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# Discrete-basis-set calculation for $e$-$N_2$ scattering cross sections in the static-exchange approximation*

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Calculations are reported for low-energy $e$-$N_2$ scattering cross sections in the static-exchange approximation. Our approach involves solving the Lippman-Schwinger equation for the transition operator in a subspace of Gaussian functions. A new feature of the method is the analytical evaluation of matrix elements of the free-particle Green's function. Another development is the use of an analytical transformation to obtain single-center expansion coefficients for the scattering amplitude from our multicenter discrete-basis-set representation of the $T$ matrix. We present results for the total elastic and rotational excitation cross sections, and the momentum-transfer cross section, for incident electron energies from 0.5 to 10 eV. Comparison is made with other theoretical results and experimental data.

## I. INTRODUCTION

The importance of electron-molecule collision processes in several areas of current research interest provides a strong incentive for development of accurate methods of *ab initio* calculation. Discrete basis set methods are of particular interest since the lack of spherical symmetry makes the application of numerical techniques considerably more difficult for molecules than for atoms. Theoretical work in electron-molecule scattering has been reviewed by Takayanagi[1] and by Golden *et al.*,[2] and more recently by Temkin.[3] Systems larger than $H_2$ for which electronically elastic scattering results have been obtained include $N_2$, CO, and $CO_2$.[4-9] Discrete basis set methods have been applied to $H_2$, $N_2$, and $F_2$.[10-13] To date the most sophisticated calculations have employed numerical techniques. The most accurate calculation using discrete-basis-set methods is the $R$-matrix calculation of Schneider[11] for $H_2$. The advantages and limitations of the various approaches referenced above have yet to be thoroughly evaluated.

The subject of this paper is the discrete basis function method for nonspherical potential scattering introduced by Rescigno, McCurdy, and McKoy.[10,14,15] The approach involves representing the potential by its projection onto a set of Gaussian basis functions and solving the Lippman-Schwinger equation for the transition operator in the discrete function subspace. We report new features of the method and its application to electronically elastic $e$-$N_2$ scattering in the static-exchange approximation.

Solving the Lippman-Schwinger equation in a basis set requires an efficient method for computing matrix elements of the free-particle Green's function. In previous calculations this involved a numerical quadrature and was in practice restricted to cases of axial symmetry.[14] As Ostlund has shown, these matrix elements may be evaluated analytically.[16] We have extended Ostlund's results for $s$- and $p$-type Gaussians[16,17] up to Gaussians of $f$-type symmetry and now we use these results in our computational procedure. An important feature of our prescription for the Green's function is that it is directly applicable to polyatomic systems.

In previous applications of the method, elastic cross sections were obtained from fixed-nuclei scattering amplitudes by numerically averaging over target orientation.[10] To calculate rotational excitation and momentum-transfer cross sections, it is desirable to treat the target orientation dependence analytically. This is now achieved by means of a single-center expansion for the scattering amplitude. We stress that the dynamical problem, represented by the Lippman-Schwinger equation, is solved as before using a multicenter basis set. The matrix elements involved in the transformation to the single-center expansion for the scattering amplitude are evaluated analytically. We also point out that, since the matrix elements used to construct the basis-set representation of the potential are evaluated using techniques developed for bound-state calculations,[18] all the matrix elements required in our prescription for scattering are now treated analytically using formulas completely applicable to polyatomic systems.

In this work our results do not include a variational correction for first order errors due to the truncation of the potential. Including the correction would require considerable additional computational effort and it is interesting to demonstrate that useful results can be obtained using moderately sized basis sets even when the correction is omitted. The calculation of variationally stable results will be the subject of future work. In Sec. II a simple method for reducing variational error at very low energies is discussed.

Results are presented for the total elastic and momentum transfer cross sections calculated in the fixed-nuclei approximation; and also for total rotational excitation cross sections calculated in the adiabatic-nuclei approximation. We compare our cross sections with the theoretical results of Burke and Sinfailam[4] and with the experimental data of Golden[19] and of Englehardt *et al.*[20] Our results are dominated by a resonance in the $^2\Pi_g$ channel in qualitative agreement with experiment and other calculations.

## II. THEORY

In the fixed-nuclei approximation the Schrödinger equation for the scattered electron is of the form (in atomic units)

$$[-\tfrac{1}{2}\nabla^2+V(R,\vec{r})-\tfrac{1}{2}k^2]\psi^+_{\vec{k}}(R,\vec{r})=0\ , \tag{1}$$

where $V(R,\vec{r})$ is an optical potential for the effective interaction between the target and the scattered electron which depends parametrically on the relative coordinates of the target nuclei (denoted by $R$). The vector subscript $\vec{k}$ indicates the dependence of the wave function on direction as well as the magnitude of the incident momentum for a nonspherical target. The scattering wave function vanishes at the origin and has the asymptotic form

$$\psi^+_{\vec{k}}(\vec{r})\to[e^{i\vec{k}\cdot\vec{r}}+f_{\vec{k}}(\hat{r})e^{ikr}/r]/(2\pi)^{3/2}\ , \tag{2}$$

as $r\to\infty$. This corresponds to the normalization

$$\langle\psi^+_{\vec{k}'}|\psi^+_{\vec{k}}\rangle=\delta(\vec{k}-\vec{k}')\ . \tag{3}$$

Rather than solve Eq. (1) directly, we work with the Lippman-Schwinger equation for the transition matrix

$$T=U+UG_0^+T\ , \tag{4}$$

where $U=2V$, and $G_0^+$ is the free-particle Green's function for the out-going wave boundary condition. The $T$ matrix solution of Eq. (4) satisfies the identity

$$\langle\vec{k}'|T|\vec{k}\rangle\equiv\langle\vec{k}'|U|\psi^+_{\vec{k}}\rangle\ , \tag{5}$$

where $\vec{k},\vec{k}'$ denote plane-wave states of the form

$$\phi_{\vec{k}}(\vec{r})=\frac{e^{i\vec{k}\cdot\vec{r}}}{(2\pi)^{3/2}}\ . \tag{6}$$

In our notation the $T$ matrix is related to the scattering matrix $S$ according to

$$S=1-i\pi\delta(E-E')T\ , \tag{7}$$

and is related to the scattering amplitude according to

$$f_{\vec{k}}(\hat{r})=-2\pi^2\langle\vec{k}'|T|\vec{k}\rangle\ , \tag{8}$$

where $\hat{r}=\hat{k}'$.

In actual calculations it is convenient to work with the $K$ matrix defined by the relation

$$\langle\vec{k}'|K|\vec{k}\rangle=-\tfrac{1}{2}\pi\langle\vec{k}'|U|\psi^{(P)}_{\vec{k}}\rangle\ , \tag{9}$$

where $\psi^{(P)}_{\vec{k}}$ is the scattering wave function for the standing-wave boundary condition. The on-shell $K$ matrix satisfies the relation

$$S=(1+iK)/(1-iK)\ . \tag{10}$$

Defining $K'=-(2/\pi)K$, the Lippman-Schwinger equation for the $K'$ matrix is

$$K'=U+UG_0^PK'\ , \tag{11}$$

where $G_0^P$ is the free-particle Green's function for the standing-wave boundary condition.

To solve Eq. (4) the potential is projected onto a subspace of square-integrable functions $\{\varphi_\alpha\}$. This forms an $N\times N$ matrix generalization of the separable potential approximation

$$V^t(\vec{r},\vec{r}')=\sum_{\alpha,\beta}\varphi_\alpha(\vec{r})\langle\alpha|V|\beta\rangle\varphi^*_\beta(\vec{r}')\ . \tag{12}$$

Inserting the truncated potential $V^t$, Eq. (4) becomes a matrix equation with solution

$$T^t=(1-U^tG_0^+)^{-1}U^t\ . \tag{13}$$

The momentum representation of the on-shell $T$ matrix is obtained by the transformation

$$\langle\vec{k}'|T|\vec{k}\rangle=\sum_{\alpha,\beta}\langle\vec{k}'|\alpha\rangle\langle\alpha|T|\beta\rangle\langle\beta|\vec{k}\rangle\ . \tag{14}$$

The truncated potential is constructed from a basis set of Cartesian Gaussian functions of the form

$$\mu^{\alpha\vec{A}}_{lmn}=N_{lmn}(x-A_x)^l(y-A_y)^m(z-A_z)^ne^{-\alpha|\vec{r}-\vec{A}|^2}\ , \tag{15}$$

where $N_{lmn}$ is a normalization factor. The basis function centers, denoted by $\vec{A}$ in Eq. (15), are placed at the target nuclei and at the center of mass. Cartesian functions are widely used in molecular bound-state calculations due to their convenient analytical properties.[18] The matrix solution $T^t$ involves Gaussian matrix elements of the free-particle Green's function

$$\langle\mu_i|G_0^+(E)|\mu_j\rangle=\lim_{\epsilon\to0^+}\int d^3k\,\frac{\langle\mu_i|\vec{k}\rangle\langle\vec{k}|\mu_j\rangle}{q^2-k^2+i\epsilon}\ , \tag{16}$$

where $E=\tfrac{1}{2}q^2$. Similarly, the matrix solution $K^t$ involves Gaussian matrix elements of the free-particle Green's function

$$\langle\mu_i|G_0^P(E)|\mu_j\rangle=P\int d^3k\,\frac{\langle\mu_i|\vec{k}\rangle\langle\vec{k}|\mu_j\rangle}{q^2-k^2}\ , \tag{17}$$

where $P$ denotes principal-value integration.

As shown by Ostlund[16] these matrix elements can be reduced analytically to an error function with complex argument for which efficient algorithms exist.[21] Based on Ostlund's techniques for evaluating scattering integrals involving Gaussian and plane-wave function, we have developed a straightforward procedure for deriving formulas for matrix elements of $G_0^+$ (or $G_0^P$) involving Gaussians of arbitrary center and symmetry type. Formulas for $s$- and $p$-type Gaussians have also been obtained by Ostlund.[17] A description of our analytical procedure and results for Gaussians of up to $f$-type symmetry will be published elsewhere.[22] Formulas for $s$- and $p$-type Gaussian matrix elements of $G_0$ are given in Appendix A.

In order to treat the target orientation dependence of the scattering analytically, we use a single-center expansion of the scattering amplitude. For simplicity consider the case of a linear molecule. In the body-fixed frame with $z$ axis along the internuclear axis, the wave function and scattering amplitude have the expansions[1]

$$\psi_{\vec{k}}^{+}(\vec{r}) = \frac{4\pi}{(2\pi)^{3/2}} \sum_{ll'm} i^{l'} g_{ll'm}(kr) Y_{lm}(\hat{r}) Y_{l'm}^{*}(\hat{k}) , \tag{18}$$

$$f_{\vec{k}}(\hat{r}) = 4\pi \sum_{ll'm} f_{ll'm}(k) Y_{lm}(\hat{r}) Y_{l'm}^{*}(\hat{k}) . \tag{19}$$

The radial wave functions have the asymptotic form

$$g_{ll'm}(kr) \rightarrow (2i/kr)(\delta_{ll'} e^{-i(kr - l\pi/2)} - S_{ll'm} e^{i(kr - l\pi/2)}) , \tag{20}$$

as $r \rightarrow \infty$. The single-center expansion coefficients for the $S$ matrix and the scattering amplitude are related according to

$$f_{ll'm} = (i^{l'-l}/2ik)(S_{ll'm} - \delta_{ll'}) . \tag{21}$$

The single-center expansion of the on-shell $T$ matrix is of the form

$$\langle \vec{k}' | T | \vec{k} \rangle = \frac{1}{k} \sum_{ll'm} i^{l'-l} T_{ll'm}(k) Y_{lm}(\hat{k}') Y_{l'm}^{*}(\vec{k}) . \tag{22}$$

Equating the right-hand sides of Eqs. (14) and (22), and using the spherical expansion of a plane wave

$$e^{i\vec{k}\cdot\vec{r}} = 4\pi \sum_{lm} j_l(kr) Y_{lm}(\hat{r}) Y_{lm}^{*}(\hat{k}) , \tag{23}$$

we obtain the single-center expansion for $T^t$:

$$T_{ll'm}^{t} = \frac{2k}{\pi} \sum_{\alpha\beta} \langle j_l Y_{lm} | \alpha \rangle \langle \alpha | T | \beta \rangle \langle \beta | j_{l'} Y_{l'm} \rangle . \tag{24}$$

Comparing Eqs. (7), (21), and (24) shows

$$f_{ll'm} = -i^{l'-l} \sum_{\alpha\beta} \langle j_l Y_{lm} | \alpha \rangle \langle \alpha | T | \beta \rangle \langle \beta | j_{l'} Y_{l'm} \rangle . \tag{25}$$

Noting that the single-center expansion of the $K'$ matrix has the same form as Eq. (22), and recalling that $K' = -2K/\pi$, we have

$$K_{ll'm}^{t} = -k \sum_{\alpha\beta} \langle j_l Y_{lm} | \alpha \rangle \langle \alpha | K' | \beta \rangle \langle \beta | j_{l'} Y_{l'm} \rangle . \tag{26}$$

The transformations (24)–(26) involve the matrix element $\langle \mu_{pqs}^{\alpha\vec{A}}(\vec{r}) | j_l(kr) Y_{lm}(\hat{r}) \rangle$. As pointed out by Schneider,[23] these matrix elements may be evaluated analytically. The technique for evaluating the single-center transformation matrix elements and formulas for $s$- and $p$-type Gaussians are given in Appendix B.

It is convenient to express the scattering amplitude in the laboratory frame with $z'$ axis in the direction of incident momentum. Using the rotational properties of spherical harmonics and introducing the rotational harmonics defined in Edmonds,[24] we find that the scattering amplitude in the laboratory frame is given by

$$f_k(R, \vec{\beta}, \hat{r}') = 4\pi \sum_{ll'mm'} \left( \frac{2l'+1}{4\pi} \right)^{1/2} f_{ll'm}(k, R) \times D_{m'm}^{(l)}(\vec{\beta}) D_{0m}^{(l')*}(\vec{\beta}) Y_{lm}(\hat{r}') , \tag{27}$$

where $R$ denotes the internuclear separation (for a diatomic) and $\vec{\beta}$ denotes the target orientation in the laboratory frame (in general a function of three Euler angles); $\hat{r}'$ denotes the scattering angles in the laboratory frame. Temkin *et al.* express the laboratory frame scattering amplitude in the form[25]

$$f_k(R, \vec{\beta}, \hat{r}') = \sum_{ll'mm'} a_{ll'm}(k, R) D_{m'm}^{(l)}(\vec{\beta}) D_{0m}^{(l')}(\vec{\beta}) Y_{lm}(\hat{r}') . \tag{28}$$

Comparing Eqs. (25), (27), and (28) yields the following prescription for the fixed-nuclei dynamical coefficients:

$$a_{ll'm}(k, R) = -[4\pi(2l+1)]^{1/2} i^{l'-l} \times \sum_{\alpha\beta} \langle j_l Y_{lm} | \alpha \rangle \langle \alpha | T | \beta \rangle \langle \beta | j_{l'} Y_{l'm} \rangle . \tag{29}$$

To calculate rotational excitation cross sections we use the adiabatic nuclei approximation

$$f_k(\hat{r}'; \Gamma' \leftarrow \Gamma) = \langle \Theta_{\Gamma'}(R, \vec{\beta}) | f_k(R, \vec{\beta}, \hat{r}') | \Theta_{\Gamma}(R, \vec{\beta}) \rangle , \tag{30}$$

where $\Theta_{\Gamma}$, $\Theta_{\Gamma'}$ are wave functions for the target nuclei. This approximation, due to Chase[26] and applied to electron-molecule scattering by Chang and Temkin,[27] is valid when the speed of the projectile is fast compared to the motion of the target nuclei.

The static-exchange approximation for the scattering potential is obtained by representing the electronic part of the scattering wave function by an antisymmetrized product state

$$\Psi^{+}_{\vec{k}} = \{1/[(N+1)!]^{1/2}\} A[\Phi(1,2,\ldots,N)\psi^{+}_{\vec{k}}(N+1)] , \tag{31}$$

where $\Phi$ is the Hartree-Fock wave function for the target and $\psi^{+}_{\vec{k}}$ is the wave function for the projectile. Substitution of the wave function (31) into Schrödinger's equation leads to the nonlocal static-exchange potential for a closed-shell target:

$$V = \sum_{i} - \frac{1}{|\vec{R}_i - \vec{r}|} + \sum_{j} (2J_j - K_j) , \tag{32}$$

where $J$ and $K$ are the usual Coulomb and exchange operators. The first term on the right-hand side of Eq. (32) is summed over target nuclei, the second is summed over occupied orbitals.

At very low scattering energies variational error due to the difference $V - V^t$ may be reduced by solving Eq. (4) at eigenenergies of the separable Hamiltonian

$$H^t = \sum_{\alpha\beta} |\alpha\rangle\langle\alpha|H|\beta\rangle\langle\beta| . \tag{33}$$

To see this, consider the positive energy eigenfunctions $\chi_k(\vec{r})$ which satisfy

$$H^t \chi_k = \tfrac{1}{2} k^2 \chi_k , \tag{34}$$

and are determined by diagonalization of $H^t$.

We are interested in the conditions under which the solution $\chi_k$ of Eq. (34) is proportional to the scattering wave function

$$\psi^{+}_{\vec{k}} = \phi_{\vec{k}} + G^{+}_{0} T^t \phi_{\vec{k}} . \tag{35}$$

Clearly, this is not true in general because the scattering wave function depends on the direction of the incident particle, and this boundary condition is not taken into account in the diagonalization of $H^t$. However, at very low energy $\psi^{+}_{\vec{k}}$ and $\chi_k$ are dominated by the lowest contributing partial wave and, hence, have approximately the same behavior at the origin. It follows that in this energy range $\psi^{t}_{\vec{k}}$ and $\chi_k$ are approximately proportional,

$$\psi^{t}_{\vec{k}}(\vec{r}) \simeq C(k)\chi_k(\vec{r}) , \tag{36}$$

if we assume that the effect of truncating the kinetic-energy operator in $H^t$ is small. The Kohn prescription for the variationally stable scattering amplitude is[28]

$$f^{s}_{\vec{k}',\vec{k}} = f^{t}_{\vec{k}',\vec{k}} - 4\pi^2 \langle \psi^{t}_{\vec{k}'} |(H - E)| \psi^{t}_{\vec{k}} \rangle . \tag{37}$$

If our discrete basis set is adequate to represent $\chi_k$ beyond the effective range of the potential, then approximation (36) may be used in Eq. (37). Since $\chi_k$ is determined by a variationally stable procedure, the second term on the right-hand side of Eq. (37) vanishes through first order. Hence

$$f^{s}_{\vec{k}',\vec{k}} \simeq f^{t}_{\vec{k}',\vec{k}} + O^2(V - V^t) , \tag{38}$$

when $E = \frac{1}{2} k^2$ is an eigenenergy of $H^t$.

## III. CALCULATIONS AND RESULTS

The truncated static-exchange potential $V^t$ is calculated in two steps. The first involves self-consistent-field (SCF) calculation for the occupied orbitals of the target. A standard basis set of contracted Cartesian Gaussian functions is used. In the second step matrix elements of the static-exchange potential, defined by Eq. (32), are computed over a larger set of uncontracted functions, called the scattering basis set. The scattering basis includes the primitive (uncontracted) Gaussians used in the target SCF calculation. This insures orthogonality between the scattering subspace and the target orbital subspace. This requirement may be relaxed under certain conditions as noted below. The scattering basis also includes functions which account for components of the scattering subspace which cannot be constructed from the target SCF basis. In this calculation the target basis set is augmented by adding diffuse functions at the center or on the nuclei.

The ground state of $N_2$ has the electron configuration ${}^1\Sigma_g(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4$. In the SCF calculation we use a $[4s3p_x3p_y3p_z2d_{xz}2d_{yx}2d_{zz}]$ contracted basis set on each nucleus plus two diffuse $p_z$ functions on the center. The $[4s3p]$ basis is constructed from a $(9s5p)$ set of primitives using the contraction coefficients suggested by Dunning.[29] The choice of $d$-type functions, which are necessary to obtain an accurate quadrupole moment, is due to Truhlar *et al.*[30] The quadrupole moment for this basis is −1.02 a.u.

For a homonuclear diatomic the scattering potential is block diagonal in the symmetries ${}^2\Sigma_g$, ${}^2\Sigma_u$, ${}^2\Pi_u$, ${}^2\Pi_g$, ..., and, hence, the Lippman-Schwinger equation may be solved separately for each case. In this work we consider scattering in the $\Sigma$ and $\Pi$ channels. Table I lists the scattering basis sets for each symmetry. Target basis functions of $d$-type symmetry are omitted in the scattering basis sets since these functions have little effect at the incident energies considered. The basis-set calculations are carried out using standard bound-state molecular integral programs.

To investigate the convergence of the scattering basis set, we varied the basis functions for each symmetry in preliminary calculations. Alternate basis sets were constructed in several ways. The use of contracted basis functions was rejected due

TABLE I. Scattering basis sets. $\vec{A}$ denotes the coordinates of the center of the basis function $\mu_{lmn}^{\alpha\vec{A}}(\vec{r})$. $(l,m,n)$ denotes the symmetry type of $\mu_{lmn}^{\alpha\vec{A}}(\vec{r})$.

| | $^2\Sigma_g$ | | | $^2\Sigma_u$ | |
|---|---|---|---|---|---|
| $\vec{A}=(0,0,\pm1.034)$ | $(0,0,\pm1.034)$ | $(0,0,0)$ | $\vec{A}=(0,0,\pm1.034)$ | $(0,0,\pm1.034)$ | $(0,0,0)$ |
| $(l,m,n)=(0,0,0)$ | $(0,0,1)$ | $(0,0,0)$ | $(l,m,n)=(0,0,0)$ | $(0,0,1)$ | $(0,0,1)$ |
| 5909.44 | 26.786 | 0.128 | 5909.44 | 26.786 | 0.1 |
| 887.451 | 5.9564 | 0.0768 | 887.451 | 5.9564 | 0.06 |
| 204.749 | 1.7074 | 0.0461 | 204.749 | 1.7074 | 0.036 |
| 59.837 | 0.5314 | 0.0276 | 59.837 | 0.5314 | 0.0216 |
| 19.9981 | 0.1654 | 0.0166 | 19.9981 | 0.1654 | 0.0130 |
| 2.686 | | 0.00995 | 2.686 | | 0.0078 |
| 7.1927 | | 0.00597 | 7.1927 | | 0.003 |
| 0.7 | | 0.003 | 0.7 | | 0.0015 |
| 0.213 | | 0.0015 | 0.213 | | |
| | | 0.006 | | | |

| $^2\Pi_u$ | | $^2\Pi_g$ | |
|---|---|---|---|
| $\vec{A}=(0,0,\pm1.034)$ | $(0,0,0)$ | $\vec{A}=(0,0,\pm1.034)$ | |
| $(l,m,n)=(1,0,0)$ | $(1,0,0)$ | $(l,m,n)=(1,0,0)$ | |
| 26.786 | 0.0992 | 26.786 | 0.0357 |
| 5.9564 | 0.0595 | 5.9564 | 0.0214 |
| 1.7074 | 0.0357 | 1.7074 | 0.0129 |
| 0.5314 | 0.0214 | 0.5314 | 0.00772 |
| 0.276 | 0.0129 | 0.276 | 0.00463 |
| 0.1654 | 0.00772 | 0.1654 | 0.00278 |
| | 0.004 | 0.0992 | 0.00167 |
| | 0.002 | 0.0595 | 0.001 |
| | 0.0007 | | |

to the lack of a criterion for choosing the contraction coefficients. One would not expect the contraction coefficients used in the SCF calculation to be appropriate, and this was verified in test calculations. Adding diffuse functions at the nuclear centers instead of at the center of mass had little effect except in certain cases when this led to linear dependence problems associated with computer round-off error. This occurred, for example, when diffuse two-center $s$-type functions were included in the calculation for $\Sigma_u$ symmetry. Varying the number of diffuse functions added to the SCF basis, or adding tight functions, also had little effect. At the scattering energies considered in this work little effect was found for $d$-type functions. These functions are probably more important at higher energy. The basis sets listed in Table I represent a consensus of our experience with basis sets to date. Apart from fluctuations associated with variational instability, and within the constraints discussed above, our results are insensitive to changes in the basis set. We estimate the uncertainty in our cross sections due to lack of basis set convergence at about 20%. Below 2 eV this error may be larger.

In these calculations we work with the Lippman-Schwinger equation for the $T$ matrix, Eq. (4), which is solved for each incident electron energy and scattering symmetry. The dynamical coefficients $a_{ll'm}$ of the fixed nuclei theory are then obtained using Eq. (29). For the range of scattering energies considered here, we find that the coupled partial-wave expansion for the scattering amplitude may be truncated with negligible error after six partial waves.

In the fixed-nuclei approximation, the total elastic cross section is given by[25]

$$\sigma=\sum_{ll'm}\frac{|a_{ll'm}|^2}{2l'+1}\ . \tag{39}$$

Our results from 0.5 to 10 eV are shown in Fig. 1, together with the experimental data of Golden[19] and the static-exchange approximation results of Burke and Sinfailam.[4] Vibrational structure present in the data of Golden is not shown. The peak in the cross sections is due to a shape resonance in the $^2\Pi_g$ channel.

Results obtained directly from $T$-matrix calculations for a selected grid of incident momenta are indicated by x's in Fig. 1. Failure of these points to form a smooth curve is attributed to variational error in the difference $V - V^t$. As Fig. 1 shows, this effect is quite small for incident energies above 3 eV; however, below 3 eV the ef-

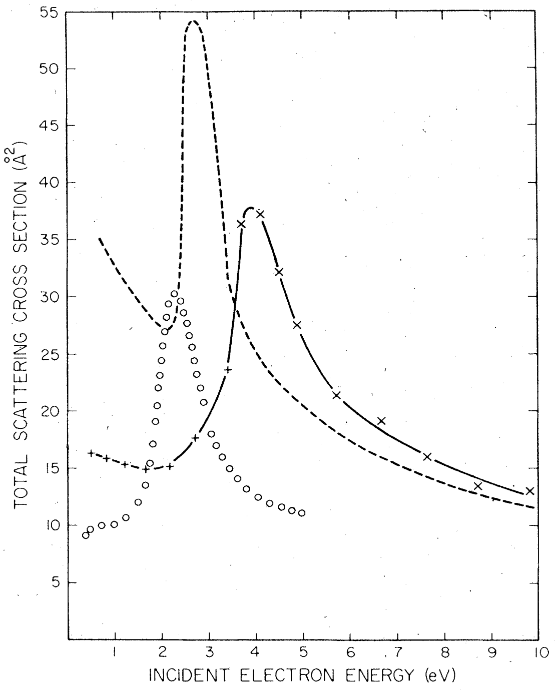

FIG. 1. Total scattering cross section. Broken solid line: this work; crosses: results obtained directly from $T$-matrix calculations; plusses: results obtained from $T$-matrix calculations at eigenenergies and interpolation of $K$ matrix; circles: experimental data of Golden (Ref. 19), observed vibrational substructure is not shown; dashed line: static-exchange results of Burke and Sinfailam (Ref. 4).

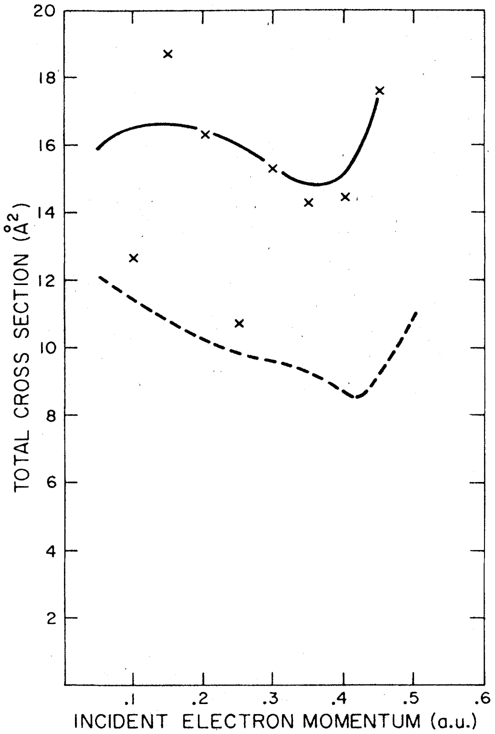

FIG. 2. Total cross section below $^2\Pi_g$ resonance. Crosses are defined as in Fig. 1; solid line: results obtained by interpolation from $T$-matrix calculation at eigenenergies; dashed line: diagonal phase-shift results of McCurdy *et al.* (Ref. 12).

fect becomes large. Our results obtained directly from $T$-matrix calculations for energies below 3 eV are shown in Fig. 2. Note that Fig. 2 is plotted in terms of incident electron momentum. As discussed in Sec. II, we expect a reduction in variational error at the eigenenergies of $H^t$. Since eigenenergies are different for different symmetries, an interpolation procedure must be used. In this work we interpolate the matrix elements of the on-shell, coupled partial-wave $K$ matrix. For energies below the $^2\Pi_g$ resonance, these matrix elements are slowly varying. Our results obtained by interpolation from $T$-matrix calculations at eigenenergies of $H^t$ are shown by the solid curve in Fig. 2 and by the + 's in Fig. 1. At very low energy the slope of the total elastic cross section should approach zero (for $S$-wave scattering in the static-exchange approximation). Instead, below $k = 0.2$ a.u. our results obtained by interpolation drop off anomalously. We attribute this behavior to the basis-set approximation for the potential which becomes increasingly inadequate at very low energy. The dashed line in Fig. 2 shows the diagonal phase shift results of McCurdy *et al.*[12]

The momentum transfer cross section is defined by

$$\sigma_m = \int d(\cos\theta)\,\frac{d\sigma}{d(\cos\theta)}(1-\cos\theta)\;. \tag{40}$$

Setting

$$\frac{d\sigma}{d(\cos\theta)} = \tfrac{1}{2}\sum_L A_L P_L(\cos\theta)\;, \tag{41}$$

we have

$$\sigma_m = A_0 - \tfrac{1}{3}A_1\;. \tag{42}$$

In the fixed-nuclei approximation, the expansion coefficients for the differential cross section are given by[7]

$$A_L = \frac{1}{2L+1}\sum_{ll'\lambda\lambda' m\mu}[(2l+1)(2\lambda+1)]^{1/2}(l\lambda 00|L0)(l'\lambda' 00|L0)(l\lambda m\mu)(l'\lambda' m\mu|Lm+m)a_{ll'm}a^*_{\lambda\lambda'\mu}\;, \tag{43}$$

where $(l_1 l_2 m_1 m_2|l_3 m_3)$ is a Clebsch-Gordan coefficient. Our results for $\sigma_m$ are shown in Fig. 3 with the

the results of Burke and Sinfailam[4] and the data, inferred from swarm experiments, of Englehardt *et al.*[20]

In the adiabatic-nuclei approximation the total rotational excitation cross section is given by[27]

$$\sigma_{j\to j'}=\frac{k_{j'}}{k_j}\sum_{ll'm\mu}a_{ll'm}a^*_{ll'\mu}\frac{(-1)^{m+n}}{(2l'+1)}\sum_J(ll'm,-m\,|J0)(ll'\mu,-\mu\,|J0)(jJ00\,|\,j0)^2\ . \tag{44}$$

In this work we set the ratio $k_{j'}/k_j$ equal to unity. Our results and the results of Burke and Sinfailam are shown in Fig. 4. Note that $\sigma_{0\to 4}$ is larger than $\sigma_{0\to 2}$ in the resonance region, indicating the nearly pure *d*-wave character of the resonance.

## IV. DISCUSSION AND CONCLUSIONS

This calculation shows that useful electron-molecule scattering information can be obtained using moderately sized basis sets and working entirely within the discrete-basis function subspace. Two methods of improving the accuracy of our results are currently being investigated. One approach is to improve the flexibility of the basis set by adding Gaussian functions of *d* type and higher symmetry. The other approach involves the calculation of a variational correction for errors in the scattering amplitude due to the difference $V-V^t$. A method for computing a variational correction for the *K* matrix is currently being applied to $e$-$H_2$ elastic scattering and will be described in a future paper. Preliminary results indicate good convergence properties for the scattering basis sets of the type used in the present calculation.

The discrepancy between our results and the diagonal phase shift results of McCurdy *et al.*[12] below 2 eV is not understood and will be investigated further. In this energy range the approximation involved in the "low-*l* spoiling" method of McCurdy *et al.* should be valid.

An important feature of our method for calculating the dynamical coefficients $a_{ll'm}$ of the fixed-nuclei theory of Temkin *et al.*[25] is that it does not involve single-center expansions of the potential or scattering wave function as part of the solution of the scattering problem. Thus the usual convergence questions concerning these expansions do not arise in our method.

The dynamical coefficients $a_{ll'm}$ refer to the asymptotic part of the scattering wave function and converge rapidly at low incident energy since then only partial waves with low *l* are significantly scat-

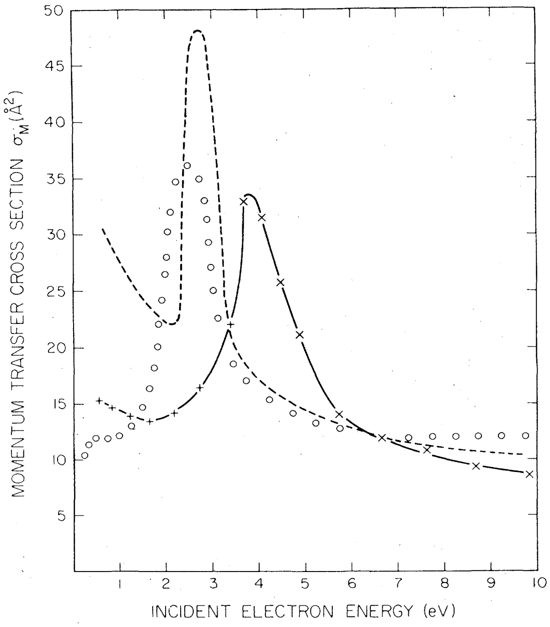

FIG. 3. Momentum-transfer cross section. Broken solid line: this work; crosses and plusses are defined as in Fig. 1; circles: experimental data of Englehardt *et al.* (Ref. 20); dashed line: static exchange results of Burke and Sinfailam.

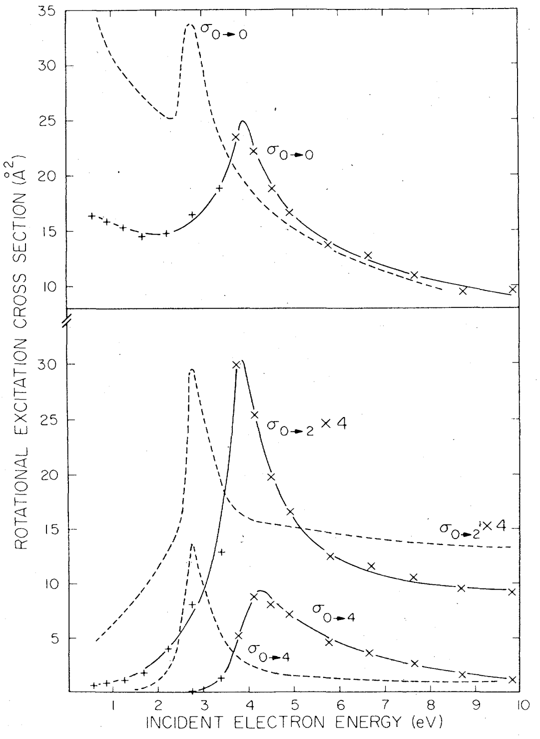

FIG. 4. Rotational excitation cross sections. Solid lines: this work; dashed lines: results of Burke and Sinfailam.

tered by the target. In the case of $e$-$N_2$ scattering below 10 eV we find that the coefficients $a_{ll'm}, l, l' = 0, 1, \ldots, 5; m = 0, \pm 1$ are sufficient to describe the scattering amplitude. This partial-wave expansion for the scattering amplitude should not be confused with the expansion for the total scattering wave function. At low incident energy many more partial waves contribute to the scattering wave function in the region of the target molecule than contribute in the asymptotic region. The high-$l$ partial-wave components of the scattering wavefunction are due to singularities in the potential at the target nuclei.

Morrison and Collins[31] have recently analyzed the partial wave close-coupling method for $e$-$N_2$ scattering in the static approximation. They find that convergence of the $^2\Sigma_g$ cross section requires that partial waves be included up to: $\lambda = 14$ in the multipole expansion of the electronic part of the potential, $\lambda = 28$ in the multipole expansion of the nuclear part of the potential, $l = 26$ in the expansion of the scattering wave function. In contrast the partial-wave close-coupling calculation of Burke and Sinfailam for $e$-$N_2$ scattering in the static exchange approximation includes only $\lambda = 0, 2, 4$ in the multipole expansion for the static potential and $l = 0, 2, 4, 6$ in the partial wave expansion for the $^2\Sigma_g$ scattering wave function. Morrison and Collins show that the unconverged static potential $^2\Sigma_g$ cross section lies above the converged result at low incident energy. Figure 1 shows that the total scattering cross section of Burke and Sinfailam is a factor of 2 larger than ours at 1 eV incident energy. Thus it is probable that lack of convergence in the calculation of Burke and Sinfailam accounts for most of the discrepancy between their results and ours. Buckley and Burke[6] have recently analyzed the calculation of Burke and Sinfailam and they find that the latter's results are not converged. Unfortunately, Buckley and Burke do not present their own static-exchange results for $e$-$N_2$ scattering.

Our results show that the static-exchange approximation for scattering is in qualitative agreement with experimental results for the total elastic and the momentum-transfer cross section although polarization and other electron correlation effects are clearly important. The displacement of our resonance peak to about 1.5 eV above the position observed experimentally, and the rapid drop in the experimental cross section below 0.5 eV incident energy are attributed primarily to polarization of the target by the scattered electron. Methods for including polarization in our prescription for scattering are currently being investigated.

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## APPENDIX A: GAUSSIAN MATRIX ELEMENTS OF FREE-PARTICLE GREEN'S FUNCTION

The Fourier transform of a normalized Cartesian Gaussian is given by

$$\langle \mu^{\alpha\vec{A}}_{lmn} | \vec{k} \rangle = \frac{(2\pi/\alpha)^{3/4} i^{l+m+n}}{[(2l-1)!!(2m-1)!!(2n-1)!!]^{1/2}} H_l\left(\frac{k_x}{2\sqrt{\alpha}}\right) H_m\left(\frac{k_y}{2\sqrt{\alpha}}\right) H_n\left(\frac{k_z}{2\sqrt{\alpha}}\right) \exp\left(i\vec{k}\cdot\vec{A} - \frac{k^2}{4\alpha}\right), \tag{A1}$$

where $H_l(x)$ is a Hermite polynomial. Substituting (A1) into the Fourier integral representation for Gaussian matrix elements of the free-particle Green's function Eq. (16),

$$\begin{aligned}\langle \mu^{\alpha\vec{A}}_{lmn} | G_0^+(E) | \mu^{\beta\vec{B}}_{l'm'n'} \rangle = &- \frac{\sqrt{2}}{\sqrt{\pi}\,(\alpha\beta)^{3/4}} [(2l-1)!!(2l'-1)!!(2m-1)!!(2m'-1)!!(2n-1)!!(2n'-1)!!]^{-1/2} \\ &\times i^{l-l'+m-m'+n-n'} \int d^3k \, \frac{e^{-ak^2 + i\vec{k}\cdot\vec{R}}}{k^2 - q^2 - i\epsilon} \\ &\times H_l\left(\frac{k_x}{2\sqrt{\alpha}}\right) H_{l'}\left(\frac{k_x}{2\sqrt{\beta}}\right) H_m\left(\frac{k_y}{2\sqrt{\alpha}}\right) H_{m'}\left(\frac{k_y}{2\sqrt{\beta}}\right) H_n\left(\frac{k_z}{2\sqrt{\alpha}}\right) H_{n'}\left(\frac{k_z}{2\sqrt{\beta}}\right),\end{aligned} \tag{A2}$$

where $\epsilon$ is a positive infinitesimal, $E=\frac{1}{2}q^2$, and

$$a=(\alpha+\beta)/4\alpha\beta \ . \tag{A3}$$

Substituting the spherical expansion for a plane wave, Eq. (22), for $e^{i\vec{k}\cdot\vec{R}}$ in Eq. (A1), and carrying out the angular integrations, the following formulas for $\Sigma$ and $\Pi$ symmetries and $s$- and $p$-type functions are obtained:

$$\langle \mu_{000}^{\alpha\vec{A}} | G_0^+ | \mu_{000}^{\beta\vec{B}} \rangle = A I_0^2 \ , \tag{A4a}$$

$$\langle \mu_{001}^{\alpha\vec{A}} | G_0^+ | \mu_{000}^{\beta\vec{B}} \rangle = (A/\sqrt{\alpha}\,) P_1(\hat{R}) I_1^3 \ , \tag{A4b}$$

$$\langle \mu_{001}^{\alpha\vec{A}} | G_0^+ | \mu_{001}^{\beta\vec{B}} \rangle = (A/\sqrt{\alpha\beta}\,)[-\tfrac{2}{3}P_2(\hat{R})\, I_2^4+\tfrac{1}{3}I_0^4] \ , \tag{A4c}$$

$$\langle \mu_{100}^{\alpha\vec{A}} | G_0^+ | \mu_{100}^{\beta\vec{B}} \rangle = (A/\sqrt{\alpha\beta}\,)[-\sqrt{\tfrac{2}{15}\pi}\; Q_{22}(\hat{R}) I_2^4 + \tfrac{1}{2}P_2(\hat{R}) I_2^4+\tfrac{1}{3}I_0^4] \ . \tag{A4d}$$

In Eqs. (A4), the integrations over $k$ are denoted by

$$I_L^n = \int_0^\infty \frac{dk\, k^n e^{-ak^2}}{k^2-q^2-i\epsilon}\, j_L(kR) \ , \tag{A5}$$

where $j_L(kR)$ is a spherical Bessel function. The constant

$$A=(2/\pi)^{1/2}(\alpha\beta)^{-3/4} \ , \tag{A6}$$

$P_L(\hat{R})$ is a Legendre polynomial, and

$$Q_{LM}=Y_{LM}(\hat{R})+Y_{L-M}(\hat{R}) \ . \tag{A7}$$

As shown in Ref. 15, the principal value part of this integral may be reduced to an error function with complex argument. Explicit expressions for the real (principal value) part of the integrals appearing in Eq. (A4) are

$$\mathrm{Re} I_0^2=(\pi/2R)e^{-aq^2}\,\mathrm{Re}[\,e^{iqR}\,\mathrm{erf}(R/2\sqrt{a}+i\sqrt{aq}\,)] \ , \tag{A8a}$$

$$\mathrm{Re} I_0^4=q^2\,\mathrm{Re} I_0^2+\tfrac{1}{4}\sqrt{\pi}\; a^{-3/2}e^{-R^2/4a} \ , \tag{A8b}$$

$$\mathrm{Re} I_1^3=\tfrac{1}{2}\pi e^{-aq^2}\,\mathrm{Re}[\,(1/R^2-iq/R)e^{iqR} \times \mathrm{erf}(R/2\sqrt{a}+i\sqrt{aq}\,) -\tfrac{1}{2}\sqrt{\pi}\; e^{-R^2/4a}a^{-1/2}/R] \ , \tag{A8c}$$

$$\mathrm{Re} I_2^4=(3/R)\,\mathrm{Re} I_1^3-\mathrm{Re} I_0^4 \ . \tag{A8d}$$

The imaginary parts are given by

$$\mathrm{Im}\, I_L^n=-\tfrac{1}{2}\pi q^{n-1}e^{-aq^2}j_L(qR) \ . \tag{A9}$$

## APPENDIX B: BESSEL GAUSSIAN OVERLAP INTEGRALS

To derive analytic formulas for the transformation matrix elements $\langle \mu_{lmn}^{\alpha\vec{A}}(\vec{r}) | j_l(kr)Y_{lm}(\hat{r})\rangle$, we insert the spherical expansion for a plane wave, Eq. (22), on both sides of Eq. (A1), the Fourier transform of a Gaussian, and equate coefficients of $Y_{LM}^*(\hat{k})$. For an $s$-type Gaussian we have immediately

$$\langle \mu_{000}^{\alpha\vec{A}} | j_L Y_{LM} \rangle = (2\pi/\alpha)^{3/4}e^{-k^2/4\alpha}j_L(kA)Y_{LM}(\hat{A}) \ . \tag{B1}$$

Derivation of formulas for Gaussian of higher symmetry is straightforward. For $p$-type Gaussians we obtain

$$\langle \mu_{001}^{\alpha\vec{A}} | j_L Y_{LM} \rangle = \left(\frac{2\pi}{\alpha}\right)^{3/4} \frac{k}{\sqrt{\alpha}}\, e^{-k^2/4\alpha}\left[\left(\frac{(L-M)(L+M)}{(2L+1)(2L-1)}\right)^{1/2} j_{L-1}(kA)Y_{L-1,M}(kA) - \left(\frac{(L+M+1)(L-M+1)}{(2L+1)(2L+3)}\right)^{1/2} j_{L+1}(kA)Y_{L+1,M}(\hat{A})\right], \tag{B2a}$$

$$\begin{aligned}\langle \mu_{100}^{\alpha\vec{A}} | j_L Y_{LM} \rangle = \left(\frac{2\pi}{\alpha}\right)^{3/4} \frac{k}{2\sqrt{\alpha}}\, e^{-k^2/4\alpha}\Bigg[&\left(\frac{(L-M)(L-M-1)}{(2L+1)(2L-1)}\right)^{1/2} j_{L-1}(kA)Y_{L-1,M+1}(\hat{A}) \\ &+\left(\frac{(L+M+2)(L+M+1)}{(2L+1)(2L+3)}\right)^{1/2} j_{L+1}(kA)Y_{L+1,M+1}(\hat{A}) \\ &-\left(\frac{(L+M)(L+M-1)}{(2L+1)(2L-1)}\right)^{1/2} j_{L-1}(kA)Y_{L-1,M-1}(\hat{A}) \\ &-\left(\frac{(L-M+2)(L-M+1)}{(2L+1)(2L+3)}\right)^{1/2} j_{L+1}(kA)Y_{L+1,M-1}(\hat{A})\Bigg] \ ,\end{aligned} \tag{B2b}$$

$$\begin{aligned}\langle \mu_{010}^{\alpha\vec{A}} | j_L Y_{LM}\rangle = i\left(\frac{2\pi}{\alpha}\right)^{3/4} \frac{k}{2\sqrt{\alpha}}\, e^{-k^2/4\alpha}\Bigg[&\left(\frac{(L-M)(L-M-1)}{(2L+1)(2L-1)}\right)^{1/2} j_{L-1}(kA)Y_{L-1,M+1}(\hat{A})\\ &+\left(\frac{(L+M+2)(L+M+1)}{(2L+1)(2L+3)}\right)^{1/2} j_{L+1}(kA)Y_{L+1,M+1}(\hat{A})\\ &+\left(\frac{(L+M)(L+M-1)}{(2L+1)(2L-1)}\right)^{1/2} j_{L-1}(kA)Y_{L-1,M-1}(\hat{A})\\ &+\left(\frac{(L-M+2)(L-M+1)}{(2L+1)(2L+3)}\right)^{1/2} j_{L+1}(kA)Y_{L+1,M-1}(\hat{A})\Bigg]. \qquad \text{(B2c)}\end{aligned}$$

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