THE APPLICATION OF BASIS SET METHODS
AND
MANY-BODY THEORY IN ELECTRON-MOLECULE SCATTERING

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ABSTRACT

Chapter I

The difficulty encountered in electron-molecule scattering, which is absent from the atomic case, is due to the nonspherical nature of the potential describing the interaction of an electron with a molecule. Therefore a prerequisite to the development of an accurate description of electron-molecule collisions is an efficient method for treating single-particle scattering from nonspherical potentials.

This chapter describes such a method. The essential idea is the approximation of the potential by a separable representation in terms of a finite set of square-integrable basis functions. This approximation gives the kernel of the Lippmann-Schwinger equation a separable form and allows us to write it as a finite matrix equation. The solution of this equation by ordinary matrix methods yields a basis set representation of the transition operator, and the scattering amplitude is easily calculated using this operator.

This method is applied to the calculation of scattering amplitudes for a model two-center Gaussian potential and to $e^- - H_2$ elastic scattering at low energies in the static exchange approximation. The $e^- - H_2$ elastic scattering calculation is compared with the results of other workers.

An entirely different approach to low-energy, elastic electron-molecule scattering from homonuclear diatomic molecules is also discussed in this chapter. It is based on the observation that, for electron scattering from homonuclear diatomic molecules at low

energies, angular momentum is approximately conserved in spite of the nonspherical nature of the molecule. This observation allows the extraction of approximate phase shifts for electron scattering in the static exchange approximation from the results of diagonalizing the Hartree-Fock Hamiltonian in a large basis. This method is applied to e^- - H_2 and e^- - N_2 elastic scattering and the results compared with those of other workers.

Chapter II.

A discussion of the application of many-body theory to electron-atom and electron-molecule scattering is presented. First a previous many-body theory of inelastic scattering is shown in first order to be a form of the distorted wave approximation. The target atom or molecule is described in the random phase approximation (RPA), while the distorting potential for the incident and scattered waves is the Hartree-Fock potential of the ground state.

The application of many-body theory to elastic scattering is also discussed using a many-body formulation of the Feshbach optical potential. The difficulty of constructing Feshbach projection operators for a system of identical particles is overcome by the use of second quantized operators. Therelationship between this theory and the optical model of Bell and Squires, in which the many-body self-energy serves as an optical potential, is discussed in detail.

Chapter III

The application of the RPA form of the distorted wave approximation to inelastic e^- - H_2 scattering is described. Differential cross

sections for excitation of the b $^3\Sigma_u^+$ and a $^3\Sigma_g^+$ states are calculated for a range of incident energies from 13 eV to 20 eV. Good agreement is obtained with the limited experimental data available for the differential cross section for excitation of the b $^3\Sigma_u^+$ state. The sum of the total cross sections for the two states is compared with the experimental cross section for electron impact dissociation of H_2, and good agreement is found. Extensive discussion of the details of the calculation is included.

Appendix

Cross sections in the Born approximation for electron impact excitation of CO_2 and CO using an RPA description of the target are presented. Generalized oscillator strengths for several states of CO_2 are found to be in agreement with experiment. For CO, substantial disagreement exists between theory and experiment for the B $^1\Sigma^+$ state. A possible explanation involving a breakdown of the Born-Oppenheimer approximation resulting from an avoided crossing is proposed.

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CHAPTER I

Basis Set Methods for Elastic Scattering from Nonspherical Potentials

INTRODUCTION

The purpose of this introduction is to place the work presented in this chapter in the context of previous work on electron-molecule scattering and to describe briefly some of the advantages of basis set methods in scattering. In central field scattering problems one begins in general by making a partial wave expansion of the scattering wavefunction, and the usual simplifications due to conservation of angular momentum ensue. If the potential has, say, the cylindrical symmetry of a linear molecule, matrix elements of the potential between spherical harmonics of different ℓ values

$$V^{m}_{\ell\ell'}(r) = \int Y_{\ell m}(\Omega)\, V(\underset{\sim}{r}) Y_{\ell' m}(\Omega) d\Omega$$

are in general nonvanishing. Thus the equations for the partial wave scattering functions are coupled. Burke and co-workers have used this straightforward approach to treat e^- - N_2 elastic scattering in the static exchange approximation.[1,2] However, the formidable set of coupled integro-differential equations that are obtained made it necessary for Burke et al. to make a local approximation to the exchange operators before they could include enough partial waves to reach convergence.[2]

An alternative for a cylindrically symmetric potential is to use prolate spheroidal coordinates in the calculation and to expand in spheroidal functions (in the nomenclature of Hara[3]) instead of ordinary spherical harmonics. This expansion is more rapidly convergent than the usual partial wave expansion, but to use it one must still solve coupled integro-differential equations.[3] Still another alternative is to numerically integrate the Schrödinger equation in two dimensions (for cylindrically symmetric potentials). This approach was used by Tully and Berry[4] for e^- - H_2 elastic

scattering in the static exchange approximation. The numerical method they used was complicated, although its application seems relatively straightforward.

It is easy to see that a need exists for a method that will allow us to avoid the complexities of numerical integration of coupled or multidimensional differential equations. Furthermore, in molecular applications it is necessary to be able to treat nonlocal exchange operators with ease, and it is imperative that we be able to make use of the spatial symmetry that exists in the molecular scattering problem. The first two papers (A and B) in this section develop such a method and demonstrate its applicability using a model nonspherical scattering problem.

The key idea in our approach is to form an approximate representation of the potential in a finite basis of N square-integrable functions

$$V \approx \sum_{\alpha,\beta}^{N} |\alpha\rangle V_{\alpha\beta} \langle\beta| \quad .$$

For electron scattering from a neutral atom or molecule, the potential will in general be of sufficiently short range that this representation is adequate. We chose Gaussian basis functions (familiar in bound state calculations on molecules) as the basis set. This choice not only affords the well-known ease in evaluating interaction matrix elements but also makes calculation of matrix elements of the free particle Green's function relatively simple. The finite basis set representation of the potential reduces the Lippmann-Schwinger equation for the T matrix to a finite matrix equation which can be solved by ordinary numerical matrix methods.

An important point is that we can choose the basis functions to transform with the irreducible representations of the point group of the

molecule, and that the Lippmann-Schwinger equation is separable in these symmetries. For a homonuclear diatomic we can solve for the σ_g, σ_u, π_g, π_u, etc. contributions to the T matrix separately. The method thus makes use of the natural symmetry of the problem in a direct and straightforward manner.

This brings us to one other important point that is not emphasized in the papers in this chapter. The Lippmann-Schwinger equation displays these convenient symmetry properties because we have expressed it in the coordinate system in which the molecule is fixed. It is easy for us to use the results of calculations in the body-fixed frame to compute cross sections in the laboratory frame because we assume that the molecule remains fixed during the scattering event. This is an excellent approximation since the molecule is far heavier and sluggish compared with electrons at the energies we have considered. However, if the molecule has a permanent dipole moment, the prescription described above will fail. The potential due to a dipole at large distances is proportional to r^{-2}, and thus a calculation in the molecule-fixed frame will have the difficulties expected from a long-range potential. The physical situation is that as the electron recedes to the asymptotic region the molecule rotates and the dipole potential averages to zero. Thus the effects of the dipole potential are only indirectly evident in the observed cross section. The methods described in this chapter are not designed to treat the case of dipolar molecules. This problem has been discussed by Chang and Fano[5] among others, but few numerical results of chemical interest are available in the literature.

The method described in the first two papers in this chapter is applied in the third paper (C) to e^- - H_2 elastic scattering in the static

exchange approximation. The results that were obtained are essentially identical to those of other workers.

Another more approximate L^2 method was developed that allows elastic scattering cross sections to be calculated for homonuclear diatomics in an extremely simple and efficient manner. The crucial assumption here is the approximate conservation of orbital angular momentum (sometimes called the low ℓ-spoiling approximation). This phrase is deceptive; it does not mean that one can ignore coupling in the partial wave expansion entirely and solve for one partial wave at a time. Instead, it means that we can construct approximate scattering solutions that are proportional to a single $Y_{\ell m}$ at large r. In the fourth paper of this chapter (D), we do this by diagonalizing the Hamiltonian in a basis set which, to a very good approximation, has only one $Y_{\ell, m}$ component at large r. The theoretical basis for this approximation was discussed by Fano[6] in 1970. Some rather interesting facts are made apparent by its success. For example, as pointed out by Fano,[6] the centrifugal barrier is responsible for the approximate decoupling of s and $d\sigma$ waves for scattering from a homonuclear molecule. In the case of a heteronuclear molecule, however, where the potential is capable of coupling s and p waves, one would not expect the centrifugal barrier to be strong enough in general to decouple them. Thus the low ℓ-spoiling approximation can be expected to fail for heteronuclear diatomics. Another point is that the effects of the asymmetry of the potential on the scattering solutions are largely due to the requirement that the scattering wavefunctions be orthogonal to the bound solutions. The method is applied successfully to e^- - H_2 and e^- - N_2 elastic scattering in the static exchange approximation in Section D.

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SECTION A

Discrete Basis Set Approach to Nonspherical Scattering

There has been much interest in the recent literature concerning the use of discrete basis sets in the calculation of electron scattering processes.[1] These methods have the advantage of requiring only standard matrix techniques in their numerical application as opposed to the more customary approach of numerically integrating the differential equations. However, except for the characterization of resonance parameters, the use of basis ——————— | sets has, until now, been limited to targets possessing spherical symmetry. This letter describes a method designed for the efficient computation of scattering amplitudes for nonspherical potentials. In spirit, the method is similar to the Jacobi-matrix technique recently proposed by Heller and Yamani[2] for use in electron-atom scattering. However, this latter method is based on the use of special L^2-basis sets which tridiagonalize the radial kinetic energy for a particular partial wave. The method we propose will be based on the use of Gaussian basis functions which are the usual choice for the multicenter molecular problem. Furthermore, we do not use a single center expansion of the potential or the wavefunction in spherical harmonics. The full scattering amplitude is solved for directly. The details of the technique to be outlined here are specific to cylindrically symmetric potentials. Extension of this approach to potentials of lower symmetry would be straightforward, but considerably more involved. This method should find immediate application in the area of low energy electron scattering by diatomic molecules, where very few theoretical studies have been made due to the computational difficulties involved.

Our starting point is the Lippmann-Schwinger equation for the transition operator, T:

$$T(E) = V + VG_0^+(E)T \quad . \tag{1}$$

The first approximation we make is to assume that the exact potential V can be well represented by an $N \times N$ matrix representation of V obtained by its

projection onto the subspace spanned by N square-integrable basis functions $\{\varphi_\alpha\}$. Denoting this truncated potential as V^T, it can be written in concise form as,

$$V^T = \sum_{\alpha,\beta=1}^{N} |\alpha\rangle\langle\beta| V_{\alpha\beta} \tag{2a}$$

where

$$V_{\alpha\beta} = \int \varphi_\alpha^*(\vec{r})\varphi_\beta(\vec{r})V(\vec{r})d^3r \quad . \tag{2b}$$

As is well-known, the approximation of Eq.(2a) leads to a separable kernel in the Lippmann-Schwinger equation, which can then be solved exactly.[2] Consistent with this approximation, we ask for matrix elements of T within the same L^2 subspace. This requires that we know the matrix elements of the free-particle Green's function, $G_0^+(E)$, that is, we require

$$\langle\alpha|G_0^+(E)|\beta\rangle \equiv \int \frac{\langle\alpha|\vec{k}\rangle\langle\vec{k}|\beta\rangle}{E - k^2 + i\epsilon} d^3k \quad . \tag{3}$$

If a Gaussian basis set is used, the Fourier transforms, $\langle\alpha|\vec{k}\rangle$, have a particularly simple form. The Fourier transform is itself a Gaussian, modulated by a product of Hermite polynomials in the components of $\vec{k}$. This remains true in the multi-center problem.

In performing the triple integration over $\vec{k}$ in the expression for the Green's function, we choose the z axis to lie along the symmetry axis of the potential and transform to spherical coordinates. With the assumption of a cylindrically symmetric potential which allows the basis functions φ_α to be chosen as a real sum of Gaussians placed on two centers, the following simplifications in calculating $\langle\alpha|G_0^+(E)|\beta\rangle$ were noted:

(1) The integration over θ could be performed analytically.

(2) If necessary, the ϕ integration could also be carried out analytically.

However, in this case, the integral is simply that of a polynomial in even powers of $\cos\phi$ and $\sin\phi$. Since these powers always remain quite low (≤ 4) for the types of basis functions used, they could be performed exactly with a low order Chebyschev quadrature of the first kind.[3]

(3) The remaining integration over k was performed using Gauss-Legendre quadrature. The singularity in the integrand was handled by the same subtraction procedure used in L^2-Fredholm calculations.[4] Denoting the k-space quadrature points and weights by k_i and ω_i, respectively, $\langle\alpha|G_0^+(E)|\beta\rangle$ is calculated by the expression:

$$\langle\alpha|G_0^+(E)|\beta\rangle = \frac{1}{(2\pi)^3}\int_0^{2\pi} d\phi \int_{-1}^{1} d\cos\theta \int_0^{\infty} k^2 dk \frac{\langle\alpha|k,\theta,\varphi\rangle\langle k,\theta,\varphi|\beta\rangle}{E - k^2 + i\epsilon}$$

$$\approx \frac{1}{(2\pi)^3}\int_0^{2\pi} d\phi \int_{-1}^{1} d\cos\theta \left[\sum_i k_i^2\omega_i \frac{\langle\alpha|k_i,\theta,\varphi\rangle\langle k_i,\theta,\varphi|\beta\rangle}{E - k_i^2} + \frac{\sqrt{E}}{2} C(E)\langle\alpha|\sqrt{E},\theta,\varphi\rangle\langle\sqrt{E},\theta,\varphi|\beta\rangle\right] \quad (4a)$$

where

$$C(E) = P\int_0^{k_{max}} \frac{dk}{\sqrt{E} - k} - \sum_i \frac{\omega_i}{\sqrt{E} - k_i} - i\pi \quad (4b)$$

where $k_{max} = \sum_i \omega_i$.

Once matrix elements of $G_0^+(E)$ have been calculated, the L^2-matrix representation of T is obtained by standard matrix inversion:

$$\underline{T}(E) = (1 - \underline{V}^T \underline{G}_0^+(E))^{-1}\underline{V}^T \quad . \quad (5)$$

It should be noted that for cylindrically symmetric potentials, $\underline{T}$ is block

diagonal in the irreducible representations belonging to the point group $D_{\infty h}$. Thus, the L^2-representations of $\underline{T}$ for Σ_g^+, Σ_u^+, Π_g, Π_u, etc., can all be solved for separately.

The on-shell T matrix (scattering amplitude) is obtained from the L^2-matrix representation of Eq. (5) by the transformation

$$\langle \vec{k}' | T(E) | \vec{k} \rangle = \sum_{\alpha, \beta} \langle \vec{k}' | \alpha \rangle \, T_{\alpha, \beta}(E) \, \langle \beta | \vec{k} \rangle \quad . \tag{6}$$

The Fourier transforms of the Gaussian basis functions required in Eq. (6) are, as previously noted, easily computed. The calculation of $\langle \vec{k}' | T(E) | \vec{k} \rangle$ for any orientations of $\vec{k}$ and $\vec{k}'$ may be rapidly performed without recomputing the L^2-matrix of T. This feature of the method is extremely valuable because in electron-molecule scattering an average of the cross section over molecular orientations is usually required. To compute the T matrix for a different energy we must reconstruct the matrix representation of the free particle Green's function using Eq. (4).

We should like to stress the advantage of the present approach over direct quadrature of the Lippmann-Schwinger equation in momentum-space, as successfully carried out by Walters,[5] for example, for the case of spherical potentials. For cylindrically symmetric potentials, this approach, coupled with an L^2-truncation of the potential as recently proposed by Schneider,[6] would involve a direct quadrature over two variables. Such a quadrature would lead to matrices much larger than those which are used in the present work.

We have applied the method outlined above to the case of scattering by a two-center Gaussian potential:

$$V(\vec{r}) = -\tfrac{1}{2}(e^{-(\vec{r}-\vec{A})^2} + e^{-(\vec{r}+\vec{A})^2}) \quad . \tag{7}$$

Note that no inherent numerical simplifications result from the choice of a Gaussian potential; this choice was made only for convenience in computing matrix elements. ——————————————————————————————— |

Our programs were checked by first setting $\vec{A} = 0$. The one-center results so obtained agreed very well with the recent numerical results of Holt and Santoso.[7] For further calculations, the distance between the centers was fixed at 2 a.u. We have chosen a test case for which the incoming wave vector lies along the axis of the potential so that only Σ_g^+ and Σ_u^+ symmetries contribute to the T matrix. A number of different basis sets were used in a convergence study. The results of this study along with amplitudes for different choices of incoming wave vectors will be presented in a later paper. Table I lists the scattering amplitude at several angles at k = 0.447 a.u. for a basis with 20 S Gaussians on each center. We have also listed the exact and approximate Born amplitudes (obtained by setting T = V and V^T, respectively). We emphasize that the results for each angle in Table I were computed using the same L^2-matrix representation of T and that our choice of the direction of the incoming wave was made purely for convenience.

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TABLE I. Scattering amplitude $f(\theta)$ for two-center Gaussian potential at k = 0.447 a.u. for incoming wave vector along symmetry axis.

θ	Exact Born	Born $(\Sigma_g^+ + \Sigma_u^+)$	$f(\theta)(\Sigma_g^+ + \Sigma_u^+)$
0	0.443	0.443	0.526 + i 0.088
$\pi/4$	0.427	0.428	0.512 + i 0.092
$\pi/2$	0.362	0.364	0.443 + i 0.095
$3\pi/4$	0.270	0.263	0.330 + i 0.089
π	0.227	0.213	0.273 + i 0.083

SECTION B

Discrete Basis Set Approach to Nonspherical Scattering. II.

I. INTRODUCTION

In a previous article, hereafter referred to as I, we outlined a method for computing scattering amplitudes for a nonspherical potential.[1] The approach involves representing the potential in a discrete set of Gaussian basis functions and solving the Lippmann-Schwinger equation for the full scattering amplitude as a matrix equation in this subspace. In this paper we present a more complete discussion of the details of the method. We also show that improved results may be obtained by a variational correction of the calculated scattering amplitudes. We report numerical results for a two-center Gaussian potential at several energies and scattering angles.

The outline of this paper is as follows. In Section II.A the details of the calculation, in particular the choice of basis functions and computation of the necessary matrix elements, are examined. Section II.B discusses a method for obtaining variationally stable results and in Section II.C we comment briefly on an alternative approach to the problem of scattering from nonspherical potentials. Our numerical results are reported in Section III. Section IV contains a brief discussion.

II. THEORY

A. Use of Gaussian Functions in Solving the Lippmann-Schwinger Equation

As discussed in I, the ansatz which forms the basis for the approach used here is the approximate representation of the potential in a finite, discrete basis. We denote this truncated potential as V^t;

$$V^t = \sum_{\alpha, \beta} |\alpha\rangle \langle\alpha| V |\beta\rangle \langle\beta| \quad . \tag{1}$$

If this approximation seems severe, it should be noted that whenever the Schrödinger equation is solved by diagonalization of the Hamiltonian in a basis set, the same approximation for the potential (as well as for the kinetic energy) is being used. The advantage of this truncation of the potential in scattering problems is that it leads to a separable kernel[2] in the Lippmann-Schwinger equation which may then be written as a finite matrix problem. Denoting the truncated transition operator as T^t, its matrix elements in the finite basis satisfy the equation

$$\langle\alpha| T^t(E) |\beta\rangle = \langle\alpha| U |\beta\rangle + \sum_{\gamma, \delta} \langle\alpha| U |\gamma\rangle \langle\gamma| G_0(E) |\delta\rangle \langle\delta| T^t |\beta\rangle \tag{2}$$

where $U = 2V$ in atomic units. The solution of this equation yields the exact scattering amplitude for the truncated potential V^t via the transformation

$$f(\vec{k}_{out} \longleftarrow \vec{k}_{in}) = -\frac{1}{4\pi} \langle \vec{k}_{out} | T^t(E) | \vec{k}_{in} \rangle$$

$$= -\frac{1}{4\pi} \sum_{\alpha, \beta} \langle \vec{k}_{out} | \alpha \rangle \langle \alpha | T^t(E) | \beta \rangle \langle \beta | \vec{k}_{in} \rangle \tag{3}$$

where

$$\langle \alpha | \vec{k} \rangle = \int e^{i\vec{k} \cdot \vec{r}} \langle \vec{r} | \alpha \rangle \, d^3r \quad . \tag{4}$$

The solution of Eq. (2) requires only matrix elements of the potential and the free-particle Green's function.

As in I, we restrict our attention to cylindrically symmetric potentials which possess a center of inversion. If one chooses basis functions which transform with the irreducible representations of the point group $D_{\infty h}$, then Eq. (2) may be solved separately for each symmetry (Σ_g^+, Σ_u^+, Π_g, etc.). This is an extremely important consideration, since it greatly reduces the size of the matrices that must be handled at any point in the calculation. The basis $\{|\alpha\rangle\}$ can then be obtained by orthonormalization of a set of functions of the form

$$\varphi_\alpha = g_\alpha(\vec{r} - \vec{A}) \pm g_\alpha(\vec{r} + \vec{A}) \tag{5}$$

where ± determines the symmetry under inversion (g or u).

In multi-center problems, it is normal to choose $g_\alpha(\vec{r})$ to be a Gaussian function.[3] This choice is particularly convenient here since it leads to great simplification in the calculation of matrix elements of the free-particle Green's function. Specifically, we choose

$$g_\alpha(\vec{r} - \vec{A}) = x^\ell y^m (z - A)^n e^{-\alpha(x^2 + y^2 + (z - A)^2)} \quad . \tag{6}$$

A matrix element of $G_0(E)$ can be written as

$$\langle \alpha | G_0(E) | \beta \rangle = \lim_{\epsilon \to 0^+} \frac{1}{(2\pi)^3} \left(\int \frac{\langle \alpha | \vec{k} \rangle \langle \vec{k} | \beta \rangle}{k_0^2 - k^2 + i\epsilon} \, d^3 k \right) \tag{7}$$

where $E = k_0^2/2$. The required Fourier transform of φ_α (Eq. (5)) can be done in closed form:[4]

$$\int e^{i\vec{k}\cdot\vec{r}} \varphi_\alpha(\vec{r}) = \left(e^{ik_z A} \pm e^{-ik_z A}\right) \left(\frac{\pi}{\alpha}\right)^{3/2} \frac{1}{(2i\sqrt{\alpha})^{\ell+m+n}} \times$$

$$\times e^{-k^2/4\alpha} H_\ell\left(-\frac{k_x}{2\sqrt{\alpha}}\right) H_m\left(-\frac{k_y}{2\sqrt{\alpha}}\right) H_n\left(-\frac{k_z}{2\sqrt{\alpha}}\right) \tag{8}$$

where H_ℓ is a Hermite polynomial.

In performing the triple integration over $\vec{k}$ in Eq. (7) we choose the z direction of $\vec{k}$ to lie along the symmetry axis. The θ integration to be performed is then of the form

$$\int_{-1}^{1} dx \; P(x) \, Q(x) \quad .$$

P(x) is a polynomial in x where $x = \cos\theta$, and Q(x) is either $\cos^2(kAx)$, $\sin^2(kAx)$ or $\sin(kAx)\cos(kAx)$ depending on the symmetry of the basis functions. This integration was performed analytically. Analytic integration over θ is important since numerical quadrature of the θ integration would be made difficult by oscillations of $\sin(kAx)$ and $\cos(kAx)$ for large values of the integration variable k. The ϕ

integration is simply that of a polynomial in even powers of cos ϕ and sin ϕ and hence a low-order Chebyschev quadrature of the first kind[5] can be employed to perform this integration exactly. The remaining integration over k requires more care, since the integrand possesses a simple pole at the point $k = k_0$. Before numerical quadrature can be used, the singularity must be subtracted off. Specifically, an integral of the form

$$\lim_{\epsilon \to 0^+} \int_0^\infty \frac{f(k)\, k^2\, dk}{k_0^2 - k^2 + i\epsilon}$$

can be approximated with little resulting error by the expression[6]

$$\sum_i \frac{f(k_i)\, k_i^2\, \omega_i}{k_0^2 - k_i^2} + \frac{f(k_0)\, k_0}{2} \left[P \int_0^{k_{max}} \frac{dk}{k_0 - k} - \sum_i \frac{\omega_i}{k_0 - k_i} - i\pi \right] \quad (9)$$

where k_i and ω_i denote quadrature weights and points, respectively, and $k_{max} = \sum_i \omega_i$. In performing the k quadrature in Eq. (7), it was found that 20 to 30 Gauss-Legendre points were sufficient to perform the integration to better than five significant figures.

After the matrix representations of $G_0(E)$ and U have been constructed, the discrete matrix $\underline{T}^t(E)$ can be obtained by a single matrix inversion:

$$\underline{T}^t(E) = (\underline{1} - \underline{U}^t\, \underline{G}_0(E))^{-1}\, \underline{U}^t \quad . \quad (10)$$

The scattering amplitude for any relative orientation of the incoming and outgoing wave vector is obtained by the transformation of Eq. (3).

$\underline{T}^t(E)$ of course only depends on the magnitude of the energy and not on the directions of $\vec{k}_{in}$ and $\vec{k}_{out}$. This is an important consideration since in any molecular problem an average over target orientations would have to be performed in order to obtain physical results. The transformation of Eq. (3) can be done quite rapidly when compared with the recomputation of $\underline{T}^t(E)$. If the energy is changed $\underline{T}^t(E)$ must be recomputed.

B. Variational Corrections

The method we have outlined provides a solution for the exact scattering amplitude corresponding to the truncated potential V^t. This amplitude, however, will generally contain errors that are first-order in the difference $(V - V^t)$ when compared with the amplitude for the exact potential V. Variational stability may be obtained by solving for the wave function corresponding to $T^t(E)$, which we denote by ψ_t, and employing it in a generalization of the Kato formula.[7] The stationary amplitude is then given by the prescription

$$\langle \vec{k}_{out} | T^s(E) | \vec{k}_{in} \rangle = \langle \vec{k}_{out} | T^t(E) | \vec{k}_{in} \rangle + 2 \langle \psi_t^{out} | H - E | \psi_t^{in} \rangle ; \quad (11)$$

$\psi_t^{in, out}$ is easily expressed in terms of $\underline{T}^t(E)$ as

$$\psi_t^{in, out} = \varphi_o^{in, out} + G_o(E)\, \underline{T}^t(E)\, \varphi_o^{in, out} \quad (12)$$

where $\varphi_o^{in, out}$ is the incoming (outgoing) plane wave. It is important

to notice that, while ψ_t certainly has components outside the truncated L^2-space employed here, only its L^2-components are needed in defining the trial scattering amplitude, as can be readily seen from the identity

$$\langle \vec{k}_{out} | T^t(E) | \vec{k}_{in} \rangle = \langle \vec{k}_{out} | U^t | \psi_t^{in} \rangle \quad . \tag{13}$$

Bearing this in mind we can write $\psi_t^{in,\,out}$ in the form

$$\psi_t^{in,\,out} = \varphi_0^{in,\,out} + \sum_{\alpha} c_{\alpha}^{in,\,out} | \alpha \rangle \tag{14}$$

and this form will be perfectly consistent with $\underline{T}^t(E)$. It is easily verified that the coefficients $c_{\alpha}^{in,\,out}$ are obtained as

$$\begin{aligned} c_{\alpha}^{in,\,out} &= \langle \alpha | \underline{G_0}(E)\, \underline{T}^t(E) | \varphi_0^{in,\,out} \rangle \\ &= \sum_{\rho,\gamma} \langle \alpha | G_0(E) | \beta \rangle \langle \beta | T^t(E) | \gamma \rangle \langle \gamma | \varphi_0^{in,\,out} \rangle \ , \end{aligned} \tag{15}$$

i.e., in computing $\underline{T}^t(E)$, we have already done all the work necessary to compute the coefficients $c_{\alpha}^{in,\,out}$. If on substituting $\psi_t^{in,\,out}$ into the Kato formula, we assume that $(H_0 + V^t - E)\, \psi_t^{in,\,out} = 0$ (which is not strictly true in this case since the scattered wave in Eq. (12) has been truncated), then the Kato formula, as Heller and Yamani pointed out, [8] reduces to the distorted wave Born formula, with U^t as the unperturbed distorting potential:

$$\langle \vec{k}_{out} | T^s(E) | \vec{k}_{in} \rangle = \langle \vec{k}_{out} | T^t(E) | \vec{k}_{in} \rangle + \langle \psi_t^{out} | U - U^t | \psi_t^{in} \rangle \ . \tag{16}$$

The price for variational stability is that bound-free and free-free matrix elements of V are now required.

C. Comment on the Direct Quadrature of the Lippmann-Schwinger Equation

Several authors have suggested calculating $\langle \vec{k}_{out} | T(E) | \vec{k}_{in} \rangle$ by direct quadrature of the Lippmann-Schwinger equation in momentum space.[9, 10] This approach was first carried out successfully for the full amplitude by Walters[9] for the case of spherical potentials. Quite recently, Schneider[10] showed that this technique could be simplified by employing the same L^2-truncation of the potential used here. In momentum space, the Lippman-Schwinger equation for the scattering amplitude reads

$$\langle \vec{k}_{out} | T(E) | \vec{k}_{in} \rangle = \langle \vec{k}_{out} | U | \vec{k}_{in} \rangle + \frac{1}{(2\pi)^3} \frac{\langle \vec{k}_{out} | U | \vec{k} \rangle \langle \vec{k} | T(E) | \vec{k}_{in} \rangle}{k_0^2 - k^2 + i\epsilon} d^3k. \quad (17)$$

If V has spherical symmetry and if one uses spherical coordinates to perform the above integration, letting the z axis coincide with the direction of $\vec{k}_{in}$, then the φ integration drops out of the above integral since $\langle \vec{k} | T(E) | \vec{k}_{in} \rangle$ is independent of the azimuthal angle that $\vec{k}$ makes with $\vec{k}_{in}$. A finite matrix equation for $\langle \vec{k}_{out} | T(E) | \vec{k}_{in} \rangle$ is then obtained by subtracting off the singularity in the integrand at $k = k_0$ and approximating the two-dimensional integral by numerical quadrature. If the potential is energy-independent, this approach can lead to an efficient algorithm for computing the scattering

amplitude at any energy after a single prediagonalization of a (possibly large) matrix is carried out. If the potential has an energy dependence, this diagonalization must be done at each energy.

If V does not possess spherical symmetry, then $\langle \vec{k}_{out} | T(E) | \vec{k}_{in} \rangle$ is not independent of the azimuthal angle between $\vec{k}_{out}$ and $\vec{k}_{in}$. However for a cylindrically symmetric potential, a simplification can be found. Since the L^2-truncation of V allows one to solve the Lippmann-Schwinger equation one symmetry (Σ_g^+, Σ_u^+, etc.) at a time, then $\langle \vec{k}_{out} | T(E) | \vec{k}_{in} \rangle$ can be written as

$$\langle \vec{k}_{out} | T(E) | \vec{k}_{in} \rangle = \langle k_{out} | T^{\Gamma}(E) | k_{in} \rangle \, e^{im(\phi_{in} - \phi_{out})} \tag{19}$$

where m is the component of the angular momentum along the symmetry axis and $\langle k_{out} | T^{\Gamma}(E) | k_{in} \rangle$ is independent of ϕ_{in} and ϕ_{out}. Thus the Lippmann-Schwinger equation for $\langle k_{out} | T^{\Gamma}(E) | k_{in} \rangle$ can again be reduced to a two-dimensional equation. We should like to stress the point that this approach would lead to matrices of much larger dimensionality than those used in the present work and that such a quadrature, even if carried out to arbitrary accuracy, would only yield the result obtainable by solving the equation for $\underline{T}^t$ as outlined in Section II.A.

III. NUMERICAL RESULTS

As a model application of the method outlined in Sections II.A and II.B we have computed amplitudes for scattering from an attractive, two-center Gaussian potential:

$$U(\vec{r}) = -1/2\,(e^{-(\vec{r}-\vec{A})^2} + e^{-(\vec{r}+\vec{A})^2}) \tag{20}$$

For these computations, we took $|\vec{A}| = 1.0$. The matrix elements of this potential between the basis functions of Eq. (5) can be written in terms of one- and two-center overlap integrals of Gaussians which are well known.[3] In this paper we report results for choices of the incoming wave vector $\vec{k}_{in}$ along the symmetry axis of the potential and perpendicular to it.

For $\vec{k}_{in}$ along the axis of the potential, non-zero matrix elements of $\underline{T}^t(E)$ exist only for basis functions of Σ_g^+ and Σ_u^+ symmetries, and, as noted earlier, $\langle \alpha | T^t(E) | \beta \rangle$ is diagonal in these symmetries. The contributions of functions transforming with other irreducible representations of $D_{\infty h}$ vanish because their Fourier transforms $\langle \alpha | \vec{k}_{in} \rangle$, with $\vec{k}_{in}$ along the axis of V, are zero. It was found that, although basis functions of Σ_g^+ and Σ_u^+ symmetry may be constructed with g_α in Eq. (5) chosen to be a z-type Gaussian ($\ell = m = 0$, $n = 1$ in Eq. (6)), the contribution of such functions is negligible at the energies considered here. Table I compares results at k = .447 a.u. for basis sets of 14 and 20 functions with g_α of S symmetry. The exponents of the Gaussian functions were chosen in geometric series over a range of values between 6×10^{-4}

and 5. Studies of convergence showed that results converged to within less than 1% could be obtained for each symmetry with 15 to 20 basis functions.

For $\vec{k}_{in}$ perpendicular to the axis of the potential, $T^t(E)$ has nonzero matrix elements for functions of Σ_g^+, Π_u and symmetries of higher angular momentum projections. The contributions of Σ_u^+ and Π_g symmetries vanish, as do the contributions of certain other symmetries, because their Fourier transforms evaluated at $\vec{k}_{in}$ are zero. A simplification involved in calculations of Π contributions should be noted. In computing the scattering amplitude we made use of the fact that the L^2-matrix representation of $T^t(E)$ is the same for basis functions of Π symmetry chosen with g_α as x-type or y-type Gaussians. However the Fourier transforms of x and y Gaussian functions are not identical. In Table II we give the contributions of Σ_g^+ and Π_u symmetries for $\vec{k}_{in}$ perpendicular to the axis of the potential for k = .447 and 1.0 a.u.

As a check on the efficacy of our numerical codes, several tests were performed. The separation of the two-center potential was made vanishingly small, and it was found that the results so obtained agreed with those of Holt and Santoso[11] for a one-center Gaussian potential at k = .447 a.u. In addition, it was also verified (by integrating $\langle \vec{k}_{out} | T^t(E) | \vec{k}_{in} \rangle$ over all orientations of $\vec{k}_{out}$) that the optical theorem holds exactly for contributions to the scattering amplitude from each symmetry. It should be expected that the optical theorem is satisfied exactly, because solution of the matrix

equation (2) should yield, as we have stated, the exact T-matrix for the particular choice of truncated potential V^t.

The application of the variational correction described in Section II.B permits the use of much smaller basis sets than those employed in the above calculations. Using Eqs. (14) and (15) we may write the second term on the right hand side of Eq. (16) for the Kato correction as:

$$\langle \psi_t^{out} | U - U^t | \psi_t^{in} \rangle = \langle \vec{k}_{out} | U | \vec{k}_{in} \rangle - \langle \vec{k}_{out} | U^t | \vec{k}_{in} \rangle$$

$$+ \sum_{\alpha,\beta,\gamma} \langle \vec{k}_{out} | \alpha \rangle \langle \alpha | T^t(E) | \beta \rangle \langle \beta | G_0(E) | \gamma \rangle \langle \gamma | U - U^t | \vec{k}_{in} \rangle \qquad (21)$$

$$+ \sum_{\alpha,\beta,\gamma} \langle \vec{k}_{out} | U - U^t | \alpha \rangle \langle \alpha | G_0(E) | \beta \rangle \langle \beta | T^t(E) | \gamma \rangle \langle \gamma | \vec{k}_{in} \rangle .$$

The usual separation of the contributions of different symmetries may be made for all but the first term in Eq. (21). As mentioned earlier, the only matrix elements appearing in (21) which have not been used in the calculation of $\underline{T}^t$ are free-free and bound-free matrix elements of the exact potential V. Due to our choice of a Gaussian potential, the free-free matrix elements may be expressed in terms of the Fourier transform of a Gaussian given in Eq. (8). The bound-free matrix elements reduce to matrix elements of $e^{ik \cdot r}$ between Gaussians on different centers, and these integrals are known in closed form.[12]

In Tables III and IV we compare the results of Kato corrected calculations using only 2 basis functions of each symmetry

(exponents of 1.0 and 2.0) with 20 function results. The agreement of these calculations suggests that, for potentials for which free-free and bound-free matrix elements can be computed, the Kato correction will allow the use of conveniently small basis sets.

It should be noted that a significant proportion of the variational improvement is carried by the leading term of the Kato correction (first line of Eq.(21)), which is simply the exact matrix element of the Born term. One would generally expect this to be true at intermediate energies, and even at very low energies for potentials without bound states. Furthermore, this leading term automatically adds in the Born contributions from all higher symmetry groups not explicitly treated and one certainly expects these contributions to be Born-dominated. As this term only involves calculation of free-free matrix elements, its addition should be quite feasible in molecular applications of this technique.

IV. DISCUSSION

In this paper we have outlined an efficient method for computing scattering amplitudes for cylindrically symmetric potentials and applied it to a model case. Our results indicate that the use of the Kato correction will allow one to obtain accurate answers with very few basis functions.

This method should find application in the area of low energy electron-diatomic molecule collisions. In this case, one would probably construct an energy-dependent optical potential[13] to describe the target. In this context the necessity for reconstructing matrix elements of the transition operator at such energy is not a drawback. A major portion of the computational effort in this work involved construction of matrix elements of the free-particle Green's function. Much of this effort (the θ and ϕ integrations in Eq. (7)) need be done only once. Applications of this technique to electron-diatomic molecule scattering are presently under study.

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metry axis of the potential.

No. basis functions	θ	Exact Born $(\Sigma_g^+ + \Sigma_u^+)$	Born (Σ_g^+)	Born (Σ_u^+)	$f(\theta)(\Sigma_g^+)$	$f(\theta)(\Sigma_u^+)$
14	0	0.443	0.336	0.112	0.405 + i .088	0.125 + i .0024
	$\pi/4$	0.427	0.354	0.080	0.427 + i .093	0.089 + i .0017
	$\pi/2$	0.362	0.373	0.0	0.449 + i .098	0.0
	$3\pi/4$	0.270	0.354	-0.080	.427 + i .093	-0.089 - i .0017
	π	0.227	0.336	-0.112	0.405 + i .088	-0.125 - i .0024
20	0	0.443	0.328	0.115	0.399 + i .086	0.127 + i .0025
	$\pi/4$	0.427	0.346	0.082	0.421 + i .090	0.091 + i .0018
	$\pi/2$	0.362	0.364	0.0	0.443 + i .095	0.0
	$3\pi/4$	0.270	0.346	-0.082	0.421 + i .090	-0.091 - i .0018
	π	0.227	0.328	-0.115	0.399 + i .086	-0.127 - i .0025

TABLE II. Scattering amplitudes with 20 basis functions per symmetry. The incident wave vector is perpendicular to the axis of the potential and the outgoing wave vector lies in the plane of the incident wave vector and the axis of the potential.

k (a.u.)	θ	Exact Born	Born (Σ_g^+)	Born (Π_u)	$f(\theta)(\Sigma_g^+)$	$f(\theta)(\Pi_u)$
	0	0.443	0.403	0.044	0.491 + i .105	0.046 + i .0003
	$\pi/4$	0.409	0.383	0.030	0.467 + i .100	0.031 + i .0002
.447	$\pi/2$	0.362	0.364	0.0	0.423 + i .095	0.0
	$3\pi/4$	0.355	0.383	-0.030	0.467 + i .100	-0.031 - i .0002
	π	0.363	0.403	-0.044	0.491 + i .105	-0.046 - i .0003
	0	0.443	0.295	0.147	0.295 + i .066	0.156 + i .0067
	$\pi/4$	0.291	0.224	0.079	0.224 + i .050	0.084 + i .0036
1.0	$\pi/2$	0.145	0.159	0.0	0.159 + i .036	0.0
	$3\pi/4$	0.143	0.224	-0.079	0.224 + i .050	-0.084 - i .0036
	π	0.163	0.295	-0.147	0.295 + i .066	-0.156 - i .0067

TABLE III. Comparison of scattering amplitudes using Kato correction and 2 basis functions per symmetry with 20 function results. Energies are k = .447 and k = 1.0 a.u. and incident wave as in Table I.

k (a.u.)	θ	$f(\theta)$ 2 basis functions uncorrected	$f(\theta)$ 2 basis functions + Kato correction	$f(\theta)$ 20 basis functions + Kato correction
.447	0	0.693 + i .163	0.515 + i .093	0.528 + i .089
	$\pi/4$	0.677 + i .170	0.499 + i .096	0.511 + i .092
	$\pi/2$	0.561 + i .168	0.431 + i .098	0.440 + i .095
	$3\pi/4$	0.446 + i .165	0.331 + i .094	0.336 + i .089
	π	0.372 + i .155	0.283 + i .090	0.287 + i .084
1.0	0	0.451 + i .073	0.465 + i .052	0.473 + i .057
	$\pi/4$	0.407 + i .071	0.382 + i .053	0.389 + i .058
	$\pi/2$	0.173 + i .043	0.141 + i .038	0.147 + i .040
	$3\pi/4$	-0.145 - i .018	-0.049 + i .008	-0.045 + i .008
	π	-0.264 - i .027	-0.097 - i .005	-0.094 - i .005

TABLE IV. Comparison of scattering amplitudes using Kato correction and 2 basis functions per symmetry with 20 function results. k = .447 and 1.0 a.u. Orientation of incident and outgoing wave vectors as in Table II.

k (a.u.)	θ	$f(\theta)$ 2 basis functions uncorrected	$f(\theta)$ 2 basis functions + Kato correction	$f(\theta)$ 20 basis functions + Kato correction
.447	0	0.724 + i .191	0.518 + i .104	0.530 + i .104
	$\pi/4$	0.667 + i .181	0.481 + i .100	0.492 + i .100
	$\pi/2$	0.583 + i .171	0.430 + i .096	0.440 + i .095
	$3\pi/4$	0.561 + i .180	0.425 + i .100	0.435 + i .099
	π	0.568 + i .189	0.435 + i .103	0.446 + i .104
1.0	0	0.558 + i .094	0.445 + i .064	0.450 + i .066
	$\pi/4$	0.371 + i .068	0.290 + i .051	0.296 + i .053
	$\pi/2$	0.178 + i .043	0.141 + i .038	0.147 + i .040
	$3\pi/4$	0.115 + i. 051	0.135 + i .045	0.140 + i .047
	π	0.081 + i .063	0.152 + i .055	0.155 + i .055

SECTION C

Low-Energy Elastic e^- - H_2 Cross Sections Using Discrete Basis Functions

I. INTRODUCTION

In two earlier papers,[1, 2] we outlined a new method for calculating cross sections for scattering involving non-spherical potentials. It was there indicated that this method would find numerous applications in low energy electron-molecule scattering problems.

Progress in the ab-initio calculation of such cross sections has been hampered because of the difficulties involved in the calculation of accurate molecular continuum wavefunctions. When compared to the advances that have been made in the area of electron-atom scattering, the study of electron-molecule collisions is still in a very unsatisfactory stage. Nevertheless, the need for accurate low energy electron-molecule cross sections is very great. For example, the excitation mechanism for many existing and proposed gas laser systems is direct excitation by electron impact in a gaseous discharge.[3] Furthermore, there is now considerable experimental low-energy data with which to compare results.

This paper describes the first results of the application of our new method to elastic scattering of low energy electrons by hydrogen molecules. We have limited ourselves here to a study of the static-exchange approximation. This model has been studied previously by others[4, 5] for e^--H_2 and we compare our results with theirs. Our point here is to show that calculations such as the present are quite feasible and, in fact, require only slightly more effort

than a standard bound-state molecular computation.

The plan of this paper is as follows. In the next section we give a general outline of the method used to calculate elastic cross sections. Section III contains our results for e^--H_2 scattering and a comparison with the work of others. Section IV contains a brief discussion.

II. THEORY

A. General formulation

Here we restrict ourselves to scattering in the static-exchange approximation, which can be formulated by writing the wavefunction for the entire system ($e^- + H_2$) as

$$\psi^+(1, 2, 3) = \mathcal{A}\,[\chi^+_{\vec{k}}(1)\,\Phi(2, 3)\,], \tag{1}$$

where $\Phi(2, 3)$ is the ground state wavefunction of H_2, which we take to be the Hartree-Fock solution. Substitution of Eq. (1) into Schroedinger equation yields an equation for the spatial part of $\chi^+_{\vec{k}}$ in which the effective potential is simply the Hartree-Fock potential of H_2

$$V = -\frac{1}{r_{N_1}} - \frac{1}{r_{N_2}} + 2\hat{J} - \hat{K}\,, \tag{2}$$

that is, the sum of the nuclear attraction and the usual coulomb and exchange operators. For a homonuclear diatomic molecule (e.g. H_2) this potential possesses cylindrical and inversion symmetry.

It should be noted that the method we are employing is by no means restricted to the static-exchange model. A more realistic inclusion of correlation effects could be accomplished either by including excited target states in the trial wavefunction given by Eq. (1) or, if a single-channel model is desired, by using an

optical potential. We have chosen the static-exchange approximation in order to keep the computational details fairly simple and to facilitate comparison with previous work.

We further assume that the molecule remains stationary during the collision, and hence its rotational motion need not be considered in the elastic scattering problem. It is well established that this is an excellent approximation for all but the lowest incident energies (less than 0.1 eV).[4-6] This allows us to perform the

calculation in the frame of the molecule, transform the result to the laboratory frame and then average the cross section over molecular orientations.[7]

Since the potential does not have spherical symmetry it is convenient to work with the integral equation for the full scattering amplitude subject to the above restrictions. We do not employ a single-center expansion of the potential.

The solution of the Lippmann-Schwinger equation using a finite set of square-integrable basis functions has been described in detail elsewhere,[1, 2] and thus only a brief outline of the method will be given here. The approximation on which our approach is based is the representation of the potential in a finite, discrete basis. This truncated potential, V^t,

$$V^t = \sum_{\alpha, \beta}' |\alpha\rangle\langle\alpha|V|\beta\rangle\langle\beta| \tag{3}$$

leads to a separable kernel in the Lippmann-Schwinger equation,[8] which becomes a linear equation for the matrix elements of the truncated transition operator T^t:

$$\langle\alpha|T^t(E)|\beta\rangle = \langle\alpha|U|\beta\rangle + \sum_{\gamma, \delta}' \langle\alpha|U|\gamma\rangle\langle\gamma|G_0(E)|\delta\rangle\langle\delta|T^t(E)|\beta\rangle \tag{4}$$

where $U = 2V$ in atomic units. The exact scattering amplitude for the truncated potential may be obtained from the matrix of T^t by the transformation to the laboratory frame

$$f(\vec{k}_{out} \leftarrow \vec{k}_{in}) = -\frac{1}{4\pi} \langle \vec{k}_{out} | T^t(E) | \vec{k}_{in} \rangle$$
$$= -\frac{1}{4\pi} \sum_{\alpha, \beta} \langle \vec{k}_{out} | \alpha \rangle \langle \alpha | T^t(E) | \beta \rangle \langle \beta | \vec{k}_{in} \rangle \quad (5)$$

where

$$\langle k | \alpha \rangle = \int e^{-i\vec{k} \cdot \vec{r}} \langle r | \alpha \rangle d^3 r \quad . \quad (6)$$

The scattering amplitude $f(\vec{k}_{out} \leftarrow \vec{k}_{in})$ depends on the orientation of the molecule as well as the scattering angle. Equation (5) renders the calculations of differential cross sections and averages over molecular orientation particularly simple since all angular dependences are contained in the Fourier transforms of Eq. (6).

The solution of Eq. (4) requires only matrix elements of the potential and the free-particle Green's function in a discrete basis. Once these matrix elements are known, the matrix $\underline{T}^t$ is obtained by a single matrix inversion,

$$\underline{T}^t = (\underline{1} - \underline{U}^t \underline{G_0}(E))^{-1} \underline{U}^t \quad . \quad (7)$$

It should be noted that the approximation of using a truncated potential is employed universally in bound state calculations on molecular systems. It arises whenever the Schroedinger equation is solved by diagonalizing the Hamiltonian in a basis set.

For molecular systems a natural approach to the solution of Eq. (4) is to construct the set $\{ | \alpha \rangle \}$ by orthogonalizing a set of the usual Gaussian basis functions of molecular bound-state

calculations.[9] Since we are restricting our attention to cylindrically symmetric systems, we first make combinations of the Gaussian functions $\mathcal{G}_\alpha$

$$\mathcal{G}_\alpha(\vec{r} - \vec{A}) = x^\ell\, y^m\, (z - A)^n\, e^{-\alpha(x^2 + y^2 + (z - A)^2)} \tag{8}$$

which have g or u inversion symmetry:

$$\varphi_\alpha = \mathcal{G}_\alpha(\vec{r} - \vec{A}) \pm \mathcal{G}_\alpha(\vec{r} + \vec{A}) \ , \tag{9}$$

and also require that the φ_α transform with irreducible representations of the point group $D_{\infty h}$. Equation (4) may then be solved separately for each symmetry, e.g. Σ_g^+, Σ_u^+, Π_g, Π_u, etc. An immediate advantage of using Gaussian basis functions is that the Fourier transforms of Eq. (6) may be done in closed form and are simply Gaussians modulated by Hermite polynomials.[10]

A number of simplifications can be realized in the calculation of the matrix elements of the free particle Green's function which reduce the computational effort required to solve Eq. (4) to little more than is expended in molecular self-consistent field calculations on bound states. In computing matrix elements of the Green's function an integration over d^3k is required. The use of Gaussians allows the two angular integrations to be performed analytically. The remaining integration over $|k|$ may be handled by a simple numerical quadrature technique; details can be found in reference 2. In addition, matrix elements of the Hartree-Fock potential were extracted from existing bound-state molecular programs.

B. Born correction

The leading term in the scattering amplitude, Eq. (5), is the matrix approximation to the Born contribution. It was found necessary to represent this term exactly. This can be accomplished by subtracting $<\alpha \mid U \mid \beta>$ from the computed value of $<\alpha \mid T^{t}(E) \mid \beta>$ and in Eq. (5) adding the exact Born matrix element $<\vec{k}_{out} \mid U \mid \vec{k}_{in}>$. In addition to improving the computed T matrix elements, this correction includes Born contributions from all symmetries not explicitly included in the computation of the scattering amplitude. One expects contributions from higher symmetries (analogous to higher partial waves in central field problems) to be well represented in the Born approximation.

Computation of $<\vec{k}_{out} \mid U \mid \vec{k}_{in}>$ requires direct and exchange free-free interaction matrix elements. The direct terms can be reduced to the Fourier transform of a product of two Gaussian basis functions on different centers; these integrals are well known.[11] The exchange matrix elements can be written in terms of error functions of a complex argument. Details are given in Appendix A. All such matrix elements depend on the scattering angle and the molecular orientation.

It should be pointed out that the Born correction discussed here is simply the leading term in a full variational correction of the computed amplitude. The details of such a correction are

discussed at length in reference 2. In this connection, it is interesting to compare this method with the more standard variational procedures such as the Kohn method. We would require bound-free and free-free matrix elements only in evaluating the Kato-correction whereas the Kohn method always needs such matrix elements. Furthermore, since we are computing the exact amplitude for an approximate potential, we would not expect to find singularities of the type that frequently occur when using the Kohn method.

C. Cross sections

The physical cross section is obtained by averaging the cross section for a particular molecular orientation over all orientations of the molecule. The cross section $\sigma\ (\Omega, \Omega_0)$ depends on the angles Ω_0 specifying the molecular orientation in the laboratory-fixed frame and on the angles Ω specifying the orientations of $\vec{k}_{in}$ and $\vec{k}_{out}$. The average over orientations is given by

$$\sigma_{av}(\theta) = \frac{1}{4\pi} \int \sigma\ (\Omega, \Omega_0)\ d\Omega_0 \tag{10}$$

The coordinate system is shown in Fig. 1. The z axis of this system lies along the momentum transfer vector $\vec{Q} = \vec{k}_{in} - \vec{k}_{out}$. This was done in order that the ranges of integration over θ and φ (see Fig. 1) could both be reduced to the interval $[\,0, \pi/2\,]$ by using the symmetry of the cross section under inversion of the molecule and under interchange of $\vec{k}_{in}$ and $\vec{k}_{out}$. This symmetry obviously applies only to homonuclear molecules.

III. RESULTS

Elastic scattering calculations were performed for incident momenta of 0.3, 0.4, 0.5, 0.6 and 0.7 a.u. A basis of 22 s-type Gaussians on each hydrogen atom was constructed from the Huzinaga[12] expansion of a 1S slater function (orbital exponent = 1.2) in 10 Gaussians by adding diffuse Gaussians with exponents chosen in a geometric series with a ratio of 1.6. A similar prescription has been used successfully by Schneider in a calculation on electron-helium scattering.[13] Diffuse basis functions were found to be necessary to properly represent the asymptotic portions of the potential. With this basis set, contributions for Σ_g^+ and Σ_u^+ symmetries may be computed. An indication of the completeness of the basis for these symmetries may be obtained by comparison of the sum of the Σ_g^+ and Σ_u^+ Born contributions (i.e., $<\vec{k}_{out} \mid U^t \mid \vec{k}_{in}>$) with the exact Born amplitude at a molecular orientation at which only these two symmetries contribute. This is the case for forward scattering with the axis of the molecule along $\vec{k}_{in}$. For k = 0.3 a.u. at this orientation the exact Born amplitude is 8.51 and the sum of the Σ_g^+ and Σ_u^+ approximate Born contributions was 8.60.

Our results for the differential cross sections at five energies and five angles are presented in Table I. The angular average for these cross sections was performed using a 6-point Gauss-Legendre quadrature in θ and φ. We compare our results

at k = 0.3, 0.4 and 0.6 a.u. with the results of Tully and Berry[4] and at k = 0.7 a.u. with the static-exchange results of Hara[5] (case C in his work) in Fig. 2. The calculation of Tully and Berry differs slightly from the present work in that they used the Weinbaum function[14] for the ground state of H_2; their cross sections were generated by direct numerical solution of the two-dimensional Schroedinger equation. Hara's results[5] were obtained by numerical solution of the Schroedinger equation in elipsoidal coordinates. The agreement between our results and those obtained by numerical integration is quite good.

The importance of including the exact Born correction can be assessed by comparison of our corrected and uncorrected cross sections at k = 0.6 a.u. with those of Tully and Berry in Fig. 3. Again, there is good agreement with our corrected results, although the uncorrected results (which are particularly easy to generate) are moderately accurate and display the correct shape. This was found to be the case at other energies also.

Our calculations were performed on an IBM 370-158 computer. The SCF calculation and the construction of the Hartree-Fock potential using the 22 S-Gaussian basis on each hydrogen required 16.6 minutes. The calculation of uncorrected cross sections for all energies and angles reported here required 2.7 minutes. The calculation of all required Born corrections which were performed with a smaller (12 S on each atom) basis required an additional 13.0 minutes. The 12 S basis gives identical results for $<\vec{k}_{out} \mid U \mid \vec{k}_{in}>$ as the 22 S basis.

IV. DISCUSSION

These results indicate that the use of Gaussian basis functions provides an efficient method for computing elastic electron-molecule cross sections. In our case, the entire scattering calculation required less time than the SCF calculation for the ground state and the construction of the potential. The bulk of the time expended in the scattering calculation was used in computing the Born corrections.

The calculations reported here were minimal; only Σ_g^+ and Σ_u^+ symmetries were included and polarization effects were ignored. Correlation effects can be easily included in this computational scheme through the use of an approximate optical potential.[15] The efficiency of the method and the accuracy of the results obtained here suggest that the prospects for more detailed calculations as well as application to larger molecules are good.

APPENDIX A

Evaluation of exchange free-free matrix elements

Consider the exchange integral for S-type Gaussians,

$$I \equiv \int d^3 r_1 \, d^3 r_2 \; e^{-ik' \cdot r_1} \; e^{-\alpha (\vec{r_2} - \vec{A})^2} \; \frac{1}{|\vec{r_1} - \vec{r_2}|} \; e^{i\vec{k} \cdot \vec{r_2}} \; e^{-\beta (\vec{r_1} - \vec{B})^2} \; . \quad \text{(A1)}$$

By completing squares in the exponents of Eq. (A1) we obtain a matrix element involving Gaussians referring to complex centers:

$$I = e^{-k^2/4\alpha} \; e^{-k'^2/4\beta} \; e^{+i\vec{k} \cdot \vec{A}} \; e^{-i\vec{k'} \cdot \vec{B}}$$

$$\times \int e^{-\alpha (\vec{r_1} - (\vec{A} + \frac{i\vec{k}}{2\alpha}))^2} \; \frac{1}{|r_1 - r_2|} \; e^{-\beta (\vec{r_2} - (\vec{B} - \frac{i\vec{k'}}{2\beta}))^2} \; d^3 r_1 \, d^3 r_2 \quad \text{(A2)}$$

Following Shavitt,[9] this integral may be performed by expressing $\frac{1}{|\vec{r_1} - \vec{r_2}|}$ as its Gaussian transform,

$$\frac{1}{|r_1 - r_2|} = \frac{1}{\sqrt{\pi}} \int_0^\infty s^{-\frac{1}{2}} \; e^{-s |r_1 - r_2|^2} \; ds \; . \quad \text{(A3)}$$

With this substitution, the integral of Eq. (A2) may be performed by elementary methods to give

$$I = \frac{2\pi^{5/2}}{\alpha\beta\sqrt{\alpha+\beta}} e^{-k^2/4\alpha} e^{-k'^2/4\beta} e^{i\vec{k}\cdot\vec{A}} e^{-i\vec{k}'\cdot\vec{B}} \quad \text{(A4)}$$

$$F_0\left(\sqrt{\frac{\alpha\beta}{\alpha+\beta}} \left|(\vec{A}-\vec{B})\, r\, i\left(\frac{\alpha\vec{k}'+\beta\vec{k}}{2\alpha\beta}\right)\right|\right)$$

where the function $F_0(X)$ is

$$F_0(X) = \frac{\sqrt{\pi}}{2X} \text{ erf } (X) \quad . \quad \text{(A5)}$$

Expressions for integrals involving p, d, etc., Gaussians may be derived from Eq. (A4) by differentiation with respect to the components of $\vec{A}$ and $\vec{B}$. An efficient algorithm for computing error functions of complex argument given by Gautschi was used in this work.[16]

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Figure Captions

Fig. 1. Coordinate system used for averaging the cross section over molecular orientations.

Fig. 2. Differential cross sections for elastic-scattering of electrons by H_2. Cross sections are given in units of a_0^2 and k is measured in atomic units. Our results are given by open circles (⊙); the solid curves are those of Tully and Berry,[4] and (at k = 0.7 a.u.) Hara.[5]

Fig. 3. Differential cross section at k = 0.6 a.u. compares our corrected (⊙) and uncorrected (△) results with those of Tully and Berry (solid curve).

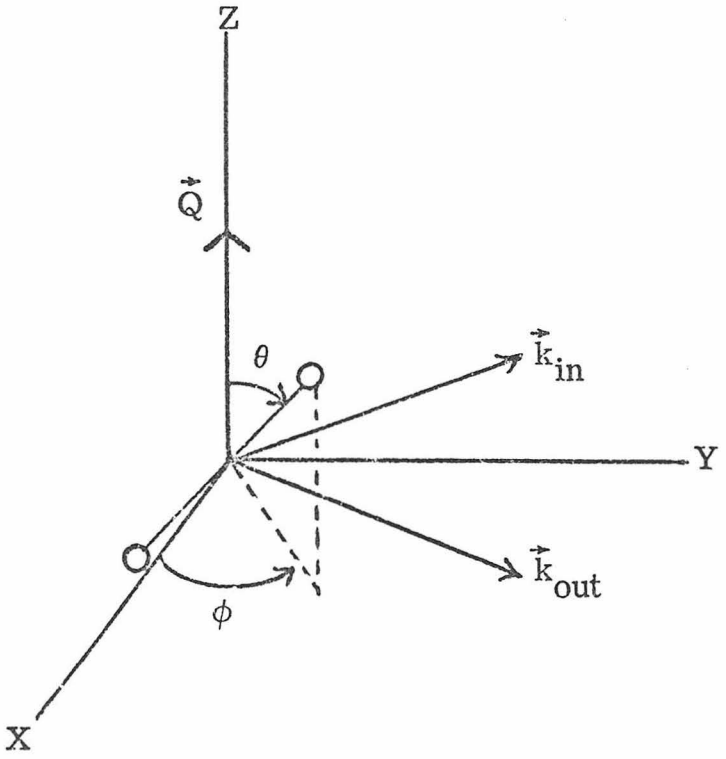
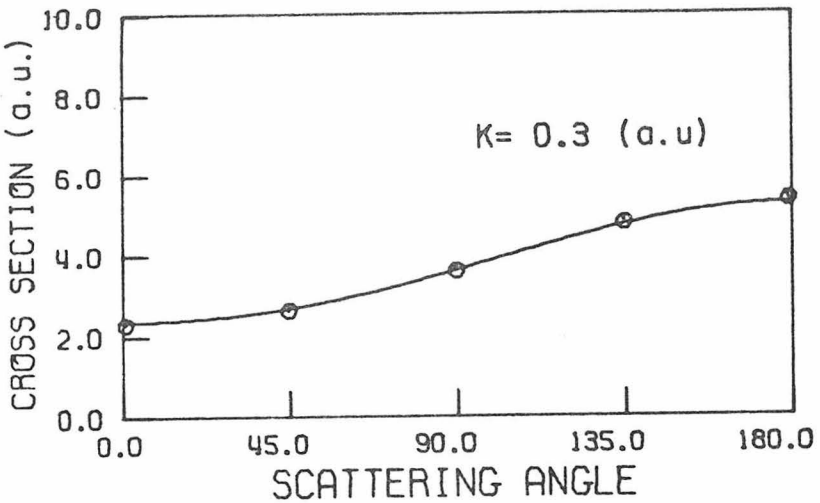
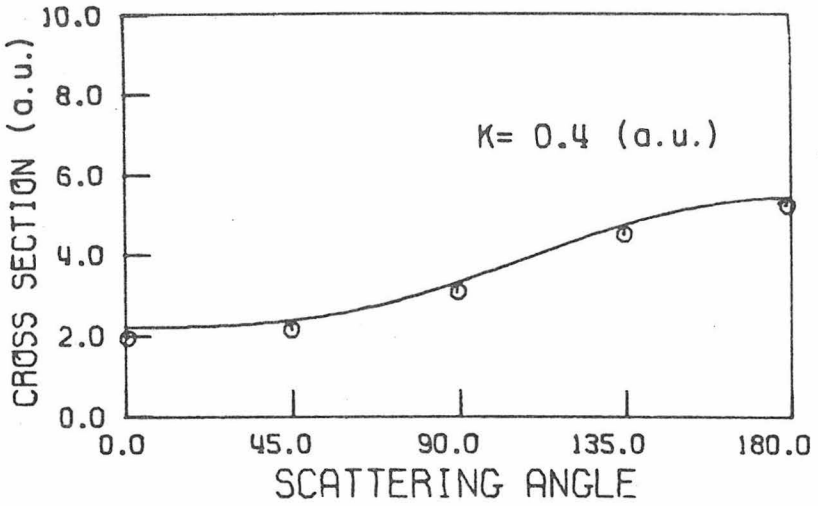
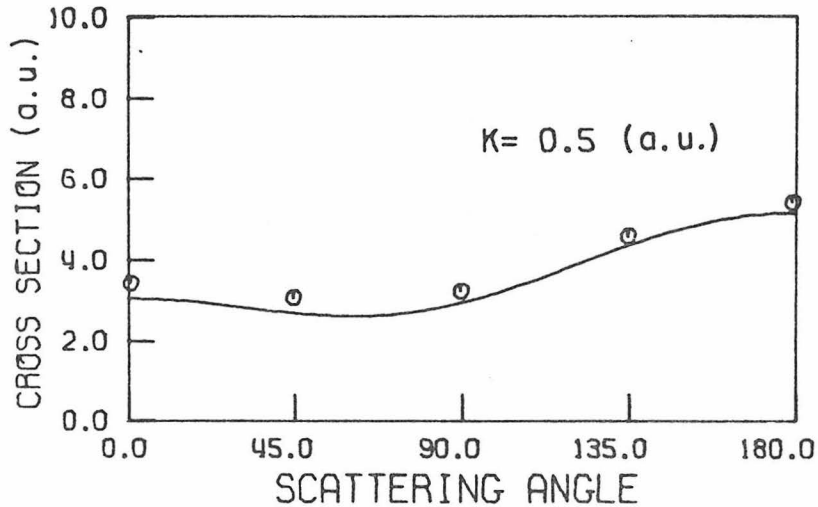


Figure 1.


CROSS SECTION (a.u.)
10.0
8.0
6.0
4.0
2.0
0.0
K= 0.3 (a.u)
0.0
45.0
90.0
135.0
180.0
SCATTERING ANGLE


CROSS SECTION (a.u.)
10.0
8.0
6.0
4.0
2.0
0.0
K= 0.4 (a.u.)
0.0
45.0
90.0
135.0
180.0
SCATTERING ANGLE


CROSS SECTION (a.u.)
10.0
8.0
6.0
4.0
2.0
0.0
K= 0.5 (a.u.)
0.0
45.0
90.0
135.0
180.0
SCATTERING ANGLE

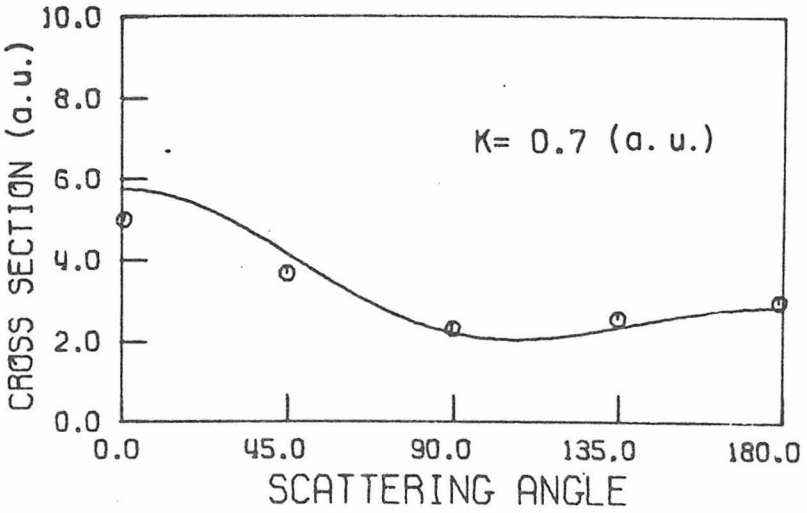

CROSS SECTION (a.u.)
10.0
8.0
6.0
4.0
2.0
0.0
K= 0.7 (a.u.)
0.0
45.0
90.0
135.0
180.0
SCATTERING ANGLE

Figure 2.

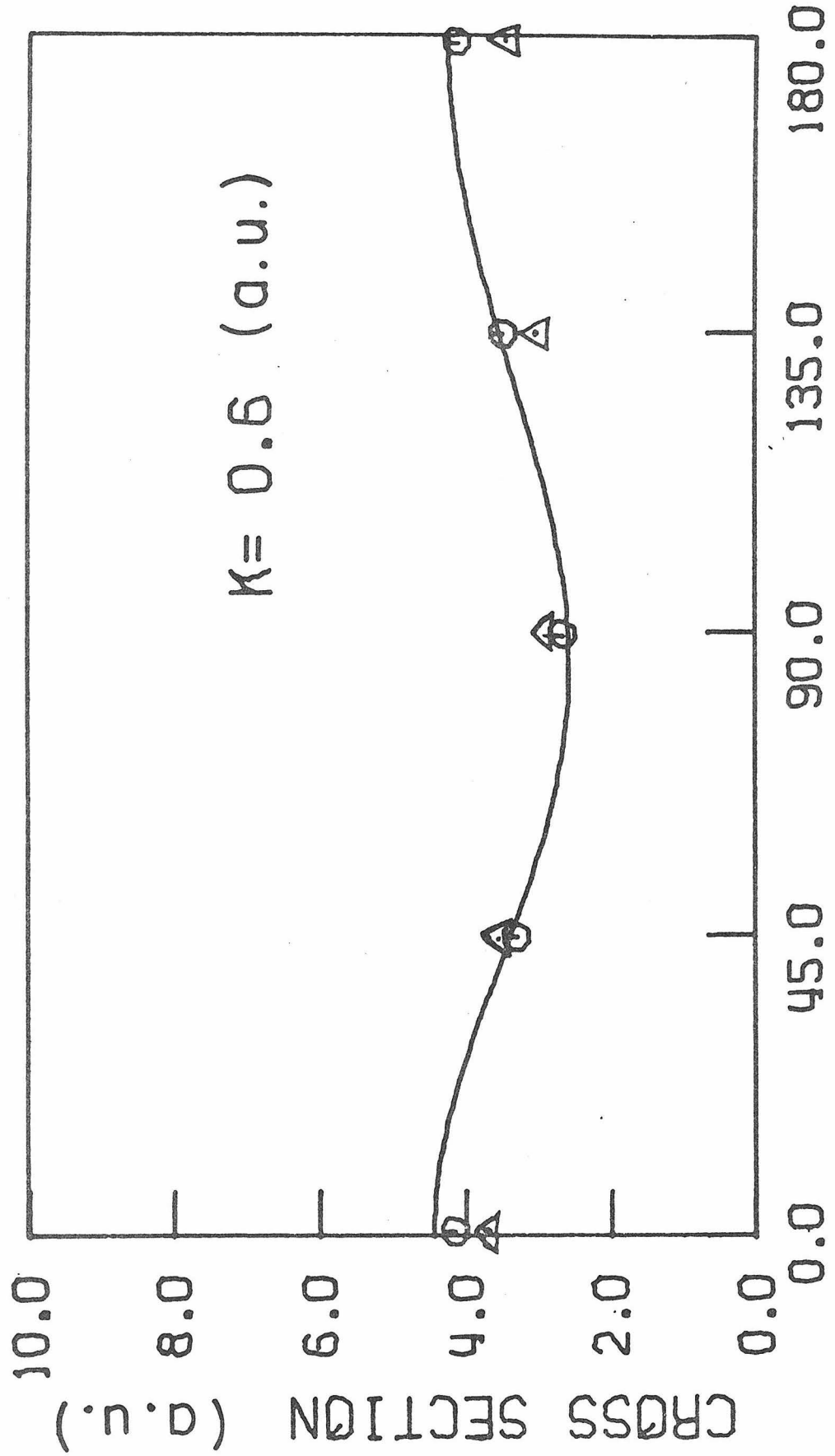

K= 0.6 (a.u.)
CROSS SECTION (a.u.)
10.0
8.0
6.0
4.0
2.0
0.0
0.0
45.0
90.0
135.0
180.0
SCATTERING ANGLE

Figure 3.

SECTION D

A Simple Method for Evaluating Low-Energy Electron-Molecule Scattering Cross Sections Using Discrete Basis Functions

1. Introduction

Electron-molecule scattering has long appeared to be a formidable problem due to the difficulties encountered in solving for continuum wavefunctions in the field of a non-spherical potential. Elastic electron scattering from a homonuclear diatomic molecule (the least anisotropic case) has been treated successfully at low energies by a variety of approaches of varying difficulty. For example, Tully and Berry (1969) numerically integrated the two dimensional Schroedinger equation, Hara (1969) made use of prolate spheroidal coordinates, and several calculations have been made using single-center expansions of the wave function (Temkin and Vasavada 1967, Lane and Henry 1969, Burke and Sinfailam 1970, Burke and Chandra 1972). Recently, more efficient methods have been developed which demonstrate that a knowledge of the wavefunction in the vicinity of the target is sufficient to calculate the scattering cross section (Rescigno, McCurdy and McKoy 1975, Schneider 1975). In all these approaches, the coupling of orbital angular momentum by the non-spherical potential can be treated properly. However, a price of increased complexity over central field calculations is inevitably paid for this capability.

The success of methods which employ purely square-integrable (L^2) basis functions to rigorously treat scattering from non-spherical targets has led to even simpler, but less rigorous, attempts to describe electron-diatomic molecule scattering. Among these are the Fredholm calculations of Winter and Lane (1975), and the method of Morrison and

Lane (1975), both of which make use of the low ℓ - spoiling approximation which we will discuss in the following section. In this paper we describe an exceedingly simple, but approximate, procedure for computing cross sections for low-energy elastic electron scattering from homonuclear diatomics. We present results for e^- - H_2 and e^- - N_2 scattering.

2. Theory

It is now well known that the square-integrable eigenfunctions at scattering energies obtained by diagonalizing the Hamiltonian for a spherical potential problem in a discrete basis are proportional to the true scattering solutions over the region spanned by the basis functions. Several approaches for resonant and non-resonant scattering make use of this fact, e.g., Hazi and Taylor (1970), Hazi and Fels (1971), Heller (1972). In general, it is necessary to develop a formula for the phase shift which is independent of the normalization of the wavefunction. For example, the Harris formula (Harris 1967) can be viewed in this manner. These methods are unfortunately not rigorously applicable to scattering from a non-spherical potential. The coupling of various partial waves by the potential gives the problem of solving for the molecular scattering wavefunction in the body-fixed frame of the molecule the same mathematical form as a multi-channel potential scattering problem. Thus at a given energy there is more than one regular solution to the radial equations and a linear combination of these must be taken to give the appropriate physical solutions. The diagonalization of the Hamiltonian in a discrete basis, however, gives only one solution at

each eigenvalue. A possible method for circumventing this difficulty, requiring several diagonalizations of the Hamiltonian in different basis sets, has been discussed by Hazi (1973).

Alternatively, if we assume that orbital angular momentum is approximately conserved (low ℓ-spoiling), then we will show how to extract scattering information from a single diagonalization of the Hamiltonian. Fano (1970) has discussed the basis for this approximation in the case of homonuclear diatomic molecules. The potential consists of the centrifugal barrier superposed on an attractive non-spherical potential of shorter range. It is known that the Rydberg series of molecules can be classified by orbital angular momentum quantum number λ (Mulliken 1964); scattering solutions for electron-homonuclear diatomic molecule scattering have been similarly classified (Tully and Berry 1969, Temkin and Vasavada 1967). Fano (1970) notes that the approximate conservation of orbital angular momentum is not due to the nearly spherical symmetry of the molecular potential at large distances. A large assymetry in the potential, even if it is of short range, is capable of coupling angular momenta. Instead, Fano (1970) concludes that the centrifugal barrier is probably responsible for preventing scattering solutions from penetrating the inner region of the potential and thus prevents the coupling of partial waves.

Approximate conservation of angular momentum should hold particularly well for homonuclear diatomics, because in those cases the center of symmetry causes even values of λ to be uncoupled from odd

values. Moreover, for linear molecules the projection of the angular momentum along the internuclear axis, m_ℓ, is a good quantum number and leads to the uncoupling of the molecular symmetries Σ, Π, etc. On the other hand, one expects the low ℓ-spoiling approximation to be less applicable to heteronuclear diatomics where s and p waves can couple and the centrifugal barrier may not be strong enough to keep them uncoupled.

We stress that the assumption of low ℓ-spoiling does not imply that the scattering wavefunction can be thought of in terms of uncoupled partial waves at all r. The fact that in the exterior region the centrifugal barrier leads to uncoupling of the partial waves means that it will also confine some solutions to the interior region where coupling is appreciable. Indeed, the bound states of the potential show a great deal of anisotropy, and the requirement that the scattering solutions remain orthogonal to the bound states implies that there may be considerable anisotropy in the scattering solutions for small r. Consequently one expects that the partial wave expansion of the molecular potential may converge very slowly.

In this paper we treat elastic electron scattering from homonuclear diatomics in the static-exchange approximation by first diagonalizing the body-fixed Hartree-Fock Hamiltonian in a discrete basis. Within the framework of low ℓ-spoiling, we may assume that the radial function, $R_{\ell m}(r)$, obtained by projecting with a spherical harmonic onto a positive energy L^2 eigenfunction, $\Psi_{\text{molecular}}(\vec{r})$,

$$R_{\ell m}(r) = \int d\Omega Y^{*}_{\ell m}(\Omega) \Psi(\vec{r})_{\text{molecular}} \qquad (1)$$

is proportional to a scattering solution for r less than some value, b, within the range of the basis set. With this assumption, a number of ways for extracting scattering information from $R_{\ell m}(r)$ suggest themselves.

One could use the value of $R_{\ell m}(r)$ at r = b as the starting point for an outward numerical integration (Morrison and Lane 1975). If b were sufficiently large, then only the direct, spherically symmetric part of the potential need be used in the integration. This procedure would be similar to the numerical R-matrix calculations of Burke, Hibbert and Robb (1971) and to the recent work of Morrison and Lane (1975). Alternatively, one could try fitting $R_{\ell m}(r)$ over the interval $\lfloor 0, b \rfloor$ to another function that had the correct asymptotic form and extracting values of the tangent of the phase shift in this manner. This procedure was tried first using a function of the form

$$\chi(r) = \sum_i C_i \varphi_i(r) + A j_\ell(kr) + B n_\ell(kr) \qquad (2)$$

where $\varphi_i(r)$ is an L^2 function and j_ℓ and n_ℓ are spherical Bessel functions. But this approach was found to be considerably less stable than the method finally adopted.

In the present work we chose to evaluate the phase shift from the radial function and its derivative at a value of r. Consider the function

$$\tan \delta_{\ell m}(r) = - \frac{R_{\ell m}(r)\, j'_\ell(kr) - R'_{\ell m}(r)\, j_\ell(kr)}{R_{\ell m}(r)\, n'_\ell(kr) - R'_{\ell m}(r)\, n_\ell(kr)} \quad . \qquad (3)$$

If one were to plot this function for the exact (low ℓ-spoiled) radial function, it would vary for small r, but then level off to a constant value as the asymptotic region were approached. This should also be the case for a basis set representation of $R_{\ell m}(r)$, provided the basis spans a sufficiently broad region of configuration space. Then $\tan \delta_{\ell m}(r)$ should approach some stable value and maintain this value until the basis set was no longer capable of representing $R_{\ell m}(r)$ accurately. Formulas for the cross section in terms of the low ℓ-spoiled phase shifts can be found in Temkin and Vasavada (1967).

3. Computational

We begin by constructing the Hartree-Fock wavefunction for the target molecule, which defines the static-exchange potential for the scattering calculation. This part of the procedure simply involves performing a standard basis set self-consistent field (SCF) calculation to obtain the occupied orbitals of the molecular target. The body-fixed, static-exchange Hamiltonian (for closed-shell targets) is then given by

$$H^{HF} = -\tfrac{1}{2}\nabla^2 + V^{direct} + V^{exchange} \qquad (4a)$$

where

$$V^{direct}(\vec{r}) = -\sum_{\text{nuclei}} \frac{Z_n}{|\vec{r} - \vec{R}_n|}$$

$$+ 2 \sum_{\alpha} \int d\vec{r}' \, \frac{\phi_\alpha^*(\vec{r}')\,\phi_\alpha(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad , \qquad (4b)$$

and

$$V^{ex}(\vec{r}, \vec{r}')F(\vec{r}') = -\sum_{\alpha}\int \frac{d\vec{r}'\,\phi_{\alpha}^{*}(\vec{r}')\phi_{\alpha}(\vec{r})F(r')}{|\vec{r} - \vec{r}'|} \quad , \tag{4c}$$

where ϕ_{α} is an occupied space orbital.

The validity of the low ℓ-spoiling approximation implies that we should be able to construct eigenfunctions of H^{HF} which for large r are proportional to a single $Y_{\ell m}$. To this end we diagonalize H^{HF} with a different basis set of Gaussian functions for each value of ℓ and $|m|$ under consideration. This basis is chosen by augmenting the basis used to perform the SCF calculation with additional diffuse functions of one particular symmetry most of which are placed at the center of the molecule. Such a choice guarantees that the positive energy eigenfunctions of H^{HF} will be orthogonal to an accurate set of non-spherical occupied orbitals and will also go asymptotically as a particular $Y_{\ell m}$. We emphasize that the SCF equations need be solved only once to define H^{HF} and that this Hamiltonian is then rediagonalized for each symmetry desired.

The choice of Gaussian basis functions makes the evaluation of the projection integral of Eq. (1) particularly simple. In a coordinate system in which the Z axis is chosen to be the internuclear axis, the projection of a spherical harmonic at the midpoint of the molecule onto a Gaussian located on the internuclear axis at a distance A from the origin can be written in the form,

$$\int Y^*_{\ell m}(\theta,\varphi)\, x^i y^j (z - A)^k e^{-\alpha(\vec{r} - \vec{A})^2}\, d\Omega =$$

$$= e^{-\alpha(r^2 + A^2)} \int Y^*_{\ell m}(\theta,\varphi)(r \sin\theta\cos\varphi)^i$$

$$\cdot\ (r \sin\theta \sin\varphi)^j (r\cos\theta - A)^k$$

$$\cdot\ e^{2\alpha r A \cos\theta} \sin\theta\, d\theta\, d\varphi \quad . \qquad (5)$$

This integral was evaluated analytically for the various cases we considered. Phase shifts were then extracted using Eq. (3) as described previously.

4. Results

We computed s and pσ phase shifts for molecular hydrogen as a test of the accuracy of the method. The basis used was a set of 22 s-type Gaussians on each hydrogen, which was used in a previous calculation (Rescigno, McCurdy and McKoy 1975). The results are compared with the R-matrix results of Schneider (1975), which were also computed in the ℓ-spoiling approximation, in figure 1.

The Hartree-Fock occupied orbitals for N_2 were computed using a basis of $[4s\ 3p]$ Gaussians contracted from a $(9s\ 5p)$ set of primitives suggested by Dunning (1970). This basis was augmented by two dπ and dσ polarization functions (Truhlar, Van-Catledge and Dunning 1972). The polarization functions are essential to the proper description of the quadrupolar part of the molecular potential (Truhlar et al.1970).

To calculate the Σ_g virtual orbitals from which s wave phase shifts were computed, this basis was augmented by three additional s-type Gaussians on each nitrogen and seven diffuse s-Gaussians at the midpoint with exponents chosen in a geometric series. The Σ_u basis consisted of these same s-type functions on the nitrogens used for Σ_g, and in addition, five uncontracted z-type Gaussians were placed on each nitrogen, seven diffuse z Gaussians at the midpoint, and two d_{z^2} Gaussians on the nitrogens. For Π_u we used seven primitive x-type Gaussians on each nitrogen with eight more at the midpoint and two $d\pi$ Gaussians on the nitrogens. The Π_g basis consisted of seven x-type Gaussians on each nitrogen, twelve xz-type Gaussians at the midpoint, and two $d\pi$ functions on the nitrogens. From these four diagonalizations of the Hartree-Fock Hamiltonian we can extract the s, $p\sigma$, $p\pi$ and $d\pi$ phase shifts. In figure 2 we show some representative plots of $\delta_{\ell m}$ obtained from equation (3) as a function of r. These demonstrate the occurrence of a region in which the phase shift is constant.

Table 1 lists the s, $p\sigma$, $p\pi$, and $d\pi$ phase shifts. In figures 3 and 4 we compare our results with those of Burke and Sinfailam (1970). We plot both the arctangent of the appropriate element of the reactance matrix from Burke and Sinfailam (1970), as well as their largest eigenphase. Note that in the complete absence of angular momentum coupling these two quantities would be identical. The extent to which they coincide is an indication of the degree of accuracy of the low ℓ-spoiling approximation. There is reasonably good agreement between the

results we find here and those of Burke and Sinfailam (1970). It is not clear whether the discrepancies between the two calculations are due to the approximate nature of the method we employed or to the fact that Burke and Sinfailam (1970) were forced to retain only a small number of terms in their one-center expansion of the potential.

A more recent calculation on e^--N_2 by Burke and Chandra (1972) shows that the Σ_g eigenphase increases as the number of terms in a single-center expansion of the potential increases. However, these calculations were performed by dropping the exchange parts of the potential and replacing them with Lagrange multipliers to enforce orthogonality to the occupied orbitals. Nevertheless, we might expect that the Σ_g phase shifts of Burke and Sinfailam (1970) would show the same behavior as the number of terms in the potential expansion was increased, bringing their results into closer agreement with ours. Unfortunately, Burke and Chandra (1970) do not show the dependence of the Σ_u and Π_u eigenphases on the number of terms in the expansion of the potential.

Some comments are in order concerning the resonance in the Π_g - $d\pi$ phase shift. Burke and Chandra (1972) found it necessary to include a polarization potential to produce a sharp resonance in the Π_g wave. We find a Π_g resonance in the present calculation and expect that the neglect of exchange effects for this symmetry in the calculation of Burke and Chandra (1972) was responsible for its disappearance as a shape resonance. Our calculations show a resonance in the $d\pi$ phase shift at 3.54 ev, compared to Burke and Sinfailam's (1970) value of 2.80 ev. We conclude that the low-energy Π_g resonance is a shape

resonance which can be described by the static-exchange model, but that the position of the resonance is affected by correlation to the extent that the static-exchange resonance is about 1 ev too high (Golden 1966).

5. Summary and Conclusions

We have described a simple method for calculating low-energy elastic electron-molecule cross sections. The method depends on the validity of the low ℓ-spoiling approximation and the ability of a discrete basis set to describe a molecular continuum wavefunction over a sufficiently large region of space. The calculations reported here were limited to the static-exchange approximation, but this restriction can be relaxed. The method should be applicable to elastic electron-scattering from any homonuclear diatomic molecule as well as from small molecules with no permanent dipole moment.

TABLE 1

e^- - N_2 Phase Shifts

S		pσ		pπ		dπ	
k(au)	δ_{00}	k(au)	δ_{10}	k(au)	δ_{11}	k(au)	δ_{21}
0.017	3.101	0.0403	3.141	0.039	3.141	0.047	0.0
0.037	3.05	0.079	3.139	0.072	3.140	0.082	0.0
0.066	2.98	0.135	3.127	0.114	3.136	0.127	0.0
0.109	2.88	0.222	3.09	0.172	3.12	0.187	0.0
0.179	2.72	0.361	2.95	0.253	3.09	0.273	0.01
0.296	2.45	0.577	2.66	0.372	3.01	0.393	0.06
0.491	2.09	0.861	2.19	0.553	2.83	0.518	0.90
0.815	1.60	1.098	1.7	0.830	2.55	0.631	2.35
						0.894	2.52
						1.182	2.33

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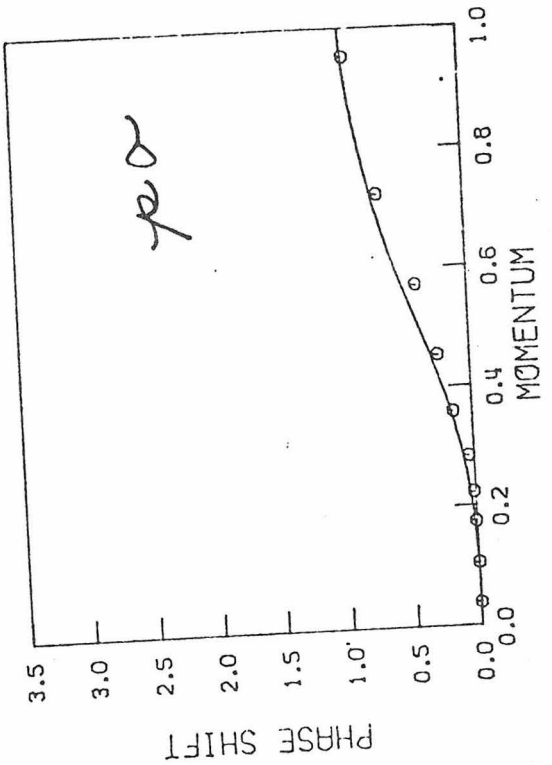
Figure Captions

Figure 1. Comparison of static-exchange phase shifts from equation (3) (circles) for e^--H_2 scattering with the low ℓ-spoiling results of Schneider (1975).

Figure 2. Some representative plots of $\delta_{\ell m}(r)$ from equation (3). The solid, dashed, and chained curves are for orbitals of $s\sigma$, $p\pi$ and $d\pi$ symmetry respectively.

Figure 3. Comparison of the $s\sigma$ and $p\sigma$ phase shifts of this work (circles) for e^--N_2 scattering with the largest eigenphase (solid) and arctangent of the appropriate diagonal element of the reactance matrix (dashed) of Burke and Sinfailam (1970). The curves for $p\sigma$ are indistinguishable on this scale.

Figure 4. Results for $p\pi$ and $d\pi$ phase shifts (circles) and the results of Burke and Sinfailam (1970) (solid) for N_2. On this scale the largest eigenphase and the arctangent of the diagonal reactance matrix element are indistinguishable.


PHASE SHIFT
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.2
0.4
0.6
0.8
1.0
MOMENTUM

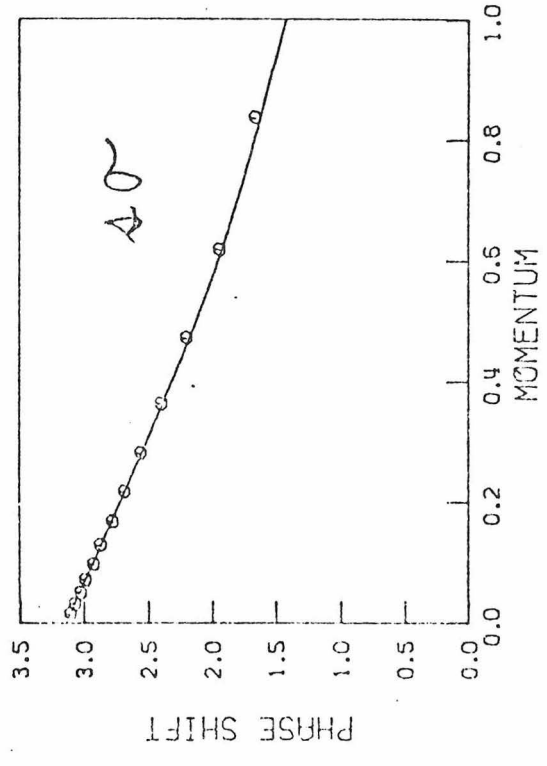

PHASE SHIFT
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.2
0.4
0.6
0.8
1.0
MOMENTUM

Figure 1.

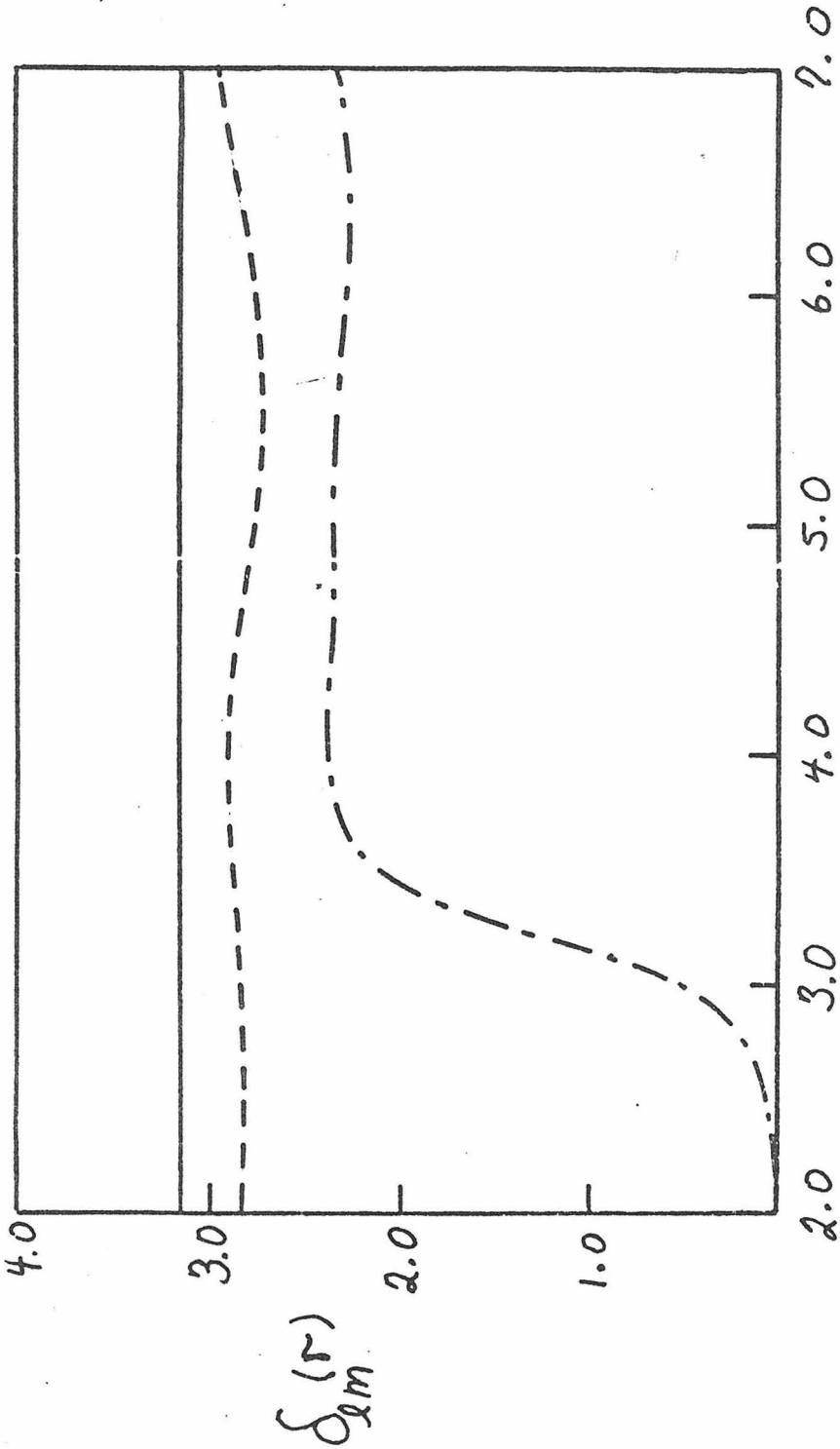
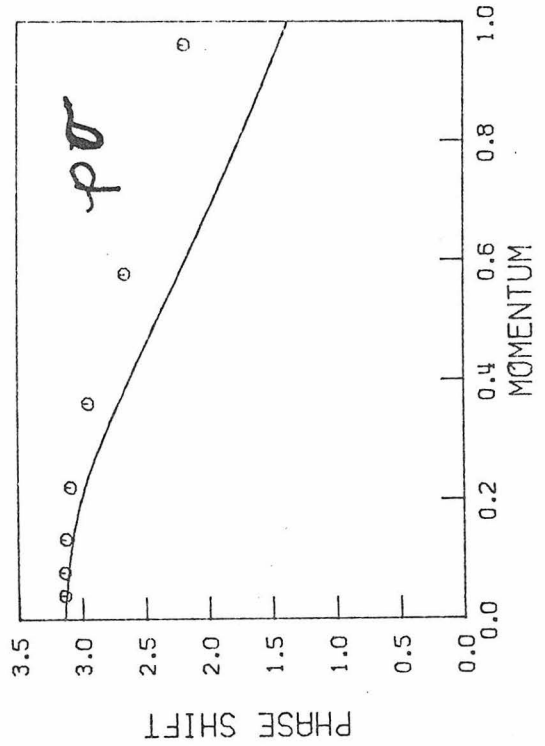


Figure 2.


pσ
PHASE SHIFT
MØMENTUM
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0.0
0.2
0.4
0.6
0.8
1.0

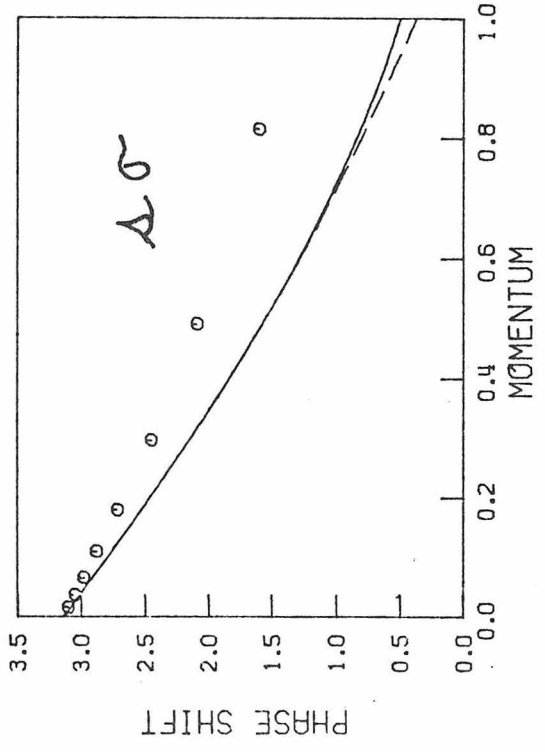
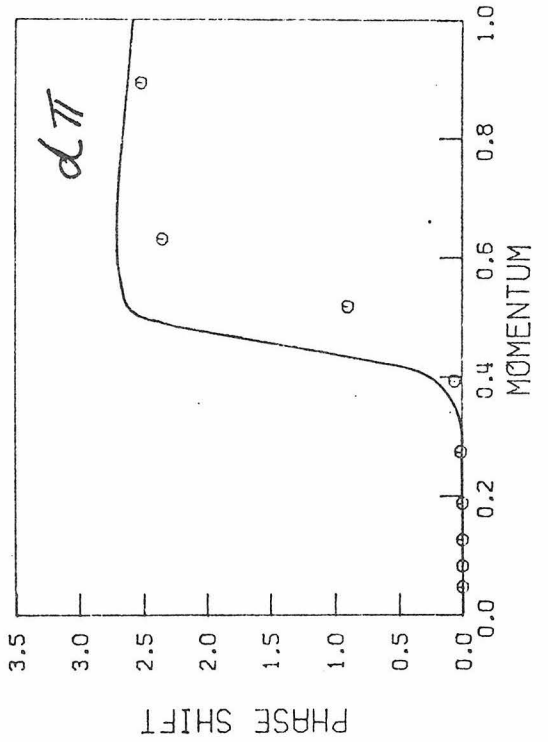

λσ
PHASE SHIFT
MØMENTUM
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0.0
0.2
0.4
0.6
0.8
1.0

Figure 3.


dπ
PHASE SHIFT
MOMENTUM
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0.0
0.2
0.4
0.6
0.8
1.0

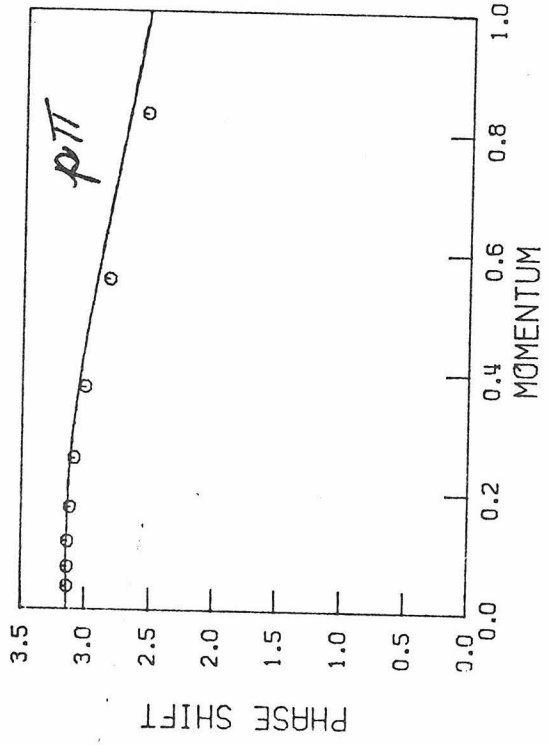

pπ
PHASE SHIFT
MOMENTUM
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0.0
0.2
0.4
0.6
0.8
1.0

Figure 4.

CHAPTER II

A Many-Body Theory Approach to Electron-Atom and Electron-Molecule Scattering

INTRODUCTION

In this chapter we will discuss some applications of many-body theory in both elastic and inelastic electron-atom and electron-molecule scattering. This introduction will first present some background discussion for Section A on the use of the distorted wave approximation in inelastic electron scattering. Some introductory discussion of Section B on elastic scattering is also included. In Section C we will give a direct relationship between the optical model for elastic scattering developed in Section B and the more standard approach in many-body theory in which the proper self-energy serves as an optical potential.

Section A gives a derivation of the first-order many-body theory for inelastic scattering originally developed by Taylor and co-workers,[1] which makes it clear that this theory is a form of the distorted wave approximation. An interesting aspect of the formula for the scattering amplitude obtained in the many-body approach is that both the incoming and outgoing waves are computed in the field of the same potential--the static-exchange potential of the ground state of the target atom or molecule. This result (and a similar formula for electron impact ionization) has been interpreted in terms of a "two-time" model.[2] Briefly, this model asserts that the time of passage of the electron, tp, is much less that the time, t_e, required for the target to respond by undergoing an excitation. With this assumption, one expects the electron to recede to the asymptotic region while the target remains in its ground state. Needless to say, this interpretation is somewhat controversial. It is hard to imagine an experiment that would unambiguously prove or disprove the two-time model. The uncertainty ΔE implied in the energy of the target times the approximate transit time

Δt (for a 40 eV electron incident on helium where, e.g., $E_{2^1S} - E_0 \approx$ 20 eV, and a generous estimate of ΔX is $5\,a_0$) is about 10^{-27} erg-sec--just within the bounds of the uncertainty principle. An experiment that would directly measure the response time of the atom would likely involve uncertainties in the measurement of the order of the response time in question.

Fortunately it is not necessary to subscribe to the two-time model in order to derive the many-body distorted wave formula. The appearance of initial and final waves in the field of the Hartree-Fock potential of the ground state comes about naturally, largely because eigenfunctions of the Hartree-Fock potential are used as the expansion basis. In Section A we give a derivation that begins with a statement of the distorted wave approximation obtained from the well-known two-potential formula. It should be mentioned that there are two forms of the distorted wave approximation that appear commonly in the literature. The first[3] is derived by considering the two-state close-coupling equations (in a standard notation)

$$\begin{aligned} (\nabla^2 + k_0^2 + U_{00})\,\varphi_0 &= U_{on}\varphi_n \\ (\nabla^2 + k_n^2 + U_{nn})\,\varphi_n &= U_{no}\varphi_0 \quad , \end{aligned} \tag{1}$$

ignoring the term $U_{on}\varphi_n$, and solving with asymptotic boundary conditions such that the incoming wave is in channel 0 and channel n has only outgoing waves with amplitude $f_{no}(\theta\varphi)$. This leads to

$$f_{no}(\theta\varphi) = -\frac{1}{4\pi}\,\langle \varphi_n^- | U_{no} | \varphi_0^+ \rangle \quad , \tag{2}$$

where φ_0^+ is solved for in the field of U_{00} with outgoing boundary conditions, and φ_n^- is solved for in the field of U_{nn} with incoming boundary conditions. The initial and final waves thus "see" different distorting potentials.

The alternate form of the distorted wave approximation[4] for electron-atom scattering is derived from the two-potential formula. We first divide the Hamiltonian into two parts, $H = H_I + V_{II}$, where

$$H_I = H_{target} + T_r + V_I \,, \tag{3}$$

T_r is the kinetic energy operator of the incident electron, and we have written the interaction potential in two parts, $V_I + V_{II}$. The two-potential formula for the transition matrix element is then written

$$T(n, k_n \leftarrow 0, k_0) = \langle k_n^I, n - | V_I | k_0, 0 \rangle + \langle k_n^I, n - | V_{II} | k_0, 0 + \rangle \,, \tag{4}$$

where $|k_n^I, n -\rangle$ is an eigenstate of H_I with incoming boundard conditions, $|k_0, 0\rangle$ is a noninteracting state, and $|k_0, 0 +\rangle$ is an eigenstate of the full Hamiltonian. The distorted wave approximation is obtained by replacing $|k_0, 0 +\rangle$ with $|k_0^I, 0 +\rangle$, an eigenfunction of H_I. In addition, we can often choose V_I so that its contribution to Eq.(4) is zero,[4] so we obtain the form of the distorted wave approximation used in Section A,

$$T(n, k_n \leftarrow 0, k_0) \approx \langle k_n^I, n - | V_{II} | k_0^I, 0 + \rangle \,, \tag{5}$$

in which both incoming and outgoing waves are in the field of V_I.

There is no a priori reason to choose Eq.(5) over Eq.(2). The only basis for the choice is whether or not one gives better results than the other in practice. In this context we can cite the work of Madison and Shelton on e^- - He inelastic scattering.[5] Before the application of the first-order many-body theory,[7] Madison and Shelton used both forms of the distorted wave approximation and found that the form with both initial and final waves in the field of the ground state gave better results.[5] Later, Pindzola and Kelly studied e^- - H atom scattering using both approximations

and again found better agreement with experiment with both the ingoing and outgoing electron in the field of the ground state.[6] To date these two computational results, together with the many-body theory results on e^- - He scattering,[7] are the best available evidence for the superiority of Eq. (5) as opposed to the other form of the distorted wave approximation (2)--the "two-time" interpretation, however, awaits further verification.

We now turn our attention to the problem of elastic scattering, to be discussed in Section B of this chapter. In most many-body theory approaches to elastic electron scattering one proceeds by constructing an effective one-particle potential, an "optical potential", which can be used to describe the scattering of an incident electron by a composite target.[8,9] This formulation is in principle exact and reduces the many-particle scattering problem to a one-particle potential scattering problem. However, the optical potential is in general nonlocal and energy dependent. It must contain the effects of antisymmetry and correlation, and above the first inelastic threshold it must be complex.

Previous many-body theories for elastic scattering have made use of the fact that the proper self energy, $\Sigma(E)$, which appears in Dyson's equation for the one-particle Green's function, is an optical potential.[8,9] This was originally proven by Bell and Squires[10] in 1959. The prescription one follows is to make approximations to $\Sigma(E)$ using various techniques of many-body theory, and then to use this approximate self energy in a scattering calculation to obtain the elastic scattering cross section.

But the optical potential is not unique. All that is required is that it be a potential whose solutions asymptotically yield the correct scattering amplitude. In fact, an alternative form of the optical model has existed in

the literature since 1962 and is due to Feshbach.[11] This formalism is general and has no direct connections with many-body theory. It has been used most often in discussions of resonant phenomena (see the references listed in Ref. 4 of Section B). However, very few numerical results for elastic electron scattering using Feshbach theory are available in the literature. To apply Feshbach theory one must construct a projection operator, P, such that when it operates on the exact, many-particle scattering wavefunction it yields asymptotically an antisymmetrized product of the ground state wavefunction of the target, Φ_0, and a scattering function, $F_0(r)$,

$$P\psi \xrightarrow[r \to \infty]{} \mathcal{A} F_0(r)\Phi_0 \ . \tag{6}$$

In other words, P projects out the elastic scattering part of the problem. The difficulty which has hindered the application of Feshbach theory is finding a suitable form of P. Unfortunately P is not an ordinary projection operator; it must antisymmetrize its result as well as project on an antisymmetric function. In Section B we show how an approximate form of P can be constructed using second quantized operators. The anticommutation properties of second quantized operators allow the proper treatment of antisymmetry with a minimum of complication.

Section C will give a direct relationship between the optical model wavefunction of the many-body approach to Feshbach theory and that of the Bell and Squires[10] optical model.

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SECTION A

A Relationship Between the Many-Body Theory of Inelastic Scattering and the Distorted Wave Approximation

1. Introduction

In a series of recent papers, H. Taylor and coworkers have developed a theory for describing elastic (Schneider, Taylor and Yaris 1970) and inelastic (Csanak, Taylor and Yaris 1971, Csanak, Taylor and Tripathy 1973) electron scattering based upon the Martin-Schwinger Green's-function technique (Martin and Schwinger 1959). The elastic theory has already been applied to electron-helium scattering with great success (Yarlagadda, Csanak, Taylor, Schneider and Yaris 1973) and their preliminary results on several inelastic transitions in helium give differential cross-sections that are in close agreement with the best experimental results available (Thomas, Yarlagadda, Csanak and Taylor 1973).

It is the inelastic scattering formulation that is the subject of our concern in this paper. The inelastic formula, which has been shown to give excellent results for several transitions in helium, is the first-order result obtained from Taylor's many-body field theory. In this order, correlation between the incident electron and the target atom is ignored. In effect, the electron is inelastically scattered by a static transition potential. The somewhat surprising occurrence is the appearance, in Taylor's formula, of a continuum orbital for the scattered electron in the exit channel that is calculated in the field of the ground state.

A similar prescription for calculating inelastic e^--He cross-sections has been recently used by Madison and Shelton (1973) in the

context of the distorted-wave Born approximation. In this work, however, there seems to have been some ambiguity over the proper choice of continuum orbital for the final state. The best results were obtained with the "unphysical" choice of computing both initial and final state orbitals in the field of the ground state. This result agrees with the first-order theory of Taylor et al. It is still difficult to assess the correctness of this choice from Madison and Shelton's work, however, because they were forced to ignore certain exchange-type orthogonality terms that appeared in their formula and because all the continuum orbitals they used were calculated over spherically averaged potentials.

Our motivation for this paper is threefold. Firstly, we wish to show that the first-order result of Csanak, Taylor and Yaris (1971) may be derived quite simply in second quantization using the Random Phase Approximation (RPA). It is not necessary to resort to approximate solutions of the Bethe-Salpeter equation nor to use the full machinery of the Martin-Schwinger formalism to obtain this theory in lowest order.

We would like to show, secondly, that identical results may be obtained by a standard application of the distorted-wave approximation coupled with the RPA. The use of the RPA in this context has several advantages over the approach used by Madison and Shelton. On the one hand, it puts correlation effects between target electrons directly into the calculation. Furthermore, the questionable omission of certain exchange-like terms is no longer a problem

since we will show that, in the RPA, all such terms cancel identically.

Finally, we will comment briefly on the possibility of extending the first-order theory presented here to include some dynamical effects of target polarization, while still retaining a distorted-wave picture of the scattering process and an RPA description of the target.

2. Inelastic Electron Scattering

2.1. Many-Body Treatment

Before deriving an expression for the matrix elements of the inelastic transition operator, it is necessary to establish some notation. The closed shell ground state and excited state wavefunctions of the N-electron target (with energies E_0 and E_f) will be denoted $\psi_0(r_1, , r_N)$ and $\psi_f(r_1, , r_N)$. In second quantization these become the state vectors $|0\rangle$ and $|f\rangle$. The momentum of the scattered electron in the initial and final asymptotic state will be denoted by k_i and k_f respectively, so that the total energy is given by

$$E = E_0 + \frac{k_i^2}{2} = E_f + \frac{k_f^2}{2} \tag{1}$$

We will employ the annihilation and creation operators a_i and a_i^+ referring to one-particle basis states which are Hartree-Fock bound and continuum spin orbitals of the ground state of the target. Hole states will be denoted by Greek subscripts and particle states by the letters r, s, m and n. The subscripts i, j, k and l will be reserved for unrestricted sums. When we consider continuum particle states we will use the notation $a(k^{\pm})$, the superscript on the momentum k indicating outgoing or incoming wave boundary conditions. Finally second-quantized operators will always be denoted with carets ($\hat{}$).

The Hamiltonian in second-quantized form is

$$\hat{H} = E_{HF} + :\hat{H}_o: + :\hat{V}: \tag{2}$$

where E_{HF} is the Hartree-Fock ground state energy of the target, and the operators (normal ordered with respect to the Hartree-Fock particle-hole vacuum) are

$$:\hat{H}_o: = \sum_i \mathcal{E}_i :a^+_i a_i: \tag{3}$$

$$:\hat{V}: = \tfrac{1}{4} \sum_{ijk\ell} (ij||k\ell)_a :a^+_i a^+_j a_\ell a_k:$$

The antisymmetrized matrix elements are defined by

$$(ij||k\ell)_a = (ij||k\ell) - (ij||\ell k) \tag{4}$$

where

$$(ij||k\ell) = \int \phi^*_i(r_1)\, \varphi^*_j(r_2)\, \frac{1}{|r_1 - r_2|}\, \phi_k(r_1)\, \varphi_\ell(r_2)\, d^3r_1\, d^3r_2 .$$

The transition matrix element for inelastic electron scattering with the target initially in its ground state $|0\rangle$ and with final state $|f\rangle$ can be expressed as[1]

$$T_{fi} = \langle f | [a(k_f^-),\ \hat{V}_{res}] | 0, k_i^+ \rangle , \tag{5}$$

where $|0,\ k_i^+\rangle$ is the exact scattering wavefunction of the N + 1

---

[1] The formulation of scattering theory in the language of second quantization is standard in nuclear physics theory. For an excellent review, see Villars (1966).

particle system. The residual interaction $\hat{V}_{res}$ is $\hat{V}_{total}$ - $\hat{V}_{Hartree\text{-}Fock}$ so $\hat{V}_{res}$ can be replaced by $:\hat{V}:$ to within an additive constant.

The potential $:\hat{V}:$ may be partitioned

$$:\hat{V}: = \hat{V}_1 + \hat{V}_2 + \hat{V}_3 \tag{6}$$

where

$$\hat{V}_1 = \tfrac{1}{4} \sum_{m\alpha n\beta} (m\,n \,||\, \alpha\,\beta)_a \, a^+_m \, a_\alpha \, a^+_n \, a_\beta + \text{h.c.}$$

$$+ \sum_{m\alpha\, n\beta} (m\,\beta \,||\, \alpha\, n)_a \, a^+_m \, a_\alpha \, a^+_\beta \, a_n \tag{7a}$$

$$\hat{V}_2 = \tfrac{1}{2} \sum_{m\alpha nr} (m\,\alpha \,||\, n\,r)_a \, a^+_m \, a^+_\alpha \, a_r \, a_n + \text{h.c.}$$

$$+ \tfrac{1}{2} \sum_{m\alpha\gamma\beta} (m\,\alpha \,||\, \gamma\,\beta)_a \, a_\gamma \, a_\beta \, a^+_m \, a^+_\alpha + \text{h.c.} \tag{7b}$$

$$\hat{V}_3 = \tfrac{1}{4} \sum_{mnrs} (m\,n \,||\, r\,s)_a \, a^+_m \, a^+_n \, a_s \, a_r$$

$$+ \tfrac{1}{4} \sum_{\alpha\beta\gamma\delta} (\alpha\,\beta \,||\, \gamma\,\delta)_a \, a_\delta \, a_\gamma \, a^+_\alpha \, a^+_\beta \tag{7c}$$

Thus $\hat{V}_1$ is the interaction between particle-hole pairs; $\hat{V}_2$ describes the scattering of a particle or hole by a particle-hole pair; and $\hat{V}_3$ is the particle-particle and hole-hole interaction.

The final target state may be written with the aid of the excitation operator defined by (Rowe 1968)

$$|f\rangle = \hat{O}^+_f |0\rangle \tag{8}$$

$$\hat{O}_f |0\rangle = 0$$

We may construct an approximation to Eq. (5) by first choosing $\hat{O}^+_f$ to be the RPA excitation operator

$$\hat{O}^+_f \approx \sum_{m\alpha} Y^{(f)}_{m\alpha} a^+_m a_\alpha - Z^{(f)}_{m\alpha} a^+_\alpha a_m$$

where $Y^{(f)}_{m\alpha}$ and $Z^{(f)}_{m\alpha}$ are amplitudes satisfying the usual RPA equations (Rowe 1968).

If we next make the lowest order approximation to $|0, k_i^+\rangle$ and, consistent with the distorted wave picture, set

$$|0, k_i^+\rangle \approx a^+(k_i^+) |0\rangle \ , \tag{9}$$

then Eq. (5) becomes

$$T_{fi} \approx \langle 0 | [O_f, [a(k_f^-), :V:] a^+(k_i^+)] | 0\rangle \tag{10}$$

The commutators in Eq. (10) lower the particle rank of the operator expression, and hence we use the same approximation to

evaluate Eq. (10) as in deriving the RPA equations of which the amplitudes specifying O_f^+ are solutions. Thus we evaluate the matrix element in Eq. (10) with respect to the Hartree-Fock particle-hole vacuum. It is then easy to show that the contributions to Eq. (10) from $\hat{V}_1$ and $\hat{V}_3$ vanish identically, as does the contribution of the part of $\hat{V}_2$ describing the interaction of a hole with a particle-hole pair. Repeated application of Wick's theorem results in the expression

$$T_{fi} \approx \sum_{m\alpha} \{Y^{*(f)}_{m\alpha} (m\, k_f^- \,||\, \alpha\, k_i^+)_a + Z^{*(f)}_{m\alpha} (\alpha\, k_f^- \,||\, m\, k_i^+)_a\} \qquad (11)$$

This is identical to the first order expression for inelastic scattering derived by Csanak, Taylor and Yaris (1971), and can also be written in the form of a matrix element of a "transition potential" between two Hartree-Fock continuum orbitals.

2.2. Distorted-Wave Approximation

We now show that the result obtained in the previous section can also be found by a straightforward use of the distorted-wave approximation coupled with the RPA.

To the interaction potential V between an incident electron and an N-electron atom or molecule, we add and subtract the operators J - K, the Hartree-Fock coulomb and exchange operators for the target in its ground state. We then partition V into two terms,

$V = V_I + V_{II}$, where

$$V_I \equiv \sum_{\text{nuclei}} - \frac{Z_n}{r_n} + J - K$$

$$V_{II} \equiv \sum_{i=1}^{N} \frac{1}{|r - r_i|} - J + K \tag{12}$$

Using the well-known two-potential formula (Messiah 1968), the transition matrix element for inelastic electron scattering can be written as

$$T_{fi} = (\psi_f(r_1, , r_N)\ e^{ik_f \cdot r} \mid V_I \mid \psi^+_{Ik_i}) + (\psi^-_{Ik_f} \mid V_{II} \mid \psi^+). \tag{13}$$

ψ^+ is the exact, antisymmetric wavefunction of the full interacting system with outgoing wave boundary conditions. $\psi^+_{Ik_i}$ and $\psi^-_{Ik_f}$ are scattering solutions of the operator $-\frac{1}{2}\nabla^2_r + H_{target} + V_I$. Thus we can write

$$\psi^+_{Ik_i} = \psi_o(r_1, , r_N)\, \phi^+_{k_i}(r)$$

$$\psi^-_{Ik_f} = \psi_f(r_1, , r_N)\, \phi^-_{k_f}(r)\,. \tag{14}$$

Note that these solutions are not antisymmetric under interchange of r with $\{r_i\}$ since they come from a non-symmetric Hamiltonian. Thus, the first term in Eq. (13) is rigorously zero due to the orthogonality of ψ_o and ψ_f. Eq. (13) is exact; we now make the

distorted-wave approximation and set ψ^+ equal to an antisymmetrized product of $\psi_0(r_1, , r_N)$ and $\phi^+_{k_i}(r)$, giving

$$T_{fi} \sim \left(\psi_f(r_1, , r_N)\, \varphi^-_{k_f}(r) \,|\, V_{II} \,|\, \mathcal{A}\, (\psi_0(r_1, , r_N)\, \varphi^+_{k_i}(r))\right). \qquad (15)$$

Without too much trouble, it can be shown that Eq. (15), which now contains direct and exchange contributions, can be conveniently grouped into two terms:

$$T_{fi} = N\left(\psi_f(r_1, , r_N)\, \varphi^-_{k_f}(r) \left| \frac{1}{|r-r_1|} \right| \Psi_0(r_1, , r_N)\, \varphi^-_{k_i}(r) - \Psi_0(r, , r_N)\, \phi^+_{k_i}(r_1)\right)$$

$$- N\left(\psi_f(r_1, , r_N)\, \varphi^-_{k_f}(r) \left| \sum_{i\neq 1} \frac{1}{|r-r_i|} - J + K \right| \varphi^+_{k_i}(r_1)\, \Psi_0(r, , r_N)\right) \qquad (16)$$

We now show that, in the RPA, the first term above gives the same result obtained previously and that the second term vanishes. In order to demonstrate this, the matrix elements in Eq. (16) must be rewritten in second-quantized form and hence permutation operators will be introduced so that the coordinates of the wave-functions appear in identical order on both sides of the matrix elements.

For example, the first term in Eq. (16) can be expressed as

$$N\left(\psi_f(r_1, , r_N)\, \varphi^-_{k_f}(r) \left| \frac{1}{|r-r_1|} (1 - P_{r, r_1}) \right| \Psi_0(r_1, , r_N)\, \varphi^+_{k_i}(r)\right)$$

$$= \sum_{ij} \langle f \,|\, a^+_i\, a_j \,|\, 0 \rangle \; u_{ij}$$

where

$$u_{ij} = (i\, k_f^- \,||\, j\, k_i^+)_a \tag{17}$$

and $P_{r,\, r_1}$ interchanges coordinates r and r_1. Employing the same strategy used in the previous section, we write this as

$$\langle 0 \,|\, [\hat{O}_f,\ \hat{U}] \,|\, 0 \rangle$$

which, in the RPA, becomes

$$\sum_{m,\alpha} u_{m\alpha}\ Y^{*(f)}_{m\alpha} + u_{\alpha m}\ Z^{*(f)}_{m\alpha}$$

coinciding with the expression derived earlier.

Finally, we consider the second part of Eq. (16). The term involving - J + K can again be written in second quantization as the matrix element of a one-electron operator,

$$-N\left(\psi_f(r_1, , r_N)\, \phi^-_{k_f}(r) \,|\, (-J+K)\, P_{r,\, r_1} \,|\, \varphi^+_{k_i}(r)\, \Psi_0(r_1, , r_N)\right) =$$

$$\sum_{ij} \langle f \,|\, a^+_i\, a_j \,|\, 0 \rangle\ w_{ij} \tag{18}$$

where

$$w_{ij} = \delta_{i,\, k_i^+} \sum_u (k_f^-\, u \,||\, j\, u)_a$$

In the RPA, this becomes

$$\sum_{\alpha,\, u} Y^{*(f)}_{k_i^+,\, \alpha}\ (k_f^-\, u \,||\, \alpha\, u)_a$$

In similar fashion, the term involving $\sum_{i\neq 1} \frac{1}{|r-r_i|}$ can be written as the matrix element of a two-electron operator:

$$- \sum_{ijk\ell} \langle f | a_i^+ a_j^+ a_k a_\ell | 0 \rangle V_{ij\ell k}$$

with

$$V_{ij\ell k} = \delta_{i, k_i^+} (k_f^- j \,||\, \ell k)$$

which, in the RPA, becomes

$$- \sum_{ijk\ell m\alpha} \langle 0 | [Y^*_{m\alpha} a^+_\alpha a_m - Z^{*(f)}_{m\alpha} a^+_m a_{\alpha'}, a_i^+ a_j^+ a_k a_\ell] | 0 \rangle V_{ij\ell k}$$

Straightforward evaluation of this expression gives

$$- \sum_{\alpha u} Y^{*(f)}_{k_i^+, \alpha} (k_f^- u \,||\, \alpha u) ,$$

which cancels the term in Eq. (18) identically, giving the same expression for T_{fi} derived in the previous section.

3. Discussion

We have shown that a many-body description of inelastic electron-scattering produces, in lowest order, a distorted-wave formula in which the scattered electron appears, both initially and finally, in continuum Hartree-Fock orbitals generated in the field of the ground state. This picture, when coupled with an RPA description of the target, gives a simple and unambiguous prescription for calculating inelastic transition matrix elements. Such a picture would be expected to incorporate the most important effects in non-resonant scattering.

We should like to point out that it would be possible to incorporate some polarization effects into the formalism and still retain the distorted-wave picture. For example, one could go through the analysis of the previous section with an elastic optical potential as the distorting potential in place of the Hartree-Fock operators. The optical potential is identical to the proper self-energy of many body theory (Bell and Squires 1959) and could be approximated in a variety of ways (Fetter and Watson, 1965; Schneider, Taylor and Yaris 1970; Rosenberg and Tolchin 1973). The continuum orbitals of Eq. (14) would become optical model wavefunctions which satisfy a one-particle Lippmann-Schwinger equation with the proper self-energy as the potential. Even though the leading term in the self-energy is the Hartree-Fock potential, the counterpart of Eq. (11) would be different as a result of the fact that the continuum orbitals are no longer

part of the orthonormal set of Hartree-Fock orbitals used to expand the excitation operator O_f^+. In addition, new contributions to T_{fi} would be made by the energy dependent part of the optical potential. An attractive feature of this scheme is that it avoids the difficulties of computing continuum orbitals in the field of the excited state. For example, we could make use of the fact that the optical potential for a closed shell, homonuclear diatomic molecule has simple cylindrical symmetry, whereas the potential of an arbitrary excited state would not.

Although the effects of polarization would be included to some extent in the approach outlined above, final state interaction effects would not be completely accounted for. However it is well known that an exact formulation of inelastic scattering can be made in which the transition matrix retains the <u>form</u> of the distorted-wave expression, i.e., a matrix element between elastic optical model continuum orbitals of an energy dependent transition potential (Gross 1969; Emrich 1971; Csanak, Taylor and Yaris 1971). In the exact theory the transition potential may no longer be constructed as simply as in the distorted-wave picture, but instead requires the solution of the Bethe-Salpeter equation of many-body theory.

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SECTION B

A Many-Body Treatment of Feshbach Theory Applied to Electron-Atom and Electron-Molecule Collisions

I. INTRODUCTION

The optical model,[1] which provides a formal method for reducing a many channel scattering problem to an equivalent one-body problem, has proven to be an effective device in the study of low energy electron-atom scattering. There are several approaches which have been used to formulate the optical model potential.

Because of its conceptual elegance and complete generality, Feshbach's theory of nuclear reactions[2] has been applied extensively to the study of atomic problems. Quite frequently, however, Feshbach's projection operator formalism serves more as an interpretive tool than a computational one. Indeed, almost all of the numerical applications of Feshbach theory have been restricted to two-electron systems, where the required projection operators can be constructed exactly.[3] The formulation lends itself most directly to the study of compound resonance states,[4] and it is certainly in this context that most applications have been made, although there have been a number of successful attempts to construct a Feshbach optical potential and use it to obtain non-resonant cross sections as well.[5]

Another approach to the optical model has been used which does not require the construction of projection operators and which can be systematically applied to larger systems. This approach is based on the fact that the proper self-energy of the one-particle Green's function of many-body theory can also serve as an elastic optical potential.[6] The self-energy can be approximated using the

diagrammatic techniques of many-body perturbation theory.[7] Alternatively, Schneider, Taylor and Yaris[8] have developed a non-perturbative approximation scheme for calculating the self-energy based on the Martin-Schwinger Green's function theory.[9] This approach has met with great quantitative success in describing low energy e^--helium scattering.[10]

In this paper, we show how the equations of motion technique[11] can be used to construct an approximate optical potential which describes the elastic scattering of an electron by a closed shell atom or molecule. The problem is formulated in the language of second quantization, which is most convenient when discussing systems of identical fermions. Rather than working with the proper self energy, however, we develop our approximation scheme in the Feshbach projection operator formalism. We will also be able to show how an approximate optical potential, quite similar to the one derived by Schneider, Taylor and Yaris[8] (hereafter referred to as STY) follows naturally from the equations-of-motion approach to Feshbach theory.

In the section that follows we derive the optical model potential at two levels of approximation, first in the Tamm-Dancoff approximation (TDA),* which ignores correlation in the target ground state, and then in the random phase approximation[11] (RPA), which implicitly includes some effects of target correlations. In Section III we compare

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* The TDA is equivalent to configuration interaction including only single excitations relative to the Hartree-Fock ground state.

the results of STY with those obtained here, and Section IV contains a brief summary and a conclusion.

II. THEORY

A. TDA description of target

Feshbach theory calls for the construction of an operator P which projects out the parts of the exact wavefunction that describe elastic scattering; that is, if ψ denotes the full wavefunction for the electron-atom (molecule) system, then P must satisfy the requirement that

$$P\psi \rightarrow \mathcal{A}\, F_0(r)\, \Phi_0(\{r_i\}) \tag{1}$$

where $\Phi_0(\{r_i\})$ is the ground state wavefunction of the target and $F_0(r)$, the optical model wavefunction, gives the correct elastic scattering. In addition to the projection operator P, we also require its orthogonal complement Q. An effective Hamiltonian can then be constructed which describes elastic scattering:[2]

$$(H_{eff} - E)\, P\psi = 0 \tag{2}$$

where

$$H_{eff} = PHP + PHQ \frac{1}{Q(E - H + i\eta)Q} QHP \tag{3}$$

In this section we will discuss a model obtained by making a number of simplifying assumptions. We first assume that the closed-shell target ground state is well represented by the Hartree-Fock ground state wave function and that the excited states of the

target may be described by the TDA. Introducing the creation and annihilation operators $a_p^\dagger$, a_p referring to the particle states φ_p of the Hartree-Fock Hamiltonian, we may formulate the model as follows.

The operators P and Q are chosen as

$$P = \sum_p a_p^\dagger \, |HF><HF| \, a_p \tag{4}$$

$$Q = \sum_{\substack{pp' \\ \lambda\lambda'}} a_p^\dagger \, |\lambda> \, S^{-1}_{p\lambda,\, p'\lambda'} \, <\lambda'| \, a_{p'} \tag{5}$$

where $|HF>$ is the HF ground state and $|\lambda>$ is an excited TDA target state which is generated by the TDA excitation operator $O_\lambda^\dagger$,

$$|\lambda> = O_\lambda^\dagger \, |HF> \tag{6}$$

$$O_\lambda^\dagger = \sum_{m\alpha} X_{m\alpha}(\lambda) \; a_m^\dagger \, a_\alpha \quad . \tag{7}$$

m and α denote particle and hole states respectively and the $X_{m\alpha}(\lambda)$'s are TDA amplitudes which satisfy the orthogonality condition

$$\sum_{m\alpha} X^*_{m\alpha}(\lambda) \, X_{m\alpha}(\lambda) = \delta_{\lambda\lambda'} \tag{8}$$

In Eq. (5) $S^{-1}_{p\lambda,p'\lambda'}$ is an element of the inverse of the overlap matrix $S_{p\lambda,\, p'\lambda'}$,

$$S_{p\lambda,\, p'\lambda'} = \langle HF \,|\, O_\lambda \, a_p \, a_{p'}^\dagger \, O_{\lambda'}^\dagger \,|\, HF \rangle$$

$$= \delta_{pp'} \, \delta_{\lambda\lambda'} - \sum_{\alpha} X_{p'\alpha}^* \, (\lambda) \, X_{p\alpha} (\lambda') \tag{9}$$

With these restrictions, it is easy to verify that P and Q are indeed projection operators and that they satisfy the necessary conditions $P \cdot Q = Q \cdot P = 0$ and $P + Q = 1$ within the space of vectors spanned by the set $a_p^\dagger \,|\, HF\rangle$, $a_p^\dagger \,|\lambda\rangle$. This implies that $P\psi$ has the form

$$P\psi = \sum_{p} C_p \, a_p^\dagger \,|\, HF \rangle \tag{10}$$

which is consistent with Eq. (1) and our assumptions about the target.

It may help to conceptualize the above approximations if we draw an analogy between the present scheme and a conventional close coupling approximation, in which TDA target states are used for the expansion and the various channel wavefunctions are all expanded in terms of Hartree-Fock particle orbitals.

We now discuss the construction of the operators in Eq. (3) with the above choice of projectors P and Q. The Hamiltonian may be written in second quantization as[12]

$$H = \sum_{i} \mathcal{E}_i : a_i^\dagger a_i : + \tfrac{1}{2} \sum_{ijk\ell} V_{ijk\ell} : a_i^\dagger \, a_j^\dagger \, a_\ell \, a_k : \tag{11}$$

where sums on i, j, k, and ℓ go over hole and particle states (spin orbitals), $V_{ijk\ell}$ is given by

$$V_{ijk\ell} = \int \varphi_i^*(r_1)\, \varphi_j^*(r_2)\, \frac{1}{|r_1 - r_2|}\, \varphi_k(r_1)\, \varphi_\ell(r_2)\, d^3r_1\, d^3r_2\,, \qquad (12)$$

$\mathcal{E}_i$ is a Hartree-Fock orbital energy and the operators are normal ordered with respect to the HF ground state. The Hartree-Fock ground state energy has been chosen as the zero of energy and has thus been subtracted from the Hamiltonian.

The operators PHP and PHQ may be formed easily from the above definitions. Repeated application of Wick's theorem to the matrix elements involved yields for H_{pp}

$$H_{pp} = \sum_p a_p^\dagger \,|\, HF > \mathcal{E}_p < HF \,|\, a_p \qquad (13)$$

If we define antisymmetrized matrix elements $\tilde{V}_{ijk\ell}$ by

$$\tilde{V}_{ijk\ell} = V_{ijk\ell} - V_{ij\ell k} \qquad (14)$$

the result for PHQ is

$$PHQ = \sum_{\substack{pqp' \\ \lambda\lambda' \\ m\gamma}} a_p^\dagger \,|\, HF > X_{m\alpha}(\lambda)\, \tilde{V}_{\alpha pmq}\, S^{-1}_{\lambda q, \lambda' p'} < HF \,|\, O_{\lambda'}\, a_{p'} \qquad (15)$$

In Eq. (15) sums on p, p′, q and m are over particle states and the sum on γ is over hole states.

The form of Q (E - H) Q is more complicated and is given in the appendix. To complete the present approximation consistently, one should diagonalize QHQ in the (non-orthogonal) basis $\{a_p^\dagger \,|\, \lambda >\}$

and then construct H_{eff} via Eq. (3). However we may develop a diagonal approximation as follows. The matrix element involved in $Q\,(E - H)\,Q$ is $\langle HF \mid O_\lambda\, a_p\, (E - H)\, a_{p'}^\dagger\, O_{\lambda'}^\dagger \mid HF \rangle$. Following a similar argument by Dietrich and Hara,[12] we assume that the states formed by adding a particle to the TDA description of the excited target are eigenfunctions of the full Hamiltonian,

$$H\, a_p^\dagger\, O_\lambda^\dagger \mid HF \rangle = (\mathcal{E}_p + \omega_\lambda)\, a^\dagger\, O_\lambda^\dagger \mid HF \rangle$$

where ω_λ is the TDA excitation energy (recall that the zero of energy has been defined as E_{HF}). With this approximation the matrix element above becomes

$$\langle HF \mid O_\lambda\, a_p\, (E - H)\, a_{p'}^\dagger\, O_{\lambda'}^\dagger \mid HF \rangle = (E - \omega_\lambda - \mathcal{E}_p)\, S_{\lambda p,\, \lambda' p'} \tag{16}$$

Further assuming $S_{\lambda p,\, \lambda' p'} = \delta_{\lambda\lambda'}\, \delta_{pp'}$ we obtain an approximate form of the optical potential

$$H_{eff} = \sum_p a_p^\dagger \mid HF \rangle\, \mathcal{E}_p\, \langle HF \mid a_p$$

$$+ \sum_{\substack{pp' \\ q\lambda \\ mn \\ \gamma\sigma}} \frac{a_p^\dagger \mid HF \rangle\, X_{m\gamma}(\lambda)\, X_{n\sigma}^*(\lambda)\; \tilde{V}_{\gamma pmq}\, \tilde{V}_{nq\sigma p'}\, \langle HF \mid a_{p'}}{E - \omega_\lambda - \mathcal{E}_p + i\eta} \tag{17}$$

This expression for H_{eff} has the analytic structure one would expect from the exact Feshbach optical potential, namely branch cuts formed by the set of continuous energies $\mathcal{E}_q$, one such cut associated

with each inelastic threshold labelled by the ω_λ's. However, H_{eff} does not possess the isolated poles associated with the resonance states of the compound system which were lost when neglecting the off-diagonal pieces of QHQ.

B. RPA description of target

One can go beyond the TDA description used in the previous section and implicitly include some of the effects of correlation in the target. In this section, we outline a method for approximating H_{eff} in the Random Phase Approximation (RPA).[11] If $|0>$ denotes the ground state of the target, then excited states $|\lambda>$ are generated by the RPA excitation operator $O_\lambda^\dagger$,

$$|\lambda> = O_\lambda^\dagger |0> \tag{18}$$

where

$$O_\lambda^\dagger = \sum_{m\alpha} Y_{m\alpha}(\lambda)\, a_m^\dagger a_\alpha - Z_{m\alpha}(\lambda)\, a_\alpha^\dagger a_m \tag{19}$$

and the sums on m and α run over particle-hole pairs.

Consider the projection operators

$$P = \sum_{pp'} a_p^\dagger |0> M^{-1}_{pp'} <0| a_{p'} \tag{20a}$$

$$Q = \sum_{\substack{pp' \\ \lambda\lambda'}} a_p^\dagger O_\lambda^\dagger |0> S^{-1}_{\lambda p, \lambda' p'} <0| O_{\lambda'} a_{p'} \tag{20b}$$

where

$$M_{pp'} = \langle 0 | a_p \, a_{p'}^{\dagger} | 0 \rangle \tag{21a}$$

$$S_{\lambda p, \lambda' p'} = \langle 0 | O_{\lambda} \, a_p \, a_{p'}^{\dagger} \, O_{\lambda'}^{\dagger} | 0 \rangle \tag{21b}$$

To verify that $P \cdot Q$ is still zero, we must consider a matrix element of the form

$$\langle 0 | a_p \, a_{p'}^{\dagger} \, O_{\lambda}^{\dagger} | 0 \rangle$$

Following Shibuya and McKoy,[11] we retain terms in $| 0 \rangle$ through first order in the correlation coefficients $C_{mn}^{\alpha\beta}$

$$| 0 \rangle \approx N_0 \left(1 + \sum_{\substack{m\alpha \\ n\beta}}^{\cdots} C_{mn}^{\alpha\beta} \, a_m^{\dagger} \, a_n^{\dagger} \, a_{\alpha} \, a_{\beta}\right) | HF \rangle \tag{22}$$

With this choice for $| 0 \rangle$, it follows that the matrix element $\langle 0 | a_p \, a_{p'}^{\dagger} \, O_{\lambda}^{\dagger} | 0 \rangle$ is zero and that the choices for P and Q are valid.

In discussing the RPA, we are faced with a problem that was not present when the TDA was used. The ground state $| 0 \rangle$ is assumed to be correlated, yet the RPA equations that are solved for the excitation operators $O_{\lambda}^{\dagger}$ do not specify the correlation coefficients. If the correlation coefficients in Eq. (22) are known (e. g. from Raleigh-Schrödinger perturbation theory), the effective Hamiltonian can be constructed in a straightforward manner from the definitions of P and Q -- although the matrix elements involved

will be quite complicated. In this section, however, we will take another approach more consistent with the derivation of the RPA. We will replace matrix elements of the form $< 0 \mid A \mid 0 >$ by equivalent commutator expressions which lower the particle rank of the operator A, and then approximate $\mid 0 >$ by the Hartree-Fock ground state.

Consider PHQ which requires matrix elements of the form

$$< 0 \mid a_p \, H \, a^\dagger_{p'} \, O^\dagger_\lambda \mid 0 >$$

If $O^\dagger_\lambda$ were an exact solution of the equations of motion for the excitation operator we would have the identity

$$O_\lambda \mid 0 > \; = \; 0 \tag{23}$$

We apply this relation followed by the approximation $\mid 0 > \approx \mid HF >$ to obtain

$$\begin{aligned} < 0 \mid a_p \, H \, a^\dagger_{p'} \, O^\dagger_\lambda \mid 0 > \; &= \; < 0 \mid [a_p \, H \, a^\dagger_{p'}, O^\dagger_\lambda] \mid 0 > \\ &\approx \; < HF \mid [a_p \, H \, a^\dagger_{p'}, O^\dagger_\lambda] \mid HF > \end{aligned} \tag{24}$$

With this approximation PHQ may be easily evaluated

$$\begin{aligned} PHQ \; = \; \sum_{\substack{pp'qq' \\ \lambda\lambda' m\alpha}} \; & a^\dagger_p \mid 0 > M^{-1}_{pq} \{ Y_{m\alpha}(\lambda) \, \tilde{V}_{q\alpha p'm} \\ & + \; Z_{m\alpha}(\lambda) \, \tilde{V}_{qmp'\alpha} \} \, S^{-1}_{p'\lambda, q'\lambda'} < 0 \mid O_{\lambda'} \, a_{q'} \end{aligned} \tag{25}$$

To complete the construction of the effective Hamiltonian in this approximation we must evaluate the matrix elements of QHQ and diagonalize it. The matrix elements of QHQ are given in the appendix. In the spirit of the previous section, we may again construct a diagonal approximation by following Dietrich and Hara[12] in assuming that states formed by adding an electron in an HF particle state to RPA excited states of the target are eigenfunctions of the full Hamiltonian,

$$H\, a_p^\dagger O_\lambda^\dagger \mid 0> = (\omega_\lambda + \mathcal{E}_p)\, a_p^\dagger O_\lambda^\dagger \mid 0> \tag{26}$$

where ω_λ is the RPA excitation energy. We also assume $S_{\lambda p,\, \lambda' p'}$ is the unit matrix. To write an approximate effective Hamiltonian which can be constructed from the results of an RPA calculation on the target without knowledge of the correlation coefficients, we must replace $a_p^\dagger \mid 0>$ in Eqs. (20a) and (25) by $a_p^\dagger \mid HF>$ which makes $M_{pp'}$ the unit matrix and PHP the same operator used in the TDA derivation. With these assumptions the effective Hamiltonian is

$$H_{eff} = \sum_p a_p^\dagger \mid HF>\, \mathcal{E}_p\, <HF \mid a_p$$

$$+ \sum_{\substack{pp'q\lambda \\ m\gamma n\delta}} a_p^\dagger \mid HF> \{Y_{m\gamma}(\lambda)\, \tilde{V}_{\gamma pmq} + Z_{m\gamma}(\lambda)\, \tilde{V}_{mp\gamma q}\}\, \frac{1}{E - \omega_\lambda - \mathcal{E}_q + i\eta}$$

$$\times \{Y^*_{n\delta}(\lambda)\, \tilde{V}_{nq\delta p'} + Z^*_{n\delta}(\lambda)\, \tilde{V}_{\delta qnp'}\} <HF \mid a_{p'} \tag{27}$$

III. COMPARISON WITH OTHER WORK

At this point, we will analyze the RPA effective Hamiltonian in its approximate diagonal form and point out the similarities and differences between this result and the expression derived by STY.

Equation (27) for H_{eff} is an operator expression which is valid in the subspace of N + 1 particle vectors spanned by the set $a_p^\dagger \mid HF >$. It has the form

$$H_{eff} = \sum_{pp'} a_p^\dagger \mid HF > H_{eff}^{pp'} < HF \mid a_{p'} \tag{28}$$

We can identify $H_{eff}^{pp'}$ as a matrix element of the effective one body Hamiltonian H^{opt} that gives the optical model wavefunction $F_0(r)$ and satisfies the equation

$$(E + \tfrac{1}{2} \nabla_r^2) F_0(r) = H^{opt} (r, r') F (r') \tag{29}$$

$H^{opt} (r, r')$ is easily extracted from Eq. (27) as

$$H^{opt}_{(r, r')} = V_{HF} (r, r') +$$

$$\sum_{\substack{m\gamma \\ n\delta \\ q\lambda}} \left\{ \left(Y_{m\gamma}(\lambda)\, V_{\gamma m}(r)\, \phi_q(r) + Z_{m\gamma}(\lambda)\, V_{m\gamma}(r)\, \phi_q(r) \right) - \left(Y_{m\gamma}(\lambda)\, V_{\gamma q}(r)\, \phi_m(r) + Z_{m\gamma}(\lambda)\, V_{mq}(r)\, \phi_\gamma(r) \right) \right\}$$

$$\times \frac{1}{E - \omega_\lambda - \mathcal{E}_q + i\eta} \left\{ \left(Y^*_{n\delta}(\lambda)\, V_{q\delta}(r')\, \phi^*_q(r') + Z^*_{n\delta}(\lambda)\, V_{\delta n}(r')\, \phi^*_q(r') \right) - \left(Y^*_{n\delta}(\lambda)\, V_{q\delta}(r')\, \phi^*_n(r') + Z^*_{n\delta}(\lambda)\, V_{qn}(r')\, \phi^*_\delta(r') \right) \right\} \tag{30}$$

where the sums on m, n and q run over particle states, the sums on γ and δ over hole states and

$$V_{ij}(r) \equiv \int \phi_i^*(r')\, \phi_j(r')\, \frac{1}{|r - r'|}\, d^3r' \quad . \tag{31}$$

The Hartree-Fock potential $V_{HF}(r, r')$ which came from PHP is

$$V_{HF}(r, r') = \sum \frac{Z_n}{R_{in}}\, \delta(r - r') + \sum_{\gamma} J_{\gamma}(r)\, \delta(r - r') - K_{\gamma}(r, r') \tag{32}$$

where the first term gives the nuclear attraction and J_{γ} and K_{γ} are the usual Coulomb and exchange operators.

Equation (30) is essentially the same as the effective Hamiltonian derived by STY by approximating the proper self-energy of the one particle Green's function with some minor differences which we now discuss. First the cut structure of Eq. (30) is the same as that of the TDA result of Eq. (17), i.e., branch cuts associated with each inelastic threshold. The STY result also has terms with energy denominators $(Z + \omega_{\lambda} - \mathcal{E}_{\mu})$ where $\mathcal{E}_{\mu}$ is a hole state orbital energy. These terms give rise to discrete poles on the negative energy axis and a left hand cut corresponding to the ionization continuum of the target. From the formal analytic structure of the proper self-energy[13] it might be expected that such terms would appear in any approximation scheme. However the Feshbach optical potential has no singularities at negative energies (that is, negative with respect to the energy of the target ground state) and consequently no such singularities appear in our approximations.

In any case we expect such terms to contribute negligibly to a scattering calculation, since at physical energies all such terms have large positive energy denominators. This supposition is verified by comparison of the results on e^--He scattering of Pu and Chang[7] with those of Yarlagadda, Csanak, Taylor, Schneider and Yaris.[10]

A more serious discrepancy between our result and that of STY is that at energies at which both optical potentials are real, the present result is symmetric in r and r′ whereas the STY optical potential is not. Consequently the STY optical potential is non-hermitian at all energies. If we use the terminology of STY, we can write Eq. (30) symbolically as

$$H_{eff} = V_{HF} + \frac{(W_{direct} - W_{exchange})\,(W^*_{direct} - W^*_{exchange})}{E - U} \qquad (33)$$

The STY result does not have the term $W_{exchange}$, is consequently non symmetric and does not couple triplet states of the target which only contribute to the term $W_{exchange}\, W^*_{exchange}/(E - U)$. This apparently did not have a serious effect on the e^--He elastic scattering computations of Yarlagadda et al.,[10] but for He, V_{HF} alone gives most of the elastic cross section.[14] This may not be the case for larger systems where the coupling to triplet target states might be more important. It has been kindly pointed out to us by Yarlagadda and Csanak that the non-hermitian potential of STY results from a non-symmetric choice of operators in their approximation scheme and may be remedied in several ways.[15]

We should also like to mention two recent studies on e^--He which bear some resemblance to the method proposed here. Temkin, Bhatia and Bardsley[16] have proposed an optical potential scheme and, considering the Q part of the problem only, successfully calculated the position and width of the lowest ^2S resonance of He^-. Murtaugh and Reinhardt,[14] using a method which they show to be equivalent to an approximate optical potential calculation, obtained similar results for the resonance position and accurate non-resonant S-wave phase shifts as well. While neither of the above references make use of second quantization in developing their approximations, it would appear that both approaches bear a strong resemblance to the "non-diagonal" optical potential we have detailed in the Appendix.[17]

IV. DISCUSSION

We have shown how to apply many-body techniques to the Feshbach projection operator formalism and obtain consistent approximations to the optical potential for closed shell target atoms and molecules in both the TDA and RPA. We have also interpreted the results of STY as a "diagonal" approximation to the equations we obtained and thus have shown why the STY optical potential is incapable of displaying resonance behavior. The form of H_{eff} given in Eq. (17) or Eq. (30) lends itself directly to numerical computation, although we reiterate that a more elaborate calculation that would also treat resonances properly could be carried out by diagonalizing QHQ as given in the appendix.

It has been shown by numerous authors that the optical potential, for purely elastic scattering, is well represented by a discrete basis set expansion which gives a finite pole representation. Thus H_{eff} as given by Eq. (30) can be formed from the results of finite basis set Hartree-Fock and RPA calculations on the target. Once the optical potential is formed, its use in a scattering calculation is no more difficult than the use of $V_{HF}(r, r')$, which is also a non-local operator. The present authors have recently shown that continuum HF calculations can be carried out for small molecules by using purely discrete basis set techniques.[18] For applications to molecular systems the restriction to closed shell targets is not a severe one since most small molecules of interest have closed shell ground states.

For energies above the first inelastic threshold the discrete pole approximation to H_{eff} is inappropriate as it stands. However in this case one could follow Nuttall[19] in performing the calculation at complex energies and obtain results at physical energies by extrapolation.

The techniques developed here can be extended to inelastic scattering by the inclusion of more than one channel in P. A similar technique has been used by Burke and Taylor[5] in calculations on e^--H scattering.[20] In a later paper we will pursue this course in developing a many-body approach to multichannel scattering.

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hence, it is implicit in the TDA optical potential. We do not expect any difficulties in the use of the RPA optical potential, judging from the results of the calculation of reference 8. We refer the reader to reference 14 for details.

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APPENDIX

Explicit formulas for QHQ

The matrix elements of the Hamiltonian given in this appendix were generated using a computer program which automates the application of Wick's theorem for arbitrary operators. We are grateful to Mr. Danny L. Yeager for instructing us in the use of his program and for modifying it to suit our needs.

a. TDA Target

$$\begin{aligned} QHQ = \sum_{\substack{pp' \\ qq \\ \lambda\lambda \\ \lambda''\lambda'''}} & a_p^\dagger O_\lambda^\dagger \mid HF > S^{-1}_{p\lambda,\, q\lambda'} \\ & \times < HF \mid O_{\lambda'}\ a_q\ H\ a_{q'}^\dagger\ O_{\lambda''}^\dagger \mid HF > \\ & \times S^{-1}_{q'\lambda'',\, p'\lambda'''} < HF \mid O_{\lambda'''}\ a_{p'} \end{aligned}$$

where $O_\lambda^\dagger$ is the TDA excitation operator of Eq. (7) and S is the overlap matrix of Eq. (9).

$$< HF \mid O_{\lambda'}\ a_q\ H\, a_{q'}^\dagger\ O_{\lambda''}^\dagger \mid HF > = \sum_{m\alpha m'\alpha'} Y^*_{m\alpha}(\lambda')\, Y_{m'\alpha'}(\lambda'')$$

$$\begin{aligned} [& \delta_{\alpha\alpha'}\, \delta_{mm'}\, \delta_{qq'}\, (\varepsilon_q + \varepsilon_m - \varepsilon_\alpha) - \delta_{\alpha\alpha'}\, \delta_{mq'}\, \delta_{m'q}\, (\varepsilon_{m'} + \varepsilon_m - \varepsilon_\alpha) \\ & + \delta_{qq'}\, \tilde{V}_{m\alpha'\alpha m'} + \delta_{pm'}\, \tilde{V}_{m\alpha' q'\alpha} + \delta_{q'm}\, \tilde{V}_{q\alpha' m'\alpha} + \delta_{mm'}\, \tilde{V}_{\alpha' qq'\alpha} \\ & + \delta_{\alpha\alpha'}\, \tilde{V}_{mqm'q'}] \end{aligned} \qquad \text{(A-1)}$$

b. RPA Target

$$QHQ = \sum_{\substack{pp' \\ \lambda\lambda' \\ \lambda''\lambda''' \\ qq'}} a_p^\dagger O_\lambda^\dagger \,|\, 0 > S^{-1}_{p\lambda,\, q\lambda'} < 0 \,|\, O_{\lambda'}\, a_q\, H\, a_{q'}^\dagger\, O_{\lambda''}^\dagger \,|\, 0 > S^{-1}_{q'\lambda'',\, p'\lambda'''} < 0 \,|\, O_{\lambda'''}\, a_{p'}$$

where $O_\lambda^\dagger$ is the RPA excitation operator of Eq. (19) and $S^{-1}_{p\lambda,\, p'\lambda'}$ is an element of the inverse of the overlap matrix $S_{p\lambda,\, p'\lambda'}$ of Eq. (21b).

Consider a general matrix element of the form $< 0 \,|\, O_\lambda\, A\, O_{\lambda'}^\dagger \,|\, 0 >$. Using the property that $O_\lambda \,|\, 0 > = 0$, this matrix element can be written as

$$< 0 \,|\, O_\lambda\, A\, O_{\lambda'}^\dagger \,|\, 0 > = < 0 \,|\, [O_\lambda,\, A,\, O_{\lambda'}^\dagger\,] \,|\, 0 >$$

$$+ \tfrac{1}{2} < 0 \,|\, A\, O_\lambda\, O_{\lambda'}^\dagger \,|\, 0 >$$

$$+ \tfrac{1}{2} < 0 \,|\, O_\lambda\, O_{\lambda'}^\dagger\, A \,|\, 0 > \qquad \text{(A-2)}$$

where the symmetric double commutator is defined by the relation

$$[A, B, C\,] = \tfrac{1}{2} \Big[A, [B, C\,]\Big] + \tfrac{1}{2} \Big[[A, B\,], C\Big]$$

In evaluating the above matrix element, we appeal to the same arguments used in Section II A of the text in replacing $|\, 0 >$ by $|\, HF >$. We also assume, for the purpose of evaluating the last two terms of Eq. (A-2), that O_λ and $O_{\lambda'}^\dagger$ are boson operators -- the quasi-boson approximation

$$[O_\lambda,\, O_{\lambda'}^\dagger\,] = \delta_{\lambda\lambda'}$$

so that

$$< 0 \mid O_\lambda \, A \, O_{\lambda'}^\dagger \mid 0 > \approx < HF \mid [O_\lambda, \, A, \, O_{\lambda'}^\dagger \,] \mid HF >$$

$$+ \, \delta_{\lambda\lambda'} < 0 \mid A \mid 0 > \qquad \text{(A-3)}$$

Note that if $\mid 0 >$ is expanded as in Eq. (22) then $< 0 \mid A \mid 0 > =$ $< HF \mid A \mid HF >$ plus terms of orders $(C_{mn}^{\alpha\beta})^2$ and $\tilde{V}_{\alpha\beta,\, pq} \cdot C_{mn}^{\alpha\beta}$ which we ignore. The results follow.

$$S_{p\lambda,\, p'\lambda'} = - \sum_{\substack{m'\alpha' \\ m\alpha}} \{ Y_{m'\alpha'}(\lambda) \, Y^*_{m\alpha}(\lambda') \, \delta_{\alpha\alpha'} \, \delta_{mp'} \, \delta_{pm'}$$

$$+ \, Z_{m'\alpha'}(\lambda) \, Z^*_{m\alpha}(\lambda') \, \delta_{\alpha\alpha'} \, \delta_{mp} \, \delta_{m'p'} \} + \delta_{\lambda\lambda'} \, \delta_{pp'} \qquad \text{(A-4)}$$

$$< \lambda \mid a_p \, H \, a_{p'}^\dagger \mid \lambda' > = \delta_{pp'} \sum_{m\alpha} \left(Y^*_{m\alpha}(\lambda) \, Y_{m\alpha}(\lambda') + Z^*_{m\alpha}(\lambda) \, Z_{m\alpha}(\lambda') \right) (\varepsilon_m - \varepsilon_\alpha)$$

$$+ \sum_{\substack{m\alpha \\ m'\alpha'}} \left(Y^*_{m\alpha}(\lambda) \, Y_{m'\alpha'}(\lambda') + Z^*_{m'\alpha'}(\lambda) \, Z_{m\alpha}(\lambda') \right)$$

$$\times \Big\{ \delta_{pp'} \, \tilde{V}_{m\alpha'\alpha m'} + \delta_{pm'} \, \tilde{V}_{m\alpha' p'\alpha}$$

$$+ \, \delta_{p'm} \, \tilde{V}_{p\alpha' m'\alpha} + \delta_{mm'} \, \tilde{V}_{\alpha' pp'\alpha}$$

$$+ \delta_{\alpha\alpha'} \, \tilde{V}_{pmp'm'} - \delta_{\alpha\alpha'} \, \delta_{mp'} \, \delta_{m'p} \, (\varepsilon_{m'} + \varepsilon_m - \varepsilon_\alpha) \Big\}$$

$$\sum_{\substack{m\alpha \\ m'\alpha'}} Y^*_{m\alpha}(\lambda) \; Z_{m'\alpha'}(\lambda')$$

$$\times\ \delta_{p'm}\,\tilde{V}_{m'p\alpha\alpha'} + \delta_{p'm'}\,\tilde{V}_{pm\alpha\alpha'} + \delta_{pp'}\,\tilde{V}_{mm'\alpha\alpha'}$$

$$+ \sum_{\substack{m\alpha \\ m'\alpha'}} Y_{m'\alpha'}(\lambda')\, Z^{*}_{m\alpha}(\lambda)\,(\delta_{pm'}\,\tilde{V}_{\alpha'\alpha mp'} + \delta_{pm}\,\tilde{V}_{\alpha'\alpha p'm'}\,\delta_{pp'}\,\tilde{V}_{\alpha'\alpha m'm})$$

$$+ \delta_{\lambda\lambda'}\,\delta_{pp'}\,\mathcal{E}_{p} \qquad \text{(A-5)}$$

SECTION C

A Direct Relationship Between the Bell and Squires Optical Model and Many-Body Feshbach Theory

In this section we develop a relationship between the Bell and Squires[1] optical model wavefunction and the optical model wavefunction obtained from the many-body Feshbach approach when the operator P is formulated using the exact target wavefunction.

The optical model wavefunction (OMW) of Bell and Squires,[1] $\chi(r)$, is defined by

$$\chi(r) \equiv \langle 0 | \hat{\psi}(r) | \Psi \rangle \ , \tag{1}$$

where $|\Psi\rangle$ is the exact N+1 particle scattering wavefunction, $|0\rangle$ is the exact N-particle ground state, and $\hat{\psi}(r)$ is an annihilation field operator. We would like to develop an expression for the OMW of many-body Feshbach theory. We begin by defining the projection operator P by

$$P = \sum_{i,j} a_i^+ |0\rangle M_{ij}^{-1} \langle 0 | a_j \ . \tag{2}$$

In Eq. (2) $|0\rangle$ is the exact ground state wavefunction of the N-particle target, the annihilation and creation operators a_i and a_i^+ refer to a complete set of one-particle functions $\{\varphi_i\}$, and M_{ij}^{-1} is an element in the matrix inverse of the matrix

$$M_{k,\ell} = \langle 0 | a_k a_\ell^+ | 0 \rangle \ . \tag{3}$$

With this definition we can write the result of P operating on the exact N+1 particle wavefunction $|\Psi\rangle$ as

$$P\Psi = \sum_{i,j} a_i^+ |0\rangle M_{ij}^{-1} \langle 0 | a_j | \Psi \rangle \ . \tag{4}$$

Equation (4) has the form

$$P\Psi = \sum_i C_i a_i^+ |0\rangle \ . \tag{5}$$

Thus $P\Psi$ is the antisymmetrized product of a one-particle wavefunction, $f_0(r)$, and the exact target ground state for all values of r. Equations (4) and (5) describe the expansion of $F_0(r)$ in terms of the complete set $\{\varphi_i\}$, so we may write

$$F_0(r) = \sum_{ij} \varphi_i(r)\, M^{-1}_{ij} \langle 0 | a_j | \Psi \rangle \ . \tag{6}$$

Multiplying Eq. (6) by $\varphi_k(r)$ and integrating over r, followed by multiplication by the matrix M yields upon using Eq. (3)

$$\sum_k \langle 0 | a_i a_k^+ | 0 \rangle \langle \varphi_j | F_0 \rangle = \langle 0 | a_i | \Psi \rangle \ . \tag{7}$$

Equation (7) may be rewritten using field operators instead of particle-hole operators as

$$\langle 0 | \hat{\psi}(r) | \Psi \rangle = \int \langle 0 | \hat{\psi}(r)\, \hat{\psi}^+(r') | 0 \rangle\, F_0(r') d^3r' \ . \tag{8}$$

The left hand side of Eq. (8) is just the Bell and Squires OMW, $\chi(r)$ defined in Eq. (1). So we have succeeded in deriving a direct relationship between the two formalisms.

We can rewrite Eq. (8) in a slightly more illuminating fashion. We may use the usual anticommutator expression along with the definition of the one-particle density matrix

$$\rho(r, r') \equiv \langle 0 | \hat{\psi}^+(r)\, \hat{\psi}(r') | 0 \rangle \tag{9}$$

to write

$$\chi(r) = F_0(r) - \int d^3r'\, \rho(r, r') F_0(r') \ . \tag{10}$$

Equation (10) shows that $\chi(r)$ and $F_0(r)$ have the same asymptotic form because, since

$$\rho(r, r') \xrightarrow[r \to \infty]{} 0$$

we have

$$\chi(r) \xrightarrow[r \to \infty]{} F_0(r) \, . \tag{11}$$

Thus we obtain the result to be expected from the non-uniqueness of the optical potential. Different optical potentials may yield optical model wavefunctions that are different in the interaction region. But, in the asymptotic region where scattering information is determined, they must be identical.

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CHAPTER III

Inelastic Electron-H_2 Scattering Calculations Using the RPA Distorted Wave Approximation

SECTION A

Ab Initio Cross Sections for Excitation of the b $^3\Sigma_u$ State of H_2 by Electron Impact in the Distorted Wave Approximation

This letter describes our first results on the electronically inelastic, low-energy, electron-molecule scattering problem. We present ab initio cross sections for the excitation of the $b\,^3\Sigma_u$ state of H_2 by electron impact. The results we report are for an incident electron energy of 15 eV. To our knowledge this is the first calculation of an electronically inelastic electron-molecule differential scattering cross section that goes beyond the high energy approximations of the Born or eikonal type.[1] We find good agreement with the previously unpublished experimental results of Srivastava and Trajmar,[2] whereas the Born approximation at this energy fails badly.

We have assumed the validity of the Born-Oppenheimer approximation in separating the electronic and nuclear portions of the scattering wavefunction. The rotational motion was treated in the usual adiabatic approximation[3] which allows one to calculate the electronic part of the transition matrix in the body-fixed frame of the molecule and then average the cross section, at a given scattering angle, over all orientations of the molecule with respect to a laboratory-fixed frame. Furthermore, we make a Franck-Condon approximation for the vibrational contribution to the cross section, by assuming that the electronic contribution to the transition matrix is independent of the internuclear separation (over the small region where the overlap of the initial and final nuclear vibrational wavefunctions $S_{\nu'\nu}$ is non-zero). With these assumptions, the cross section for the excitation of a particular electronic/vibrational state is given by

$$\sigma(k_f, \nu' \leftarrow k_i, \nu) = \frac{k_f}{k_i} \frac{1}{4\pi^2} S_{\nu'\nu} \cdot \frac{1}{4\pi} \int d\Omega \left| T_{fi}^{e\ell} \right|^2 \qquad (1)$$

where the integral is over all orientations of the molecule and k_i and k_f, the initial and final momenta, are given by

$$\frac{k_i^2}{2} = \Delta E_{fi} + \frac{k_f^2}{2} \tag{2}$$

and ΔE_{fi} is the excitation energy between the initial and final electronic/vibrational states. For the electronic transition energy, we used the value given by Kolos and Wolniewicz[4] at the equilibrium internuclear separation of 1.4 a_0.

In the present calculation we employ the distorted wave approximation for the electronic transition matrix, using the ground state Hartree-Fock potential as the distorting potential and the random phase approximation (RPA) for the electronic transition densities. This approximation is described at length in reference 5, and allows us to write the transition matrix element $T_{fi}^{e\ell}$ in the particularly simple form,

$$T_{fi}^{e\ell} = \sum_{m,\alpha} U_{m\alpha}\, Y^*_{m\alpha}(f) + U_{\alpha m}\, Z^*_{m\alpha}(f) \tag{3}$$

where $Y_{m\alpha}(f)$ and $Z_{m\alpha}(f)$ are RPA amplitudes[4] and $U_{m\alpha}$ is defined by

$$U_{m\alpha} = \int d^3r\, d^3r'\ \phi^*_m(r)\ \varphi^{(-)}_{\vec{k}_f}(r')^*\ \frac{1}{|r-r'|}\ \phi_\alpha(r)\ \phi^{(+)}_{\vec{k}_i}(r') - \text{exchange}. \tag{4}$$

In Eq. (4) ϕ_m is an unoccupied Hartree-Fock spin orbital and φ_α is the occupied σ_g spin orbital of H_2. The distorted waves $\phi^{(+)}_{\vec{k}_i}$ and $\varphi^{(-)}_{\vec{k}_f}$ are Hartree-Fock continuum spin orbitals with incoming (+) and

outgoing (-) boundary conditions.

In computing $\phi_{\vec{k}}^{(\pm)}$ we make use of an expansion technique using square-integrable basis functions developed previously by the authors[6] and applied to elastic electron-H_2 scattering.[7] In this approach the Lippman-Schwinger equation for $\phi_{\vec{k}}^{(\pm)}$ is reduced to a finite matrix problem by expanding the ground-state Hartree-Fock potential in a finite set of two-center Gaussian functions, $\varphi_\alpha(r)$,

$$\phi_{\vec{k}}^{\pm}(r) = \sum_\alpha \varphi_\alpha(r)\ C_\alpha(\vec{k}) \tag{5a}$$

$$C_\alpha(\vec{k}) = \langle \alpha \,|\, \vec{k} \rangle + \sum_{\beta,\gamma} G^0_{\alpha\beta}\ V_{\beta\gamma}\ C_\gamma(\vec{k}) \tag{5b}$$

This is an important simplification, since it allows us to avoid one-center expansions and/or numerical integration of the Schroedinger equation for the distorted waves in the presence of a non-spherical potential.

The electronic transition matrix elements were then computed so as to compensate for the fact that a truncated basis set representation of $\phi_{\vec{k}}^{\pm}$ was used. Since the first term in $\phi_{\vec{k}}^{\pm}$ (Eq. 5b) is simply a plane wave, $U_{m\alpha}$ (Eq. 4) will contain a plane wave contribution which we can write as

$$U_{m\alpha}^{\text{Born}} = \langle m\ \vec{k}_f \,|\, \frac{1}{r_{12}} \,|\, \alpha\ \vec{k}_i \rangle \text{ - exchange} \tag{6}$$

The basis set representation of $U_{m\alpha}^{\text{Born}}$ was thus subtracted from $U_{m\alpha}$ and replaced by the exact plane wave matrix element. This substitution also includes the Born contributions from the higher

symmetry types not included in the basis.[6]

The basis set used to generate the RPA amplitudes (Eq. 3) consisted of a [7s/5p] basis, contracted from a [10s/5p] set of primative Gaussians on each center. The distorted wave basis, which must contain a significant number of diffuse functions in order to represent the tails of the continuum orbitals, consisted of a set of [20s/7z/15x/15y] Gaussians on each center, whose exponents were chosen in a geometric series. With this basis, the Σ_g, Σ_u, Π_g and Π_u contributions to the electronic amplitude could be constructed; other symmetries were included only to the extent that they contributed to the exact Born terms of Eq. (6).

The results we are reporting are for the excitation of the total vibrational band corresponding to the $b\,^3\Sigma_u$ electronic state of H_2; that is, the cross section of Eq. (1) is summed over all final states ν'. Since the $b\,^3\Sigma_u$ state is dissociative, the Franck-Condon factor involves the overlap of a bound and a continuum nuclear vibrational function. This overlap was evaluated by numerical quadrature, using a harmonic oscillator initial state with parameters taken from Herzberg,[8] and a final vibrational wavefunction that was generated numerically, using the $b\,^3\Sigma_u$ potential energy curve of Kolos and Wolniewicz[4] and a Runge-Kutta integration scheme. Our computed Franck-Condon curve was found to be in good agreement with the shape of the observed dissociative feature in the electron-impact energy loss spectrum,[2] and was thus used to extend the latter feature for the purpose of computing the total area under the

dissociative curve, which should be proportional to the total cross section we evaluated.

The results of our computation are shown in Fig. 1 along with the previously unpublished results of Srivastava and Trajmar.[2] The latter relative figures have been normalized to our values at 90°. The agreement of our computed differential cross section with experiment is seen to be good. We have also plotted the plane-wave approximation obtained by setting $U_{m\alpha} = U_{m\alpha}^{Born}$; this is frequently referred to as the Born-Oppenheimer minus core approximation (BOMC).[9] In contrast to the full distorted wave approximation, the BOMC fails badly at this low incident electron energy of 15 eV. Absolute total cross sections for the dissociation of H_2 by electron impact have been measured by Corrigan.[10] Our value for the integrated cross section at 15 eV is 0.994 (πa_0^2). This number is consistent with Corrigan's observed value of 0.98 for the total cross section for dissociation of H_2 by 15 eV electrons, and this supports the supposition that the low-energy electron impact dissociation of H_2 proceeds mainly through direct excitation of the $b\,^3\Sigma_u$ state.

The preliminary results we have obtained for the $X\,^1\Sigma_g \rightarrow b\,^3\Sigma_u$ transition in H_2 at 15 eV are very encouraging. Further calculations at other incident electron energies and for different electronic states are under way and will be described in a future publication.

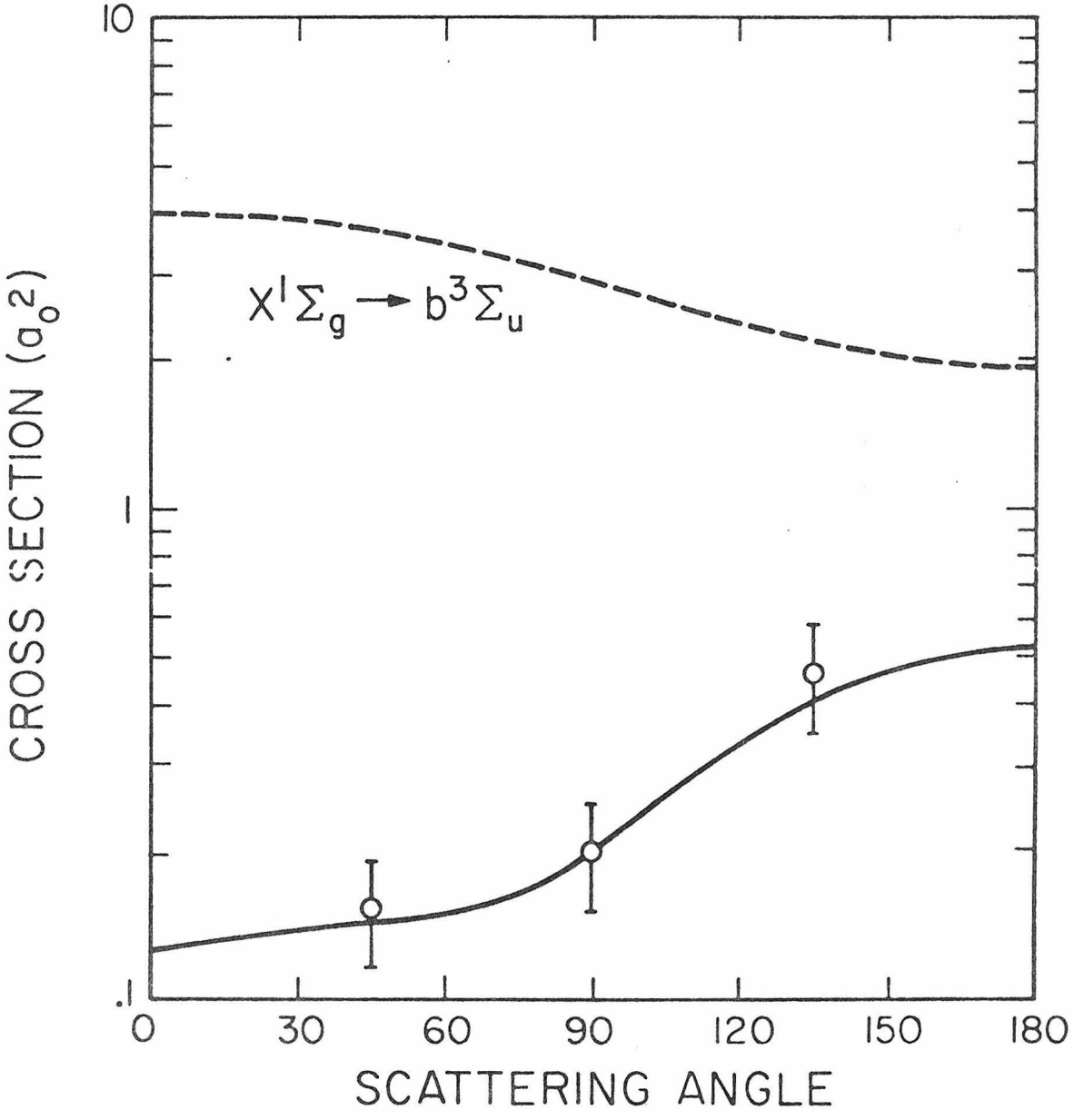
The authors would like to express their appreciation to Drs. Trajmar and Srivastava for undertaking this experiment and furnishing us with their observed cross sections.

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Figure Caption

Fig. 1. Differential cross section for the excitation of the $b\,^3\Sigma_u$ state of H_2 by 15 eV incident electrons. Numerical results using the distorted wave approximation (solid curve) are compared with normalized experiment and with the results obtained in the Born approximation (broken curve). Cross sections are for excitation of the entire vibrational band and are given in atomic units.


10
1
.1
CROSS SECTION (a_o^2)
$X^1\Sigma_g \rightarrow b^3\Sigma_u$
0
30
60
90
120
150
180
SCATTERING ANGLE

SECTION B

The Low-Energy Electron-Impact Excitation of the Hydrogen Molecule

I. INTRODUCTION

Current efforts in the identification and development of new gas laser systems have sparked a renewed interest in gas dynamic processes and, in particular, have created a need for accurate low energy electron-molecule scattering cross sections. The precise evaluation of cross sections for processes involving the collision of slow electrons with molecules has been greatly hindered in the past because of the severe difficulties introduced into the calculation of molecular continuum wavefunctions by the non-spherical nature of the molecular force field. In most cases, numerical complications have restricted the computations to a rather low level of approximation; indeed, for cases involving molecular electronic excitation, the calculations almost invariably fall under the category of Born-type calculations in the case of spin-allowed transitions, or in the case of singlet-triplet transitions, Born-Oppenheimer or Ochkur-type calculations.[1] Experience gained in the calculation of electron-atom cross sections has shown that the validity of such approximate schemes at low electron impact energies (<50 eV) is highly questionable.[2,3]

In a previous letter,[4] we reported differential cross sections for the excitation of the dissociative $b^3\Sigma_u^+$ state of H_2 at 15 eV incident electron energy. The results were in good agreement with experimental data. The computations were carried out using the so-called "first-

order many-body formula"[5] which, as the authors have shown,[6] is simply a form of the distorted-wave approximation. The distorted waves were obtained by an efficient expansion technique which involves solving the Lippmann-Schwinger equation for the molecular continuum orbitals in a discrete set of Gaussian basis functions.[7, 8] This approach allowed us to treat the non-central nature of the scattering process by explicitly including the Σ_g^+, Σ_u^+, Π_g and Π_u contributions to the transition amplitude without resorting to a one-center expansion. The fact that no numerical integrations were performed also enabled us to treat the exchange forces properly in computing the distorted waves.

These computations have now been extended to other energies between 13 and 20 eV. We have also considered the excitation of the second ($a\,^3\Sigma_g^+$) triplet state of H_2 over the same energy range. As will be shown, these two cross sections can be combined to give a total cross section for the dissociation of H_2 that is in good agreement with the experimental cross section over this range of electron impact energies. The general theory and approximation schemes employed in these calculations will also be considered in some detail.

II. THEORY

A. Separation of Electronic, Vibrational and Rotational Motion

Within the framework of the Born-Oppenheimer approximation, we denote the electronic, vibrational and rotational quantum numbers

of the initial (final) state of the electron-H_2 system by n, ν, ℓ and m (n', ν', ℓ', m') and write the wavefunction for this state as

$$\Psi_{i(f)}^{total} = \Psi_{n(n')}^{+(-)} (\{\vec{x}\}, \vec{R}) \zeta_{\nu(\nu')}^{n(n')} (R)\, Y_{\ell(\ell')}^{m(m')} (\theta, \varphi), \tag{1}$$

where $\Psi_{n'}^{+}$, the electronic wavefunction, depends explicitly on the electronic space and spin coordinates $\{\vec{x} \equiv \vec{r}, \vec{s}\}$ in a body-fixed coordinate system and on the internuclear separation R. There is also an implicit dependence on the orientation of the molecule with respect to a laboratory-fixed frame, which comes about through the imposition of asymptotic, scattering boundary conditions. The vibrational wavefunction, ζ_{ν}^{n}, is assumed to be independent of the rotational quantum numbers ℓ and m and $Y_{\ell}^{m} (\theta, \varphi)$ is a spherical harmonic, with polar angles referring to the orientation of the molecular axis with respect to the laboratory frame.

If we label the incident electron as particle 1, the cross section for the excitation of a particular electronic/vibrational/rotational state is given (in atomic units) by,

$$\sigma(\vec{k}_f \leftarrow \vec{k}_i) = \frac{1}{4\pi^2} \frac{k_f}{k_i} \Big| \int e^{-i\vec{k}_f \cdot \vec{r}_1} \chi^*(\vec{s}_1)\, \Phi_{n'}^{*} (\vec{x}_2, \vec{x}_3; R)$$

$$\zeta_{\nu'}^{*n'}(R)\, Y_{\ell'}^{*m'} (\theta, \varphi) \left(-\frac{1}{r_{1A}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} + \frac{1}{r_{13}}\right) \Psi_{n}^{+} (\vec{x}_1, \vec{x}_2, \vec{x}_3; \vec{R})$$

$$\zeta_{\nu}^{n}(R)\, Y_{\ell}^{m}(\theta, \varphi)\, d\vec{x}_1 d\vec{x}_2 d\vec{x}_3\, d\vec{R} \Big|^2, \tag{2}$$

where $\chi(s_1)$ is the spin wavefunction of the scattered electron, $\Phi_{n'}$ is the normalized final-state electronic wavefunction of H_2, and A and B denote the two hydrogen nuclei. $\vec{k}_i$ and $\vec{k}_f$, the wavevectors for the incident and scattered electrons, are determined by the relation

$$k_f^2 = k_i^2 - 2\,(E_f - E_i) \qquad (3)$$

where E_f (E_i) is the final (initial) energy of the molecule. In defining the cross section we have used the post-interaction representation[9] in which the non-interacting form of $\Psi_{n'}^-$ appears, and Ψ_n^+ ($\{\vec{x}\}$, R) is the fully antisymmetrized outgoing electronic wavefunction for the $e^- - H_2$ system.

We can first treat the contribution to the cross section arising from the rotational motion of the molecule. Since rotational levels are typically not resolved in current experiments, it is customary to treat them as being effectively degenerate and to sum the cross section of Eq. (2) over all final rotational levels ℓ' and m′ and average over all initial states ℓ and m. If we also neglect the slight dependence of the molecular energy upon ℓ and ℓ', it then follows, from the completeness properties of the spherical harmonics, that the rotationally averaged cross section can be written as,[10]

$$\sigma^{\text{rot. av.}}(k_f \leftarrow k_i) =$$

$$\frac{1}{4\pi^2} \cdot \frac{k_f}{k_i} \int \left| \int e^{-i\vec{k}_f \cdot \vec{r}_i} \chi^*(\vec{s}_1)\, \Phi_{n'}^*(\vec{x}_2, \vec{x}_3; R)\, \zeta_{\nu'}^{*n'}(R) \right.$$

$$\left. \left(-\frac{1}{r_{1A}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} + \frac{1}{r_{13}}\right) \Psi_n^+(\vec{x}_1, \vec{x}_2, \vec{x}_3; \vec{R}) \right.$$

$$\left. \zeta_{\nu}^{n}(R)\, R^2\, dR\, d\vec{x}_1\, d\vec{x}_2\, d\vec{x}_3 \right|^2 \frac{d\Omega}{4\pi} \,. \qquad (4)$$

This result, which is equivalent to an adiabatic treatment of molecular rotation,[11] simply amounts to averaging the cross section over all possible orientations of the molecular target.

A further approximation may be made by realizing that the electronic wavefunctions are more slowly varying functions of the internuclear separation R than the vibrational wavefunctions and hence replacing the former by their values at the equilibrium internuclear separation. This approximation works best when the initial vibrational state is $\nu = 0$ (which is the case for hydrogen at room temperature) since the vibrational wavefunction is then nearly Gaussian and centered about the equilibrium internuclear separation, R_e. The vibrational component of the cross section can then be separated from Eq. (4) and gives a multiplicative factor of

$$q_{\nu' \nu} \equiv \left| \int R\, \zeta_{\nu'}^{n'*}(R)\, R\, \zeta_{\nu}^{n}(R)\, dR \right|^2 \qquad (5)$$

which is the familiar Franck-Condon overlap integral.[10] The cross section for exciting all the vibrational levels of a particular

electronic state can then be obtained by summing over all ν' values to give

$$\sigma_{tot.}^{rot.\,av.}(\vec{k}_f \leftarrow \vec{k}_i) = \sum_{\nu'} \frac{1}{4\pi^2} \frac{k_f}{k_i} q_{\nu\nu'} \times$$

$$\int \left| \int e^{-i\vec{k}_f \cdot \vec{r}_i} \chi^*(\vec{s}_1)\, \Phi_n^*, (\vec{x}_2, \vec{x}_3; R_e) \left(-\frac{1}{r_{1A}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} \frac{1}{r_{13}}\right) \times \right.$$

$$\left. \Psi_n^+ (\vec{x}_1, \vec{x}_2, \vec{x}_3; \vec{R}_e)\, d\vec{x}_1, d\vec{x}_2, d\vec{x}_3 \right|^2 \frac{d\Omega}{4\pi} \,. \qquad (6)$$

A final approximation consists of ignoring the dependence of the electronic portion of the scattering amplitude on the vibrational quantum number; that is, for each value of the incident electron energy under consideration, a single electronic transition amplitude was calculated, with a final wavenumber corresponding to a vertical transition from the $\nu = 0$ ground state into the vibrational level of the upper electronic state with the largest Franck-Condon overlap. Using the electronic potential energy curves of Kolos and Wolniewicz,[12,13] this corresponds to a vertical transition energy of 10.14 eV for the $b\ ^3\Sigma_u^+$ state and 12.12 eV for the $a\ ^3\Sigma_g^+$ state. Relaxing this approximation would have required computing a different electronic transition matrix for every possible final vibrational state--a procedure that would have involved a considerable amount of computer time. The final form of the differential, rotationally averaged, total vibrational cross section used in this work is

$$\sigma_{tot.}^{rot.\,av.} = \frac{1}{4\pi^2} \int \left| T_{el}(\vec{k}_f \leftarrow \vec{k}_i) \right|^2 \frac{d\Omega}{4\pi} \sum_{\nu'} \frac{k_f}{k_i} q_{\nu\nu'} \qquad (7)$$

where

$$T_{el}(\vec{k}_f \leftarrow \vec{k}_i) = \int e^{-i\vec{k}_f(R_e)\cdot\vec{r}_1} \chi^*(s_1)\, \Phi_n^*(\vec{x}_2, \vec{x}_3; R_e)\left(-\frac{1}{r_{1A}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} + \frac{1}{r_{13}}\right)$$

$$\Psi_n^+(\vec{x}_1, \vec{x}_2, \vec{x}_3; \vec{R}_e)\, d\vec{x}_1\, d\vec{x}_2\, d\vec{x}_3 \ . \qquad (8)$$

In the case of the dissociative b $^3\Sigma_u^+$ state, the sum over ν' in Eq. (7) is replaced by an integral.

B. The Distorted Wave-Random Phase Approximation (DW-RPA) for the Electronic Transition Matrix

For the computations reported in this paper, the electronic transition matrix T_{el} was calculated using the first-order many-body formula. This approximation was first introduced into electron scattering by H. S. Taylor and his coworkers[5] and applied to e^--He scattering.[3] As the present authors have shown,[6] the first-order many-body formula is simply a form of the distorted-wave (DW) approximation in which both distorted waves are computed in the field of the initial state and the electronic target states are treated in the random phase approximation (RPA). Other DW calculations have appeared in the literature recently, on e^--He[14] and e^--H,[15] and in both studies it was shown that better results were obtained when the initial and final state orbitals were both computed in the field of the ground state--

in agreement with the DW-RPA prescription.

The DW-RPA[6] can be easily obtained for the general case of scattering from an n-electron closed shell atom or molecule by using the two potential formula.[16] To the interaction potential V between an incident electron and an n-electron atom or molecule, we add and subtract the operators J-K, the Hartree-Fock Coulomb and exchange operators for the target in its ground state. We then partition V into two terms, $V = V_I + V_{II}$, where

$$V_I = \sum_{\text{nuclei}} - \frac{Z_N}{|r - R_N|} + J - K \tag{9a}$$

and

$$V_{II} = \sum_{i=1}^{n} \frac{1}{|r - r_i|} - J + K \tag{9b}$$

We may then write the electronic transition matrix element for inelastic scattering as

$$T_{el}(\vec{k}_f \leftarrow \vec{k}_i) = (\Phi_n, (x_1, , , x_n) e^{i\vec{k}_f \cdot \vec{r}} \chi(s) | V_I | \Psi^+_{Ik_i}(x, x_1, , , x_n)) + \\ + \left(\Psi^-_{Ik_f}(x, x_1, , , x_n) | V_{II} | \Psi^+(x, x_1, , , x_n)\right) \quad , \tag{10}$$

where Ψ^+ is the exact, antisymmetric electronic wavefunction for the full interacting system with outgoing wave boundary conditions, and $\Psi^+_{Ik_i}$ and $\Psi^-_{Ik_f}$ are eigenfunctions of the operator $-\frac{1}{2}\nabla^2_r +$ $H_{target} + V_I$. Thus $\Psi^+_{Ik_i}$ and $\Psi^+_{Ik_f}$ are products of target

eigenstates and scattering solutions of the static exchange Hamiltonian $-\frac{1}{2}\nabla_r^2 + V_I$. The distorted wave approximation is made by replacing Ψ^+ by an antisymmetrized product of the target ground-state wavefunction and a Hartree-Fock continuum spin-orbital. The choice of the ground state J-K operators in the definition of V_I leads naturally to a distorted wave approximation in which the distorting potential is the static-exchange potential of the ground state. However this is a somewhat artificial choice whose justification lies mainly in the better agreement obtained for e^--H[15] and e^--He[14] cross sections using the field of the ground state than were obtained using the field of the excited state. In the theory of Taylor and coworkers[3,5] the replacement of certain operators in the Bethe-Salpeter equation by their Hartree-Fock values leads to the same final result. In fact this is a result to be expected in first order from a many-body theory approach to scattering which starts from a set of hole and particle (bound and continuum) orbitals which are eigenfunctions of the ground-state Hartree-Fock Hamiltonian.[6]

The distorted wave approximation to the transition element may be written as a matrix element of a simple operator between the ground and excited states of the target. This expression is then evaluated in the RPA (details are given in reference 6) to yield

$$T_{el}(\vec{k}_f \leftarrow \vec{k}_i) = \sum_{m\alpha} Y^{*(f)}_{m\alpha} (m\, k_f^- || \alpha\, k_i^+)_a + Z^{*(f)}_{m\alpha} (\alpha\, k_f^- || m\, k_i^+)_a \,, \qquad (11)$$

where $Y^{(f)}_{m\alpha}$ and $Z^{(f)}_{m\alpha}$ are amplitudes satisfying the usual RPA equations, m and α refer to Hartree-Fock unoccupied and occupied spin-orbitals respectively, $k^{+(-)}_{i(f)}$ is a Hartree-Fock continuum spin-orbital at the incident (exiting) wavenumber with outgoing (incoming) wave boundary conditions and the antisymmetrized matrix elements and defined by

$$(ij||kl)_a = (ij||kl) - (ij||lk) \qquad (12)$$

where

$$(ij||kl) = \int \phi_i^*(\vec{x}_1)\, \phi_j^*(\vec{x}_2)\, \frac{1}{|\vec{r}_1 - \vec{r}_2|}\, \phi_k(x_1)\, \phi_\ell(x_2)\, d\vec{x}_1\, d\vec{x}_2 \,. \qquad (13)$$

For the calculations presented here we require an expression for the cross section in the special case of excitation from a closed-shell singlet ground state to a triplet state. By using the spin-adapted excitation operators of Shibuya and McKoy,[17] and following the derivation of reference 6, specializations of Eq. (11) for exciting each of the degenerate components of the excited-state are obtained. The cross section is found by summing over components of the final state of the target and over the spin projection of the exiting electron. We assume an unpolarized incident beam and thus average the cross section over spin projections of the incident electron. The resulting expression for the cross section is

$$\sigma^{\text{triplet}}(\vec{k}_f \leftarrow \vec{k}_i) = \frac{3}{2} \frac{1}{(2\pi)^2} \frac{1}{4\pi} \int d\Omega \, | T_{el}^{\text{triplet}}(\vec{k}_f \leftarrow \vec{k}_i) |^2 \sum_{\nu'} \frac{k_f}{k_i} q_{\nu\nu'} \, , \tag{14}$$

where

$$T_{el}^{\text{triplet}}(\vec{k}_f \leftarrow \vec{k}_i) = \sum_{m,\alpha} Y_{m\alpha}^{(f)*} (m\, k_f^- || k_i^+ \, \alpha) + Z_{m\alpha}^{(f)*} (\alpha\, k_f^- || k_i^+ \, m) \, . \tag{15}$$

In Eq. (15) m, α, k_f^- and k_i^+ are Hartree-Fock space-orbitals evaluated at the equilibrium internuclear separation, the spin integrations having been performed in the derivation of Eq. (14).

A similar analysis for exciting a singlet state gives

$$\sigma^{\text{singlet}}(\vec{k}_f \leftarrow \vec{k}_i) = \tfrac{1}{2} \frac{1}{(2\pi)^2} \frac{1}{4\pi} \int d\Omega | T_{el}^{\text{singlet}}(\vec{k}_f \leftarrow \vec{k}_i) |^2 \sum_{\nu'} \frac{k_f}{k_i} q_{\nu\nu'} \, , \tag{16}$$

with

$$T_{el}^{\text{singlet}}(\vec{k}_f \leftarrow \vec{k}_i) = \sum_{m\alpha} Y_{m\alpha}^{(f)*} (2(m\, k_f^- || \alpha\, k_i^+) - (m\, k_f^- || k_i^+ \, \alpha)) + Z_{m\alpha}^{(f)*} (2(\alpha\, k_f^- || m\, k_i^+) - (\alpha\, k_f^- || k_i^+ \, m)) \, , \tag{17}$$

and where the orbitals are again space-orbitals.

C. Evaluation of Molecular Continuum Orbitals

The successful execution of a distorted wave calculation depends on an efficient technique for computing the continuum orbitals. This is particularly true in molecular applications where the distorted waves must be computed with a non-spherical Hartree-Fock potential. A partial wave expansion of the scattering wavefunction leads to coupled equations whose solutions can, in principle, be found by direct numerical integration. In practice, the relatively slow convergence of single-center expansions[18] and the difficulties of handling exchange operators render calculations by this method tedious. Other investigators who have chosen this approach have often found it necessary to make severe approximations to the non-local portions of the potential to make the calculations tractable.[19, 20]

The Hartree-Fock scattering solutions used in this work, $\phi_k^{\pm}(\vec{r})$, were computed by direct solution of the Lippmann-Schwinger equation for the wavefunction. The Lippmann-Schwinger equation can be reduced to a finite matrix equation by expanding the wavefunction in a set of square-integrable basis functions, which in this case were chosen to be ordinary Gaussian functions, $\varphi_\alpha(\vec{r})$, centered on the two nuclei[7, 8]

$$\phi_k^{\pm}(\vec{r}) = \sum_\alpha \varphi_\alpha(\vec{r})\, c_\alpha^{\pm}(\vec{k}) \quad . \tag{18}$$

The Lippmann-Schwinger equation becomes an algebraic equation for the coefficients $c_\alpha^{\pm}(\vec{k})$,

$$c_\alpha^{\pm}(\vec{k}) = \langle \alpha | \vec{k} \rangle + \sum_{\beta,\gamma} G_{\alpha\beta}^{0\pm} V_{\beta\gamma} c_\gamma^{\pm}(\vec{k}), \tag{19}$$

where $V_{\beta\gamma}$ is a matrix element of the Hartree-Fock potential, $\langle \alpha | \vec{k} \rangle$ is the Fourier transform of $\varphi_\alpha(\vec{r})$, and $G_{\alpha\beta}^{0\pm}$ is a matrix element of the free-particle Green's function. The formulas for the matrix elements in Eq. (19) are given in references 7 and 8. In this approach, non-local potential operators pose no more serious problems than in bound state calculations since only matrix elements of the potential between square integrable basis functions are required.

The basis set expansion of $\phi_k^{\pm}(\vec{r})$ obtained by the solution of Eq. (10) is only valid over a finite range of r, but with a sufficiently large set of basis functions a representation is obtained which can be used to accurately evaluate the matrix elements of Eq. (15). If one chooses basis functions which transform with the irreducible representations of the point group $D_{\infty h}$, Eq. (19) may be solved separately for each molecular symmetry (Σ_g^+, Σ_u^+, Π_g, etc.). This constitutes a major simplification, since it reduces the size of the matrices which must be handled at any point in the calculation. It should be noted that the solution of Eq. (19) for $\phi_{\vec{k}}^{\pm}$ is carried out in the body-fixed frame and that the orientation of the molecule with respect to the incident direction $\vec{k}$ enters the calculation through the Fourier transforms $\langle \alpha | \vec{k} \rangle$. Thus we compute distorted waves for a number of orientations of the molecule and

use these to construct the cross section at enough points to perform the average over molecular orientations numerically. The details of this numerical integration in Eq. (14) will be discussed in the following section.

We may correct the electronic transition matrix elements in Eq. (15) to a certain extent so as to compensate for the fact that a finite basis representation of $\phi_{\vec{k}}^{\pm}$ is being used. Since the first term in $\phi_{\vec{k}}^{\pm}$ [Eq. (18) and (19)] is a plane wave, the matrix element (for example), $(m\ \vec{k}_f^- \,||\, \vec{k}_i^+\ \alpha)$ will contain a plane wave contribution $(m\ \vec{k}_f \,||\, \vec{k}_i\ \alpha)$. We can substract the basis set representation of this contribution and replace it by the exact plane wave matrix element. This substitution also has the effect of including first Born contributions to the scattering amplitude from higher symmetries not included in the basis.[8] For the basis sets and number of molecular symmetries considered in this work, the plane wave correction was found to be small in all cases. These plane-wave corrections require the evaluation of free-free matrix elements. Multicenter bound-free and free-free matrix elements can be evaluated in closed form when Gaussian orbitals are used.[21,22]

III. COMPUTATIONAL

The first step in the calculation was to compute an accurate Hartree-Fock ground-state wavefunction and the RPA amplitudes $Y_{m\alpha}$ and $Z_{m\alpha}$ of Eq. (11). For this purpose a [7s 5p] set of contracted Gaussian basis functions was used which was formed from the 10s and 5p sets of Huzinaga[23] (effective Slater exponent of 1.2) by contracting the four tightest s functions. The distorted waves $\phi_{\vec{k}}^{\pm}$ of Eq. (18) were then expanded in larger basis sets. Only Σ_g^+, Σ_u^+, Π_g and Π_u components of the distorted waves were computed using the Lippmann-Schwinger equation; higher symmetries were included through the plane-wave corrections, as discussed previously.

For the Σ_g^+ and Σ_u^+ components, a (20s $5p_z$) set of Gaussians on each center was used, with s exponents chosen in a geometric series (most diffuse $\alpha = 4 \times 10^{-4}$) to extend the Huzinaga[23] 10s set and p_z exponents also chosen in a geometric series (ratio 1.9, most diffuse $\alpha = 0.102$). For Π_g and Π_u symmetries, a 15p set of primitive Gaussians was formed with exponents ranging from 15.3 to 0.001. The Π_x and Π_y components were solved for separately but the potential matrix $V_{\alpha\beta}$ in Eq. (19) is the same for both.

Since a smaller basis was used to expand the occupied σ_g orbital of H_2 than was used to expand the distorted waves $\phi_{\vec{k}}^{(\pm)}$, considerable economy was realized in the computation of the two-electron integrals which contribute to the potential matrix $V_{\alpha\beta}$ of

Eq. (19). The smaller [7s 5p] set was also used in solving the RPA equations so that the Hartree-Fock virtual orbitals m in Eq. (15) were also expressed in this basis. Thus only the distorted waves in Eq. (15) are expressed in the larger basis sets and consequently many fewer two-electron integrals are required than would be if the same basis was for both $\varphi_k^{(\pm)}$ and m and α. It is important to realize that the distorted wave formula [Eq. (15)] can couple the different components of the distorted waves depending on the symmetry of final electronic state. For example, in the case of the $b\ ^3\Sigma_u^+$ state, the matrix element $(k_f^- m \| \alpha k_i^+)$ connects the g and u components of the two distorted waves, but still leaves the Σ, Π, Δ, etc., symmetries uncoupled.

Eq. (15) may be used to compute $T_{el}(\vec{k}_f \leftarrow \vec{k}_i)$ for a given orientation of the molecule relative to the directions of $\vec{k}_i$ and $\vec{k}_f$. This is accomplished by solving Eq. (19) for the incident and final distorted waves, specifying the molecular orientation through the Fourier transforms. To compute the cross section we must perform the integral over molecular orientations in Eq. (14). We may write this integral as

$$\int_0^{2\pi} \int_{-1}^{1} d(\cos\theta)\, d\varphi \left| T_{el} \right|^2,$$

the polar angles θ and φ specifying the orientation of the molecular axis with respect to the axis perpendicular to the bisector of the angle

between $\vec{k}_f$ and $\vec{k}_i$ and lying in the plane of those vectors. The integration was performed in this coordinate system using six point Gauss-Legendre Quadrature in each of the variables $\cos\theta$ and φ. The integral is symmetric in φ and need only be computed on the interval $[0, \frac{\pi}{2}]$. At each orientation the plane wave correction discussed in the previous section was made to $T_{el}(\vec{k}_f \leftarrow \vec{k}_i)$ and the corrected value was used in the integration over orientations.

Since we are ignoring the dependence of $T_{el}(\vec{k}_f \leftarrow \vec{k}_i)$ on the internuclear separation, and thus on vibrational quantum numbers, the only factor left in the computation of the cross section is $\sum_{\nu'} \frac{k_f}{k_i} q_{\nu\nu'}$. Conservation of energy requires that k_f depend on ν'; ν was chosen as the lowest vibrational level of the ground state in all cases. The Franck-Condon factors for transitions to the discrete vibrational levels of the $a\ ^3\Sigma_g^+$ excited state were taken from the work of Cartwright and Kuppermann.[24] No continuum vibrational states were included in the sum over ν' for this state, because the sum of $q_{0\nu'}$ for the first eight levels was sufficiently close to the expected value of unity.

The $b\ ^3\Sigma_u^+$ state is dissociative and thus has only continuum vibrational states. Vibrational wavefunctions were computed for this state by numerical integration using the potential energy curve of Kolos and Wolniewicz.[12] The wavefunction of the lowest vibrational level of the ground state was also computed in this manner and the Franck-Condon envelope is shown in Figure 1. It was found to be in

excellent agreement with the shape of the dissociative feature in the energy loss spectrum for the b $^3\Sigma_u^+$ state at 15 eV incident energy in the unpublished experimental results of Srivastava and Trajmar.[4] This agreement gives some indication that the neglect of the dependence of $T_{el}(k_f \leftarrow k_i)$ on the internuclear separation is justified in this case.

IV. RESULTS

Differential cross sections at incident electron energies of 13, 14, 15, 16, 17 and 20 eV for excitation of the b $^3\Sigma_u^+$ and a $^3\Sigma_g^+$ states are shown in Figures 2 and 3, and Tables 1 and 2 respectively. The DW-RPA gives similar angular distributions for both states. These cross sections are backward peaked at 13 eV and develop a well-formed minimum at 90° as the incident energy increases.

There is unfortunately little experimental data with which to compare these results. Srivastava and Trajmar[4] have measured angular distributions for the excitation of the b $^3\Sigma_u^+$ state at 15 eV and their results agree very well with those predicted by the DW-RPA. The energy dependence of the differential cross sections we find for the b $^3\Sigma_u^+$ state shows that the backward peaking becomes less pronounced as the energy increases and indicates the development of a maximum in the cross section near 30° at higher energies. The experimental angular distribution of Trajmar et al.[25] for this transition shows a maximum between 30° and 40° for incident energies between 35 and 60 eV.

Cartwright[25, 26] has also calculated differential cross sections for the b $^3\Sigma_u^+$ state using the Ochkur-Rudge[27] (OR) approximation. This theory predicts a maximum near 40° for incident energies between 15 and 85 eV. While this type of behavior does agree with the experimental measurements (which only extend to 80°) at energies above 35 eV,[25] it disagrees with the distributions we find below 20 eV in shape, although the magnitudes are similar. The Ochkur-Rudge approximation is however a high energy theory based on first-order perturbation principles and should not be expected to be accurate at the low energies we have considered.

In the case of the a $^3\Sigma_g^+$ excitation, no experimental data are available for the comparison. The energy loss spectrum shows a strong overlap of the a $^3\Sigma_g^+$ vibrational bands with those of the c $^3\Pi_u$ state and this interference makes angular distributions for the excitation of the a $^3\Sigma_g^+$ state difficult to measure.[25] The only other results available for comparison are the (OR) calculations of Cartwright,[25, 26] and once again these differential cross sections do not agree with our results in shape, although the magnitudes are similar.

Since singlet-to-triplet radiative transitions are not observed in molecular hydrogen and the lowest triplet state is repulsive, electron impact excitation of any triplet state must lead eventually to dissociation. Values for the dissociation cross section of H_2, obtained by summing the total cross sections for excitation of the two lowest triplet states,

are shown in Figure 4. Also shown are the (OR) results of Cartwright,[24,26] the Ochkur(O) calculations of Khare[28] and the experimental results of Corrigan.[29]

At energies above 15.4 eV, Corrigan's data must be corrected to account for the effects of H_2 ionization. The experimental curve shown in Figure 4 thus represents the difference between Corrigan's measurement and the ionization cross section at the same impact energy measured by Harrison.[24,30] Our results, as well as the theoretical results of Cartwright[24,26] and Khare,[28] show a peak in the ionization cross section between 14 and 15 eV, while the experimental data[29] shows this peak at ~ 16 eV. Considering the possible errors involved in correcting Corrigan's data for the effects of ionization, the agreement between theory and experiment is satisfactory. There is also qualitative agreement between our total cross sections and the (O) and (OR) results. This agreement suggests that total cross sections computed using the (O) or (OR) approximations may be more reliable at low energies than the corresponding differential cross sections.

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TABLE I. Differential and total cross sections for the $X^1\Sigma_g^+ \rightarrow b\,^3\Sigma_u^+$ transition in molecular hydrogen. The differential cross sections are in units of a_0^2; total cross sections are in units of πa_0^2.

θ \ E	13 eV	14 eV	15 eV	16 eV	17 eV	20 eV
0°	3.682(-2)	9.583(-2)	1.284(-1)	1.690(-1)	1.819(-1)	1.851(-1)
30°	5.466(-2)	1.128(-1)	1.418(-1)	1.777(-1)	1.897(-1)	2.037(-1)
45°	7.453(-2)	1.263(-1)	1.478(-1)	1.746(-1)	1.815(-1)	1.785(-1)
60°	1.031(-1)	1.409(-1)	1.536(-1)	1.669(-1)	1.658(-1)	1.464(-1)
90°	2.009(-1)	2.170(-1)	2.044(-1)	1.907(-1)	1.718(-1)	1.154(-1)
120°	3.497(-1)	3.685(-1)	3.357(-1)	2.962(-1)	2.573(-1)	1.531(-1)
135°	4.253(-1)	4.492(-1)	4.103(-1)	3.600(-1)	3.101(-1)	1.805(-1)
150°	4.879(-1)	5.167(-1)	4.740(-1)	4.150(-1)	3.553(-1)	2.041(-1)
180°	5.445(-1)	5.776(-1)	5.327(-1)	4.687(-1)	3.964(-1)	2.248(-1)
total cross section (πa_0^2)	9.317(-1)	1.050(-1)	1.011(-1)	9.595(-1)	8.757(-1)	6.244(-1)

TABLE II. Differential and total cross sections for the $X\,^1\Sigma_g^+ \rightarrow a\,^3\Sigma_g^+$ transition in molecular hydrogen. The differential cross sections are in units of a_0^2; total cross sections are in units of $\pi\, a_0^2$.

θ \ E	13 eV	14 eV	15 eV	16 eV	17 eV	20 eV
0°	8.779(-3)	1.599(-2)	3.081(-2)	5.170(-2)	6.889(-2)	9.632(-2)
30°	8.611(-3)	1.253(-2)	2.145(-2)	3.462(-2)	4.534(-2)	5.945(-2)
45°	8.878(-3)	1.073(-2)	1.563(-2)	2.368(-2)	3.053(-2)	3.939(-2)
60°	9.784(-3)	1.076(-2)	1.277(-2)	1.695(-2)	2.071(-2)	2.603(-2)
90°	1.413(-2)	1.876(-2)	1.978(-2)	2.012(-2)	1.918(-2)	1.664(-2)
120°	2.153(-2)	3.825(-2)	4.661(-2)	4.920(-2)	4.687(-2)	3.580(-2)
135°	2.563(-2)	5.033(-2)	6.457(-2)	6.985(-2)	6.787(-2)	5.251(-2)
150°	2.926(-2)	6.137(-2)	8.128(-2)	8.931(-2)	8.789(-2)	6.880(-2)
180°	3.273(-2)	7.217(-2)	9.780(-2)	1.086(-1)	1.079(-1)	8.522(-2)
total cross section (πa_0^2)	6.490(-2)	1.067(-1)	1.341(-1)	1.530(-1)	1.589(-1)	1.486(-1)

Figure Captions

Figure 1. Continuum Franck-Condon factor, $q_{o\nu'}$, for the transition $X^1\Sigma_g^+ \rightarrow b^3\Sigma_u^+$ in molecular hydrogen. Normalization is chosen so that $\int_o^\infty q_{o\nu'} d\, k_{nuc} = 1$, where k_{nuc} is the relative momentum of the dissociating protons in atomic units.

Figure 2. Differential cross sections for the transition $X^1\Sigma_g^+ \rightarrow b^3\Sigma_u^+$ in molecular hydrogen. Cross sections are given in units of a_o^2. Curves on the left (running top to bottom) are for incident electron energies of 13, 14 and 15 eV respectively; curves on the right (top to bottom) are for electron energies of 16, 17 and 20 eV.

Figure 3. Differential cross sections for the transition $X^1\Sigma^1 \rightarrow a^3\Sigma_g^+$ in molecular hydrogen. Cross sections are given in units of a_o^2. Incident electron energies are the same as in Figure 2.

Figure 4. Dissociation cross section of H_2 into 2H by electron impact. Cross sections are in units of πa_o^2. (o), present results; (————), experimental curve (ref. 29), after subtraction of ionization cross section (see refs. 30 and 24); (- - -), Ochkur-Rudge calculations (ref. 24); (— — — —), Ochkur calculation (ref. 28).

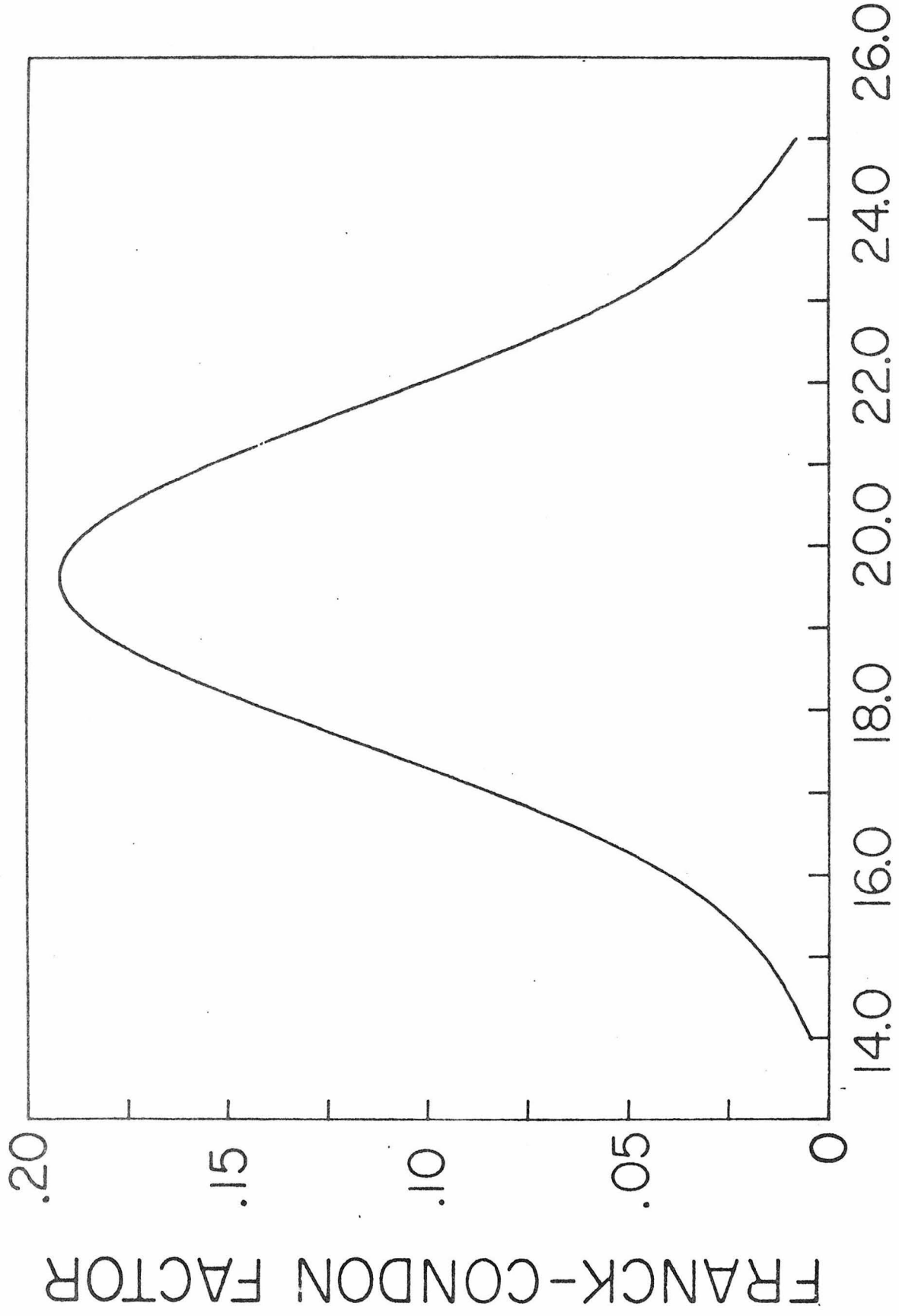

FRANCK-CONDON FACTOR
.20
.15
.10
.05
0
14.0
16.0
18.0
20.0
22.0
24.0
26.0
NUCLEAR MOMENTUM (a.u.)

Figure 1.

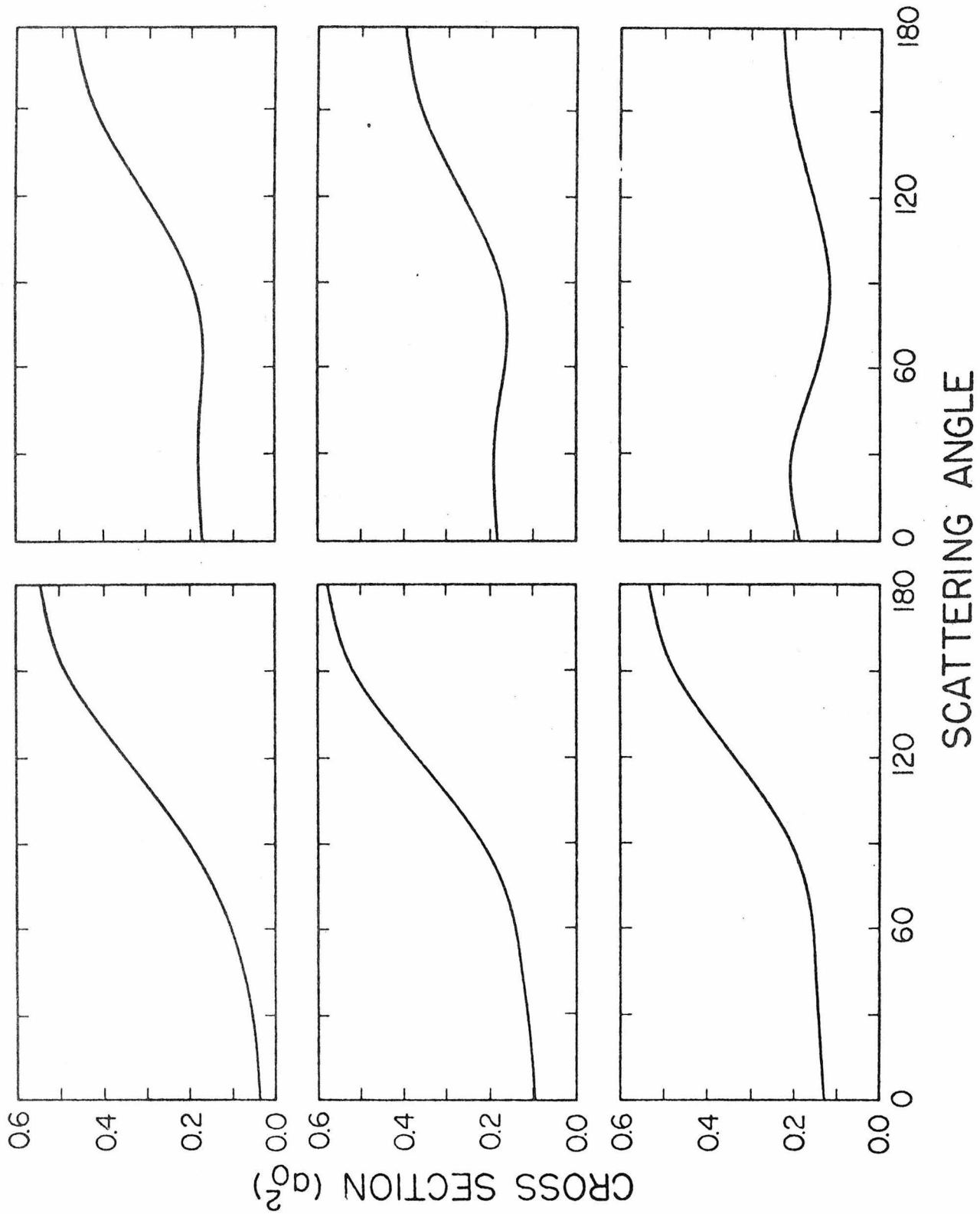


Figure 2.

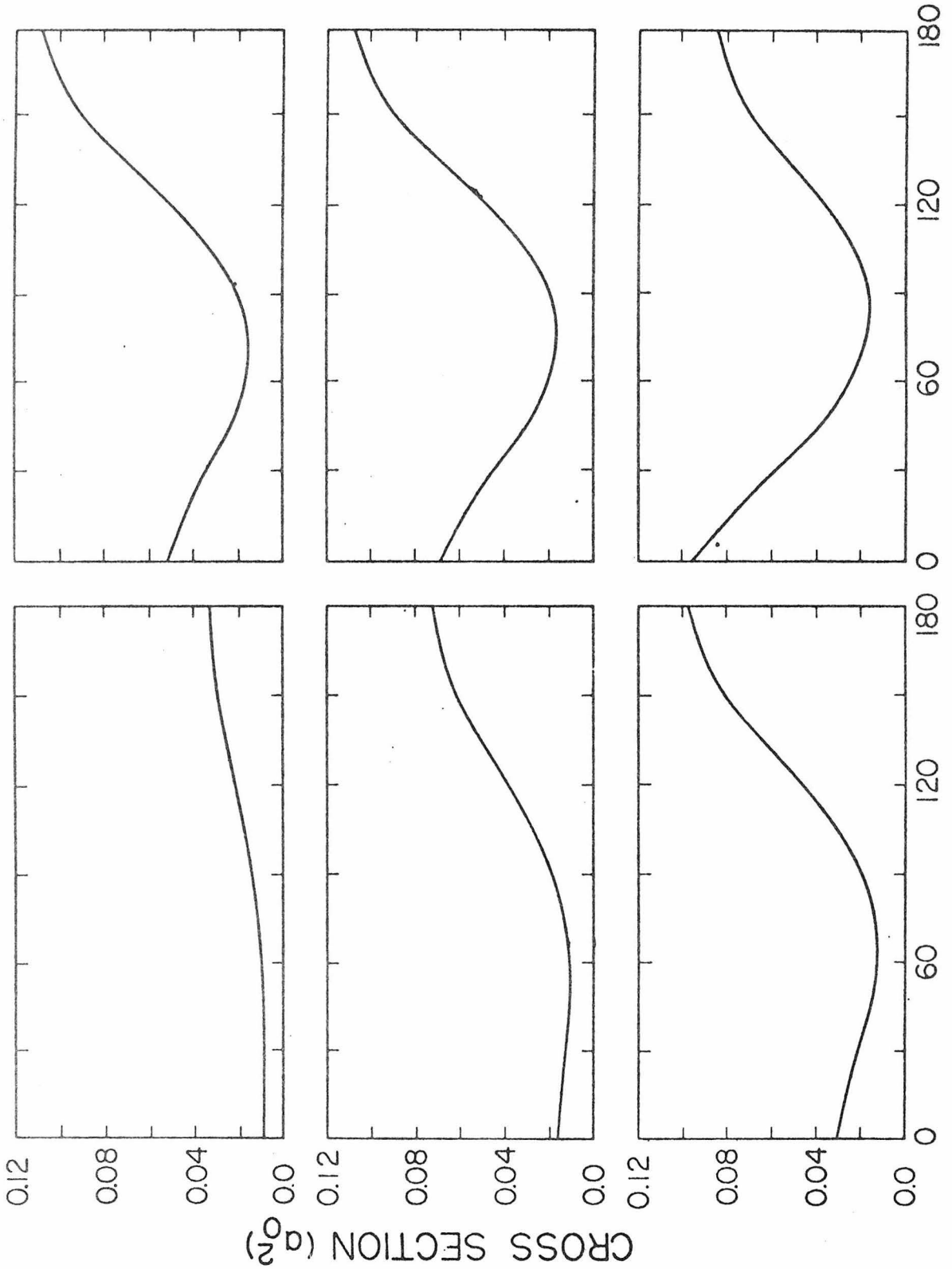

CROSS SECTION (a_0^2)
0.12
0.08
0.04
0.0
0
60
120
180
SCATTERING ANGLE

Figure 3.

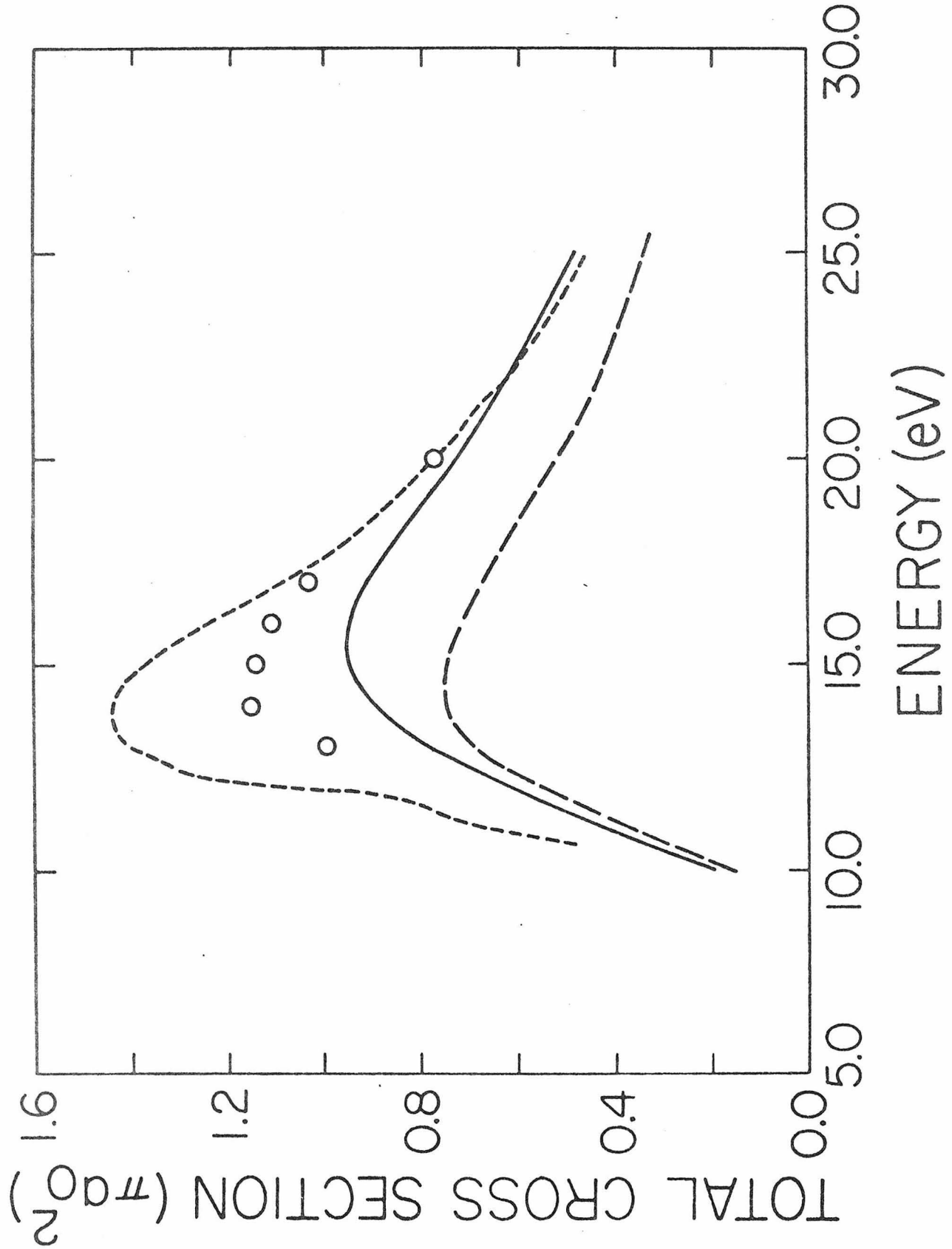

TOTAL CROSS SECTION (πa_0^2)
1.6
1.2
0.8
0.4
0.0
5.0
10.0
15.0
20.0
25.0
30.0
ENERGY (eV)

Figure 4.

APPENDIX

The Born Approximation in Electron-Molecule Scattering Using the Random Phase Approximation

SECTION A

The Equations of Motion Method: Inelastic Electron Scattering for Helium and CO_2 in the Born Approximation

I. INTRODUCTION

We have previously discussed the equations of motion (EOM) method as an approach for directly calculating spectroscopic properties of molecules, e.g., transition energies and optical intensities.[1,2] The EOM is a theory specifically designed for calculating relative and response properties of atoms and molecules and does not entail the calculation of highly accurate wavefunctions and absolute energies for each electronic state. We solve the equations of motion for the operator O_λ^+ which generates the excited state $|\lambda\rangle$ from the ground state $|0\rangle$, and express transition amplitudes and matrix elements between the ground and excited states in terms of this operator. In the EOM the approximation, including single particle-hole (1p-1h) and two-particle--two-hole (2p-2h) components in O_λ^+, gives results for transition energies and intensities in N_2, CO, C_2H_4,[3] C_6H_6,[4] and H_2CO[5] which are in good agreement with experiment.

The calculation of Born differential cross sections and generalized oscillator strengths requires the computation of the matrix elements of a simple operator between the ground and excited electronic states. The equations of motion approach is ideally suited for calculating such quantities with a minimum of computational effort. In this paper we present results of calculations on generalized oscillator strengths of helium and carbon dioxide. Our results for helium agree well with the very extensive calculations of Kim and Inokuti.[6] Our results on carbon dioxide are compared with experiment,

and assignments in the CO_2 spectrum are discussed. In particular, we can identify the experimental generalized oscillator strengths of Lassettre and Shiloff[7] for transitions at 8.61 and 9.16 eV with that of the $^1\Pi_g$ state of CO_2.

In the following two sections we briefly outline the theory of the Born approximation and the equations of motion method. Sections V and VI give the results for helium and carbon dioxide.

II. BORN APPROXIMATION

Consider a process in which an electron of mass m, charge e, and initial momentum $\hbar\vec{k}$ is scattered inelastically by a stationary atom or molecule into solid angle element $d\omega$ in the center of mass coordinate system. The final momentum of the electron is $\hbar\vec{k}'$, and the target atom or molecule is left in excited state n. The differential cross section in the Born approximation is[8]

$$d\sigma_n = \left(\frac{2me^2}{\hbar^2K^2}\right)^2 \frac{k'}{k} \left|\epsilon_n(K)\right|^2 d\omega, \tag{1}$$

where $\hbar\vec{K} = \hbar(\vec{k} - \vec{k}')$ is the momentum transfer vector. If the target is an N electron atom the matrix element $\epsilon_n(\vec{K})$ is[8]

$$\epsilon_n(\vec{K}) = \int \varphi_n^* \sum_{j=1}^{N} e^{i\vec{K}\cdot\vec{r}_j} \varphi_0 \, d^3r_1 \cdots d^3r_N, \tag{2}$$

where φ_0 and φ_n are the ground and excited state eigenfunctions of the atom in terms of the electronic coordinates $\vec{r}_i$. For a molecular

target with M nuclei and N electrons $\epsilon_n(\vec{K})$ is given by

$$\epsilon_n(\vec{K}) = \int \psi_n^* \sum_{j=1}^{N} e^{i\vec{K}\cdot\vec{r}_j} \psi_0 \; d^3r_1 \cdots d^3r_N \, d^3R_1 \cdots d^3R_M, \quad (3)$$

where ψ_0 and ψ_n are the ground and excited state eigenfunctions of the molecule and depend on both the electronic coordinates $\vec{r}_i$ and nuclear coordinates $\vec{R}_i$.

Several simplifying assumptions can be applied to Eq. (3). First we make the Born-Oppenheimer separation and neglect rotational-vibrational coupling.[8] Since rotational levels are not usually resolved in current experiments, a sum over final and an average over initial rotational states can be performed yielding an average over molecular orientations.[8-10] The expression for $\epsilon_n(\vec{K})$ is now an integral involving vibrational and electronic wavefunctions only. We will not consider vibrational levels explicitly in our calculations, and a sum over final vibrational states gives an expression for scattering into all vibrational levels of the excited electronic configuration.[9] The expression for $\epsilon_n(\vec{K})$ for molecular targets becomes

$$\epsilon_n(\vec{K}) = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \left| \langle u_n | \sum_{j=1}^{N} e^{i\vec{K}\cdot\vec{r}_j} | u_0 \rangle \right|^2 \sin\theta d\theta \, d\psi \quad (4)$$

u_0 and u_n are the ground and excited electronic eigenfunctions respectively. The inner integration in Eq. (4) is over electronic coordinates only. In Eq. (4) the Euler angles θ and ψ between a system of coordinates fixed in the molecule and a space-fixed frame (in which the momentum transfer vector $\hbar\vec{K}$ lies along the Z axis)

are defined in Figure 1. The dependence of the electronic matrix element on θ and ψ appears explicitly in $\vec{K} \cdot \vec{r}_j$ as

$$\vec{K} \cdot \vec{r}_j = K(x_j \sin\theta\sin\psi + y_i \sin\theta\cos\psi + z_j\cos\theta), \qquad (5)$$

where x_j, y_j, and z_j are electronic coordinates in the molecule-fixed frame. The integration over molecular orientations must in general be performed numerically. This is discussed further in section IV. It should be noted that $\epsilon_n(\vec{K})$ in Eq. (2) or (4) is a function of only the magnitude of $\vec{K}$.

The generalized oscillator strength, which, though directly related to the differential cross section, is more useful in the comparison of experimental and theoretical results.[22] If ΔE_n is the transition energy between the ground and excited states, and R and a_0 denote the Rydberg energy and Bohr radius respectively, the generalized oscillator strength $f_n(K)$ is defined by[8]

$$f_n(K) = \frac{\Delta E_n/R}{(Ka_0)^2} \left| \epsilon_n(K) \right|^2. \qquad (6)$$

This quantity is independent of incident energy at energies for which the Born approximation is valid, and approaches the familiar optical oscillator strength as the momentum transfer K goes to zero. For further details of the application of the Born approximation to electron-molecule scattering, including sum rules satisfied by $f_n(K)$, the reader is referred to the excellent review on the subject by Inokuti.[8]

III. EQUATIONS OF MOTION METHOD

The equations of motion method has been discussed in detail elsewhere,[1,2] and only a brief summary of the theory will be given here. The operator O_λ^+ which generates excited state $|\lambda\rangle$ from the ground state $|0\rangle$ can be shown to be exactly a solution of the equation of motion[11]

$$\langle 0 \,|[\delta O_\lambda, H, O_\lambda^+]\,| 0\rangle = \omega_\lambda \langle 0 \,|[\delta O_\lambda, O_\lambda^+]\,|0\rangle \tag{7}$$

for all variations δO_λ^+ in the amplitudes specifying O_λ^+. In equation (7) ω_λ denotes the excitation frequency and the double commutator is defined as

$$2[A, B, C] = [[A, B], C] + [A, [B, C]]. \tag{8}$$

If O_λ^+ is restricted to single particle-hole (1p-1h) form, Eq. (7) becomes the matrix equation for the amplitudes $\{Y_{m\gamma}\}$ and $\{Z_{m\gamma}\}$.

$$\begin{bmatrix} \underset{\sim}{A} & \underset{\sim}{B} \\ -\underset{\sim}{B}^* & -\underset{\sim}{A}^* \end{bmatrix} \begin{bmatrix} Y(\lambda) \\ Z(\lambda) \end{bmatrix} = \omega_\lambda \begin{bmatrix} \underset{\sim}{D} & 0 \\ 0 & \underset{\sim}{D} \end{bmatrix} \begin{bmatrix} Y(\lambda) \\ Z(\lambda) \end{bmatrix} \tag{9}$$

The elements of the matrices $\underset{\sim}{A}$, $\underset{\sim}{B}$, and $\underset{\sim}{D}$ are given elsewhere.[1] It has been shown that the theory including two-particle--two-hole (2p-2h) components is equivalent to the 1p-1h theory with a renormalized interaction.[2] In addition an approximate perturbative scheme has been developed for calculating the correction to the transition energies due to the effect of the 2p-2h components.[2] In the 1p-1h theory the matrix element $M_{o\lambda}$ of any one electron operator between

state $|\lambda\rangle$ and the ground state $|0\rangle$ is given (to second order in the correlation coefficients of the ground state) by[3]

$$M_{0\lambda} = \langle 0|M|\lambda\rangle = \sqrt{2} \sum_{m\gamma} \{Y^*_{m\gamma}(\lambda)M_{m\gamma} + Z^*_{m\gamma}(\lambda)M_{m\gamma}\}, \qquad (10a)$$

$$M_{m\gamma} = M^\circ_{m\gamma} + \sum_{\delta} M^\circ_{m\delta}\rho^{(2)}_{\gamma\delta} - \sum_{n} M^\circ_{n\gamma}\rho^{(2)}_{mn} \qquad (10b)$$

$M^\circ_{m\gamma}$ is the matrix element between a hole orbital γ and a particle orbital m, and $\rho^{(2)}_{ij}$ is the contribution to the density matrix which is quadratic in the correlation coefficients. We will make use of Eq. (10) in computing $\epsilon_n(K)$ of equations (2) and (4) in the 1p-1h approximation. The 2p-2h amplitudes will have only a small effect on the matrix elements of single particle operators, and hence we neglect 2p-2h contributions to $M_{o\lambda}$.

IV. COMPUTATIONAL DETAILS

The first step in the calculation of the generalized oscillator strengths is to carry out a Hartree-Fock calculation on the ground state of the target atom or molecule to generate a particle-hole basis. The SCF calculations were done in a basis of Gaussian orbitals. A [12S/8P] basis for the calculation on helium was constructed using exponents suggested by Huzinaga[12] as well as additional diffuse S functions and one additional valence P Gaussian. Contraction coefficients for the S functions were obtained from calculations by Guberman.[13] For the calculation on CO_2 a valence [3S/2P] basis of contracted Gaussian orbitals was constructed from the (7S/3P)

set suggested by Whitman and Hornback.[14] This basis was augmented by a (1S/1P) set of diffuse functions. The basis functions in our calculations are given in Table I.

With the particle-hole basis from the SCF calculation, the 1p-1h equations of motion are solved for the $Y(\lambda)$ and $Z(\lambda)$ amplitudes and the 1p-1h approximation to the transition energies, and the 2p-2h corrections to the transition energies are computed. Then the matrix elements for the generalized oscillator strength are calculated using equation (10). The matrix elements of $\exp(i\vec{K}\cdot\vec{r})$ can be expressed in terms of integrals involving Gaussian orbitals on different centers A and B

$$N_A N_B I_x I_y I_z = \int dV \exp(i\vec{K}\cdot\vec{r})\varphi_A\varphi_B \tag{11}$$

where φ_A and φ_B are Gaussian orbitals at centers A and B, and N_A and N_B are normalization constants. I_x, I_y, and I_z denote the integrals over x, y, and z, i.e.,

$$I_x = \int_{-\infty}^{\infty} dx' (x'-A_x)^{\ell}(x'-B_x)^{m}\exp[\, iKq_x x' - \zeta_A(x'-A_x)^2 - \zeta_B(x'-B_x)^2\,]\, dx' \tag{13}$$

where A_x and B_x are the x coordinates of centers A and B; ζ_A and ζ_B are Gaussian exponents and the vector $q=(\sin\theta\sin\psi,\ \sin\theta\cos\psi,\ \cos\theta)$. This integral can be performed to give[15]

$$I_x = \left(\frac{\pi}{\lambda}\right)^{\frac{1}{2}} \exp\left[iKq_x p_x - \frac{(Kq_x)^2 + 4\zeta_A\zeta_B(A_x - B_x)^2}{4\lambda}\right]$$

$$\times \sum_{k=0}^{\ell} \binom{\ell}{k} \left(\frac{\zeta_B(B_x - A_x)}{\lambda}\right)^{\ell-k} \sum_{j=0}^{m} \binom{m}{j} \left(\frac{\zeta_A(A_x - B_x)}{\lambda}\right)^{m-j} \tag{14}$$

$$\times \left(\frac{i}{2\lambda^{\frac{1}{2}}}\right)^{k+j} H_{k+j}\left(\frac{Kq_x}{2\lambda^{\frac{1}{2}}}\right)$$

where $\lambda = (\zeta_A + \zeta_B)$, $p_x = (\zeta_A A_x + \zeta_B B_x)/\lambda$, H_n is a Hermite polynomial, and $\binom{\ell}{k}$ is a binomial coefficient.

To compute the generalized oscillator strength for molecules an integration over molecular orientations is required. For the linear geometry of CO_2, we may perform the ψ integration analytically to obtain a factor of 2π. The θ integration was performed using 8 point Gauss-Legendre quadrature in $\cos\theta$.

V. HELIUM

Helium provides a test case for the equations of motion approach to high-energy inelastic electron scattering uncomplicated by the necessity of numerical averaging over orientations. No particle states were truncated from the particle basis for helium prior to performing the EOM calculation. The results of the EOM calculation are compared with experiment and other theoretical results in Table II, and the agreement for both transition energies and optical oscillator strengths is quite good. The generalized oscillator strengths were computed

over a grid of thirty points between zero and sixteen atomic units in K^2, and are shown in Table III as $f_n(K)/\Delta E$. Our results agree well with a similar calculation on helium by Schneider.[26]

Measurements of absolute cross sections are difficult to make, and consequently experimental data is often scaled to a known optical limit or normalized to a theoretical calculation.[16] However, for helium the definitive calculations of Kim and Inokuti[6] provide an excellent standard of comparison. Kim and Inokuti[6] have used accurate Weiss CI wavefunctions to compute generalized oscillator strengths for transitions from the ground state to the 2^1S, 3^1S, 2^1P, and $3\ ^1P$ states as well as for a number of other transitions. The accuracy of their results is demonstrated by close agreement with experiment as well as by agreement of their results using the "length" and "velocity" formulas for the generalized oscillator strength. The results of our calculations using the equations of motion method are compared in Table IV with the results of Kim and Inokuti at representative points, and in Figure 2 our results are plotted with those of Kim and Inokuti.[6] In calculating $f_n(K)$ using equation (6) we use the transition energy ΔE_n in the 1p-1h approximation to be consistent with the fact that the $Y_{m\gamma}$ and $Z_{m\gamma}$ amplitudes are computed using only 1p-1h components. Agreement is good; an average deviation of less than 5% is found for the four transitions for $K^2 < 9$ a.u.

VI. CARBON DIOXIDE

Tables V, VI, and VII give orbital energies of CO_2 from the Hartree-Fock calculation and the results of the equations of motion

calculation on transition energies and optical oscillator strengths. In the EOM calculation hole states with energies less than -10 Hartrees and particle states above 10 Hartrees were truncated from the particle-hole basis. There are many features in the carbon dioxide UV absorption[17] and electron impact[18] spectra with uncertain assignments. The transition energies from the EOM calculation can aid in the identification of several of these features. However, transition energies do not constitute a complete description of the spectrum, and the generalized and optical oscillator strengths for the singlet-singlet transitions can also play an important part in determining assignments.

The generalized oscillator strengths calculated for seven states of CO_2 are given in Figure 3 and Table VIII. Of these seven states only the $1\ ^1\Delta_u$ is completely valence like, and there is no minimum in the generalized oscillator strength for this state.[21] The $f_n(K)$ for the other states, with the exception of the $^1\Sigma_g^+$ state, show minima of different depths.

The assignment of the $1\ ^1\Delta_u$ and $^1\Pi_g$ states in the optical and electron impact spectra is a problem of current interest. In the UV absorption spectrum the peaks observed at 9.31 and 8.41 eV[19] have been variously assigned as two components of the $^1\Pi_g$ transition split by vibrational effects,[7] as the $^1\Pi_g$ and $^1\Delta_u$, respectively,[19] and together as the $^1\Delta_u$.[20] Lassettre and Shiloff[7] have reported the differential generalized oscillator strength f′ for peaks in the electron impact energy loss spectrum at 8.61 and 9.16 eV,[7] and their data

is plotted in Figure 4. The integral of f′ over a peak in the energy loss spectrum gives the generalized oscillator strength for that transition assuming only one transition contributes to the peak.[22] As an approximation one may assume that the ratio b of peak area to height is constant over scattering angle so that the generalized oscillator strength is $f \simeq bf'$, where f′ is measured at the maximum of the peak.[22] Lassettre and Shiloff[7] find that as the scattering angle increases the two peaks at 9.16 and 8.61 eV merge into one peak at 9.12 eV.[7] Thus they were unable to determine a value of b for each peak separately. It should be noted from Figure 4, however, that the two differential generalized oscillator strengths are qualitatively very much the same. Lassettre and Shiloff[7] assert on the basis of this evidence and an argument relating the shape of the envelope of the 9.12 eV transition to vibronic effects, that the two peaks observed are components of the $^1\Pi_g$ transition.

The theoretical results for the generalized oscillator strengths of the $^1\Pi_g$ and 1 $^1\Delta_u$ transitions are compared in Figure 4 with the experimental f′ data for the 9.16 eV peak. Since no $\underline{b}$ value is given by Lassettre and Shiloff, a value found by least squares analysis was used for purposes of qualitative comparison. Also because the computed transition energies and the energies of the experimental peaks differ slightly, the oscillator strengths were divided by their associated transition energies to make comparison easier. It can be seen from Figure 4 that the theoretical $f_n(K)$ of the $^1\Pi_g$ state is qualitatively much the same as the f′ for both the 9.16 and 8.61 eV peaks, whereas

that of the $^1\Delta_u$ is not. Lassettre and Shiloff[7] perform an extrapolation of the f′ curves to obtain maxima at $K^2 \simeq 0.2$ a.u.,[2] in good agreement with the calculated maximum at about 0.25 of the $^1\Pi_g$ state. The maximum in the theoretical $f_n(K)$ for the $^1\Delta_u$ state is at a much higher value of momentum transfer, $K^2 \simeq 4.5$ a.u.[2]

The above comparison strongly supports the assertion of Lassettre and Shiloff[7] that the generalized oscillator strengths they observe at 8.61 and 9.16 eV are due (at least predominantly) to the $^1\Pi_g$ transition. However, the UV absorption spectrum of these two peaks show markedly different vibrational structure.[19] This fact leads Rabalais et al.,[19] to assign the 8.41 eV peak in the optical spectrum to the $^1\Delta_u$ transition and the 9.31 eV peak to the $^1\Pi_g$. The unambiguous assignment of these two peaks in the CO_2 spectrum must await higher resolution electron impact measurements as well as careful vibrational analysis of the optical spectrum. Tentatively we can assign at least the 9.31 eV peak in the optical spectrum to the $^1\Pi_g$ and speculate that the 8.4 eV peak contains contributions from both the $^1\Pi_g$ and $^1\Delta_u$ transitions.

The two lowest optically allowed transitions of CO_2 occur at 11.08 and 11.4 eV, and these peaks have been assigned by different investigators to the $^1\Sigma_u^+$ and $^1\Pi_u$ states and vice versa.[18,19,23] The transition energies from the EOM calculation suggest assigning these peaks as $^1\Sigma_u^+$ at 11.08 eV and $^1\Pi_u$ at 11.4 eV. The calculated optical oscillator strength of 0.116 for the $^1\Sigma_u^+$ state agrees well with the experimental value for the 11.08 eV transition of 0.12.[24]

Lassettre and Shiloff[7] have measured the generalized oscillator strength for the 11 eV transition. They note that there may be a weak maximum in the $f_n(K)$ of this peak at $K^2 \simeq 2$ a.u.[2] Our theoretical $f_n(K)$ for the $^1\Sigma_u^+$ state shows a maximum at $K^2 \simeq 1.75$ a.u.[2] in agreement with the location of the maximum tentatively identified experimentally, while the $^1\Pi_u$ generalized oscillator strength has a maximum only beyond 4 a.u.[2] Otherwise both theoretical generalized oscillator strength curves are qualitatively the same as the experimental results for the transition at 11 eV. Although the above comparison is not conclusive it tends to substantiate the assignment of the 11.08 eV peak in the optical spectrum as the $^1\Sigma_u^+$ transition.

Krauss et al.[27] and Lawrence[28] have suggested that there is an underlying continuum absorption in CO_2 in the range 11-14 eV due to a transition to a valence-like interloper state of $^1\Sigma_u^+$ symmetry. Our calculations yield a valence-like $^1\Sigma_u^+$ state occurring with a vertical transition energy of approximately 12-12.5 eV (from results of two independent calculations), which has an optical oscillator strength f = 0.64. We cannot definitely assign this state to the continuum absorption without first computing its energy surface. However it seems likely this state corresponds to the valence $^1\Sigma_u^+$ state calculated by Krauss et al.[27] using an approximate SCF method.

The threshold electron impact spectrum of CO_2 has been measured by Hubin-Franskin and Collins by the SF_6 scavenger technique.[25] The energies of transitions seen in this spectrum are displaced by a few tenths of an electron volt from their counterparts in the optical spectrum. Peaks are observed in the threshold spectrum at 8.55 at 9.3 eV corresponding to the 8.41 and 9.31 eV transitions in the optical spectrum. Just below these transitions a peak is observed at 8.0 eV whose intensity decreases markedly for energies just above threshold suggesting that this peak is due to a transition to a triplet state. From the EOM transition energies we may tentatively assign this peak to the $^3\Delta_u$ state which is calculated to lie at 8.06 eV. The next transition of lower energy observed in the threshold electron impact spectrum is at 7.5 eV, and we may assign it in a similarly tentative manner to the $^3\Sigma_u^+$ state.

The assignments in the CO_2 spectrum which we have made are tabulated and the calculated transition energies compared with experiment in Table IX.

VII. CONCLUSIONS

We have discussed calculations on the excited states of helium and carbon dioxide, including the computation of generalized and optical oscillator strengths, as an application of the equations of motion method. Generalized oscillator strengths calculated for helium using the EOM agree well with other theoretical calculations. We have discussed assignments in the electronic spectrum of carbon

dioxide including the $^1\Pi_g$, $^1\Delta_u$, $^1\Sigma_u^+$ and $^1\Pi_u$ states. The error in the calculated transition energies of the states we have assigned is less than 10% in all cases. The comparison of our theoretical generalized oscillator strengths with those measured for carbon dioxide by Lassettre and Shiloff[7] proves helpful in making spectral assignments.

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Table I. Basis Functions

Helium			
S		P	
Exponent	Coefficient	Exponent	Coefficient
3293.69	0.004615	4.50000	1.0
488.894	0.036575	1.45337	1.0
108.772	0.197834	0.34627	1.0
30.1799	0.827072	0.11191	1.0
9.78905	1.0	0.04216	1.0
3.52226	1.0	0.01702	1.0
1.35244	1.0	0.01127	1.0
0.55261	1.0	0.00510	1.0
0.24092	1.0		
0.10795	1.0		
0.04837	1.0		
0.02167	1.0		
0.00971	1.0		
0.00300	1.0		
0.00100	1.0		

Table I. (Cont'd)

Oxygen			
S		P	
Exponent	Coefficient	Exponent	Coefficient
2200.0	0.009108	8.3560	0.221135
332.20	0.066636	1.7190	0.872694
76.930	0.288115	0.3814	1.0
21.740	0.730114	0.0400	1.0
6.7730	1.0		
1.1030	0.454600		
0.3342	0.605065		
0.0480	1.0		

Carbon			
S		P	
Exponent	Coefficient	Exponent	Coefficient
994.70	0.011529	4.2970	0.209524
160.00	0.075741	0.8699	0.881228
39.910	0.291275	0.2036	1.0
11.820	0.716418	0.0300	1.0
3.6980	1.0		
0.6026	0.410040		
0.1817	0.648033		
0.0360	1.0		

Table II. Transition Energies and Optical Oscillator Strengths for Helium.

State	ΔE^a (1p-1h)	ΔE^a (1p-1h) + (2p-2h)	ΔE^b Exper	f_n	$f_n{}^c$ Other work
$2\,^3S$		20.00	19.82		
$2\,^1S$	22.22	20.88	20.61		
$2\,^3P$		21.24	20.96		
$2\,^1P$	22.78	21.51	21.22	0.2643	0.276
$3\,^3S$		22.91	22.72		
$3\,^1S$	24.47	23.14	22.92		
$3\,^3P$		23.22	23.01		
$3\,^1P$	24.63	23.32	23.09	.0735	0.0734

[a] Basis set is [12s18p] and energies are in eV. See text.

[b] C. E. Moore, Natl. Bur. Std. Circular No. 467 (1949).

[c] B. Schiff and C. L. Pekeris, Phys. Rev., 134, A638 (1964).

Table III. $f_n(K)/\Delta E_n$ for Helium[a]

K^2[b]	$2\ ^1S$	$3\ ^1S$	$2\ ^1P$	$3\ ^1P$
0.018	1.3840(-3)	3.0402(-4)	2.5670(-1)	7.1774(-2)
0.071	5.1150(-3)	1.1489(-3)	2.3535(-1)	6.7041(-2)
0.160	1.0112(-2)	2.3480(-3)	2.0423(-1)	5.9854(-2)
0.284	1.5074(-2)	3.6483(-3)	1.6841(-1)	5.1105(-2)
0.444	1.8934(-2)	4.7921(-3)	1.3264(-1)	4.1786(-2)
0.640	2.1120(-2)	5.5876(-3)	1.0035(-1)	3.2820(-2)
0.871	2.1572(-2)	5.9512(-3)	7.3365(-2)	2.4864(-2)
1.138	2.0595(-2)	5.9019(-3)	5.2148(-2)	1.8253(-2)
1.440	1.8654(-2)	5.5277(-3)	3.6244(-2)	1.3050(-2)
1.778	1.6214(-2)	4.9447(-3)	2.4760(-2)	9.1340(-3)
2.151	1.3648(-2)	4.2639(-3)	1.6702(-2)	6.2894(-3)
2.560	1.1205(-2)	3.5718(-3)	1.1171(-2)	4.2797(-3)
3.004	9.0255(-3)	2.9254(-3)	7.4327(-3)	2.8892(-3)
3.484	7.1668(-3)	2.3551(-3)	4.9346(-3)	1.9415(-3)
4.000	5.6319(-3)	1.8717(-3)	3.2770(-3)	1.3024(-3)
4.551	4.3938(-3)	1.4738(-3)	2.1811(-3)	8.7411(-4)
5.138	3.4120(-3)	1.1532(-3)	1.4572(-3)	5.8808(-4)
5.760	2.6427(-3)	8.9877(-4)	9.7840(-4)	3.9719(-4)
6.418	2.0049(-3)	6.9904(-4)	6.6076(-4)	2.6962(-4)
7.111	1.5829(-3)	5.4339(-4)	4.4915(-4)	1.8411(-4)
7.840	1.2268(-3)	4.2267(-4)	3.0746(-4)	1.2654(-4)
8.604	9.5288(-4)	3.2927(-4)	2.1204(-4)	8.7599(-5)
9.404	7.4208(-4)	2.5707(-4)	1.4739(-4)	6.1098(-5)

Table III. (Cont'd)

K^{2b}	$2\,^1S$	$3\,^1S$	$2\,^1P$	$3\,^2P$
10.240	5.7972(-4)	2.0125(-4)	1.0330(-4)	4.2950(-5)
11.111	4.5447(-4)	1.5805(-4)	7.3007(-5)	3.0438(-5)
12.018	3.5761(-4)	1.2454(-4)	5.2042(-5)	2.1749(-5)
12.960	2.8250(-4)	9.8500(-5)	3.7415(-5)	1.5669(-5)
13.938	2.2407(-4)	7.8196(-5)	2.7127(-5)	1.1381(-5)
14.951	1.7845(-4)	6.2317(-5)	1.9829(-5)	8.3321(-6)
16.000	1.4270(-4)	4.9857(-5)	1.4608(-5)	6.1468(-6)

[a] Notation is, e.g., 1.3840(-3) = 1.3840×10^{-3}.

[b] In atomic units.

Table IV. Comparison at Selected Points with Calculations Using Accurate Weiss CI Wavefunctions for Helium.

K^2 (a.u.)	$2\,^1S$ This work[a]	$2\,^1S$ Kim and Inokuti[b]	$3\,^1S$ This work[a]	$3\,^1S$ Kim and Inokuti[b]
0.25	1.3903×10^{-2}	1.4683×10^{-2}	3.3284×10^{-3}	3.3168×10^{-3}
1.00	2.1235×10^{-2}	2.2493×10^{-2}	5.9738×10^{-3}	5.9352×10^{-3}
4.00	5.6319×10^{-3}	5.9528×10^{-3}	1.8717×10^{-3}	1.8502×10^{-3}
9.00	8.4059×10^{-4}	8.6148×10^{-4}	2.9085×10^{-4}	2.7911×10^{-4}
	$2\,^1P$		$3\,^1P$	
0.25	1.7753×10^{-1}	1.8596×10^{-1}	5.3385×10^{-2}	5.3618×10^{-2}
1.00	6.2049×10^{-2}	6.5431×10^{-2}	2.1381×10^{-2}	2.1671×10^{-2}
4.00	3.3277×10^{-3}	3.4485×10^{-3}	1.3024×10^{-3}	1.3116×10^{-3}
9.00	1.7661×10^{-4}	1.7346×10^{-4}	7.3088×10^{-5}	6.7427×10^{-5}

[a] EOM results with [12s/8p] basis.

[b] Reference 6.

Table V. SCF Molecular Orbital Eigenvalues for CO_2.[a]

MO		ϵ_γ[b]	MO		ϵ_m	MO		ϵ_m
1	$1\sigma u^+$	-20.7220	12	$5\sigma g^+$	0.0389	26	$8\sigma g^+$	0.5437
2	$1\sigma g^+$	-20.7204	13	$2\pi ux$	0.0577	27	$5\pi ux$	1.0049
3	$2\sigma g^+$	-11.5469	14	$2\pi uy$	0.0577	28	$5\pi uy$	1.0049
4	$3\sigma g^+$	- 1.5737	15	$4\sigma u^+$	0.0667	29	$7\sigma u^+$	1.0414
5	$2\sigma u^+$	- 1.5414	16	$6\sigma g^+$	0.1390	30	$8\sigma u^+$	1.2242
6	$4\sigma g^+$	- 0.7967	17	$2\pi gx$	0.1450	31	$3\pi gx$	1.8319
7	$3\sigma u^+$	- 0.7456	18	$2\pi gy$	0.1450	32	$3\pi gy$	1.8319
8	$1\pi ux$	- 0.7437	19	$3\pi ux$	0.1728	33	$6\pi ux$	2.0289
9	$1\pi uy$	- 0.7437	20	$3\pi uy$	0.1728	34	$6\pi uy$	2.0289
10	$1\pi gx$	- 0.5460	21	$5\sigma u^+$	0.1734	35	$9\sigma u^+$	2.0469
11	$1\pi gy$	- 0.5460	22	$4\pi ux$	0.2047	36	$9\sigma g^+$	2.0710
			23	$4\pi uy$	0.2047	37	$10\sigma g^+$	13.0305
			24	$7\sigma g^+$	0.2294	38	$11\sigma g^+$	23.0554
			25	$6\sigma u^+$	0.2808	39	$10\sigma u^+$	24.3690

[a] In a ([3s/2p] + R(1s/1p)) basis of contracted Gaussians, with R_{C-O} = 2.192 a.u. This basis gives a ground state E_{SCF} = -187.29846 a.u.

[b] In atomic units.

Table VI . EOM Calculation of Singlet Excited States of CO_2.

Transition	ΔE^a (1p-1h)	$\Delta E^{a,b}$ (1p-1h) + (2p-2h)	$f_o{}^c$	$\Delta(\langle x^2\rangle + \langle y^2\rangle)^d$	Dominant[d] Components
$^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^-$	11.63	8.53		1.24	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow 1\,{}^1\Delta_u$	11.98	8.56		1.36	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow {}^1\Pi_g$	11.87	8.62		15.3	$1\pi_g \rightarrow \sigma_g^*$
$^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$	13.87	10.29	0.116	35.5	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow 2\,{}^1\Delta_u$	13.91	10.42		35.3	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow {}^1\Pi_u$	14.20	10.97	0.1680	22.4	$1\pi_g \rightarrow \sigma_u^*$
$^1\Sigma_g^+ \rightarrow {}^1\Delta_g$	15.56	12.60		20.9	$1\pi_g \rightarrow \pi_g^*$
$^1\Sigma_g^+ \rightarrow {}^1\Sigma_g^+$	16.09	12.63		24.0	$1\pi_g \rightarrow \pi_g^*$
$^1\Sigma_g^+ \rightarrow {}^1\Sigma_g^-$	15.42	12.78		15.1	$1\pi_g \rightarrow \pi_g^*$

[a] In electron volts.

[b] Best approximation to transition energies.

[c] Optical oscillator strength assuming Franck-Condon factor of unity for vertical excitation.

[d] Difference in ground and excited state expectation value of $x^2 + y^2$ [in $(a.u.)^2$].

Table VII. EOM Calculation of Triplet Excited States of CO_2.

Transition	ΔE^a (1p-1h) + (2p-2h)	$\Delta(\langle x^2\rangle + \langle y^2\rangle)^b$	Dominant Components
$^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$	7.35	1.00	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow 1\,{}^3\Delta_u$	8.06	1.09	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^-$	8.39	1.24	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow {}^3\Pi_g$	8.40	12.2	$1\pi_g \rightarrow \sigma_g^*$
$^1\Sigma_g^+ \rightarrow 2\,{}^3\Delta_u$	10.43	34.7	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow {}^3\Pi_u$	10.99	20.1	$1\pi_g \rightarrow \sigma_u^*$
$^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^+$	11.33	2.28	$1\pi_u \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow {}^3\Delta_g$	12.42	5.99	$1\pi_u \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$	12.67	15.5	$1\pi_g \rightarrow \pi_g^*$

[a] In electron volts.

[b] Difference in ground and excited state expectation value of $x^2 + y^2$ [in $(a.u.)^2$].

Table VIII. $f_n(K)/\Delta E_n$ for CO_2[a]

K^2[b]	$1\,^1\Delta_u$	$^1\Pi_g$	$^1\Sigma_u^+$	$2\,^1\Delta_u$	$^1\Pi_u$	$^1\Delta_g$	$^1\Sigma_g^+$
0.01	1.373(-6)	2.209(-3)	1.044(-1)	2.426(-5)	1.491(-1)	1.465(-3)	9.770(-3)
0.04	1.280(-5)	7.768(-3)	8.254(-2)	9.694(-5)	1.191(-1)	4.891(-3)	3.290(-2)
0.09	5.895(-5)	1.415(-2)	5.583(-2)	5.752(-4)	8.311(-2)	8.226(-3)	5.588(-2)
0.16	1.791(-4)	1.834(-2)	3.229(-2)	1.339(-3)	5.179(-2)	9.938(-3)	6.782(-2)
0.25	4.144(-4)	2.052(-2)	1.584(-2)	2.170(-3)	2.975(-2)	9.802(-3)	6.629(-2)
0.36	7.868(-4)	1.926(-2)	6.426(-3)	2.542(-3)	1.626(-2)	8.481(-3)	5.569(-2)
0.49	1.284(-3)	1.603(-2)	2.003(-3)	2.470(-3)	8.629(-3)	6.759(-3)	4.211(-2)
0.64	1.863(-3)	1.197(-2)	4.365(-4)	2.129(-3)	4.434(-3)	5.131(-3)	2.978(-2)
0.81	2.471(-3)	8.001(-3)	2.376(-4)	1.714(-3)	2.142(-3)	3.795(-3)	2.034(-2)
1.00	3.059(-3)	4.685(-3)	5.647(-4)	1.336(-3)	9.112(-4)	2.777(-3)	1.378(-2)
1.21	3.600(-3)	2.266(-3)	9.917(-4)	1.024(-3)	2.948(-4)	2.032(-3)	9.475(-3)
1.44	4.080(-3)	7.728(-4)	1.318(-3)	7.682(-4)	4.430(-5)	1.504(-3)	6.735(-3)
1.69	4.496(-3)	9.911(-5)	1.466(-3)	5.559(-4)	1.609(-5)	1.152(-3)	5.014(-3)
1.96	4.855(-3)	5.845(-5)	1.432(-3)	3.801(-4)	1.231(-4)	9.499(-4)	3.910(-3)
2.25	5.164(-3)	4.330(-4)	1.261(-3)	2.409(-4)	3.071(-4)	8.806(-4)	3.146(-3)
2.56	5.433(-3)	1.016(-3)	1.015(-3)	1.399(-4)	5.225(-4)	9.248(-4)	2.548(-3)

Table VIII. (Cont;d)

K^{2b}	$1\,^1\Delta_u$	$^1\Pi_g$	$^1\Sigma_u^+$	$2\,^1\Delta_u$	$^1\Pi_u$	$^1\Delta_g$	$^1\Sigma_g^+$
2.89	5.665(-3)	1.640(-3)	7.527(-4)	7.566(-5)	7.304(-4)	1.057(-3)	2.027(-3)
3.24	5.861(-3)	2.196(-3)	5.171(-4)	4.267(-5)	9.002(-4)	1.246(-3)	1.553(-3)
3.61	6.017(-3)	2.629(-3)	3.300(-4)	3.244(-5)	1.013(-3)	1.458(-3)	1.131(-3)
4.00	6.124(-3)	2.922(-3)	1.959(-4)	3.595(-5)	1.064(-3)	1.661(-3)	7.762(-4)
5.76	5.913(-3)	3.015(-3)	1.395(-5)	6.739(-5)	8.502(-4)	2.016(-3)	1.004(-4)
7.84	4.748(-3)	2.232(-3)	6.535(-6)	5.533(-5)	5.172(-4)	1.655(-3)	6.020(-5)
10.24	3.309(-3)	1.313(-3)	6.912(-6)	3.252(-5)	2.825(-4)	1.128(-3)	5.800(-5)
12.96	2.156(-3)	6.712(-4)	5.214(-6)	1.785(-5)	1.392(-4)	7.182(-4)	2.753(-5)
16.00	1.384(-3)	3.359(-4)	2.806(-6)	1.031(-5)	6.726(-5)	4.486(-4)	1.359(-5)

[a] Notation is, e.g., 1.373(-6) = 1.373×10^{-6}.

[b] In atomic units.

Table IX. Assignments in the CO_2 Spectrum

State	ΔE[a] (1p - 1h) + (2p - 2h)	ΔE[a] Experimental	% Error[b]	f	f exp
$^3\Sigma_u^+$	7.35	7.5[c]	2%		
$^3\Delta_u$	8.06	8.0[c]	1%		
$^1\Delta_u$	8.56	8.41[d]	2%[g]		
$^1\Pi_g$	8.62	9.31[d]	7%		
$^1\Sigma_u^+$	10.29	11.08[d]	7%	0.116	0.12[f]
$^1\Pi_u$	10.97	11.4[e]	4%	0.1680	

[a] In electron volts.

[b] Relative to experimental value.

[c] Reference 25.

[d] Reference 19.

[e] Reference 7.

[f] Reference 24.

[g] Tentative assignment, see section VI.

FIGURE CAPTIONS

Figure 1. Definition of the Euler angles used in Eq. (3) and (4).

Figure 2. Comparison of EOM generalized oscillator strengths (solid lines) for helium with the results of Kim and Inokuti[6] (dashed). K^2 is in atomic units.

Figure 3. Calculated generalized oscillator strengths for CO_2. K^2 is in atomic units.

Figure 4. Upper: Experimental differential generalized oscillator strengths for CO_2 measured at 8.61 eV (triangles) and 9.16 eV (octagons) by Lassettre and Shiloff.[7] Lower: Comparison of theoretical results for the $^1\Pi_g$ (solid) and $^1\Delta_u$ states with the differential generalized oscillator strength of the 9.16 eV peak times 0.76.

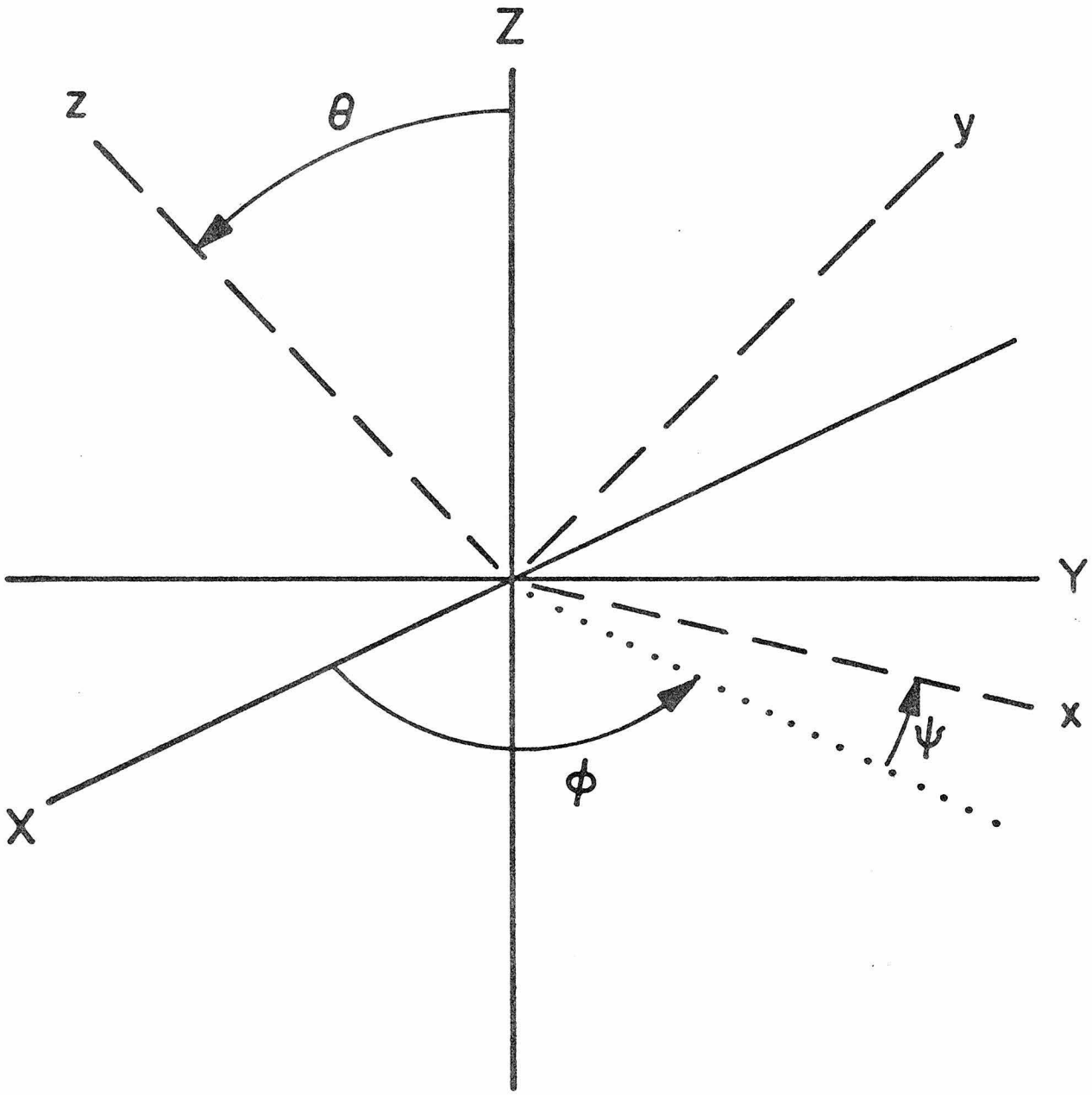


Fig. 1

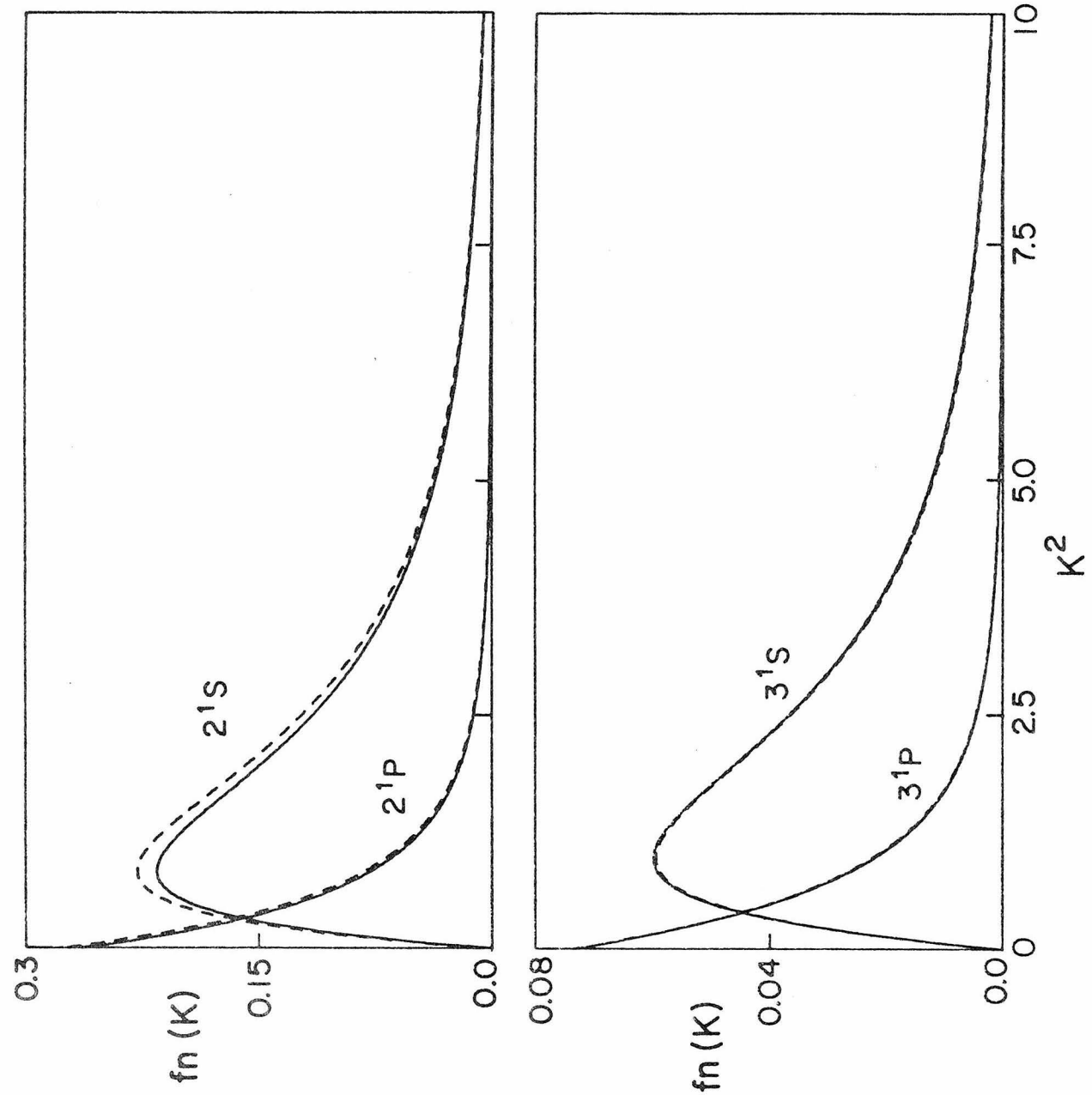


Fig. 2

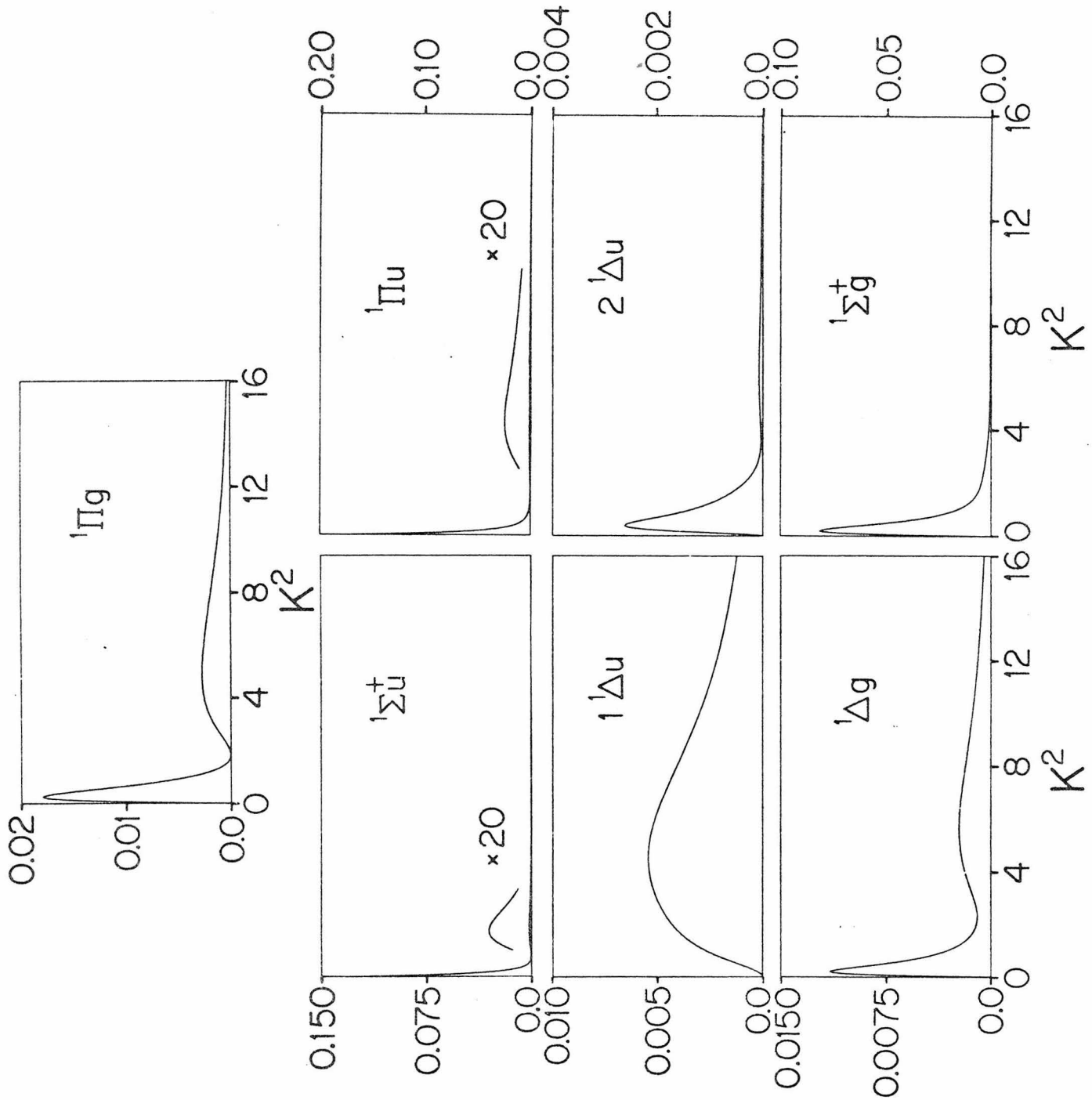

$^1\Pi_g$
$^1\Sigma_u^+$
$^1\Pi_u$
$2\,^1\Delta_u$
$^1\Sigma_g^+$
$1\,^1\Delta_u$
$^1\Delta_g$
×20
×20
K^2
K^2
K^2

Fig. 3

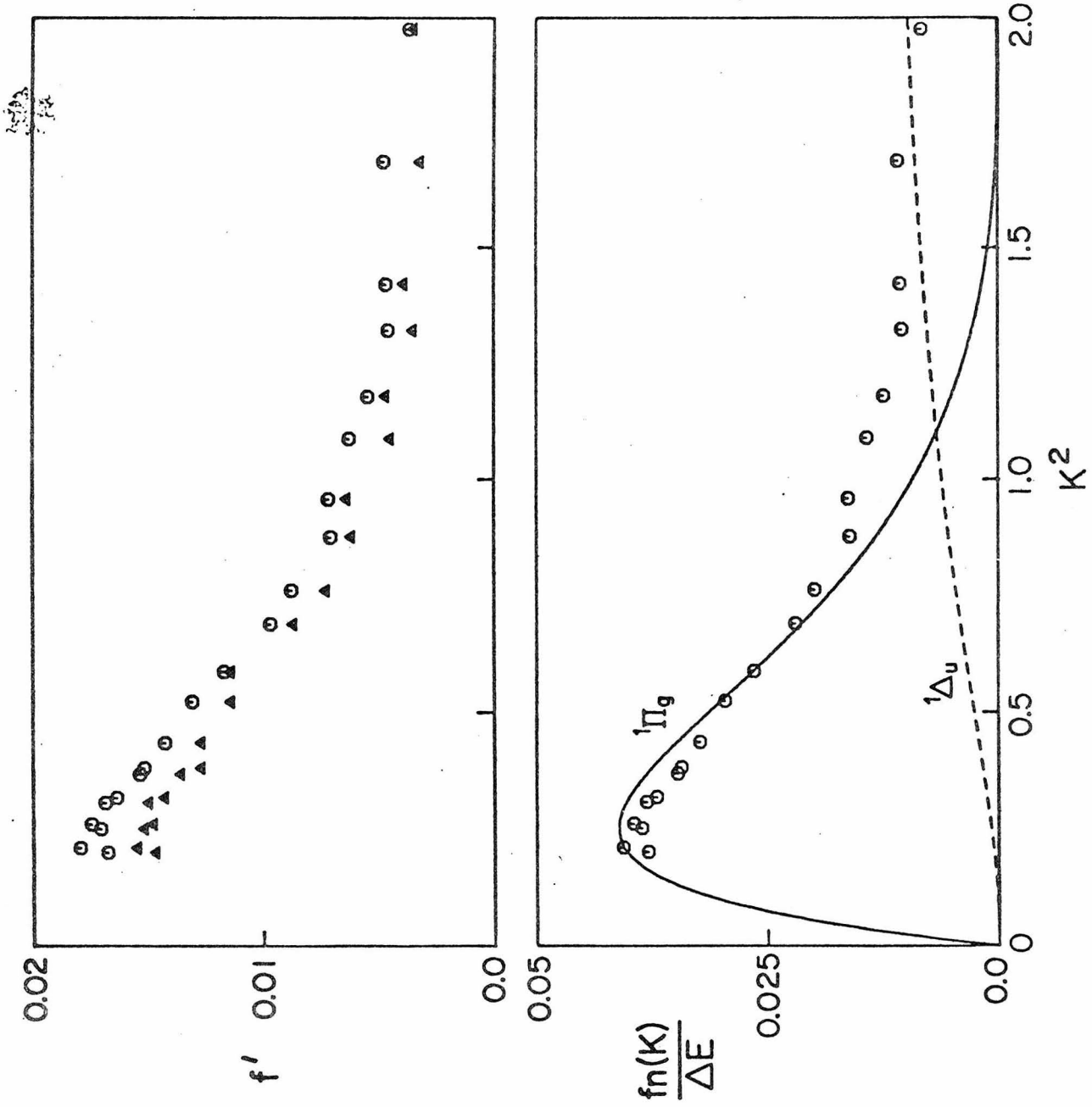


Fig. 4

SECTION B

Generalized Oscillator Strengths for CO

I. INTRODUCTION

Recent experimental studies of the electron impact spectrum of carbon monoxide by Skerbele and Lassettre[1] and by Klump and Lassetre[2] have revealed unusual behavior in the generalized oscillator strengths of the $B\ ^1\Sigma^+$ and $C\ ^1\Sigma^+$ states. Lassettre has shown that deviations from the Born approximation should occur at relatively high energies for transitions between states with the same term symbol.[3] In accordance with this theory, measurements of the generalized oscillator strength, $f_n(K)$, of the $B\ ^1\Sigma^+$ state of CO vary considerably over the range of incident energy between 300 and 500 eV, and smaller deviations are observed for the $C\ ^1\Sigma^+$ state.[1] A more striking feature of the generalized oscillator strength of the $B\ ^1\Sigma^+$ state is a large change in slope and the occurence of a minimum at small momentum transfer K (see Fig. 1).[1,4] Minima in $f_n(K)$ due to Rydberg character of the excited state have been observed only at larger values of momentum transfer.[5,6] Moreover, we have recently obtained a value of 0.04 for the oscillator strength of the $X\ ^1\Sigma^+ \rightarrow B\ ^1\Sigma^+$ transition by the equations of motion method. This value is significantly larger than that of 0.015 determined by Lassettre from high energy electron impact data. On the other hand, the calculated oscillator strengths for the $X\ ^1\Sigma^+ \rightarrow A\ ^1\Pi$ and $X\ ^1\Sigma^+ \rightarrow C\ ^1\Sigma^+$ transition agree reasonably well with the measured values.

In this paper we report the generalized oscillator strengths, $f_n(K)$, for excitation of the $A\ ^1\Pi$, $B\ ^1\Sigma^+$, and $C\ ^1\Sigma^+$ and $D\ ^1\Delta$

states of CO using the equations of motion (EOM) method and compare them with the experimental determinations for the $A\,^1\Pi$, $B\,^1\Sigma^+$, and $C\,^1\Sigma^+$ states.[1] The agreement with the measured values of $f_n(K)$ is satisfactory for the $A\,^1\Pi$ state and the calculated values for the $C\,^1\Sigma^+$ state reproduce the general trend of the measured values. However, at low momentum transfer we find no minimum in the generalized oscillator strength for the $B\,^1\Sigma^+$ state. The calculated optical oscillator strength for the $B\,^1\Sigma^+$ state is also about three times larger than the experimental value. We have suggested that this discrepancy between theory and experiment may be due to the interaction between the $B\,^1\Sigma^+$ state and other $^1\Sigma^+$ states which we have shown can approach one another closely.[8] Recently Klump and Lassettre[2] have reexamined the relative intensities for excitation of the $\nu = 0$ and $\nu = 1$ vibrational levels of the $B\,^1\Sigma^+$ state by electron impact and determined that these relative intensities change by a factor of 10 over the range of scattering angle from 0° to 20° at 400 eV incident energy. This variation is in contrast to the constant ratio of intensities observed in other vibrational progressions[9, 10] and suggests a breakdown of the Born-Oppenheimer approximation.

In the following section we briefly describe the theoretical techniques of the calculation and in Section III we further discuss the results.

II. THE EQUATIONS OF MOTION APPROACH TO ELECTRON SCATTERING IN THE BORN APPROXIMATION

The application of the EOM to the computation of Born cross sections has been described previously,[11] and thus only a brief summary of the method will be given here. The operator O_n^+ which generates excited state $|n\rangle$ from the ground state $|0\rangle$ can be shown to be exactly a solution of the equation of motion[12]

$$\langle 0|[\delta O_n, H, O_n^+]|0\rangle = \Delta E_n \langle 0|[\delta O_n, O_n^+]|0\rangle \qquad (1)$$

for all variations δO_n^+ in the amplitudes specifying O_n^+. In Eq. (1) ΔE_n denotes the excitation energy and the double commutator is defined as

$$2[A, B, C,] = [[A, B],C] + [A,[B, C]] \qquad (2)$$

If O_n^+ is restricted to single particle-hole (1p-1h) form, Eq. (1) becomes a matrix equation for the amplitudes $\{Y_{m\gamma}\}$ and $\{Z_{m\gamma}\}$.

$$\begin{bmatrix} \underset{\sim}{A} & \underset{\sim}{B} \\ -\underset{\sim}{B}^* & -\underset{\sim}{A}^* \end{bmatrix} \begin{bmatrix} Y(n) \\ Z(n) \end{bmatrix} = \Delta E_n \begin{bmatrix} \underset{\sim}{D} & O \\ O & \underset{\sim}{D} \end{bmatrix} \begin{bmatrix} Y(n) \\ Z(n) \end{bmatrix} \qquad (3)$$

The elements of the matrices $\underset{\sim}{A}$, $\underset{\sim}{B}$, and $\underset{\sim}{D}$ are given elsewhere.[13] It has been shown that the theory including two-particle--two hole (2p-2h) components is equivalent to the 1p-1h theory with a

renormalized interaction.[14] In addition an approximate perturbative scheme has been developed for calculating the correction to the transition energies due to the effect of 2p-2h components.[14] In the 1p-1h theory the matrix element M_{on} of an arbitrary one electron operator between state $|n>$ and ground state $|0>$ is given (to second order in the correlation coefficients of the ground state) by[7]

$$M_{on} = \langle 0|M|n\rangle = \sqrt{2} \sum_{m\gamma} Y^{*}_{m\gamma}(n)\, M_{m\gamma} + Z^{*}_{m\gamma}(n)\, M_{m\gamma} \tag{4a}$$

$$M_{m\gamma} = M^{0}_{m\gamma} + \sum_{\delta} M^{0}_{m\delta}\, \rho^{(2)}_{\gamma\delta} - \sum_{p} M^{0}_{p\gamma}\, \rho^{(2)}_{mp} \tag{4b}$$

$M^{0}_{m\gamma}$ is the matrix element between a hole orbital γ and a particle orbital m, and $\rho^{(2)}_{ij}$ is the contribution to the density matrix which is quadratic in the correlation coefficients. The approximation we employ in this work has been referred to specifically as the Higher Random Phase Approximation (HRPA) with 2p-2h corrections to the transition energies.[13,14]

If K is the momentum transfer, and R and a_o denote the Rydberg energy and Bohr radius respectively, the generalized oscillator strength $f_n(K)$ is defined by[15]

$$f_n(K) = \frac{\Delta E_n/R}{(Ka_o)^2} \left|\epsilon_n(\vec{K})\right|^2_{Av} \tag{5}$$

In Eq. (5) $\epsilon_n(\vec{K})$ is the electronic matrix element between excited state $|n\rangle$ and ground state $|0\rangle$

$$\epsilon_n(\vec{K}) = \langle n | \sum_{j=1}^{n} e^{i\vec{K}\cdot\vec{r}_j} | 0 \rangle \qquad (6)$$

where $\vec{r}_j$ is an electronic coordinate, and the average is over molecular orientations.[16,17] We compute the electronic matrix element of $\Sigma e^{i\vec{K}\cdot\vec{r}_j}$ using Eqs. (4). The average over molecular orientations was performed using an 8 point Gauss-Legendre quadrature in the cosine of the Euler angle θ (in the notation of reference 11) over the reduced interval $[0, \pi/2]$. For a further discussion of the details of the angular average see references 11 and 18.

A [3S/2P] basis of Gaussian atomic orbitals contracted from a (9S/5P) set of primitive Gaussian functions was used for the calculation.[19] This set was augmented by diffuse primitive Gaussian functions on carbon (with exponents $\zeta_s = .0488$ and $\zeta_p = .0365$) and oxygen ($\zeta_s = .0906$, $\zeta_p = .0680$) and by diffuse s, p_z and d_π functions at the center of charge ($\zeta_s = .022$, $\zeta_p = .016$, $\zeta_d = .01$). The ground state Hartree-Fock claculation in this basis gave an energy of E_{HF} - 112.6899 a.u. In the EOM calculation the hole space was truncated by eliminating the two lowest occupied orbitals 1σ and 2σ. The particle space was not truncated.

III. DISCUSSION

The results of the EOM calculation of transition energies and optical oscillator strengths for the $A\,^1\Pi$, $B\,^1\Sigma^+$, $C\,^1\Sigma$, and $D\,^1\Delta$ states are compared with experiment in Table I. Although the optical oscillator strength f_o of the $A\,^1\Pi$ state is in good agreement with experiment, those of the B and C states are not. In particular the f_o calculated for the $B\,^1\Sigma^+$ state is in excess of the experimental value by more than a factor of three. The results of a previous EOM calculation on CO at the equilibrium internuclear distance using a completely different basis set compared similarly with experiment.[7] A comparison of the theoretical and experimental generalized oscillator strengths in Fig. 1 shows that, while agreement is close for the $A\,^1\Pi$ state, only the general trend of the measurements for the $C\,^1\Sigma^+$ state is reproduced by the calculation. Of particular interest is the fact that the low momentum transfer behavior of the theoretical and experimental $f_n(K)$ for the $B\,^1\Sigma^+$ state are qualitatively different.

Previous calculation of generalized oscillator strengths using the EOM have compared well with available experimental data.[11] We believe that a breakdown in the Born-Oppenheimer approximation which is employed in our calculations may be responsible for the disagreement between our results and experiment in the case of the $B\,^1\Sigma^+$ state and possibly also the $C\,^1\Sigma^+$ state. Klump and Lassettre's[2] observation of wide variation in the ratio of intensities

of transitions to the $\nu = 0$ and $\nu = 1$ vibrational levels of the B state strongly suggests the presence of a perturbing state. Previous calculations of potential energy durves for CO using the EOM[8] show that the character of the lowest excited state of $^1\Sigma^+$ symmetry changes from the $\sigma \rightarrow 3S$ character of the B state to $\pi \rightarrow \pi^*$ with larger internuclear separation. The calculated potential energy curves show the usual behavior associated with an avoided crossing. The present calculation yields a $^1\Sigma^+$ state of $\pi \rightarrow \pi^*$ character above 15 eV with a large optical oscillator strength (.17), although 2p-2h corrections were not computed for the energy of this transition.

The configuration of potential energy curves schematically represented in Fig. 2, which shows a repulsive state of $^1\Sigma^+$ symmetry "crossing" B and C states, would explain the observations of the B and C states in the electron impact spectrum. The adiabatic curves (utilizing the noncrossing rule) for the B and C states would be quite complicated and the near degeneracies associated with avoided crossings would probably result in a breakdown of the Born-Oppenheimer approximation. [It should be noted that Krupenie[20] has asserted that experimental data on the predissociation of the B state is inconsistent with dissociation through a repulsive state.] We can only hypothesize that the perturbation of the B state that we propose occurs in addition to predissociation through the a $^3\Sigma^+$ ($\pi \rightarrow \pi^*$) state.

Unfortunately a complete calculation of Born cross-sections without making the Born-Oppenheimer approximation is well beyond

the present capabilities of our method. A complete explanation of the unusual behavior of the B state in the electron impact spectrum of CO must await more definitive experimental or theoretical evidence.

Finally we make some comparisons between our calculated generalized oscillator strengths and those obtained by Szabo and Ostlund[21] and Chung and Lin.[22] Szabo and Ostlund[21] calculated the generalized oscillator strength for the $A\,^1\Pi$ state in the RPA. Apart from some small differences this should be close to the EOM for this transition. The fact that their $f(K^2)$ values do not agree with experiment as well is mainly due to their use of a minimal basis set Hartree-Fock set of orbitals.

Ching and Lin[22] calculated their $f(K^2)$ values in the Hartree-Fock approximation. Our results for the $A\,^1\Pi$ state are in better agreement with experiment than theirs although this difference is not very large. This is probably due to the inclusion of some correlation effects in the EOM method. Their generalized oscillator strength for the $D\,^1\Delta$ state is about twice as large as ours but this may be due to their use of the unoccupied $^2\Pi$ orbital of the ground state Hartree-Fock calculation. The discrepancy between their calculated generalized oscillator strength for the $B\,^1\Sigma^+$ state and ours may be quite significant. For example we predict an optical oscillator strength of 0.056 for this transition while they obtained a value of 0.0098. This may be due to their approximations in carrying out the SCF calculation for this state. For the $^1\Sigma^+$ states one has two open-shells of the same

symmetry and their SCF procedure could not handle those cases. However Rose and McKoy[23] have shown how SCF calculations can be done correctly for these states of CO and in fact obtained an f-value for the $B\,^1\Sigma^+$ state of 0.031, about three times larger than their value.

TABLE I. Results of EOM Calculation

State	ΔE^a (1p-1h)	ΔE^a (1p-1h) +(2p-2h)	ΔE^a_{exp}	f_o	f_{exp}
$A\ ^1\Pi$	10.1	8.66	8.4[b]	0.050[d]	0.043[e]
$D\ ^1\Delta$	12.3	10.1	10.5[c]	--	--
$B\ ^1\Sigma^+$	12.9	10.8	10.8	0.056	0.016[f]
$C\ ^1\Sigma^+$	13.6	11.3	11.4	0.10	0.16[f]

[a] In electron volts

[b] The experimental results for the $A\ ^1\Pi$, $B\ ^1\Sigma^+$ and $C\ ^1\Sigma^+$ are from V. Meyer, A. Skerbele and E. N. Lassetre, J. Chem. Phys. 43, 805 (1965).

[c] G. Herzberg, T. Hugo, S. Tilford and J. Simons, Can. J. Phys. 48, 3004 (1970).

[d] Theoretical result multiplied by Franck-Condon Factor of 0.24 for

[e] Measured for $\nu' = o \rightarrow \nu'' = 2$ transition, see f.

[f] E. N. Lassetre and A. Skerbele, J. Chem. Phys. 54, 1597 (1971).

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[4] It should be noted that for very small values of momentum transfer ($K^2 < 0.02$) variations in $f_n(K)$ of the B state are quite small and that it has been shown (the limit theorem) that the Born approximation holds exactly at zero momentum transfer for transitions of all symmetries. See E. N. Lassettre, A. Skerbele, and M. A. Dillon, J. Chem. Phys. 50, 1829 (1969).

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FIGURE CAPTIONS

FIG. 1. Generalized oscillator strengths (divided by (1p-1h) transition energies) for four states of CO. A Franck-Condon factor of 0.24 is incorporated in the theoretical results for the $A\,^1\Pi$ state. K^2 is in atomic units

FIG. 2. Schematic representation of the configuration of potential energy curves of CO leading to the proposed breakdown of the Born-Oppenheimer approximation.

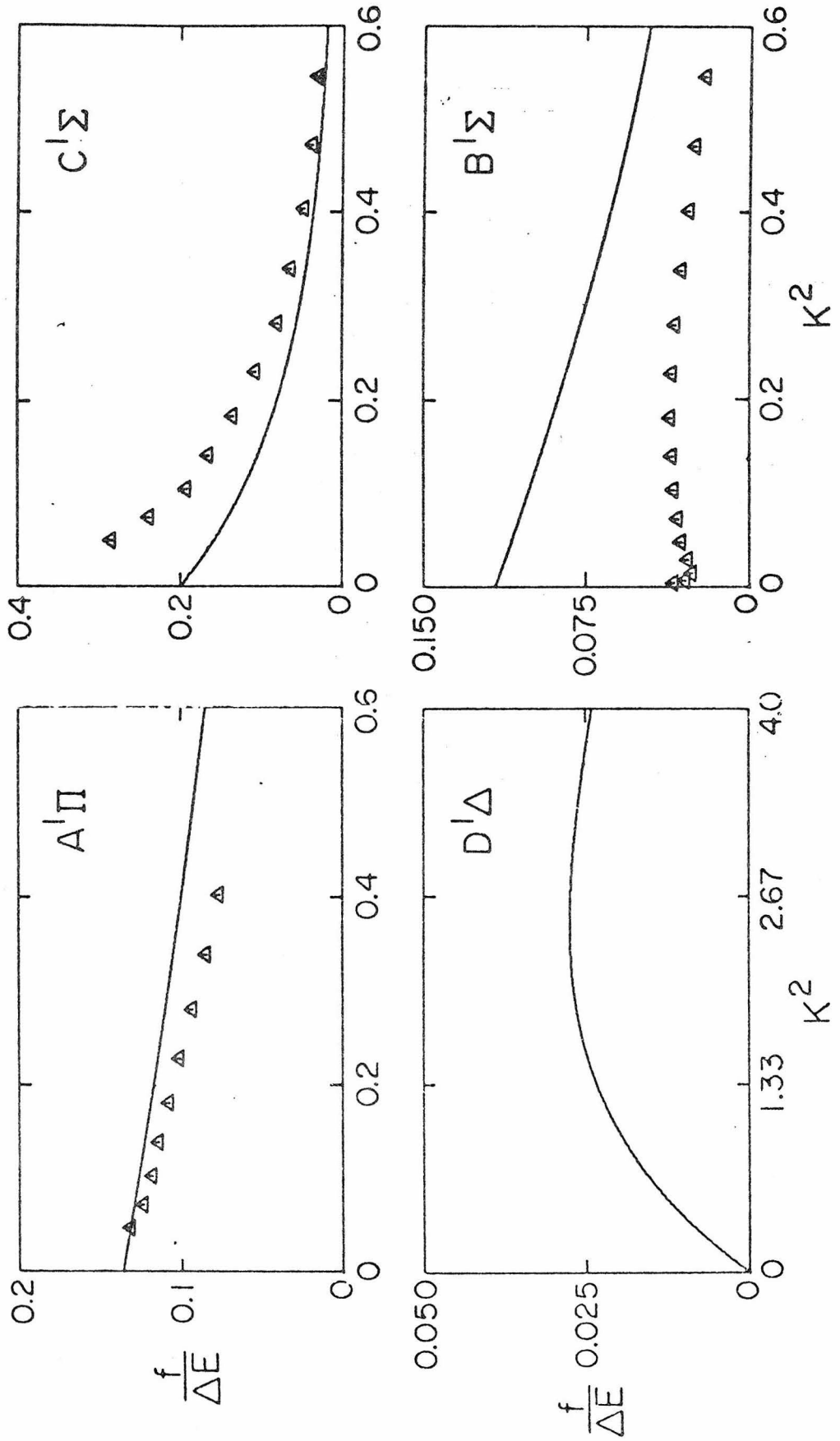

$A^1\Pi$
$B^1\Sigma$
$C^1\Sigma$
$D^1\Delta$
$\frac{f}{\Delta E}$
K^2
0.2
0.1
0
0.4
0.6
0.150
0.075
0.050
0.025
1.33
2.67
4.0

Figure 1.

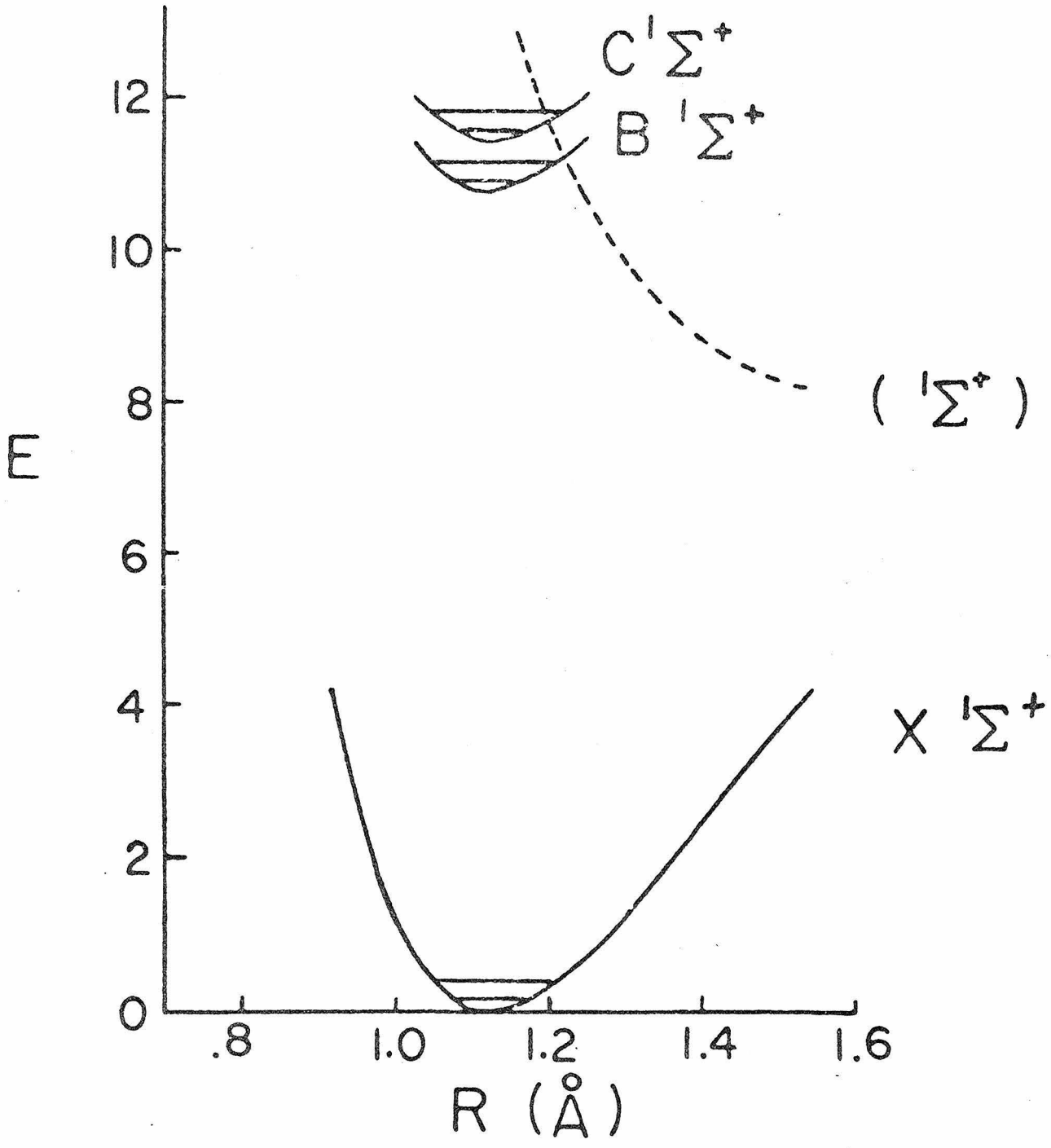


Figure 2.