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BY

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Norman, Oklahoma

1969

A STUDY OF THEORETICAL METHODS OF CALCULATION OF EXCITATION CROSS SECTIONS OF TWO-ELECTRON SYSTEM BY ELECTRON IMPACT

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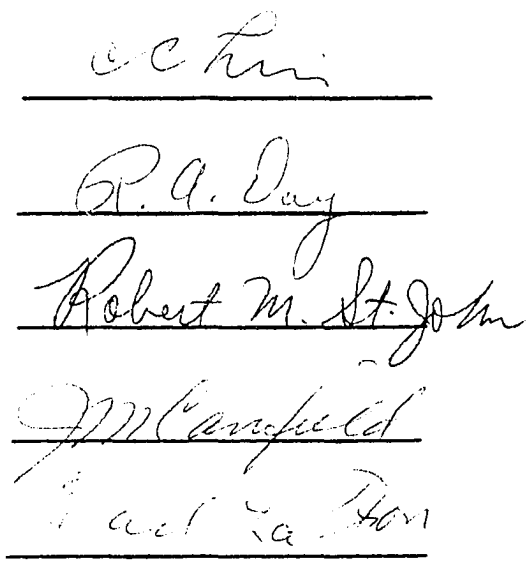

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PART I

SIMULTANEOUS IONIZATION-EXCITATION CROSS SECTION OF HELIUM BY BORN APPROXIMATION

CHAPTER I

INTRODUCTION

The production of excited ionized helium atoms by electron impact has been observed by optical method.[1,2] In these experiments the intensity of the transition $n=4 \rightarrow n=3$ (4686-Å) of He^+ which resulted from a beam of electrons passing through a container of helium was measured. Because of the near L degeneracy in He^+, the observed radiation is the total intensity of the five transitions $4S \rightarrow 3P$, $4P \rightarrow 3S$, $4P \rightarrow 3D$, $4D \rightarrow 3P$, and $4F \rightarrow 3D$. If the emission of the 4686-Å radiation is believed to result primarily from direct ionization-excitation induced by electron impact, the cross section of the 4686-Å radiation can be calculated from the ionization-excitation cross sections of the 4S, 4P, 4D and 4F states of He^+. Calculations for the 4P and 4D

states have been made by Dalgarno and McDowell.[3] In the paper of St. John and Lin,[1] it was assumed that the ionization-excitation cross section of the 4S state of He^+ lies somewhere between those of 4P and 4D as suggested in Ref. 3. Using a cross section of the 4S state estimated in this manner, it was found that the 4S → 3P transition alone constitutes more than the sum of all other 4 transitions. This happens because the 4S state cascades only to 3P and 2P with an intensity ratio of 3:4, whereas the majority of the atoms in 4P cascade to 1S, leaving a small fraction of the population for the 4P → 3S and 4P → 3D transitions. The ionization-excitation cross section for 4F can be well expected to be much smaller than that of 4D, and the 4F → 3D transition should be quite insignificant compared to the other members of the 4686-Å group.

Taking the ionization-excitation cross section of 4S to be somewhere between 4P and 4D, as suggested in Ref. 3, one finds the calculated cross section of n=4 → n=3 to be too small compared with experiment.[1] Because of the importance of the 4S → 3P transition in its contribution to the intensition of the 4686-Å radiation it is necessary to calculated the ionization-excitation cross sections for the 4S state of He^+ more carefully. For the range of incident energy of the electrons considered, Born approximation seems to be sufficient. The theoretical cross sections for the 4686-Å radiation are then determin-

ed and compared with the experimental results. In the case of the excitation of the triplet states of the neutral helium atoms, St. John, Miller and Lin[4] have found that the observed cross sections are much larger than the theoretical values, leading to the conclusion that the observed population of the triplet states in their discharge experiment is produced mainly by processes other than direct excitation. It is therefore of interest to see if the observed intensity of the 4686-Å radiation can be ascribed mainly to direct ionization-excitation processes.

The calculation can be readily extended to give cross sections for $n=5 \rightarrow n=3$ (3203-Å), $n=6 \rightarrow n=3$ (2733-Å) and $n=7 \rightarrow n=3$ (2511-Å).

Recently the five individual transitions of the 4686-Å have been resolved.[18] The broadening of each line is due to the following effects: natural line-width, pressure broadening, thermal Doppler broadening and recoiled Doppler broadening. A distribution of recoiled velocity of the ionized-excited atom can be obtained from the differential cross section. It is interesting to calculate the amount of broadening due to recoil to see if its contribution is significant and to see if the total calculated line-width agrees with experimental measurements. The half-width of the $4S \rightarrow 3P$ line due to recoiled velocity alone is calculated and compared with experimental value in Appen. IV.

CHAPTER II

FORMULATION OF EXCITATION CROSS SECTION OF TWO-ELECTRON SYSTEMS BY ELECTRON IMPACT[4]

§2.1 Direct Excitation

Consider the excitation of a two-electron system by electron bombardment. The mass of the electron is small compared with the target and the motion of the latter in the collision can be neglected. Let the intensity of the incident beam of electrons be such that one particle crosses unit area per unit time. Denote the propagation vector of the scattered electron by $\vec{k}'$, (k', θ, ϕ) being its polar coordinates. The number of electrons that are scattered per unit time into a solid angle $d\omega$, in the direction of $\vec{k}'$, after having excited the two-electron atom into its higher state n is $I(\theta, \phi)d\omega$. This number has the dimension of an area and will be called the differential cross section for scattering into the solid angle $d\omega$. The total cross section Q_n corresponding to the excitation will be obtained by integrating over all angles of scattering so that

$$Q_n = \int_0^{\pi} \int_0^{2\pi} I_n(\theta, \phi) \sin\theta \, d\theta d\phi \ . \qquad (2.1)$$

Let the atomic electrons be distinguished by suffices 1 and 2 and the incident electron by suffix 3. In atomic units the Hamiltonian of the system of incident electron and the atom is

$$H = H_a - \nabla_3^2/2 + r_{13}^{-1} + r_{23}^{-1} + V(\vec{r}_3) \ , \qquad (2.2)$$

where $\nabla_i^2 = (\partial^2/\partial x_i^2) + (\partial^2/\partial y_i^2) + (\partial^2/\partial z_i^2)$

is the Laplacian operator in the space of the ith electron, H_a is the Hamiltonian of the atomic system and $r_{ij} = |\vec{r}_i - \vec{r}_j|$, $\vec{r}_i$ being the position vector of the ith electron. H_a can be written as

$$H_a = -2/r_1 - 2/r_3 + r_{12}^{-1} + H' \ ,$$

where H' includes spin-orbit coupling and other small effects. $V(\vec{r}_3)$ is the potential between the incident electron and the core. The wave equation of the system is then

$$H\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = E\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) \ . \qquad (2.3)$$

Expand $\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ in terms of the complete orthonormal set of eigenfunction $\psi_n(\vec{r}_1, \vec{r}_2)$ of the atomic Hamiltonian operator H_a:

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = (\Sigma + \int)\psi_n(\vec{r}_1, \vec{r}_2) F_n(\vec{r}_3) \ , \qquad (2.4)$$

and $$H_a \psi_n(\vec{r}_1, \vec{r}_2) = E_n \psi_n(\vec{r}_1, \vec{r}_2) \ . \qquad (2.5)$$

The integral sign denotes integration over the functions of the con-

tinuous spectrum. Substituting equ. (2.4) into LHS of equ. (2.3) the following expression is obtained:

$$(\sum+\int)(E - E_n + \nabla_3^2/2)\psi_n(\vec{r}_1, \vec{r}_2) F_n(\vec{r}_3) = (r_{13}^{-1} + r_{23}^{-1} + V(\vec{r}_3)) \times \Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) \ . \qquad (2.6)$$

Because of the ortho-normal conditions of the $\psi_n(\vec{r}_1, \vec{r}_2)$ wave functions on multifying equ. (2.6) on both sides by $\psi_n^*(\vec{r}_1, \vec{r}_2)$ and integrating, the following differential equation is obtained:

$$(E - E_n + \nabla_3^2/2)F_n(\vec{r}_3) = \iint(r_{13}^{-1} + r_{23}^{-1} + V(\vec{r}_3))\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) \times \psi_n^*(\vec{r}_1, \vec{r}_2)d\vec{r}_1 d\vec{r}_2 \ . \qquad (2.7)$$

Without loss of generality the atom is assumed to be in its ground state before excitation. The required asymptotic solutions of equ. (2.7) are

$$F_o(\vec{r}) \to \exp(ik_o z_o) + r^{-1}\exp(ik_o r)f_o(\theta, \phi) \ , \qquad (2.8)$$

and

$$F_n(\vec{r}) \to r^{-1}\exp(ik_n r)f_n(\theta, \phi) \ . \qquad (2.9)$$

The function $F_o(\vec{r})$ represents the sum of amplitudes of the incident and scattered waves while $F_n(\vec{r})$ must represent the scattered wave amplitude only. Construct a sphere of radius r with the target atom as the center. The number of electrons, after having excited the atom to a state n, crossing a unit area of the sphere per unit time is $k_n r^{-2}|f_n(\theta, \phi)|^2$. The flux of the incident beam of electrons is k_o. Thus the differential

cross section of the mode of excitation being considered is

$$I_n(\theta,\phi)\,d\omega = (k_n/k_0)\left|f_n(\theta,\phi)\right|^2 d\omega \ . \qquad (2.10)$$

The differential equation (2.7) cannot be solved exactly. Several approaches to the equation are discussed in Ref. 4 to give approximate solutions. Only the Born approximation[6] will be considered here. At higher incident energy, the interaction between the in coming plane wave and the target atom may be considered as small perturbation on the incident wave. As a zero-order approximation $\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3)$ can be taken as

$$\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3) = \exp(i\vec{k}_o\cdot\vec{r}_3)\psi_n(\vec{r}_1,\vec{r}_2) \ , \qquad (2.11)$$

where $\vec{k}_o$ is the propagation vector of the incident electron. Equ. (2.7) then becomes

$$(\nabla_3^2 + k_n^2)F_n(\vec{r}_3) = 2\iint(r_{13}^{-1} + r_{23}^{-1} + V(\vec{r}_3))\exp(i\vec{k}_o\cdot\vec{r})\psi_o(\vec{r}_1,\vec{r}_2)\ X$$

$$\psi_n(\vec{r}_1,\vec{r}_2)d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \ , \qquad (2.12)$$

where

$$k_n^2 = 2(E - E_n) \ . \qquad (2.13)$$

Now equ. (2.12) can be solved.[4] The solution corresponding to the excited state n has the asymptotic form

$$F_n(\vec{r}) \to [\exp(ik_n r)/(2\pi r)]\iint\exp[i(\vec{k}_o-\vec{k}_n)\cdot\vec{r}_3][r_{13}^{-1} + r_{23}^{-1} + V(\vec{r}_3)]\ X$$

$$\psi_o(\vec{r}_1,\vec{r}_2)\psi_n^*(\vec{r}_1,\vec{r}_2)d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \ , \qquad (2.14)$$

where $\vec{k}_n$ has the magnitude satisfying equ. (2.13) and is in the direction

of the scattered electron. The differential cross section is then given by

$$I_n(\theta,\phi) = k_n/(4\pi^2 k_o)\left|\int \exp(i\vec{K}\cdot\vec{r}_3)[r_{13}^{-1}+r_{23}^{-1}+V(\vec{r}_3)]\psi_o(\vec{r}_1,\vec{r}_2)\,X\right.$$

$$\left.\psi_n^*(\vec{r}_1,\vec{r}_2)d\vec{r}_1 d\vec{r}_2 d\vec{r}_3\right|^2 , \qquad (2.15)$$

where

$$\vec{K} = \vec{k}_o - \vec{k}_n , \qquad (2.16)$$

is the change of propagation vector of the incident electron. The zero-order approximation can be refined by putting the expression (2.14) in the RHS of equ. (2.7) and integrating the expression a second time. This would then give the first-order correction of Born approximation. However the method becomes very tedious and it is better to use the method of distorted waved or some other method discussed in Ref. 4.

Expression (2.15) can be simplified in the following manner. The $V(\vec{r}_3)$ term is zero because $\psi_o(\vec{r}_1,\vec{r}_2)$ is orthogonal to $\psi_n(\vec{r}_1,\vec{r}_2)$. The wave functions are either symmetric or antisymmetric with respect to interchanging atomic electrons 1 and 2:

$$\psi_m(\vec{r}_1,\vec{r}_2) = \pm\psi_m(\vec{r}_2,\vec{r}_1) . \qquad (2.17)$$

The initial and final wave functions ψ_o and ψ_n must have the same symmetry with respect to the operation of interchanging atomic electrons otherwise r_{13}^{-1} and r_{23}^{-1} terms will contribute equal and opposite amount to the integral and cause it to vanish. When they are of

the same symmetry, the first two terms of the RHS of equ. (2.15) are equal. This can be expressed as

$$\int \exp(i\vec{K}\cdot\vec{r}_3)(r_{13}^{-1}+r_{23}^{-1})\psi_o(\vec{r}_1,\vec{r}_2)\psi_n(\vec{r}_1,\vec{r}_2)d\vec{r}_1 d\vec{r}_2 d\vec{r}_3$$

$$= 2\int \exp(i\vec{K}\cdot\vec{r}_3)r_{13}^{-1}\psi_o(\vec{r}_1,\vec{r}_2)\psi_n^*(\vec{r}_1,\vec{r}_2)d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \ . \qquad (2.18)$$

Expression (2.15) can be simplified further by using the following formula derived by Bethe:[7]

$$\int \exp(i\vec{K}\cdot\vec{r}_i)r_{ij}^{-1}d\vec{r}_i = (4\pi K^{-2})\exp(i\vec{K}\cdot\vec{r}_j) \ . \qquad (2.19)$$

When equ. (2.19) is applied to equ. (2.18) and the resulting equation is inserted into equ. (2.15) the following expression results:

$$I_n(\theta,\phi) = 16k_n/(k_o K^4)\left|\int \exp(i\vec{K}\cdot\vec{r}_1)\psi_o(\vec{r}_1,\vec{r}_2)\psi_n^*(\vec{r}_1,\vec{r}_2)d\vec{r}_1 d\vec{r}_2\right|^2, \qquad (2.20)$$

In some cases there exists a symmetry about ϕ and $I_n(\theta,\phi)$ is independent of ϕ. The cross section then is given by the following expressions:

$$I_n(\theta) = 32\pi k_n/(k_o K^4)\left|\int \exp(i\vec{K}\cdot\vec{r}_1)\psi_o(\vec{r}_1,\vec{r}_2)\psi_n^*(\vec{r}_1,\vec{r}_2)d\vec{r}_1 d\vec{r}_2\right|^2, \qquad (2.21)$$

$$Q_n = \int_0^\pi I_n(\theta)\sin\theta\, d\theta \ . \qquad (2.22)$$

Often it is convenient to use the momentum variable instead of angular variable. The magnitude of $\vec{K}$ as defined by expression (2.15) is given by

$$K^2 = k_n^2 + k_o^2 - 2k_o k_n \cos\theta \ , \qquad (2.23)$$

since the axis is chosen in the direction of $\vec{k}_o$. From the last equa-

tion it is seen that

$$KdK = k_o k_n \sin\theta d\theta \,. \tag{2.24}$$

In terms of momentum variable expression (2.19) becomes

$$I_n(K)dK = 32\pi/(k_o^2 K^3)\left|\int \exp(i\vec{K}\cdot\vec{r}_1)\psi_o(\vec{r}_1,\vec{r}_2)\psi_n^*(\vec{r}_1,\vec{r}_2)d\vec{r}_1 d\vec{r}_2\right|^2. \tag{2.25}$$

Formula (2.25) gives the expression of differential cross section for momentum change between K and K+dK.

The Born approximation seems to have a wider range of validity than it might have been anticipated. A detailed discussion and comparison between experimental and theoretical results is given in Chapter III of Ref. 4.

§2.2 Excitation by Electron Exchange[4]

When spin-orbit coupling is neglected it is impossible to excite an atom to a state with a different multiplicity. With no spin-orbit coupling there is no singlet-triplet mixing. The configuration part of the singlet wave function is symmetric with respect to interchanging of atomic electrons 1 and 2 while that of the triplet is antisymmetric. As is seen in the previous section Born approximation predicts zero cross section for direct excitation. Oppenheimer[8] proposed the mode of excitation by electron exchange: the incident elec-

tron is captured by the atom and one of the atomic electrons is ejected. This excitation by means of electron exchange can change the multiplicity by ±2 only.[9,5] The electrons are treated as distinguishable only when their spins are antiparallel.

The formulation for excitation by exchange is similar to the previous section. Instead of equ. (2.4) the expansion is

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = (\sum + \int)\psi_n(\vec{r}_2, \vec{r}_3)G_n(\vec{r}_1) , \tag{2.27}$$

where $G_n(\vec{r}_1)$ is assumed to have the asymptotic form of

$$G_n(\vec{r}_1) \rightarrow r^{-1}\exp(ik_n r)g_n(\theta, \phi) . \tag{2.28}$$

Substituting equ. (2.27) into wave equation (2.3), multiplying on both sides by $\psi_n^*(\vec{r}_2, \vec{r}_3)$ and integrating over $\vec{r}_2$ and $\vec{r}_3$ the following differential equation for $G_n(\vec{r}_1)$, corresponding to equ. (2.7), is obtained:

$$(k_n^2 + \nabla_1^2)G_n(\vec{r}_1) = 2\int[r_{13}^{-1} + r_{23}^{-1} + V(\vec{r}_3)]\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3)\psi_n^*(\vec{r}_2, \vec{r}_3)d\vec{r}_2 d\vec{r}_3 . \tag{2.29}$$

Previously the nuclear interaction term $V(\vec{r}_3)$ does not contribute. This is not the case here. A difficulty arises in the choice of the potential for the nuclear interaction as to whether it should be $V(\vec{r}_3)$, the prior interaction or $V(\vec{r}_1)$, the post interaction. If the wave functions are exact solutions of the wave equation then both terms give the same result.[10] This is also true when Hartree self-consisten field wave

functions are used,[9,10] provided the energy difference between the states is taken as to be that given by the same approximation. It is not true for Hartree-Fock wave functions or wave functions by other approximations.

There exists no means of deciding which of the two interactions or some mean between them is the best choice. The seriousness of the difficulty is shown by the following example. The $1^1S \rightarrow 2^3S$ intercombination transition in helium is calculated to have a maximum cross section at 23 eV incident energy of 0.2 a.u. with prior interaction and 0.65 a.u. with post interaction.[11] The later actually exceedes the maximum possible inelastic cross section.

In order to solve equ.(2.29) Born's approximation will be introduced. However instead of expression (2.11) the following expression for $\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ is appropriate:[8]

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \exp(i\vec{k}_o \cdot \vec{r}_1)\psi_n(\vec{r}_2, \vec{r}_3) + \epsilon\exp(i\vec{k}_o \cdot \vec{r}_2)\psi_n(\vec{r}_1, \vec{r}_3) + \epsilon^2\exp(i\vec{k}_o \cdot \vec{r}_3)\psi_n(\vec{r}_1, \vec{r}_2) , \qquad (2.30)$$

where

$$\epsilon = (i - 3^{1/2})/2 ,$$

and

$$\psi_n(\vec{r}_i, \vec{r}_j) = -\psi_n(\vec{r}_j, \vec{r}_i) . \qquad (2.31)$$

Substituting expression (2.30) into equ.(2.29) a solution of $G_n(\vec{r}_1)$ can be obtained in a manner similar to that for $F_n(\vec{r}_3)$, with the re-

quired asymptotic form as given in expression (2.28). The differential cross section is then given by

$$I_n(\theta,\phi) = 3k_n/(4\pi^2 k_o)\left|\int[r_{13}^{-1} + r_{23}^{-1} + V(\vec{r}_3)]\,\psi_o(\vec{r}_1,\vec{r}_2)\psi_n^*(\vec{r}_1,\vec{r}_3)\ X\right.$$
$$\left.\exp[i(\vec{k}_o\cdot\vec{r}_3 - \vec{k}_n\cdot\vec{r}_2)]\,d\vec{r}_1 d\vec{r}_2 d\vec{r}_3\right|^2 . \qquad (2.32)$$

The total cross section is then given by

$$Q_n = \int I_n(\theta,\phi)\sin\theta d\theta d\phi . \qquad (2.33)$$

When the Born approximation is used in the calculation of excitation cross sections by means of electron exchange, this is known as the Born-Oppenheimer approximation as distinct from the direct excitation.

CHAPTER III

THEORY OF THE 4686-Å LINE OF He^+ BY ELECTRON IMPACT*

The processes to be investigated in this and the next chapters can be described quantitatively as

$$He(1s)^2 \xrightarrow{e} He^+(4L) + e,$$

$$He^+(4L) \rightarrow He^+(3L') + h\nu(4686\text{-Å}) .$$

§3.1 Direct Ionization-excitation Cross Section for 4S

The excitation energy for exciting neutral helium to 4S of He^+ is 75.58 eV. The range of incident energy to be considered is from 200 eV to 450 eV. For this range Born approximation is expected to be valid.

According to equ. (2.25) the differential cross section for momentum change between K and K+dK of the incident electron, the

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ejected electron having a propagation vector $\vec{\kappa}$ whose magnitude lies between κ and $\kappa + d\kappa$ and in the solid angle $d\sigma$ is

$$I_{\kappa}(K)dKd\kappa\, d\sigma = 32\pi/(k_o^2 K^3)\left|\int \exp(i\vec{K}\cdot\vec{r}_1)\psi_o(\vec{r}_1,\vec{r}_2)\psi_n^*(\vec{r}_1,\vec{r}_2)d\vec{r}_1 d\vec{r}_2\right|^2 X$$
$$dKd\kappa d\sigma \ . \qquad (3.1)$$

Slater orbitals will be used as an approximation for the ground state of helium. The ground state wave function can be written as

$$\psi_o(\vec{r}_1,\vec{r}_2) = \phi_{1s}(Z|\vec{r}_1)\phi_{1s}(Z|\vec{r}_2) \ , \qquad (3.2)$$

where

$$\phi_{1s}(Z|\vec{r}) = \pi^{-1/2}Z^{3/2}\exp(-Zr) \ . \qquad (3.3)$$

Z is chosen to be 1.69 in accordance with the work of Mott and Massey.[62] For the excited state the wave function $\psi_n^*(\vec{r}_1,\vec{r}_2)$ can be written as†

$$\psi_n^*(\vec{r}_1,\vec{r}_2) = 2^{-\frac{1}{2}}[\phi^*_{n\ell m}(Z'|\vec{r}_1)\phi^*_{\kappa}(Z''|\vec{r}_2) + \phi^*_{\kappa}(Z''|\vec{r}_1)\phi^*_{n\ell m}(Z'|\vec{r}_2)], \qquad (3.4)$$

where $\phi_{n\ell m}(Z'|\vec{r})$ is the hydrogenic wave function with the nuclear charge Z'=2 and $\phi_{\kappa}(Z''|\vec{r})$ is a state in the continuous spectrum with propagation vector $\vec{\kappa}$. An approximate wave function for $\phi_{\kappa}(Z''|\vec{r})$ is to take the hydrogenic wave function in the continuum, with the nu-

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† The suffix n on the LHS of equ. (3.3) denotes an excited state while that on the RHS carries its usual meaning in Quantum Mechanics as the principal quantum number; ℓ is the azimuthal quantum number.

clear charge taken as 1.69.[62] The solution of the hydrogen wave equation in the continuum was first obtained by Sommerfeld:[12]

$$\phi_{\kappa}^{*}(Z''|r) = \kappa(2\pi)^{-1} s^{\frac{1}{2}} w e^{i\kappa r}[\Gamma(1-is)]^{-1} \int_0^{\infty} e^{-is} e^{-u} J_o[2(i\kappa\xi' u)^{\frac{1}{2}}]\, du, \quad (3.5)$$

where

$$\xi' = r(1+\cos\lambda),$$

$$\cos\lambda = \cos\theta\cos\chi + \sin\theta\sin\chi\cos(\phi-\psi),$$

$$s = Z''/\kappa, \quad (3.6a)$$

and

$$w = [1 - \exp(-2\pi s)]^{-1}. \quad (3.6b)$$

In expression (3.5) $J_m(z)$ is the Bessel function of the first kind of order m and argument z, λ is the angle between the incident and the ejected electrons, χ and ψ are the polar angles of the ejected electron and θ and ϕ are the polar angles of the scattered electron. This approximate wave function has the merit of being orthogonal to the ground state. Its normalization is such that it represents an outgoing plane wave plus an outgoing spherical wave.

Substituting equs. (3.2) and (3.3) into equ. (3.1) gives

$$I_n(K)d\kappa\, dK d\sigma = 16\pi/(k_o^2 K^3)\left|h_1 + h_2\right|^2 d\kappa dK d\sigma, \quad (3.7)$$

where

$$h_1 = \int \exp(i\vec{K}\cdot\vec{r}_1)\phi_{1s}(Z|\vec{r}_1)\phi_{n\ell m}^{*}(Z'|\vec{r}_1)d\vec{r}_1 \int \phi_{1s}(Z|\vec{r}_2)\phi_{\kappa}^{*}(Z''|\vec{r}_2)d\vec{r}_2, \quad (3.8)$$

and

$$h_2 = \int \exp(i\vec{K}\cdot\vec{r}_1)\phi_{1s}(Z|\vec{r}_1)\phi_{\kappa}^{*}(Z''|\vec{r}_1)d\vec{r}_1 \int \phi_{1s}(Z|\vec{r}_2)\phi_{n\ell m}^{*}(Z'|\vec{r}_2)d\vec{r}_2. \quad (3.9)$$

If Z'' is chosen as 1.69 as is required in the calculation of the 4S state of He^+ cross section to make $\phi_\kappa(Z''\vec{r})$ orthogonal to $\phi_{1s}(Z\vec{r})$, h_1 vanishes. Except for the modifying factor

$$C = 2\int \phi_{1s}(Z|\vec{r}_2)\phi^*_{n\ell m}(Z'|\vec{r}_2)d\vec{r}_2 \Big|^2 , \tag{3.10}$$

the differential cross section is the same as in the case of ionization of hydrogen.[62] The factor 2 comes from the fact that there are two terms in the potential which contribute a factor of 4, but has to be divided by 2 because of the normalization constant of the wave function. This modifying factor C can be evaluated readily and is found to be equal to 1.26×10^{-3}, with Z=1.69 and Z'=2.0. The first integral of h_2 was performed by Massey and Mohr.[13] It gives for the differential cross section the following expression:

$$I_\kappa(K)d\kappa dK d\sigma = C 2^9 Z^6 \kappa k_o^{-2} K^{-2} w \exp[-2Z\kappa^{-1}\arctan\{2Z\kappa/(Z^2+K^2-\kappa^2)\}] \times$$
$$(Z^2+K^2+\kappa^2-2K\kappa\cos\theta)^{-4}[(K-\kappa\cos\theta)^2 + Z^2\cos^2\theta][(Z^2+K^2-\kappa^2)^2+4Z^2\kappa^2]^{-1} \times$$
$$d\kappa dK d\sigma , \tag{3.11}$$

where θ is the angle between $\vec{K}$ and the direction of ejected electron. The integration over the angles of the ejected electron can be performed to give the differential cross section corresponding to a momentum change of the incident electron between K and K+dK and momentum of the ejected electron between κ and $\kappa+d\kappa$.

After integration, equ. (3.11) becomes

$$I_\nu(K)\,d\nu dK = C2^{11}\pi\nu\, k_o^{-2}K^{-1}w\,Z^6[K^2+\tfrac{1}{3}(Z^2+K^2)]\,[Z^4+2Z^2(K^2+\nu^2)+(K^2-\nu^2)^2]^3\exp[-2Z\nu^{-1}\arctan\{2Z\nu/(Z^2+K^2-\nu^2)\}]\,d\nu dK. \qquad (3.12)$$

In order to get the total cross section it is necessary to integrate over ν and K. This can only be performed by numerical methods. The expression for cross section is

$$Q_{4S} = \int_0^{\nu_{max}}\int_{K_{min}}^{K_{max}} I_\nu(K)d\nu dK\,, \qquad (3.13)$$

where

$$\nu_{max} = (k_o^2 - 2E_n)^{\frac{1}{2}}\,, \qquad (3.14)$$

$$K_{min} = k_o - k_\nu\,, \qquad (3.15)$$

$$K_{max} = k_o + k_\nu\,, \qquad (3.16)$$

$$k_\nu = (k_o^2 - \nu^2 - 2E_n)^{\frac{1}{2}}\,,$$

and $E_n = 75.58$ eV $= 2.778$ a.u.

E_n is the ionization-excitation energy, and $k_o^2/2$ is the kinetic energy of the incident electron.

Numerical integration has been carried out on the computer for the incident energies at 200, 270, 350, 405 and 450 eV. The numerical method used is the two dimensional Simpson's rule. The values obtained are listed in the first row of Table I on p. 22.

§3.2 Direct Ionization-excitation Cross Sections of 4P, 4D and 4F

For $L \neq 0$, h_2 becomes zero because of the angular dependence of $\phi_n^*(Z'|\vec{r}_2)$. If Z'' is chosen to be 1.69 then the cross sections will be zero. However the orthogonality requirement between $\psi_o(\vec{r}_1, \vec{r}_2)$ and $\psi_n(\vec{r}_1, \vec{r}_2)$ no longer demands Z'' to be chosen as 1.69. Hence Z'' can be varied as a parameter.

The first integral on the RHS of equ. (3.8) is an elementary integral. Let it be denoted by $I_{n\ell}(K)$. Choose the axis along $\vec{K}$, then by a straightforward integration the following results can be obtained:

$$I_{4P}(K) = \int \exp(i\vec{K}\cdot\vec{r}_1)\phi_{1s}(Z|\vec{r}_1)\phi^*_{n\ell m}(Z'|\vec{r}_1)d\vec{r}_1 = [i(Z'Z)^{3/2}KB^{-5}5^{-\frac{1}{2}}] \times$$

$$[10cB^2 - 5(5c^2-K^2)B + 3c(5c^2-3K^2)]\delta_{0m} , \qquad (3.18)$$

$$I_{4D}(K) = [(Z'Z)^{3/2}K^2B^{-4}][-6c+(7c^2-K^2)/B]\delta_{0m} , \qquad (3.19)$$

$$I_{4F}(K) = [-i8(Z'Z)^{3/2}cK^3]B^{-5}5^{-1/2}\delta_{0m} , \qquad (3.20)$$

$c = Z' + Z/n = 2.19$,

$B = c^2 + K^2$.

The integration for the second integral on the RHS of equ. (3.8) is given in Appen. I. This is carried out in a similar manner to the integration of the first integral on the RHS of equ. (3.9). The result is:

$$I_{1\kappa} = \int \phi_{1s}(Z|\vec{r}_1)\phi^{*}_{\kappa}(Z''|\vec{r}_2)d\vec{r}_2 = -4Z^{3/2}\pi^{-1/2}(Z''\kappa w)^{1/2}\exp[-2Z''\kappa^{-1} X$$

$$\arctan(\kappa/Z)](Z-Z'')(Z^2+\kappa^2)^{-2} . \qquad (3.21)$$

For a given κ, $\left|I_{1\kappa}\right|^2$ is a rapidly varying function of Z''. It has a minimum of zero at Z''=1.69 and increases rapidly on either side. Thus the cross sections Q_{4P}, Q_{4D} and Q_{4F} depend sensitively on the choice of the parameter Z''.

Now $h_1 = I_{4L}(K)I_{1\kappa}(\kappa, K)$ is given by equs. (3.18) to (3.21). Substituting equs. (3.18) to (3.21) for h_1 in equ. (3.7) the differential cross section becomes a function of κ and K only. Integration over angles of ejection can be performed immediately to give a factor of 4π. The final integrations over κ and K again have to be carried out by numerical methods on the computer to give the direct ionization-excitation cross sections for 4P, 4D and 4F.

By varying Z'' Dalgarno and McDowell's results can be reproduced for the following values of Z'':

Z'' = 1.455 for 4P,

Z'' = 1.446 for 4D.

Dalgarno and McDowell did not report any value for 4F. However the direct excitation cross section for 4F is found to be small and its contribution to the $n=4 \rightarrow n=3$ transition is small. An estimation is made by averaging over the values calculated using Z''=1.455 and Z''=1.446.

§3.3 Variation of Q_{4S} with Z'' as a Parameter

It will be shown in the next chapter that the direct ionization-excitation cross section of 4S state of He^+ contributes about 90% to the intensity of the n=4→n=3 transition. In view of the fact that the cross sections of 4P, 4D and 4F of He^+ are very sensitive to the choice of the parameter Z'' and the choice of Z'' to be 1.69 is somewhat arbitrary, it is interesting to investigate the dependence of Q_{4S} of He^+ on Z''. When Z'' is varied, $\phi^*_\kappa(Z''|\vec{r})$ as given in expression (3.4) will not be orthogonal to $\phi_{1s}(Z|\vec{r})$. Orthogonality can be achieved in the following manner.[10] Instead of using $\phi^*_\kappa(Z''|\vec{r})$ the wave function $\phi^*_\kappa(Z'', Z|\vec{r})$ will be constructed:

$$\phi^*_\kappa(Z'', Z|\vec{r}) = \alpha\,\phi^*_\kappa(Z''|\vec{r}) + \beta\,\phi^*_{1s}(Z|\vec{r}) \ , \qquad (3.22)$$

and by varying α and β, $\phi^*_\kappa(Z'', Z|\vec{r})$ can be made to be orthogonal to $\phi_{1s}(Z|\vec{r})$ and normalised. The normalization condition is[14]

$$\lim_{\Delta\kappa\to 0} \int_0^\infty d\vec{r}\,\phi_\kappa(Z'', Z|\vec{r}) \int_{\kappa-\Delta\kappa}^{\kappa+\Delta\kappa} \phi^*_\kappa(Z'', Z|\vec{r})\,d\kappa = 1 \ . \qquad (3.23)$$

This gives: $\alpha = 1$. Multiplying equ. (3.22) on both sides by $\phi_{1s}(Z|\vec{r})$ and integrating gives

$$\beta(Z'', Z) = -\int \phi_{1s}(Z|\vec{r})\phi^*_\kappa(Z''|\vec{r})d\vec{r} = I_{1\kappa} \ . \qquad (3.25)$$

Substituting equs. (3.22) and (3.25) into equ. (3.9) the following expression for h_2 is obtained:

$$h_2 = h_{21} \times h_{22} \ , \tag{3.26}$$

where

$$h_{21} = \int \phi_{1s}(Z|\vec{r}_2)\phi^*_{n\ell m}(Z'|\vec{r}_2)d\vec{r}_2 \ , \tag{3.27}$$

and $$h_{22} = \int \exp(i\vec{K}\cdot\vec{r})\phi_{1s}(Z|\vec{r}][\phi^*_{\kappa}(Z''|\vec{r}_1) + \beta\phi^*_{1s}(Z|\vec{r}_1]d\vec{r}_1 \ . \tag{3.28}$$

The first integral in expression (3.28) has been carried out in detail in Appen. II. The second integral is an elementary integral:

$$\int \exp(i\vec{K}\cdot\vec{r}_1)\phi_{1s}(Z|\vec{r}_1)\phi^*_{1s}(Z|\vec{r}_1)d\vec{r}_1 = -16Z^4(4Z^2+K^2)^{-2}. \tag{3.29}$$

The differential cross section is then given by equ. (3.7) and the total cross section becomes

$$Q = C(Q_1 + Q_2 + Q_3) \ , \tag{3.30}$$

where C is the modifying factor given by equ. (3.10) and

$$Q_1 = 512\pi Z^3 Z'' k_o^{-2} \int \kappa K^{-3} w \exp[-2Z''\kappa^{-1}\arctan\{2Z\kappa/(Z^2-\kappa^2+K^2)\}][(Z^2+\kappa^2+K^2)^2-4\kappa^2K^2]^{-3}[(Z''-Z)^2(Z^2+\kappa^2)+(Z''+Z)^2K^2-4\kappa^2K^2\{(Z''^2-Z^2/3)+\tfrac{2}{3}Z''^2Z^2\kappa^{-2}\}]d\kappa\,dK \ ,$$

$$Q_2 = 128\pi Z^3 k_o^2 \int K^{-3} Z''\kappa w \exp[-2Z''\kappa^{-1}\arctan(\kappa/Z)]4(Z-Z'')^2 \times (Z^2+\kappa^2)^{-4} d\kappa dK \ ,$$

$$Q_3 = 256\pi k_o^2 Z^3(Z''-Z)\int Z''\kappa w(Z^2+\kappa^2)^{-2}K^{-3}\exp[-Z''\kappa^{-1}\arctan\{\kappa(3Z^2-\kappa^2+K^2)Z^{-1}(Z^2-3\kappa^2K^2)\}][R\cos(\tfrac{1}{2}Z''\kappa^{-1}\ln A)+S\sin(\tfrac{1}{2}Z''\kappa^{-1}\ln A)](Z^2+\kappa^2+K^2-2\kappa K\cos\theta)^{-2}[(Z^2+\kappa^2+K^2)^2-4\kappa^2K^2]^{-1}\sin\theta\,d\theta d\kappa dK \ ,$$

$$A = [(Z^2-\kappa^2+K^2)^2+4Z^2\kappa^2][Z^2+\kappa^2+K^2-2\kappa K\cos\theta]^{-2} \ ,$$

$$R = 2Z''(Z^2+\varkappa^2-K^2)(\varkappa^2+Z^2+K^2-2\varkappa K\cos\theta) - 2Z[(Z^2-\varkappa^2+K^2)^2+4\varkappa^2Z^2] ,$$

$$S = 4Z''ZK[\cos\theta(Z^2+\varkappa^2+K^2) - 2\varkappa K] .$$

Again for Q_1 and Q_2 the final integrations over $\varkappa$ and K have to be done numerically. For Q_3 even the angle of ejection has to be integrated numerically. The triple integration takes considerable time on the IBM1410 computer and the numbers of intervals for $\varkappa$ and K have to be reduced in order to have the program to be run within a reasonable amount of time (approximately two hours). However it is found that Q_3 is of one to two orders of magnitude smaller than Q_1. An inaccuracy of even 50% in Q_3 will not effect the final numerical result too much. Typical values for Q_1, Q_2 and Q_3 are shown in Table I.

It is to be noticed that the dependence of Q_{4S} on Z'' is far less critical than Q_{4P}, Q_{4D} and Q_{4F}. As an illustration it has been calculated that when Z'' varies from 1.45 to 1.55, a variation of 7%, Q_{4P}, Q_{4D} and Q_{4F} vary approximately by a factor of 4, as compared with a 13% variation in Q_{4S}. Corresponding to Z''=1.45 the value of the excitation cross section of the 4S state of He^+ at 405 eV is 8.7×10^{-21} cm^2. This is 25% larger than the value listed in Table III.

TABLE I

Typical Values of Q_1, Q_2 and Q_3 at 405 eV Incident Energy for Four Values of Z'' in Atomic Units

Z''	Q_1	Q_2	Q_3	Q
1.00	0.411	0.0732	0.0810	0.56
1.30	0.289	0.0105	0.0061	0.306
1.54	0.225	0.00131	0.0013	0.228
1.69	0.196	0	0	0.196
1.75	0.186	0.000179	-0.00033	0.187

CHAPTER IV

COMPARISON WITH EXPERIMENT AND CONCLUSION

§4.1 Comparison with Experiment

Let I(nL/n'l') denote the spontaneous transition probability from nL state to n'L' state and I(nL) the total spontaneous transition probability to all possible states, given by

$$I(nL) = \sum_{n'L'} I(nL/n'L'). \tag{4.1}$$

The branching ratio of the transition from nL state to n'L' state denoted by B(nL→n'L') is then defined by

$$B(nL \rightarrow n'L') = I(nL)/I(nL/n'L') . \tag{4.2}$$

The calculated values of the direct ionization-excitation cross sections for 4S, 4P, 4D and 4F states of He^+ are listed in the first four rows of Table II. But before the n=4→n=3 transition cross sections can be calculated and compared with experimental results the following five branching ratios are needed: B(4S→3P), B(4P→3S), B(4P→3D), B(4D→3P) and B(4F→3D). The spontaneous transition probabilities of He^+ is proportional to that of the excited hydrogen atom, the constant

of proportionality being Z'^{-2}. The branching ratios are therefore the same as those in the case of hydrogen atom. Spontaneous transition probabilities of hydrogen are taken from a Table published by Lawrence Radiation Laboratory.[15]

TABLE II

Spontaneous Transition Probabilities in 10^8 sec^{-1} and Branching Ratios†

I(4S/3P) = 0.0184	I(4S) = 0.0441	B(4S→3P) = 2.40
I(4P/3S) = 0.0306	I(4P) = 0.813	B(4P→3S) =26.6
I(4P/3D) = 0.00348	I(4P) = 0.813	B(4P→3D) =234
I(4D/3P) = 0.0704	I(4D) = 0.277	B(4D→3P) =3.93
I(4F/3D) = 0.138	I(4F) = 0.138	B(4F→3D) = 1

† The branching ratios given here differ slightly from and are more accurate than those quoted in the paper.[16] Those values were calculated from spontaneous transition probabilities given on p. 266 of Ref. 14.

Let T_{4L} denote the contribution from the direct excitation cross section Q_{4L} to the n=4→n=3 transition cross section, $Q(He^+, 4\rightarrow 3)$. Then T_{4L} is given by the following relation:

$$T_{4L} = Q_{4L}/B(4L\rightarrow 3L\pm 1), \tag{4.2}$$

where when both $B(4L\rightarrow 3L+1)$ and $B(4L\rightarrow 3L-1)$ exist, T_{4L} is the sum of the two terms. The cross section is given by:

$$\begin{aligned} Q(He^+, 4\rightarrow 3) &= \sum_L T_{4L} \\ &= Q_{4S}/B(4S\rightarrow 3P) + Q_{4P}/B(4P\rightarrow 3S) + Q_{4P}/B(4P\rightarrow 3D) \\ &\quad + Q_{4D}/B(4D\rightarrow 3P) + Q_{4F}/B(4F\rightarrow 3D) . \end{aligned} \tag{4.3}$$

It is to be noted that the experimental values in Table III include the contribution from both the direct ionization-excitation processes and the cascading from the upper states.

Theoretical cascading contribution from n=7, 6, 5 levels to n=4 levels is calculated in the next chapter. It is estimated that the total cascading contribution from all possible upper states will increase the calculated values of $Q(He^+, 4\rightarrow 3)$ by 4%.

§4.2 Discussion and Conclusion

It is seen from Table III (p. 28) that 90% of the n=4→n=3 radiation resulted from Q_{4S}. In §3.3 it has been shown that a varia-

TABLE III

Cross Sections (10^{-21} cm^2) for Ionization-excitation of He by Electron Impact

	Incident Electron Energy in eV				
	200	270	340	405	450
$Q(He^+, 4S)$[a]	8.1	8.2	7.6	6.9	6.6
$Q(He^+, 4P)$[b]	2.9	3.1	2.9	2.8	2.7
$Q(He^+, 4D)$[b]	0.68	0.69	0.66	0.62	0.57
$Q(He^+, 4F)$[c]	0.03	0.03	0.02	0.02	0.02
T_{4S}	3.4	3.4	3.2	2.9	2.7
T_{4P}	0.12	0.13	0.12	0.12	0.11
T_{4D}	0.17	0.18	0.17	0.16	0.15
T_{4F}	0.03	0.03	0.02	0.02	0.02
$Q(He^+, 4 \rightarrow 3)$ Theor.	3.7	3.7	3.5	3.2	3.0
$Q(He^+, 4 \rightarrow 3)$ Exptal.	9.8	9.1	7.9	7.0	6.5

[a] Calculated by using Z''=1.69

[b] Taken from Ref. 3

[C] Obtained from the average of the calculated values using Z''=1.446 and Z''=1.455

tion of the effective charge Z'' in the Coulomb continuum wave function may produce a change of 25% in the cross section. Considering the uncertainty of the effective charge, the approximate nature of the wave functions used and the use of the Born approximation in the calculation the agreement between the theoretical and the experimental cross sections is quite satisfactory.

The most serious approximations in this calculation are in the use of the Slater orbitals for the ground state of the helium atom and the Coulomb continuum wave function for the ejected electron. The Slater orbitals for light atoms have been considered sufficiently accurate in many cases. However in the present case, for the process of simultaneous ionization and excitation to be possible, there must be some correlation between the two atomic electrons in the ground state. The only correlation between the two atomic electrons arises from the use of Slater orbital is the shielding effect, i.e., the effective nuclear charge is 1.69 instead of 2.0. Because the simultaneous ionization-excitation cross section arises mainly from the interaction of the atomic electrons, the Slater type orbital is not expected to give as accurate results as in some other cases, such as the energy of the ground state of helium or excitation cross sections. For a more refined calculation it is suggested that Hylleraas wave function, which takes care of the correlation of the atomic electrons

in greater detail, be used for the ground state.

The second approximation is more difficult to improve. A step in this direction would be to use self-consistent field wave function for the ejected electron.

The cross sections Q_{4P} and Q_{4D} quoted in Table III are only good to within a factor of 5, as has been pointed out by the authors.[3] The accuracy for Q_{4F} is even worse. Fortunately the total contribution to the $n=4 \rightarrow n=3$ radiation from Q_{4P} and Q_{4D} amounts to only 10%. The contribution from Q_{4F} is almost negligible. Hence in spite of the large uncertainty of these cross sections the value of $Q(He^+, 4 \rightarrow 3)$ should remain fairly accurate.

Both theoretical and experimental curves show a maximum at approximately 230 eV incident energy. This has also been observed by R. J. Anderson for 4686-Å as well as for the 3203-Å, 2733-Å and 2511-Å lines which are the radiation from $n=5 \rightarrow n=3$, $n=6 \rightarrow n=3$ and $n=7 \rightarrow n=3$ respectively.

In conclusion, it has been shown that, unlike the case of the excitation of triplet series of neutral He, the population of the 4S state of He^+ is produced primarily by direct ionization-excitation rather than indirect mechanisms. The intensity of the radiation from $n=4 \rightarrow n=3$ of He^+ transition can be explained quantitatively by direct excitation and subsequent decay.

CHAPTER V

EXTENSION OF THE CALCULATION TO 3203-Å, 2733-Å, 2511-Å LINES OF HELIUM

§5.1 Calculation of Direct Ionization-excitation Cross Sections of Q_{nS}, n=5, 6, 7

The cross sections will be calculated at different energies but with Z''=1.69 only. The differential cross sections are given by equ. (3.12) where the modifying factors C can be evaluated readily for different values of n:

$$C = 2\left|\int \phi_{1s}(Z|\vec{r})\phi^{*}_{n\ell m}(Z'|\vec{r})d\vec{r}\right|^2 , \qquad (3.10)$$

$$Z = 1.69 , \qquad Z' = 2.0 .$$

n	4	5	6	7
C	1.26×10^{-3}	5.77×10^{-4}	3.20×10^{-4}	1.96×10^{-4}

Expression on the RHS of equ. (3.12) can be integrated in exactly the same manner as in the previous case, except that the excitation energy has to be changed for different values of n; the numerical procedure is otherwise the same. The ionization-excitation energies are:

n=4, $E_n = 75.58$ eV ,

n=5, $E_n = 76.83$ eV ,

n=6, $E_n = 77.47$ eV ,

n=7, $E_n = 77.87$ eV ,

The values of Q_{nS} for n=5, 6, 7 at five different incident energies with Z''=1.69 are given in Tables IV, V, VI respectively.

§5.2 Calculation of Q_{nP}, Q_{nD}, Q_{nF} for n=5, 6, 7

The difficulty in these cases is that there is no way of determining the effective Coulomb charge Z''. It is however anticipated that the contribution from Q_{nP}, Q_{nD} and Q_{nF} to the n=5, 6, 7 $\rightarrow$ n=3 transition cross sections will be small, as in the case for n=4. As an approximation the effective Coulomb charge Z'' is chosen as 1.455 for Q_{nP}, 1.446 for Q_{nD} and Q_{nF} will be the average of the values calculated at these two values of Z'' for n=5, 6, 7.

Now the cross section is given by

$$Q_{nL} = \int I_{\mu}(K) d\mu dK d\sigma \qquad (5.1)$$

$$= 64\pi^2 k_o^{-2} \int_0^{\varkappa_{max}} d\varkappa \int_{K_{min}}^{K_{max}} K^{-3} \left| h_l \right|^2 dK , \qquad (5.2)$$

for L=1, 2, 3. The limits are given by equs. (3.14) to (3.16) and the excitation energies E_n are listed on the previous page. Again h_l may be decomposed as

$$h_l = I_{nL}(K)\, I_{l\varkappa}(\varkappa, K) , \qquad (5.3)$$

where $I_{l\varkappa}(\varkappa, K)$ is given by equ. (3.12) and $I_{nL}(K)$ can be obtained by straightforward integration. The nine functions $I_{nL}(K)$ for n=5, 6, 7 and L=1, 2, 3 are listed in Appen. III. Also listed in the appendix are the hydrogenic wave functions for 7S, 7P, 7D and 7F which are derived from the Laguerre Polynomials. The branching ratios used in calculating T_{nL} are obtained from transition probabilities from Ref. 15.

The direct ionization-excitation cross sections decrease fairly regularly as n^{-3}. It is observed that while the maxima of the cross sections of nS and nP remain approximately at 230 eV those of nD shift towards lower incident energy as n increases. This can be explained by the spreading outwards of the D wave functions as n increases and hence increases interaction between the slower incident electron and the atomic electrons.

§5.3 Estimation of Cascade Contributions.

TABLE IV

CROSS SECTIONS (10^{-21} cm^2) FOR IONIZATION-EXCITATION OF HELIUM BY ELECTRON IMPACT

	Incident Electron Energy in eV				
	200	270	340	405	450
$Q(He^+, 5S)$[a]	3.8	3.8	3.5	3.2	3.0
$Q(He^+, 5P)$[b]	1.4	1.4	1.4	1.3	1.3
$Q(He^+, 5D)$[c]	0.36	0.36	0.34	0.32	0.30
$Q(He^+, 5F)$[d]	0.02	0.02	0.02	0.02	0.02
T_{5S}	1.2	1.2	1.1	1.0	1.0
T_{5P}	0.059	0.061	0.059	0.057	0.055
T_{5D}	0.084	0.086	0.081	0.076	0.072
T_{5F}	0.01	0.01	0.01	0.01	0.01
$Q(He^+, 5 \rightarrow 3)$ Theor.	1.4	1.4	1.3	1.2	1.1
$Q(He^+, 5 \rightarrow 3)$ Exptal.	2.6	2.8	2.4	---	---

[a] Calculated by using Z''=1.69

[b] Calculated by using Z''=1.455

[c] Calculated by using Z''=1.446

[d] Obtained from the average of the calculated values using Z''=1.446 and Z''=1.455

TABLE V

CROSS SECTIONS (10^{-21} cm^2) FOR IONIZATION-EXCITATION OF HELIUM BY ELECTRON IMPACT

	Incident Electron Energy in eV				
	200	270	340	405	450
$Q(He^+, 6S)$[a]	2.1	2.1	1.9	1.8	1.7
$Q(He^+, 6P)$[b]	0.78	0.80	0.77	0.74	0.71
$Q(He^+, 6D)$[c]	0.13	0.12	0.10	0.09	0.09
$Q(He^+, 6F)$[d]	0.01	0.01	0.01	0.01	0.01
T_{6S}	0.56	0.57	0.52	0.48	0.46
T_{6P}	0.03	0.03	0.03	0.03	0.03
T_{6D}	0.03	0.03	0.02	0.02	0.02
T_{6F}	0.007	0.007	0.006	0.006	0.005
$Q(He^+, 6 \rightarrow 3)$ Theor.	0.63	0.63	0.59	0.54	0.51
$Q(He^+, 6 \rightarrow 3)$ Exptal.	1.9	1.8	1.7	---	---

[a] Calculated by using $Z''=1.69$

[b] Calculated by using $Z''=1.455$

[c] Calculated by using $Z''=1.446$

[d] Obtained from the average of the calculated values using $Z''=1.446$ and $Z''=1.455$

TABLE VI

CROSS SECTIONS (10^{-21} cm^2) FOR IONIZATION-EXCITATION OF HELIUM BY ELECTRON IMPACT

	Incident Electron Energy in eV				
	200	270	340	405	450
$Q(He^+, 7S)$[a]	1.3	1.3	1.2	1.1	1.0
$Q(He^+, 7P)$[b]	0.48	0.49	0.48	0.45	0.44
$Q(He^+, 7D)$[c]	0.08	0.08	0.07	0.06	0.05
$Q(He^+, 7F)$[d]	0.008	0.008	0.008	0.007	0.006
T_{7S}	0.31	0.31	0.29	0.27	0.25
T_{7P}	0.02	0.02	0.02	0.02	0.02
T_{7D}	0.02	0.02	0.01	0.01	0.01
T_{7F}	0.004	0.004	0.004	0.003	0.003
$Q(He^+, 7\rightarrow3)$ Theor.	0.35	0.35	0.31	0.29	0.27
$Q(He^+, 7\rightarrow3)$ Exptal.	1.3	1.2	1.1	---	---

[a] Calculated by using Z''=1.69

[b] Calculated by using Z''=1.455

[c] Calculated by using Z''=1.446

[d] Obtained from the average of the calculated values using Z''=1.446 and Z''=1.455

The experimental values as in the case when n=4 include cascade contributions. Hence before making any comparison it is necessary to add cascade contributions to the calculated cross sections. Estimation of the cascade contributions can be done in the following manner. Firstly it will be assumed that Q_{nL} decreases as n^{-3} as n increases. This is an asymptotic behaviour. When n is large the overlap between the excited wave function and the ground state wave function remains fairly constant while the normalization constant changes as $n^{-3/2}$. Thus the cross sections, while depend on the square of the normalization constant, vary as n^{-3}. The fact that the direct ionization-excitation cross sections listed in Table IV to VI show fairly regular variation as n^{-3} gives justification for this assumption. Secondly it will be assumed that the branching ratio B(nL, n'L') remains approximately constant as n increases. In reality the branching ratio B(nL, n'L') tends to a limit asymptotically from below as n increases. This assumption will introduce smaller branching ratios and hence larger cascading contributions which may be regarded as upper limits. It will be seen that cascading contributions thus estimated amounts to only a few per cent which are smaller than experimental uncertainty and can be neglected.

The cascade contribution to the intensity of the 4686-Å (4-3)

line at 200 eV is estimated as follows. The contributions from n=5, 6, 7 can be calculated from direct ionization-excitation cross sections tabulated in Tables IV to VI. The sum of which is found to be 2.5%. The sum of cascade contributions from n=m to infinity is given by

$$m^3 \sum_{n=m}^{\infty} n^{-3} \cong m^3 \int_m^{\infty} x^{-3} dx = m/2 \ ,$$

where the cascade contribution from the mth term has been normalized to unity. Thus the sum of contributions for all $n \geq 8$ is estimated to be 0.95% and the total cascade contribution to the 4686-Å radiation is 3.4%.

Similarly the cascade contribution to the 3203-Å (5→3) and the 2733-Å (6→3) radiations are estimated to be 3.7% and 3.8% respectively. The cascade contribution to the 2511-Å (7→3) radiation can be estimated by extrapolation from those of n=4, 5, 6 or from the hyperthetical n=8 cross sections since cross sections are assumed to decrease as n^{-3}. Both methods give its cascade contribution of the 2511-Å (7→3) radiation as 3.8%.

Although the estimation is carried out at the incident energy of 200 eV, because of the similar shapes of the excitation functions the cascade contributions at all energies, except very close to the thresholds, should be almost the same. It is safe to say that the cas-

cade contributions, in the energy range being considered, to the intensities of the radiations are less than 4%. This being less than experimental uncertainty, can be neglected.

§5.4 Comparison between Calculated and Experimental Results and Conclusion

In Table IV, V, VI the second last lines are the calculated direct ionization-excitation cross sections. Because theoretical cascade contributions are found to be neglegible comparison between calculated and experimental values can be done by inspecting the last two lines of these tables. The experimental values are extrapolated from curves of excitation functions taken by Anderson.[19] The agreement is found to be compatible with the case of 4686-Å. Hence it is concluded that, as in the case of the 4686-Å radiation, the populations of the 5S, 6S, 7S states of He^+ are produced primarily by direct excitation rather than by indirect means.

PART II

CHAPTER VI

EXCITATION OF MERCURY BY ELECTRON IMPACT

§6.1 Introduction

Mercury with an atomic number 80 has two valence electrons and a ground state configuration 6^1S. The first 78 electrons form closed shells. If only the excitation of the valence electrons is to be considered, then it may be treated approximately as a two electron system with a central potential.

Excitation of mercury has been studied experimentally by several authors.[22] More recently the investigation has been carried out extensively by Jongerius[23,24] and Anderson.[25,26] Theoretical calculations for the excitation cross sections of mercury has previously been performed by Penney,[27] using Slater wave function. The prior nuclear interaction potential was used. It is the objective of this section of the thesis to calculate the excitation cross sections of 7^1S_o, 6^3D_2, 6^3D_3

and 7^3P_2 configurations of the mercury from ground state by electron impact. For the 7^1S_o configuration Born approximation will be used and for the 7^3P_2 and 6^3D_3 configurations which involve a change of multiplicity but no singlet-triplet mixing, the Born-Oppenheimer (B-O) approximation is appropriate. For the 6^3D_2 state which according to one configuration approximation is a mixture of $6^1\underline{D}_2$ † and $6^3\underline{D}_2$, Born approximation will be used to calculate the contribution from the $6^1\underline{D}_2$ configuration and B-O approximation for the $6^3\underline{D}_2$ state.

§6.2 Wave Function

The self-consistent field (SCF) wave function will be used for the radial part of the basis function for the uncoupled representation:

$$\phi_{n\ell m}(\vec{r}) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi) , \qquad (6.1)$$

where the radial function $R_{n\ell}(r)$ has been tabulated by Mishra.[28] The configuration portion of the uncoupled wave function will have to be symmetric or antisymetric with respect to the interchange of the two atomic electrons according to whether it is a singlet or a triplet. The uncoupled representation with the proper symmetry is given by

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†An underline is used to denote a pure state, without mixing. Thus 6^3D_2 is a mixture of $6^1\underline{D}_2$ and $6^3\underline{D}_2$.

$$\phi(\vec{r}_1, \vec{r}_2) = 2^{-1/2}[\phi_{n\ell m}(\vec{r}_1)\phi_{n'\ell'm'}(\vec{r}_2) \pm \phi_{n\ell m}(\vec{r}_2)\phi_{n'\ell'm'}(\vec{r}_1)]. \qquad (6.2)$$

The Hamiltonian will be approximated as

$$H = H_o + H_1 . \qquad (6.3)$$

In the last expression the explicit form of H_o is

$$H_o = \sum_{i=1,2} [-\nabla_i^2/2 + V(\vec{r}_i)] + r_{12}^{-1} , \qquad (6.4)$$

where the suffices 1 and 2 refer to the atomic valence electrons and H_1 stands for spin-orbit coupling. All other fine structure terms will be neglected. For H_1 the following approximation will be used:

$$H_1 = \sum_{i=1,2} \xi_i(\vec{r})\vec{\ell}_i \cdot \vec{s}_i . \qquad (6.5)$$

The Hamiltonian of the atom, H_o, is diagonal in the $LSJM_J$ coupled representation. Let $\psi(^aL_{J, M_J})$ be the wave function of the coupled representation, where a denotes spin multiplicity, then $\psi(^aL_{J, M_J})$ is a linear combination of $\phi(\vec{r}_1, \vec{r}_2)S_{\pm, m_S}$:

$$\psi(^aL_{J, M_J}) = \sum_{m_L} c_{LS}(J, M_J; m_L, m_S)\phi(\vec{r}_1, \vec{r}_2)S_{\pm, m_S} \qquad (6.6)$$

where $S_{\pm, m_S}$ is the spin function; S_{+, m_S} stands for symmetric triplets and S_{-, m_S} for antisymmetric singlet:

$$S_{-, 0} = 2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] ,$$

$$S_{+, 1} = \alpha(1)\alpha(2) ,$$

$$S_{+,0} = 2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] ,$$

$$S_{+,-1} = \beta(1)\beta(2) ,$$

and $c_{LS}(J, M_J; m_L, m_S)$ is the Clesch-Gordan coefficient. The introduction of the spin-orbit interaction causes a mixing between states of the same L, J, M_J but different S. Thus mixing is possible between all the $^3P_{-1}$ and $^1P_{-1}$ states and between the $^3D_{-2}$ and $^1D_{-2}$ states. The D-states, for example, can arise from many different configurations: it can be from the (ns)(n'd) configuration or the (np)(n'p) configuration, etc. The one configuration approximation, which ignores mixing between different configurations, will be introduced. Hence for the 6^3D_2 and 6^1D_1 the mixing is assumed to be only between the singlet and triplet states from the (6s)(6d) configuration. The wave function then can be written as

$$\begin{aligned} \Psi(^1P_1) &= \alpha\psi(^1P_{-1}) + \beta\psi(^3P_{-1}) , \\ \Psi(^3P_1) &= -\beta\psi(^1P_{-1}) + \alpha\psi(^3P_{-1}) ; \end{aligned} \qquad (6.7)$$

and similarly for $\Psi(^3D_2)$ and $\Psi(^1D_2)$. The constants α and β are the mixing coefficients and can be expressed in terms of the exchange integrals $K_{6s,n\ell}$ and the spin-orbit coupling constant $\lambda_{n\ell}$. K and λ are determined from the three spacing of the four states. Thus K and λ are over determined and there is a range of values for K and λ which is

satisfactory but does not fit the three spacings exactly. Wolfe[29] introduced an extra parameter by including spin-other-orbit interaction in the Hamiltonian. Thus there are three parameters to be fitted by three spacings. Because of the one configuration approximation the mixing coefficients thus obtained do not have too much meaning. Alternatively the mixing coefficients can be obtained from experimentally measured g factor[30] or life time measurements.[30] For the 6^1D_2 and 6^3D_2 states the value for β adopted is 0.58 ± 0.02. This is taken from the paper by Van Kleef and Fred.[31] The error limit given here is associated with the experimental errors of measurements. The value of β may be subject to a larger uncertainty because of the approximate nature of the theoretical model used. For the (6s)(7p) states the value adopted for β is 0.54 ± 0.08 from fine-structure energies since no g factor or life time data are available.

The wave function thus chosen has one difficulty: it cannot explain the experimentally observed inversion of the 6^1D_2 and 6^3D_2 levels. This is probably due to the neglect of configuration interaction and the spin-other-orbit interaction in the present approximation. Wolfe's equation[32] can produce the mixing coefficients regardless of the anomalous inversion of the D states. However it is not clear that one can ascribe the anomalous inversion of the D states completely to the spin-

other-orbit interaction. Bacher[32] showed that configuration interaction alone may also produce such an inversion. A calculation has been performed by including the D states arising from the (6p)(6p) configuration. The result does show an inversion. However the separation of the singlet and triplet levels is of several orders of magnitude too large compared with observed value. This is probably due to the fact that the SCF wave functions used are not accurate enough for this purpose. Besides the approximate nature of the SCF method the 6p wave function used for the (6p)(6p) configuration is the same as for (6s)(6p) configuration. The calculated value of the separation is the difference of the $^1D_2$ and $^3D_2$ levels. Since the experimentally observed separation is of several order of magnitude smaller than the energy levels, in order to reproduce such energy separation by theoretical calculation extremely refined wave functions are needed. Since no such wave functions are available at the present we will be contented to know that such an inversion of singlet and triplet can be explained by configuration interaction or by configuration interaction and spin-other-orbit interaction.

§6.3 Calculation

The Born cross sections for 7^1S can be obtained readily from equs. (2.21) and (2.22). For 6^3D_2, 6^3D_3 and 7^3P_2 the B-O cross sections can be obtained from equs. (2.32) and (2.33). Let the position

vector of the incident electron be denoted by $\vec{r}_3$ then the B-O cross sections for excitation from an initial state o to a final state n is given by

$$Q(o \rightarrow n) = \int_0^{\pi} \int_0^{2\pi} I_n(\theta, \phi) \sin\theta d\theta d\phi = Q(n^a L_{J, M_J}) \tag{2.33}$$

$$I_n(\theta, \phi) = 3k_n (4\pi^2 k_o)^{-1} \left| I_{gn}(\theta, \phi) \right|^2 , \tag{6.8}$$

and $$I_{gn}(\theta, \phi) = \int (r_{13}^{-1} + r_{23}^{-1} - 2r_3^{-1}) \exp[i(\vec{k}_o \cdot \vec{r}_3 - \vec{k}_n \cdot \vec{r}_1)] \psi_6 1_{S_o} (\vec{r}_1, \vec{r}_2) \times$$

$$\psi_n a_{L_{J, M_J}} (\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 . \tag{6.9}$$

Equ. (2.33) gives the excitation cross section $Q(n^a L_{J, M_J})$ of a state specified by the set of quantum numbers $\{a, L, J, M_J\}$. To obtain the excitation cross section $Q(n^a L_J)$ corresponding to the states $(n^a L_J)$ it is necessary to sum over M_J.

The final states are then the pure triplet states. Because the ground state is un-mixed, the required cross sections will be the sum of the separate contributions from the singlet and triplet states whenever there is mixing.

It is noticed that prior potential is used in equ. (6.9). The difference between the results from using prior or post nuclear interaction potential is not expected to be too serious, because Mishra's wave functions are fair approximations to the Hartree wave functions. This is would not be true had the Slater wave functions been used, like

in the calculation performed by Penney.[27]

Now for the ground state the configuration portion of the wave function is

$$\psi_{6^1S_o}(\vec{r}_1, \vec{r}_2) = \phi_{6s}(\vec{r}_1)\phi_{6s}(\vec{r}_2) \ , \tag{6.10}$$

and the antisymmetric singlet state S_- constitutes the spin wave function. For the excited state it is given by equ. (6.6). Substituting equs. (6.10) and (6.6) into equ. (6.9) the following expression for I_{gn} is obtained:

$$I_{gn}(\theta) = \sum_{m_L} c_{LS}(J, M_J; m_L, m_S) I_{gnm}(\theta) \ , \tag{6.11}$$

where

$$I_{gnm}(\theta) = \int (r_{13}^{-1} + r_{23}^{-1} - 2/r_3) \exp[i(\vec{k}_o \cdot \vec{r}_3 - \vec{k}_n \cdot \vec{r}_1)] \phi_{6s}(\vec{r}_1) \ X$$

$$\phi_{6s}(\vec{r}_2)\phi_{n\ell m}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \ . \tag{6.12}$$

Substituting equ. (6.2)† for $\phi_{n\ell m}(\vec{r}_1, \vec{r}_2)$ into the last expression, I_{gnm} becomes

$$I_{gnm}(\theta) = 2^{-\frac{1}{2}}[J_1(\theta) + J_2(\theta) + J_3(\theta)] \ , \tag{6.13}$$

where

$$J_1(\theta) = \int (r_{13}^{-1} - r_3^{-1}) \exp[i(\vec{k}_o \cdot \vec{r}_3 - \vec{k}' \cdot \vec{r}_1)] \phi_{6s}(\vec{r}_1)\phi_{6s}(\vec{r}_2) \ X$$

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† "-" sign for triplets.

$$\phi^*_{6s}(\vec{r}_2)\phi^*_{n\ell m}(\vec{r}_3)d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \ , \qquad (6.14)$$

$$J_2(\theta) = \int(r_{23}^{-1} - r_3^{-1})\exp[i(\vec{k}_o\cdot\vec{r}_3 - \vec{k}'\cdot\vec{r}_1)]\,\phi_{6s}(\vec{r}_1)\phi_{6s}(\vec{r}_2)\phi^*_{6s}(\vec{r}_2)\ X$$

$$\phi^*_{n\ell m}(\vec{r}_3)d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \ , \qquad (6.15)$$

$$J_3(\theta) = -\int(r_{23}^{-1} - r_3)\exp[i(\vec{k}_o\cdot\vec{r}_3 - \vec{k}'\cdot\vec{r}_1)]\,\phi_{6s}(\vec{r}_1)\phi_{6s}(\vec{r}_2)\phi^*_{6s}(\vec{r}_3)\ X$$

$$\phi^*_{n\ell m}(\vec{r}_2)d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \ . \qquad (6.16)$$

Note that the integral

$$\int(r_{13}^{-1} - r_3^{-1})\exp[i(\vec{k}_o\cdot\vec{r}_3 - \vec{k}'\cdot\vec{r}_1)]\,\phi_{6s}(\vec{r}_1)\phi_{6s}(\vec{r}_2)\phi^*_{6s}(\vec{r}_3)\phi^*_{n\ell m}(\vec{r}_2)d\vec{r}_1 d\vec{r}_2 d\vec{r}_3$$

is zero because $\int \phi_{6s}(\vec{r}_2)\phi^*_{n\ell m}(\vec{r}_2)d\vec{r}_2 = 0$. The evaluation of the integrals J_1, J_2 and J_3 is carried out in Appen. V. The integration over θ to obtain the total cross section, $Q(^aL_{J,M_J})$, has to be carried out numerically.

§6.4 Results and Discussion

The calculated cross sections are plotted in Fig. I. For $Q(6^3D_2)$ it is the sum of $\alpha^2 Q(6^3\underline{D}_2)$ and $\beta^2 Q(6^1\underline{D}_2)$. Recently Ochkur[34] has suggested a simplified method for calculating cross sections of exchange excitation. What he did essentially was to expand the expression for B-O cross section in inverse power of k_o. By keeping only the first term and dropping terms containing higher inverse powers of k_o he obtained a much simplied expression for excitation cross section from sin-

glet to triplet states:

$$Q_{\alpha\to\beta} = 3k'k_o^{-1}\int\left|g_{\alpha\beta}(\theta,\phi)\right|^2 \sin\theta\, d\theta\, d\phi, \tag{6.16}$$

$$g_{\alpha\beta}(\theta,\phi) = 2k_o^{-2}\int\psi_\beta^*(\vec{r}_2,\vec{r}_1)\psi_\alpha(\vec{r}_1,\vec{r}_2)\exp[i(\vec{k}_o-\vec{k}')\cdot\vec{r}_1]\, d\vec{r}_1 d\vec{r}_2. \tag{6.17}$$

The evaluation of Ochkur's cross sections is very simple and will not be detailed here. Results by using Ochkur's expression are also plotted in Fig. I. As incident energy increases the B-O and the Ochkur cross sections converge.

The calculated values are compared with Anderson's[25] experimental measurements with cascade contributions substracted. The comparison is made at 15 eV only. At higher energies the cascade analysis becomes inaccurate because of the distortion of excitation functions by the presence of the adjacent lines. Below 15 eV the excitation curves begin to rise rapidly with decreasing electron energy. Since the electron beam has an energy spread of about 0.6 eV the observed cross sections represent weighed averages of the actual values and may be subject to considerable error. Indeed with energy spread limited to about 0.1 eV Jongerius showed[24] that the rise of the triplet excitation function is faster than has been previously reported. With direct excitation cross sections available at just one electron energy only a very limited comparison with theoretical calculations can be made. This is shown in Table VII. The theoretical excitation cross section of the 7^1S_o level is a-

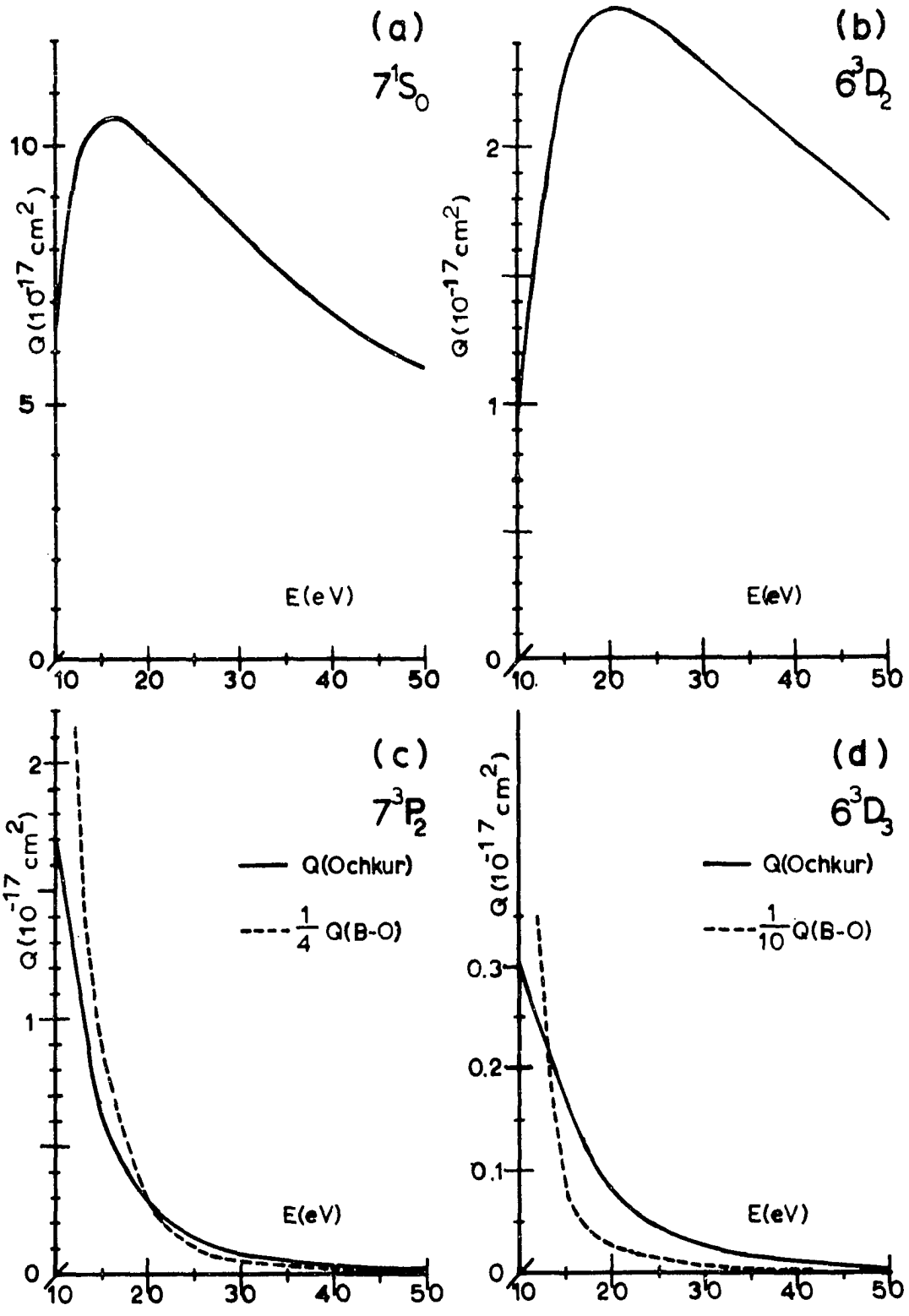


DIAGRAM I. CALCULATED EXCITATION FUNCTIONS OF Hg

TABLE VII

COMPARISON BETWEEN THE EXPERIMENTAL AND THEORETICAL VALUES OF THE DIRECT EXCITATION CROSS SECTIONS AT 15 eV

(in units of 10^{-18} cm^2)

State	Experimental Cross Section	Theoretical Cross Section Born, B-O	Ochkur
7^1S_o	5.5 ±2.6	106	
6^3D_2	66 ±14	25	
6^3D_3	7.5 ±1.3	8.0	1.7
7^3P_2	25 ±8	37	6.4

bout 20 times larger than the experimental value. Even in the extreme case of zero cascade, the maximum experimental value of the direct excitation cross section is equal to the apparent excitation cross section which is 9×10^{-18} cm^2. This discrepancy is therefore most likely due to the inaccuracy of theoretical value, although one would normally expect the Born approximation to give cross sections of the correct

order of magnitude for the singlet states. More accurate calculations of the excitation cross section of the 7^1S_o state are needed. Improved calculation can be made by using more refined wave functions and by employing the close coupling formulation instead of Born approximation. Because the singlet component of the wave function is the major contributor to the excitation cross section of the 6^3D_2 state, the latter depends quite strongly on the mixing coefficient β. Nevertheless, the observed cross section of the 6^3D_2 state agrees reasonably well with theory. The agreements between the experimental and theoretical values of $Q(6^3D_3)$ and $Q(7^3P_2)$ are also regarded as reasonbale in view of the uncertainty of the approximate methods used in the theoretical calculations. However, similar studies of the direct excitation cross sections at several higher electron energies must be made before one can arrive at more general conclusions as to the over-all agreement between theory and experiment.

PART III

VIBRATIONAL EXCITATION OF HYDROGEN MOLECULES BY ELECTRON IMPACT

CHAPTER VII

INTRODUCTION

Rotational and vibrational excitations are important mechanism for energy loss for slow electrons in gases. Due to the growth of the research in upper atmosphere interest in the vibrational and rotational excitation cross sections of diatomic molecules has grown in the recent years.

Previous calculations of the vibrational excitation cross sections of H_2 have been carried out by Wu,[35] Morse[36] and Carson.[37] In all these calculations Born approximation was assumed. The interaction potential between the incident electron and the target molecule was considered to be purely due to electrostatic interaction. This Coulomb

interaction is of short range since when the electron is, say, only a few a.u. away it is effectively outside the electron cloud and the potential decreases exponentially. Thus even the most refined calculation[37] is of two orders of magnitude too small. If the Born approximation is assumed to be correct, as it has proved to be for atomic excitation processes, then a long range interaction potential is needed.

Recent theoretical works[38] on electron-atom collision have pointed out the important contribution from the polarization interaction to the cross section. Thus it seems that the induced dipole-monopole interaction may be the answer to the missing long range interaction. Breig and Lin[39] have investigated the effect of this dipole-monopole polarization interaction. Again Born approximation was used. Since the dipole-monopole interaction behaves asymptotically as r^{-4} an empirical polarization potential of the form αr^{-4} has been used, where r is the distance between the incident electron and the center of the homo-diatomic molecule. The center of the homo-diatomic molecule is the midpoint of the line joining the two nuclei, and is also chosen as the origin. When the electron is at a distance of several a.u. away from the origin the polarization potential will deviate from r^{-4} behaviour markedly. In fact this polarization potential diverges at the origen and the potential has to be either modified or cut off at a certain

distance a.

Several models of the potential were used by Breig and Lin[39] with several values of the parameter a. Each model has a different procedure of modifying the potential for $r<a$.

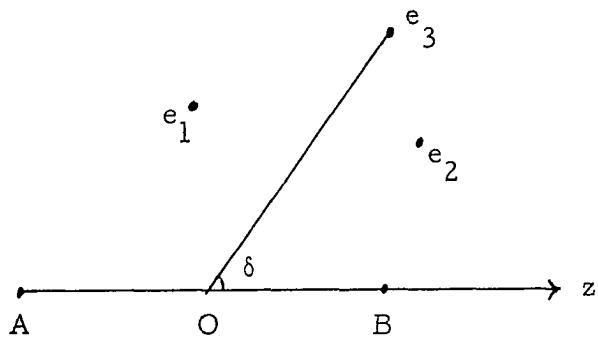
By using this type of interaction potential the calculated values of the vibrational excitation cross section are brought up to the same order of magnitude as the experimental values. Thus this work shows that induced dipole-monopole interaction is important for the vibrational excitation cross section of diatomic molecules.

The undesirable feature in this calculation is that there is no way of determing what model to choose or what the value of the cut-off parameter should be. Different models with the same parameter may result in cross sections differing by a factor of 4. The cross section obtained with a=1.1 is approximately 5 times that with a=1.8.

Because of the importance of the induced diple-monopole interaction in the calculation of the vibrational excitation of homodiatomic molecules and because of the lack of a priori for cut-off procedure for the empirical polarization interaction, it seems that a first principle calculation is necessary. It is the purpose of this section of the thesis to carry out a calculation of the vibrational excitation cross section of H_2 with a more refined method than Born approximation and using a polarization potential obtained from first principle.

CHAPTER VIII

FORMULATION OF $e\text{-}H_2$ COLLISIONS



A, B protons

e_1, e_2 molecular electrons

e_3 incident electron

DIAGRAM I

Let $\vec{r}_1$, $\vec{r}_2$ denote the position vectors of the molecular electrons and $\vec{r}_3$ that of the incident electron. The axis of the molecule is the line joining from A to B. The midpoint of AB, O is taken as the origin unless otherwise specified. $\vec{\xi}$ denotes the nuclear coordinates with polar coordinates (ξ, Θ, Φ). ξ is the normal coordinate of vibra-

tion: it is the change of the distance r_{AB} from its equilibrium position. (Θ, Φ) describe its rotational motion.

The wave equation for the system consisting of the hydrogen molecule and the incident electron is

$$H\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi}) = E\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi}) , \tag{8.1}$$

$$H = H_{mol} + H' , \tag{8.2}$$

$$H_{mol} = H_o - (2M')^{-1}\nabla_\xi^2 , \tag{8.3}$$

where M' is the reduced mass of proton or equals to half of the mass of proton. The explicit form of H_o and H' are

$$H_o = -\nabla_1^2/2 - \nabla_2^2/2 - r_{1A}^{-1} - r_{2A}^{-1} - r_{1B}^{-1} - r_{2B}^{-1} + r_{12}^{-1} + r_{AB}^{-1}, \tag{8.4}$$

$$H' = r_{31}^{-1} + r_{23}^{-1} - r_{3A}^{-1} - r_{3B}^{-1} - \nabla_3^2/2 . \tag{8.5}$$

Denote the eigenfunctions of H_{mol} by $\Psi_\sigma(\vec{r}_1, \vec{r}_2, \vec{\xi})$ where σ represents the set of quantum numbers necessary to specify its electronic, vibrational and rotational states. Let n be the electronic quantum numbers, ν be the vibrational quantum number and J, M the rotational quantum numbers, then σ stands for $\{n, \nu, J, M\}$. Because of the large difference between the proton and the electron masses, $\Psi_\sigma(\vec{r}_1, \vec{r}_2, \vec{\xi})$ can be approximated as[40]

$$\Psi_\sigma(\vec{r}_1, \vec{r}_2, \vec{\xi}) = \psi_n(\vec{r}_1, \vec{r}_2, \vec{\xi})\psi_o(\vec{\xi}) \tag{8.6}$$

$$= \psi_n(\vec{r}_1, \vec{r}_2, \vec{\xi})\xi^{-1}\chi_\nu(\xi) Y_{JM}(\Theta, \Phi) , \tag{8.7}$$

where a good approximation for $\chi_\nu(\xi)$ is the harmonic oscillator wave function. $Y_{JM}(\Theta, \Phi)$ is the spherical harmonics and is the rotational wave function for the molecule. The wave function $\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi})$ can be expanded in terms of the complete set $\Psi_\sigma(\vec{r}_1, \vec{r}_2, \vec{\xi})$. However in order to include the polarization the following alternate expansion is more desirable. Because of the presence of e_3 the electronic wave function is distorted. The distorted electronic states can be expressed as a linear combination of $\psi_n(\vec{r}_1, \vec{r}_2, \vec{\xi})$, where the coefficients depend upon $\vec{r}_3$:

$$\psi_n(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi}) = \sum_{n'} c_{n'}(\vec{r}_3)\psi_{n'}(\vec{r}_1, \vec{r}_2, \vec{\xi}) . \tag{8.8}$$

When $\vec{r}_3$ tends to infinity all $c_{n'}(\vec{r}_3)$, $n' \neq n$, tend to zero and $c_n(\vec{r}_3)$ tends to 1. This can be expressed as

$$\psi_n(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi}) \xrightarrow{|\vec{r}_3| \to \infty} \psi_n(\vec{r}_1, \vec{r}_2, \vec{\xi}) . \tag{8.9}$$

Denote $\Psi_\sigma(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi})$ for $\psi_n(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi})\xi^{-1}\chi_\nu(\xi)Y_{JM}(\Theta, \Phi)$. Expand $\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi})$ in terms of $\psi_n(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi})$ rather than $\psi_n(\vec{r}_1, \vec{r}_2, \vec{\xi})$ to include induced polarization of the molecule:

$$\begin{aligned}\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi}) &= \sum_\sigma F_\sigma(\vec{r}_3)\Psi_\sigma(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi}) \\ &= \sum_\sigma F_\sigma(\vec{r}_3)\psi_n(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi})\xi^{-1}\chi_\nu(\xi) Y_{JM}(\Theta, \Phi) . \end{aligned} \tag{8.10}$$

Let the polar coordinates of $\vec{r}_3$ be (r, θ, ϕ), where r is the

distance between e_3 and the midpoint of AB and (θ, ϕ), the polar angles with respect to some fixed reference frame. Expand $F_\sigma(\vec{r}_3)$ in terms of spherical harmonics $Y_{\ell m}(\theta, \phi)$:

$$F_\sigma(\vec{r}_3) = \sum_{\gamma'} F_{\gamma'}(\sigma|r) Y_{\ell' m'}(\theta, \phi) , \tag{8.11}$$

where

$$\gamma' = \{\sigma', \ell', m'\} = \{n', \nu', J', M', \mathcal{U}, m'\} . \tag{8.12}$$

The coefficients $F_\gamma(\sigma|r)$ depends on the initial state of the target molecule. By substituting expression (8.9) into equ. (8.8) the following expansion is obtained:

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi}) = \sum_{\gamma'} F_{\gamma'}(\sigma|r) \psi_n(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi}) \xi^{-1} \chi_\nu(\xi) Y_{JM}(\Theta, \Phi) \; X$$

$$Y_{\ell m}(\theta, \phi) . \tag{8.13}$$

Inserting equ. (8.13) into the wave equation (8.1), multiplying by $\Psi^*_{\sigma''}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi}) Y^*_{\ell'' m''}(\theta, \phi)$ and integrating over $d\vec{r}_1, d\vec{r}_2$, $d\vec{\xi}$ and the solid angle of $\vec{r}_3$ the following set of coupled differential equations is obtained:

$$[k^2_{\sigma''} + \partial^2/\partial r^2 - \ell(\ell+1)/r^2] G_{\gamma''}(\sigma|r) = \sum_{\gamma'} U_{\gamma''\gamma'}(r) G_{\gamma'}(\sigma|r) , \tag{8.14}$$

$$k^2_{\sigma'} = k^2_\sigma - 2(E_{\sigma'} - E_\sigma) , \tag{8.15}$$

$$G_{\gamma''}(\sigma|r) = r F_{\gamma''}(\sigma|r) ,$$

$$U_{\gamma''\gamma'}(r) = 2 \int \Psi^*_{\sigma''}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi}) Y^*_{\ell'' m''}(\theta, \phi) H \Psi_{\sigma'}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi}) \; X$$

$$Y_{\ell' m'}(\theta, \phi) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \sin\theta \, d\theta d\phi . \tag{8.16}$$

The terms $\nabla_\xi^2 \psi_n(\vec{r}_1, \vec{r}_2, \vec{\xi})$ and $\vec{\nabla}_3 \psi_n(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi})$ have been neglected. Equ. (8.15) expresses the conservation of energy: $k_{\sigma'}^2/2$ being the kinetic energy of the scattered electron, $k_\sigma^2/2$ being the kinetic energy of the incident electron, E_σ being the energy of the target molecule in its initial state and $E_{\sigma'}$ being the energy of the molecule in one of the channels.

For large value of r, $U_{\gamma''\gamma'}(r)$ tends to zero, since there can be no interaction between the electron and the neutral molecule when they are far apart. The asymptotic solution of $G_{\gamma'}(\sigma|r)$ is

$$k^{-\frac{1}{2}}\{ \exp[-i(kr-\ell\pi/2)]\, \delta_{\sigma\sigma''} - \exp[i(kr-\ell\pi/2)]\, S_{\gamma\gamma''}\} , \qquad (8.17)$$

where $S_{\gamma\gamma''}$ is the scattering matrix.[41]

Define

$$T = 1 - S . \qquad (8.18)$$

By comparing equ. (8.17) with equs. (2.1), (2.8), (2.9) and (2.10) the cross section from initial state σ to final state σ' is given by

$$Q(\sigma \to \sigma') = \pi k_{\sigma'}^{-2} \sum |T(\sigma, \sigma')|^2/(2J+1), \qquad (8.19)$$

where the summation is over ℓ, ℓ' the incident and scattered partial waves, J', M', the final rotational states and J, M, the initial rotational states. There is no degeneracy in the vibrational states.

Theoretically if the coupled differential equation for $G_{\gamma'}(\sigma|r)$ can be solved, its asymptotical form gives the required cross section.

However this set of coupled differential equations cannot be solved exactly and numerical methods have to be used. If only a few of the channels are to be considered, the expansion in equ. (8.12) is no longer exact and the resulting solution does not satisfy the wave equation. Fortunately it often happens that only a few of the channels are important for a particular excitation cross section; the presence of other channels will not effect the cross section significantly. For these cases, although the expansion of (8.13) is not exact and hence does not satisfy the wave equation it is a very good approximation. The consideration of convergence is only important when the kinetic energy of the incident electron is near the threshold of excitation. For the range of excitation energy that is to be considered the convergence should be rapid and it will be assumed that expansion in terms of a finite number of terms in expression (8.13) is a good approximation.

The formulation presented so far in this chapter has been in terms of uncoupled representation. Percival and Seaton[42] has shown the advantage of using coupled representation in the case of excitation of hydrogen atom by electron collision. The coupled representation, therefore, will be used in the calculation that is to follow. The following coupling scheme will be adopted. The spin angular momentum is zero for the ground state of H_2 and is separately conserved.

The only coupling then will be between the angular momentum of the partial waves of the incident electron $\vec{\ell}$ and the initial rotational angular momentum $\vec{J}$ to form a total angular momentum $\vec{L}$ and between the scattered partial waves $\vec{\ell}'$ and $\vec{J}'$, the rotation angular momentum of the molecule after collision, to form a total angular momentum $\vec{L}'$. The law of conservation of angular momentum then demands that

$$\vec{L} = \vec{L}' .$$

Thus the coupling scheme can be expressed simply as

$$\vec{\ell} + \vec{J} = \vec{\ell}' + \vec{J}' = \vec{L} . \tag{8.20}$$

The expansion of equ. (8.13) is in terms of the uncoupled representation $Y_{\ell m}(\theta, \phi)Y_{JM}(\Theta, \Phi)$ or $<\ell, m, J, M|$ using Condon-Shortley notation. The same formulation can be carried through with the coupled representation $<\ell, J, L, m_L|$, where $<\ell, J, L, m_L|$ is a linear combination of $<\ell, m, J, M|$:

$$<\ell, J, L, m_L| = \sum_m c_{\ell J}(L, m_L; m, M)<\ell, m, J, M| . \tag{8.21}$$

In the last expression $c_{\ell J}(L, m_L; m, M)$ is the Clesch-Gordan coefficient and is given by

$$c_{\ell J}(L, m_L; m, M) = <\ell, m, J, M | \ell, J, L, m_L> . \tag{8.22}$$

In equ. (8.22) $<\psi_a(\vec{r}) | \psi_b(\vec{r})>$ means $\int \psi_a^*(\vec{r})\psi_b(\vec{r})d\vec{r}$. The resulting set of coupled differential equations is

$$[k_{\sigma'}^2 + \partial^2/\partial r^2 - \ell(\ell+1)/r^2] G_{\Gamma''}(\sigma|r) = \sum_{\Gamma'} U_{\Gamma''\Gamma'}(r)G_{\Gamma'}(\sigma|r), \tag{8.23}$$

where Γ stands for $\{n, \nu, \ell, J, L, m_L\}$.

Alternatively equ. (8.23) can be obtained from equ. (8.14) by a transformation.[42] Seaton's notation will be adopted:

$$
\begin{aligned}
&\langle \Gamma | = \langle n, \nu, \ell, J, L, m_L |\,, \\
&\langle \gamma | = \langle n, \nu, \ell, m, J, M |\,, \\
&\langle \gamma' | \gamma \rangle = \delta_{\gamma'\gamma}\,, \qquad \langle \Gamma' | \Gamma \rangle = \delta_{\Gamma'\Gamma}\,, \\
&|\gamma'\rangle\langle\gamma| = I\delta_{\gamma'\gamma}\,, \qquad |\Gamma'\rangle\langle\Gamma| = I\delta_{\Gamma'\Gamma}\,,
\end{aligned}
\tag{8.24}
$$

where I is a unit matrix. For the rest of the Chapter summation over indices which appear twice is implied. For a given initial state σ, equ. (8.14) can be written, according to Seaton's notation, as

$$
[k_{\sigma'}^2 + \partial^2/\partial r^2 - \ell(\ell+1)/r^2]\, \langle G_{\gamma''}(\sigma|r)| = |\gamma''\rangle U \langle\gamma'|\, \langle G_{\gamma'}(\sigma|r)|\,,
$$

where U=2H. Multiplying the last equation by $|\Gamma''\rangle\langle\gamma''|$ on both sides, it becomes

$$
[k_{\sigma'}^2 + \partial^2/\partial r^2 - \ell(\ell+1)/r^2]\, |\Gamma''\rangle\langle\gamma''|\, \langle G_{\gamma''}(\sigma|r)| = |\Gamma''\rangle U \langle\Gamma'|\ X
$$

$$
|\Gamma'\rangle\langle\gamma'|\, \langle G_{\gamma'}(\sigma|r)|\,.
$$

Denote $\langle G_{\Gamma''}(\sigma|r)|$ for $|\Gamma''\rangle\langle\gamma''|\, \langle G_{\gamma''}(\sigma|r)|$. The equation is identical to equ. (8.23) if previous notation is used:

$$
[k_{\sigma'}^2 + \partial^2/\partial r^2 - \ell(\ell+1)/r^2]\, \langle G_{\Gamma''}(\sigma|r)| = |\Gamma''\rangle U \langle\Gamma'|\, \langle G_{\Gamma'}(\sigma|r)|\,. \tag{8.25}
$$

The asymptotic form of $G_{\Gamma'}(\sigma|r)$ is

$$k^{-1/2}\{\exp[-i(kr-\ell\pi/2)]\,\delta_{\Gamma\Gamma''} - \exp[i(kr-\ell\pi/2)]\,S_{\Gamma''\Gamma}\}\ ,$$

where it can be shown[42] that

$$S_{\gamma\gamma'} = \langle\gamma|\Gamma\rangle\, S_{\Gamma\Gamma'}\langle\Gamma'|\gamma'\rangle\ , \qquad (8.26)$$

and that the matrices $S_{\gamma\gamma'}$ and $S_{\Gamma\Gamma'}$ are unitary and symmetric. The matrix $S_{\Gamma''\Gamma}$ is diagonal in L and m_L. Thus each block characterized by L and m_L can be examined individually. By the use of the coupled representation the infinite, coupled set of differential equations (8.14) has been decoupled into blocks and each block has only a finite number of channels. This is the main reason for using the coupled representation.

The cross section of excitation from initial state σ to final state σ' is

$$Q(\sigma\to\sigma') = \pi k^{-2}\,\Omega(\sigma,\sigma')/(2J+1)\ , \qquad (8.27)$$

where

$$\Omega(\sigma,\sigma') = \sum_{\ell,\ell',L}(2L+1)\left|T(\sigma',\ell',L;\sigma,\ell,L)\right|^2\ , \qquad (8.28)$$

and T is defined by equ. (8.18).

Before attempting to solve equ. (8.23) to obtain the asymptotic solution of $G_{\Gamma'}(\sigma|r)$ and hence the excitation cross section, the potential $U_{\Gamma''\Gamma'}$ has to be calculated.

CHAPTER IX

ELECTRIC AND POLARIZATION POTENTIAL

§9.1 Interaction Potential $U_{n''n}(\vec{r}_3, \vec{\xi})$

Define $U_{\Gamma''\Gamma}(r)$ and $U_{n''n}(\vec{r}_3, \vec{\xi})$ as

$$U_{\Gamma''\Gamma}(r) = \langle n''\nu''\ell''J''Lm_L | 2H | n\nu\ell JLm_L \rangle \ , \tag{9.1}$$

$$U_{n''n}(\vec{r}_3, \vec{\xi}) = \langle n'' | 2H | n \rangle \tag{9.2}$$

$$= 2 \int \psi^*_{n''}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi}) H \psi_n(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi}) d\vec{r}_1 d\vec{r}_2 \ .$$

If the kinetic energy of the incident electron is less then the energy necessary to excite the target to the next electronic state, then all higher electronic states are closed. The closed channels are usually not important in the calculation of excitation cross section. Hence as an approximation the expansion in equ. (8.13) will include $\psi_o(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi})$, the ground electronic state only.

If $\psi_o(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi})$ and the eigenfunctions of H_{mol}, $\psi_n(\vec{r}_1, \vec{r}_2, \vec{\xi})$ were known, then theoretically $\psi_o(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi})$ could be expanded in

terms of $\psi_n(\vec{r}_1, \vec{r}_2, \vec{\xi})$. However $\psi_o(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi})$ is unknown and $\psi_n(\vec{r}_1, \vec{r}_2, \vec{\xi})$ is not known sufficiently accurately. Thus it is necessary to resort to some variational function as an approximation to the ground electronic state of the perturbed hydrogen molecule $\psi_o(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi})$. The scheme will be as follows. For the electronic wave function of the unperturbed ground state the Weibaum wave function[43] will be used. Define ϕ_o as:

$$\phi_o = \psi_o(\vec{r}_1, \vec{r}_2, \vec{\xi}) = N^{-1}\{[a(1)b(2)+a(2)b(1)] + c[a(1)a(2)+b(1)b(2)]\}, \quad (9.4)$$

$$a(1) = \pi^{-1/2} Z^{3/2} \exp(-Zr_{1a}) ,$$

$$b(1) = \pi^{-1/2} Z^{3/2} \exp(-Zr_{1b}),$$

$$N^2 = 2[(1+c^2)^2 + (c+S)^2] , \quad (9.5a)$$

$$S = \int a(1)b(1)d\vec{r}_1 , \quad (9.5b)$$

where Z and c are functions of ξ. Defind Φ as:

$$\Phi = (\phi_o + \psi') \cong \psi_o(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi}) , \quad (9.6)$$

where ψ' is a function of $\vec{r}_1$ and $\vec{r}_2$ and contains one or more parameters. By substituting equ. (9.6) into equ. (9.2) and varying the parameters until the potential is a minimum, $U_{n''n}(\vec{r}_3, \vec{\xi})$ is the required potential and Φ, the variational function for $\psi_o(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{\xi})$. The potential can be written as

$$U_{n''n}(\vec{r}_3, \vec{\xi}) = \langle \Phi | 2H | \Phi \rangle \quad (9.7)$$

$$= E_o + \langle \phi_o | 2H' | \phi_o \rangle + [\langle \Phi | 2H | \Phi \rangle \langle \Phi | \Phi \rangle^{-1} - \langle \phi_o | 2H' | \phi_o \rangle - E_o] \ ,$$

where E_o is the unperturbed ground state energy of the hydrogen molecule. The second term on the RHS of equ. (9.8) represents the interaction energy of the incident electron with the target electrons and nuclei. The electronic density distribution is not distorted and hence is the electric term. The quantities in the parenthesis represent the lowering of the potential energy as a result of distortion of the electronic cloud density and hence is the polarization term.

Physically the potential $U_{n''n}(\vec{r}_3, \vec{\xi})$ should depend only upon r, ξ and δ, where δ is the angle between $\vec{r}_3$ and the axis of the molecule. For the considerations of electric and polarization potentials the molecular axis will be taken as the z-axis and assumed to be fixed.

§9.2 The Electric Potential

The integrals encountered in the electric potential can be evaluated analytically:

$$E(r, \xi, \delta) = \langle \phi_o | 2H' | \phi_o \rangle$$

$$= 2 \langle \phi_o | r_{31}^{-1} + r_{23}^{-1} - r_{3A}^{-1} - r_{3B}^{-1} | \phi_o \rangle$$

$$= -2(r_{3A}^{-1} + r_{3B}^{-1}) + 4N^{-1}[c_t(I_{4A} + I_{4B}) + 2c_s I_5] \ ,$$

where N and the overlap integral S are given by equ. (9.5), and

$$c_t = 1 + c^2 + 2cS ,$$

$$c_s = S + c^2 S + 2c .$$

The integrals I_{4A} and I_{4B} are listed in Appen. VI.

Expand $E(r, \xi, \delta)$ in Legendre polynomial $P_n(\cos\delta)$. Because of the symmery of the H_2 molecule the coefficients of the odd terms are zero:

$$E(r, \xi, \delta) = \sum_{\lambda=0}^{\infty} E_{2\lambda}(r, \xi) P_{2\lambda}(\cos\delta) . \tag{9.11}$$

Subject the coefficients $E_{2\lambda}(r, \xi)$ to a Taylor expansion of the variable ξ about the equilibrium position. Denote $\partial^k E_{2\lambda}(r, \xi)/\partial \xi^k \Big|_{\xi = 0}$ by $E^k_{2\lambda}(r)$ then equ. (9.11) becomes

$$E(r, \xi, \delta) = \sum_{\lambda=0}^{\infty} \sum_{k=0}^{\infty} E^k_{2\lambda}(r) \xi^k / k! P_{2\lambda}(\cos\delta) . \tag{9.12}$$

For low vibrational states, the amplitude of vibration is small. Hence the Taylor series will be terminated after the second term:

$$E(r, \xi, \delta) \cong \sum_{\lambda=0}^{\infty} [E^o_{2\lambda}(r) + E^1_{2\lambda}(r)] P_{2\lambda}(\cos\delta) . \tag{9.13}$$

The calculation by Breig and Lin[39] indicates that the cross section is mainly due to the spherical symmetric term $P_o(\cos\delta)$. The contribution from the $P_2(\cos\delta)$ is of two orders of magnitude smaller. It is anticipated that the $P_4(\cos\delta)$ or higher terms will contribute less than the P_2 term and hence will be neglected. Thus only the first two

terms in the Legendre polynomial series will be kept. The electric potential can then be written as

$$E(r,\xi,\delta) \cong \sum_{\lambda=0,1} [E^{o}_{2\lambda}(r) + E^{1}_{2\lambda}(r)\xi\,]\, P_{2\lambda}(\cos\delta)\ . \qquad (9.14)$$

Upon multiplying equ. (9.14) by $P_{2\lambda}(\cos\delta)$ and integrate over $\cos\delta$, the following result is obtained:

$$E_{2\lambda}(r,\xi) = (4\lambda+1)/2 \int E(r,\xi,\delta)P_{2\lambda}(\cos\delta)\sin\delta d\delta \qquad (9.15)$$

$$\cong E^{o}_{2\lambda}(r) + E^{1}_{2\lambda}(r)\xi\ ,$$

where $E^{o}_{2\lambda}(r)$ is given by the last equation with $\xi = 0$. In order to obtain $E^{1}_{2\lambda}(r)$, $E_{2\lambda}(r,\xi)$ is calculated for five values of ξ, at $\xi = -0.2,\ -0.1,\ 0,\ 0.1,\ 0.2$, corresponding to the nuclear separation at R_{AB}=1.23, 1.33, 1.43, 1.53, 1.63 respectively. Then the five points are fitted to a polynomial of fourth degree and a differentiation at $\xi = 0$ is obtained from the polynomial. The values of parameters c and Z in the Weibaum's wave function at different nuclear separations are calculated and tabulated in Table VIII.

It is found that for $r \geq 2.0$ the electric coefficients decay exponentially, i.e. behave like $c_1\exp(-c_2 r)$. The values of $E_{2\lambda}(r)$ and $E^{1}_{2\lambda}(r)$ are listed in Table IX. The constants c_1 and c_2 are also listed in the same Table.

TABLE VIII

PARAMETERS FOR THE WEIBAUM WAVE FUNCTION AT VARIOUS NUCLEAR SEPARATIONS

R_{AB}	ξ	Z	c	E(eV)
1.23	-.2	1.2420	0.26231	-3.79224
1.33	-.1	1.2167	0.26453	-3.97354
1.43	0	1.1937	0.26438	-4.02516
1.53	.1	1.1729	0.26220	-3.98487
1.63	.2	1.1535	0.25852	-3.87984

TABLE IX

COEFFICIENTS OF ELECTRIC POTENTIAL (a. u.)

r	$E_o^o(r)$	$E_2^o(r)$	$E_o^1(r)$	$E_2^1(r)$
0	-0.8982	0	1.2759	0
0.1	-0.9035	-0.05077	1.2885	0.1084
0.35	-0.9570	-0.6277	1.3566	1.3383
0.50	-1.0150	-1.2932	1.4269	2.7514
0.60	-1.0628	-1.8755	1.4777	4.1182
0.80	-0.8780	-1.8754	-.3634	-2.6440
1.0	-0.5024	-0.9009	-.2597	-1.3517
1.5	-0.1354	-0.04311	-.1040	-0.08438
2.0	-0.03848	-0.01157	-.03876	-0.02508
2.5	-0.0112	-0.00324	-0.1389	-0.00770
c_1	-5.224	-1.8039	-2.4766	-2.6307
c_2	2.4553	2.5246	2.0786	2.3265

§9.3 Polarization Potential

From equ. (9.8) the polarization potential is given by

$$V(r,\xi,\delta) = \langle\bar{\Phi}|2H'|\bar{\Phi}\rangle\langle\bar{\Phi}|\bar{\Phi}\rangle^{-1} - \langle\phi_o|2H'|\phi_o\rangle - E_o \ . \qquad (9.16)$$

An approximate expansion same as for the electric potential can be obtained:

$$V(r,\xi,\delta) \cong \sum_{\lambda=0,1} [V^o_{2\lambda}(r) + V^1_{2\lambda}(r)\xi\,]\, P_{2\lambda}(\cos\delta) \ . \qquad (9.17)$$

Equ. (9.6) defines ψ' as

$$\bar{\Phi} = \phi_o + \psi' \ .$$

Fowllowing the work of Das and Berson[45] ψ' will be chosen to be of the following form:

$$\psi' = p\phi_o \ ,$$

where p is chosen to be of the following form:

$$p = p_1 + p_2 \ ,$$

$$p_i = c'(x_i+y_i) + b'z_i + [c''(x_i+y_i)+b''z_i]\exp(-\varepsilon r_{i3}) \ , \qquad (9.18)$$

$$i = 1,2 \ ,$$

c', c'', b', b'' are the variational parameters, r_{13}, r_{23} are distances between the molecular electrons and the incident electron. It takes too much time on the computer to average over cosδ, like it has been done for the electric term. Instead, e_3 will be placed on the z-axis to get the z polarization and then on the x-axis to get the x, y polariza-

tion. From $V(r, \xi, 0)$ and $V(r, \xi, \pi/2)$ the coefficients of P_o and P_2 in Equ. (9.17) can be obtained:[39]

$$
\begin{aligned}
V_o(r) &= [V(r, \xi=0, 0) + 2V(r, \xi=0, \pi/2)]/3 \ , \\
V_2(r) &= [V(r, \xi=0, 0) - V(r, \xi=0, \pi/2)]\tfrac{2}{3} \ , \\
V_o^1(r) &= [V^1(r, \xi, 0) + 2V^1(r, \xi, \pi/2)]/3 \ , \\
V_2^1(r) &= [V^1(r, \xi, 0) - V^1(r, \xi, \pi/2)]\tfrac{2}{3} \ ,
\end{aligned}
\qquad (9.19)
$$

where $V_o^1(r)$ and $V_2^1(r)$ are obtained in the same manner as in the case of $E_o^1(r)$ and $E_2^1(r)$.

The 3-center integrals encountered in the polarization potential can be reduced by Gauss Transformation[46] to double integrals which can be evaluated readily on computer. The integrals are listed in Appen. VI. An example of the use of Gauss Transformation in dealing with 3-center integrals is also given in the same Appendix. The values of $V(r, \xi, 0)$, $V(r, \xi, \pi/2)$, $V^1(r, \xi, 0)$ and $V^1(r, \xi, \pi/2)$ are listed in Table X.

When the polarization coefficients are plotted against r on log-log graph paper, it is observed that they attain the asymptotic behaviour somewhere about $r \cong 7.0$ a.u. from the center of the molecule. The constants c_3 are the factors necessary to bring the polarizabilities to agree with experimental values. The experimental values[47, 48] of $\alpha_\perp$,

TABLE X

COEFFICIENTS OF POLARIZATION POTENTIAL (a.u.)

r	$V(r, 0, \pi/2)$	$V(r, 0, 0)$	$V^1(r, 0, \pi/2)$	$V^1(r, 0, 0)$
0	0	0	0	0
0.1	-0.003129	-0.01829	0.00274	0.01041
0.35	-0.02959	-0.1472	0.02124	0.02926
0.50	-0.04735	-0.2055	0.02840	-.01252
1.0	-0.07054	-0.2943	0.01776	-.1270
1.5	-0.05625	-0.2173	-.000355	-.1554
2.0	-0.03691	-0.1377	-.007464	-.1282
2.5	-0.02268	-0.08284	-.007918	-.09200
3.0	-0.01380	-0.04939	-.006260	-.06185
3.5	-0.008556	-0.02988	-.004459	-.04049
4.0	-0.005476	-0.01858	-.003066	-.02648
4.5	-0.003636	-0.01194	-.002103	-.01755
5.0	-0.002504	-0.007943	-.001465	-.01189
6.0	-0.001305	-0.003858	-.000764	-.00585
7.0	-0.000749	-0.002080	-.000439	-.00319
c_3†	1.235	0.6114	1.598	0.4487

†c_3 is the normalization constant.

$\alpha_{//}$, the x and z-polarizability are 4.443 and 6.107 respectively. The V^{-1}'s are so normalized that they agree with experimental data of the intensities of Raman spectra.[49] The coefficients will be called normalized when they are multiplied by the respective constants. It is the normalized polarization coefficients that will be used for calculations of vibrational excitation cross sections.

CHAPTER X

CROSS SECTIONS BY BORN APPROXIMATION AND BY CLOSE COUPLING FORMULATION, DISCUSSION AND CONCLUSION

§10.1 Cross Section by Born Approximation

Since all previous calculations were done with Born approximation, the Born cross sections will be obtained and compared with earlier results. According to equ. (2.15) the Born cross section is given by

$$Q(o \to n) = k_o^{-2} \int_0^{2\pi} d\eta \int_{K_{min}}^{K_{max}} \left| f_{o,n}(K,\eta) \right|^2 K dK d\eta \ , \qquad (10.1)$$

$$f_{o,n}(K,\eta) = (2\pi)^{-1} \int \exp(iKr\cos\theta)\, V_{on}(r) d\vec{r} \ , \qquad (10.2)$$

$$V_{on}(r) = \tfrac{1}{2} U_{\gamma''\gamma}(r) = \tfrac{1}{2} \langle \nu''\ell''J''Lm_L \left| U_{n''n}(r, \xi, \delta) \right| \nu\ell JLm_L \rangle . \qquad (10.3)$$

If the approximate expansions of equs. (9.4) and (9.17) are substituted into the last equation and integrated over $\vec{\xi}$ and $\sin\Theta d\Theta d\Phi$, the following expression for $V_{on}(r)$ is obtained:

$$V_{on}(r) = [A_o^o(r)\delta_{\nu\nu''} + \xi_{\nu\nu''} A_o^1(r)]\, \delta_{JJ''} \delta_{MM''} + [A_2^o(r)\delta_{\nu\nu''} + \xi_{\nu\nu''} A_2^1(r)] (4\pi/5)^{\frac{1}{2}} C_2(J, M, J'', M'') Y_{2, M-M''}(\theta, \phi) \ , \qquad (10.4)$$

where

$$A_n^m(r) = (E_n^m(r) + V_n^m(r))/2 \ , \tag{10.5}$$

$$\xi_{\nu\nu''} = \langle \nu | \xi | \nu'' \rangle \ , \tag{10.6}$$

$$C_\lambda(J, M, J'', M'') = (-1)^M (2\lambda+1)^{\frac{1}{2}} (4\pi)^{-\frac{1}{2}} \int Y^*_{J, M} Y_{\lambda, M-M''} Y_{J'', M''} d\omega \ . \tag{10.7}$$

Also the addition theorem of Legendre polynomials has been used:

$$P_{2\lambda}(\cos\delta) = \sum_{M=-2\lambda}^{2\lambda} [4\pi/(4\lambda+1)]^{\frac{1}{2}} Y^*_{2\lambda, M}(\theta, \phi) Y^*_{2\lambda}(\Theta, \Phi) \ . \tag{10.8}$$

The vibrational excitation to be considered is from the ground state (ν=0) to the first excited state (ν''=1). It will have to be averaged over all initial rotational states and summed over all final rotational states. In equ. (10.4) the terms involving $\delta_{\nu\nu''}$ drop out and $V_{on}(r)$ becomes

$$V_{on}(r) = \beta[A^1_o(r)\delta_{\nu, \nu''+1}\delta_{JJ''}\delta_{MM''} + A^1_2(r)\delta_{\nu, \nu''+1}](4\pi/5)^{\frac{1}{2}} \ X$$

$$C_2(J, M, J'', M'') Y_{2, M-M''}(\theta, \phi) \ , \tag{10.9}$$

where

$$\beta = \xi_{0,1} = 0.1695 \ .$$

The plane wave exp(iKrcosθ) can be expanded in terms of partial waves with the help of the following formula:

$$\exp(iKr\cos\theta) = \sum_{\ell=0}^{\infty} (2\ell+1) i^\ell P_\ell(\cos\theta) j_\ell(kr) \ , \tag{10.10}$$

where

$$\begin{aligned} j_\ell(Kr) &= [\pi/(2Kr)]^{\frac{1}{2}} J_{\ell+\frac{1}{2}}(Kr) \ , \\ j_o(Kr) &= \sin Kr/(Kr) \ . \end{aligned} \tag{10.11}$$

Substituting equs. (10.9), (10.10) into equ. (10.2) and integrating over $\sin\theta\, d\theta\, d\phi$ the following expression is obtained:

$$f_{on}(K,\eta) = 2\beta(\pi/2K)^{1/2}[J_A \delta_{JJ''} - 5^{-1} C_2(J, M, J'', M) J_B]\, \delta_{MM''} ,$$

where

$$J_A = \int J_{\frac{1}{2}}(Kr) A_o^1(r)\, r^{3/2} dr ,$$

and

$$J_B = \int J_{5/2}(Kr) A_2^1(r)\, r^{3/2} dr .$$

Thus the expression for Born cross section becomes

$$Q(\nu=0, J, M \rightarrow \nu''=1, J'', M) = (4\pi^2\beta^2/k_o^2) \sum_{J'', M} (2J+1)^{-1} \int [J_A \delta_{JJ''} - 5^{-1} C_2(J, M, J'', M) J_B]^2 dK.$$

Using the formulas[49]

$$\sum_M C_2(J, M, J, M) = 0 ,$$

and

$$\sum_{J'', M} |C_2(J, M, J'', M)|^2 = 1/5\,(2J+1) ,$$

the Born Cross section then is given by the following expression:

$$Q(\nu=0 \rightarrow \nu''=1) = 4\pi^2\beta^2 k_o^{-2} \int_{K_{min}}^{K_{max}} [J_A^2(K) + J_B^2(K)/125]\, dK . \quad (10.14)$$

If only the vibrational excitation energy is taken into account, i.e. the small rotational excitation energy is neglected, the Born cross section is then the same for all initial values of J.

The $E_o^1(r)$ term as tabulated in Table IX has a discontinuity at $r=0.715=\rho_o$. This arises from the Coulomb interaction between the

incident electron and the nuclei. During the process of averaging over all angles an infinitely thin shell of charge 2e is produced. The potential between the incident electron and the thin shell is well known --- it is $-1/\rho_o$ inside the shell and decays as $-1/r$ when $r > \rho_o$. When it is subsequently subjected to a Taylor expansion the discontinuity results. In actual case, if vibration is taken into account, the infinitely thin shell of positive charge will smear out with charge density decreasing on either side. Thus the first order approximation in the Taylor expansion in equ. (9.13) is not valid at $r=\rho_o$. A detailed calculation for $\langle \nu=0 | \int r_{3A}^{-1} d\omega | \nu''=1 \rangle$ has been carried through. It is found that discontinuity can be avoided by employing, in the region from r=0.45 to r=0.90, a straight line joining the two end points. This approximate potential curve for the electric potential is adequate for the reason that its contribution to cross section is less important than the polarization potential.

The electric potentials are curve fitted regionalwise to a polynomial with five parameters.† The regions overlap at the boundaries so as to ensure continuity of the curve, except, of course, where discontinuity occurs. For r>2.0, the electric potentials decay ex-

---

†The program was originally written by R. Channey and was adapted by S. Chung

TABLE XI

BORN CROSS SECTION (a. u.)

Incident Kinetic Energy (eV)	A	B	C
2	0. 310	0. 004	0. 343
4	0. 176	0. 029	0. 199
6	0. 119	0. 020	0. 135
8	0. 0895	0. 015	0. 102
10	0. 0732	0. 013	0. 0820

Column A: Electric Potential has a discontinuity at r=0. 715; Polarization Potential normalized.

Column B: Electric Potential (with discontinuity) alone.

Column C: The discontinuity in the Electric Potential has been avoided by a straight line joining the two points (r=0. 45, r=0. 90), Polarization Potential included.

ponentially, and the parameters are given in Table IX.

The polarization potentials are curve fitted in the same manner up to r=7.0. For r> 7.0, they are proportional to r^{-4} and the constants of proportionality, the α's are tabulated in Table X.

In Table XI the values of Born cross section at several different incident energies are listed.

§10.2 Born Partial Wave Cross Sections.

The incident electron is treated in the Born approximation as a plane wave, represented by $\exp(i\vec{k}_o \cdot \vec{r})$. This can be expanded in terms of partial waves according to equ. (10.10) and the cross section $Q_\ell(o \to n)$ due to each partial wave ℓ examined. Often Born cross section exceeds the experimental value at low energy. Then the Born partial wave cross section provides a test of validity of the approximation, because the law of conservation of angular momentum requires the following to hold:[51]

$$Q_\ell^{in}(o \to n) \leq \pi(2\ell+1)/k_o^2 \ . \qquad (10.15)$$

In the present case the Born cross section is smaller than experimental value and the Born partial wave cross sections fall far below the maximum limit. However, this expansion of the Born cross section affords some physical insight and hence will be carried through.

The Born cross section in terms of angular variables is

$$Q(o \to n) = \int\int I_n(u, v) \sin u \, du \, dv, \tag{10.16}$$

where (u, v) are the scattered polar angles and

$$I_n(u, v) = (k_n / k_o) \left| f_n(u, v) \right|^2 , \tag{10.17}$$

$$f_n(u, v) = (2\pi)^{-1} \int\int \exp(i\vec{k}_o \cdot \vec{r} - \vec{k}' \cdot \vec{r}) V_{on}(r) d\vec{r}. \tag{10.18}$$

In the last expression $V_{on}(r)$ is defined by equ. (10.9).

By the use of equs. (10.9), (10.10) and after some tedious but straightforward manipulation the following formula for $Q_\ell(o \to n)$ can be derived:

$$Q_\ell(o \to n) = 4\beta^2 \pi^3 k_o^{-2} \sum_{i=1,4} T_{\ell i} , \tag{10.19}$$

$$T_{\ell 1} = (2\ell+1) I_\ell^2 \delta_{JJ''} \delta_{MM''} ,$$

$$T_{\ell 2} = C_2(J, M, J'', M)(2\ell+1)^{1/2} \delta_{JJ''} \delta_{MM''} I_\ell [-(2\ell+5)^{1/2} \times C_2(\ell+2, 0, \ell, 0) I'_{\ell+2, \ell} + (2\ell+1)^{1/2} C_2(\ell, 0, \ell, 0) I'_{\ell, \ell} - (2\ell-3)^{1/2} C_2(\ell-2, 0, \ell, 0) \times I'_{\ell-2, \ell}] ,$$

$$T_{\ell 3} = C_2(J, M, J'', M'')(2\ell+1)^{1/2} \delta_{JJ''} \delta_{MM''} \delta_{m'0} [-I_{\ell-2} I'_{\ell, \ell-2} \times (2\ell-1)^{1/2} C_2(\ell, 0, \ell-2, 0) + (2\ell+1)^{1/2} I_\ell I'_{\ell, \ell} C_2(\ell, 0, \ell, 0) - (2\ell+5)^{1/2} \times I_{\ell+2} I'_{\ell, \ell+2} C_2(\ell, 0, \ell+2, 0)] ,$$

$$T_{\ell 4} = C_2(J, M, J'', M'')(2\ell+1)^{1/2} \delta_{m', M-M''} [(2\ell+1)^{1/2} \times I'^2_{\ell, \ell-2} C_2(\ell, 0, \ell-2, m')^2 - (2\ell-3)^{1/2} I'_{\ell-2, \ell-2} I'_{\ell, \ell-2} C_2(\ell, 0, \ell-2, m') \times$$

$$C_2(\ell-2, 0, \ell-2, m') + (2\ell-7)^{1/2} I'_{\ell, \ell-2} I'_{\ell-4, \ell-2} C_2(\ell, 0, \ell-2, m') \times$$

$$C_2(\ell-4, 0, \ell-2, m') - (2\ell+5)^{1/2} I'_{\ell, \ell} I'_{\ell+2, \ell} C_2(\ell, 0, \ell, m') C_2(\ell+2, 0, \ell, m')$$

$$+ (2\ell+1)^{1/2} I'^{2}_{\ell, \ell} C_2(\ell, 0, \ell, m')^2 - (2\ell-3)^{1/2} I'_{\ell, \ell} I'_{\ell-2, \ell} C_2(\ell, 0, \ell, m') \times$$

$$C_2(\ell-2, 0, \ell, m') + (2\ell+9)^{1/2} I'_{\ell, \ell+2} I'_{\ell+4, \ell+2} C_2(\ell, 0, \ell+2, m') \times$$

$$C_2(\ell+4, 0, \ell+2, m') - (2\ell+5)^{1/2} I'_{\ell, \ell+2} I'_{\ell+2, \ell+2} C_2(\ell, 0, \ell+2, m') \times$$

$$C_2(\ell+2, 0, \ell+2, m') + (2\ell+1)^{1/2} I'^{2}_{\ell, \ell+2} C_2(\ell, 0, \ell+2, m')^2] \ ,$$

where

$$I_\ell = \int J_{\ell+\frac{1}{2}}(k_o r) J_{\ell+\frac{1}{2}}(k' r) A^1_o(r) r dr$$

and $$I'_{\ell, \ell'} = \int J_{\ell+\frac{1}{2}}(k_o r) J_{\ell'+\frac{1}{2}}(k' r) A^1_2(r) r dr \ .$$

The Born partial wave cross sections are tabulated in Table XII.

§10.3 Close Coupling Calculation

The set of coupled differential equations to be solved is

$$[k^2_{\sigma'} + \partial^2/\partial r^2 - \ell(\ell+1)/r^2) \langle G_{\Gamma'}(\sigma|r)| = \langle \Gamma''|U|\Gamma'\rangle \langle G_{\Gamma'}(\sigma|r)|, \quad (8.15)$$

where

$$\langle \Gamma''|U|\Gamma'\rangle = \langle \nu'', \ell'', J'', L, m_L | U_{n''n}(r, \xi, \delta) | \nu', \ell', J', L, m_L \rangle .$$

(10.20)

Note that $U_{n''n}(r, \xi, \delta)$ is the sum of the two approximate expansions of equ. (9.14) and (9.17):

TABLE XII

BORN PARTIAL WAVE CROSS SECTION (a.u.)

Incident Kinetic Energy (eV)		A		C
2	$\ell=0$:	0.273	$\ell=0$:	0.286
	$\ell=1$:	0.0360	$\ell=1$:	0.036
	$\ell=2$:	0.0030	$\ell=2$:	0.0030
4	$\ell=0$:	0.121	$\ell=0$:	0.130
	$\ell=1$:	0.050	$\ell=1$:	0.050
	$\ell=2$:	0.006	$\ell=2$:	0.006

The potentials used in Column A and C are the same as those used in the corresponding Columns in Table XI.

$$U_{n''n}(r,\xi,\delta) = \sum_{\lambda=0,1}[B^{o}_{2\lambda}(r)+B^{1}_{2\lambda}(r)\xi]\,P_{2\lambda}(\cos\delta)\ , \qquad (10.21)$$

where

$$B^{j}_{2\lambda}(r) = E^{j}_{2\lambda}(r) + V^{j}_{2\lambda}(r)\ ,\ j=0,1\ . \qquad (10.22)$$

Using the notation of Seaton,[42] denote $\langle \ell, J, L, m_L | P_k(\cos\delta) | \ell', J', L, m_L \rangle$

by $f_k(\ell, J; \ell'', J''; L)$ and because of the following relations:

$$\langle \nu \mid \nu'' \rangle = \delta_{\nu\nu''} ,$$

$$\langle \nu=0 | \xi | \nu'' \rangle = \beta \delta_{1,\nu''} = 0.1695\, \delta_{1,\nu''} ,$$

$$\langle \ell, J, L, m_L | \ell'', J'', L, m_L \rangle = \delta_{\ell\ell''}\delta_{JJ''} ,$$

the expression for $\langle \Gamma'' | U | \Gamma \rangle$ can be written as

$$\langle \Gamma'' | U | \Gamma \rangle = [B_o^o(r)\delta_{\nu\nu''} + \beta B_o^1(r)\delta_{1,\nu''}]\delta_{\ell\ell''}\delta_{JJ''} + [B_2^1(r)\delta_{\nu\nu''} + \beta B_2^1(r)\delta_{1,\nu''}] f_2(\ell, J; \ell'', J''; L) . \qquad (10.24)$$

The coefficients $f_2(\ell, J; \ell'', J''; L)$ has been programmed. † This greatly reduces the labour involved. In order to calculate the vibrational excitation cross section $Q(\nu=0 \rightarrow \nu''=1)$ of H_2 at temperature T, it is necessary to calculate, first of all , the cross sections $Q(\nu=0, J, M \rightarrow \nu''=1, J'', M'')$ corresponding to different initial rotational states J, M. It is, of course,necessary to average over initial states (same J but different M) and sum over all possible final states (J'', M''). Then all the $Q(\nu=0, J, M \rightarrow \nu''=1, J'', M'')$ are added with the respective statistical weights at temperature T. It is to be noted that there are two species of H_2,[52] according to whether the nuclear spins

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†The values of the coefficients are taken from a more complete table supplied by S. Chung.

are parallel (ortho-) or anti-parallel (para-). For the para-hydrogen the rotational quantum numbers can only be even and the ortho-hydrogen, odd. The conversion between para- and ortho-hydrogen is slow and the ratio of ortho-hydrogen to para-hydrogen is 3:1.

Because of limited available computer time, the close coupling cross sections are calculated with the electric and polarization (normalized) potentials as tabulated in Tables IX and X only. The Numerov method is used to solve the set of coupled differential equations. The numerical procedure has been discussed in detail by Lane and Lin[56] and Lane[57] and will not be reproduced. Lane's original program, adapted by S. Chung has been used. The results are listed in Table XIII.

At 300°T 80% of the hydrogen are in the first two rotational states. If it is assumed that $Q(v=0, J=2n \rightarrow v''=1)$ and $Q(v=0, J=2n+1 \rightarrow v''=1)$ are independent of n, then

$$Q(v=0 \rightarrow v''=1) = Q(v=0, J=0 \rightarrow v''=1)/4 + (3/4)Q(v=0, J=1 \rightarrow v''=1) .$$

The vibration excitation cross sections from ground state to the first excited state of H_2 (a mixture of 75% of ortho- and 25% of para-) is tabulated in Table XV.

TABLE XIII

CLOSE COUPLING VIBRATIONAL EXCITATION CROSS SECTION OF PARA-HYDROGEN FOR $J=0$ (a. u.)

Inc. K. E. (eV)	L=0	L=1	L=2	sum over L	sum over L (10^{-17} cm^2)
2	0.0875	0.0813	0.0032	0.172	0.482
4	0.0587	0.148	0.0075	0.214	0.599
6	0.0452	0.173	0.0106	0.228	0.638
8	0.0374	0.171	0.0129	0.221	0.619
10	0.0322	0.157	0.0145	0.204	0.517

Each channel is labelled by (ν, J, ℓ). The channels used are:

for L=0, (0, 0, 0), (1, 0, 0);

for L=1, (0, 0, 1), (0, 2, 1), (0, 2, 3), (1, 0, 1), (1, 2, 1), (1, 2, 3);

for L=2, (0, 0, 2), (0, 2, 0), (0, 2, 2), (0, 2, 4), (1, 0, 2), (1, 2, 0), (1, 2, 2), (1, 2, 4).

TABLE XIV

CLOSE COUPLING VIBRATIONAL EXCITATION CROSS SECTION OF ORTHO-HYDROGEN FOR J=1 (a.u.)

Inc. K.E. (eV)	L=0	L=1	L=2	L=3	sum over L	sum over L (10^{-17} cm^2)
2	0.0178	0.0500	0.0495	0.0015	0.113	0.32
4	0.0363	0.0394	0.0924	0.0037	0.168	0.47
6	0.0449	0.0333	0.109	0.0050	0.187	0.52
8	0.0460	0.0297	0.119	0.0064	0.185	0.52
10	0.0430	0.0271	0.100	0.0073	0.171	0.48

Each channel is labelled by (ν, J, ℓ). The channels used are:

for L=0, (0,1,1), (0,3,3), (1,1,1), (1,3,3);

for L=1, (0,1,0), (0,1,2), (0,3,2), (0,3,4), (1,1,0), (1,1,2), (1,3,2), (1,3,4);

for L=2, (0,1,1), (0,1,3), (0,3,1), (0,3,3), (1,1,1), (1,1,3), (1,3,1), (1,3,3);

for L=3, (0,1,2), (0,3,0), (0,3,2), (1,1,2), (1,3,0), (1,3,2).

TABLE XV

CLOSE COUPLING VIBRATIONAL EXCITATION CROSS SECTION FOR H_2 (A MIXTURE OF 75% ORTHO- AND 25% PARA-HYDROGEN) at 300°T

Inc. K. E. (eV)	Q(a. u.)	$Q(10^{-17} cm^2)$
2	0.128	0.36
4	0.180	0.50
6	0.197	0.55
8	0.194	0.54
10	0.179	0.50

§10.4 Discussion And Conclusion

By comparing columns A and B in Table XI it is observed that the cross section becomes one order smaller if polarization potential is not included. This clearly shows the importance of the polarization potential in the excitation process. At 2 eV the vibrational excitation cross section with electric potential alone is com-

petible with calculations by Wu[35] and Carson.[37]

For the case of para-hydrogen with J=0, the contribution from L=0 has also been calculated using four channels. The results are tabulated in Table XVI together with the 2-channel calculations from column one of Table XIII. Although the 2-channel and 4-channel calculations give results which are quite different their contributions to the total cross section remain relatively small and hence does not effect the cross section too seriously. For this particular

TABLE XVI

COMPARISON BETWEEN 2-CHANNEL AND 4-CHANNEL CLOSE COUPLING PARTIAL CROSS SECTIONS FOR J=0, L=0 (a.u.)

	Incident K.E. (eV)				
	2	4	6	8	10
2-channel[a]	0.0875	0.0582	0.0452	0.0374	0.0322
4-channel[b]	0.0494	0.0377	0.0308	0.0265	0.0234

[a] The two channels are (0, 0, 0) and (1, 0, 0).

[b] The four channels are (0, 0, 0), (0, 2, 2), (1, 0, 0) and (1, 2, 2).

case the 2-chanel calculation corresponds to the contribution from the $\ell=0$ partial wave. This affords a direct comparison with the Born partial S-wave ($\ell=0$) cross section. This will be discussed later. The unexpected drastic differences in the 2-channel and 4-channel calculation are probably due to the following reason. The L=0 cross sections are very sensitive to any change in the potential. The 2-channel cross sections depend on only the $P_o(\cos\delta)$ term, however the 4-channel cross sections depend upon the P_o, P_2 and also on the P_4 terms. Thus for the 4-channel calculation an additional approximation is involved: the effect of the P_4 term in the potential is excluded. Because the coefficients of P_2 and P_4 are of opposite signs, it is anticipated that if P_4 is included, the 4-channel calculations will yield resuts which are much closer to the 2-channel values. Indeed, when P_2 is arbitrarily set to zero, the 4-channel values agree very well with the 2-channel results.

It is to be noticed that as the incident kinetic energy increases, the agreement between the two sets of values becomes better. This is because of the fact that the faster electron spends less time in the molecular electron cloud and the inicdent partial waves becomes less and less distorted. As the S-wave becomes less distorted (Born approximation becomes more valid), it becomes

less sensitive to the potential and the agreement improves.

According to Born approximation if the small rotational excitation energy is neglected the vibrational excitation cross section $Q(\nu=0, J \rightarrow \nu''=1)$ is independent of the initial J. $Q(\nu=0, J=0 \rightarrow \nu''=1)$ is close to $Q(\nu=0, J=1 \rightarrow \nu''=1)$ by partial wave calculation and hence is in agreement with results of Born approximation. The numerical values of the two calculations are of the same order of magnitude. Other than that the agreement between the two calculations is poor. The Born approximation indicates a peak near or below 2 eV while the partial wave calculation shows a peak around 7 eV. This can be understood by the following physical interpretation. Born approximation treats scattering as a small perturbation on the incident plane wave. This is a fair assumption when the incident electron is "high", such that the incident electron does not spend too much time in the target electron cloud. At 2 eV although it is four times the energy required for vibrational excitation the velocity of the incident electron is rather slow. It therefore remains in contact with the target electron cloud for a considerable period of time and as a result the plane wave will be distorted. This distortion of the plane wave is also observable from results in Tables XII and XIII. In Table XII the Born partial wave cross section indicates that the $\ell=0$

TABLE XVII

COMPARISON BETWEEN THEORETICAL AND EXPERIMENTAL VIBRATIONAL EXCITATION CROSS SECTIONS AT 2 eV (10^{-17} cm^2)

From Table XI, Column B (with electric potential only)	0.12
Wu[35] (theoretical)	0.08
Carson[37] (theoretical)	0.19
Breig and Lin[39] (theoretical) (model A, cut-off parameter at a=1.7)	0.90
(model B, cut-off parameter at a=1.7)[39]	4.0
From Table XI, Column C (Born)	0.96
From Table XIII (Close Coupling)	0.38
Schulz[53] (experimental)	5.5
Phelps[54] (experimental)	4.0

partial wave contributes a major portion of the total Born cross section, while the close coupling calculation for J=0 shows that major contribution is from the ℓ=1 partial wave. The distortion is probably due to the exceptionally large elastic scattering cross section of the ground state of H_2 which is of four orders of magnitude larger

than the vibrational excitation cross section. When the potential responsible for elastic scattering is artificially set to zero, the Born cross section is reproduced. This clearly indicates that the plane wave has been grossly distorted by elastic scattering and that the vibrational excitation is the interaction between the scattering center and the distorted wave.

The existing experimental data are scarce and contradicting. The early swarm experiments were not too reliable.[55] More recently measurements have been made by Schulz[53] and Engelhardt and Phelps.[54] Schulz's experimental curve shows a maximum at 2 eV while the experimental work of Engelhardt and Phelps indicates a peak at 4.5 eV. Thus Born cross section has the energy dependence similar to Schulz's measurement and close coupling cross section has a functional dependence similar to the curve of Engelhardt and Phelps. The calculated values are consistently smaller than experimental measurements. This is not unexpected because of the simple variational function used in producing the polarization potential. As has been mentioned before that the parameter ϵ in p_i of equ. (9.18) has been set to 1 due to lack of computing facilities. It is not unreasonable to expect that when ϵ is treated as a parameter and more terms are added, the polarization may be lowered by a factor of 2 to 3 in

the potential-sensitive region $1.5 \leq r \leq 3.0$. This will then increase the vibrational cross section by a factor of 4 or more and bring the theoretical calculation to agree with the experimental values. Hence it is concluded that the theoretical calculation can yield vibrational excitation cross sections that agree with experimental measurements if the polarization interaction is taken care of in sufficient detail.

Appendix I

To evaluate the integral $I_{1\kappa}(\kappa, K)$, given that

$$I_{1\kappa}(\kappa, K) = \int \phi_{1s}(Z)\, \phi^{*}_{\kappa}(Z'')\, d\vec{r}, \tag{I.1}$$

$$\phi_{1s}(Z) = (Z^3/\pi)^{\frac{1}{2}} \exp(-Zr), \tag{I.2}$$

$$\phi^{*}_{\kappa}(Z'') = (\kappa/2\pi)[n/(1-e^{-2\pi n})]^{\frac{1}{2}} \exp(i\kappa r)[\Gamma(1-in)]^{-1} \int_0^{\infty} u^{-in} e^{-u} X$$

$$J_o[2(i\kappa\xi' u)^{\frac{1}{2}}]\, du, \tag{3.5}$$

where $\xi' = r(1+\cos\rho)$, and $n = Z''/\kappa$. (3.6)

$J_m(z)$ is the Bessel Function of the first kind of order m and argument z. Equ. (I.1) can be expressed as:

$$I_{1\kappa} = (Z^3/\pi)^{\frac{1}{2}} (\kappa/2\pi)[n/(1-e^{-2\pi n})]^{\frac{1}{2}} [\Gamma(1-in)]^{-1} I, \tag{I.3}$$

where

$$I = \int du \int u^{-in} e^{-u} J_o[2(i\kappa\xi' u)^{\frac{1}{2}}] \exp(-Zr + i\kappa r)\, d\vec{r}. \tag{I.4}$$

Choose the direction of ejection as axis, then $\xi' = \xi$ and ξ, η are the parabolic coordinates defined by

$$\xi = r(1+\cos\theta), \qquad \eta = r(1-\cos\theta), \tag{I.5}$$

$$r = (\xi+\eta)/2, \qquad r\cos\theta = (\xi-\eta)/2, \tag{I.6}$$

$$d\vec{r} = (\xi+\eta)\, d\xi\, d\eta\, d\phi/4, \tag{I.7}$$

The explicit form of I is

$$I = (1/4) \int du \int u^{-in} e^{-u} J_o[2(i\kappa\xi u)^{\frac{1}{2}}] \exp[(i\kappa - Z)\xi/2 + (i\kappa - Z)\eta/2]\ X$$

$$(\xi+\eta)\, d\xi\, d\eta\, d\phi.$$

Integrating over ϕ gives a factor of 2π. Using the expression

$$\exp[(i\varkappa-Z)\xi/2+(i\varkappa-Z)\eta/2](\xi+\eta) = -2(\partial/\partial Z)\exp[(i\varkappa-Z)\xi/2+(i\varkappa-Z)\eta/2] ,$$

and interchanging the order of differentiation and integration, the expression for I can be written as

$$I = -\pi(\partial/\partial Z)\int du \int u^{-in} e^{-u} J_o[2(i\varkappa\xi u)^{\frac{1}{2}}] \exp[(i\varkappa-Z)\xi/2+(i\varkappa-Z)\eta/2] \quad X$$

$$d\xi\, d\eta . \qquad (I.9)$$

Integrating over η gives

$$\int \exp[-(Z-i\varkappa)\eta/2]\, d\eta = 2/(Z-i\varkappa) .$$

Integration over ξ can be performed by using the formula first derived by Weber:[59]

$$\int \exp(-\lambda\xi)\, J_o(2r\xi^{\frac{1}{2}})\, d\xi = (1/\lambda)\exp(-r^2/\lambda). \qquad (I.10)$$

Integrating over ξ gives

$$\int \exp[-(Z-i\varkappa)\xi/2]\, J_o[2(i\varkappa\xi u)^{\frac{1}{2}}]\, d\xi = \frac{2}{Z-i\varkappa} e^{-2i\varkappa u/(Z-i\varkappa)} .$$

The expression for I becomes

$$I = -4\pi(\partial/\partial Z)(Z-i\varkappa)^{-2}\int_0^\infty u^{-in}\exp[-(Z+i\varkappa)u/(Z-i\varkappa)]\, du .$$

By changing the variable from u to $v=(Z+i\varkappa)u/(Z-i\varkappa)$ the integral in the last expression becomes a gamma function. The result is

$$I = -4\pi\Gamma(1-in)(\partial/\partial Z)[(Z-i\varkappa)^{-in-1}/(Z+i\varkappa)^{-in+1}] .$$

After having carried out the differentiation and by means of the following trigonometric relation

$$\arctan x = (i/2)\ln[(1-i\varkappa)/(1+i\varkappa)] \qquad (I.11)$$

I can be expressed as

$$I = 4\pi\Gamma(1-in)\exp[-(2Z''/\varkappa)\arctan(\varkappa/Z)]\,2(Z-Z'')(Z^2+K^2)^{-2}.$$

Hence the integral $I_{l\varkappa}$ is equal to

$$-4(Z^3/\pi)^{\frac{1}{2}}[Z''\varkappa/(1-e^{-2\pi Z''/\varkappa})]^{\frac{1}{2}}(Z-Z'')(Z^2+\varkappa^2)^{-2}\exp[-(2Z''/\varkappa)\ X$$

$$\arctan(\varkappa/Z)]\ .$$

Appendix II

To calculate the ionization-excitation cross section of the 4S state of He^+ as a function of the effective Coulomb charge Z''. From equs. (3.7), (3.9), (3.26), (3.27) and (3.28) the cross section may be expressed as

$$Q_{4S}(Z'') = C(32\pi^2/k_o^2)\int K^{-3}\left|h_{22}\right|^2 d\kappa dK\,, \qquad \text{(II.1)}$$

where C is given by equ. (3.10) and h_{22} is equal to

$$\int \exp(i\vec{K}\cdot\vec{r})\phi_{1s}(Z|\vec{r})[\phi^*_{\kappa}(Z''|\vec{r}) + \beta\phi^*_{1s'}(Z|\vec{r})]\,d\vec{r}\,. \qquad \text{(II.2)}$$

Let the first integral on the RHS of (II.2) be denoted by $h_{2\kappa}(\kappa, K)$ and the second integral by $b_{2\kappa}(\kappa, K)$:

$$b_{2\kappa}(\kappa, K) = \beta\int \exp(i\vec{K}\cdot\vec{r})\phi_{1s}\phi^*_{1s}\,d\vec{r}$$

$$= -64(Z''^{11}/\pi)^{\frac{1}{2}}(4Z^2+K^2)^{-2}(Z-Z'')(Z^2+\kappa^2)^{-2}[Z''\kappa/(1-e^{-2\pi Z''/\kappa})]^{\frac{1}{2}}X$$

$$\exp[-(2Z''/\kappa)\arctan(\kappa/Z)]\,, \qquad \text{(II.3)}$$

$$h_{2\kappa}(\kappa, K) = \int \exp(i\vec{K}\cdot\vec{r})\phi_{1s}(Z)\phi^*_{\kappa}(Z'')d\vec{r}\,, \qquad \text{(II.4)}$$

where $\phi_{1s}(Z)$ and $\phi^*_{\kappa}(Z'')$ have been given in Appen. I. The integral can be written explicitly as

$$h_{2\kappa} = (Z^3/\pi)^{\frac{1}{2}}(\kappa/2\pi)n^{\frac{1}{2}}(1-e^{-2\pi n})^{-\frac{1}{2}}\Gamma(1-in)^{-1}\,I\,, \qquad \text{(II.5)}$$

$$I = \int du \int u^{-in}e^{-u}J_o[2(i\kappa\xi' u)^{\frac{1}{2}}]\exp[(i\kappa-Z)r]\exp(i\vec{K}\cdot\vec{r})d\vec{r}\,. \qquad \text{(II.6)}$$

Choose axis along $\vec{K}$, then

$$\vec{K}\cdot\vec{r} = Kr\cos\theta\,. \qquad \text{(II.7)}$$

In equ. (II. 6) ξ' is the parabolic coordinate referring to the direction of ejection as axis. It is connected to the parabolic coordinates ξ, η referring to the new axis by the following relation:

$$\xi' = \xi\cos^2\tfrac{1}{2}\theta + \eta\sin^2\tfrac{1}{2}\theta + (\xi\eta)^{\frac{1}{2}}\cos\tfrac{1}{2}\theta\,\sin\tfrac{1}{2}\theta\cos\phi\,,$$

where θ is the angle between the direction of ejection and $\vec{K}$. Then J_o may be expanded as follows:[60]

$$J_o[2(i\varkappa\xi' u)^{\frac{1}{2}}] = \sum_m J_m[2(i\varkappa\eta u\sin^2\tfrac{1}{2}\theta)^{\frac{1}{2}}]\, J_m[2(i\varkappa\xi u\cos^2\tfrac{1}{2}\theta)^{\frac{1}{2}}]\cos m\phi. \quad \text{(II. 9)}$$

By changing to parabolic coordinates and putting expressions (I. 7), (I. 8), (II. 9) into equ. (II. 7) the expression for I becomes:

$$I = -\tfrac{1}{2}(\partial/\partial Z)\int du\int u^{-in}\exp[-u+(i\varkappa - Z)(\xi+\eta)/2+iK(\xi-\eta)/2]\sum_m J_m[2(i\varkappa\eta u\,X$$

$$\sin^2\tfrac{1}{2}\theta)^{\frac{1}{2}}]\, J_m[2(i\varkappa\xi u\cos^2\tfrac{1}{2}\theta)^{\frac{1}{2}}]\cos m\phi\, d\xi\, d\eta\, d\phi\,.$$

Integrating over ϕ yields a factor of $2\pi\delta_{0,m}$. (II. 10)

Again using Weber's formula (I. 10) integrating over ξ yields

$$\int\exp[-(Z-i\varkappa-iK)\xi/2]\, J_o[2(i\varkappa u\cos^2\tfrac{1}{2}\theta)^{\frac{1}{2}}\xi^{\frac{1}{2}}]\, d\xi = 2(Z-i\varkappa-iK)^{-1}\,X$$

$$\exp[-2(i\varkappa u\cos^2\tfrac{1}{2}\theta)/(Z-i\varkappa-iK)]\,. \quad \text{(II. 11)}$$

Similarly integration over η yields

$$\int\exp[-(Z-i\varkappa+iK)\eta/2]\, J_o[2(i\varkappa u\sin^2\tfrac{1}{2}\theta)^{\frac{1}{2}}\eta^{\frac{1}{2}}]\, d\eta = 2(Z-i\varkappa+iK)^{-1}\,X$$

$$\exp[-2(i\varkappa u\sin^2\tfrac{1}{2}\theta)/(Z-i\varkappa+iK)]\,. \quad \text{(II. 12)}$$

Thus the expression for I becomes

$$I = -4\pi(\partial/\partial Z)(Z^2-\varkappa^2+K^2-2i\varkappa Z)^{-1}\int\exp[-u(Z^2+\varkappa^2+K^2-2\varkappa K\cos\theta)/(Z^2-\varkappa^2+$$

$$K^2-2i\varkappa Z)]\, u^{-in}\, du\,.$$

Recognizing the last integral to be a gamma function the expression can be written as

$$I = -4\pi\Gamma(1-in)(\partial/\partial Z)[(Z^2-\varkappa^2+K^2-2i\varkappa Z)^{-in}(Z^2+\varkappa^2+K^2-2\varkappa K\cos\theta)^{in-1}] .$$

After having carried out the differentiation, substituting $Z''/\varkappa$ for n and by means of the relation (I. 11) I becomes

$$I = -4\pi\Gamma(1-in)\exp[-(Z''/\varkappa)\arctan(\frac{2Z}{Z^2-\varkappa^2+K^2})][\cos(\frac{Z''}{2\varkappa}\ln A) - i\sin(\frac{Z''}{2\varkappa}\ln A)] X$$

$$f(Z'', \varkappa, K, \theta) , \qquad \text{(II. 13)}$$

where

$$f(Z'', \varkappa, K, \theta) = [(Z-i\varkappa)^2+K^2]^{-1}(\varkappa^2+Z^2+K^2-2\varkappa K\cos\theta)^{-2} \quad X$$

$$\{-2[Z''(\varkappa^2-Z^2+K^2-2\varkappa K\cos\theta)+Z(Z^2-\varkappa^2+K^2)] + i[-4ZZ''(\varkappa-K\cos\theta)+4Z^2]\} , \qquad \text{(II. 14)}$$

$$A = [(Z^2-\varkappa^2+K^2)^2+4Z^2\varkappa^2](Z^2+\varkappa^2+K^2-2\varkappa K\cos\theta)^{-2} .$$

By substituting the expression for I into equ. (II. 6) and the resulting equation, together with expressions (II. 5), (II. 3) and (II. 2) into equ. (II. 1) the cross section $Q_{4S}(Z'')$ has the form as is given on p. 21.

Appendix III

Explicit forms of $I_{nL}(K)$ for n=5, 6, 7 and L=P, D, F

$B = c^2 + K^2$

n=5, c_2=0.8, c=2.09

$$I_{5P} = i(16/25\sqrt{10})(Z'Z)^{3/2}c_2KB^{-3}[70c - 15c_2(5c^2-K^2)/B+18c_2^2c\ X$$
$$(5c^2-3K^2)/B^2 - c_2^3(35c^4-42c^2K^2+3K^4)/B^3]$$

$$I_{5D} = (32/25\sqrt{14})(Z'Z)^{3/2}c_2^2K^2B^{-4}[-21c+7c_2(7c^2-K^2)/B - 4c_2^2c\ X$$
$$(7c^2-3K^2)/B^2]$$

$$I_{5F} = i(63/25\sqrt{10})(Z'Z)^{3/2}c_2^3K^3B^{-5}[-8c+c_2(9c^2-K^2)/B]$$

n=6, c_2=2/3, c=2.023

$$I_{6P} = i(4/9\sqrt{70})(Z'Z)^{3/2}c_2KB^{-3}[70c -70c_2(5c^2-K^2)/B+126c_2^2c(5c^2 -$$
$$3K^2)/B^2 - 14c_2^3(35c^4-42c^2K^2+3K^4)/B^3+20c_2^4c(7c^4-14c^2K^2 +$$
$$3K^4)/B^4]$$

$$I_{6D} = (8/3\sqrt{21})(Z'Z)^{3/2}c_2^2K^2B^{-4}[-14c+7c_2(7c^2-K^2)/B - 8c_2^2(7c^2 -$$
$$3K^2)/B^2 + c_2^3(21c^4-18c^2K^2+K^4)/B^3$$

$$I_{6F} = i(16/9\sqrt{5})(Z'Z)^{3/2}c_2^3K^3B^{-5}[-12c+3c_2(9c^2-K^2)/B - 5c_2^2c(3c^2 -$$
$$K^2)/B^2]$$

n=7, c_2=4/7, c = 1.9757142

$$I_{7P} = i(4/49\sqrt{7})(Z'Z)^{3/2}c_2KB^{-3}[112c -140c_2(5c^2-K^2)/B+336c_2^2c(5c^2 -$$

$$3K^2)/B^2 - 56c_2{}^3(35c^4 - 42c^2K^2 + 3K^4)/B^3 + 160c_2{}^4c(7c^4 - 14c^2K^2 + 3K^4)/B^4$$

$$- 12c_2{}^5(21c^6 - 63c^4K^2 + 27c^2K^4 - K^6)/B^5]$$

$$I_{7D} = (32/49\sqrt{21})(Z'Z)^{3/2}c_2{}^2K^2B^{-4}[-63c + 42c_2(7c^2 - K^2)/B - 72c_2{}^2c \times$$

$$(7c^2 - 3K^2)/B^2 + 18c_2{}^3(21c^4 - 18c^2K^2 + K^4)/B^3 - 5c_2{}^4c(21c^4 - 30c^2K^2 + 5K^4) \times$$

$$B^{-4}]$$

$$I_{7F} = i(16/9\sqrt{5})(Z'Z)^{3/2}c_2{}^3K^3B^{-3}[-12c + 3c_2(c^2 - K^2)/B - 5c_2{}^2c(3c^2 - K^2)/B^2]$$

The Hydrogenic Radial Wave Functions for n=7, ℓ=0, 1, 2, 3

v=2Zr/n

$$R_{7s}(v) = Z^{3/2}(17640\sqrt{7})^{-1}(5040 - 15120v + 12600v^2 - 4200v^3 + 630v^4 -$$

$$-42v^5 + v^6)\exp(-v/2)$$

$$R_{7p}(v) = Z^{3/2}(11760\sqrt{21})^{-1}(6720 - 8400v + 3360v^2 - 560v^3 + 40v^4 - v^5)ve^{-v/2}$$

$$R_{7d}(v) = Z^{3/2}(7056\sqrt{105})^{-1}(3024 - 2016v + 432v^2 - 36v^3 + v^4)v^2e^{-v/2}$$

$$R_{7f}(v) = Z^{3/2}(17640\sqrt{42})^{-1}(720 - 270v + 30v^2 - v^3)v^3e^{-v/2}$$

Appendix IV

The five individual lines of the 4686-Å group have recently been resolved[18] and the line widths measured. It is of interest to see if the recoiled velocity distribution has any significent effect in the broadening of the line widths.

In atomic units the conservation of momentum before and after the ionization-excitation process gives

$$\vec{k} = \vec{k}' + \vec{\kappa} + \vec{p}\,, \tag{IV.1}$$

where $\vec{k}$, $\vec{k}'$, $\vec{\kappa}$, $\vec{p}$ are in a. u., the momenta of the incident electron, the scattered electron, the ejected electron and the recoiled atom respectively. Denote $\vec{k} - \vec{k}'$ as $\vec{K}$, then

$$\vec{K} = \vec{\kappa} + \vec{p}\,. \tag{IV.2}$$

Because of the set up of the experiment, $\vec{k}$ is completely random, the scattered and ejected electrons have no angular dependence. In the calculation it has to be averaged over the angles of $\vec{\kappa}$ and $\vec{p}$.

The differential cross section in equ. (3.1) is a function of K and $\vec{\kappa}$, (κ, χ, ψ) being the polar coordinates of $\vec{\kappa}$. Previously it has been integrated over angles of $\vec{K}$, since the differential cross section is independent of its angles. It is convenient to take $\vec{K}$ as the axis. $\vec{K}$ and $\vec{\kappa}$ completely determine $\vec{p}$. In equ. (3.1) the set of independent variables are (K, κ, χ, ψ). It is a simple matter to change to another

set of independent variables (K, p, θ, ϕ), p, θ, ϕ being polar coordinates of $\vec{p}$. Thus the cross section becomes

$$\Omega = \int I_{\varkappa}(K) dK d\varkappa \sin\chi d\chi d\psi$$

$$= \int I_p(K) \sin\chi \, dK[\partial(\varkappa, \chi, \psi)/\partial(p, \theta, \phi)] \, d\theta d\phi dp \, , \qquad \text{(IV. 3)}$$

where $\sin\chi$ is expressed as a function of p, θ, ϕ. The differential cross section corresponding to a given p is then given by

$$I_p = \int I_p(K) \sin\chi dK[\partial(\varkappa, \chi, \psi)/\partial(p, \theta, \phi)] \, d\theta d\phi \, . \qquad \text{(IV. 4)}$$

I_p is proportional to the probability of the ionized-excited atom having a recoiled speed p/M, and I_p/p^2 is proportional to the probability of the target atom having a recoiled velocity p/M in any direction; M is the mass of the target atom.

At 200 ev I_p/p^2 is calculated and plotted against p. The halfwidth is obtained in the following manner. Normalized I_p/p^2 so that at the peak (p=0) it is equal to 1.. Let p_h be the corresponding value of p when $I_p/p^2 = 0.5$. The recoiled velocity v of the atom is obtained by divided p_h by the mass of the helium atom. Doppler shift is given by the following relation

$$\Delta\nu = \nu_o v/c \, .$$

The half-width due to recoil alone of the 4S line at 200 eV incident energy is found to be 24 mK. At 30°K the Doppler shift due

to thermal velocity is 42 mK and with a life-time of 1.42×10^{-8} sec. the natural line-width is 15mK. The pressure broadening is negligible because the averaged time between collision is 10^{-5} sec. which is much longer than the life-time of the excited atom. To obtain the total calculated half-width it is necessary to supperimpose the two velocity distributions, namely the thermal and the recoiled, and find the velocity corresponding to the intensity which is half of the maximum. This indeed has been done.[18] However a rough estimate is to just add the half-widths together. The results in this case happens to be almost the same. The experimental measurement gives 103 mK for the half-width of the 4S line as compared with 80 mK for the calculated value. Part of the discrepency can be explained by the spread of the incident electron energy during the measurement. The spread is estimated to be about 50 eV. Any fluctuation in temperature may further increase the half-width.

It is seen that at approximately 30°K the recoiled velocity causes an increment of about 30% in the line width. At lower temperature it will become the major cause for the broadening of the 4686-Å line.

Appendix V

To evaluate $J_1(\theta)$, $J_2(\theta)$ and $J_3(\theta)$ of equs. (6.15), (6.16) and (6.17). $J_1(\theta)$ is defined as

$$J_1(\theta) = \int (r_{13}^{-1} - r_3^{-1}) \exp[i(\vec{k}_o \cdot \vec{r}_3 - \vec{k}' \cdot \vec{r}_1)] \phi_{6s}(1)\phi_{6s}^2(2)\phi_{n\ell m}(3) d\vec{r}_1 d\vec{r}_2 \, X \, d\vec{r}_3 . \qquad (6.15)$$

Integrating over $d\vec{r}_2$ gives unity. Using the expansion of r_{13}^{-1} in terms of spherical harmonics, $(r_{13}^{-1} - r_3^{-1})$ can be written as

$$r_{13}^{-1} - r_3^{-1} = \sum_{\nu=0}^{\infty} \sum_{p=-\nu}^{\nu} 4\pi/(2\nu+1)\gamma_\nu(1,3)\Theta_{\nu,p}(\theta_3)\Theta_{\nu,p}(\theta_1)\Phi_p(\phi_1)\Phi_p^*(\phi_3), \quad (V.1)$$

where

$$\gamma_o = 0 \qquad \text{if } r_3 > r_1 ,$$

$$= r_1^{-1} - r_3^{-1} \qquad \text{if } r_1 > r_3$$

and $\gamma_\nu = r_<^\nu / r_>^{\nu+1}$, $\nu \geq 1$.

In the expression above $r_<$ ($r_>$) is the smaller (greater) of r_1 and r_3.

Take axis along $\vec{k}_o$, then

$$\vec{k}_o \cdot \vec{r}_3 - \vec{k}' \cdot \vec{r}_1 = k_o r_3 \cos\theta_3 - k' r_1 (\sin\theta_1 \cos\phi \sin\theta + \cos\theta_1 \cos\theta) , \qquad (V.2)$$

where θ is the angle between $\vec{k}_o$ and $\vec{k}'$ and hence is the scattered angle Substituting equs. (V.1) and (V.2) into expression (6.15) the following result is obtained:

$$J_1(\theta) = \sum_{\nu=0}^{\infty} \sum_{p=-\nu}^{\nu} 4\pi/(2\nu+1) \int \gamma_\nu(1,3)\Theta_{\nu,p}(\theta_1)\Theta_{\nu,p}(\theta_3)\Phi_p(\phi_1)\Phi_p^*(\phi_3) \exp\{i[k_o \, X$$

$$r_3\cos\theta_3 - k' r_1(\sin\theta_1\cos\phi_1\sin\theta + \cos\theta_1\cos\theta)]\} R_{6s}(1) Y_{oo}(1) \phi_{n\ell m}^*(3) d\vec{r}_1 d\vec{r}_3 .$$

Integrating over ϕ_3 gives δ_{pm}. Integrating over ϕ_1 gives

$$\int \Phi_m(\phi_1)\exp(-ik'r_1\sin\theta_1\cos\phi_1\sin\theta)d\phi_1 = 2\pi^{\frac{1}{2}}(-i)^m J_m(k'r\sin\theta_1\sin\theta). \quad (V.5)$$

Integration over θ_1 can be effected by using Gegenbauer's integral:[59]

$$\int \Theta_{\nu,m}(\theta_1)\exp(-ik'r_1\cos\theta_1\cos\theta)J_m(k'r_1\sin\theta_1\sin\theta)\sin\theta_1 d\theta_1 = [(2\nu+1)/2]^{\frac{1}{2}} \times$$

$$[(\nu-|m|)!/(\nu+|m|)!][2\pi/(k'r_1)]^{\frac{1}{2}} i^{\nu-m} P_\nu^{|m|}(\cos\rho) J_{\nu+\frac{1}{2}}(k'r_1), \quad (V.6)$$

where

$$\rho = \pi - \theta . \quad (V.7)$$

Substituting equs. (V.4), (V.5) and (V.6) into expression (V.3) the following result is obtained:

$$J_1(\theta) = \sum_{\nu=0}^{\infty}(2\pi)^{3/2}(2\nu+1)^{-\frac{1}{2}}(-1)^m i^\nu[(\nu-|m|)!/(\nu+|m|)!]^{\frac{1}{2}} P_\nu^{|m|}(\cos\rho) \times$$

$$\int \gamma_\nu(1,3)\Theta_{\nu,m}(\theta_3)\exp(ik_o r_3)(k'r_1)^{-\frac{1}{2}} J_{\nu+\frac{1}{2}}(k'r_1)R_{6s}(1)R_{n\ell}(3) \times$$

$$\Theta_{\ell,m}(\theta_3) r_1^2 dr_1 r_3^2 dr_3 \sin\theta_3 d\theta_3 . \quad (V.8)$$

In order to integrate over θ_3, expand the product $\Theta_{\nu,m}(\theta_3)\Theta_{\ell,m}(\theta_3)$ in terms of Legendre polynomials:

$$\Theta_{\nu,m}(\theta_3)\Theta_{\ell,m}(\theta_3) = \sum_k b_k(\nu,\ell,m)P_k(\theta_3) . \quad (V.9)$$

Multiply the last equation on both sides by $\Theta_{k,0}(\theta_3)$ and integrate over $\sin\theta_3 d\theta_3$:

$$b_k(\nu,\ell,m) = (2k+1)2^{-1} c^k(\nu,m;\ell,m) ,$$

where

$$c^k(\nu,m;\ell,m) = [2/(2k+1)]^{\frac{1}{2}} \int \Theta_{\nu,m}\Theta_{\ell,m}\Theta_{k,0} d\cos\theta ,$$

and its explicit form is given by Graunt' formula.[61] Only a limited number of c^k's can be non-zero, since the triangle rule has to be satisfied:

$$|\nu - \ell| \leq k \leq |\nu + \ell| .$$

Now the expansion gives

$$\int \Theta_{\nu,m}(3)\,\Theta_{\ell,m}(3)\exp(ik_o r_3\cos\theta_3)\sin\theta_3 d\theta_3 = \sum_k b_k(\nu,\ell,m)\ X$$

$$\int P_k(\theta_3)\exp(ik_o r_3\cos\theta_3)\sin\theta_3 d\theta_3 . \qquad (V.11)$$

Using the relation

$$J_{n+\frac{1}{2}}(z) = (-i)^n (z/2\pi)^{\frac{1}{2}} \int_{-1}^{1} \exp(ixz) P_n(x) dx ,$$

integration over θ_3 yields

$$\sum_k b_k(\nu,\ell,m) i^k (2\pi/k_o r_3)^{\frac{1}{2}} J_{k+\frac{1}{2}}(k_o r_3) . \qquad (V.12)$$

Hence it is seen that

$$J_1(\theta) = \sum_{\nu=0}^{\infty} \sum_k a_k(\nu,\ell,m) \int \gamma_\nu(1,3) J_{\nu+\frac{1}{2}}(k'r_1) J_{k+\frac{1}{2}}(k_o r_3)(k'r_1)^{-\frac{1}{2}}\ X$$

$$(k_o r_3)^{-\frac{1}{2}} R_{6s}(1) R_{n\ell}(3) r_1^2 dr_1 r_2^2 dr_2 ,$$

where

$$a_k(\nu,\ell,m) = (2\pi)^2 i^{\nu+k+2m} [(\nu-|m|)!/(\nu+|m|)!]^{\frac{1}{2}} b_k(\nu,\ell,m)(2\nu+1)^{-\frac{1}{2}} \qquad (V.13)$$

The first ten values of ν are included in the summation over ν. The convergence of the series has not been tested rigorously, but it is expected to be fairly close to the actual sum of the series. Due to the limitation of computer facilities available it is impratical to include more terms.

$J_2(\theta)$ will be considered next. Substituting equs. (V.1) and (V.2) into (6.16) the following expression for $J_2(\theta)$ is obtained:

$$J_2(\theta) = \sum_{\nu=0}^{\infty} \sum_{p=-\nu}^{\nu} 4\pi/(2\nu+1) \int \gamma_\nu(2,3)\, \Theta_{\nu,p}(\theta_2)\, \Theta_{\nu,p}(\theta_3)\, \Phi_p(\phi_2)\, \Phi_p^*(\phi_3) \;\; X$$

$$\exp\{i[k_o r_3 \cos\theta - k' r_1 (\sin\theta_1 \cos\phi_1 \sin\theta + \cos\theta_1 \cos\theta)]\}\, \phi_{6s}(1)\, \phi_{6s}(2)\, \phi_{6s}^*(2) \;\; X$$

$$\phi_{n\ell m}(3)\, d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 . \qquad (V.14)$$

Integrating over ϕ_2 gives

$$\int \Phi_p \Phi_o \Phi_o^* d\phi_2 = 2^{-\frac{1}{2}} \delta_{p,0} .$$

Integrating over ϕ_3 gives $\delta_{p,m}$. Integrating over ϕ_1 yields

$$\int \Phi_o \exp(ik' r_1 \sin\theta \cos\phi_1 \sin\rho) d\phi_1 = (2\pi)^{\frac{1}{2}} J_o(k' r_1 \sin\theta_1 \sin\rho).$$

Integrating over θ_2 gives a factor of $2^{-\frac{1}{2}} \delta_{\nu,0}$.

$J_2(\theta)$ then becomes

$$4\pi/2^{\frac{1}{2}} \int \gamma_\nu(2,3)\, \Theta_{\nu,0}(\theta_3) \exp[i(k_o r_3 \cos\theta + k' r_1 \cos\theta_1 \cos\rho)]\, J_o(k' r_1 \sin\theta_1 \sin\rho) \;\; X$$

$$R_{6s}(1)\, \Theta_{0,0}(1)\, R_{6s}^2(2)\, R_{n\ell}(3)\, \Theta_{\ell,0}(3)\, r_1^2 dr_1 r_2^2 dr_2 r_3^2 dr_3 d\cos\theta_1 d\cos\theta_3 .$$

By means of Gegenbauer's integral θ_1-integration yields

$$\int \exp(ik' r_1 \cos\theta_1 \cos\rho)\, J_o(k' r_1 \sin\theta_1 \sin\rho)\, \Theta_{0,0}(1) d\cos\theta_1 = (\pi/k' r_1)^{\frac{1}{2}} J_{\frac{1}{2}}(k' r_1) .$$

Integrating over θ_3 gives

$$2^{-\frac{1}{2}} \int \exp(ik_o r_3 \cos\theta)\, \Theta_{\ell,0}(\theta_3) d\cos\theta_3 = [(2\ell+1)/2]^{\frac{1}{2}} i^\ell (\pi/k_o r_3)^{\frac{1}{2}} J_{\ell+\frac{1}{2}}(k_o r_3) .$$

Hence the integral $J_2(\theta)$ can be expressed as:

$$2\pi^2 (2\ell+1)^{\frac{1}{2}} i^\ell (k_o k')^{-1} [\int J_{\frac{1}{2}}(k' r_1) R_{6s}(1) r_1^{3/2} dr_1] [\int\int \gamma_\nu(2,3) J_{\ell+\frac{1}{2}}(k_o r_3) \;\; X$$

$$R_{6s}(2)R_{6s}(2)R_{n\ell}(3)r_2^{\,2}dr_2 r_3^{\,3/2}dr_3] \ .$$

Lastly consider the integral $J_3(\theta)$. Substituting the expansion for $(r_{23}^{-1} - r_3^{-1})$ and taking axis alon $\vec{k}_o$ it becomes

$$J_3(\theta) = \sum_{\nu=0}^{\infty} \sum_{p=-\nu}^{\nu} 4\pi/(2\nu+1) \int \gamma_\nu(2,3)\Theta_{\nu,p}(\theta_2)\Theta_{\nu,p}(\theta_3)\Phi_p(2)\Phi_p^*(3)\exp\{i[k_o \ X$$

$$r_3\cos\theta_3 - k'r_1(\sin\theta_1\cos\phi_1\sin\theta+\cos\theta_1\cos\theta)]\}\phi_{6s}(1)\phi_{6s}(2)\phi_{6s}^*(3)\phi_{n\ell m}^*(2)d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 .$$

Integrating over ϕ_3 yields $\delta_{\nu,\ell}$. Integrating over ϕ_2 gives $(2\pi)^{-\frac{1}{2}}\delta_{p,m}$. Integrating over ϕ_1 gives

$$\int \exp(ik'r_1\sin\theta_1\cos\phi_1\sin\rho)\Phi_o(1)d\phi_1 = (2\pi)^{\frac{1}{2}} J_o(k'r_1\sin\theta_1\sin\rho).$$

Integrating over θ_2 yields $\delta_{\nu,\ell}$. Integrating over θ_1 gives

$$\int \exp(ik'r_1\cos\theta_1\cos\rho)J_o(k'r_1\sin\theta_1\sin\rho)d\cos\theta_1 = (2\pi/k'r_1)^{\frac{1}{2}}J_{\frac{1}{2}}(k'r_1).$$

Integrating over θ_3 gives

$$\int \Theta_{\ell,0}(3)\exp(ik_o r_3\cos\theta_3)d\cos\theta_3 = [(2\ell+1)/2]^{\frac{1}{2}} i^{\ell}(2\pi/k_o r_3)^{\frac{1}{2}} J_{\ell+\frac{1}{2}}(k_o r_3) \ .$$

Hence $J_3(\theta)$ can finally be expressed as:

$$J_3(\theta) = i^{\ell}\pi^2[(2\ell+1)k'k_o]^{-\frac{1}{2}}[\int J_{\frac{1}{2}}(k'r_1)R_{6s}(1)r_1^{\,3/2}dr_1][\int\int \gamma_\ell(2,3) \ X$$

$$J_{\ell+\frac{1}{2}}(k_o r_3)R_{6s}(2)R_{n\ell}(2)R_{6s}(3)r_2^{\,2}dr_2 r_3^{\,3/2}dr_3] \ .$$

The single and double integrals are numerically integrated by Gaussian-Legendre Quardrature method. The upper limit is so chosen that the wave function are practically zero beyond that limit. The wave functions are taken from Mishra's paper.[28] For each wave function a curve is plotted and intermediate points extrapolated.

Appendix VI

The nuclear Coulomb terms $-1/r_{3A}$ and $-1/r_{3B}$ in equ. (9.17) cancel out and if H_2' is used to denote the sum of $1/r_{13}$ and $1/r_{23}$ then it becomes

$$V(r,\xi,\delta) = \langle\Phi|2H_2|\Phi\rangle/\langle\Phi|\Phi\rangle - \langle\phi_o|2H_2'|\phi_o\rangle - E_o \qquad \text{(VI.1)}$$

$$= 2\sum T_i/\langle\Phi\,\Phi\rangle ,$$

$$T_1 = -2B\langle\phi_o|\psi'\rangle ,$$

$$T_2 = 2\langle\phi_o|H_2'|\psi'\rangle ,$$

$$T_3 = \langle\psi'|H_o - E_o|\psi'\rangle = \sum_{k=1,2}\langle\Phi|\nabla_k p\cdot\nabla_k p|\Phi\rangle$$

$$T_4 = \langle\psi'|H_2'|\psi'\rangle$$

$$T_5 = -B\langle\psi'|\psi'\rangle$$

$$B = (4/N)\left(c_t\frac{I_{4A}+I_{4B}}{2} + c_s I_5\right) ,$$

$$c_t = 1 + c^2 + 2cS ,$$

$$c_s = S + c^2 S + 2c ,$$

$$\Phi = \phi_o + \psi' , \qquad (9.6)$$

$$\psi' = p\phi_o ,$$

$$p = p_1 + p_2 ,$$

$$p_i = c'(x_i+y_i) + b'z_i + [c''(x_i+y_i) + b''z_i]\exp(-\epsilon r_{13}).$$

In the expressions above, N is defined by equ. (9.5); ϕ_o is the Weibaum wave function. Because of the limited access to a computer, ϵ is set to equal to 1 arbitrarily. However ϵ will be carried through the mani-

pulation. The RHS of the second equality sign of T_3 can be derived from the LHS by the use of Green's Theorem[50] and with the approximation that

$$H_o|\phi_o> = E_o|\phi_o> .$$

The operator ∇_k is

$$\nabla_k = (\partial/\partial x_k)\hat{i} + (\partial/\partial y_k)\hat{j} + (\partial/\partial z_k)\hat{k} .$$

To obtain the x, y-polarization, e_3 is placed on the x-axis. V then has no b or b' term and the minimum is at b=b'=0. Hence p_i can be written as

$$p_i = c'(x_i+y_i) + c''(x_i+y_i)\exp(-\epsilon r_{i3}) ,$$

and $T_1 = c''R_{1a}$,

$$T_2 = c'R_{2a} + c''R_{2b} ,$$

$$T_3 = 2c'^2 + c''^2R_{3bb} + cc'R_{3ab} ,$$

$$T_4 = c'^2R_{4aa} + c'c''R_{4ab} + c''^2R_{4bb} ,$$

$$T_5 = c'^2R_{5aa} + c'c''R_{5ab} + c''^2R_{5bb} ,$$

$$R_{1b} = -B(8/N)(c_tI_{26} + c_sI_{27}) = -BS_{1b} ,$$

$$R_{2a} = (4/N)(c_tI_1 + c_sI_2) ,$$

$$R_{2b} = (8/N)[(c_tI_{22} + c_sI_{23}) + I_{26}(c_uI_4 + c_vI_5) + I_{27}(c_vI_4 + c_uI_5)] ,$$

$$c_u = 1 + c^2 , \quad c_v = 2c ,$$

$$R_{3bb} = (2/N)\{2(c_tI'_3 + c_sI'_{12}) - 2\epsilon[c_t(I'_{28} + 2I'_{13} - rI'_{22}) + c_s(I'_{29} + 2I'_{14} - rI'_{23})] + \epsilon^2[c_t(2I'_{15} + I'_{30}) + c_s(2I'_{16} + I'_{31})]\} ,$$

where r is the distance of e_3 from the midpoint of nuclei A and B,

$$R_{3ab} = (4/N)\{c_t[2I_3 - e(I_{28}+2I_{13}-rI_{22})] + c_s[2I_{12}-e(I_{29}+2I_{14}-rI_{23})]\},$$

$$R_{4aa} = (4/N)\{2[Z^{-2}(c_uI_4+c_vI_5) + P(c_vI_4+c_uI_5) + c_tI_8+c_sI_9] + c_tI_6 + c_sI_{11}\},$$

$$P = [15 + 15ZR + 6(ZR)^2 + (ZR)^3]\, e^{-ZR}/(15Z^2),$$

where R is the internuclear distance,

$$R_{4ab} = (8/N)\{c_t(2I_{13}+I_{28}) + c_s(2I_{14}+I_{29}) + (2I_{15}+I_{30})(c_uI_4+c_vI_5) + (2I'_{16}+I'_{31})(c_uI_5+c_vI_4)\} + (4/N)[I_{26}(c_uI_1+c_vI_2)+I_{27}(c_uI_2+c_vI_1)],$$

$$R_{4bb} = (4/N)[c_t(2I'_{13}+I'_{28})+c_s(2I'_{14}+I'_{29})+(2I'_{15}+I'_{30})(c_uI_4+c_vI_5) + (2I'_{16}+I'_{31})(c_uI_5+c_vI_4)] + (8/N)[I_{22}(c_uI_{26}+c_vI_{27}) + I_{23}\,X\,(c_uI_{27}+c_vI_{26})],$$

$$R_{5aa} = -BS_{5aa} = -B(8/N)(c_tZ^{-2} + c_sP);$$

$$R_{5ab} = -BS_{5ab} = -B(8/N)[c_t(2I_{15}+I_{30})+c_s(2I_{16}+I_{31})],$$

$$R_{5bb} = -BS_{5bb} = -B(4/N)[c_t(2I'_{15}+I'_{30})+c_s(2I'_{16}+I'_{31})+c_u(I_{26}^2 + I_{27}^2) + 4c_vI_{26}I_{27})],$$

$$\langle\Phi|\Phi\rangle = 1+c''S_{1b}+c'^2S_{5aa}+c''c'S_{5ab}+c''^2S_{5bb}.$$

V can be written explicitly as

$$V(r,\xi,\pi/2) = [c'R_{2a} + c''(R_{1a}+R_{2b}) + c'^2(2+R_{4aa}+R_{5aa}) + c'c''(R_{3ab} + R_{4ab}+R_{5ab}) + c''^2(R_{3bb}+R_{4bb}+R_{5bb})](1+c''S_{1b}+c'^2S_{5aa}+c'c''S_{5ab}+c''^2S_{5bb})^{-1}.$$

The minimum is obtained by iteration process: a value for c' is assumed and c'' is varied to make V a minimum. Insert c'' thus

obtained into equ. (VI. 5) and vary c' to make V a minimum. This procedure is repeated until c' and c'' converge.

LIST OF ONE, TWO AND THREE CENTER INTEGRALS OF $V(r, \xi, \frac{1}{2}\pi)$

R is the distance between nuclei A and B, R_{3A} and R_{3B} are the distances between e_3^- and nuclei A and B respectively.

The limits of integration are from 0 to 1 for both u and w.

$$f = (1-u)uw^2R^2 + w(1-w)R_{3A}^2 \quad , \quad g = Z^2[4u(1-u)w]^{-1} \quad ,$$

$$g_c = \sigma^2[4u(1-u)w(1-w)]^{-1} \quad , \quad \sigma = [Z^2(1-w) + \epsilon^2u(1-u)w]^{\frac{1}{2}} \quad ,$$

$$x = 2(fg)^{\frac{1}{2}} \quad , \quad x_c = 2(fg_c)^{\frac{1}{2}} \quad , \quad a = 2ZR_{3A} \quad ,$$

$$I_1 = 2\int x_1 r_{13}^{-1} a^2(1)\, d\vec{r}_1 = 2Z^{-1}ra^{-3}[8 - e^{-a}(a^3+4a^2+8a+8)] \quad ,$$

$$I_2 = 2\int x_1 r_{13}^{-1} a(1)b(1)\, d\vec{r}_1 = 4Z^3r\pi^{-1}\int[u(1-u)]^{-1/2}\int w^{-1}(1-w)^{\frac{1}{2}}K_2(x)fdwdu,$$

where $K_n(x)$ is the Bessel Function of the second kind of order n.

$$I_3 = \int e^{-\epsilon r_{13}} a^2(1)d\vec{r}_1 = (Z^4\epsilon/8)\int u(1-u)\,\eta^{-5}e^{-t}\,(3+3t+t^2)\,du,$$

where $\eta = [Z^2(1-u) + \epsilon^2u/4]^{\frac{1}{2}}$, $t = 2R_{3A}$,

$$I_4 = \int r_{13}^{-1} a^2(1)d\vec{r}_1 = R_{3a}^{-1}[1-e^{-a}(1+a/2)] \quad ,$$

$$I_5 = \int r_{13}^{-1} a(1)b(1)d\vec{r}_1 = (2Z^3/\pi)\int[u(1-u)]^{-\frac{1}{2}}\int w^{-1}(1-w)^{-\frac{1}{2}}K_2(x)fdwdu,$$

I_5 can also be integrated and expressed in terms of log-integral.[44]

$$I_6 = \int (x_1^2 - y_1^2)r_{13}^{-1} a^2(1)d\vec{r}_1 = (Zr^2/2)\int (1-u)^{3/2}(1+t)e^{-t}du,$$

$$I_8 = \int y_1^2 r_{13}^{-1} a^2(1)d\vec{r}_1 = (8Z)^{-1}\int u(1-u)^{-\frac{1}{2}} e^{-t}(3+3t+t^2)du,$$

$$I_9 = \int y_1^2 r_{13}^{-1} a(1)b(1)d\vec{r}_1 = 2Z^2\pi^{-1}\iint [w(1-w)]^{-\frac{1}{2}} K_3(x) f^{3/2} dwdu ,$$

$$I_{11} = \int (x_1^2 - y_1^2) r_{13}^{-1} a(1)b(1)d\vec{r}_1 = 2Z^3 r^2 \pi^{-1}\int [u(1-u)]^{-\frac{1}{2}} \int w^{-1}(1-w)^{3/2} \times$$

$$K_2(x) f\, dwdu ,$$

$$I_{12} = \int \exp(-\epsilon r_{13}) a(1)b(1)d\vec{r}_1 = 2\epsilon Z^5/\pi \iint w^{-\frac{1}{2}} K_3(x_c) f^{3/2} \sigma^{-3} dwdu$$

$$I_{13} = \int y_1^2 \exp(-\epsilon r_{13}) r_{13}^{-1} a^2(1)d\vec{r}_1 = (Z^4/8)\int u(1-u)^2 \eta^{-5} e^{-t}(3+3t+t^2)du,$$

$$I_{14} = \int y_1^2 \exp(-\epsilon r_{13}) r_{13}^{-1} a(1)b(1)d\vec{r}_1 = 2Z^5/\pi \iint w^{-\frac{1}{2}} (1-w) K_3(x_c) \times$$

$$f^{3/2} \sigma^{-3} dwdu ,$$

$$I_{15} = \int y_1^2 \exp(-\epsilon r_{13}) a^2(1)d\vec{r}_1 = (Z^4 \epsilon/32)\int u^2(1-u)^2 \eta^{-3} e^{-t}(15+15t+6t^2+t^3)du,$$

$$I_{16} = \int y_1^2 \exp(-\epsilon r_{13}) a(1)b(1)d\vec{r}_1 = 2Z^5 \epsilon/\pi \int [u(1-u)]^{\frac{1}{2}} \int (1-w)^{\frac{1}{2}} K_4(x_c) f^2 \sigma^{-4} \times$$

$$dwdu$$

$$I_{22} = \int x_1 \exp(-\epsilon r_{13}) r_{13}^{-1} a^2(1)d\vec{r}_1 = (Z^4 r/2)\int (1-u)^2 e^{-t}(1+t) \eta^{-3} du ,$$

$$I_{23} = \int x_1 \exp(-\epsilon r_{13}) r_{13}^{-1} \times a(1)b(1)d\vec{r}_1 = (2Z^5 r/\pi)\int [u(1-u)]^{-\frac{1}{2}} \times$$

$$\int w^{-1}(1-w)^{3/2} K_2(x_c) f \sigma^{-2} dwdu ,$$

$$I_{26} = \int x_1 \exp(-\epsilon r_{13}) a^2(1)d\vec{r}_1 = (Z^4 r \epsilon/8)\int u(1-u)^2 e^{-t}(3+3t+t^2) \eta^{-5} du ,$$

$$I_{27} = \int x_1 \exp(-\epsilon r_{13}) a(1)b(1)d\vec{r}_1 = (2Z^5 \epsilon r/\pi)\iint w^{-\frac{1}{2}} (1-w) K_3(x_c) f^{3/2} \sigma^{-3} dwdu,$$

$$I_{28} = \int (x_1^2 - y_1^2) \exp(-\epsilon r_{13}) r_{13}^{-1} a^2(1)d\vec{r}_1 = (Z^4 r^2/2)\int (1-u)^3 \eta^{-3} \times$$

$$e^{-t}(1+t)\, du ,$$

$$I_{29} = \int(x_1^2 - y_1^2)\exp(-\epsilon r_{13})r_{13}^{-1}a(1)b(1)d\vec{r}_1 = (2Z^5r^2/\pi)\int[u(1-u)]^{-\frac{1}{2}} X$$

$$\int w^{-1}(1-w)^{5/2}K_2(x_c)f\sigma^{-2}dwdu ,$$

$$I_{30} = \int(x_1^2 - y_1^2)\exp(-\epsilon r_{13})a^2(1)d\vec{r}_1 = (Z^4\epsilon r^2/8)\int u(1-u)^3\eta^{-5}e^{-t}(3+3t+t^2)du,$$

$$I_{31} = \int(x_1^2 - y_1^2)\exp(-\epsilon r_{13})a(1)b(1)d\vec{r}_1 = (2Z^5\epsilon r^2/\pi)\int\int w^{-\frac{1}{2}}(1-w)^2K_3(x_c) X$$

$$f^{3/2}\sigma^{-3}dwdu ,$$

$$I'_n(\epsilon) = I_n(2\epsilon) .$$

All the single integrals can be integrated and expressed in terms of exponential functions or log-integrals.

To obtain the z-polarization e_3 is placed on the z-axis. The difference between z-polarization and the x, y-polarization is that nuclei A and B are no longer inter-changeable, i. e. integrals centered at e_3 and A are no longer equal to the corresponding integrals centered at e_3 and B. T_i in terms of R have the same form as before except that the parameters are b', b'' instead of c', c'' and

$$T_3 = b'^2 + b''^2R_{3bb} + b'b''R_{3ab} .$$

$$R_{1b} = -B'(4/N)[c_tJ_{26} + 2c_sI_{27}] = -B'S_{1b} ,$$

$$B' = (2/N)[c_tJ_4 + 2c_sI_5] ;$$

$$R_{2a} = (2/N)[c_tJ_1 + 2c_sI_2] ,$$

$$R_{2b} = (8/N)c_sI_{23} + (4/N)[c_tJ_{22} + I_{26A}(I_{4B}+c^2I_{4A}+c_vI_5) + I_{26B}(I_{4A} +$$

$$c^2 I_{4b} + c_v I_5) + I_{27}(2c_u I_5 + c_v J_4)] \ ,$$

$$R_{3bb} = N^{-1} c_t [J'_3 + \epsilon^2 (J'_{15} + J'_{30}) - 2\epsilon(J'_{13} + J'_{28}) + 2\epsilon r J'_{22}] + 2N^{-1} c_s [I'_{12} +$$

$$\epsilon^2 (I'_{16} + I'_{31}) - 2\epsilon(I'_{14} + I'_{29}) + 2\epsilon r I'_{23}]$$

$$R_{3ab} = (2/N)\{c_t [J_3 - \epsilon(J_{13} + J_{28}) + \epsilon r J_{22}] + 2c_s [I_{12} - \epsilon(I_{14} + I_{29}) + \epsilon r I_{23}]\},$$

$$R_{4aa} = (2/N)[c_t (J_8 + J_6) + 2c_s (I_9 + I_{11}) + (Z^{-2} + R^2/4)(G_4 + G_5) + P' G_6] \ ,$$

$$P' = [60 + 60ZR + 27(ZR)^2 + 7(ZR)^3 + (ZR)^4] \exp(-ZR)(60Z^2)^{-1}$$

$$= \int z_1^2 a(1) b(1) d\vec{r}_1 \ ,$$

$$G_1 = I_{26B} + c^2 I_{26A} + c_v I_{27} \ ,$$

$$G_2 = I_{26A} + c^2 I_{26B} + c_v I_{27} \ ,$$

$$G_3 = 2c_u I_{27} + c_v J_{26} \ ,$$

$$G_4 = I_{4B} + c^2 I_{4A} + c_v I_5 \ ,$$

$$G_5 = I_{4A} + c^2 I_{4B} + c_v I_5 \ ,$$

$$G_6 = 2c_u I_5 + c_v J_4 \ ,$$

$$R_{4ab} = (4/N)[c_t (J_{13} + J_{28}) + 2c_s (I_{14} + I_{29}) + G_4 (I_{15A} + I_{30A}) + G_5 (I_{15B} +$$

$$I_{30B}) + G_6 (I_{16} + I_{31})] + (2/N)(G_1 I_{1A} + G_2 I_{1B} + G_3 I_2) \ ,$$

$$R_{4bb} = (2/N)[c_t (J'_{13} + J'_{28}) + 2c_s (I'_{14} + I'_{29})] + (4/N)[G_1 I_{22A} + G_2 I_{22B} +$$

$$G_3 I_{23} + G_4 (I'_{15A} + I'_{30A}) + G_5 (I'_{15B} + I'_{30B}) + G_6 (I'_{16} + I'_{31})] \ ,$$

$$R_{5aa} = (4/N)[c_t(Z^{-2}+R^2/4) + c_s P'] ,$$

$$R_{5ab} = (4/N)[c_t(J_{15}+J_{30}) + 2c_s(I_{16}+I_{31})] ,$$

$$R_{5bb} = (2/N)[c_t(J'_{15}+J'_{30}) + 2c_s(I'_{16}+I'_{31})] + (4/N)[I_{26A}I_{26B} + c_v I_{27}J_{26} + c^2(I_{26A}^2+I_{26B}^2) + 2c_u I_{27}^2] ,$$

$$J_m = I_{mA} + I_{mB} , \qquad J'_m = I'_{mA} + I'_{mB} .$$

LIST OF ONE, TWO AND THREE CENTER INTEGRALS OF $V(r, \xi, 0)$

$a = 2ZR_{3A}$ for I_{mA} integrals (A-integrals), m being an integer,

$= 2ZR_{3B}$ for I_{mB} integrals (B-integrals) ,

$\eta^2 = Z^2(1-u) + \epsilon^2 u/4$, $p = 2R_{3A}$ for A-integrals ,

$= 2R_{3B}$ for B-integrals ,

$$f = u(1-u)w^2R^2 + (1-u)w(1-w)R_{3B}^2 + u(1-w)wR_{3A}^2 ,$$

$$g = Z^2[4wu(1-u)]^{-1} , \quad x = 2(fg)^{\frac{1}{2}} , \quad g_c = \sigma^2[4u(1-u)w(1-w)]^{-1} ,$$

$$\sigma^2 = Z^2(1-w) + \epsilon^2 u(1-u)w , \quad x_c = 2(fg_c)^{\frac{1}{2}} ,$$

$d^2(1) = a^2(1)$ for A-integrals ,

$= b^2(1)$ for B-integrals ,

$$I_{1A,B} = 2\int z_1 r_{13}^{-1} d^2(1) d\vec{r}_1 = Z\int (1-u)^{-\frac{1}{2}}[Ru/2 + r(1-u)](1+p)e^{-p}du ,$$

$$J_1 = I_{1A} + I_{1B} ,$$

$$I_2 = 2\int z_1 r_{13}^{-1} a(1)b(1) d\vec{r}_1 = 4Z^3/\pi \iint [u(1-u)]^{-\frac{1}{2}} \int w^{-1}(1-w)^{-\frac{1}{2}}[(1-2u)wR/2 +$$

$$r(1-w)]\,K_2(r)\,f\,dwdu\ ,$$

$$I_{3A,B} = \int \exp(-\epsilon r_{13}) d^2(1) d\vec{r}_1 = (\epsilon Z^4/8)\int u(1-u)\,\eta^{-5} e^{-p}(3+3p+p^2)du\ ,$$

$$I_{4A,B} = \int r_{13}^{-1} d^2(1) d\vec{r}_1 = (2Z/a)[1 - e^{-a}(1+a/2)]\ ,$$

$$I_5 = \int a(1)b(1) r_{13}^{-1} d\vec{r}_1 \quad \text{(see ref. 44)}\ ,$$

$$I_{6A,B} = \int (z_1^2 - y_1^2) r_{13}^{-1} d^2(1) d\vec{r}_1 = (Z/2)\int (1-u)^{-\frac{1}{2}} [uR/2 \mp (1-u)r]^2 \quad X$$

$$e^{-p}(1+p)\ du\ ,$$

where "$\mp$" means that for I_{6A} the sign should be "-" and for I_{6B} the sign is "+".

$$I_{8A,B} = \int y_1^2 r_{13}^{-1} d^2(1) d\vec{r}_1 = (8Z)^{-1}\int u(1-u)^{-\frac{1}{2}} e^{-p}(3+3p+p^2)du\ ,$$

$$I_9 = \int y_1^2 r_{13}^{-1} a(1)b(1) d\vec{r}_1 = 2Z^2/\pi \int\int w^{-\frac{1}{2}}(1-w)^{-\frac{1}{2}} K_3(x)\, f^{3/2}\, dwdu\ ,$$

$$I_{11} = \int (z_1^2 - y_1^2) r_{13}^{-1} a(1)b(1) d\vec{r}_1 = 2Z^3/\pi \iint [u(1-u)]^{-\frac{1}{2}} [r(1-w)+Rw(1-2u)/2]^2 X$$

$$w^{-1}(1-w)^{-\frac{1}{2}} K_2(x)\, f\, dwdu\ ,$$

$$I_{12} = \int \exp(-\epsilon r_{13}) a(1)b(1) d\vec{r}_1 = 2Z^5 \epsilon/\pi \int\int w^{-\frac{1}{2}} K_3(x_c)\, f^{3/2} \sigma^{-3}\, dwdu\ ,$$

$$I_{13A,B} = \int y_1^2 \exp(-\epsilon r_{13}) r_{13}^{-1} d^2(1) d\vec{r}_1 = (Z^4/8)\int u(1-u)^2 \eta^{-5} e^{-p}(3+3p +$$

$$p^2)du\ ,$$

$$I_{14} = \int y_1^2 \exp(-\epsilon r_{13}) r_{13}^{-1} a(1)b(1) d\vec{r}_1 = 2Z^5/\pi \iint w^{-\frac{1}{2}}(1-w) K_3(x_c) f^{3/2} \sigma^{-3}\, dwdu,$$

$$I_{15A,B} = \int y_1^2 \exp(-\epsilon r_{13}) d^2(1) d\vec{r}_1 = (Z^4 \epsilon/32)\int [u(1-u)]^2 \eta^{-3} e^{-p}(15+15p +$$

$$6p^2+p^3)du\ ,$$

$$I_{16} = \int y_1^2 \exp(-\epsilon r_{13}) a(1) b(1) d\vec{r}_1 = 2Z^5 \epsilon/\pi \int [u(1-u)]^{\frac{1}{2}} \int (1-w)^{\frac{1}{2}} K_4(x_c) f^2 \; X$$

$$\sigma^{-4} dwdu \ ,$$

$$I_{22A,B} = \int z_1 \exp(-\epsilon r_{13}) r_{13}^{-1} d^2(1) d\vec{r}_1 = (Z^4/2) \int (1-u)[r(1-u) \mp Ru/2] \; X$$

$$\eta^{-3} e^{-p} (1+p) du \ ,$$

$$I_{23} = \int z_1 \exp(-\epsilon r_{13}) r_{13}^{-1} a(1) b(1) d\vec{r}_1 = (2Z^5/\pi) \int [u(1-u)^{-\frac{1}{2}} w^{-1} (1-w)^{\frac{1}{2}} \; X$$

$$[w(1-2u)R/2 + (1-w)r] K_2(x_c) f \sigma^{-2} dwdu \ ,$$

$$I_{26A,B} = \int z_1 \exp(-\epsilon r_{13}) d^2(1) d\vec{r}_1 = (Z^4 \epsilon/8) \int u(1-u)[r(1-u) \mp Ru/2] \; X$$

$$\eta^{-5} e^{-p} (3+3p+p^2) du \ ,$$

$$I_{27} = \int z_1 \exp(-\epsilon r_{13}) a(1) b(1) d\vec{r}_1 = 2Z^5 \epsilon/\pi \iint w^{\frac{1}{2}} [w(1-2u)R/2 + r(1-w)] \; X$$

$$K_3(x_c) f^{3/2} \sigma^{-3} dwdu \ ,$$

$$I_{28A,B} = \int (z_1^2 - y_1^2) \exp(-\epsilon r_{13}) r_{13}^{-1} d^2(1) d\vec{r}_1 = (Z^4/2) \int (1-u)[r(1-u) \mp$$

$$Ru/2]^2 \eta^{-3} e^{-p} (1+p) du \ ,$$

$$I_{29} = \int (z_1^2 - y_1^2) \exp(-\epsilon r_{13}) r_{13}^{-1} a(1) b(1) d\vec{r}_1 = 2Z^5/\pi \iint [u(1-u)]^{-\frac{1}{2}} \; X$$

$$w^{-1} (1-w)^{\frac{1}{2}} [w(1-2u)R/2 + (1-w)r]^2 K_2(x_c) f \sigma^{-2} dwdu \ ,$$

$$I_{30A,B} = \int (z_1^2 - y_1^2) \exp(-\epsilon r_{13}) d^2(1) d\vec{r}_1 = (Z^4 \epsilon/8) \int u(1-u)[r(1-u) \mp$$

$$uR/2]^2 \eta^{-5} e^{-p} (3+3p+p^2) du \ ,$$

$$I_{31} = \int (z_1^2 - y_1^2) \exp(-\epsilon r_{13}) a(1) b(1) d\vec{r}_1 = 2Z^5 \epsilon/\pi \int \int w^{-\frac{1}{2}} [Rw(1-2u)/2 +$$

$$(1-u)r]^2 K_3(x_c) f^{3/2} \sigma^{-3} dwdu \ .$$

As before all the single integrals can be integrated and expressed in terms of exponential function or log-integrals.

As an example the Gauss Transformation will be applied to a three center integral, namely I_{23}, to reduce it to an ordinary double integral. The following relations will be useful:

$$1/r = \pi^{-\frac{1}{2}}\int_0^\infty \alpha^{-\frac{1}{2}}\exp(-\alpha r^2)\,d\alpha \ , \quad (r>0) \ , \tag{VI.2}$$

$$\exp(-\alpha r) = \alpha 2^{-1}\pi^{-\frac{1}{2}}\int_0^\infty s^{-3/2}\exp(-\alpha^2/4s)\exp(-sr^2)ds \ , \tag{VI.3}$$

$$r^{-1}\exp(-\alpha r) = \pi^{-\frac{1}{2}}\int_0^\infty s^{-\frac{1}{2}}\exp(-\alpha^2/4s)\exp(-sr^2)ds \ , \tag{VI.4}$$

$$\exp(-s_1 r_{1a}^2 - s_2 r_{1b}^2 - s_3 r_{1c}^2) = \exp(-s_1 s_2 R_{ab}^2/s - s_2 s_3 R_{bc}^2/s - s_3 s_1 R_{ca}^2/s)\exp(-s r_{1g}^2) \ , \tag{VI.5}$$

where $s = s_1+s_2+s_3$, $\quad \vec{G} = (s_1\vec{A}+S_2\vec{B}+S_3\vec{C})/s$, $\tag{VI.6}$

$$a(1) = (Z^3/\pi)^{\frac{1}{2}}\exp(-Zr_{1a}) = (Z^3/\pi)^{\frac{1}{2}}Z2^{-1}\pi^{-\frac{1}{2}}\int s_1^{-3/2}\exp(-Z^2/4s_1)\ X \exp(-s_1 r_{1a}^2)ds_1 \ , \tag{VI.7}$$

$$b(1) = (Z^3/\pi)^{\frac{1}{2}}\exp(-Zr_{1b}) = (Z^3/\pi)^{\frac{1}{2}}Z(2\pi^{\frac{1}{2}})^{-1}\int s_2^{-3/2}\exp(-Z^2/4s_2)\ X \exp(-s_2 r_{1b}^2)ds_2 \ , \tag{VI.8}$$

$$\exp(-\epsilon r_{13})/r_{13} = \pi^{-\frac{1}{2}}\int s_3^{-1/2}\exp(-\epsilon^2/4s_3)\exp(-s_3 r_{13}^2)ds_3 \ . \tag{VI.9}$$

By substituting the transformations (VI. 7) to (VI. 9) into integral

I_{23} it becomes

$$I_{23} = \int z_1 \exp(-\epsilon r_{13}) r_{13}^{-1} a(1)b(1)d\vec{r}_1 = Z^5(4\pi^{5/3})^{-1}\int (s_1 s_2)^{-3/2} s_3^{-\frac{1}{2}} \text{ X}$$

$$\exp(-Z^2/4s_1 - Z^2/4s_2 - \epsilon^2/4s_3)\exp(-s_1 s_2 R^2/s - s_2 s_3 R_{3B}^2/s - s_3 s_1 R_{3A}^2/s) \text{ X}$$

$$\int z_1 \exp(-s r_{1g}^2) d\vec{r}_1 ds_1 ds_2 ds_3 \ .$$

Equ. (VI. 5) has been used to obtain the last expression for I_{23}. If e_3 is on the z-axis, then

$$\vec{G} = (s_1\vec{A} + s_2\vec{B} + s_3\vec{C}) = [(-s_1+s_2)R/2 + s_3 r]/s\ \hat{k} \qquad \text{and}$$

$$z_1 = z_{1g} + [(-s_1+s_2)R/2 + s_3 r]/s \ ,$$

where z_{1g} is the z coordinate of e_1 with $\vec{G}$ as origin. A simple straightforward integration gives the following relation:

$$\int z_1 \exp(-s r_{1g}^2) d\vec{r}_1 = [(-s_1+s_2)R/2 + s_3 r]/s\ (\pi/s)^{3/2} \ .$$

Inserting the last expression into the expression for I_{23} it becomes

$$I_{23} = Z^5(4\pi^{5/2})^{-1}\int (s_1 s_2)^{-3/2} s_3^{-\frac{1}{2}} \exp(-Z^2/4s_1 - Z^2/4s_2 - \epsilon^2/4s_3) \text{ X}$$

$$\exp(-s_1 s_2 R^2/s - s_2 s_3 R_{3B}^2/s - s_3 s_1 R_{3A}^2/s)[(-s_1+s_2)R/2 + s_3 r]\, s^{-1}(\pi/s)^{3/2} \text{ X}$$

$$ds_1 ds_2 ds_3 \ .$$

Make the following transformation of variables:

$$s_1 = uws, \quad s_2 = (1-u)ws \ , \quad s_3 = (1-w)s \ ,$$

$$u = s_1/(s_1+s_2) \ ; \quad w = (s_1+s_2)/(s_1+s_2+s_3) \ ; \quad s = s_1 + s_2 + s_3 \ .$$

It is seen that the limits of integration for u and w are 0 to 1, while those of s are from 0 to ∞, and that

$$ds_1 ds_2 ds_3 = s^2 w ds du dw .$$

Define f as

$$f = u(1-u)w^2R^2 + (1-u)w(1-w)R_{3B}^2 + u(1-w)wR_{3A}^2 ,$$

then fs can be written as

$$fs = s_1 s_2 R^2/s + s_2 s_3 R_{3B}^2/s + s_3 s_1 R_{3A}^2/s .$$

Define g_c as

$$g_c = \sigma^2[4u(1-u)w(1-w)]^{-1} ,$$

where

$$\sigma^2 = Z^2(1-w) + \epsilon^2 u(1-u)w,$$

then g_c/s can be written as

$$g_c/s = Z^2/4s_1 + Z^2/4s_2 + \epsilon^2/4s_3 .$$

With this transformation of variables and the definitions of f and g_c the expression for I_{23} becomes

$$I_{23} = Z^5(4\pi)^{-1}\int[u(1-u)^{-3/2}w^{-2}(1-w)^{\frac{1}{2}}[w(1-2u)R/2 + r(1-w)] \; X$$

$$\int s^{-3}\exp(-fs - g_c/s)ds\,dw\,du .$$

Using the following relation

$$\int_0^\infty s^{-(n+1)}\exp(-fs - g/s)ds = 2(f/g)^{n/2}K_n[(2(fg)^{\frac{1}{2}}) ,$$

I_{23} becomes

$$2Z^5\pi^{-1}\int[u(1-u)]^{-\frac{1}{2}}w^{-1}(1-w)^{\frac{1}{2}}[w(1-2u)R/2+(1-w)r]\,K_2[2(fg_c)^{\frac{1}{2}}]\;X$$

$$f\sigma^{-2}dwdu$$

as is given in the list.

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