Accurate *Ab Initio* Treatment of Low-Energy Electron Collisions with Polyatomic Molecules: Resonant Electron-Formaldehyde Scattering

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We report the first results of a fully *ab initio* treatment of the scattering of low-energy electrons by formaldehyde. The calculations are carried out using the complex Kohn variational method, which is an anomaly-free algebraic variational procedure, and are implemented by a combination of analytic and adaptive, three-dimensional quadrature techniques. The calculations reveal a low-energy shape resonance of ${}^2B_1$ symmetry, which is prominent in the elastic differential cross section only at large scattering angles, and which has been observed experimentally. Its position is sensitive to target distortion effects which are accurately handled by inclusion of an optical potential calculated from first principles.

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Although the mechanisms of electron scattering by small molecules and resonant vibrational excitation are well understood qualitatively,[1] except perhaps very close to electronic and vibrational thresholds,[2] our ability to quantitatively describe these processes from first principles is still quite limited. Although much progress has been made in this area for diatomic or linear triatomic molecules by exploiting their spatial symmetry, only a few *ab initio* calculations on nonlinear polyatomic targets have appeared in the literature, and those have been limited to the static-exchange approximation.[3-6] The inclusion of channel coupling or *ab initio* treatments of target polarization in electronic collisions with polyatomic molecules are formidable computational tasks, and, to our knowledge, no results of such calculations have been published prior to this work.

The principal computational barrier in electron-polyatomic molecule scattering, even in the simplest case of a one-state approximation for the molecule, is that one must solve for scattering from an arbitrarily nonspherical target, without the effective reduction to two dimensions which linear symmetry allows. The problem is compounded by the inclusion of additional target states or electronic correlation effects. On the other hand, electron scattering from polyatomics is intrinsically more interesting than scattering from diatomics because the former possess additional energy-transfer possibilities between electronic and vibrational degrees of freedom as well as a more complicated electronic structure. The calculations on formaldehyde (CH_2O) which we report here demonstrate a newly developed procedure[5] for solving the electron-polyatomic molecule scattering problem and do so in the context of including target polarization effects. Moreover, formaldehyde is a particularly complicated test case for our methods because the molecule possesses a strong permanent dipole. Thus the potential experienced by the scattered electron is long range, and the transformation from the body-fixed frame of reference to the laboratory-fixed frame requires additional care.

A low-energy shape resonance, corresponding to a ${}^2B_1$ state of CH_2O^-, has been observed in elastic electron-formaldehyde collisions[7] as well as in vibrational excitation.[8] Target distortion effects are critical in determining the positions and widths of such resonances. In our calculations on formaldehyde we include these electronic effects through the use of a Feshbach optical potential constructed using the techniques of *ab initio* electronic structure theory.[9] This formalism allows the description of the elastic scattering problem in terms of an effective, energy-dependent, nonlocal Hamiltonian, H_{eff},

$$H_{\text{eff}} = PHP + P(H-E)Q[Q(E-H)Q]^{-1}Q(H-E)P$$
$$\equiv PHP + V_{\text{opt}} \,. \qquad (1)$$

Equation (1) is in a standard notation[9,10] referring to projection operators P and Q which formally satisfy the conditions that the sum of P and Q is the unit operator and $PQ=0$. In our case, P projects on the space appropriate to the static-exchange approximation which is spanned by configurations of the form

$$\Phi_P(\mathbf{r}_{1'},\mathbf{r}_{N+1}) = A[\chi(\mathbf{r}_{1'},\mathbf{r}_N)\phi(\mathbf{r}_{N+1})] \,, \qquad (2)$$

where χ denotes the Hartree-Fock ground-state wave function of CH_2O and ϕ denotes a basis orbital constructed from a linear combination of Gaussian basis functions. The physics included by the optical potential is determined by the choice of configurations which span the Q space. In these calculations we have chosen 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 electronic configuration of formaldehyde in the Hartree-Fock approximation is $(1a_1^2 2a_1^2 3a_1^2 4a_1^2 1b_2^2 5a_1^2 1b_1^2 2b_2^2)$. The configurations in the Q space all consist of antisymmetrized products of a basis orbital (ϕ) and target configurations which are singlet-coupled, single excitations from the occupied Hartree-Fock orbitals to virtual orbitals of the same symmetry. We have 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. This effect has been modeled in several calculations on homonuclear diatomics by constructing a static-exchange potential using orbitals from a Hartree-Fock calculation on the anion.[11,12] However, the use of anion orbitals in the construction of an effective potential drastically alters the dipole moment of the molecule and therefore would change the background scattering both on and off resonance. The present approach is far more preferable because 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.[9]

The optical-potential Hamiltonian, H_{eff}, defines a one-electron scattering problem with an energy-dependent, nonlocal potential with the symmetry of CH_2O. To solve that problem we use a recently developed implementation[5] of the complex Kohn variational principle for electron-molecule scattering.

There is a long-standing problem in the traditional Kohn method, and other related techniques, that concerns the appearance of unphysical, basis-set-dependent, spurious singularities.[13] This problem has been completely eliminated in the present approach by formulating the principle with complex, outgoing-wave boundary conditions.[14,15] Furthermore, all exchange matrix elements of the Hamiltonian involving continuum basis functions, which would be particularly difficult to evaluate, are systematically and rigorously eliminated in the present formulation,[16] resulting in an efficient computational method especially well suited to molecular applications. We evaluate direct matrix elements of the Hamiltonian involving continuum functions by a novel, adaptive three-dimensional quadrature scheme,[5] thus avoiding numerical single-center expansions which generally converge very slowly for polyatomic systems. All other matrix-element evaluation is implemented by standard quantum electronic-structure methodology.

The physical content of the formalism can be characterized briefly by considering the form of the trial scattering wave function,

$$\psi(\mathbf{r}_{1'},\mathbf{r}_{N+1}) = A[\chi(\mathbf{r}_{1'},\mathbf{r}_N)F(\mathbf{r}_{N+1})] , \tag{3}$$

where χ is the Hartree-Fock wave function and the continuum functions, F, are further expanded using a combination of continuum and square-integrable basis functions,

$$\begin{aligned} rF(\mathbf{r}) = \sum_l [f_l(r)\delta_{ll'}\delta_{mm'} + T_{lml'm'}g_l(r)]Y_{lm}(\hat{\mathbf{r}}) \\ + \sum_k c_k\phi_k(\mathbf{r}) , \end{aligned} \tag{4}$$

where $Y_{lm}(\hat{\mathbf{r}})$ is a spherical harmonic and $\phi_k(\mathbf{r})$ denotes a square-integrable basis function which is generally a linear combination of Gaussians. The continuum functions appearing in the expansions have the form,

$$\begin{aligned} f_l(r) &= h(r)j_l(kr)/\sqrt{k} \underset{r\to\infty}{=} \sin(kr - l\pi/2)/\sqrt{k} , \\ g_l(r) &= ih(r)[j_l(kr) + in_l(kr)c(r)]/\sqrt{k} \\ &\underset{r\to\infty}{=} [i(kr - l\pi/2)]/\sqrt{k} , \end{aligned} \tag{5}$$

where the functions $c(r)$ and $h(r)$ are cutoff functions; $c(r)$ is chosen to regularize n_l at $r=0$ and $h(r)$ can further exclude both the regular and irregular functions from the inner portion of the interaction region. The T-matrix elements which we desire to compute, and which provide both differential and integral scattering information are the coefficients $T_{lml'm'}$ in the expansion in Eq. (3). The Kohn variational principle can be used to characterize the T matrix as the stationary value of the functional:[17]

$$[\underline{T}] = \underline{T} - 2\int \Psi(H_{\text{eff}} - E)\Psi . \tag{6}$$

The result of the variation is

$$[\underline{T}] = -2(\underline{M}_{00} - \underline{M}_{q0}\underline{M}_{qq}^{-1}\underline{M}_{q0}) , \tag{7}$$

where the elements of $\underline{M}_{00}$ are matrix elements of the effective Hamiltonian including the optical potential and are defined as

$$(M_{00})_{lml'm'} = \int A(\chi f_l Y_{lm})(H_{\text{eff}} - E)A(\chi f_{l'} Y_{l'm'}) . \tag{8}$$

The matrices $\underline{M}_{0q}$ and $\underline{M}_{qq}$ are similarly defined as matrix elements of $H_{\text{eff}} - E$ with q referring to the subspace spanned by functions $A(\chi g_l Y_{lm})$ and $A(\chi\phi_k)$. Because of the outgoing-wave definition of the functions g_l, the matrix $\underline{M}_{qq}$ is complex symmetric and *its inverse is nonsingular for real energies*. Thus the complex Kohn variational principle is anomaly free.

The essence of the entire calculation can be reduced to the evaluation of the matrix elements of $H_{\text{eff}} - E$ over bound and continuum basis functions. 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) 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 polyatomics. 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 representation of all exchange operators and by orthogonalizing the continuum basis functions to the square-integrable basis used in the representation of exchange. We will give no further details of that step here because it has been discussed in detail elsewhere.[16] The only remaining matrix elements involving continuum functions are "direct" and thus require a single three-dimensional integration. The second step in rendering the polyatomic problem tractable is to evaluate those using an efficient and accurate three-dimensional quadrature which can readily take advantage of vector supercomputers.

The key to making this quadrature practical is to make it adaptive so that the 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. We begin by constructing the integrand so we need to evaluate integrals of the form

$$I=\int F(\mathbf{r})d^3r\,. \tag{9}$$

We then define the change of variable,

$$\mathbf{r}(\mathbf{q})=\mathbf{q}-\sum_{\text{nuc}}(\mathbf{q}-\mathbf{R}_{\text{nuc}})S_{\text{nuc}}(\mathbf{q})\,, \tag{10}$$

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

$$S_{\text{nuc}}(\mathbf{q}) \underset{q\to\infty}{\longrightarrow} 0\,. \tag{11}$$

This property is necessary so that the transformation in Eq. (10) will reduce to the identity, and $\mathbf{r}$ will be the same as $\mathbf{q}$ at large distances from the molecule. Typically we choose the strength function as a weighted Gaussian centered at the nucleus in question with an exponent of sufficient magnitude to draw the points to the singularity. The efficacy of the choice is tested by integrating a Yukawa potential numerically and comparing it with the known analytic result. If the choice is appropriate the numerical integral should be much more accurate with the transformed grid. This may be repeated for various exponents until the desired accuracy is achieved. For the present calculation we chose $S_{\text{nuc}}(\mathbf{q})=g_{\text{nuc}}(\mathbf{q})^2/\sum g_{\text{nuc}}(\mathbf{q})$, where $g_{\text{nuc}}(\mathbf{q})=\exp[-\alpha(\mathbf{q}-\mathbf{R}_{\text{nuc}})^2]$ with $\alpha=15.0$. With this change of variable the integral we wish to evaluate becomes

$$I=\int F[\mathbf{r}(\mathbf{q})]\,|\partial\mathbf{r}/\partial\mathbf{q}|\,d^3q\,. \tag{12}$$

Now we choose a quadrature in $\mathbf{q}$ 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. (12) transforms the points under the mapping $\mathbf{r}(\mathbf{q})$ so that they are distributively adaptive while the Jacobian, $|\partial\mathbf{r}/\partial\mathbf{q}|$, provides the correct weights. The integrals involving continuum functions in the present calculation on formaldehyde were calculated using a grid of less than 60000 points. Further details and an evaluation of the accuracy of such quadratures are given elsewhere.[5]

We now turn to the physical aspects of electron scattering from formaldehyde. 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 T-matrix elements $T_{lml'm'}$ fails to converge,[18] as does the differential cross section in the forward direction. A treatment of this problem, which has been used with great success in the case of polar diatomics, was proposed by Norcross and Padial,[19] and is summarized by the expression for the laboratory-frame differential cross section for the rotational transition $j\to j'$, where j denotes all relevant rotational quantum numbers,

$$\left(\frac{d\sigma}{d\Omega}\right)_{j\to j'}=\left(\frac{d\sigma}{d\Omega}\right)^{\text{Born}}_{j\to j'}+\Delta\left(\frac{d\sigma}{d\Omega}\right)_{j\to j'}. \tag{13}$$

In Eq. (13), $(d\sigma/d\Omega)^{\text{Born}}_{j\to j'}$ is the Born approximation to the cross section for a rotating point dipole (whose magnitude is that of the molecule's permanent dipole) and $\Delta(d\sigma/d\Omega)_{j\to j'}$ denotes the difference between the contribution due to the computed T-matrix elements $T_{lml'm'}$ and that due to their counterparts, $T^{\text{Born}}_{lml'm'}$, in the Born approximation for the point dipole. The latter is evaluated in the fixed-nuclei approximation. This treatment is called the multipole extracted adiabatic nuclei (MEAN) method 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.[1]

Specifically, our calculations on formaldehyde were performed as follows. In these preliminary calculations, the Kohn equations were solved only for b_1 symmetry; we expect the other symmetries to be dominated by the dipole potential and hence included them in Eq. (13) in the Born approximation. The Gaussian basis used in the expansion of the continuum orbital was a standard contracted basis of Dunning[20] augmented by nine Gaussians of b_1 symmetry located on the carbon and oxygen nuclei and at the center of charge. Continuum functions with l and $|m|$ values up to 4 (which contribute to b_1 symmetry) were also used in the expansion of the continuum orbital. We found that the results of Eq. (13) for the differential cross section (summed over allowed j' values) at a scattering angle of 90° were completely insensitive to the initial value of j. The Born differential cross section used in Eq. (13), which is given by Crawford, Dal-

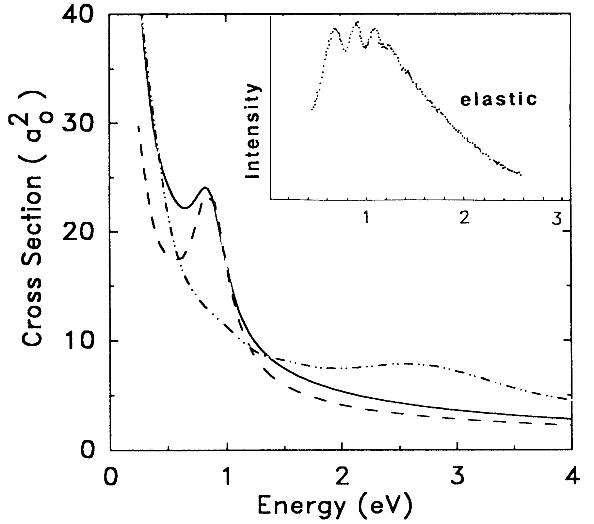

FIG. 1. Elastic differential cross section for e^--CH_2O. Solid curve: optical-potential results at 90°; dashed curve: optical-potential results at 120°; dash-dotted curve: static-exchange result at 90°. Inset: Experimental results of Benoit and Abouaf (Ref. 8).

garno, and Hays,[18] is therefore computationally equivalent to Altshuler's[21] result for elastic scattering.

Our results are summarized in Fig. 1. In the static-exchange approximation the resonance appears at an energy nearly 2 eV above the correct position and with a far broader width than both the optical-potential results and experiment. The results of the optical-potential calculation place the resonance essentially exactly at the experimentally observed position,[7,8] as in earlier calculations on electron-N_2 collisions.[9] 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 Fig. 1 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 Fig. 1 display vibrational structure due to 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, either by the "boomerang"[22] method using the *ab initio* resonance parameters or by vibrational close coupling. Only then will it be clear whether the apparently narrower width in the optical-potential calculations is consistent with experiment.

The calculations we present here demonstrate that the combination of our implementation of the complex Kohn approach and an *ab initio* optical potential is capable of treating general polyatomic systems accurately. The principle barriers remaining to, for example, electronic close-coupling calculations on polyatomic molecules involve the development of accurate but compact representations of the electronic wave functions of the target states. The difficulties involved in solving the scattering problem for general nonspherical, nonlocal or energy-dependent potentials have been surmounted for electron-polyatomic molecule scattering.

Calculations of electron-formaldehyde scattering in other molecular symmetries than b_1 and for other molecular geometries are underway and will be published elsewhere.

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