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NEW THEORETICAL APPROACHES FOR STUDYING ELECTRON COLLISIONS WITH SMALL MOLECULES*

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I. INTRODUCTION

There has been a recent resurgence of interest in the use of algebraic variational methods for studying a variety of collision problems. Much of this interest stems from the discovery that spurious singularities, which plagued the traditional methods, can be eliminated when the variational principle is formulated with outgoing-wave boundary conditions.[1],[2] Another reason for the recent activity is the obvious suitability of these methods to present-day supercomputers. My purpose here is to describe an implementation of the complex Kohn method[3], an algebraic variational technique, for studying electron collisions with small molecules, both linear and non-linear. Unlike variational principles based on the integral form of the Schroedinger equation (Lippmann-Schwinger equation), the method only requires Hamiltonian matrix elements. I will also show how the formalism allows one to develop a variational principle for computing first-order properties, such as bound-free dipole transition amplitudes. I will show results for the electron-impact dissociation of hydrogen as a function of initial vibrational quantum number. I will also illustrate the method for polyatomic molecules with results for elastic scattering of electrons by formaldehyde.

II. THEORY

A. Trial Wave Function

To describe the scattering of low energy electrons, incident in a channel denoted by the label Γ', by an N-electron target molecule, we formulate the problem in body-frame coordinates within the framework of the fixed-nuclei approximation using an antisymmetrized trial wave function of the form,

$$\Psi_{\Gamma'} = \sum_{\Gamma} \mathcal{A}(\chi_\Gamma F_{\Gamma\Gamma'}) + \sum_{\mu} d_\mu^{\Gamma'} \Theta_\mu . \tag{1}$$

where the first sum runs over the energetically open N-electron target states, denoted by the normalized functions χ, and the operator $\mathcal{A}$ antisymmetrizes the orbital functions F into the functions χ. The Θ are an orthonormal set of antisymmetric, square-integrable (N+1)-electron functions used to represent polarization and correlation effects not included in the first summation. The symbol Γ is being used to label all the quantum numbers needed to represent a physical state of the composite system, ie. the internal state of the target molecule as well as the energy and orbital angular momentum of the scattered electron.

To calculate physical differential cross sections, it is necessary to express the scattering amplitude in the laboratory frame[4]. Since this is easily accomplished by projecting the T-matrix onto a set of angular functions, the channel continuum functions, F, are further expanded as:

$$rF_{\Gamma\Gamma'}(\vec{r}) = \sum_{\ell m}[f_\ell^\Gamma(r)\delta_{\ell\ell'}\delta_{mm'}\delta_{\Gamma\Gamma'} + T_{\ell m\ell' m'}^{\Gamma\ \Gamma'}\ g_\ell^\Gamma(r)]\ Y_{\ell m}(\hat{r}) + \sum_k c_k^{\Gamma\Gamma'}\varphi_k^\Gamma(\vec{r}) \qquad (2)$$

where $Y_{\ell m}$ is a normalized spherical harmonic, the φ_k are a set of square-integrable functions, and the functions {f} and {g} are linearly independent continuum orbitals which are *regular* at the origin and, in the case of neutral targets, behave asymptotically as regular and *outgoing* Riccati-Bessel functions, respectively,

$$\begin{aligned} f_\ell^\Gamma(r) &\underset{r\to\infty}{=} \sin(k_\Gamma r - \ell\pi/2)/\sqrt{k_\Gamma}\ ; \\ g_\ell^\Gamma(r) &\underset{r\to\infty}{=} \exp(i(k_\Gamma r - \ell\pi/2\ ))/\sqrt{k_\Gamma}\ . \end{aligned} \qquad (3)$$

The channel momenta are determined by energy conservation,

$$k_\Gamma^2/2 = E - E_\Gamma \ , \qquad (4)$$

where E is the total energy and E_Γ is the energy of target state χ_Γ. The functions {f} and {g} may be modified to Coulomb form to treat ionic targets. The coefficients [T] are elements of the T-matrix and are the fundamental dynamical quantities that determine scattering amplitudes and cross sections.

If the target molecule has symmetry, we can use it to restrict the sum over angular quantum numbers that appear in Eq. (2). For example, in linear molecules, m is a good quantum number and the sum over m collapses to the single term with $m=m'$. Moreover, the sum over ℓ-values can be restricted to the number of "asymptotic ℓ's" needed to represent the channel wave function at large distances and to provide converged cross sections at a particular energy.

Electron scattering cross sections can be expressed solely in terms of the T-matrix. In such cases, all we need is the open-channel part of the wave function and the correlation functions Θ can be formally incorporated into an effective optical potential. This is accomplished using Feshbach partitioning with operators P and Q that project onto the open- and closed-channel subspaces, respectively. However, there are cases where we need the full wave function. For example, if we wish to calculate properties such as dipole transition matrix elements, we will need both $P\Psi$ and $Q\Psi$. In such cases, it may be simpler to work with Eq. (1) directly.

B. Variational Principles

The Kohn principle[5] can be used to characterize the T-matrix as the stationary value of the functional:

$$T^{\Gamma\Gamma'}_{\text{stat}} = T^{\Gamma\Gamma'} - 2 \int \Psi_{\Gamma} \, (H - E) \, \Psi_{\Gamma'} \quad . \tag{5}$$

Trial values for the coefficients T , c and d, which define the "Kohn trial wave function", are determined from the linear equations obtained by requiring that the derivatives of elements of $T^{\Gamma\Gamma'}_{\text{stat}}$ with respect to these parameters vanish. These coefficients, when substituted back into Eq. (5), give a stationary expression for the T-matrix. In a condensed matrix notation, in which open-channel indices are supressed, the result is[3]

$$[\underset{\sim}{T}_{\text{stat}}] = -2 \; (\underset{\sim}{M}_{oo} - \underset{\sim}{M}_{qo} \underset{\sim}{M}^{-1}_{qq} \underset{\sim}{M}_{qo} \;) \tag{6}$$

where o refers to $\mathcal{A}(\chi_\Gamma \, f^{\Gamma}_{\ell} \, Y_{\ell m})$ and q to $\mathcal{A}(\chi_\Gamma \, g^{\Gamma}_{\ell} \, Y_{\ell m})$, $\mathcal{A}(\chi_\Gamma \, \varphi^{\Gamma}_{k})$ and Θ_{μ}. For example, the elements of $\underset{\sim}{M}_{qo}$ are defined as

$$(M_{qo})^{\Gamma\Gamma'}_{k \; \ell' m'} = \int \mathcal{A}(\chi_\Gamma \, \varphi^{\Gamma}_{k}) \; (H - E) \; \mathcal{A}(\chi_{\Gamma'} \, f^{\Gamma'}_{\ell'} \, Y_{\ell' m'}) \quad . \tag{7}$$

Because of the outgoing-wave behavior of the functions {g}, the matrix M_{qq} will be complex-symmetric and thus its inverse will be non-singular for real energies[1,2]. Thus with complex, outgoing-wave boundary conditions, the Kohn method leads to an anomaly-free expression for the T-matrix.

The Kohn trial wave function, when substituted into Eq. (5), gives a stationary expression for the T-matrix. Less obvious, but nonetheless true, is that this same wave function, when used to compute any first-order property, will also give a value accurate through second-order. Suppose we wish to calculate the amplitude,

$$B \equiv \langle W | \Psi_{\Gamma'} \rangle \tag{8}$$

where W is some known function. For example, if $|W\rangle = \mu |\Psi_0\rangle$, where μ is the dipole operator and Ψ_0 is the initial state of the target, then B is simply the bound-free dipole transition amplitude for photoabsorption. We start with a stationary principle for B given by Gerjouy, Rau and Spruch[6]:

$$B' \equiv \langle W | \Psi_{\Gamma'} \rangle + \langle h' | M | \Psi_{\Gamma'} \rangle \tag{9}$$

where $M = H - E$ and h' is some auxillary function. The second term in Eq. (9) obviously vanishes when $\Psi_{\Gamma'}$ is exact. The auxillary function is required to satisfy the equation:

$$M | h' \rangle + | W \rangle = 0 \tag{10}$$

along with the boundary condition

$$\langle h' | M | \delta\Psi_{\Gamma'} \rangle - \langle \delta\Psi_{\Gamma'} | M | h' \rangle = 0 \quad , \tag{11}$$

where

$$\delta\Psi_{\Gamma'} = \Psi_{\Gamma'}^{\text{exact}} - \Psi_{\Gamma'} \ . \qquad (12)$$

Because of the asymptotic boundary conditions specified by Eqs. (2) and (3), Eq. (11) will be satisfied if h' is chosen to be regular at the origin and to behave as a purely outgoing scattered wave asymptotically. Thus we take, in analogy with Eqs. (1)-(3),

$$h' = \sum_{\Gamma} \mathcal{A}(\chi_{\Gamma}\, G_{\Gamma\Gamma'}) + \sum_{\mu} e_{\mu}^{\Gamma'}\, \Theta_{\mu} \ . \qquad (13)$$

with

$$rG_{\Gamma\Gamma'}(\vec{r}) = \sum_{\ell}[U_{\ell m \ell' m'}^{\Gamma\ \Gamma'}\ g_{\ell}^{\Gamma}(r)]\ Y_{\ell m}(\hat{r}) + \sum_{k} i_{k}^{\Gamma\Gamma'}\, \varphi_{k}^{\Gamma}(\vec{r}) \qquad (14)$$

The derivation proceeds as before. We substitute Eqs. (1), (2), (13) and (14) into Eq. (9) and set the derivatives of B' with respect to the trial coefficients in both h' and $\Psi_{\Gamma'}$ equal to zero. The result, when substituted back into Eq. (9), gives:

$$B' = \langle W|\mathcal{A}(\chi_{\Gamma'}\ f_{\ell'}^{\Gamma'}\ Y_{\ell' m'})\rangle - V_{q}\ \underset{\sim}{M}_{qq}^{-1}\ \underset{\sim}{M}_{qo} \qquad (15)$$

where **M** is as in Eq. (6) and **V** is a vector whose elements are:

$$V_{q} = \langle W|q\rangle \qquad (16)$$

where q again refers to the space spanned by $\mathcal{A}(\chi_{\Gamma}\ g_{\ell}^{\Gamma}\ Y_{\ell m})$, $\mathcal{A}(\chi_{\Gamma}\ \varphi_{k}^{\Gamma})$ and Θ_{μ}. But Eq. (15), which we have now shown to be a stationary expression, is simply the result one would have obtained by using the Kohn trial wave function in Eq. (8).

C. Orthogonality and Separable Expansions

The essence of the entire calculation can be reduced to the evaluation of the matrix elements of one- and two-body operators over bound and continuum basis functions. The first practical step is to reformulate the entire procedure in terms of mutually orthogonal bound and continuum functions. This can be done quite rigorously and follows from a property of the Kohn principle called *transfer invariance* which has been described elsewhere[7,8]. The matrix elements involving only bound functions can be evaluated using the standard techniques of bound-state molecular electronic structure theory. The matrix elements involving continuum (Bessel or Coulomb) functions are more problematic, and the principal difficulty of any molecular scattering calculation is their evaluation. There are two critical steps in making this problem tractable for molecules. The first is the rigorous relegation of exchange forces to matrix elements over the square-integrable part of the basis. That reformulation is accomplished by constructing a separable represention of all exchange operators and by orthogonalizing the continuum basis functions to the square-integrable basis used in the representation of exchange. If an optical potential is used, it too is treated in separable form. I will give no further details of that step here because it has been discussed in detail elsewhere[3,8]. The only remaining matrix elements involving continuum functions are "direct". Thus the second step in rendering the molecular problem tractable is to devise an efficient numerical scheme for evaluating these intergals.

D. Adaptive Quadratures

All direct "bound-free" and "free-free" matrix elements can be reduced to single three-dimensional integrals. For diatomic targets, single-center expansions can be used to further reduce these to sums of radial integrals, which can be quadratured numerically, times known angular factors. For polyatomic targets, single-center expansions can converge quite slowly so we evaluate the three-dimensional integrals directly using novel quadrature schemes.

The key to making this quadrature practical is to make it adaptive so that points are clustered with nearly spherical symmetry around each nucleus while the points at large distances from the molecule are arranged with spherical symmetry around its center[9]. We begin by defining a new variable:

$$\vec{r}(\vec{q}) = \vec{q} - \sum_{nuc} (\vec{q} - \vec{R}_{nuc})\, S_{nuc}(\vec{q}\,) \tag{17}$$

where $S_{nuc}(\vec{q})$ is a strength function depending on the distance of a point from the nuclear position R_{nuc}. The function S_{nuc} may be chosen in any number of ways, but it must have the property that

$$S_{nuc}(\vec{q}) \xrightarrow[q \to \infty]{} 0 \tag{18}$$

so that the transformation in Eq.(17) will reduce to the identity, and r will be the same as q at large distances from the molecule. With this change of variable, a typical integral we wish to evaluate becomes

$$I = \int F(\vec{r}(\vec{q}))\ |\partial\vec{r}/\partial\vec{q}|\ d^3q \tag{19}$$

Now we choose a quadrature in $\vec{q}$ consisting of shells of points around the center of the molecule which we can construct from standard Gauss quadrature points and weights. Applying that quadrature to Eq.(19) transforms the points under the new mapping so that they are distributed adaptively while the Jacobian, $|\partial r/\partial q|$, provides the correct weights. Further details and an evaluation of the accuracy of such quadratures are given elsewhere[9].

III. EXAMPLES

A. Electron Impact Dissociation of Hydrogen

At low energies, electron-impact dissociation of molecular hydrogen proceeds mainly through excitation of the lowest triplet electronic state, which dissociates to neutral ground-state hydrogen atoms. Cross sections for this process, and particularly their dependence on initial vibrational quantum number, are required for accurate modelling of hydrogen plasmas. We previously calculated these cross sections[10] in a two-state close-coupling approximation using the complex Kohn method. The complex Kohn equations were solved by using Cartesian Gaussian basis sets in each of four symmetries, $\sigma_g, \sigma_u, \pi_g$, and π_u, along with regular and outgoing-wave Bessel functions up to $\ell=12$. The details of these computations, including basis set information, target state description and assumptions about the nuclear dynamics, have all been given previously and will not be repeated here. I have since extended these calculations to lower energies than were originally reported and these new results are shown here. Figure 1 gives the energy dependence of the excitation(dissociation) cross sections for hydrogen starting in each of the first ten vibrational levels.

B. Low Energy Electron-Formaldehyde Scattering

A low energy shape resonance, corresponding to a $^2B_1$ state of CH_2O^-, has been observed in elastic electron-formaldehyde collisions as well as in vibrational excitation[11,12]. Target distortion effects are critical in determining the positions and widths of such resonances. In our calculations on formaldehyde[13] we included these effects through the use of a Feshbach optical potential constructed using the techniques of *ab initio* electronic structure theory. This formalism allows the description of the elastic scattering problem in terms of an effective, energy-dependent, nonlocal Hamiltonian. In our case P projects on the space appropriate to the static-exchange approximation while the physics included by the optical potential is determined by the choice of configurations which span the Q-space. In these calculations we chose configurations representing the dominant effect of correlation in a shape resonance, which is the relaxation of the occupied target orbitals in the presence of the scattered electron. The ground state of formaldehyde was represented by a closed-shell Hartree-Fock wave function. The configurations in the Q-space

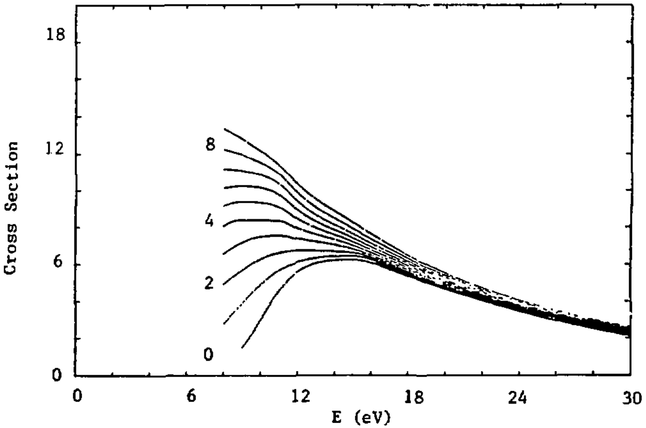

Figure 1. Total cross sections (a_0^2) for excitation of the $b^3\Sigma_u^+$ state of H_2 from various vibrational levels of the ground state.

all consisted of antisymmetrized products of a basis orbital and target configurations which are singlet-coupled, single excitations from the occupied Hartree-Fock orbitals to virtual orbitals of the same symmetry. We used 624 such Q-space configurations to effectively allow the target orbitals to relax in the presence of a scattered electron at the resonance energy. The *ab initio* optical potential has the correct energy dependence to represent the enhancement of target orbital relaxation near the resonance energy and its reduction elsewhere, while preserving the correct asymptotic dipole behavior of the interaction.

Except in b_1 symmetry, where there is a shape resonance, electron scattering from CH_2O at low energies can be expected to be dominated by its permanent dipole potential. This presents us with an additional physical problem, because the partial wave expansion of the total cross section in terms of the body-frame T-matrix elements fails to converge, as does the differential cross section in the forward direction. A simple remedy for this problem was proposed by Norcross and Padial[14]. It is summarized by the expression for the laboratory frame differential cross section for the rotational transition j→j′, where j denotes all relevant rotational quantum numbers,

$$\left[\frac{d\sigma}{d\Omega}\right]_{j\to j'} = \left[\frac{d\sigma}{d\Omega}\right]^{\rm Born}_{j\to j'} + \Delta\left[\frac{d\sigma}{d\Omega}\right]_{j\to j'}. \qquad (20)$$

In Eq. (20) the first term is the Born approximation to the cross section for a rotating point dipole (whose magnetude is that of the molecule's permanent dipole) and the second term denotes the difference between the contribution due the computed T-matrix elements and that due to their counterparts in the Born approximation for the point dipole. The latter is evaluated in the fixed-nuclei approximation. This treatment is called the

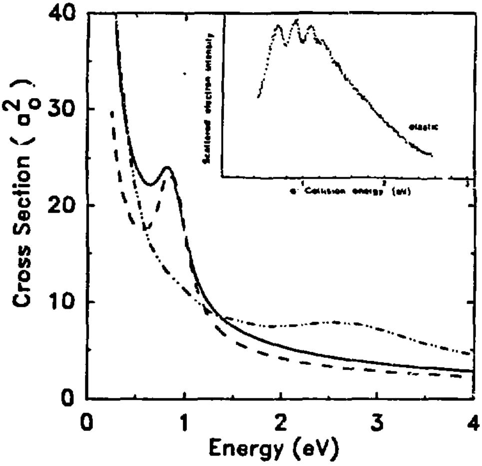

Figure 2. Elastic differential cross section for e^--CH_2O. Solid curve: optical potential results at 90°; dashed curve: optical potential results at 120°; dashed-dot curve: static-exchange result at 90°. Insert shows expermental results of Benoit and Abouaf (ref. 12).

multipole extracted adiabatic nuclei (MEAN) method[14] because it is the result of adding and subtracting the Born cross section in two different representations: the analytic expression for the laboratory cross section and its body-frame partial wave expansion. Additional details of the transformation of the partial wave amplitudes from the body-fixed to laboratory-fixed frames are given by Lane[4].

Our results[13] are summarized in Figure 2. In the static-exchange approximation the resonance appears at an energy nearly two eV above the correct position and with a far broader width than both the optical potential results and experiment[12]. The results of the optical potential calculation place the resonance essentially exactly at the experimentally observed position. Our calculations at the molecule's equilibrium geometry produce a width which is somewhat narrower than the experimentally observed resonance peak in elastic scattering. Also shown in Figure 2 is the cross section from the optical potential calculation at a scattering angle of 120°. The resonance peak is increasingly visible at higher angles and is essentially invisible near the forward direction where scattering from the dipole potential dominates.

The experimental elastic scattering measurements shown in Figure 2 display vibrational structure due to the vibrational states of the metastable formaldehyde anion. A complete comparison between theory and experiment must wait for theoretical calculations which have been performed over a range of nuclear positions so that vibrational motion can be included.

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