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Inclusion of exact exchange in the noniterative partial-differential-equation method of electron-molecule scattering: Application to e-N_2

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A method for including exchange exactly in the framework of the noniterative partial-differential-equation (PDE) approach [Phys. Rev. A **28**, 621 (1983)] to electron-molecule scattering is presented. The method consists of breaking down the exchange equation into a set of inhomogeneous equations without integral terms. The difference form of the latter can then be solved by a straightforward generalization of the uncoupled noniterative PDE technique. Application is made to e-N_2 scattering in the fixed-nuclei approximation. The method is checked by comparing with other static- (exact) exchange calculations; agreement is found to be satisfactory particularly with new (unpublished) linear-algebraic results of Collins. A polarization potential, previously derived on the basis of a polarized-orbital treatment generalized to molecular targets, is then added; comparison is made with our previous results based on a Hara local exchange (HFEGE) approximation. The results show that HFEGE, as we had previously modified it, was less attractive than exact exchange. With exact exchange we are led alternatively to weaken the short-range part of the polarization potential with the consequence that agreement with other (exact) exchange-adiabatic calculations is excellent. The modified polarization potential is expected to be very useful in more elaborate scattering calculations.

I. INTRODUCTION

In this paper, we continue our study of the application of the noniterative partial-differential-equation (PDE) technique[1] to electron-molecule collisions.[2,3] The immediate precondition for application of the noniterative technique is that the potential be local. On the other hand, an essential requirement of low-energy electron scattering is the incorporation of exchange, and exchange is well known to be equivalent to a nonlocal interaction. Thus it would appear that exchange is incompatible with the direct application of the noniterative technique. However, in electron-atom scattering, if one confines oneself to exchange or exchange-adiabatic approximations, the exchange terms are Hermitian (i.e., a sum of separable terms) and one can eliminate them. (It is, of course, possible to include them directly and solve the equations iteratively. This iteration process should not be confused with the kind of iteration that is avoided by our noniterative PDE technique, which refers to the elimination of the kind of relaxation procedures that are usually employed to solve elliptic partial-differential equations.)

In Sec. II we derive the noniterative exchange technique, which as stated above is the main object of this paper. In Sec. III we describe an effective method for propagating the solution to large values of r, which is necessary in the presence of the long-range potentials that are a particularly important part of low-energy electron-molecule scattering. In Sec. IV we first test our method of including exchange by comparing our static-exchange results with other such calculations. We next describe the changes necessary in our previous polarization potential[3] as a result of including static exchange exactly rather than in terms of a local-exchange approximation. Fixed-nuclei results are graphically given in Sec. IV and compared with a limited number of other calculational and experimental results. We conclude with a few remarks relating to the effect of the approximate target wave functions.

II. EXACT EXCHANGE PROCEDURE

We shall confine ourselves here to the fixed-nuclei approximation.[4] The essential implication of this idealization is that the scattering equations can be reduced to equations in the molecular frame (defined by the direction of the fixed internucleus axis) which are independent of the orientation of the molecular frame with respect to the laboratory frame (the latter most conveniently defined by the direction of the incoming electron[4]). These equations can be conveniently written (in atomic units; cf., for example, Ref. 5)

$$(\tfrac{1}{2}\nabla^2+\tfrac{1}{2}k^2)F^{(m)}(\mathbf{r}) = V(\mathbf{r})F^{(m)}(\mathbf{r})-\sum_{\alpha=1}^{N_{\mathrm{occ}}} W_{\alpha}^{(m)}(\mathbf{r})\Phi_{\alpha}(\mathbf{r}) , \quad (2.1)$$

where $F^{(m)}(\mathbf{r})$ represents a partial wave designated by (m), of the scattered electron [with vector coordinates $\mathbf{r}=(r,\theta,\phi)$]. ∇^2 is the usual three-dimensional Laplacian with $\mathbf{r}$ representing the displacement of the scattered electron from a fixed point in space, usually the midpoint of the internuclear axis for a homonuclear diatomic target. In (2.1) $V(\mathbf{r})$ is the local potential (which always includes the static and may include the induced polarization potential as well) while the last term represents the static exchange kernels:

$$W_\alpha^{(m)}(\mathbf{r})=\int d\mathbf{x}\,\Phi_\alpha(\mathbf{x})\,|\mathbf{r}-\mathbf{x}|^{-1}F^{(m)}(\mathbf{x})\ . \tag{2.2}$$

The above form of exchange assumes that the continuum orbital is orthogonal to all bound orbitals. Thus is justified for closed-shell molecules such as N_2. Equation (2.2) contains the bound electrons orbitals Φ_α which in the ground state Σ_g of N_2 are occupied in pairs as indicated by

$$\Phi_g=\Phi_g(1\sigma_g^2 2\sigma_g^2 3\sigma_g^2 1\sigma_u^2 2\sigma_u^2 1\pi_{xu}^2 1\pi_{yu}^2)\,|\,{}^1\Sigma_g{}^{(+)})\ . \tag{2.3}$$

The cylindrical symmetry may then be further exploited by writing

$$F^{(m)}(\mathbf{r})=r^{-1}f^{(m)}(\mathbf{z})(-1)^m(2\pi)^{-1/2}e^{im\varphi}\ , \tag{2.4a}$$

$$\Phi_\alpha(\mathbf{r})=r^{-1}\phi_\alpha(\mathbf{z})(-1)^{m_\alpha}(2\pi)^{-1/2}e^{im_\alpha\varphi}\ , \tag{2.4b}$$

where $\mathbf{z}=(r,\theta)$ is a two-dimensional vector in terms of which, by substitution of (2.4) into (2.2), the exchange kernel can also be written:

$$W_\alpha^{(m)}(\mathbf{r})=r^{-1}w_\alpha^{(m)}(\mathbf{z})(-1)^{m-m_\alpha}e^{i(m-m_\alpha)\varphi}\ . \tag{2.5}$$

Thus (2.1) can be reduced to a two-dimensional partial integro-differential equation in $\mathbf{z}$:

$$[\Delta(m)+k^2]f^{(m)}(\mathbf{z})=2V(\mathbf{z})f^{(m)}(\mathbf{z})-2\sum_{\alpha=1}^{N_{\text{occ}}}\frac{1}{r}\phi_\alpha(\mathbf{z})w_\alpha(\mathbf{z})\ . \tag{2.6}$$

Here $\Delta(m)$ is the two-dimensional Laplacian

$$\Delta(m)\equiv\frac{\partial^2}{\partial r^2}+\frac{1}{r^2}\left[\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}-\frac{m^2}{\sin^2\theta}\right]\ . \tag{2.7}$$

We now come to the method whereby the integral term in $W_\alpha^{(m)}$ can be removed from (2.1). The procedure is in effect a generalization to PDE's of a method that has long been used in ordinary integro-differential equations (ODE's).[6] To demonstrate, apply ∇^2 to both sides of (2.5) using the fact that the Coulomb potential is in fact the Green's function of the Laplacian operator:

$$\nabla^2(\,|\mathbf{r}-\mathbf{x}|^{-1})=-4\pi\delta(\mathbf{r}-\mathbf{x})\ . \tag{2.8}$$

Using (2.8) in the right-hand side (rhs) and Eqs. (2.4) on the left-hand side (lhs) allows (2.2) to be reduced to two-dimensional PDE:

$$\Delta(m-m_\alpha)w_\alpha(\mathbf{z})=-\frac{2}{r}\phi_\alpha(\mathbf{z})f^{(m)}(\mathbf{z})\ . \tag{2.9}$$

We see that (2.9) combined with (2.6) is a set of $N_{\text{occ}}+1$ coupled equations for the scattering function $f^{(m)}$ and the reduced exchange kernels $w_\alpha(\mathbf{z})$. The latter may be considered a set of N_{occ} pseudo-orbitals. The main thing is that the set of equations has no integral terms and may be solved by a straightforward generalization of the noniterative PDE technique of Refs. 2 and 3. Specifically, the boundary conditions for the pseudo-orbitals which may readily be derived from their definitions (2.2) and (2.4b) are

$$w_\alpha(r,\theta)\,|_{r=0}=0 \tag{2.10a}$$

and

$$\lim_{\rho\to\infty} w_\alpha(\rho,\theta)=0\ . \tag{2.10b}$$

In practice, (2.10b) is imposed at finite but large ρ, as were the boundary conditions for the polarized orbitals in Ref. 3. The angular boundary conditions are similarly imposed: specifically, each orbital ϕ_α has the same symmetry as the lowest spherical harmonic $Y_{l_\alpha m_\alpha}(\Omega)$ in terms of which the ϕ_α are expanded. The symmetry of the partial wave, $f^{(m)}$, is determined by the quantum numbers which define the partial wave, and the associated Y_{lm} corresponds to the lowest l $(\geq m)$ which is consistent with its parity. The symmetry of $w_\alpha(\mathbf{z})$ in terms of its lowest spherical harmonic $Y_{l_w m_w}(\Omega)$ is determined from (2.9). This means specifically

$$m_w=m-m_\alpha\ , \tag{2.11}$$

and the parity of l_w is the product of the parities of ϕ_α and $f^{(m)}$ with the magnitude of l_w being the smallest integer which allows l_α to be vector coupled to l.

The results are given in Table I both in terms of the lowest spherical harmonic $(Y_{l_w m_w})$ and the vanishing of the $w_\alpha(r,\theta)$ indicated by $(\times)$ or its derivatives $(-)$ at $\theta=0$ (upper entry) and $\theta=\pi/2$ (lower entry). The latter may be readily deduced from the symmetry of $Y_{l_w m_w}(\Omega)$ at those boundaries, which are given in Ref. 3. (For some of the higher $l_w m_w$ both conditions obtain, and this is indicated in Table I by an asterisk.)

To apply the noniterative technique[1] to a coupled set of PDE's having defined a grid in r and θ, one must enlarge the solution vector to include the $w_\alpha(z)$:

$$\underline{\mathbf{g}}(\mathbf{z})=\begin{bmatrix} f^{(m)}(\mathbf{z}) \\ w_1(\mathbf{z}) \\ \vdots \\ w_{N_{\text{occ}}}(\mathbf{z}) \end{bmatrix}\ . \tag{2.12}$$

The solution vector is then discretized in the form $g_{i,j}(k)$ where $k=1,2,\ldots,N_{\text{occ}}+1$ defines the function and i,j the mesh point in r,θ at which they are all being computed.

The noniterative technique[1] then gets put into effect exactly as described in Ref. 1, except that every element of the solution vector becomes a vector of $N_{\text{occ}}+1$ components, and every element of the difference matrix becomes an $(N_{\text{occ}}+1)\times(N_{\text{occ}}+1)$ submatrix representing the set of PDE's. The final form of the difference equation for Eqs. (2.6) and (2.9) is of the form

$$\underline{\mathcal{A}}\,\underline{\mathbf{g}}=\underline{\mathbf{R}}\ , \tag{2.13a}$$

where $\underline{\mathbf{R}}$ is the expanded vector representing the known boundary conditions for the set of functions representing the solution. More specifically, the difference equation can be written

$$[\alpha_{ij}^{+}(k)g_{i+1,j}(k)+\alpha_{ij}^{-}(k)g_{i-1,j}(k)+\beta_{i,j}^{+}(k)g_{i,j+1}(k)+\beta_{ij}^{-}(k)g_{i,j-1}(k)]+\sum_{k'}\gamma_{ij}(k,k')g_{i,j}(k')=0\ . \tag{2.13b}$$

Equation (2.13b) is the generalization of Eq. (2) of Ref.

TABLE I. The lowest symmetry $(l_w m_w)$ of the exchange kernels w_α for all bound orbitals and the lower partial waves. Boundary conditions at $\theta = 0, \pi/2$ are indicated by the second column of symbols for each entry; cf. text. The entries in this table are independent of n for each symmetry of φ_α.

α		1,2,3	4,5	6	7
φ_α		$n\sigma_g$	$n\sigma_u$	π_{xu}	π_{yu}
$(l_\alpha m_\alpha)$		(00)	(10)	(11)	(1,−1)
Partial wave $f(m)$	(lm)				
$^2\Sigma_g$	(00)	(00) $\begin{bmatrix}-\\-\end{bmatrix}$	(10) $\begin{bmatrix}-\\\times\end{bmatrix}$	(1,−1) $\begin{bmatrix}\times\\-\end{bmatrix}$	(11) $\begin{bmatrix}\times\\-\end{bmatrix}$
$^2\Sigma_u$	(10)	(10) $\begin{bmatrix}-\\\times\end{bmatrix}$	(00) $\begin{bmatrix}-\\-\end{bmatrix}$	(2,−1) $\begin{bmatrix}\times\\\times\end{bmatrix}$	(21) $\begin{bmatrix}\times\\\times\end{bmatrix}$
$^2\Pi_g$	(21)	(21) $\begin{bmatrix}\times\\\times\end{bmatrix}$	(11) $\begin{bmatrix}\times\\-\end{bmatrix}$	(10) $\begin{bmatrix}-\\\times\end{bmatrix}$	(32) $\begin{bmatrix}*\\\times\end{bmatrix}$
$^2\Pi_u$	(11)	(11) $\begin{bmatrix}\times\\-\end{bmatrix}$	(21) $\begin{bmatrix}\times\\\times\end{bmatrix}$	(00) $\begin{bmatrix}-\\-\end{bmatrix}$	(22) $\begin{bmatrix}*\\-\end{bmatrix}$
$^2\Delta_g$	(22)	(22) $\begin{bmatrix}*\\-\end{bmatrix}$	(32) $\begin{bmatrix}*\\\times\end{bmatrix}$	(32) $\begin{bmatrix}*\\-\end{bmatrix}$	(33) $\begin{bmatrix}*\\-\end{bmatrix}$
$^2\Delta_u$	(32)	(32) $\begin{bmatrix}*\\\times\end{bmatrix}$	(22) $\begin{bmatrix}*\\-\end{bmatrix}$	(22) $\begin{bmatrix}*\\-\end{bmatrix}$	(43) $\begin{bmatrix}*\\\times\end{bmatrix}$

1; it demonstrates with respect to the new index (k) that the only off-diagonal term occurs in nonderivative terms, and in fact for the specific coupling involved in (2.6) and (2.9) only the $\gamma_{ij}(k,1)$ and $\gamma_{ij}(1,k')$ elements are nonzero (for $k \neq k'$).

Figure 1 illustrates the structure of the A matrix for the simplified case of $N_{\text{occ}} = 3$, $N_\theta = 3$, $N_r = 5$ (N_θ and N_r being the illustrative number of points in the θ and r direction, respectively). Each filled square now corresponds to a 4×4 block matrix and squares with diagonal lines represent 4×4 blocks with diagonal elements only. All other blocks are empty.

The factorization of $\underline{A}$ into a lower times an upper triangular matrix, from which the consecutive inversion of, in this case, the $[(N_{\text{occ}}+1)N_\theta] \times [(N_{\text{occ}}+1)N_\theta]$ blocks proceeds, is in complete analogy to the method of Ref. 1, as carried out in Ref. 3. In practice, we have introduced some additional technical modifications of which we will describe here only those having to do with large-r contributions to the solution.

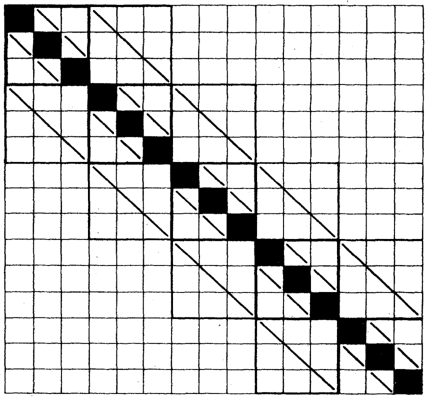

FIG. 1. Example of the block tridiagonal structure of the coefficient matrix corresponding to $N_{\text{occ}} = 3$, $N_e = 3$, $N_r = 5$. Cf. text for more details.

III. PHASE-AMPLITUDE PROPAGATION METHOD

In this section, we develop a method of propagating the solution to convergence as a function of r, so as to obtain, ultimately, the elements of the K matrix. First let it be noted, since the exchange pseudo-orbitals (w_α) are exponentially damped, that the complete set of PDE's is only carried to an inner radius $r_e < r_\rho$ (cf. Fig. 2). Beyond r_e the PDE for the scattering function $f^{(m)}(\mathbf{z})$ is integrated without exchange coupling terms to r_ρ. At that boundary the reaction matrix is extracted as we have described elsewhere.[2].

The propogation technique refers to the extension of the solution beyond $r > r_\rho$, to a point where convergence to a specified accuracy has taken place. The key to obtaining the solution in region III is to recognize that the solution there can be decomposed into a spherical har-

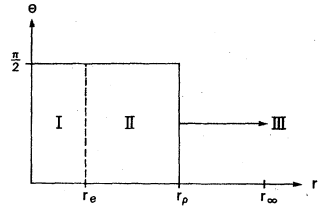

FIG. 2. Integration regions. I, PDE including exchange; II, PDE without exchange; III, propagation region as described in text.

monic expansion *which is rapidly convergent.* The decomposition allows the PDE [derived as described above from (2.6)]

$$[\Delta(m)+k^2]f^{(m)}(\mathbf{z})=2V(\mathbf{z})f^{(m)}(\mathbf{z}) \tag{3.1}$$

to be written as a set of coupled ODE's. Specifically expanding $f(\mathbf{z})$ (dropping the diagonal m index)

$$f_\lambda(\mathbf{z})=\sum_{l'}{}'' f_{l'}^{(\lambda)}(r)P_{l'm}(\theta) , \tag{3.2}$$

we can reduce (3.1) to the coupled ODE's:

$$\left[\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}+k^2\right]f_l^{(\lambda)}(r)=2\sum_{l'}{}'' V_{l,l'}(r)f_{l'}^{(\lambda)}(r') , \tag{3.3}$$

where

$$V_{l,l'}(r)=\int_0^\pi P_{lm}(\theta)[V_{e\text{-nuc}}(r,\theta)+V_{\text{pol}}(r,\theta)]P_{l'm}(\theta)\sin\theta\, d\theta . \tag{3.4}$$

The superscript (λ) here refers to the specific PDE solution of (3.1), defined by the $P_{\lambda m}(\theta)$ on the $r=r_\rho$ boundary, that is being considered. It will be recalled that a convergent linear combination of such solutions in the PDE sense is required to obtain the physical solution,[2] in practice no more than three λ's are necessary. The asymptotic form of the solution of (3.3) defines the K matrix

$$f_l^{(\lambda)}(r)\sim k^{-1/2}[\sin(kr-\pi l/2)\delta_{l\lambda}+K_{l\lambda}\cos(kr-\pi\lambda/2)] \text{ as } r\rightarrow\infty . \tag{3.5}$$

In principle one could integrate (3.3) as far as necessary to obtain a converged K matrix. In practice, however, the following phase-amplitude method is much more stable and greatly shortens the machine time and storage that would otherwise by required. Let us note that a formal solution of (3.3) can be written:

$$f_l^{(\lambda)}(r)=S_l(r)p_l^{(\lambda)}(r)+C_l(r)q_l^{(\lambda)}(r) , \tag{3.6}$$

where

$$\begin{aligned}S_l(r)&=k^{1/2}rj_l(kr)\sim k^{-1/2}\sin(kr-\pi l/2) \text{ as } r\rightarrow\infty ,\\ C_l(r)&=-k^{1/2}rn_l(kr)\sim k^{-1/2}\cos(kr-\pi l/2) \text{ as } r\rightarrow\infty\end{aligned} \tag{3.7}$$

(j_l and n_l are spherical Bessel functions with phase as defined in Morse and Feshbach[7]) and

$$\begin{aligned}p_l^{(\lambda)}(r)&=\delta_{l\lambda}+2\sum_{l'}\int_{r_\rho}^{r} C_{l'}(x)V_{ll'}(x)f_{l'}^{(\lambda)}(x)dx ,\\ q_l^{(\lambda)}(r)&=-2\sum_{l'}\int_{r_\rho}^{r} S_{l'}(x)V_{ll'}(x)f_{l'}^{(\lambda)}(x)dx .\end{aligned} \tag{3.8}$$

Comparison of Eqs. (3.6)—(3.8) with (3.5) shows that the K matrix as a function of r, is given by

$$K_{\lambda l}(r)=[p^{-1}(r)q(r)]_{\lambda l}=\sum_\mu [p^{-1}(r)]_{\lambda\mu}q_{\mu l}(r) , \tag{3.9a}$$

from which the final K matrix is

$$K_{\lambda l}=\lim_{r\rightarrow\infty} K_{\lambda l}(r) . \tag{3.9b}$$

Up to this point, the analysis and decomposition in terms of $p(r)$ and $q(r)$ is essentially that of Smith and Henry.[8] Below we shall give a brief analysis leading to our specific method of propagation. We believe this treatment is worthwhile, because it is brief and it applies directly to our problem. It is emphasized that the essential ideas here are also not new and that a general development of a concatenated expression for the asymptotic amplitude has been given by Norcross.[9]

Suppressing index labels (l,λ) in this discussion, we start with a Taylor expansion of the solution

$$f_i=f_{i-1}+f'_{i-1}\Delta r , \tag{3.10}$$

where $f_i=f(r_i)$, etc. Utilizing (3.6) leads in first order to

$$f_i=S_ip_{i-1}+C_iq_{i-1} . \tag{3.11}$$

But from (3.8) we have

$$\begin{aligned}p_i&=1+2\sum_{j=\rho}^{i}\omega_jS_jV_jf_j=p_{i-1}+2\omega_iC_iV_if_i ,\\ q_i&=-2\sum_{j=\rho}^{i}\omega_jS_jV_jf_j=q_{i-1}-2\omega_iS_iV_if_i .\end{aligned} \tag{3.12}$$

In the derivation of (3.12) the integral in (3.8) has been replaced by a summation with weight factors ω_j. (In practice, we use trapezoidal rule: $\omega_\rho=\omega_i=\frac{1}{2}$; all other $\omega_j=1$.) Inserting (3.11) into the rhs of (3.12) for f_i gives rise to a difference equation for p_i and q_i which is conveniently written in matrix form as

$$\underline{\mathbf{p}}_i=\underline{A}(i)\underline{\mathbf{p}}_{i-1} , \tag{3.13}$$

where

$$\underline{\mathbf{p}}_i=\begin{bmatrix}p_i\\ q_i\end{bmatrix} \tag{3.14}$$

and $\underline{A}(i)$ turns out to be

$$\underline{A}(i)=\begin{bmatrix}1+2\omega_iC_iV_iS_i & 2\omega_iC_iV_iC_i\\ -2\omega_iS_iV_iS_i & 1-2\omega_iS_iV_iC_i\end{bmatrix} . \tag{3.15}$$

Repeated use of (3.13) allows the desired $\underline{\mathbf{p}}$ to be evaluated as a "concatenated" product:

$$\underline{\mathbf{p}}_i=\underline{A}(i)\underline{A}(i-1)\cdots\underline{A}(\rho)\underline{\mathbf{p}}_\rho . \tag{3.16}$$

From the components of $\underline{\mathbf{p}}_i$, the K matrix at r_i may be evaluated from (3.9), and r_i may be extended as far as necessary for convergence. The methodology therefore accomplishes the goal of propagating and at the same time avoiding the integration of the ODE's in region III.

In actual calculations (both with and without polarization) the exchange integrals were dropped at $r_e=5a_0$ (cf. Fig. 2); that radius was sufficient to insure four-figure accuracy in the eigenphase sums. In production runs r_ρ was set to $10a_0$ and r_∞ at $60a_0$. In the Π_g case three λ values ($\lambda=2,4,6$) (and the corresponding three l values) of $K_{\lambda l}$ were determined. When the process was repeated with inclusion of a fourth λ value, the resulting eigenphase sum

TABLE II. Comparison of e-N_2 static-exchange results. Calculations based on the Cade, Sales, and Wahl (Ref. 12) ground state. Entries are partial cross sections in Å^2, and eigenphase sums in radians (in parentheses). Empty entries mean particular results have not been given. CRM denotes results of Collins, Robb, and Morrison (Ref. 11). CS denotes results of Collins and Schneider (unpublished) using the linear-algebraic code (Ref. 13). Cf. text.

Partial wave	Calculations[b]	k^2 (Ry) 0.1	0.3	0.5	1.0
Σ_g	Present	14.95 (2.417)	9.756 (1.983)	6.805 (1.747)	3.503 (1.350)
	CRM	18.86 (2.311)	(1.808)	8.974 (1.524)	3.092 (1.043)
	CS	15.155 (2.406)		6.827 (1.723)	3.17 (1.296)
Σ_u	Present	0.862 (2.976)	2.14 (2.692)	2.77 (2.479)	2.90 (2.149)
	CRM	0.8222 (2.937)	3.14 (2.584)	3.76 (2.316)	3.33 (1.908)
Π_g	Present	0.0105 (0.24)	42.68 (1.760)	7.70 (2.574)	4.47 (2.546)
	CRM	0.011 (0.26)	43.92 (1.461)	10.4 (2.454)	5.26 (2.453)
Π_u	Present	0.55 (-0.0705)	3.01 (-0.269)	4.63 (-0.536)	5.95 (-0.646)
	CRM	0.63 (-0.075)	(-0.290)	5.52 (-0.455)	6.38 (-0.694)

was again unaffected to three significant figures. Adequate mesh sizes were found to be $\Delta\theta=\pi/60$ and $\Delta r=0.05$ in regions I and II and $\Delta r=0.1$ in region III. We estimate that the final cross sections that we deduce have an overall accuracy of better than 5%. As in other calculations, we found the cross sections for the Δ symmetries to be almost negligible in the energy range of present interest (0–10 eV).

A valuable check of the method of including exchange as well as the asymptotic program is afforded by the static-exchange approximation. Here there are two previous calculations in which exchange has been included exactly.[10,11] Of these, the one by Collins *et al.*[11] uses the Cade-Sales-Wahl ground-state (N_2) wave function,[12] to which therefore we can directly compare. In Table II results are given both in terms of eigenphase sums and cross sections. The respective results are one the whole in satisfactory agreement with each other, to the accuracy estimated in Ref. 11; however, within that accuracy it was felt that the Σ_g results were most in need of improvement [L. A. Collins (private communication)]. Collins has therefore just redone the Σ_g utilizing the new linear-algebraic code recently developed at Los Alamos.[13] Those results are also given in Table II; the agreement with our results is now truly remarkable. In view of how different the methodologies and programs are, we consider the agreement a cogent confirmation of the validity of both methods.

IV. THE POLARIZATION POTENTIAL: RESULTS

In Ref. 3, a polarization potential for the e-N_2 system was derived using the basic ideas of the (static part) of the method of polarized orbitals:[14] the cutoff dipole approximation of the static interaction between the incoming and the target electrons. In the molecular application, however, although the nonspherical aspects of that static interaction could also be nicely handled by the noniterative PDE technique,[3] including the additional and complicated coupling involved in those equations was considered to be unwarranted given the nature of the above approximations. Thus we made additional approximations which rendered the inside part of the derived polarization potential of less than fundamental quantitative significance.

That aspect of the polarization potential which we consider to be of qualitative importance, however, is the relative strength of the monopole and quadrupole parts of the potential:

$$V_{\text{pol}}(\mathbf{r})=V_{\text{pol}}^{(0)}(r)+V_{\text{pol}}^{(2)}(r)P_2(\cos\theta) \ . \tag{4.1}$$

Specifically, it was found[3] that $V_{\text{pol}}(\mathbf{r})$ was attractive along $\theta=0$ but repulsive along $\theta=\pi/2$ for small values r. Wishing to retain that character, we have therefore taken our present polarization potential to be

$$V_{\text{pol}}(\mathbf{r})=B(r)V_{\text{pol}}^{\text{OT}}(\mathbf{r}) \tag{4.2}$$

with

$$B(r)=1-e^{-(r/r_0)^2} \tag{4.3}$$

and $V_{\text{pol}}^{\text{OT}}(\mathbf{r})$ given by the polarization potential of Ref. 3. In order to facilitate comparison with other exchange-adiabatic (fixed-nuclei) calculations we first report on results using a value of r_0 selected so as to give the $^2\Pi_g$ resonance in the vicinity of previous results[15–17] (which range from 2.07 to 2.24 eV). A value of $r_0=2.635\,85$ was found to give $E_r=2.103$ eV with a width $\Gamma_r=0.356$. This is in satisfactory agreement with other exchange-adiabatic results ($E_r=2.24$, 2.07, 2.17 eV; $\Gamma_r=0.34$, 0.47, 0.301) coming from Refs. 15, 17, and 18, respectively. It is seen that there are differences among the other exchange-adiabatic calculations as well, each of which is based on a different methodology. The authors of Ref. 18 have had some reservation that their results may suffer from overcorrelation.[18]

In Fig. 3, we present our total cross section in comparison with several calculations[16,17] and experiments.[19–21] In this calculation we have chosen $r_0=2.934$ to achieve a resonance at $E=2.39$ eV which is closer to the experimental value. This value of $r_0=2.934$ gives $\Gamma_r=0.37$ eV, which shows that width is only minimially affected. But it should be stressed that the experimental cross section contains substructure,[19,22] so that any fixed-nuclei width can have only semiquantitative significance. To obtain the substructure, as is by now well known, one must in one way[23] or another[24,25] include vibrational motion. From the point of view of the hybrid theory,[23] exact exchange can also be included in the vibrational close-coupling portion of the theory in direct analogy to what has been done here, and we are starting to implement that part of the calculation.

Apart from the resonant energy region the fixed-nuclei should be a quantitatively accurate approximation.[23] In Fig. 3, however, one sees that our cross sections are slightly lower than experiment at the high-energy and more noticeably lower at the low-energy end. But all calculations in Fig. 3 were based on a single-configuration self-consistent-field (SCF) target (N_2) wave function.[12] The importance of an accurate target state wave function has recently been stressed by Burke, Noble, and Salvini.[26] Very recently, Rumble *et al.*[27] have examined the effect of using an improved [multiconfiguration SCF (MCSCF)] ground-state wave function. They find—relative to the single-configuration target—a slight lowering of the cross section at the high-energy end and a more noticeable lowering at energies below the Π_g resonance. These qualitative effects cannot yet be considered definitive, because they[27] have used a model HFEGE exchange potential[28] in each case. But the model exchange is the same for both targets, thus we consider their results provocatively suggestive, and we look forward to utilizing the static potential based on the improved ground-state wave function[27] in future calculations.

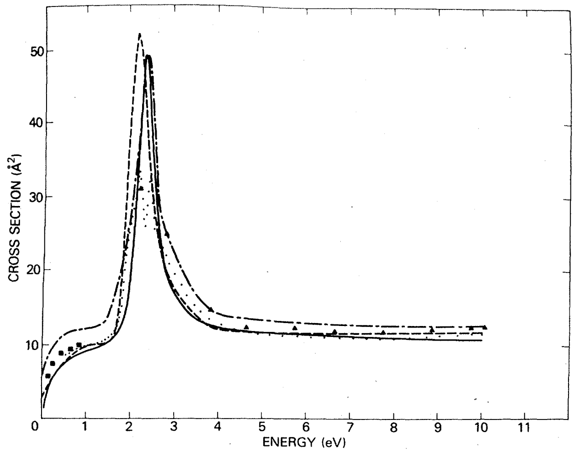

FIG. 3. Total cross sections for scattering of electrons by N_2: results of Padial and Norcross (Ref. 17) (— — —); Morrison and Collins (Ref. 16) (–·–·); present results (———); experimental data of Kennerly (Ref. 19) (· · ·); Hoffman *et al.* (Ref. 20) (▲); Jost. *et al.* (Ref. 21) (■).

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