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Pseudopotential Method for Inelastic Processes in Atoms and Molecules. I. General Method and Photodetachment of O^-

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With the ultimate goal of elucidating inelastic processes in molecules, we have developed a pseudopotential method by which one can compute the wave functions for electron scattering states around atoms, molecules, and their respective ions. The method depends upon knowledge of the phase shift, obtained from scattering experiments or from Quantum Defect calculations. A one-parameter model is chosen to fit the boundary conditions and an approximate pseudowave function derived from it. First-order perturbation theory is then carried out in the Green's function formalism, both to yield an improved wave function and to fit the parameter which optimizes our model. As a test of our model, we apply the theory to the calculation of the s-wave continuum wave function and cross section for the photodetachment of electrons from O^-.

I. OUTLINE

The theoretical treatment of inelastic collision processes of electrons with molecules requires a knowledge of scattering functions, not only in the asymptotic region, but also close to and inside the molecular scatterer itself. In the region of the bound atomic or molecular electrons, which we shall call the inner region, scattering functions and bound excited one-electron functions have strong oscillatory behavior. These oscillations, which are imposed on the scattering function by the requirement of orthogonality to the occupied core orbitals, make it difficult to obtain accurate solutions of the one-electron Schrödinger equation by straightforward numerical methods based on effective potentials, whether local or nonlocal, or real or coupled. In this paper we adopt the physically intuitive viewpoint that if low-energy continuum functions are forced to fit simultaneously the known asymptotic boundary conditions and empirically determined phase shifts, and to be orthogonal to the occupied bound states of the $N+1$ electron system, little flexibility is left in their form.

It was pointed out by Phillips and Kleinman[1] and by Cohen and Heine[2] that the condition of orthogonality can be included as an effective nonlocal repulsive potential which we shall call V_R. The potential V_R cancels most of the real potential V in the inner region. The sum $V+V_R$ is the pseudopotential. The reformulated problem based on the pseudopotential leads to a new Schrödinger equation whose solution is called a pseudofunction. The pseudofunction is smooth and generally of low amplitude in the inner region, and is identical to the true eigenfunction in the outer region. The true scattering function may be obtained by orthogonalizing the pseudofunction to the occupied core orbitals. Because of its smoothness, the pseudofunction is well suited to numerical calculation. Moreover the method lends itself to approximations whose nature is easily understood. In effect, the pseudopotential method puts the burden of accuracy largely onto the accuracy of the known bound-state functions, which define the orthogonality properties of the desired scattering function. We wish to use this property to help us determine scattering functions that are accurate enough in the inner region to be useful for treating inelastic collisions and photoionization of molecules.

The viewpoint of the treatment that follows is this. The long-range properties of a scattering function are contained in the short-range part of the phase shift and in the asymptotic form of the potential and the solutions to the corresponding Schrödinger equation. If one knows the short-range part of the phase shift and the regular and irregular solutions for the scattering problem based on the asymptotic potential alone, then one has all the long-range information about the asymptotic region. Such phase shifts are often known, either from scattering experiments or from quantum defects. The behavior of the solution in the innermost region is determined in large part by the boundary condition at the origin. In the remainder of the inner region, the form of the wave function is governed by the orthogonality conditions, at least for scattering states whose asymptotic deBroglie wavelength is large compared with characteristic linear dimensions of the scatterer.

In this paper we utilize our knowledge of the boundary conditions to be satisfied by the scattering function and the experimentally determined short-range phase shifts to find a simple model potential approximation to the true pseudopotential. The model potential is parameterized to assure that the desired function has the proper long- and short-range behavior. The accuracy and utility of the method, in lowest order, depends on the small amplitude and smooth shape of the pseudofunction in the inner region and on the accuracy of the functions, representing occupied states. We also present a perturbation method for improving the accuracy beyond that of the zero-order function. Last, we carry out a model calculation for photodetachment of electrons from O^-.

II. GENERAL METHOD

A. The Zero-Order Function

Let $|\phi\rangle$, which we call a "pseudofunction," be a solution of the equation

$$(\mathcal{H}+V_R)|\phi\rangle=(T+V+V_R)|\phi\rangle=E|\phi\rangle\,, \tag{1}$$

where V_R is the "pseudopotential." As Austin, Heine and Sham[3] have shown, the most general form of the pseudopotential is given by

$$V_R=\sum_c|\varphi_c\rangle\langle F_c|\,, \tag{2}$$

where $|\varphi_c\rangle$ are the occupied core states of the Hamiltonian of our system and $|F_c\rangle$ are completely arbitrary functions. For any potential V_R of this form, the true continuum orbital $|\varphi\rangle$ satisfying

$$\mathcal{H}|\varphi\rangle=(T+V)|\varphi\rangle=E|\varphi\rangle \tag{3}$$

can be obtained from the pseudofunction $|\phi\rangle$ by the relation

$$|\varphi\rangle=|\phi\rangle-\sum_c|\varphi_c\rangle\langle\varphi_c|\phi\rangle\,. \tag{4}$$

Our procedure is to approximate the effective potential $(V+V_R)$ in Eq. (1) with a rough but convenient model potential V_0 to obtain an approximation to the pseudofunction $|\phi\rangle$. We then obtain our zero-order approximation to the true continuum function $|\varphi\rangle$ according to Eq. (4) by orthogonalizing $|\phi\rangle$ to the occupied core states $|\varphi_c\rangle$, which we assume are known. The worth of our method depends upon the extent to which an effective potential $(V+V_R)$ can be more accurately approximated by a simple model than can the true potential V.

Cohen and Heine[2] and Austin *et al.*[3] have discussed methods of constructing pseudopotentials which satisfy Eq. (2), and which cancel the true potential V as completely as possible in the region of the core. In our approach, we need not specify the pseudopotential V_R explicitly in the lowest order of approximation; the form of V_R enters only in the more refined perturbation calculation. In the lowest order we assume the existence of a V_R satisfying these conditions: (a) V_R can be expressed in the form of Eq. (2) with some undetermined set of functions F_c; (b) V_R cancels the true potential V sufficiently that the solutions to a Schrödinger equation based on $V+V_R$ are smooth and have low amplitude in the core region; (c) the sum $V+V_R$ can be well-represented by a model potential V_0 sufficiently simple that exact analytic eigenfunctions based on V_0 may be used to approximate the pseudofunction $|\phi\rangle$. One other rather obvious condition must be applied to V_0, namely that V_0 behave like V for distances far from the scatterer.

The method we describe is obtained by taking V_0 inside the core to be a spherical square barrier or well, and outside, to be equal to $-Z/r$, where Z is the charge of the isolated scatterer. The parameters of the potential V_0 are chosen so that the pseudofunction has the correct experimental (or quantum-defect-determined) phase shift and has a continuous logarithmic derivative on the surface where V_0 becomes $-Z/r$.

More explicitly, the method we propose is as follows. We wish to obtain an approximate solution $|\phi^-\rangle$ of Eq. (1) which, for photoionization, is of the form

$$|\phi^-\rangle\sim\exp[i\vec{k}\cdot\vec{r}-i\gamma\ln(kr+\vec{k}\cdot\vec{r})] +r^{-1}f^-(\hat{r})\exp[-ikr+i\gamma\ln 2kr]\,, \tag{5}$$

for asymptotically large values of r. (For photodetachment, $\gamma=0$.) The corresponding wave function $|\varphi^-\rangle$ obtained by orthogonalizing $|\phi^-\rangle$ to the *bound* core states will be an approximate solution to the Schrödinger Eq. (3) with the same asymptotic behavior given by Eq. (5). As stated above, we replace the effective potential $(V+V_R)$ in Eq. (1) with a model potential V_0. We restrict this model potential $V_0=V_0(l,m,E;r)$ to be spherically symmetric, but allow it to be nonlocal in the sense that it depends upon the symmetry and energy of the pseudofunction. For molecular systems, by taking V_0 to be spherical we are assuming that, to a good approximation, there exists a pseudopotential V_R which completely cancels all of the nonspherical part of V; i.e., that the nonspherical nature of the scattering wave function can be well described in terms of the core functions. It would require little additional effort, in molecular problems, to allow V_0 to be elliptic and to define the partial wave expansion in terms of spheroidal harmonics. Here, however, we assume V_0 is spherical and employ the usual partial wave expansion

$$|\phi^-\rangle=\sum_{l,m}r^{-1}y_{lm}(r)Y_{lm}(\theta,\varphi)\,, \tag{6}$$

where each $y_{lm}(r)$ is a radial function satisfying a pseudo wave equation

$$\left(-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+V_0(l,m,E;r)-\frac{1}{2}k^2\right)y_{lm}(r)=0\,. \tag{7}$$

All that remains to define our zero-order method is to choose a specific form for the model potential $V_0(l,m,E;r)$. We choose V_0 as follows:

$$V_0(l,m,E;r)=C_{lm}(E),\quad r<r_c\,, \tag{8a}$$

$$=-Z/r,\quad r>r_c\,. \tag{8b}$$

Thus our model potential is a square well (barrier) inside the core, and is equal to the long-range part of the real potential outside the core. Z is the net charge of the isolated scatterer. For scattering by neutrals (photodetachment) $Z=0$, and so strictly speaking the long-range behavior of V is $-\alpha/r$.[4] In actual practice it makes little difference if we set $V_0=0$ for $r>r_c$ according to Eq. (8b). (This is a consequence of the fact that the asymptotic functions in a polarization potential have the same sine-like form as those in a constant potential, even though, at finite distances, a single spherical Bessel function is not an appropriate radial eigenfunction for a polarization potential.[4])

The length of the well (barrier) r_c is an arbitrary parameter. Physical considerations suggest that r_c should be chosen to be equal to the core radius, e.g., the region within which 90 to 95% of the core electron density is confined. Estimates of r_c based on other physical properties such as crystal radii, are usually in good agreement with the values obtained from core density measurements.

The other parameters $C_{lm}(E)$, which give the depth (height) of the well (barrier), are determined semiempirically, as follows: We assume from this point on that, in addition to knowing the occupied core wave functions, we know the low-energy phase shifts of each of the more important partial waves, either from experimental scattering data or from Quantum Defect extrapolations.[5] If $\delta_{\mathrm{exp};lm}$ is the experimental phase shift and S is the number of occupied bound states of the same symmetry as the continuum function we are trying to calculate, then the phase shift we use for our pseudofunction is

$$\delta_{lm}=\delta_{\mathrm{exp},lm}-S\pi\,. \tag{9}$$

The physical meaning of Eq. (9) is as follows. We transform to the pseudopotential formalism to obtain a wave function which is smooth within the core. All the oscillations imposed on the real wave function by its orthogonality to the core states should be removed and contained in the potential V_R. Since orthogonalization to each bound state of the same symmetry introduces another node, we subtract π times the number of bound states from the experimental phase shift to get the phase shift δ_{lm} for the pseudofunction.

For our choice of V_0, Eq. (6) becomes

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+C_{lm}(E)-\frac{1}{2}k^2\right]y_{lm}(r)=0,\quad r<r_c\,, \tag{10}$$

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}-\frac{Z}{r}-\frac{1}{2}k^2\right]y_{lm}(r)=0\,,\quad r>r_c\,.$$

Using Eq. (9) we have

$$y_{lm}{}^0(r)=R_l(kr)+\tan\delta_{lm}G_l(kr),\quad r>r_c\,, \tag{11}$$

where $R_l(kr)$ and $G_l(kr)$ are the regular and irregular solutions to our model Hamiltonian in the asymptotic region. For photodetachment $R_l(kr)$ and $G_l(kr)$ are the spherical Bessel and Neumann functions multiplied by r. For photoionization they become the regular and irregular spherical Coulomb functions. The form of the solution for $r<r_c$ depends on the magnitude of C_{lm} compared to $\frac{1}{2}k^2$. If we define

$$K^2=2C_{lm}-k^2,\quad 2C_{lm}-k^2>0,\quad \text{Case I}$$

$$K^2=k^2-2C_{lm},\quad 2C_{lm}-k^2<0,\quad \text{Case II}$$

we have, for $r<r_c$,

$$y_{lm}{}^0=A_{lm}rI_l(kr)\,,\quad \text{Case I} \tag{12a}$$

$$y_{lm}{}^0=A_{lm}rj_l(kr)\,,\quad \text{Case II} \tag{12b}$$

where I_l is the spherical hyperbolic Bessel function and j_l the ordinary spherical Bessel function. The continuity of the logarithmic derivative at r_c determines that

$$\frac{d}{dr}\ln[rI_l(Kr)]\bigg|_{r=r_c}=\frac{d}{dr}\ln[R_l(kr)+\tan\delta_{lm}G_l(kr)]\bigg|_{r=r_c}\,,\quad \text{Case I;} \tag{13a}$$

$$\frac{d}{dr}\ln[rj_l(Kr)]\bigg|_{r=r_c}=\frac{d}{dr}\ln[R_l(kr)+\tan\delta_{lm}G_l(kr)]\bigg|_{r=r_c}\,,\quad \text{Case II.} \tag{13b}$$

If we choose a value of r_c for which we believe the wave function has essentially taken on its asymptotic form, we can calculate the corresponding K and C_{lm} from (13a) or (13b), whichever has a solution for that value of r_c. Thus the known phase shift and the continuity conditions determine one parameter in the model potential. We also require $y_{lm}{}^0$ to be as smooth as possible, consistent with our chosen k and fixed δ_{lm}, so that the nodal properties of the wave function are determined by the occupied core states and not by the model potential. This means we want K to be small, which in turn means that only one of the Eqs. (13a) or (13b) will have such a solution for real K.

The first approximation to the true continuum orbital is obtained by orthogonalizing $y_{lm}{}^0$ to the occupied bound states of our Hamiltonian $\mathcal{H}$.

$$\varphi_{lm}{}^0(r) = y_{lm}(r) - \sum_{\text{core}} \langle \varphi_c(r) | y_{lm}(r) \rangle \, \varphi_c(r) , \tag{14}$$

where the sum is over all core states of the same symmetry as $y_{lm}(r)$.

B. Improvement by Perturbation

It is possible to make systematic improvements on our model pseudofunction using perturbation theory. We begin by rewriting Eq. (1) as follows:

$$(T + V_0 - V_0 + V + V_R)\,|\phi\rangle = [H_0 + (V + V_R - V_0)]\,|\phi\rangle = E|\phi\rangle \, . \tag{15}$$

We now choose the pseudopotential V_R to be of specific form[2]

$$V_R = -\sum\nolimits_c |\varphi_c\rangle\langle\varphi_c|(V - V_0) . \tag{16}$$

Substituting Eq. (16) into Eq. (15) gives

$$(E - \mathcal{H}_0)|\phi\rangle = [(V - V_0) - \sum\nolimits_c |\varphi_c\rangle\langle\varphi_c|(V - V_0)]\,|\phi\rangle . \tag{17}$$

The starting point for our perturbation treatment is Eq. (17) which can be rewritten as

$$|\phi\rangle = |\phi_m\rangle + (E - \mathcal{H}_0 - i\epsilon)^{-1}(V + V_R - V_0)|\phi\rangle \, . \tag{18}$$

If, as we have assumed, $(V + V_R - V_0)$ is a relatively weak potential, it should be sufficient to solve (18) to first order. To this approximation we get

$$|\phi_1\rangle = |\phi_m\rangle + (E - \mathcal{H}_0 - i\epsilon)^{-1}(V + V_R - V_0)|\phi_m\rangle \, . \tag{19}$$

One of the more useful features of our model is that the Green's function, $(E - \mathcal{H}_0 - i\epsilon)^{-1}$, may be evaluated quite simply. In the next section we show how this may be done for a photodetachment problem. The extension to systems with long-range potentials is simply a matter of redefining the solutions to the model Hamiltonian and need not concern us for the present.

It is possible using perturbation theory not only to improve the wave function, but to optimize the value of the parameter r_c at the same time. If our model gives a good approximation to the exact solution for some sequence of values of r_c, then the first-order correction will be small. By solving the perturbation equation for a range of values of r_c, we can choose that solution which shows the smallest change upon perturbation in order to optimize our model. Such a procedure is only valid when the zero-order function is close to the exact solution and must be used with great care. In the energy range we have studied, the optimization need only be carried out for one value k because the value of the optimum r_c is not a sensitive function of energy. Thus after fixing a value of r_c for one energy, we can use this value to compute other zero order, or if need be, first-order wave functions for other energies in the same region. Proceeding in this manner, we calculate, with minimal effort, all the wave functions needed to get a detailed description of the way cross sections for inelastic processes behave with energy. The method will hopefully provide a usefully accurate way of elucidating inelastic processes in molecular gases.

III. A SIMPLE MODEL CALCULATION: THE PHOTODETACHMENT OF ELECTRONS FROM O$^-$

In this section we apply the theory developed in the previous section to the process

$$\mathrm{O}^- + h\nu \rightarrow \mathrm{O} + e^- \, .$$

This problem was chosen because, with a suitable model Hamiltonian, we are able to carry out both zero-order and first-order pseudopotential calculations and compare these with an "exact" numerical calculation based on the same potential. We use the results as a justification for the application presented in the following article.

In order to remove inessentials from the calculation, we chose for our Hamiltonian one of the same form used by Klein and Brueckner[6] in their calculation of electron detachment from O$^-$ and N$^-$, namely,

$$\mathcal{H}_r = -\frac{1}{2}\frac{d^2}{dr^2} - \frac{\delta}{r} + U(r) - \frac{1}{2}\alpha(r_p{}^2 + r^2)^{-1} \, , \tag{20}$$

$$U(r) = r^{-1}\int_0^r (P_{1s}{}^2 + P_{2s}{}^2 + 2P_{2p}{}^2)\,dr_1$$

$$+\int_r^\infty (P_{1s}{}^2+P_{2s}{}^2+2P_{2p}{}^2)r_1{}^{-1}dr_1 . \qquad (21)$$

The P_n are the solutions of the Hartree-Fock equations for the oxygen ^3P state as given by Clementi, Roothaan, and Yoshimine.[7] The term $U(r)$ is the usual Coulomb potential. The parameter α is a combined exchange-polarization factor chosen to reproduce the binding energy of the $2p$ electron in O^-, and r_p is a screening distance. Let us denote by the symbol $V(r)$ everything in Eq. (20) except the kinetic energy

$$\mathcal{H}_r = -\tfrac{1}{2}(d^2/dr^2)+V(r); \qquad (22)$$

we now transform to the pseudopotential formalism and look for s-wave solutions of the following equation

$$(\mathcal{H}_r + V_R)y_0(kr) = \tfrac{1}{2}k^2 y_0(kr). \qquad (23)$$

In obtaining the zero-order approximation to y_0, in place of experimental phase shifts δ_{exp} we use the phase shifts $\bar{\delta}$ obtained from numerical integration of the true Schrödinger equation with the Hamiltonian $\mathcal{H}_R$. The s-wave phase shifts obtained in this way, for k approaching zero, approach the value 2π from below. According to Eq. (9), the phase shift δ which will result in a smooth pseudofunction is obtained by subtracting 2π from this value. This results in the phase shift $\bar{\delta}_0$ of the pseudofunction being small and negative, and therefore, the solution to our model Hamiltonian belongs to case I: V_0 is a barrier. Explicitly we have

$$y_0{}^0(kr) = A\sinh(Kr), \qquad r<r_c, \qquad (24a)$$

$$y_0{}^0(kr) = B\sin(kr+\bar{\delta}_0), \qquad r>r_c. \qquad (24b)$$

The continuity condition at r_c gives

$$K^{-1}\tanh(Kr_c) = k^{-1}\tan(kr_c+\bar{\delta}_0). \qquad (25)$$

The model wave functions obtained from Eqs. (23) and (24) were orthogonalized to the bound state $1s$ and $2s$ functions of Eq. (20). These functions were then used to compute the photodetachment cross section of O^- from the formula,

$$\sigma = 8\pi^3 e^2 \nu (3c)^{-1} \left| \int y_0{}^0(kr) r P_{2p}(r) dr \right|^2 . \qquad (26)$$

The calculation of σ was repeated with the exact solution to Eq. (20) obtained by numerical integration of the differential equation. In Table I we give the results of our calculation of the total cross section as a function of the wave vector of the outgoing electron. The computation was carried out using the value 3.5 Bohr units for r_c. Our choice was guided by the core-density criterion discussed earlier, and is in good agreement with measurements of the univalent crystal radius of O^-. However, in calculations of e-He s-wave scattering states by the same procedure, the resulting optimal value of r_c was somewhat larger than what is generally considered to be the radius of the helium atom.[8] Therefore we are not certain how much confidence can be placed in the core-density criteria for choosing r_c. Nevertheless, the fact that the model pseudofunctions are not very sensitive to changes in r_c, as illustrated by Fig. 1, indicates that it is not too critical that r_c be determined accurately.

The agreement between the exact values of the total cross section and the values computed from our model wave functions are quite good, especially considering the simplicity of our zero-order method. As a result, we feel that this procedure, even in its simplest form, might be very useful in atomic and molecular continuum calculations.

It is possible to improve the results of our simple model calculation using perturbation theory. For atomic (spherically symmetric) systems, this perturbation procedure involves roughly the same numerical effort as solving the exact equation by numerical integration, and so it will not be useful for such systems. For molecular systems for which the potential is not separable, numerical solution of the exact (partial differential) equation becomes quite laborious, and for these systems the perturbation method might provide a very tractable way of obtaining accurate wave functions.

TABLE I. Calculated and experimental photodetachment cross sections of electrons from O^-.

k(a.u.)	V_0	Cross section for unperturbed function	Cross section for perturbed function	Cross section for exact(18) solution	% error	Experimental cross section (Ref. 10)
10^{-4}	0.078 84	0.984×10^{-21}	0.102×10^{-20}	0.101×10^{-20}	1.19	
10^{-2}	0.078 86	0.984×10^{-19}	0.102×10^{-18}	0.101×10^{-18}	1.8	
10^{-1}	0.079 88	0.960×10^{-18}	0.100×10^{-17}	0.973×10^{-18}	2.8	0.45×10^{-17}
0.3	0.092 45	0.208×10^{-17}	0.202×10^{-17}	0.199×10^{-17}	1.5	0.625×10^{-17}
0.5	0.126 37	0.173×10^{-17}	0.177×10^{-17}	0.176×10^{-17}	0.6	

To carry out the perturbation procedure we return to Eq. (23) which may be rewritten as

$$(\tfrac{1}{2}k^2 - \mathcal{H}_0)y_0(kr) = (V + V_R - C_0)y_0(kr)\,, \tag{27}$$

where
$$\mathcal{H}_0 = -\frac{1}{2}\frac{d^2}{dr^2} + C_0\,, \quad r<r_c\,, \tag{28a}$$

$$\mathcal{H}_0 = -\frac{1}{2}\frac{d^2}{dr^2}\,, \qquad r>r_c\,. \tag{28b}$$

Here we form the pseudopotential V_R according to Eq. (16)

$$V_R = -P_{1s}(r)\langle P_{1s}\,|\,V - C_0\,|\,y_0\rangle - P_{2s}(r)\langle P_{2s}\,|\,V - C_0\,|\,y_0\rangle\,, \tag{29}$$

where we define

$$\langle P_{ns}\,|\,V - C_0\,|\,y_0\rangle = \int_0^{r_c} P_{ns}(r)(V - C_0)y_0(r)dr + \int_{r_c}^{\infty} P_{ns}(r)Vy_0(r)dr\,. \tag{30}$$

To first order, the solution to Eq. (27) is

$$y_0^{(1)}(kr) = y_0^{0}(kr) + (\tfrac{1}{2}k^2 - \mathcal{H}_0)^{-1}(V + V_R - C_0)y_0^{0}(kr)\,. \tag{31}$$

The Green's function[9] $(\frac{1}{2}k^2 - \mathcal{H}_0)^{-1}$ satisfies the equation

$$(\tfrac{1}{2}k^2 - \mathcal{H}_0)G(r\,|\,r') = \delta(r - r')\,; \tag{32}$$

$$\left(\frac{d^2}{dr^2} + k^2 - 2C_0\right)G(r\,|\,r') = 2\delta(r - r')\,, \quad r<r_c\,; \tag{33a}$$

$$\left(\frac{d^2}{dr^2} + k^2\right)G(r\,|\,r') = 2\delta(r - r')\,, \qquad r>r_c\,. \tag{33b}$$

The solution to Eq. (31) satisfying the boundary conditions

$$y_0^{1}(0) = 0\,, \tag{34a}$$

$$\left.\frac{dy_0^{1}}{dr}\right|_{r=0} = 1\,, \tag{34b}$$

may be constructed using the Green's function

$$G(r\,|\,r') = 0\,, \qquad r<r'\,, \tag{35a}$$

$$G(r\,|\,r') = [\theta_1(r')\theta_2(r) - \theta_1(r)\theta_2(r')] \times [J(\theta_1, \theta_2)]^{-1}\,, \quad r>r'\,, \tag{35b}$$

where

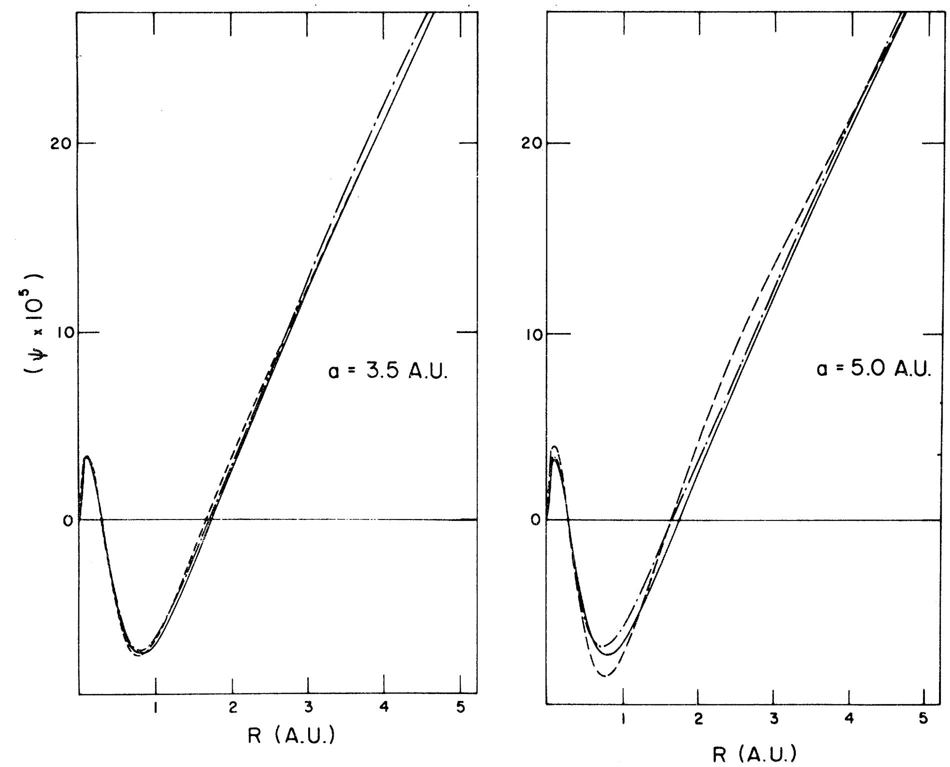

FIG. 1. Wave functions for various values of the length parameter a. (a) Solid curve is exact solution to Eq. 18. (b) Dashed curve is a square-barrier wave function orthogonalized to the P_{1s} and P_{2s} states of Eq. 18. (c) Dot-dashed curve is the first-order perturbed square-barrier function after orthogonalization to the P_{1s} and P_{2s} states of Eq. 18.

$$\theta_1(r) = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \left(H(r_c - r)\, \frac{\sin(kr_c + \bar{\delta}_0)}{\sinh Kr_c} \sinh Kr \right.$$

$$\left. + H(r - r_c) \sin(kr + \bar{\delta}_0) \right) ,$$

$$\theta_2(r) = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \left(H(r_c - r)\, \frac{\sin(kr_c + \eta_0)}{\cosh Kr_c} \cosh Kr \right.$$

$$\left. + H(r - r_c) \sin(kr + \eta_0) \right) ,$$

and $H(r)$ is the Heaviside step function,

$$H(r) = 0, \quad r < 0 ,$$
$$\qquad 1, \quad r > 0 .$$

The Wronskian

$$J(\theta_1, \theta_2) = \theta_1 \frac{d\theta_2}{dr} - \theta_2 \frac{d\theta_1}{dr}$$

$$= - \frac{2K}{\pi} \frac{\sin(kr_c + \bar{\delta}_0) \sin(kr_c + \eta_0)}{\sinh Kr_c \cosh Kr_c} ;$$

η_0 is a parameter automatically fixed once $\bar{\delta}_0$ and r_c are chosen by the following equation

$$K^{-1} \coth Kr_c = k^{-1} \tan(kr_c + \eta_0) . \tag{36}$$

The final integral equation is

$$y_0{}^{(1)}(kr) = y_0{}^0(kr) + \int G(r \mid r')(V + V_R - C_0) y_0{}^0(kr')\, dr' , \tag{37}$$

i.e., for $r < r_c$

$$y_0{}^{(1)}(kr) = K^{-1} \sinh Kr + K^{-1} \sinh Kr \int_0^r \cosh Kr' F_1(r') dr' - K^{-1} \cosh Kr \int_0^r \sinh Kr' F_1(r') dr' , \tag{38a}$$

and for $r > r_c$

$$y_0{}^{(1)}(kr) = \frac{\sinh(Kr_c) \sin(kr + \bar{\delta}_0)}{K \sin(kr_c + \bar{\delta}_0)} \times \left[1 + \frac{\cosh Kr_c}{\sin(kr_c + \eta_0)} \times \left(\frac{\sin(kr_c + \eta_0)}{\cosh Kr_c} \int_0^{r_c} \cosh(Kr') F_1(r') dr' + \int_{r_c}^r \sin(kr' + \eta_0) F_2(r') dr' \right) \right.$$

$$\left. + \frac{\sin(kr + \eta_0)}{\sin(kr + \bar{\delta}_0)} \frac{\cosh(Kr_c)}{\sin(kr_c + \eta_0)} \times \left(\frac{\sin(kr_c + \delta_0)}{\sinh(Kr_c)} \int_0^{r_c} \sinh(Kr') F_1(r') dr' + \int_{r_c}^r \sin(kr' + \bar{\delta}_0) F_2(r') dr' \right) \right] , \tag{38b}$$

where

$$F_1(r) = 2(V - C_0) y_0{}^0(kr) - 2P_{1s}(r) \langle P_{1s} \mid V - C_0 \mid y_0{}^0 \rangle - 2P_{2s}(r) \langle P_{2s} \mid V - C_0 \mid y_0{}^0 \rangle ,$$

$$F_2(r) = 2V y_0{}^0(kr) - 2P_{1s}(r) \langle P_{1s} \mid V - C_0 \mid y_0{}^0 \rangle - 2P_{2s}(r) \langle P_{2s} \mid V - C_0 \mid y_0{}^0 \rangle .$$

We normalize so that the final first-order function has the same amplitude at some distant point a as our model. The solution to our original Schrödinger equation based on the Hamiltonian $\mathcal{H}_r$ can be recovered by simple orthogonalization to the 1s and 2s core states:

$$\psi_0{}^{(1)} = y_0{}^{(1)}(kr) - P_{1s}(r) \langle P_{1s} \mid y_0{}^{(1)} \rangle - P_{2s}(r) \langle P_{2s} \mid y_0{}^{(1)} \rangle . \tag{39}$$

In Table I, we have included the values of the total cross section calculated using $\psi_0{}^{(1)}$ for completeness. As expected, the change in the value of the cross section in going from the model to the perturbed wave function is small. In Fig. 1 we show a plot of the orthogonalized model function, the orthogonalized perturbed function, and the exact solution to Eq. (20) for four choices of r_c. From examination of these curves it is easy to see that a value of 3.0 or 3.5 a.u. gives the smallest difference between the perturbed functions and model function. Comparison of the perturbed functions with the exact solution shows that for almost all values of r_c, the perturbed function is very close to being exact. The comparison also shows that the perturbed functions for a barrier length of 3.0 or 3.5 a.u. are closest to the exact function. This confirms our belief that the best value of r_c may be estimated by making the perturbed and unperturbed functions as similar as possible. For the value of 3.5 a.u., even the unperturbed function is an excellent approximation to the exact solution.

The results of the calculations for O$^-$ based on the simple step-function model potential, are accurate enough to dissuade us from pursuing more elaborate model potentials at this time. Even in zero order, the method appears promising enough to be applied to complex systems, i.e., to molecular problems.

Let us examine the relationship between the psuedopotential $V+V_R$ and the model potential V_0. It is certainly true that $V+V_R$ is not a constant in the core. Figure 2 shows that it has both a positive and negative part between zero and about one bohr unit. Why is it then that even such a simple model as a square well with a properly chosen length can give such good results? The answer lies not so much in the model as in the effect of the orthogonalization of the pseudofunction to the core states. It is a well-known property of high-energy valence and continuum functions of the same symmetry that they look alike within the core of the atom.[11,12] This reflects the condition that they must be orthogonal to the core functions. By taking some simple smooth function and orthogonalizing to the occupied core states, we are able to reproduce the general shape and nodal characteristics of continuum of high-energy bound-state functions. The essential effect of the model function $y_0{}^0$ is to insure the proper boundary conditions and asymptotic form of our wave function from our knowledge of the phase shift. It is not surprising that a model function of the form sinhKr can give an excellent result when K is chosen properly, and when it is orthogonalized to accurate core functions.

With this behavior in mind one can look forward to treating reasonably complicated systems. All one needs are the experimental phase shifts, a simple smooth model function, and sufficiently accurate bound-state functions of the system to get a useful approximation to the correct continuum function.

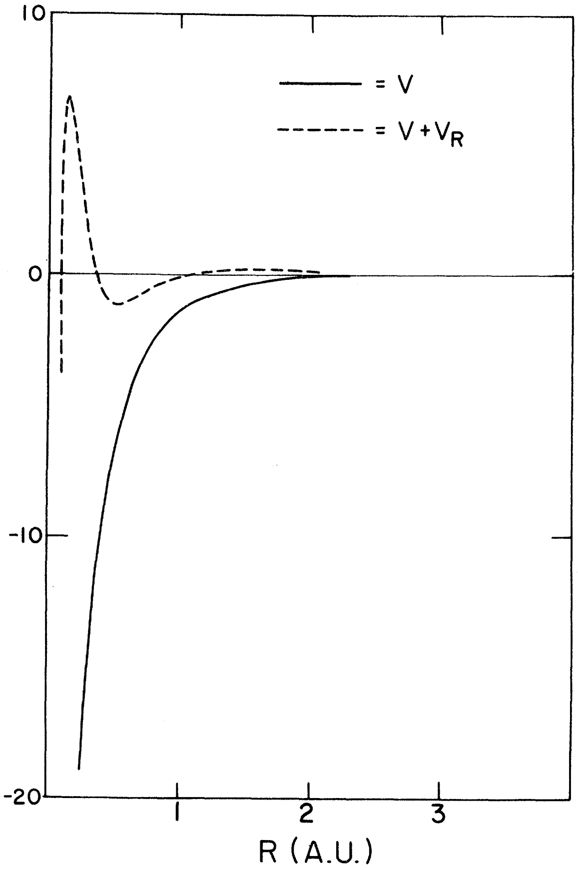

FIG. 2. Hartree-plus-polarization potential (V), and the potential $V-\Sigma|\varphi_c\rangle\langle\varphi_c|V$, which is V less its projection on the core states. This is essentially the same as $V+V_R=V-\Sigma\,|\varphi_c\rangle\langle\varphi_c(V-V_0)$, and is so labeled.

It is interesting to note that a method strikingly similar to ours was developed quite independently for treating energy bands in solids.[13,14] This formulation of the pseudopotential method seems to be well adapted to generate energies and wave functions of Hartree-Fock quality in solid-state problems.

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[1] J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).

[2] M. H. Cohen and V. Heine, Phys. Rev. 122, 1821 (1961).

[3] B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. 127, 276 (1962).

[4] T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. 2, 491 (1961); R. O. Berger, T. F.

O'Malley, and L. Spruch, Phys. Rev. 137, A1068 (1965).

[5] See M. J. Seaton, Monthly Notices Roy. Astron. Soc. 118, 504 (1958); M. J. Seaton, Proc. Phys. Soc. (London) 88, 801 (1966); M. Weinberg, Ph.D. thesis, University of Chicago, 1967 (unpublished); M. Weinberg, R. S. Berry, and J. Tully, J. Chem. Phys. 49, 122 (1968).

[6] M. M. Klein and K. A. Brueckner, Phys. Rev. 111, 1115 (1958); see also E. J. Robinson and S. Geltman, Phys. Rev. 153, 4 (1967); W. R. Garrett and H. T. Jackson, Jr., Phys. Rev. 153, 28 (1967) and J. W. Cooper and J. B. Martin, Phys. Rev. 123, 1482 (1962), for other calculations of the photodetachment cross section of O$^-$.

[7] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. 127, 1618 (1962).

[8] J. C. Tully, Ph.D. thesis, University of Chicago (1968) (unpublished).

[9] B. Friedman, Principles and Techniques of Applied Mathematics (John Wiley & Sons, Inc., New York, 1956), pp. 169–172.

[10] L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, Phys. Rev. 111, 504 (1958).

[11] E. Brown, Phys. Rev. 126, 421 (1962).

[12] J. C. Slater, Quantum Theory of Atomic Structure (McGraw-Hill Book Company, Inc., New York, 1960), pp. 229–232.

[13] I. V. Abarenkov and V. Heine, Phil. Mag. 12, 529 (1965).

[14] I. V. Abarenkov and I. M. Antonova, Phys. Stat. Solids 20, 643 (1967).

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Pseudopotential Method for Inelastic Processes in Atoms and Molecules. II. Photoionization of N_2[†]

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The pseudopotential method developed in Paper I is applied to the photoionization of N_2. From the known quantum defects of two Rydberg series of N_2, we obtain the phase shifts of the photoionized electron. These phase shifts are used to construct a simple model potential approximation to the true pseudopotential. The model wave functions are then orthogonalized to the known Hartree-Fock wave functions of the N_2^+ core. Using these wave functions we calculate the total and differential cross section for photoionization of electrons from N_2 as a function of the energy of the outgoing electron. The results of the calculation are discussed and compared with some of the more recent experimental measurements of the aforementioned quantities.

I. INTRODUCTION

The photoionization of N_2 has been the subject of intensive efforts in a large number of laboratories during the past ten years. This work culminated in experimental measurements of the total cross section for the photoionization of electrons from N_2 as a function of incident light energy.[1–4] Quite recently the angular distribution of the photoelectrons from N_2 has been studied for formation of specific electronic states of the ion.[5]

The electronic structure of the N_2 molecule may be represented as

$$(1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2 1\pi_u{}^4 3\sigma_g{}^2)\ {}^1\Sigma_g^+ \tag{1}$$

in the molecular orbital picture. The photoionization process with the lowest threshold energy

$$N_2({}^1\Sigma_g^+) + h\nu \rightarrow N_2^+({}^2\Sigma_g^+) + e \tag{2}$$

begins to occur at an energy of 15.58 eV (795.9 Å). Using the selection rules for dipole radiation, we find that the only allowed states of the outgoing electron are $k\sigma_u$ and $k\pi_u$. The corresponding configurations and states of the $e - N_2^+$ system may be represented as

$$(1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2 1\pi_u{}^2 3\sigma_g k\sigma_u)\ ,\quad {}^1\Sigma_u^+ \tag{3}$$

and

$$(1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2 1\pi_u{}^4 3\sigma_g k\pi_u)\ ,\quad {}^1\Pi_u\ ,$$

where k is the wave number of the escaping electron. As the energy of the photons is increased, channels corresponding to excited core N_2^+ states