A THEORETICAL STUDY OF EXCITATION CROSS SECTION FOR HELIUM ATOM AND CALCULATION OF ITS GROUND STATE ENERGY

Submitted to the Central Department of Physics
University Campus, Tribhuvan University
In the partial fulfillment of the requirement for
MASTER'S DEGREE OF SCIENCE
IN PHYSICS

By
Dhanik Lal Kushwaha
Central Department of Physics
Tribhuvan University
Kathmandu, Nepal

A THEORETICAL STUDY OF EXCITATION CROSS SECTION FOR HELIUM ATOM AND CALCULATION OF ITS GROUND STATE ENERGY

Submitted to the Central Department of Physics

University Campus, Tribhuvan University

In the partial fulfillment of the requirement for

MASTER'S DEGREE OF SCIENCE

IN PHYSICS

By

Dhanik Lal Kushwaha

Central Department of Physics

Tribhuvan University

Kathmandu, Nepal

Aug-2010

RECOMMENDATION

It is certified that **Mr. Dhanik Lal Kushwaha** has carried out the dissertation work entitled **"A Theoritical Study Of Excitation Cross Section For Helium Atom And Calculation Of Its Ground State Energy "** under my supervisions and guidance. I recommend the dissertation in the partial fulfillment for the requirement of **Master's Degree of Science in Physics** at Tribhuvan University.

……………………………………………
………

Professor Dr. Jeevan Jyoti Nakarmi
Central Department of Physics
Tribhuvan University, Kirtipur
Kathmandu, Nepal

Date :-………………………………….

EVALUATION

We certify that we have read this dissertation and in our opinion, it is satisfactory in the scope and quality as a dissertation in the partial fulfillment for the requirement of Master's Degree of Science in Physics.

Evaluation Committee

……………………………………………

……………………………………

Prof. Dr. Jeevan Jyoti Nakarmi

Supervisor

Central Department of Physics

Tribhuvan University, Kirtipur

Kathmandu, Nepal

Prof. Dr.Lok Narayan Jha

Head

Central Department of Physics

Tribhuvan University, Kirtipur

Kathmandu, Nepal

………………………..…………

……………………………………..

External Examiner

Internal Examiner

Date :-……………………………..…

ACKNOWLEDGEMENT

I would like to express my sincere gratitude to my supervisor Prof. Dr. Jeevan Jyoti Nakarmi for suggesting the problem and providing proper guidance with constant inspiration throughout the work. His wide knowledge, logical way of thinking and cooperativeness has been a great value for me. His motivation and assistance at all times has been of immense value.

I express my sincere gratitude to all the my teachers of Central Department of Physics, Tribhuvan University, Kirtipur, especially Prof. Dr. L. N. Jha (Head central Department of Physics), and to my all respected teachers Prof.Dr. D. R. Mishra, Prof. Dr. S. Gurung, Prof. Dr. S. K. Aryal, Prof. Dr. M. M. Aryal, Prof. Dr. S.R. Byahut, Dr. N. B. Maharjan, Dr. Raju Khanal, Dr. Binil Aryal, Dr. Narayan Adhikari, A.D. Panta for their valuable guidance and knowledge given to me during throughout my work.

I would like to extend the acknowledgement to all my friends especially Nabraj Pyakurel, Subash shah, Dharmendra Singh, Shabbir Hussain, Arun Gupta, Rajendra Kushwaha, Rahul singh, Satendra Sah, Surya Singh, D.L. Mahato, Aachal Singh & Anil Kushwaha.

Finally, I must express my deepest gratitude and appreciation to my parents & my lovely wife Kajol Singh for providing me academic environment.

Dhanik Lal Kushwaha

ABSTRACT

The present work deals with the theoretical study of excitation cross section for Helium atom & calculation of its ground state energy. The excitation scattering of electrons from helium atom is investigated in order to examine quantitatively errors introduced by the fact that the description of the helium target is only approximately known. The cross section is calculated in Born Approximation using matrix elements which weight wave functions differently. Similar shapes for angular distribution and total cross section versus energy curves are obtained although absolute values differ. The ground state energy of Helium atom is calculated by: (i) Perturbation method (ii) Variational method and (iii) Hartree-Fock method. The ground state energy of helium atom obtained by the Hartree-Fock method is much close to the experimental value than the variational and the perturbation method.

CONTENTS

Chapter I

FUNDANENTAL OF EXCITATION

1.1 Introduction

Helium is an element and the next simplest atom to solve after the hydrogen atom. Helium is composed of two electrons in orbit around a nucleus containing two protons along with either one or two neutrons, depending on the isotope. The hydrogen atom is used extensively to aid in solving the helium atom. The Niles Bohr model of the atom gave a very accurate explanation of the hydrogen spectrum, but when it came to helium it collapsed. Werner Heisenberg developed a modification of Bohr's analysis but it involved half-integral values for the quantum number. Thomas-Fermi theory, also known as density functional theory, is used to obtain the ground state energy levels of the helium atom along with the Hartree-Fock method.

Helium is the least reactive noble gas after neon and thus the second least reactive of all elements. It is inert and monatomic in all standard conditions. Due to helium's relatively low molar (atomic) mass, in the gas phase its thermal conductivity, specific heat, and sound speed are all greater than any other gas except hydrogen. For similar reasons, and also due to the small size of helium atoms, helium's diffusion rate through solids is three times that of air and around 65% that of hydrogen. Helium is less water soluble than any other gas known, and helium's index of refraction is closer to unity than that of any other gas. Helium has a negative Joule-Thomson coefficient at normal ambient temperatures, meaning it heats up when allowed to freely expand. Only below its Joule-Thomson inversion temperature (of about 32 to 50 K at 1 atmosphere) does it cool upon free expansion. Once pre cooled below this temperature, helium can be liquefied through expansion cooling.

Most extraterrestrial helium is found in a plasma state, with properties quite different from those of atomic helium. In plasma, helium's electrons are not bound to its nucleus, resulting in very high electrical conductivity, even when the gas is only partially ionized. The charged particles are highly influenced by magnetic and electric fields. For example, in the solar wind together with ionized hydrogen, the particles interact with the Earth's magnetosphere giving rise to Birkeland currents and the aurora.

Excitation is an elevation in energy level above an arbitrary baseline energy state. In physics, there is a specific technical definition for energy level which is often associated with an atom being excited to an excited state. In quantum mechanics an excited state of a system (such as an atom, molecule or nucleus) is any quantum state of the system that has a higher energy than the ground state (that is, more energy than the absolute minimum). Total cross sections for the ionization and excitation of atoms and molecules by electron impact is one of the essential sets of data needed in a wide range of applications, such as modeling plasmas for plasma processing of semiconductors, designing mercury-free fluorescent lamps, assessing the efficiency of ion gauges, normalizing mass spectrometer output, diagnosing plasmas in magnetic fusion devices, and modeling radiation effects on materials.

The accuracy of standard theoretical methods for ionization cross sections depends both on the quality of wave functions as well as the collision theory used. Many theories work well at high incident energies, but few can be trusted at low incident energies, particularly near the ionization threshold. Also, theories that require continuum wave functions are difficult to use on molecules because calculating continuum wave functions for molecules suitable for ionization cross sections is in general a very difficult task, particularly for polyatomic molecules. To date, major sources of ionization cross sections for molecules were experiments and theories-- often semi empirical--that worked well only on limited types of targets and/or limited ranges of energy.

The excitation scattering of electrons from helium atom is investigated in order to examine quantitatively the errors introduced by the fact that the description of the helium target is only approximately known. The cross section is calculated in Born Approximation using matrix elements which weight wave functions differently. Similar shapes for angular distribution and total cross section versus energy curves are obtained although absolute values differ. Theoretical Born-approximation total cross sections are presented for the simultaneous ionization and excitation to the 2p state of the helium atom under electron impact. Cross sections are computed to 200 ev incident electron energy. These results fall substantially below a recent measurement and the cause of this discrepancy is investigated by performing second Born calculations for selected triply differential cross sections. Approximation using equivalent matrix elements, which weight the wave functions differently in space. Similar shapes for angular distribution and total cross section.

Inelastic collisions between fast electron and atoms can be considered by means of the Born approximation. The condition for the Born approximation to be applicable is that the velocity of the incident electron should be large compared with those of the atomic electrons. The energy loss in the collision may have any value. If the electron loses a considerable part of its energy, the atom is ionized, the energy being transferred to one of its electron. However, we can always regard as the scattered electron that which has the greater velocity after the collision; thus, if the velocity of the incident electron is large, that of the scattered electron is also large .

In a collision between an electron and an atom, the coordinate system in which their centre of mass is at rest. An inelastic collision is accompanied by a change in the internal state of the atom. The atom may go from the normal state to an excited state of the discrete or continuous spectrum, the latter case signifies an ionization of the atom. In deriving the general formulae we can consider the two cases together. We start from the general formula for the transition probability between the states of the continuous spectrum and apply it to the system consisting of the incident electron and the atom.

1.2 Helium atom excitation reviews

The first recorded He diffraction experiment was completed in 1930 by Estermann and Stern [1] on the (100) crystal face of lithium fluoride. This experimentally established the feasibility of atom diffraction when the de Broglie wavelength, λ, of the impinging atoms is on the order of the interatomic spacing of the material. At the time, the major limit to the experimental resolution of this method was due to the large velocity spread of the helium beam. It wasn’t until the development of high pressure nozzle sources capable of producing intense and strongly monochromatic beams in the 1970’s that has gained popularity for probing surface structure. Interest in studying the collision of rarefied gases with solid surfaces was helped by a connection with aeronautics and space problems of the time. Plenty of studies showing the fine structures in the diffraction pattern of materials using helium atom scattering were published in the 1970s. However, it wasn't until a third generation of nozzle beam sources was developed, around 1980, that studies of surface phonons could be made by helium atom scattering. These nozzle beam sources were capable of producing helium atom beams with an energy resolution of less than 1 meV, making it possible to explicitly resolve the very small energy changes resulting from the inelastic collision of a helium atom with the vibrational modes of a solid surface, so HAS could now be used to probe lattice dynamics. The first measurement of such a surface phonon dispersion curve was reported in 1981 [3], leading to a renewed interest in helium atom scattering applications, particularly for the study of surface dynamic

Phlip M. becker and John S.bahler in 1964 A.D. carried out the theory and calculation of cross section for the electron-impact excitation of double excitation states in Helium which are stable to autoionisation. The cross section are found to exhibit sharp peak just above the threshold energies for excitation and to decrease rapidly with further increase of energy.

Electron-impact Helium double excitation within the S-wave model was given by C.plottke, P.Nicol and I. Bray as published in journal of physics B:Atomic, Molecular and optics physics. According this paper the Laguerre-based Convergent close coupling method is used to calculated the electron-impact excitation cross section of the auto ionization states $2s2s^1S$,$2s3s^1S$ and $2s3s^3S$, various ionization, as well as other cross section for scattering from the 1^1s , 2^1s and 2^3s initial states of helium. The calculations are done with the S-wave model.

The Excitation function of Helium by J.H.Lees in 1932, published by The Royal Society. In that paper cross-section for excitation of the 2sup3\supP state of helium from the ground state have been calculated by the distorted wave method. The polarization of radiation emitted as a result of the excitation is also calculated.

Excitation of the Helium by H^+ and polarization of the resulting radiation by F.J.de Heer and J.Van den Bos and Published by Elsevier science B.V, Netherland. In this paper absolute excitation cross-section have been determined for He^+ incident on He by measuring the intensities of the singlet and triplet lines of the He I spectrum emitted by the target atom between 2900Å and

6000Å.The polarization of the photons has also been measured. The impact energy was between 5 and 100Kev.

Chapter II

FUNDAMENTAL EQUATION

In this chapter the fundamental equation of quantum mechanics are introduced. These fundamental equation are the Schrodinger equation, wave equation Transitions under the action of a periodic perturbation, Transitions in the continuous spectrum, Potential energy as a perturbation, Born's formula, Born approximation.

2.1 Wave equation & Schrodinger wave equation

Since the correspondence between quantum and classical motion serves as a guide in the construction , by supervision of harmonic waves of wave packet that propagate like classical particles but exhibit quantum mechanical spreading in space and time . Although the plane wave (Fourier representation) gives the most general form of free particle wave function. For this we find a linear partial differential equation and its general solution, provide the relation between angular frequency ω and wave function $\vec{k}$.

The time dependent Schrodinger equation for free particle is given by

$$i\hbar\frac{\partial\psi(r,t)}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi(r,t)+V(x,y,zt)\psi(r,t)\ldots\ldots\ldots \text{(2.1.1)}$$

The solution of this equation is

$$\psi(r,t)=e^{i(k.r-wt)}$$

With

$$\hbar w(k)=\frac{\hbar^2}{2m}\left(k_{x^2}+k_{y^2}+k_{y^2}\right)+v$$

Where v is constant

The equation (2.1.1)as the fundamental equation of non relativistic quantum mechanics for particle without spin i.e. wave equation or time dependant Schrodinger equation where ψ is called wave function and ψ itself can't give probability of finding electron. Since probability are real and positive .So the probability of finding electron is proportional to the square of amplitude of the wave function $\psi(r,t)$i.e. $|\psi|^2$. The probability of finding the particles in some finite region of space is then proportional to the integral of $\psi^*\psi$ over this region. The consistency of this probabilistic interpretation of the wave function requires that if the probability of finding the particle in some bounded region of space decrease as time goes on, then the probability of finding it outside of the region must increase by the same amount. The probability of interpretation of the ψ waves can be made consistently only if this conservation of probability is guaranteed .This requirement is fulfilled, owing to Gauss integral theorem, if it is possible to define probability current density J with together probability density $\rho = \psi^*\psi$ satisfy the continuity equation.

$$\frac{\partial \rho}{\partial t} + \nabla.\vec{J} = 0 \ldots\ldots\ldots\ldots (2.1.2)$$

Schrodinger in 1926 started with de Broglie relationship between momentum of a particle and wavelength of the associated matter waves and developed it into a rigorous mathematical theory known as wave mechanics. The essential feature of this theory is the remarkable success with which it describes the behavior of atomic system and their interaction with other particles and electromagnetic radiation.

Since according to Max Born $|\psi|^2$ doesn't measure the particle density at any point but gives the probability of finding the particle at that point at any given moment. For total probability of finding the probability somewhere is unity i.e. particle is certainty to be found somewhere in space.

$$\iiint |\psi|^2 dxdydz = 1$$

The wave function ψ also follows the orthogonal & orthonormal condition i.e. if the product of the function $\psi_1(r)$and the complex conjugate $\psi_2^x(r)$ of a function $\psi_2(r)$ vanishes ,when integrate with respect to r over interval $a \le x \le b$ if

$$\int_a^b \psi_2^*(r)\psi_1(r)dr = 0$$

& normalized condition is

$$\int \psi_1^*(r)\psi_1(r)dr = 1$$

Now from above discussion it has been seen that the absolute square of the wave function is a measure of a probability of finding a particle at a particular point in space. when a large number of measurement are made on some dynamical quantity which is define by space-coordinate or momenta ,then the relative no. of times the particle is observed in any particular volume or the expected value of any function is define as

$$\langle f \rangle \int \psi^* f(x)\psi dx$$

This formula holds only if the wave function normalized, if the wave function is not normalized, then the following formula is used.

$$\langle f \rangle = \frac{\int \psi^* f(x)\psi dx}{\int \psi^* \psi dx}$$

2.2 Transitions under the action of a periodic perturbation

Suppose the system nth unperturbed stationary state $E_n^{(0)}$ of $\hat{H}_0$ when the perturbation operator $\hat{V}$ is applied at t = 0. It can be prepared in infinite time (-∞ < t<0) so that the uncertainty principles allows $E_n^{(0)}$ to be precisely known. The probability amplitude of the first order transition from state n to k is given by

$$a_{kn} = -\frac{i}{\hbar}\int_0^t V_{kn} e^{i\omega_{kn}t'} dt' \ldots\ldots\ldots (2.2.1)$$

(See quantum mechanics non- relativistic theory by L.D. Landau and E.M. Lifshitz page no. 146)

Here we have introduced the frequencies $\omega_{kn} = \left(E_k^{(0)} - E_n^{(0)}\right)/\hbar$. This determines the wave functions in the first approximation. Let us now consider in more detail the case of a perturbation which is periodic with respect to time, of the form

$$\hat{V} = \hat{F}e^{-i\omega t} + \hat{G}e^{i\omega t} \ldots\ldots\ldots (2.2.2)$$

Where $\hat{F}$ and $\hat{G}$ are operators independent of time. Since $\hat{V}$ is hermitian, we must have V_{nm}=V_{mn}^* ,or

$$F_{nm}e^{-i\omega t} + G_{nm}e^{i\omega t} = F_{mn}^* e^{i\omega t} + G_{mn}^* e^{-i\omega t}$$, from which we get

$$G_{nm} = F_{mn}^*, \quad \ldots\ldots\ldots (2.2.3)$$

Equation (2.2.3) determines the relation between the operators $\hat{G}$ and $\hat{F}$. Using this relation, we have

$$V_{kn}(t) = V_{kn}e^{i\omega_{kn}t} = F_{kn}e^{i(\omega_{kn}-\omega)t} + F_{nk}^* e^{i(\omega_{kn}+\omega)t} \ldots\ldots (2.2.4)$$

Now to find the transition under the action of a periodic perturbation we shall assume the frequency ω of the periodic perturbation is such that

$\hbar\omega > E_{\min} - E_n^{(0)}$, where E_{min} is the value of the energy where the continuous spectrum begins. From the equation (2.2.4) taking only the first term ($\omega_{kn} - \omega$, close to zero). Substituting this term in equation (2.2.1) and integrating, we obtain

$$a_{kn} = -F_{kn}\,\frac{e^{-i\left(w_{k_n} - w\right)t} - 1}{\hbar\left(w_{kn} - w\right)}$$

The lower limit of integration is chosen so that $a_{kn} = 0$ for $t = 0$, in accordance with the initial condition imposed. Hence we find for the squared modulus of a_{kn}

$$\left|a_{kn}\right|^2 = \left|F_{kn}\right|^2 .4\sin^2\left[\tfrac{1}{2}\left(w_{kn} - w\right)t\right] \big/ \hbar^2\left(w_{kn} - w\right)^2 \text{ .... (2.2.6)}$$

It is easy to see that, for large t, this function can be regarded as proportional to t. To show this, we notice that

$$\lim_{t\to\infty} \frac{\sin^2 \alpha t}{\pi t \alpha^2} = \delta(\alpha) \text{ .... (2.2.7)}$$

For when $\alpha \neq 0$ this limit is zero, while for $\alpha = 0$ we have $\left(\sin^2 \alpha t\right)/t\alpha^2 = t$, so that the limit is infinite; finally, integrating over α from $-\infty$ to $+\infty$, we have (with the substituting $\alpha t = \xi$)

$$\frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\sin^2 \alpha t}{t\alpha^2}\, d\alpha = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\sin^2 \xi}{\xi^2}\, d\xi = 1 .$$

Thus the function on the left-hand side of equation (2.2.4) in fact satisfies all the conditions which define the delta function. Accordingly, we can write for large t

$$|a_{kn}|^2 = (1/\hbar^2)|F_{kn}|^2 \pi t \delta(\tfrac{1}{2} w_{kn} - \tfrac{1}{2} w),$$

Or, substituting $\hbar w_{kn} = E_k - E_n{}^{(0)}$ and using the fact $\delta(ax) = (1/\alpha)\delta(x)$,

$$|a_{kn}|^2 = (2\pi/\hbar)|F_{kn}|^2 \delta(E_k - E_n^{(0)} - \hbar w)t \; .$$

The expression $|a_{kn}|^2 dv$ is the probability of a transition from the original state to one in the interval from v to $v + dv$.we see that, for large t, it is proportional to the time interval elapsed since $t = 0$.The probability dw_{nk} of the transition per unit time is

$$dw_{nk} = (2\pi/\hbar)|F_{kn}|^2 \delta(E_k - E_n^{(0)} - \hbar w)dv \ldots\ldots \text{ (2.2.8)}$$

As we should expect, it is zero expect for transitions to states with energy $E_k = E_n^{(0)} + \hbar w$, and the probability of a transition to this state is

$$w_n E = (2\pi/\hbar)|F_{En}|^2$$

2.3 Transitions in the continuous spectrum

One of the most important applications of perturbation theory is to calculate the probability of a transition in the continuous spectrum under the action of a constant (time-independent) perturbation. We have known that the states of the continuous spectrum are almost always degenerate. Having chosen in some manner the set of unperturbed wave functions corresponding to some given energy level, we can put the problem as follows. It is known that, at the initial instant, the system is in one of these states; it is required to determine the probability of the transition to another state with the same energy. If we denote the initial state by the suffix v_o, then for transitions to states between v and $v+dv$ we have at once from (2.2.8)(putting ω =0 and changing the notation)

$$dw_{v_0 v} = (2\pi/\hbar)|V_{vv_0}|^2 \delta(E_v - E_{v_0})dv \ldots\ldots\ldots\ldots (2.3.1)$$

2.4 Potential energy as a perturbation

The case where the total potential energy of the particle in an external field can be regarded as a perturbation merits special consideration. The unperturbed Schrodinger's equation is then the equation of the motion of the particle.

$$\Delta\psi^{(0)} + k^2\Psi^{(0)} = 0, \; k = \sqrt{(2mE/\hbar^2)} = p/\hbar, \ldots\ldots\ldots (2.4.1)$$

Solutions of which represent plane waves. The energy spectrum of free motion is continuous, so that we are concerned with an unusual case of perturbation theory in a continuous spectrum. The solution of the problem is here more conveniently obtained directly, without having recourse to general formulae. The equation for the correction $\psi^{(1)}$ to the wave function in the first approximation is

$$\Delta\psi^{(1)} + k^2\psi^{(1)} = (2mU/\hbar^2)\psi^{(0)}, \ldots\ldots\ldots (2.4.2)$$

Where U is the potential energy, the solution of this equation, as we know from electrodynamics, can be written in the form of retarded potentials i.e. in the form

$$\Delta\psi^{(1)}(x,y,z) = -(m/2\pi\hbar^2)\int \psi^{(0)}U(x',y',z;')e^{ikr}\, dV'/r, \ldots\ldots (2.4.3)$$

Where, $dV = dx'dy'dz'$, $r^2 = (x-x')^2 + (y-y')^2 + (z-z')^2$.

Let us find what condition must be satisfied by the field U in order that it may be regarded as a perturbation. The condition of applicapability of perturbation theory is contained in the requirement that $\psi^{(1)} \ll \psi^{(0)}$. Let a be the order of magnitude of the dimension of the region of space in which the field is noticeably different from zero. We shall first suppose that the energy of the particle is so small that ka is at most of the order of the unity. Then the factor e^{ikr} in the integrand of (2.4.3) is unimportant in an order of magnitude estimate, and the integral is of the order of $\psi^{(0)}|U|a^2$, so that

$$\psi^{(1)} \sim m|U|a^2 \psi^{(0)}/\hbar^2$$

And we have the condition

$$|U| \ll \hbar^2/ma^2, \quad (\text{For } ka < 1) \;\ldots\ldots\ldots\; (2.4.4)$$

We notice that the expression on the right has a simple physical meaning; it is the order of magnitude of the kinetic energy which the particle would have if enclosed in a volume of linear dimension a (since, by the uncertainty relation, its momentum would be of the order of $\hbar/a$). Let us consider, in particular, a potential well so shallow that the condition (2.4.4) holds for it. It is easy to see that in such a well there are no negative energy levels. For the particular case of a spherically symmetric well when E=0, the unperturbed wave function reduces to a constant, which can be arbitrarily taken as unity: $\psi^{(0)} = 1$. Since $\psi^{(1)} \ll \psi^{(0)}$, it is clear that the wave function $\psi = 1 + \psi^{(1)}$ for motion in the well no where vanishes; the Eigen function being without nodes, belongs to the normal state, so that E=0 remains the least possible value of the energy of the particle. Thus, if the well is sufficiently shallow, only an infinite motion of the particle is possible: the particle cannot be captured by the well. Attention must be paid to the fact that this result is peculiar to quantum theory; in classical mechanics a particle can execute a finite motion in a potential well. It must be emphasized that all that has been said refers only to a three dimensional well. In a one or two dimensional well (i.e. one in which the field is a function of only one or two co-ordinate), there are always negative energy levels. This is related to the fact that, in the one and two dimensional cases, the perturbation theory under consideration is inapplicable for an energy E which is zero or very small. For large energies, when ka≫ 1, the factor e^{ikr} in the integrand plays an important part, and a markedly reduces the value of the integral. The solution (2.4.3) in this case can be transformed; the alternative form, however, is more conveniently derived by returning to equation (2.4.2), we take as x-axis the direction of the unperturbed motion; the unperturbed wave function then has the form $\psi^{(0)} = e^{ikx}$(the constant factor is arbitrarily taken as unity) let us seek a solution of the equation

$$\Delta\psi^{(1)} + k^2\psi^{(1)} = \left(2m/\hbar^2\right)Ue^{ikx}$$

In the form $\psi^{(1)} = e^{ikxf}$, in view of the assumed large value of k, it is sufficient to retain in $\Delta\psi^{(1)}$ only those term in which the factor e^{ikx} is differentiated one or more times. We then obtain for f, the equation

$$2ik\,\partial f/\partial x = 2mU/\hbar^2 \text{ , whence}$$

$$\psi^{(1)} = e^{ikxf} = -\left(im/\hbar^2 k\right)e^{ikx}\int Udx. \;\ldots\ldots\; (2.4.5)$$

An estimation of this integral gives $\psi^{(1)} \sim mUa/\hbar^2 k$, so that the condition of applicability of perturbation theory in this case is

$$|U| \ll \left(\hbar^2/ma^2\right)ka = \hbar v/a \;\; (ka \gg 1)\ldots\ldots\ldots (2.4.6)$$

Where $v = k\hbar/m$ is the velocity the particle. It is to be observed that this condition is weaker than (2.2.4). Hence, if the field can be regarded as a perturbation at small energies of the particle, it can always be so regarded at large energies, where as the converse is not necessarily true. The applicability of the perturbation theory developed here to a coulomb field requires special consideration. In a field $U = \alpha/r$, it is impossible to separate a finite region of space outside which U is considerably less than inside it. The required condition can be obtained by writing in (2.4.6) a variable distance r instead of the parameter a; this leads to the inequality

$$\alpha/\hbar v \ll 1 \quad \ldots\ldots \ (2.4.7)$$

Thus, for large energies of the particle, a coulomb field can be regarded as a perturbation. Finally we shall derive a formula which approximately determines the wave function of the particle whose energy E everywhere considerably exceeds the potential energy U(no other conditions being imposed). In the first approximation, the wave function depends on the co-ordinates in the same way as for the free motion (whose direction is taken as the x-axis). Accordingly, let us look for ψ in the form $\psi = e^{ikxF}$, where F is a function of the co-ordinates which varies slowly in the comparison with the factor e^{ikx}. Substituting Schrodinger's equation, we obtain for F the equation

$$2ik\,\partial F/\partial x = \left(2m/\ \hbar^2\right)UF\,, \quad \ldots\ldots \ (2.4.8)$$

$$\text{Whence, } \psi = e^{ikx}F = \text{ constant} \times \ e^{ikx}e - ^{(i/\ \hbar v)\int U dx} \quad \ldots\ldots \ (2.4.9)$$

This is required expression. It should, however, be borne in mind that this formula is not valid at large distances. in equation (2.4.8) a term ΔF has been omitted which contains second derivatives of F. The derivative $\frac{\partial^2 F}{\partial x^2}$, together with the first derivative $\frac{\partial F}{\partial x}$, tends to zero at large distances, but the derivatives with respect to transverse co-ordinates y and z do not tends to zero, and can be neglected only if $x \ll ka^2$.

2.5 Born's formula

The effective scattering cross -section can be calculated in a general form in a very important case, namely that where the scattering field may be regarded as a perturbation. It has been shown in equation (2.4.4) and (2.4.6) that is possible when either of the two conditions

$$|U| \ll \hbar^2/ma^2 \;\ldots\ldots\; (2.5.1)$$

Or $$|U| \ll \hbar v/a = \left(\hbar^2/ma^2\right)ka \;\ldots\ldots\ldots\; (2.5.2)$$

holds, a being the range of action of the field $U(r)$ and U the order of magnitude of the field in the range where it is significant. When the first condition is satisfied, the approximation is valid for all velocities; the second condition shows that it is always applicable for sufficiently fast particles.

We seek the wave function in the form $\psi = \psi^{(0)} + \psi^{(1)}$ where $\psi^{(0)} = e^{ikr}$ corresponds to an incident particle having wave vector $\vec{k} = \frac{\vec{p}}{\hbar}$. Form equation (2.4.3) we have

$$\psi^{(1)}(x, y, z) = -\frac{m}{2\pi\hbar^2}\int U(x', y', z')e^{i(k.r+kR)}\frac{dV'}{R} \;\ldots\ldots\ldots\; (2.5.3)$$

Taking the origin at scattering centre, we introduce the radius vector $\vec{R}_0$ from the origin to the point where the value of $\psi^{(1)}$ is required, and denoted by $\vec{n}'$ a unit vector along $\vec{R}_0$. Let the radius vector of a volume element dV' be $\vec{r}'$; then $\vec{R} = \vec{R}_0 - \vec{r}'$. At large distances from the centre, $R_0 \gg r'$, so that

$$R = \left|\vec{R}_0 - \vec{r}'\right| \cong \vec{R}_0 - \vec{r}.'\vec{n}'$$

Substituting this in (4.3), we have the following asymptotic expression for $\psi^{(1)}$:

$$\psi^{(1)} \approx -\frac{m}{2\pi\hbar^2}\frac{e^{ikR_0}}{R_0}\int U(\vec{r}\,')e^{i(k-k').r'}dV' \text{........ (2.5.3)}$$

(Where $k' = kn'$ is the wave factor of the particle after scattering).comparing this with the scattering amplitude given by formula (3), we find for the latter the expression

$$f = -\frac{m}{2\pi\hbar^2}\int Ue^{-i\vec{K}.\vec{r}}dV\,, \text{ .... (2.5.4)}$$

Where we have renamed the variable of integration and introduced the vector

$$\vec{K} = \vec{k}' - \vec{k}\,, \text{ ...... (2.5.5)}$$

Whose absolute magnitude is $K = 2k\sin\frac{\theta}{2}$ ...... (2.5.6)

θ being the angle between k and k' i.e. the scattering angle. Finally, squaring the modulus of the scattering amplitude, we have the following expression for the effective cross section for the scattering into the solid angle elementd_0:

$$d\sigma = \frac{m^2}{4\pi^2\hbar^4}\left|\int Ue^{-i\vec{K}.\vec{r}}dV\right|^2 d_0 \text{ .... (2.5.7)}$$

We see that the scattering with the momentum change $\hbar\vec{K}$ is determined by the squared modulus of the corresponding Fourier component of the field U.In the theory of collisions, the approximation considered here is often called the born approximation. It may be noted that, in this approximation, the relation

$$f(\vec{k},\vec{k}') = f^*(\vec{k}',\vec{k}) \text{ ...... (2.5.8)}$$

Holds between the amplitudes of the direct and inverse scattering process, i.e. processes differing by the interchange of the initial & final momenta, without the change of sign such as occur in time reversal. Thus another symmetry property, in addition to the reciprocity theorem appears in scattering. This property is closely related to the smallness of the scattering amplitudes in perturbation theory, and follows immediately from the unitarity condition (2.5.8) if we neglect the integral term quadratic in f. Equation (2.5.7) also is obtained by another method (which however does not determine the phase of the scattering amplitude). We can start from the general formula (2.3.1), according to which the transition probability between states of the continuous spectrum is given by the expression

$$dw_{\nu_0\nu} = (2\pi/\hbar)\left|U_{\nu\nu_0}\right|^2 \delta(E_\nu - E_{\nu_0})d\nu \text{ ...... } (2.5.9)$$

In the case under consideration, we have to apply this formula to this transition from the state of the incident particle with a given initial momentum $\vec{p}$ to the state of the particle, with momentum $\vec{p}'$, scattered into the element of solid angle do. As the "integral" of the states $d\nu$ we can take the volume element $dp'_x\, dp'_y\, dp'_z$ in momentum space. Substituting for $E_\nu - E_\nu$ the difference $p'^2 - p^2/2m$ of the energies of the free particles with momenta $\vec{p}'$ and $\vec{p}$, we obtain

$$d\psi_{pp'} = (4\pi m/\hbar)\left|U_{pp'}\right|^2 \delta\left(p'^2 - p^2\right)dp'_x dp'_y dp'_z \text{ .... } (2.5.1.1)$$

The wave function of the incident and scattered particles are the functions for the free motion, i.e. plane waves:

$$\psi_p = cons\tan t \times e^{i\vec{p}.\vec{r}/\hbar}, \psi_{p'} = cons\tan t \times e^{i\vec{p}'.\vec{r}/\hbar}$$

Since we have taken as the " dv' an element of momentum space, the wave function $\psi_{p'}$ must be normalized by the delta function in momentum space:

$$\psi_{p'} = e^{(i/\hbar)p'.r} / (2\pi\hbar)^{3/2} \text{ .... } (2.5.1.2)$$

We normalized the function ψ_p to unit current density:

$$\psi_p = \sqrt{(m/p)} e^{(i/\hbar)\vec{p}.\vec{r}} \text{ .... } (2.5.1.3)$$

Then the probability (4.9) will have the dimensions of area, and is the differential effective scattering cross-section. The presence of the delta function in formula (2.5.9) means that $p' = p$, I.e. the absolute magnitude of the momentum is unchanged, as it should be in elastic scattering. We can remove the delta function by changing to "spherical coordinates" in momentum space (i.e. by replacing $dp'_x\, dp'_v\, dp'_z$ by $p'^2\, dp'\, do' = \frac{1}{2} p'\, d(p'^2\ )do'$) and integrating over p'^2. The integration amounts to replacing p' by p in the integrand, and we obtain

$$d\sigma = (2\pi m\frac{p}{\hbar})\left|\int \psi_p{}^* U \psi_p dV\right|^2 do' \quad \text{......... (2.5.1.4)}$$

2.6 Born approximation

In Born approximation, perturbation in Hamiltonian and wave function are taken into consideration to obtain Green solution for the out going wave as

$$\psi(\vec{r}) = \psi^{(0)}(\vec{r}) + \int G_{0k}(\vec{r},\vec{r}\,')F(\vec{r}\,')d^3r' \quad \text{...... (2.6.1)}$$

Where $\psi^{(0)}(\vec{r}) = e^{i\vec{k}.\vec{r}} = e^{ikz}$

$$F(\vec{r}\,') = -U(\vec{r}\,')\psi^{(0)}(\vec{r}\,') = -\frac{2\mu V(\vec{r}\,')e^{ik.\vec{r}\,'}}{\hbar^2}$$

$$\psi(\vec{r}\,') = e^{ikz} - \frac{1}{4\pi}\int \frac{e^{ik|\vec{r}-\vec{r}\,'|}}{|\vec{r}-\vec{r}\,'|}U(r')e^{ik.r'}d^3r' \quad \text{...... (2.6.2)}$$

From the above figure

$$|\vec{r}-\vec{r}\,'| = \sqrt{r^2 - 2rr' + r'^2}$$

$$= r\left[1 - \frac{2rr'\cos\Theta}{r^2} + \left(\frac{r'}{r}\right)^2\right]^{\frac{1}{2}} \text{for } r' \gg r \text{ we can write}$$

$\cong r - r'\cos\Theta$ .... (2) Now from equation (2.6.2) we get

$$\psi(\vec{r}) = e^{ikz} - \frac{1}{4\pi}\int \frac{e^{ik(r - r'\cos\Theta) + i\vec{k}.\vec{r}}}{r} U(\vec{r}\,')d^3r'$$

$$\psi(\vec{r}) = e^{ik_p z} - \frac{1}{4\pi}\int \frac{e^{ikr}}{r} e^{-ikr'\cos\Theta + ik.r'} U(\vec{r}\,')d^3r'$$

Comparing with $\psi(\vec{r}) = e^{ik_p z} + f(\theta)\frac{e^{ikr}}{r}$ we get

$$f(\theta) = -\frac{1}{4\pi}\int e^{-ikr'\cos\Theta} e^{i\vec{k}.\vec{r}\,'} U(\vec{r}\,')d^3\vec{r}\,' \ldots\ldots\ldots (2.6.4)$$

The momentum transfer vector $\vec{K}$ is given as

$$\vec{K} = \vec{k} - \vec{k}'$$

$$\left|\vec{K}\right| = \sqrt{k^2 - 2kk'\cos\theta + k'^2}$$

$$= \sqrt{2k^2(1 - \cos\theta)} \text{ as } |k| = |k'| = k$$

$$= \sqrt{2k^2 2\sin^2\tfrac{\theta}{2}}$$

$$K = 2k\sin\tfrac{\theta}{2} \ldots\ldots\ldots\ldots\ldots\ldots(2.6.5)$$

And $kr'\cos\Theta = (k'.r')$, so equation (2.6.4) become

$$f(\theta) = -\frac{1}{4\pi}\int e^{-i(\vec{k} - \vec{k}').\vec{r}\,'} U(\vec{r}\,')d^3r'$$

$$= -\frac{1}{4\pi}\int e^{i(\vec{k} - \vec{k}').\vec{r}\,'} U(\vec{r}\,')d^3r'$$

$$= -\frac{1}{4\pi}\int e^{iK.r'} \frac{2\mu V(\vec{r}\,')}{\hbar^2} d^3r'$$

Differential cross-sectional is given by

$$\frac{d\sigma}{d\Omega} = \sigma(\theta) = |f(\theta)|^2 \ldots\ldots\ldots (2)$$

Chapter III

ANALYTICAL STUDY

3.1 Introduction

In this section we discuss the inelastic collision between fast electron and atom and use this phenomenon to find the excitation cross-section for He atom using Born approximation. In the section 1, for the transition 1^1S to 2^1P and 1^1S to 3^1P, the excitation cross section is calculated with help of Born approximation. Similarly in the section 2, for the transition 1^1S to 2^1S, the excitation cross section is calculated.

3.2 Inelastic collisions between fast electron and atom (helium)

Inelastic collisions between fast electron and atoms can be considered by means of the Born approximation. The condition for the Born approximation to be applicable is that the velocity of the incident electron should be large compared with those of the atomic electrons. The energy loss in the collision may have any value. If the electron loses a considerable part of its energy, the atom is ionized, the energy being transferred to one of its electron. However, we can always regard as the scattered electron that which has the greater velocity after the collision; thus, if the velocity of the incident electron is large, that of the scattered electron is large also.

In a collision between an electron and an atom, the coordinate system in which their centre of mass is at rest .An inelastic collision is accompanied by a change in the internal state of the atom. The atom may go from the normal state in to an excited state of the discrete or continuous spectrum, the latter case signifies an ionization of the atom. In deriving the general formulae we can consider the two cases together. We start from the general formula for the transition probability between the states of the continuous spectrum as in equation (2.3.1) with certain change in symbol, and apply it to the system consisting of the incident electron and the atom. Let $\vec{p}\,,\vec{q}$ be the momenta of the incident electron before and after the collision, and E $_0$,E$_n$ the corresponding energies of the atom. For the transition probability, we have the expression

$$dw_n = \frac{2\pi}{\hbar}\left|U_{E_n q}^{E_0 p}\right|^2 \delta\left(\frac{q^2 - p2}{2m} + E_n - E_0\right) dq_x dq_y dq_z, \ldots\ldots \text{(3.2.1)}$$

Where $U_{E_n q}^{E_0 p}$ is the matrix element of the energy of interaction between the incident electron and the atom,

$$U = Z\,e^2 \Big/ r - \sum_{a=1}^{Z} e^2 \Big/ \left|r - r_a\right|;$$

Here r is the radius vectors of the incident electron, $\vec{r}_a$ those of the atomic electron; the origin is at the nucleus of the atom, and m is the mass of the electron. The wave functions Ψ_p and Ψq of the electron are determined as given in equation (2.5.1.2) and (2.5.1.3), then dw is the effective cross section dI_n for the collision. The wave functions of the of the atom in the initial and final states we denote by Ψ_0 and Ψ_n.If the final state of the atom belongs to the discrete spectrum, then Ψ_n $(like\Psi_0)$ is normalized to unity in the usual manner. If, on the other hand, the atom enters a state of the continuous spectrum, the wave function is normalized by the delta functions of the parameters v which determine these states (these parameters may be, for instance, the energy of the atom, and the momentum components of the electron which leaves the atom in the ionization). The effective cross section thus obtained give the probability of a collision in which the atom enters states of the continuous spectrum lying in the range of parameters between v and dv

Integration of (3.2.1) over the absolute magnitude $\vec{p}'$ gives

$dI_n = \frac{2\pi m p'}{\hbar} \left| U_{nq}^{0p} \right|^2 d_0'$, where $\vec{q}$ is determined from the law of conservation of energy:

$$\left(p^2 - q^2\right)/2m = E_n - E_0 \ldots\ldots\ldots \text{ (3.2.2)}$$

Substituting in the matrix element $U_{np'}^{0p}$, the wave functions of the electron from equation (2.5.1.2) and (2.5.1.3), we obtain

$$dI_n = \frac{m^2}{4\pi^2\hbar^4} \frac{q}{p} \left| \iint U e^{-iK.r} \psi_n^* \psi_0 \, d\tau dV \right|^2 d_0 \quad \ldots\ldots\ldots\ldots \text{ (3.2.3)}$$

Where $d\tau = dV_1 dV_2 ....dV_z$ is the element of configuration space of the Z electrons in the atom, and we omit the prime to d_o. In this form, this is a general formula of perturbation theory, applicable not only to collisions of electrons with an atom, but also to any inelastic collisions of two particles, and gives the effective scattering cross section in a system of co-ordinates in which the centre of mass of the particles is at rest; m is then the reduced mass of the two particles. For n=0 and $\vec{p} = \vec{q}$ equation (3.2.3) becomes the formula for the effective elastic scattering cross section.

Since the functions ψ_n and ψ_0 are orthogonal, the term in U this contains the interaction Ze^2/r with the nucleus vanishes on integration over τ, and so we have for inelastic collisions

$$dI_n = \frac{m^2}{4\pi^2\hbar^4} \frac{q}{p} \sum_a \left| \iint \frac{e^2}{\left| r - r_a \right|} e^{-iK.r} \psi_n^* \psi_0 \, d\tau dV \right|^2 d_0 \ldots\ldots\ldots \text{ (3.2.4)}$$

The integration is over V. The integral

$\phi_K(r_a) = \int e^{-iK.r} dV / |r - r_a|$ is formally the same as the Fourier component of the potential at the point r due to charges distributed in space with density $\rho = \delta(r - r_a)$. And using Fourier Series which gives

$$\phi_{K(r_a)} = (4\pi/K^2)e^{-iK.r_a} \ldots\ldots\ldots (3.2.5)$$

Substituting this expression in equation (3.2.4), we finally obtain the following general expression for the inelastic cross-section:

$$dI_n = \left(\frac{e^{-2}m}{\hbar^2}\right)^2 \frac{4k_q}{k_p K^4} \left|\int \sum_a e^{-iK.r_a} \psi_n^* \psi_0 d\tau\right|^2 d_0; \quad \ldots\ldots (3.2.6)$$

Here we have introduced, in place of the momenta $\vec{q}$ and $\vec{p}$, the wave vectors $\vec{k}_q = \frac{\vec{q}}{\hbar}$, $\vec{k}_p = \frac{\vec{p}}{\hbar}$. This formula gives the probability of a collision in which the electron is scattered into an element of solid angle d_0 and the atom enters the nth excited state. The vector $-\hbar\vec{K}$ is the momentum given to the atom by the electron in the collision.

In effecting the calculations, it is more convenient to refer the effective cross section, not to the element of solid angle, but to the element dK of the absolute magnitudes of the vector $\vec{K}$. The vector $\vec{K}$ is defined by $\vec{K} = \vec{k}_q - \vec{k}_p$ for its absolute magnitude we have

$$K^2 = k_p^2 + k_q^2 - 2k_p k_q \cos\theta \ldots\ldots\ldots (3.2.7)$$

Hence for a given loss of energy by the electron,

$$KdK = k_p k_q \sin\theta d\theta = (k_p k_q / 2\pi)d_o \ldots\ldots\ldots\ldots (3.2.8)$$

Therefore equation (3.2.6) can be written as

$$dI_n = 8\pi\left(\frac{e^2}{\hbar\upsilon}\right)^2 \frac{dK}{K^3} \left|\int \sum_a e^{-iK.r_a} \psi_n^* \psi_0 d\tau\right|^2 \ldots\ldots\ldots\ldots\ldots (3.2.9)$$

The vector K plays an important part in all the following calculations. Let us examine more closely its relation to the scattering angle θ and to the energy $E_n - E_0$ transferred in the collision. We shall see below that the most important collision are those cause scattering through small angles ($\theta \ll 1$), with a transfer of energy which is small in comparison with the energy E=1/2mv^2 of the incident

Electron: $E_n - E_0 \ll E$. The difference $k_p - k_q$ is in this case also small, ($k_p - k_q \ll k_p$); and

$$E_n - E_0 = \hbar^2 \left(k_p^2 - k_q^2\right)/2m \cong \hbar^2 k\left(k_p - k_q\right)/m = \hbar v\left(k_p - k_q\right)$$

Since θ is small, we have from equation (3.2.7)

$$K^2 \cong \left(k_p - k_q\right)^2 + \left(k_p\theta\right)^2, \ldots\ldots\ldots \text{(3.2.8)}$$

And finally, $K = \sqrt{\left[\left\{\left(E_n - E_0\right)/\hbar v\right\}^2 + \left(k_p\theta\right)^2\right]}, \ldots\ldots$ (3.2.9)

The minimum value of K is $K_{\min} = \left(E_n - E_0\right)/\hbar v$, in the region of small angles we can further distinguish between different regions depending on the relation between the small quantities θ and $\frac{v_0}{v}$, where v_0 is of the velocity of the atomic electrons. If we consider energy ϵ_0 of the atomic electrons

($E_n - E_0 \sim \epsilon_0 \sim mv_0^2$), then for $\left(\frac{v_0}{v}\right)^2 \ll \theta \ll 1$ we have

$$K = k_p\theta = \left(\frac{mv}{\hbar}\right)\theta \ldots\ldots\ldots \text{(3.2.10)}$$

3.3 Excitation cross section for helium atom (section-1)

Since exact wave functions for complex atoms are not available, there is an uncertainty introduced in scattering calculations which is distinct from those inherent in the Born approximation. The approximate wave functions, such as those of Slater, usually are well determined with respect to the energy of the state and are less well determined in regions other than those which contribute the most to the energy. For scattering problems such errors may be quite serious. A similar situation occurs in the calculation of the optical transition probabilities, and investigations have been reported. This difficulty has never been quantitatively examined for collision problems.

To make this study, I have followed the suggestion, advanced by Bates, Fundaminsky, and Massey, of employing two formally equivalent expressions for the differential cross section, both of which are within the Born Approximation. These expressions are not necessarily the same in the actual calculation since they weight the various regions of coordinate space differently. The cross section for a momentum change dK for excitation of an atom from state p to the state q is given in Born approximation by

$$I(K)dK = \frac{8\pi dK}{k_p^2 K^2}\left|\sum_i^n \int e^{-iK_{zi}} \psi_p \psi_q^* d\tau_1 d\tau_2 ......d\tau_n\right|^2 \text{ .... (3.3.1)}$$

Where the summation is made over the atomic electrons, and where $K = k_q - k_p$ k_p = wave number of the incident electron, k_q = wave number of the scattered electron, $k_q^2 = k_p^2 - 2\Delta E$, and $\Delta E = E_q - E_p$, the internal energy change of the target; in all of these symbols Hartree units have been used. The summation over the atomic electrons is made readily if product type wave functions are used. The summation over the atomic electrons is made readily if product type wave function is used. For the ground state of Helium

$\Psi_p = \Psi_0(N/r_1)\Psi_0(N/r_2)$, (where, N=1.687).

While for the excited state-other than an S state-the Eckhart approximation to the wave is used , i.e. $\psi_q = 2^{-1/2}\{\psi_0(2/r_1)\psi_{nlm}(1/r_2) + \psi_0(2/r_2)\psi_{nlm}(1/r_1)\}$, where

$\psi_{nlm}(N/r)$is a wave function of single electron in the nml state moving in a field of charge N. with these assumptions,

$$\sum_{i}^{n} e^{-iK_{zi}} \psi_p \psi_q^* dr_1 ....dr_n = \sqrt{2}\int e^{-iK_z} \psi_0 (N/r) \psi_{nlm}^* (1/r) dr \, .$$

Choosing the final states with their polar axis along the momentum transfer vector K establishes the selection rule Δm = 0 for the process. Therefore, the differential cross section becomes

$$I(K)dK = \frac{16\pi dK}{k_p^2 K^3} \left| \int e^{-iK_z} \psi_0 (N/r) \psi_{nl} (1/ \ r) dr \right|^2 \ldots\ldots\ldots (3.3.2)$$

By making use of the equations satisfied by exact helium atom wave functions,$\psi_p$and ψ_q, the product $\psi_q^* \psi_p = \dfrac{\psi_q^* \left(\nabla_1^2 + \nabla_2^2\right) \psi_p - \psi_p \left(\nabla_1^2 + \nabla_2^2\right) \psi_q^*}{2\left(E_q - E_p\right)}$

and by a straightforward analysis, using the Eckhart wave functions, an alternative expression for the differential cross section can be shown to be

$$I(k)dk = \frac{4\pi dk}{(\Delta E)^2 K k_p^2} \left| \int e^{-iK_z} \left\{ \psi_{nl}^* (1/r) \frac{\partial}{\partial z} \psi_0 (N/r) - \psi_0 (N/r) \frac{\partial}{\partial z} \psi_{nl}^* (1/r) \right\} dr \right| \ldots\ldots\ldots (3.3.3)$$

Equation (3.3.2) and Eq^n (3.3.3) have been applied to two cases, namely, the transition 1^1S to 2^1P and 1^1s to 3^1P. All results using Eq^n (3.3.2) is designated as method I, and those results obtained using Eq^n(3.3.3) will is designated as method II. For the transition 1^1S to 2^1P, the differential cross section per unit solid angle, $I(\theta)$, in the units of πa_0^2, after transforming from momentum to angular variables is

$$2\pi I(\theta) = 1.176 \times 10^4 \frac{k_q}{k_p} \frac{1}{K^2 \left(p^2 + K^2\right)^6} \qquad \text{By method I} \ldots\ldots\ldots (3.3.4)$$

and similarly

$$2\pi I(\theta)=2.532\times10^{2}\frac{k_q}{k_p}\frac{\left[8.069-0.687K^{2}\right]^{2}}{K^{2}\left(p^{2}+K^{2}\right)^{6}}$$ By method II ……… (3.3.5)

Where p^2= 4.783.F or this transition ΔE =0.779 in Hartree units.

The corresponding total cross sections, $\int_0^{\pi} 2\pi I(\theta)\sin\theta d\theta$, are

$$Q_1(k_p)=\frac{1.176\times10^{2}}{k_p^{2}}\left[\frac{1}{X^{5}}\left\{\begin{array}{l}2.091+0.546X+0.1523X^{2}+4.777\times10^{-2}X^{3}\\+1.977\times10^{-2}X^{4}+4.176\times10^{-3}X^{5}\ln\dfrac{K^{2}}{X}\end{array}\right\}\right]_{k_p-k_q}^{k_p+k_q}$$

……… (3.3.6) by method I

$$Q_{II}(k_p)=1.42Q_I+\frac{2.987}{k_p^{2}}\left[\frac{5K^{2}-89.18}{X^{5}}\right]_{k_p-k_q}^{k_p+k_q}$$ …… (3.3.7) by method II

Where $X=p^{2}+K^{2}$,

Similarly, for the transition 1^1S to 3^1P, using, $\Delta E=0.8474$, the differential cross section per unit solid angle, $I(\theta)$, in the units of πa_0^2, after transforming from momentum to angular variables,

is calculated as

$$2\pi I(\theta)=1.507\frac{k_q}{k_p}\frac{\left[52.55K^{2}+1.168\times10^{2}\right]^{2}}{K^{2}\left(p^{2}+K^{2}\right)^{8}}$$ By method I …… (3.3.8)

and

$$2\pi I(\theta)=0.5245\frac{k_q}{k_p}\frac{\left[-8.28K^{4}+87.62K^{2}+228.8\right]^{2}}{K^{2}\left(p^{2}+K^{2}\right)^{8}}$$ By method II …… (3.3.9)

Where p^2 = 4.093;

The corresponding total cross sections, $\int_0^{\pi} 2\pi I(\theta)\sin\theta d\theta$, are given by

$$Q_1(k_p)=\frac{1.507}{k_p^2}\left[\frac{1}{X^7}\left\{\begin{matrix}-1.012\times10^3-2.301\times10^2K^2 67.93X+19.92X^2+6.084X^3\\ +1.982X^4+0.7265X^5+0.3550X^6+8.675\times10^{-2}X^7\ln\dfrac{K^2}{X}\end{matrix}\right\}\right]_{k_p-k_q}^{k_p+k_q}$$

...... (3.3.9.1) by method I

$$Q_{II}(k_p)=1.333Q_I-\frac{05245}{k_p^2}\left[\frac{1}{X^7}\left\{8.57K^6-1.241\times10^2K^4-1.303\times10^3K^2-2.175\times10^3\right\}\right]_{k_p-k_q}^{k_p+k_q}$$

...... (3.3.9.2) by method II

Where $X=p^2+K^2$

3.4 Excitation cross section for helium atom (section-2)

In the last section, the differential cross section per unit solid angle, $I(\theta)$ and total excitation cross section for electron impact with helium atom for transition 1^1S to 2^1P and 1^1S to 3^1P was determined. The present work follows the analysis in previous section results but pertains to the transition to the first excited metastable state of the helium atom. Those two formally equivalent expressions for the differential cross section in Born approximation are employed, and these expressions do not lead to the same results in actual calculations because of the approximate nature of the helium atomic wave functions. As in the last section method I is refered to the standard matrix element for the excitation differential cross section while method II refers to results derived from the alternative expression obtained by the transformation.

$$\psi_q^* \psi_p = \frac{\psi_q^*\left(\nabla_1^2 + \nabla_2^2\right)\psi_p - \psi_p\left(\nabla_1^2 + \nabla_2^2\right)\psi_q^*}{2\left(E_q - E_p\right)} \quad \text{.....(3.4.1)}$$

Here Ψ_q and Ψ_p refer to the exact wave functions for the final and initial states, respectively. Hartree units are employed everywhere. The wave function for the (1s 2s)^{1}S level was originally suggested by Vinti and already employed by Massey and Mohr and is given by

$\Psi_q = B\left(\Phi_2 - \gamma\Psi_p\right), \gamma = \int \Psi_p \Phi_2 dr_1 dr_2$, where Ψ_p is the ground state wave function of helium atom taken to be $\Psi_p = \Psi_{100}(N/r_1)\Psi_{100}(N/r_2)$, (N = 1.687),

$$\text{While, } \Phi_2 = \frac{\Psi_{100}(\alpha/r_1)\Psi_{200}(\beta/r_2) + \Psi_{100}(\alpha/r_2)\Psi_{200}(\beta/r_1)}{\left\{2\left(1+b^2\right)\right\}^{\frac{1}{2}}}$$

$$\text{With } (2x)^3(x-1)^2/\left(x+\tfrac{1}{2}\right)^8;\ x = \alpha/\beta;\ \beta = \left(1-\gamma^2\right)^{-\frac{1}{2}}$$

$\Psi_{nlm}(Z/r)$ is the wave function of a single electron in the nlm state moving in a field of charge Z. the values of the screening parameters α and β were found by the Ritz condition of minimum energy to be

α = 1.98, β = 1.20.

It is clear that Ψ_q is properly normalized to the ground state. The differential cross section for a momentum change of magnitude dk for excitation transition 1^1S $\rightarrow 2^1$S is then calculated by Method I and is given by

$$I(K)dK = \frac{8\pi dK}{k_p^2 K^3}\left|\frac{36.879}{\left(13.447+K^2\right)^2} + \frac{(11.457)\left(2.547+2.887K^2\right)}{\left(5.2304+K^2\right)^3} - \frac{52.863}{11.384+K^2}\right|^2 \ldots..$$

(3.4.2)

The matrix element for the excitation differential cross section by Method I is transformed by using Eq.(3.4.1), with the result

$$\sum_{i=1}^{2} e^{-iK_{zi}}\Psi_p\Psi_q^* dr_1 dr_2 = \frac{1}{\left(1-\gamma^2\right)^{\frac{1}{2}}\Delta E}\left[K^2\int \Phi_2 e^{-iK_{z1}}\Psi_p dr_1 dr_2 + 2iK\int \Phi_2 e^{-iK_{z1}}\frac{\partial}{\partial z_1}\Psi_p dr_1 dr_2\right]$$

…. (3.4.3)

In which $\Delta E = E_q - E_p$, the transition energy change, equals 0.75584. The final results of the cross section for momentum change is given by

$$I(K)dK = \frac{8\pi dK}{k_p^2 K^3}\left|3.7372\times10^2 K^2\left[\frac{5.2159\times10^{-3}}{\left(13.4469+K^2\right)^2} + \frac{6.9338\times10^{-2} - 9.876\times10^{-3}K^2}{\left(5.2304+K^2\right)^3}\right]\right|^2$$

…… (3.4.4) by method II

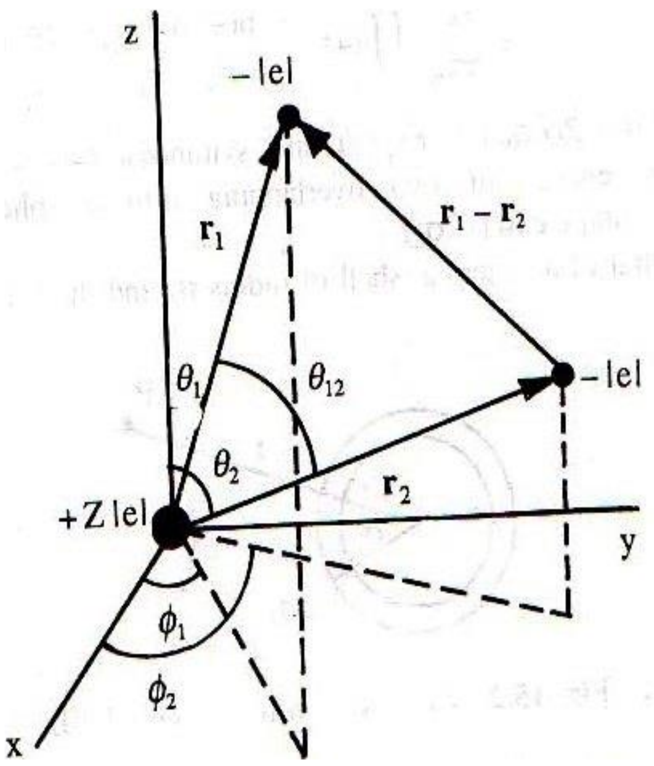
3.5 Ground state energy of Helium atom by

3.5.1) Time independent perturbation method

3.5.2) Variational method

3.5.3) Hartree-Fock method

The helium atom consists of a nucleus with atomic number Z=2 and two electrons in the k-shell. The position of the electrons in the atom with respect to the nucleus can be shown by the following figure.



The Hamiltonian of the Helium atom can be written as:

$$H = \frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - e^2\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right) \ldots\ldots\ldots\ldots \text{(3.5.1.1)}$$

Where we have neglected any reduced mass effects. The terms in the above expression represent the kinetic energy of the first electron, the kinetic energy of the second electron, the electrostatic attraction between the nucleus and the first electron, the electrostatic attraction between the nucleus and the second electron, and the electrostatic repulsion between the two electrons, respectively.

It is the final term which causes all of the difficulties. Indeed, if this term is neglected then we can write

$$H_0 = H_{01} + H_{02}$$

$$H_0 = \left(\frac{p_1^2}{2m} - \frac{Ze^2}{r_1}\right) + \left(\frac{p_2^2}{2m} - \frac{Ze^2}{r_2}\right)$$

= unperturbed Hamiltonian

And H^1 = The electron- electron interaction term $= \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} = \frac{e^2}{|\vec{r}_{12}|}$

The unperturbed wave function for the Helium atom can be written as:

$$U^0_{nlm}(\vec{r}_1, \vec{r}_2) = U^0_{n_1 l_1 m_1}(\vec{r}_1) U_{n_2 l_2 m_2}(\vec{r}_2) \ldots\ldots \text{(3.5.1.2)}$$

Where $U^0_{n_1 l_1 m_1}(\vec{r}_1)$ and $U^0_{n_2 l_2 m_2}(\vec{r}_2)$ are the unperturbed Hydrogen atom wave functions.

Let us write SWE for the two electrons separately assuming two electrons are independent

i.e. $H_{o1} U^o_{n_1 l_{1} m_1}(\overrightarrow{r_1}) = E^o_{n_1} U^o_{n_1 l_{1} m_1}(\overrightarrow{r_1})$ and $H_{o2} U^o_{n_2 l_2 m_2}(\overrightarrow{r_2}) = E^o_{n_2} U^o_{n_2 l_2 m_2}(\overrightarrow{r_2})$

Putting H_{o1} and H_{o2} we get,

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{r_1}\right) U^0_{n_1 l_1 m_1}(\vec{r}_1) = E^0_{n_1} U^0_{n_1 l_1 m_1}(\vec{r}_1)$$

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{r_2}\right) U^0_{n_2 l_2 m_2}(\vec{r}_2) = E^0_{n_2} U^0_{n_2 l_2 m_2}(\vec{r}_2)$$

These above two equations are the same as for a hydrogen atom. Therefore we can immediately write the solutions of these equations as follows.

$$E^0_{n_1} = -\frac{mZ^2e^4}{2n_1^2\hbar^2} = -\frac{Z^2}{n_1^2}\left(\frac{me^4}{2\hbar^2}\right) = -\frac{Z^2}{n_1^2}E_H$$

And $E^o_{n_2}$ = -$\frac{Z^2}{n_2^2}$ E_H , where E_H=$\frac{me^4}{2\hbar^2}$ = 13.6ev is the ground state energy of H-atom.

Since in the ground state of Helium atom, both electron are in 1s state designated as $1s^2$ configuration (i.e. $n_1 = n_2 = 1$), the total ground state energy of the Helium atom is given by

$$E^0_{n_1n_2} = E^0_{n_{1=1}} + E^0_{n_{2=1}}$$

$$E^0_{n_1n_2} = -Z^2E_H - Z^2E_H$$

$$E^0_{11} = -2Z^2E_H \text{ ...... (3.5.1.3)}$$

$$= -8\times 13.6\text{ev} \qquad (Z = 2)$$

$$E^0_{n_1n_2} = E^0_{11} = -108.8ev$$

But the experimental value of ground state energy of Helium atom is -79ev. That means the total ground state energy of Helium atom must include the repulsive interaction such that:

$$E_{11} = E^0_{11} + E^1_{11} \text{ .... (3.5.1.4)}$$

First order correction in E^1_{11}:

According to the first order perturbation theory, the first order correction in the ground state energy is given by:

$$E^1_{11} = \left\langle U^0_{100}(r_1, r_2)\middle|H^1\middle|U^0_{100}(r_1, r_2)\right\rangle$$

Since $U_{100}^{0}(r_1) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr_1}{a_0}}$ and

$$U_{100}^{0}(r_2) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr_2}{a_0}}$$

are the ground state wave functions of H-atom, the total ground state wave functions of Helium atom is given by

$$U_{100}^{0}(r_1, r_2) = \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^{3} e^{-\frac{Z}{a_0}(r_1+r_2)} \quad \ldots\ldots\ldots (3.5.1.5)$$

$$E_{11}^{1} = \frac{e^2}{\pi^2}\left(\frac{z}{a_0}\right)^{6} \int d^3 r_1 e^{-2Zr_1/a_0} \int d^3 r_2 e^{-2Zr_2/a_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \quad \ldots\ldots\ldots\ldots (3.5.1.6)$$

Evaluation of $\frac{1}{|\vec{r}_1 - \vec{r}_2|}$

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{\left\{r_1^2 + r_2^2 - 2r_1 r_2 \cos(\theta_2 - \theta_1)\right\}^{1/2}} = \frac{1}{r_1\left\{1 + \left(\frac{r_2}{r_1}\right)^2 - \frac{2r_2}{r_1}\cos\theta\right\}^{1/2}} = \frac{1}{r_1}\left\{1 + \left(\frac{r_2}{r_1}\right)^2 - \frac{2r_2}{r_1}\cos\theta\right\}^{-1/2}$$

For $r_1 > r_2$,using Binomial expansion,

$(1+x)^n = 1 + nx + n(n-1)\frac{x^2}{2} + \ldots\ldots\ldots$ we get

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{r_1}\left[1 - \frac{1}{2}\left(\frac{r_2}{r_1}\right)^2 + \cos\theta + \frac{3}{8}\frac{r_2}{r_1}\left\{\left(\frac{r_2}{r_1}\right)^2 - \frac{2r_2}{r_1}\cos\theta\right\}^2 + \ldots\ldots\right] = \frac{1}{r_1}\left[1 - \frac{1}{2}\left(\frac{r_2}{r_1}\right)^2 + \cos\theta + \frac{3}{8}\left\{\left(\frac{r_2}{r_1}\right)^4 - 2.\left(\frac{r_2}{r_1}\right)^2 .2\frac{r_2}{r_1}\cos\theta + 4\left(\frac{r_2}{r_1}\right)^2 \cos^2\theta\right\}\right]$$

Neglecting higher power of $\frac{r_2}{r_1}$ we get

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{r_1}\left[1 + \frac{r_2}{r_1}\cos\theta + \frac{3}{2}\left(\frac{r_2}{r_1}\right)^2 \cos^2\theta\right] \quad \ldots\ldots\ldots\ldots (3.5.1.7)$$

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{r_1}\sum_{l=0}^{\infty}\left(\frac{r_2}{r_1}\right)^l p_l(\cos\theta), \text{ For } r_1 \geq r_2 \quad \text{………} (3.5.1.8)$$

Similarly,

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{r_2}\sum_{l=0}^{\infty}\left(\frac{r_1}{r_2}\right)^l p_l(\cos\theta), \text{ For } r_2 \geq r_1 \quad \text{………} (3.5.17.9)$$

Where $p_{l(\cos\theta)}$ are the Legendre polynomials.

Let $\frac{2Zr_1}{a_o} = \rho_1$, $\frac{2Zr_2}{a_o} = \rho_2$ …………(3.5.1.10)

And choosing $d^3r_2 = r_2^2 \mathrm{d}r_2 \sin\theta d\theta d\varphi$……… (3.5.1.11)

Since, $d^3r_1 = r_1^2 \mathrm{d}r_1 \sin\theta_1 d\theta_1 d\varphi_1$

From eq^n (3.5.1.10) we get $r_1 = \left(\frac{a_o}{2Z}\right)\rho_1$

$$d^3r_1 = \left(\frac{a_0}{2Z}\right)^2 \rho_1^2 \left(\frac{a_0}{2Z}\right) d\rho_1^2 \left(\frac{a_0}{2Z}\right) d\rho_1 \sin\theta_1 d\theta_1 d\phi_1 = \left(\frac{a_0}{2Z}\right)^3 \rho_1^2 d\rho_1 \sin\theta_1 d\theta_1 d\phi_1$$

…… (3.5.1.12)

Similarly from eq^n (3.5.1.10), $r_2 = \left(\frac{a_o}{2Z}\right)\rho_2$

$$d^3r_2 = \left(\frac{a_0}{2Z}\right)^2 \rho_2^2 \left(\frac{a_0}{2Z}\right) d\rho_2^2 \left(\frac{a_0}{2Z}\right) d\rho_2 \sin\theta d\theta d\phi = \left(\frac{a_0}{2Z}\right)^3 \rho_2^2 d\rho_2 \sin\theta d\theta d\phi$$

..

(3.5.1.13)

Now putting eq^n (3.5.1.8),(3.5.1.9),(3.5.1.10),(3.5.1.11)(3.5.1.12)&(3.8.1.13) in eq^n (3.5.1.6),we get

$$E_{11}^{1}=\frac{e^2}{\pi^2}\left(\frac{Z}{a_0}\right)^6\left(\frac{a_0}{2Z}\right)^6\iiint \rho_1^2 d\rho_1 \sin\theta_1 d\theta_1 d\phi_1 e^{-\rho_1}\iiint \rho_2^2 d\rho_2 \sin\theta d\theta d\phi e^{-\rho_2}.$$

$$\left\{\left(\frac{2Z}{a_0}\right)\frac{1}{\rho_1}\sum_{l=0}^{\infty}\left(\frac{\rho_2}{\rho_1}\right)^l \rho_l(\cos\theta)+\left(\frac{2Z}{a_0}\right)\frac{1}{\rho_2}\sum_{l=0}^{\infty}\left(\frac{\rho_1}{\rho_2}\right)^l \rho_l(\cos\theta)\right\}$$

Where we write

$\frac{1}{|\vec{r}_1-\vec{r}_2|} = \frac{1}{|\vec{r}_1-\vec{r}_2|}$ for $r_1 \geq r_2$ + $\frac{1}{|\vec{r}_1-\vec{r}_2|}$ for $r_2 \geq r_1$, to include both $r_1 \geq r_2$ & $r_2 \geq r_1$ cases.

$$E_{11}^{1}=\frac{e^2}{\pi^2}\frac{1}{2^6}\frac{2Z}{a_0}\iiint \rho_1^2 d\rho_1 e^{-\rho_1}\sin\theta_1 d\theta_1 d\phi_1 \times$$

$$\left[\frac{1}{\rho_1}\int_0^{\rho_1}\rho_2^2 d\rho_2 e^{-\rho_2}\times\sum_l\left(\frac{\rho_1}{\rho_2}\right)^l\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}p_l(\cos\theta)\sin\theta d\theta d\phi+\int_{\rho_1}^{\infty}\rho_2 d\rho_2 e^{-\rho_2}\times\sum_l\left(\frac{\rho_1}{\rho_2}\right)^l\int_{\theta}^{\pi}\int_{\phi}^{2\pi}\rho_l(\cos\theta)\sin\theta d\theta d\phi\right]$$

Using the relation, $\int_0^{\pi}\rho_l(\cos\theta)\sin\theta d\theta = 2,$ for l=0 and

$\int_0^{\pi}\rho_l(\cos\theta)\sin\theta d\theta = 0,$ for $l = l \geq 1$……… (3.5.1.14)

We get

$$E_{11}^{1}=\frac{e^2}{\pi^2}\frac{1}{2^5}\frac{Z}{a_0}\iiint \rho_1^2 d\rho_1 e^{-\rho_1}\sin\theta_1 d\theta_1 d\phi_1\left[\frac{4\pi}{\rho_1}\int_0^{\rho_1}\rho_2^2 e^{-\rho_2}d\rho_2+4\pi\int_{\rho_1}^{\infty}\rho_2 e^{-\rho_2}d\rho_2\right]$$

$$E_{11}^{1} = \frac{e^2}{\pi^2}\frac{1}{32}\frac{Z}{a_0}4\pi\iiint \rho_1^2 d\rho_1 e^{-\rho_1}\sin\theta_1 d\theta_1 d\phi_1\left[\frac{1}{\rho_1}\int_0^{\rho_1}\rho_2^2 e^{-\rho_2}d\rho_2 + \int_{\rho_1}^{\infty}\rho_2 e^{-\rho_2}d\rho_2\right]$$

After integration we get

$$E_{11}^{1} = \frac{5}{8}\frac{Ze^2}{a_0} \text{ , since } a_0 = \frac{\hbar^2}{me^2}$$

$$E_{11}^{1} = \frac{5}{8}\frac{Ze^2}{\hbar^2}me^2 = \frac{5}{4}Z\left(\frac{me^4}{2\hbar^2}\right)$$

$$E_{11}^{1} = \frac{5}{4}ZE_H \text{ .... } (3.5.1.15)$$

From eq^n (3.5.1.3), (3.5.1.4) & (3.5.1.15) we have:

$$E_{11}^{1} = -2Z^2E_H + \frac{5}{4}ZE_H$$

$$E_{11}^{1} = \left(-Z^2 + \frac{5}{8}Z\right)2E_H \text{ .... } (3.5.1.16)$$

Eq^n (3.5.1.16) is total ground state energy of Helium atom up to first order correction. For Helium atom Z=2 & E_H = +13.6ev. So from eq^n (3.5.1.16) we get

$$E_{11}^{1} = \left(-4 + \frac{5}{4}\right)27.2\,\text{ev}$$

$$E_{11}^{1} = -74.8\,\text{ev}$$

This value of ground state energy of Helium atom differ from experimental value (= -79ev) by 4.2ev

3.5.2 Variational Method

Owing to the screening of the one electron to the nucleus by the other electron, the nuclear charge is not exactly 2e but expected to be lesser. This suggests that the effective atomic number Z' may be regarded as the variable parameter and the function in Eq^n (3.5.1.5) corresponding to the nuclear charge Z'e may be taken as the trial wavefunction. It is convenient to rewrite the Hamiltonian as

$$H = \left(-\frac{\hbar^2 \nabla_1^2}{2m} - \frac{Z' e^2}{r_1} \right) + \left(-\frac{\hbar^2 \nabla_2^2}{2m} - \frac{Z' e^2}{r_1} \right) + \left(Z' - Z \right) e^2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{r_{12}} \quad \ldots\ldots\ldots\ (3.5.2.1)$$

The expectation value of H with the trial wavefunction in Eq^n(3.5.1.5) when Z replaced by Z'is given

$$\langle H \rangle = \left\langle U_1 \left| \frac{\hbar^2 \nabla_1^2}{2m} - \frac{Z' e^2}{r_1} \right| U_1 \right\rangle + \left\langle U_2 \left| \frac{\hbar^2 \nabla_2^2}{2m} - \frac{Z' e^2}{r_2} \right| U_2 \right\rangle + \left(Z' - Z \right) \left\langle U_1 \left| \frac{e^2}{r_1} \right| U_1 \right\rangle + \left(Z' - Z \right) \left\langle U_2 \left| \frac{e^2}{r_2} \right| U_2 \right\rangle + \left\langle U_1 U_2 \left| \frac{e^2}{r_{12}} \right| U_1 U_2 \right\rangle$$

………(3.5.2.2)

The value of the first and second terms on the right are equal and each is

$-Z'^2 E_H$, where $E_H = \left(\frac{me^4}{2\hbar^2} \right)$. Then

$$\left\langle U_1 \left| \frac{e^2}{r_1} \right| U_1 \right\rangle = \frac{Z' e^2}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta_1 d\theta_1 \int_0^{\infty} r_1 e^{-2Z' r_1 / a_0} dr_1 = \frac{Z'^3 e^2}{\pi a_0^3} 4\pi \frac{1}{\left(2Z' / a_0 \right)^2} = 2Z' E_H \quad \ldots\ldots..$$

(3.5.2.3)

$$\left\langle U_2 \left| \frac{e^2}{r_2} \right| U_2 \right\rangle = 2Z' E_H \quad \ldots\ldots\ldots\ldots\ (3.5.2.4)$$

And

$$\left\langle U_1 U_2 \left| \frac{e^2}{r_{12}} \right| U_1 U_2 \right\rangle = \frac{5}{4} Z' E_H \ \ldots\ldots\ldots\ (3.5.2.5)$$

Putting all the terms together in Eq^n (3.5.2.2), we get

$$\langle H\rangle = -2Z'^2E_H + 4(Z'-Z)Z'E_H + \frac{5}{4}Z'E_H$$

Minimizing $\langle H\rangle$ with respect to Z'

$$0 = -4Z'E_H + 8Z'E_H - 4ZE_H + \frac{5}{4}E_H \ldots\ldots\ldots (3.5.2.6)$$

$Z' = Z - \frac{5}{16}$ With this value of Z' from Eq ^{n}(3.5.2.6)

$$E = \langle H\rangle = -2\left(Z - \frac{5}{16}\right)^2 E_H$$

Substitution of E_H = 13.6 ev leads to a ground state energy of -77.46eV for helium atom, where as the experimental value is -78.975eV.

3.5.3 Hartree-Fock Method

In the Hartree method, the simple product wave function $\psi(\overrightarrow{r_1},\overrightarrow{r_2},\cdots\cdots\overrightarrow{r_n}) = u_1(\overrightarrow{r_1})u_2(\overrightarrow{r_2})\cdots\cdots u_n(\overrightarrow{r_n})$ neglects the contributions in the motion of electrons caused by the asymmetry of the complete wave functions. As a result, the exchange term in the energy is missing. Therefore the Hartree method gives same energy for the Para and Ortho states of Helium. To improve this Hartree method, V-Fock used the correct antisymmetrized wave function is given by the following Slater determinant:

$$\psi = \frac{1}{\sqrt{2}}\begin{vmatrix} u_a(1) & u_b(1) \\ u_a(2) & u_b(2) \end{vmatrix} \ldots\ldots\ldots (3.5.3.1)$$

Where u_a and u_b are mutually orthogonal normalized spin orbitals involving space and spin parts i.e

$\langle u_a|u_a\rangle$=1, $\langle u_b|u_b\rangle$ ………… (3.5.3.2)

$\langle u_a|u_b\rangle$=0, $\langle u_b|u_a\rangle$=0 …… (3.5.3.3)

The Hamiltonian of the system of two- electrons is given by,

$H = H_1^0 + H_2^0 + V_{12}$ ………… (3.5.3.4)

Where H_1^0 operates only on the co-ordinates of electron 1 and similarly H_2^0

$$\langle\phi|H|\phi\rangle = \frac{1}{2}\left[\left\langle u_a(1)u_b(2) - u_a(2)u_b(1)\right|H^0 + V_{12}\left|u_a(1)u_b(2) - u_a(2)u_b(1)\right\rangle\right]$$

$$\langle\phi|H|\phi\rangle = \langle u_a(1)u_b(2)|H^0|u_a(1)u_b(2)\rangle + \langle u_a(2)u_b(1)|H^0|u_a(2)u_b(1)\rangle + \langle u_a(1)u_b(2)|V_{12}|u_a(1)u_2(b)\rangle - \langle u_a(1)u_b(2)|V_{12}|u_a(2)u_b(1)\rangle - \langle u_a(2)u_b(1)|V_{12}|u_a(2)u_b(1)\rangle + \langle u_a(2)u_b(1)|V_{12}|u_a(2)u_b(1)\rangle$$

Since, $H^0 = H_1^0 + H_2^0$

$$\langle\phi|H|\phi\rangle = \langle u_a(1)u_b(2)|H_1^0|u_a(1)u_b(2)\rangle + \langle u_a(1)u_b(2)|H_2^0|u_a(1)u_b(2)\rangle + \langle u_a(2)u_b(1)|H_1^0|u_a(2)u_b(1)\rangle + \langle u_a(2)u_b(1)|H_2^0|u_a(2)u_b(1)\rangle + (\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots)$$

Since H_1^0 operates only on the co-ordinates of electron 1 and H_2^0 operates only

On the co-ordinates of electron 2 we have:

$$\langle\phi|H|\phi\rangle = \langle u_a(1)|H_1^0|u_a(1)\rangle + \langle u_b(2)|H_2^0|u_b(2)\rangle + \langle u_b(1)|H_1^0|u_b(1)\rangle + \langle u_a(2)|H_2^0|u_a(2)\rangle + \langle u_a(1)u_b(2)|V_{12}|u_a(1)u_b(2)\rangle - \langle u_a(1)u_b(2)|V_{12}|u_a(2)u_b(1)\rangle - \langle u_a(2)u_b(1)|V_{12}|u_a(1)u_b(2)\rangle + \langle u_a(2)u_b(1)|V_{12}|u_a(2)u_b(1)\rangle$$

……….

(3.5.3.5)

Combining eq^n (3.5.3.3)&(3.5.3.5) by using the lagranges multipliers to get the variational eq^n

$\delta[\langle\varphi|H|\varphi\rangle - \lambda_{aa}\langle u_a(1)|u_a(1)\rangle - \lambda_{ab}\langle u_a(1)|u_b(1)\rangle - \lambda_{bb}\langle u_b(1)|u_b(1)\rangle - \lambda_{ba}\langle u_b(1)|u_a(1)\rangle]$ =0

Let us suppose this eq[n] as δI=0

Then $\frac{\partial I}{\partial\langle u_a(1)}$ =0 gives

$H_1^0 u_a(1)$ + $v_{bb}u_a(1)$ - $v_{ba}u_b(1)$ - $\lambda_{aa}u_a(1)$ - $\lambda_{ab}u_b(1)$ =0

$[H_1^0 + v_{bb}]u_a(1)$ - $v_{bb}u_b(1)$ = $\lambda_{aa}u_a(1)$ + $\lambda_{ab}u_b(1)$……………….(3.5.3.6)

Similarly, Then $\frac{\partial I}{\partial\langle u_b(1)}$ =0, gives

$[H_1^0 + v_{aa}]u_b(1)$ - $v_{ab}u_b(1)$ = $\lambda_{bb}u_a(1)$ + $\lambda_{ba}u_b(1)$…… (3.5.3.7)

Eq[n] (3.5.3.6) & (3.5.3.7) can be written in the matrix form as:

$\begin{pmatrix} H_1^0 + v_{bb} & -v_{ba} \\ -v_{ab} & H_1^0 + v_{aa} \end{pmatrix}\begin{pmatrix} u_a(1) \\ u_b(1) \end{pmatrix} = \begin{pmatrix} \lambda_{aa} & \lambda_{ab} \\ \lambda_{ba} & \lambda_{bb} \end{pmatrix}$ …………… (3.5.3.8)

Where,

$v_{bb} = \langle u_b(2)|V_{12}|u_b(2)\rangle$ is coulomb integral

$v_{ab} = \langle u_a(2)|V_{12}|u_b(2)\rangle$ is exchange integral

$v_{ba} = \langle u_b(2)|V_{12}|u_a(2)\rangle$ is exchange integral

$v_{aa} = \langle u_a(2)|V_{12}|u_a(2)\rangle$ is coulomb integral

Let us consider the $\lambda^{,s}$ matrix

$\Lambda = \begin{pmatrix} \lambda_{aa} & \lambda_{ab} \\ \lambda_{ba} & \lambda_{bb} \end{pmatrix}$

Since $\lambda_{ab}^* = \lambda_{ba}$,Λ is Hermition. Therefore a unitary operator A must exit that diagonalizes Λ i.e.

A ΛA^{-1} =E ………………(3.5.3.9)

Where E is diagonal matrix with eigen values E_a and E_b i.e.

E $=\begin{pmatrix} E_a & 0 \\ 0 & E_b \end{pmatrix}$

Thus eq^n (3.5.3.8) can be written as:

$$\begin{pmatrix} H_1^0 + v_{bb} & -v_{ba} \\ -v_{ab} & H_1^0 + v_{aa} \end{pmatrix} \begin{pmatrix} u_a \\ u_b \end{pmatrix} = \begin{pmatrix} E_a & 0 \\ 0 & E_b \end{pmatrix} \begin{pmatrix} u_a \\ u_b \end{pmatrix}$$

$\Rightarrow$ $(H_1^0 + v_{bb})\, u_a$- $v_{ba}\, u_b = E_a u_a$ and

-$v_{ab}\, u_a$ +$(H_1^0 + v_{aa})\, u_b = E_b u_b$

$\Rightarrow (H_1^0 + v_{bb} - E_a) u_a = v_{ba}\, u_b$………… (3.5.3.10) and

$(H_1^0 + v_{aa} - E_a\,) u_b = v_{ab}\, u_a$…………… (3.5.3.11)

Eq^n (3.5.3.10) & (3.5.3.11) are the Hartree – Fock equations. These are solved simultaneously by the method of successive approximation to achieve self-Consistency.

From eq^n (1) we get, $\varphi = \frac{1}{\sqrt{2}} \begin{vmatrix} u_a(1) & u_b(1) \\ u_a(2) & u_b(2) \end{vmatrix}$ ………… (3.5.3.12)

$$\varphi = \frac{1}{\sqrt{2}} \begin{vmatrix} u_{1s\uparrow}(1) & u_{1s\downarrow}(1) \\ u_{1s\uparrow}(2) & u_{1s\downarrow}(2) \end{vmatrix}$$

Where, $u_a(1) = u_{1s\uparrow}(1) = \frac{1}{\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{\frac{3}{2}} e^{-\frac{2r_1}{a_0}}$

$u_a(2) = u_{1s\uparrow}(2) = \frac{1}{\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{\frac{3}{2}} e^{-\frac{2r_2}{a_0}}$

$u_b(1) = u_{1s\downarrow}(1) = \frac{1}{\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{\frac{3}{2}} e^{-\frac{2r_1}{a_0}}$

$$u_b(2) = u_{1s\downarrow}(2) = \frac{1}{\sqrt{\pi}}\left(\frac{2}{a_0}\right)^{\frac{3}{2}} e^{-\frac{2r_2}{a_0}} \text{ and } V_{12} = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

Now we have exchange integral,

$$v_{ab} = \langle u_a(2)|V_{12}|u_b(2)\rangle$$

$$= \int \frac{1}{\sqrt{\pi}}\left(\frac{2}{a_0}\right)^{\frac{3}{2}} e^{-\frac{2r_2}{a_0}} \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \frac{1}{\sqrt{\pi}}\left(\frac{2}{a_0}\right)^{\frac{3}{2}} e^{-\frac{2r_2}{a_0}} d^3r_2$$

$$= \frac{1}{\pi}\left(\frac{2}{a_0}\right)^3 \int e^{-\frac{4r_2}{a_0}} \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} d^3r_2$$

$$v_{ab} = \frac{e^2}{\pi}\left(\frac{2}{a_0}\right)^3 \int e^{-\frac{4r_2}{a_0}} \frac{1}{|\vec{r}_1 - \vec{r}_2|} d^3r_2 \text{...........} \quad (3.5.3.13)$$

In the similar manner coulomb integral are calculated, and the values of these integral are substituted in equation (3.5.3.10) and (3.5.3.11). Then with the help of E matrix the final energy of ground state can be calculated by the Hartree-fock method. But this procedure is tedious and needs a lot of effort, so we have used here Gaussian program to calculate the ground state energy of helium atom by Hartree-fock method using different basis set. The value of ground state energy by using different basis set is tabulated below.

Serial no.	Basis set	Energy in a.u./ Hartree unit	Energy in eV
1.	3-21G	-2.83567987	-77.16168494
2.	3-21G*	-2.83567987	-77.16168494
3.	6-31G	-2.85516043	-77.69177046
4.	6-31G*	-2.85516043	-77.69177046

Chapter IV

Result and discussion

This chapter includes the result of the theoretical discussion related to analytical study related to analytical study of excitation cross-section of helium atom by electron impact. The general expression for the differential cross-section per unit solid angle for the different transitions were derived in the chapter III

Excitation differential cross- section (1^1S to 2^1P)

For the transition from 1^1S to 2^1P as given by equation (3.3.4) and (3.3.5) the differential cross section are given as

$$2\pi I(\theta) = 1.176\times 10^4 \frac{k_q}{k_p}\frac{1}{K^2\left(p^2+K^2\right)^6} \qquad \text{By method I}$$

and similarly

$$2\pi I(\theta) = 2.532\times 10^2 \frac{k_q}{k_p}\frac{\left[8.069-0.687K^2\right]^2}{K^2\left(p^2+K^2\right)^6} \qquad \text{By method II}$$

Where, k_p = wave number of the incident electron.

k_q =wave number of the scattered electron.

$\vec{K} = \vec{k}_q - \vec{k}_p = 2k_p \sin\frac{\theta}{2}$

$p^2 = 4.783$

$\Delta E = 0.779$ In Hartree units

The graph plotted below shows cross section ($2\pi I(\theta)$) in the units of πa_0^2 versus angle of scattering in radians, in which scattering angle increases from zero to

0.4 radians. It is clearly seen from the plot below that as the angle of scattering increases from zero to 0.4 radians, the differential cross section go on decreasing.

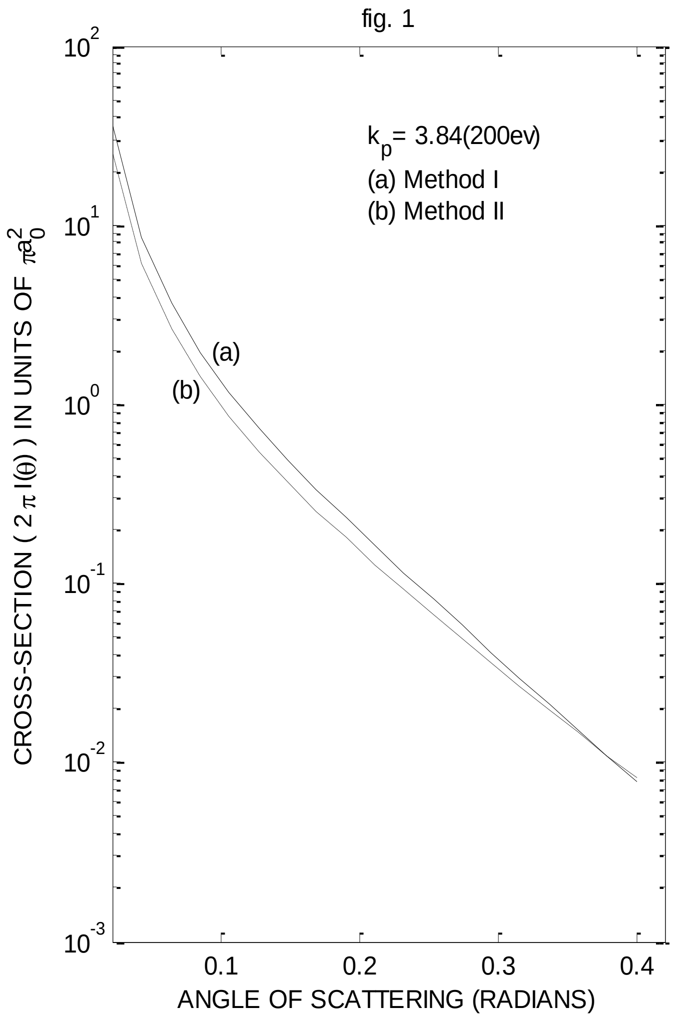


Fig.1 Angular distributions for excitation scattering of electrons by helium atoms (^1S to 2^1P transition)

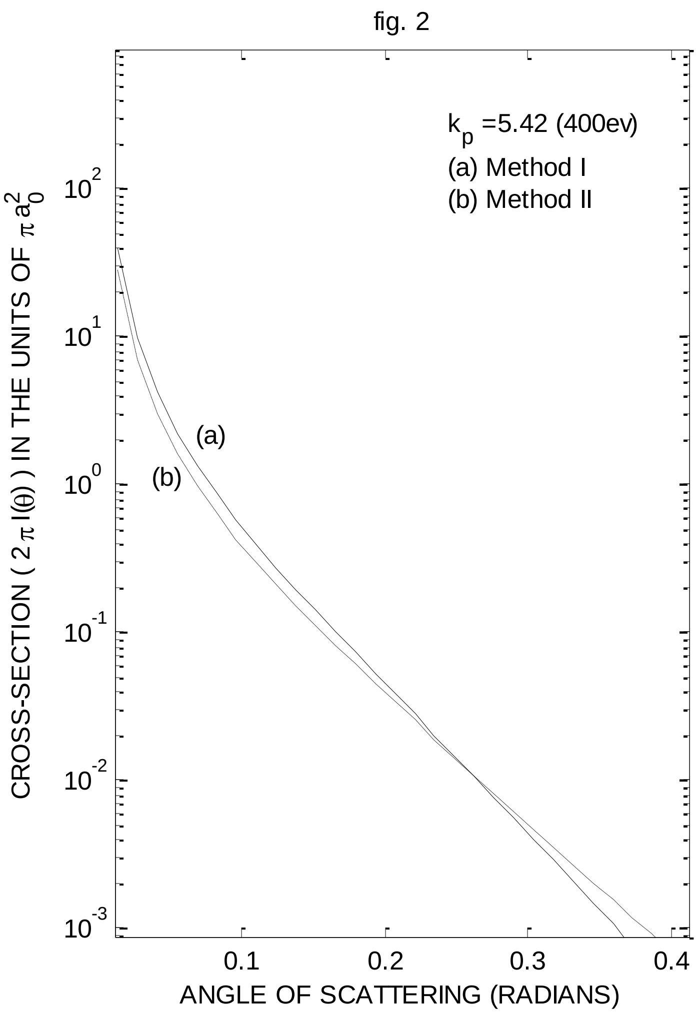


Fig.2 Angular distribution for excitation scattering of electrons by helium atoms (^1S to 2^1P transition)

The total excitation cross-section

The corresponding total cross sections as given by equation (3.3.6) and (3.3.7) are

$$Q_1(k_p) = \frac{1.176\times10^2}{k_p^2}\left[\frac{1}{X^5}\left\{\begin{matrix}2.091 + 0.546X + 0.1523X^2 + 4.777\times10^{-2}X^3 \\ +1.977\times10^{-2}X^4 + 4.176\times10^{-3}X^5 \ln\dfrac{K^2}{X}\end{matrix}\right\}\right]_{k_p-k_q}^{k_p+k_q}$$ by method I

And similarly

$$Q_{II}(k_p) = 1.42Q_I + \frac{2.987}{k_p^2}\left[\frac{5K^2 - 89.18}{X^5}\right]_{k_p-k_q}^{k_p+k_q}$$ By method II

Where $X = p^2 + K^2$,

Here, the total cross sections are presented in figs. 3 and 4. Particular significance is attached to the results since, except for magnitudes of the cross sections, the general behaviour is quit similar for the two methods. Therefore , the results of either may be successfully normalised to measure cross sections.

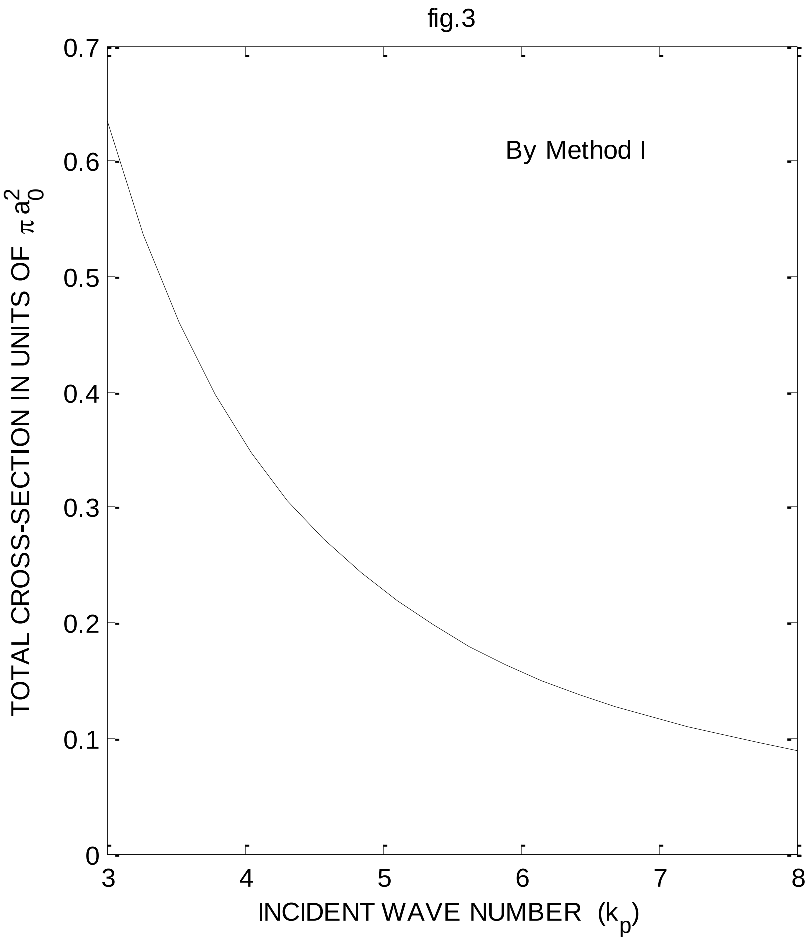


Fig..3 Total excitation cross section for electron impact with helium atoms as a function of a incident energy(^1S to 2^1P) by method I

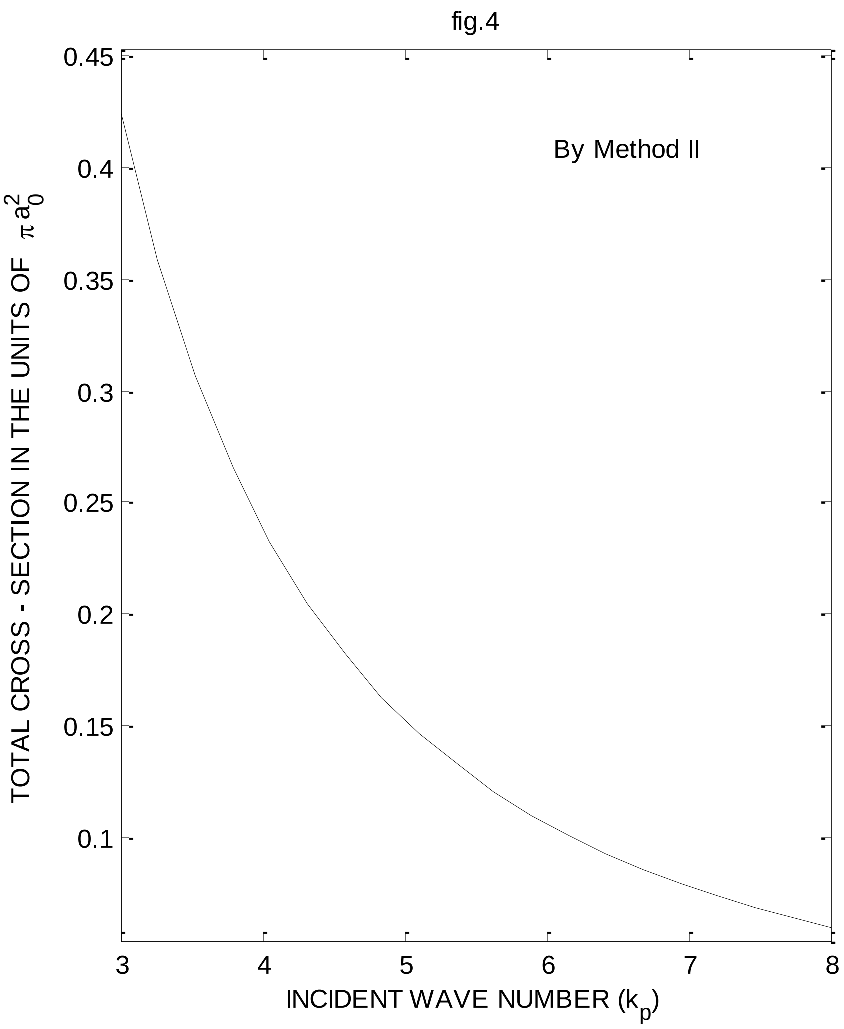


Fig..4 Total excitation cross section for electron impact with helium atoms as a function of a incident energy(^1S to 2^1P)by method II

Excitation differential cross- section(1^1S to 3^1P)

For the transition from state 1^1S to state 3^1P as given by equation (3.3.8) and (3.3.9) the differential cross section are given as

$$2\pi I(\theta) = 1.507\frac{k_q}{k_p}\frac{\left[52.55K^2 + 1.168\times 10^2\right]^2}{K^2\left(p^2 + K^2\right)^8}$$ By method I …………(3.3.8)

and similarly

$$2\pi I(\theta) = 0.5245\frac{k_q}{k_p}\frac{\left[-8.28K^4 + 87.62K^2 + 228.8\right]^2}{K^2\left(p^2 + K^2\right)^8}$$ By method II ……….. (3.3.9)

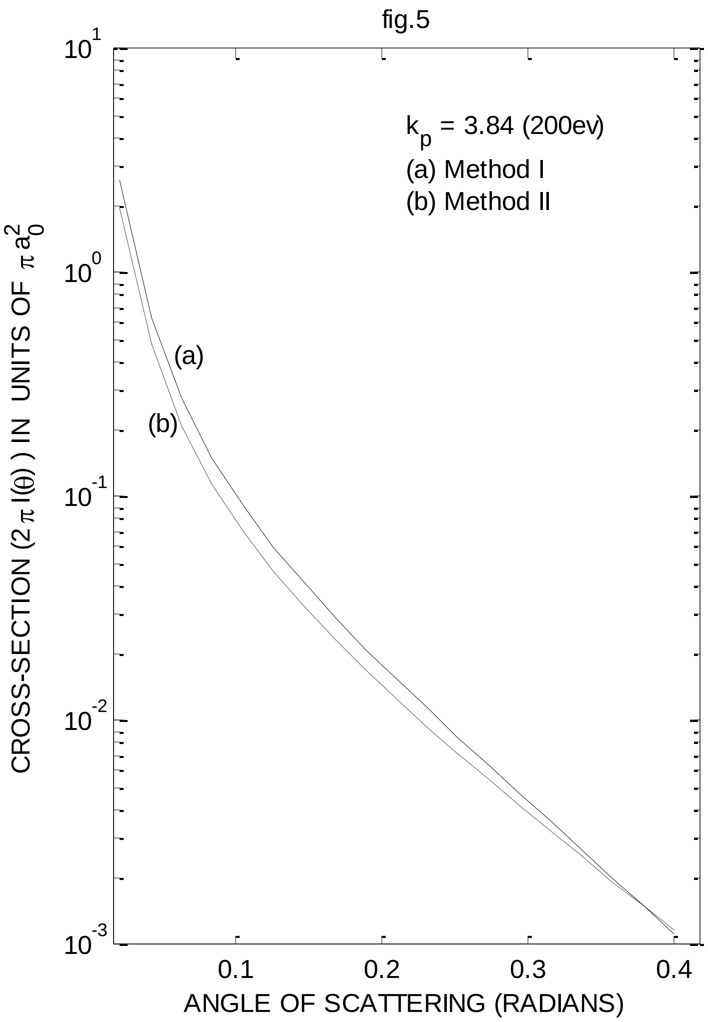
Where $p^2 = 4.093$; $\Delta E = 0.8474$,

k_p = wave number of the incident electron.

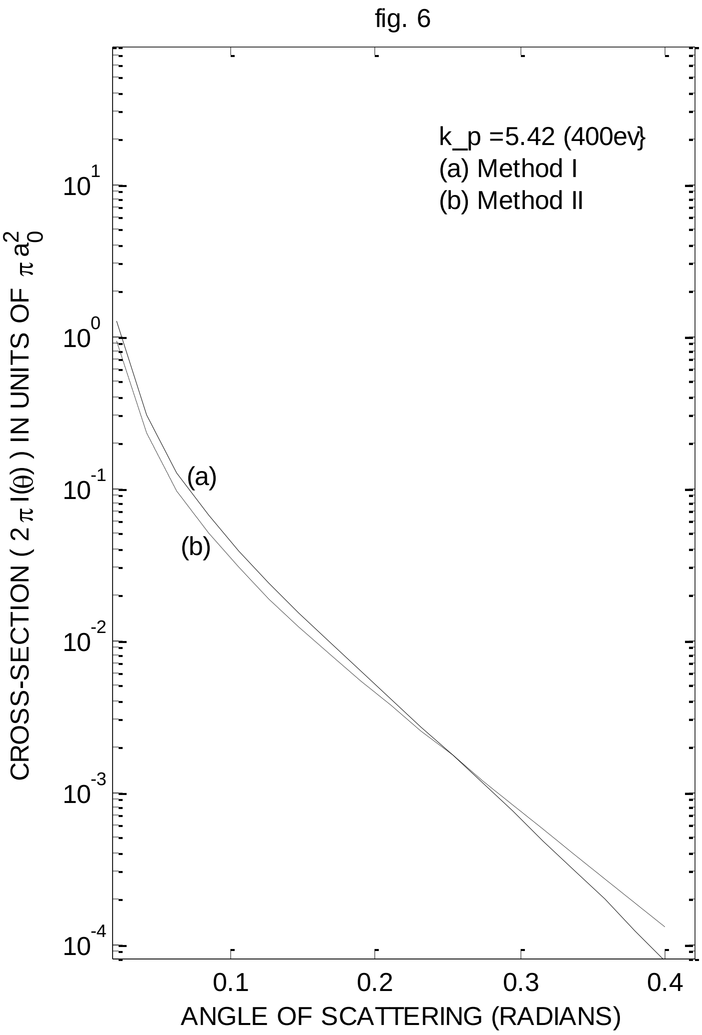
k_q =wave number of the scattered electron.

$\vec{K} = \vec{k}_q - \vec{k}_p = 2k_p \sin\frac{\theta}{2}$

The graph plotted below shows cross section ($2\pi I(\theta)$) in the units of πa_0^2 versus angle of scattering in radians, in which scattering angle increases from zero to 0.4 radians. It is clearly seen from the plot below that as the angle of scattering increases from zero to 0.4 radians, the differential cross section go on decreasing. More or less the result given by both the method is similar in nature though the numerical value differs slightly.



fig…5 Angular distribution for excitation scattering of electrons by helium atoms (^1S to 3^1P transition)



fig…6 Angular distribution for excitation scattering of electrons by helium atoms (^1S to 3^1P transition)

The total excitation cross -section

The corresponding total cross sections as given by equation are given by (3.3.9.1) and (3.3.9.2) are

$$Q_1\left(k_p\right)=\frac{1.507}{k_p^2}\left[\frac{1}{X^7}\left\{\begin{array}{l}-1.012\times10^3-2.301\times10^2K^2 67.93X+19.92X^2+6.084X^3\\+1.982X^4+0.7265X^5+0.3550X^6+8.675\times10^{-2}X^7\ln\dfrac{K^2}{X}\end{array}\right\}\right]_{k_p-k_q}^{k_p+k_q}$$

by method II

And similarly

$$Q_{II}\left(k_p\right)=1.333Q_I-\frac{05245}{k_p^2}\left[\frac{1}{X^7}\left\{8.57K^6-1.241\times10^2K^4-1.303\times10^3K^2-2.175\times10^3\right\}\right]_{k_p-k_q}^{k_p+k_q}$$

by method II,

Where $X=p^2+K^2$

From the figures 7 and 8 it can clearly interpret that the total excitation cross-section given by method follows the same nature, but slightly differs in numerical value.

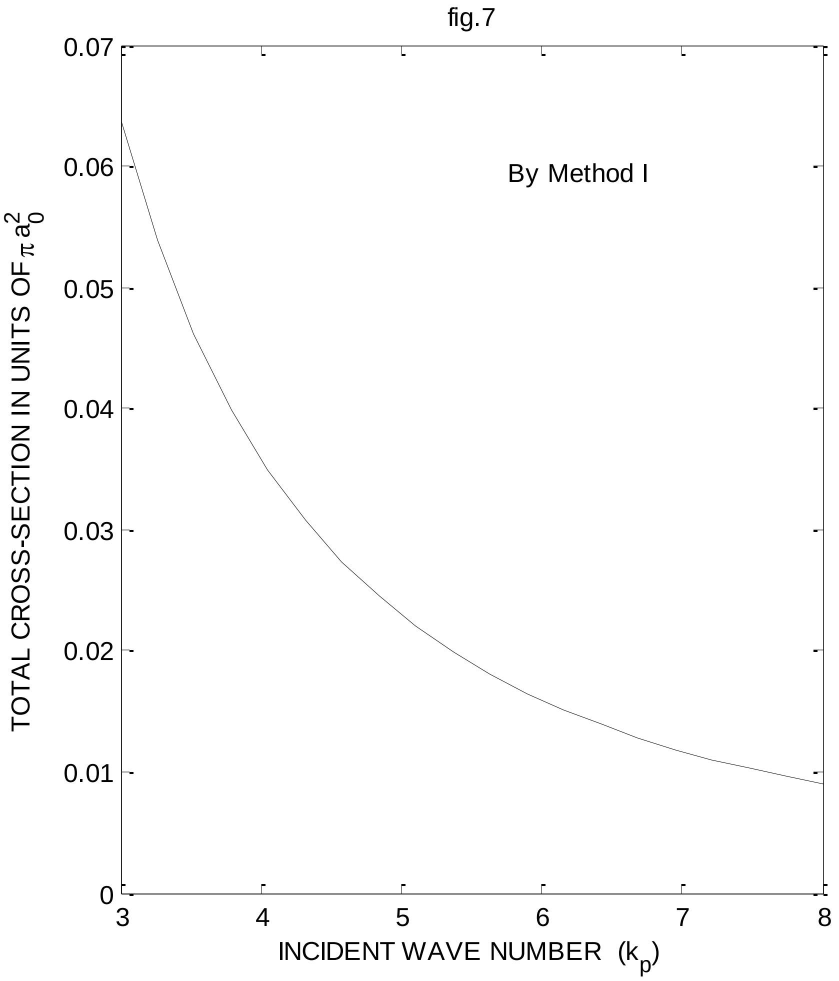


Fig..7 Total excitation cross section for electron impact with helium atoms as a function of a incident energy(^1S to 3^1P)by method I

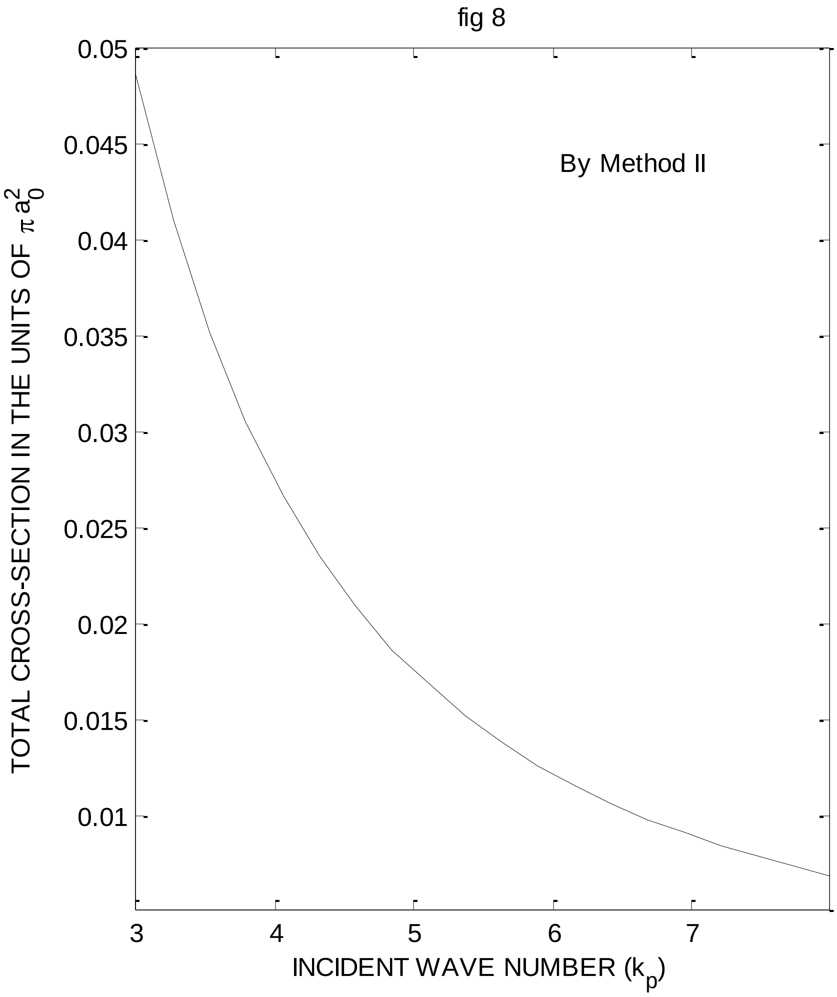


Fig..8 Total excitation cross section for electron impact with helium atoms as a function of a incident energy(^1S to 3^1P)by method II

Excitation differential cross-section (1^1S to 2^1S) from section -2

The differential cross section for a momentum change of magnitude dK for excitation transition $1^1S \rightarrow 2^1S$ calculated by Method I as given in equation (3.4.1) and (3.4.2) is given by

$$I(K)dK = \frac{8\pi dK}{k_p^2 K^3}\left|\frac{36.879}{\left(13.447+K^2\right)^2}+\frac{(11.457)\left(2.547+2.887K^2\right)}{\left(5.2304+K^2\right)^3}-\frac{52.863}{11.384+K^2}\right|^2$$

And similarly by method II is given as

$$I(K)dK = \frac{8\pi dK}{k_p^2 K^3}\left|3.7372\times10^2 K^2\left[\frac{5.2159\times10^{-3}}{\left(13.4469+K^2\right)^2}+\frac{6.9338\times10^{-2}-9.876\times10^{-3}K^2}{\left(5.2304+K^2\right)^3}\right]\right|^2$$

Just as in the case of transitions to P-states (section 1) we observe that the cross section for either of the two methods may be normalized to measured values. However, such is not the case for the angular distributions in the case of the transition to the first excited to the metastable state. The disagreement in the shape of the angular distribution indicates that the Vinti function does not describe the metastable state as well as the Eckhart functions for the P-states (section 1).

In order to discriminate between the results of the either method it will be necessary to have accurate experimental data. Nevertheless, an argument may be advanced which favors the results of the method II.

fig.9

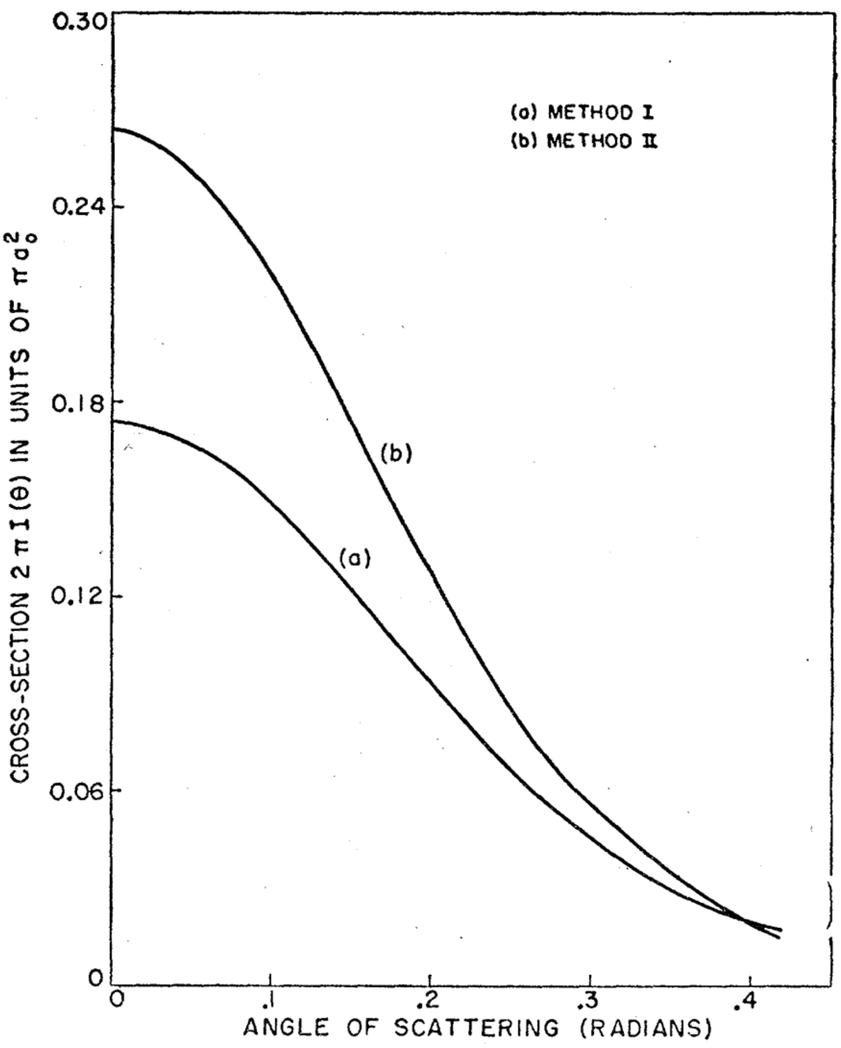


Fig.9 Angular distributions for excitation of electrons from helium atoms (1^1S to 2^1S transition) at incident energy of 200ev.

Conclusion

The nature of the curve of differential cross section and total cross section as given by the method I and method II is slightly different. This may be due to the numerical factor difference that arises in these two methods. No doubt the both of the methods nearly have the same nature of curves. For the method I, to calculate the differential cross section, the wave function of the Helium atom in the ground state are the product of unperturbed hydrogen atom wave functions where as the wave function of the helium atom in excited state is considered by the Eckhart approximation. Similarly for the method II, the equations satisfied by exact Helium atom wave functions ψ_p and ψ_q are used. The product $\psi_q^* \psi_p$ is calculated to find the differential cross section. It is seen that with increase in the angle of scattering, the differential cross section go on decreasing and so for the total excitation cross section. Here increase in the value of incident wave vector (k_p) means, the energy of the incident electron is increased. The ground state energy of helium atom obtained by the Hartree-Fock method is much close to the experimental value than the variational and the perturbation method.

References

1. L.D. Landau and E.M. Lifshitz, Quantum Mechanics, Non-relativistic theory

(Institute of physical problem, U.S.S.R Academy of sciences, vol. 3, second edition, 1965)

2. B.K. Agrawal and Hari Prakash, Quantum Mechanics, prentice Hall of India private limited, fifth printing, September (2005)

3. Estermann, O. Stern: Z. Phys. 61, 95 (1930)

4. J. B. Hudson, Surface Science - An Introduction, John Wiley & Sons, Inc, New York (1998)

5. B.H. Bransden and C.J. Joachain's Physics of Atoms and Molecules 2nd edition Pearson Education, Inc Introduction to Quantum Mechanics Second edition (2002)

6. David I. Griffiths Pearson Education, Inc (2005)

7. Cramer, Christopher J. Essentials of Computational Chemistry. Chichester: John Wiley & Sons, Ltd. pp. 153–189. ISBN 0-471-48552-7 (2002).

8. Physica, volume 31, issue 3, Pages 365-384 F.J.Heer and J.Van Den Bos, march (1965)

9. G.Aruldhas, Quantum mechanics, prentice Hall of India private limited, seventh printing, October (2007).

10. Eugen Merzbacher, Quantum mechanics, John Willy & Sons, Third edition (1998).

11. D.R. Bates and A. Damgaard, Trans. Roy.Soc.(London) Physical Rev. **A242**, 101 (1949);

12. Bates, Fundaminsky, and Massey, Trans. Roy. Soc. (London) physical Rev. **A243**, 93 (1950);

13. N.F. Mott and H.S.W. Massey, Theory of Atomic Collisions, Clarendon Press, Oxford, England,second edition(1949)

14. V.K.Thankappan, Quantum Mechanics, New age international (P) Ltd, publishers.second edition January (1993)

15. Gupta, Kumar & Sharma, Quantum Mechanics, Jai Prakash Nath & Company, Meerut India, (1999)

16. John David Jackson Classical Electrodynamics Third edition (1998)

17. Schiff, Leonard. Quantum Mechanics. New York: McGraw-Hill (1968)

APPENDIX

The alternative matrix element which is the basis of Method II ,as given in Eq.(3.4.3),is established as follows:

In the case of the transition considered in this note, $\psi_p \psi^*{}_q$ is symmetric. Therefore,

$$J \equiv \sum_{i=1}^{2} \int e^{-iKzi} \psi_p (\vec{r}_1, \vec{r}_2) \psi_q^* (\vec{r}_1, \vec{r}_2) dr_1 r_2$$

$$=2 \int e^{-iKz1} \psi_p \psi_q^* dr_1 dr_2 \ ,$$

And, substituting from Eq.(3.4.1) , we have

$$J = \frac{1}{\Delta E} \int e^{-iKz1} \left\{ \psi_q^* \left(\nabla_1^2 + \nabla_2^2 \right) \psi_p - \psi_p \left(\nabla_1^2 + \nabla_2^2 \right) \psi_q^* \right\} dr_1 dr_2$$

$$= \frac{1}{\Delta E} \left[\int e^{-iKz1} \left\{ \psi_q^* \nabla_1^2 \psi_p - \psi_p \nabla_1^2 \psi_q^* \right\} dr_1 dr_2 + \int e^{-iKz1} \left\{ \psi_q^* \nabla_2^2 \psi_p - \psi_p \nabla_2^2 \psi_q^* \right\} dr_1 dr_2 \right]$$

The second term on the right vanishes identically because of the Hermitian property of ∇_2^2.

Consequently (since the 2^1S state is real),

$$J = \frac{1}{\Delta E} \int e^{-iKz1} \left\{ \psi_q \nabla_1^2 \psi_p - \psi_p \nabla_1^2 \psi_q \right\} dr_1 dr_2 \, .$$

Introducing

$$\psi_q = B \left(\varphi_2 - \gamma \psi_p \right),$$

We have

$$J = \frac{B}{\Delta E} \left[\int e^{-iKz1} \left(\varphi_2 - \gamma \psi_p \right) \nabla_1^2 \psi_p dr_1 dr_2 - \int e^{-iKz1} \psi_p \nabla_1^2 \left(\varphi_2 - \gamma \psi_p \right) dr_1 dr_2 \right]$$

$$= \frac{B}{\Delta E} \left[\int e^{-iKz1} \left(\varphi_2 \nabla_1^2 \psi_p - \psi_p \nabla_1^2 \varphi_2 \right) dr_1 dr_2 \right].$$

We now employ the identity:

$$\int e^{-iKz1} \psi_p \nabla_1^2 \varphi_2 dr_1 dr_2 = \int \varphi_2 \nabla_1^2 \left(\psi_p e^{-iKz1} \right) dr_1 dr_2$$

$$= \int \varphi_2 \left\{ \psi_p \nabla_1^2 e^{-iKz1} + e^{-iKz1} \nabla_1^2 \psi_p + 2\nabla \psi_p \cdot \nabla e^{-iKz1} \right\} dr_1 dr_2 .$$

Substituting, the expression for J becomes

$$J = \frac{B}{\Delta E} \left[\int \left\{ -\varphi_2 \psi_p \nabla_1^2 e^{-iKz1} - 2\varphi_2 \nabla_1 \psi_p \cdot \nabla_1 e^{-iKz1} \right\} dr_1 dr_2 \right]$$

$$= \frac{B}{\Delta E} \left[K^2 \int \varphi_2 e^{-iKz1} \psi_p dr_1 dr_2 + 2iK \int \varphi_2 e^{-iKz1} \frac{\partial}{\partial Z_1} \psi_p dr_1 dr_2 \right]$$

Matlab programme

Matlab programme for fig.1

```
clear all;
close all;
theta=linspace(0,0.4,20);
kp=3.84;
kq=3.63;
kp1=3.84;
kq1=3.63;
psq=4.783;
K=2*kq*sin(theta/2);
K1=2*kq*sin(theta/2);
Ksq=K.^2;
Ksq1=K1.^2;
denm=Ksq.*(psq+Ksq).^6;
denm1=Ksq1.*(psq+Ksq1).^6;
itheta=1.176e4*(kq/kp)*1./(2*pi*denm);
itheta1=2.532e2*(kq1/kp1)*(8.069-0.687*K1.^2).^2./(2*pi*denm);
semilogy(theta,itheta,'k--',theta,itheta1,'k')
```

Matlab programme for fig.2

```
clear all;
close all;
theta=linspace(0,0.4,30);
kp=5.42;
kq=5.27;
kp1=5.42;
kq1=5.27;
psq=4.783;
K=2*kq*sin(theta/2);
K1=2*kq*sin(theta/2);
```

```
Ksq=K.^2;
Ksq1=K1.^2;
denm=Ksq.*(psq+Ksq).^6;
denm1=Ksq1.*(psq+Ksq1).^6;
itheta=1.176e4*(kq/kp)*1./(2*pi*denm);
itheta1=2.532e2*(kq1/kp1)*(8.069-0.687*K1.^2).^2./(2*pi*denm);
semilogy(theta,itheta,'k--',theta,itheta1,'k')
```

Matlab programme for fig.3

```
clear all
close all
theta=0.1;
a=1.76e2;
kp=linspace(3,8,20);
kq=3.63;

psq=4.783;
K=2*kq*sin(theta/2);
Ksq=K.^2;
 X1=kp+kq;
X2=kp-kq;
y=log(K^2./X1);
z=log(K^2./X2);
a1=2.091+0.5464*X1;
a2=0.1523*X1.^2;
a3=4.77e-2*X1.^3;
a4=1.997e-2*X1.^4;
a5=4.176e-3*y.*X1.^5;
f=(a1+a2+a3+a4+a5);
b1=2.091+0.5464*X2;
b2=0.1523*X1.^2;
b3=4.77e-2*X2.^3;
b4=1.997e-2*X2.^4;
```

```
b5=4.176e-3*z.*X2.^5;
h=(b1+b2+b3+b4+b5);
g=f/X1.^5;
k=h/X2.^5;
fx=a*(k-g)./kp.^2;
plot(kp,fx)
```

Matlab programme for fig.4

```
clear all
close all
theta=0.1;
a=1.176e2;
kp=linspace(6,8,20);
kq=3.84;
psq=4.783;
K=2*kq*sin(theta/2);
Ksq=K.^2;
X1=kp+kq;
X2=kp-kq;
y=log(K^2./X1);
z=log(K^2./X2);
a1=2.091+0.5464*X1;
a2=0.1523*X1.^2;
a3=4.77e-2*X1.^3;
a4=1.997e-2*X1.^4;
a5=4.176e-3*y.*X1.^5;
f=(a1+a2+a3+a4+a5);
b1=2.091+0.5464*X2;
b2=0.1523*X1.^2;
b3=4.77e-2*X2.^3;
b4=1.997e-2*X2.^4;
b5=4.176e-3*z.*X2.^5;
h=(b1+b2+b3+b4+b5);
```

```
g=f/X1.^5;
k=h/X2.^5;
fx=a*(k-g)./kp.^2;
c1 = 5*K^2 - 89.18;
d1 = c1./X1.^5;
d2 = c1./X2.^5;
d = (d1-d2);
l=2.987./kp.^2;
yx = 1.402*fx + l.*d;
 plot(kp,yx)
```

Matlab programme for fig.5

```
clear all;
close all;
theta=linspace(0,0.4,20);
kp=3.84;
kq=3.61;
kp1=3.84;
kq1=3.61;
psq=4.783;
K=2*kq*sin(theta/2);
K1=2*kq*sin(theta/2);
Ksq=K.^2;
Ksq1=K1.^2;
denm=Ksq.*(psq+Ksq).^8;
denm1=Ksq1.*(psq+Ksq1).^8;
itheta=1.507*(kq/kp)*(52.55*K.^2.+1.168*10.^2.).^2./(2*pi*denm
);
itheta1=0.5245*(kq1/kp1)*(-
8.28*K1.^4+87.62*K1.^2+228.8).^2./(2*pi*denm);
semilogy(theta,itheta,'k--',theta,itheta1,'k')
```

Matlab programme for fig.6

```
clear all;
close all;
theta=linspace(0,0.4,20);
kp=5.42;
kq=5.26;
kp1=5.42;
kq1=5.26;
psq=4.783;
K=2*kq*sin(theta/2);
K1=2*kq*sin(theta/2);
Ksq=K.^2;
Ksq1=K1.^2;
denm=Ksq.*(psq+Ksq).^8;
denm1=Ksq1.*(psq+Ksq1).^8;
itheta=1.507*(kq/kp)*(52.55*K.^2.+1.168*10.^2.).^2./(2*pi*denm
);
itheta1=0.5245*(kq1/kp1)*(-
8.28*K1.^4+87.62*K1.^2+228.8).^2./(2*pi*denm);
semilogy(theta,itheta,'k--',theta,itheta1,'k')
```

Matlab programme for fig.7

```
clear all
close all
theta=0.01;
a=1.507;
kp=linspace(3,8,20);
kq=5.27;

psq=4.093;
```

```
K=2*kq*sin(theta/2);
Ksq=K.^2;

X1=kp+kq;
X2=kp-kq;
y=log(K^2./X1);
z=log(K^2./X2);
a1=-1.012e3-2.301e2*K.^2*67.93*X1;
a2=19.92*X1.^2;
a3=6.084*X1.^3;
a4=1.982*X1.^4;
a5=0.7265*X1.^5;
a6=0.3550*X1.^6;
a7=8.675e-2*y.*X1.^7;
f=(a1+a2+a3+a4+a5+a6+a7);
b1=-1.012e3-2.301e2*K.^2*67.93*X2;
b2= 19.92*X2.^2;
b3= 6.084*X2.^3;
b4=1.982*X2.^4;
b5=0.7265*X2.^5;
b6=0.3550*X2.^6;
b7=8.675e-2*z.*X2.^7;
h=(b1+b2+b3+b4+b5+b6+b7);
g=f/X1.^7;
k=h/X2.^7;
fx=a*(g-k)./kp.^2;
plot(kp,fx)
```

Matlab programme for fig.8

```
close all
theta=0.01;
a=1.507;
kp=linspace(7,8,20);
```

```
kq=5.27;
psq=4.093;
K=2*kq*sin(theta/2);
Ksq=K.^2;
X1=kp+kq;
X2=kp-kq;
y=log(K^2./X1);
z=log(K^2./X2);
a1=-1.012e3-2.301e2*K.^2*67.93*X1;
a2=19.92*X1.^2;
a3=6.084*X1.^3;
a4=1.982*X1.^4;
a5=0.7265*X1.^5;
a6=0.3550*X1.^6;
a7=8.675e-2*y.*X1.^7;
f=(a1+a2+a3+a4+a5+a6+a7);
b1=-1.012e3-2.301e2*K.^2*67.93*X2;
b2= 19.92*X2.^2;
b3= 6.084*X2.^3;
b4=1.982*X2.^4;
b5=0.7265*X2.^5;
b6=0.3550*X2.^6;
b7=8.675e-2*z.*X2.^7;
h=(b1+b2+b3+b4+b5+b6+b7);
g=f/X1.^7;
k=h/X2.^7;
fx=a*(g-k)./kp.^2;
c1 = 8.570*K^6-1.241e2*K^4-1.303e3*K^2-2.175e3;
d1 = c1./X1.^7;
d2 = c1./X2.^7;
d = (d1-d2);
l=0.5245./kp.^2;
yx = 1.402*fx + l.*d;
plot(kp,yx)
```