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Calculation of the polarization potential for e-N_2 collisions

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A polarization potential (V_{pol}) for e-N_2 collisions is calculated by the generalization of the static part of the method of polarized orbitals to molecular targets. Partial differential equations (PDE) are derived for polarized orbitals, which are functions of the distance (r) from the molecular center and angle (θ) from the molecular axis. The equations are solved with the use of the noniterative PDE technique. From the polarized orbitals a polarization potential can be constructed whose r and θ dependence is found to be significantly different from the well-known phenomenological one. The two potentials are further compared by carrying out limited hybrid-theory scattering calculations. Only those scattering results based on the calculated V_{pol} are in satisfactory accord with experiment.

I. INTRODUCTION

The e-N_2 scattering system has now become the canonical standard of low-energy scattering from homonuclear diatomic targets in which resonance substructure figures prominently. As such, much theoretical and calculational effort has gone into the study of this system[1,2]; however, even those studies which are *ab initio* in character and which reveal substructure, all (with one exception,[3] to be discussed in Sec. IV) invoke a polarization potential in addition to (an approximation of) exchange as a necessary ingredient of their approach.

We have in mind primarily the hybrid theory and calculations,[4] where for the first time an essentially *ab initio* theory gave rise to the famous observed substructure of the 2.4-eV resonance.[5] In detail, however, the calculation involved a phenomenological polarization potential

$$V_{\text{pol}}^{(\text{phen})}(r,\theta)=-\left[1-e^{-(r/r_0)^6}\right]\times\left[\frac{\alpha_0(R)+\alpha_2(R)P_2(\cos\theta)}{2r^4}\right], \quad (1.1)$$

which is essentially the one introduced in the fixed-nuclei calculation of Burke and Chandra,[6] minimally generalized to encompass the dependence of α_λ on internuclear separation (R), so that vibrational motion, which in one way or another[7,4] is responsible for the substructure, could also be included.

In our earlier papers[4] a two-term linear expansion of the $\alpha_\lambda(R)$ was used with constants adjusted to "experimental" values of $\alpha_\lambda(R_0)$, where $R_0=2.068$ (a.u. are used throughout) is the equilibrium separation of N_2; our fit fortunately also agreed approximately with slopes of the $\alpha_\lambda(R)$ inferred from Raman data by Truhlar.[8]

The cutoff parameter r_0 in Eq. (1.1) was, as in Burke and Chandra,[6] adjusted so that the resonance occurred at the observed energy. For the hybrid theory, the adjustment of a single parameter r_0 is a severe demand, because it is a series of peaks which constitutes the substructure that must come out of the calculation: That the hybrid theory was able to do this,[4] at least in a semiquantitative way, was a testimonial to the validity of physical and mathematical underpinnings of the theory (cf. Ref. 2). In detail, however, the calculations suffered on two accounts: First, the angular expansion needed in addition to the vibrational close-coupling part of the theory was extremely slowly convergent,[4] to the extent that final quantitative results could not be achieved. Second, but related to the first, the phenomenological polarization potential (1.1) could not be definitively tested, but it was clear that it was unlikely to be quantitatively accurate either in its R or small-r dependence.

In a sense, therefore, the solution of the first problem is a precondition for an examination of the second. We shall find that the key to the solution of both problems is the formulation and accurate numerical integration of partial differential equations (PDE).[9] In that regard we shall also show that whereas the application of the noniterative PDE technique was first suggested to the molecular scattering problem[10]; it equally well suits the adiabatic problem that we shall deal with here, from which an essentially nonphenomenological V_{pol} is derived. In a sequel,[11] we shall report on the use of this V_{pol} in a detailed scattering calculation; however, in this paper a more limited scattering calculation has been carried out which is sufficient to indicate that our calculated V_{pol} is significantly different from and better than $V_{\text{pol}}^{(\text{phen})}$.

In Sec. II we generalize the static (first) part of the method of polarized orbitals[12] to deal with a (homonuclear) molecular target. In Sec. III we apply it to the N_2 target. Results including limited scattering calculations and discussion are given in Sec. IV.

II. EQUATIONS FOR POLARIZED ORBITALS

The basic idea of the (first part-static problem of the) method of polarized orbitals[12] is the adiabatic approximation: The treatment of the (dipole part of the) interaction between the incoming electron and the target as if the projectile electron were stationary. The resulting perturbed (polarized-orbital) wave function becomes, thereby, a parametric function of the position $\vec{r}_1$ of the incoming electron. That function is then used as part of the dynamical ansatz for the total wave function from which one

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derives scattering equations and ultimately phase shifts.

Originally the static perturbation was calculated using the method of Sternheimer,[13] although it was recognized from the beginning[14,12] that that was only an approximation to perturbation theory. In the present extension to molecular targets we will immediately start with a more complete consideration of the static equations. It is assumed that the unperturbed bound molecular orbitals $\varphi_\lambda^{(0)}$ are determined in the Hartree-Fock approximation

$$\left[-\tfrac{1}{2}\Delta_i-\sum_{A=1}^{2}\frac{Z_A}{r_{iA}}+\sum_{\beta=1}^{N_{\rm occ}}[2J_\beta(\vec{r}_i)-K_\beta]\right]\varphi_\alpha^{(0)}(\vec{r}_i)=E_\alpha^{(0)}\varphi_\alpha^{(0)}(\vec{r}_i)\ , \tag{2.1}$$

where the Coulomb integral is defined as

$$J_\beta(\vec{r}_i)=\int|\varphi_\beta^{(0)}(\vec{r}_j)|^2\frac{1}{r_{ij}}d\vec{r}_j \tag{2.2}$$

and exchange integral as

$$K_\beta\varphi_\alpha^{(0)}(\vec{r}_i)=\left[\int\varphi_\beta^{(0)*}(\vec{r}_j)r_{ij}^{-1}\varphi_\alpha^{(0)}(\vec{r}_j)d\vec{r}_j\right]\varphi_\beta^{(0)}(\vec{r}_i)\ . \tag{2.3}$$

Here and throughout this paper, atomic units are used. We take the origin of our coordinate system at the center of mass of the molecule, and its z axis along the internuclear axis. Z_A is a charge of nucleus A ($A=1,2$); $N_{\rm occ}$ is the number of molecular orbitals occupied by bound molecular electrons, and α, β, etc., collectively denote a set of quantum numbers specifying the orbital. (Inner products of spin coordinates are assumed.) In addition, $\vec{r}_{ij}=\vec{r}_i-\vec{r}_j$, $\vec{r}_{iA}=\vec{r}_i-\vec{R}_A$, where $\vec{r}_i$ is a position vector of the ith electron, and $\vec{R}_A$ is a position vector of nucleus A.

Now, let us consider a distortion of unperturbed bound molecular orbital $\varphi_\alpha^{(0)}(r_i)$ caused by an incoming but static electron. The adiabatic interaction is

$$V_{\rm ad}(\vec{r}_1;\vec{r}_i)=\sum_{i=2}^{N+1}\frac{1}{r_{1i}}-\sum_{A=1}^{2}\frac{Z_A}{r_{1A}}\ . \tag{2.4a}$$

The interaction is expanded in terms of Legendre polynomials, and only the dipole term is retained, i.e., r_{1i}^{-1} is approximated by the cut-off dipole term[12,15]; i.e.,

$$V_{\rm ad}\rightarrow V_{\rm cd}\ , \tag{2.4b}$$

where

$$V_{\rm cd}=\lambda\sum_{i=2}^{N+1}\Theta(r_1,r_i)v(\hat{r}_1;\vec{r}_i)\ , \tag{2.4c}$$

$$v(\hat{r}_1;\vec{r}_i)=r_i\cos(\hat{r}_1\cdot\hat{r}_i)\ , \tag{2.5}$$

$$\lambda=1/r_1^2\ , \tag{2.6a}$$

and Θ is a step function

$$\Theta(r_1,r_i)=\begin{cases}1, & r_1\geq r_i\\ 0, & r_1<r_i\ .\end{cases} \tag{2.6b}$$

The step function $\Theta(r_1,r_i)$ partially remedies the breakdown of separable approximation: If the scattered electron is inside any specific molecular electron, the effect of charge polarization is neglected.[15]

Analogous orbitals perturbed by the presence of V of Eq. (2.4c) (ψ_α) satisfy the equation

$$\left[-\tfrac{1}{2}\nabla_i^2-\sum_{A=1}^{2}\frac{Z_A}{r_{iA}}+\lambda v(\hat{r}_1;\vec{r}_i)+\sum_{\beta=1}^{N_{\rm occ}}[2\tilde{J}_\beta(\vec{r}_i)-\tilde{K}_\beta]\right]\psi_\alpha(\vec{r}_i)=E_\alpha\psi_\alpha(\vec{r}_i)\ , \tag{2.7}$$

where $\tilde{J}_\beta$ and $\tilde{K}_\beta$ are, respectively, defined by Eqs. (2.2) and (2.3) with polarized orbitals $\psi_\alpha(\vec{r}_i)$ replacing the $\varphi_\alpha^{(0)}(\vec{r}_i)$. In order to solve Eq. (2.7), we assume λ, Eq. (2.6a), is small (which is surely so for $r_1\gg r_i$) compared with other terms on the left-hand side (lhs) of (2.7), and apply perturbation theory; i.e., we expand

$$\psi_\alpha=\varphi_\alpha^{(0)}+\lambda\sum_{\gamma=1}^{N_{\rm pol}}\varphi_{\alpha\rightarrow\gamma}+O(\lambda^2)\ , \tag{2.8a}$$

$$E_\alpha=E_\alpha^{(0)}+\lambda E_\alpha^{(\rm pol)}+O(\lambda^2)\ . \tag{2.8b}$$

Inserting Eqs. (2.8) into (2.7) and equating powers of λ, we obtain the equation for polarized orbitals $\varphi_{\alpha\rightarrow\gamma}$ [Δ_i is the two-dimensional Laplacian; cf. Eq. (3.10)]

$$\begin{aligned}\left[-\tfrac{1}{2}\Delta_i-\sum_{A=1}^{2}\frac{Z_A}{r_{iA}}+\sum_{\beta=1}^{N_{\rm occ}}[2J_\beta(\vec{r}_i)-K_\beta]-E_\alpha^{(0)}\right]&\varphi_{\alpha\rightarrow\gamma}(\vec{r}_i)\\
=-v(\hat{r}_1;\vec{r}_i)\varphi_\alpha^{(0)}(\vec{r}_i)&+\left[\int\varphi_\alpha^{(0)*}(\vec{r}_j)r_{ij}^{-1}\varphi_\alpha^{(0)}(\vec{r}_j)d\vec{r}_j\right]\varphi_{\alpha\rightarrow\gamma}(\vec{r}_i)\\
&-\left[2\int\varphi_\alpha^{(0)*}(\vec{r}_j)r_{ij}^{-1}\varphi_{\alpha\rightarrow\gamma}(\vec{r}_j)d\vec{r}_j+\int\varphi_{\alpha\rightarrow\gamma}^{*}(\vec{r}_j)r_{ij}^{-1}\varphi_\alpha^{(0)}(\vec{r}_j)d\vec{r}_j\right]\varphi_\alpha^{(0)}(\vec{r}_i)\\
&-\sum_{\beta(\neq\alpha)=1}^{N_{\rm occ}}\sum_{\delta=1}^{N_{\rm pol}}2\left[\int\varphi_\beta^{(0)*}(\vec{r}_j)r_{ij}^{-1}\varphi_{\beta\rightarrow\delta}(\vec{r}_j)d\vec{r}_j+\int\varphi_{\beta\rightarrow\delta}^{*}(\vec{r}_j)r_{ij}^{-1}\varphi_\beta^{(0)}(\vec{r}_j)d\vec{r}_j\right]\varphi_\alpha^{(0)}(\vec{r}_i)\\
&+\sum_{\beta(\neq\alpha)=1}^{N_{\rm occ}}\sum_{\delta=1}^{N_{\rm pol}}\left[\left[\int\varphi_\beta^{(0)*}(\vec{r}_j)r_{ij}^{-1}\varphi_\alpha^{(0)}(\vec{r}_j)d\vec{r}_j\right]\varphi_{\beta\rightarrow\delta}(\vec{r}_i)+\left[\int\varphi_{\beta\rightarrow\delta}^{*}(\vec{r}_j)r_{ij}^{-1}\varphi_\alpha^{(0)}(\vec{r}_j)d\vec{r}_j\right]\varphi_\beta^{(0)}(\vec{r}_i)\right]\ .\end{aligned} \tag{2.9}$$

In deriving (2.9) we have used $E^{(\rm pol)}=0$, which is a consequence of parity conservation and the dipole approximation. Also in (2.8) and (2.9), $N_{\rm pol}$ is the number of polarized orbitals of different symmetry for a given α induced by the perturbation. The last two sums on the right-hand side (rhs) take account of coupling between polarized orbitals which have different symmetries, or originate from different unperturbed molecular orbitals.

We next consider approximations to (2.9); first, we drop coupling on the rhs, noting that this was implicit even in Sternheimer's and related work.[13,12,14] The new aspect of this application is that we do *not* drop the exchange terms on the lhs or the $\beta=\alpha$ terms on the rhs of (2.9). [Rather we shall apply the free-electron gas-exchange model[16] to them; cf. (2.13).] This gives, after combining similar terms on the rhs and lhs of (2.9)—specifically diagonal exchange terms,

$$[-\tfrac{1}{2}\Delta_i+V_{\mathrm{st}}^{(\alpha)}(\vec{\mathrm{r}}_i)+\epsilon V_{\mathrm{ex}}^{(\alpha)}-E_\alpha^{(0)}]\varphi_{\alpha\to\gamma}(\vec{\mathrm{r}}_i)$$
$$=-v(\hat{r}_1;\vec{\mathrm{r}}_i)\varphi_\alpha^{(0)}(\vec{\mathrm{r}}_i)\ , \qquad (2.10)$$

where

$$V_{\mathrm{st}}^{(\alpha)}(\vec{\mathrm{r}}_i)=-\sum_{A=1}^{2}\frac{Z_A}{r_{iA}}+\sum_{\beta=1}^{N_{\mathrm{occ}}}(2-\delta_{\alpha\beta})J_\beta(\vec{\mathrm{r}}_i)\ . \qquad (2.11)$$

In (2.10) we also use the notation

$$V_{\mathrm{ex}}^{(\alpha)}\varphi_{\alpha\to\gamma}=-\sum_{\beta=1}^{N_{\mathrm{occ}}}K_\beta\varphi_{\alpha\to\gamma}(\vec{\mathrm{r}}_i)$$
$$+\left[3\int\varphi_\alpha^{(0)*}(\vec{\mathrm{r}}_j)r_{ij}^{-1}\varphi_{\alpha\to\gamma}(\vec{\mathrm{r}}_j)d\vec{\mathrm{r}}_j\right]$$
$$\times\varphi_\alpha^{(0)}(\vec{\mathrm{r}}_i)\ . \qquad (2.12)$$

In this application we shall approximate the exchange potential by the free-electron-gas model[16]

$$V_{\mathrm{ex}}^{(\alpha)}\to V_{\mathrm{FEG}}^{(\alpha)}=-\frac{2k_F}{\pi}\left[\frac{1}{2}+\frac{1-\eta_\alpha^2}{4\eta_\alpha}\ln\left|\frac{1+\eta_\alpha}{1-\eta_\alpha}\right|\right]\ , \qquad (2.13)$$

where

$$\eta_\alpha=\kappa_\alpha/k_F\ , \qquad (2.14)$$

$$k_F=[3\pi^2\rho(\vec{\mathrm{r}}_i)]^{1/3}\ , \qquad (2.15)$$

$$\kappa_\alpha=(2\,|\,E_\alpha^{(0)}\,|\,)^{1/2}\ , \qquad (2.16)$$

and

$$\rho(\vec{\mathrm{r}}_i)=\sum_{\alpha=1}^{N_{\mathrm{occ}}}N_\alpha\,|\,\varphi_\alpha^{(0)}(\vec{\mathrm{r}}_i)\,|^2\ . \qquad (2.17)$$

V_{FEG} can be derived from (2.12) by approximating the polarized orbitals $\varphi_{\alpha\to\gamma}^{(\mathrm{pol})}(r_i)$ as well as the unpolarized orbitals $\varphi_\alpha^{(0)}(r_i)$ as a plane waves in the exchange integrals in Eq. (2.12); in addition ϵ will have the approximate value

$$\epsilon\cong[(N-3)/N]_{N=14}=0.786\ldots\ . \qquad (2.18)$$

However, since the free-electron-gas value is not always optimum, we shall take ϵ as an adjustable parameter, to be determined so that dipole polarizabilities (see below) agree with available reliable values. We shall find that adjusted value is in fact not far different from (2.18).

There is one additional emendation we shall make to (2.10)—orthognalization. The polarized orbitals should be orthogonal to all bound orbitals of the same symmetry. The method of incorporating that condition is by now well known and applies to PDE's as well as ordinary differential equations: One appends successive terms $(1-\delta_{0n})\varphi_{n\gamma}^{(0)}$ to the rhs of (2.10), where $n=1,2,\ldots,N_{\mathrm{sym}}$ the latter being the number of unperturbed orbitals of the given symmetry in the target (for example, $N_{\mathrm{sym}}=3$ for σ_g symmetry corresponding to the filled $1\sigma_g$, $2\sigma_g$, and $3\sigma_g$ orbitals in the N$_2$ target). From the homogeneous $(\varphi_{\alpha\to 0\gamma})$ and N_{sym} inhomogeneous solutions, one constructs

$$\varphi_{\alpha\to\gamma}=\varphi_{\alpha\to 0\gamma}+\sum_{n=1}^{N_{\mathrm{sym}}}a_n\varphi_{\alpha\to n\gamma}\ , \qquad (2.19)$$

wherein the a_n are determined by the orthogonality conditions

$$\langle\varphi_{\alpha\to\gamma}\varphi_{n\gamma}^{(0)}\rangle=0,\quad n=1,2,\ldots,N_{\mathrm{sym}}\ . \qquad (2.20)$$

III. POLARIZATION POTENTIAL, POLARIZABILITIES, AND APPLICATION TO e-N$_2$ SCATTERING

The method of polarized orbitals[12] projects a total wave function (for a given molecular partial wave Λ)

$$\Psi_{\mathrm{po}}^{(\Lambda)}=\mathscr{A}\{F^{(\Lambda)}(\vec{\mathrm{r}}_1)\mathscr{Y}_S[\Phi_0(2,\ldots,N+1)$$
$$+\Phi_{\mathrm{pol}}(1;2,\ldots,N+1)]\}\ , \qquad (3.1)$$

in which the polarized part Φ_{pol} is constructed from the unpolarized Φ_0 (Hartree-Fock) target function by replacing each orbital consecutively by its polarized parts[12]

$$\varphi_\alpha^{(0)}(i)\to\lambda\sum_\gamma\varphi_{\alpha\to\gamma}(i)\ . \qquad (3.2)$$

In (3.1) $\mathscr{A}$ is the antisymmetrizer between electron 1 and the orbital electrons $(2,3,\ldots,N+1)$, the functions Φ_0 and Φ_{pol} being assumed antisymmetric in their orbital $(2,\ldots,N+1)$ coordinates. We will not go into any detail on this as the method is well known[12] and has been reviewed elsewhere[17]; suffice it to repeat that equations for the scattering functions $F^{(\Lambda)}(\vec{\mathrm{r}}_1)$ are obtained from the projection on the *unperturbed* target function[15,17]

$$\int\Phi_0^*\mathscr{Y}_S^*(H-E)\Psi_{\mathrm{po}}^{(\Lambda)}d\vec{\mathrm{r}}^{(1)}=0\ . \qquad (3.3)$$

In (3.1) and (3.3) $\mathscr{Y}_S$ represents the coupling of all angular and spin variables involving the scattered particle to the target molecule (again the notation here is very abbreviated). H is the total Hamiltonian and E the total energy of the electron-molecule system. Specifically,

$$E=E_0+\tfrac{1}{2}k^2\ , \qquad (3.4)$$

where E_0 is the energy of the target state.

The $d\vec{\mathrm{r}}^{(1)}$ in Eq. (3.3) signifies integration is over all coordinates *except* the vector $\vec{\mathrm{r}}_1=(r_1,\theta_1)$. This leads to a scattering equation which may be symbolically written

$$[-\tfrac{1}{2}\Delta_1+V_{\mathrm{st}}(\vec{\mathrm{r}}_1)+V_{\mathrm{st}}^{(\mathrm{ex})}+V_{\mathrm{pol}}(\vec{\mathrm{r}}_1)+V_{\mathrm{pol}}^{(\mathrm{ex})}-\tfrac{1}{2}k^2]$$
$$\times F^{(\Lambda)}(\vec{\mathrm{r}}_1)=0\ . \qquad (3.5)$$

The four "potentials" above came from the direct and exchange parts, Φ_0 and Φ_{pol}, of $\Psi_{\mathrm{po}}^{(\Lambda)}$, Eq. (3.1), respectively.

We shall only consider the direct polarization potential V_{pol} in detail. Note first that all potentials as well as the scattering functions $F^{(\Lambda)}(\vec{r}_1)$ are functions of the vector coordinates of the scattered particle $\vec{r}_1$. Thus all the relevant equations are partial differential equations, and this is the main distinction between the molecular as opposed to the atomic application of the method of polarized orbitals. In particular, the polarization potential in (3.5) derived from (3.3) is

$$V_{\text{pol}}(\vec{r}_1)=\int \Phi_0^*(2,\ldots,N+1)\left[\sum_{i=2}^{N+1}\frac{1}{r_{1i}}-\sum_{A=1}^{2}\frac{Z_A}{r_{1A}}\right]\times\Phi_{\text{pol}}(1;2,\ldots,N+1)d\vec{r}_1^{\,(1)}\ . \tag{3.6a}$$

It may be reduced to the form

$$V_{\text{pol}}(\vec{r}_1)=\sum_{\alpha=1}^{N_{\text{occ}}}\sum_{\gamma=1}^{N_{\text{pol}}}N_\alpha\int \varphi_\alpha^{(0)*}(\vec{r}_i)\left[\frac{1}{r_{1i}}-\sum_{A=1}^{2}\frac{Z_A}{r_{1A}}\right]\times\lambda(1;i)\varphi_{\alpha\to\gamma}(\vec{r}_i)d\vec{r}_i\ , \tag{3.6b}$$

where N_{occ} and N_{pol} have been defined above and N_α is the number of electrons in the spatial orbital $\varphi_\alpha^{(0)}$.

At this point we shall specialize the N_2 target in its ground $({}^1\Sigma_g^+)$ state:

$$\Phi_0=\Phi_{N_2}(1\sigma_g^2 2\sigma_g^2 3\sigma_g^2 1\sigma_u^2 2\sigma_u^2 1\pi_u^4)\ . \tag{3.7}$$

The specific ground-state approximation we use is that of Cade, Sales, and Wahl[18]; in Table I, we give energies for the various orbitals as a function of internuclear separation (R). It is obvious that the $(1\sigma_g)$ and $(1\sigma_u)$ orbitals are much more tightly bound than the others; thus they make a negligible contribution to polarization and according to our prescription[12] are neglected.

To find the polarized orbitals, the task is to integrate Eq. (2.10). Here we use the specific symmetry of the homonuclear diatomic target and the cut-off dipole approximation V_{cd} [Eq. (2.4c)] on the rhs of (2.10). The net result is that for each unperturbed $\varphi_\alpha^{(0)}$ there are two linearly independent polarized orbitals, which can be conveniently classified as parallel ($||$) and perpendicular ($\perp$) which refer to directions of approach to the fixed internuclear axis. For each of these, the appropriate dipole perturbation $v_{||}$ or $v_\perp$, where

$$v(\vec{r}_i)=\begin{cases} v_{||}=r_i\cos\theta_i, & (3.8\text{a})\\ v_\perp=r_i\sin\theta_i e^{i\varphi_i}\ , & (3.8\text{b})\end{cases}$$

is to be used in Eq. (2.10). The actual dipole perturbation of the ith electron due to an electron approaching perpendicular to the internuclear (z) axis, which can be taken to be along the x axis, is from (2.4c) $r_i\sin\theta_i\cos\varphi_i$; but because of the nature of Δ_i operator in (2.10), we can equally take the perpendicular perturbation as in (3.8b). The φ_i dependence of the solution of (2.10) can be taken out by writing (dropping the subscript i)

$$\varphi_{\alpha\to\gamma}(\vec{r})=r^{-1}h_{\alpha\to\gamma}(r,\theta)(-1)^{m_\gamma}e^{im_\gamma\varphi}/\sqrt{2\pi}\ , \tag{3.9}$$

where the $(-1)^{m_\gamma}$ is inserted for convenience. The resulting PDE for $h_{\alpha\to\lambda}(r,\theta)$ is

$$\left[\frac{\partial^2}{\partial r^2}+\frac{1}{r^2}\left[\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}-\frac{m_\gamma^2}{\sin^2\theta}\right]-2V_{\text{eff}}^{(\alpha)}(r,\theta)+2E_\alpha^{(0)}\right]h_{\alpha\to\gamma}(r,\theta)=(-1)^{m_\gamma}\begin{Bmatrix}2\cos\theta\delta_{m_\gamma 0}\\ \sin\theta\delta_{m_\gamma 1}\end{Bmatrix}r^2\varphi_\alpha^{(0)}(r,\theta)\ , \tag{3.10}$$

in which it is understood that the equations are augmented to construct orthogonalized solutions as described above. From (3.10) it is clear that the parallel perturbation ($m_\gamma=0$) does not change the m character relative to the unperturbed orbital, whereas the perpendicular perturbation ($m_\gamma=1$) changes it by one unit. On the other hand, the polarized orbital has opposite parity from its associated unperturbed orbital in all cases. The potential in (3.10) is the sum of the two potentials in (2.10):

$$V_{\text{eff}}^{(\alpha)}(r,\theta)=V_{\text{st}}^{(\alpha)}(r,\theta)+\epsilon V_{\text{FEG}}^{(\alpha)}(r,\theta)\ . \tag{3.11}$$

TABLE I. Orbital energies obtained by Cade, Sales, and Wahl (Ref. 18) (hartree).

R (a_0)	$1\sigma_g$	$2\sigma_g$	$3\sigma_g$	$1\sigma_u$	$2\sigma_u$	$1\pi_u$
1.85	−15.639	−1.558	−0.645	−15.631	−0.739	−0.671
1.95	−15.659	−1.519	−0.640	−15.653	−0.757	−0.644
2.05	−15.678	−1.480	−0.636	−15.674	−0.775	−0.619
2.068	−15.682	−1.474	−0.635	−15.678	−0.778	−0.615
2.15	−15.697	−1.442	−0.631	−15.694	−0.792	−0.597
2.20	−15.706	−1.423	−0.628	−15.704	−0.800	−0.587
2.292	−15.719	−1.388	−0.621	−15.717	−0.813	−0.568
2.45	−15.745	−1.338	−0.612	−15.743	−0.839	−0.542

All potentials are functions of r and θ, including even $V_{\rm FEG}^{(\rm ex)}$, Eq. (2.13).

We conclude this section by writing explicitly expressions for the polarization potentials from (3.6) in terms of the functions $h_{\alpha\to\gamma}$, Eq. (3.9), which are the ones actually solved for

$$V_{\rm pol}^{(||)}(r_1)=\frac{4}{r_1^4}\left\{\int_0^{r_1}dr\,r^2\left[\int_0^{\pi/2}\left[\sum_{n=2}^{3}\varphi_{n\sigma_g}^{(0)*}h_{n\sigma_g\to\sigma_u}+\varphi_{2\sigma_u}^{(0)*}h_{2\sigma_u\to\sigma_g}-2\varphi_{1\pi_u}^{(0)*}h_{1\pi_u\to\pi_g}\right]\cos\theta\sin\theta\,d\theta\right]\right\}, \tag{3.12a}$$

$$V_{\rm pol}^{(\perp)}(r_1)=\frac{4}{r_1^4}\left\{\int_0^{r_1}dr\,r^2\left[\int_0^{\pi/2}\left[-\sum_{n=2}^{3}\varphi_{n\sigma_g}^{(0)*}h_{n\sigma_g\to\pi_u}-\varphi_{2\sigma_u}^{(0)*}h_{2\sigma_u\to\pi_g}+2\varphi_{1\pi_a}^{(0)*}h_{1\pi_u\to\sigma_g}+2\varphi_{1\pi_u}^{(0)*}h_{1\pi_u\to\Delta_g}\right]\sin^2\theta\,d\theta\right]\right\}. \tag{3.12b}$$

From the above we can construct

$$V_{\rm pol}(\vec{r}_1)=V_{\rm pol}^{(0)}(r_1)+V_{\rm pol}^{(2)}(r_1)P_2(\cos\theta_1)\,, \tag{3.13}$$

where

$$V_{\rm pol}^{(0)}(r_1)=\tfrac{1}{3}[V_{\rm pol}^{(||)}(r_1)+2V_{\rm pol}^{(\perp)}(r_1)] \tag{3.14a}$$

and

$$V_{\rm pol}^{(2)}(r_1)=\tfrac{2}{3}[V_{\rm pol}^{(||)}(r_1)-V_{\rm pol}^{(\perp)}(r_1)]\,. \tag{3.14b}$$

Finally, the (dipole polarizabilities) are generated from the asymptotic form of $V_{\rm pol}^{(\lambda)}$ in the well-known way

$$\alpha_\lambda=\lim_{r_1\to\infty}[-2r_1^4V_{\rm pol}^{(\lambda)}(r_1)]\,, \tag{3.15}$$

where λ can be 0, 2, $||$, or $\perp$.

IV. BOUNDARY CONDITIONS, NUMERICAL SOLUTIONS, RESULTS, AND DISCUSSION

We discuss first the numerical solutions. The method used in all equations, whether the polarized orbitals or scattering, is the noniterative PDE technique.[9] Because all equations are elliptic, one needs boundary conditions on all boundaries. The boundaries and boundary conditions for $h_{\alpha\to\gamma}(r,\theta)$ are indicated by the rectangle in Fig. 1. The right-hand-most line $r=\rho\gg 1$ is an approximation of limit $r\to\infty$; in practice, ρ is taken to be a constant large enough so that physical results will be insensitive to its precise value; in practice, this was tested and the final $\rho=15a_0$ was found to be satisfactorily large enough. Clearly, the polarized-orbital functions are quadratically integrable and therefore they must vanish as $\rho\to\infty$. By virtue of their definition, Eq. (3.9), all solutions must also vanish along $r=0$.

The less obvious boundary conditions are along $\theta=0$ and $\pi/2$. These are determined by the angular content of the functions in question. This in turn can be determined by the behavior of the lowest spherical harmonic in terms of which the function can *naturally* be expanded. A compilation is given in Table II; they are to accompany the remaining boundary conditions shown in Fig. 1. Note in Table II that for some of the higher partial waves both the function and its first derivative are zero; this means that higher-order differences at the boundaries would have to be used in those cases.

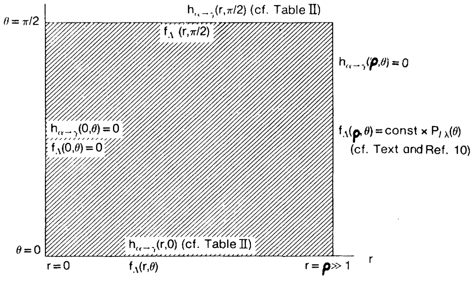

FIG. 1. Boundaries and boundary conditions for polarized orbitals and scattering functions.

The other important boundary condition is associated with the Coulomb (attractive) singularity at the nuclei. In cases where the wave function does not vanish, the wave function must have a cusp according to Kato's theorem.[19] We see from Table II that polarized orbitals $h_{\alpha\to\gamma}(r,\theta)$ do not vanish along $\theta=0$ (and specifically at the nuclei $r=R/2$, $\theta\to 0$) for $\gamma=\sigma_g$ and $\gamma=\sigma_u$ symmetries. Here we take the polarized orbitals to be

$$h_{\alpha\to\gamma}(r,\theta)=h_{\alpha\to\gamma}(\tfrac{1}{2}R,0)e^{-Z|\vec{R}/2-\vec{r}|}\,, \tag{4.1}$$

for R and r such that

$$|\tfrac{1}{2}\vec{R}-\vec{r}|\leq c\ll 1\,. \tag{4.2}$$

Explicitly, this takes care of the cusp at one nucleus. At the opposite nucleus $-R/2$ the function automatically has the same behavior by virtue of the reflection symmetry of $h_{\alpha\to\gamma}(r,\theta)$ about $\theta=\pi/2$ (which is the reason we can confine the boundaries within $\theta\leq\pi/2$). Again, numerical experimentation determines that a suitable value of $c=h_r/2$, where h_r is the mush size in the r direction.

All results presented here are for the e-N_2 collision system. The value of ϵ in (2.10) is adjusted so that electric dipole polarizabilities agree with reliable values. The use of an adjustable parameter ϵ here as well as in the scattering portion of the calculation (below) renders the present investigation as not completely *ab initio*. We believe that the quantitative alterations due to these phenomenological aspects are small; however, until the exchange kernel can be well incorporated into the noniterative PDE method,[9,10] a completely *ab initio* calculation from this point of view is not yet feasible. The results are given in Table III together with our previous analytic fit[20] slightly modified to experimental results[2] and other calculated values.[22,23] All results are seen to be in reasonable accord with one another.

The partial differential equations, essentially Eq. (2.10), with appropriate boundary conditions, were solved using the noniterative technique.[19] Some preliminary results of this work have been reported.[24]

Two-dimensional perspective graphs of the polarized orbitals $h_{\alpha\to\gamma}$, defined in Eq. (3.9), are shown in Figs. 2–4.

TABLE II. Boundary conditions for $h_{\alpha\to\gamma}(r,\theta)$ along $\theta=0$ and $\pi/2$. × indicates that the particular boundary condition obtains.

		$\theta=0$		$\theta=\pi/2$	
γ	lowest Y_{lm}	$\frac{\partial}{\partial\theta}h_{\alpha\to\gamma}=0$	$h_{\alpha\to\gamma}=0$	$\frac{\partial}{\partial\theta}h_{\alpha\to\gamma}=0$	$h_{\alpha\to\gamma}=0$
σ_g	Y_{00}	×		×	
σ_u	Y_{10}	×			×
π_u	Y_{11}		×	×	
π_g	Y_{21}		×		×
Δ_g	Y_{22}	×	×	×	
Δ_u	Y_{32}	×	×		×

These are the orthogonalized solutions, where required, as described above. Note that those functions which do not vanish along $\theta=0$ are seen to have cusps at $r=R/2$. Note also that the functions are not trivial in their θ dependence. It is particularly gratifying that the noniterative PDE technique which was originally put forward in the molecular context for the scattering problem[10] has proved to be so effective in solving for polarized orbitals as well.

From the polarized orbitals, so obtained, we can obtain the polarization potentials by quadrature, Eqs. (3.12), for perpendicular and parallel approach of the incoming electron to the direction of the internuclear axis. Results as a function of r at the equilibrium separation $R=2.068$ are compared to other calculations in Table IV. There is reasonable agreement among the various calculations as expected at larger r, but the differences at small r, particularly in $V_{\text{pol}}^{(\perp)}(r)$, are notable; specifically, we see that our potential becomes positive (repulsive). If the polarization potential were rigorously the result of an adiabatic perturbation, then it would necessarily be negative at all r, but as we have long emphasized,[12,17] by virtue of the step function and other elements of the method, our polarized orbital potential attempts to simulate nonadiabatic effects, which are important for small r, and need not be attractive. The θ dependence of the polarization potential, Eq. (3.13), is particularly dramatic as seen in Fig. 5 in comparison to the phenomenological potential, Eq. (1). Here $V_{\text{pol}}^{(\text{po})}(r)$ manifests itself as a repulsive potential for perpendicular approach to the N_2 molecule. This is compared with $V_{\text{pol}}^{(\text{phen})}(r)$, which is seen to be attractive for all directions of approach θ. The contrast between the shorter-range part of these respective polarization potentials can be rather pictorially stated: Whereas the phenomenological potential can be described as a rather "sticky egg," the polarized-orbital potential is more like the reverse of a true egg—longitudinally soft but traversally stiff. [It is emphasized that this polarization potential assumes that the remaining and major portion of the short-range potential is described (ideally) in the exchange (Hartree-Fock) approximation.] It will be seen that this has an important effect on the scattering and that only $V_{\text{pol}}^{(\text{po})}$ is able to reproduce the normalization of the substructure of the e-N_2 resonance correctly.

We now come to the internuclear separation (R) dependence of $V_{\text{pol}}(r)$. The calculated V_{pol} are plotted for different R in Figs. 6 and 7. Although it is not so obvious, the R dependence of these potentials is also quite complex and different from the phenomenological potential as originally generalized.[4] The main consequence of this difference occurs in the vibrational close-coupling portion of the theory, because matrix elements of $V_{\text{pol}}^{(\text{po})}$ between vibrational states of N_2 will be quite different from those of $V_{\text{pol}}^{(\text{phen})}$.

TABLE III. Electric dipole polarizabilities (a_0^3).

R (a_0)	ϵ in Eq. (2.10)[a]				Present results	Temkin (Ref. 20)	Morrison and Hay (Ref. 22)	Schneider[b]	Experiment
							α_0 (a_0^3)		
1.85	0.786	0.786	0.60	1.23	10.43	10.50	9.88		
1.95	0.786	0.786	0.64	1.20	11.08	11.18	10.59		
2.068	0.786	0.786	0.65	1.19	11.66	11.90	11.43	11.455	11.90[c]
2.15	0.786	0.60	0.67	1.12	12.66	12.34	12.01		11.74[d]
2.292	0.786	0.50	0.695	1.11	13.13	12.99	13.03		
2.45	0.786	0.37	0.72	1.07	13.90	13.55	14.15		
							α_2 (a_0^3)		
1.85	0.786	0.786	0.60	1.23	2.20	2.24	2.22		
1.95	0.786	0.786	0.64	1.20	2.70	2.60	2.74		
2.068	0.786	0.786	0.65	1.19	3.09	3.07	3.36	3.464	3.08[c]
2.15	0.786	0.60	0.67	1.12	3.33	3.42	3.79		
2.292	0.786	0.50	0.695	1.11	3.95	4.06	4.54		
2.45	0.786	0.37	0.72	1.07	4.93	4.81	5.37		

[a] The same ϵ apply to α_0 and α_2. The four columns refer to $\alpha=2\sigma_g$, $3\sigma_g$, $2\sigma_u$, and $1\pi_u$ in $\varphi_{\alpha\to\gamma}$ equations.

[b] B. Schneider, Chem. Phys. Lett. 51, 578 (1977).

[c] Bridge and Buckingham (Ref. 21).

[d] Zeiss and Meath (Ref. 21).

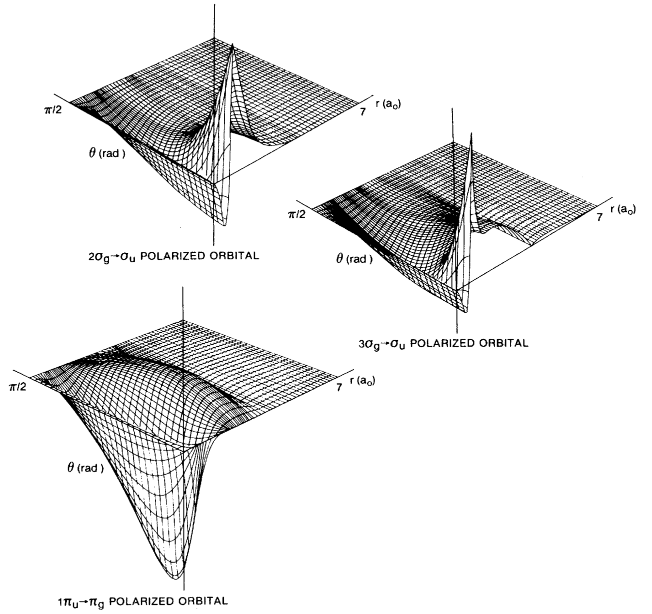

FIG. 2. Perspective plots of three (parallel) polarized orbitals, $h_{\alpha\to\gamma}$, for e-N_2. Here and in Figs. 3 and 4, N_2 is taken as its equilibrium value $R=2.068a_0$.

Let us turn to the scattering calculation that we have done in order to test the major aspects of V_{pol}. Since these results will be augmented by a much more extensive set of calculations,[11] we will be brief here. The hybrid theory[4] as we have applied it to e-N_2 scattering reduces to a set of vibrational close-coupling calculations for the Π_g partial wave derived from Eq. (3.5) with approximations[10] analogous to those made in (3.10) for the polarized orbitals

$$[-\tfrac{1}{2}\Delta_{(1)}+\langle v'|\mathscr{V}|v'\rangle-\tfrac{1}{2}k_{v'}^2]F_{v'}^{(\Pi_g)}(\vec{r}) = -\sum_{v\,(\neq v')}\langle v'|\mathscr{V}|v\rangle F_v^{(\Pi_g)}(\vec{r})\,, \qquad (5.1)$$

where $\mathscr{V}$ is sum of the static, (model) exchange,[16] and polarization potentials

$$\mathscr{V}(R,\vec{r})=V_{\text{st}}+\epsilon V_{\text{FEG}}+V_{\text{pol}}\;. \qquad (5.2)$$

Here V_{FEG} is of the form of (2.13) but with $\kappa_\alpha^2\to\kappa^2=k^2+2I+k_F^2$, where I is the ionization potential of the molecule;

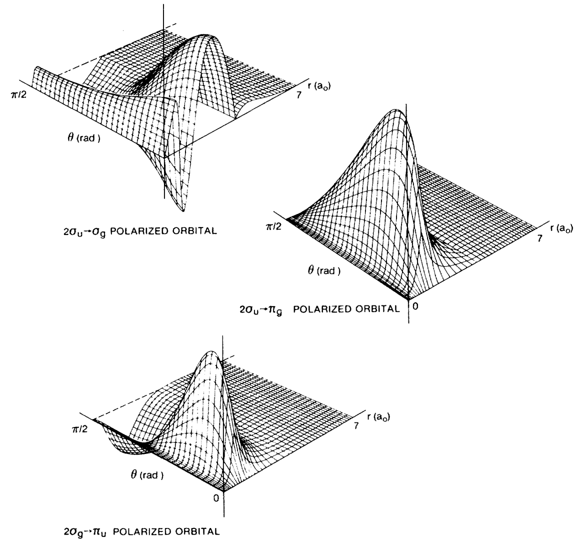

FIG. 3. Perspective plots of three different polarized orbitals.

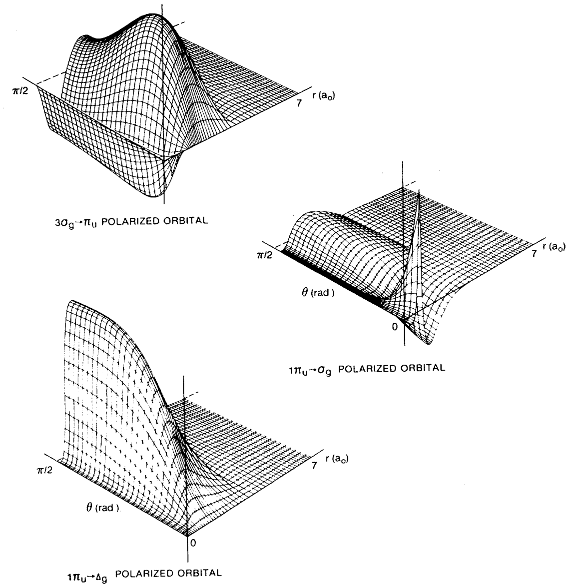

FIG. 4. Perspective plots of three (perpendicular) polarized orbitals.

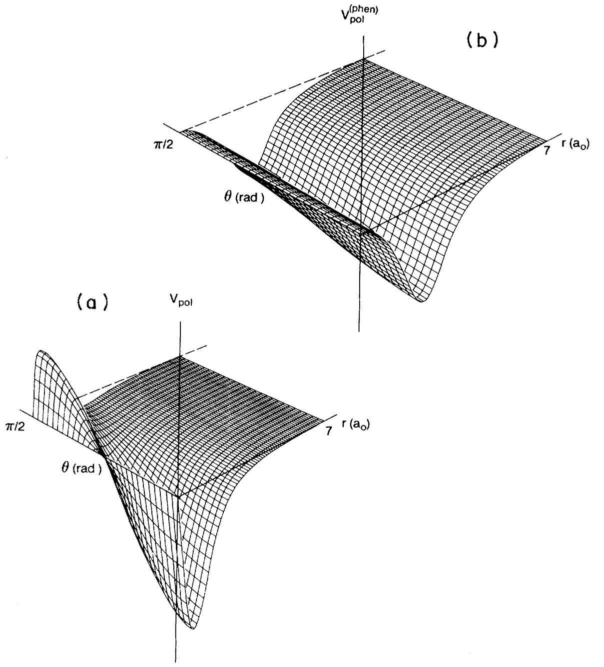

FIG. 5. Perspective plots of polarization potential for $R=R_0$: (a) calculated, polarized orbital, (b) phenomenological.

TABLE IV. Polarization potentials (hartree) for e-N$_2$ ($R = 2.068a_0$).

	$V_{\rm pol}^{(\|\|)}(r)$			$V_{\rm pol}^{(\perp)}(r)$		
r (a_0)	Present results	Morrison and Hay[a]	Eades, Truhlar, and Dixon[b]	Present results	Morrison and Hay[a]	Eades, Truhlar, and Dixon[b]
0.1	$-1.52(-1)$[c]			$+1.09(-1)$		
0.3	$-4.47(-1)$			$+2.83(-1)$		
0.5	$-7.04(-1)$		$-5.39(-1)$	$+3.53(-1)$		$-4.10(-1)$
0.75	$-8.96(-1)$		$-6.14(-1)$	$+2.89(-1)$		$-3.42(-1)$
1.0	$-8.82(-1)$			$+1.42(-1)$		
1.25	$-7.85(-1)$		$-7.23(-1)$	$+3.65(-2)$		$-2.07(-1)$
1.5	$-5.71(-1)$		$-6.72(-1)$	$-1.36(-2)$		$-1.58(-1)$
2.0	$-2.67(-1)$	$-4.936(-1)$	$-4.73(-1)$	$-5.54(-2)$	$-9.45(-2)$	$-9.54(-2)$
2.5	$-1.34(-1)$		$-2.32(-1)$	$-5.49(-2)$		$-6.02(-2)$
3.0	$-7.48(-2)$	$-1.347(-1)$	$-1.19(-1)$	$-4.11(-2)$	$-4.13(-2)$	$-3.84(-2)$
3.5	$-4.45(-2)$		$-6.75(-2)$	$-2.79(-2)$		$-2.46(-2)$
4.0	$-2.76(-2)$	$-4.37(-2)$	$-3.96(-2)$	$-1.84(-2)$	$-1.71(-2)$	$-1.59(-2)$
4.5	$-1.77(-2)$			$-1.21(-2)$		
5.0	$-1.17(-2)$	$-1.18(-2)$	$-1.55(-2)$	$-8.05(-3)$	$-7.57(-3)$	$-7.10(-3)$

[a] Including effects of higher multipole components (Ref. 22).

[b] Including effects of higher multipole components. Here the results from basis 5 are presented (Ref. 23).

[c] $(-1)=10^{-1}$, etc.

$$\Delta_{(\Lambda)}=\frac{\partial^2}{\partial r^2}+\frac{1}{r^2}\left[\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}-\frac{\Lambda^2}{\sin^2\theta}\right] . \quad (5.3)$$

For other than Π_g waves we use the fixed-nuclei approximation[25]

$$[-\tfrac{1}{2}\Delta_{(\Lambda)}+\mathscr{V}(R_0,\vec{r})-\tfrac{1}{2}k^2]F^{(\Lambda)}(\vec{r})=0 \ . \quad (5.4)$$

In both cases $\vec{r}$ signifies (r,θ) and the same noniterative technique[9] is used to solve the (two-dimensional) PDE's avoiding the l expansion which was the major cause of convergence difficulties in our original treatment.[4] In contrast of Ref. 4, we use a model exchange potential $V_{\rm FEG}$ in place of orthogonalization.[6] But as opposed to the calculation of polarized orbitals, Eq. (2.10), ϵ is here fine-tuned to have a single value: For the resonant partial wave, ϵ is determined such that the first resonance occurs at the experimental value as determined by Kennerly,[26] whereas the nonresonant partial waves have a different value of ϵ, chosen such that the even lower-energy nonresonant scattering is correctly given, again according to the experiment of Kennerly.[26] (Actually only the Σ_g partial wave is significant here, but that value of ϵ is used for all non-Π_g partial waves.)

For comparison we have also used $V_{\rm pol}^{(\rm phen)}$ in similar calculation. There we chose $\epsilon=1$ and fine-tuned r_0 to get the first resonance at the correct position ($k^2=1.98$ eV). In the close-coupling (Π_g) part of the calculation, seven vibrational states were retained. The vibrational functions were taken as Morse functions appropriate to a Morse curve optionally fitted to a spectroscopically determined potential-energy curve of Shimanouchi.[27] From our final calculations,[11] we determined that seven states are suffi-

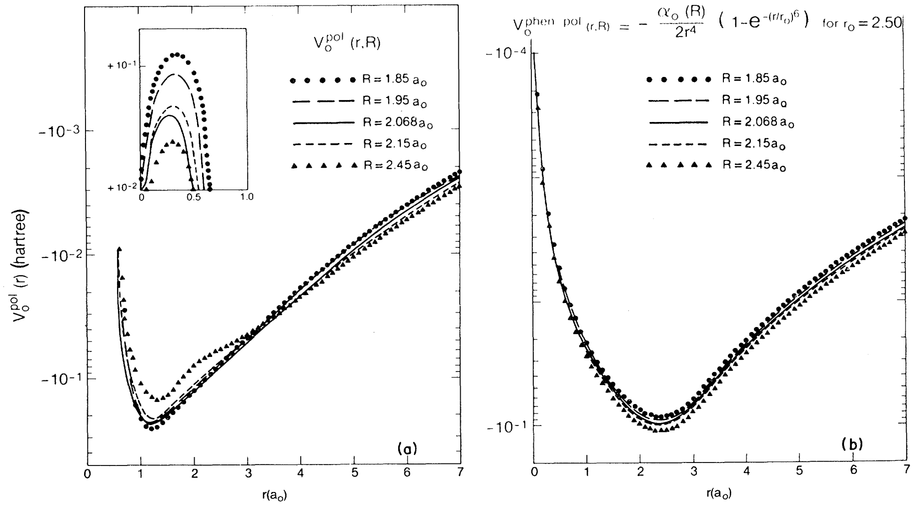

FIG. 6. $V_{\rm pol}^{(0)}(r)$ for different R: (a) calculated, polarized orbital, (b) phenomenological.

TABLE V. Integrated cross sections for the e-N_2 collision system.

$\sigma_{v'v}$	σ_{00}		σ_{10}				σ_{20}				$\sigma_T=\sum_{v=0}^{6}\sigma_{v0}$		σ_T (expt.)
E (eV)	I[a,b]	II[c,b]	I	II	R matrix[d]	Expt.[e]	I	II	R matrix[d]	Expt.[e]	I	II	Kennerly (Ref. 26)
1.80	12.5	11.5	0.568	0.325	0.54	2.1	0.079	0.0834	~0	0.3	13.2	11.9	15.6
1.85	13.7	11.9	1.04	0.529	1.20	3.0	0.192	0.171	0.25	0.7	15.0	12.7	18.2
1.90	15.5	12.6	2.07	0.919	2.7	4.75	0.526	0.394	0.5	1.3	18.2	14.0	21.6
1.95	17.4	13.1	4.15	1.60	4.3	5.6	1.53	0.983	1.5	3.9	23.6	16.3	25.4
2.00	15.7	12.4	5.19	1.61	4.7	3.9	3.03	1.62	2.7	3.8	25.2	17.0	25.8
2.05	12.6	12.0	2.70	0.506	2.5	2.2	2.90	0.988	2.6	3.5	20.0	14.9	23.9
2.10	14.0	13.1	0.955	0.258	0.5	1.6	2.30	0.427	1.9	2.9	19.4	15.0	24.1
2.15	19.0	14.9	0.803	0.662	0.3	2.8	1.87	0.163	1.5	2.0	24.9	17.0	29.1
2.20	25.2	17.2	2.82	1.72	1.1	5.15	1.18	0.0718	1.0	0.7	34.0	20.5	33.2
2.25	22.9	19.3	5.36	3.63	4.2	5.85	0.359	0.228	0.6	0.7	33.3	25.1	31.7
2.30	15.9	18.9	5.42	5.64	5.5	4.5	0.316	0.773	0.75	2.0	24.8	27.6	27.5

[a] I: Effective potential consists of the sum of static, free-electron gas-exchange potential multiplied by a factor of 0.482, and polarization potential obtained by polarized orbital method. All cross sections in units of 10^{-16} cm^2.

[b] Contribution to elastic scattering from nonresonant partial waves ($\Sigma_{g,u}$ and Π_u) calculated in the fixed-nuclei approximation at $R=2.068a_0$ and added to the Π_g resonant partial wave obtained from seven-channel vibrational close-coupling calculations. For nonresonant partial waves $\epsilon=0.73$.

[c] II: Same as I, except for use of phenomenological polarization potential with $r_0=2.50a_0$, with $\epsilon=1$ multiplying Z_{FEG}.

[d] Schneider, Le Dourneuf, and Vo Ky Lan (Ref. 3).

[e] Absolute normalization deduced from S. F. Wong [in Ref. 28, given in more detail in Ref. 7(b)] using the formula $\sigma_{v0}=4\pi(\frac{14}{15})d\sigma_{v0}/d\Omega$ $(\theta=\pi/2)$. These results as well as those of Ref. 3 (cf. footnote d) were numerically interpolated from graphical data; aside from values at maxima they are probably not very accurate.

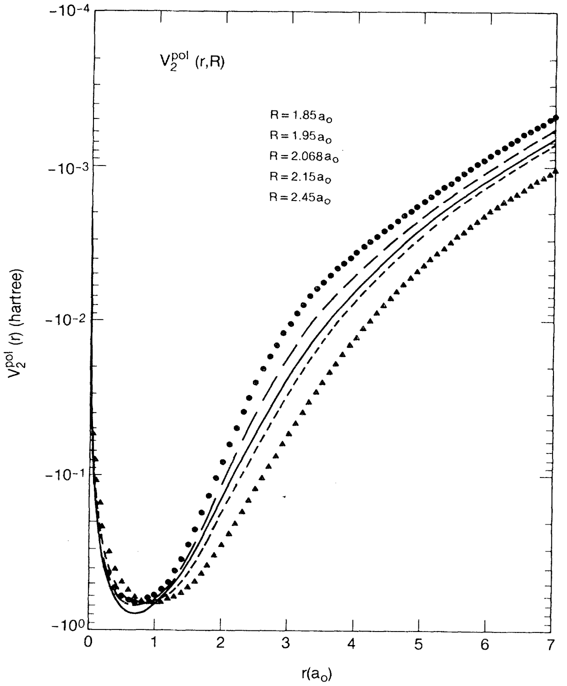

FIG. 7. $V_{\rm pol}^{(2)}(r)$ for different R. The $\lambda=2$ and 0 components of $V_{\rm pol}^{(\rm phen)}$ have the same dependence on R, cf. Fig. 6.

cient to get convergence in the range $k^2 \le 2.20$ eV.

Numerical results are presented in Table V. We see that the total cross section σ_T, which is the most secure experimental measurement[26] with regard to absolute normalization, is in fact very well fit by our calculation using the polarized-orbtial polarization potential $V_{\rm pol}^{(\rm po)}$ whereas the $V_{\rm pol}^{(\rm phen)}$ results fail both as regards height of the first peak and position of the second.

Coming now to the individual vibrational cross sections, also in Table V, we compare our results with experimental results of Wong[28] whose normalization is inferred (footnote e) from the experimental normalization (which was measured at 90°) assuming a pure Π_g partial wave. The normalization is estimated to be correct to $\pm 25\%$ [S. F. Wong (private communication)], and thus the uncertainty is relatively larger than those of σ_T. But they are accurate enough to show again that those results based on $V_{\rm pol}^{(\rm po)}$ are substantially more accurate than those coming from $V_{\rm pol}^{(\rm phen)}$. To repeat, we believe the angular (θ) dependence of $V_{\rm pol}$ is the key element of these improvements and that indicates that the polarized-orbital method is of value in giving this dependence (as well as the small-r dependence, which it gives in atomic scattering as well). The *ab initio* results of Schneider *et al.*[3] are also included, because they are of comparable accuracy.

The scattering calculation is being augmented to include up to 13 vibrational states. This is expected to yield convergence to $k^2 \le 3$ eV, which contains the bulk of the substructure. At that time we will present a more complete set of scattering results.

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