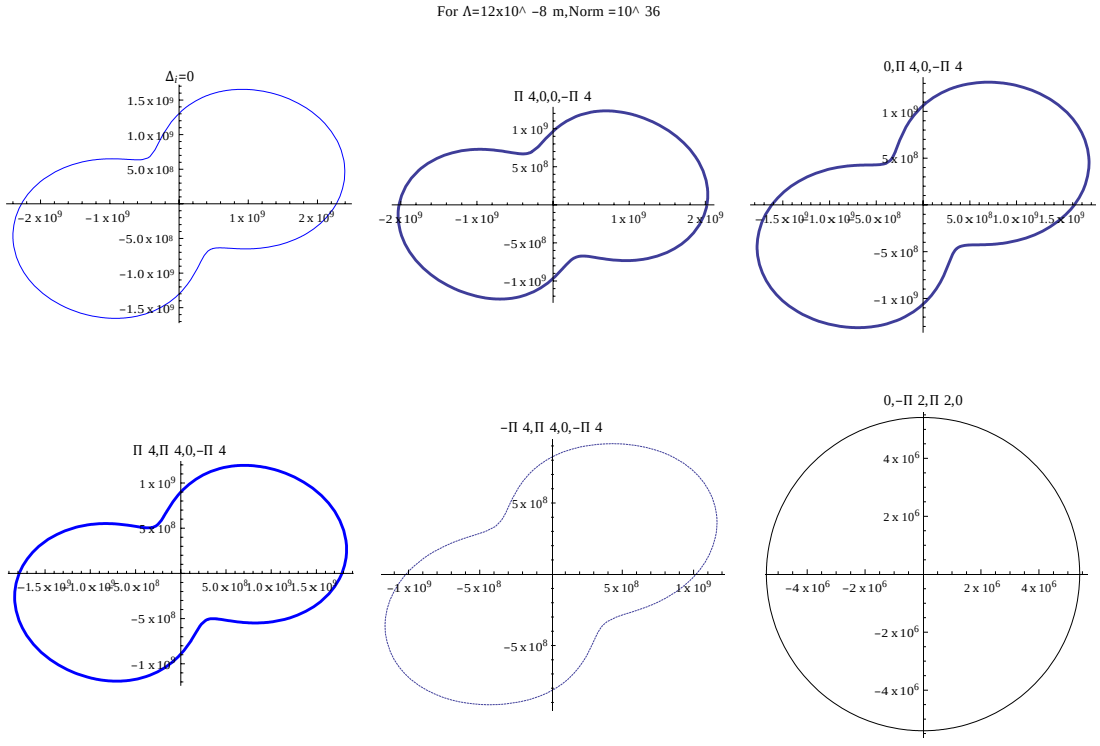


Figure 5.15: Changing phases for two photos three beams with $\lambda = 12 \times 10^{-8} m$ and Norm = 10^{36}

Changing normalization for two photon

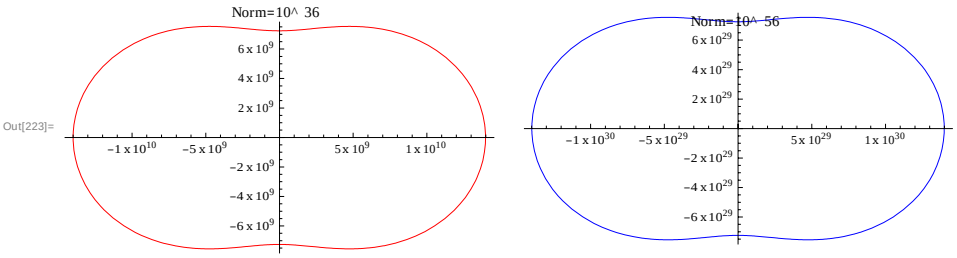


Figure 5.16: Changing normalization for two photon for $\lambda = 18 \times 10^{-8} m$

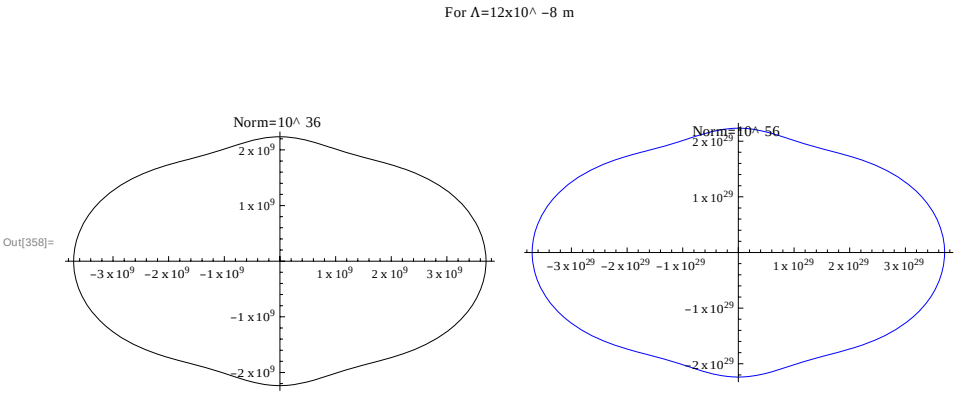


Figure 5.17: Changing normalization for two photos for $\lambda = 12 \times 10^{-8} m$, without phase

Polarization Dependance of Two photon

Two Photon, two Beams

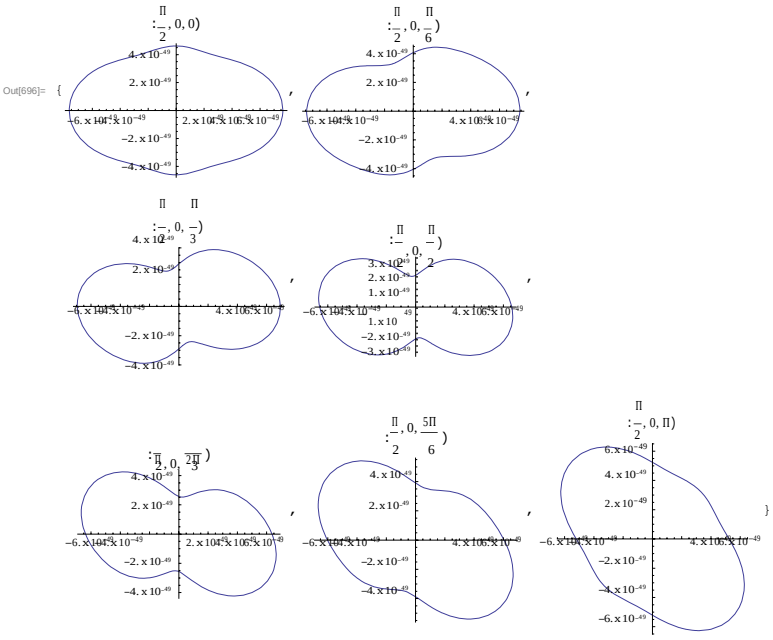


Figure 5.18: Polar plots of differential cross-section of two-photon ionization with two beams changing polarization, for $\delta_1 = \pi/2,\ \delta_2 = 0,$ and $\zeta_2 = 0$, but varying $\zeta_1 = 0$,to $\pi/6$, the co-ordinates in bracket are $(\vartheta = \pi/2,\ \zeta_2,\ \zeta_1\ )$

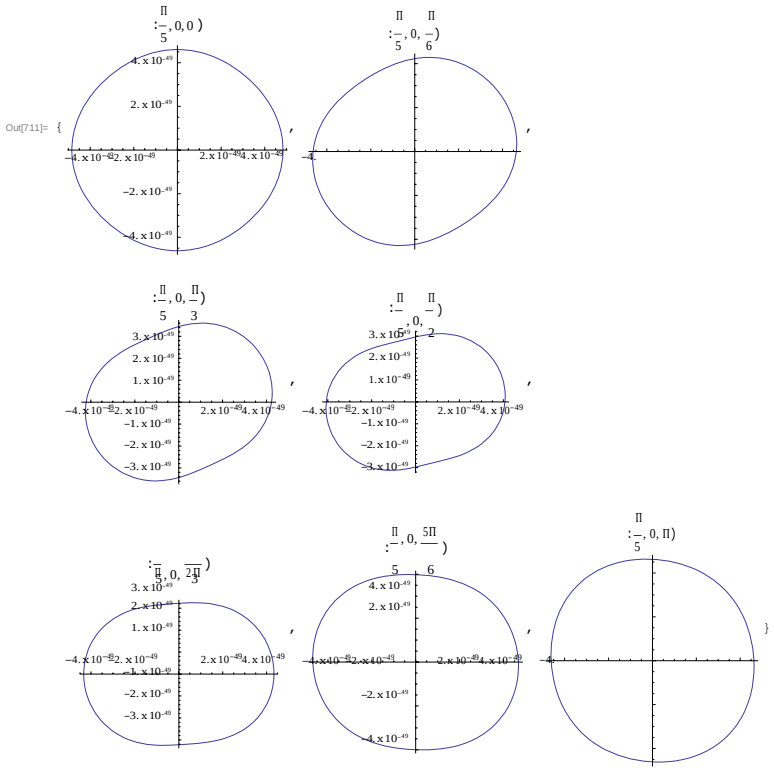


Figure 5.19: Polar plots of differential cross-section of two-photon ionization with two beams, $\delta_1 = \pi/2$, $\delta_2 = 0$, For $\zeta_2 = 0$, Varying $\zeta_1 = 0$,to $\pi/6$, the co-ordinates in bracket are ($\vartheta = \pi/5$, ζ_2, ζ_1)

Two photon, three beams

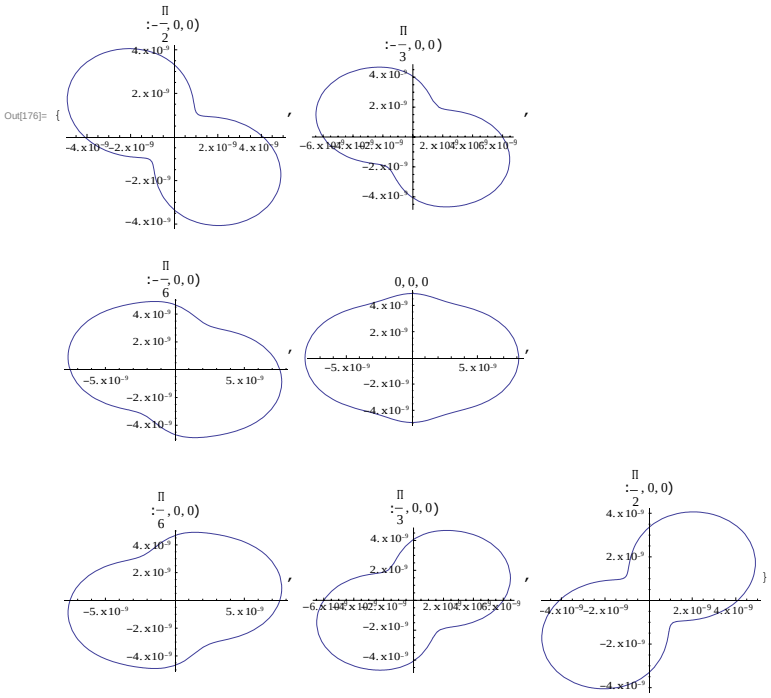


Figure 5.20: Polar plots of differential cross-section of two-photon ionization with three beams, $\delta_2 = \pi/2$, $\delta_1 = \delta_3 = 0$, For Varying $\zeta_1 = -\pi/2$,to $\pi/6$, the co-ordinates in bracket are $(\zeta_1, \zeta_2, \zeta_3)$

Two photon, four beams

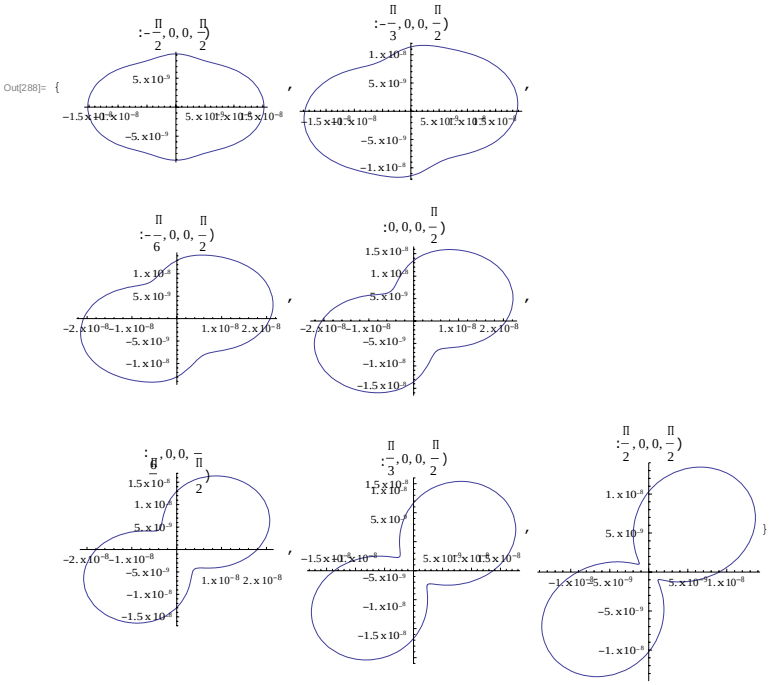


Figure 5.21: Polar plots of differential cross-section of two-photon ionization with four beams, $\delta_2 = \pi/2$, $\delta_1 = \delta_3 = \delta_4 = 0$, For Varying $\zeta_1 = -\pi/2$, to $\pi/6$, the co-ordinates in bracket are $(\zeta_1, \zeta_2, \zeta_3, \zeta_4)$

Three-photon symmetry

With the new notation the angular integrals are given by

$$\Theta^{(1)}_{j_1 j_2 j_3} = \hat{k}\cdot\hat{\epsilon}_{j_1}\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_2}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_3}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_2}$$

and

$$\Theta^{(3)}_{j_1 j_2 j_3} = 5(\hat{k}\cdot\hat{\epsilon}_{j_1})(\hat{k}\cdot\hat{\epsilon}_{j_2})(\hat{k}\cdot\hat{\epsilon}_{j_3}) - \Theta^{(1)}_{j_1 j_2 j_3}$$

$$M^{(1)} = \frac{4\sqrt{\pi}}{15}(-i)\int drR^*_{k1}\left(5r^3 g_0 + 2r^5 g_2\right)e^{-r} \tag{5.17}$$

$$M^{(3)} = \frac{6\sqrt{\pi}}{5}(i)\int drR^*_{k3}\, r^5 g_2\, e^{-r} \tag{5.18}$$

$$M_{j_1 j_2 j_3} = M^{(1)}\Theta^{(1)}_{j_1 j_2 j_3} + M^{(3)}\Theta^{(3)}_{j_1 j_2 j_3}. \tag{5.19}$$

With the new notation the angular integrals are given by

$$\Theta^{(1)}_{j_1 j_2 j_3} = \hat{k}\cdot\hat{\epsilon}_{j_1}\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_2}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_3} + \hat{k}\cdot\hat{\epsilon}_{j_3}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_2}$$

and

$$\Theta^{(3)}_{j_1 j_2 j_3} = 5(\hat{k}\cdot\hat{\epsilon}_{j_1})(\hat{k}\cdot\hat{\epsilon}_{j_2})(\hat{k}\cdot\hat{\epsilon}_{j_3}) - \Theta^{(1)}_{j_1 j_2 j_3}$$

Ionization rate, for 3-photon transition is given by

$$\Gamma^{(3)} \propto \left(\frac{I}{I_0}\right)^3 |M^{(3)}|^2$$

where

$$M^{(3)} = \sum_{j_1 j_2 j_3} e^{-i(\delta_{j_1}+\delta_{j_2}+\delta_{j_3})} \; M^{(1)}\Theta^{(1)}_{j_1 j_2 j_3} + M^{(3)}\Theta^{(3)}_{j_1 j_2 j_3}$$

Phase dependance of Three photon

Three photon, two beams

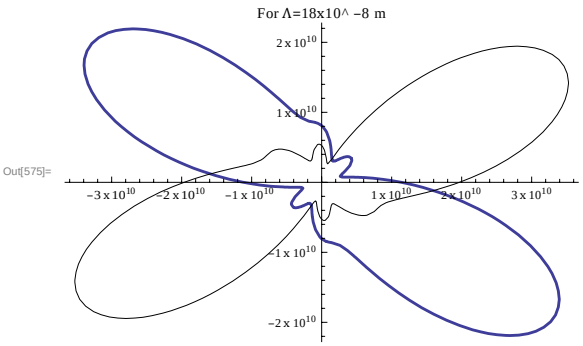


Figure 5.22: Polar plot of the differential cross -section of the three-photon ionization with two beams with phase diff of $\pi/2$.

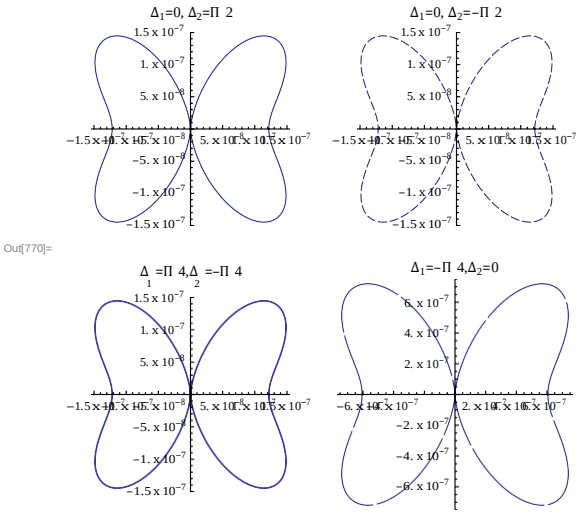


Figure 5.23: Polar plot of the differential cross -section of the three-photon ionization with two beams by varying phase.

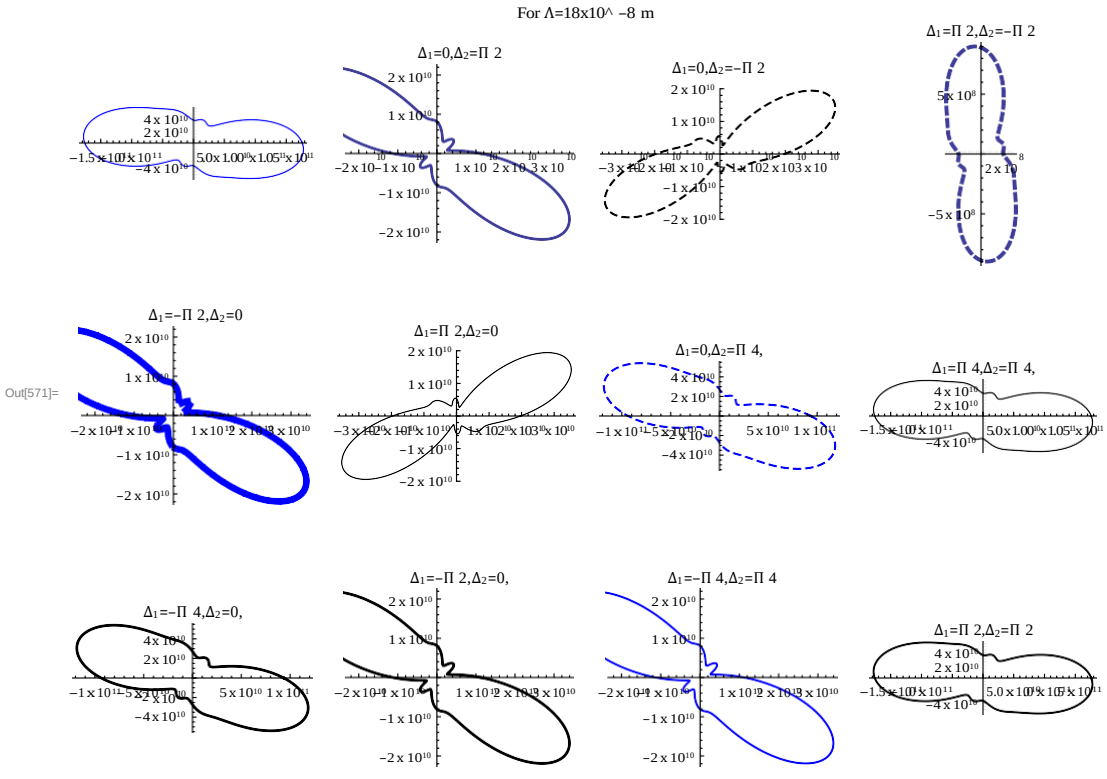


Figure 5.24: Changing phases for three photon with $\lambda = 18\times10^{-8}m$ and Norm = 10^{36}

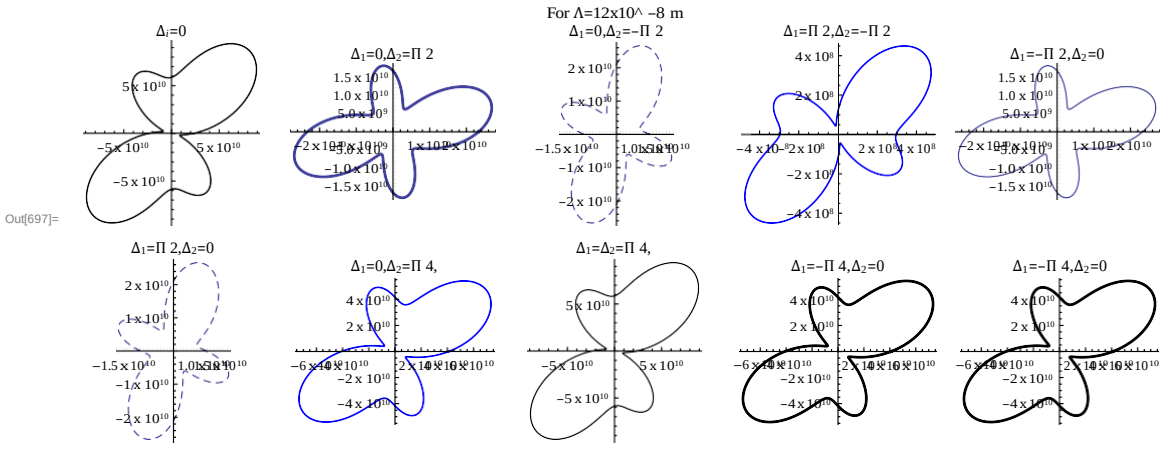


Figure 5.25: Changing phases for three photon with $\lambda = 12\times10^{-8}m$ and Norm = 10^{36}

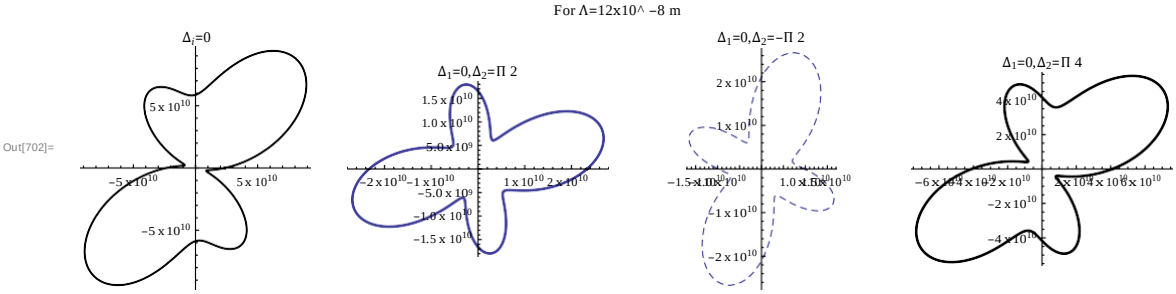


Figure 5.26: Changing phases for three photon two beams with $\lambda = 12 \times 10^{-8}m$ and Norm = 10^{36}

Three photon, three beams

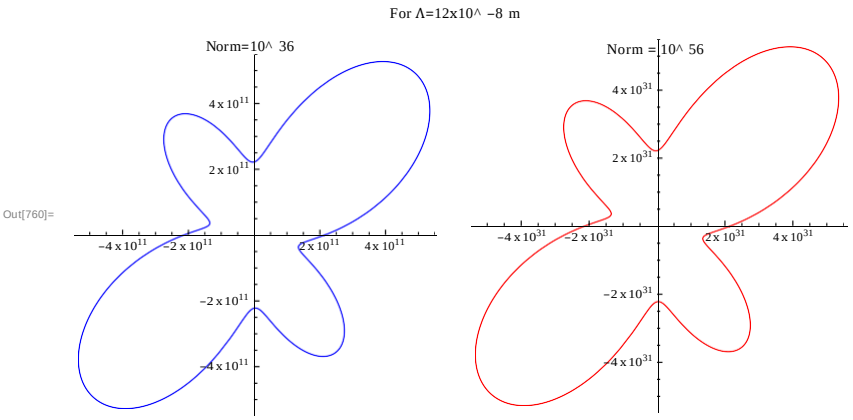


Figure 5.27: Changing Normalization same phase($\delta_i = 0$) and same polarization with $\zeta_1 = \zeta_3 = 0, \zeta_2 = \pi/2$

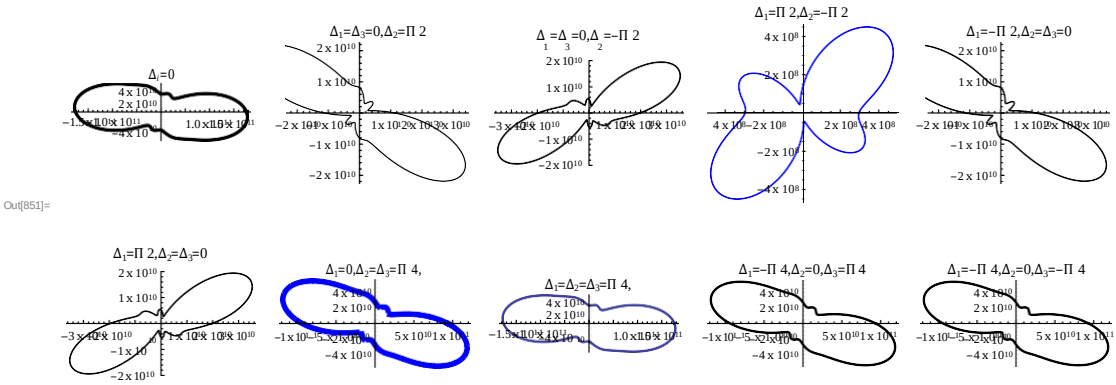


Figure 5.28: Changing phases for three photon three beams with $\lambda = 18 \times 10^{-8} m$ and Norm = 10^{36}

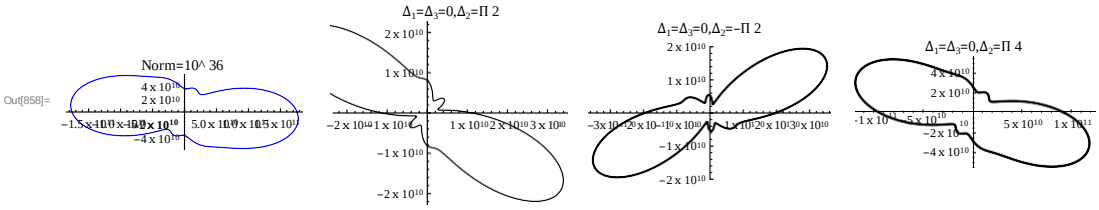


Figure 5.29: Changing phases for three photon three beams with $\lambda = 18 \times 10^{-8} m$ and Norm = 10^{36}

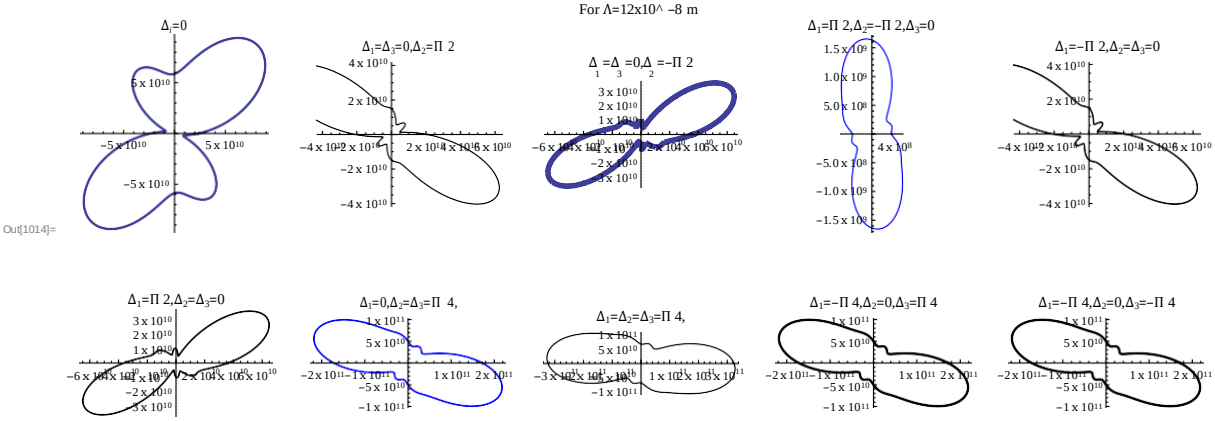


Figure 5.30: Changing phases for three photon three beams with $\lambda = 12 \times 10^{-8}$m

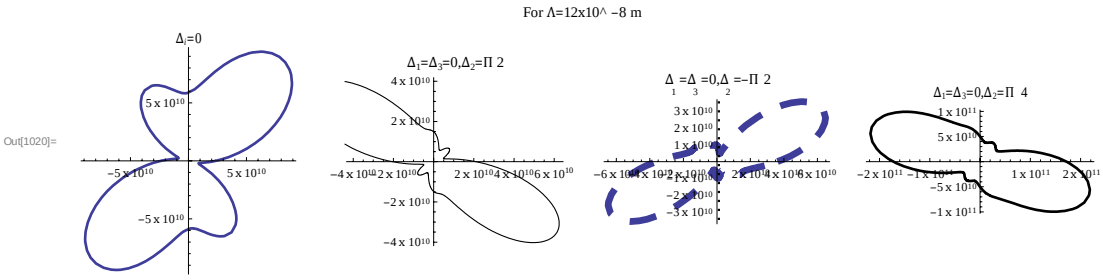


Figure 5.31: Changing phases for three photon three beams with $\lambda = 12 \times 10^{-8}$m

Three photon, four beams

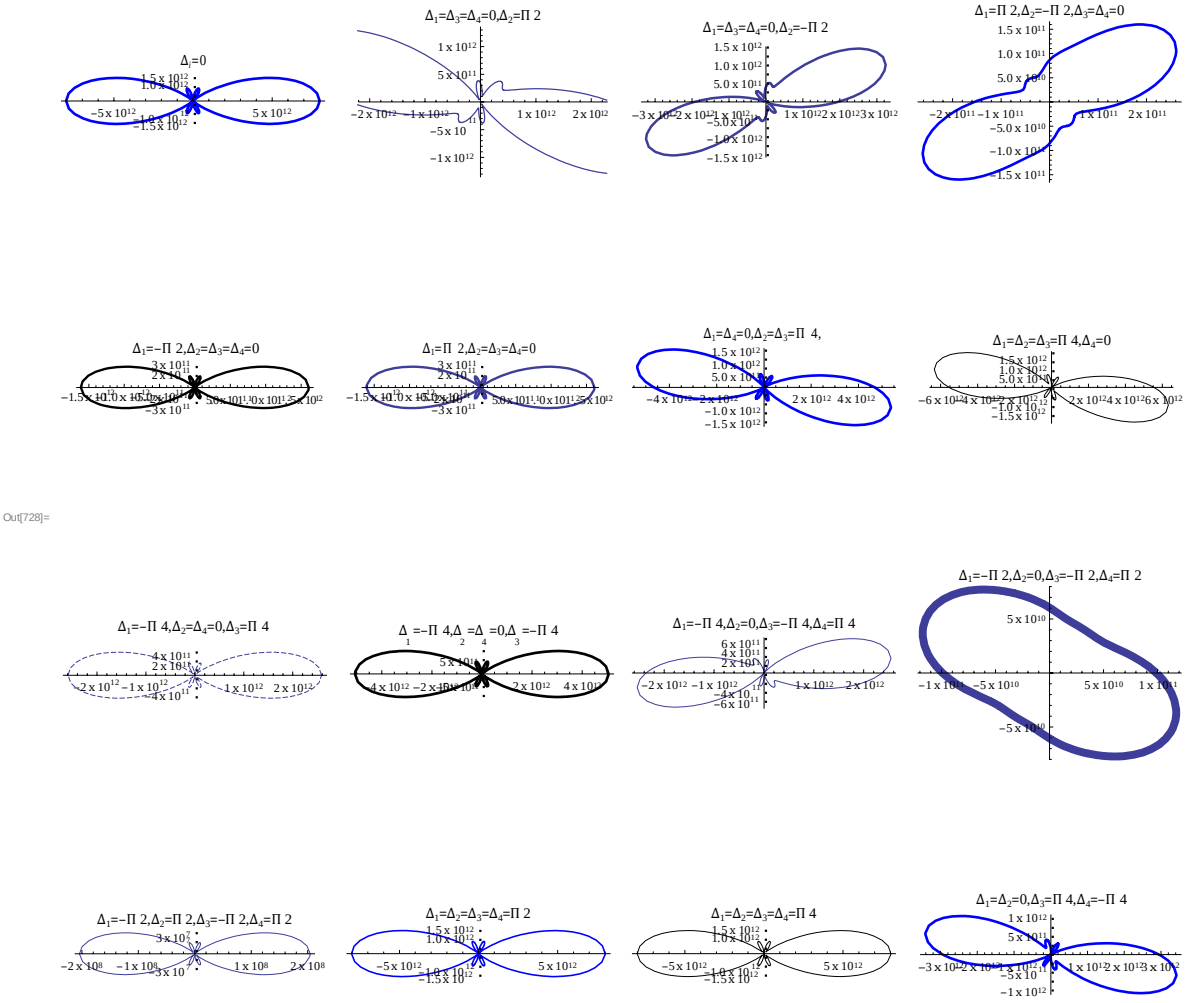


Figure 5.32: Changing phases for three photon four beams with $\lambda = 18 \times 10^{-8}m$ and Norm = 10^{36}

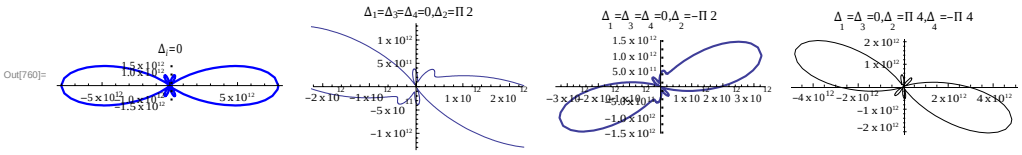


Figure 5.33: Changing phases for three photon four beams with $\lambda = 18 \times 10^{-8} m$ and Norm = 10^{36}

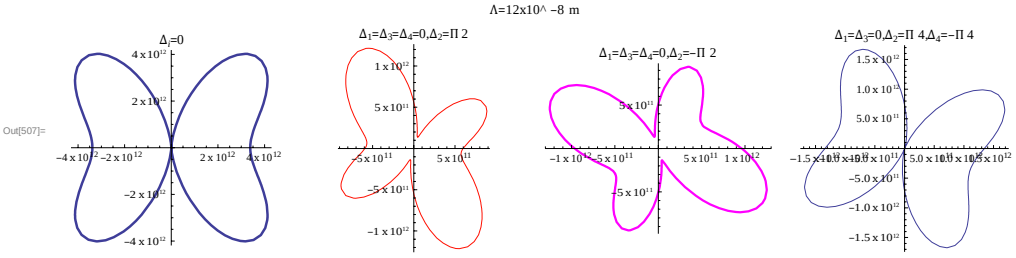


Figure 5.34: Changing phases for three photon four beams with $\lambda = 12 \times 10^{-8} m$ and Norm = 10^{36}

Three photon, five beams

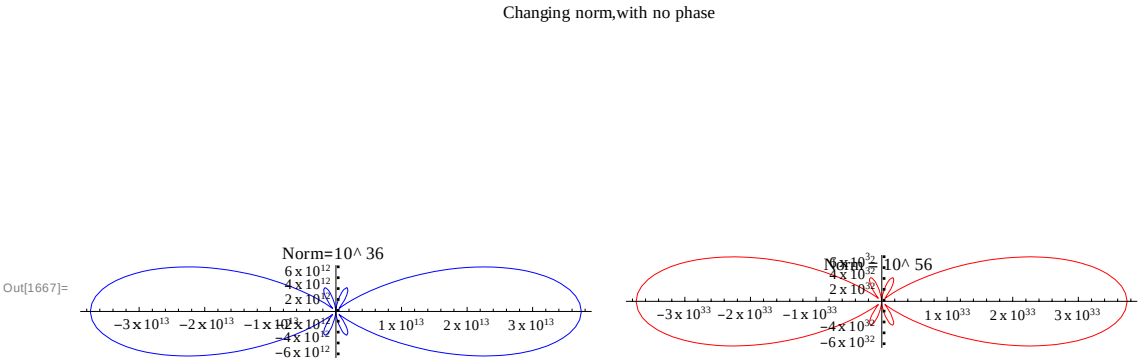


Figure 5.35: Changing phases for three photon five beams with $\lambda = 18 \times 10^{-8}$ m, without phase

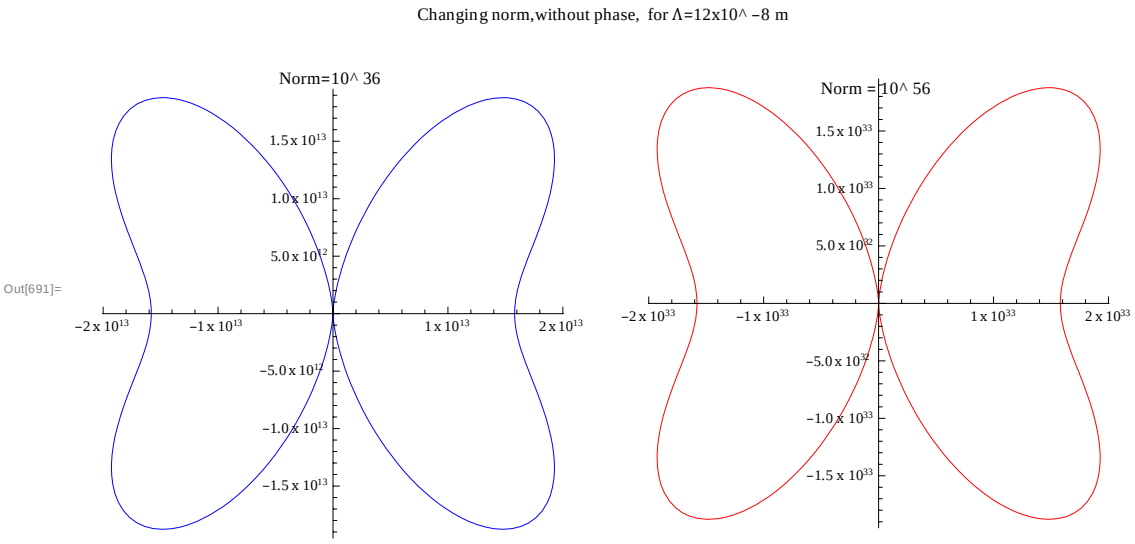


Figure 5.36: Changing phases for three photon five beams with $\lambda = 12 \times 10^{-8}$ m, without phase

Changing phases for Three photon, five beams

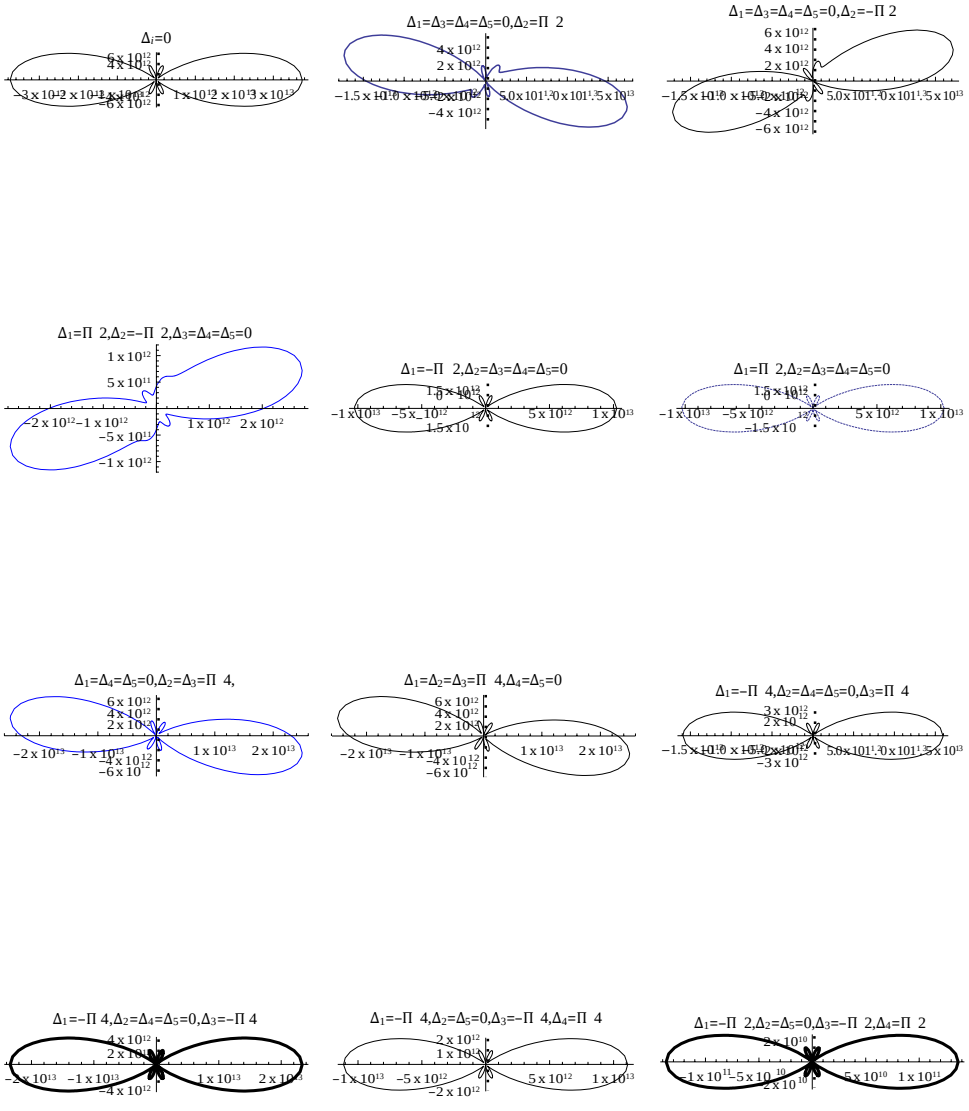


Figure 5.37: Changing phases for three photon five beams with $\lambda = 18 \times 10^{-8}$ m and Norm = 10^{36}, with phase

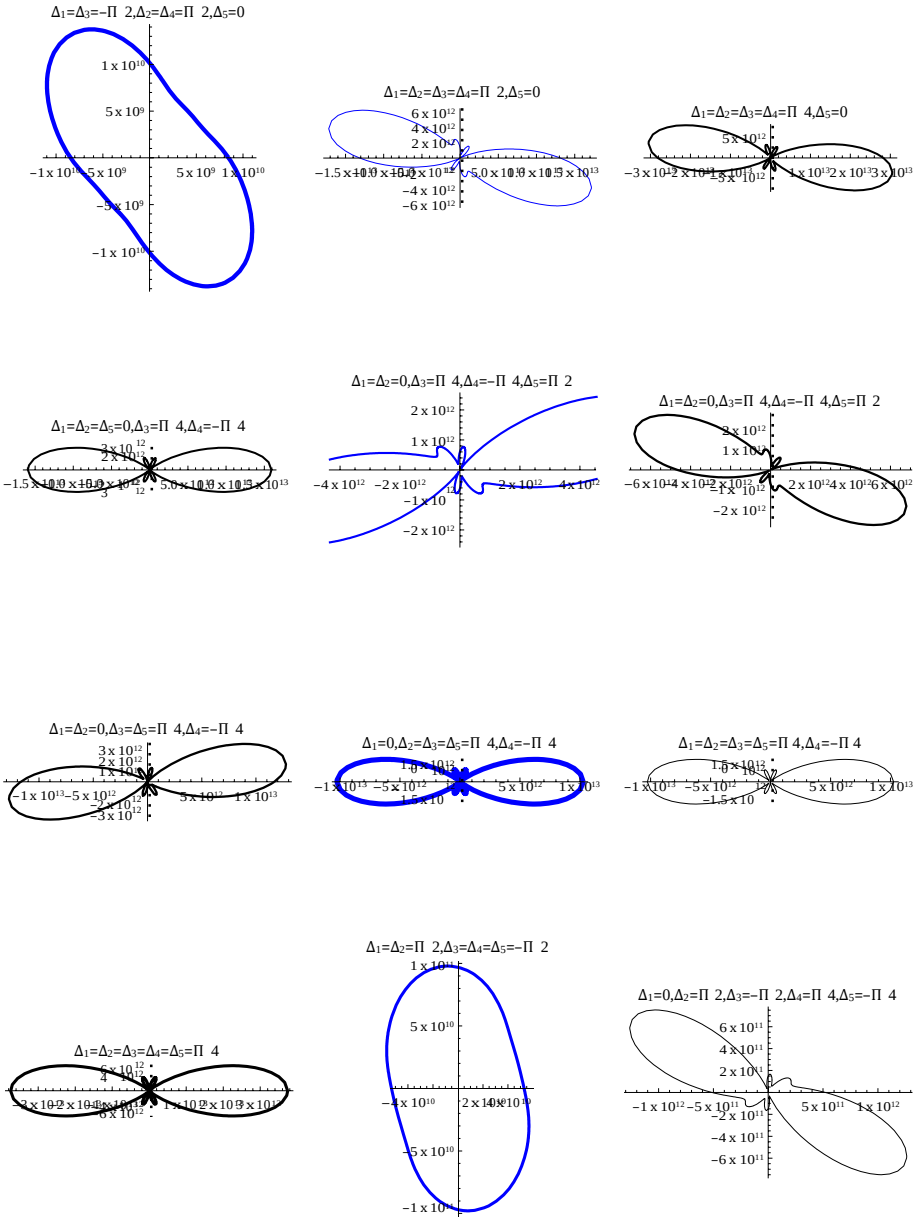


Figure 5.38: Changing phases for three photon five beams with $\lambda = 18 \times 10^{-8}$ m and Norm = 10^{36}, with phase

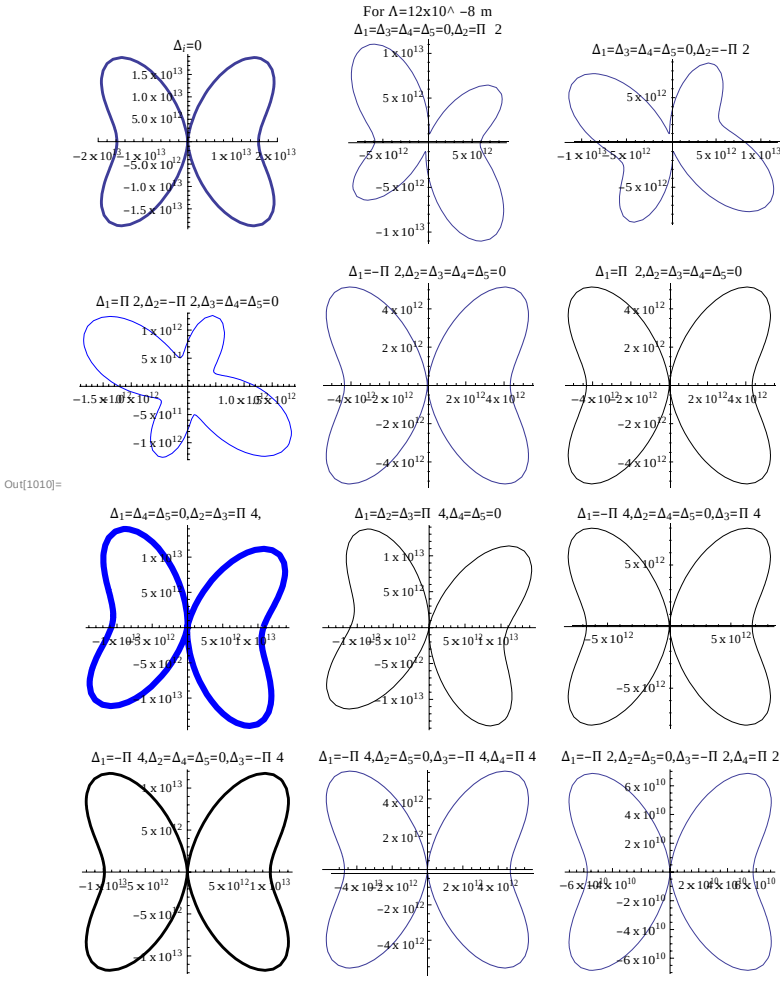


Figure 5.39: Changing phases for three photon five beams with$\lambda = 12 \times 10^{-8}$m and Norm = 10^{36}

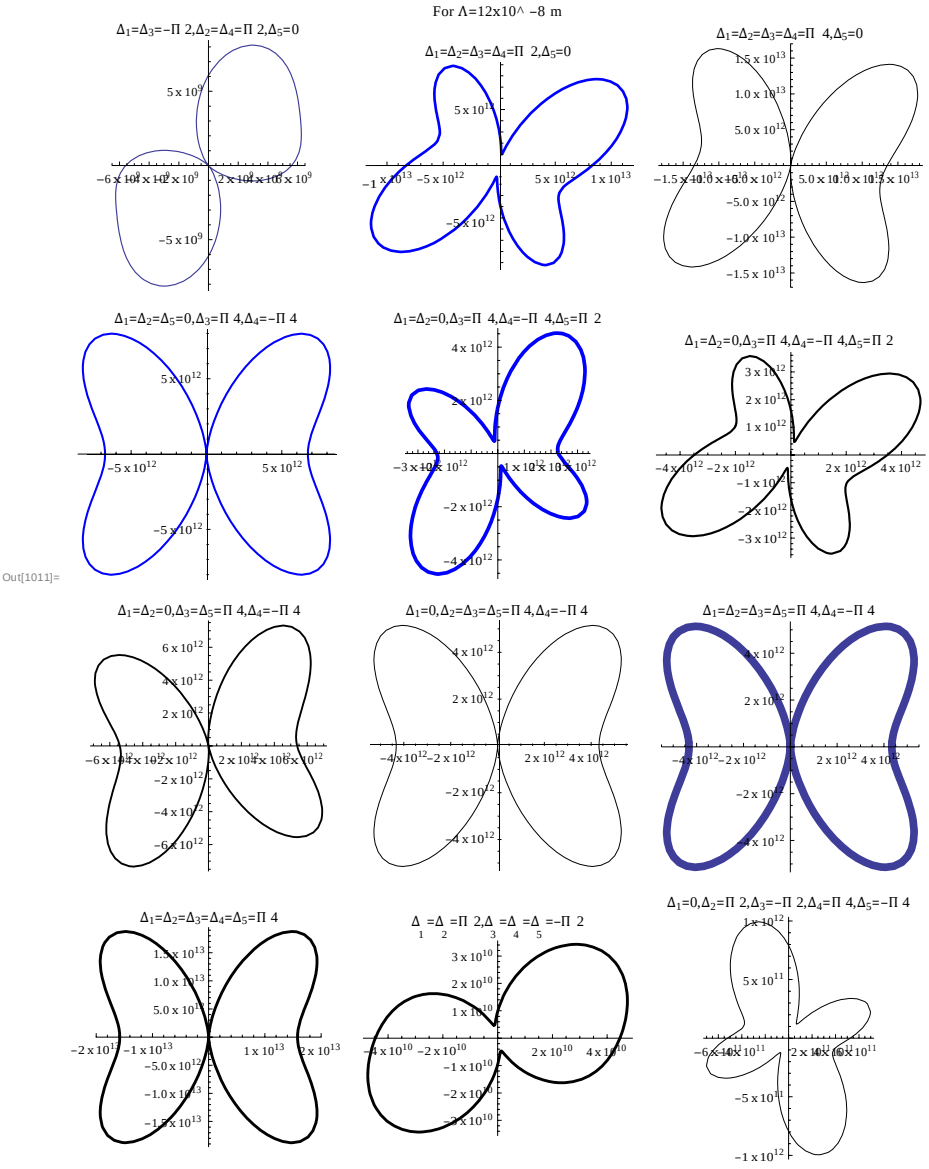


Figure 5.40: Changing phases for three photon five beams with $\lambda = 12 \times 10^{-8}$m and Norm = 10^{36}

Changing normalization for three photon

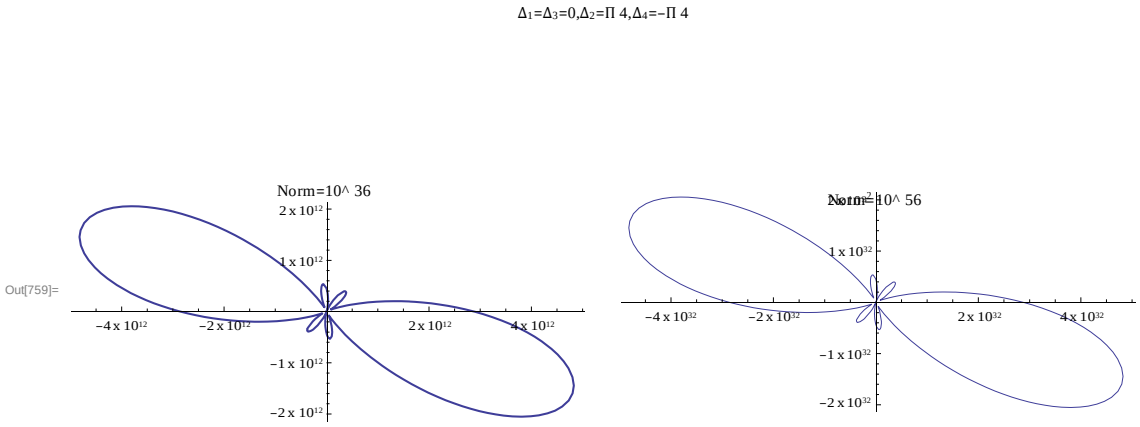


Figure 5.41: Changing normalization for three photon four beams,with phase

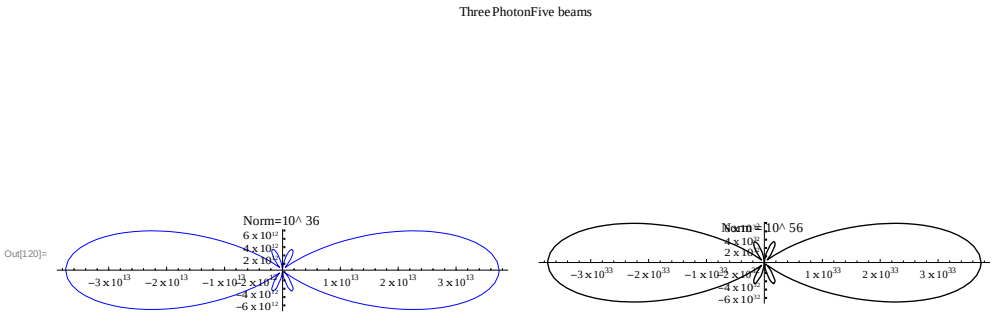


Figure 5.42: Changing normalization for $\lambda = 18 \times 10^{-8}$m, without phase

Polarization Dependance for Three photon

Three Photon, two beams

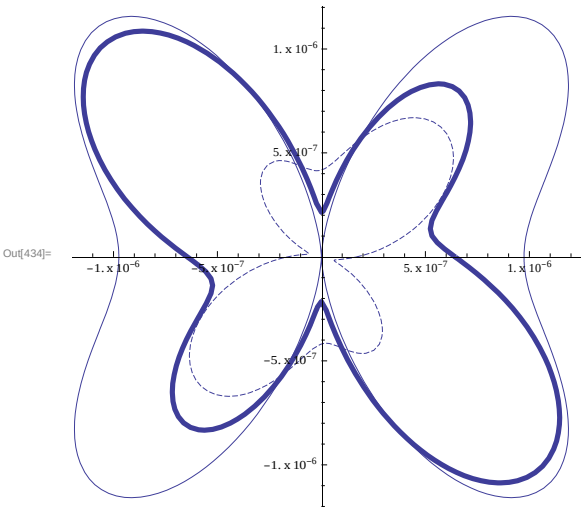


Figure 5.43: Polar plot of the differential cross -section of the three-photon ionization with two beams. Thick line $\zeta_1 = 0, \zeta_2 = -\pi/4$, Thin line, $\zeta_1 = \zeta_2 = 0$ and Dashed line $\zeta_1 = 0, \zeta_2 = \pi/2$

Three photon, three beams

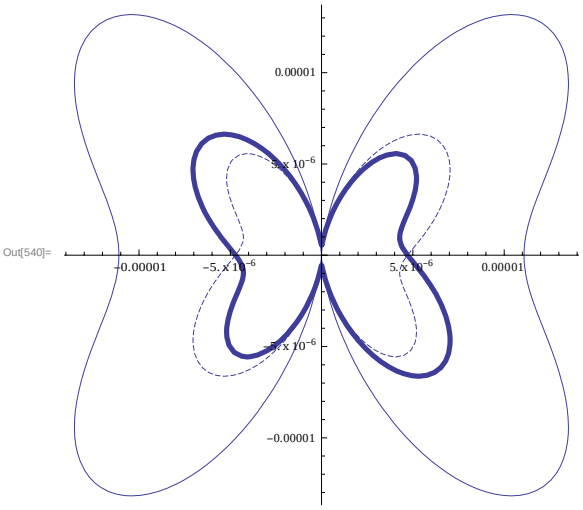


Figure 5.44: Polar plot of the differential cross -section of the three-photon ionization with two beams. Thick line $\zeta_1 = 0, \zeta_2 = -\pi/4, \zeta_3 = \pi/4$ Thin line, $\zeta_1 = \zeta_2 = \zeta_3 = 0$ and Dashed line $\zeta_1 = 0, \zeta_2 = \pi/2, \zeta_3 = -\pi/4$

Three photon, four beams

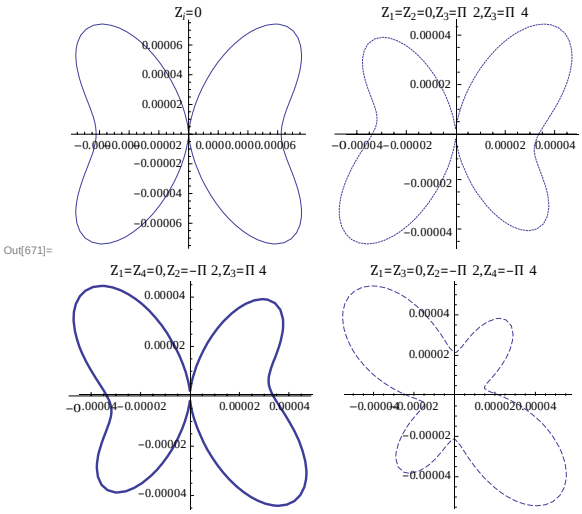


Figure 5.45: Polar plot of the differential cross -section of the three-photon ionization with four beams by changing polarization

Changing wavelength, with phases

Two photon, two beams

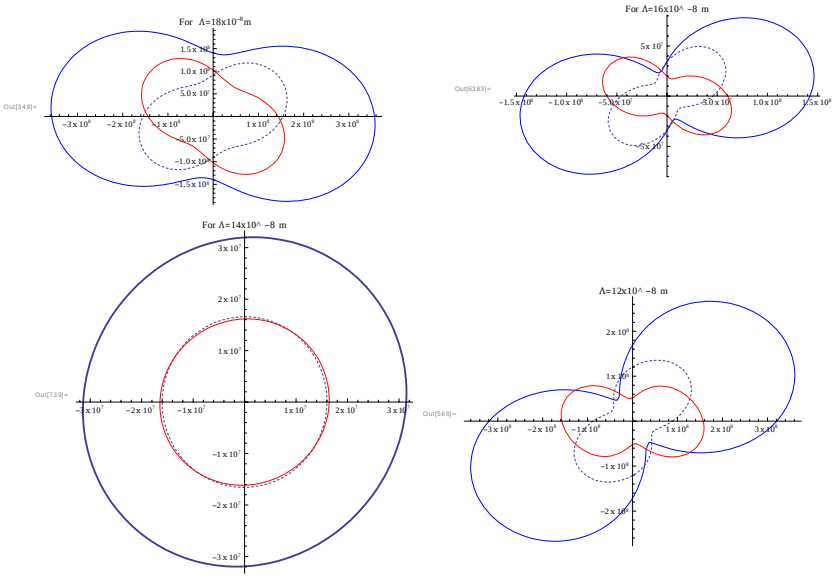


Figure 5.46: Changing wavelength 2ph, Thick line $\delta_i = 0$, Dashed line $\delta_1 = \pi/4$, $\delta_2 = -\pi/4$ and Thin line for $\delta_1 = -\pi/4$, $\delta_2 = -\pi/4$

Three photon, two beams

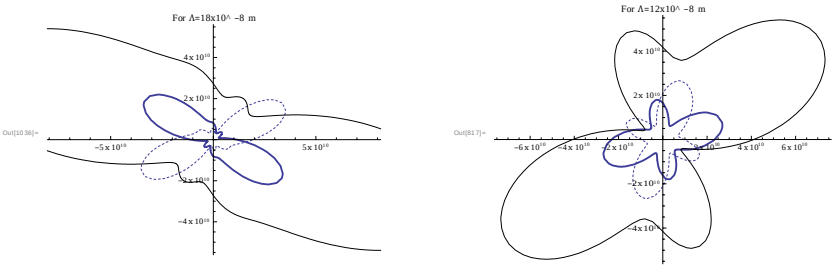


Figure 5.47: Changing wavelength 3ph, Thick line $\delta_1 = 0$, $\delta_2 = \pi/2$, Dashed line $\delta_1 = \pi/2$, $\delta_2 = 0$ and Thin line for $\delta_1 = -\pi/4$, $\delta_2 = 0$

Three photon, four beams

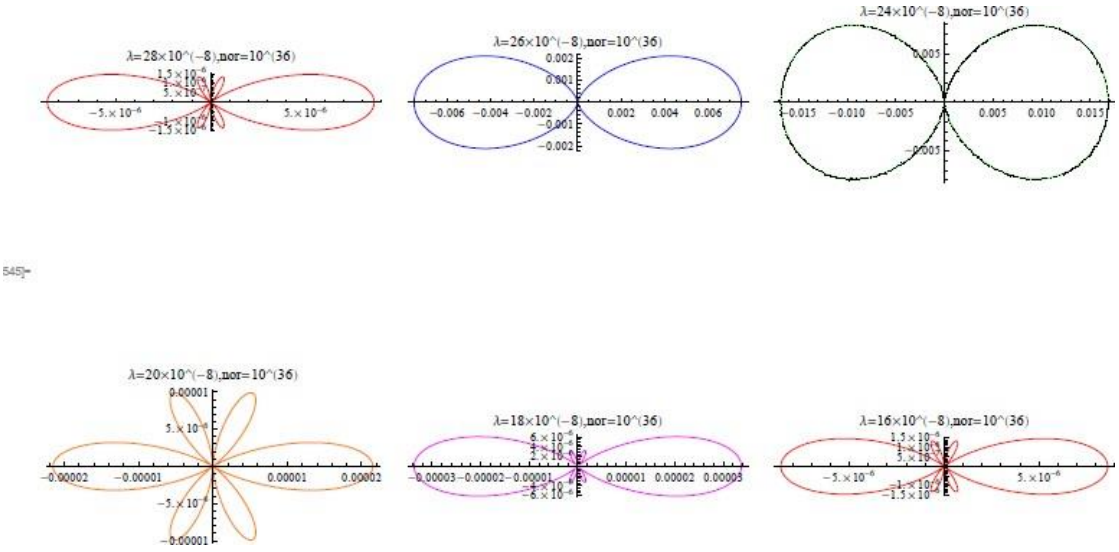


Figure 5.48: Polar plot of the differential cross -section of the three-photon ionization with four beams by varying wavelength of the photon.

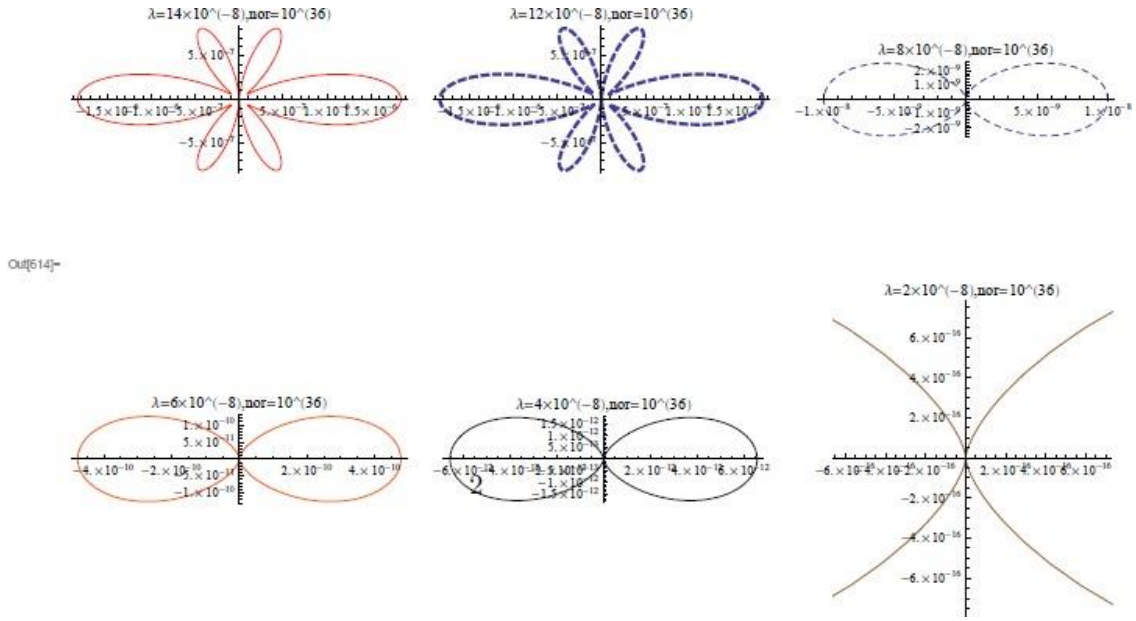


Figure 5.49: Polar plot of the differential cross -section of the three-photon ionization with four beams by varying wavelength of the photon.

Discussions

We have presented analytical and numerical results for the two and three-photon ionization of ground state hydrogen atom due to simultaneous interaction with two or more laser beams of same frequency, but different polarization states. We have shown in different polar plots, the dependance of the two and three photon differential cross-section, on phase, polarization and photon wavelength, with polar angle $\vartheta = \pi/2$ and varying azimuthal angle from $\varphi = 0$ to 2π. The graphical output is placed immediately after its corresponding input command as it appears in Mathematica notebooks. Arbitrary units are used in these graphs. In the present work we have found that photo ionization with different beams of same frequency gives quite different pattern of angular distribution.

From the phase part of figure 5.3 to 5.3.1 shows, for two beams to five beams with phase difference of $\pi/2$. Hence as far as angular distribution of photo-electron is concerned, it changes the shape.

Figure 5.4 if one of the beam is circularly polarized and other beam is linearly polarized the azimuthal angular distribution of ejected photoelectron is dramatically modified by the change of linearly polarized beam. The magnitude and alignment of

azimuthal angular distribution for circular polarization is quite different than that for the right circular polarization. There are some more plots like in figures 5.6 and 5.11, for changing the phase angle for different beams, changes the symmetry. Similar is the case for thee-photon but modified the shape as shown in different plots 5.3.6. The interference effects are caused by phase difference δ between the different beams.

By changing the wavelength for two photon two beams as figure 5.46, and for three photon as in figure 5.47 for two beams and 5.49 four beams, also changes the shape.

In the polarization part for two photon figure 5.3.4 and for three photon figure 5.3.8 to 5.3.9, shows the asymmetry. By increasing the normalization constant as shown in figure 5.16, for two photon and figure 5.41, 5.3.7 and 5.3.7, for three photon, increases the magnitude of the shape.

The asymmetry does indeed vary as the phase difference, polarization of individual beams and number beams. Thus differential cross-section shows strong dependance on the phase, polarization and photon wavelength and the number of beams.

CHAPTER 6

Conclusions and Recommendations

Conclusions

This thesis is devoted to a multiphoton ionization approach for solving laser-atom Time Dependent Schrodinger Equation (TDSE) of a Hydrogen atom in intense multiple laser beams by using Dalgarno-Lewis technique. We followed the perturbation theory in dipole approximation to obtain expressions corresponding to higher order matrix element. A general text book description is presented for the derivation of second and third order transition amplitude. We have succeeded in developing the solution for separating the contribution into angular part on one hand, and radial part on the other hand. The eigenfunction of the angular dependent part of the Schrodinger equation for Hydrogen atom is the spherical harmonics $Y_{lm}(\vartheta, \varphi)$, where ϑ is the angle between direction of ejected electrons and polarization of laser beams. In the case of N-photon ionization of atoms, the photoelectron angular distribution is described by the photo electron angular differential cross-section. Based on our analytical expression, the various spherical polar plots of differential ionization cross-section on angular distribution of ejected photo- electrons by varying intensity, phase, and polarization of different beams show that, there is asymmetry in multiphoton ionization. The results illustrate the influence of laser wavelength, arbitrary beams, intensities, polarization of different beams and their phase differences on the differential ionization cross-section. It is found that differential ionization cross-section strongly depends on phase and polarization of absorbed beams.

Recommendation

The unique polarization dependency of multiphoton ionization has not been exploited very much, despite its interesting application. The experimental work still remains to be seen in near future. It is a simple method for determining and studying the symmetries of the excited states. Another application is to use its ability to distinguish species on behalf of polarization ratio. The last decade multiphoton fluorescence has especially emerged within the field of biology and neuroscience as an instrument to look deep within biological samples and is already very mature. It is also used as an instrument to deliver or activate biological active substances at specific places within tissue.

Thus, the study of **MPI** in presence of **multiple beams** is very useful spectroscopy for image processing (Joseph, 2008) and also to gather useful information from the light carrying form cosmos use as photons (photonics) rather than electrons) (Santomato, 2004). This novel approach widely used in the investigations and unique insights into the physics of energy transfer. The most important application is the industrial application such as micromatching (Shalom and Kunioki, 2009).

Multiphoton processes cover the areas as diverse as precision measurements, studies of ultra fast dynamics, laser acceleration of charged particles, laser machining of solid-state materials and medical applications. With the advent of lasers the nonlinear, or multiphoton, interactions between radiation and matter have become a key area in basic and applied research.

It is believed that over a decade from now, it will approach a fundamental limit, as electrical insulation of gate oxide will break down when its thickness becomes less than 0.7nm. In this case it will not be possible to further reduce the size of transistor and consequently it could not be possible to increase the density of individual components integrated in a single chip. An attractive alternate to use as photons (photonics) as information carriers (Manual, 2004). This studies can give a concept for the advanced scientific theories and serve as indication for future research direction, which are important in a number of application, like in laser driven plasma heating, or in the development of fast optical electronic devises (Antoine, 2010).

CHAPTER 7

SUMMARY

Summary

In the family of multiphoton phenomena, multiple beams ionization represents a topic of increasing experimental and theoretical interest. Generally, in two-color ionization process the electron is ejected as a result of the atom interaction with two or three fields of same frequency, but different polarization, same principle is assumed for the three-color process. All the theoretical investigations of the ionization processes are based on the solution of Time Dependent Schrodinger Equation (TDSE). Since the exact analytical solution of the TDSE does not exist even for the simplest atomic system, there are two possible approaches to solve the TDSE. The first possibility is the direct numerical solutions of TDSE using different basis sets but they are not efficient for complex system.Again they converge very slowly at high radiation field intensities and also involve extensive numerical calculation with high computational costs. The second possibility is approximate solution of TDSE, which has advantage that involves much less computations, but they provide less accurate results.

The goal of my research is to introduce the concept of transition amplitudes, which is essential for the quantum description of interaction between atom and photon. The transition amplitudes associated with a physical process is the evolution-operator matrix element between the initial and final states of the process under study. For the calculation of these amplitudes, we have used the perturbation theory, which is based on the splitting of the total Hamiltonian H into H_0 and the coupling part $H^{I}(t)$. Our present approach is based on the solution of TDSE, where the Coulomb interaction between the active electron and the target nucleus is taken as perturbation. While the use of perturbational approach has been shown to be

adequate in many practical application (Chin and Lambroupoulos, 1984), detailed quantitative evaluation has been difficult due mainly to the task of summing over the complete set of intermediates states. Thus we have solved TDSE analytically in the presence of multiple laser beams by Dalgarno and Lewis (DL) method. This method in principle should be more advantageous both in terms of computational efficacy and numerical accuracy than any other methods. The idea of DL method is to define an auxiliary operator such that the evaluation of intermediate sum is not needed. We have succeed in separating the angular and radial parts, for the evaluation of the transition amplitudes, and the physical quantities that can be deduced from these transition amplitudes are ionization rate, ionization cross-section, etc.

Angular distributions of the ionization probabilities of the photoelectrons are studied for different laser beams by changing the laser frequencies. We have shown that the ionization rate for two and three-photon ionization of a one-electron atom depend on polarization and phase of incident light. For the given path the radial part of the Dalgarno's operators are solved, which only depend on the frequency of the laser beams, the angular part is different for different polarization of multiple beams.

This thesis is grouped into four main chapters. Before we come to deal with multiphoton process due to multiple beams, in first two chapters we have discussed the brief review of the physical "one-photon" context in the presence of ultra-short laser pulse, in which quantum optics was born, and the remaining chapters describe multiphoton ionization due to multiple beams.

- Chapter 1, we have explained the history of multiphoton ionization, and introduction to MPI, ATI, TI, OBI etc.
- Chapter 2 describes some reviews of work done and some of the methods on perturbative and non-perturbative for solving the transition amplitudes.
- Chapter 3, we describe the theoretical method for the derivation of transition amplitude by two-photon ionization due to multiple beams.
- Chapter 4, which we mainly concentrate on three-photon ionization due to multiple beams.
- In chapter 5, has explained the results and discussion of our entire work.

- Chapter 6 presents concluding remarks and recommendation, Chapter 7, summarizes the work with future research and finally in Chapter 8, we have presented the bibliography.

We can conclude that, *Because of dependence of transition amplitudes on polarization of absorbed light beams, it is not a surprise that absorption of intensity depends on polarization, hence multiphoton ionization is more sensitive than single photon ionization.*

Future research

- To calculate and plot, by varying intensity on ionization cross-section of atomic hydrogen for multiple beams.
- Analytical and Computational analysis on Multiphoton ionization of Hydrogen atom for multiple beams of different frequencies.
- To verify experimentally on ionization cross-section of hydrogen atom for same and different frequencies of multiple beams.
- Look for analytical and computational analysis on Multiphoton ionization for multiple beams of other atoms like He, lithium etc.

Bibliography

Andrei (2007), MIT Department of Chemistry, pp 2-42, http://home.uchicago.edu/ /tokmakoff/TDQMS/Notes/2.5.

Antoine M., Weber S., and Chatel B. (2010), *J. Phys. B: At. Mol. Opt. Phys.*, 43, 103001-103005.

Aurelia C (1992), International Center for Theoretical Physics, IC 33, Trieste.

Awasthi M.(2009), dissertation, *Molecules in strong laser fields*, 32.

Aymar M. and Crance M. (1981), *J. Phys. B: At. Mol. Phys.*, Vol.14, 3585-3601.

Bailey P.B. (1965), *Proc, Phys. Soc.*, 85,1127-1131

Banerjee S., Valenzuela A. R., Shah R.C, Maksimchuk A. and D. Umstadter D. (2003), *J. Opt. Soc. Am. B*, 20(1), 10182-10199.

Barna I. F., Wang J., and Burgdörfer (2006), *Phys. Rev. A:*, 73(1), 065602-065609.

Barry B. H. and Gold A. (1966), *Phy. Rev.* Vol 143(1), 1-24.

Barry B. H. (1967), *Phy. Rev.* Vol 153(1), 23-28.

Bassani F., Forney J. J., Quattropani A. (1977), *Physical Review Letters*, Vol 39(17), 1070-1073.

Bassi M. (2000), *Pramana J. Phys.* vol 54, 379-384.

Bauer J. (1997), *Laser Physics* , Vol 8 (1), 76-77.

Baumert T., Grosser M., Thalweiser R., and Gerber G.(1991), *Phy. Rev. Lett.* , 67, 3753-3756.

Beiser A. (2001), *Concepts of M.Physics,* fifth edition, Tata McGraw-Hill tenth reprint 2001, 161-188.

Bethe H. A. and Salpeter E. E. (1957), *Quantum mechanics of one or two electrons atom*, Springer, 253-267.

Bhardwaj R., Hnatovsky C., Pattathil R., Simova E., Rayner D. M., Taylor R. S., and Corkum P. B. (2007), *Modification of fused silica using femtosecond multiphoton ionization*, Ottawa, ON Canada.

Bivona S., Burlon R., and Leone C. (1991), *IL NUOVO CIMENTO*, Vol 13(9), 1111-1115.

Bivona S., Bonanno G., Burlon R., and Leone C. (2008), *The European Physical Journal Special Topics*,Vol 160, Issue 1, 23-31.

Bojer M. L. (1998), Thesis,*Strong Field Ionization*, Institute of Physics and Astronomy, University of Aarhus.

Borbèly S., Póra K., and Nagy L. (2009), *J. Phys.*, 14th Int. conf. on the physics of highly charged ions, Conference series, 163, IOP publishing, 012067.

Borbèly S., Tőkési K., and Nagy L. (2008), *Phy. Rev A:*, 77, 033412-11pages.

Bottcher M., Rottke H., Zhavoronkov N. Sandner W., Agostini P., Gisselbrecht M., and Huetz A. (2007), *Phys. Rev. A:*, 75, 033408-4 pages.

Brandi H. S., Davidovich L., and Zagury N., *Journal De Physique*, Colluque C2, supplement au n°11, Tome 43, C2(397)-C2(405).

Bransden B. H. and Joachain C. J. (2003), *Physics of atoms and molecules*, 2nd edition, Pearson Education, 416-421.

Bredy R., Camp H. A., Nguyen H., Awata T., Shan B., Chang Z., and DePaola B. D. (2004), *J. Opt. Soc. Am. B*, 21(12), 2221-2226.

Bulanov S. V. and Naumova N. M.(1994), *Phys. Plasmas*, 1(3), 745-757.

Cerent L., and Mazur E. (2007), *Femtosecond laser-micromaching*, Draft 6.4 of 6/11/07.

Chandra A. K. (2000), *An Introductory Quantum Chemistry*, Tata McGraw-Hill Limited, New Delhi, 123-139.

Chandre C., and Uzer T. (2002), *Phys. Rev. E*, 65, 026211-026218.

Chang T. N. and Poe R. T. (1976), *J. Phys. B: Atom. Moles. Phys.*,9 (11), L311-L315.

Chichinin A. I., Shternin P. S., Gödecke N., Kauczok S., Maul C., Vasyutinskii O. S., and Gericke K. H. (2006), *J. Chem. Phys*, 125, 034310-14.

Chin S. L. and Lambroupoulos P. (1984), *Multiphoton Ionization Of Atoms,* World Scientific, 115-135.

Cloude C. T. (1991), *Atom-photon interactions*, Physics for Wiley and Sons publisher, 7-15.

Cohen-Toannoudji C. (2004), *Atoms in electromagnetic fields*, World Scientific, Vol. 3, 347-367.

Constants E. (1996), *Phy. Rev. Lett.* , 76(22), 4140 - 4143.

Corcum P. B., Burnett N. H., and Brunel F. (1989). *Phy. Rev. Lett.* , Vol 62(11), 1259-1262.

Corkum P. B., Christoph E., Manjusha M., Peter D., Steven H., Sergey A., David R. and David V. (1999), *Royal Society of Chemistry*, Faraday Discuss, 113, 47-59.

Corkum P. B.(1993), *Phy. Rev. Lett.*, Vol 71(13), 1994-1997.

Crance M. and Aymar M. (1979), *J. Phy. B, Atom, Molec.*, Vol 12, 3665-3678.

Ding D., Mingxing J., Hang LIU, Lu K.T.(1989), *Chinese, Phys. Lett.*, Vol 6(3), 128-129.

Dörner R., Weber T., Weckenbrock M., Staudte A., Kammer S., and Schmidt-Böcking H. (2001), IN: Photonic Electronic and Atomic Collisons, *Proceedings of ICPEAC*, Ringtone press.

Dörner R., Weber T., Wecknbrock M., Staudte A. and Kammer S. (2001), *Double Ionization in Strong laser field*, ICPEAC.

Dalgarno A. and Lewis J.T.(1956), *Proc. Phys. Soc. A:*, 69, 628-630.

David J. G. (2002), *Introduction to Electrodynamics*, Third edition, Printice Hall of place country-region India Private Lmt, 1-20.

David A. B. (2008), *Quantum Mechanics for scientists and engineers*, Cambridge University press, 60-65.

Delone N. B., and Krainov V. (1999),*Multiphoton Processes in Atoms*, Springer-Verlag Berlin Heilberg, 190-210.

Devananthan V. (2002), *Angular momentum techniques in quantum mechanics*, Kluwer Academic Publishers, 115-130.

Dimitrovski D. (2005), *Time dependence of ionization and excitation by intense short electric pulses*, Dissertation.

Dong-Ik L and Chandrashekhar C (2003), *Optical Express*, 11(8), 946-951.

Doo W. B., Yasushi O., Andersen L. H., and Lineberger W. C. (1997), J. Phys. Chem. A 1997, 101, 6688-6696.

Drachman R. J., Bhatia A. K., and Shabazz A. A. (1990), Phy. Rev A:, 42(11), 6333-6335.

Duchateau G., Illescas C., Pons B., Cormier E., and Gayet R. (2000), *J. Phy. B: At. Mol. Opt. Phy.*, 33, L571-L581.

Duchateau G., Cormier E., and Gayet R. (2002), *Phy. Rev. A:*, 66, 023412-7pages.

Edwards M. (1992), Phys. Rev. A: 46, 7228-7234.

Faisal F. H. M., Wallenstein W., and Zacharias H.(1977), *Phy. Rev. Vol.*, 39(18), 1138-1141.

Faisal F. H. M. (1986), *Theory of multiphoton processes*, Plenum press, 128-143.

Fedorov I., Koziol L., Mollner A. K., Krylov A. I., and Reisler H. (2009), *J. Phys. Chem. A:*, 113, 7412-7421.

Fedorov M. V. (1997), *Atomic and free electrons and in a strong light field*, World Scientific, 20-28.

Fedorov M. V., and Poluektov N. P. (2003), *arXiv: quant-ph*, Vol 1, 0311025-0311029.

Fifirig M. and Stroe M. (2002), *Laser Phys.*, Vol 12(6), 963-970.

Fifirig M., Florescu V., Maquet A., and Taïeb R. (2000), *J. Phy. At. Mol. Opt. Phy.*, 33, 5313-5327.

Fifirig M. (2000), *Laser physics*, Vol 10(2), 588-593.

Fifirig M (2001), *Laser physics*, Vol 11(9), 989-993.

Fifirig M. and Florescu V. (2003), *Romanian Report on Physics*, Vol 55(4), 532-548.

Fox M. (2006), *Quantum Optica, An Introduction* , Oxford university press, 169-178.

Gao B., and Starace A. F. (1988), *Phy. Rev. Lett.*, Vol 61, 404-407.

Gao B., and Starace A. F. (1989), Phy. Rev A,Vol. 39 (9), 4550-4560.

Garrett A. W., and Zwier T. S. (1992), *J. Chem. Phys*, 96(5), 3405-3409.

Gasiorowicz S. (2000), *Quantum Physics*, John Wiley and Sons, Inc., 341-359.

Gerery C. and Night P. (2005), *Introductory Quantum Optics*, United Kingdom at University of Press, Cambridge, 75-85.

http://www.atom.uni-frankfurt.de/research /synchrotron/photonmolecule/H2_double/4_photo

Gontier Y. and Trahin M.(1971), *Phy. Rev. A:* , Vol 4(5), 1897-1906.

Gontier Y., Poirier M. and Trahin M.(1980), *J. Phys. B:* , 13, 1381-1387.

Grossmann F. (2008), *Theoretical Femtosecond physics*, Springer series on Atomic, Optical and Plasma physics, 99-113.

Heitler W.(1957), *The Quantum Theory of Radiation*, 175-186.

Hill W. T. III and Chi H. L. (2007), *Light - matter interaction*, WILEY-VCH Verlag GmbH and Co. KGaA, 30-39.

Imre F. B. , Jianyi W., and Joachin B. (2006), *Phy. Rev.*, 73, 1-6.

Ince E. L. (1956), *Ordinary Differential Equations*, New York, Dover Publications, 187-206.

Jinghua H. and Yaguo L., (2011), *Interaction Between Pulsed Laser and Materials*, 117-120 www.intechopen.com

Jingtao Z.(2007), *Phy. Rev.A:*, Vol 75, 043403-9pages.

Joshi R. (2007), Phys. Lett. A, Vol 361(4), 352-355.

John S. T. (2000), *A modern Approach to quantum mechanics*, University Science books print, 93-105.

Jones M., and Tennyson J. (2010), *J. Phy. B: At. Mol. Opt. Phys.*, 43(4), 045101.

Joseph R. L. (2008), *Principles of fluoresce spectroscopy*, Springer, 623-634.

Karule E., and Gailitis A. (2010), *J.Phys. B: At. Mol. Opt, Phys.*, 43, 065601-08.

Karule E. (1988), *J. Phy. Phy. B At. Mol. and Opt Phy.*, 21, 1997-2014.

Keldysh L. V. (1965), *Soveit physics, JETP*, Vol 20(5), 1307-1314.

Kenichi I. and Katsumi M. (2002), *Phys. Rev. A*, 65, 043405-7.

Kenneth J. S. and Kenneth C. K. (1992), *Phy. Rev. A:*, 45, 8026.

Klepper D. et al(1997), *Atomic, Molecular and optical physics workshop report*, 21-29.

Koval P. (2004), Thesis,*Two photon ionization of atomic inner shells*, University of Kassel, 25-26.

Kundiliya R., Bhatra K. and Man Mohan(2001), *J. Phys. B: Atom. Mol. Opt. Phys.*, 34, 4083-4089.

Kundiliya R, Bhatra K., Man Mohan (2001), *Phys. Rev. A*, 64, 043404-11.

Lambropoulos P. and Petrosyan D. (2007), *Fundamental of Quantum Optics and Quantum Information*, Springer-Verlag Berlin Heidelberg, 76-82.

Lambropoulos P.(1972), *Phy. Rev. lett*, 28, 585-589.

Landau L. D. and Lifshitz E. M. (1965), *Quantum Mechanics*, Pergamon Press, 51-67.

Lang T. et al , *Rare gas Atoms in strong laser fields*, mht. document.

Leplanche G., Durrieu A., Flank Y., Jaouenet M., and Rachmanal A. (1976), *J.Phys. B: Atom.Molec. Phys.*, 9(8), 1263-1277.

Lewenstein M. and L Huilleir A.,(2008), Edited by Thomas Brabec, *Strong Field Laser*, Springer Science and Business Media, 148-150.

Lezius M., Blanchet V., Ivanov M. Y., and Stolow A. (2002),*J. Chem. Phys.*, 117, 1575-1588.

Likhatov P. V., and Telnov D. A. (2009) , *J. Phy. B: At. Mol. Opt. Phys.*, 42(10), 105603-10.

Lin S. H., Vilaeys, and Fugimura Y. (2004), *Advances in Multiphoton Processes and Spectroscopy*, Vol 16, World Scientific, 249-270.

Loud B. B. (1991), *Lasers and Non-Linear Optics*, Wiley Eastern Ltd, New-Delhi, 17-.

Magnus W., Oberhettinger F. and Soni R. O. (1966), *Formulas and theorems for the special functions of mathematical physics*, 3rd ed, Springer, New York publication, 49-59.

Mainfray G. and Manus C. (1999), *Rep. Prog. Phys*., 54, 1333-1372.

Mainfray G. and Manus C. (1980), *Applied Optics*, Vol. 19(23), 3934-3940.

Manual F. F. (2004), Thesis, *Two color spectroscopy of energy transfers in Si:Er*.

Mark F. (2006), *Quantum Optics, An introduction*, Oxford University Press, 53-67.

Marques M. A. L., and Gross E. K. U. (2004), *Annu.Rev. Phys. Chem.*, 55, 427-55.

Martin S. (2008), Thesis, *Attosecond real time observation of ionization and electron-electron interactions*, Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1 , 12.

Mathews P. M. and Venkatesan K. (1976), *A Text book of Quantum Mechanics*, Tata McGraw-Hill publishing company ltd, New Delhi, 282 - 295.

Messaih A. (1962), *Quantum Mechanics, Part II*, North Holland publishing company, 494-515.

Mickoy V. et al (1986), *Aust J. Phys.*, 29, 761-777.

Mikhail V. F. (1997), *Atomic and free electrons in strong light field*, World Scientific publishing, 20-29.

Miladen M. and Marko S. (2000), *FIZIKA A*, 9(3), 115-128.

Mizushima M.(1970), *Quantum Mechanics of Atomic spectra and Atomic Structure*, W. A. Benjamin, Inc., NY, 03-10.

Moore G.(2005), SIAM (Society for Industrial and Applied Mathematics), *J. NUMER. ANAL.*, Vol 42(6), 2522-2568.

Morellec J., Normand D., Mainfray G., and Manus C. (1980), *Phy. Rev. Lett.*, Vol 44(21), 1394-1397.

Mott N. F. (1962), *Elements of Wave Mechanics*, Cambridge University Press, 121-131.

Nandi T. K., Bera P. K., Panja M. M., and Talukdar B. (1996), *J. Phy. Maths. Gen.*, 29, 1101-1105.

Nikura H., and Corkum P. B. (2006),*Atomic, Molecular and Optical Phys*., 54, 511-522.

Noureddine C., and Dalabeeh M. A. (2005), *J. Phys. Math, Gen.*, 38, 1553-1558.

O'Keeffe P., Lòpez-Martens R., Mauritsson J., Johansson A., L'Huillier A., Véniard V., Taïeb R., Maquet A., Meyer M. (2004), Phy. Rev. A:, 69, 051401(1)-051401(4).

Parashar B. P. (1989), *Ordinary Differential Equation*, 47-57.

Peter K and Gerry C. (2005), *Introduction to Quantum Optics*, Cambridge University Press, 75-85.

Petite G.,Fabre F., and Agostini P. (1984), *Phy. Rev. A:*, Vol 29(5), 2677-2689.

Potvliege R. M. and Smith P. H. G. (1991), *J. Phys. B; At. Mol. Opt. Phys.*, 24, L641-L646.

Pyykko P.(1967), Proc. Phy. Soc. 92, 842-844.

Quattropani A., Bassani F., and Carillo S. (1982), *Phy. Rev. A:*, Vol 26, pp 3079, and Vol 25, 2869-2876.

Radhakrishnan R. and Thayyullathil R. B. (2004), *Phy. Rev. A:*, 69, 033407(1)-033407(5).

Rajini N. (1989), Thesis, *Three Photon absorption Spectroscopy of Diatomic Molecules*, McMaster University, Ontario , 5-25.

Requate A.(2007), Thesis, *S-matrix Analysis of Vibrational and Alignment Effects in intense Field Multiphoton Ionization of Molecules*, an der Fakulät für Physik der Universität Bielefeld.

Rolf W. (2005), Thesis, *Experimental Ionization Processes Of Noble gases in strong laser fields*, Albert Ludwigs Universität, Freiburg.

Rosendroff S. and Schlaile H. G. (1993), *Phy. Rev. A:*, 48(4), 2798-2810.

Rosendroff S. and Schlaile H. G. (1989), *Phy. Rev. A:*, 40(12), 6892-6896.

Sælen L., Birkeland T., Sisourat N., Dubois A., and Hansen J. P. at al (2010), *Phy. Rev. A:*, 81, 022718(1)-022718(7).

Santomato E. (2004),*Photon orbital angular momentum: problems and Perspectives*, Fortshchr., Phy. 52, 1141-1153.

Schultze M. (2008), Thesis,*Attosecond real time observation of ionization and electron-electron interactions*, der Ludwig-Maximilians-Universität München.

Schwartz C.(1959), *Annals of Physics*, 2, 156-169.

Schwartz C.(1959), *Annalas of Physics*, 2, 170-177.

Schwartz C.(1959), *Annalas of Physics*, 2, 178-187.

Selstø S., Alicia P., Fernández J., and Fernando M. (2006), *Phy. Rev.*, 133(1)-133(5).

Shalom E. and Kunioki M. (2009), *Application of laser plasma interactions*, CRC press, 246-256.

Sheehy B., DiMauro L. F. (1996), *Annu. Rev. Phys. Chem.*, Vol. 47, 463-494.

Shih-I C. (1986), *Chinese Journal of Physics*, Vol 24(1), 1-18.

Shrestha N., and Nakarmi J. J. (2008), *An introduction to multiphototon ionization and study of ionization rate and cross-section of hydrogen atom*, 3rd IUPAP, ICWIP, Seoul, South Korea, AIP Conference proceedings, Abstract, Vol. 1119, 243.

Snyder E. M., Buzza S. A., and Castleman A. W. Jr.,(1996), *Phys. Rev. Lett.*, 77(16), 3347-3352.

Stancalie V., Pais V., Mihailescu A., Budriga O., and Oprea A (2010), *Romanian Reports in Physics*, Vol 62(3), 528-545.

Steinman J. (2007), Dissertation, *MPI of laser cooled lithium*.

Steinmann J. (2007), Dissertation ,*Multiphoton ionization of laser cooled lithium* .

Takashi N. and Gabrila B.(2006), *Phy. Rev.A:*, 74, 023411(1)-023411(9).

Taylor K. T. and Dundas D. (1999), *Royal. Soc. Lon. A*, 357, 1331-1358.

Thayyullathil R. B. and Prasanna K. J. (1994), *Phy. Rev. A:*, 49 (4), 2432-2434.

Thayyullathil R. B., Radhakrishnan R. and Seema (2003), *J. Phy. A: Math., Gen.*, 36, 8473-8478.

Thomas B. (2008), *Strong field laser physics*, Springer science business media, 400-420.

Umstadlter D. (2003), *J. Phys. D: Appl. Phys.*, 36, R151-R165.

Unnikrishan K. (1991), *J. Phys. B: At. Mole. Opt. Phys.* 24, L161-L164.

Wang P. J. and Fang Y. (2008), *Chinese Phy. B:*, Vol 17(10), 3668-3671.

Weckenbrock M., Zeidler D., Staudte A., Weber Th., Schöffler M., Meckel M., Kammer S., Smolarski M., Jagutzki O., Bhardwaj V. R., Rayner D. M., Villeneuve D. M., Corkum P. B., and Dörner R.(2004), *Phys. Rev. Lett*, 92(21), 213002.

Wickenhauser M. (2006), *Phy. Rev. A:*, 74, 041402(1)-041402(4).

Xi C. (1995), Thesis, *Atomic and Molecular multiphoton process in intense laser fields*,Nankai University.

Xiao-Min T. and Shih-I C. (2001), *Phy. Rev A:*, Vol 64, 013417(1)-013417(8).

Yoon O. K., Hwang W. G., Choe J. C., and Kim M. S.(1999), *Rapid Commun. Mass Spectrom.*, 13, 1515-1521 .

Yudin G. L., and Ivanov M. Y. (2001), *Phys. Rev. A*, 63(3), 033404, 3404-3408.

Zhang X., Quan W., Wang Y., Kang H., Liu H., and Liu X. (2010), *Chinese Optics Lett.* , Vol 8 (3), 338-341.

Appendix A

Scientific Publications

Asymmetries in multiphoton ionization of the ground state of a hydrogen atom

IOP Publishing Journal of Physics B: Atomic, Molecular and Optical Physics

J. Phys. B: At. Mol. Opt. Phys. **47** (2014) 105002 (7pp) doi:10.1088/0953-4075/47/10/105002

Asymmetries in multiphoton ionization of the ground state of a hydrogen atom

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Received 2 January 2014, revised 19 March 2014
Accepted for publication 31 March 2014
Published 1 May 2014

Abstract

This paper illustrates the study on asymmetry of the angular distribution of the ejected electrons in a multiphoton process from the ground state of a hydrogen atom. General expressions for the multiphoton ionization rates have been derived based on a variation of the Dalgarno–Lewis method for the evaluation of matrix elements in higher order perturbation theory. In addition, these analytical expressions for the various multiphoton transition rates and their variation as a function of polarization, phase, frequency and intensity of the incident radiation have been studied extensively. The general expression obtained can be used to analyse any number of incident beams with arbitrary polarization, phase and intensity.

Keywords: multiphoton ionization, asymmetry, polarization, phase dependence, Dalgarno–Lewis method

(Some figures may appear in colour only in the online journal)

1. Introduction

Multiphoton processes involving multiple laser beams represent a topic of increasing experimental and theoretical interest [1–6]. Here we have made a unified approach to study the dependence of various parameters of the incident radiation on the differential scattering cross section for the multiphoton ionization of a hydrogen atom with many beams. It is shown that the inclusion of multiple beams considerably modifies the shape of the angular distribution of ejected photoelectrons [7]. The asymmetry in the angular distribution of the scattering cross section is found to be controlled by the relative phase difference between the beams and the results obtained can be used for a different frequency range of the incident photons.

This paper is an extension of our previous work [8], where the closed form analytical expressions were obtained for ionization cross sections for interaction of a single beam on a hydrogen atom. Here we have generalized our previous formulation so that many beams with arbitrary polarization and phase can be included in the expression for the ionization cross section. In addition to this advantage, we can use these results to study above threshold ionization (ATI) also. We have shown that the final parametrized analytic expression for the multiphoton ionization cross section is very compact and convenient for analytical and numerical studies.

In section 2 we have discussed in detail the method of Dalgarno–Lewis (DL) for performing the intermediate sums present in higher order transition matrix elements and a convenient extension is performed to include many incident beams. Sturmian expansion of the Coulomb Green function is another widely used method to evaluate these matrix elements [10, 11]. But, in general, it is difficult to evaluate higher order matrix elements present in perturbation theory [8–11] and particularly ATI.

We consider second and third order matrix elements in the subsections and finally obtained the closed form analytical expressions for these transition amplitudes. In section 3, we consider the differential cross section and its dependence on the polarization, phase and amplitude of the incident radiation. In order to show the elegance of our method, a detailed analytical evaluation has been performed for simple situations involving linear, right and left circular polarizations and is presented in section 3.2. In the concluding section 4, we discuss the numerical and analytical results. Numerical results on ATI have been presented for various values of polarization and relative phases of the incident beams.

2. DL method and transition matrix elements

The DL method was originally introduced for the evaluation of long range forces between atoms [12] and later on it was modified by Schwartz [13]. The method depends on auxiliary dimensionless operators which enable us to perform the summation over the complete set of states of the whole spectrum exactly. These operators are determined by a certain inhomogeneous differential equation which depends functionally on the initial state of the atom. For example in order to calculate the N-photon matrix element, it is necessary to solve $(N-1)$ differential equations. This method is more advantageous both in terms of computational efficiency and numerical accuracy than other methods which approximate the summation by various truncation schemes. Here we explicitly consider two- and three-photon ionization of the ground state of the hydrogen atom. We take the interaction part of the Hamiltonian involving many beams in the dipole approximation as $H^{r} = -\sum_j E_{0j}\, \mathrm{e}^{-\mathrm{i}(\omega t+\delta_j)}\, \epsilon_j \cdot r$ with electric field of the j-th beam, $E_{0j} \propto I_j$, where I_j, δ_j, and ϵ_j are, respectively, intensity, phase and polarization of the j-th beam. For simplicity we consider the situation where different beams have the same frequency ω. For a given frequency ω the ionization rate is [8]:

$$\Gamma^{(N)} \propto |M_{fg}^{(N)}|^2. \tag{1}$$

We use atomic units and $M_{fg}^{(N)}$ refers to the N-th order transition amplitude corresponding to a transition from the ground state $|g\rangle$ to a final continuum state $|f\rangle$ by absorbing N photons.

2.1. Two-photon ionization

In this section we consider N_b number of beams interacting with the hydrogen atom and it absorbs two photons (labelled with i, j) simultaneously from any of these beams. Following second-order time-dependent perturbation theory, the transition matrix element is given by

$$M_{fg}^{(2)} = \sum_{i,j} \sqrt{I_i I_j}\, \mathrm{e}^{-\mathrm{i}(\delta_i+\delta_j)} M_{ij}^{(2)} \tag{2}$$

where the i, j can go from 1 to N_b and

$$M_{ij}^{(2)} = \sum_n \frac{\langle f|\epsilon_i \cdot r|n\rangle\langle n|\epsilon_j \cdot r|g\rangle}{\omega_{ng} - \omega}. \tag{3}$$

The infinite intermediate sum includes both discrete as well as continuum states. In the DL method we define an auxiliary operator, F_j such that the evaluation of the intermediate sum is completely taken into account as follows:

$$(\epsilon_j \cdot r)|g\rangle = H_0 F_j - F_j H_0 - \omega F_j\ |g\rangle \tag{4}$$

using equation (4) and the closure relation $\sum_n |n\rangle\langle n| = I$ in equation (3), the second-order matrix element reduces to

$$M_{ij}^{(2)} = \langle f|\epsilon_i \cdot r F_j|g\rangle. \tag{5}$$

Taking the initial state as the ground state of the hydrogen atom, i.e. $|g\rangle = \mathrm{e}^{-r}/\sqrt{\pi}$ (in atomic units) the angular separation can be achieved by taking $F_j(\mathbf{r}) = (\epsilon_j \cdot r) f_1(r)$ and the equation (4) reduces to

$$r f_1'' + (4 - 2r) f_1' + (2\omega r - 2) f_1 = -2r \tag{6}$$

here the prime denotes the derivative with respect to r.

Three-photon ionization

A similar procedure can be followed for the case of the three-photon transition matrix element

$$M_{fg}^{(3)} = \sum_{i,j,k} \sqrt{I_i I_j I_k}\, \mathrm{e}^{-\mathrm{i}(\delta_i+\delta_j+\delta_k)} M_{ijk}^{(3)} \tag{7}$$

where

$$M_{ijk}^{(3)} = \sum_{m,n} \frac{\langle f|\epsilon_i \cdot r|m\rangle\langle m|\epsilon_j \cdot r|n\rangle\langle n|\epsilon_k \cdot r|g\rangle}{(\omega_{mg} - 2\omega)(\omega_{ng} - \omega)}. \tag{8}$$

Since the third-order matrix elements involve two summations of intermediate states in addition to the operator $F_j(\mathbf{r})$ in equation (4), we now have one more auxiliary operator $G_{jk}(\mathbf{r})$ such that

$$(\epsilon_j \cdot r)F_k|g\rangle = H_0 G_{jk} - G_{jk} H_0 - 2\omega G_{jk}\ |g\rangle. \tag{9}$$

Using equations (4) and (9) in equation (8) and the closure relation, equation (8) reduces to

$$M_{ijk}^{(3)} = \langle f|(\epsilon_i \cdot r) G_{jk}|g\rangle. \tag{10}$$

Now the angular separation of the operator $G_{jk}(\mathbf{r})$ can be carried out by taking

$$G_{jk}(\mathbf{r}) = \frac{r^2}{2} Q_{jk}(\hat{r}) g_2(r) + q_{jk} g_0(r) \tag{11}$$

where $Q_{jk} = (\epsilon_j \cdot r)(\epsilon_k \cdot r) - \frac{1}{3}(\epsilon_j \cdot \epsilon_k)$ and $q_{jk} = (\epsilon_j \cdot \epsilon_k)$. Substituting equation (11) in equation (9) it is easy to show that the differential equation satisfied by the radial terms $g_0(r)$ and $g_2(r)$ are

$$r g_0'' + (2 - 2r) g_0' + 4\omega r g_0 = \tfrac{2}{3} r^3 f_1 \tag{12}$$

$$r g_2'' + (6 - 2r) g_2' + (4\omega r - 4) g_2 = \tfrac{4}{3} r f_1 \tag{13}$$

here again the prime denotes the differentiation with respect to r.

Solutions of differential equations

Using the method of the Laplace transform, one can find the solutions to the differential equations (6), (12) and (13). This can be done by defining the following function:

$$\Phi(p, q, \lambda, t, r) = \int_{\lambda}^{t} \mathrm{e}^{-r(s-1)} K(p, q, \lambda, s)\, \mathrm{d}s, \tag{14}$$

where

$$K(p, q, \lambda, s) = \frac{1-\lambda}{1+\lambda}^{\frac{1}{\lambda}} (s+\lambda)^{p+\frac{1}{\lambda}} (s-\lambda)^{q-\frac{1}{\lambda}}. \tag{15}$$

Here p and q are real and in general λ can be complex.

Now the solutions to differential equations (6), (12) and (13) can be expressed in terms $\Phi(\cdot)$ [8, 9] as

$$f_1(r) = \frac{1}{\omega} - \frac{1}{2\omega^3}\Phi(1, 1, \lambda_1, 1, r) \tag{16}$$

$$g_2(r) = \frac{1}{3\omega^2} - \frac{1}{3\omega^4}\Phi(1, 1, \lambda_1, 1, r) + \frac{2}{3\omega^4}\int_{\lambda_1}^{1} \mathrm{d}t\, \frac{K(1, 1, \lambda_1, t)t}{K(3, 3, \lambda_2, t)}\Phi(2, 2, \lambda_2, t, r) \tag{17}$$

$$g_0(r) = \frac{2}{3\omega^2}\frac{r^2}{4} + \frac{1}{4\omega^2}(1-2\lambda_1) - \frac{3}{8\omega} - \frac{1}{3\lambda_1\omega^4}\phi(0,0,\lambda_2,1,r) - \frac{1}{6\omega^4}\left(\frac{1}{2}\frac{\lambda_1}{r} + \frac{1}{\omega}r - \frac{1}{\omega}\frac{1+\lambda_1}{r}\right)\phi(1,1,\lambda_1,1,r) + \frac{1}{\lambda_1}\frac{\lambda_1}{2}\frac{1}{1}\frac{1}{1}$$

$$\int \mathrm{d}t \frac{K(1,1,\lambda_1,t)}{K(1,1,\lambda,t)} \frac{t}{2} + \frac{2}{\quad}$$

$$\frac{1}{3\omega}\frac{1}{1}\frac{\lambda}{-2\omega} \times$$

It is useful to note that the above expression is spherically symmetric, therefore, the angular distribution of the ejected electron is isotropic for a given polarization state of the radiation.

We now have the integral

$$\int P_2(\hat{k}\cdot\hat{r})\epsilon_i\cdot\hat{r}\epsilon_j\cdot\hat{r}\,\mathrm{d}\Omega = \frac{2\pi}{5}\left(k\cdot\epsilon_i k\cdot\epsilon_j + k\cdot\epsilon_j k\cdot\epsilon_i\right)$$

$$\frac{4\pi}{15}$$

$$\frac{}{}(\epsilon\cdot\epsilon) \qquad (23)$$

$$M = \sqrt{\pi}$$

and the matrix element corresponding to a $\Delta l = 2$ transition

$$\omega(1+\lambda_1)\ \bar{}\ \omega\ \bar{}\ t+\lambda_1 \qquad (t+\lambda_1)^2$$

is

$M^{(2)}$

l $\sqrt{\pi}$ kl 1

$$P_l(\hat{k}\cdot\hat{r})\hat{\epsilon}_j \cdot \hat{r}\,\mathrm{d}\blacktriangle = 3 \quad j_1 \quad \frac{1}{4\pi} \quad \hat{} \quad \hat{} \quad \hat{}$$

3 i j k 105 i j k

Since

j_1 j_2 3 j_1 j_2 j_1 j_2 j_3 $\overline{5}$ $k1$ 2

$\times\Phi(0, 0, \lambda_2, t, r)$ (18) 2 $\hat{k}$ $\hat{k}$ 4π

$\hat{k}$ $\hat{k}$

$j_1 j_2 =$

where $\lambda_1 = \sqrt{1 - 2\omega}$ and $\lambda_2 = \sqrt{1 - 4\omega}$.

$$\begin{pmatrix} \hat{\epsilon}_{j_1} & \hat{\epsilon}_{j_2} \\ \hat{\epsilon}_{j_1} & \hat{\epsilon}_{j_2} \end{pmatrix}$$

$j_1 j_2$

Two-photon transitions. First we consider

Angular integrals

photon processes and label the beams from which the photons

the two-

$$\int \times \quad r^4 R_{k2}(r)\, f_1(r)\, e^{-r}\, dr. \tag{24}$$

Three-photon transitions. Now we consider the three- photon processes and label the beams from which the photons are absorbed as j_1, j_2 and j_3 with respective polarizations ϵ_{j_1}, ϵ_{j_2} and ϵ_{j_3}. Using equation (19) in equation (10), the third-order transition matrix element now takes the form:

are absorbed by j_1 and j_2 and denote the corresponding

polarization states by ϵ_{j_1} and ϵ_{j_2}. These j_i $(i \quad 1, 2)$ can go from 1 to N_b, where N_b is the number of available incident beams from which the atoms can absorb photons. Using

$$P_l(\hat{k}\cdot\hat{r})$$

the following partial wave expansion of the final state wave fun ction

$$f(\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)(e^{2i\delta_l}-1)P_l(\cos\theta)$$

$$C^{(3)}_{j_1 j_2 j_3} \qquad (-\mathrm{i})^l$$

$$_{l}\,\underline{(2l+1)}\ \int \qquad R^{*}_{kl}$$

—

the following relations for the Legendre polynomials:

$$\frac{4\pi}{3}$$

—

$$M_{j_1 j_2 j_3} = -\mathrm{i}4 \quad \overline{\pi} \quad \mathrm{d}r R_{k1}(r) \quad r\ g_0(r) - \overline{2} g_2(r)$$

—

$$^{1\quad 2\qquad 3}$$

——

$$r^2\,\mathrm{d}r\,\mathrm{e}^{-r}$$

$$l \qquad \int$$

l

the two-photon transition matrix element in equation (5)

becomes

$$\frac{r^3}{2} g_2(\hat{\epsilon}_{j_1} \cdot \hat{r}) Q_{j_2 j_3} + r g_0(\hat{\epsilon}_{j_1} \cdot \hat{r}) q_{j_2 j_3} \qquad P_l(\hat{k} \cdot \hat{r}). \tag{25}$$

× d▲

$$M^{(2)} = i^l (2l+1) \int r^2 dr\, e^{-r} R^* f(r)$$

$$\times \int d\Omega (\hat{\epsilon}_{j_1} \cdot \hat{r})(\hat{\epsilon}_{j_2} \cdot \hat{r}) P_l(\hat{k} \cdot \hat{r}). \quad (20)$$

Using a spherical harmonic addition theorem and the orthogonal properties of the spherical harmonics, we have the following integrals involving Legendre polynomials:

$$\int P_1(\hat{k} \cdot \hat{r})(\hat{\epsilon}_k \cdot \hat{r})(\hat{\epsilon}_i \cdot \hat{\epsilon}_j)\, d\Omega = \hat{k} \cdot \hat{\epsilon}_k \hat{\epsilon}_i \cdot \hat{\epsilon}_j \quad (26a)$$

$$\int P_1(\hat{k} \cdot \hat{r})(\hat{\epsilon}_i \cdot \hat{r})(\hat{\epsilon}_j \cdot \hat{r})(\hat{\epsilon}_k \cdot \hat{r})\, d\Omega = \frac{4\pi}{15}(\hat{k} \cdot \hat{\epsilon}_i \hat{\epsilon}_j \cdot \hat{\epsilon}_k + \hat{k} \cdot \hat{\epsilon}_j \hat{\epsilon}_i \cdot \hat{\epsilon}_k + \hat{k} \cdot \hat{\epsilon}_k \hat{\epsilon}_i \cdot \hat{\epsilon}_j) \quad (26b)$$

The angular integral in equation (25) can be carried out using

$$\int P_l(\hat{k} \cdot \hat{r})\, d\Omega = \begin{cases} 4\pi, & l = 0 \end{cases}$$

$0, l \quad 0 \quad \int \qquad \int \frac{4\pi}{} \hat{k} \cdot \hat{\epsilon} \;, l = 1 \qquad P_1(\hat{k} \cdot \hat{r})(\hat{\epsilon}_k \cdot \hat{r})_2 \; 3(\hat{\epsilon}_i \cdot \hat{r})(\epsilon_j \cdot \hat{r}) - (\hat{\epsilon}_i \cdot \hat{\epsilon}_j) \; d\blacktriangle$

$$= \frac{1}{15}[3\hat{k}\cdot\hat{\epsilon}_i\hat{\epsilon}_j\cdot\hat{\epsilon}_k + 3\hat{k}\cdot\hat{\epsilon}_i\hat{\epsilon}_j\cdot\hat{\epsilon}_k - 2\hat{k}\cdot\hat{\epsilon}_k\hat{\epsilon}_i\cdot\hat{\epsilon}_j] \quad (26c)$$

$$\int P_1(\hat{k}\cdot\hat{r})(\hat{\epsilon}_{j_1}\cdot\hat{r})(\hat{\epsilon}_{j_2}\cdot\hat{r})\,d\blacktriangle = 0. \quad (21)$$

We can see that the two-photon transitions are allowed to a final state with either $l = 0$ or $l = 2$.

$$\int \hat{\epsilon}\cdot\hat{r}\hat{\epsilon}\cdot\hat{r}\,d\blacktriangle = \frac{4\pi}{}\hat{\epsilon}\cdot\hat{\epsilon},$$

the transition to a final state with $l = 0$, i.e., the matrix element

corresponding to a $\Delta l = 0$ transition is

$$M^{(2)} \quad \frac{4\pi}{} \quad \int \quad r^4 R$$

$$_{j_1 j_2} = \quad _3 \quad (\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_2}) \qquad r\ f\ r\ e^{-r}\,dr \quad (22)$$
$$_{k0}(\ )\ _1(\ ) \qquad .$$

$$\int P_2(\hat{k}\cdot\hat{r})(\hat{\epsilon}\cdot\hat{r})(\hat{\epsilon}\cdot\hat{r})(\hat{\epsilon}\cdot\hat{r})\,d\blacktriangle = \frac{12\pi}{}[5\hat{k}\cdot\hat{\epsilon}\,\hat{k}\cdot\hat{\epsilon}\,\hat{k}\cdot\hat{\epsilon}$$
$$-\hat{k}\cdot\hat{\epsilon}_i\hat{\epsilon}_j\cdot\hat{\epsilon}_k - \hat{k}\cdot\hat{\epsilon}_j\hat{\epsilon}_i\cdot\hat{\epsilon}_k - \hat{k}\cdot\hat{\epsilon}_k\hat{\epsilon}_i\cdot\hat{\epsilon}_j] \quad (26d)$$

and we obtain the final form of the three-photon transition matrix element as

$$^{(3)} \quad \sqrt{\ } \int \quad * \sqrt{\ }_{\pi}^{3} \int \quad r^5$$
$$\times e^{-r\hat{k}\cdot\hat{\epsilon}}\hat{\epsilon}\cdot\hat{\epsilon}_j - i\hat{k}\cdot\hat{\epsilon}_j\hat{\epsilon}_j\cdot\hat{\epsilon}_j \quad dr R^*(r)r^5 g(r)$$
$$\times e^{-r}[\hat{k}\cdot\hat{\epsilon}_j\hat{\epsilon}_j\cdot\hat{\epsilon}_j + \hat{k}\cdot\hat{\epsilon}_j\hat{\epsilon}_j\cdot\hat{\epsilon}_j + \hat{k}\cdot\hat{\epsilon}_j\hat{\epsilon}_j\cdot\hat{\epsilon}_j]$$
$$3\sqrt{\ }_{\pi} \int \quad * \quad 5$$

$$2\ 1\ 3 \qquad 3\ 1\ 2$$

$$-i \quad _{10} \qquad dr R_{k3}(r) r \quad g_2(r)\ e^{-r}[5\hat{k}\cdot\hat{\epsilon}_{j_1}\hat{k}\cdot\hat{\epsilon}_{j_2}\hat{k}\cdot\hat{\epsilon}_{j_3}$$

$$-k\cdot\hat{\epsilon}_{j_1}\hat{\epsilon}_{j_2}\cdot\hat{\epsilon}_{j_3} - k\cdot\hat{\epsilon}_{j_2}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_3} - k\cdot\hat{\epsilon}_{j_3}\hat{\epsilon}_{j_1}\cdot\hat{\epsilon}_{j_2}], \quad (27)$$

To make the final expression compact, we define functions which depend on the direction of the emitted electrons (ϑ, φ) and the polarization of the radiation in the following way:

$$\mathcal{A}^{(0)}_{j_1 j_2} = \frac{4\pi}{3}(\hat{\epsilon}_{j_1} \cdot \hat{\epsilon}_{j_2}) \tag{28}$$

$$\mathcal{A}^{(2)}_{j_1 j_2} = 2\pi(\hat{k} \cdot \hat{\epsilon}_{j_1}\hat{k} \cdot \hat{\epsilon}_{j_2} + \hat{k} \cdot \hat{\epsilon}_{j_1}\hat{k} \cdot \hat{\epsilon}_{j_2} + \hat{k} \cdot \hat{k}\hat{\epsilon}_{j_1} \cdot \hat{\epsilon}_{j_2}) - \frac{2\pi}{15}(\hat{\epsilon}_{j_1} \cdot \hat{\epsilon}_{j_2}) \tag{29}$$

$$\mathcal{A}^{(1)}_{j_1 j_2 j_3} = \hat{k} \cdot \hat{\epsilon}_{j_1}\hat{\epsilon}_{j_2} \cdot \hat{\epsilon}_{j_3} + \hat{k} \cdot \hat{\epsilon}_{j_2}\hat{\epsilon}_{j_1} \cdot \hat{\epsilon}_{j_3} + \hat{k} \cdot \hat{\epsilon}_{j_3}\hat{\epsilon}_{j_1} \cdot \hat{\epsilon}_{j_2} \tag{30}$$

and

$$\mathcal{A}^{(3)}_{j_1 j_2 j_3} = 5(\hat{k} \cdot \hat{\epsilon}_{j_1})(\hat{k} \cdot \hat{\epsilon}_{j_2})(\hat{k} \cdot \hat{\epsilon}_{j_3}) - \mathcal{A}^{(1)}_{j_1 j_2 j_3}. \tag{31}$$

The resulting expressions can be used to study the entire angular distributions of both two- and three-photon ionization rates. Later on in section 3, we can see that these parameters determine the angular distributions and it is easy to control the asymmetry using them.

2.5. Radial integrals

We also need the following radial integrals for finding the ionization rates:

$$M^{(0)} = \sqrt{\frac{3}{8\pi}} \int_{k0}^{1} dr R^*_{k0}\, r^4 f_1(r)\, e^{-r} \tag{32}$$

$$M^{(2)} = i\sqrt{\frac{\pi}{16}} \int dr R^*_{k2}\, r^4 f_1(r)\, e^{-r} \tag{33}$$

$$M^{(1)} = \frac{i\sqrt{\pi}}{3} \int dr R^*_{k1}\, 5r^3 g_1 - 2r^5 g_1\, e^{-r} \tag{34}$$

$$M^{(3)} = \frac{i6\sqrt{\pi}}{5} \int_{k1}^{} dr R^*_{k3}\, r^5 g_2\, e^{-r}. \tag{35}$$

By taking the final state wave function as

$$R_{kl}(r) = e^{\frac{\pi\nu}{2}} \frac{\Gamma(l+1-i\nu)}{\Gamma(2l+2)} \times (2rk_f)^l e^{ik_f r} F(l+1-i\nu, 2l+2, -2ik_f r), \tag{36}$$

the radial integrals can be performed using the integrals involving confluent hypergeometric functions [8]. With these definitions we can write the transition amplitudes $M^{(2)}_{j_1 j_2}$ and $M^{(3)}_{j_1 j_2 j_3}$ as

$$M^{(2)}_{j_1 j_2} = M^{(0)} \mathcal{A}^{(0)}_{j_1 j_2} + M^{(2)} \mathcal{A}^{(2)}_{j_1 j_2}, \tag{37}$$

$$M^{(3)}_{j_1 j_2 j_3} = M^{(1)} \mathcal{A}^{(1)}_{j_1 j_2 j_3} + M^{(3)} \mathcal{A}^{(3)}_{j_1 j_2 j_3}. \tag{38}$$

We can clearly see that the radial integrals presented here (i.e., $M^{(0)}$, $M^{(1)}$, $M^{(2)}$ and $M^{(3)}$) are exactly the same functions that we obtained for the single beam [8]. All of its analytical properties and convenience has already been discussed. We have performed the angular separation for the auxiliary operators (F and G) in such a way that these radial integrals will be the same and at the same time, the expressions preserve the tensor structure. Because of this formulation, the quantum interference occurring due the presence of multiple beams can be treated easily.

3. Asymmetries in multiphoton ionization

In this section we study the asymmetries on the angular distribution and its variation and dependence on the phase and polarization of the incident beams. Here we refer to the asymmetry in reflection about the principal polarization axes. When we include two or more incident beams with a different state of polarization and phase difference, the energy conservation can be achieved by the quantum interference of various routes, so we have to sum over all the possible configurations.

3.1. Two- and three-photon ionization rates

The ionization rate for two-photon transition is given by

$$\Gamma^{(2)} \propto |\mathsf{M}^{(2)}_{fg}|^2$$

where

$$\mathsf{M}^{(2)}_{fg} = \sum_{j_1 j_2} e^{-i(\delta_i + \delta_j)} M^{(0)} \mathcal{A}^{(0)}_{j_1 j_2} + M^{(2)} \mathcal{A}^{(2)}_{j_1 j_2} \tag{39}$$

The ionization rate for three-photon transition is

$$\Gamma^{(3)} \propto |\mathsf{M}^{(3)}_{fg}|^2$$

where

$$\mathsf{M}^{(3)}_{fg} = \sum_{j_1 j_2 j_3} e^{-i(\delta_{j_1} + \delta_{j_2} + \delta_{j_3})} M^{(1)} \mathcal{A}^{(1)}_{j_1 j_2 j_3} + M^{(3)} \mathcal{A}^{(3)}_{j_1 j_2 j_3} \tag{40}$$

from 1 to N_b, where N_b is the number of incident beams from which the photons are simultaneously absorbed. An important point to be noted is that, here j_1, j_2 and j_3 goes

3.2. Polarization dependence on three-photon ionization

In order to show the analytical simplicity, we have carried out a detailed analysis of the polarization dependence on the transition matrix elements and presented it in this section.

We label the beams by the subscripts; for example, $\hat{\epsilon}_j$ corresponds to the polarization vector of the jth beam and in general, there can be any number of beams. The polarization vectors are normalized such that $\epsilon^*_j \cdot \epsilon_j = 1$. For simplicity we consider parallel beams along the z direction, so that the polarization is in the $x-y$ plane. Thus, for elliptical polarization we have

$$\hat{\epsilon}_j = \cos(\zeta_j/2)\hat{e}_x + i\sin(\zeta_j/2)\hat{e}_y$$

here $e_x(e_y)$ represents the unit polarization vector along the direction $x(y)$ axis. The ellipticity angle ζ_j takes the values $-\pi/2 \le \zeta \le \pi/2$. The value $\zeta = 0$ corresponds to linear polarization and $\zeta = \pm\pi/2$ corresponds to circular polarization. It is very clear from the above expressions for the ionization rate that the polarization dependence can be well studied by using the following functions: $\mathcal{A}^{(0)}_{j_1 j_2}$, $\mathcal{A}^{(2)}_{j_1 j_2}$, $\mathcal{A}^{(1)}_{j_1 j_2 j_3}$ and $\mathcal{A}^{(3)}_{j_1 j_2 j_3}$.

We will now consider three-photon transition matrix elements for various situations with a different number of incident beams. In this section M refers to third-order transition amplitude $\mathsf{M}^{(3)}_{fg}$.

Single beam. Now all three photons are taken from a single incident beam. For a linearly polarized light, i.e., $\zeta = 0$ we have

$$\mathrm{M} = A_1 \cos\phi + A_3 \cos^3\phi$$

where, $A_1 = 3(M^{(1)} - M^{(3)})$, $A_3 = 5M^{(3)}$. Similarly for a right circular light we have

$$\mathrm{M} = \frac{A_3}{2\sqrt{2}} e^{3i\phi}$$

so that the angular distribution for the ionization rates will be *spherically symmetric*. We can see that for left circularly polarized light a replacement of i to $-i$ can be performed.

$$\mathrm{M} = \frac{5}{2\sqrt{2}} M^{(3)} e^{-3i\phi}.$$

For an elliptical polarization of $\zeta = \pi/3$ we get

$$\mathrm{M} = \frac{A_1}{4}\sqrt{3}\cos\phi + i\sin\phi + \frac{A_3}{8}\sqrt{3}\cos\phi + i\sin\phi^3$$

where A_1 and A_3 are defined above. Similarly for arbitrary polarization states we can construct the amplitudes from ①'s given in equations (30)–(31).

Two beams. Now the atom takes three photons fromdifferent routes of the two beams. Indices j_1, j_2, j_3 in equation (40) runs from 1 to 2. For linearly polarized lights with phase difference zero, i.e., $\delta_1 = \delta_2 = 0$ we have

$$\mathrm{M} = 24(M^{(1)} - M^{(3)})\cos(\phi) + 40M^{(3)}\cos^3(\phi).$$

It can be seen that if we keep one beam linear and other circularly polarized, i.e., $\zeta_1 = 0$, $\zeta_2 = \pi/2$ we get

$$\begin{aligned}\mathrm{M} &= 3(M^{(1)} - M^{(3)})\cos\phi + 5M^{(3)}\cos^3\phi \\ &+ 3(M^{(1)} - M^{(3)})e^{i\phi} + \frac{5M^{(3)}}{2\sqrt{2}} e^{3i\phi} \\ &+ \frac{3}{\sqrt{2}} M^{(1)}(3\cos\phi + i\sin\phi) \\ &+ \frac{15}{\sqrt{2}} M^{(3)}\cos^2\phi\, e^{i\phi} + \frac{\cos\phi}{\sqrt{2}} e^{2i\phi}\end{aligned}$$

similarly if one is left and the other right circularly polarized, i.e., $\zeta_1 = -\pi/2$, $\zeta_2 = \pi/2$ we get

$$\mathrm{M} = 6\sqrt{2}M^{(1)} + \frac{3M^{(3)}}{\sqrt{2}}\cos(\phi) + \frac{5M^{(3)}}{\sqrt{2}}\cos(3\phi).$$

Again for a phase shift of $\pi/3$ to one beam i.e., $\zeta_1 = -\pi/2$, $\zeta_2 = \pi/2$, $\delta_1 = 0$, $\delta_2 = \pi/3$ we get

$$\begin{aligned}\mathrm{M} &= \frac{-5iM^{(3)}}{\sqrt{2}}\sin(3\phi) + \frac{3i}{2\sqrt{2}}(4M^{(1)} + M^{(3)}) \\ &\times(\sqrt{3}\cos(\phi) + \sin(\phi))\end{aligned}$$

Three beams. The indices j_1, j_2, j_3 run from 1 to 3.

For linearly polarized lights with relative phase differences zero, we get

$$\mathrm{M} = 27\ 3(M^{(1)} - M^{(3)})\cos(\phi) + 5\cos^3(\phi)$$

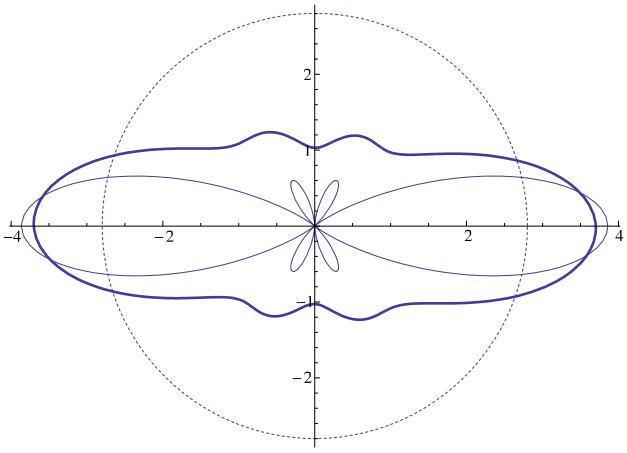

Figure 1. Polar plot of the differential scattering cross section of the three-photon ionization with a single beam. Thin line, $\zeta = 0$; thick line, $\zeta = \pi/4$; dashed line, $\zeta = \pi/2$; the cross section is normalized by a factor of 10^{-48}.

When one of the beams is circularly polarized, i.e., $\zeta_1 = 0$, $\zeta_2 = 0$, $\zeta_3 = \pi/2$ we get

$$\begin{aligned}\mathrm{M} &= (24 + 18\sqrt{2})(M^{(1)} - M^{(3)})\cos(\phi) \\ &+ 6i\sqrt{2}(M^{(1)} - M^{(3)})\sin(\phi) + 40M^{(3)}\cos^3(\phi) \\ &+ [6(M^{(1)} - M^{(3)}) + 30M^{(3)}\cos^2(\phi)]e^{i\phi} \\ &+ \frac{5}{2\sqrt{2}} M^{(3)} e^{3i\phi} + 15M^{(3)}\cos(\phi)e^{2i\phi}\end{aligned}$$

Similarly if two beams are circularly polarized ($\zeta_1 = 0$, $\zeta_2 = \pi/2$, $\zeta_3 = \pi/2$), then

$$\begin{aligned}\mathrm{M} &= 3(M^{(1)} - M^{(3)})\cos(\phi) + 5M^{(3)}\cos^3(\phi) \\ &+ [(12 + 3\sqrt{2})(M^{(1)} - M^{(3)}) + 30\sqrt{2}M^{(3)}\cos^2(\phi)]e^{i\phi} \\ &+ 60M^{(3)}\cos(\phi)e^{2i\phi} + 10\sqrt{2}M^{(3)}e^{3i\phi}\end{aligned}$$

3.2.4. Four beams. Now the atom has four beams from where it can take three photons, so the indices j_1, j_2, j_3 run from 1 to 4. For linearly polarized beams with relative phase difference zero, we have

$$\mathrm{M} = 192(M^{(1)} - M^{(3)})\cos(\phi) + 320M^{(3)}\cos^3(\phi)$$

if one beam is circularly polarized. Let $\zeta_4 = \pi/2$

$$\begin{aligned}\mathrm{M} &= 81(M^{(1)} - M^{(3)})\cos(\phi) + 135M^{(3)}\cos^3(\phi) \\ &+ 9M^{(1)}e^{i\phi} + \frac{5}{2\sqrt{2}} M^{(3)} e^{3i\phi} + \frac{9}{4}M^{(3)}(e^{i\phi} + 5e^{3i\phi}) \\ &+ 27(M^{(1)} - M^{(3)})(3\cos(\phi) + i\sin(\phi)) \\ &+ \frac{135}{\sqrt{2}} M^{(3)}\cos^2(\phi)\, e^{i\phi}.\end{aligned}$$

Similarly if two beams are circularly polarized, for example $\zeta_3 = \pi/2$, $\zeta_4 = \pi/2$

$$\begin{aligned}\mathrm{M} &= 24(M^{(1)} - M^{(3)})\cos(\phi) + 40M^{(3)}\cos^3(\phi) \\ &+ 24M^{(1)}e^{i\phi} + 10\sqrt{2}e^{3i\phi} + 60\sqrt{2}M^{(3)}\cos^2(\phi)\, e^{i\phi} \\ &+ \frac{24}{\sqrt{2}}(M^{(1)} - M^{(3)})(3\cos(\phi) + i\sin(\phi))\end{aligned}$$

$$+24M^{(3)}e^{i\phi} + 120M^{(3)}\cos(\phi)\,e^{2i\phi}.$$

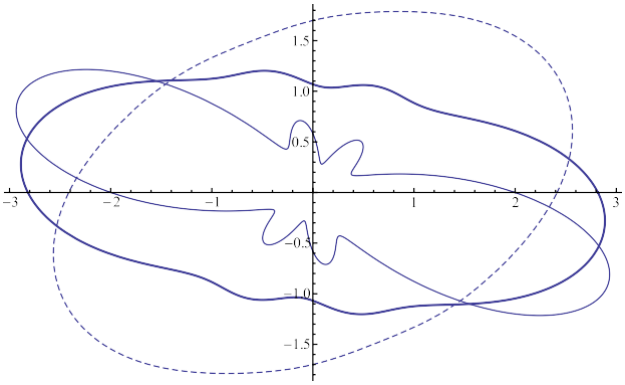

Figure 2. Polar plot of the differential scattering cross section of the three-photon ionization involving two beams. Thin line, $\zeta_1 = 0$; thick line, $\zeta_1 = \pi/4$; dashed line, $\zeta_1 = \pi/2$ and $\zeta_2 = \pi/3$, $\delta_2 = \pi/2$. Cross section is normalized by a factor of 10^{-48}.

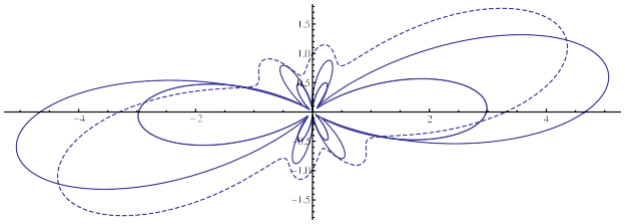

Figure 3. Polar plot of the differential scattering cross section of the three-photon ionization involving five beams. Thin line, $\zeta_1 = 0$; thick line, $\zeta_1 = -\pi/2$; dashed line, $\zeta_1 = \pi/2$. $\zeta_2 = \zeta_4 = \pi/3$, $\zeta_5 = 0$. Phase of the beams: $\delta_1 = \delta_4 = \delta_5 = 0$, $\delta_2 = \delta_3 = \pi/2$. Cross sections are normalized by 10^{-45}.

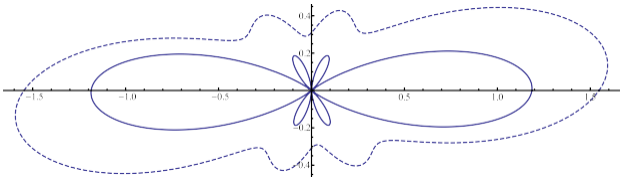

Figure 4. Differential scattering cross section of the three-photon ionization involving three beams $\zeta_2 = \pi/3$, $\zeta_3 = 0$ and $\delta_3 = \pi/4$, thin and thick lines correspond to $\zeta_1 = \pm\pi/4$. Cross section is normalized by a factor of 10^{-45}.

Similarly the angular distribution of the ejected electron with many beams can be derived with elementary trigonometry. Thus the angular dependence of the ejected electron for any situation involving beams with arbitrary polarization and phase can be studied easily with our formalism.

4. Results and discussions

In this section we will analyse in detail various results obtained in this paper. In addition to the analytical expressions presented in the previous section we have plotted the differential cross section per unit intensity. The angular distributions presented are in the plane of polarization, i.e., $\vartheta = \pi/2$. For various plots we have chosen $\lambda = 1600$ Å, an incident frequency which corresponds to the range where two-photon ionization is energetically possible (or in other words, above the two-photon ionization threshold). Also we can see that as the number of beams increases the amplitude of the cross section also changes, therefore we have to multiply the amplitudes shown in the figures by appropriate factors.

First we consider the simplest of all situations, i.e., when the atom is interacting with only one beam, the question of asymmetry does not arise here. It is clearly shown in figure 1 that the distribution is symmetric with respect to both the polarization axes. As we have discussed in section 3.2.1 it is clear from the analytical expression that, for the right circularly polarized light the distribution is spherically symmetric.

In figure 2 we have considered two beams, The second beam is right circularly polarized, i.e., $\zeta_2 = \pi/3$ and polarization of the first beam is varied. A phase difference of $\delta_2 = \pi/2$ is given to the second beam to introduce the asymmetry. Similarly in figure 4 we have considered three beams, polarization of the first beam is varied and all other parameters kept constant. Similarly in figures 3 and 4 we have considered three and five beams respectively. For the case of figure 3, the polarization of the first beam is varied and all other parameters kept constant. And in figure 4 we can clearly observe the asymmetry due to change in different parameters.

In order to show the freedom of choosing an arbitrary polarization state to the incident beams we have taken three beams and the angular distribution is given in figure 5. The polarization state of the second beam is fixed ($\zeta_2 = \pi/3$)

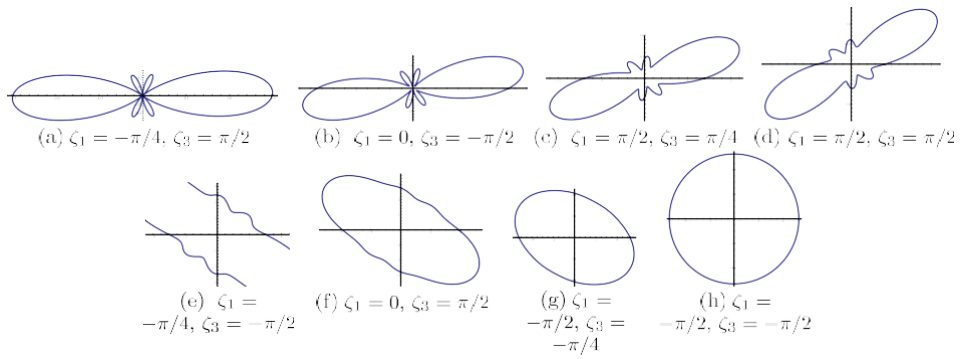

Figure 5. Polar plots of the differential scattering cross section of the three-photon ionization involving three beams showing asymmetry. Cross section is normalized by a factor of 10^{-46}. Phase of the beams: $\delta_1 = 0$, $\delta_2 = \pi/3$, $\delta_3 = \pi/2$.

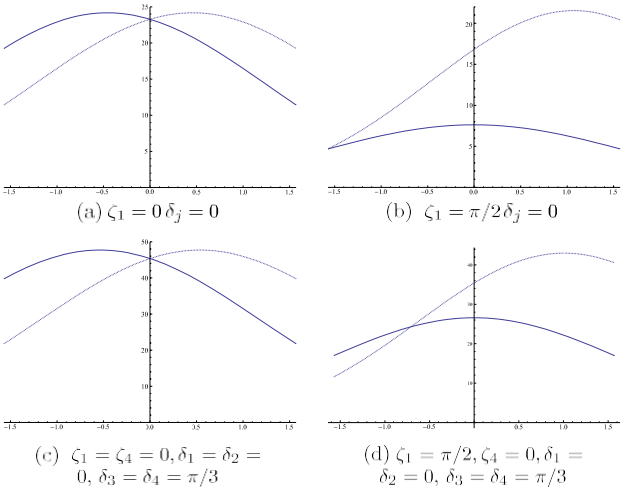

Figure 6. The differential scattering cross section is plotted against ζ_3 for four incident photons. Dotted/continuos line corresponds to right/left circular polarization of the second beam (i.e., $\zeta_2 = \pm\pi/2$).

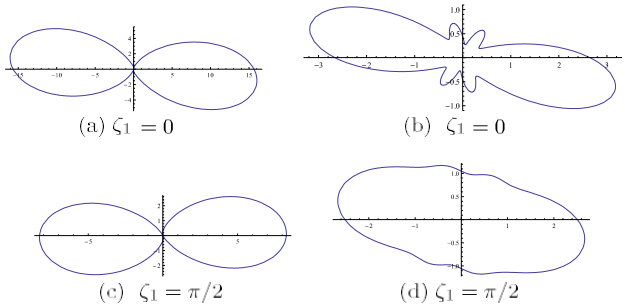

Figure 7. Polar plot of the differential scattering cross section of the three-photon ionization showing the dependence of incident photon frequency. Here we have four incident beams with polarization states: $\zeta_2 = 0$, $\zeta_3 = \pi/2$, $\zeta_4 = \pi/3$. Phase of the beams: $\delta_1 = \delta_2 = 0$, $\delta_3 = \pi/2$, $\delta_4 = 0$. For (a) and (c) λ 600 Å, cross sections are normalized by 10^{-49}. For (b) and (d) λ =1600 Å, cross sections are normalized by 10^{-45}.

and polarization of the first and third beams is varied. In this case, the amplitude is normalized by a factor of 10^{-46}. Dependence of polarization is studied considering the four beams in figure 6, where $\zeta_4 = \pi/3$ is linearly polarized and $\zeta_3 = \pi/3$ is varied for different values of ζ_1. We can clearly see how the amplitude varies for both right and left circularly polarized lights.

In order to study the dependence of frequency we have considered two frequencies from two ranges, corresponding to above one-photon (λ = 600 Å) and to above two-photon (λ = 1600 Å) ionization thresholds. It is already shown that these radial closed form expressions can be used for photons with any incident frequency. The variation is presented in figure 7. As expected, we can see the difference in their amplitudes and there is a huge variation of the angular distribution. It is worthwhile to mention that here we have considered the system absorbing photons simultaneously from four different beams and the evaluation is easy in the present formalism.

It has been shown that, our formalism can be used to study ATIs effectively [8]. In such situations we have to analytically continue the expressions in the complex λ plane, we have used this property in various plots.

5. Conclusion

We obtained analytical expressions for two- and three-photon ionization rates as a function of incident frequency, intensity, phase difference and polarization state of the absorbed radiation. Analytical expressions showing the dependence of the polar angles on the transition amplitude are presented explicitly and finally numerical evaluation is carried out for many beams with arbitrary polarizations. Analytical expressions are presented as a sum of products of radial and angular parts preserving the tensor nature. In order to demonstrate the elegance of the analysis presented in this paper, we have derived analytical expressions showing the polarization dependence. Finally these expressions presented in the current paper provide a new possibility to explore the theoretical understanding of the experimentally observed angular distributions of ejected electrons from multiphoton ionization of hydrogen-like atoms.

Acknowledgments

We are grateful to INSA-NAST bilateral exchange program for the funding to pursue this research work at Cochin University of Science and Technology (CUSAT), Kerala, India (April–Oct, 2010) and awarding grants for research at UGC, Nepal.

References

[1] Seipt D and Kampfer B 2013 *Phys. Rev.* A **88** 012127
[2] Matula O *et al* 2013 *J. Phys. B: At. Mol. Opt. Phys.* **46** 205002
[3] Bai L *et al* 2006 *Phys. Rev. Lett.* **97** 193002
[4] Muller H G *et al* 1986 *J. Phys. B: At. Mol. Phys.* **19** L733
[5] L'Huillier A *et al* 1989 *J. Opt. Soc. Am.* B **6** 1790
[6] Wang P J and Fang Y 2008 *Chin. Phys.* B **17** 3668
[7] Fifirig M and Stroe M 2002 *Laser Phys.* **12** 963–70
[8] Radhakrishnan R and Ramesh Babu T 2004 *Phys. Rev.* A **69** 033407
[9] Ramesh Babu T, Radhakrishnan R and Seema M 2003 *J. Phys. A: Math. Gen.* **36** 8473
[10] Karule E and Moine B 2003 *J. Phys. B: At. Mol. Opt. Phys.* **36** 1963
[11] Karule E and Gailitis A 2010 *J. Phys. B: At. Mol. Opt. Phys.* **43** 065601
[12] Dalgarno A and Lewis J T 1955 *Proc. R. Soc.* A **233** 70
[13] Schwartz C 1959 *Ann. Phys.* **2** 156

*Journal of Institute of Science and Technology, 2013, **18(1):** 144-147, © Institute of Science and Technology, T.U.*

An Alternate Approach of Multi-photon Processes by Dalgarno-Lewis Method in Prencence of Multiple Laser Beams

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ABSTRACT

The transition amplitude for the multiphoton process in presence of multiple laser beams has been evaluated analytically. The method is based on the generalization of a method by Dalgarno and Lewis. It is shown that this technique forms an independent perturbation theory and can be used to deal with both bound and continuum state problems.

Key words: multiple laser beams, multi-photon processes, H-atom, scalar function, differential equations.

INTRODUCTION

Multiphoton processes is the absorption due to multi photons, predicted by Koval (2004) theoretically in 1931 by M. Geoppert, were for a long time considered to be mainly of academic interest. This view changed when laser technology has raised the intensity higher and higher in the early 1960 (Lin *et al.* 2004). Multiphoton absorptions are described by higher order perturbation theory, which is valid when the radiation field strength is less than the atomic field strength (Thayyullathil *et al.* 1994).

Dalgarno-Lewis method provides an elegant method to obtain exact results for various orders in perturbation theory, while avoiding infinite sums which arise in each order. It consists in the solution of a system of inhomogeneous differential equations. For example in order to calculate K-photon matrix element, it is necessary to solve (K-1) differential equation (Dalgarno & Lewis, 1956). In this method, the perturbed ground state Ö□, which is assumed to be related to the ground state in the form Ö□□□ □ □Ö, where □ is the scalar function of the variables that occur in Hamiltonian, and then use of □□□□ □ ¡Ö□□¡Ö□□□¡ □ □□□¡Ö¡Ö□□□¡ □ ¡Ö□□¡Ö□□□¡

□ϱ being the perturbing Hamiltonian and Ö is the ground state wave function for the hydrogen atom. The first-order equation in perturbations theory is given as.

□□□ □ □□Ö□□□ □ □□ϱ □ □□□□Ö □ T

Setting Ö□□□ □ □Ö and defining a reduced potential by □ϱ □ □ϱ □ □□□□ □ □ϱ □ ¡Ö□□¡Ö□□□¡, then the equation becomes

□□¡□Ö □ □ħϱÖ □ T

Where, □□ □□ □□ □□□□□□ is the unperturbed Hamiltonian for the H-atom and □□□□ □ □□ is the Coulombic potential. Because □□□□ and □ commute, then we can show that the □ is the solution of inhomogeneous differential equations.

Two-Photon Processes

Consider an atomic system interaction with two laser beams (j_1 and j_2) of radiation of same frequency Z with different polarization H_{j_1} and H_{j_2}. Assume that the atom makes a transition from the initial state $|g$ to a final state $|f$ by absorbing two photons. The matrix element for two photon process is,

$$M_{fg}^{(2)} = \sum_{j_1 j_2} \frac{\langle f|H_{j_2}\cdot r|n\rangle\langle n|H_{j_1}\cdot r|g\rangle}{(Z_{ng} - Z)} \qquad (1)$$

Where, $|H_{j_1}\cdot r|$ is the perturbation part of Hamiltonian. The infinite sum runs over the complete set of states that includes both discrete and continuum states

which is very difficult to evaluate. This summation can be removed by the variation of Dalgarno-Lewis method. While calculating, we have used two dimensionless operators D_1 for two- photon and D_2 for three -photon, which enable us to perform summation over the whole spectrum exactly. These operators are defined by certain inhomogeneous differential equations which depend functionally on initial wave function of the atom. We define D_1 such as, Chang (1976),

$$(H - E_1)D_1 = [H_0, D_1] = ZD_1 \qquad (2)$$

After taking scalar product to equation (2) by bra vector and using closure relation, the equation (1) becomes, $M^{(2)}_{fg} = \langle f | (H - E_2)D_1 | g \rangle$

Now difficulties associated with the infinite summation is reduced to the problem of finding an appropriate expressions for the operators D_1.

Evaluation of D_1:

$$D_1H_0 - H_0D_1 = ZD_1$$
$$-\frac{1}{2}D_1'' - \frac{1}{r}D_1' + \frac{1}{2r^2}D_1 = ZD_1$$

After some rearrangement equation becomes

$$(H - E)D_1 = -\frac{1}{2}D_1'' - D_1' = ZD_1$$

For simplicity, we consider radiation to be linearly polarized along 'z' direction i.e.

$$H = z = r\cos\theta$$

By inspection we can see that D_1 have a radial part of function $f_1(r)$ and an angular dependence given by $P_1(\cos\theta)$, where $P_l(\cos\theta)$ Lengendre polynomial of order l.

Let us define, $D_1 = f_1(r)P_1(\cos\theta)$ *(3)*

Then, by some little bit algebra we obtained the above equation as, $-\frac{1}{2}f_1'' - \frac{f_1'}{r} + (Z - \frac{1}{r^2})f_1 = \varepsilon f_1$

Here, f_1 depends on r only, we now introduce $g(r,Z)$ such as

$$f_1 = rg(r,Z) \qquad (4)$$

We thus obtained the following differential equation for the unknown radial function as

$$xg'' + (4 - 2x)g' + (2Z - 2)g = 0$$

To solve this equation it is advantageous to make the substitution

$$g = e^{(t-1)x}u(x,Z)$$

Where, $t = \sqrt{1 - \varepsilon}$, Now taking derivatives on g and by substitutions we get

$$u'' + \frac{(4 - 2xt)}{x}u' - \frac{(4t - 2)}{x}u = 0$$

This equation is non homogenous differential equation of second order of the form.

$$u'' + P(x)u' + Q(x)u = R(x)$$

Where, $P(x) = \frac{(4 - 2xt)}{x}$, $Q(x) = -\frac{(4t - 2)}{x}$ and $R(x) = 0$

The general solution has the form, $u(x,Z) = C_1u_1(x) + C_2u_2(x)$, where C's are constants, Now from the method of variation parameters changing the constants into two unknown functions $v_1(x)$ and $v_2(x)$ such as, $u = v_1u_1 + v_2u_2$

The equation after rearrangement becomes,

$$v_1(u_1'' + Pu_1' + Qu_1) + v_2(u_2'' + Pu_2' + Qu_2)$$
$$+ v_1'u_1' + v_2'u_2' = R(x)$$

Thus the solutions u_1 and u_2 in determinant form is expressed as

$$W = \begin{vmatrix} u_1 & u_2 \\ u_1' & u_2' \end{vmatrix}$$ which is known as Wronskian

Hence the required solution is

$$u(x,Z) = u = \int_0^x \frac{u_2(x')}{W(u_1,u_2)}e^{(t-1)x}dx' + u_2\int_0^x \frac{u_1(x')}{W(u_1,u_2)}e^{(t-1)x}dx'$$
$$+ C_1u_1 + C_2u_2$$

Here the two functions u_1 and u_2 are the fundamental solution of the homogenous equations. The two constants of C's are determined by the conditions of finiteness. Now the two independent solutions of the homogeneous equation, which is called the Kummer's

equations are the regular solution (Magnus *et al.* 1954).

$$xu'' + (4 - 2xt)u' - (4t - 2)u = 0$$

Comparing this to Kummer's equations

$$a = 2 - \frac{1}{t}, \; b = 4 \text{ and } z = 2tx$$

Thus the required solutions are

$$u_1(x) = u_1 = M(a,b;z) = {}_1F_1(a,b;z) = 1 + \frac{(2 - 1/t)}{2}tx$$

$$u_2(x) = u_2 = U(a,b;z) = \frac{(1 - 1/t)}{(2 - 1/t)(-3)2^3 t^3 x^3} M(2 - 1/t - 4 + 1, 2 - 4; 2tx)$$

Here, $M(2 - 1/t - 4 + 1, 2 - 4; 2tx) = 1 - (1 - 1/t)tx$

Where, $M(a,b;z)$ and $U(a,b;z)$ are the confluent hypergeometric functions of first order type with regular singular point at $x = 0$ and irregular singular point at infinity respectively.

$$u_1(0) = 1$$

$$u_2(0) = \frac{-(1 - 1/t)}{8t^3 x^3 (2 - 1/t)(-3)}$$

For calculation of Wronskian (W)

$$W = \frac{1}{4x} - \frac{3}{4t^3(2 - 1/t)} - \frac{3}{4t^3(2 - 1/t)}x,$$

For, $x = 0$,

$$W = -\frac{3}{4t^3(2 - 1/t)}$$

We therefore have,

$$v_1 = -\int_0^x \frac{u_2 R(x)}{W(u_1,u_2)}dx - \int_0^x \frac{{}_1F_1(2 - 1/2, 4; 2tx)e^{(t-1)x}}{W(u_1,u_2)}dx$$

$$v_2 = -\int_0^x \frac{U(2 - 1/t, 4; 2tx)e^{(t-1)x}}{W(u_1,u_2)}dx$$

Hence

$$u(x,Z) = v_1u_1 + v_2u_2 \quad x$$
$$u(0,Z) = \frac{4}{t^3(2 - 1/t)} - \frac{3}{3} \quad {}_1F_1(2 - 1/t, 4; x') - e^{(t-1)x} \quad 4 \quad o \quad U(2 \quad (x') \quad dx'$$

Hence

$$g(x,Z) = e^{-(t-1)x}u(x,Z)$$

Thus,

$$f_1(r) = rg(x,Z)$$

And $D_1 = f_1(r)P_1(\cos\theta)$

Dalgarno operator for two photon ionization is

$$D_1 = \frac{4t^3(2 - 1/t)}{3}\left[F(2 - 1/t, 4; 2tx) \int_0^x U(2 \quad 1/t, 4; 2tx')e^{(t-1)x'} \quad 4 \quad (x') \, dx' \right.$$
$$\left. + U(2 - 1/t, 4; 2tx) \int_0^x {}_1F_1(2 - 1/t, 4, 2tx')e^{(t-1)x'} \quad 4 \quad (x') \, dx' \right] e^{-(t-1)x}$$

Three-Photon Processes

In three photon processes, where three photons with frequency Z are simultaneously are absorbed in one event and make a transition from initial state $|g\rangle$ to final $|f\rangle$ state, allowed by three photon selection rules. We have used third-order perturbation theory for studying this effect. The three photon matrix element is

$$M_{fg}^{(3)} = \sum_{j_1 j_2 j_3} \frac{\langle f|H_{j_3}|r\rangle\langle m|H_{j_2}|r\rangle\langle n|H_{j_1}|r|g\rangle}{(Z_{ng} - Z)(Z_{mg} - 2Z)} \qquad (5)$$

Where, j's, are three laser beams of same frequency Z and different polarization H_{j_1}, H_{j_2}, H_{j_3} For three-photon absorption, we have to define one more auxiliary operator D_2 in addition to D_1.

$$(H_{j_2} - rD_1|g = (D_2H_0 - H_0D_2 - 2ZD_2)|g\rangle$$

Hence for K-photon, we can write,

$$H_j - rD_{K-1}|g = (D_KH_0 - H_0D_K - KZD_K)|g\rangle$$

Now proceeding as two photon, the operator D_1 can be used to remove one of the energy denominator, we can express the compact from of matrix element as

$$M_{fg}^{(3)} = \langle f|H_{j_3} - rD_2|g\rangle$$

RESULTS AND DISCUSSION

The unknown radial part of Dalgarno operator has been solved analytically in terms of integral representation, which only depend on frequency of the laser beams. The angular part will be different for different polarization of multiple beams, which remains to be seen. The transition amplitude associated with the matrix element $M_{fg}^{(K)}$ for two and three photon can be evaluated, which is essential for the quantum description of the interaction between

atom and photon. This method is also used as perturbation and determining energy levels of diatomic molecular ion (Bailey, 1965) as sum rule (Pyykko, 1967). It is shown that this technique forms an independent perturbation theory and can be used to deal with both bound- and continuum-state problems (Nandi *et al.* 1996).

ACKNOWLEDGEMENT

I would like to express my sincere gratitude to my supervisors Prof. Dr. J. J. Nakarmi and Prof Dr. L. N. Jha, Central Department of Physics, Tribhuvan University, Kirtipur and Prof. Dr. Ramesh Babu Thayyullathil, CUSAT, Kochi, India for their continuous supports, indispensable advices and guidance. I am also very grateful to the INSA-NAST bilateral exchange program for funding my research work at Cochin University of Science and Technology (CUSAT), Kerala, India (April-Oct, 2010) and awarding grants for research work at UGC, Nepal. Special thanks to Prof. Dr. Sitaram Byahut for his invaluable suggestion, TU.

REFERENCES

Bailey, P. B. 1965. On perturbation treatment of the one-electron diatomic molecular ion. *Proc, Phys. Soc.* **85**: 1127-1131.

Dalgarno, A. and Lewis, J. T. 1956. The equvalace of variational and perturbation calculation of small disturbances. *Proc. Phys. Soc. A* **69:** 628-630**.**

Koval, V. P. 2004. *Two- Photons ionization of atomic inner-shells*, University Kassel, Germany.

Lin, S. H. , Villaeys, A. A. and Fujimura, Y. 2004. From multiphoton to tunnel ionization (S.L. Chin). In: *Advances in Multiphoton processes and spectroscopy*, World scientific publishing, Singapore, 249p.

Magnus, W. and Oberhettinger F. 1954. The confluent hypergeometric function and its special cases. In: *Formulas and Theorems for the Functions of Mathematical Physics*, Chelsea Publishing Company, New York, 86p.

Nandi, T. K., Bera P. K. et al. 1996. The Dalgarno-Lewis method as a perturbation theory. *J. Phy. Maths. Gen*. **29**: 1101-1105.

Pyykko, P. 1967. 2^l-pole sum rule for the hydrogen atom. *Proc, Phy, Soc*. **92**: 842-844.

Thayyullathil, R. and Prasanna, K. J. 1994. Two photon transition in atomic hydrogen: an alternative approach. *Physical Rev. A, Vol 49*(**4**): 2432-2434.

Nepal Journal of Science and Technology Vol. 14, No. 2 (2013) 165-170

Perturbation Theory and Dalgarno-Lewis (DL) Method in Presence of Multiple Laser Beams

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Abstract
The evaluation of second and higher order perturbation of energy by iterative solution of Schrodinger's equation, rather than evaluation of matrix element is described.

Key words: perturbed hamiltonian, dalgarno operator

Introduction
While there are many ways to solve Schrodinger equation (SE) analytically, we cannot always obtain an exact solution. Therefore, we must move on to different approaches to obtain more precise results. For example, if the potential energies are known then we can formulate their corresponding Hamiltonians to solve Schrodinger equations very precisely. Hence no such approximations are required for the preceding case. While there are many such Hamiltonians which can be solve fairly easily, there are many more whose solutions can only be approximated numerically. We therefore have to use the widely accepted Perturbation Theory to find approximate solutions of such Hamiltonians—provided that they are similar to the ones which are fairly easy to solve.

Perturbation theory works best when the system's total energy is "perturbed" by a small additional potential energy (Messsiah 1962). The total Hamiltonian can be expressed as a sum of an unperturbed Hamiltonian ($\hat{H}_o$) and a perturbed Hamiltonian ($\hat{H}$),

$$\hat{H} = \hat{H}_o + \hat{H}'$$

The plan is to expand the system of Hamiltonian, and hence the total energy, into a sum of terms involving higher and higher powers of $\hat{H}'$, similar to a Taylor series expansion of a function around some value. Since the perturbation is small, we only have to keep the first few terms (typically two or three terms) to obtain a close approximation to the actual total energy.

We must be careful when using the perturbation theory because the perturbing potential should not change the number of bound states of the considered atoms in the system. We can also assume that the unperturbed states of the atoms in consideration form a complete set. We can then express the corrected states as linear combinations of the unperturbed states.

However, if the perturbing potential changes the Hamiltonian of the system such that the number of bound states is increased by one, this new state must have come from the unbounded region. This is a problem because the unbounded region contains a continuum of energies. So while perturbation theory is a very useful tool, it is not *always* the method of choice.

The time independent (TI) form of the theory is best suited to the problems with discrete energy spectrum. The time dependent (TD) form is useful for problems where there is a continuum of energy states; and here, the product $H't/\hbar$ must less than unity. In both the forms, the solution is obtained by expanding Eigen-values and Eigen-functions in a series of small parameters that represents the strength of perturbing terms. The TISE

$$\hat{H}\Psi = E\Psi$$

and for TDSE,

$$\hat{H}\Psi(r,t) = i\hbar\frac{\partial\Psi(r,t)}{\partial t}$$

The solution of TDSE as,

$$\Psi(r,t) = \sum_n C_n(t)\psi_n(r)e^{-\frac{i}{\hbar}E_n t}$$

Here $C_n(t)$ is the expansion coefficient which is our more interest.

From TDSE, and using initial state as ground state

$(H_0\ \psi_n = E_n\psi_n)$

Hence, writing in Dirac Notation

$$i\hbar\sum_n\frac{\partial C_n(t)}{\partial t}e^{-\frac{i}{\hbar}E_n t}|\psi_n(r)\rangle = \sum_n C_n(t)e^{-\frac{i}{\hbar}E_n t}H^1|\psi_n(r)\rangle$$

Multiplying by bra vector $\psi_m^*|$ in both sides and integrating over all the space

$$i\hbar\dot{C}_m(t) = \sum_n C_n(t)e^{-\frac{i}{\hbar}(E_n-E_m)t}H^1_{mn}$$

$$= \sum_n C_n(t)e^{-i\omega_{nm}t}H^1_{mn} \quad \ldots\ldots(1)$$

Where, $\hbar\omega_{nm} = E_n - E_m$

$h\omega_{nm}$ is known as transition energy.

Assuming the system is in Eigen-state $|\psi_n\rangle$ at t = 0, we can express the expansion coefficient for the first order perturbation as

$$i\hbar\dot{C}_m^{(1)}(t) = C_n^{(0)}e^{-i\omega_{nm}t}H^1_{mn},\ m \neq n$$

$$C_n^{(1)}(t) = (i\hbar)^{-1}\int dt e^{-i\omega_{nm}t}H^1_{mn}(t') \quad \ldots\ldots(2)$$

Thus, this equation can be directly integrated, if the perturbed Hamiltonian is known.

Hence the new wave function is known and we can calculate the behavior of the system from this new wave function.

$$|\Psi\rangle = e^{-\frac{i}{\hbar}E_n t}|\psi_n\rangle + \sum_n C_n^{(1)}(t)e^{-\frac{i}{\hbar}E_n t}|\psi_n\rangle$$

For the second order

$$C_m^{(2)}(t) = (i\hbar)^{-1}\sum_n C_n^{(1)}(t)e^{-i\omega_{nm}t}H^1_{mn} \quad \ldots\ldots(3)$$

For the higher order (S'*th*) of perturbation, the expansion coefficient becomes,

$$i\hbar C_m^{(s+1)}(t) = \sum_n C_n^{(s)}(t)e^{-i\omega_{nm}t}H^1_{mn},$$

s= 0,1,2..... order of perturbation.

Here, H^1_{mn} is the perturbed Hamiltonian in matrix form $\langle\psi_m^*(r)|H^1|\psi_n(r)\rangle$.

The equation (3) is the set of coupled differential equations for $C_n(t)$.

The matrix element $\langle\psi_m^*(r)|H^1|\psi_n(r)\rangle$ is non zero, and thus we will use the selection rule by which all the matrix elements for given perturbation vanish, except for a few "select" ones characterized by special changes in the quantum numbers.

We now consider a hydrogen atom, and then expose this system to an electric field treated classically in dipole approximation. The electric field alters the Hamiltonian of the initial system, which in turn alters the corresponding Eigen-energies and Eigen-states. Perturbation theory allows us to find approximate solutions to the perturbed Eigen-value problems by beginning with the known exact solutions of the unperturbed problems and then making small corrections to be based on the new perturbing potential.

Then, the perturbation part of the Hamiltonian is

$$H^1 = -\sum_j E_{0j}e^{-i(\omega t+\delta_j)}\hat{\varepsilon}_j\cdot r \quad \ldots\ldots(4)$$

Where, ω is the angular frequency of the external radiation and δ_j the phase difference between different beams and $\hat{\varepsilon}_j$ represent polarization vector of the different beams are propagating along the same direction.

Now, we have evaluated the transition between the continuum states of two Eigen states $|g\rangle$ as initial state for (t=0) and $|f\rangle$ as final states at later time t.

Let,, $\hbar\omega_0 = E_f - E_g$,

where, is ω_0 the frequency of the transition between two states.

$\hbar\omega_0 \rangle 0$ means atom has absorbsed the photon,

$\hbar\omega_0 \langle 0$ means atom has emitted the photon.

Plugging equation (4) into equation (1) after performing t integral (Shrestha *et al.* 2011)

$$C_f^{(1)}(t)$$

$$= E_0 \langle f|\hat{\varepsilon}_j \cdot r|g\rangle \left[\frac{e^{i(\omega_0+\omega)t}-1}{(\omega_0+\omega)} + \frac{e^{i(\omega_0-\omega)t}-1}{(\omega_0-\omega)}\right]$$

Let the external frequency ω, be nearly equal to the transition frequency ω_0. Then the second term in the above equation becomes arbitrarily large with respect to the first. Still for the fixed time t and H (t), since we cannot have $C_f(t) \rangle 1$. We choose sufficiently small amount of time such that our perturbation expansion works even when is almost equal to. Thus, we can neglect the first term giving

$$C_{fg}^{(1)}(t) = E_0 \langle f|\hat{\varepsilon}_j \cdot r|g\rangle \left[\frac{e^{i(\omega_{fg}-\omega)t}-1}{(\omega_0-\omega)}\right]$$

The probability of atom at time t is

$$P_f = \left|C_f^{(1)}(t)\right|^2$$

$$= E_0^2 \left|\langle f|\hat{\varepsilon}_j \cdot r|g\rangle\right| \left[\frac{e^{i(\omega_{fg}-\omega)t}-1}{(\omega_0-\omega)}\right]^2$$

Using the identity operator,

$$|e^{i\theta}-1|^2 = 2(1-\cos\theta) = 4\sin^2\theta/2$$

Hence, the probability at time t is,

$$P_f(t) = E_0^2 \left|\langle f|\hat{\varepsilon}_j \cdot r|g\rangle\right|^2 \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$

The transition rate

$$\Gamma^{(1)}{}_f = E_0^2 \left|\langle f|\hat{\varepsilon}_j \cdot r|g\rangle\right|^2 \delta(\omega_0-\omega)$$

The first order correction gives the ordinary, linear optical properties of material.

For second order correction

$$C_{fn}^{(2)}(t) = \int_0^t dt \sum_n C_n^{(1)}(t) e^{-i(\omega_{fg})t} H^1_{fn}$$

$$= \int_0^t dt E_0 \langle n|\hat{\varepsilon}_k \cdot r|g\rangle \times \left[\frac{e^{i(\omega_{ng}-\omega)t}-1}{(\omega_0-\omega)}\right] e^{-i(\omega_{fg})t} H^1_{fn}$$

Here, $\hbar\omega_0 = E_n - E_g = \hbar\omega_{ng}$

$$C_f^{(2)}(t) = E_0^2 \frac{1}{(\omega_0-\omega)} \langle f|\hat{\varepsilon}_j \cdot r|n\rangle\langle n|\hat{\varepsilon}_k \cdot r|g\rangle \times \left[\frac{e^{i(\omega_{fg}-2\omega)t}-1}{(\omega_{fn}-\omega)} - \frac{e^{i(\omega_{fn}-\omega)t}-1}{(\omega_{fn}-\omega)}\right]$$

The probability is

$$P^{(2)}_f = \left| E_0^2 \frac{1}{(\omega_0-\omega)} \langle f|\hat{\varepsilon}_j \cdot r|n\rangle\langle n|\hat{\varepsilon}_k \cdot r|g\rangle \times \left[\frac{e^{i(\omega_{fg}-2\omega)t}-1}{(\omega_{fg}-2\omega)} - \frac{e^{i(\omega_{fn}-\omega)t}-1}{(\omega_{fn}-\omega)}\right]\right|^2$$

Similarly for three photon, after performing integration,

$$C_f^{(3)}(t)$$

$$= E_0^3 \langle f|\hat{\varepsilon}_j \cdot r|m\rangle\langle m|\hat{\varepsilon}_k \cdot r|n\rangle\langle n|\hat{\varepsilon}_l \cdot r|g\rangle \times \left[\frac{e^{i(\omega_{fg}-\omega-2\omega-3\omega)t}-1}{(\omega_{mg}-\omega)(\omega_{ng}-2\omega)(\omega_{fg}-3\omega)} - \frac{e^{i(\omega_{fm}-\omega)t}-1}{(\omega_{ng}-\omega)(\omega_{ng}-2\omega)(\omega_{fm}-\omega)}\right]$$

The probability of atom in $|f\rangle$ at time t is

$$P_f^{(3)}(t) \propto \left| E_j^3 \sum_m \sum_n \frac{\langle f|\hat{\varepsilon}_j \cdot r|m\rangle\langle m|\hat{\varepsilon}_k \cdot r|n\rangle\langle n|\hat{\varepsilon}_l \cdot r|g\rangle}{(\omega_{mg} - \omega)(\omega_{ng} - 2\omega)} \times \left[\frac{e^{i(\omega_{fg}-3\omega)t} - 1}{(\omega_{fg} - 3\omega)}\right] \right|^2$$

The transition rate for multiple beams j, k and l, can be expressed as

For first order correction

$$\Gamma^{(1)}_f \propto E_{0j}^2 \left|\langle f|\hat{\varepsilon}_j \cdot r|g\rangle\right|^2$$

For two and three photons

$$\Gamma^{(2)}_f \propto E_{0j}^2 E_{0k}^2 \left|\sum_m \langle f|\hat{\varepsilon}_k \cdot r|n\rangle\langle n|\hat{\varepsilon}_j \cdot r|g\rangle\left[\frac{1}{(\omega_{ng} - \omega)}\right]\right|^2$$

$$\Gamma^{(3)}_f \propto E_{0j}^2 E_{0k}^2 E_{0l}^2 \left|\sum_m \sum_n \langle f|\hat{\varepsilon}_j \cdot r|m\rangle\langle m|\hat{\varepsilon}_k \cdot r|n\rangle \times \langle n|\hat{\varepsilon}_l \cdot r|g\rangle\left[\frac{1}{(\omega_{ng} - \omega)(\omega_{ng} - 2\omega)}\right]\right|^2$$

The calculation of ionization rate has been reducing to a matter of evaluating matrix element.

Let us denote the matrix element of the form by M as

For first order correction

$$M^{(1)}_f \propto \langle f|\hat{\varepsilon}_j \cdot r|g\rangle$$

For second order correction

$$M^{(2)}_f \propto \left[\frac{\sum_m \langle f|\hat{\varepsilon}_k \cdot r|n\rangle\langle n|\hat{\varepsilon}_j \cdot r|g\rangle}{(\omega_{ng} - \omega)}\right] \quad \ldots\ldots\ldots(5)$$

For third order correction

$$M^{(3)}_f \propto \left[\frac{\sum_m \sum_n \langle f|\hat{\varepsilon}_j \cdot r|m\rangle\langle m|\hat{\varepsilon}_k \cdot r|n\rangle\langle n|\hat{\varepsilon}_l \cdot r|g\rangle}{(\omega_{ng} - \omega)(\omega_{ng} - 2\omega)}\right] \quad \ldots(6)$$

Dalgarno and Lewis (Dalgarno *et al*. 1956) developed a simple and practical method to solve perturbation equations; the method was later adopted by many authors to tackle a variety of problems. This method (Francisco 1952) consists of writing the perturbation correction to the Eigen function as

$$\Psi_p(r) = F_p(r)\Psi_0(r), \quad p = 0, 1, 2\ldots\ldots$$

And solving the resulting equations; the Dalgarno operator $F_p(r)$ thus becomes,

$$-\frac{1}{2}\nabla F_p - \frac{1}{\Psi_0}\nabla\Psi_0 \cdot \nabla F_p + V F_{p-1} - \sum_{k=1}^{p} E_k F_{p-k} = 0$$

In this equation, ∇ is the gradient vector operator and the dot stand for the standard scalar product. These equations are easier to solve than the original differential equation for the perturbation corrections. In many cases the correction factors F_p are simple polynomial function of the coordinates. For $F_0 = 1$ is suitable solution to the equation of order zero, and E_0 does not appear in the perturbation equation. The Dalgarno–Lewis method (Nandi *et al*. 1996) allows us to calculate the perturbation series to higher orders for non degenerate states. The method is based on conversion of Eigen value problem into series of inhomogeneous differential equation. These equations determine successively the correction to the Eigen function and the energy correction are obtained by simple expectation value (Schiff 1968).

In our calculations as shown in equation (5) and equation (6), we have assumed two auxiliary dimensionless operators for two photons as F_j, and G_{jk} for three photons, where j, k are the number of beams having same frequency, but different polarization vectors propagating along the same direction.

Equation (5) is evaluated by defining F_j such as

$$(\hat{\varepsilon}_j \cdot \vec{r})|g\rangle = [F_j H_0 - H_0 F_j + \omega F_j]|g\rangle$$
$$(\hat{\varepsilon}_j \cdot \vec{r})\psi = [F_j H_0 - H_0 F_j + \omega F_j]\psi$$

Now, the equation (5) becomes,

$$M_{fi}^{(2)} = \left\langle f \left| (\hat{\varepsilon}_i \cdot \vec{r}) F_i \right| g \right\rangle$$

Here, $H_0 = -\frac{1}{2}\nabla^2 - \frac{1}{r}$

Thus, $(\hat{\varepsilon}_i \cdot \vec{r})\psi$

$$= \frac{\nabla^2 F_i}{2}\psi + \nabla F_i \cdot \nabla\psi + \omega F_i \psi \quad \ldots\ldots(7)$$

Similarly for three photon ionization, we define G_{fi} such as,

$$(\hat{\varepsilon}_i \cdot \vec{r}) F_i \left| g \right\rangle = \left[G_{fi} H_0 - H_0 G_{fi} + \omega G_{fi} \right] \left| g \right\rangle$$

Then equation (6) becomes,

$$M_{fi}^{(3)} = \left\langle f \left| (\hat{\varepsilon}_i \cdot \vec{r}) G_{fi} \right| g \right\rangle$$

$$(\hat{\varepsilon}_i \cdot \vec{r}) F_i \psi$$

$$= \frac{\nabla^2 G_{fi}}{2}\psi + \nabla G_{fi} \cdot \nabla\psi + \omega G_{fi}\psi \quad \ldots\ldots(8)$$

In general for the higher order, this can be done by defining a set of $n-1$ operators F_n with $n = 1, 2, \cdots n-1$ such as (Delone 1999).

$$(\hat{\varepsilon}_i \cdot \vec{r}) F_{n-1} \left| g \right\rangle = \left(F_n H_0 - H_0 F_n + n\omega F_n \right) \left| g \right\rangle$$

In hydrogen atom, the electron potential is the well known spherically symmetric coulomb potential, owing to the spherically symmetric; it is very convenient to solve TDSE in spherical coordinates (Griffiths 1999).

Let $F_i = (\hat{\varepsilon}_i \cdot \vec{r}) f(\omega, r)$

Where, $(\hat{\varepsilon}_i \cdot \vec{r})$ is the angular part given by Legendre polynomial and unknown $f(\omega, r)$ simply as f is the radial part.

After a few manipulations the differential equation for two photon ionization takes the form,

$$rf'' + (4 - 2r) f' + (2\omega r - 2) f = 2r$$

Similarly for three photon, after assuming

$$G_{ijk} = \left[\frac{3}{2} \hat{\varepsilon}_i \cdot r' \hat{\varepsilon}_k \cdot r' - \frac{1}{2} \hat{\varepsilon}_i \cdot \hat{\varepsilon}_k r'^2 \right] g_2 + \hat{\varepsilon}_i \cdot \hat{\varepsilon}_k g_0$$

Then after some algebra, we can have the simpl differential equation as

$$rg_0'' + (2 - 2r) g_0' + 4\omega r = \frac{2}{3} r^3 f$$

$$rg_2'' + (6 - 2r) g_2' + (4\omega r - 4) g = \frac{4}{3} rf$$

Here we have used the method of Laplace transfor (Ince 1956) for the solution of this differential equatic (Radhakrishanan *et al.* 2004).

$$\Phi(p, q, \lambda, t, r) = \int_0^\infty ds e^{-rs} K(p, q, \lambda, s)$$

$$K(p, q, \lambda, s) = \left(\frac{1 - \lambda}{1 + \lambda} \right)^{p/2} (s + \lambda)^{-(p+q)/2} (s - \lambda)^{(q-p)/2}$$

Finally, we can have $f(r)$, as

$$f(r) = \frac{1}{\omega} - \frac{1}{2\omega^2} \Phi(1, 1, \lambda_1, 1, r)$$

$$g_0(r) = \frac{1}{3\omega^2} - \frac{1}{3\omega^4} \Phi(1, 1, \lambda_1, 1, r) + \frac{2}{3\omega^4} \int_0^\infty dt \frac{K(1, 1, \lambda_1, 1, t) t}{K(3, 3, \lambda_2, t)} \Phi(2, 2, \lambda_2, t, r)$$

where $\lambda_1 = \sqrt{(1 - 2\omega)}$ and $\lambda_2 = \sqrt{(1 - 4\omega)}$

$$g_2(r) = \frac{2}{3\omega^2} \left[\frac{r^2}{4} + \frac{1}{4\omega^2}(1 - 2\lambda_1) - \frac{3}{8\omega} \right] - \frac{1}{3\lambda_2 \omega^2} \Phi(0, 0, \lambda_2, t, r) - \frac{1}{6\omega^4} \left[r^2 + \frac{\lambda_1}{\omega} r - \frac{1}{\omega}\left(1 + \frac{1}{\lambda_1}\right) \right] \Phi(1, 1, \lambda_1, 1, r) - \frac{1}{3\omega} \left(1 + \frac{1}{\lambda_1} \right) \int_0^\infty dt \frac{K(1, 1, \lambda_1, 1, t) t}{K(1, 1, \lambda_2, t)} \times \left[\frac{1 - 2\omega}{\omega(1 + \lambda_1)} - \frac{t}{\omega} - \frac{2}{t + \lambda_1} + \frac{2}{(t + \lambda_1)^2} \right] \times \Phi(0, 0, \lambda_2, t, r)$$

Results and Discussion

The idea of DL method is to define an auxiliary operator such that the evaluation of intermediate sum is not

needed. Now, the difficulties associated with the infinite summation is reduced to the problem of finding an appropriate expressions for the operators F_j and G_{jk}.

We have explored the technique of evaluating higher-order perturbation theory for the multiple beams of same frequency but different polarization from the point of view of Schrodinger's differential equation. The method seems very well adaptable for the problems such as that of the hydrogen atom (Charles 1959).

Acknowledgements

I would like to thank my supervisors Prof. Dr. J. J. Nakarmi and Prof. Dr. L. N. Jha, for their guidance and encouragement. I express a sincere gratitude to Prof. Ramesh Babu Thauullathil for his fruitful remarks on multiphoton ionization by multiple laser beams, Cochin University of Science and Technology, CUSAT, Kerala, and gratefully acknowledge INSA-NAST bilateral exchange program for funding research at CUSAT, Kerala, India. This work has been supported in part by University Grant Commission, Sanothimi, Bhaktapur.

References

Charles, S. 1959. Calculation in Schrodinger perturbation theory. *Annals of Physics* **2:** 159-169.

Dalgarno, A. and J.T. Lewis. 1956 . An equivalence of variational and perturbation calculations of small disturbances. *Proc. Roy. Soc. A* **69:** 628-630.

Delone N. B. and V.P. Krainov. 1999. Multiple ionization of atom. In: *Multiphoton Processes in Atoms.* Springer- Verlag , Berlin, Heidelberg, pp 190-221.

Francisco, M. F. 1952. Perturbation theory in coordinate representation. In: *Introduction to Perturbation Theory*. CRC Press, Boca Ratan, 13-23.

Griffiths, D. J. 1999. Vector analysis. In: *Introduction to Electrodynamics.* 3rd edition, Printice Hall of place country-region India Private Lmt, 1-10.

Ince, E. L. 1926. The solution of linear differential equation by definite integral. In: *Ordinary Differential Equations*. New York, Dover Publications, 187-203pp.

Messsiah, A. 1962. Stationary perturbation theory. In: *Quantum Mechanics Volume II*.North Holland Publishing Company, Amsterdam, pp 685-739.

Nandi, T.K. and P.K. Bera. 1996. The Dalgarno-Lewis method as small perturbation theory. *J. Phys. A. Maths. Gen*. **29:** 1101-1105.

Radhakrishanan R. and R.B. Thayyullathil 2004. Nonresonant multiphoton ionization in atomic hydrogen. *Phy. Rev. A.* **69:** 033407(1)-033407(5).

Schhiff, L.I. 1968. An alternative treatment of the perturbation series. In: *Quantum Mechanics.* 3rd edition, Mc Graw Hill Book Company, pp 263-267.

Shrestha, N. and J.J. Nakarmi. 2011. One, two and three photon absorption in atomic hydrogen. *Nepal Journal of Science and Technology*, **12:** 324-329.

Nepal Journal of Science and Technology 12 (2011) 324-329

One, Two and Three Photon Absorption in Atomic Hydrogen

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Abstract
Non relativistic, semi-classical in dipole approximation, based on time dependent Schrodinger equation under the framework of perturbation theory, three different absorption processes in hydrogen atom are studied and calculated transition matrix element from an initial state to final state.

Key words: multiphoton ionization, perturbation and ionization rate

Introduction
Multiphoton ionization results from the simultaneous absorption of several photons, predicted(Koval 2004) theoretically in 1931 by M. Geoppert, were for a long time considered to be mainly of academic interest. This view changed when it was shown (Delone, Mainfray, Charles) that a two-photon absorption process could, because of a quadratic dependence of excitation on intensity, produce a spatially confined excitation useful for three-dimensional data storage and imaging. Two-photon absorption has received considerable attention recently because of the development of highly efficient two-photon-sensitive materials, leading to numerous technological applications. These successes have created interest in exploring applications based on three-photon excitations (3PA)(Joseph 2008). 3PA works when three photons (identical or different frequencies) are simultaneously absorbed in one event and make a transition from initial state $|g\rangle$ to and excited state or final state $|f\rangle$ allowed by three photon selection rules (Thayyullathil *et al.* 2003). The energy difference between the involved lower and upper states of the atom is equal to the sum of the energies of the three photons. The three photon absorption most commonly occurs in longer wavelengths (near infrared), some scientists see hope for it in terms of biomedical and photonic applications (Joseph 2008).

Multiphoton absorptions are described by higher order perturbation theory, which is valid when the radiation field strength is less than the atomic field strength. If a quantum system is represented by the time dependent Hamiltonian H, then from TDSE (Peter *et al.* 2005).

$$H|\Psi(t)\rangle = E|\Psi(t)\rangle \qquad (1)$$

Here H is the total Hamiltonian, which is the sum of unperturbed Hamiltonian H_0 and interaction Hamiltonian $H'(t)$ such as;
$H = H_0 + H'(t)$
$H'(t)$ has the form

$$H'(t) = H'(t) \ if \ \ 0 \le t \le \tau$$
$$= 0 \ if, t \le 0 \ and, t \ge \tau \qquad (2)$$

Assuming the solution of this equation to be linear combination of basis set $\{|n\rangle\}$, which are the engienstates of the unperturbed Hamiltonian,

$$|\Psi(t)\rangle = \sum_n \ C_n(t)\varphi_n(r)e^{-iE_nt/\hbar} \qquad (3)$$

Unperturbed Hamiltonian H_0 has eigenvalues as:

$$H_0|n\rangle = E_n|n\rangle \qquad (4)$$

The quantities to be determined here are the expansion coefficient $C_n(t)$ and these are our direct physical interest. $\varphi_n(r)$ is the eigenfunction of the Hamiltonian. The square of this expansion coefficient is the probability, and divided by time is the transition rate (Γ_{fg}).

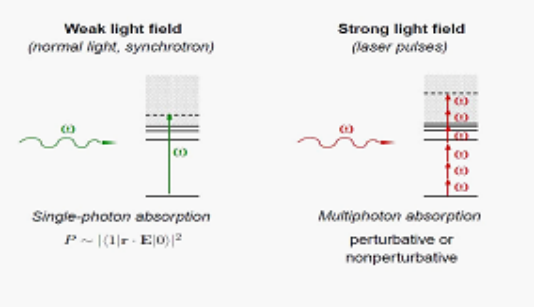

Fig. 1. Laser - Matter Interaction

$|C_n(t)|^2$, with which is the system is described by $|\Psi(t)\rangle$ will be found in the energy eigenstate $|n\rangle$ at time t. Using atomic units as $\hbar = m = e = a_0 = 1$; We can write, interaction Hamiltonian for three different laser frequency such as:

$$H' = \sum_{j=1to3} \hat{\varepsilon}_j \cdot \vec{r} E_{0j} e^{i(\omega_j t - \delta_j)} \quad (5)$$

$$H' = \hat{\varepsilon}_1 \cdot \vec{r} E_{01} e^{-i(\omega_1 t + \delta_1)} + \hat{\varepsilon}_2 \cdot \vec{r} E_{02} e^{-i(\omega_2 t - \delta_2)} + \hat{\varepsilon}_3 \cdot \vec{r} E_{03} e^{-i(\omega_3 t - \delta_3)} \quad (6)$$

Let, $H_1 = \hat{\varepsilon}_1 \cdot \vec{r} E_{01}$ Similarly we can write for H_2 and, H_3 . Here, E_{01} is the amplitude of the electromagnetic field along the direction of the polarization vector $\hat{\varepsilon}_1$. Similarly E_{02} and E_{03} are the amplitudes along the direction $\hat{\varepsilon}_2$ and $\hat{\varepsilon}_3$ for the beam 2 and 3 respectively. The interaction Hamiltonian for the same laser frequency ω with different polarization should be:

$$H' = \sum_j \hat{\varepsilon}_j \cdot \vec{r} E_0 e^{i(\omega t - \delta_j)} \quad (7)$$

One-photon ionization

The transition of electron from ground state to the final state by the absorption of one photon. Single-photon absorption is described by first order perturbation theory.

Calculation for first order perturbation:

$$\frac{dC_n^{(1)}(t)}{dt} = \frac{1}{i} \sum_g C_g^{(0)}(t) e^{i\omega_{ng} t} \langle n|H'|g\rangle e^{-i\omega t} \quad (8)$$

Here, ω is the frequency of the linearly polarized light. The ionization rate for the same frequency and different polarization can be expressed as (Shrestha *et al.* 2008):

$$\frac{\left|C_n^{(1)}(t)\right|^2}{t} = E_0^2 \left|\langle n|\hat{\varepsilon}_j \cdot \vec{r}|g\rangle\right|^2 \delta(\omega_{ng} - \omega)$$

Since atoms are small compared to the wavelength of light, the amplitudes of electric field will not vary significantly over the dimensions of atom. We can therefore take them constants out from the calculation of integrals (Mark 2006). Thus,

$\Gamma_{ng}^{(1)} \propto |\langle n|H'|g\rangle|^2 \delta(\omega_{ng} - \omega)$

Here we can see that a resonance occurs at $\omega_{ng} = \omega$ corresponding to one photon transition from ground state $|g\rangle$ to the final state $|n\rangle$.

Two photon absorption (2PA)

2PA works when two photons (identical or different frequencies) are simultaneously absorbed in one event and make a transition from initial state as ground state $|g\rangle$ to and final state $|m\rangle$ allowed by two photon selection rules (Bethe *et al.* 1957). The two photon absorption is described by the second order perturbation theory.

$$\frac{dC_m^{(2)}(t)}{dt} = \frac{1}{i} \sum_n C_n^{(1)}(t) \langle m|H'|n\rangle e^{i(\omega_{mn} - \omega)t} \quad (9)$$

By integrating and substituting the value of $C_n^{(1)}(t)$ (Shrestha *et al.* 2009),

$$C_m^{(2)}(t) \propto \sum_n \langle m|H'|n\rangle\langle n|H'|g\rangle \left[\frac{-e^{i(\omega_{mn} - \omega)t}}{(\omega_{mn} - \omega)(\omega_{ng} - \omega)}\right] \propto \left[\frac{1 - e^{i(\omega_{mn} + \omega_{ng} - 2\omega)t}}{(\omega_{mg} - 2\omega)(\omega_{ng} - \omega)}\right] \quad (10)$$

Assuming the two different beams are j and k.

Let, $M_{mg}^{(2)}$, is the transition matrix element for two-photon ionization, for same frequency (ω) of different polarization. We can derive by dropping the antiresonance terms such as

$$M_{mg}^{(2)} = \sum_{j,k} \sum_{n} \frac{\langle m|\vec{\varepsilon}_k \cdot \vec{r}|n\rangle\langle n|\vec{\varepsilon}_j \cdot \vec{r}|g\rangle}{(\omega_{ng} - \omega)} \quad (11)$$

The transition rate (Thayyullathil *et al.* 1994) becomes:

$$\Gamma_{mg}^{(2)} \infty \left|M_{mg}^{(2)}\right|^2 \delta(\omega_{mg} - 2\omega)$$

Where we have retained only those terms in which the denominators approaches zero. Here we can see that a resonance occurs at $\omega_{mg} = 2\omega$ corresponding to the two photon transition for the identical laser frequency ω, from the ground state $|g\rangle$ to the final state $|m\rangle$ through one intermediate state $|n\rangle$.

For different laser frequency with different polarization

The second order expansion coefficient for different laser frequency with different polarization:

$$C_m^{(2)}(t) = \sum_n \frac{\langle m|H_1|n\rangle\langle n|H_1|g\rangle}{\omega_{ng} - \omega_1} \delta(\omega_{mg} - 2\omega_1) \quad (12)$$

$$+ \sum_n \frac{\langle m|H_2|n\rangle\langle n|H_1|g\rangle}{(\omega_{ng} - \omega_1)} \delta(\omega_{mn} + \omega_{ng} - \omega_1 - \omega_2)$$

$$+ \sum_n \frac{\langle m|H_3|n\rangle\langle n|H_1|g\rangle}{(\omega_{ng} - \omega_1)} \delta(\omega_{mn} + \omega_{ng} - \omega_1 - \omega_3)$$

$$+ \sum_n \frac{\langle m|H_1|n\rangle\langle n|H_2|g\rangle}{(\omega_{ng} - \omega_1)} \delta(\omega_{mn} + \omega_{ng} - 2\omega_2)$$

$$+ \sum_n \frac{\langle m|H_1|n\rangle\langle n|H_2|g\rangle}{(\omega_{ng} - \omega_2)} \delta(\omega_{mn} + \omega_{ng} - \omega_1 - \omega_2)$$

$$+ \sum_n \frac{\langle m|H_3|n\rangle\langle n|H_2|g\rangle}{(\omega_{ng} - \omega_2)} \delta(\omega_{mn} + \omega_{ng} - \omega_2 - \omega_3)$$

$$+ \sum_n \frac{\langle m|H_3|n\rangle\langle n|H_3|g\rangle}{(\omega_{ng} - \omega_3)} \delta(\omega_{mn} + \omega_{ng} - 2\omega_3)$$

$$+ \sum_n \frac{\langle m|H_1|n\rangle\langle n|H_3|g\rangle}{(\omega_{ng} - \omega_3)} \delta(\omega_{mn} + \omega_{ng} - \omega_1 - \omega_3) \quad (13)$$

$$+ \sum_n \frac{\langle m|H_2|n\rangle\langle n|H_3|g\rangle}{(\omega_{ng} - \omega_3)} \delta(\omega_{mn} + \omega_{ng} - \omega_2 - \omega_3)$$

Hence the transition matrix becomes:

$$M_{mg}^{(2)} = \sum_{i,k} \sum_{n} \frac{\langle m|H_k|n\rangle\langle n|H_j|g\rangle}{(\omega_{ng} - \omega_j)} \quad (14)$$

Three photon absorption(3PA)

3PA works when three photons (identical or different frequencies) are simultaneously absorbed in one event and make a transition from $|g\rangle$ to excited state $|f\rangle$ allowed by three photon selection rules. We require third order perturbation theory such as, for the same frequency and linearly polarized:

$$\frac{dC_f^{(3)}(t)}{dt} = \frac{1}{i} \sum_m \langle f|H'|m\rangle C_m^{(2)}(t) e^{i(\omega_{fm} - \omega)t} \quad (15)$$

Then, integrating and substituting the value of $C_m^{(2)}$,

$$C_f^{(3)}(t) = \sum_m \sum_n \langle f|H'|m\rangle\langle m|H'|n\rangle\langle n|H'|g\rangle \times$$

$$\left[\frac{1 - e^{i(\omega_{fm} - \omega)t}}{(\omega_{fm} - \omega)(\omega_{mn} - \omega)(\omega_{ng} - \omega)}\right] - \left[\frac{1 - e^{i(\omega_{fm} + \omega_{mn} - 2\omega)t}}{(\omega_{fm} + \omega_{mn} - 2\omega)(\omega_{mn} - \omega)(\omega_{ng} - \omega)}\right]$$

$$\left[\frac{1 - e^{i(\omega_{fm} - \omega)t}}{(\omega_{fm} - \omega)(\omega_{mg} - 2\omega)(\omega_{ng} - \omega)}\right] - \left[\frac{1 - e^{i(\omega_{fm} + \omega_{mn} + \omega_{ng} - 3\omega)t}}{(\omega_{fm} + \omega_{mn} + \omega_{ng} - 3\omega)(\omega_{mg} - 2\omega)(\omega_{ng} - \omega)}\right]$$

Here we can see that a resonance occurs at $\omega_{fm} + \omega_{mn} + \omega_{ng} = \omega_{fg} = 3\omega_1$ corresponding to three photon transition for identical laser frequency ω_1, from ground state $|g\rangle$ to the final state $|f\rangle$ through two intermediate states $|n\rangle$ and $|m\rangle$. By dropping the antiresonance term the matrix elements for three-photon of same frequency (ω) with different polarization becomes:

$$M_{fg}^{(3)} = \sum_{j,k,l} \sum_{m,n} \frac{\langle f|(\vec{\varepsilon}_l \cdot \vec{r})|m\rangle\langle m|(\vec{\varepsilon}_k \cdot \vec{r})|n\rangle\langle n|(\vec{\varepsilon}_j \cdot \vec{r})|g\rangle}{(\omega_{ng} - \omega)(\omega_{mg} - 2\omega)} \quad (17)$$

Similarly the matrix element for three different frequencies and polarization we have obtained 27 terms with different dirac function such as:

$$M_{fg}^{(3)} = \sum_m \sum_n \frac{\langle f|H_3|m\rangle\langle m|H_2|n\rangle\langle n|H_1|g\rangle}{(\omega_{mg} - 2\omega_1)(\omega_{ng} - \omega_1)} \delta(\omega_{fg} - 3\omega_1) \quad (18)$$

$$+ \sum_m \sum_n \frac{\langle f|H_2|m\rangle\langle m|H_1|n\rangle\langle n|H_1|g\rangle}{(\omega_{mg} - 2\omega_1)(\omega_{ng} - \omega_1)} \delta(\omega_{fg} - 2\omega_1 - \omega_2)$$

$$+ \sum_m \sum_n \frac{\langle f|H_3|m\rangle\langle m|H_1|n\rangle\langle n|H_1|g\rangle}{(\omega_{mg} - 2\omega_1)(\omega_{ng} - \omega_1)} \delta(\omega_{fg} - 2\omega_1 - \omega_3)$$

$$+ \sum_m \sum_n \frac{\langle f|H_1|m\rangle\langle m|H_2|n\rangle\langle n|H_1|g\rangle}{(\omega_{mg} - \omega_1 - \omega_2)(\omega_{ng} - \omega_1)} \delta(\omega_{fg} - 2\omega_1 - \omega_2)$$

$$+ \sum_m \sum_n \frac{\langle f|H_3|m\rangle\langle m|H_2|n\rangle\langle n|H_1|g\rangle}{(\omega_{mg} - \omega_1 - \omega_2)(\omega_{ng} - \omega_1)} \delta(\omega_{fg} - \omega_1 - \omega_2 - \omega$$

$$+ \sum_m \sum_n \frac{\langle f|H_2|m\rangle\langle m|H_2|n\rangle\langle n|H_1|g\rangle}{(\omega_{mg} - \omega_1 - \omega_2)(\omega_{ng} - \omega_1)} \delta(\omega_{fg} - 2\omega_2 - \omega_1)$$

$$+\sum_m \sum_n \frac{\langle f|H_1|m\rangle\langle m|H_3|n\rangle\langle n|H_2|g\rangle}{(\omega_{mg}-\omega_2-\omega_3)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-\omega_1-\omega_2-\omega$$

$$+\sum_m \sum_n \frac{\langle f|H_3\ m\rangle\langle m|H_3|n\rangle\langle n|H_3|g\rangle}{(\omega_{mg}-2\omega_3)(\omega_{ng}-\omega_3)}\delta(\omega_{fg}-3\omega_3)$$

$$+\sum_m \sum_n \frac{\langle f|H_1|m\rangle\langle m|H_1|n\rangle\langle n|H_3|g\rangle}{(\omega_{mg}-\omega_1-\omega_3)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-2\omega_1-\omega_3)$$

$$+\sum_m \sum_n \frac{\langle f|H_2|m\rangle\langle m|H_1|n\rangle\langle n|H_3|g\rangle}{(\omega_{mg}-\omega_1-\omega_3)(\omega_{ng}-\omega_3)}\delta(\omega_{fg}-\omega_1-\omega_2-\omega$$

$$+\sum_m \sum_n \frac{\langle f|H_1|m\rangle\langle m|H_3|n\rangle\langle n|H_2|g\rangle}{(\omega_{mg}-\omega_2-\omega_3)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-\omega_1-\omega_2-\omega$$

$$+\sum_m \sum_n \frac{\langle f|H_3|m\rangle\langle m|H_1|n\rangle\langle n|H_3|g\rangle}{(\omega_{mg}-\omega_1-\omega_3)(\omega_{ng}-\omega_3)}\delta(\omega_{fg}-\omega_1-2\omega_3)$$

$$+\sum_m \sum_n \frac{\langle f|H_1|m\rangle\langle m|H_3|n\rangle\langle n|H_1|g\rangle}{(\omega_{mg}-\omega_1-\omega_3)(\omega_{ng}-\omega_1)}\delta(\omega_{fg}-2\omega_1-\omega_3)$$

$$+\sum_m \sum_n \frac{\langle f|H_3|m\rangle\langle m|H_3|n\rangle\langle n|H_1|g\rangle}{(\omega_{mg}-\omega_1-\omega_3)(\omega_{ng}-\omega_1)}\delta(\omega_{fg}-2\omega_3-\omega_1)$$

$$+\sum_m \sum_n \frac{\langle f|H_3|m\rangle\langle m|H_1|n\rangle\langle n|H_2|g\rangle}{(\omega_{mg}-\omega_1-\omega_2)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-\omega_1-\omega_2-\omega$$

$$+\sum_m \sum_n \frac{\langle f|H_1|m\rangle\langle m|H_3|n\rangle\langle n|H_1|g\rangle}{(\omega_{mg}-\omega_2-\omega_3)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-\omega_1-\omega_2-\omega$$

$$+\sum_m \sum_n \frac{\langle f|H_3|m\rangle\langle m|H_3|n\rangle\langle n|H_2|g\rangle}{(\omega_{mg}-\omega_2-\omega_3)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-\omega_2-2\omega_3)$$

$$+\sum_m \sum_n \frac{\langle f|H_1|m\rangle\langle m|H_3|n\rangle\langle n|H_3|g\rangle}{(\omega_{mg}-2\omega_3)(\omega_{ni}-\omega_3)}\delta(\omega_{fg}-\omega_1-2\omega_3)$$

$$+\sum_m \sum_n \frac{\langle f|H_2|m\rangle\langle m|H_3|n\rangle\langle n|H_3|g\rangle}{(\omega_{mg}-2\omega_3)(\omega_{ng}-\omega_3)}\delta(\omega_{fg}-\omega_2-2\omega_3)$$

$$+\sum_m \sum_n \frac{\langle f|H_1|m\rangle\langle m|H_2|n\rangle\langle n|H_3|g\rangle}{(\omega_{mg}-\omega_2-\omega_3)(\omega_{ng}-\omega_3)}\delta(\omega_{fg}-\omega_1-\omega_2-\omega$$

$$+\sum_m \sum_n \frac{\langle f|H_2|m\rangle\langle m|H_2|n\rangle\langle n|H_3|g\rangle}{(\omega_{mg}-\omega_2-\omega_3)(\omega_{ng}-\omega_3)}\delta(\omega_{fg}-2\omega_2-\omega_3)$$

$$+\sum_m \sum_n \frac{\langle f|H_3|m\rangle\langle m|H_2|n\rangle\langle n|H_3|g\rangle}{(\omega_{mg}-\omega_2-\omega_3)(\omega_{ng}-\omega_3)}\delta(\omega_{fg}-\omega_2-2\omega_3)$$

$$+\sum_m \sum_n \frac{\langle f|H_2|m\rangle\langle m|H_3|n\rangle\langle n|H_1|g\rangle}{(\omega_{mg}-\omega_2-\omega_3)(\omega_{ng}-\omega_1)}\delta(\omega_{fg}-\omega_1-\omega_2-\omega$$

$$+\sum_m \sum_n \frac{\langle f|H_2|m\rangle\langle m|H_2|n\rangle\langle n|H_2|g\rangle}{(\omega_{mg}-2\omega_2)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-3\omega_2$$

$$+\sum_m \sum_n \frac{\langle f|H_3|m\rangle\langle m|H_2|n\rangle\langle n|H_2|g\rangle}{(\omega_{mg}-2\omega_2)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-2\omega_2-\omega_3)$$

$$+\sum_m \sum_n \frac{\langle f|H_1|m\rangle\langle m|H_1|n\rangle\langle n|H_2|g\rangle}{(\omega_{mg}-\omega_1-\omega_2)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-2\omega_1-\omega_2)$$

$$+\sum_m \sum_n \frac{\langle f|H_2|m\rangle\langle m|H_1|n\rangle\langle n|H_2|g\rangle}{(\omega_{mg}-\omega_1-\omega_2)(\omega_{ng}-\omega_2)}\delta(\omega_{fg}-2\omega_2-\omega_1)$$

We can expressed representing three different beams j, k, and l as:

$$M_{fg}^{(3)} = \sum_{j,k,l}\sum_{m,n} \frac{\langle f|\hat{\varepsilon}_l\cdot\vec{r}|m\rangle\langle m|\hat{\varepsilon}_k\cdot\vec{r}|n\rangle\langle n|\hat{\varepsilon}_j\cdot\vec{r}|g\rangle}{(\omega_{ng}-\omega_j)(\omega_{mg}-\omega_j-\omega_k)} \qquad (19)$$

Where we have retained only those terms in which the denominators approaches zero. Here we can see that a resonance occurs at $\omega_{fm}+\omega_{mn}+\omega_{ng}=\omega_{fg}=3\omega$ corresponding to three photon transition from the ground state $|g\rangle$ to the final state $|f\rangle$ through two intermediate states $|n\rangle$ and $|m\rangle$ processes. Therefore the rate of three photon absorption becomes

$$\Gamma_{fg}^{(3)} \infty \left|M_{fg}^{(3)}\right|^2 \delta(\omega_{fg}-3\omega) \qquad (20)$$

Results and Discussion

1. In general, all the transitions which satisfies the Bohr's quantum condition (for the single photon) are not allowed.
2. The radiative transitions can take place only the states allowed by certain selection rules. The parity rule follows by odd parity of dipole operator.
3. The spin selection rules follows from the fact that, the photon does not interact with electron spin and so the spin quantum number never change in the transitions.
4. In a non linear medium two and three photon absorptions occurs between the states of same parity, while in the single photon absorption states involved are opposite parity. Hence as the intensity of the radiation field increases, the transition which is forbidden by single photon transitions can occur by two and three photon absorption.
5. Probability of two or three photon is proportional to the respectively, fourth and sixth power electric field i.e square and cube of the intensity of radiation field(I^n).

6. In general, $\Gamma_{fg}^{(n)} \propto \sigma_n I^n$, where σ_n is the generalized cross-section of the n^{th} photon ionization (Chin *et al.* 1984).

In the case for two photon ionization for laser radiation containing different frequency

For two fields (ω_k, ω_j)

The same final continuum state is reached by:

- the absorption of two identical laser photons (ω_k) or (ω_j) with the polarization vectors $\hat{\varepsilon}_k$.
- the absorption of two different laser photons $(\omega_k$ and $\omega_j)$ with different polarization vectors $\hat{\varepsilon}_k$ and $\hat{\varepsilon}_j$ respectively,
- the absorption of two different laser photons $(\omega_j$ and $\omega_k)$ with different polarization vectors $\hat{\varepsilon}_j$ and $\hat{\varepsilon}_k$ respectively.
- the absorption of two identical laser photons (ω_j) or (ω_k) with $\hat{\varepsilon}_j$.

For three fields:

The same final continuum state is reached by the interference of six different routes connected to the absorption of two identical laser photons with polarization vectors ($\hat{\varepsilon}_k$ and $\hat{\varepsilon}_j$) and absorption of two laser photons with different polarization vectors.

In the case for three photon ionization the laser radiation containing different frequency

For two fields The same final continuum state is reached

by the interference of three different routes connected to the absorption of three identical laser photons with polarization vectors($\hat{\varepsilon}_l$, $\hat{\varepsilon}_k$ and $\hat{\varepsilon}_j$).

by the interference of six different routes connected to the absorption of three different laser photons with polarization vectors($\hat{\varepsilon}_j$, $\hat{\varepsilon}_k$ and $\hat{\varepsilon}_l$).

For three fields:

The same final continuum state is reached

by the interference of nine different routes connected to absorption of three identical laser beams with the polarization vectors($\hat{\varepsilon}_j$, $\hat{\varepsilon}_k$ and $\hat{\varepsilon}_l$) respectively.

by the interference of eight different routes connected to absorption of three different laser beams with the polarization vectors($\hat{\varepsilon}_j$, $\hat{\varepsilon}_k$ and $\hat{\varepsilon}_l$) respectively.

by the interference of ten different routes connected to absorption of three different laser beams with different polarization vectors($\hat{\varepsilon}_j$, $\hat{\varepsilon}_k$ and $\hat{\varepsilon}_l$) respectively.

Thus the same final continuum state is reached in total by the interference of twenty seven different routes connected to the absorption of three identical or different laser photons with polarization vectors($\hat{\varepsilon}_j$, $\hat{\varepsilon}_k$ and $\hat{\varepsilon}_l$).

Besides the energy conservation the total angular momentum of the system (Atom + Photon) has to be conserved. The transition probability therefore depends on polarization of the absorbed or emitted electromagnetic radiation.

Acknowledgements

We would like to express our sincere gratitude to advisor Prof. Dr. Ramesh Babu Thayyullathil, Dept of Physics, Cochin University of Science and Technology(CUSAT), Kerela, India, for his guidance and helpful comments. It is our pleasure to acknowledge INSA-NAST bilateral exchange program for funding research at Cochin University of Science and Technology (CUSAT), Kerala, India (April-Oct,2010Without their funding and support, this research work would not have been possible. We are also thankful to Prof. Dr. Lok Narayan Jha, Head of Central Department of Physics, Tribhuvan University, Kirtipur for providing the necessary facilities and UGC, Sanothimi, Bhaktpur for the financial support to carry out this doctoral research work.

References

Bethe, H. A. and E. E. Salpeter. 1957. Interaction with radiation. In: *Quantum Mechanics of One or Two Electrons Atom.* Springer-verlag, Berlin, Acdemicc Press inc, New York, pp 248-263.

Rhodes, Charles K. 1985. Multiphoton ionization of atoms. *Science* **229**: 4720,

Delone, N. B. and V. P. Krainov. 1999. Exitation of higher harmonics. In: *Multiphoton Processes in Atoms.* 2nd edition, Springer Berlin, pp 187-193.

Demtröder, W. 2006: Emission, absorption of Electromagnetic Radiation by Atoms. In: *Atoms, Molecules and Photons.* Springer Berlin Heidelberg New York, pp 242-277.

Lakowice, Joseph R. 1983. Fluorescence Sensing. In: *Principles of Fluorescence Spectroscopy.* Plenum Press 1983, 233 Spring Str. New York, pp 623 - 664.

Koval, Von Peter. 2004. *Two- Photons Ionization of Atomic Inner-shells*. Ph.D dissertation, vorgelegt beim Fachbereich Naturwissenschaften der Universitat Kassel, University Kassel, Kassel, pp 1-127.

Mainfray, G. and Manus C. 1991. Multiphoton ionization of atoms. *Rep. Prog. Phys* . **54**: 1333-1372.

Fox ,Mark. 2006. Radiative transition in atoms. In: *Quantum Optics, An introduction*, Oxford University Press, pp 48-71.

Knight , Peter and C. Gerry. 2005. Emission and absorption of radiation by atoms, In: *Introduction to Quantum Optics*,Cambridge University Press, UK, pp 75-114.

Shrestha, Nilam, J. J. Nakarmi and L. N. Jha .2008 . An introduction to Multiphoton Ionization and study of ionization rate and cross-section of hydrogen atom. In: *Proceedings of 3rd IUPAP International conference on Women in Physics (ICWIP)* (oct ,8-10,2008), Seoul, South Korea. **1119**: 243.

Shrestha, Nilam, J. J. Nakarmi and L. N. Jha. 2009 . Two Photon ionization of hydrogen atom, In: *Abstract of International Conference on Frontiers of Physics Kathmandu (ICFP)* (June 2-4,2009), pp 64.

Thayyullathil, R.B. , Radhakrishnan R. and Seema M. 2003. Three-Photon transition from ground state to bound states in atomic hydogen. *J. Phy. A: Math. Gen* **36**: 8473-8478.

Thayyullathi, R.B.. and K. J. Prasanna. 1994. Two-photon transition in atomic hydrogen: An alternative approach. *Phy. Rev. A* **49** (9): 2432-2434.

An Introduction to Multiphoton Ionization and Study of Ionization Rate of Hydrogen Atom:

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Abstract

We have discussed the problems of non linear interaction between electromagnetic radiations with atoms from semi-classical point of view. Time dependent Schrödinger equation for single electron system is solved by using perturbative technique to obtain transition probability. Higher order perturbation is also discussed which is used in multiple processes, in which two or more quanta are emitted instead of a single photon. The theory is based on assumption that the perturbation is small. From this transition probability ionization rate and absorption cross-section of hydrogen atom is calculated. Its variation with photon energy and field strength is analyzed which agrees very well with experimental observations.

Keywords: *non linear interaction, perturbative technique, multiple processes, absorption cross-section.*

Introduction

An atom can be ionized by photons with energy $h\nu$ much less than ionization energy, if the photon flux is strong enough, which, from a practical point of view can only be achieved with laser radiation [1]. This process is designated as Multiphoton Ionization and results from the simultaneous absorption of a number N-photons defined as[2].

$$Nh\nu + X = X^*$$

The first lasers in the early 1960s equipped physicists with extraordinary tool. It became possible to study not only multiphoton transitions between bound states, but also between bound free multiphoton transition i.e. Multiphoton ionization [3]. The multiphoton excitation and ionization processes have received an increasing interest, both from the experimental as well as from the theoretical side.

When photons, meets the atom, the atomic electron(s) can take up the energy of one or many photons [4]. If the electron is released by absorption of only one single photon then the ionization probability will be proportional to the number of photons which interacts with the atom. Hence in one-photon ionization the probability linearly depends on the number of interacting photons (photon flux) [5,6].

$$\text{N-photon Ionization rate} \propto \sigma_N I^N ,$$

Where, σ_N generalized cross-section and I^N laser intensity numerically equal to photon flux, for N photons.

Ionization Rate of Hydrogen Atom

We now calculate the probability of ionization of a hydrogen atom initially in its ground state [7], when it is placed in a harmonically time varying electric field [8].

The perturbation

$H^1 = 2eE_0 r\cos\omega t$ (Electric dipole approximation)

Fermi-Golden rule for the transition rate, [9]

$$\Gamma_{i-f} = \frac{2\pi}{\hbar}\left|\langle f|H^1|i\rangle\right|^2 \delta(E_f - E_i - \hbar\omega)$$

Taking the incoming wave to be an electromagnetic field having vector potential

$$\vec{A}(\vec{r},t) = A_0\cos(k\cdot\vec{r} - \omega t)$$

Hence the interaction Hamiltonian is given by replacing the electron kinetic energy term

$$H^1 = \frac{e}{m}\cos(\vec{k}\cdot\vec{r} - \omega t)\vec{A}_0\cdot\vec{p}$$

$$= \left[H^{10}e^{-i\omega t} + (H^{10})^* e^{i\omega t}\right]\vec{\varepsilon}\cdot\vec{p}$$

(Under dipole approximation)

Density of states (DOS)

We make the assumption that the final state is the plane wave state, $|\vec{k}_f\rangle \propto e^{ik'\cdot\vec{r}}$ [10] which has to be confined into a box of side L and use the boundary conditions. The normalized plane wave state becomes:

$$|\vec{k}\rangle = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} = \frac{1}{L^{3/2}} e^{i\vec{k}\cdot\vec{r}}$$

Thus, DOS becomes,

$$\rho(E)\Delta E = 4\pi k^2 \left(\frac{L}{2\pi}\right)^3 \frac{m}{\hbar^2 k} \Delta E$$

Matrix Element for hydrogen atom:

The ground state wave function for hydrogen is

$$|100\rangle = \left(\frac{1}{\sqrt{\pi a_0^3}}\right) e^{-r/a_0}$$

Here, the interaction Hamiltonian matrix for the hydrogen atom is [11]

$$H^1_{if} = \langle f | H^1 | i \rangle$$

$$= \left(\frac{1}{L}\right)^{3/2} \left(\frac{e}{2m}\right) \frac{1}{\sqrt{\pi a_0^3}} \int d^3 r\, e^{-i\vec{k}_f\cdot\vec{r}} \vec{A}_0 \cdot (-i\hbar\nabla) e^{-r/a_0}$$

Integrating by parts gives the gradient operator acting on the plane wave states,

Solving the integration, and using Fermi-Golden Rule:

$$\Gamma_{i-f} = \frac{2\pi}{\hbar} |\langle f | H^1 | i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

$$= \frac{2\pi}{\hbar} \left|(1/L)^{3/2} \left(\frac{e}{2mc}\right) \frac{1}{\sqrt{\pi a_0^3}} \frac{(\vec{A}_0 \cdot \vec{p}_f)\, 8\pi / a_0}{(a_0^{-2} + k_f^2)^2}\right|^2 \delta(E_f - E_i - \hbar\omega)$$

Here δ - function measures the density of possible outgoing states. The ejected electrons are measured by a sensitive detector to some small solid angle $d\Omega$.

Hence,

$$\Gamma_{i-f} = \frac{2\pi}{\hbar} |\langle f | H^1 | i \rangle|^2 \rho(k, d\Omega)$$

$$= \frac{2\pi}{\hbar} \left|(1/L)^{3/2} \left(\frac{e}{2m}\right) \frac{1}{\sqrt{\pi a_0^3}} \frac{(\vec{A}\cdot\vec{p})\, 8\pi / a_0}{(a_0^{-2} + k_f^2)^2}\right|^2 (L/2\pi)^3 k_f (m/\hbar^2) d\Omega$$

Here, $(\vec{A}_0 \cdot \vec{p}_f)^2 = A_0^2 p_f^2 \cos^2\vartheta$ ejection is most likely to be parallel to the electric field. The total ionization rate is given by the integrating the rate over all angles, and on the unit sphere $\cos^2\vartheta = z^2 = 1/3$, thus,

$$(\vec{A}_0 \cdot \vec{p}_f)^2 d\Omega = 4\pi A_0^2 p_f^2 / 3$$

The total ionization rate is , Γ_{i-f}

$$= \frac{\pi}{\hbar} \left|(1/L)^2 \left(\frac{e}{2m}\right) \frac{1}{\sqrt{\pi a_0^3}} \frac{8\pi / a_0}{(a_0^{-2} + k_f^2)^2}\right|^2 \frac{4\pi}{3} A_0^2 p_f^2 (L/2\pi)^3 k_f (m/\hbar^2)$$

$$\Gamma_{i-f} = \frac{16 e^2 A_0^2 p_f^3}{3mc^2 \hbar^4 a_0^5 (a_0^{-2} + (p_f/\hbar)^2)^4}$$

Ionization Cross-section

The area of the disc equivalent to one atom is the ionization cross-section. Since during ionization an atom takes energy of $\hbar\omega$ from the incident beam, the rate of energy absorption

is just $\hbar\omega\ \Gamma_{i-f}$ [12], hence,

$$\hbar\omega\ \Gamma_{i-f} = c < E_\rho(\omega) > \times Cross - section(\sigma(\omega))$$

Energy density is given by ,

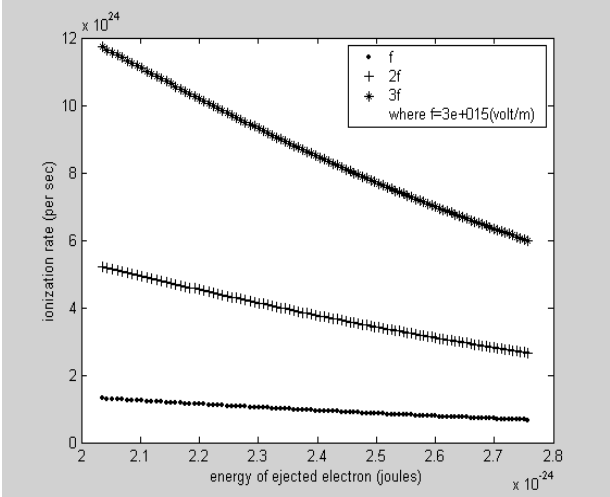
$$E_\rho(\omega) = \frac{1}{8\pi}\left(|\vec{E}|^2 + |\vec{B}|^2\right) = \frac{1}{8\pi}\left(2\frac{\omega^2}{c^2} A_0^2 \sin^2(k\cdot r - \omega t)\right)$$

Averaging over $\sin^2(k\cdot r - \omega t)$, gives the energy absorption density,

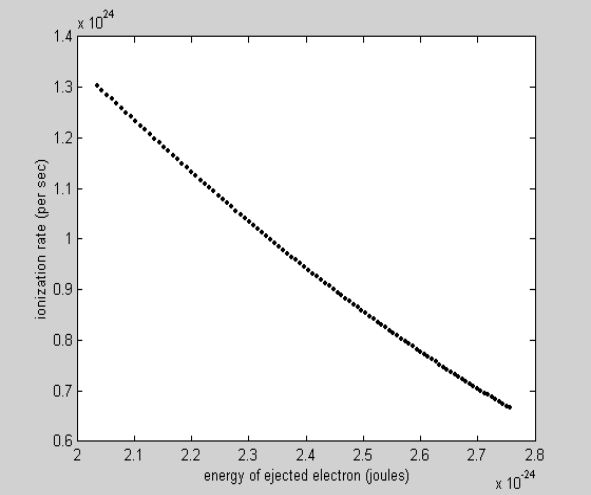
$$< E_\rho(\omega) > = \frac{A_0^2 \omega^2}{8\pi c^2}$$

Hence, the absorption cross section is

$$= \frac{128}{\omega} \frac{e^2}{a_0^5 \hbar^3} \frac{\pi p_f^3}{3m} \left(\frac{1}{a_0^{-2} + (p_f/\hbar)^2}\right)^4$$



Plot (1)



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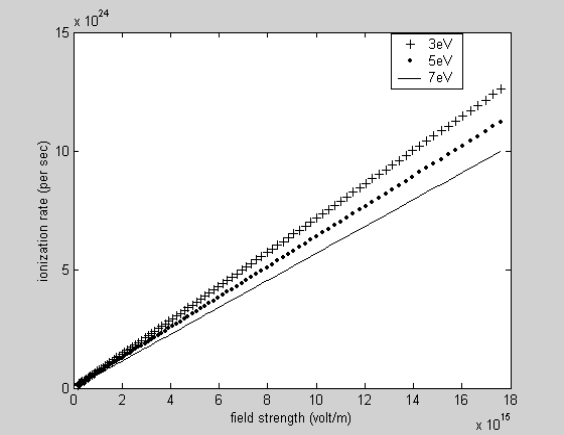

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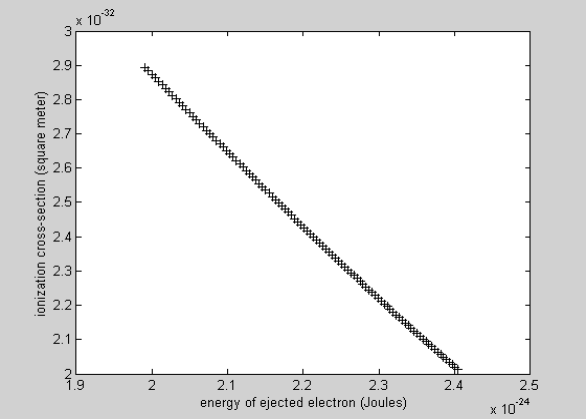

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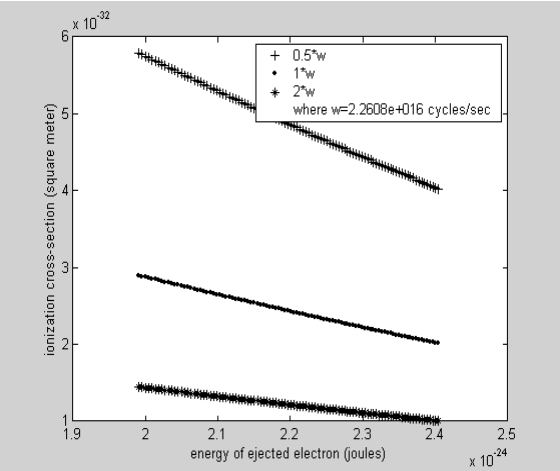

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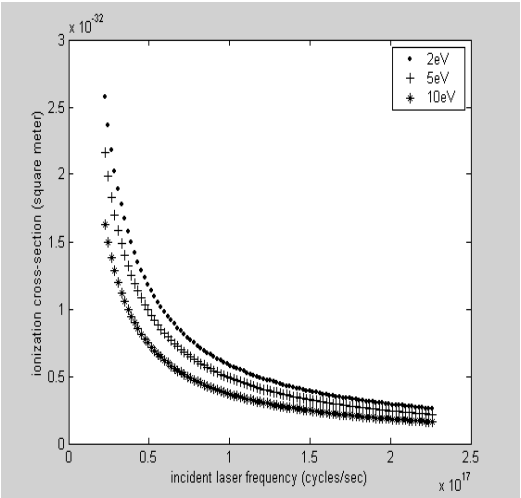

Plot (6)

Results and Discussion

The results are presented in the various plots: in the plot (1) and (2) we have shown that ionization rate decreases with energy of ejected electron. In plot (3), ionization rate increases with increase of field strength for three different values of energy of ejected electron. From plot (4) to (6), it shows that ionization cross-section is independent of field strength; it depends inversely to energy of ejected electron for fixed value and three different values of photon energy, but in plot(6), it gradually decreases with incident photon frequency.

Conclusion

We have solved the time dependent Schrödinger equation and calculated ionization rate and cross-section of the simplest atom like hydrogen by using perturbative technique.

Acknowledgement

It is my pleasure to acknowledge National Science Council, Taiwan for the financial support for the paper presentation on 3rd IUPAP, ICWIP 2008 in Seoul, South Korea and in parts by grants from University of Grant Commission, Sanothimi, Bhaktapur, Nepal.

References

[1] G. Mainfray and C. Manus 1980. Resonance Effects in multiphoton Ionization of atoms, *Applied Optics, 19,* 3934 -3940.

[2] Charles K. Rhodes 1985, Multiphoton ionization of atoms, Vol 229, No. 4720 , www.sciencemag.org

[3] G. Mainfray and C. Manus, 1991, Multiphoton Ionization of Atoms, *IOP publishing Ltd, Phys. 54,* 1333-1372.

[4] L. D. Landau and E.M. Lifshitz, 1965, Quantum Mechanics, Pergamon Press, pp 136.

[5] N. B. Delone and V. P. Krainov, 1999, Multiphoton processes in Atoms, 2nd edition, Springer Berlin, pp 187.

[6] Von Peter Koval,2004, Two- Photons ionization of atomic inner-shells, Ph. D. Dissertation., University Kassel.

[7] E. Merzbazcher,, 2004 Quantum Mechanics, John Wiley and Sons, Inc., pp 509.

[8] N. F. Mott, 1962, Elements of Wave Mechanics, Cambridge University Press, pp 121.

[9] Kenneth Krane, 1998, Modern physics, John wiley and sons, Inc., NY, pp 146

[10] L. I. Schiff, 1968, Quantum Mechanics, McGraw-Hill International editions, pp 287.

[11] Michael Fowler, 2007, *Photoelectric effects in Hydrogen atom* e-net

[12] B. H. Bransden and C. J. Joachain,1983, *Physics of Atoms and Molecules,* Longman Inc., NY, pp 521, and pp 552 .

Symmetry, Vol. 8, p 37-39(2013).

Dalgarno Lewis method as a Perturbation Theory for Multiphoton ionization

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Abstract:
Dalgarn-Lewis summation technique as used in perturbation theory is discussed. Within the semi classical, dipole approximation treatment, the transition amplitude of multiphon ionization interaction between atom and photon is evaluated.

Introduction:
Perturbation theory allows one to find approximate solutions to the perturbed eigenvalue problem by beginning with the known exact solutions of the unperturbed problem and then making small corrections to it based on the new perturbing potential. The limit of the infinite summation of corrections to the unperturbed solution is the exact solution to the perturbed problem. Of course, this infinite sum is very difficult to calculate, the summation must be truncated at some point--hence the approximate nature of the solutions produced by perturbation theory. Luckily, subsequent corrections to the Hamiltonian become smaller and smaller, so the series can usually be truncated after only a few corrections.
Consider time dependent perturbation in Hamiltonian with H_0 exactly soluble

$$H = H_0 + \lambda H'(t)$$

We set the dummy perturbation parameter λ equal to unity for simplicity of the equation.
Here the interaction part of the Hamiltonian $H'(t)$ is small compared to time independent part H_0 and it can be treated as perturbation.
From TDSE,

$$i\hbar \frac{\partial \left| \Psi_n(r,t) \right\rangle}{\partial t} = H \left| \Psi_n(r,t) \right\rangle$$

With time dependent coefficient, the solution

$$\Psi_n(r,t) = \sum_n C_n(t) e^{-iE_n t/\hbar}$$

Inner product with $\langle \Psi_m | i\omega_{mn} t$ [1]

$$\dot{C}_m(t) = H'_{mn} e$$

Where, $H'_{mn} = \langle \Psi_m | H' | \Psi_n \rangle$ is the matrix element.

There is no direct photon to photon interaction. A photon cannot absorb or scatter other photons nor does it decay of its own. No known force can mediate interaction between photons. The transformation of photons can be brought about only through intermediary –a quantum system such as an atom or a molecule characterized by a system of discrete energy levels. An atom or a molecule can absorb or emit photons and in the process may undergo a transition from one energy level to the other [2].
For nearly a century, it has been known that atom can be photo-ionized by absorbing a single photon from radiation whose wavelength is such that the photon energy is higher than or equal to the ionization energy of the atom. The atomic response is a linear function of the weak intensity of radiation, and the process is described by the famous Bohr's quantum rule.

The Bohr's quantum condition,

$$E_f - E_i = \hbar\omega \tag{1}$$

Where, E_f and E_i are the final and initial state energies respectively, and ω is the frequency of the incident photon. But In general all transitions which satisfy above condition are not allowed. The radiative transition can take place only between the states allowed by certain selection rule. Apart from energy conservation given in equation(1), angular momentum also has to be conserved and leads to selection rules and the dependence of the transition probability on the polarization of the incident radiation, described by famous Fermi Golden Rule.

It was found recently that, at high intensity laser pulses, the density of photons is so high that an electron could absorb simultaneously two or more photons i.e nonlinear effect. This process is designated Multiphoton Ionization and results from the simultaneous absorption of N number of - photons. Thus for the N photons the Bohr's quantum condition changes to

$$E_f - E_i = N\hbar\omega$$

Here, N is the number of photons. ω_{fi} is the transition frequency, and ω the threshold frequency, which is much smaller if the intensity of the beam increases. The photoelectric effect therefore, depends both on the intensity and on the frequency of radiation. It may be called Multiquantum photoelectric effect [3].

Perturbation theory is valid only when the radiation field is much less than the atomic field strength and Keldysh parameter or adiabaticity parameter $\gamma \geq 1$, then the ionization can take place as a result of multiphoton ionization and we assume that the kinetic energy of ejected electron is not perturbed by the electromagnetic field.

Consider the simplest case, ground state of hydrogen atom, interacting with the laser beam of frequency ω such that,

$$H(1s) + \sum_{n_b} N\cong\omega = H^+ + e^-(E_k,\ k)$$

Only by 1931, however, Goppert-Mayer noticed that the second-order perturbation theory is able to describe another, different from the scattering, process of two photon absorption. Furthermore, it became clear after Goppert-Mayer's work that higher-order perturbation theory reveals multiphoton absorption processes [4].

Following the perturbation theory, the Nth-order transition amplitude $M_{fg}^{(N)}$ corresponding to a transition from the initial ground state g to final f state in atomic unit is

$$M_{fg}^{(N)} = \sum_{i_{N-1}\ldots.\,i_1} \frac{\left\langle f\left|H'\right|i_{N-1}\right\rangle \ldots\ldots \left\langle i_2\left|H'\right|i_1\right\rangle \left\langle i_1\left|H'\right|g\right\rangle}{(E_{g_{N-1}} - E_g - (N-1)\omega)\ldots\ldots\ldots(E_{i_1} - E_g - \omega)} \tag{2}$$

Here, in dipole approximation $H' = \hat{\varepsilon}\cdot\vec{r}e^{-i(\omega t+\delta)}$ is the interaction part of Hamiltoninan , ω frequency of the incident beam and δ is the phase shift. The intermediate sum runs over the discrete including the continuum states. Various standard procedures are there to evaluate this matrix element, which includes explicit summation technique as well as indirect for summation and variational methods.

Dalgarno- Lewis method[5]

Dalgarno and Stewart[6] developed a simple and practical method for the solution of perturbation equations, later adopted by many authors in the treatment of variety of problem[7]. For simplicity we apply this method to a one particle model Hamiltonian operator, which in dimensionless form reads,

$$H_0 = -\frac{\nabla^2}{2} + V(r)$$

Where, ∇^2 is Laplacian operator, and V(r) is a dimentionless potential energy function.

In the first order perturbation, we obtain expression for the rate at which an atom absorbs light. In these calculations, we had retained the linear term and neglected the higher term on the ground that they are very weak. They are not however, so weak for light from laser source. The very high photon flux and the associated high field of radiation enable the atom or molecule to interact with more than one photon, but we have to solve TDSE directly to study this effect by using higher order perturbation theory.

Two-Photon Process

In two photon absorption the two photons are simultaneously transfer their energy to the atom for their transition. Thus following the second order perturbation theory, we have the transition matrix element as

$$M_{fg}^{(2)} = \sum_n \frac{\langle f|H'|n\rangle\langle n|H'|g\rangle}{(\omega_{ng} - \omega)} \tag{3}$$

Now we will apply Dalgarno-Lewis's principle, the idea of DL method is to define an auxiliary operator such that the evaluation of intermediate sum is not needed. Suppose an operator D_1 exists in such a way that,

$D_1\psi_o^0 = \psi_0^1$ or, $|1\rangle = D_1|0\rangle$

Therefore,

$$\hat{\varepsilon}\cdot r|g\rangle = (H_0 D_1 - D_1 H_0)|g\rangle - \omega D_1|g\rangle \tag{4}$$

Multiplying by bra vector $\langle n|$

$$=(\omega_{ng} - \omega)\langle n|D_1|g\rangle$$

and using identity operator

$$M_{fg}^{(2)} = \langle f|\hat{\varepsilon}\cdot\vec{r}D_1|g\rangle \tag{5}$$

Three-Photon Process

In three photon absorption the three photons are simultaneously transfer their energy to the atom for their transition. Thus following the third order perturbation theory, we have the transition matrix element as $M_{fg}^{(3)} = \sum_{n,m} \frac{\langle f|H'|n\rangle\langle n|H'|m\rangle\langle m|H'|g\rangle}{(\omega_{ng} - 2\omega)(\omega_{mg} - \omega)}$ (6)

There are two summation, now applying Dalgarno-Lewis's principle, we first remove one summation using D_1, operator, then we have to assume one more operator in addition to D_1, to remove the second summation. Let D_2 exists as,

$$(\hat{\varepsilon}\cdot\vec{r})\psi = \left[H_0, D_1\right]\psi - \omega D_1\psi$$

$$(\hat{\varepsilon}\cdot\vec{r})\left|g\right\rangle = (D_1H_0 - H_0D_1 - \omega D_1)\left|g\right\rangle \quad (7)$$

$$(\hat{\varepsilon}\cdot r\, D_1 \mid g\rangle = (D_2H_0 - H_0D_2 - 2\omega D_2)\mid g\rangle$$

$$M_{fg}^{(3)} = \left\langle f\left|\hat{\varepsilon}\cdot\vec{r}D_2\right|g\right\rangle$$

In general for N-photon

$$\hat{\varepsilon}\cdot\vec{r}\, D_{N-1}\mid g\rangle = (D_NH_0 - H_0D_N - N\omega D_N)\mid g\rangle$$

The transition amplitude for N-photon after the inclusion of Dalgarno method reads as

$$M_{fg}^{(N)} = \left\langle f\left|\hat{\varepsilon}\cdot\vec{r}D_{N-1}\right|g\right\rangle$$

Evaluation of Dalgarno's operator

We have unperturbed Hamiltonian, in S. I units

$$H_0 = -\frac{\nabla^2}{2} - \frac{1}{r}$$

$$\left|g\right\rangle = \left|\psi\right\rangle = e^{-r}/\sqrt{\pi}$$

$$H_0\left|\psi\right\rangle = -1/2\left|\psi\right\rangle$$

Plugging this into eq (4)

$$(\hat{\varepsilon}\cdot\vec{r})\psi = \frac{\nabla^2 D_1}{2}\psi + \nabla D_1\cdot\nabla\psi + \omega D_1\psi \quad (8)$$

For linearly polarized beam along the z axis,

$$(\hat{\varepsilon}\cdot\vec{r}) = z = r\cos\theta$$

By inspection, we can say that, D_1 is the product of radial and angular part

Let, $D_1 = f_1(r)P_1(\cos\theta)$ (9)

Where, $f_1(r)$ is the unknown radial part that has can be determined, and $P_1(\cos\theta)$ is the Legendre polynomial of first order.

Plugging equation (9) into equation (8),

We can express in terms of inhomogeneous differential equation satisfied by $f_1(r)$, that can be solved.

Similarly for three photon, we can express D_2 in terms of two inhomogeneous differential equations, which depends on the solution of $f_1(r)$. In this way, once the Dalgarno's operators are known, we are able to evaluate the transition matrix element for various multiphoton processes. Then we can calculate transition rate and the scattering cross-section of the given system and also show the dependence of polarization, phase and intensity on ionization rate by numerical method.

Conclusion:

We conclude by noting that the technique of Dalgarno and Lewis has always been regarded as the supplement to Rayleigh Schrodinger Perturbation theory(RSPT). It is an accurate and efficient procedure in calculation of multiphoton ionization process. In addition to the calculation advantage, this procedure also enable us to study the relative contribution of resonant and non resonant intermediate states[8].

Acknowledgement:

I would like to thank Prof J. J. Nakarmi and Prof. L. N. Jha for much helpful discussion on multiphoton ionization. This work is supported in part by UGC Nepal.

References:

1. Nilam Shrestha and J. J. Nakarmi, 2011, *One, two and three photon absorption in atomic hydrogen*, Nepal journal of science and technology, NAST, 12, p 324-329.
2. G. Mainfray and C. Manus, 1991, *Multiphoton ionization of atoms*, Rep. Prog. Phys. 54, p1333-1372.
3. G. Mainfray and C. Manus , 1980, *Resonance effect in multiphoton ionization of atom*, Applied Optics, Vol. 19(23), p 3934-3940.
4. Nilam Shrestha and J. J. Nakarmi, and L.N. Jha, 2012, *An introduction to multiphoton ionization and study of ionization rate of Hydrogen atom, The Himalayan Physics*, Vol.3(3), p 40-43.
5. Dalgarno, A. and Lewis, J. T. 1956. *The equvalace of variational and perturbation calculation of small disturbances, Proc. Phys. Soc. A* 69, p 628-630.
6. Nandi, T. K., Bera P. K. et al, 1996, *The Dalgarno-Lewis method as a perturbation theory, J. Phy. Maths. Gen.* 29: p 1101-1105.
7. Francisco M. Fernandez, Ph.D, 2000, *An introduction to Perturbation Theory*, CRC press, Chapter 2, p 13-17.
8. Chang, T. N. and Poe, R. T., 1976, *Calculation of multiphoton ionization processes, J. Phys. B: Atom. Moles. Phys.9* (11), p L311-L315.

Symmetry, Vol 7 (2012), pp 08-11.

Schrödinger wave function of Harmonic oscillator using Runge-Kutta in matlab program

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Abstract:

In the present work time independent Schrödinger wave equation of one dimensional harmonic oscillator has been developed using Runge-Kutta Method in matlab program. The solutions of the wave equation describing the physical stationary states of the harmonic oscillator are obtained for different values of energies. And the stationary states corresponding to the eigen values have been presented in the form of plots.

I. Introduction:

Schrödinger wave equation (SWE) describes the time evolution of the wavefunction. The Hamiltonian for the harmonic oscillator describes a particle of mass 'm' in a quadratic potential. Displacing the mass from equilibrium produces a linear restoring force. We have focused on the 1D oscillator since a 3D oscillator can be decomposed into three 1D oscillator and coupling between three 1D is required. Considering Schrödinger time independent equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{x}) = [E - V(x)]\psi(\mathbf{x})$$

Where, $\hbar = h/2\pi$ [1]

Peculiarity of this equation is that it is second order in space coordinates. This second order time independent differential equation in essence describes the non-relativistic motion of a particle of mass m and energy E in the field having potential V. Hence, inclusion of the potential accounts for the interaction of the particle with a force field. In one-dimensional case the equation reads as:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = [E - V(x)]\psi(x) \quad \textbf{[2]}$$

The wave function $\psi(x,t)$ or $\psi(x)$ (for time dependent of independent respectively) describes the particle's state and trajectory. It is not a physically observable quantity, but the square of the wavefunction at point (x,t) gives the probability of finding the particle (oscillator) at a point x at time t.

II.Form of potential:

In our presentation we are interested in potential which is symmetric in position coordinate, that is,

$$V(x) = V(-x) \qquad [4]$$

The symmetric transformation, $x \rightarrow -x$, requires that if $\psi(x)$ is the solution then $\psi(-x)$ is also the solution. The parities of the solution are thus,

$$P = \pm 1$$

It means the wave function obtained as solution of Eqn (1) must possess either odd (P = –1) or even parity (P = +1). The parity operator P is a further quantity, which can be used for identification of the bound states.

For the present case, we consider harmonic potential as symmetric potential:

$$V(x) = \frac{1}{2} kx^2 \qquad [5]$$

Where, the equilibrium position occurs at the origin, x=0.

Spring constant $k=m\omega^2$ and $\omega = 2\pi\upsilon$ (angular frequency) must be +ve, $k > 0$, and it describe the curvature of the potential. (i.e. magnitude of the force in classical harmonic).

The quantum mechanical Hamiltonians using operators **x** and **p** [where $\mathbf{p}=\frac{\hbar}{i}\frac{\partial}{\partial x}$ and **x**=x] becomes:

The SWE with this form is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x)}{\partial x^2} + \frac{1}{2} m\omega^2 x^2 \Psi(x) = E\Psi(x) \qquad [6]$$

The boundary condition for the harmonic oscillator requires the wavefunction to approach zero as x goes infinity ($\Psi(x \to \pm\infty) \to 0$)

III. Eigen Value Problem:

Rescaling the constants ($' = 1$ and m = 1) the equation (2), reduces to the eigen value equation

$$\frac{d^2\psi(x)}{dx^2} = -2[E - V(x)]\psi(x) \qquad [7]$$

For given form of the potential V(x), we may use any of the computational methods available to solve a second order differential equation. It should be born in mind that for bound states the energy eigen values E of the equation (6) are discrete. Each of the solutions corresponding to the eigen values describes some physical stationary states.

IV. Reduction of the Schrödinger equation:

The Eigen value equation (6) can be resolved into two simultaneous first order equations by letting

$$\frac{d\psi(x)}{dx} = z \qquad [8]$$

So that

$$\frac{dz}{dx} = -2[E - V(x)]\psi(x) \qquad [9]$$

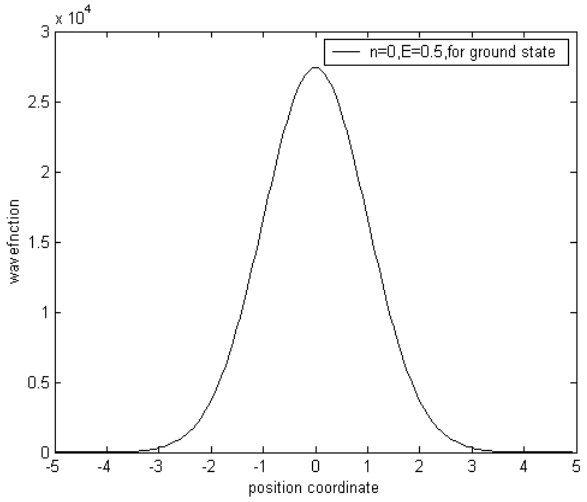
Hence, we obtained the required set of first order equations.

V. Results:

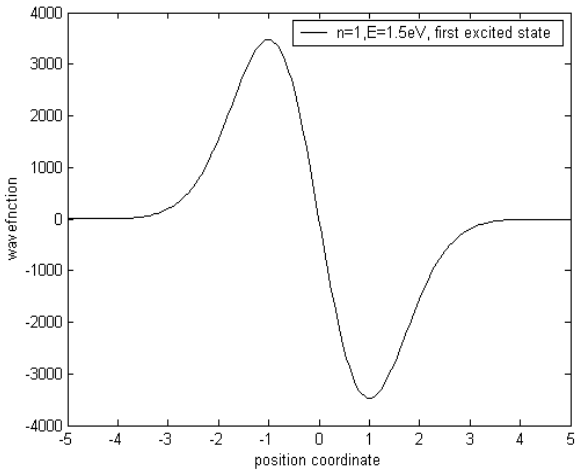
In this program we shall numerically integrate the one dimensional Schrödinger equation to obtain eigenfunctions and eigen values for variety of one dimentional potential functions.

Fig (1): Variation of Wave function with position co-ordinate:

Plot (1)



Plot (2)



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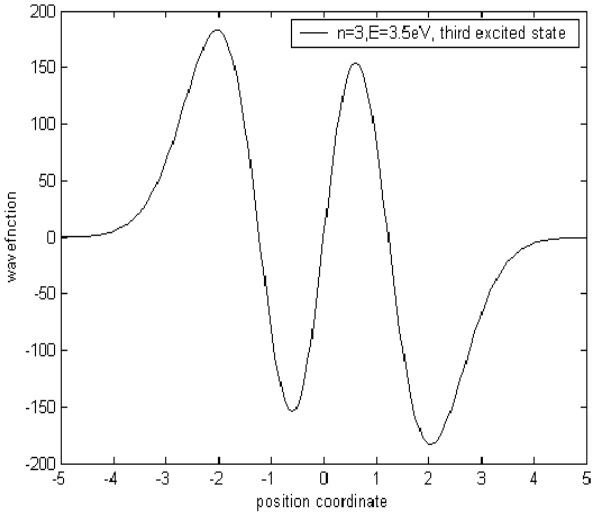

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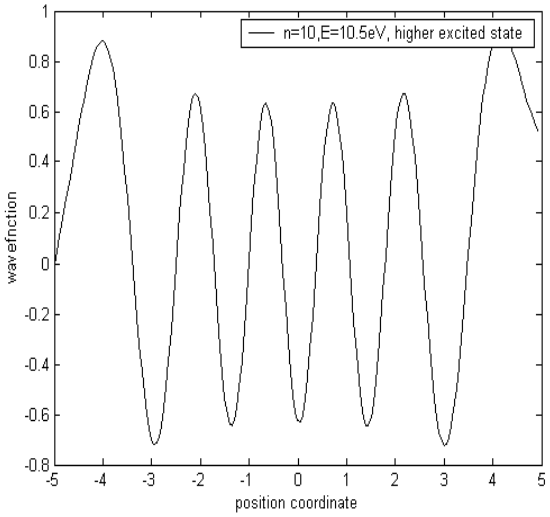
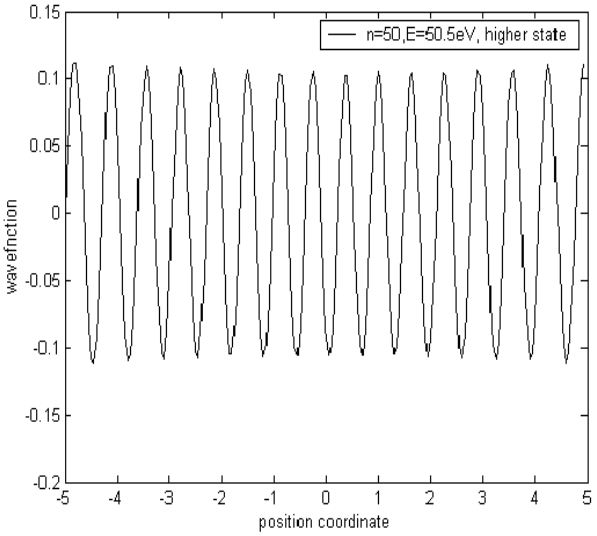


Plot (5)



Plot (6)

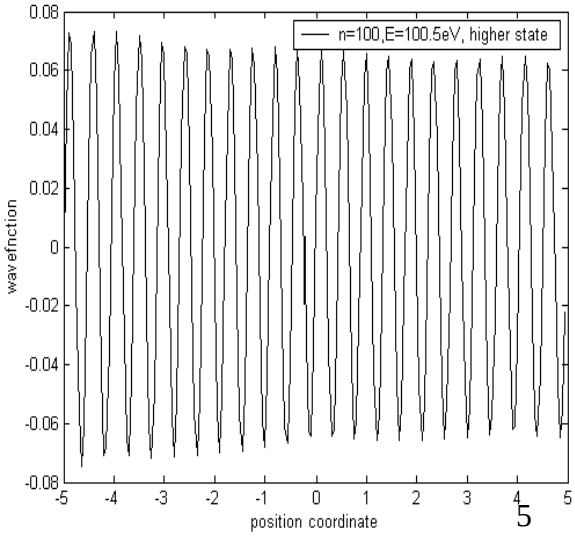
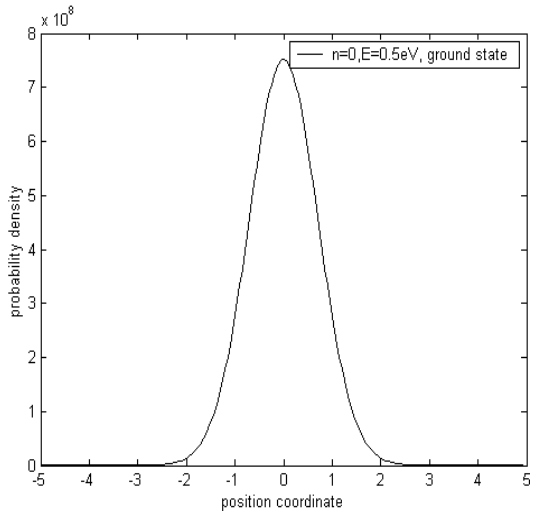
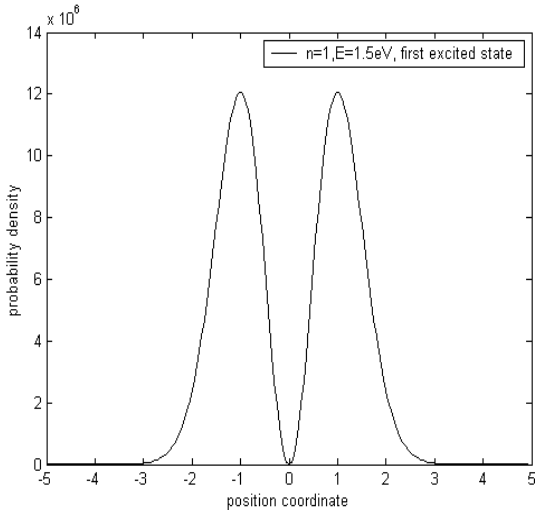


Fig. (2): Variation of Probability density with position co-ordinates:

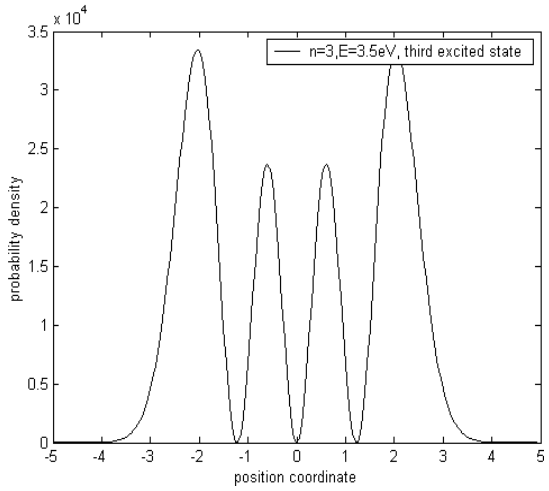
Plot (7)



Plot (8)



Plot (9)



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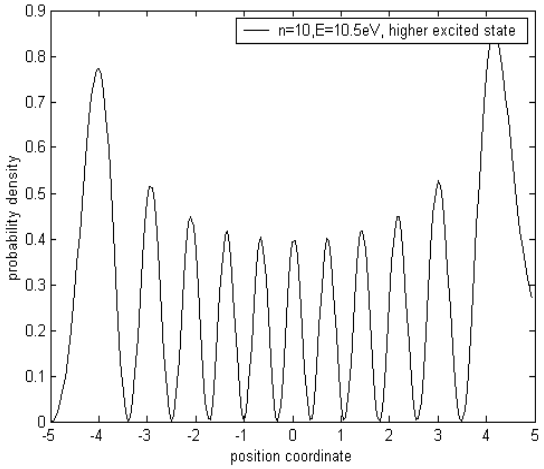

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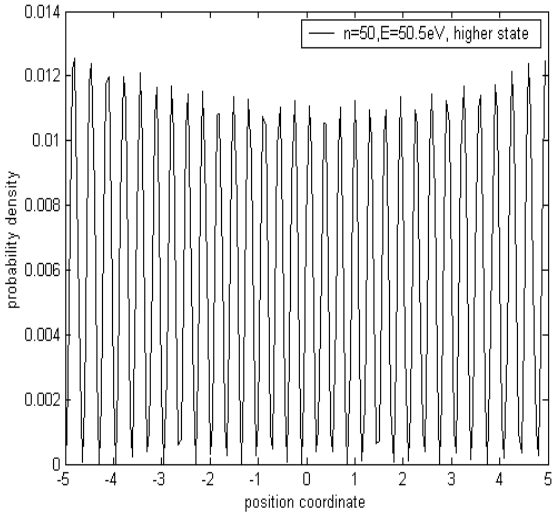

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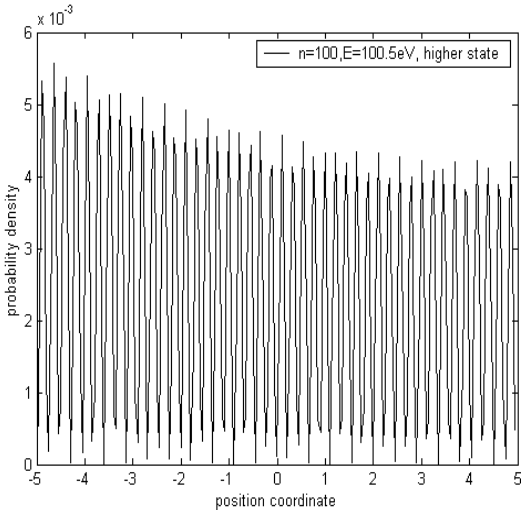

VI. Conclusion:

The most probable value of position for the lower states is very different from the classical harmonic oscillator, where it spends more time near the end of its motion. But as the quantum number increases, the probability distribution becomes more like that of classical oscillator. This tendency of approach the classical behavior for the high quantum numbers is called the correspondence principle.

The first three plots of quantum mechanical solution to the harmonic oscillator, the probability density at the point x does not resemble the classical one.

Acknowledgement: I would like to express my gratitude to Dr. Jeevan Jyoti Nakarmi who gave the initial idea of matlab program to outcome this work. This work has also been supported by partial grant of University of Grant Commission, Sanothimi, and acknowledgement is also made to Central Department of Physics, TU for providing me space to do the work.

References:

1. Matlab User's guide, 1995
2. Quantum Mechanics, third edition, Eugen Merzbacher, 2004.
3. Schaum's outline series, Modern Differential Equations, (1973).
4. Computational Physics,R.C.Verma,P.K.Ahuwalia and K.C. Sharma (1999).
5. Numerical Methods for Engineers, Steven C. Charpa and Raymond P.Canale, 4th edition,(2002).
6. Numerical methods, E.Balagurusamy (2004).
7. Sameep Sangakar (094-70-3044).

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Jyotsna pp 89-90(2013)

Multiphoton ionization of atoms by multiple laser beams and its applications.

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A study of Multiphoton ionization of atoms in presence of multiple laser beams is a subject of much current importance in science and technology. In particular the recent advancement of intense ultra-short laser pulse technology has led to the discovery of a host of novel and very high order multiphoton and non linear optical phenomena which can not be understood by the traditional perturbation theories. More over currently there exist no adequate methods capable of treating many electrons for both atoms and molecular systems; again time dependent dynamics is limited to the one electron systems.

In 1931, Maria Goppert-Mayer predicted theoretically that an atom might absorbs two or more photons simultaneously, thus allowing an electron to occupy states unreachable by a single photon absorption [1]. The multi-photon transition amplitude W_{if} between two discrete energy states $|i\rangle$ and $|f\rangle$ strongly depends on the intensity of the radiation interacting with the atomic system and can be generally expressed as [2].

$$W_{if} \alpha \sigma I^n$$

Here n is the number of photons involved in the multiphoton absorption; I is the radiation intensity in Watt/cm^2 and σ is the multi-photon absorption cross section.

Multiphoton absorptions are described by higher order perturbation theory, which is valid when the radiation field strength is much less than the atomic field strength. If a quantum system is represented by the time dependent Hamiltonian H, then from TDSE [3].

$$H|\psi,t\rangle = i\hbar\frac{\partial}{\partial t}|\psi,t\rangle$$

$$H = H_0 + H'(t)$$

Where H' is the perturbing Hamiltonian of the form

$$H'(t) = H'(t) \text{ if } 0 \le t \le \tau$$

$$= 0 \text{ if }, t \le 0 \text{ and, } t \ge \tau$$

The investigation of multiphoton ionization is important for the applications where high power lasers interact with matter as e.g. for the study of laser induced plasma. If an atom is irradiated by photons having energy less than the ionization potential of atom, the atom cannot be ionized in a single photon process. It is, however, possible to ionize the atom by simultaneous absorption of several photons. The phenomena are known as Multiphoton ionization of atoms. In general the cross section for such a non linear process is very low and high power lasers are required for the observation of multiphoton ionization.

Because of dependence of transition amplitudes on intensity of absorbed light beams, it is not a surprise that absorption of intensity depends on polarization, hence multiple beams ionization is more sensitive than single photon ionization.

The unique polarization dependency of multiphoton ionization has not been exploited very much, despite its interesting application. It is a simple method for

determining and studying the symmetries of the excited states. Another application is to use its ability to distinguish species on behalf of polarization ratio. The last decade multiphoton fluorescence has especially emerged within the field of biology and neuroscience as an instrument to look deep within biological samples and is already very mature. It is also used as an instrument to deliver or activate biological active substances at specific places within tissue.

Thus, the study of **MPI** in presence of **multiple beams** is very useful spectroscopy for image processing [4] and also to gather useful information from the light carrying form cosmos (i.e as information carrier to use as photons (photonics) rather than electrons) [5]. This novel approach widely used in the investigations and unique insights into the physics of energy transfer. The most important application is the industrial application such as micromatching [6].

Multiphoton processes cover the areas as diverse as precision measurements, studies of ultra fast dynamics, laser acceleration of charged particles, laser machining of solid-state materials and medical applications. With the advent of lasers the nonlinear, or multiphoton, interactions between radiation and matter have become a key area in basic and applied research.

This studies can give a concept for the advanced scientific theories and serve as indication for future research direction, which are important in a number of application, like in laser driven plasma heating, or in the development of fast optical electronic devises [7].

Acknowlegement:

My sincere gratitude to supervisors Prof. J. J. Nakarmi, and Prof. L. N. Jha, CDP, TU. This work has been supported in part by University Grant Commission, Bhaktapur, Nepal.

References:

1. Maria Goppert-Mayer (1931), Ann. Physik 9, 273.
2. Loud B. B. (1991), *Lasers and Non-Linear Optics*, Wiley Eastern Ltd, New-Delhi.
3. Nourendine Zettile(1962), *Quantum Mechanics Concepts and Application* John Wily and Sons, New York .
4. Joseph R. Lakowice (2008), *Principles of fluoresce spectroscopy,* pp 623.
5. Santomato E. (2004), Fortshchr., Phy. 52, pp 1141.
6. Shalom Eliezer and Kunioki Mima (2009), *Application of laser plasma interactions*, CRC press, pp 246.
7. Antoine M., et al (2010), J. Phys. B: At. Mol. Opt. Phys., 43, pp 103001.

BMC,Journal of Physics,Vol 2, ISSN 2362-1494,pp16-21(2014)

AN ANALYTICAL APPROACH TO MULTIPHOTON IONIZATION IN ATOMIC HYDROGEN BY PRESENCE OF MULTIPLE BEAMS

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ABSTRACT
Analytical expression for the various multiphoton transition rates are evaluated, in the frame work of higher order perturbation theory and using the variation of Dalgarno Lewis method. It is shown that, the rate depends on a function of polarization, phase shift, intensities and frequency of the incident photon. In this formulation we can use any number of incident beams with arbitrary polarization.

I. INTRODUCTION

The advent of powerful laser in the early 1960s and its capability to create breakdown in gases has a sparked a strong interest both from the experimental as well as theoretical side. The measurements of two-photon ionization in alkali and alkaline atoms have confirmed the theoretical predictions on total cross-sections and electronic angular distributions [1]. At the sufficiently high photon ux densities, there is an increasing probability for simultaneous absorption of two or even more photons by the atom and hence the process is called Multiphoton Ionization. We consider the ground state hydrogen atom simultaneously interacts with multiple laser beams of same frequency (ω!) having different polarization, propagating along the same direction. The interaction Hamiltonian for multiple beams

$$H' = \sum_{j=1}^{n_b} \sqrt{I_j} \quad e^{-i(\omega t+\delta_j)}(\hat{\epsilon}_j \cdot \vec{r}) \tag{1}$$

II. IONIZATION RATE

The differential ionization rate for N photon absorption in a. u. has expression [2]

$$\frac{d\Gamma^{(N)}}{d\Omega} = \frac{\pi\alpha^2}{(k_f)^4}\left(\frac{\bar{I}}{I_0}\right)^N |M_{fg}^{(N)}|^2$$

where, $\bar{I}$ is mean intensity of the beams, $I_0 = 7.019\times10^{-16}\, w/cm^2$ is the atomic unit of the field strength intensity. $M_{fg}^{(N)}$ refers to the Nth order transition amplitude corresponding to a transition from the ground state g to a final continuum state f and k_f is the momentum of the ejected electron and its magnitude for an N-photon process is given by $k_f = \sqrt{2N\omega - 1}$

III. DALGARNO-LEWIS (DL) METHOD

Dalgarno-Lewis method was originally introduced for the evaluation of long range forces between atoms [3] and later on it was modified by Schwartz [4] for various orders in higher perturbation theory, while avoiding infinite sums which arise in each order. The method depends on auxiliary dimensionless operator, which enables us to perform the summation over the whole spectrum exactly. These operators are determined by a certain inhomogeneous differential

$$(\hat{\epsilon}_j \cdot \vec{r})|g\rangle = (F_j H_0 - H_0 F_j)\,|g\rangle + \omega F_j|g\rangle \tag{2}$$

$$(\hat{\epsilon}_k \cdot \vec{r})F_j|g\rangle = (G_{kj}H_0 - H_0 G_{kj})\,|g\rangle + 2\omega G_{kj}|g\rangle \tag{3}$$

For N-Photon,

$$(\hat{\epsilon}_j \cdot \vec{r})D_{N-1}|g\rangle = (D_N H_0 - H_0 D_N)\,|g\rangle + N\omega D_N|g\rangle$$

Where, $(\hat{\varepsilon}_j \cdot \vec{r})$ is the interaction part of Hamiltonian and H_0 is the unperturbed Hamiltonian.

$$H_0 = -\frac{\nabla^2}{2} - \frac{1}{r} \tag{4}$$

A. Two-photon process

In the two-photon absorption, the two-photons simultaneously transfer their energy to the atom for their transition. In the case when laser radiation contains two fields with polarization vector $\hat{\varepsilon}_j$ and $\hat{\varepsilon}_k$, the final continuum of energy $E = E_1 + 2\cong\omega$ (E_1 is the ground state energy), is reached by quantum interference of four different routes. Similar situation occurs for three beams (jth, kth and lth) of same frequency with different polarization vectors. Here the final state is obtained by quantum interference of six different routes. From second order perturbation theory, the matrix element for two photon process has the form

$$\mathcal{M}_{fg}^{(2)} = \sum_{j,k}\sum_{n} \frac{\langle f|\hat{\epsilon}_k \cdot \vec{r}|n\rangle\langle n|\hat{\epsilon}_j \cdot \vec{r}|g\rangle}{(\omega_{ng} - \omega)} \tag{5}$$

The infinite intermediate sum includes both discrete and continuum states. Now we will apply Dalgarno-Lewis's principle by defining an operator Fj such as in (2). The compact form of two photon transition amplitude becomes

$$\mathcal{M}_{fg} = \langle f|(\hat{\epsilon}_k \cdot \vec{r})F_j|g\rangle \tag{6}$$

B. Differential equation for F_j

From (2) and (4), the differential equation has the form

$$(\hat{\epsilon}_j \cdot \vec{r})\psi = \frac{\nabla^2 F_j}{2}\psi + \nabla F_j \cdot \nabla\psi + \omega F_j \psi$$

By inspection, Fj depends on unknown radial function (fj(r)) and angular function $(\hat{\varepsilon}_j \cdot \vec{r})$.

Let us define Fj as

$$F_j = (\hat{\epsilon}_j \cdot \vec{r}) f_j(r)$$

Thus the differential equation satisfied by unknown radial function f_j is

$$r f_j'' + (4 - 2r) f_j' + (2\omega r - 2) f_j = 2r \qquad (7)$$

The solution for f_j [7, 8] are given ,

$$f_j(r) = \frac{1}{\omega} - \frac{1}{2\omega^3} \Phi(1, 1, \lambda_1, 1, r)$$

Where, $\lambda_1 = \sqrt{(1 - 2\omega)}$

$$\Phi(p, q, \lambda, t, r) = \int_{\lambda}^{t} e^{-r(s-1)} K(p, q, \lambda, s) ds$$

$$K(p, q, \lambda, s) = \left(\frac{1 - \lambda}{1 + \lambda}\right)^{\frac{1}{\lambda}} (s + \lambda)^{p + \frac{1}{\lambda}} (s - \lambda)^{q - \frac{1}{\lambda}}$$

Here p and q are real numbers λ's are in general complex.

C. Three-photon Process

In 3PP, where three photons are simultaneously absorbed in one event and make a transition, allowed by three photon selection rules [9]. We have used third-order perturbation theory for studying these effects. The three photon transition matrix element is expressed as where

$$\mathcal{M}_{fg} = \sum_{m,n} \frac{\langle f|\hat{\epsilon}_l \cdot \vec{r}|m\rangle \langle m|\hat{\epsilon}_k \cdot \vec{r}|n\rangle \langle n|\hat{\epsilon}_j \cdot \vec{r}|g\rangle}{(\omega_{mg} - 2\omega)(\omega_{ng} - \omega)} \qquad (8)$$

Here, the polarization vector $\hat{\varepsilon}_j$, these vectors are normalized (such as $\hat{\epsilon}_j^* \cdot \hat{\epsilon}_j = 1$)and are propagating along z direction, i.e. polarization is in the x - y plane [10]. Since the transition matrix element for three-photon (8) includes two intermediate sums (m; n). We define one more auxiliary operator G_{jk} in addition to first operator Fj . Now proceeding in a similar manner as above, the operator Fj can be used to remove one of the energy denominator. Finally the equation becomes as

$$\mathcal{M}_{fg}^{(3)} = \langle f|\hat{\epsilon}_l \cdot \vec{r} G_{jk}|g\rangle \qquad (9)$$

D. Differential equation for G_{jk}

From (3) and (4), the differential equation has the form as:

$$\hat{\epsilon}_k \cdot \vec{r} F_j \psi \;=\; -\frac{\nabla^2 G_{jk}}{2}\psi - \nabla G_{jk} \cdot \nabla \psi - 2\omega G_{jk}\psi \qquad (10)$$

Let us define G_{jk} as,

$$G_{kj} = \left[\frac{3}{2}(\hat{\epsilon}_k \cdot \vec{r})(\hat{\epsilon}_j \cdot \vec{r}) - \frac{1}{2}(\hat{\epsilon}_k \cdot \hat{\epsilon}_j)r^2\right] g_2 + (\hat{\epsilon}_k \cdot \hat{\epsilon}_j) g_0$$

Where, the unknown radial functions g_2 and g_0 are used for l= 2 and l= 0 respectively. The differential equations satisfied by the unknown radial functions are

$$r g_0'' + (2 - 2r) g_0' + 4\omega r g_o = \frac{2}{3} r^3 f_j \qquad (11)$$

$$r g_2'' + (6 - 2r) g_2' + (4\omega r - 4) g_2 = \frac{4}{3} r f_j \qquad (12)$$

The radial part g_2 and g_0 are evaluated [8].

$$g_2(r) = \frac{1}{3\omega^2} - \frac{1}{3\omega^4}\Phi(1,1,\lambda_1,1,r) + \frac{2}{3\omega^4}\int_{\lambda_1}^{1} dt \frac{K(1,1,\lambda_1,t)t}{K(3,3,\lambda_2,t)}\Phi(2,2,\lambda_2,t,r)$$

Where, $\lambda_2 = \sqrt{1 - 4\omega}$

$$g_0(r) = \frac{2}{3\omega^2}\left[\frac{r^2}{4} + \frac{1}{4\omega^2}(1 - 2\lambda_1) - \frac{3}{8\omega}\right] - \frac{1}{3\lambda_1\omega^4}\Phi(0,0,\lambda_2,1,r) - \frac{1}{6\omega^4}\left[r^2 + \frac{\lambda_1}{\omega}r - \frac{1}{\omega}(1 + \frac{1}{\lambda_1})\right]\Phi(1,1,\lambda_1,1,r)$$
$$- \frac{1}{3\omega}\left(1 + \frac{1}{\lambda_1}\right)\int_{\lambda_1}^{1} dt \frac{K(1,1,\lambda_1,t)}{K(1,1,\lambda_2,t)} \times \left[\frac{1 - 2\omega}{\omega(1 + \lambda_1)} - \frac{t}{\omega} - \frac{2}{t + \lambda_1} + \frac{2}{(t + \lambda_1)^2}\right]\Phi(0,0,\lambda_2,t,r)$$

IV. RESULTS AND DISCUSSION

The radial parts are evaluated numerically and angular part can be performed in terms of the spherical harmonics using the orthogonality property of the Legendre Polynomials. The amplitudes for the considered process are usually added and subsequently squared. This leads to signals which are dependent on relative phase between multiple beams. Hence the multiphoton ionization rate varies with the relative phase of the two or three color beams. Because of dependence of transition probability on polarization of absorbed beams, the two and three color ionization is more sensitive than one color.

V. ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my supervisors Prof. J. J. Narkarmi and Prof. L. N. Jha. Central department of Physics (CDP), Tribhuvan University, Nepal. Many heartfelt thanks to Prof. Ramesh babu Thayyullathil, CUSAT, Kerela, India, Dr. Radhakrishanan, University of Madras, Chhenai, India and Prof. Sitaram Bhyahut CDP, TU. This work has been supported in part by University Grant Commission, Kathmandu, Nepal. INSA-NAST bilateral exchange program for funding research at Cochin University of science and technology, CUSAT, Kerala, India.

REFERENCES:

[1] Delone N. B. and Krainov V.P. (1999), Multiphoton Processes in Atoms, Springer-Verlag Berlin Heidelberg, p 190.
[2] Fifrig M. and Stroe M. (2002), Asymmetries in two photon ionization, Laser Phys., Vol 12(6), p 963.
[3] A. Dalgarno and J.T. Lewis (1955), the equivalence of variational and perturbation calculation of small disturbances, Proc. R. Soc. Lon. A 233, p 70.
[4] Charles Schwartz (1959), New Calculation of Numerical Value Lamb Shift Annals of Physics 2, p 156.
[5] Ramesh Babu T. and Prasanna K.J. (1994), Two-photon transition in atomic hydrogen Phy. Rev. A 49, p 2432.
[6] Jayadevan A. P. and Ramesh Babu T.(2001), Two-photon ionization of atomic hydrogen above the one photonn ionization
threshold J. Phys. B, At. Mol. Opt. Phy. 34, p 699.
[7] Ramesh Babu T., R. Radhakrishanan and Seema (2003), Three photon transition from ground state to bound state in atomic
hydrogen J. Phy. A, Math., Gen. 36, p 8473.
[8] R. Radhakrishanan and Seema (2003), Nonresonant multi photon ionization in atomic hydrogen, Phy. Rev. A 69, p 8473.
[9] John S. Townsend (2000), A modern Approach to quantum mechanics, University Science books print, p 93.
[10] Fifrig M. (2001), Hydrogen ionization by a coherent superposition of three harmonics, Laser physics, Vol 11(9), p 989.

Revo-science, Vol II, No. VII, page 25-26, March 2013

What is Multiphoton Ionization (MPI)

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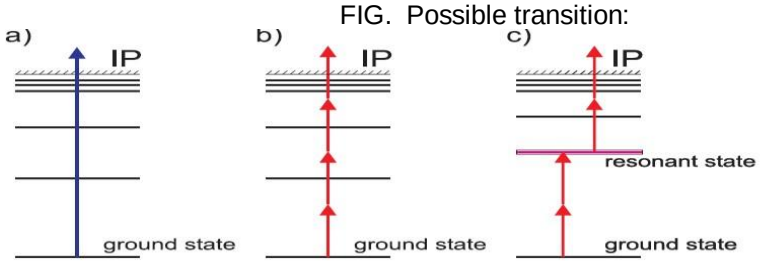
One photon ionization was first observed a hundred years ago by Hertz. It laid the foundation for the quantum treatment of light. At the sufficiently high photon flux densities, however, there is an increasing probability for simultaneous absorption of two or even more photons by the atom and hence the process is called Multiphoton Ionization. If the total energy (E) of these K absorbed photons is greater than ionization potential (E0) energy of atom, the atom A is ionized by light field, whose single photon energy ⊚ is much less than ionization energy.

$$A + K\circledcirc = A^+ + e^-$$

MPI of atom by the minimum energetically necessary number of photon was first observed by Voronov and Delone [1] only the few years after invention of laser. As atom posses discrete negative energy spectra, there are resonant and non-resonant multiphoton processes. In the case of non resonant mpi, no intermediate states have the same energy as the atomic states in the discrete spectrum. When one or more intermediate states coincide with atomic states we have resonance-enhance multiphoton ionization processes [2].

FIG. Possible transition:



Photoionization of an atom:a) Single photon ionization (photo effect); b) Non-resonant multiphoton ionization (NRMPI or simply MPI); c) Resonance enhanced multiphoton ionization (REMPI).

In strong fields atom may absorb not only the minimum energetically necessary of photons, but one or more excess photons, called ATI [3], [4]. The energy of extra absorbed photon is converted entirely into the kinetic electron of emitted electron. Therefore the photon electron energy spectra must be studied, which became possible only with the development of methods of photoelectron spectroscopy with very high energy resolution. The first experiment on ATI was carried out by Agostini et al [5].

Energy conservation mandates that the photoelectron leaves the atom with the energy [6], [7].

$$E = K\circledcirc - E_0 = (N + S)\circledcirc - E_0, \quad S = 0, 1, 2, 3 \ldots\ldots$$

Where, ⊚ is the energy of the photon, E_0 is the ionization potential energy of atom, N is the minimum energetically necessary number of photons for the ionization and S is the number excess photons. Atomic units are used.

Most MPI are performed with rare gases [8]. Until now there have been few MPI and ATI experiments for atomic hydrogen, Luven et al (1976), Muller(1986), Fieldmen et al(1987), Wolf et al(1988) [9], though as the simplest of the atoms atomic hydrogen is of interest in its own right. The wave function of atomic hydrogen are well known. Therefore, rather good approximation may be obtained. Besides the results of calculations of cross-sections for atomic hydrogen provide an estimate of the lowest limits for cross-sections of other atoms [10]. A moderate intensities nonresonant multiphoton ionization may be considered within the framework of perturbation theory. Perturbation theory proves to be valid up to intensity of light I = 10^{13}Wcm^{-2} in the case of ionization from the ground state and N ⊚ 8.

Starting with the pioneering work of Goppert-Mayer(1931) on two -photon absorption up, until now perturbation theory is the most widely used in multiphoton calculations for atomic hydrogen. At moderate intensities, direct multiphoton ionization as well as above threshold ionization may be satisfactorily treated by the method of perturbation theory. There are three methods that are used to investigate multiphoton processes: the method of solving the set of inhomogenous differential equations, the Green function method [11] and [12] and variational method [13], [14].

Zernik(1964) and Zernik and Klopfenstein(1965) started with two photon ionization of atomic hydrogen in the 2s metastable state. To calculate transition matrix elements, they solved the first-order inhomogenous differential equations. This technique was first proposed by Dalgarno and Lewis[15] and later reformulated by Schwartz and Tiemen[16].

The first to investigate MPI of atomic hydrogen, rare gases, and alkali atoms when large number of photon participate were Bebb and Gold[17] and Bebb[18]. They used Green function method. The Green's function energy eiegnfunction expansion

$$G_{L}(r,r',\omega) = -\frac{R_{nL}(r)R_{nL}(r')}{\omega - E_{n}} - \int_{0}^{\infty}\frac{R_{EL}(r)R_{EL}(r')dE}{\omega - E}$$

was employed. In the case of atomic hydrogen R_{nL} and R_{EL} are the radial parts of discrete and continuum states wavefunctions of atomic hydrogen.

For two-photon absorption [19]

Let,$M_{mg}^{(2)}$, is the transition matrix element for two-photon ionization, for same frequency (ω) of different polarization. We can derive by dropping the antiresonance terms such as

$$M_{mg}^{(2)} = \sum_{j,k}\sum_{n}\frac{(m|\$_{k}\cdot r|n)(n|\$_{j}\cdot r|g)}{(\omega_{ng}-\omega)}$$

Similarly, for three-photon absorption

$$M_{fg}^{(3)} = \sum_{j,k,l}\sum_{m,n}\frac{(f|(s_{j}\hat{}\cdot r)|m)(m|(s_{k}\hat{}\cdot r)|n)(n|(s_{j}\hat{}\cdot r)|g)}{(\omega_{ng}-\omega)(\omega_{mg}-2\omega)}$$

Importance of MPI

A spectrum of these multiphoton transitions often displays quite different information from normal single photon spectrum because of altered selection rules and transition intensities. Entirely new states and vibration are seen in multiphoton spectra that provide a much more complete understanding of excited state structure. Atoms, molecules and ions are the basic building blocks of all complete structures in the universe and understanding of their structure and dynamics of their interaction is of fundamental relevance not only in physics, but also in chemistry, biology, medicine, astronomy and material science and scientific treatment of many systems on physical quantum level is becoming of increasing importance.

Acknowledgement:

My heartfelt thanks to my supervisors Prof. Dr. J. J. Nakarmi and Prof. Dr. L. N. Jha, Central Department of Physics, TU, Kritipur.

References:

1. Delone N. B. and Krainov V. (1999), Multiphoton Processes in Atoms, pp 190.
2. Fox M. (2006), Quantum Optica, An Introduction Oxford university press, pp 169.
3. Lin S. H. et al (2004), Advances in Multiphoton Processes and Spectroscopy, Vol 16, World Scientific.
4. Mikhail V. Fedorov (1997), Atomic and free electrons in a strong light field, World scientific.
5. Agostini P. et al (1979), Free-Free transition following Six photon ionization of Xenon atoms, Phy. Rev. Lett., Vol 42(17), pp 1127.
6. Karule E. et al (2010), J. Phys. B: At. Mol. Opt, Phys., 43, pp 065601.
7. Karule E.et al (1988), J. Phy.Phy. B At. Mol. and Opt Phy. 21, pp 1997.
8. R. Bhardwaj et al, Modification of fused silica using femtosecond multiphoton ionization, Ottawa, ON Canada.
9. Morellec J. et al (1980), Phy. Rev. Lett. Vol 44(21), pp 1394.
10. Lambropoulos P. and Petrosyan D. (2007), Fundamental of Quantum Optics and Quantum Information, Springer-Verlag Berlin Heidelberg, pp 76.
11. G.Leplanche et al (1976), J. Phys. B: Atom.Molec. Phys. 9(8), pp 1263.
12. Mark Edwards (1992), Phys. Rev. A: 46, pp 7228.
13. Gao Bo et al (1988), Phy. Rev. Lett., Vol 61, pp 404.
14. Gao Bo et al (1989), Phy. Rev A,Vol. 39 (9), pp 4550,
15. Dalgarno A. and Lewis J.T.(1956), Proc. Phys. Soc. A: 69, pp 628.
16. Schwartz C. (1959), Annals of Physics 2, pp 156.
17. Bebb H. Barry (1967), Phy. Rev. Vol 153(1), pp 153.
18. Bebb H. Barry and Gold Albert(1966), Phy. Rev. Vol 143(1), pp 1.
19. N.Shrestha and J.J. Nakarmi (2011), One, Two and Three Photon Absorption in Atomic Hydrogen , Nepal Journal of Science and Technology, Vol 12, pp 324-329.

Appendix B

Atomic Units and Q C relation

Atomic Units

For the theoretical purpose, it is more convenient to introduce an atomic units, in which certain of these universal constants are set equal to unity. Four fundamental physical constants are set to unity such as:

$$\mathrm{k} = m = e = a_0 = 1 a.u.$$

Since the Bohr radius is defined as

$$a_0 = \frac{4\pi\epsilon_0 \mathrm{k}^2}{me^2}$$

this system of units is of Gaussian type, where $\epsilon_0 = \frac{1}{4\pi}$ The atomic unit of energy is Hartree, with

$$1 \text{ Hartree} = \frac{e^2}{4\pi\epsilon_0 a_0} = 27.2116 eV$$

The atomic unit of time is derived from the atomic unit of energy as

$$\mathrm{k} = a.u._{\text{energy}} \times a.u._{\text{time}} \Longrightarrow a.u._{\text{time}} = \frac{\mathrm{k} a_0}{e^2} = 24.2 \times 10^{-18} \mathrm{s}$$

The atomic field strength in ground state of Hydrogen atom is obtained from Coulomb law

$$|E_0| = \frac{e}{4\pi\epsilon_0 a_0^2} = 5.14 \times 10^9 \frac{\mathrm{V}}{\mathrm{cm}}$$

and from this one derives the atomic unit of intensity as

$$1a.\ u.\ of\ Intensity = \frac{1}{2} c\epsilon_0 E_0^2 = 3.5 \times 10^{16} \frac{W}{cm^2}$$

Some atomic units for physical quantities are:

- 1 a.u. intensity = $3.51 \times 10^{16} W cm^{-2} -> |F|$(Electric field) = 1 a.u.$->$ applied electric field = Coulomb field at 1 a.u. from a Coulomb center.
- 1 a.u. length = a_0= Bohr radius
- 1 a.u. frequency = 1 a.u. energy = 2R (Reydberg Constant)= 27.2 eV $->$ λ = $45.56 nm$

Quantum and Classical relation

We have used the following Classical and Quantum mechanical relation, where, the symbols have their own meanings, i. e. m = mass of the electron, e = charge of electron and v = velocity of electron.

Serial number	Classical dynamical variables	Classical mathematical symbol	Quantum mechanical operator
1	Linear momentum for a single particle	P(t)=mv(t)	$-i\mathrm{k}\nabla$
2	Kinetic energy for a single particle	$\frac{1}{2}mv^2$	$(-\frac{\mathrm{k}^2}{2m})\nabla^2$
3	Potential energy for a single particle	V(r,t)	V(r,t)
4	Orbital angular momentum for a single particle	r×p	$\mathrm{L}=\frac{1}{\mathrm{k}}[r \times (-i\mathrm{k}\nabla)]$
5	Linear momentum for many particles	$\sum_j p_j(A)$	$\sum_j -i\mathrm{k}\nabla_j$
6	Kinetic energy for many particles	$\sum_j \frac{1}{2} m_j v_j^2$	$\sum_j (-\frac{\mathrm{k}^2}{2m})\nabla_j^2$
7	Potential energy for many particles	$\sum_{ij} V(r_i, r_j, t)$	$\sum_{ij} V(r_i, r_j, t)$

Appendix C

Some useful vector derivatives

Some useful vector derivatives

Cartesian

$$dl = dx\,\hat{x} + dy\,\hat{y} + dz\,\hat{z}, \qquad \text{and} \qquad d\tau = dx\,dy\,dz$$

Gradient: $$\nabla t = \frac{\partial t}{\partial x}\hat{x} + \frac{\partial t}{\partial y}\hat{y} + \frac{\partial t}{\partial z}\hat{z}$$

Divergence: $$\nabla \cdot v = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}$$

Curl:

$$\nabla \times v = \left(\frac{\partial v_z}{\partial y} - \frac{\partial v_y}{\partial z}\right)\hat{x} + \left(\frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x}\right)\hat{y} + \left(\frac{\partial v_y}{\partial x} - \frac{\partial v_x}{\partial y}\right)\hat{z}$$

Laplacan: $$\nabla^2 t = \frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2}$$

Spherical

Gradient : $$\nabla v = \frac{\partial v}{\partial r}\hat{r} + \frac{1}{r}\frac{\partial v}{\partial \vartheta}\hat{\vartheta} + \frac{1}{r\sin\vartheta}\frac{\partial v}{\partial \varphi}\hat{\varphi}$$

Divergence: $$\nabla \cdot v = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 v_r) + \frac{1}{r\sin\vartheta}\frac{\partial}{\partial \vartheta}(\sin\vartheta\, v_\vartheta) + \frac{1}{r\sin\vartheta}\frac{\partial v_\varphi}{\partial \varphi}$$

Curl:

$$\nabla \times v = \frac{1}{r\sin\vartheta}\left[\frac{\partial}{\partial\vartheta}(\sin\vartheta v_\varphi) - \frac{\partial v_\vartheta}{\partial\varphi}\right]\hat{r} + \frac{1}{r}\left[\frac{1}{\sin\vartheta}\frac{\partial v_r}{\partial\varphi} - \frac{\partial}{\partial r}(rv_\varphi)\right]\hat{\vartheta} + \frac{1}{r}\left[\frac{\partial}{\partial r}(rv_\vartheta) - \frac{\partial v_r}{\partial\vartheta}\right]\hat{\varphi}$$

Laplacian:

$$\nabla^2 v = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial v}{\partial r}\right) + \frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial v}{\partial\vartheta}\right) + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2 v}{\partial\varphi^2}$$

Here,

$$\hat{r} = \frac{\vec{r}}{r}$$

$$\nabla(\hat{\epsilon}_i \cdot \vec{r}) = \nabla(\hat{\epsilon}_i \cdot \hat{r}\, r) = (\hat{\epsilon}_i \cdot \hat{r})\nabla r = (\hat{\epsilon}_i \cdot \hat{r})\hat{r} = \hat{\epsilon}_i$$

We also have,

$$\begin{aligned} x &= r\sin\vartheta\cos\varphi \\ y &= r\sin\vartheta\sin\varphi \\ z &= r\cos\vartheta \\ r &= \sqrt{(x^2 + y^2 + z^2)} \\ \vartheta &= \tan^{-1}\left(\frac{\sqrt{x^2 + y^2}}{z}\right) \\ \varphi &= \tan^{-1}(y/x) \end{aligned}$$

The unit vectors of polar co-ordinates are,

$$\begin{aligned} \hat{r} &= \sin\vartheta\cos\varphi\hat{x} + \sin\vartheta\sin\varphi\hat{y} + \cos\vartheta\hat{z} \\ \hat{\vartheta} &= \cos\vartheta\cos\varphi\hat{x} + \cos\vartheta\sin\varphi\hat{y} - \sin\vartheta\hat{z} \\ \hat{\varphi} &= -\sin\varphi\hat{x} + \cos\varphi\hat{y} \end{aligned}$$

And,

$$\hat{r} \times \hat{r} = 0, \quad \hat{r} \times \hat{\vartheta} = \varphi \quad and \quad \hat{\vartheta} \times \hat{r} = -\varphi$$

Where the unit vectors $\hat{x}$, $\hat{y}$, and $\hat{z}$ are

$$\begin{aligned} \hat{x} &= \sin\vartheta\cos\varphi\hat{r} + \cos\vartheta\cos\varphi\hat{\vartheta} - \sin\varphi\hat{\varphi} \\ \hat{y} &= \sin\vartheta\sin\varphi\hat{r} + \cos\vartheta\sin\varphi\hat{\vartheta} + \cos\varphi\hat{\varphi} \\ \hat{z} &= \cos\vartheta\hat{r} - \sin\vartheta\hat{\vartheta} \end{aligned}$$

$$\int \hat{r}_\alpha \hat{r}_\beta \, d\Omega = \frac{4\pi}{3}\delta_{\alpha\beta}$$

$$\int \hat{r}_\alpha \hat{r}_\beta \hat{r}_\lambda \hat{r}_\gamma \, d\Omega = \frac{4\pi}{15}[\delta_{\alpha\beta}\delta_{\lambda\gamma} + \delta_{\alpha\gamma}\delta_{\beta\lambda} + \delta_{\alpha\lambda}\delta_{\beta\gamma}]$$

$$\hat{\epsilon}_j \cdot \hat{r} = \sum_l (\hat{\epsilon}_j)_l \hat{r}_l$$

$$\hat{\epsilon}_j \cdot \hat{r}\hat{\epsilon}_k \cdot \hat{r} = \sum_l (\hat{\epsilon}_j)_l \hat{r}_l \sum_n (\hat{\epsilon}_k)_n \hat{r}_n$$

$$\sum_{ln} (\hat{\epsilon}_j)_l (\hat{\epsilon}_k) \int \hat{r}_n \hat{r}_l d\Omega = (\hat{\epsilon}_j)_l (\hat{\epsilon}_k) \frac{4\pi}{3}\delta_{ln}$$

$$\int (\hat{\epsilon}_j \cdot \hat{r})(\hat{\epsilon}_k \cdot \hat{r}) d\Omega = \sum_{ln} (\hat{\epsilon}_j)_l (\hat{\epsilon}_k)_n \int \hat{r}_l \hat{r}_n d\Omega$$

$$= \frac{4\pi}{3}(\hat{\epsilon}_j)_l \cdot (\hat{\epsilon}_k)_n \delta_{ln}$$

And

$$\int (\hat{\epsilon}_j \cdot \hat{\epsilon}_k) d\Omega = 4\pi(\hat{\epsilon}_j \cdot \hat{\epsilon}_k)$$

$$dl = dr\,\hat{r} + r\,d\vartheta\,\hat{\vartheta} + r\,\sin\vartheta\,d\varphi\,\hat{\varphi} \qquad \text{and} \qquad d\tau = r^2 \sin\vartheta\, dr\, d\vartheta\, d\varphi$$

Some Legendre polynomial integration

We have

$$P_0(x) = 1,\ P_1(x) = x,\ P_2(x) = 1/2(3x^2 - 1),\ P_3(x) = 1/2(5x^3 - 3x)$$

For two-photon ionization

Case(I) D *For* $l = 0$

$$\int P_l(\hat{k} \cdot \hat{r}) d\Omega = \int P_0(\hat{k} \cdot \hat{r}) d\Omega$$

$$= \int_0^\pi 1 \times \sin\vartheta d\vartheta \int_0^{2\pi} d\varphi$$

$$= [-\cos\vartheta]_0^\pi [2\pi]$$

$$= [2\pi]\, 2\pi$$

$$= 4\pi$$

$$\int P_0(\hat{k} \cdot r)\hat{\epsilon}_i \cdot \hat{r}\hat{\epsilon}_j \cdot \hat{r} d\Omega = \frac{4\pi}{3}\,\hat{\epsilon_i} \cdot \hat{\epsilon_j}$$

Case(II) D *For* $l = 2$

$$\int P_2(\hat{k}\cdot r)\hat{\epsilon}_i\cdot\hat{r}\hat{\epsilon}_j\cdot\hat{r}d\Omega$$

$$= \frac{1}{2}\int [3(\hat{k}\cdot r)^2 - 1]\hat{\epsilon}_i\hat{r}\hat{\epsilon}_j\hat{r}d\Omega$$

$$= \frac{1}{2}\frac{4\pi}{15}3\left[\hat{k}\cdot\hat{\epsilon}_i\hat{k}\cdot\hat{\epsilon}_j + \hat{k}\cdot\hat{\epsilon}_j\hat{k}\cdot\hat{\epsilon}_i + \hat{\epsilon}_i\cdot\hat{\epsilon}_j\right] - \frac{1}{2}\frac{4\pi}{3}\hat{\epsilon}_i\hat{\epsilon}_j$$

$$= \frac{1}{2}\frac{4\pi}{15}\left[3(\hat{k}_i\cdot\hat{\epsilon})(\hat{k}_j\cdot\hat{\epsilon}) - \hat{\epsilon}_i\hat{\epsilon}_j\right]$$

For three photon ionization

Case(I) D *For* $l = 1$

$$\int P_l(\hat{k}\cdot\hat{r})(\hat{\epsilon}_i\cdot\hat{r})d\Omega = \int P_1(\hat{k}\cdot\hat{r})(\hat{\epsilon}_i\cdot\hat{r})d\Omega$$

$$= \int_0^{\pi}(\hat{k}\cdot\hat{r})(\hat{\epsilon}_i\cdot\hat{r})\times\sin\vartheta d\vartheta\int_0^{2\pi}d\varphi$$

$$= (\hat{k}\cdot\hat{r})(\hat{\epsilon}_i\cdot\hat{r})[-\cos\vartheta]_0^{\pi}[2\pi]$$

$$= (\hat{k}\cdot\hat{r})[2\pi]2\pi = \frac{4\pi}{3}\hat{k}\cdot\hat{\epsilon}_i$$

$$\int P_1(\hat{k}\cdot r)(\hat{\epsilon}_i\cdot\hat{r})(\hat{\epsilon}_j\cdot\hat{r})(\hat{\epsilon}_k\cdot\hat{r})d\Omega = \int P_1(\hat{k}\cdot r)(\hat{\epsilon}_k\cdot\hat{r})(\hat{\epsilon}_j\cdot\hat{\epsilon}_i)d\Omega \qquad \text{(C.1)}$$

$$\int P_1(\hat{k}\cdot r)(\hat{\epsilon}_i\cdot\hat{r})(\hat{\epsilon}_j\cdot\hat{r})(\epsilon_k\cdot\hat{r})d\Omega = \frac{4\pi}{15}\left[\hat{k}\cdot\hat{\epsilon}_i\hat{\epsilon}_j\cdot\hat{\epsilon}_k + \hat{k}\cdot\hat{\epsilon}_j\hat{\epsilon}_i\cdot\hat{\epsilon}_k + \hat{k}\cdot\hat{\epsilon}_k\hat{\epsilon}_i\cdot\hat{\epsilon}_j\right]$$

$$\int P_1(\hat{k}\cdot r)(\hat{\epsilon}_k\cdot\hat{r})(\hat{\epsilon}_i\cdot\hat{\epsilon}_k)d\Omega = \frac{4\pi}{3}\hat{k}\cdot\hat{\epsilon}_k\hat{\epsilon}_i\cdot\hat{\epsilon}_j$$

$$\int P_1(\hat{k}\cdot r)(\hat{\epsilon}_k\cdot\hat{r})\frac{1}{2}\left[3(\hat{\epsilon_i}\cdot\hat{r})(\hat{\epsilon_j}\cdot\hat{r}) - (\hat{\epsilon_i}\cdot\hat{\epsilon_j})\right]d\Omega$$

$$= \frac{1}{2}\frac{4\pi}{15}\left[3\hat{k}\cdot\hat{\epsilon}_i\epsilon_j\cdot\hat{\epsilon}_k + 3\hat{k}\cdot\hat{\epsilon}_i\hat{\epsilon}_j\cdot\hat{\epsilon}_k - 2\hat{k}\cdot\hat{\epsilon}_k\hat{\epsilon}_i\cdot\hat{\epsilon}_j\right]$$

Case II D *For* $l = 3$

$$\int (\hat{k}\cdot\hat{r})^3(\hat{r}\cdot\hat{\epsilon}_k)(\hat{\epsilon}_i\cdot\hat{\epsilon}_j)d\Omega = \frac{4\pi}{15}(\hat{\epsilon}_i\cdot\hat{\epsilon}_j)\times 3(\hat{k}\cdot\hat{\epsilon}_k)$$

$$\int (\hat{k}\cdot\hat{r})(\hat{r}\cdot\hat{\epsilon}_k)(\hat{\epsilon}_i\cdot\hat{\epsilon}_j)d\Omega = \frac{4\pi}{3}(\hat{k}\cdot\hat{\epsilon}_k)(\hat{\epsilon}_i\cdot\hat{\epsilon}_j)$$

$$\int P_3(\hat{k}\cdot\hat{r})(\hat{r}\cdot\hat{\epsilon}_k)(\hat{\epsilon}_i\cdot\hat{\epsilon}_j)d\Omega$$

$$= \frac{1}{2}\times\frac{4\pi}{15}\times 5\hat{k}\cdot\hat{\epsilon}_k(\hat{\epsilon}_i\cdot\hat{\epsilon}_j) - \frac{1}{2}\times 3\frac{4\pi}{3}\hat{k}\cdot\hat{\epsilon}_k(\hat{\epsilon}_i\cdot\hat{\epsilon}_j)$$

$$= \frac{1}{2}\frac{4\pi}{3}\times -2(\hat{k}\cdot\hat{\epsilon}_k)(\hat{\epsilon}_i\cdot\epsilon_j)$$

$$\int (\hat{k}\cdot\hat{r})^3(\hat{\epsilon}_i\cdot\hat{r})(\hat{\epsilon}_j\cdot\hat{r})(\hat{\epsilon}_k\cdot\hat{r})d\Omega = \frac{4\pi}{105}\times$$

$$\left[6\hat{k}\cdot\hat{\epsilon}_i\hat{k}\cdot\hat{\epsilon}_j\hat{k}\cdot\hat{\epsilon}_k + 3\hat{k}\cdot\hat{\epsilon}_i\hat{\epsilon}_j\cdot\hat{\epsilon}_k + 3\hat{k}\cdot\epsilon_j\epsilon_i\cdot\epsilon_k + 3\hat{k}\cdot\hat{\epsilon}_k\hat{\epsilon}_i\cdot\hat{\epsilon}_j\right]$$

$$\int (\hat{k}\cdot\hat{r})(\hat{\epsilon}_i\cdot\hat{r})(\epsilon_j\cdot\hat{r})(\hat{\epsilon}_k\cdot\hat{r})d\Omega = \frac{4\pi}{15}\left[\hat{k}\cdot\hat{\epsilon}_i\hat{\epsilon}_j\cdot\hat{\epsilon_k} + \hat{k}\cdot\hat{\epsilon}_j\hat{\epsilon}_i\cdot\hat{\epsilon}_k + \hat{k}\cdot\hat{\epsilon}_k\hat{\epsilon}_i\cdot\hat{\epsilon}_j\right]$$

$$\int P_3(\hat{k}\cdot\hat{r})(\hat{\epsilon}_i\cdot\hat{r})(\hat{\epsilon}_j\cdot\hat{r})(\hat{\epsilon}_k\cdot\hat{r})d\Omega$$

$$= \frac{1}{2}\times\frac{4\pi}{105}\times 5\left[6\hat{k}\cdot\hat{\epsilon}_i\hat{k}\cdot\hat{\epsilon}_j\hat{k}\cdot\hat{\epsilon}_k + 3\hat{k}\cdot\hat{\epsilon}_i\hat{\epsilon}_j\cdot\hat{\epsilon_k} + \cdots\right] + 3\frac{4\pi}{15}\left[\hat{k}\cdot\hat{\epsilon}_i\hat{\epsilon}_j\cdot\hat{\epsilon_k}\right]$$

$$= \frac{1}{2}\frac{4\pi}{105}6\left[5\hat{k}\cdot\hat{\epsilon}_i\hat{k}\cdot\hat{\epsilon}_j\hat{k}\cdot\hat{\epsilon}_k - \hat{k}\cdot\hat{\epsilon}_i\hat{\epsilon}_j\cdot\hat{\epsilon_k} - \hat{k}\cdot\hat{\epsilon}_j\epsilon_i\cdot\epsilon_k - \hat{k}\cdot\hat{\epsilon}_k\hat{\epsilon}_i\cdot\hat{\epsilon}_j\cdots\right]$$