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OF HELIUM ATOM AND NITROGEN MOLECULE.

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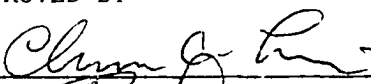
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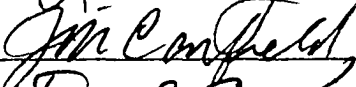
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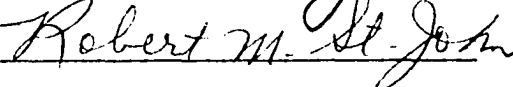
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A STUDY OF ELECTRON EXCITATION CROSS SECTIONS
OF HELIUM ATOM AND NITROGEN MOLECULES

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PART I

A STUDY OF INDIRECT COUPLING EFFECTS
ON THE ELECTRON EXCITATION
CROSS SECTIONS OF HELIUM

CHAPTER I

INTRODUCTION

Shortly after the introduction of modern quantum mechanics, Born formulated a rather simple approximate scheme to compute the excitation cross sections. This method, known as the Born approximation, has been quite extensively used since then for theoretical investigations of collision processes.¹⁻⁸ From the beginning it is well understood that the Born approximation is a high energy approximation, that is, it is valid only if the incident electron passes by the target atom with great speed. However, the fact that the Born approximation is also a "two-state approximation" was not as widely recognized. As in other areas of atomic physics, the excitation process is not dictated only by those states of atom between which electronic transition takes place. Rather, all eigenstates of the atom play roles for an electronic transition(excitation) between any pair of states. It is the object of this part of the thesis to investigate to what extent an excitation process is influenced by the presence of other(intermediate) states, and to single out the important intermediate states, given an initial and a final states of excitation. To this end, the

formalism of the close-coupling method^{9,10} is adopted, which permits one to systematically examine the effects of intermediate states(indirect coupling effects).

To be sure, there are other difficulties associated with the use of the Born approximation.^{10,22} Since it is a first order perturbation type of method, the use of the Born approximation requires that the coupling potential (perturbation) be small. Although the close-coupling formalism removes such difficulty,¹⁰ this aspect will not be discussed in detail. Rather, the major effort is directed toward the case where the direct coupling is too small to account for the observed cross sections.

In the literature there are abundant experimental data reported by several laboratories on the electron excitation cross sections of He atom.^{1,12-15} Helium being an inert gas of light atom, many experimental difficulties are alleviated, and experimental data of the excitation cross sections are more reliable than those for any other atoms. For these reasons He atom was chosen as the subject of the investigation.

Regardless of the formalisms adopted to compute excitation cross sections, the outcome depends ultimately on the wave functions used, which in themselves are approximations except the special case of hydrogen atom. Therefore, in order

to test the variations in excitation cross sections due to the choice of approximate wave functions used, wave functions of varying degree of accuracy are used, ranging from the semi-empirical hydrogenic functions to the highly accurate correlated wave functions with more than 50 terms. At 100 eV the plane wave approximation portion of the Born approximation is expected to be valid; therefore, the effect of the indirect coupling may be examined by comparing the results of the Born approximation and those of the close-coupling method.

Although the attention will be focused on the indirect coupling effects on the n^1D cross sections of He, it should be pointed out that the indirect coupling becomes even more important in numerous cases³ where the direct coupling alone gives vanishing cross sections.

CHAPTER II

FORMULATION

When a beam of electrons is passed through a chamber containing He atoms, the electrons collide elastically or inelastically with the atoms, and are scattered to a certain direction $(\theta\phi)$. The coordinate system along with collision process is shown in Fig. 1. The number of scattered elec-

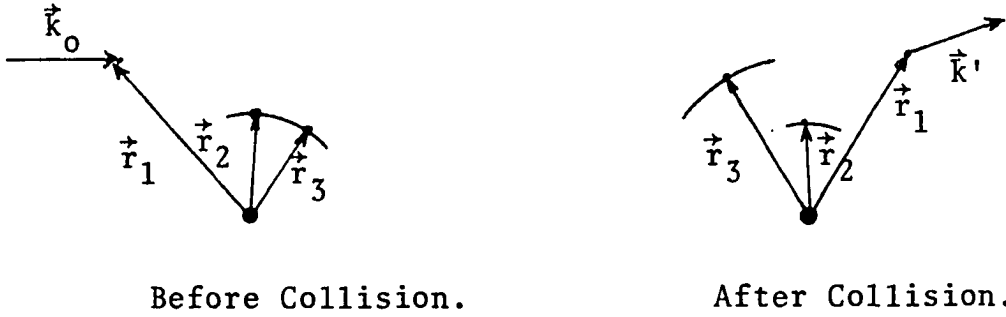


Figure 1. The Collision Process and Coordinate system.

trons per unit time in the $(\theta\phi)$ direction within a solid-angle element $d\Omega$, after having suffered a particular kind of collision, is proportional to the number of atoms in a unit volume, and to the flux of the incident electron beam. The proportionality constant $I(p' \rightarrow p | \theta\phi) d\Omega$ has a dimension of an area, and is referred to as the differential cross section for scattering into a solid angle $d\Omega$,¹⁶ the notation $p' \rightarrow p$ describing the

internal excitation process of the atom. The total excitation cross section $Q(p' \rightarrow p)$ is obtained by integrating over the entire solid angle.

Expansion and Cross Section Formulae

The colliding electron is labeled by subscript 1 and two atomic electrons by subscripts 2 and 3. In the time-independent formalism, the Hamiltonian H of the entire colliding system in atomic units is

$$H = H_a - \nabla_1^2/2 - Z/r_1 + r_{12}^{-1} + r_{13}^{-1}, \quad (2.1)$$

where

$$H_a = -\nabla_2^2/2 - Z/r_2 - \nabla_3^2/2 - Z/r_3 + r_{23}^{-1}, \quad (2.2)$$

and $r_{ij} = |\vec{r}_i - \vec{r}_j|$ and Z is the nuclear charge.

The wave function Ψ^T describing the entire collision system must satisfy the Schroedinger equation, i.e.,

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

The solution Ψ^T of Eq.(2.3), which satisfies the appropriate boundary conditions, would contain all the information relevant to the collision process. However, due to the interactions of type r_{ij}^{-1} in the Hamiltonian the exact solutions are not attainable. Herein lies the problem, and one is forced to search various approximate schemes which will

adequately reflect the physical processes under consideration.

One may expand Ψ^T in terms of the basis functions which are the products of the atomic eigenfunctions and the partial waves (angular momentum ℓ) of the colliding electron as

$$\Psi^T(\gamma'|\vec{r}_1, \vec{r}_2, \vec{r}_3) = \sum_{p\ell m} r_1^{-1} G_{p\ell m}(\gamma'|r_1) Y_{\ell m}(\hat{r}_1) \psi_p(\vec{r}_2, \vec{r}_3) . \quad (2.4)$$

The notation γ' in Ψ^T specifies the initial condition before collision; and $(r_1^{-1} G_{p\ell m})$, $Y_{\ell m}$ and ψ_p are respectively the unknown coefficient function to be solved, the spherical harmonic,¹⁷ and the atomic wave function; and p represents a collection of quantum numbers necessary to specify the atomic state. The set (p, ℓ, m) is said to define a channel and represented by γ for short. In principle $\Psi^T(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ must be properly anti-symmetrized. However, the resulting effect of electron exchange between the incident and the atomic electrons is expected to be unimportant at the energy of interest (100 eV). Therefore, such electron exchange will not be considered.

Since the cross section is determined by the asymptotic behavior of $G_\gamma(\gamma'|r_1)$, this behavior is examined before proceeding to the solutions. As $r_1 \rightarrow \infty$, the scattered electron becomes a free particle, the target atom being a neutral one, so that the general asymptotic solution of $G_\gamma(\gamma'|r_1)$ is a

superposition of the incoming and outgoing free waves, i.e.,

$$G_{\gamma}(\gamma' | r_1) \underset{r_1 \rightarrow \infty}{\sim} k_p^{-1/2} [A(\gamma', \gamma) \exp\{-i(k_p r - \ell\pi/2)\} - B(\gamma', \gamma) \exp\{i(k_p r - \ell\pi/2)\}], \quad (2.5)$$

$$k_p^2/2 + E_p = k_{p'}^2/2 + E_{p'}, \quad (2.6)$$

where k_p and $k_{p'}$ are the magnitudes of wave vectors in the channels γ and γ' . The factor $k_p^{-1/2}$ is inserted in the RHS of Eq. (2.5) to make A and B amplitudes of flux. The coefficient matrices $\underline{A}$ and $\underline{B}$ are not independent of each other; rather, $\underline{B}$ is related to $\underline{A}$ through a certain transformation, since once the incoming flux is known, the outgoing flux is uniquely determined by the property of the collision system. This transformation matrix is called the scattering matrix¹⁸ and defined through

$$\underline{B} = \underline{S} \underline{A}. \quad (2.7)$$

In order to determine $\underline{A}$ and $\underline{B}$ matrices, attention is given to a particular initial condition of the incident electron impinging upon a target atom in the p'^{th} eigenstate. For convenience, the direction of the incident electron is chosen as $\hat{z}$ direction. As the interest lies in the asymptotic behavior ($r_1 \rightarrow \infty$), the product function of $[(k_{p'})^{-1/2} \exp(ik_{p'} z_1) \times \psi_p(\vec{r}_2, \vec{r}_3)]$ adequately describes this condition. Next the plane wave is expanded as

$$\begin{aligned}
(k_{p'})^{-1/2} \exp(ik_{p'} z_1) \psi_{p'}(\vec{r}_2, \vec{r}_3) &= (4\pi/k_{p'})^{1/2} \\
&\times \sum_{\ell} i^{\ell'} (2\ell'+1)^{1/2} j_{\ell'}(k_{p'} r_1) Y_{\ell'0}(\hat{r}_1) \psi_{p'}(\vec{r}_2, \vec{r}_3) \\
&\approx (4\pi/k_{p'})^{1/2} (2ik_{p'} r_1)^{-1} \sum_{\ell} i^{\ell'} (2\ell'+1)^{1/2} \\
&\times [\exp\{i(k_{p'} r_1 - \ell'\pi/2)\} - \exp\{-i(k_{p'} r_1 - \ell'\pi/2)\}] \\
&\times Y_{\ell'0}(\hat{r}_1) \psi_{p'}(\vec{r}_2, \vec{r}_3) , \tag{2.8}
\end{aligned}$$

where the spherical Bessel function $j_{\ell'}$ is approximated by the asymptotic form as

$$j_{\ell'}(k_{p'} r) \approx (k_{p'} r)^{-1} \sin(k_{p'} r - \ell'\pi/2) . \tag{2.9}$$

By comparing Eqs. (2.4) and (2.8) with the aid of Eq. (2.5), it is easy to see that

$$A(\gamma', \gamma) = \delta_{m0} \delta_{pp'} \delta_{\ell\ell'} i^{\ell'+1} \pi^{1/2} (2\ell'+1)^{1/2} k_{p'} . \tag{2.10}$$

In the case of an inelastic scattering ($\gamma \neq \gamma'$), the off-diagonal elements of $\underline{B}$ are the partial amplitudes of the flux scattered through an angle $(\theta\phi)$. However, in the case of an elastic scattering ($\gamma = \gamma'$), a diagonal element of $\underline{B}$ matrix contains an amplitude equal in magnitude to the corresponding element of $\underline{A}$. This portion is due to the incident wave as seen in Eq. (2.8) and must be excluded. Thus, the transition matrix, which represents amplitudes solely due to scattering, is defined as¹⁹

$$\underline{T} = \underline{I} - \underline{S} . \tag{2.11}$$

The differential cross section for exciting an atom from p' to p state is then given by

$$I(p' \rightarrow p | \theta \phi) d\Omega = \pi (k_{p'})^{-2} \left| \sum_{\ell, i} i^{\ell'+1} (2\ell'+1)^{1/2} \times \sum_{\ell m} T(p' \ell' 0; p \ell m) Y_{\ell m}(\theta \phi) \right|^2 d\Omega. \quad (2.12)$$

The spherical harmonics $Y_{\ell m}$ being an orthonormal set, the corresponding total cross section is easily obtained,

$$Q(p' \rightarrow p) = \pi k_{p'}^{-2} \sum_{\ell m} \left| \sum_{\ell'} i^{\ell'+1} (2\ell'+1)^{1/2} T(p' \ell' 0; p \ell m) \right|^2. \quad (2.13)$$

Differential Equations

Thus, the cross sections are easily obtained through the $\underline{S}$ matrix, once the latter is known. In the preceding section the uncoupled representation is used in order to bring out more clearly the physical processes involved; for the computation purposes, however, it is more convenient to expand Ψ^T in the coupled representation characteristic of the total angular momentum of the system L and the z component thereof M as

$$\begin{aligned} \Psi^T(\Gamma' | \vec{r}_1, \vec{r}_2, \vec{r}_3) &= \sum_{LM} \Psi^{LM}(\Gamma' | \vec{r}_1, \vec{r}_2, \vec{r}_3) \\ &= \sum_{LM\mu} r_1^{-1} F_{\mu}^{LM}(\Gamma' | r_1) \chi_{\mu}^{LM}(\Gamma' | \hat{r}_1, \vec{r}_2, \vec{r}_3), \end{aligned} \quad (2.14)$$

where $(r_1^{-1}F)$ and χ are the unknown coefficient functions to be solved and the basis functions of expansion respectively.

The explicit expression of the latter is given in Eq. (2.15). μ represents a collection of quantum numbers n , j , and ℓ , where n and j are the principal and azimuthal quantum numbers of atom respectively, and ℓ is the angular momentum of the partial wave of the colliding electron. The set (L, M, μ) defines a channel and is written as Γ for short. The basis function in the coupled representation is related to that in the uncoupled representation by a unitary transformation as

$$\begin{aligned} \chi_{\mu}^{LM}(\Gamma' | \hat{r}_1, \vec{r}_2, \vec{r}_3) = \sum_{m_{\ell} m_j} C(\ell j m_{\ell} m_j; \ell j LM) Y_{\ell m_{\ell}}(\hat{r}_1) \\ \times \psi_{njm_j}(\vec{r}_2, \vec{r}_3) , \end{aligned} \quad (2.15)$$

where C is the Clebsch-Gordan coefficient.¹⁷ Confining to the configurations of type $(1s)(nj)$ of the He atom, the anti-symmetrized singlet wave functions ψ 's are

$$\begin{aligned} \psi_{njm}(\vec{r}_2, \vec{r}_3) = 2^{-1/2} [a_{1s}(r_2)b_{nj}(r_3)Y_{00}(\hat{r}_2)Y_{jm}(\hat{r}_3) \\ + a_{1s}(r_3)b_{nj}(r_2)Y_{00}(\hat{r}_3)Y_{jm}(\hat{r}_2)] , \end{aligned} \quad (2.16)$$

where a and b are radial parts of one electron wave functions. The coupled representation offers an advantage over the uncoupled representation in that L and M are conserved throughout the collision process, which permits one to examine each Ψ^{LM} separately.

In practice only a finite number of atomic states can be included in the expansion in Eq. (2.14). The method based on such a truncated expansion is known as the close-coupling method. When the variational principle is applied to Eq. (2.3), the following set of differential equations results.⁹

$$\begin{aligned} \left[\frac{d^2}{dr^2} - \ell(\ell+1)/r^2 + k_{nj}^2 \right] F_{\mu}^{LM}(\mu' | r) \\ = \sum_{\mu''} U_{\mu\mu''}(r) F_{\mu''}^{LM}(\mu' | r), \end{aligned} \quad (2.17)$$

where the subscript in r_1 is now dropped without confusion. The coupling potential $U_{\mu\mu''}(r)$ in Eq. (2.17) is

$$\begin{aligned} U_{\mu\mu''}(r_1) &= 2 \int \chi_{\mu}^*(\mu' | \hat{r}_1, \vec{r}_2, \vec{r}_3) [-Zr_1^{-1} + r_{12}^{-1} + r_{13}^{-1}] \\ &\times \chi_{\mu''}(\mu' | \hat{r}_1, \vec{r}_2, \vec{r}_3) d\hat{r}_1 d\vec{r}_2 d\vec{r}_3 = -2Zr_1^{-1} \delta_{\mu\mu''} \\ &+ 2 \sum_{\lambda} f_{\lambda}(\ell j \ell'' j''; L) y_{\lambda}(\phi_{nj}, \phi_{n''j''} | r_1), \end{aligned} \quad (2.18)$$

where ϕ is used symbolically for radial parts in Eq. (2.16), and

$$\begin{aligned} y_{\lambda}(\phi_{nj}, \phi_{n'j'} | r) &= 2[r^{-\lambda-1} \int_0^r \phi_{nj}(t_1, t_2) t_1^{\lambda} \phi_{n'j'}(t_1, t_2) \\ &\times t_1^2 dt_1 t_2^2 dt_2 + r^{\lambda} \int_r^{\infty} \phi_{nj}(t_1, t_2) t_1^{-\lambda-1} \phi_{n'j'}(t_1, t_2) \\ &\times t_1^2 dt_1 t_2^2 dt_2], \end{aligned} \quad (2.19)$$

and

$$f_{\lambda}(\ell j \ell' j'; L) = \int \sum_{m_{\ell} m_j m_{\ell'}, m_{j'}} C(\ell j m_{\ell} m_j; LM)$$

$$\begin{aligned}
& \times Y_{\ell m_\ell}^*(\hat{r}_1) Y_{jm_j}^*(\hat{r}_2) Y_{00}^*(\hat{r}_3) [4\pi/(2\lambda+1)]^{1/2} \\
& \times \sum_{g=-\lambda}^{\lambda} Y_{\lambda g}^*(\hat{r}_1) Y_{\lambda g}(\hat{r}_2) C(\ell' j' m_\ell, m_j, ; LM) Y_{\ell' m_\ell}(\hat{r}_1) \\
& \times Y_{jm_j}(\hat{r}_2) Y_{00}(\hat{r}_3) d\hat{r}_1 d\hat{r}_2 d\hat{r}_3 . \quad (2.20)
\end{aligned}$$

Using the results of Racah's work on the theory of complex spectra,²⁰ Eq. (2.20) may be reduced to a more compact expression, i.e.,

$$\begin{aligned}
f_\lambda(\ell j \ell' j'; L) &= (-1)^{\ell+\ell'-L} (2\lambda+1)^{-1} C(\ell j 00; \lambda 0) \\
&\times C(\ell' j' 00; \lambda 0) [(2\ell+1)(2j+1)(2\ell'+1)(2j'+1)]^{1/2} \\
&\times W(\ell j \ell' j'; L\lambda) , \quad (2.21)
\end{aligned}$$

where W is the Racah coefficient.²⁰ The coefficient $f_\lambda(\ell j \ell' j'; L)$ vanishes unless each of the sets $(\ell j L)$, $(\ell' j' L)$, $(\ell \ell' \lambda)$, and $(j j' \lambda)$ satisfies the "triangular rule" and the "parity rule", i.e., for (abc)

$$a+b \geq c, \quad c+a \geq b, \quad b+c \geq a$$

and

$$(2.22)$$

$$a+b+c = \text{even}.$$

For the solutions F of Eq. (2.17) to represent the physical problem of collision process, F must be finite everywhere (the origin included), and must have the asymptotic form similar to Eq. (2.5), i.e.,

$$F_{\mu}^{LM}(\mu' | r) \underset{r \rightarrow \infty}{\sim} (k_{n'j'})^{-1/2} [\delta_{\mu\mu'} \exp\{-i(k_{nj}r - \ell\pi/2)\} - \exp\{i(k_{nj}r - \ell\pi/2)\} S_{\mu\mu'}] . \quad (2.23)$$

As the basis functions in the coupled and the uncoupled representations are related by the unitary transformation as shown in Eq. (2.15), the corresponding scattering matrices are related as¹⁸

$$S(nj\ell m_j m_{\ell}, n'j'\ell' m_j, 0) = \sum_{L=0}^{\infty} \sum_{M=-L}^L C(j\ell m_j m_{\ell}; LM) \times S(nj\ell LM, n'j'\ell' LM) C(j'\ell' m_j, 0; LM) . \quad (2.24)$$

The total cross section is then given as (See Appendix I for detailed derivation.)

$$Q^T(n'j' \rightarrow nj) = \sum_L Q^L(n'j' \rightarrow nj) . \quad (2.25)$$

$$Q^L(n'j' \rightarrow nj) = (\pi/k_{n'j'}^2) (2L+1) \sum_{\ell\ell'} (2j'+1)^{-1} |T(Lnj\ell, Ln'j'\ell')|^2 . \quad (2.26)$$

The conservation theorem²¹ of particle imposes the condition that the scattering matrix be a unitary matrix. The consequence of this theorem is to put an upper limit to the total inelastic cross section as

$$Q^L(\text{inelastic}) = \sum_{nj} Q^L(n'j' \rightarrow nj) \leq (\pi/k_{n'j'}^2) (2L+1) (2j'+1)^{-1} . \quad (2.27)$$

The scattering matrix is also symmetric, which relates the

cross sections of excitation with de-excitation between the two given states (detailed balancing). As will be discussed shortly, the conservation theorem is well satisfied in the close-coupling formalism. However, it is noted in passing that the conservation theorem is violated in using the Born approximation, when the direct coupling potential is too strong.²²

For computational purposes, it is advantageous to put the asymptotic form in Eq. (2.23) in another form, i.e.,

$$F_{\mu}^{LM}(\mu' | r) \underset{r \rightarrow \infty}{\sim} (k_{nj})^{-1/2} [\sin(k_{nj}r - \ell\pi/2) \delta_{\mu\mu'} + \cos(k_{nj}r - \ell\pi/2) R_{\mu\mu'}] , \quad (2.28)$$

where the "reactance" matrix $\underline{R}$ is related to the scattering matrix as

$$\underline{S} = (\underline{I} + i\underline{R})(\underline{I} - i\underline{R})^{-1}. \quad (2.29)$$

The fact that the Hamiltonian is real and symmetric assures that the coupling potentials U 's in Eq. (2.18) are real and symmetric; the latter in turn assures that $\underline{R}$ is real and symmetric. Finally it is evident from Eq. (2.29) that $\underline{S}$ matrix is unitary.

CHAPTER III

METHOD OF COMPUTATION

Lane and co-workers¹⁰ give the numerical procedure for solution of differential equations of Eq. (2.17) and determination of $\underline{R}$ and $\underline{S}$ matrices. Although, in principle, the determination of $\underline{R}$ matrix (and hence $\underline{S}$ matrix) should be done at infinite separation of the scattered electron from the target atom, the range of integration is limited in practice to 100 or 200 atomic units. In this limited range of r , $\underline{R}$ matrix shows a variance with respect to the value of r where $\underline{R}$ matrix is determined, especially when the number of channels are large. For this reason, it is desirable to have a corrective scheme to obtain a "converged" $\underline{R}$ matrix. Earlier, Burke and Schey¹¹ used a scheme based on an asymptotic expansion in terms of the inverse power series in r . However, the asymptotic series do not converge, when the atomic eigenstates have near-degeneracy like the case of He atom where the energy levels of the same n are rather close together. Thus, a new scheme³¹ is devised which is applicable regardless of the degeneracy.

Solution of Differential Equations

For computational purposes Eq. (2.17) is written as

$$\frac{d^2}{dr^2} F_{in} = \sum_m [\delta_{im} \{-k_i^2 + \ell_i(\ell_i+1)/r^2\} + U_{im}(r)] F_{mn}(r) . \quad (3.1)$$

or in matrix notation (denoting the second derivative by "double prime"),

$$\underline{F}'' = \underline{G} \underline{F} , \quad (3.2)$$

where

$$G_{im} = \delta_{im} \{-k_i^2 + \ell_i(\ell_i+1)/r^2\} + U_{im} . \quad (3.3)$$

To facilitate the numerical solution of Eq. (3.1), the method of Numrov²³ is used which is based on the relationship between the second derivative of a function f and its second differences,

$$\delta^2 f = h^2 [f'' + \delta^2 f''/12] + O(h)^4 , \quad (3.4)$$

where the second difference $\delta^2 f$ is

$$\delta^2 f_n = f_{n+1} - 2f_n + f_{n-1} , \quad (3.5)$$

and

$$\begin{aligned} h &= r_{n+1} - r_n , \\ f_n &= f(r_n) . \end{aligned} \quad (3.6)$$

From Eqs. (3.4) and (3.5) the following recurrence formula is obtained.

$$\begin{aligned} \underline{F}_{n+1} = & [\underline{I} - h^2 \underline{G}_{n+1}/12]^{-1} \{ [2\underline{I} + 5h^2 \underline{G}_n/6] \underline{F}_n \\ & - [\underline{I} - h^2 \underline{G}_{n-1}/12] \underline{F}_{n-1} \} . \end{aligned} \quad (3.7)$$

For optimum computing efficiency, it is desirable to put the recurrence formula in another form as

$$\underline{P}_{n+1} = \underline{W}_n \underline{P}_n - \underline{P}_{n-1} , \quad (3.8)$$

where

$$\underline{P}_n = [\underline{I} - h^2 \underline{G}_n/12] \underline{F}_n , \quad (3.9)$$

$$\underline{W}_n = [(1/12)\underline{I} - h^2 \underline{G}_n/144]^{-1} - 10\underline{I} .$$

Once the solutions $\underline{F}_n$ are known at two adjacent points ($n=1,2$, for example), the recurrence formula may be used to generate solutions at all succeeding points. It is simple to show [See Eq. (2.19).] that all the coupling potentials U_{nm} approach at most constant values near the origin except the diagonal ones which behave as $-2Z/r$. Thus, at sufficiently small values of r ($\sim 10^{-3}a_0$), Eq. (3.1) is de-coupled. The two starting solutions are thus provided by means of the Frobenius method as (discarding the ill-behaved ones),

$$\begin{aligned} F_{mm}(r) &= c_{mm} r^{\ell+1} [1 - Zr/(\ell+1) + \dots] , \\ F_{mn}(r) &= 0 , \quad m \neq n , \end{aligned} \quad (3.10)$$

with $r=r_0$ for one and $r=r_0+h$ for the other solutions. The arbitrary constant c_{mm} may be chosen as unity, and one or two terms in Eq. (3.10) is all that is necessary. The boundary

condition imposes that the solutions must behave for large r as

$$\underline{F}^B \sim k_m^{-1/2} [\underline{J} + \underline{Y} \underline{R}] , \quad (3.11)$$

where the diagonal matrices $\underline{J}$ and $\underline{Y}$ are defined as

$$\begin{aligned} J_{mm} &= (k_m r)^{-1} j_{\ell_m}(k_m r) , \\ Y_{mm} &= -(k_m r)^{-1} y_{\ell_m}(k_m r) , \end{aligned} \quad (3.12)$$

where j and y are the spherical Bessel functions of the first and the second kinds respectively. Because of the arbitrariness c_{mm} in the starting solutions, the Numrov-integrated solutions will have the form

$$\underline{F}^N = [\underline{J} \underline{A} + \underline{Y} \underline{B}] , \quad (3.13)$$

where $\underline{A}$ and $\underline{B}$ are the "constant" matrices (See the following section). By a linear transformation

$$\underline{F}^N \underline{A}^{-1} = \underline{J} \underline{I} + \underline{Y} \underline{B} \underline{A}^{-1} , \quad (3.14)$$

the $\underline{R}$ matrix is identified as

$$\underline{R} = \underline{B} \underline{A}^{-1} . \quad (3.15)$$

The matrices $\underline{A}$ and $\underline{B}$ may be determined by solving the simultaneous matrix equations.

$$\begin{aligned} \underline{F}^N(a) &= \underline{J}(a) \underline{A} + \underline{Y}(a) \underline{B} , \\ \underline{F}^N(b) &= \underline{J}(b) \underline{A} + \underline{Y}(b) \underline{B} , \end{aligned} \quad (3.16)$$

where a and b indicate the matching values $r=a$ and $r=b$ ($=a+h$,

usually).

The starting solutions [Eq. (3.10)] may be initiated safely from $r=10^{-3}a_0$. A test calculation with the starting value of $r=10^{-6}a_0$ showed completely identical results. In the region of small r , the accuracy of the numerical integration depends largely on how close to a unit matrix the matrix $[I-h^2\underline{G}/12]$ is. Noting that the largest contribution to $\underline{G}$ comes from the term $\ell(\ell+1)/r^2$ (except when $\ell=0$), it is easy to see that the numerical accuracy would increase as the ratio $[h^2\ell(\ell+1)/r^2]$ is decreased. In practice the values of h have been chosen so as to keep the ratio (h/r) less than $(1/20)$, which proved to be quite satisfactory in all cases of interest. In the outer region ($r>1.0a_0$) the step-size h is dictated by the "frequency" of F . Since for large r the solutions F become linear superposition of $\sin(k_i r)$ and $\cos(k_i r)$ [See Eq. (3.11)], the value of h has been chosen so as not to exceed one tenth of $(\pi/k_{\max})$, $k_{\max}$ being the magnitude of the largest wave vector. The matching, that is, the determination of $\underline{R}$ matrix, may start as soon as all the coupling potentials take the asymptotic forms

$$U_{mn}(r) = d_{mn} r^{-\lambda-1}, \quad \lambda \geq 1. \quad (3.17)$$

Correction to R Matrix

It is tacitly assumed in Eq. (3.16) that $\underline{A}$ and $\underline{B}$ are constant; however, due to the limited range of integration and due to the case of $\lambda=1$, $\underline{A}$ and $\underline{B}$, and hence $\underline{R}$ vary slowly with r .

A first order corrective scheme is developed to avoid this variance. The functions $\underline{J}(r)$ and $\underline{Y}(r)$ defined in Eq. (3.12) are in reality the two independent homogeneous solutions of Eq. (3.1), and they satisfy the condition,

$$\underline{J}'(r)\underline{Y}(r) - \underline{J}(r)\underline{Y}'(r) = \underline{I} , \quad \text{for all } r, \quad (3.18)$$

where "prime" indicates the derivative with respect to r .

Therefore, the general solution is²⁴

$$\underline{F}(r) = \underline{J}(r) \int_a^r dr \underline{Y}(r) \underline{U}(r) \underline{F}(r) - \underline{Y}(r) \int_b^r dr \underline{J}(r) \underline{U}(r) \underline{F}(r) . \quad (3.19)$$

The arbitrary constants a and b may be chosen so that $\underline{F}$ satisfy the boundary conditions, i.e.,

$$\underline{F}(\infty) = \underline{J} \int_a^\infty dr \underline{Y} \underline{U} \underline{F} - \underline{Y} \int_b^\infty dr \underline{J} \underline{U} \underline{F} = \underline{J} \underline{I} + \underline{Y} \underline{R} . \quad (3.20)$$

Substitution of Eq. (3.20) in Eq. (3.19) gives

$$\underline{F}(r) = \underline{J} [\underline{I} - \int_r^\infty dr \underline{Y} \underline{U} \underline{F}] + \underline{Y} [\underline{R} + \int_r^\infty dr \underline{J} \underline{U} \underline{F}] . \quad (3.21)$$

The subscript o will be used to distinguish the approximate $\underline{R}$ matrix obtained by Eqs. (3.15) and (3.16) from the "true" $\underline{R}$. As before, the Numrov-integrated solutions will differ from

those in Eq. (3.21) by a linear transformation. For convenience, this transformation matrix may be taken as $(\underline{A}^{-1}\underline{C})$, where $\underline{C}$ matrix (as yet unknown) is to be determined. Then from Eqs. (3.13) and (3.21) one arrives at

$$[\underline{J} + \underline{Y} \underline{R}^0] \underline{C} = \underline{J} [\underline{I} - \int_r^\infty dr \underline{Y} \underline{U} \underline{F}] + \underline{Y} [\underline{R} + \int_r^\infty dr \underline{J} \underline{U} \underline{F}] . \quad (3.22)$$

To obtain the corrective matrices, the approximate $\underline{F}$ is inserted on the RHS of Eq. (3.22) with

$$\underline{F} \approx \underline{J} + \underline{Y} \underline{R}^0 . \quad (3.23)$$

By equating the coefficient matrices of $\underline{J}$ the matrix $\underline{C}$ is determined as

$$\underline{C} = [\underline{I} - \int_r^\infty \underline{Y} \underline{U} \underline{J} dr - \int_r^\infty \underline{Y} \underline{U} \underline{Y} dr \underline{R}^0] . \quad (3.24)$$

Finally the corrected $\underline{R}$ is

$$\begin{aligned} \underline{R} = \underline{R}^0 [\underline{I} - \int_r^\infty \underline{Y} \underline{U} \underline{J} dr - \int_r^\infty \underline{Y} \underline{U} \underline{Y} dr \underline{R}^0] - \int_r^\infty \underline{J} \underline{U} \underline{J} dr \\ - \int_r^\infty \underline{J} \underline{U} \underline{Y} dr \underline{R}^0 . \end{aligned} \quad (3.25)$$

The use of the corrective scheme gives substantially improvement in that the matrix elements matched at $80a_0$ and $200a_0$ agree typically to five significant figures. In a practical way, this scheme allows one to obtain more accurate cross sections without having to integrate to a large value of r , thus leading to a considerable saving in computer usage.

CHAPTER IV

RESULTS AND CONCLUSION

Essential to any theoretical calculations of excitation cross sections is the quality of the wave functions employed in computation. Therefore, the dependence of the cross sections on the accuracy of the wave functions is first examined by using the Born approximation and the close-coupling method. Next, given the final state (the initial state being the ground state), a detailed examination of the effects of the intermediate states is made. This is done by including various combinations of the states in the scattering equation. The results of a comprehensive study in this regard are presented. The atomic states examined include $(1s)(nj)$ for $n=1-4$, $j=0-3$; $(1s)(np)$ for $n=2-8$; and the doubly excited states $(2s)(2p)$, $(2s)(3p)$, $(3s)(2p)$, and $(3s)(3p)$. The close-coupling results are then compared with those of the Born approximation and the experimental cross sections.

Wave Functions

The He wave functions have been calculated by numerous workers.²⁵ They may be classified as (i) hydrogenic functions

with empirical effective charge;²⁶ (ii) Hartree-Fock or Hartree-Fock-Slater type;^{25,27} (iii) wave functions containing inter-electronic distance explicitly.²⁸⁻³⁰ The functions of class (i) are satisfactory for highly excited states ($n \geq 4$), but distinctly poor for the ground state both from the energy criterion and as reflected in the computed cross sections. The wave functions of class (ii) assumes product type as those of class (i), the distinction being that the former are obtained by ab initio calculations whereas the latter are empirical in nature. The Hartree-Fock equation may be solved either in tabular form or by linear variations for the coefficients of pre-chosen exponential basis functions, both leading to a virtually identical energy value. The major limitation of these functions arises from the assumed product form, by which the electron correlation cannot be properly accounted for. This correlation effect is particularly important for the ground state where two electrons share the same shell, but not too critical for the excited states where two electrons stay apart from each other (in classical sense). By virtue of including the inter-electronic distance explicitly, far superior wave functions are obtained, which, for example, predict the ground state energy within the limits of the spectroscopic measurements. Some of these functions are

$$\begin{aligned}\Psi(1^1S) = & 1.38189\exp(-1.82s)[1 - 0.100828s \\ & + 0.353808u + 0.033124s^2 + 0.128521t^2 \\ & - 0.031799u^2] , \quad \text{by Hylleraas},^{28}\end{aligned}$$

$$\begin{aligned}\Psi(1^1S) = & \exp(-1.755s)[1.38084 + 0.46552u \\ & - 0.051189u^2 - 0.202095s + 0.187694v \\ & - 0.245212w] , \quad \text{by Stewart and Webb},^{30}\end{aligned}$$

where $s=r_1+r_2$, $t=r_2-r_1$, $u=|\vec{r}_1-\vec{r}_2|$, $v=r_1^2+r_2^2$, and $w=r_1r_2$.

Weiss²⁹ gives the correlated wave functions of 1^1S , 2^1S , 3^1S , 2^1P , 3^1P , and 3^1D as

$$\Psi(n^1j) = \sum_{pqt} C_{pqt}^{nj} \phi_{pqt}^{nj} ,$$

where C_{pqt}^{nj} are the weight coefficients, and

$$\begin{aligned}\phi_{pqt}^{nj} = & (\zeta^3 \pi^{-1/2}/4) [\rho_1^p \rho_2^{q+j} \rho_{12}^t \exp(-\rho_1 - \chi \rho_2) Y_{jm}(\hat{r}_2) \\ & + \rho_2^p \rho_1^{q+j} \rho_{12}^t \exp(-\rho_2 - \chi \rho_1) Y_{jm}(\hat{r}_1)] ,\end{aligned}$$

where $\rho=\zeta r$, and ζ and χ are the parameters. The numerical values are reproduced as communicated by Weiss in Table I.

The variance of the cross sections with the use of the first two classes of wave functions are summarized in Table II. The effective nuclear charges for hydrogenic functions are chosen as 1.65 for the ground (1s) orbital, and 2.0 and 1.0 respectively for (1s) and (nj) orbitals of the excited states. The Hartree-Fock wave functions are those of

TABLE I

NUMERICAL PARAMETERS

 1^1S : 53 terms $\zeta=2.19239116$ $\chi=1.000$

p	q	t	C	p	q	t	C
0	0	0	-1.1542299 (0) (a)	0	1	0	-2.3132474 (-1)
0	0	1	-2.3829439 (-1)	0	2	0	-1.7489135 (-1)
1	1	0	5.4438241 (-2)	0	1	1	-1.1395662 (-1)
0	0	2	6.9675030 (-2)	0	3	0	-2.2772606 (-2)
1	2	0	3.7845311 (-2)	0	2	1	6.6986175 (-2)
1	1	1	-4.2225240 (-2)	0	1	2	-4.2207900 (-3)
0	0	3	-1.9209468 (-2)	0	4	0	-1.2402138 (-3)
1	3	0	-4.2380360 (-3)	2	2	0	-5.4466292 (-4)
0	3	1	2.2705319 (-3)	1	2	1	-1.6319744 (-2)
0	2	2	-1.9213872 (-2)	1	1	2	1.3097475 (-2)
0	1	3	6.1758107 (-3)	0	0	4	3.1036666 (-3)
0	5	0	3.9754628 (-4)	1	4	0	-1.0839976 (-3)
2	3	0	1.1439479 (-3)	0	4	1	-1.1371931 (-4)
1	3	1	3.4880588 (-3)	2	2	1	-7.6751013 (-4)
0	3	2	-2.6724531 (-3)	1	2	2	1.4147480 (-3)
0	2	3	5.9103197 (-3)	1	1	3	-1.5934956 (-3)
0	1	4	-3.1852010 (-3)	0	0	5	8.2626579 (-5)
0	5	1	-2.3503277 (-4)	1	4	1	5.5213657 (-5)
2	3	1	-2.7275591 (-4)	0	5	2	7.1466333 (-6)
1	4	2	-2.1652129 (-5)	2	3	2	-1.5210611 (-5)
0	4	2	5.0679259 (-4)	1	3	2	9.6494887 (-6)
2	2	2	4.7969623 (-4)	0	3	3	-2.8193889 (-4)
1	2	3	-1.2838034 (-3)	0	4	3	-1.5680515 (-5)
1	3	3	5.2815999 (-5)	2	2	3	1.3704848 (-5)
0	2	4	-5.0137824 (-5)	1	1	4	7.1629358 (-4)
0	1	5	2.1204731 (-5)	0	2	5	8.4148947 (-6)
1	1	5	-2.0971917 (-5)				

(a) Numbers inside the parentheses indicate the power of 10.

TABLE I-Continued

 2^1S : 54 terms $\zeta=2.12285706$ $\chi=0.370$

p	q	t	C	p	q	t	C
0	0	0	-3.8987008 (-1)	0	1	0	1.1627869 (-1)
1	0	0	5.2892227 (-2)	0	2	0	-8.7853457 (-3)
1	1	0	-1.1654868 (-2)	2	0	0	-1.4032278 (-3)
0	3	0	2.7600543 (-3)	1	2	0	-7.5035481 (-5)
2	1	0	9.2686527 (-4)	3	0	0	1.6282962 (-4)
0	4	0	-5.4097288 (-5)	1	3	0	1.9934886 (-4)
2	2	0	-2.7686468 (-4)	3	1	0	-1.1280909 (-5)
0	0	1	-6.8764753 (-2)	0	1	1	3.0632952 (-2)
1	0	1	-1.6459900 (-2)	0	2	1	-1.2965706 (-3)
1	1	1	5.8402414 (-3)	2	0	1	3.8134982 (-4)
0	3	1	-1.5572461 (-4)	1	2	1	-4.8250331 (-4)
2	1	1	1.2151425 (-4)	3	0	1	-1.2946421 (-4)
0	4	1	1.0509838 (-5)	1	3	1	-2.7842899 (-6)
2	2	1	3.1472710 (-5)	3	1	1	8.4140227 (-6)
0	0	2	9.6424816 (-3)	0	1	2	-4.6781916 (-3)
1	0	2	4.6440650 (-4)	0	2	2	3.6735055 (-4)
1	1	2	-1.4736136 (-4)	2	0	2	-5.8952714 (-7)
0	3	2	-8.1991005 (-6)	1	2	2	2.1771491 (-5)
2	1	2	-3.0343312 (-5)	3	0	2	3.9141410 (-6)
0	0	3	-5.7193667 (-4)	0	1	3	3.0117459 (-4)
1	0	3	4.8011348 (-6)	0	2	3	-1.5116722 (-5)
1	1	3	1.5624648 (-6)	2	0	3	6.2707273 (-6)
0	0	4	5.6653478 (-6)	0	1	4	-1.1214881 (-5)
1	0	4	-1.3686807 (-6)	0	2	4	5.3020272 (-7)
1	1	4	-3.4576873 (-7)	0	0	5	5.3152916 (-7)
0	1	5	1.3935763 (-7)	1	0	5	8.5035149 (-8)
0	2	5	-6.5028816 (-9)	1	1	5	2.4479303 (-9)

TABLE I-Continued

 3^1S : 54 terms $\zeta=2.04999998$ $\chi=0.231$

p	q	t	C	p	q	t	C
0	0	0	2.3161238 (-1)	0	1	0	-1.0135069 (-1)
1	0	0	-3.5784863 (-2)	0	2	0	8.0920891 (-3)
1	1	0	1.5748018 (-2)	0	0	1	3.4167829 (-2)
0	1	1	-9.6344882 (-3)	1	0	1	-1.2643723 (-4)
0	2	1	1.1114842 (-4)	1	1	1	-2.2616512 (-4)
2	0	0	2.2156101 (-5)	0	3	0	1.6421958 (-5)
1	2	0	-2.6195787 (-3)	2	1	0	6.7284803 (-4)
3	0	0	-3.2714730 (-4)	0	4	0	1.4469396 (-5)
1	3	0	3.6190568 (-5)	2	2	0	8.6691500 (-5)
3	1	0	-6.2063970 (-6)	2	0	1	-5.3334209 (-4)
0	3	1	-3.2331918 (-5)	1	2	1	2.4143654 (-4)
2	1	1	-2.3336803 (-4)	3	0	1	7.1243588 (-5)
0	4	1	1.0225509 (-6)	1	3	1	-7.6796440 (-6)
2	2	1	-1.3794617 (-5)	3	1	1	1.8389411 (-6)
0	0	2	-4.4122216 (-3)	0	1	2	7.9430197 (-4)
1	0	2	9.4180399 (-6)	0	2	2	-3.7640578 (-5)
1	1	2	1.2490334 (-5)	2	0	2	1.1753584 (-4)
0	3	2	9.1585648 (-8)	1	2	2	1.7549426 (-5)
2	1	2	2.8710175 (-5)	3	0	2	-4.1471503 (-6)
0	0	3	5.5434534 (-4)	0	1	3	2.6611162 (-5)
1	0	3	-5.6608170 (-5)	0	2	3	-8.6655241 (-8)
1	1	3	-3.7931935 (-5)	2	0	3	-1.3827207 (-5)
0	0	4	-6.6781765 (-5)	0	1	4	2.2516934 (-6)
1	0	4	1.8958775 (-5)	0	2	4	-4.2415668 (-8)
1	1	4	4.6198350 (-7)	0	0	5	7.2509766 (-7)
0	1	5	-2.8375798 (-8)	1	0	5	-2.8313491 (-7)
0	2	5	5.5532594 (-10)	1	1	5	-1.1682415 (-9)

TABLE I-Continued

 2^1P : 52 terms $\zeta=2.05535704$ $\chi=0.370$

p	q	t	C	p	q	t	C
0	0	0	5.7757176 (-2)	0	1	0	8.9511880 (-4)
1	0	0	6.5153669 (-4)	0	0	1	9.0727367 (-3)
0	2	0	2.5673028 (-3)	1	1	0	-2.5398049 (-3)
2	0	0	-7.7475159 (-4)	0	1	1	-2.0518903 (-3)
1	0	1	3.3689650 (-3)	0	0	2	-3.8664079 (-4)
0	3	0	-1.8295131 (-4)	1	2	0	2.2302753 (-4)
2	1	0	2.1944635 (-4)	3	0	0	9.0896587 (-6)
0	2	1	1.3744678 (-4)	1	1	1	1.1814862 (-5)
2	0	1	-6.0268080 (-5)	0	1	2	1.3163275 (-4)
1	0	2	-3.3484444 (-4)	0	0	3	-3.3533606 (-6)
0	4	0	5.4908784 (-6)	1	3	0	7.8935150 (-6)
2	2	0	-2.6200092 (-5)	3	1	0	3.5758271 (-6)
4	0	0	-7.0818027 (-6)	0	3	1	2.6797637 (-6)
1	2	1	-3.6302950 (-5)	2	1	1	5.5667837 (-6)
3	0	1	-5.5535395 (-6)	0	2	2	-6.1583089 (-6)
1	1	2	2.7412209 (-5)	2	0	2	1.3699313 (-5)
0	1	3	-8.9876792 (-6)	1	0	3	1.0610272 (-5)
0	0	4	3.0769860 (-6)	0	4	1	2.5733936 (-7)
1	3	1	-7.4624494 (-7)	2	2	1	1.8249069 (-6)
3	1	1	3.1143417 (-7)	4	0	1	6.3508019 (-7)
0	3	2	-9.4811165 (-7)	1	2	2	2.3304944 (-6)
2	1	2	-1.8138947 (-6)	3	0	2	-2.8215363 (-7)
0	2	3	1.2031440 (-6)	1	1	3	-2.0072711 (-6)
2	0	3	-2.1464172 (-7)	0	1	4	-3.3408787 (-7)
1	0	4	1.4239658 (-7)	0	2	4	-1.2327863 (-9)
1	1	4	4.1862207 (-9)	2	0	4	1.4338893 (-8)

TABLE I-Continued

 3^1P : 52 terms $\zeta=2.13749999$ $\chi=0.225$

p	q	t	C	p	q	t	C
0	0	0	2.8832695 (-2)	0	1	0	-2.9139890 (-3)
1	0	0	1.9335333 (-3)	0	0	1	4.0233635 (-3)
0	2	0	5.6962431 (-4)	1	1	0	-7.3616040 (-4)
2	0	0	-2.2883047 (-4)	0	1	1	-5.3054188 (-4)
1	0	1	7.6296777 (-4)	0	0	2	-3.5700996 (-4)
0	3	0	-4.2983190 (-5)	1	2	0	-5.1526141 (-5)
2	1	0	3.3876037 (-5)	3	0	0	4.9816931 (-5)
0	2	1	2.2983028 (-5)	1	1	1	1.8050748 (-4)
2	0	1	1.4196966 (-5)	0	1	2	-9.5172691 (-6)
1	0	2	-1.3591963 (-4)	0	0	3	4.5545117 (-5)
0	4	0	-2.7484112 (-7)	1	3	0	2.1003824 (-6)
2	2	0	2.4840079 (-5)	3	1	0	-6.4013286 (-6)
4	0	0	-7.6597586 (-6)	0	3	1	2.4551485 (-6)
1	2	1	-8.6356310 (-6)	2	1	1	-5.0823996 (-5)
3	0	1	3.3726545 (-6)	0	2	2	-1.4197064 (-6)
1	1	2	7.6623895 (-6)	2	0	2	2.2653711 (-5)
0	1	3	-8.3527685 (-7)	1	0	3	-1.8187429 (-6)
0	0	4	-1.0447704 (-6)	0	4	1	-4.9051268 (-8)
1	3	1	1.8465673 (-8)	2	2	1	-1.6301357 (-6)
3	1	1	2.1876119 (-7)	4	0	1	5.5277005 (-7)
0	3	2	7.3719674 (-8)	1	2	2	1.6919395 (-7)
2	1	2	3.1745091 (-6)	3	0	2	-2.6969389 (-7)
0	2	3	-6.2937052 (-8)	1	1	3	-4.2518952 (-7)
2	0	3	-1.4327777 (-6)	0	1	4	6.1665321 (-8)
1	0	4	2.6055099 (-7)	0	2	4	-3.0252369 (-10)
1	1	4	-7.7468169 (-10)	2	0	4	-2.3237604 (-9)

TABLE I-Continued

 3^1D : 52 terms $\zeta=2.09343511$ $\chi=0.220$

p	q	t	C	p	q	t	C
0	0	0	1.2308399 (-3)	0	1	0	2.2176628 (-5)
1	0	0	5.0207283 (-5)	0	0	1	7.7588469 (-5)
0	2	0	6.9143526 (-6)	1	1	0	-2.2707990 (-5)
2	0	0	-9.4589205 (-6)	0	1	1	-2.5448978 (-6)
1	0	1	2.9823628 (-5)	0	0	2	-5.6054122 (-6)
0	3	0	-4.7717836 (-8)	1	2	0	4.6444102 (-6)
2	1	0	4.0737996 (-8)	3	0	0	-1.0774665 (-6)
0	2	1	-1.5339749 (-7)	1	1	1	-5.9975017 (-6)
2	0	1	2.2364004 (-6)	0	1	2	3.2216093 (-7)
1	0	2	9.2003002 (-7)	0	0	3	1.8074514 (-7)
0	4	0	9.1226091 (-9)	1	3	0	-1.8829744 (-7)
2	2	0	-2.2626727 (-7)	3	1	0	1.6787811 (-7)
4	0	0	3.5250599 (-8)	0	3	1	-1.5544549 (-8)
1	2	1	2.0575796 (-7)	2	1	1	3.6172834 (-7)
3	0	1	-7.1175312 (-8)	0	2	2	1.5306883 (-9)
1	1	2	3.8228153 (-8)	2	0	2	-2.8385965 (-7)
0	1	3	1.0362075 (-8)	1	0	3	-2.1911020 (-8)
0	0	4	-1.3713227 (-8)	0	4	1	7.7694550 (-11)
1	3	1	6.0000573 (-9)	2	2	1	1.0501379 (-8)
3	1	1	-5.8356372 (-9)	4	0	1	-1.5995372 (-9)
0	3	2	7.2198473 (-12)	1	2	2	-1.0403868 (-8)
2	1	2	-1.7252987 (-8)	3	0	2	3.8552659 (-9)
0	2	3	-1.8855092 (-10)	1	1	3	4.1812060 (-9)
2	0	3	1.0857037 (-8)	0	1	4	2.5960215 (-10)
1	0	4	-5.4855133 (-10)	0	2	4	-7.4394541 (-13)
1	1	4	7.8120025 (-12)	2	0	4	-3.4908282 (-11)

TABLE II
SENSITIVITY OF CROSS SECTIONS
TO WAVE FUNCTIONS

Ground	Hyd ^(a)	Hyd	H-F	H-F
Excited	Hyd	H-F ^(b)	Hyd	H-F
3^1P	.287(+3) ^(c)	.300(+3)	.343(+3)	.359(+3)
4^1P	.115(+3)	.121(+3)	.136(+3)	.143(+3)
3^1D	.484(+1)	.496(+1)		.864(+1)
4^1D	.271(+1)	.270(+1)	.458(+1)	.459(+1)
4^1F	.141(-1)	.140(-1)	.337(-1)	.337(-1)

(a) Hydrogenic function ground state $(1s)^2$ with $Z=1.65$. Excited states $(1s)(nj)$ with $Z_{1s}=2.0$ and $Z_{nj}=1.0$.

(b) Hartree-Fock tabular function of this work.

(c) All cross sections in units of 10^{-20}cm^2 at 100 eV. Numbers in parentheses indicate power of 10.

this work computed in tabular forms. It is seen that the agreements between columns two and three, and between four and five are within 5% at most, leading to the conclusion that the cross sections do not depend sensitively on the accuracy of the excited state wave functions. However, the discrepancy between the two groups of columns is quite severe especially for 3^1D , 4^1D , and 4^1F cross sections, which indicates the desirability of an accurate ground state wave functions for computing cross sections. The variance of the cross sections with the use of the second and the third classes of the wave functions are summarized in Table III. When the correlated wave functions are used for the ground state, the cross sections vary little (less than 10%) with the choice of excited state functions. Somewhat greater (about 20%) variance is noted when the Hartree-Fock wave function is employed for the ground state.

The results of the similar test calculations by the close-coupling method also show typically about 35% change in cross sections going from the hydrogenic to the Hartree-Fock wave functions, but less than 10% difference between the latter and the correlated wave functions.

TABLE III
SENSITIVITY OF CROSS SECTIONS
TO WAVE FUNCTIONS

Ground	H-F ^(a)	SW ^(b)	SW ^(c)	Weiss ^(d)
Excited	H-F	H-F	H-F	Weiss
2 ¹ P		.129(+4) ^(e)	.123(+4)	.131(+4)
3 ¹ P	.359(+3)	.311(+3)	.312(+3)	.322(+3)
4 ¹ P	.143(+3)	.119(+3)	.128(+3)	.130(+3)
3 ¹ D	.864(+1)	.881(+1)	.882(+1)	.907(+1)
4 ¹ D	.459(+1)	.470(+1)	.468(+1)	

(a) This work with Hartree-Fock wave functions.

(b) This work with Stewart and Webb function for ground state.

(c) Ref. 4 with Stewart and Webb ground state function.

(d) Ref. 2 with Weiss functions.

(e) Cross sections at 100 eV in units of 10^{-20} cm^2 .

Numbers inside the parentheses indicate power of 10.

Preliminary Results

In comparing the Born excitation cross sections of He atom with those by experiment,¹² it is immediately noticeable that the agreement between theory and experiment is satisfactory for the dipole-allowed n^1P cross sections. However, for the dipole-forbidden n^1S , n^1D and n^1F states, the Born approximation seems to underestimate the cross sections compared with experiments. It is felt that the discrepancy is possibly due to the omission of the other atomic states, the Born approximation being a two-state approximation. Thus, it is of theoretical interest to see the influence on the cross sections exerted by intermediate states which were previously left out in the formalism of the Born approximation.

For the purpose of studying the indirect coupling effects per se the analyses do not depend critically on the choice of wave functions, sufficed that the quality of the wave functions should remain the same for all computations to be compared. Thus, in the initial stage of this research the wave functions were approximated by the hydrogenic type for simplicity. Guided by the energy criterion of the perturbation theory, the important intermediate states were conjectured (later verified) to be those states of the same principal quantum number. Therefore, the preliminary close-

coupling calculations were made for the incident electron energy of 100 eV, including 1^1S , 3^1S , 3^1P , and 3^1D states, and including 1^1S , 4^1S , 4^1P , 4^1D , and 4^1F states in the scattering equations.

The results of these calculations are tabulated in Table IV and V along with the cross sections by the Born approximation for comparison. It is seen that the excitation cross sections for n^1P states are little influenced by inclusion of other atomic states. On the other hand, by inclusion of n^1P state as an intermediary, the n^1D and 4^1F cross sections are enhanced by factors of four and forty respectively. These results demonstrate the significant roles of the intermediate states, and it is desired to conduct more systematic studies on the indirect coupling effects.

Detailed Analyses

As noted previously there are considerable uncertainties in the computed cross sections associated with using the empirical hydrogenic wave functions. To eliminate this extra variable the correlated wave functions given by Weiss²⁹ are adopted for 1^1S , 2^1S , 3^1S , 2^1P , 3^1P , and 3^1D states. For other states, the Hartree-Fock type wave functions are computed in tabular form to replace the hydrogenic functions.

In order to see how an indirect coupling potential

TABLE IV

CROSS SECTIONS AT 100 eV IN UNITS OF a_0^2
 BY $1^1S-3^1S-3^1P-3^1D$ CLOSE-COUPPLING

L	$Q^L(3^1S)$	$Q^L(3^1P)$	$Q^L(3^1D)$
0	0.797(-3) ^(a)	1.286(-3)	0.305(-4)
1	2.624	0.062	1.320
2	1.931	4.780	1.017
3	1.089	11.054	1.975
4	0.576	14.044	4.832
5	0.312	14.051	7.498
6	0.182	12.458	9.003
7	0.172	10.860	9.268
8	0.081	8.177	8.752
9	0.060	6.342	7.635
10	0.046	4.862	6.470
11	0.036	3.705	5.325
12	0.028	2.810	4.332
13	0.023	2.129	3.475
14	0.018	1.608	2.783
15	0.014	1.216	2.211
16	0.011	0.917	1.758
Q^T	8.000(-3)	1.004(-1)	7.796(-3)
Q^{Born}	5.770(-3)	1.024(-1)	1.770(-3)

(a) Numbers inside the parentheses indicate power of 10.

TABLE V

CROSS SECTIONS AT 100 eV IN UNITS OF a_0^2
 BY $1^1S-4^1S-4^1P-4^1D-4^1F$ CLOSE-COUPPLING

L	$Q^L(4^1S)$	$Q^L(4^1P)$	$Q^L(4^1D)$	$Q^L(4^1F)$
0	0.447(-4) ^(a)	0.395(-3)	0.113(-4)	0.429(-5)
1	2.270	0.083	1.058	0.353
2	3.429	1.733	0.598	0.340
3	3.269	4.256	0.582	0.939
4	2.327	5.603	2.283	1.569
5	1.512	5.746	3.662	1.983
6	1.013	5.169	4.434	2.122
7	0.718	4.311	4.557	2.065
8	0.537	3.446	4.240	1.895
9	0.412	2.687	3.693	1.664
10	0.319	2.068	3.086	1.418
11	0.246	1.580	2.506	1.178
12	0.189	1.202	2.000	0.964
13	0.144	0.913	1.578	0.777
14	0.109	0.692	1.235	0.622
15	0.083	0.525	0.961	0.494
Q^T	1.702(-3)	4.041(-2)	3.659(-3)	1.881(-4)
Q^{Born}		4.114(-2)	0.968(-3)	0.050(-4)

(a) Numbers inside the parentheses indicate power of 10.

affects the cross section, a portion of the scattering equation [Eq. (2.17)] is explicitly written out with $1^1S \rightarrow 3^1D$ excitation as a specific example.

$$\begin{aligned} \mathcal{L} F(3D+) &= U(3D+, 1S) F(1S) + U(3D+, 2P+) F(2P+) \\ &+ U(3D+, 2P-) F(2P-) + U(3D+, 3P+) F(3P+) \\ &+ U(3D+, 3P-) F(3P-) + \dots, \end{aligned} \quad (4.1)$$

where the initial (ground) state index is dropped and the other index (subscript) is written inside the parentheses. "+" and "-" signs following nP indicate $\ell=L+1$ and $\ell=|L-1|$ respectively, and $\mathcal{L}$ is used for the operator in the LHS of Eq. (2.17). It is tacitly assumed in the Born approximation that the direct coupling term [the first term on the RHS of Eq. (4.1)] dominates over all others. Such a reasoning relies heavily on the fact that, the initial state being the 1^1S state, $F(1S)$ is much larger than other $F(nj)$ for $nj \neq 1S$. Though this observation is quite correct, it is noted that the products $U(3D+, nj) F(nj)$ are more meaningful quantities to compare. Indeed, an analysis by "successive approximation" scheme (See Appendix III) shows that the direct coupling term is rather small compared with other (indirect coupling) terms in Eq. (4.1). This is graphically illustrated in Figure 2. One can see the possibility of the indirect coupling term becoming important when the direct coupling term is small such as shown in Figure 2.

Although this illustration is helpful for qualitative

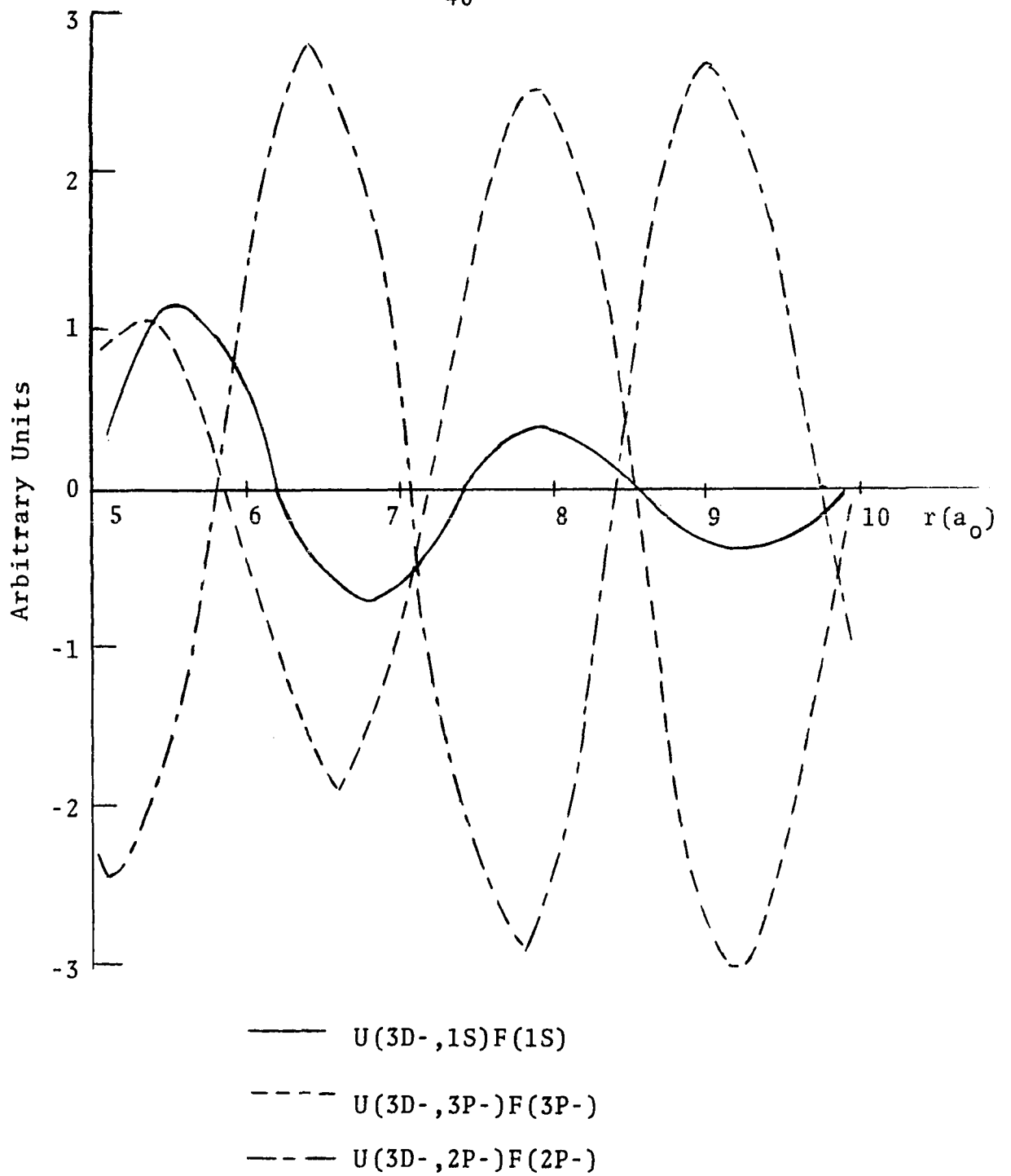


Figure 2. Relative Contributions of Coupling Potentials

understanding of the significant consequence of the intermediate states, the quantitative measure of such effects due to various atomic states can only be measured by repeated calculations of cross sections with different combinations of atomic states included in the scattering equation. For this testing purpose it is adequate to compute some typical partial cross sections corresponding to the total angular momentum L of the system. From the effects exhibited in the partial cross sections, the dependence of cross sections with respect to inclusion of different atomic states can be satisfactorily predicted. Among the numerous calculations, the partial cross sections corresponding to $L=3$ and $L=8$ with inclusion of the following atomic states are presented in Table VI: (1) $1^1S, 2^1S$; (2) $1^1S, 3^1S$; (3) $1^1S, 2^1P$; (4) $1^1S, 3^1P$; (5) $1^1S, 3^1D$; (6) $1^1S, 2^1S, 2^1P$; (7) $1^1S, 2^1P, 3^1P$; (8) $1^1S, 3^1S, 3^1P$; (9) $1^1S, 2^1P, 3^1D$; (10) $1^1S, 3^1P, 3^1D$; (11) $1^1S, 3^1S, 3^1P, 3^1D$; (12) $1^1S, 2^1P, 3^1S, 3^1P, 3^1D$; (13) $n=1,2,3$; (14) $n=1,2,3,4$; (15) $n=1,2,3,4$, and $5^1P, 6^1P, 7^1P, 8^1P$; and (16) $n=1,2,3$, and $(2s)(2p)^1P, (2s)(3p)^1P, (3s)(2p)^1P, (3s)(3p)^1P$. For brevity the notations of $n=1,2,3$, etc. are used to denote the inclusion of all atomic states consistent with the principal quantum numbers indicated. Except those specified in calculation (16), all other states have the singly excited configurations. These calculations are done for the case of incident electron

TABLE VI
EFFECTS OF INTERMEDIATE STATES ON CROSS SECTIONS
AT 100 eV IN UNITS OF a_0^2

Calculation		2^1S	3^1S	2^1P	3^1P	3^1D
(1)	L=3	.120(-1) ^(a)				
	L=8	.651(-4)				
(2)	L=3		.266(-2)			
	L=8		.456(-5)			
(3)	L=3			.375(-1)		
	L=8			.378(-1)		
(4)	L=3				.103(-1)	
	L=8				.105(-1)	
(5)	L=3					.154(-3)
	L=8					.313(-3)
(6)	L=3	.762(-2)		.441(-1)		
	L=8	.986(-3)		.375(-1)		
(7)	L=3			.378(-1)	.109(-1)	
	L=8			.364(-1)	.926(-2)	
(8)	L=3		.131(-2)		.118(-1)	
	L=8		.251(-3)		.103(-1)	
(9)	L=3			.363(-1)		.130(-2)
	L=8			.370(-1)		.798(-3)
(10)	L=3				.103(-1)	.171(-3)
	L=8				.966(-2)	.123(-2)

TABLE VI-Continued

Calculation	2^1S	3^1S	2^1P	3^1P	3^1D
(11) L=3		.120(-2)		.141(-1)	.283(-3)
L=8		.276(-3)		.105(-1)	.128(-2)
(12) L=3		.127(-2)	.411(-1)	.156(-1)	.274(-3)
L=8		.249(-3)	.375(-1)	.103(-1)	.326(-3)
(13) L=3	.728(-2)	.115(-2)	.428(-1)	.139(-1)	.359(-3)
L=8	.102(-2)	.210(-3)	.356(-1)	.962(-2)	.333(-3)
(14) L=3	.782(-2)	.125(-2)	.485(-1)	.156(-1)	.277(-3)
L=8	.107(-2)	.242(-3)	.369(-1)	.987(-2)	.341(-3)
(15) L=3	.742(-2)	.129(-2)	.432(-1)	.141(-1)	.369(-3)
L=8	.115(-2)	.266(-3)	.431(-1)	.118(-1)	.360(-3)
(16) L=3	.779(-2)	.139(-2)	.427(-1)	.139(-1)	.395(-3)
L=8	.116(-2)	.190(-3)	.434(-1)	.122(-1)	.347(-3)

(a) Numbers inside the parentheses indicate power of 10.

energy of 100 eV. The elastic cross sections do not vary much (less than 15%), and are not included in Table VI. The calculations (1) through (5) are two-state close-coupling calculations, and as such the effects of the intermediate states are not included. Other calculations include one or more intermediate states, however.

The comparisons of the 2^1S partial cross sections, computed by calculations (1), (6), and the rest in Table VI, show that the 2^1P state is by far the most important intermediary for the 2^1S cross sections. Similarly, the 3^1P state is seen to be most important for the 3^1S cross sections by comparing calculations (2), (8), and the rest. Although the partial cross sections of the n^1S states do change, the total cross sections are not much affected by inclusion of intermediate states as will be seen later. Thus, the significance of the intermediate states (2^1P and 3^1P states for 2^1S and 3^1S cross sections respectively) is to redistribute the partial cross sections, the consequence of which lies in the angular distribution (the differential cross sections).

Although no great change (20%) in n^1P cross sections is observed by including various intermediate states, it is noted that the 2^1S state affects the 2^1P cross sections more than other states; similarly the 3^1S affects 3^1P cross sections. Furthermore, these changes in n^1P cross sections due to n^1S

states occur for partial cross sections of small angular momentum ($L=3$), indicating the short-range nature of the potential between the 1^1S and n^1S states. It had been expected to see only a small change in the n^1P cross sections, since the direct coupling potentials (1^1S - n^1P) are indeed much larger than the indirect coupling potentials via other atomic states.

Somewhat more complex pattern of the interplay among the intermediate states is seen for the 3^1D cross sections. Compared with the results of calculation (5) (direct coupling alone), the inclusion of the 2^1P or 3^1P states separately [calculations (9) and (10) respectively] enhances the cross sections by an order of magnitude; however, when both the 2^1P and 3^1P states are included simultaneously [calculation (12)], the 3^1D cross sections become much smaller again. Further inclusion of higher states beyond those already included in calculation (12) or (13) does not contribute significantly toward the 3^1D cross sections as evidenced by calculations (12) through (16). The n^1S states do not affect the n^1D cross sections as severely as the n^1P states. Furthermore, by comparing calculations (10) and (11), and (12) and (13), the effect of n^1S states is evidenced only for the partial cross section of small angular momentum ($L=3$). This is due to the fact that in the indirect coupling scheme of 1^1S - n^1S - 3^1D , the 1^1S - n^1S potentials are short range (decaying exponentially for large r), compared

with the 1^1S - n^1P potentials in 1^1S - n^1P - 3^1D scheme, which behaves as r^{-2} for large r .

The destructive interference effect of 2^1P and 3^1P states on the cross sections of the 3^1D state is further analyzed by means of the successive approximation (Appendix III). The severe destructive interference is graphically illustrated in Figure 2. It is expected that the interference should be generally destructive in nature. However, what is surprising is the almost "completeness" of the destructive interference. To understand this phenomenon, it is necessary to examine the "periods" of the channel waves associated with the 2^1P and 3^1P states, and the relative magnitudes and the signs of the coupling potentials connecting 2^1P and 3^1D , and 3^1P and 3^1D states. At high incident electron energy the magnitudes of the wave vectors of all channels become quite close to one another. Therefore, under this circumstance all channel waves would remain approximately in phase in the range of r where the coupling potentials are expected to be effective. It is true not only for the He problem of this research, but also probably for most other cases of electron-atom collision problems. In view of this the relative signs and magnitudes of coupling potentials would dictate whether the interference be constructive or destructive. To see this, the theorem of completeness is helpful, by which the quadrupole matrix element is expanded by the products of dipole

matrix elements as (omitting multiplicative constant),

$$\langle 1^1S | r^2 | 3^1D \rangle = \sum_n \langle 1^1S | r | n^1P \rangle \langle n^1P | r | 3^1D \rangle, \quad (4.2)$$

with the numerical values

n	$\langle 1^1S r n^1P \rangle$	$\langle n^1P r 3^1D \rangle$	Product
2	0.728439	4.827257	3.516363
3	0.360300	-10.014785	-3.608332
4	0.230588	1.275664	0.294153
5	0.162309	0.502958	0.081634
6	0.122379	0.279039	-0.034148
7	0.096596	0.185336	0.017903
8	0.078788	0.135956	0.010712

$$\langle 1^1S | r^2 | 3^1D \rangle = 0.504494 \quad \text{Total} \quad 0.346581$$

Had the summation in Eq. (4.2) covered over the entire complete set, the total would have been exactly equal to 0.504494 as shown. Further, it is noted that the various matrix elements in Eq. (4.2) are in reality the coefficients of the coupling potentials in the asymptotic region. It is immediately obvious from the numerical values in the first two rows why such a severe cancellation occurs between the effects of the 2^1P and 3^1P states. Such a severe cancellation (+3.516 vs. -3.608) found in this work on He may possibly be an exception rather than a rule. Certainly, there appear to be no a priori reasons to suggest the extension of present findings to other collision problems, since the coupling potentials are determined by the

characteristics of atomic states of particular atom under consideration. Moreover, the small increase in 3^1D cross sections with the inclusions of high n^1P states [calculation (15)] is understood by the numerical coefficients for the asymptotic potentials listed above.

In summary it may be stated that the cross sections of the dipole-allowed states are not influenced by the presence of other atomic states, whereas those of the dipole-forbidden states are affected to a significant degree by the indirect coupling routes of 1^1S - n^1P - $n^1S(D)$ type, particularly by those n^1P states which lie between the ground and the upper states.

Comparison with Born Approximation and with Experiments

The total cross sections are computed by the close-coupling method including 1^1S , 2^1S , 3^1S , 2^1P , 3^1P , and 3^1D states at 100 eV of incident electron energy. The partial and the total cross sections are tabulated in Table VII. As mentioned before, the wave functions employed for this calculation are those due to Weiss.²⁹ In Table VIII the comparison is made between the present results and those by the Born approximation, and the experimental data. The Born approximation cross sections are those computed by Bell et al⁴ (also independently by Kim and Inokuti²) using the same wave functions

TABLE VII
TOTAL CROSS SECTIONS AT 100 eV IN UNITS OF a_0^2
BY 1^1S - 2^1S - 3^1S - 2^1P - 3^1P - 3^1D CLOSE-COUPPLING^(a)

L	$Q^L(1^1S)$	$Q^L(2^1S)$	$Q^L(3^1S)$	$Q^L(2^1P)$	$Q^L(3^1P)$	$Q^L(3^1D)$
0	$1.0900 \times 10^{+0}$	0.8334×10^{-2}	1.9571×10^{-3}	0.0768×10^{-1}	0.0267×10^{-1}	0.0382×10^{-3}
1	0.3353	2.8335	6.9687	0.0371	0.0134	0.1492
2	0.0577	1.7103	3.6894	0.2137	0.0727	0.3980
3	0.0107	0.7278	1.1517	0.4280	0.1393	0.3305
4	0.0026	0.2899	0.2794	0.5437	0.1687	0.2907
5	0.0010	0.1591	0.1603	0.5591	0.1681	0.3116
6	0.0005	0.1307	0.2041	0.5111	0.1480	0.3438
7	0.0003	0.1194	0.2273	0.4353	0.1220	0.3571
8	0.0002	0.1038	0.2096	0.3560	0.0962	0.3417
9	0.0002	0.0846	0.1734	0.2834	0.0757	0.3082
10	0.0001	0.0649	0.1308	0.2202	0.0591	0.2623
11	0.0001	0.0491	0.1019	0.1745	0.0451	0.2143
12	0.0001	0.0362	0.0752	0.1328	0.0347	0.1687
13	0.0001	0.0260	0.0573	0.1064	0.0266	0.1321
14		0.0189	0.0430	0.0823	0.0206	0.1030
15		0.0133	0.0328	0.0651	0.0157	0.0769
Q^T	1.4890	7.2009	15.4620	4.2255	1.2326	3.8263

^(a)Wave functions due to Weiss.²⁹

TABLE VIII
COMPARISON WITH BORN CROSS SECTIONS AND WITH EXPERIMENTS

	1^1S	2^1S	3^1S	2^1P	3^1P	3^1D
Present ^(a)	4196 ^(b)	201.6	43.29	1183	345.1	10.71
Born ^(c)	3626	195.6	43.95	1306	322.4	9.07
Expt. ^(d)			28		320	21
Expt. ^(e)			26	870	260	16.6

^(a) Close-coupling including 1^1S - 2^1S - 3^1S - 2^1P - 3^1P - 3^1D with Weiss functions. ²⁹

^(b) All cross sections are in units of 10^{-20} cm^2 .

^(c) Ref. 4.

^(d) Ref. 12.

^(e) Ref. 15.

as those of this work. The results of Van den Bos,⁵ employing somewhat inferior wave functions to those cited above, are not included, the sensitivity of cross sections on the accuracy of wave functions having been discussed earlier.

As expected, the close-coupling results for 2^1P and 3^1P cross sections are quite close to the corresponding Born cross sections. Somewhat unexpectedly, the difference for 2^1S and 3^1S cross sections between the two formalisms is very small, which suggests a possibility that the short-range potentials may be more important than the long-range ones for excitation to n^1S states. This is further borne out by the fact that the most of the contributions to n^1S cross sections come from partial waves of small angular momenta as seen in Table VII. The Born 3^1D cross section at 100 eV seems well established to be $9 \times 10^{-20} \text{ cm}^2$ with very minute differences due to wave functions.^{2,4,5} Fox^{6a} reported the 3^1P and 3^1D cross sections by Born approximation at 100 eV to be 313 and $8.37 \times 10^{-20} \text{ cm}^2$ respectively. The subsequent correction^{6b} to this paper states that these cross sections are to be multiplied by two. This correction would make his computed 3^1D cross section greater than $16 \times 10^{-20} \text{ cm}^2$, but this correction appears to be somewhat unrealistic, since it would also make the 3^1P cross section twice as large.

The measured cross sections of 3^1D by several groups¹²⁻¹⁵

are greater than theoretical values by a factor of two or more. By an optical method St. John, Miller, and Lin¹² obtained 3^1D cross section of $21 \times 10^{-20} \text{ cm}^2$ at 100 eV. The recent results of time-resolved spectroscopy by Anderson, Hughes, and Norton¹⁴ show the value of $23 \pm 3 \times 10^{-20} \text{ cm}^2$ which is in good agreement with that by St. John et al.¹² The 3^1D cross section of $16.6 \times 10^{-20} \text{ cm}^2$ obtained by Moustafa Moussa, De Heer, and Schutten¹⁵ (by optical means) is considerably smaller than other experimental values cited above. It is noted that the experimental cross sections of other states by the latter group are also uniformly smaller than the ones by the former group. However, the ratio $Q(3^1D)/Q(3^1P)$ is seen to agree much better (0.0665 vs. 0.064) between the two groups. Regardless which experimental data one chooses to compare the theoretical values with, the discrepancy is very serious. By including 2^1S , 3^1S , 2^1P , and 3^1P states in the scattering equation, some improvement (16%) is made. However, the present results by no means remove the serious discrepancy between theory and experiment. The fact that the mutual cancellation of the 2^1P - and 3^1P -indirect coupling effects are severe is responsible for the small increase in the 3^1D cross section. Although further inclusion of higher n^1P states or doubly excited 1P states shows a tendency of increasing 3^1D cross section (Table VI), the increase in cross section with each addition of a higher state is too small to

pursue further at this time.

In conclusion the indirect coupling effects have been examined by means of the close-coupling method and found to be significant. Due to the slow rate of convergence in the 3^1D cross section, only a small improvement is made toward removing the discrepancy between theory and experiment.

PART II

APPLICATION OF GAUSSIAN-TYPE ORBITALS TO
COLLISION PROBLEM: ELECTRON EXCITATION
CROSS SECTIONS OF NITROGEN MOLECULE
BY BORN APPROXIMATION

CHAPTER V

INTRODUCTION

Although a great deal of efforts have been directed toward characterizing the electron excitation functions of atoms and comparing the experimental excitation cross sections with the theoretical values in recent years,¹⁻¹⁰ similar studies for molecules are rather sparse in the literature. Even with the simplification of using the Born approximation, computation of the cross sections of electron excitation of the electronic states of diatomic molecules is complicated by the necessity of evaluating multicenter integrals. Indeed calculations of cross sections for diatomic molecules using accurate molecular wave functions have been reported for only a few cases.³³⁻³⁵ The introduction of the Gaussian-type orbitals (GTO), which has been used extensively in the calculations of electronic structure of molecules^{36,37} and more recently of crystalline solids,³⁸ has circumvented the difficulty of multicenter integration to the point that the computational procedure for electron excitation cross sections of molecules is no more complex than the corresponding atomic cases.^{35,39}

A large part of the experimental efforts of measuring electron excitation cross sections of the electronic states of molecules has been devoted to the N_2 molecule. Experimental studies of a number of triplet states have been reported from several laboratories.⁴⁰⁻⁴⁵ Recently the excitation functions of the Lyman-Birge-Hopfield band ($a^1\Pi_g$) and of the $a''^1\Sigma_g^+$ state have been measured.⁴⁶⁻⁴⁹ The availability of these experimental data makes it possible to conduct a comprehensive comparison between theoretical calculations with experiments.

In this thesis are presented the calculations with the Born-type approximations of the electron excitation cross sections of the $a^1\Pi_g$, $c'^1\Sigma_u^+$, $a''^1\Sigma_g^+$, $w^1\Delta_u$, $b'^1\Sigma_u^+$, $b^1\Pi_u$, $A^3\Sigma_u^+$, $B^3\Pi_g$, $C^3\Pi_u$, $D^3\Sigma_u^+$, $W^3\Delta_u$, and $E^3\Sigma_g^+$ states of N_2 by means of the technique of GTO. The cross sections are computed by using different sets of wave functions to test how sensitively the former depend on the accuracy of the latter. Theoretical Born-type cross sections of the $a^1\Pi_g$ and $b^1\Pi_u$ states have been reported by Rozsnyai,⁵⁰ and those of the six triplet states by Cartwright.³⁴ In both Refs. 50 and 34, the molecular wave functions were expressed as linear combinations of the Slater-type orbitals (STO), thus certain approximations were made in order to evaluate the Born integrals. Indeed, in several cases, quite substantial differences are found between the

present results and those of Refs. 50 and 34. Moreover, in comparing the algebraic expressions of cross sections given in Cartwright's paper to those of this thesis, it is noted that Eq. (17) of Ref. 34 gives cross sections which are twice larger than the ones computed according to the present formulation, as noted in the paper.³⁹ This discrepancy is due to an error in the integration over spin variables in Cartwright's work, and the correction for this error has been given.⁵¹

The experimental data of the $a^1\Pi_g$ state furnish a test of the accuracy of the Born approximation (without exchange) as applied to electronic excitation of diatomic molecules since the measurements are extended to energies as high as 2000 eV. For the sake of completion the calculated cross sections (Born approximation) are given for incident energies down to the threshold; however, the interests lie mainly in the high-energy region, since the plane-wave approximation is no longer valid in the near-threshold region. It may be mentioned that while systematic comparisons of theoretical excitation cross sections calculated by the Born approximation with the experimental values have been made for atoms, similar studies for electronic excitation of molecules are very sparse in the literature.

For calculations of singlet-triplet excitation cross sections, modifications of the Born-Oppenheimer approximation

have been introduced by Ochkur⁵² and by Rudge.⁵³ Although the use of the plane-wave approximation is expected to be valid only at high energies, these modifications could possibly provide sufficient degree of improvement over the Born-Oppenheimer scheme so that their applicability may extend to much lower energies than does the Born-Oppenheimer approximation. The singlet-triplet excitation functions fall off with energy much more rapidly than the singlet-singlet counterpart; indeed in most of the experimental work, the energy range of interest lies between threshold and about 50 eV rather than the high-energy region where the triplet cross sections become very small. Accordingly, the discussions of calculated triplet cross sections (by Ochkur's and Rudge's modifications) and their comparison with the experimental data will be confined to incident energies below 40 eV.

CHAPTER VI

FORMULATION

The process of prime interest is the excitation of N_2 from the ground electronic and ground vibrational state to a particular vibrational level of a certain excited electronic state. The rotational structure of the molecule will be neglected; instead, the excitation cross sections are averaged over the orientation of the molecular axis with respect to the direction of incident electron. This is essentially equivalent to summing over the rotational levels of the final state and averaging over those of the initial state.

Born and Born-Oppenheimer Approximations

Consider a system of an incident electron with a diatomic molecule with N electrons (N being even) and denote the spatial and spin coordinates of an electron r_i and σ_i respectively, and the interatomic distance of the molecule by R . To derive a general expression for the excitation-scattering amplitude, a procedure similar to that of Seaton⁵⁴ is adopted for treating an $(N+1)$ -electron system corresponding to an electron-molecule collision process. The first step is

to expand the (N+1)-electron wave function Ψ in terms of the coupled-representation basis functions ψ which are characterized by the total spin quantum numbers S, M_S of the entire system, i.e.,

$$\begin{aligned} \Psi(SM_S | \vec{r}_1, \vec{r}_2, \dots, \vec{r}_{N+1}; \sigma_1 \dots \sigma_{N+1}; R) \\ = (N+1)^{-1/2} \sum_{mv} \sum_{n=1}^{N+1} (-1)^{n-1} \rho_{1,n} \\ \times \psi_m(SM_S | \vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1 \dots \sigma_{N+1}; R) \chi_{mv}(R) F_{mv}(\vec{r}_1) , \end{aligned} \quad (6.1)$$

where the operator $\rho_{1,n}$ exchanges $\vec{r}_1, \sigma_1$ with $\vec{r}_n, \sigma_n$, and the products $\psi_m \chi_{mv}$ constitute the basis functions of expansion. χ_{mv} 's are the vibrational wave functions of the molecule, F_{mv} is the unknown coefficient function to be solved, and the explicit form of ψ_m will be given later. The Hamiltonian of the entire system is

$$\begin{aligned} H = - \sum_{i=1}^{N+1} (\nabla_i^2 / 2 + Z/r_{iA} + Z/r_{iB}) + \sum_{i=1}^N \sum_{j=i+1}^{N+1} |\vec{r}_i - \vec{r}_j|^{-1} \\ - \frac{1}{2\mu} \frac{d^2}{dR^2} + Z^2/R , \end{aligned} \quad (6.2)$$

where Z is the charge of each nucleus and μ is the reduced mass of the two nuclei in the molecule. Unless otherwise specified all the equations are in Hartree's atomic units.

In the Born-type approximation only the terms

appropriate to the initial and final states are retained in Eq. (6.1). The initial (o) state is a spin-singlet state, whereas the final state (n) may be a spin-singlet or -triplet state. ψ_m 's in the basis function are constructed by coupling the spin of the incident electron with that of the molecule so as to form the eigenfunctions of the total spin $S=1/2$, and $M_S=1/2$ as (denoting the spin of the scattered electron by ξ)

$$\begin{aligned} \psi_n(SM_S | \vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_2, \dots, \sigma_{N+1}; R) \\ = \sum_{m_S m_\xi} C(s\xi m_S m_\xi; 1/2 \ 1/2) \\ \times \phi_n(sm_S | \vec{r}_2 \dots \vec{r}_{N+1}; \sigma_2 \dots \sigma_{N+1}; R) \zeta(\xi m_\xi | \sigma_1) , \quad (6.3) \end{aligned}$$

where C , ζ , and ϕ_n are respectively the Clebsch-Gordan coefficient, the spin function, and the anti-symmetrized (determinantal) wave function of N_2 . The application of the variational principle to the Schroedinger equation

$$H\Psi = E\Psi \quad (6.4)$$

leads to

$$\begin{aligned} \sum_{\sigma} \int \psi_m^* (SM_S | \vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_2, \dots, \sigma_{N+1}; R) \chi_{mv}^* (R) [H-E] \\ \times \Psi (SM_S | \vec{r}_1, \vec{r}_2, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_2, \dots, \sigma_{N+1}; R) \\ \times d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_{N+1} R^2 dR = 0 , \quad (6.5) \end{aligned}$$

where $\sum_{\sigma}$ indicates the summation over all spin variables.

When the permutation operation in Eq. (6.1) is effected

Eq. (6.5) becomes

$$\begin{aligned}
& (N+1)^{-1/2} \int_{\sigma} d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_{N+1} R^2 dR \int_{m_s, m_{\xi}} C(s' \xi' m_s, m_{\xi}; SM_S) \\
& \times \phi_m^*(s' m_s, |\vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_2, \sigma_3, \dots, \sigma_{N+1}; R) \\
& \times \zeta^*(\xi' m_{\xi}, |\sigma_1) \chi_{m_V}^*(R) [H-E] \int_{nV} \int_{m_s m_{\xi}} C(s \xi m_s m_{\xi}; SM_S) \\
& \times \{ \phi_n(sm_s | \vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_2, \sigma_3, \dots, \sigma_{N+1}; R) \zeta(\xi m_{\xi} | \sigma_1) \\
& \times F_{nV}(\vec{r}_1) - \phi_n(sm_s | \vec{r}_1, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_3, \dots, \sigma_{N+1}; R) \\
& \times \zeta(\xi m_{\xi} | \sigma_2) F_{nV}(\vec{r}_2) \\
& + \phi_n(sm_s | \vec{r}_2, \vec{r}_1, \dots, \vec{r}_{N+1}; \sigma_2, \sigma_1, \dots, \sigma_{N+1}; R) \\
& \times \zeta(\xi m_{\xi} | \sigma_3) F_{nV}(\vec{r}_3) - + \dots \} \chi_{nV}(R) = 0 \quad (6.6)
\end{aligned}$$

Since $\vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N+1}$, and $\sigma_1, \sigma_2, \dots, \sigma_{N+1}$ are merely the integration coordinates in Eq. (6.6), the indexing of the coordinates may be rearranged such that F_{nV} 's are functions of $\vec{r}_2$ in the second term through the $(N+1)^{th}$ term inside the curly bracket in Eq. (6.6). When this is done, remembering that ϕ_n 's are determinantal functions, all the terms inside the curly bracket except the first term are shown to be equivalent to the second term. For example, the third term is

$$\phi_n(sm_s | \vec{r}_2, \vec{r}_1, \dots, \vec{r}_{N+1}; \sigma_2, \sigma_1, \dots, \sigma_{N+1}; R) \zeta(\xi m_{\xi} | \sigma_3) F_{nV}(\vec{r}_3)$$

$$\begin{aligned}
&= \phi_n(\text{sm}_S | \vec{r}_3, \vec{r}_1, \dots, \vec{r}_{N+1}; \sigma_3, \sigma_1, \dots, \sigma_{N+1}; R) \zeta(\xi m_\xi | \sigma_2) F_{nv}(\vec{r}_2) \\
&= -\phi_n(\text{sm}_S | \vec{r}_1, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_3, \dots, \sigma_{N+1}; R) \zeta(\xi m_\xi | \sigma_2) F_{nv}(\vec{r}_2) ,
\end{aligned}$$

which is equivalent to the second term. Thus, Eq. (6.6) may be written as

$$\begin{aligned}
&\sum_{\sigma} \int d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_{N+1} R^2 dR \psi_m^*(\text{SM}_S | \vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_2, \dots, \sigma_{N+1}; R) \\
&\times \chi_{mv}^*(R) [H-E] \sum_{nv} \{ \psi_n(\text{SM}_S | \vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_2, \dots, \sigma_{N+1}; R) \\
&\times F_{nv}(\vec{r}_1) - N \psi_n(\text{SM}_S | \vec{r}_1, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_2, \dots, \sigma_{N+1}; R) \\
&\times F_{nv}(\vec{r}_2) \} \chi_{nv}(R) = 0 .
\end{aligned} \tag{6.7}$$

Since the target molecule wave functions are known (or assumed) to be exact, Eq. (6.7) becomes

$$\begin{aligned}
&[\nabla_1^2 + k_{mv}^2] F_{mv}(\vec{r}_1) = 2 \sum_{nv} [V_{mv, nv}(\vec{r}_1) F_{nv}(\vec{r}_1) \\
&- W_{mv, nv}(\vec{r}_1)] ,
\end{aligned} \tag{6.8}$$

where

$$\begin{aligned}
V_{mv, nv}(\vec{r}_1) &= \sum_{\sigma} \int d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_{N+1} R^2 dR \\
&\times \psi_m^*(\text{SM}_S | \vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_2, \dots, \sigma_{N+1}; R) \\
&\times \chi_{mv}^*(R) [-Z/r_{1A} - Z/r_{1B} + \sum_{i=2}^{N+1} |\vec{r}_1 - \vec{r}_i|^{-1}] \\
&\times \psi_n(\text{SM}_S | \vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_2, \dots, \sigma_{N+1}; R) \chi_{nv}(R) ,
\end{aligned} \tag{6.9}$$

and

$$\begin{aligned}
W_{mv,nv}(\vec{r}_1) &= N \int d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_{N+1} R^2 dR \\
&\times \psi_m^*(SM_S | \vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_2, \dots, \sigma_{N+1}; R) \chi_{mv}^*(R) \\
&\times \mathcal{H} \psi_n(SM_S | \vec{r}_1, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_2, \dots, \sigma_{N+1}; R) \chi_{nv}(R) \\
&\times F_{nv}(\vec{r}_2) , \tag{6.10}
\end{aligned}$$

where the operator $\mathcal{H}$ may assume, according to either "prior" or "post" formalism,⁵⁴ as

$$\mathcal{H} = -\nabla_2^2 / 2 - Z/r_{2A} - Z/r_{2B} - k_{nv}^2 / 2 + \sum_{i \neq 2}^{N+1} |\vec{r}_2 - \vec{r}_i|^{-1} , \text{ prior}, \tag{6.11}$$

$$\mathcal{H} = -\nabla_1^2 / 2 - Z/r_{1A} - Z/r_{1B} - k_{mv}^2 / 2 + \sum_{i \neq 1}^{N+1} |\vec{r}_1 - \vec{r}_i|^{-1} , \text{ post}. \tag{6.12}$$

In accordance with the Born approximation, Eq. (6.8) is approximated as

$$[\nabla_1^2 + k_{nv}^2] F_{nv}(\vec{r}_1) = 2 \{ V_{nv,oo}(\vec{r}_1) F_{oo}(\vec{r}_1) - W_{nv,oo}(\vec{r}_1) \} , \tag{6.13}$$

where the ground and the excited states are labeled by oo and nv respectively. The potentials V and W are due to direct (no electron exchange) and exchange of electrons respectively. The former is interpreted as the incident electron being scattered while causing an excitation of a molecular electron to a higher orbital, whereas the latter is interpreted as the incident electron being captured in an excited orbital while

ejecting a molecular electron as a scattered electron. For an excitation process of no spin multiplicity change, it is customary to keep only V , the exchange term W making no significant contribution at high energies. On the other hand, for a process of spin multiplicity change, the direct potential V vanishes due to spin orthogonality; hence, the exchange term W is the only contributor. In terms of physics, this means that an electron of opposite spin must be substituted (exchange) in order to change the spin multiplicity of a molecule.

Using the well-known technique,²⁴ the scattered amplitudes in $(\theta\phi)$ direction are

$$f_{nv}(\theta\phi;\theta') = -(2\pi)^{-1} \int \exp(-i\vec{k}_{nv} \cdot \vec{r}_1) V_{nv,oo}(\vec{r}_1) \times F_{oo}(\vec{r}_1) d\vec{r}_1, \text{ direct}, \quad (6.14)$$

$$g_{nv}^{\pm}(\theta\phi;\theta') = (2\pi)^{-1} \int \exp(-i\vec{k}_{nv} \cdot \vec{r}_1) W_{nv,oo}^{\pm}(\vec{r}_1) d\vec{r}_1, \quad \text{exchange}, \quad (6.15)$$

where θ' designates the orientation of the molecular axis with respect to the direction of the incident electron, and "+" and "-" signs refer to the spin non-exchange, and spin exchange processes respectively. The averaged differential cross sections for exciting the molecule from the ground to an electronic-vibrational excited state nv are

$$I^S(o \rightarrow nv | \theta \phi) = (\omega_n k_{nv} / 2k_{oo}) \int_0^\pi |f_{nv}(\theta \phi; \theta')|^2 \sin \theta' d\theta' , \quad (6.16)$$

$$I^T(o \rightarrow nv | \theta \phi) = (\omega_n k_{nv} / 2k_{oo}) \int_0^\pi |g_{nv}^-(\theta \phi; \theta')|^2 \sin \theta' d\theta' , \quad (6.17)$$

where I^S and I^T refer to a singlet and a triplet final state respectively, the integration $\sin \theta' d\theta'$ results from averaging over the orientation of the molecular axis with respect to the direction of the incident electron, and ω_n is the degeneracy of the final electronic state. For a diatomic molecule, electronic states are doubly degenerate with respect to $\Lambda = |\pm M|$ except the case $M=0$, where M is the component of the angular momentum in the direction of the molecular axis.⁵⁵ Thus all but Σ state ($\Lambda=0$) are doubly degenerate.

In order to evaluate f_{nv} and $g_{nv}^\pm$, the basis functions are explicitly written as

$$\begin{aligned} & \psi_o(1/2 \ 1/2 | \vec{r}_1, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_2, \dots, \sigma_{N+1}; R) \\ &= (N!)^{-1/2} \begin{vmatrix} u_1(1) & u_2(1) & \dots & u_{N-2}(1) & u_{N-1}(1) & u_N(1) \\ u_1(3) & u_2(3) & \dots & u_{N-2}(3) & u_{N-1}(3) & u_N(3) \\ \vdots & & & & & \\ u_1(N+1) & \dots & & & & u_N(N+1) \end{vmatrix} \alpha(2) \\ &= D^{(u)} [u_1(1)u_2(3)\dots u_{N-1}(N)u_N(N+1)] \alpha(2) , \quad (6.18) \end{aligned}$$

$$\psi_n(1/2 \ 1/2 | \vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_2, \dots, \sigma_{N+1}; R)$$

$$= (N!)^{1/2} \sqrt{\frac{1}{2}} \left[\begin{array}{c} \left| \begin{array}{cccccc} b_1(2) & b_2(2) & \dots & b_{N-2}(2) & b_{N-1}(2) & b_N(2) \\ b_1(3) & b_2(3) & \dots & b_{N-2}(3) & b_{N-1}(3) & b_N(3) \\ \vdots & \vdots & & \vdots & \vdots & \vdots \\ b_1(N+1) & \dots & & & & b_N(N+1) \end{array} \right| \\ \left. \begin{array}{c} \left| \begin{array}{cccccc} c_1(2) & c_2(2) & \dots & c_{N-2}(2) & c_{N-1}(2) & c_N(2) \\ c_1(3) & c_2(3) & \dots & c_{N-2}(3) & c_{N-1}(3) & c_N(3) \\ \vdots & \vdots & & \vdots & \vdots & \vdots \\ c_1(N+1) & \dots & & & & c_N(N+1) \end{array} \right| \\ \alpha(1) \end{array} \right] \\ = \sqrt{1/2} \{ D^{(b)} [b_1(2) \ b_2(3) \ \dots \ b_{N-1}(N) \ b_N(N+1)] \\ - D^{(c)} [c_1(2) \ c_2(3) \ \dots \ c_{N-1}(N) \ c_N(N+1)] \} \alpha(1) , \\ \text{for singlet,} \quad (6.19)$$

$$\psi_n(1/2 \ 1/2 | \vec{r}_2, \vec{r}_3, \dots, \vec{r}_{N+1}; \sigma_1, \sigma_2, \dots, \sigma_{N+1}; R)$$

$$= (N!)^{1/2} \left[\begin{array}{c} \sqrt{\frac{2}{3}} \left| \begin{array}{cccccc} a_1(2) & a_2(2) & \dots & a_{N-2}(2) & a_{N-1}(2) & a_N(2) \\ a_1(3) & a_2(3) & \dots & a_{N-2}(3) & a_{N-1}(3) & a_N(3) \\ \vdots & \vdots & & \vdots & \vdots & \vdots \\ a_1(N+1) & \dots & & & & a_N(N+1) \end{array} \right| \end{array} \right] \beta(1)$$

$$\begin{aligned}
& - \sqrt{\frac{1}{3}} \sqrt{\frac{1}{2}} \left\{ \begin{vmatrix} b_1(2) & b_2(2) & \dots & b_{N-2}(2) & b_{N-1}(2) & b_N(2) \\ b_1(3) & b_2(3) & \dots & b_{N-2}(3) & b_{N-1}(3) & b_N(3) \\ \vdots & & & & & \\ b_1(N+1) & \dots & & & & b_N(N+1) \end{vmatrix} \right\} \alpha(1) \\
& + \left\{ \begin{vmatrix} c_1(2) & c_2(2) & \dots & c_{N-2}(2) & c_{N-1}(2) & c_N(2) \\ c_1(3) & c_2(3) & \dots & c_{N-2}(3) & c_{N-1}(3) & c_N(3) \\ \vdots & & & & & \\ c_1(N+1) & \dots & & & & c_N(N+1) \end{vmatrix} \right\} \alpha(1) \\
& = \sqrt{2/3} D^{(a)} [a_1(2) a_2(3) \dots a_{N-1}(N) a_N(N+1)] \beta(1) \\
& - \sqrt{1/3} \sqrt{1/2} \{ D^{(b)} [b_1(2) b_2(3) \dots b_{N-1}(N) b_N(N+1)] \\
& + D^{(c)} [c_1(2) c_2(3) \dots c_{N-1}(N) c_N(N+1)] \} \alpha(1) , \\
& \text{for triplet,} \quad (6.20)
\end{aligned}$$

where u_i , a_i , b_i , c_i are the orthonormal one electron spin-orbitals which depend on R as parameter, and α and β are the spinfunctions. The electron coordinates $\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{N+1}$ are simply denoted inside the parentheses by numerics 1, 2, ..., $N+1$. The factors $\sqrt{2/3}$ and $-\sqrt{1/3}$ are the appropriate Clebsch-Gordan coefficients consistent with the spin assignments given in Eq. (6.22), and the factor $\sqrt{1/2}$ is the normalization constant for two determinantal functions. The short notation "D" is

used for convenience to denote the normalized determinants with the principal diagonals written inside the brackets. To the extent of dealing with single electron excitation processes, all spin-orbitals except two in Eqs. (6.18), (6.19), and (6.20) are identical, e.g.,

$$u_i = a_i = b_i = c_i, \quad \text{for } i=1, \dots, N-2. \quad (6.21)$$

The remaining two spin-orbitals are

$$\begin{aligned} u_{N-1}(\vec{r}, \sigma) &= p(\vec{r})\alpha(\sigma) \\ u_N(\vec{r}, \sigma) &= p(\vec{r})\beta(\sigma) \\ a_{N-1}(\vec{r}, \sigma) &= p(\vec{r})\alpha(\sigma) \\ a_N(\vec{r}, \sigma) &= p'(\vec{r})\alpha(\sigma) \\ b_{N-1}(\vec{r}, \sigma) &= p(\vec{r})\alpha(\sigma) \\ b_N(\vec{r}, \sigma) &= p'(\vec{r})\beta(\sigma) \\ c_{N-1}(\vec{r}, \sigma) &= p(\vec{r})\beta(\sigma) \\ c_N(\vec{r}, \sigma) &= p'(\vec{r})\alpha(\sigma), \end{aligned} \quad (6.22)$$

where p and p' are respectively the ground and the excited orbitals. With the substitution of Eqs. (6.18) and (6.19), Eq. (6.9) is evaluated

$$\begin{aligned} V_{nv,00}(\vec{r}_1) &= \int \chi_{nv}^*(R) \chi_{00}(R) R^2 dR \int_{\sigma} d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_{N+1} \\ &\times \sqrt{1/2} \{D^{(b)}\}^* [b_1(2) b_2(3) \dots b_{N-1}(N) b_N(N+1)] \end{aligned}$$

$$\begin{aligned}
& - D^{(c)*} [c_1(2) c_2(3) \dots c_{N-1}(N) c_N(N+1)] \} \\
& \times \alpha^*(1) [-Z/r_{1A} - Z/r_{1B} + \sum_{i=2}^{N+1} |\vec{r}_1 - \vec{r}_i|^{-1}] \\
& \times D^{(u)} [u_1(2) u_2(3) \dots u_{N-1}(N) u_N(N+1)] \alpha(1) . \quad (6.23)
\end{aligned}$$

In substituting Eq. (6.18), $\vec{r}_1$ is replaced by $\vec{r}_2$ as indicated in Eq. (6.9). As far as two pairs of determinants $[D^{(b)*}$ and $D^{(u)}$, and $D^{(c)*}$ and $D^{(u)}$] in Eq. (6.23) are concerned the term $(-Z/r_{1A} - Z/r_{1B})$ is constant, whereas $\sum_i |\vec{r}_1 - \vec{r}_i|^{-1}$ is a one-electron operator. The two determinants in each pair differing by a column, the former makes no contribution (orthogonality), whereas the latter gives an identical result for each pair, viz.,

$$\begin{aligned}
V_{nv,00}(\vec{r}_1) &= 2\sqrt{1/2} \int \chi_{nv}^*(R) \chi_{00}(R) R^2 dR \int p'^*(\vec{r}_2) |\vec{r}_1 - \vec{r}_i|^{-1} \\
&\times p(\vec{r}_2) d\vec{r}_2 . \quad (6.24)
\end{aligned}$$

The properties of determinantal functions are found in the literature.⁵⁶ The evaluation of the exchange integrals is somewhat more complex because ψ_m and ψ_n in Eq. (6.10) are not functions of the same electron coordinates. However, the exchange integrals for excitations to a singlet and a triplet state may be constructed as

$$\begin{aligned}
W_{nv,00}^+(\vec{r}_1) &= \int \chi_{nv}^*(R) \chi_{00}(R) R^2 dR \sqrt{1/2} [W^{(b)}(\vec{r}_1) - W^{(c)}(\vec{r}_1)] , \\
&\text{for singlet,} \quad (6.25)
\end{aligned}$$

$$\begin{aligned}
W_{nv,00}^-(\vec{r}_1) &= \int \chi_{nv}^*(R) \chi_{00}(R) R^2 dR [\sqrt{2/3} W^{(a)}(\vec{r}_1) \\
&\quad - \sqrt{1/6} W^{(b)}(\vec{r}_1) - \sqrt{1/6} W^{(c)}(\vec{r}_1)] , \quad \text{for triplet.}
\end{aligned}
\tag{6.26}$$

$$\begin{aligned}
W^{(i)}(\vec{r}_1) &= N \int_{\sigma} d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_{N+1} \mathcal{D}^{(i)*} \mathcal{H} \\
&\quad \times D^{(u)} [u_1(1) \ u_2(3) \ \dots \ u_{N-1}(N) \ u_N(N+1)] \alpha(2) F_{00}(2) , \\
&\quad i=a,b,c, \tag{6.27}
\end{aligned}$$

where

$$\begin{aligned}
\mathcal{D}^{(a)} &= D^{(a)} [a_1(2) \ a_2(3) \ \dots \ a_{N-1}(N) \ a_N(N+1)] \beta(1) \\
\mathcal{D}^{(b)} &= D^{(b)} [b_1(2) \ b_2(3) \ \dots \ b_{N-1}(N) \ b_N(N+1)] \alpha(1) \tag{6.28} \\
\mathcal{D}^{(c)} &= D^{(c)} [c_1(2) \ c_2(3) \ \dots \ c_{N-1}(N) \ c_N(N+1)] \alpha(1) ,
\end{aligned}$$

and the prior form of $\mathcal{H}$ is grouped as

$$\begin{aligned}
\mathcal{H} &= H' + \sum_{m=3}^{N+1} |\vec{r}_2 - \vec{r}_m|^{-1} \\
H' &= -\nabla_2^2/2 - Z/r_{2A} - Z/r_{2B} - k_{00}^2/2 + |\vec{r}_1 - \vec{r}_2|^{-1} .
\end{aligned}
\tag{6.29}$$

After substitution of Eq. (6.28) in Eq. (6.27), each of the two determinants $D^{(i)}$ and $D^{(u)}$ are expanded by its first row elements, e.g.,

$$\begin{aligned}
W^{(a)}(\vec{r}_1) &= N \int_{\sigma} d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_{N+1} \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N (-1)^{i+j} \beta^*(1) a_i^*(2) \\
&\quad \times \Delta_i^{(a)*} [H' + \sum_{m=3}^{N+1} |\vec{r}_2 - \vec{r}_m|^{-1}] u_j(1) \Delta_j^{(u)} \alpha(2) F_{00}(2) , \tag{6.30}
\end{aligned}$$

where $\Delta_i^{(a)}$ and $\Delta_i^{(u)}$ are respectively the normalized minor determinants formed from the determinants $D^{(a)}$ and $D^{(u)}$ by omitting the first row and the i^{th} column. H' is a constant as far as the minor determinants are concerned; thus, integration and summation over coordinates 3 through $N+1$ give vanishing results, unless $i=j=N$ in which case the result is unity. Because $\sum_{m=3}^{N+1} |\vec{r}_2 - \vec{r}_m|^{-1}$ is a one-electron operator, there are more terms resulting from the integration. The results, after integration and summation over coordinates 4 through $N+1$, are

$$\begin{aligned}
 W^{(a)}(\vec{r}_1) &= \int_{\sigma} d\vec{r}_2 d\vec{r}_3 \beta^*(1) p'^*(2) \alpha^*(2) p^*(3) \alpha^*(3) \\
 &\times H' p(1) \beta(1) p(3) \alpha(3) \alpha(2) F_{oo}(2) \\
 &+ \sum_{i=1}^{N-1} \int_{\sigma} d\vec{r}_2 d\vec{r}_3 \{ [\beta^*(1) a_i^*(2) p'^*(3) \alpha^*(3) r_{23}^{-1} u_i(1) p(3) \beta(3) \\
 &+ \beta^*(1) p'^*(2) \alpha^*(2) a_i^*(3) r_{23}^{-1} p(1) \beta(1) u_i(3)] \alpha(2) F_{oo}(2) \} , \\
 &\hspace{15em} (6.31)
 \end{aligned}$$

$$\begin{aligned}
 W^{(b)}(\vec{r}_1) &= \int_{\sigma} d\vec{r}_2 d\vec{r}_3 \alpha^*(1) p'^*(2) \beta^*(2) p^*(3) \alpha^*(3) \\
 &\times H' p(1) \beta(1) p(3) \alpha(3) \alpha(2) F_{oo}(2) \\
 &+ \sum_{i=1}^{N-1} \int_{\sigma} d\vec{r}_2 d\vec{r}_3 \{ [\alpha^*(1) b_i^*(2) p'^*(3) \beta^*(3) r_{23}^{-1} u_i(1) p(3) \beta(3) \\
 &+ \alpha^*(1) p'^*(2) \beta^*(2) b_i^*(3) r_{23}^{-1} p(1) \beta(1) u_i(3)] \alpha(2) F_{oo}(2) \} , \\
 &\hspace{15em} (6.32)
 \end{aligned}$$

$$\begin{aligned}
W^{(c)}(\vec{r}_1) = & - \sum_{\sigma} \int d\vec{r}_2 d\vec{r}_3 \alpha^*(1) p'^*(2) \alpha^*(2) p^*(3) \beta^*(3) \\
& \times H' p(1) \alpha(1) p(3) \beta(3) \alpha(2) F_{00}(2) \\
& + \sum_{i=1}^{N-1} \sum_{\sigma} \int d\vec{r}_2 d\vec{r}_3 \{ [\alpha^*(1) c_i^*(2) p'^*(3) \alpha^*(3) r_{23}^{-1} u_i(1) p(3) \alpha(3) \\
& + \alpha^*(1) p'^*(2) \alpha^*(2) c_i^*(3) r_{23}^{-1} p(1) \alpha(1) u_i(3)] \alpha(2) F_{00}(2) \} ,
\end{aligned} \tag{6.33}$$

where $r_{23} = |\vec{r}_2 - \vec{r}_3|$, and the minus sign in the first member of Eq. (6.33) arises from interchange of two columns in the minor determinant. It is also noted that the first member of Eq. (6.32) vanishes due to the spin orthogonality.

Ochkur's and Rudge's Modifications

With the expressions of W^+ and W^- given in Eqs. (6.25) and (6.26), and with replacement of $F_{00}(\vec{r})$ by $\exp(i\vec{k}_{00} \cdot \vec{r})$, the Born-Oppenheimer exchange amplitudes could be evaluated. However, there is a serious discrepancy between the results obtained using the prior and the post interaction formulations in practice, although the two formulations would give an identical result if the wave functions of the collision system were exact.⁵⁷ Moreover, the computed cross sections by the Born-Oppenheimer approximation exceed the conservation limit of incident electron flux, which is traceable to lack of orthogonality between wave functions, $\exp(i\vec{k}_{00} \cdot \vec{r}_1) \psi_0(\vec{r}_2, \vec{r}_3, \dots)$

and $\exp(i\vec{k}_{nv} \cdot \vec{r}_2) \psi_n(\vec{r}_1, \vec{r}_3, \dots)$, which describe the conditions before and after the exchange collision process.¹ Ochkur⁵² and subsequently Rudge⁵³ made modifications to the Born-Oppenheimer approximation, both of which remove the major shortcomings of the Born-Oppenheimer approximation.

In his work on e-He problem, Ochkur⁵² has shown by partial differentiations that

$$\begin{aligned} I(r_{12}^{-1}) &= \int r_{12}^{-1} \exp\{i(\vec{k}_{oo} \cdot \vec{r}_2 - \vec{k}_{nv} \cdot \vec{r}_1)\} \\ &\times p^*(\vec{r}_3) p'^*(\vec{r}_2) p(\vec{r}_1) p(\vec{r}_3) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \\ &= 4\pi k_{>}^{-2} \int \exp\{i(\vec{k}_{oo} - \vec{k}_{nv}) \cdot \vec{r}_1\} p'^*(\vec{r}_1) p(\vec{r}_1) d\vec{r}_1, \quad (6.34) \end{aligned}$$

$$\begin{aligned} I(r_{23}^{-1}) &= \int r_{23}^{-1} \exp\{i(\vec{k}_{oo} \cdot \vec{r}_2 - \vec{k}_{nv} \cdot \vec{r}_1)\} \\ &\times p^*(\vec{r}_3) p'^*(\vec{r}_2) p(\vec{r}_1) p(\vec{r}_3) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \\ &= O(k_{>}^{-6}), \quad (6.35) \end{aligned}$$

$$\begin{aligned} I(r_2^{-1}) &= \int r_2^{-1} \exp\{i(\vec{k}_{oo} \cdot \vec{r}_2 - \vec{k}_{nv} \cdot \vec{r}_1)\} \\ &\times p^*(\vec{r}_3) p'^*(\vec{r}_2) p(\vec{r}_1) p(\vec{r}_3) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \\ &= O(k_{>}^{-6}), \quad (6.36) \end{aligned}$$

where $k_{>}$ is the greater of k_{oo} and k_{nv} . In evaluating the exchange collision amplitudes, Ochkur discards the terms of type as in Eqs. (6.35) and (6.36) since they are of higher

order of smallness compared with the terms of type as in Eq. (6.34). Within the framework of the Ochkur's modification, Eqs. (6.31), (6.32), and (6.33) become operationally equivalent to

$$\begin{aligned} W^{(a)}(\vec{r}_1) &\rightarrow 4\pi k_{oo}^{-2} p'^*(\vec{r}_1) p(\vec{r}_1) , \\ W^{(b)}(\vec{r}_1) &\rightarrow 0 , \\ W^{(c)}(\vec{r}_1) &\rightarrow -4\pi k_{oo}^{-2} p'^*(\vec{r}_1) p(\vec{r}_1) , \end{aligned} \quad (6.37)$$

where k_{γ} is replaced by k_{oo} (excitation). Now by means of Eqs. (6.25) and (6.26), the exchange amplitudes in Eq. (6.15) become

$$\begin{aligned} g_{nv}^+(\theta\phi; \theta') &= \sqrt{2} k_{oo}^{-2} \int \exp\{i(\vec{k}_{oo} - \vec{k}_{nv}) \cdot \vec{r}_1\} p'^*(\vec{r}_1) p(\vec{r}_1) d\vec{r}_1 \\ &\times \chi_{nv}^*(R) \chi_{oo}(R) R^2 dR , \end{aligned} \quad (6.38)$$

$$\begin{aligned} g_{nv}^-(\theta\phi; \theta') &= 2\sqrt{3/2} k_{oo}^{-2} \int \exp\{i(\vec{k}_{oo} - \vec{k}_{nv}) \cdot \vec{r}_1\} \\ &\times p'^*(\vec{r}_1) p(\vec{r}_1) d\vec{r}_1 \chi_{nv}^*(R) \chi_{oo}(R) R^2 dR . \end{aligned} \quad (6.39)$$

The Rudge's modification⁵³ entails to the replacement of k_{oo}^2 by $(k_{nv} - i\varepsilon^{1/2})^2$, where ε is the ionization potential of the initial state in Rydberg units. The direct collision amplitude is obtained by substitution of Eq. (6.24) in Eq. (6.14) with $F_{oo}(\vec{r}_1)$ replaced by $\exp(i\vec{k}_{oo} \cdot \vec{r}_1)$ as

$$\begin{aligned} f_{nv}(\theta\phi; \theta') &= -(2\pi)^{-1} \sqrt{2} \int \exp\{i(\vec{k}_{oo} - \vec{k}_{nv}) \cdot \vec{r}_1\} \\ &\times r_{12}^{-1} p'^*(\vec{r}_2) p(\vec{r}_2) \chi_{nv}^*(R) \chi_{oo}(R) R^2 dR d\vec{r}_1 d\vec{r}_2 \end{aligned}$$

$$= -2\sqrt{Z} K^{-2} \int \exp(i\vec{K} \cdot \vec{r}) p'^*(\vec{r}) p(\vec{r}) \chi_{nv}^*(R) \chi_{oo}(R) R^2 dR d\vec{r} , \quad (6.40)$$

where $\vec{K} = \vec{k}_{oo} - \vec{k}_{nv}$. Introducing the transition amplitude

$$\mathcal{O}_{on}(K; \theta', R) = -\sqrt{Z} \int \exp(i\vec{K} \cdot \vec{r}) p'^*(\vec{r}) p(\vec{r}) d\vec{r} , \quad (6.41)$$

the differential cross sections may be expressed as

$$I^S(oo \rightarrow nv | \theta \phi) = (\omega_n k_{nv} / 2k_{oo}) \int_0^\pi | \int (2K^{-2} - T^{-2}) \mathcal{O}_{on}(K; \theta', R) \\ \times \chi_{nv}^*(R) \chi_{oo}(R) R^2 dR |^2 \sin \theta' d\theta' , \quad (6.42)$$

$$I^T(oo \rightarrow nv | \theta \phi) = (3\omega_n k_{nv} / 2k_{oo}) \int_0^\pi | \int -T^{-2} \mathcal{O}_{on}(K; \theta', R) \\ \times \chi_{nv}^*(R) \chi_{oo}(R) R^2 dR |^2 \sin \theta' d\theta' , \quad (6.43)$$

where

$$T^2 = \begin{cases} k_{oo}^2 , & \text{excitation,} \\ k_{nv}^2 , & \text{de-excitation,} \end{cases} \quad \text{Ochkur ,} \quad (6.44)$$

$$T^2 = (k_{nv} - i\varepsilon^{1/2})^2 , \quad \text{Rudge.}$$

Franck-Condon Factor Approximation

When the vibrational function χ_{oo} of the initial state has a localized form, the overlap between χ_{oo} and χ_{nv} is appreciable only for a small range R . Within this limited range of R , $\mathcal{O}_{on}(K; \theta', R)$ is found to be a slowly varying function of R .^{33,35} In such a case, a substantial simplification is made

by suppressing the dependence of $\mathcal{E}_{\text{on}}(K; \theta', R)$ on R , and evaluating $\mathcal{E}_{\text{on}}(K; \theta', R)$ at R_0 which is the equilibrium bond length of the molecule. This is known as the Franck-Condon factor approximation. With this approximation,

$$I^S(\text{oo} \rightarrow \text{nv} | \theta \phi) = (\omega_n k_{\text{nv}} q_{\text{nv}} / 2k_{\text{oo}}) \int_0^\pi | (2K^{-2} - T^{-2}) \times \mathcal{E}_{\text{on}}(K; \theta', R_0) |^2 \sin \theta' d\theta' , \quad (6.45)$$

$$I^T(\text{oo} \rightarrow \text{nv} | \theta \phi) = (3\omega_n k_{\text{nv}} q_{\text{nv}} / 2k_{\text{oo}}) \int_0^\pi | T^{-2} \mathcal{E}_{\text{on}}(K; \theta', R_0) |^2 \times \sin \theta' d\theta' , \quad (6.46)$$

where the Franck-Condon factor q_{nv} is

$$q_{\text{nv}} = | \int \chi_{\text{nv}}^*(R) \chi_{\text{oo}}(R) R^2 dR |^2 , \quad (6.47)$$

The total cross sections for excitation to an electronic-vibrational state are obtained by integration of the differential cross sections over all solid angle $\sin \theta d\theta d\phi$. Using the momentum-change variable,

$$K^2 = k_{\text{oo}}^2 + k_{\text{nv}}^2 - 2k_{\text{oo}}k_{\text{nv}} \cos \theta , \quad (6.48)$$

$$Q^S(\text{oo} \rightarrow \text{nv}) = (\pi \omega_n q_{\text{nv}} / k_{\text{oo}}^2) \int_{K_{\text{min}}}^{K_{\text{max}}} K dK \int_0^\pi | (2K^{-2} - T^{-2}) \times \mathcal{E}_{\text{on}}(K; \theta', R_0) |^2 \sin \theta' d\theta' , \quad (6.49)$$

$$Q^T(\text{oo} \rightarrow \text{nv}) = (3\pi \omega_n q_{\text{nv}} / k_{\text{oo}}^2) \int_{K_{\text{min}}}^{K_{\text{max}}} K dK \int_0^\pi | T^{-2} \mathcal{E}_{\text{on}}(K; \theta', R_0) |^2 \times \sin \theta' d\theta' ,$$

where

$$\begin{aligned} K_{\min} &= k_{oo} - k_{nv} , \\ K_{\max} &= k_{oo} + k_{nv} . \end{aligned} \quad (6.50)$$

The total cross sections for excitation to an electronic state are

$$\begin{aligned} Q^S(o \rightarrow n) &= \sum_v Q^S(oo \rightarrow nv) , \\ Q^T(o \rightarrow n) &= \sum_v Q^T(oo \rightarrow nv) . \end{aligned} \quad (6.51)$$

Although in principle the values of $K_{\max}$ and $K_{\min}$ depend on v , except near the threshold one can ignore their variations due to the vertical excitation energies to different vibrational levels of the upper electronic state and simply use some mean value $\bar{K}_{\max}$ and $\bar{K}_{\min}$ for all vibrational components, i.e.,

$$\begin{aligned} Q^S(o \rightarrow n) &\approx (\sum_v q_{nv}) (\pi \omega_n / k_{oo}^2) \int_{\bar{K}_{\min}}^{\bar{K}_{\max}} K dK \\ &\times \int_0^\pi | (2K^{-2} - T^{-2}) \mathcal{E}_{on}(K; \theta', R_o) |^2 \sin \theta' d\theta' \\ &= (\pi \omega_n / k_{oo}^2) \int_{\bar{K}_{\min}}^{\bar{K}_{\max}} K dK \int_0^\pi | (2K^{-2} - T^{-2}) \mathcal{E}_{on}(K; \theta', R_o) |^2 \\ &\times \sin \theta' d\theta' . \end{aligned} \quad (6.52)$$

The error in the total cross section due to this approximation is about 2% at 40 eV, and at energies greater than 100 eV the error is completely negligible. However, the use of Eq. (6.51)

requires reliable Franck-Condon factors whereas the use of Eq. (6.52) does not. In this work the cross sections of the all triplet states and the $a^1\Pi_g$ state are computed by Eq. (6.51). The Franck-Condon factors used in this work are due to Benesch et al⁵⁸ for $a^1\Pi_g$, $B^3\Pi_g$, $C^3\Pi_u$, and $A^3\Sigma_u^+$; and due to Cartwright³³ for $W^3\Delta_u$, $E^3\Sigma_g^+$, and $D^3\Sigma_u^+$ states. For other singlet states ($b^1\Pi_u$, $b'^1\Sigma_u^+$, $w^1\Delta_u$, $a''^1\Sigma_g^+$, $c'^1\Sigma_u^+$), the cross sections are computed by using Eq. (6.52).

It is convenient to introduce the quantity

$$G_{on}(K) = (\omega_n/K^2) \int_0^\pi |\mathcal{E}_{on}(K; \theta', R_0)|^2 \sin\theta' d\theta' , \quad (6.53)$$

from which one can easily obtain both the singlet and the triplet excitation cross sections. The function $G_{on}(K)$ depends only on the wave functions of the initial and the final states; therefore, it is especially suitable for testing the sensitivity of cross sections on the accuracy of the wave functions used. The generalized oscillator strength $\mathcal{G}_{on}(K)$ is related to $G_{on}(K)$ as

$$\mathcal{G}_{on}(K) = (\Delta E) G_{on}(K) , \quad (6.54)$$

where ΔE is the vertical excitation energy.

CHAPTER VII

METHODS OF COMPUTATION

The wave function of a molecule is customarily expressed as a linear combination of atomic orbitals (LCAO) of the constituent atoms. Further, the atomic orbitals have been traditionally expressed by the Slater-type orbitals (STO), which are the products of exponential and polynomial functions. Indeed, an examination of atomic Hartree-Fock equation shows that the solutions (i.e., atomic orbitals) would have the form of STO; therefore, STO is the natural choice as far as atomic problems are concerned. However, in applications of quantum mechanics beyond atoms to molecules and solids, the progress is impeded to a large extent by the extreme computational difficulty of evaluating multicenter integrals associated with the use of STO's. On the other hand, the Gaussian-type orbitals (GTO), admittedly inferior to STO in representing an atomic orbital, do not lead to such a computational difficulty. Thus, even if several GTO's are needed to represent an atomic orbital to the same fidelity as one STO would, such a disadvantage is far outweighed by the advantage gained in computational ease. In fact the advantage

of using GTO functions is amply demonstrated in the molecular structure calculations,³⁶ in the electronic band structure calculations of solids,³⁸ and in the studies of electron-molecule collision problems.^{35,39} Therefore, the technique of GTO is adopted in this work.

Transition Amplitudes

To avoid a duplication of notations, the ground and the excited molecular orbitals in Eq. (6.41) are denoted by ϕ_λ and ϕ_λ^* , respectively. With these notations transition amplitude is

$$\mathcal{O}_{\text{on}}(K; \theta') = -\sqrt{2} \int \phi_\lambda^*(\vec{r}) \exp(i\vec{K} \cdot \vec{r}) \phi_\lambda(\vec{r}) d\vec{r} , \quad (7.1)$$

where the subscript in $\vec{r}_1$ is dropped, and the R-dependence is suppressed by using the Franck-Condon factor approximation. Thus, it is understood that the molecular orbitals ϕ_λ and ϕ_λ^* , are those corresponding to the equilibrium internuclear separation R_0 of the ground state. Each molecular orbital is given in LCAO form as

$$\phi_\lambda = \sum_{\ell} c_{\ell} [u_{\ell}(\vec{r}_A) + M(\lambda, \ell) u_{\ell}(\vec{r}_B)] , \quad (7.2)$$

where $u_{\ell}(\vec{r}_A)$ and $u_{\ell}(\vec{r}_B)$ are atomic orbitals centered at nuclei A and B respectively. Here, ℓ represents a collection of quantum numbers for an atomic orbital and c_{ℓ} 's are the coefficients of LCAO expansion determined by self-consistent

field (SCF) calculation, and $M(\lambda, \ell)$ takes +1 or -1. With ϕ 's given as in Eq. (7.2),

$$\mathcal{E}_{\text{on}} = -\sqrt{2} \sum_{\ell \ell'} c_{\ell} c_{\ell'} J(\lambda, \ell; \lambda', \ell') , \quad (7.3)$$

where

$$J(\lambda, \ell; \lambda', \ell') = \int [u_{\ell}(\vec{r}_A) + M(\lambda', \ell') u_{\ell'}(\vec{r}_B)]^* \times \exp(i\vec{k} \cdot \vec{r}) [u_{\ell}(\vec{r}_A) + M(\lambda, \ell) u_{\ell}(\vec{r}_B)] d\vec{r} . \quad (7.4)$$

If the atomic orbital u 's in Eq. (7.4) are expressed by STO, J would contain series of multicenter integrals of type

$$I = \int r_A^{t'} \exp(-\alpha' r_A) Y_{\ell', m'}^*(\theta_A \phi) \exp(i\vec{k} \cdot \vec{r}) \times r_B^t \exp(-\alpha r_B) Y_{\ell m}(\theta_B \phi) d\vec{r} . \quad (7.5)$$

The evaluation of integrals of type Eq. (7.5) is rather difficult, and one must resort to an approximation such as ζ -function expansion technique which was adopted by Cartwright.^{33,34}

Even with such an approximation, the computational complexity increases rapidly with inclusion of higher atomic orbitals, so that, for example, in the Cartwright's work,³⁴ the atomic orbitals other than 1s, 2s, 2p had to be excluded from computation. However, if u 's are expressed as GTO's, such an integral can be evaluated in a closed form by the following procedure. For convenience the notations of Gaussian functions will be adopted as denoting a 1s-type Gaussian (function) of exponent $\underline{a}$ centered at a point A by $s(\underline{a}, A)$, the similar 2p-types

by $p_x(a,A)$, etc., and 3d-types by $d_{xy}(a,A)$, etc., i.e.,

$$\begin{aligned} s(a,A) &= \exp\{-a[(x-A_x)^2+(y-A_y)^2+(z-A_z)^2]\} , \\ p_i(a,A) &= (i-A_i)s(a,A) , \\ d_{ij}(a,A) &= (i-A_i)(j-A_j)s(a,A) , \end{aligned} \quad (7.6)$$

where i and j represent x, y, z , and A_x, A_y, A_z are the Cartesian coordinates of the point A . It is well known that a product of two Gaussians centered at two different points A and B may be expressed by another Gaussian centered at a third point C as³⁷

$$\begin{aligned} s(a,A)s(b,B) &= \exp[-ab(\overline{AB})^2/(a+b)]s(a+b,C) , \\ (\overline{AB})^2 &= (A_x-B_x)^2+(A_y-B_y)^2+(A_z-B_z)^2 , \\ C_i &= (aA_i+bB_i)/(a+b) , \quad i=x,y,z . \end{aligned} \quad (7.7)$$

Thus, using the Cartesian coordinates with the origin at the midpoint of N_2 molecule, the integral

$$\begin{aligned} \langle s(a,A) | \exp(i\vec{K} \cdot \vec{r}) | s(b,B) \rangle &= \int_{-\infty}^{+\infty} s^*(a,A) \\ &\quad \times \exp[i(K_x x + K_y y + K_z z)] s(b,B) dx dy dz \end{aligned} \quad (7.8)$$

can easily be evaluated by substitution of

$$\begin{aligned} x' &= x - (aA_x + bB_x)/(a+b) , \\ y' &= y - (aA_y + bB_y)/(a+b) , \\ z' &= z - (aA_z + bB_z)/(a+b) , \end{aligned} \quad (7.9)$$

with the result

$$\begin{aligned}
 \langle s(a,A) | \exp(i\vec{k} \cdot \vec{r}) | s(b,B) \rangle &= [\pi/(a+b)]^{3/2} \\
 &\times \exp[-K^2(a+b)^{-1}/4] \exp[-ab(\overline{AB})^2/(a+b)] \\
 &\times \exp\{i(a+b)^{-1}[(aA_x+bB_x)K_x + (aA_y+bB_y)K_y + (aA_z+bB_z)K_z]\} .
 \end{aligned}
 \tag{7.10}$$

Integrals involving p- and d-type orbitals may be obtained by successive partial differentiation with respect to A_x , B_x , etc. and manipulations of Eq. (7.10). They are listed in Appendix IV. For an electron-diatomic molecule collision problem, it is convenient to choose the coordinate axes such that $\vec{k}$ lies on the y-z plane without loss of generality. This gives $K_x=0$, $K_y=K\sin\theta$, $K_z=K\cos\theta$, where θ is the angle between $\vec{k}$ and the molecular axis as shown in Figure 3. The nuclei A and B are placed at $(0,0,R_0/2)$ and $(0,0,-R_0/2)$ respectively as shown in Figure 3. When the symmetries of the molecular orbitals ϕ_λ and ϕ_λ , are specified, Eq. (7.4) may be expressed in analytical form, e.g.,

$$\begin{aligned}
 J(\sigma_g, 1s; \sigma_u, 1s) &= \langle s(a,A) + s(a,B) | \exp(i\vec{k} \cdot \vec{r}) | s(b,A) - s(b,B) \rangle \\
 &= 2iW[\text{sint}_1 - e\text{sint}_2] ,
 \end{aligned}
 \tag{7.11}$$

where

$$\begin{aligned}
 W &= [\pi/(a+b)]^{3/2} \exp[-K^2(a+b)^{-1}/4] , \\
 e &= \exp[-abR_0^2/(a+b)] ,
 \end{aligned}
 \tag{7.12}$$

$$t_1 = KR_0 \cos \theta / 2 ,$$

$$t_2 = KR_0 (a-b)(a+b)^{-1} \cos \theta / 2 .$$

Substitution of Eq. (7.11) in Eq. (7.3) gives $\mathcal{E}_{on}$ as a function of K and θ . It should be pointed out that θ differs from θ' which was defined in Chapter VI as the angle between the direction of the incident electron and the molecular axis. However, for the purpose of averaging $|\mathcal{E}_{on}|^2$ over all orientations, θ' may be replaced by θ without any change in substance.

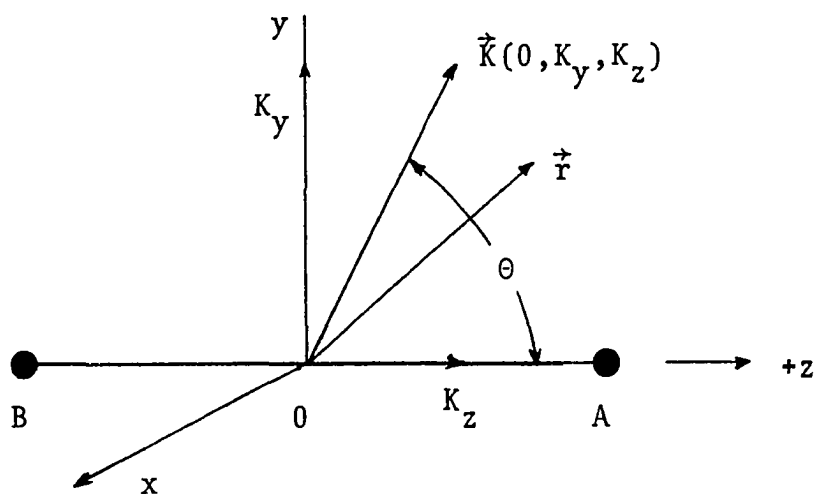


Figure 3. Momentum Change Vector $\vec{K}$
Relative to the Molecular Axis

Generalized Oscillator Strengths

To compute $G(K)$, which is related to the generalized oscillator strength by a multiplicative constant of ΔE as shown in Eq. (6.54), the averaging process is carried out numerically. For the electron-homonuclear diatomic molecule collision problem, Eq. (6.53) can be reduced to

$$G(K) = 2\omega_n K^{-2} \int_0^{\pi/2} |\mathcal{E}_{on}(K; \theta)|^2 \sin \theta d\theta . \quad (7.13)$$

The integrand is computed for values of θ from $\theta=0^\circ$ to $\theta=90^\circ$ with $\Delta\theta=1^\circ$ for a total of 91 quadrature points. The numerical integration is performed by means of the Newton-Cotes' six-term interpolation scheme. In order to test the accuracy of this procedure a provision is made in the computer program so as to pick out the values of integrand at every other quadrature points ($\Delta\theta=2^\circ$ and 46 quadrature points), and the integration is carried out similarly. The difference in the results between the two cases (91 and 46 quadrature points) occurs in the fourth significant figure at worst, indicating that the accuracy of this procedure is good at least for four significant figures. Using this scheme, $G(K)$ is computed for as many as 65 values of K . Next, the tabular values of $G(K)$ are curve-fitted to a quotient of two polynomials according to the known behavior of the generalized oscillator strengths of the optically-allowed and -forbidden transitions as

$$G(K) = [b_1 + b_2 x + b_3 x^2] / [1 + \sum_{i=1}^7 a_i x^i] , \quad \text{allowed, (7.14)}$$

$$G(K) = [b_1 x + b_2 x^2 + b_3 x^3] / [1 + \sum_{i=1}^7 a_i x^i] , \quad \text{forbidden, (7.15)}$$

where $x=K^2$. In certain cases where $G(K)$'s show "structures", it becomes necessary to improvise the curve-fitting schemes by making separate fits which are valid in different regions of K values.

Finally, for excitations to triplet states, Eq. (6.49) is integrated by the Simpson's rule from $K=0$ to certain upper limit of K with $\Delta K=10^{-3}$ throughout. For excitations to singlet states, the integration is carried out from $K=10^{-2}$ with the starting $\Delta K=10^{-4}$, doubling ΔK after each 100 quadrature points of K . The small starting ΔK used for the singlet excitation cross sections is necessitated to accurately evaluate the diverging integrand in Eq. (6.49) in the case of excitation to an optically-allowed states.

Conversion of STO to GTO

To carry out the computational procedures described in the preceding section, the wave functions must be expressed in GTO. One may obtain such a wave function of N_2 by performing the SCF calculation using the GTO basis functions as is done in this work. However, all N_2 wave functions in the

literature⁶⁰⁻⁶⁴ are in STO form, in which case STO's are converted to GTO by the following procedure. For a given molecular orbital, the constituent atomic orbitals are grouped by symmetry (i.e., by ns, np, nd types), and each group is curve-fitted to seven Gaussian functions. The non-linear least square curve-fitting technique of Marquardt⁵⁹ is adopted, by which the linear (multiplier of Gaussian) and the non-linear (exponent of Gaussian) are allowed to vary simultaneously. Typically, in the region where the value of the function is greater than 10^{-2} of its peak value, the fit is good within a few tenths of a percent. In the region where the value is order of 10^{-3} of the peak the fit is about 1%. The fit becomes poorer (>10%) as the value of the function becomes less than 10^{-5} of the peak value. In order to see how sensitively the computed cross section depends on the "goodness" of GTO expansion of a STO, a test calculation was made, using 1s→2p excitation of hydrogen atom.³⁹ It was found that the six-term GTO expansions for both 1s and 2p atomic wave functions of hydrogen atom give cross sections within 1% of the exact values over the incident electron energies 60-1000 eV.

Judging from the quality of curve-fitting, the present work should be of comparable accuracy as in the test case cited above.

CHAPTER VIII

RESULTS AND DISCUSSION

Generalized Oscillator Strengths

Before making an extensive comparison between the theoretical and the experimental excitation cross sections of the N_2 molecule, it is important to ascertain how sensitively the theoretical values vary with the choice of the electronic wave functions. To this end several sets of the wave functions are used, which are given by Nesbet,⁶⁰ Richardson,⁶¹ Ransil,⁶² Sahni and De Lorenzo,⁶³ and Lefebvre-Brion and Moser.⁶⁴ The wave functions of Ransil and those of Sahni and De Lorenzo contain in the basis functions $n=1$ and $n=2$ atomic orbitals, with the distinction that the exponents of atomic orbitals were optimized in the former set, whereas they were not in the latter. The wave functions of Richardson differ from those above in that the number of $n=2$ atomic orbitals were doubled. The 3d atomic orbitals were included in Nesbet's wave functions which give better energies. For comparison a SCF calculation has been performed on the electronic structure of N_2 using 13 s-type and seven p-type GTO's as the basis functions. The exponents and the "contractions" of the

Gaussians were taken from the work of Huzinaga and Sakai;⁶⁵ however, the "contractions" on the 2p GTO's were relaxed to gain more variational freedom. To show the relative accuracy of these wave functions, the total and the orbital energies of the ground $X^1\Sigma_g^+$ state of various SCF calculations are tabulated in Table IX. The numerical parameters of the active orbitals of the present GTO wave function and the typical curve-fit results are shown in Appendix V.

For convenience Nesbet's wave functions for both the ground and the excited orbitals will be designated by set (i), Richardson's wave functions by set (ii), and the present GTO functions by set (iii). In the cases of excitation to the Rydberg excited states (c'^1 , $D^3\Sigma_u^+$ and a''^1 , $E^3\Sigma_g^+$), the wave functions of the excited orbitals given by Lefebvre-Brion and Moser were used in combination with Nesbet's, with Richardson's, and with the GTO ground state functions. However, the same designations will be used without confusion, since those wave functions by Lefebvre-Brion and Moser are the only ones available for the Rydberg excited orbitals of $(3s)\sigma_g$ and $(3p)\sigma_u$. Set (iv) will refer to the combinations of the Ransil's ground state and the excited state functions of Sahni and De Lorenzo's "restricted treatment".

Since both the singlet and the triplet excitation cross sections are proportional to the generalized oscillator strengths,

TABLE IX
COMPARISON OF DIFFERENT WAVE FUNCTIONS
OF N_2 GROUND STATE

	GTO ^(a)	NESB ^(b)	RICH ^(c)	RANS ^(d)
E^T	-108.8894 ^(e)	-108.9730	-108.7853	-108.6336
$1\sigma_g$	-15.71564	-15.69623	-15.70512	-15.46705
$1\sigma_u$	-15.71203	-15.69262	-15.70192	-15.64423
$2\sigma_g$	-1.53154	-1.48569	-1.49301	-1.42106
$2\sigma_u$	-0.77741	-0.78581	-0.76287	-0.71370
$3\sigma_g$	-0.63005	-0.64278	-0.62225	-0.55548
$1\pi_u$	-0.63082	-0.62261	-0.61378	-0.54540

(a) Present calculation.

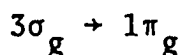
(b) Nesbet (Reference 60).

(c) Richardson (Reference 61).

(d) Ransil (Reference 62).

(e) All energies are expressed in atomic units.

a detailed examination is made on the various versions of the functions $G_{\text{on}}(K)$ computed by different sets of wave functions.⁶⁶ The singlet cross sections are particularly sensitive to the behavior of $G_{\text{on}}(K)$ for small values of $K(\leq 1.0)$, whereas the triplet cross sections are governed mainly by $G_{\text{on}}(K)$ for larger values of K [See Eq. (6.49)]. When the electronic states of the molecule are represented by those of a single electron configuration, as in Eqs. (6.18), (6.19), and (6.20), each excitation can be characterized as a one-electron transition from one molecular orbital to another. Each of the $3\sigma_g \rightarrow 1\pi_g$, $2\sigma_u \rightarrow 1\pi_g$, $1\pi_u \rightarrow 1\pi_g$, $3\sigma_g \rightarrow (3s)\sigma_g$, and $3\sigma_g \rightarrow (3p)\sigma_u$ transitions is discussed, which are the underlying one-electron transitions of all the excitation processes considered in this thesis. The generalized oscillator strengths, computed by using the Nesbet's functions, are tabulated in Tables X and XI.



This transition corresponds to the $a^1\Pi_g$ and $R^3\Pi_g$ of the $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)(1\pi_g)$ configuration.⁶⁷ Different versions of $G_{\text{on}}(K)$ have been calculated by using all four sets of wave functions. Fig. 4 shows the curves of $G_{\text{on}}(K)$ calculated by sets (i), (iii), and (iv) along with the experimental values of Lassettre and Krasnow.⁶⁸ The results of set (ii) lie between sets (i) and (iii) and are left out for clarity.

TABLE X

$G_{\text{on}}(K)$ FOR OPTICALLY-ALLOWED
TRANSITIONS IN a.u.

K	$3\sigma_g \rightarrow (3p)\sigma_u$	$1\pi_u \rightarrow 1\pi_g^{(a)}$	$2\sigma_u \rightarrow 1\pi_g^{(b)}$
0.01	1.277(-1) ^(c)	2.942(+0)	1.397(+0)
0.02	1.276	2.941	1.397
0.05	1.262	2.935	1.394
0.10	1.210	2.915	1.382
0.15	1.134	2.881	1.364
0.20	1.027	2.835	1.339
0.30	.775	2.708	1.269
0.40	.573	2.540	1.178
0.50	.288	2.341	1.073
0.60	.130	2.120	.959
0.70	.408(-2)	1.888	.841
0.80	.776(-3)	1.655	.727
0.84	.567		
0.90	.101(-2)	1.428	.618
1.00	.280	1.213	.520
1.20	.597	.839	.357
1.40	.606	.550	.241
1.60	.424	.343	.162
1.80	.234	.204	.112
2.40	.399(-3)	.316(-1)	.403(-1)
2.80	.328	.657(-2)	.202
3.20	.225	.962(-3)	.916(-2)
3.60	.950(-4)	.291	
4.00	.306	.360	.133
5.00	.115(-5)	.822(-4)	.103

(a) Appropriate for $1, 3\Sigma_u^+$ states.

(b) Computed by using GTO wave functions.

(c) Numbers inside the parentheses indicate the power of 10.

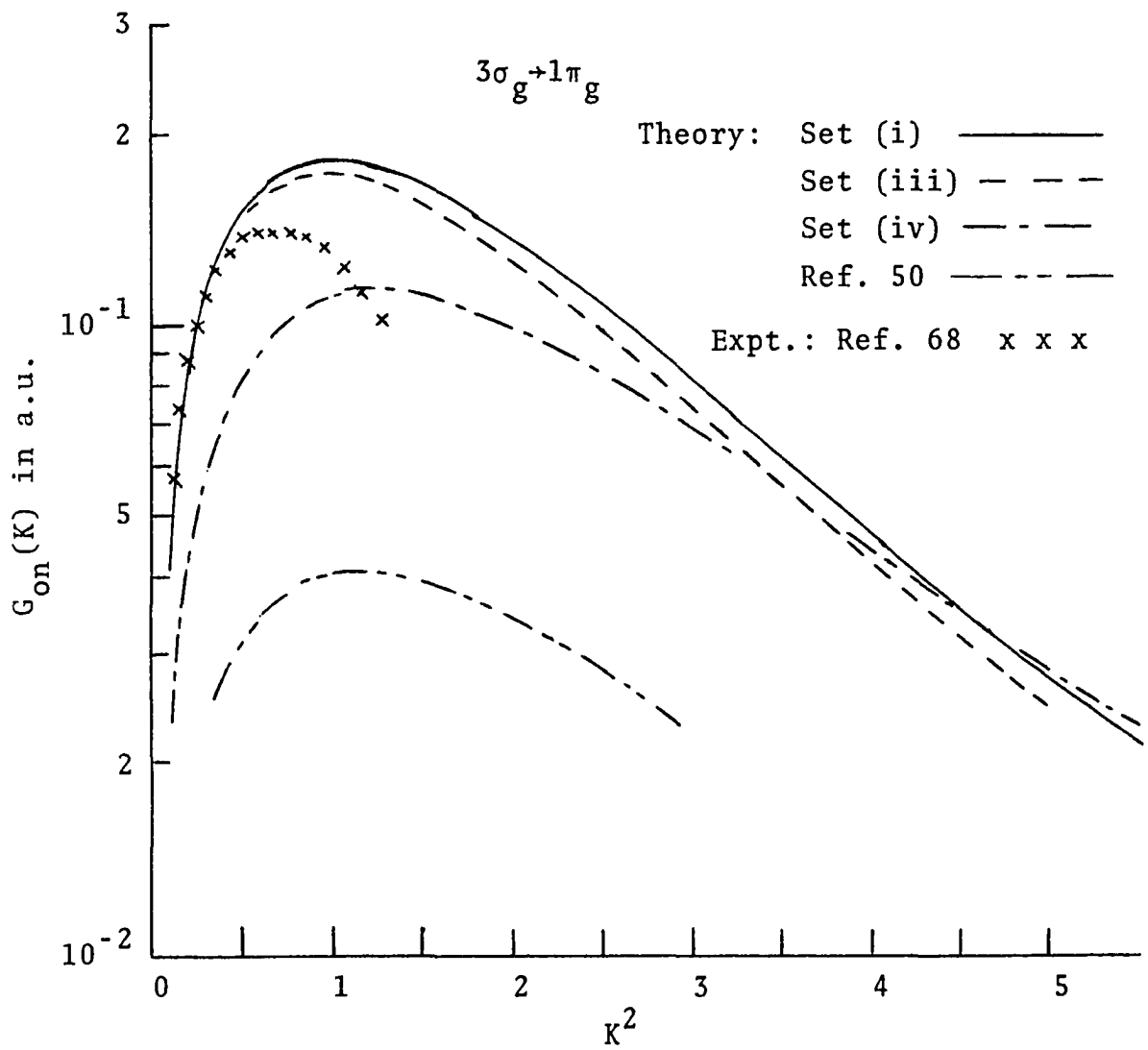
TABLE XI

$G_{\text{on}}(K)$ FOR OPTICALLY-FORBIDDEN
TRANSITIONS IN a.u.

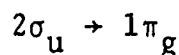
K^2	$3\sigma_g \rightarrow 1\pi_g$	$1\pi_u \rightarrow 1\pi_g$ (a)	$3\sigma_g \rightarrow (3s)\sigma_g$
0.05	.252(-1) (b)	.110(-3)	.165(-1)
0.1	.477	.421	.284
0.2	.856	.154(-2)	.436
0.3	.115(+0)	.318	.508
0.4	.138	.518	.528
0.5	.156	.744	.519
0.6	.168	.984	.492
0.7	.176	.123(-1)	.456
0.8	.182	.148	.417
0.9	.184	.173	.378
1.0	.185	.197	.341
1.2	.181	.242	.276
1.4	.173	.281	.225
1.6	.162	.315	.186
1.8	.150	.344	.158
2.0	.138	.366	.136
2.4	.113	.396	.108
2.8	.916(-1)	.408	.907(-2)
3.2	.733	.408	.777
3.6	.585	.399	.668
4.0	.467	.383	.570
5.0	.273	.331	.368
6.0	.172	.274	.225
7.0	.119	.222	.133
8.0	.900(-2)	.179	.787(-3)
9.0	.729	.143	.481
10.0	.614	.115	.315

(a) Appropriate for Δ state.

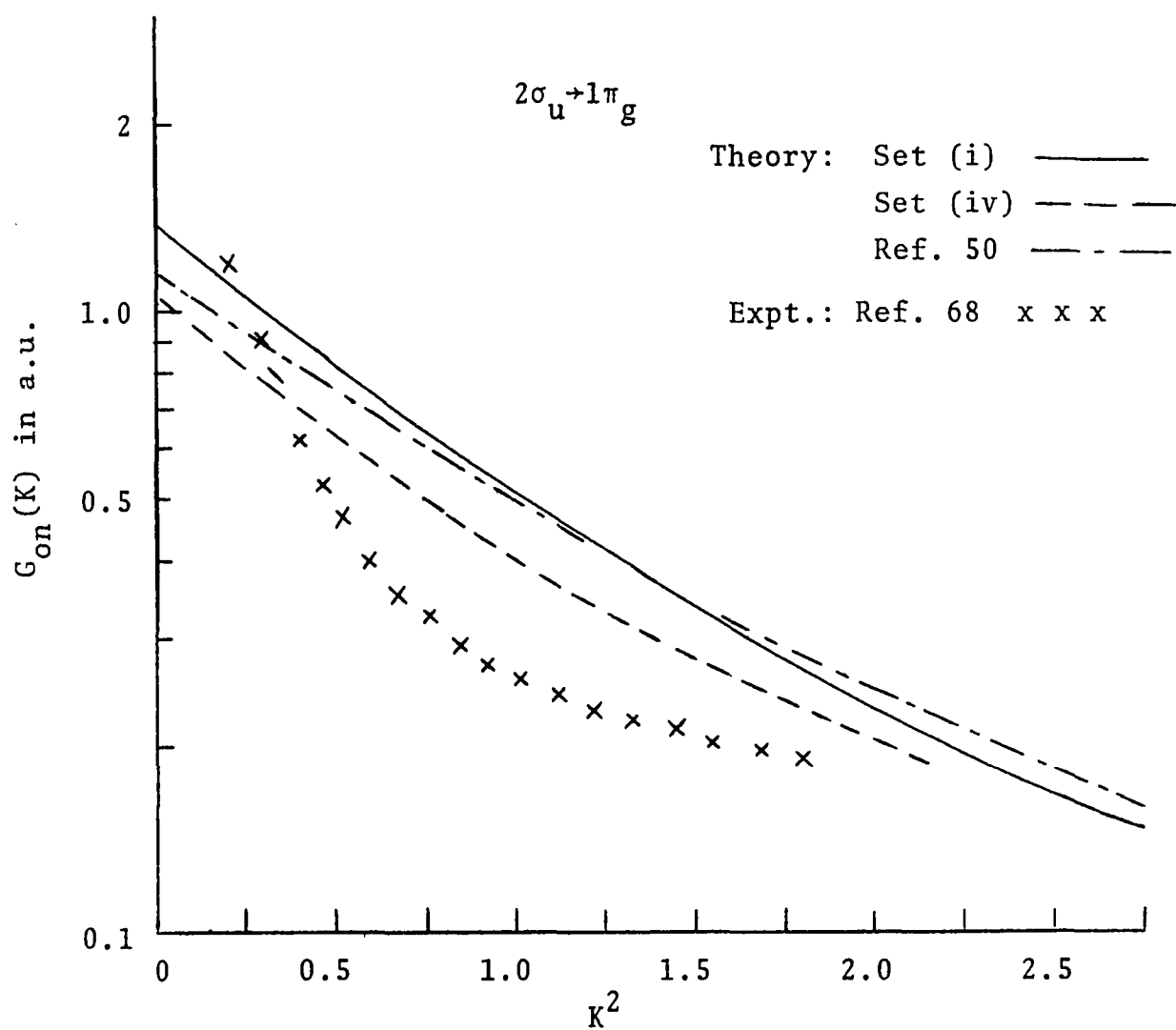
(b) Numbers inside the parentheses indicate the power of 10.

Figure 4. $G_{on}(K)$

The theoretical values calculated using sets (i), (ii), and (iii) agree very well with one another (within 10%) and also show a reasonable agreement with the experimental data for small values of K . The theoretical generalized oscillator strengths have been reported by Rozsnyai (based on the Ransil's functions with unoptimized exponents for both the ground and the excited states).⁵⁰ His values are lower than all four sets of theoretical values mentioned above (Fig. 4). The Rozsnyai's approximate scheme of evaluating multicenter integrals may be subject to some errors. The discrepancy of a factor greater than two is difficult to reconcile, however. As will be seen in the next subsection, his values for $2\sigma_u \rightarrow 1\pi_g$ transition agree much better (20%) with the present results. Rozsnyai was able to increase the value of the oscillator strengths by dropping the $1s$ and $2s$ constituents from the $3\sigma_g$ molecular orbital, but there appears to be no theoretical justification for this step. The close agreement between the theoretical values calculated from the wave functions of Nesbet, of Richardson, and the present GTO wave functions is especially encouraging.



The electronic configuration $(2\sigma_u)(3\sigma_g)^2(1\pi_u)^4(1\pi_g)$ gives rise to the $C^3\Pi_u$ state⁶⁹ and to one $^1\Pi_u$ state; the

Figure 5. $G_{on}(K)$

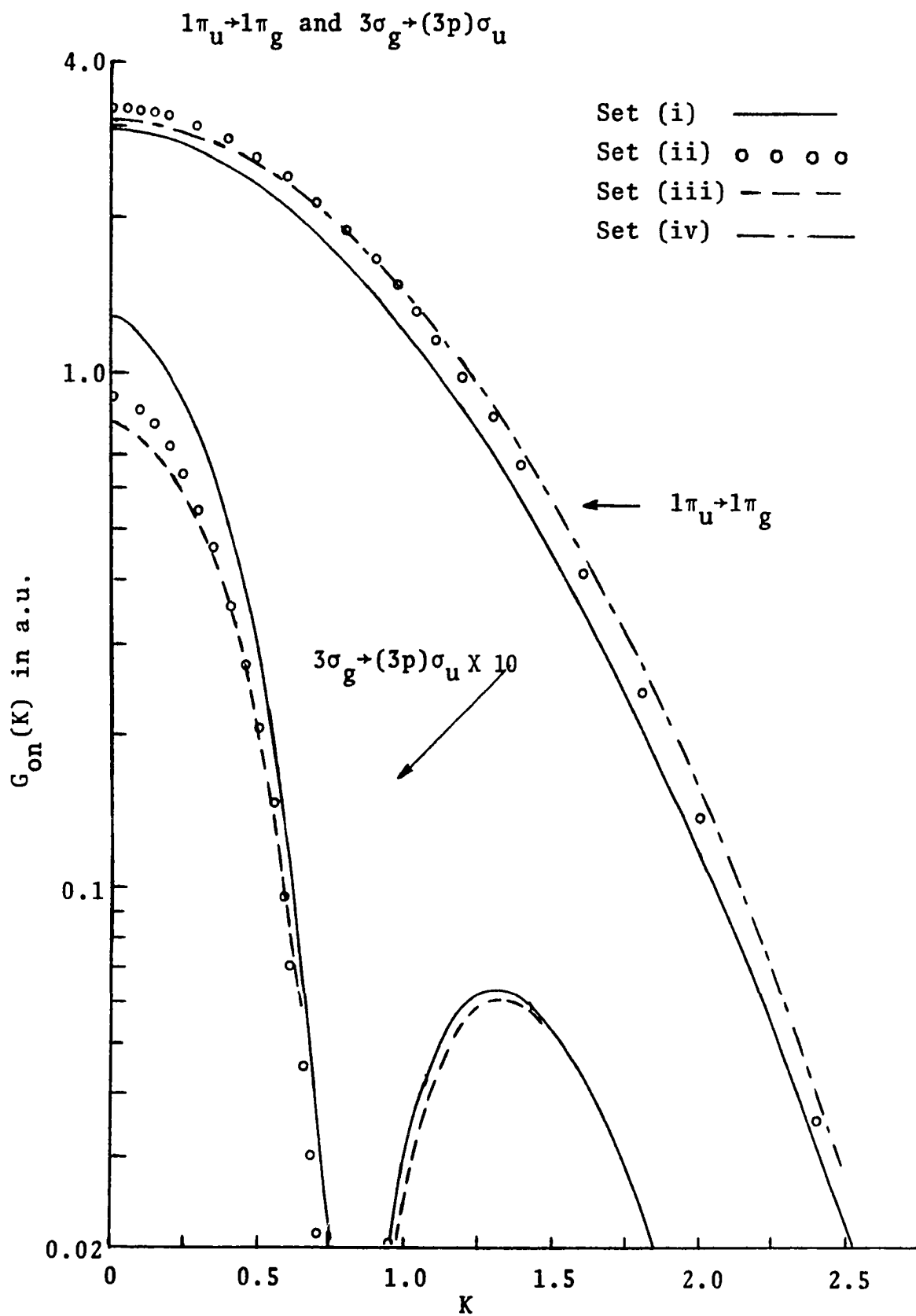
latter ($b^1\pi_u$), however, is believed to be mixed with the $(2\sigma_u)^2(3\sigma_g)(1\pi_u)^3(1\pi_g)^2$ configuration. The graphs of $G_{on}(K)$ calculated by sets (i) and (iv) along with Rozsnyai's values⁵⁰ and Lassetre and Krasnow's experimental values⁶⁸ are displayed in Fig. 5. The results of sets (ii) and (iii), which are not shown in Fig. 5, differ from those of set (i) by no more than 8.5% and 2.6% respectively. All four calculated $G_{on}(K)$ curves show a maximum at $K=0$, characteristic of the generalized oscillator strengths of a dipole-allowed transition. Moreover, they are not very sensitive to the choice of wave functions for this transition. From electron-impact energy loss experiment, Lassetre and Krasnow obtained the generalized oscillator strengths for the energy loss $\Delta E=12.85$ eV.⁶⁸ It was suggested that the spectrum of this energy loss probably includes contributions from vibrational levels of $c'^1\Sigma_u^+$, $c^1\pi_u$ as well as $b^1\pi_u$.⁷¹ Because of these uncertainties no comparison between theory and experiment will be made for this transition.

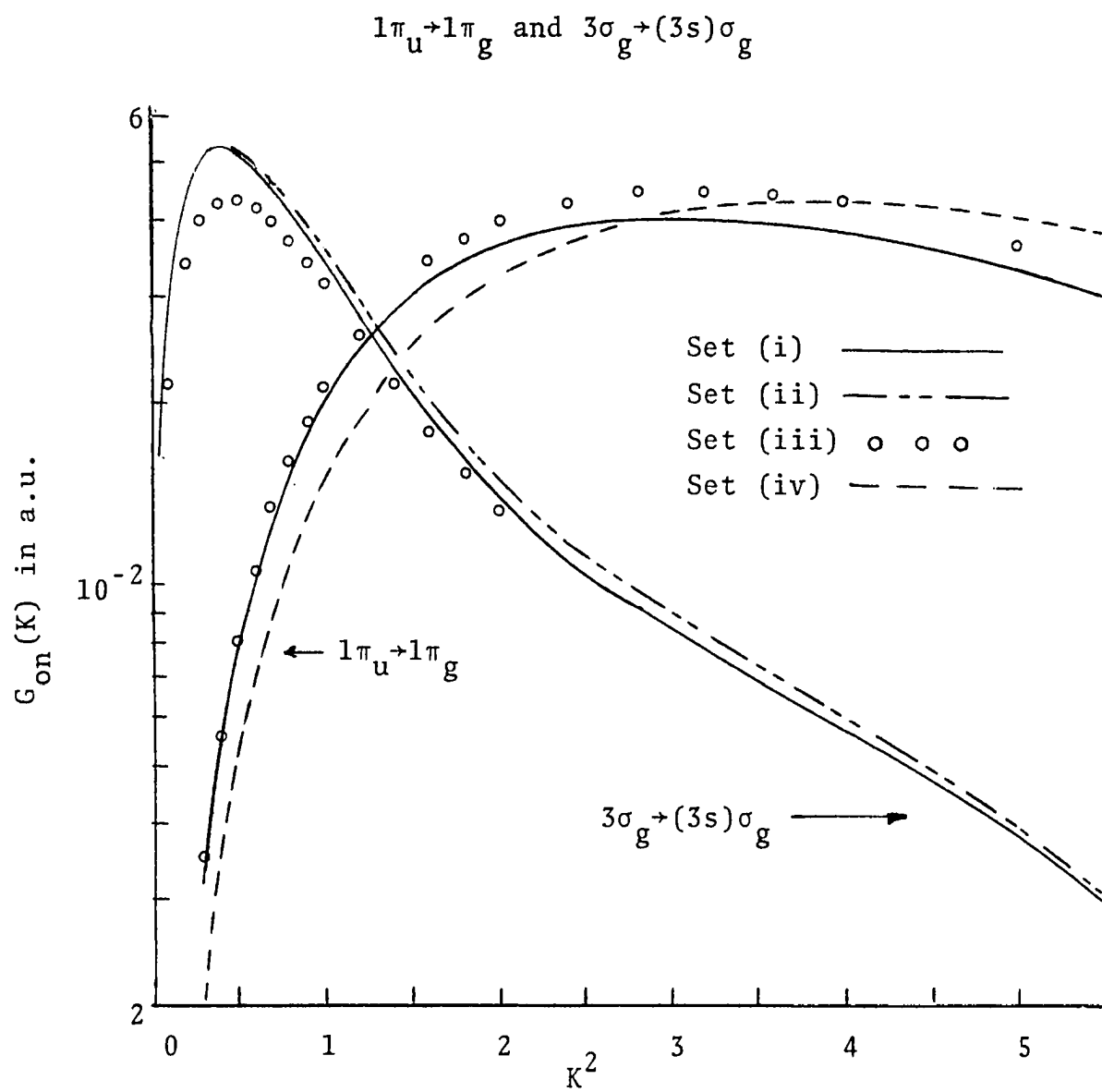
$$1\pi_u \rightarrow 1\pi_g$$

When an electron in the degenerate $1\pi_u$ is promoted to another degenerate $1\pi_g$ orbital, four different assignments may be made, which are responsible for Σ_u^+ , Σ_u^- and doubly degenerate Δ_u states.⁷² The $^1\Sigma_u^+$ state (designated as $b'^1\Sigma_u^+$) is an optically-allowed one, and its triplet counterpart is the $A^3\Sigma_u^+$ state.

The other states ($a, {}^1\Sigma_u^-, B, {}^3\Sigma_u^-, w, {}^1\Delta_u, W, {}^3\Delta_u$) are all dipole-forbidden. The shape of the $G_{\text{on}}(K)$ curves indeed properly reflect the optical nature of the transitions as may be seen in Figs. 6 and 7 [$G_{\text{on}}(K)$ is identically zero for symmetry-forbidden transition to Σ_u^-]. Fig. 6 shows the $G_{\text{on}}(K)$ appropriate to ${}^1, {}^3\Sigma_u^+$ computed by sets (i) and (iv), and the results by set (ii) are represented simply by dots for clarity. Set (iii) gives values which are between sets (i) and (ii) except near $K=0$ where they are about 5% larger than those of set (ii). Sets (i) and (iv) differ most, but the difference is within 25% for $K \leq 3.0$. An interesting feature of the secondary extrema (not shown in Fig. 6) has been observed beyond $K=3.5$ (by all sets of wave functions). However, these extrema occur at too large values of K and the magnitude is too small (less than 10^{-3} of the value at $K=0$) to affect the total cross sections in any appreciable way.

Fig. 7 shows $G_{\text{on}}(K)$ appropriate for ${}^1, {}^3\Delta_u$ computed by sets (i), (iv) and (iii)[by dots]. The results by set (ii) are smaller by 10% at $K=0.1$ and larger by 10% at $K=6.0$ compared with those of set (i). A much broader peak in this curve is noted, compared with other optically-forbidden transitions. As will be seen later, this broad peak is responsible for a broad peak in the excitation functions of the $w, {}^1\Delta_u$ and $W, {}^3\Delta_u$ states.

Figure 6. $G_{on}(K)$

Figure 7. $G_{on}(K)$

$$3\sigma_g \rightarrow (3p)\sigma_u \text{ and } 3\sigma_g \rightarrow (3s)\sigma_g$$

The $3\sigma_g \rightarrow (3p)\sigma_u$ transition corresponds to excitation to the Rydberg $c'^1\Sigma_u^+$ and $D^3\Sigma_u^+$ states. In Fig. 6 is presented the $G_{on}(K)$ curves for the $3\sigma_g \rightarrow (3p)\sigma_u$ transition. As designated before, for this and the $3\sigma_g \rightarrow (3s)\sigma_g$ transitions, sets (i), (ii), and (iii) refer to the $3\sigma_g$ orbitals of Nesbet, Richardson, and GTO in order in combination with $(3p)\sigma_u$ and $(3s)\sigma_g$ orbitals of Lefebvre-Brion and Moser. The generalized oscillator strengths depend much more sensitively on the initial $3\sigma_g$ as seen in Fig. 6. The discrepancy is particularly severe (as much as a factor of two) below $K=1.2$. This will be reflected much more strongly in the singlet cross sections than in the triplet cross sections.

From the measurements of absorption spectrum, Lawrence, Mickey, and Dressler⁷³ obtained the absolute optical oscillator strength to be 0.14 ± 0.04 for the $p'^1\Sigma_u^+$ band which is the first vibrational member of $c'^1\Sigma_u^+$ state. By comparing the transition probability deduced from their oscillator strength and the one from the life-time measurement, they conclude that the Franck-Condon factor for the p' level to be very close to unity. Assuming the Franck-Condon factor of the p' level to be unity, the present computed $G_{on}(K=0)$ leads to an optical oscillator strength of 0.0607 which is about 2.3 times smaller than the

measured value. Unlike other transitions studied in this thesis, the $G_{\text{on}}(K)$ function for $c'^1\Sigma_u^+$ shows an unusual behavior of decreasing very rapidly from $K=0$ to $K=0.84$ by a factor greater than 200 and then rising again to a broad maximum around $K=1.3$ (Fig. 6). This sharp decrease in $G_{\text{on}}(K)$ indicates a strong angular dependence of the differential cross section. The relative intensities measurements of electron-impact energy loss spectra also show the strong angular dependence. This point is discussed in fuller detail later.

The generalized oscillator strengths of the $3\sigma_g \rightarrow (3s)\sigma_g$ transition, which yields⁷⁴ the $a'^1\Sigma_g^+$ and $E^3\Sigma_g^+$ states, are seen to have the qualitative behavior of those of a dipole-forbidden state (Fig. 7). Compared with the values obtained by set (i), set (ii) results are about 7% larger for $K \geq 1.0$. On the other hand, set (iii) gives values which are about 20% smaller for $K \leq 0.5$, but practically identical for $K \geq 2.0$.

Excitation Cross Sections for Singlet States

The $a'^1\Pi_g$ State (Lyman-Birge-Hopfield Bands)

The $a'^1\Pi_g$ state is the only singlet state for which a considerable amount of experimental work on the measurements of the absolute excitation cross sections has been reported

in the literature; therefore, it is a particularly good case for testing the Born cross sections. In applying the Born approximation to the singlet-singlet excitation problems, it has been customary to ignore the exchange effect. By means of the Ochkur⁵² and Rudge⁵³ modifications, the exchange effect can be taken into account more satisfactorily than by the Born-Oppenheimer approximation. Accordingly, the singlet excitation cross sections have been computed by these two versions of exchange treatment and by neglecting exchange, using wave functions set (i), and the results are compared in Fig. 8. It is seen that the Ochkur exchange tends to decrease the computed cross sections in the low energy region, whereas the use of the Rudge formula reduces only slightly the cross sections above 40 eV but gives a substantial increase over the non-exchange values as the incident electron energy is decreased. In fact, it is easy to see from Eqs. (6.42) and (6.44) that for incident electron energy less than $5\epsilon/3 + \Delta E$ (in Ry) the Rudge exchange term tends to increase the cross sections. A similar increase of cross sections (at low energies) has been observed, associated with the use of the Rudge modification for all the other singlet states studied in this thesis. It may be pointed out in passing that the same kind of behaviors were also noted in the excitation functions of the 1P and 1D states of He.⁷⁵ From the available experimental data

of N_2 , it is difficult to decide which version of the exchange approximation works better for singlet-singlet excitation. Moreover, the difference between the non-exchange Born approximation and the two modifications is appreciable only at relatively low energies where such effects as polarization and distortion, which were not included in all the Born-type theory, may play important roles in determining the cross sections. Without a quantitative measure of these effects, it is impractical to attempt a critical appraisal of the two versions of exchange formula by comparing the theoretical values with the experimental data. However, the steep rise of cross sections with reducing energies below 30 eV according to Rudge's modification could be somewhat unrealistic. For this reason and the reason that the Rudge's modification lacks the detailed balancing in the case of the singlet-to-singlet excitation,⁷⁶ the Ochkur modification will be adopted to include exchange effect. Unless otherwise specified, all singlet cross sections presented in this thesis are computed with exchange by the Ochkur's modification.

The theoretical excitation cross sections calculated by using the wave functions of set (i), (ii), and (iii) agree very well with one another, of which the results of set (i) are shown in Fig. 8. The excitation functions by the other two sets are about 5% smaller than the one shown. The exci-

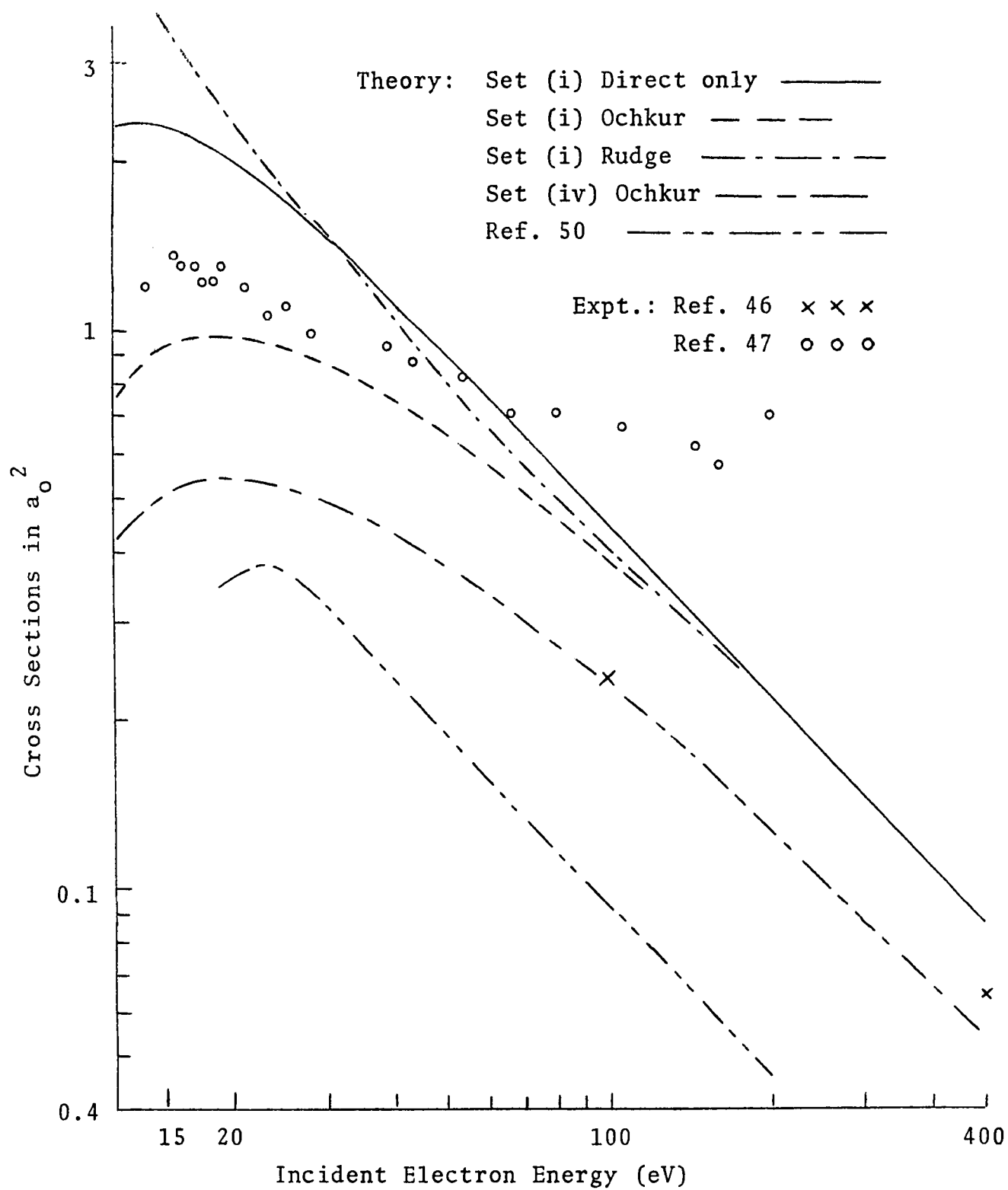


Figure 8. Cross Sections of $a^1\Pi_g$

tation function computed with set (iv) is markedly smaller, however (See Fig. 8). The sensitivity of cross sections on the choice of wave functions for this and other singlet states is summarized in Table XII.

These theoretical cross sections based on wave functions (i), (ii), and (iii) are somewhat larger than the experimental values reported by Holland,⁴⁶ above 500 eV the agreement is within 25%. This provides an experimental test of the accuracy of the first Born approximation for electron-molecule excitation since at energies above 500 eV the exchange effect is entirely negligible.

Experimental measurements of the excitation cross sections have been reported also by Ajello⁴⁷ for the energy range of 10-200 eV. His cross sections are much larger than those of Holland in the energy range where the two sets of data overlap. Between 100 and 200 eV, Ajello's cross sections are substantially larger than the theoretical values.

Aarts and De Heer⁴⁸ have studied the electron-impact emission of the $a^1\Pi_g \rightarrow X^1\Sigma_g^+$ transitions and by normalizing the cross sections to the experimental data of Lassetre and Krasnow⁶⁸ at 500 eV, obtained the excitation cross sections of the $a^1\Pi_g$ state. Their results are in very good agreement with those of Holland.⁴⁶ Brinkmann and Trajmar⁴⁹ reported electron excitation measurements for a number of states of N_2 .

By normalizing to the absolute cross sections of other workers and by extrapolation they gave an electron excitation function of the $a^1\Pi_g$ state which agree well with Holland's values. Other cross-section measurements of the $a^1\Pi_g$ state include the work of Borst⁴⁵ and of Freund⁷⁷ in the region of 0-40 eV.

It should be mentioned that the measured cross sections of Holland and of Ajello were not corrected for cascade contributions. Ajello⁴⁷ estimated the probable cascade to be less than 10%. In Holland's work evidence has been cited to indicate that the cascade contribution is not large.⁴⁶ However, it was pointed out in Ref. 46 that if radiative lifetime of the $a^1\Pi_g$ state is as short as 40 μ sec, the cross sections may include a cascade contribution of 25%-35%. Recent measurements of Borst and Zipf give the lifetime of the $a^1\Pi_g$ state of N_2 as 115 ± 20 μ sec,⁷⁸ supporting the idea of small cascade contribution to the observed cross sections.

Included in Fig. 8 are the theoretical cross sections reported by Rozsnyai.⁵⁰ The latter values are much lower than the present theoretical cross sections calculated from all four sets of wave functions as was noted previously. There also exist other calculations of cross sections by semi-empirical means,⁷⁹ but the method employed was quite different from the one used here, hence no comparison of the results will be made.

The $a''^1\Sigma_g^+$ State

The $a''^1\Sigma_g^+$ state arises from the $(1\pi_u)^4(3\sigma_g)(3s\sigma_g)$ configuration.⁷⁴ In Fig. 9 are shown the theoretical excitation functions of $a''^1\Sigma_g^+$ computed using sets (i) and (iii). The excitation cross sections do not seem to depend too sensitively on the choice of wave functions, sets (i) and (iii) differing about 20%. The theoretical cross sections show E^{-1} dependence beyond 250 eV. The experimental excitation function reported by Brinkmann and Trajmar⁴⁹ is about 50% of the present theoretical counterpart above 80 eV, although agreement is considerably better at lower energy. The E^{-1} dependence of their excitation function starts at much lower energy than 250 eV found in this theoretical work. Brinkmann and Trajmar studied electron impact energy-loss spectra at 15, 20, 30, 60, and 80 eV of incident electron energy. They have normalized their data to different known experimental cross sections according to the incident electron energy. At incident electron energies greater than 80 eV, they extrapolated to obtain the cross sections. Their procedures of reducing experimental data may account for some of the discrepancy found between the theory and the experiment.

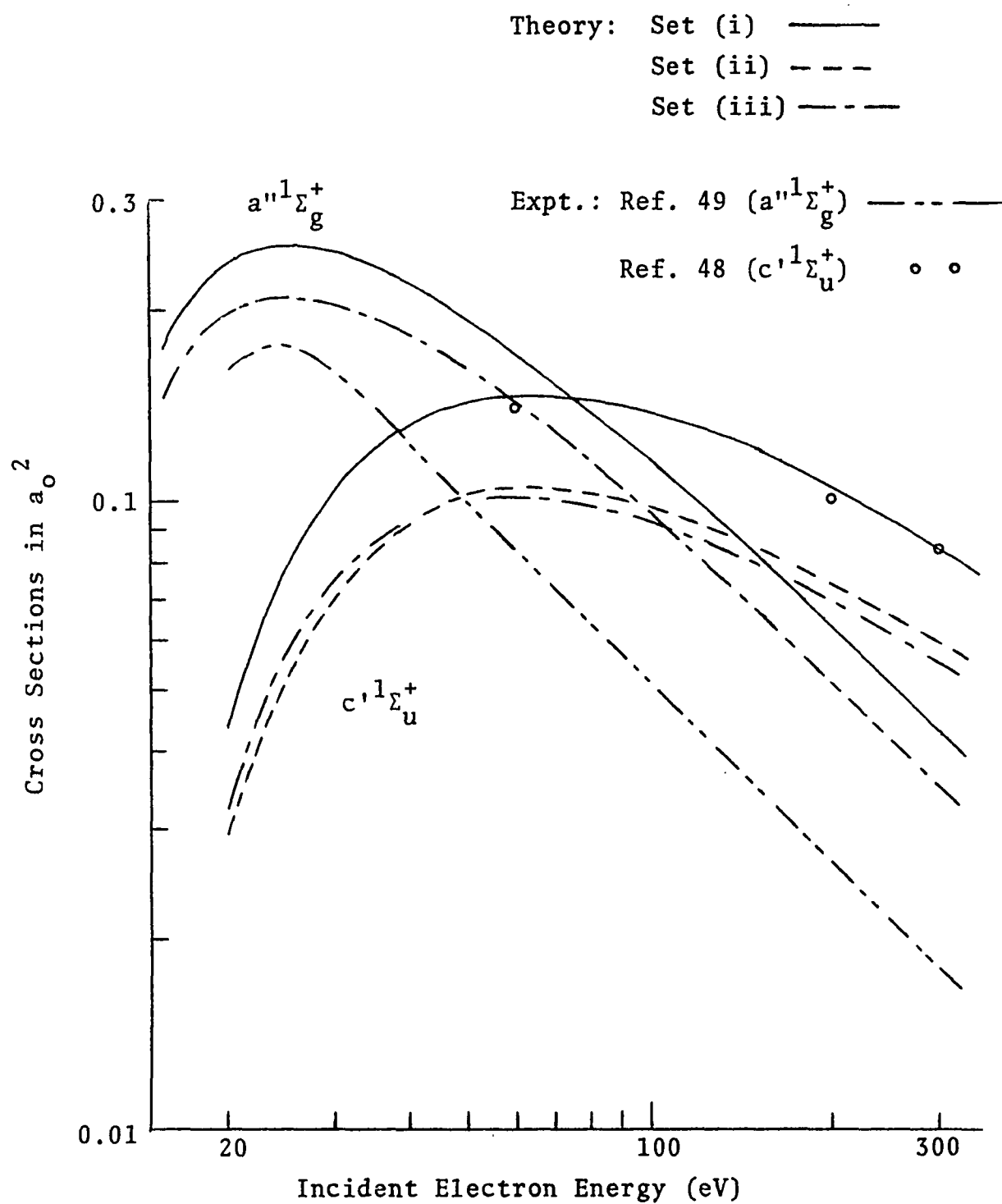


Figure 9. Cross Sections of $a''^1\Sigma_g^+$ and $c'^1\Sigma_u^+$

The $c'^1\Sigma_u^+$ State

The $c'^1\Sigma_u^+$ state which belongs to the $(1\pi_u)^4(3\sigma_g)(3p\sigma_u)$ configuration, is a dipole-allowed state; thus, it is of special interest to study its excitation properties. The excitation functions obtained using wave functions (i), (ii), and (iii) are shown in Fig. 9. The broad peak of the excitation function reminds one of the corresponding case of the dipole-allowed excited states of atoms. For this state unusually large variations are noted of the cross sections due to the choice of wave functions (as large as 50%), the shape of the theoretical curves remaining nearly the same. Recently the $p'^1\Sigma_u^+$ state has been identified as the lowest vibrational level of the $c'^1\Sigma_u^+$ state.⁷⁰ The optical excitation function of $p'^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ ($v''=1$) has been measured by Aarts and De Heer,⁴⁸ and the shape of their excitation function is in good agreement with the present calculations. Since only one vibrational component ($v'=0 \rightarrow v''=1$) of the $c'^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transitions and one component of $c'^1\Sigma_u^+ \rightarrow a^1\Pi_g$ were reported in the measurements of Aarts and De Heer, it is not possible to compare the magnitude of the present theoretical cross sections with experiments. Instead, the optical cross sections of Aarts and De Heer is normalized to the theoretical cross section [by set (i)] at 2000 eV in order to compare the shape of the excitation functions.

The normalized cross sections of Aarts and De Heer are included in Fig. 9. The agreement is seen to be quite good.

As the case of a dipole-allowed atomic excited state, the differential excitation cross sections of $c'^1\Sigma_u^+$ are sharply peaked in the forward direction as illustrated in Fig. 10 which shows the differential cross sections at various incident electron energies as a function of scattering angle, including that of $a'^1\Pi_g$ at 15 eV for comparison. This is in qualitative agreement with the experiment by Williams and Doering.⁸⁰ Lassettre⁸¹ has pointed out the sharp decrease in relative intensity at zero angle of the 12.93 eV transition of the electron impact spectra of Heideman, Kuyatt and Chamberlain,⁸² and identified this peak as $p'^1\Sigma_u^+$ state. The present calculations give a theoretical value of 8 for the ratio of the differential cross section at $\theta=0$ of the $p'^1\Sigma_u^+$ state at 35 eV to that at 20 eV in qualitative agreement with the observation cited above.

The $w'^1\Delta_u$ and $b'^1\Sigma_u^+$ States

The configuration $(1\pi_u)^3(3\sigma_g)^2(1\pi_g)$ gives rise to three singlet states $w'^1\Delta_u$, $b'^1\Sigma_u^+$, and $a'^1\Sigma_u^-$. The author is not aware of any direct experimental measurements of electron excitation of the $w'^1\Delta_u$ state; however, Freund has pointed out a possible experimental evidence of such an excitation process.⁸³

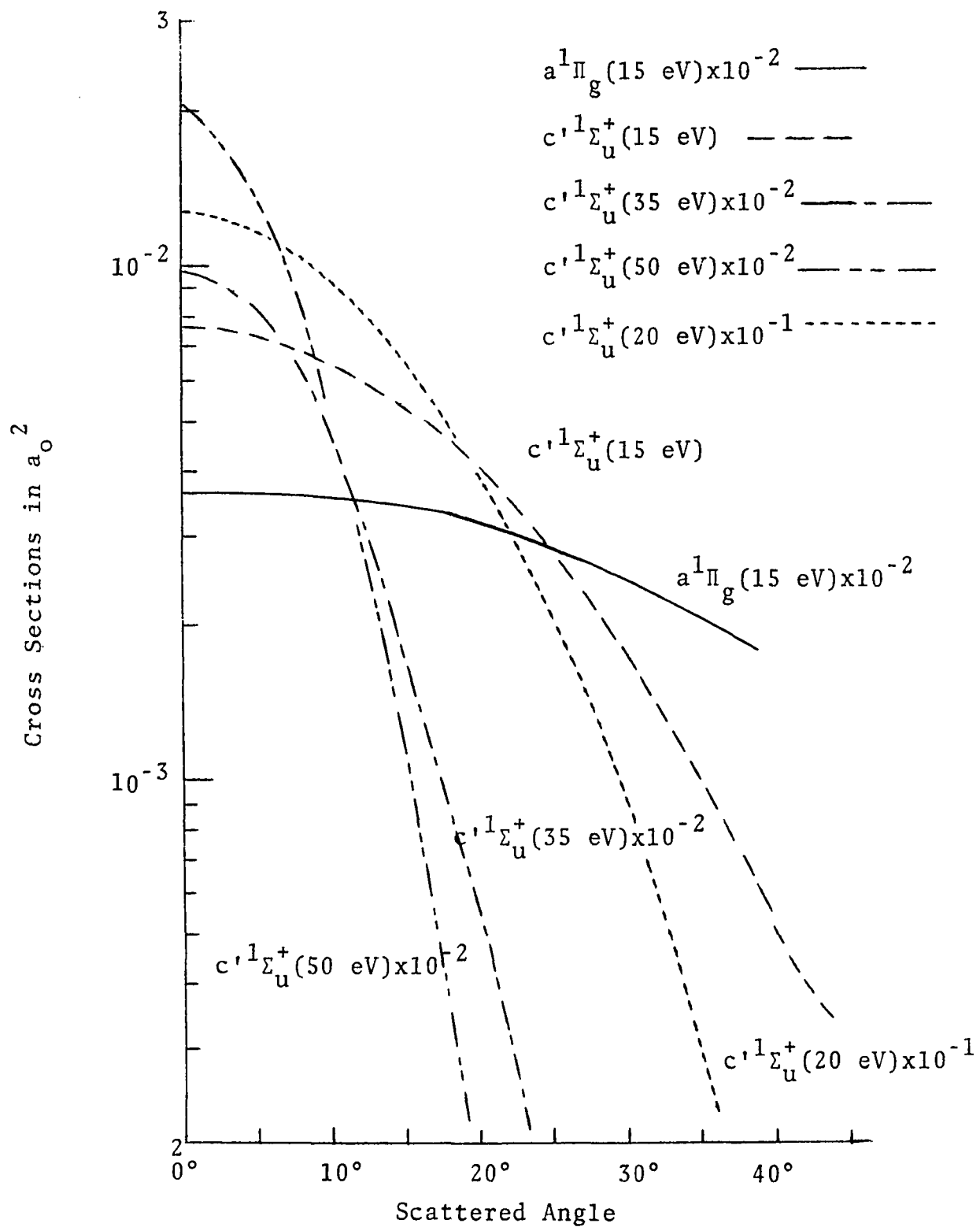


Figure 10. Differential Cross Sections of $a^1\Pi_g$ and $c',^1\Sigma_u^+$

The excitation functions of $w^1\Delta_u$ state computed by using wave function set (i) is displayed in Fig. 11. Compared with the results shown, the cross sections by set (ii) are about 5% smaller at low energy but 5% larger at high energy. Set (iii) gives cross sections which are uniformly larger by 10% than the ones shown. Below 40 eV, the cross sections by set (iv) are about 20% smaller than the ones by set (i), but above 200 eV the agreement is within 5%. The broad shape of $G_{on}(K)$ for this transition is reflected in the broad peak of the excitation function with E^{-1} dependence starting around 400 eV.

The $b'^1\Sigma_u^+$ state is another dipole-allowed state. However, theoretical calculations here are complicated by the mixing with the $(1\pi_u)^4(3\sigma_g)(3\sigma_u)$ configuration (35%) and possible vibrational perturbation of the high vibrational levels.^{84,70} The latter will not be treated in this work, but the former can be analyzed in some detail. In Fig. 11 are shown theoretical cross sections to the pure $(1\pi_u)^3(3\sigma_g)^2(1\pi_g)^1\Sigma_u^+$ state, to the pure $(1\pi_u)^4(3\sigma_g)(3\sigma_u)^1\Sigma_u^+$ state, and to the state of 65-35% weighted mixture of the above two (using Richardson's functions). Although the pure cross sections of $1\pi_u \rightarrow 1\pi_g$ and $3\sigma_g \rightarrow 3\sigma_u$ excitations are quite similar both in magnitude and shape, the severe destructive interference in $\mathcal{C}_{on}(K)$ results in the "mixed" cross sections

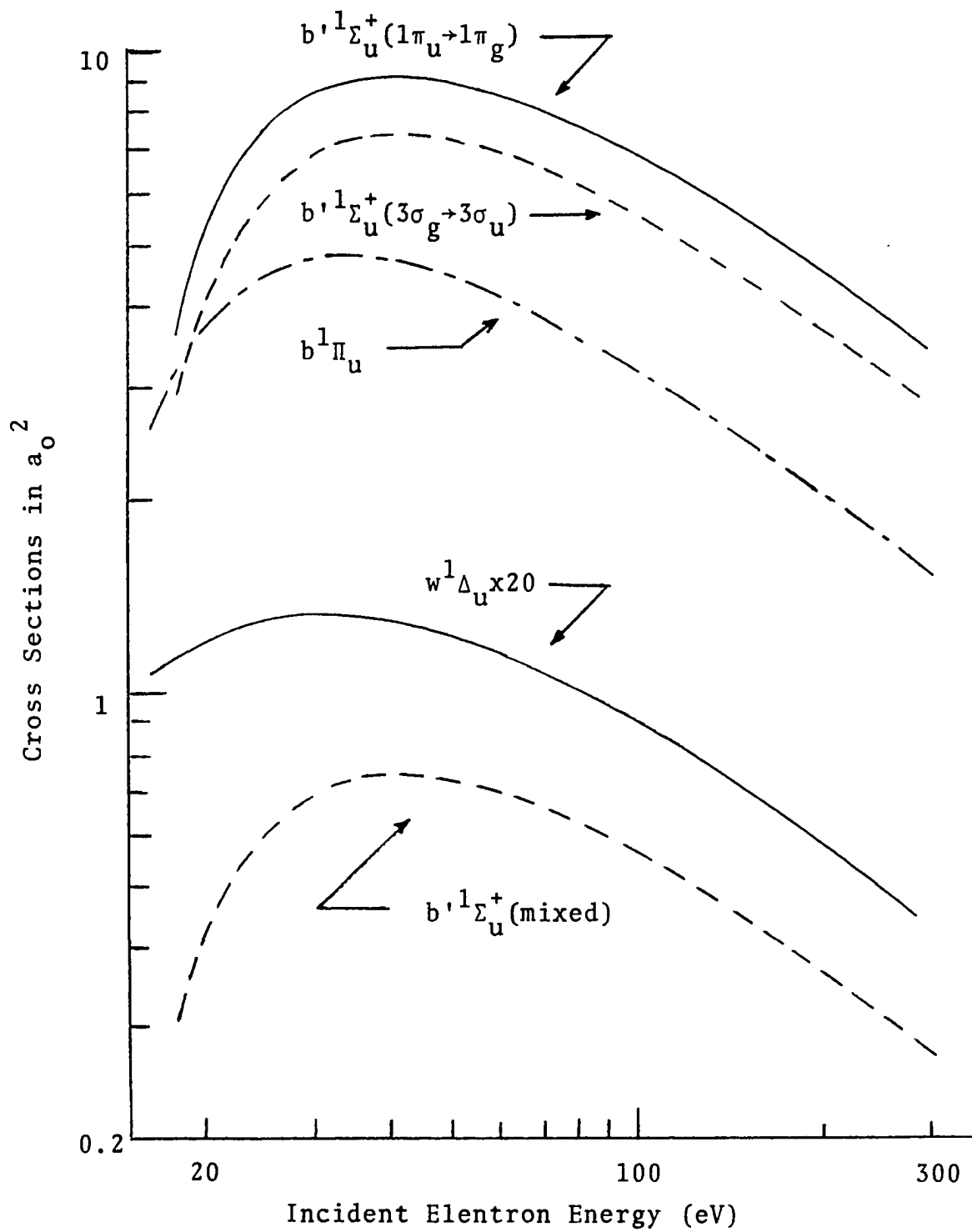


Figure 11. Cross Sections of $b',^1\Sigma_u^+$, $b'^1\Pi_u$, and $w'^1\Delta_u$

which are about one tenth of either of the pure cross sections. The sensitivity of the "mixed" cross sections indicates that in order to obtain reliable excitation cross sections of $b'^1\Sigma_u^+$ state, it would be necessary to conduct an accurate analysis of the configuration mixing.

Under the first Born approximation (including Ochkur's or Rudge's exchange term), the excitation cross sections of the $a'^1\Sigma_u^-$ state becomes zero. To analyze theoretically excitation to this state, one must consider the indirect coupling between $X^1\Sigma_g^+$ and $a'^1\Sigma_u^-$ through the various intermediate states. Calculations of excitation cross sections involving indirect coupling are beyond the scope of this research. Nevertheless, it may be pointed out that a somewhat similar case is known of excitation of neon atoms in which the Born cross sections (exclusive of exchange terms) of a number of the excited states of the $2p^5np$ and $2p^5nd$ configuration are zero.³

The $b^1\Pi_u$ State

The $b^1\Pi_u$ state may be described as deriving from the $(2\sigma_u)(1\pi_u)^4(1\pi_g)$ configuration mixed with $(1\pi_u)^3(3\sigma_g)(1\pi_g)^2$. Since the wave function for the latter configuration is not available, the discussions for this state are only qualitative in nature. Nevertheless, the computations have been made for the excitation cross sections for the pure $(2\sigma_u)(1\pi_u)^4(1\pi_g)^1\Pi_u$.

In Fig. 11 is shown the excitation function calculated by using set (i). The sensitivity to the choice of wave function is not too great (See Table XII). The excitation function exhibits the broad maximum characteristic of the dipole-allowed states. The shape of the excitation function and the magnitude of the cross sections are in fact rather similar to those of the $b'^1\Sigma_u^+$ state.

It is well known^{1,3} that for the singlet-singlet excitations at high incident electron energies, the cross sections depend on energy as $E^{-1}\ln E$ in the case of the dipole-allowed transitions and as E^{-1} in the case of dipole-forbidden transitions. The present theoretical calculations using Nesbet's functions show that within 5% the cross sections of the dipole-allowed $b'^1\Sigma_u^+$ (pure $1\pi_u \rightarrow 1\pi_g$), $b^1\Pi_u$, and $c'^1\Sigma_u^+$ states begin to have such asymptotic energy dependence at 500, 700, and 1400 eV respectively. The cross sections of the dipole-forbidden $a^1\Pi_g$, $a''^1\Sigma_g^+$, and $w^1\Delta_u$ states show within 5% E^{-1} dependence from 300, 250, and 400 eV respectively.

Excitation Cross Sections for Triplet States

Compared with the singlet states, a considerably larger amount of experimental data are available for excitation cross sections of the triplet states. Particularly the $B^3\Pi_g$ (first positive system) and $C^3\Pi_u$ (second positive system) states

TABLE XII

SENSITIVITY OF THE SINGLET CROSS SECTIONS^(a)
ON THE CHOICE OF WAVE FUNCTIONS

States ^(b)	Set (i) ^(c)	Set (ii)	Set (iii)	Set (iv)
$a^1\Pi_g$	0.980 (18.5) 0.0442	0.945 (18.5) 0.0427	0.931 (18.5) 0.0417	0.551 (19.0) 0.0276
$a''^1\Sigma_g^+$	0.253 (26) 0.0134	0.255 (26) 0.0134	0.210 (26) 0.0110	
$c'^1\Sigma_u^+$	0.148 (60) 0.0383	0.104 (60) 0.0272	0.101 (60) 0.0249	
$w^1\Delta_u$	0.0674 (30) 0.00715	0.0664 (32) 0.00751	0.0773 (30) 0.00783	0.0553 (34) 0.00708
$b'^1\Sigma_u^+$	8.287 (40) 1.214	9.392 (40) 1.391	9.409 (40) 1.411	9.324 (40) 1.347
$b^1\Pi_u$	4.875 (34) 0.620	5.275 (34) 0.670	4.950 (34) 0.625	4.442 (32) 0.542

(a) All cross sections are computed by Ochkur's² modification and expressed in units of a_0^2 .

(b) For each state there are three rows which are respectively the peak cross section, the position of the peak in eV, and the cross section at 1000 eV.

(c) See the text for designations.

TABLE XIII

SENSITIVITY OF THE TRIPLET CROSS SECTIONS^(a)
ON THE CHOICE OF WAVE FUNCTIONS

States ^(b)	Set (i) ^(c)	Set (ii)	Set (iii)	Set (iv)
$C^3\Pi_u$	1.609 (14.5) 0.367	1.676 (14.5) 0.365	1.615 (14.5) 0.364	1.613 (15.0) 0.403
$A^3\Sigma_u^+$	4.354 (11.0) 0.491	5.035 (11.0) 0.569	4.197 (11.0) 0.536	5.263 (11.5) 0.619
$B^3\Pi_g$	0.997 (13.5) 0.187	0.968 (13.5) 0.179	0.928 (13.0) 0.172	0.706 (14.5) 0.175
$D^3\Sigma_u^+$	0.0334 (18) 0.00713	0.0320 (18) 0.00701	0.0322 (18) 0.00709	
$W^3\Delta_u$	0.257 (21) 0.148	0.275 (22) 0.169	0.284 (21) 0.163	0.273 (24) 0.183
$E^3\Sigma_g^+$	0.133 (15) 0.0257	0.142 (15) 0.0272	0.123 (15) 0.0247	

(a) All cross sections are computed by Rudge's modification and expressed in units of a_0^2 .

(b) For each state there are three rows which are respectively the peak cross section, the position of the peak in eV, and the cross section at 60 eV.

(c) See the text for designations.

have been investigated experimentally by several groups.⁴⁰⁻⁴⁴

Unlike the case of some of the singlet states, there is no evidence of serious configuration mixing or of perturbation of vibrational levels in the triplet electronic states.

Since the electron exchange effect is entirely responsible for exciting the triplet states, one expects a much larger difference between the Ochkur-type and the Rudge-type calculations than in the singlet counterparts. From Eqs. (6.43) and (6.44) it is seen that if the vertical excitation energy ΔE is equal to the ionization potential ϵ of the initial state, the two approximations would give identical results.

Thus for the excitation to the triplet states of the helium atom for which the excitation energy is more than 80% of the ionization energy, one finds a close agreement between the results of two approximations.⁵³ However, for the $B^3\Pi_g$ state of N_2 which is about halfway between the ground state and the ionization limit, the Ochkur approximation gives markedly larger cross sections than does the Rudge modification.³⁹

The Rudge formula was derived in a first-principle manner based on the variational method, thus it will be adopted in the present calculations of the triplet excitation cross sections. Unless otherwise specified, all the calculated cross sections of the triplet states are of the Rudge-type. Computations have been made using both the theoretical and the

experimental values of the ionization energy ϵ in Eq. (6.44), of which the results using the latter are presented. The replacement of the latter by the former may reduce the cross sections by as much as 20% for $B^3\Pi_g$, $C^3\Pi_u$, $D^3\Sigma_u^+$ and $E^3\Sigma_g^+$, and increase by as much as 20% for $A^3\Sigma_u^+$ and $W^3\Delta_u$.

The sensitivity of the triplet cross sections to the choice of wave functions employed is summarized in Table XIII.

The $C^3\Pi_u$ State (Second Positive System)

The excitation function of the $C^3\Pi_u$ state calculated by using the Nesbet's wave functions (with Rudge's exchange) is shown in Fig. 12. For the purpose of comparison, also included is the excitation function (scaled to one half) calculated by means of the Ochkur exchange. The results by using wave function sets (i), (ii), and (iii) agree within 4%, and the results of set (iv) differ no more than 10% from the above group (See Table XIII). The theoretical excitation function of Cartwright is uniformly twice as large as the present one for the reason explained earlier.

Included in Fig. 12 are the experimental excitation functions (apparent) reported by Jobe, Sharpton and St. John⁴⁰ and by Burns, Simpson and McConkey.⁴² The $C^3\Pi_u$ state receives little cascade contribution, thus it is particularly suited for making comparison between theory and experiment. The magni-

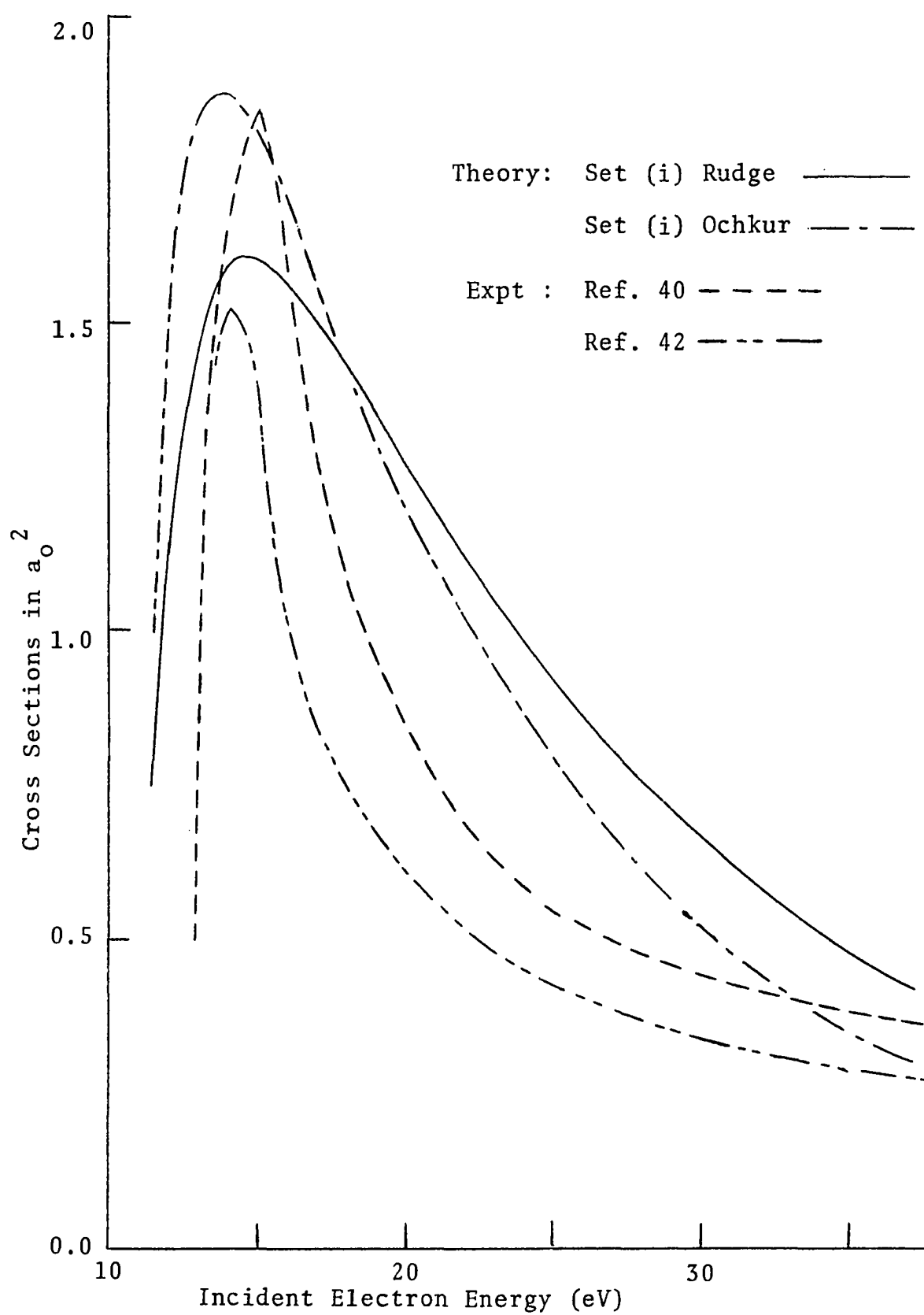


Figure 12. Cross Sections of $C^3\Pi_g$

tude and the position of the peak of the present theoretical curve (1.61 a_0^2 at 14.5 eV) agree well with the experimental values of 1.85 a_0^2 at 15 eV by Jobe et al and with 1.52 a_0^2 at 14.0 eV by Burns et al, but the shape of the theoretical excitation function is broader than the experimental counterpart. The recent optical measurements by Shemansky and Broadfoot⁸⁵ show a peak cross section of 1.35 a_0^2 at 14.7 eV. The unnormalized optical excitation function of Freund⁷⁷ has a somewhat broader shape than those in Refs. 40 and 42. The cross sections reported by Skubenich and Zapesochny,⁴¹ however, are much smaller than those of Refs. 40 and 42. The good agreement between the present theoretical cross sections and the experimental results of two different groups^{40,42} suggests the possibility that the Born-Rudge approximation may be reasonably adequate in describing electron-impact excitation of the triplet states of N_2 . The Born-Ochkur cross sections, however, are more than two times greater than the Born-Rudge counterpart near the peak, and by 40% at 40 eV and by 27% at 60 eV.

The $A^3\Sigma_u^+$ State (Vegard-Kaplan Bands)

The transitions between $A^3\Sigma_u^+$ and $X^1\Sigma_g^+$ have been observed by various methods.^{86,87} The mechanism of population of $A^3\Sigma_u^+$ is of aeronomical interest. In their analysis of

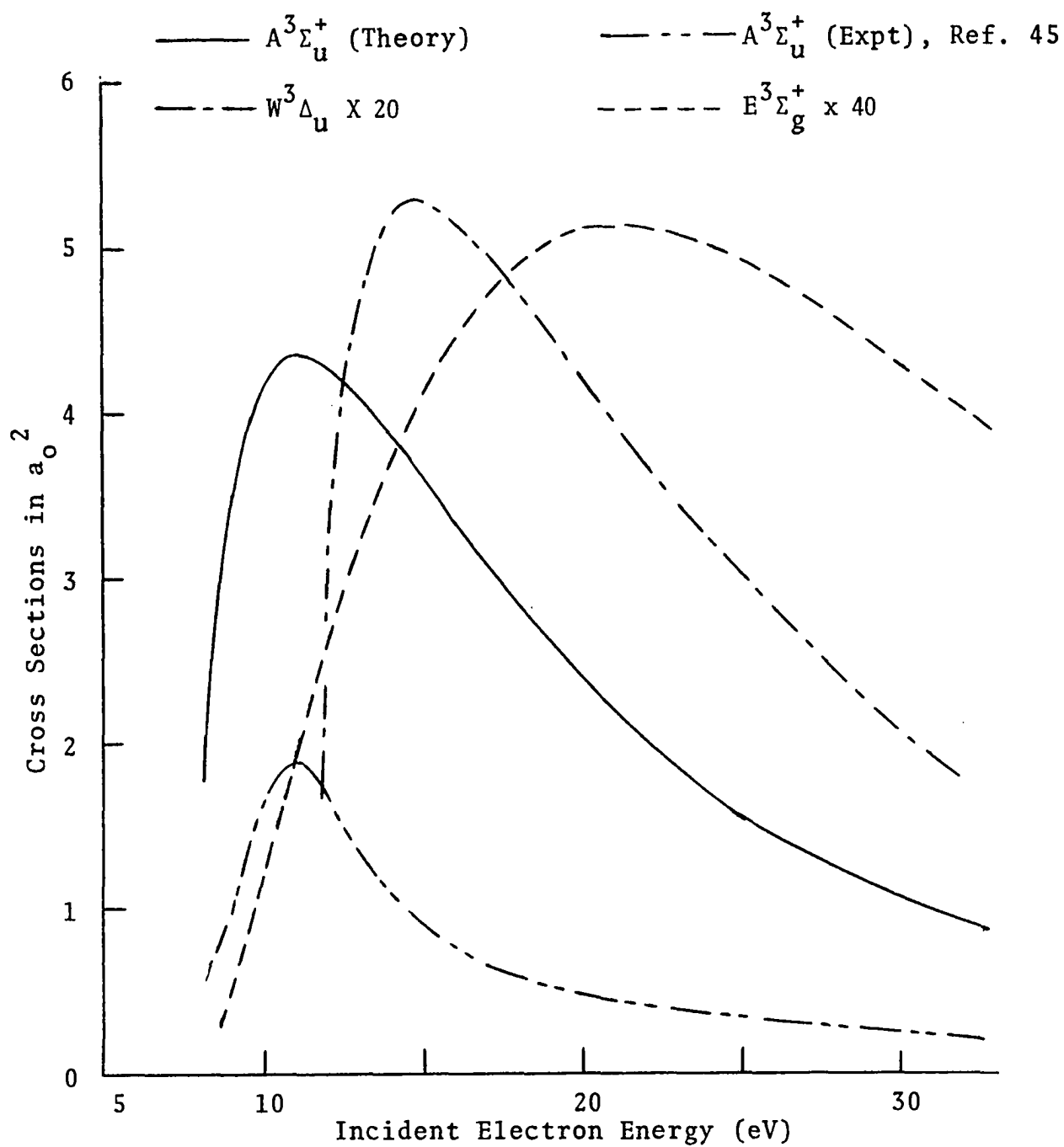


Figure 13. Cross Sections of $A^3\Sigma_u^+$, $W^3\Delta_u$, and $E^3\Sigma_g^+$

auroral spectrum, Broadfoot and Hunten⁸⁸ concluded that the population of $A^3\Sigma_u^+$ is almost entirely due to cascade. Very recently Borst⁴⁵ has reported direct experimental measurements of the $A^3\Sigma_u^+$. In Fig. 13 are shown the present calculated cross sections (Nesbet's wave functions) along with Borst's experimental results. The excitation functions obtained by using other sets of wave functions are somewhat (15-20%) larger than the one shown in Fig. 13, but their shapes and the positions of peak agree very well with one another. While the peaks of both curves occur at about the same energy, the theoretical cross sections are substantially larger than the experimental ones lying beyond the limits of uncertainty given by Borst. Cartwright's theoretical values are consistent with the present results except for the difference of a factor two mentioned previously.

The $B^3\Pi_g$ State (First Positive System)

The excitation function computed by using Nesbet's wave functions is shown in Fig. 14. It agrees with the theoretical curves resulted from sets (ii) and (iii) to within 8%. When the wave functions of set (iv) were used, the peak cross section is found to undergo a 30% reduction, while the cross sections above 40 eV are not much affected (8%). Although the present cross sections had been expected to be

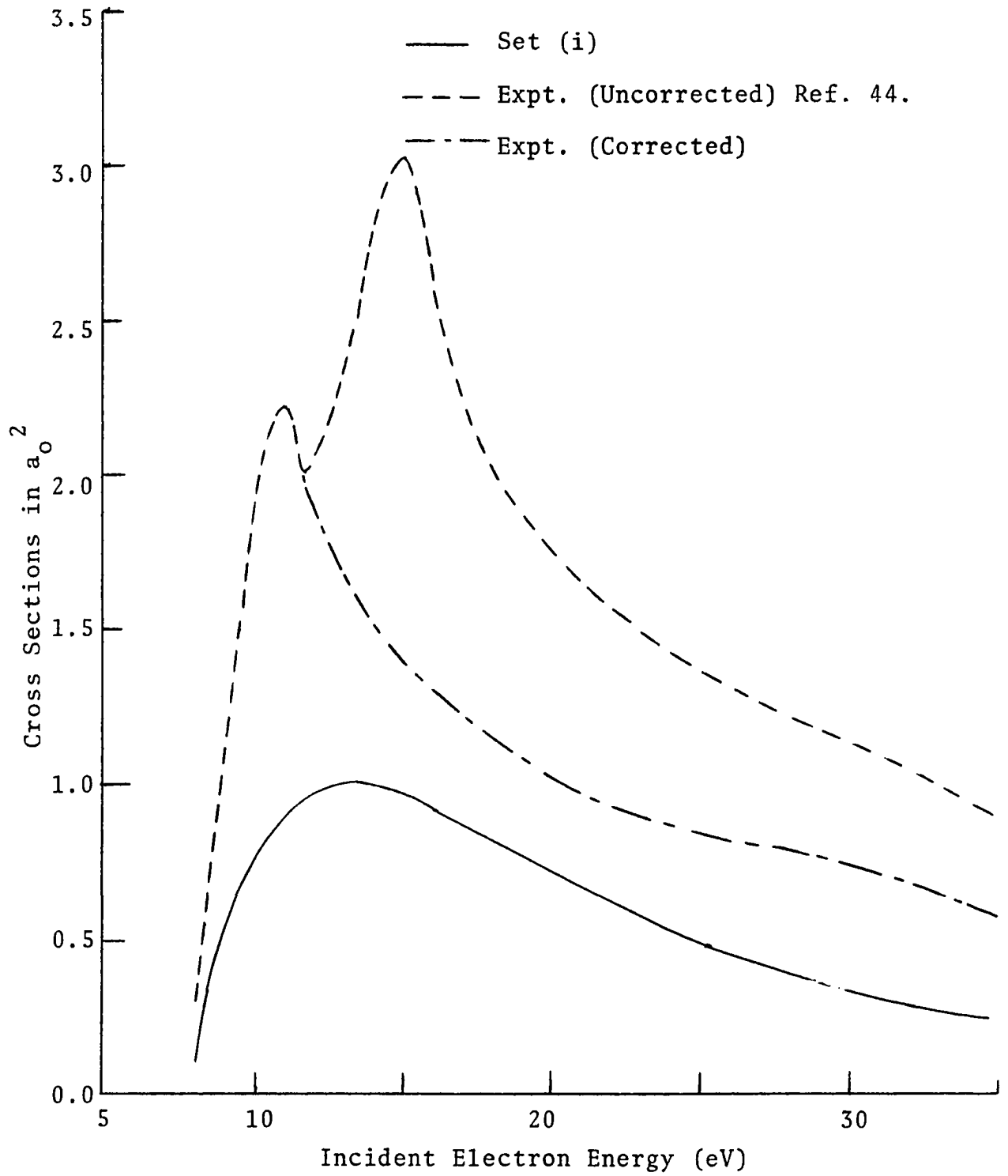


Figure 14. Cross Sections of $B^3\Pi_g$

about one-half of those of Cartwright's,³³ the latter are found to be about three times larger than the present values using similar wave functions. This discrepancy is difficult to reconcile.

Experimental measurements of the apparent excitation functions have been reported by Stanton and St. John,⁴⁴ by McConkey and Simpson,⁴³ and by Skubenich and Zapesochny.⁴¹ The first two sets of data are quite close to each other, whereas the Skubenich and Zapesochny cross sections differ quite appreciably from those of Refs. 44 and 43 for incident energies below 16 eV. These apparent excitation functions contain, in addition to direct excitation, the cascade contributions from higher states. Among the states which may cascade to the $B^3\Pi_g$ state, the $C^3\Pi_u$ and $C'^3\Pi_u$ states are probably the most important ones. By using the experimental data of the optical excitation function of the $C^3\Pi_u \rightarrow B^3\Pi_g$ transition reported by St. John and co-workers,⁴⁰ "correction" was made to the experimental data of Ref. 44 for cascade from the $C^3\Pi_u$ state. This corrected excitation function along with the uncorrected apparent excitation function of Stanton and St. John are included in Fig. 14. There are no experimental data of excitation cross sections of the $C'^3\Pi_u$ state to estimate its cascade contribution. The $C'^3\Pi_u$ state [configuration $(1\pi_u)^3(3\sigma_g)(1\pi_g)^2$] involves two electrons in excited orbitals,

and no accurate wave functions for this state have been published to the author's knowledge. Of the other triplet states which may cascade to $B^3\Pi_g$, the cross sections of the $W^3\Delta_u$ and $D^3\Sigma_u^+$ states are much smaller than the direct excitation cross sections of $B^3\Pi_g$ as will be seen in the next two subsections. Under the Born-Rudge (or Born-Ochkur) approximation, the collision amplitude of excitation of the $B'^3\Sigma_u^-$ vanishes. Thus no further cascade subtraction will be made to the "corrected" excitation function in Fig. 14. It is seen that the experimental excitation cross sections of $B^3\Pi_g$ are considerably larger than the present theoretically calculated values. From their recent optical measurements, Shemansky and Broadfoot⁸⁵ estimated the peak cross section as $4.28 a_0^2$ which is about two times larger than the ones reported in Refs. 41, 43 and 44.

Gilmore⁸⁹ pointed out the interesting possibility of cascade scheme of $A^3\Sigma_u^+(\text{high } v) \rightarrow B^3\Pi_g(\text{low } v) \rightarrow A^3\Sigma_u^+(\text{low } v)$. The present calculations indeed indicate that the excitation cross sections of $A^3\Sigma_u^+$ is about five times larger than those of $B^3\Pi_g$ and that the Franck-Condon factors of $A^3\Sigma_u^+$ favor excitation to the vibrational levels around $v=10$ which may cascade to the lower vibrational levels of $B^3\Pi_g$. Such a double cascade mechanism may be responsible for at least part of the discrepancy between the theoretical and the experimental curves.

The $D^3\Sigma_u^+$ State

The present theoretical excitation function of the $D^3\Sigma_u^+$ state computed with set (i) is shown in Fig. 15 along with the experimental data of Skubenich and Zapesochny.⁴¹ Wave functions set (ii) and set (iii) give results within 4% of the one shown. The shape of the excitation function is markedly different between theory and experiment. The broad secondary peak around 25 eV reported in Ref. 41 is in distinct contrast with the present theoretical results. A recent experimental optical excitation function by Freund⁷⁷ also shows somewhat similar shape to the one in Ref. 41. The theoretical cross sections of Cartwright³³ are some six to eight times larger than the present values. This discrepancy may be partly due to the fact that in the Cartwright's calculations of the excitation function of the $D^3\Sigma_u^+$ state, the multicenter terms in the transition amplitude were neglected. To examine this point, separate calculations of the cross sections have been made omitting all the three-center integrals and the results become rather close to one-half of Cartwright's values (within typically 50%) as would be expected.

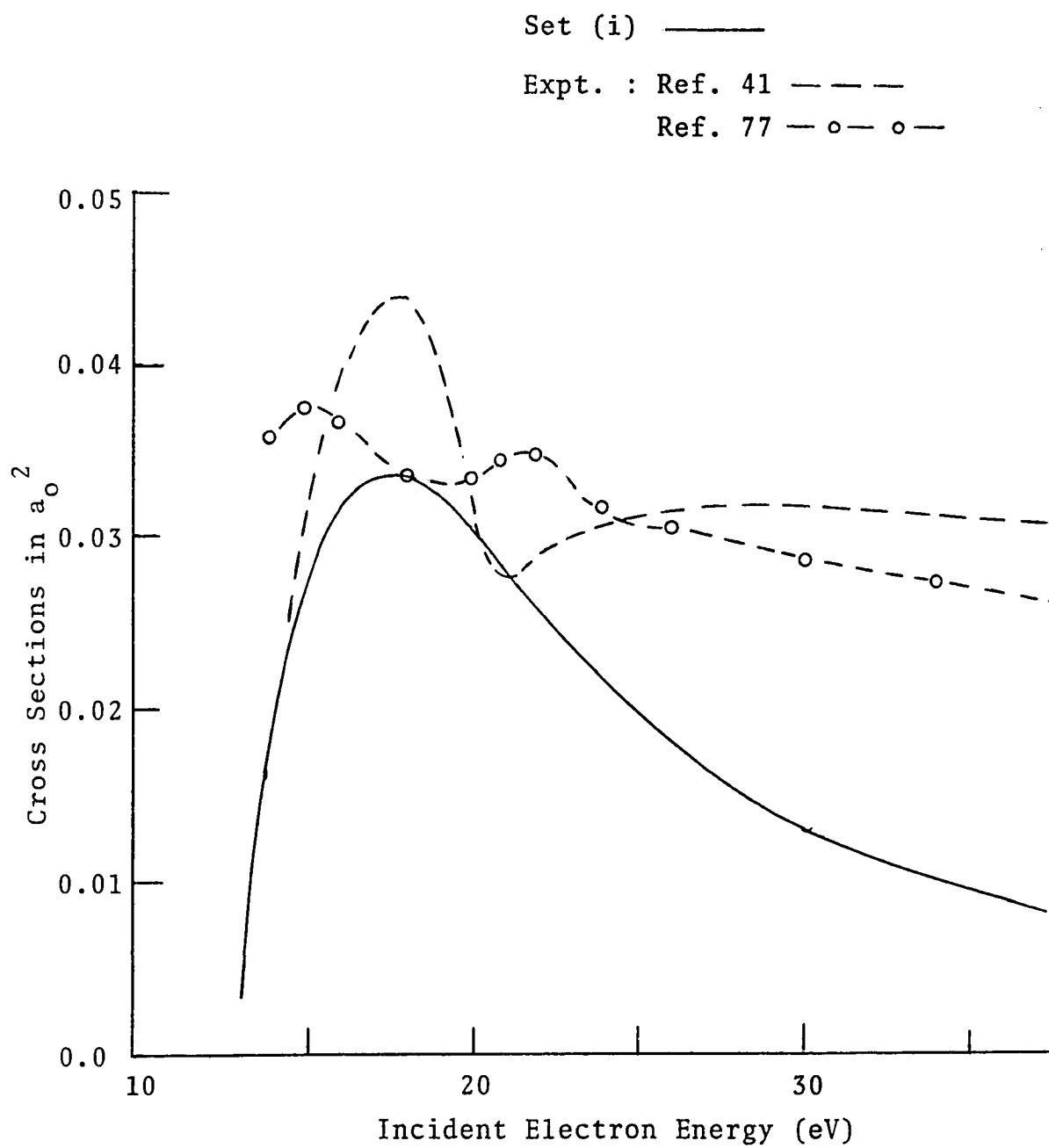


Figure 15. Cross Sections of $D^3\Sigma_u^+$

The $W^3\Delta_u$ and $E^3\Sigma_g^+$ States

The theoretical excitation function of the $W^3\Delta_u$ state shows a peak around 22 eV which is distinctly broader than those of the other triplet states studied in this work (Fig. 13). The excitation function shown in Fig. 13 is obtained by using wave function set (i). The other three sets of wave functions give cross sections which are somewhat larger (about 15%) than the ones shown. There do not appear to be any experimental measurements of the excitation cross sections of the $W^3\Delta_u$ in the literature to compare with the present theoretical values. Although discrepancy of a factor of two had been expected between the present and the Cartwright's cross sections,³³ his excitation function for $W^3\Delta_u$ is virtually identical to the present one.

In Fig. 13 is also included the calculated excitation function of the $E^3\Sigma_g^+$ by using set (i). Sets (ii) and (iii) give the cross sections that are about 8% larger and smaller respectively than the ones shown in Fig. 13. In his cross section calculations for this state, Cartwright neglected the multicenter terms in the transition amplitude (like the case of $D^3\Sigma_u^+$), and his cross sections are some four to nine times larger than the present values. The separate calculations without the multicenter terms show that again much of the dis-

crepancy (beyond the factor of two) is due to the neglect of multicenter terms in Ref. 33. Several investigators⁹⁰ have found a sharp peak around 12.3 eV attributed to the $E^3\Sigma_g^+$ state in their excitation experiments, the latest being the experimental measurement by Borst⁴⁵ with the peak cross section of 0.25 a_0^2 . The present theoretical excitation function shows a much broader shape with the peak cross section of 0.133 a_0^2 at 15 eV. Since the experimental evidence is suggestive of a resonance-type mechanism, no further comparison will be made.

For the singlet-triplet excitations, the cross sections depend on energy as E^{-3} at high incident electron energy. The present theoretical calculations using Nesbet's functions show such energy dependence starting within 5% at 170 eV ($A^3\Sigma_u^+$), 190 eV ($B^3\Pi_g$), 160 eV ($C^3\Pi_u$), 85 eV ($D^3\Sigma_u^+$), 100 eV ($E^3\Sigma_g^+$), and 190 eV ($W^3\Delta_u$).

Conclusion

By using the GTO as the basis functions of the molecular orbitals, the Born-approximation cross sections of electron-impact excitation of the electronic states of diatomic molecules can be calculated by a very simple procedure which is no more complicated than the corresponding case of excitation of atoms. In this thesis are presented the theoretical excitation functions for twelve states of the N_2 molecule.

When molecular wave functions of sufficiently high accuracy (such as those of Nesbet and of Richardson) are used, the computed cross sections do not appear to vary too sensitively with the choice of the wave functions.

For the excitation of the singlet states one can use the Born approximation for the direct-excitation scattering amplitude neglecting the exchange term, or alternatively include the exchange amplitude by the Ochkur or the Rudge scheme. At energies well above the threshold all three schemes (Ochkur, Rudge, and non-exchange) result in nearly the same cross sections. Near the threshold region, the Rudge-modification cross sections substantially exceed the other two types; however, at the low-energy range the Born approximation is not expected to be reliable for singlet-singlet excitation. Thus the difference between the three schemes is not of great interest. Comparison of the present calculated singlet excitation cross sections with the available experimental data shows about 25% agreement for the $a^1\Pi_g$ state at 500 eV but for the $a''^1\Sigma_g^+$ state at 80 eV the experimental cross section is 50% of the theoretical value.

..In the case of singlet-triplet excitation, the low-energy range is of prime interest in most of the experimental work. For the theoretical calculations of the cross sections, the Rudge modification has been adopted. The present theo-

retical excitation cross sections of the $C^3\Pi_u$ state are in good agreement with the experimental values, whereas for the $A^3\Sigma_u^+$ and $B^3\Pi_g$ states the discrepancy becomes considerably larger.

In conclusion it may be stated that with the use of the GTO, the Born approximation along with the Rudge modification provides a simple, practical scheme to compute the electronic excitation cross sections of N_2 , and the results are in reasonable agreement with the available experimental data.

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APPENDIXES

APPENDIX I

DERIVATION OF CROSS SECTION FORMULA

The algebra of derivation is considerably simplified by using the results of the Racah's works on the theory of complex spectra,²⁰ which elucidate the coupling schemes of more than two angular momenta. Also useful are the symmetry relations of the Clebsch-Gordan coefficients¹⁷ (also known as vector addition and Wigner coefficients). For this reason, the properties of the Clebsch-Gordan, the Racah, and the related coefficients are listed first.

The Clebsch-Gordan (C-G) coefficients have the following symmetry relations with respect to interchange of the parameters,

$$C(ab\alpha\beta; c\gamma) = (-1)^{a-\alpha} [(2c+1)/(2b+1)]^{1/2} C(ca\gamma -\alpha; b\beta) \quad (\text{I-1a})$$

$$= (-1)^{b+\beta} [(2c+1)/(2a+1)]^{1/2} C(bc -\beta\gamma; a\alpha) . \quad (\text{I-1b})$$

Racah gives the formula (Racah's sum rule)²⁰ for the sum over a magnetic quantum number of the product of three Clebsch-Gordan coefficients as

$$\sum_{\beta} C(ab\alpha\beta; e\alpha+\beta) C(ed\alpha+\beta\gamma-\alpha-\beta; c\gamma) C(bd\beta\gamma-\alpha-\beta; f\gamma-\alpha) \\ = [(2e+1)(2f+1)]^{1/2} C(af\alpha\gamma-\alpha; c\gamma) W(abcd; ef), \quad (\text{I-2})$$

where W is the Racah's coefficient. The Racah coefficient is defined as²⁰

$$W(abcd;ef) = \Delta(abe)\Delta(cde)\Delta(acf)\Delta(bdf)w(abcd;ef) , \quad (I-3)$$

where the "triangula" coefficient $\Delta(abc)$ is

$$\Delta(abc) = [(a+b-c)(c+a-b)(b+c-a)/(a+b+c+1)!]^{1/2} , \quad (I-4)$$

and

$$\begin{aligned} w(abcd;ef) = \sum_z (-1)^{z+a+b+c+d} (z+1)! / [(z-a-b-e)! \\ \times (z-c-d-e)!(z-a-c-f)!(z-b-d-f)!(a+b+c+d-z)! \\ \times (a+d+e+f-z)!(b+c+e+f-z)!] , \end{aligned} \quad (I-5)$$

where in Eq. (I-5) the summation over z runs as long as the factorials are valid. Some of the symmetry relations²⁰ of the Racah coefficients are

$$W(abcd;ef) = W(badc;ef) \quad (I-6a)$$

$$= W(cdab;ef) \quad (I-6b)$$

$$= W(acbd;fe) \quad (I-6c)$$

$$= (-1)^{e+f-a-d} W(ebcf;ad) \quad (I-6d)$$

$$= (-1)^{e+f-b-c} W(aefd;bc) . \quad (I-6e)$$

Finally a coefficient related to the Racah coefficient is defined as

$$\begin{aligned} Z(abcd;ef) = i^{f-a+c} [(2a+1)(2b+1)(2c+1)(2d+1)]^{1/2} \\ \times C(ac00;f0)W(abcd;ef) . \end{aligned} \quad (I-7)$$

In particular the following reduction³² is useful, i.e.,

$$Z(abcd; e0) = \delta_{ac} \delta_{bd} (-1)^{b-e} (2b+1)^{1/2} . \quad (I-8)$$

Blatt and Biedenharn³² give the general derivation of the cross section formula. The purpose of this Appendix is to specialize the derivation with fuller detail to the problem of electron-atom collision process.

The scattered amplitude B in $(\theta\phi)$ direction is from Eqs. (2.7) and (2.10),

$$B(n'j'm_j, \rightarrow njm_j) = \pi^{1/2}/k' \sum_{\ell'=0}^{\infty} i^{\ell'-1} (2\ell'+1)^{1/2} \\ \times \sum_{\ell=0}^{\infty} \sum_{m=\ell}^{\ell} i^{-\ell} S(n'j'\ell'm_j, 0; nj\ell m_j m_{\ell}) . \quad (I-9)$$

Substitution of Eq. (2.24) followed by rearrangement of summing order yields

$$B = \pi^{1/2}/k' \sum_{L=0}^{\infty} \sum_{m=-L}^L \sum_{\ell=|L-j|}^{L+j} \sum_{\ell'=|L-j'|}^{L+j'} \sum_{m=-\ell}^{\ell} \\ \times i^{\ell'-\ell-1} (2\ell'+1)^{1/2} C(\ell'j'0m_j, ; LM) C(\ell j m m_j; LM) \\ \times S(nj\ell LM, n'j'\ell'LM) . \quad (I-10)$$

The differential cross section is then

$$I(n'j'm_j, \rightarrow njm_j | \theta\phi) d\Omega = |B(n'j'm_j, \rightarrow njm_j) Y_{\ell m}(\theta\phi)|^2 d\Omega . \quad (I-11)$$

Since the excitation from $n'j'$ to nj state is of major

interest, it is customary to average over the initial magnetic substates ($m_{j,}$) and to sum over the final magnetic substates (m_j). Then,

$$\begin{aligned}
 I(n'j' \rightarrow nj | \theta\phi) = & \pi(k')^{-2} (2j'+1)^{-1} \sum_{L_1 \ell_1 \ell_1' L_2 \ell_2 \ell_2'} \\
 & \times i^{\ell_1 - \ell_1' + \ell_2' - \ell_2} [\delta_{nn'}, \delta_{jj'}, \delta_{\ell_1 \ell_1'} \\
 & - S^*(nj \ell_1 L_1 M_1, n'j' \ell_1' L_1 M_1)] [\delta_{nn'}, \delta_{jj'}, \delta_{\ell_2 \ell_2'} \\
 & - S(nj \ell_2 L_2 M_2, n'j' \ell_2' L_2 M_2)] K(L_1 \ell_1 \ell_1'; L_2 \ell_2 \ell_2'; jj' | \theta\phi),
 \end{aligned}
 \tag{I-12}$$

where subscripts "1" and "2" are introduced to distinguish the two sets of summing indices, and

$$\begin{aligned}
 & \sum_{M_1 M_2 m_1 m_2 m_j m_j'} C(\ell_1' j' 0 m_j'; L_1 M_1) C(\ell_2' j' 0 m_j'; L_2 M_2) \\
 & \times C(\ell_1 j m_1 m_j; L_1 M_1) C(\ell_2 j m_2 m_j; L_2 M_2) \\
 & \times Y_{\ell_1 m_1}^*(\theta\phi) Y_{\ell_2 m_2}(\theta\phi) .
 \end{aligned}
 \tag{I-13}$$

Although sums over six magnetic quantum numbers are formally written out, only two of them (m_1 and $m_{j,}$, for example) are independent due to the restrictions on the C-G coefficients,

$$\begin{aligned}
 M_1 &= M_2 = m_j, \\
 m_j &= M_1 - m_1 = m_{j,} - m_1 \\
 m_2 &= M_2 - m_j = m_{j,} - m_j = m_1
 \end{aligned}
 \tag{I-14}$$

Substitution of

$$\begin{aligned}
 Y_{\ell_1 m_1}^* (\theta \phi) Y_{\ell_2 m_2} (\theta \phi) &= (-1)^{m_1} \sum_{L=|\ell_1 - \ell_2|}^{\ell_1 + \ell_2} \\
 &\times [(2\ell_1 + 1)(2\ell_2 + 1)/4\pi(2L + 1)]^{1/2} C(\ell_1 \ell_2 -m_1 m_1; L 0) \\
 &\times C(\ell_1 \ell_2 0 0; L 0) Y_{L 0} (\theta \phi) \quad (I-15)
 \end{aligned}$$

along with the symmetry relation (I-1a) applied to the first member of the C-G coefficient in Eq. (I-15), gives

$$\begin{aligned}
 K &= (-1)^{\ell_1} [(2\ell_1 + 1)(2\ell_1' + 1)(2\ell_2' + 1)/4\pi]^{1/2} \\
 &\times \sum_{L m_j} C(\ell_1' j' 0 m_j; L_1 m_j) C(\ell_2' j' 0 m_j; L_2 m_j) \\
 &\times C(\ell_1 \ell_2 0 0; L 0) \sum_{m_1} C(\ell_1 j m_1 -m_j, -m_1; L_1 m_j) \\
 &\times C(L \ell_1 0 m_1; \ell_2 m_1) Y_{L 0} (\theta \phi) . \quad (I-16)
 \end{aligned}$$

Eq. (I-16) is reduced by using Eq. (I-2) as

$$\begin{aligned}
 K &= (-1)^{\ell_1} [(2\ell_1 + 1)(2\ell_1' + 1)(2\ell_2 + 1)(2\ell_2' + 1)(2L_1 + 1)/4\pi]^{1/2} \\
 &\times \sum_{L m_j} C(\ell_1 \ell_2 0 0; L 0) C(\ell_1' j' 0 m_j; L_1 m_j) C(\ell_2' j' 0 m_j; L_2 m_j) \\
 &\times C(LL_1 0 m_j; L_2 m_j) W(L \ell_1 L_2 j; \ell_2 L_1) Y_{L 0} (\theta \phi) . \quad (I-17)
 \end{aligned}$$

Application of Eq. (I-1b) to each of the third and the fourth C-G coefficients in Eq. (I-17) followed by application of Eq. (I-2) gives

$$K = (-1)^{\ell_1 - \ell_2' - L + 2j'} (2L_1 + 1)(2L_2 + 1)$$

$$\begin{aligned}
& \times [(2\ell_1+1)(2\ell_1'+1)(2\ell_2+1)(2\ell_2'+1)]^{1/2} \\
& \times \sum_L C(\ell_1\ell_2 00; L0) C(\ell_1'\ell_2' 00; L0) W(L\ell_1 L_2 j; \ell_2 L_1) \\
& \times W(\ell_1' j' L L_2; L_1 \ell_2') [4\pi(2L+1)]^{-1/2} Y_{L0}(\theta\phi) . \quad (I-18)
\end{aligned}$$

Using the symmetry relation of W in Eqs. (I-6a) through (I-6e), and the definition of Z coefficient in Eq. (I-7), Eq. (I-18) is expressed as

$$\begin{aligned}
K &= (-1)^{\ell_1+\ell_2+j'-j} (2L_1+1)(2L_2+1) \\
& \times [(2\ell_1+1)(2\ell_1'+1)(2\ell_2+1)(2\ell_2'+1)]^{1/2} \\
& \times \sum_L C(\ell_1\ell_2 00; L0) C(\ell_1'\ell_2' 00; L0) (-1)^L W(\ell_1 L_1 \ell_2 L_2; jL) \\
& \times W(\ell_1' L_1 \ell_2' L_2; j'L) [4\pi(2L+1)]^{-1/2} Y_{L0}(\theta\phi) \\
& = (-1)^{\ell_1+\ell_2+j'-j} \sum_L (-1)^L i^{\ell_2-\ell_1+\ell_1'-\ell_2'-2L} \\
& \times Z(\ell_1 L_1 \ell_2 L_2; jL) Z(\ell_1' L_1 \ell_2' L_2; j'L) [4\pi(2L+1)]^{-1/2} \\
& \times Y_{L0}(\theta\phi) . \quad (I-19)
\end{aligned}$$

When Eq. (I-19) is substituted in Eq. (I-11) and integrated over $(\theta\phi)$, one would obtain the expression for the total excitation cross section

$$Q(n'j' nj) = \int d\Omega I(n'j' \rightarrow nj | \theta\phi) . \quad (I-20)$$

The angular dependence of $Y_{L0}(\theta\phi)$ appears only in the expression of K ; therefore, for the purpose of obtaining the

total cross sections, the integration over $(\theta\phi)$ is performed for K function. The spherical harmonics forming an orthonormal set, the integration simply leads to

$$\begin{aligned} \bar{K}(L_1 \ell_1 \ell_1'; L_2 \ell_2 \ell_2'; jj') &= \int d\Omega K(L_1 \ell_1 \ell_1'; L_2 \ell_2 \ell_2'; jj' | \theta\phi) \\ &= \delta_{L_0} (-1)^{\ell_1 + \ell_2 + j' - j} \binom{\ell_2 - \ell_1 + \ell_1' - \ell_2' - 2L}{(i)} \\ &\times Z(\ell_1 L_1 \ell_2 L_2; j0) Z(\ell_1' L_1 \ell_2' L_2; j'0) . \end{aligned} \quad (I-21)$$

By means of Eq. (I-8), Eq. (I-20) is further reduced as

$$\bar{K} = (2L_1 + 1) \delta_{L_0} \delta_{\ell_1 \ell_2} \delta_{\ell_1' \ell_2'} \delta_{L_1 L_2} . \quad (I-22)$$

Finally substitution of Eqs. (I-22) and (I-12) in Eq. (I-20) gives the well-known formula

$$\begin{aligned} Q(n'j' \rightarrow nj) &= (\pi/k'^2) (2j'+1)^{-1} \sum_L (2L+1) \sum_{\ell=|L-j|}^{L+j} \sum_{\ell'=|L-j'|}^{L+j'} \\ &\times |\delta_{nn'} \delta_{jj'} \delta_{\ell\ell'} - S(nj\ell LM; n'j'\ell'LM)|^2 , \end{aligned} \quad (I-23)$$

where the subscripts are now dropped, the two sets of summing indices having been reduced as seen in Eq. (I-22).

APPENDIX II

COMPUTATION OF POTENTIAL USING CORRELATED WAVE FUNCTIONS

The problem to be dealt with is the evaluation of the integrals of type,

$$V_{\mu\mu},(r_1) = 4 \int \chi_{\mu}^*(\hat{r}_1, \vec{r}_2, \vec{r}_3, r_{23}) r_{12}^{-1} \chi_{\mu}(\hat{r}_1, \vec{r}_2, \vec{r}_3, r_{23}) \\ \times d\hat{r}_1 d\vec{r}_2 d\vec{r}_3 . \quad (II-1)$$

With the Weiss functions χ 's have the form

$$\chi_{\mu} = \sum_m C(\ell j \ M-m \ m; LM) Y_{\ell \ M-m}(1) [R(r_2, r_3, r_{23}) Y_{jm}(3) Y_{00}(2) \\ + R(r_3, r_2, r_{23}) Y_{jm}(2) Y_{00}(3)] . \quad (II-2)$$

Thus,

$$V_{\mu\mu},(r_1) = 4 \sum_{mm'} C(\ell j \ M-m \ m; LM) C(\ell' j' \ M-m' \ m'; LM) r_{12}^{-1} \\ \times [R_A(r_2, r_3, r_{23}) Y_{\ell \ M-m}^*(1) Y_{jm}^*(3) Y_{00}^*(2) Y_{\ell', \ M-m'}(1) \\ \times Y_{j', m'}(3) Y_{00}(2) + R_B(r_2, r_3, r_{23}) Y_{\ell \ M-m}^*(1) Y_{jm}^*(3) \\ \times Y_{00}^*(2) Y_{\ell', \ M-m'}(1) Y_{j', m'}(2) Y_{00}(3) \\ + R_C(r_2, r_3, r_{23}) Y_{\ell \ M-m}^*(1) Y_{jm}^*(2) Y_{00}^*(3) Y_{\ell', \ M-m'}(1) \\ \times Y_{j', m'}(3) Y_{00}(2) + R_D(r_2, r_3, r_{23}) Y_{\ell \ M-m}^*(1) Y_{jm}^*(2) \\ \times Y_{00}^*(3) Y_{\ell', \ M-m'}(1) Y_{j', m'}(2) Y_{00}(3)] d\hat{r}_1 d\vec{r}_2 d\vec{r}_3 , \quad (II-3)$$

where R_A , R_B , R_C , and R_D are the appropriate products of R 's which are shown in Eq. (II-2). Since the functions R_A , R_B , R_C , and R_D contain $\cos\theta_{23}$ dependence through r_{23} , it is advantageous to change either set of the integration coordinates $(\theta_2\phi_2)$ and $(\theta_3\phi_3)$ to $(\theta_{23}\phi_{23})$ and hence, to $(r_{23}\phi_{23})$. Accompanied by this rotation of coordinate system, it is necessary to transform the spherical harmonics accordingly. Rose¹⁷ gives the relation,

$$Y_{jm}(\theta_{23}\phi_{23}) = \sum_m D_{mm'}^j(\phi_2\theta_2^0) Y_{jm}(\theta_3\phi_3) , \quad (\text{II-4})$$

where $D_{mm'}^j$ is the matrix representation of the rotations of azimuthal angle ϕ_2 followed by polar angle θ_2 . From Eq. (II-4) it is easy to arrive at

$$Y_{jm}(\theta_3\phi_3) = \sum_m D_{mm'}^{j*}(\phi_2\theta_2^0) Y_{jm}(\theta_{23}\phi_{23}) . \quad (\text{II-5})$$

In particular, the following formulas¹⁷ are useful, deriving the expressions of V , viz.,

$$D_{m0}^{j*}(\phi\theta) = [4\pi/(2j+1)]^{1/2} Y_{jm}(\theta\phi) , \quad (\text{II-6})$$

and

$$\begin{aligned} Y_{j_1 m_1}(\theta\phi) Y_{j_2 m_2}(\theta\phi) &= \sum_{J=|j_1-j_2|}^{j_1+j_2} [(2j_1+1)(2j_2+1)/4\pi(2J+1)]^{1/2} \\ &\times C(j_1 j_2 m_1 m_2; J \ m_1+m_2) C(j_1 j_2 00; J0) Y_{J \ m_1+m_2}(\theta\phi) . \end{aligned} \quad (\text{II-7})$$

The expansion of r_{12}^{-1} is also well-known, i.e.,

$$r_{12}^{-1} = \sum_k \sum_{g=-k}^k [4\pi/(2k+1)] [r_<^k/r_>^{(k+1)}] Y_{kg}(\theta_1\phi_1) Y_{kg}^*(\theta_2\phi_2) , \quad (\text{II-8})$$

where $r_>$ and $r_<$ are respectively the greater and the lesser of r_1 and r_2 . Now Eq. (II-3) is re-written as

$$V_{\mu\mu'}(r_1) = 4 \int_i \int r_1^2 dr_1 r_2^2 dr_2 dr_{23} R_i(r_2, r_3, r_{23}) I_i(r_{23}) , \\ i=A, B, C, D . \quad (\text{II-9})$$

The explicit form and evaluation of I_i 's are now given, e.g.,

$$I_A = \sum_{mm'} C(j \ M-m \ m; LM) C(j' \ M-m' \ m'; LM) \\ \times \sum_k \sum_g [4\pi/(2k+1)] [r_<^k/r_>^{(k+1)}] Y_{kg}(1) Y_{kg}^*(2) Y_{\ell \ M-m}^*(1) \\ \times Y_{jm}^*(3) Y_{00}^*(2) Y_{\ell' \ M-m'}(1) Y_{j' m'}(3) Y_{00}(2) d\Omega_1 d\Omega_2 d\Omega_3 . \quad (\text{II-10})$$

Applications of Eq. (II-7) followed by Eq. (II-5) gives

$$\int Y_{jm}^*(3) Y_{j' m'}(3) \sin\theta_3 d\theta_3 d\phi_3 \\ = (-1)^m \sum_J [(2j+1)(2j'+1)/4\pi(2J+1)]^{1/2} \\ \times C(jj' \ -m \ m'; Jm' -m) C(jj' 00; J0) \\ \times \int \sum_{\mu} D_{m' -m, \mu}^{J*}(\phi_2 \theta_2 0) Y_{J\mu}(\theta_{23} \phi_{23}) \sin\theta_{23} d\theta_{23} d\phi_{23} \\ = (-1)^m \sum_J [(2j+1)(2j'+1)/4\pi(2J+1)]^{1/2} \\ \times C(jj' \ -m \ m'; Jm' -m) C(jj' 00; J0) \\ \times 2\pi Y_{Jm' -m}(\theta_2 \phi_2) P_J(\cos\theta_{23}) \sin\theta_{23} d\theta_{23} , \quad (\text{II-11})$$

where in the last step, Eq. (II-6) and the following relations among the Legendre, the associated Legendre functions and the spherical harmonics are used, viz.,

$$Y_{\ell m}(\theta\phi) = \sqrt{2\pi} \exp(im\phi) P_{\ell}^{|m|}(\cos\theta) , \quad (\text{II-12})$$

$$P_{\ell}^0(\cos\theta) = [(2\ell+1)/2]^{1/2} P_{\ell}(\cos\theta) .$$

Substitution of Eq. (II-11) in Eq. (II-10) yields

$$\begin{aligned} I_A = & \sum_{mm'} (-1)^m C(\ell j \ M-m \ m; LM) C(\ell' j' \ M-m' \ m'; LM) \\ & \times \sum_k \sum_g (2k+1)^{-1} [r_{<}^k / r_{>}^{(k+1)}] \sum_J 2\pi [(2j+1)(2j'+1)/4\pi(2J+1)]^{1/2} \\ & \times C(jj' \ -m \ m'; Jm' -m) C(jj' 00; J0) \int Y_{kg}^*(2) Y_{Jm' -m}(2) d\Omega_2 \\ & \times \int Y_{\ell \ M-m}^*(1) Y_{kg}(1) Y_{\ell' \ M-m'}(1) d\Omega_1 P_J(\cos\theta_{23}) \sin\theta_{23} d\theta_{23} . \end{aligned} \quad (\text{II-13})$$

In Eq. (II-13), $d\Omega_2$ -integration restricts

$$J = k , \quad (\text{II-14})$$

$$g = m' - m .$$

Re-naming k by λ and performing the $d\Omega_1$ -integration,

$$\begin{aligned} I_A = & \frac{1}{2} \sum_{\lambda} [r_{<}^{\lambda} / r_{>}^{(\lambda+1)}] (2\lambda+1)^{-1} \\ & \times [(2j+1)(2j'+1)(2\ell'+1)/(2\ell+1)]^{1/2} \\ & \times \sum_{mm'} (-1)^m C(\ell j \ M-m \ m; LM) C(\ell' j' \ M-m' \ m'; LM) \\ & \times C(jj' \ -m \ m'; Lm' -m) C(jj' 00; \lambda 0) C(\lambda \ell' \ m' -m \ M-m'; \ell \ M-m) \end{aligned}$$

$$\begin{aligned}
& \times C(\lambda \ell' 00; \ell 0) P_{\lambda}(\cos \theta_{12}) \sin \theta_{12} d\theta_{12} \\
& = \frac{1}{2} \sum_{\lambda} [r_{<}^{\lambda} / r_{>}^{(\lambda+1)}] f_{\lambda}(\ell j \ell' j'; L) P_{\lambda}(\cos \theta_{23}) \sin \theta_{23} d\theta_{23} ,
\end{aligned}
\tag{II-15}$$

where the identification is made in the last step of $f_{\lambda}(\ell j \ell' j'; L)$. By the similar procedure, the other integrals are obtained with the results

$$\begin{aligned}
I_B &= I_A P_j(\cos \theta_{23}) / P_{\lambda}(\cos \theta_{23}) , \\
I_C &= I_A P_{j'}(\cos \theta_{23}) / P_{\lambda}(\cos \theta_{23}) , \\
I_D &= I_A P_0(\cos \theta_{23}) / P_{\lambda}(\cos \theta_{23}) .
\end{aligned}
\tag{II-16}$$

To evaluate the integral in Eq. (II-9), use is made of the relation,

$$r_{23}^2 = r_2^2 + r_3^2 - 2r_2 r_3 \cos \theta_{23} . \tag{II-17}$$

Thus,

$$V_{\mu\mu'}^{\lambda}(r) = 2 \sum_{\lambda} f_{\lambda}(\ell j \ell' j'; L) V_{\mu\mu'}^{\lambda}(r) ,$$

where

$$\begin{aligned}
V_{\mu\mu'}^{\lambda}(r) &= \sum_{nn'} c_n c_{n'} \sum_i [r^{-\lambda-1} \int_0^r \exp\{-\alpha(i)r_2\} r_2^{\lambda+1+p(i)} dr_2 \\
&\times r^{\lambda} \int_r^{\infty} \exp\{-\alpha(i)r_2\} r_2^{-\lambda+p(i)} dr_2] [\int_0^r \exp\{-\beta(i)r_3\} r_3^{q(i)+1} dr_3 \\
&\times \int_{r_2-r_3}^{r_2+r_3} r_{23}^{t(i)+1} Q_N(i, r_{23}) dr_{23} + \int_r^{\infty} \exp\{-\beta(i)r_3\} \\
&\times r_3^{q(i)+1} dr_3 \int_{r_3-r_2}^{r_3+r_2} r_{23}^{t(i)+1} Q_N(i, r_{23}) dr_{23}] , \\
& i=A, B, C, D ,
\end{aligned}
\tag{II-18}$$

where c_n and $c_{n'}$ are the weight coefficients in the wave functions of the initial and the final states, and the $Q_N(i, r_{23})$ is the associated Legendre function $P_N(\cos\theta_{23})$ expressed in terms of r_{23} by Eq. (II-17), and

$$t(i) = t_n + t_{n'}, \quad i = A, B, C, D,$$

and the other parameters are

$$\begin{aligned} \alpha(A) &= \zeta_n + \zeta_{n'}, & \beta(A) &= \chi_n \zeta_n + \chi_{n'} \zeta_{n'}, \\ p(A) &= p_n + p_{n'}, & q(A) &= q_n + q_{n'} + j + j', \text{ and } N = \lambda; \\ \alpha(B) &= \zeta_n + \chi_{n'} \zeta_{n'}, & \beta(B) &= \chi_n \zeta_n + \zeta_{n'}, \\ p(B) &= p_n + q_{n'} + j', & q(B) &= q_n + j + p_{n'}, \text{ and } N = j; \end{aligned} \tag{II-19}$$

$$\begin{aligned} \alpha(C) &= \beta(B), & \beta(C) &= \alpha(B), \\ p(C) &= q(B), & q(C) &= p(C), \text{ and } N = j'; \\ \alpha(D) &= \beta(A), & \beta(D) &= \alpha(A), \\ p(D) &= q(A), & q(D) &= p(A), \text{ and } N = 0. \end{aligned}$$

The parameters ζ_n , χ_n , p_n , q_n , t_n , etc. are listed in Table I. In Eq. (II-18), the integrations over r_{12} and r_2 are done analytically. Although the last integration (over r_1) may also be done analytically, due to an exceedingly large number of resulting terms, no computing savings are foreseen; therefore, the last integration has been done numerically.

APPENDIX III

SUCCESSIVE APPROXIMATION

The following approximation to the close-coupling equation is helpful for understanding how an indirect coupling affects the cross sections of a state which is weakly coupled to the ground state. Using the notation

$$\mathcal{L}_{nj\ell} = \frac{d^2}{dr^2} - \ell(\ell+1)/r^2 + k_{nj}^2, \quad (\text{III-1})$$

the approximations of the differential equations of Eq. (2.17) are written

$$\mathcal{L}_{1SJ} F_{1SJ}(r) = U_{1SJ,1SJ}(r) F_{1SJ}(r), \quad (\text{III-2})$$

$$\mathcal{L}_{nPJ} F_{nPJ}(r) = U_{nPJ,1SJ'}(r) F_{1SJ'}(r), \quad (\text{III-3})$$

$$\begin{aligned} \mathcal{L}_{nDJ} F_{nDJ}(r) = & U_{nDJ,1SJ'}(r) F_{1SJ'}(r) \\ & + \sum_{nJ''} U_{nDJ,nPJ''}(r) F_{nPJ''}(r), \end{aligned} \quad (\text{III-4})$$

where the initial state being the ground state, its channel index has been omitted in F_{njJ} . For a given total angular momentum of the system L , the angular momenta J 's of the partial scattered waves may take

$$\begin{aligned} J &= L \quad \text{for } j = S \\ J &= |L-1|, L+1 \quad \text{for } j = P \\ J &= |L-2|, L, L+2 \quad \text{for } j = D. \end{aligned} \quad (\text{III-5})$$

Eq. (III-2) is first solved for F_{1SJ} which is substituted in the RHS of Eq. (III-3), and Eq. (III-3) is solved for each F_{nPJ} . Then these values are substituted on the RHS of Eq. (III-4) to obtain F_{nDJ} 's.

Although the utility of this approximation lies mainly in qualitative understanding of the indirect coupling effects, the validity of such a scheme is illustrated in Table A, where the partial cross sections ($L=3$) obtained by this method are compared with those by close-coupling [Calculation (13) of Table VI].

TABLE A

$Q^{L=3}$ BY SUCCESSIVE APPROXIMATION
IN UNITS OF $10^{-3} a_0^2$

	1^1S	2^1P	3^1P	3^1D
Succ. Approx.	9.197	51.03	14.85	0.3327
Close-Coupling ^(a)	10.066	42.80	13.93	0.3305

^(a) Calculation (13) in Table VI.

APPENDIX IV

MULTICENTER INTEGRALS IN THE BORN COLLISION AMPLITUDE

For convenience the following notations are used in this Appendix:

$$\langle 00| = s(a, A),$$

$$\langle p0| = \langle 0p| = (p - A_p) s(a, A),$$

$$\langle pq| = (p - A_p)(q - A_q) s(a, A),$$

$$|00\rangle = s(b, B),$$

$$|r0\rangle = |0r\rangle = (r - B_r) s(b, B),$$

$$|rt\rangle = (r - B_r)(t - B_t) s(b, B),$$

$$(\overline{AB})_p = (A_p - B_p) \text{ etc.},$$

$$\hat{O} = \exp(i\vec{K} \cdot \vec{r}) = \exp\{i(K_x x + K_y y + K_z z)\},$$

$$\delta_{pq} = \begin{cases} 1, & \text{if } p=q, \\ 0, & \text{if } p \neq q, \end{cases}$$

where $p, q, r, t = x, y, z$.

$$\langle p0|\hat{O}|00\rangle = (2a)^{-1} \frac{\partial}{\partial A_p} \langle 00|\hat{O}|00\rangle$$

$$= [-b(\overline{AB})_p / (a+b) + iK_p / 2(a+b)] \langle 00|\hat{O}|00\rangle.$$

$$\langle 00|\hat{O}|r0\rangle = (2b)^{-1} \frac{\partial}{\partial B_r} \langle 00|\hat{O}|00\rangle$$

$$\begin{aligned}
&= [a(\overline{AB})_r / (a+b) + iK_r / 2(a+b)] \langle 00 | \hat{O} | 00 \rangle. \\
\langle p0 | \hat{O} | r0 \rangle &= (2b)^{-1} \frac{\partial}{\partial B_r} \langle p0 | \hat{O} | 00 \rangle \\
&= (a+b)^{-2} [\{\delta_{pr} (a+b)/2 - ab(\overline{AB})_p (\overline{AB})_r - K_p K_r / 4\} \\
&\quad + (i/2) \{-bK_r (\overline{AB})_p + aK_p (\overline{AB})_r\}] \langle 00 | \hat{O} | 00 \rangle. \\
\langle pq | \hat{O} | 00 \rangle &= (2a)^{-1} [\delta_{pq} \langle 00 | \hat{O} | 00 \rangle + \frac{\partial}{\partial A_q} \langle p0 | \hat{O} | 00 \rangle] \\
&= (a+b)^{-2} [\{\delta_{pq} (a+b)/2 + b^2 (\overline{AB})_p (\overline{AB})_q - K_p K_q / 4\} \\
&\quad - (ib/2) \{K_p (\overline{AB})_q + K_q (\overline{AB})_p\}] \langle 00 | \hat{O} | 00 \rangle. \\
\langle 00 | \hat{O} | rt \rangle &= (2b)^{-1} [\delta_{rt} \langle 00 | \hat{O} | 00 \rangle + \frac{\partial}{\partial B_t} \langle 00 | \hat{O} | r0 \rangle] \\
&= (a+b)^{-2} [\{\delta_{rt} (a+b)/2 + a^2 (\overline{AB})_r (\overline{AB})_t - K_r K_t / 4\} \\
&\quad + (ia/2) \{K_r (\overline{AB})_t + K_t (\overline{AB})_r\}] \langle 00 | \hat{O} | 00 \rangle. \\
\langle pq | \hat{O} | r0 \rangle &= (2b)^{-1} \frac{\partial}{\partial B_r} \langle pq | \hat{O} | 00 \rangle \\
&= (a+b)^{-2} [\delta_{pq} a(\overline{AB})_r / 2 - (b/2) \{\delta_{pr} (\overline{AB})_q + \delta_{qr} (\overline{AB})_p\} \\
&\quad + (1/4) (a+b)^{-1} \{bK_r (K_p (\overline{AB})_q + K_q (\overline{AB})_p) - aK_p K_q (\overline{AB})_r\} \\
&\quad + ab^2 (\overline{AB})_p (\overline{AB})_q (\overline{AB})_r / (a+b)] \langle 00 | \hat{O} | 00 \rangle \\
&\quad + i(a+b)^{-2} [(\delta_{pq} K_r + \delta_{pr} K_q + \delta_{qr} K_p) / 4 \\
&\quad + (b/2) (a+b)^{-1} \{bK_r (\overline{AB})_p (\overline{AB})_q - a(\overline{AB})_r (K_p (\overline{AB})_q \\
&\quad + K_q (\overline{AB})_p)\} - K_p K_q K_r / 8(a+b)] \langle 00 | \hat{O} | 00 \rangle. \\
\langle p0 | \hat{O} | rt \rangle &= (2a)^{-1} \frac{\partial}{\partial A_p} \langle 00 | \hat{O} | rt \rangle
\end{aligned}$$

$$\begin{aligned}
&= (a+b)^{-2} [(a/2) \{ \delta_{pr} (\overline{AB})_t + \delta_{pt} (\overline{AB})_r \} - (b/2) \delta_{rt} (\overline{AB})_p \\
&+ (1/4) (a+b)^{-1} \{ -a K_p (K_r (\overline{AB})_t + K_t (\overline{AB})_r) + b K_r K_t (\overline{AB})_p \} \\
&- a^2 b (\overline{AB})_p (\overline{AB})_r (\overline{AB})_t / (a+b)] \langle 00 | \hat{O} | 00 \rangle \\
&+ i(a+b)^{-2} [(\delta_{pt} K_r + \delta_{pr} K_t + \delta_{rt} K_p) / 4 \\
&- (a/2) (a+b)^{-1} \{ b (\overline{AB})_p (K_r (\overline{AB})_t + K_t (\overline{AB})_r) \\
&- a K_p (\overline{AB})_r (\overline{AB})_t - K_p K_r K_t / 8 (a+b) \}] \langle 00 | \hat{O} | 00 \rangle. \\
\langle pq | \hat{O} | rt \rangle &= (2b)^{-1} [\delta_{rt} \langle pq | \hat{O} | 00 \rangle + \frac{\partial}{\partial B_t} \langle pq | \hat{O} | r0 \rangle] \\
&= (a+b)^{-2} [(\delta_{pq} \delta_{rt} + \delta_{pr} \delta_{qt} + \delta_{pt} \delta_{qr}) / 4 \\
&+ (1/2) (a+b)^{-1} \{ a^2 \delta_{pq} (\overline{AB})_r (\overline{AB})_t + b^2 \delta_{rt} (\overline{AB})_p (\overline{AB})_q \\
&- ab (\delta_{pr} (\overline{AB})_q (\overline{AB})_t + \delta_{pt} (\overline{AB})_q (\overline{AB})_r + \delta_{qr} (\overline{AB})_p (\overline{AB})_t \\
&+ \delta_{qt} (\overline{AB})_p (\overline{AB})_r) \} - (1/8) (a+b)^{-1} \{ \delta_{pq} K_r K_t \\
&+ \delta_{pr} K_q K_t + \delta_{pt} K_q K_r + \delta_{qr} K_p K_t + \delta_{qt} K_p K_r + \delta_{rt} K_p K_q \} \\
&- (1/4) (a+b)^{-2} \{ a^2 K_p K_q (\overline{AB})_r (\overline{AB})_t + b^2 K_r K_t (\overline{AB})_p (\overline{AB})_q \\
&- ab (K_p K_r (\overline{AB})_q (\overline{AB})_t + K_p K_t (\overline{AB})_q (\overline{AB})_r + K_q K_r (\overline{AB})_p (\overline{AB})_t \\
&+ K_q K_t (\overline{AB})_p (\overline{AB})_r) \} + a^2 b^2 (\overline{AB})_p (\overline{AB})_q (\overline{AB})_r (\overline{AB})_t / (a+b)^2 \\
&+ K_p K_q K_r K_t / 16 (a+b)^2] \langle 00 | \hat{O} | 00 \rangle \\
&+ i(a+b)^{-2} [(1/4) (a+b)^{-1} \{ \delta_{pq} a (K_r (\overline{AB})_t + K_t (\overline{AB})_r) \\
&- b \delta_{rt} (K_p (\overline{AB})_q + K_q (\overline{AB})_p) + \delta_{pr} (a K_q (\overline{AB})_t \\
&- b K_t (\overline{AB})_q) + \delta_{pt} (a K_q (\overline{AB})_r - b K_r (\overline{AB})_q) + \delta_{qr} (a K_p (\overline{AB})_t
\end{aligned}$$

$$\begin{aligned}
& - bK_t(\overline{AB})_p) + \delta_{qt}(aK_p(\overline{AB})_r - bK_r(\overline{AB})_p) \\
& + (ab/2)(a+b)^{-2}\{b(\overline{AB})_p(\overline{AB})_q(K_r(\overline{AB})_t + K_t(\overline{AB})_r) \\
& - a(\overline{AB})_r(\overline{AB})_t(K_p(\overline{AB})_q + K_q(\overline{AB})_p)\} \\
& + (1/8)(a+b)^{-2}\{bK_rK_t(K_p(\overline{AB})_q + K_q(\overline{AB})_p) \\
& - aK_pK_q(K_r(\overline{AB})_t + K_t(\overline{AB})_r)\}\} \langle 00 | \hat{O} | 00 \rangle.
\end{aligned}$$

APPENDIX V

RESULTS OF GTO SCF CALCULATION OF N_2 AND RESULTS OF CURVE FITS

GTO Wave Function

The molecular orbital theory and the formulation of the self-consistent field (SCF) equations are well described in the literature;^{91,36} therefore, these will not be repeated here. The present GTO SCF calculation has been performed with the fixed internuclear distance of $2.0675 a_0$ corresponding to the equilibrium bond length of the N_2 molecule. Although the computation was performed explicitly for the ground configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4X^1\Sigma_g^+$, certain valence excited molecular orbitals may be obtained to a good approximation.^{91,72}

The total wave function of N_2 is expressed as the anti-symmetrized product of one-electron molecular spin-orbitals. The spatial part of each constituent molecular spin-orbitals are in turn expressed as

$$\phi_{\lambda n} = \sum_n c_{\lambda n i} \chi_{\lambda i} , \quad (V-1)$$

where λ designates the symmetry of the molecular orbital ($\sigma_g, \sigma_u, \pi_g, \pi_u$), and χ and c are respectively the symmetry

basis functions of expansion and its weight coefficients.

The basis function χ 's are constructed as

$$\chi_{\lambda i} = N_m [u_i(\ell|\vec{r}_A) + M(\lambda, \ell)u_i(\ell|\vec{r}_B)] , \quad (V-2)$$

where u 's are the Gaussian functions of type $\ell(1s, 2p_x, 2p_y, 2p_z)$ centered at points A and B as indicated by $\vec{r}_A$ and $\vec{r}_B$; N_m is to normalize $\chi_{\lambda i}$; and $M(\lambda, \ell)$ is 1 or -1. With the coordinate system as shown in Fig. 3 of Chapter VII,

$$\begin{aligned} M=+1 & \quad \text{for } \lambda=\sigma_g, \ell=1s; \text{ for } \lambda=\sigma_u, \ell=2p_z; \\ & \quad \text{for } \lambda=\pi_u, \ell=2p_x, 2p_y; \text{ and} \\ M=-1 & \quad \text{for } \lambda=\sigma_u, \ell=1s; \text{ for } \lambda=\sigma_g, \ell=2p_z; \\ & \quad \text{for } \lambda=\pi_g, \ell=2p_x, 2p_y . \end{aligned} \quad (V-3)$$

For numerical reasons,^{65,36} each u is expressed as a weighted combination of several single Gaussians, i.e., for a given symmetry ,

$$u_i(\ell|\vec{r}) = \sum_{j=J}^{J'} w_j v_j(\ell|\vec{r}) , \quad (V-4)$$

where w 's are the weight coefficients, and

$$\begin{aligned} v(\ell=1s|\vec{r}) &= \exp\{-\alpha(x^2+y^2+z^2)\} , \\ v(\ell=2p_z|\vec{r}) &= z \exp\{-\alpha(x^2+y^2+z^2)\} , \text{ etc.} \end{aligned} \quad (V-5)$$

The Gaussian exponents α and weight coefficients are listed in Table B. The original "contracted" set of Gaussians is due to Huzinaga and Sakai;⁶⁵ the "contractions" have been relaxed,

TABLE B

GAUSSIAN BASES

	v_i	Exponents (α)	Coefficients (w)
$\ell=1s$	1	.13383000(+5)	.431550985(+1)
	2	.17667800(+4)	.797192370(+1)
	3	.39633800(+3)	.130898833(+2)
	4	.11167000(+3)	.199877984(+2)
	5	.35971400(+2)	.252715196(+1)
	6	.12961000(+2)	.211273502(+1)
	7	.50561300(+1)	.874282819(+0)
	8	.19422900(+1)	.762518033(-1)
	9	.57643022(+1)	-.344240421(+0)
	10	.94693704(+0)	.321038623(+0)
	11	.48554083(+0)	.252111769(+0)
	12	.24389741(+0)	.198654923(+0)
	13	.11196526(+0)	.296348196(-1)
$\ell=2p_z$	14	.58942500(+2)	.274709690(+1)
$=2p_x$	15	.13450200(+2)	.302032414(+1)
$=2p_y$	16	.42517100(+1)	.261956559(+1)
	17	.15962300(+1)	.182463839(+1)
	18	.64129900(+0)	.408194187(+0)
	19	.25757300(+0)	.120232456(+0)
	20	.10164000(+0)	.120120136(-1)

however, as seen in Table B. The contractions of the Gaussian are done as in Eq. (V-4) with indices

i	J	J'
1	1	4
2	5	8
3	9	11
4	12	13
5,9	14	15
6,10	16	17
7,11	18	19
8,12	20	20

Here, $i=1$ to 4 refer to 1s type Gaussian, $i=5$ to 8 refer to $2p_z$ type, and $i=9$ to 12 refer to $2p_x$ or $2p_y$ type. For a given u_i , two different χ 's are formed depending on the inversion symmetry ("g" and "u"). The normalization constants in Eq. (V-2) are listed in Table C. In Table D are listed the expansion coefficients [c's in Eq. (V-1)].

Conversion of STO to GTO

The results of the curve-fit which converts the STO atomic orbitals into GTO functions are given below. The unnormalized GTO's are defined as

$$\begin{aligned}
 \text{GTO}(1s) &= \exp(-\beta r^2) , \\
 \text{GTO}(2p) &= \exp(-\beta r^2) \begin{Bmatrix} x \\ y \\ z \end{Bmatrix} , \\
 \text{GTO}(3d_{\pi}) &= \exp(-\beta r^2) \begin{Bmatrix} xy \\ yz \end{Bmatrix} , \\
 \text{GTO}(3d_{\sigma}) &= \exp(-\beta r^2) (3z^2 - r^2) .
 \end{aligned}
 \tag{V-6}$$

In Table E are tabulated the Gaussian exponents β 's and the expansion coefficients c 's for all molecular orbitals used in this work.

TABLE C

NORMALIZATION CONSTANTS

$\chi_{\lambda i}$	N_g	N_u	$\chi_{\lambda i}$	N_g	N_u
1	0.707107	0.707107	7	0.695941	0.911522
2	0.707038	0.707176	8	6.523571	3.992016
3	0.624478	0.834574	9	7.934248	7.934248
4	0.551858	1.181441	10	0.744365	0.729126
5	7.934248	7.934248	11	1.032148	0.655182
6	0.693530	0.788906	12	10.897734	3.584532

TABLE D
GTO SCF MOLECULAR ORBITALS

C_i	$1\sigma_g$	$2\sigma_g$	$3\sigma_g$
1	.978498383(-1) ^(a)	.214437186(-1)	-.686887102(-2)
2	.950647523(+0)	.251188750(+0)	-.861705348(-1)
3	.154416285(-2)	-.654236173(+0)	.162913762(+0)
4	.151663781(-3)	-.222730212(+0)	.580489097(+0)
5	-.115102441(-2)	.144156507(-1)	.305469586(-1)
6	-.345039951(-2)	.209365570(+0)	.378369190(+0)
7	.740935408(-3)	.252936147(+0)	.630129435(+0)
8	-.253703507(-3)	-.470082854(-1)	-.338389016(-2)
C_i	$1\sigma_u$	$2\sigma_u$	
1	.979072096(-1)	-.198434132(-1)	
2	.951067918(+0)	-.233506779(+0)	
3	-.221890391(-3)	.487303521(+0)	
4	-.130080084(-2)	.361075736(+0)	
5	-.113099927(-2)	.144393616(-1)	
6	-.230631984(-2)	.146035329(+0)	
7	.228878834(-2)	.179110121(+0)	
8	-.119101536(-4)	.249503492(-1)	
C_i	$1\pi_g$ ^(b)	$1\pi_u$	
9	.295829696(-1)	.295529290(-1)	
10	.314175792(+0)	.313856756(+0)	
11	.746008411(+0)	.745250862(+0)	
12	.638981202(-1)	.638332337(-1)	

(a) Numbers inside the parentheses indicate the power of 10.

(b) Unoccupied orbital.

TABLE E
CURVE-FIT RESULTS

Nesbet $3\sigma_g$					
1s		2p		3d	
β	c	β	c	β	c
.8041(-1)	-.3670(-2)	.9647(-1)	-.2442(-2)	.1194(+0)	.4151(-4)
.1634(+0)	-.3851(-1)	.1989(+0)	-.3971(-1)	.2204(+0)	.1103(-2)
.3528(+0)	-.9269(-1)	.4467(+0)	-.1694(+0)	.4223(+0)	.6737(-2)
.7572(+0)	-.7896(-1)	.1155(+1)	-.4966(+0)	.8869(+0)	.1734(-1)
.5319(+1)	.1548(+0)	.3125(+1)	-.9769(+0)	.2150(+1)	.2521(-1)
.1701(+2)	.2395(+0)	.9779(+1)	-.1120(+1)	.6514(+1)	.2506(-1)
.6158(+2)	.2311(+0)	.4292(+2)	-.9268(+0)	.3008(+2)	.1971(-1)

TABLE E-Continued

<u>Nesbet $2\sigma_u$</u>					
<u>1s</u>		<u>2p</u>		<u>3d</u>	
<u>β</u>	<u>c</u>	<u>β</u>	<u>c</u>	<u>β</u>	<u>c</u>
.7953(-1)	.3186(-2)	.9658(-1)	.1209(-2)	.1194(+0)	-.5672(-5)
.1625(+0)	.3960(-1)	.1991(+0)	.1958(-1)	.2204(+0)	-.1507(-3)
.3529(+0)	.1563(+0)	.4467(+0)	.8260(-1)	.4222(+0)	-.9205(-3)
.7911(+0)	.2112(+0)	.1154(+1)	.2344(+0)	.8869(+0)	-.2369(-2)
.5497(+1)	-.4037(+0)	.3132(+1)	.4516(+0)	.2150(+1)	-.3445(-2)
.1579(+2)	-.6685(+0)	.9824(+1)	.5124(+0)	.6514(+1)	-.3425(-2)
.5687(+2)	-.6816(+0)	.4309(+2)	.4221(+0)	.3008(+2)	-.2694(-2)

TABLE E-Continued

<u>Nesbet $1\pi_g$</u>			
<u>2p</u>		<u>3d</u>	
β	c	β	c
.9220 (-1)	.3174 (-2)	.1828 (+0)	.1228 (-3)
.1846 (+0)	.5444 (-1)	.3346 (+0)	.3587 (-2)
.3939 (+0)	.2330 (+0)	.6343 (+0)	.2345 (-1)
.9652 (+0)	.5331 (+0)	.1312 (+1)	.6352 (-1)
.2666 (+1)	.8981 (+0)	.3111 (+1)	.9608 (-1)
.8636 (+1)	.9958 (+0)	.9092 (+1)	.9845 (-1)
.3978 (+2)	.8018 (+0)	.3921 (+2)	.8015 (-1)
<u>Nesbet $1\pi_u$</u>			
<u>2p</u>		<u>3d</u>	
β	c	β	c
.9598 (-1)	.2416 (-2)	.1836 (+0)	.2336 (-3)
.1971 (+0)	.3949 (-1)	.3365 (+0)	.6758 (-2)
.4393 (+0)	.1668 (+0)	.6390 (+0)	.4377 (-1)
.1129 (+1)	.4617 (+0)	.1324 (+1)	.1176 (+0)
.3074 (+1)	.8846 (+0)	.3145 (+1)	.1768 (+0)
.9674 (+1)	.1006 (+1)	.9199 (+1)	.1802 (+0)
.4268 (+2)	.8284 (+0)	.3961 (+2)	.1463 (+0)

TABLE E-Continued

<u>Richardson $3\sigma_g$</u>			
1s		2p	
β	c	β	c
.7768(-1)	.3701(-2)	.9427(-1)	.1242(-2)
.1519(+0)	.3596(-1)	.2067(+0)	.2285(-1)
.3076(+0)	.7230(-1)	.4794(+0)	.1708(+0)
.6511(+0)	.5801(-1)	.1115(+1)	.5436(+0)
.4717(+1)	-.1164(+0)	.2880(+1)	.8471(+0)
.1472(+2)	-.2385(+0)	.9058(+1)	.8313(+0)
.5572(+2)	-.2705(+0)	.4093(+2)	.6330(+0)

<u>Richardson $2\sigma_u$</u>			
1s		2p	
β	c	β	c
.7557(-1)	.6912(-2)	.9533(-1)	-.6914(-3)
.1470(+0)	.7515(-1)	.1939(+0)	-.6600(-2)
.3085(+0)	.1936(+0)	.5476(+0)	.3975(-1)
.7216(+0)	.2087(+0)	.1090(+1)	.2016(+0)
.5473(+1)	-.3666(+0)	.2636(+1)	.3878(+0)
.1606(+2)	-.6789(+0)	.8140(+1)	.4300(+0)
.5787(+2)	-.7707(+0)	.3782(+2)	-.3395(+0)

TABLE E-Continued

<u>Richardson $1\pi_g$</u>		<u>Richardson $1\pi_u$</u>	
<u>2p</u>		<u>2p</u>	
β	c	β	c
.8723(-1)	.3287(-2)	.9047(-1)	.1842(-2)
.1771(+0)	.5289(-1)	.1899(+0)	.3048(-1)
.3843(+0)	.2341(+0)	.4312(+0)	.1691(+0)
.9198(+0)	.5374(+0)	.1028(+1)	.4870(+0)
.2478(+1)	.7414(+0)	.2707(+1)	.7429(+0)
.8130(+1)	.6861(+0)	.8658(+1)	.7209(+0)
.3847(+2)	.5004(+0)	.3986(+2)	.5422(+0)

<u>Ransil $1\pi_u$</u>		<u>Sahni-De Lorenzo $1\pi_g$</u>	
<u>2p</u>		<u>2p</u>	
β	c	β	c
.1336(+0)	.2142(-2)	.1336(+0)	.2863(-2)
.2567(+0)	.4696(-1)	.2567(+0)	.6276(-1)
.5154(+0)	.2368(+0)	.5154(+0)	.3165(+0)
.1142(+1)	.5092(+0)	.1142(+1)	.6805(+0)
.2923(+1)	.6335(+0)	.2923(+1)	.8467(+0)
.9206(+1)	.5553(+0)	.9206(+1)	.7422(+0)
.4146(+1)	.4041(+0)	.4146(+2)	.5400(+0)

TABLE E-Continued

<u>Ransil $3\sigma_g$</u>			
<u>1s</u>		<u>2p</u>	
β	c	β	c
.9541(-1)	.5313(-3)	.1400(+0)	.4398(-3)
.1720(+0)	.1573(-1)	.2585(+0)	.2111(-1)
.3281(+0)	.7885(-1)	.5025(+0)	.1860(+0)
.7036(+0)	.1015(+0)	.1088(+1)	.5828(+0)
.5308(+1)	-.1439(+0)	.2756(+1)	.9026(+0)
.1575(+2)	-.2630(+0)	.8698(+1)	.8774(+0)
.5731(+2)	-.2980(+0)	.3990(+2)	.6588(+0)

<u>Ransil $2\sigma_u$</u>			
<u>1s</u>		<u>2p</u>	
β	c	β	c
.9333(-1)	.1023(-2)	.1400(+0)	.1705(-3)
.1688(+0)	.3375(-1)	.2585(+0)	.8182(-2)
.3232(+0)	.1789(+0)	.5025(+0)	.7212(-1)
.6970(+0)	.2363(+0)	.1088(+1)	.2259(+0)
.5214(+1)	-.3603(+0)	.2756(+1)	.3499(+0)
.1534(+2)	-.7121(+0)	.8698(+1)	.3401(+0)
.5648(+2)	-.8267(+0)	.3990(+2)	.2554(+0)

TABLE E-Continued

<u>Lefebvre-Brion and Moser (3s)σ_g</u>					
<u>1s</u>		<u>2p</u>		<u>3d</u>	
β	c	β	c	β	c
.1094(-1)	-.4895(-2)	.8064(-2)	.4563(-2)	.8253(-2)	-.1675(-4)
.3623(-1)	-.2783(-1)	.3508(-1)	-.4253(-3)	.1593(-1)	-.3185(-4)
.1905(+0)	.2665(-1)	.1584(+0)	.2284(-3)	.3652(-1)	.1294(-3)
.2824(+0)	.3069(-1)	.4322(+0)	.3834(-3)	.8441(-1)	.6476(-3)
.6018(+0)	.9064(-1)	.4182(+0)	.4232(-1)	.2056(+0)	.1127(-2)
.8573(+1)	-.1964(+0)	.1283(+1)	.1354(+0)	.6181(+0)	.1268(-2)
.4382(+2)	-.2624(+0)	.6416(+1)	.1539(+0)	.2937(+1)	.1061(-2)

TABLE E-Continued

<u>Lefebvre-Brion and Moser (3p)σ_u</u>					
<u>1s</u>		<u>2p</u>		<u>3d</u>	
<u>β</u>	<u>c</u>	<u>β</u>	<u>c</u>	<u>β</u>	<u>c</u>
.5159(-2)	.8864(-1)	.9493(-2)	-.3113(-2)	.8240(-2)	.1944(-4)
.2118(-1)	-.5285(-1)	.1625(-1)	.5300(-3)	.1541(-1)	.3385(-4)
.3853(-1)	-.5442(-1)	.5655(-1)	-.4372(-2)	.3630(-1)	-.3179(-4)
.2331(+0)	.4171(-1)	.6024(-1)	.2809(-3)	.8494(-1)	-.2697(-3)
.5873(+0)	.8277(-1)	.6130(+0)	.1783(-1)	.2106(+0)	-.4539(-3)
.8536(+1)	-.1690(+0)	.2089(+1)	.3114(-1)	.6275(+0)	-.5016(-3)
.4368(+2)	-.2238(+0)	.1090(+2)	.3114(-1)	.2953(+1)	-.4227(-3)