

Second-order nonadiabatic polarization potentials for positron-hydrogen and positron-helium elastic scattering

Y.-C. Jean* and D.M. Schrader

Chemistry Department, Marquette University, Milwaukee, Wisconsin 53233

(Received 21 June 1976; revised manuscript received 2 February 1978)

A self-consistent field theory for one-positron, many-electron systems derived by Schrader [Phys. Rev. A **1**, 1070 (1970)] is solved in first order for positron-hydrogen and -helium elastic scattering below the positronium formation threshold. The perturbation is the positron-electron interaction, and the zeroth-order target, in the case of helium, is the Hartree-Fock atom. The first-order target equation is solved variationally. Unlike the polarized-orbital method of Callaway-Temkin, no further simplifying approximations are made here for s -wave phase shifts except the use of a finite basis in which to expand the perturbed electronic orbitals, and in the case of helium the neglect of a certain small and intractable integral at an intermediate stage of the calculation. In addition, for non- s -wave phase shifts we follow much previous work and neglect contributions of an excited target. Our approach is fully nonadiabatic, and is contrived in such a way that the zeroth-order target equation contains the positronic Laplacian operator. The nonadiabatic polarization potential thus generated by the positron differs significantly from that in other more approximate nonadiabatic theories. The positronic scattering phase shifts of the s , p , and d waves are calculated and compared to the best available results from other methods. Our calculated phase shifts for the hydrogen target lie midway between those for a static target and the exact results, thus revealing a serious lack of accuracy for any first-order method, at least when applied to systems similar to hydrogen. Our results for helium are more accurate but still not satisfactory. Our results thus cast doubt on the validity of many earlier calculations in which the polarization potential obtained from a first-order perturbation calculation is adjusted to improve the resulting phase shifts.

I. INTRODUCTION

Positron and electron scattering from hydrogen and helium atoms is the central problem in scattering theory. Only if these simple systems can be quantitatively understood on the basis of methods applicable to more complicated targets can we claim to understand those targets. Hence we see the significance of the concept of the polarization potential.

Progress in scattering calculations has been much slower than in bound-state calculations on corresponding systems. Hylleraas¹ produced accurate wave functions and energies for the ground state of heliumlike atoms soon after the introduction of quantum mechanics. His calculations have been refined numerically by later workers, but his results are essentially quantitatively correct. Indeed, his wave functions are still used today in various applications. For scattering systems of the same complexity, an electron or positron scattering from a hydrogen atom, accurate calculations were presented much later, in 1961, by Schwartz.² Schwartz's results, presented in the form of s -wave phase shifts in the elastic region, have since been numerically refined and extended by Bhatia, Temkin, Drachman, and Eiserike,³ and by Register and Poe,⁴ but are essentially quantitatively correct. For the next most complicated target, helium, accurate s - and p -wave phase shifts for

an incident positron were reported quite recently by Humberston.⁵ Humberston's method, as that of Hylleraas, is not practically extensible to arbitrary targets.

One's goal in devising an extensible method is first to demonstrate that the method reproduces these accurate results for these simple systems. The methods involving a polarization potential are very appealing and have been widely used. The notion that the incident particle distorts the target atom and thereby creates for itself an attractive potential in which the scattering takes place can be traced to Slater⁶ and Bethe.⁷ Of course, for the simplest targets, those considered here, the calculation of the scattering potential is an intermediate step which can be eliminated by treating the projectile-plus-target systems as a simple problem in many-body quantum mechanics, as was done by Schwartz for hydrogen and by Humberston for helium. However, for more complicated targets, the calculation of the polarization potential provides certain advantages not found in more fundamental methods, namely, physical insight into the scattering process, and computational convenience as well, in that the unpolarized target wave functions are now known in the Hartree-Fock approximation for most atoms and many small molecules. It is surprising that this extensible method had not, until now, been given a definitive test for simple targets for which accurate phase

shifts are available. In the present work, we believe we have provided such a test.

Modern approaches to the calculation of polarization potentials are usually based upon perturbative calculations of corrections to the unpolarized Hartree-Fock orbitals of the target; hence the name, the method of polarized orbitals. Very early workers in this area were Bethe⁷ and Ludwig,⁸ although the rebirth of interest in this problem which is still alive today dates from more recent work by Callaway⁹ and Temkin.¹⁰ Both of these latter authors assumed, in their first works, that the target is instantaneously polarized by the projectile regardless of the mass and energy of the latter, an approach called the adiabatic approximation. Other approximations also made in these early works have to do with inexact treatment of exchange (in the case of incident electrons), neglect of the effects of penetration of the incident particle into the interior of the target, incomplete multipole expansions of the perturbed target orbitals and *per force* of the polarization potential, and various numerical approximations made for convenience. Subsequent effort has been directed at studying one or another of these approximations (see Drachman and Temkin¹¹ and Callaway¹² for reviews), although three assumptions seem to be nearly uniformly accepted in work performed so far: the use of Hartree-Fock wave functions for the target (in the case of helium), the use of first-order perturbative methods on that target, and the neglect of virtual excitation of the target for non-s-wave phase shifts.

We accept these three assumptions in the present work, and remove all others essentially completely. The use of a Hartree-Fock wave function for the target is probably a reasonable self-imposed restriction in view of the availability of such wave functions for simple molecular targets. As for a first-order method, we note that all other approximations (nonpenetration, incomplete multipole expansions, etc.) have not (until the present work) been completely removed in a first-order calculation, and should be in order to assess the utility of this restriction before going on to higher orders. Other workers have obtained good agreement with experimental phase shifts,¹³ binding energies,¹⁴ etc., using methods of calculation in which several of these other approximations are made. Under these circumstances, one never knows whether good agreement is a consequence of a good theory or of a fortuitous cancellation of error arising from the several approximations.

Another nearly universal approximation is the use of adiabatically determined polarized orbitals to estimate nonadiabatic contributions to the polarization potential. That is, if nonadiabatic effects

are considered explicitly, the first-order orbitals are first calculated in the adiabatic approximation, and then these are inserted into expressions for nonadiabatic contributions to the polarization potential. This amounts to an inconsistent mixing of orders in a perturbation expansion: the nonadiabatic effects are treated as though they arise from a second-order interaction, but the corresponding Coulomb interactions are not obtained. In Sec. VI we discuss a few of the dozen or more examples of this procedure.

In the present work we calculate *dynamically* polarized orbitals in first order, and furthermore we remove all other numerical approximations having to do with nonpenetration and incomplete multipolar expansions by solving the first-order orbital equations exactly, within the variational framework (except for ignoring a small integral in an intermediate stage of the calculation for the helium target). Our work should thus be regarded as a definitive test of the use of first-order perturbative methods for electron- and positron-atom scattering.

Schrader¹⁵ in 1970 pointed out that calculating accurate positron annihilation parameters depends on calculating an accurate wave function in the region of coalescence of the positron and an electron. He presented a self-consistent-field (SCF) theory for one-positron, many-electron systems for this purpose. His theory, which amounts to a variational (i.e., all orders of perturbation) polarized orbital method, permits one to take all positron-electron correlation effects into account in a fully self-consistent way. However, attempts to solve this self-consistent problem have met with severe computational difficulties.¹⁶ In this paper we simplify those difficulties by expanding Schrader's SCF equations in a perturbation scheme. The zeroth-order equations are for a Hartree-Fock target and a zero-energy, noninteracting incident positron. The first-order equations, which we solve in this work for hydrogen and helium targets, are generalizations of the Callaway-Temkin polarized orbital equations in that ours introduce diabatic corrections in a transparent manner and to a consistent order in the perturbation. Our approach is directly extensible to larger targets, for which it is an extension of the coupled Hartree-Fock perturbation theory.¹⁷ We include all nonadiabatic terms in our theory, both in the first-order equation and in the second-order energy-correction term, and calculate the phase shifts for hydrogen and helium to compare with the existing exact and adiabatic results. From these results we assess the applicability and validity of an effective potential theory by the polarized-orbital method or any first-order perturbative method.

II. DERIVATION OF THE FIRST-ORDER TARGET EQUATIONS

In Schrader's presentation of the theory,¹⁵ the positron is assumed bound to an atom or molecule, the electrons of which constitute a closed shell. The theory is equally applicable to positron elastic scattering, and from targets which differ from a closed shell by one electron, so that an approximate target wave function of the correct symmetry can be written as a single determinant. Positron scattering from hydrogen and helium targets are the simplest such systems.

In Schrader's approach the positron-plus-target trial wave function is written for the two systems considered here (equations in this work are designated *a* and *b* if they are specific for the hydrogen or helium target, respectively),

$$\Psi_H = \phi_p(\vec{r}_p) \phi_e(\vec{r}_1, \vec{r}_p), \quad (1a)$$

$$\Psi_{He} = \phi_p(\vec{r}_p) \phi_e(\vec{r}_1, \vec{r}_p) \phi_e(\vec{r}_2, \vec{r}_p). \quad (1b)$$

Spin functions are factorable and always integrate to unity in the present work, and are therefore suppressed. ϕ are orbitals and the subscripts denote either the positron or an electron, which are numbered. These trial wave functions have a form which is extensible to a complicated target: the product of a positronic function and a Slater determinant of perturbed electronic orbitals. Equation (1a) is not a savings in labor for the hydrogen target for it is potentially exact, but it provides a prototype of the desired form.

The electronic orbitals ϕ_e are determined uniquely by Schrödinger-like equations and the additional constraint

$$\langle \phi_e(\vec{r}_1, \vec{r}_p) | \phi_e(\vec{r}_1, \vec{r}_p) \rangle_1 = 1. \quad (2)$$

Integrals in this work are indicated by angular brackets, and a subscript on the ket denotes the integration variables. In Eq. (2), for example, the integration is over the spatial coordinates of the electron. The integration variables will be indicated when their identity is not clear from the context.

Schrader shows in detail that minimizing the expectation value of the Hamiltonian subject to the constraint (2) leads to the electronic equations

$$\left(-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_p^2 - \frac{1}{r_1} - \frac{1}{r_{1p}} - \epsilon_e(r_p) \right) \phi_e(\vec{r}_1, \vec{r}_p) = 0, \quad (3a)$$

$$\left(-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_p^2 - \frac{2}{r_1} - \frac{1}{r_{1p}} + 2J(\vec{r}_1, \vec{r}_p) - K(\vec{r}_1, \vec{r}_p) - \vec{B}(\vec{r}_1, \vec{r}_p) \cdot \vec{\nabla}_p - \epsilon_e(r_p) \right) \phi_e(\vec{r}_1, \vec{r}_p) = 0, \quad (3b)$$

where

$$\begin{aligned} J(\vec{r}_1, \vec{r}_p) &= \left\langle \phi_e(\vec{r}_2, \vec{r}_p) \left| \frac{1}{r_{12}} \right| \phi_e(\vec{r}_2, \vec{r}_p) \right\rangle_2, \\ K(\vec{r}_1, \vec{r}_p) F(\vec{r}_1, \vec{r}_2) &= \left\langle \phi_e(\vec{r}_2, \vec{r}_p) \left| \frac{1}{r_{12}} \right| F(\vec{r}_2, \vec{r}_1) \right\rangle_2 \phi_e(\vec{r}_1, \vec{r}_p), \\ \vec{B}(\vec{r}_1, \vec{r}_p) \cdot \vec{G}(\vec{r}_1, \vec{r}_2) &= -\langle \phi_e(\vec{r}_2, \vec{r}_p) | \vec{G}(\vec{r}_2, \vec{r}_1) \rangle_2 \cdot \vec{\nabla}_p \phi_e(\vec{r}_1, \vec{r}_p), \end{aligned} \quad (4)$$

and where $\epsilon_e(r_p)$ is a Lagrange multiplier that normalizes $\phi_e(\vec{r}_1, \vec{r}_p)$ identically according to Eq. (2).

The equations obeyed by the positronic scattering functions, ϕ_p in Eqs. (1) are given by Schrader as

$$\left(-\frac{1}{2} \nabla_p^2 + \frac{1}{r_p} + \epsilon_e(r_p) - E \right) \phi_p(\vec{r}_p) = 0, \quad (5a)$$

$$\left(-\frac{1}{2} \nabla_p^2 + \frac{2}{r_p} + 2\epsilon_e(r_p) - V_{ee}(r_p) - E \right) \phi_p(\vec{r}_p) = 0,$$

$$\begin{aligned} V_{ee}(r_p) &= \langle \phi_e(\vec{r}_1, \vec{r}_p) | 2J(\vec{r}_1, \vec{r}_p) \\ &\quad - K(\vec{r}_1, \vec{r}_p) - \vec{B}(\vec{r}_1, \vec{r}_p) \cdot \vec{\nabla}_p | \phi_e(\vec{r}_1, \vec{r}_p) \rangle_1, \end{aligned} \quad (5b)$$

where E is the total energy of the positron plus target. Equations (3) must be solved first for ϕ_e and ϵ_e , and these functions are inserted in Eqs. (5), a simple central-field problem which is then solved for the positron-scattering function. We propose to solve Eqs. (3), the target equations, in first order.

For each zeroth-order target we take a zero-energy positron and an isolated target. Then the zeroth-order equations are

$$\left(-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_p^2 - \frac{1}{r_1} - \epsilon_e^{(0)} \right) \phi_e^{(0)}(r_1) = 0, \quad (6a)$$

$$\left(-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_p^2 - \frac{2}{r_1} + 2J^{(0,0)}(r_1) - K^{(0,0)}(r_1) - \vec{B}^{(0,0)} \cdot \vec{\nabla}_p - \epsilon_e^{(0)} \right) \phi_e^{(0)}(r_1) = 0. \quad (6b)$$

Aside from the positronic differential operators, these equations are simply the Schrödinger equation for the hydrogen atom and the Hartree-Fock equation for helium. The superscripts on J , K , and \vec{B} indicate the order of ϕ_e that appear in Eqs. (4). Equations (6) contain the leading terms in the perturbation expansions

$$\begin{aligned} \phi_e(\vec{r}_1, \vec{r}_p) &= \phi_e^{(0)}(r_1) + \phi_e^{(1)}(\vec{r}_1, \vec{r}_p) + \dots, \\ \epsilon_e(r_p) &= \epsilon_e^{(0)} + \epsilon_e^{(1)}(r_p) + \dots, \end{aligned} \quad (7)$$

where

$$\epsilon_e^{(0)} = -\frac{1}{2}, \quad \phi_e^{(0)}(r_1) = e^{-r_1/\sqrt{\pi}}, \quad (8a)$$

$$\epsilon_e^{(0)} = -0.91796, \quad (8b)$$

and $\phi_e^{(0)}$ for helium is the normalized Hartree-Fock orbital.¹⁸ The first-order equations are now seen to be

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_p^2 - \frac{1}{r_1} + \frac{1}{2}\right)\phi_e^{(1)}(\vec{r}_1, \vec{r}_p) + \left(-\frac{1}{r_{1p}} - \epsilon_e^{(1)}(r_p)\right)\phi_e^{(0)}(r_1) = 0, \quad (9a)$$

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_p^2 - \frac{2}{r_1} + J^{(0,0)}(r_1) - \epsilon_e^{(0)}\right)\phi_e^{(1)}(\vec{r}_1, \vec{r}_p) + \left(-\frac{1}{r_{1p}} + 2J^{(0,1)}(\vec{r}_1, \vec{r}_p) - \epsilon_e^{(1)}(r_p)\right)\phi_e^{(0)}(r_1) = 0. \quad (9b)$$

$\phi_e^{(0)}$ and ϕ_e are each normalized, from which it follows that $\phi_e^{(1)}$ must obey the constraint

$$\langle \phi_e^{(0)}(r_1) | \phi_e^{(1)}(\vec{r}_1, \vec{r}_p) \rangle_1 = 0, \quad (10)$$

where we have assumed $\phi_e^{(1)}$ to be real. The first-order eigenvalues in Eqs. (9) are now seen to be, using Eqs. (6) and (10),

$$\epsilon_e^{(1)}(r_p) = -J^{(0,0)}(r_p), \quad (11a)$$

$$\epsilon_e^{(1)}(r_p) = -J^{(0,0)}(r_p) + 2\langle \phi_e^{(0)}(r_1) | J^{(0,0)}(r_1) | \phi_e^{(1)}(\vec{r}_1, \vec{r}_p) \rangle_1. \quad (11b)$$

It is important to realize the implication of assigning the kinetic energy of the incident particle to the zeroth-order Hamiltonian in Eqs. (9). This procedure, not original with us, gives rise to nonadiabatic contributions to the potential seen by the incident particle.^{19,20} These contributions arise in first-order implicitly [Eqs. (11)] via the effect of the incident Laplacian on the first-order target orbitals. In all previous work known to us (but see Sec. VI), this contribution is lost due to the use of adiabatically determined first-order target orbitals.

III. SOLUTION OF THE FIRST-ORDER TARGET EQUATIONS

We wish to solve Eqs. (9) subject to the constraint (10). Variational functionals which have Eqs. (9) as their Euler-Lagrange equations are

$$Q^{(2)} = \left\langle \phi_e^{(1)} \left| -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_p^2 - \frac{1}{r_1} + \frac{1}{2} \right| \phi_e^{(1)} \right\rangle_{1,p} + 2\left\langle \phi_e^{(1)} \left| -\frac{1}{r_{1p}} \right| \phi_e^{(0)} \right\rangle_{1,p}, \quad (12a)$$

$$Q^{(2)} = \left\langle \phi_e^{(1)} \left| -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_p^2 - \frac{2}{r_1} + J^{(0,0)}(r_1) - \epsilon_e^{(0)} \right| \phi_e^{(1)} \right\rangle_{1,p} + 2\left\langle \phi_e^{(1)} \left| -\frac{1}{r_{1p}} + J^{(0,1)}(\vec{r}_1, \vec{r}_p) \right| \phi_e^{(0)} \right\rangle_{1,p}. \quad (12b)$$

Up to this point we have made no approximations whatever in solving the scattering problem for incident low-energy positrons and Hartree-Fock targets except the use of first-order perturbation theory. Now we introduce minor approximations.

One of them, the use of a finite basis in which to expand $\phi_e^{(1)}$ is unavoidable. The other approximation consists of dropping $\langle \phi_e^{(1)} | J^{(0,1)} | \phi_e^{(0)} \rangle_{1,p}$ from $Q^{(2)}$ for helium. $J^{(0,1)}$ is the potential generated by an electron in a charge distribution which contains a total charge of zero and hence is probably small. If we try to get a rough idea of the magnitude of $J^{(0,1)}$ from the Mulliken approximation,²¹ well known in molecular quantum mechanics, we get zero. In terms of the interparticle coordinate $r_{ij} = |\vec{r}_i - \vec{r}_j|$, the integrand of $J^{(0,1)}$ depends upon r_2 , r_p , r_{2p} , and r_{12} . In the language of molecular quantum mechanics, it is a three-center integral, the centers being the positions of the nucleus, the positron, and the external electron (number 1). Some three-center integrals can be simply evaluated by use of Fourier transforms. By restricting the basis set for our expansion of $\phi_e^{(1)}$, we could have managed to obtain an integral sufficiently simple to use this method. We choose instead to ignore the $J^{(0,1)}$ integral in Eq. (12b) and use an unrestricted basis set for $\phi_e^{(1)}$. General methods for evaluating $J^{(0,1)}$ are available,²² but their use would have multiplied the complexity and cost of our calculation prohibitively. It should be noted that the same troublesome integral appears in the expression for $\epsilon_e^{(1)}$, Eq. (11b); however, it appears in the form $\langle \phi_e^{(0)} | J^{(0,1)} | \phi_e^{(0)} \rangle$, its zeroth-order average, which is easily evaluated by interchanging the order of integration, as indicated. Our second approximation consists, therefore, of calculating the perturbed orbital $\phi_e^{(1)}$, while ignoring $J^{(0,1)}$ in $Q^{(2)}$ but keeping $J^{(0,1)}$ in the first-order energy, $\epsilon_e^{(1)}$, which appears as part of the potential in the scattering equation for the positron [Eq. (5b)]. It turns out that a cancellation of this part of $\epsilon_e^{(1)}$ with a part of $V_{ee}^{(1)}$ takes place, so $J^{(0,1)}$ does not actually appear in the scattering problem, Eq. (5b). This small integral thus influences the scattering problem in a very indirect and probably numerically insignificant way, and omitting it from Eq. (12b) seems like a safe approximation.

A third approximation is implicit in the use of a unique Hartree-Fock target. For p -waves (as well as higher l -waves) a p -target and an s -projectile also contribute to the scattering process.

Now we expand $\phi_e^{(1)}$ as an orthogonalized linear combination of Hylleraas-type basis functions:

$$\phi_e^{(1)}(\vec{r}_1, \vec{r}_p) = \left(1 - |\phi_e^{(0)}\rangle\langle\phi_e^{(0)}|\right) \sum_{i=1}^N C_i X_i(r_1, r_p, r_{1p}), \quad (13)$$

$$X_i(r_1, r_p, r_{1p}) = r_1^{\alpha_i} r_p^{\beta_i} r_{1p}^{\gamma_i} e^{-(\alpha_i r_1 + \beta_i r_p + \gamma_i r_{1p})}.$$

TABLE I. First-order electronic orbital for the hydrogen target [Eq. (31)].

i	C_i	$n_i l_i m_i$	α_i	β_i	γ_i	$Q^{(2)^a}$
1	0.311 602	0 0 0	0.8	-0.184	0.7	-4.831
2	-0.008 866	0 0 2	1.0	0.7	-0.2	-7.573
3	-0.338 374	0 0 0	0.97	0.93	-0.135	-8.021
4	-0.016 916	1 1 0	1.26	-0.37	1.22	-8.355
5	-0.022 140	0 2 0	0.892	0.033	1.032	-8.400
6	0.178 176	0 0 0	1.0	1.75	-0.15	-8.482
7	-0.059 483	1 1 0	1.217	0.94	0.0	-8.536
8	-0.000 283	0 3 1	1.12	0.0	0.8	-8.681
9	-0.001 745	0 3 0	1.14	0.056	0.7	-8.811
10	0.000 155	0 4 0	1.07	-0.065	0.6	-8.985

^a Equation (12a) as N [Eq. (13)] is increased from one to ten.

$Q^{(2)}$ is evaluated in terms of the coefficients C_i by performing the operations indicated in Eqs. (12). Minimizing $Q^{(2)}$ with respect to the C_i leads to a linear algebraic system of equations with the C_i as solutions.

The C_i values obtained for hydrogen and helium are given in Tables I and II. The parameters n , l , m , β , and γ are separately optimized for each basis function. The calculated $Q^{(2)}$ are given as successively larger basis sets are used as a means to assay the convergence of the expansion. Convergence is seen to be good.

A major concern with using Hylleraas-type expansion is in getting the correct long-range behavior in the polarization potential. However, the variational principle together with some basis functions which have a very long extent (the last three in Tables I and II) give $V^{(2)}(r_p)$ the correct behavior for large r_p (~ 10). The functional values of $V^{(2)}(r_p)$ converge nicely as N in Eq. (13) increases. Beyond $r_p = 10$, a stratagem (see below) is used to get the proper behavior.

IV. SOLUTION OF THE SCATTERING EQUATION; THE NONADIABATIC POLARIZATION POTENTIAL

In Eqs. (5) the positron scatters from the nucleus and electrons. The electron-positron effective po-

tential $V(r_p)$ which enters there is

$$V(r_p) = \epsilon_e(r_p), \quad (14a)$$

$$V(r_p) = 2\epsilon_e(r_p) - V_{ee}(r_p), \quad (14b)$$

where V_{ee} is defined in Eq. (5b). We of course want the most accurate potential available to us and that means the highest-order perturbation expansion:

$$V(r_p) = V^{(0)} + V^{(1)}(r_p) + V^{(2)}(r_p). \quad (15)$$

We already have $V(r_p)$ to the first order:

$$V^{(0)} + V^{(1)} = -\frac{1}{2} - J^{(0,0)}(r_p), \quad (16a)$$

$$V^{(0)} + V^{(1)} = -2.86168 - 2J^{(0,0)}(r_p). \quad (16b)$$

The number in Eq. (16b) is Clementi's¹⁸ Hartree-Fock energy for helium. Equations (16) provides only the unperturbed target energy and the static target part of the effective potential V . Second- and higher-order contributions to V constitute what is commonly called the polarization potential. We calculate $V^{(2)}$ from the first-order electronic orbital. The desired expression comes from Eqs. (14) with $V_{ee}^{(2)}$ deducible from Eq. (5b) and $\epsilon_e^{(2)}$ from the second-order electronic equation. This can be derived by extending the expansions in Eqs. (7) and collecting second-order terms in Eqs. (3). The result of these operations is

TABLE II. First-order electronic orbital for the helium target [Eq. (31)].

i	C_i	$n_i l_i m_i$	α_i	β_i	γ_i	$Q^{(2)^a}$
1	0.151 863	0 0 0	1.61	-0.43	0.96	-2.160
2	-0.178 294	0 0 2	1.41	1.37	0.0	-2.41
3	0.451 200	1 1 0	1.34	0.845	1.25	-2.43
4	-4.959 45	0 0 0	1.673	2.50	0.01453	-2.44
5	-0.004 645	0 2 0	6.67	-0.26	0.923	-2.45
6	0.006 060	0 3 0	1.47	0.0	0.7	-2.63
7	0.001 153	0 3 1	4.03	0.0	0.8	-2.641

^a Equation (12b) as N [Eq. (13)] is increased from one to seven.

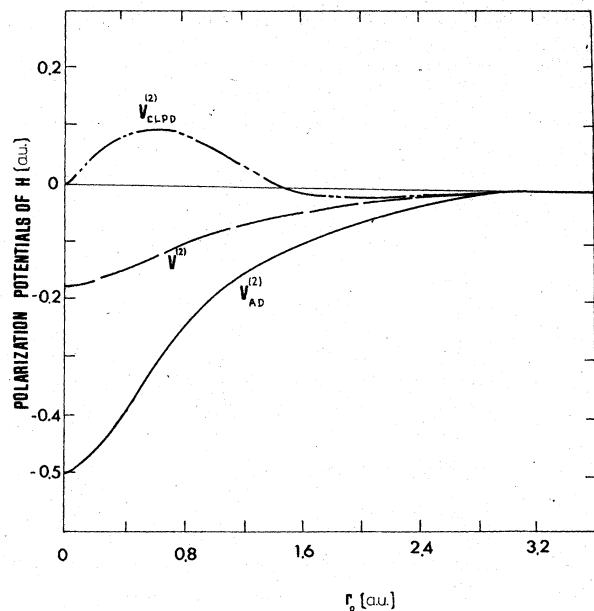


FIG. 1. Polarization potentials for hydrogen. $V^{(2)}$ —nonadiabatic potential, this work [Eq. (17a)]; $V_{AD}^{(2)}$ —adiabatic potential of Dalgarno and Lynn (Ref. 27); $V_{CLPD}^{(2)}$ —nonadiabatic potential given by Callaway, LaBahn, Pu, and Duxler (Ref. 37).

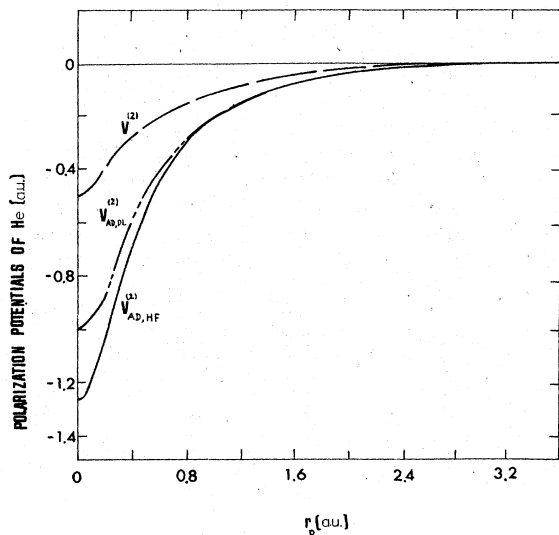


FIG. 2. Polarization potentials for helium. $V^{(2)}$ —nonadiabatic potential, this work [Eq. (17b)]; $V_{AD,DL}^{(2)}$ —adiabatic potential [calculated by the present authors from the work of Dalgarno and Lynn (Ref. 27) with the screened nuclear charge parameter in the orbital taken to be 1.6875]; $V_{AD,HF}^{(2)}$ —adiabatic polarization potential resulting from a Hartree-Fock target (present work). $V^{(2)}$ also uses a Hartree-Fock target (present work).

$$V^{(2)} = \frac{1}{2} \langle \vec{\nabla}_p \phi_e^{(1)} \cdot | \vec{\nabla}_p \phi_e^{(1)} \rangle_1 + \left(\left\langle \phi_e^{(1)} \left| -\frac{1}{2} \nabla_1^2 - \frac{1}{r_1} + \frac{1}{2} \left| \phi_e^{(1)} \right\rangle_1 \right. \right. \\ \left. \left. + 2 \left\langle \phi_e^{(1)} \left| -\frac{1}{r_{1p}} \left| \phi_e^{(0)} \right\rangle_1 \right. \right. \right), \quad (17a)$$

$$V^{(2)} = \langle \vec{\nabla}_p \phi_e^{(1)} \cdot | \vec{\nabla}_p \phi_e^{(1)} \rangle_1 + 2 \left(\left\langle \phi_e^{(1)} \left| -\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} + J^{(0,0)}(r_1) - \epsilon_e^{(0)} \left| \phi_e^{(1)} \right\rangle_1 \right. \right. \\ \left. \left. + 2 \left\langle \phi_e^{(1)} \left| -\frac{1}{r_{1p}} \left| \phi_e^{(0)} \right\rangle_1 \right. \right. \right). \quad (17b)$$

These expressions are the integrands of the variational functionals $Q^{(2)}$, Eqs. (12), and hence can be regarded as possessing a kind of bounded character in the local sense. The “locally” variational form of the polarization potential has not been used before in a calculation, to our knowledge. Such a form, while not quite satisfying all the postulates of Empedocles’s range relaxation theorem²³ and thus not demonstrably rigorously variational point by point, nevertheless has a very desirable characteristic which one associates with pointwise boundedness: as we use progressively more basis functions to improve the accuracy of $\phi_e^{(1)}$, the approach to convergence of $V^{(2)}$ as given by Eq. (17) is much more rapid and more nearly point by point monotonic than that shown by any other form. The nonadiabatic potentials are shown in Figs. 1 and 2 as $V^{(2)}$.

For example, one such alternative form, frequently used in more approximate nonadiabatic treatments, is

$$\frac{1}{4} \nabla_p^2 \langle \phi_e^{(1)}(\vec{r}_1, \vec{r}_p) | \phi_e^{(1)}(\vec{r}_1, \vec{r}_p) \rangle_1 + \left\langle \phi_e^{(0)}(r_1) \left| -\frac{1}{r_{1p}} \left| \phi_e^{(1)}(\vec{r}_1, \vec{r}_p) \right\rangle_1 \right. \right), \quad (18a)$$

$$\frac{1}{2} \nabla_p^2 \langle \phi_e^{(1)}(\vec{r}_1, \vec{r}_p) | \phi_e^{(1)}(\vec{r}_1, \vec{r}_p) \rangle_1 + 2 \left\langle \phi_e^{(0)}(r_1) \left| -\frac{1}{r_{1p}} \left| \phi_e^{(1)}(\vec{r}_1, \vec{r}_p) \right\rangle_1 \right. \right). \quad (18b)$$

The forms (17) and (18) are equivalent if the exact solutions $\phi_e^{(1)}$ to Eqs. (9) are used, but if a finite expansion (13) introduces even the tiniest error in $\phi_e^{(1)}$ at $r_p = 0$, the forms (18) diverge at that point. $V^{(2)}$ given by Eqs. (17) is very much to be preferred over (18) for this reason. This point was noted by Reeh²⁴ and by Eissa and Opik,¹⁹ but our work represents the first use of this expression in a calculation.

The first term in each of the above equations is a dynamic correction term, calculated with the first-order electronic orbital which implicitly con-

tains nonadiabatic effects. Other nonadiabatic theories lead to a dynamic term of this form, but in all previous work known to us, it is calculated approximately by using the adiabatic first order orbital, a procedure which introduces an error. This point is discussed further in Sec. VI. The second terms in (18) are called the "polarization potential" in Bethe's original work.⁷ All polarization potential theories, whether adiabatic or nonadiabatic, give rise to such a term, but only in the present work is it evaluated with a fully nonadiabatic first-order electronic orbital.

The total energy of the target plus positron of Eq. (9) equals

$$E = -\frac{1}{2} + \frac{1}{2}k^2, \quad (19a)$$

$$E = -2.86168 + \frac{1}{2}k^2. \quad (19b)$$

Substituting the above equations and $V^{(0)} + V^{(1)} + V^{(2)}$ as V into Eqs. (5) by use of Eqs. (14), we obtain the scattering equations for the positron with potentials up to second order. We then integrate these equations to a large value of r_p (10a.u.), using the Bulirsch-Stoer numerical-integration method.²⁵ The integrations are carried beyond $r_p = 10$ until the calculated phase shifts stabilize to five significant figures. In the asymptotic region ($r_p \geq 5$), $V^{(2)}$ is taken to be $C_4/r_p^4 + C_6/r_p^6$, where C_4 and C_6 are calculated by fitting $V^{(2)}$ at $r_p \leq 5$. The method reproduces the phase shifts of previous authors when their polarization potentials are used in place of our $V^{(2)}$. The results, tabulated in Tables III and IV and compared with other results in Figs. 3-8, are discussed below.

V. ADIABATIC POLARIZATION POTENTIAL FOR THE HARTREE-FOCK HELIUM ATOM

In the adiabatic approximation, one completely neglects any dynamic effect due to positronic motion. In the first-order equation, the perturbed electronic orbital $\phi_{e,ad}^{(1)}$ depends on the positronic coordinate only parametrically [i.e., $\nabla_p \phi_{e,ad}^{(1)}(\vec{r}_1; \vec{r}_p) = \vec{0}$]. Therefore the first-order-target equations (9) are reduced to

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_1} + \frac{1}{2}\right)\phi_{e,ad}^{(1)}(\vec{r}_1; \vec{r}_p) + \left(-\frac{1}{r_{1p}} - \epsilon_{e,ad}^{(1)}(r_p)\right)\phi_e^{(0)}(r_1) = 0, \quad (20a)$$

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + J^{(0,0)}(r_1) - \epsilon_e^{(0)}\right)\phi_{e,ad}^{(1)}(\vec{r}_1; \vec{r}_p) + \left(-\frac{1}{r_{1p}} - \epsilon_{e,ad}^{(1)}(r_p)\right)\phi_e^{(0)}(r_1) = 0, \quad (20b)$$

where $\phi_{e,ad}^{(1)}$ obeys the same orthogonalization constraint as $\phi_e^{(1)}$, Eq. (10). The equation for hydro-

TABLE III. Phase shifts for hydrogen-target nonadiabatic calculation.^a

k	s wave, η_0	k^2	p wave, η_1	d wave, η_2
0.00	-1.039 ^b	0.00	4.50 ^c	4.50 ^d
0.01	0.0099	0.01	0.0073	0.0013
0.02	0.0188	0.02	0.0131	0.0026
0.03	0.0268	0.03	0.0181	0.0038
0.04	0.0338	0.04	0.0223	0.0050
0.05	0.0400	0.05	0.0261	0.0062
0.1	0.0589	0.1	0.0396	0.0114
0.2	0.0556	0.2	0.0519	0.0198
0.3	0.0235	0.3	0.0548	0.0259
0.4	-0.0200	0.4	0.0531	0.0305
0.5	-0.0667	0.5	0.0489	0.0338
0.6	-0.1125	0.6	0.0433	0.0362
0.7	-0.1554	0.7	0.0370	0.0377
0.8	-0.1943	0.8	0.0303	0.0386
0.9	-0.2289	0.9	0.0235	0.0389
1.0	-0.2591	1.0	0.0168	0.0387

^a k in atomic units of momentum, phase shifts in radians.

^b Scattering length, $\lim_{k \rightarrow 0} (-\eta_0/k)$.

^c Dipole polarizability, $\lim_{k \rightarrow 0} (15\eta_1/\pi k^2)$.

^d Dipole polarizability, $\lim_{k \rightarrow 0} (105\eta_2/\pi k^2)$.

TABLE IV. Phase shifts for helium-target nonadiabatic calculation.^a

k	s wave, η_0	k^2	p wave, η_1	d wave, η_2
0.00	-0.352 ^b	0.00	1.323 ^c	1.323 ^d
0.01	0.0034	0.01	0.0024	0.0004
0.02	0.0065	0.02	0.0046	0.0008
0.03	0.0093	0.03	0.0066	0.0012
0.04	0.0119	0.04	0.0084	0.0016
0.05	0.0141	0.05	0.0101	0.0020
0.1	0.0219	0.1	0.0173	0.0038
0.2	0.0219	0.2	0.0271	0.0074
0.3	0.0072	0.3	0.0330	0.0106
0.4	-0.0166	0.4	0.0364	0.0135
0.5	-0.0458	0.5	0.0379	0.0160
0.6	-0.0777	0.6	0.0382	0.0183
0.7	-0.1107	0.7	0.0375	0.0203
0.8	-0.1436	0.8	0.0360	0.0220
0.9	-0.1755	0.9	0.0341	0.0234
1.0	-0.2062	1.0	0.0317	0.0247

^a k in atomic units of momentum, phase shifts in radians.

^b Scattering length, $\lim_{k \rightarrow 0} (-\eta_0/k)$.

^c Dipole polarizability, $\lim_{k \rightarrow 0} (15\eta_1/\pi k^2)$.

^d Dipole polarizability, $\lim_{k \rightarrow 0} (105\eta_2/\pi k^2)$.

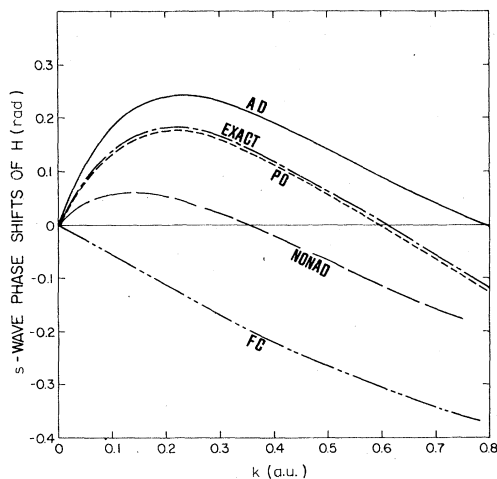


FIG. 3. *s*-wave phase shifts for hydrogen. AD—adiabatic results (Ref. 13); EXACT—essentially exact results (Ref. 3); PO—polarized orbital results (Ref. 13); NONAD—present work; FC—frozen-core (static) approximation.

gen, Eq. (20a), has been solved approximately by Temkin²⁶ and exactly by Dalgarno and Lynn²⁷ in a prolate coordinate system. The exchangeless electronic perturbed equation for electron-helium

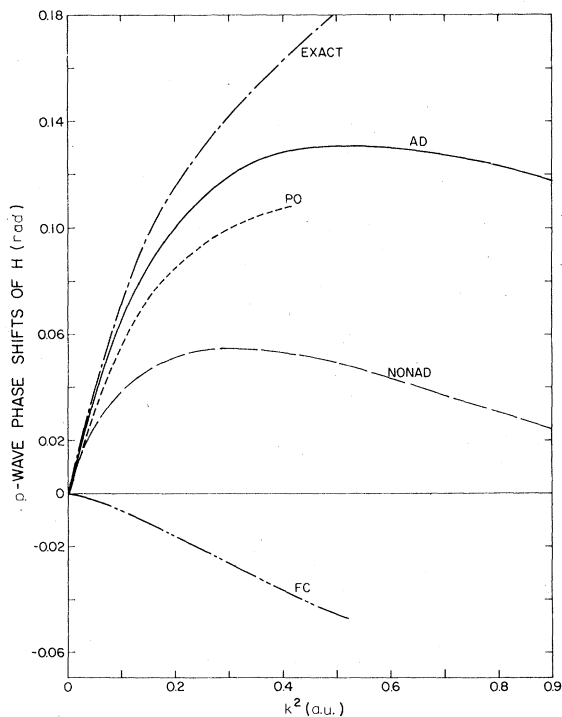


FIG. 4. *p*-wave phase shifts for hydrogen. EXACT—essentially exact results (Ref. 53); AD—adiabatic results (Ref. 13); PO—polarized orbital results (Ref. 13); NONAD—present work; FC=frozen-core (static) approximation.

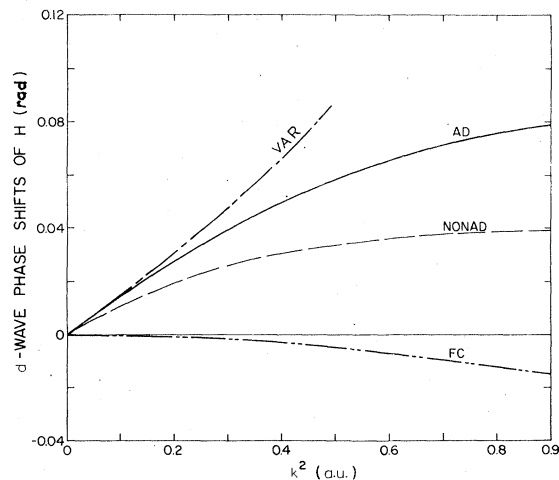


FIG. 5. *d*-wave phase shifts for hydrogen. Same labels as in Fig. 4, except VAR—essentially exact results of Ref. 4.

scattering, Eq. (20b) except for a sign, was solved by LaBahn and Callaway²⁸ by a numerical method in multipole components, but several simplifying approximations were made. McEachran *et al.*²⁹ gave solutions for helium which result from suppressing the monopole part of the perturbation

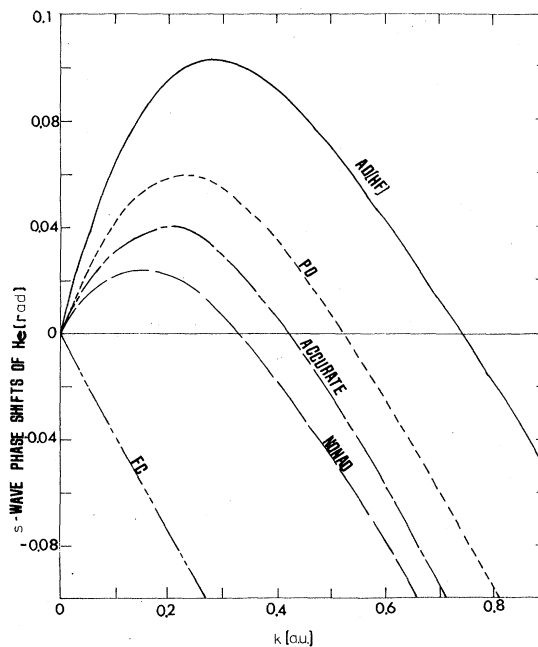


FIG. 6. *s*-wave phase shifts of helium. AD(HF)—adiabatic results (present work) PO—polarized potential results (Ref. 29); ACCURATE—accurate results (Ref. 5); NONAD—present work; FC—frozen-core (static) approximation.

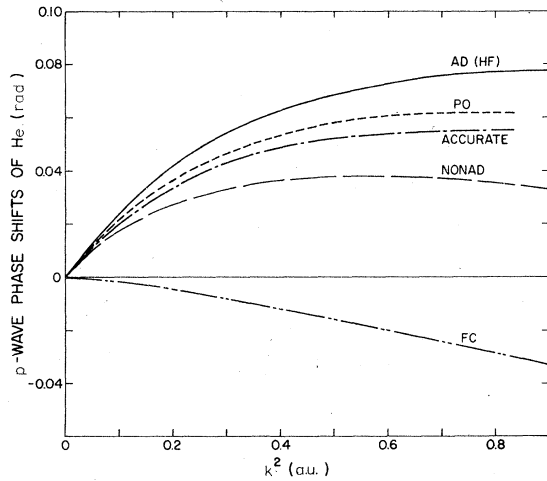


FIG. 7. p -wave phase shifts for helium. Same symbols as Fig. 6.

$-1/r_{1p}$. An accurate variational solution for Eq. (20b) has thus not been given before. It is presented in this section in order to have a comparison with our nonadiabatic results of the previous sections. We now describe our method for solving Eq. (20b).

The variational functional $Q_{ad}^{(2)}$, for Eq. (20b) is

$$Q_{ad}^{(2)}(r_p) = \left\langle \phi_{e,ad}^{(1)} \left| -\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} + J^{(0,0)}(r_1) - \epsilon_e^{(0)} \right| \phi_{e,ad}^{(1)} \right\rangle_1 + 2 \left\langle \phi_{e,ad}^{(1)} \left| -\frac{1}{r_{1p}} \right| \phi_e^{(0)} \right\rangle_1, \quad (21b)$$

where, unlike the nonadiabatic treatment, the integration is only over the electronic space [cf. Eq. (12b)]. We expand $\phi_{e,ad}^{(1)}$ in a basis,

$$\phi_{e,ad}^{(1)} = (1 - |\phi_e^{(0)}\rangle\langle\phi_e^{(0)}|) \sum_{i=1}^{\lambda} C_i(r_p) X_{i,ad}(r_1, r_{1p}), \quad (22)$$

$$X_{i,ad}(r_1, r_{1p}) = r_1^{\alpha_i} r_{1p}^{\beta_i} e^{-(\alpha_i r_1 + \beta_i r_{1p})}.$$

Here the expansion coefficients C_i depend upon r_p

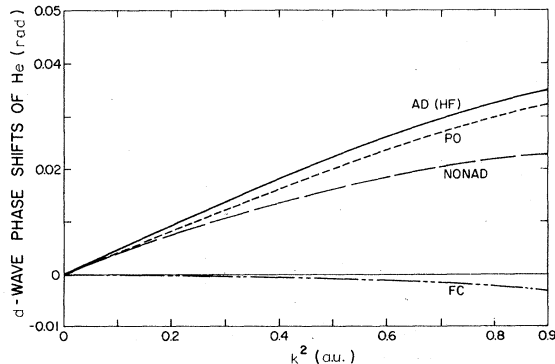


FIG. 8. d -wave phase shifts for helium. Same symbols as Fig. 6.

as indicated; they are not constants as those in the nonadiabatic case. The functional $Q_{ad}^{(2)}(r_p)$ is minimized at each value of r_p to be used in the scattering problem, thus providing the coefficients as functions of r_p . Thus $\phi_{e,ad}^{(1)}$ is endowed with the correct r_p dependence for both long and short range as an automatic consequence of minimizing $Q_{ad}^{(2)}(r_p)$ for each value of r_p separately, and all questions pertaining to those problems for the nonadiabatic $\phi_e^{(1)}$ are irrelevant here.

The second-order contribution to the scattering potential for the positron has the same form as the polarization potential part in the nonadiabatic case,

$$V_{ad}^{(2)} = 2 \langle \phi_{e,ad}^{(1)} | -\frac{1}{r_{1p}} | \phi_e^{(0)} \rangle_1, \quad (23b)$$

but $\phi_{e,ad}^{(1)}$ above is the adiabatically perturbed orbital, quite different from nonadiabatically perturbed orbital calculated in the previous sections (see Sec. VI). As a consequence of minimizing $Q_{ad}^{(2)}$, there is no distinction here analogous to that between the variational and nonvariational forms of $V^{(2)}$ [Eqs. (19) and (18)].

In order to assure the accuracy of the basis set employed, we first solve Eq. (20a) for the perturbed hydrogenic electronic orbital by the same method, reproducing the Dalgarno-Lynn potential²⁷ in the range of interest to about six significant figures. Then we employ the same basis functions with reoptimized exponential parameters to the Hartree-Fock helium orbital. We find that the expansion for $\phi_{e,ad}^{(1)}$ converges more rapidly than in the nonadiabatic case, and the exponential parameters do not vary much for different values of r_p . Of course the coefficients C_i vary for different r_p . We use 18 basis functions for the range of r_p from the origin to 10 a.u., and obtain the adiabatic polarization potential to five significant figures. The adiabatic polarization potential is exhibited in Fig. 2.

The solution of the positronic scattering equation and the derivation of the s -, p -, and d -wave phase shifts proceeds as before. They are given in Figs. 6–8 with other results. The scattering length obtained is -0.807 , and the dipole polarizability from the p - and d -wave results is 1.323 which agrees with the perturbed Hartree-Fock result.³⁰

VI. DISCUSSION

The calculation for the adiabatic case is much simpler than for the nonadiabatic. Unfortunately, when one applies the method used for the former problem to the latter, one arrives at a set of coupled differential equations which have proven so far to be intractable. The equations have the coefficients c_i as their solutions. The c_i are known

asymptotically, but integration inwards from the asymptotic region has proven to be unfruitful due to round-off losses.¹⁶

A third-order contribution to the adiabatic polarization potential,

$$V_{\text{ad}}^{(3)} = \epsilon_{e,\text{ad}}^{(3)} = \langle \phi_{e,\text{ad}}^{(1)} | -\frac{1}{r_{1p}} | \phi_{e,\text{ad}}^{(1)} \rangle_1 - \epsilon_{e,\text{ad}}^{(1)} \langle \phi_{e,\text{ad}}^{(1)} | \phi_{e,\text{ad}}^{(1)} \rangle_1, \quad (24a)$$

$$V_{\text{ad}}^{(3)} = 2\epsilon_{e,\text{ad}}^{(3)} + V_{ee}^{(3)} \\ = 2 \left[\langle \phi_{e,\text{ad}}^{(1)} | -\frac{1}{r_{1e}} | \phi_{e,\text{ad}}^{(1)} \rangle_1 - \epsilon_{e,\text{ad}}^{(1)} \langle \phi_{e,\text{ad}}^{(1)} | \phi_{e,\text{ad}}^{(1)} \rangle_1 \right], \quad (24b)$$

is available from a first-order calculation of the electronic orbital, in accordance with the celebrated $2n+1$ rule,³¹ although no authors except Drachman⁵⁰ have used it in a calculation to our knowledge. The corresponding expression for the nonadiabatic case is

$$V^{(3)} = \frac{1}{2} \nabla_p^2 \langle \phi_e^{(1)} | \phi_e^{(2)} \rangle_1 + \langle \phi_e^{(1)} | -\frac{1}{r_{1p}} - \epsilon_e^{(1)} | \phi_e^{(1)} \rangle_1, \quad (25a)$$

$$V^{(3)} = \nabla_p^2 \langle \phi_e^{(1)} | \phi_e^{(2)} \rangle_1 + 2 \langle \phi_e^{(1)} | -\frac{1}{r_{1p}} - \epsilon_e^{(1)} | \phi_e^{(1)} \rangle_1; \quad (25b)$$

i.e., the unknown second-order nonadiabatic orbital $\phi_e^{(2)}$ cannot be eliminated owing to the nonhermiticity in electronic space of the generalized Hartree-Fock-type operators in Eqs. (3). $V^{(3)}$ is therefore not available in a first-order nonadiabatic calculation; in general, $\phi_e^{(n)}$ yields at best $V^{(n+1)}$ in the nonadiabatic case. This nonhermiticity seems to be very widespread in treatments of diabatic effects^{6,32} and was first commented upon in electron-positron-atom scattering theory by Mittleman.³³

The adiabatic polarization potential for hydrogen²⁷ is known to be much too attractive and an *ad hoc* reduction of this potential has been shown to give improved phase shifts.^{13,29} In the case of the helium, the adiabatic polarization potential calculated here for an accurate Hartree-Fock target is even more attractive than that of the less realistic single-zeta orbital results.²⁷ As a result the s-wave phase shifts for these two adiabatic potentials are each higher than the accurate phase shifts.

In the past, most authors attempted to reduce this excessively attractive potential using semiempirical arguments¹³ or by developing an approximate nonadiabatic correction.^{19,20,33,38} All of these attempts to moderate the excess of the adiabatic potential are based upon the first-order adiabatically perturbed orbital. In the present work

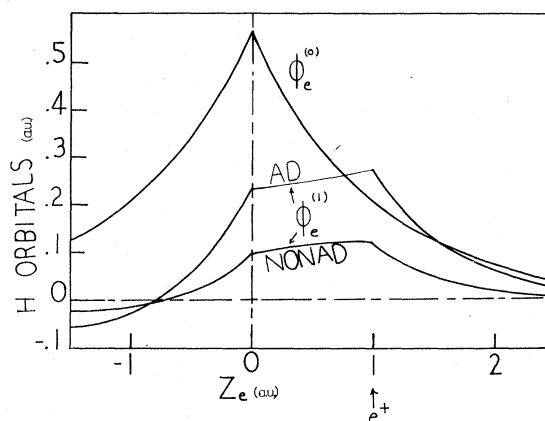


FIG. 9. Zeroth- and first-order electronic orbitals for hydrogen. Z_e is the z coordinate of the electron measured from the nucleus. The positron is on the z axis at a distance of 1 a.u. from the nucleus. The values of orbitals are those along the nuclear-positronic axis (i.e., the z axis).

we use quite a different method in that we solve directly, without significant approximation, the first-order problem with nonadiabatic effects. The nonadiabatic operator, $-\frac{1}{2}\nabla_p^2$, which appears in the zeroth-order Hamiltonian [Eqs. (6)], as well as in the second-order energy correction, has never been dealt with before in this direct fashion except in Taylor's application of the RPA method³⁹⁻⁴¹ and in the nonextensible methods of Schwartz,² of Humberston,⁵ and of Hunter and Kuriyan.⁴² By including the nonadiabatic operator in this way, we find that the first-order orbital is very much different from the adiabatic orbital, especially for the short range, as is seen in Figs. 9 and 10. The

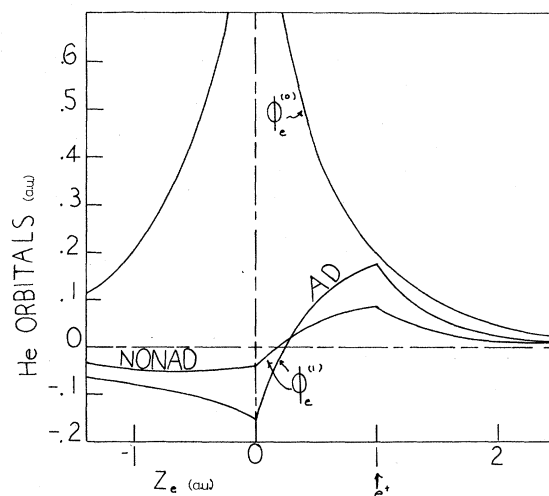


FIG. 10. Zeroth (Hartree-Fock) and first-order electronic orbitals for helium. See the caption of Fig. 9 for an explanation. Figures 9 and 10 are drawn to the same scale.

quantity $\langle Q_{ad}^{(1)} \rangle_p$ is calculated by numerically integrating the Dalgarno-Lynn adiabatic hydrogen potential over \vec{r}_p . The result, -17.5 a.u., is about twice the value for the corresponding quantity involving the nonadiabatic potential for hydrogen (Table I), -8.985 a.u. Thus nonadiabatic effects reduce the first-order polarization potential by about one half in some average sense.

Although the adiabatic approximation has been widely used in scattering and bound-state calculations, one should be aware of the very large approximation embedded in such a procedure. Nonadiabatic effects influence the polarization potential not only in the short-range part but they also spread out to a large range. The nonadiabatic effects are not simply additive, but rather they influence the polarization potential in a complicated way, as can be seen by comparing $V_{ad}^{(2)}$ and $V^{(2)}$ (Figs. 1 and 2).

The widespread practice^{19,28,34,35,37-39,43-47} of calculating the nonadiabatic potential $V^{(2)}$ with the adiabatically perturbed orbital $\phi_{e,ad}^{(1)}$ substituted for $\phi_e^{(1)}$ in Eqs. (17) is not to be recommended either; for example, it is found that the polarization potential calculated in this way for hydrogen is zero at the origin. This result is an artifact resulting from the use of the adiabatic orbital in the nonadiabatic expression. $V_{CLPD}^{(2)}$ in Fig. 1 was given some time ago by Callaway, LaBahn, Pu, and Duxler³⁷ as the nonadiabatic polarization potential for an exchangeless electron (and hence also a positron) scattering off hydrogen. These authors made a number of approximations in calculating their potential, the main of which is, in our opinion, the substitution of $\phi_{e,ad}^{(1)}$ for $\phi_e^{(1)}$ in their expression for the polarization potential. When this and other approximations are removed, one obtains $V^{(2)}$ in Fig. 1. $V_{CLPD}^{(2)}$ and $V^{(2)}$ differ qualitatively, which suggests the approximation is poor.

Our first-order nonadiabatic phase shifts for hydrogen are very inaccurate; they lie midway between adiabatic and frozen-core results. Our results are a little more accurate for helium than

for hydrogen, as we can see for Figs. 3-8. This reveals to us that a first-order approximation can get only about half of the polarization effect into account. Second-order contributions to the perturbed orbital are also significant and must be calculated in order to obtain acceptable accuracy in the phase shifts. The need for higher orders is shown also in Figs. 9 and 10, where it is seen that $\phi_e^{(1)}$ is not small compared to $\phi_e^{(0)}$. Thus, the principal conclusion to be drawn from this work is negative in character, although still useful: first-order approaches to positron- (and electron-) atom scattering are inadequate. This conclusion has been reached by others on different grounds.⁴⁷

Various approximate improvements can be (and have been) devised for the first-order calculation,^{14,48-52} but the failure of our essentially exact calculation shows that such procedures lack rigor. Nevertheless, our approach has a unique combination of virtues; it is extensible to more complicated targets and it includes nonadiabatic effects in a realistic and orderly manner. It is also extensible to higher orders, as it must in order to obtain phase shifts of satisfactory accuracy. Finally, we note that our approach is applicable to electron-atom scattering, although in such systems allowance must be made for exchange.

ACKNOWLEDGMENTS

The authors are grateful to the NSF and to the Marquette University Committee on Research for support of this work; acknowledgment is also made to the donors of the Petroleum Research Fund administered by the American Chemical Society for support. Part of this work was performed at the University of Nottingham with support from the Science Research Council (U.K.), and at Virginia Polytechnic Institute and State University. We are grateful to Professor G. G. Hall and to Professor H. J. Ache for making this support available.

*Present address: Chemistry Dept., Univ. of British Columbia, Vancouver, B. C. V6T 1W5, Canada.

¹E. Hylleraas, *Z. Phys.* **54**, 347 (1929).

²C. Schwartz, *Phys. Rev.* **124**, 1468 (1961).

³A. K. Bhatia, A. Temkin, R. J. Drachman, and H. Eiserike, *Phys. Rev. A* **3**, 1328 (1971).

⁴D. Register and R. T. Poe, *Phys. Lett.* **51A**, 431 (1975).

⁵J. W. Humberston, *J. Phys. B* **6**, L305 (1973); R. I. Campeanu and J. W. Humberston, *ibid.* **8**, L244 (1975).

⁶J. C. Slater, *Proc. Natl. Acad. Sci. (U.S.)* **13**, 423 (1927).

⁷H. A. Bethe, *Handbuch der Physik*, 24/1 (Springer-Ver-

lag, Berlin, 1933), pp. 324-349.

⁸G. Ludwig, *Helv. Phys. Acta.* **1**, 273 (1934).

⁹J. Callaway, *Phys. Rev.* **106**, 868 (1957).

¹⁰A. Temkin, *Phys. Rev.* **107**, 1004 (1957); **116**, 358 (1959); A. Temkin and J. C. Lamkin, *ibid.* **121**, 788 (1961).

¹¹R. J. Drachman and A. Temkin, *Case Studies in Atomic Collision Physics II*, edited by E. W. McDaniel and M. R. C. McDowell (North-Holland, Amsterdam, 1973), p. 399.

¹²J. Callaway, *Comput. Phys. Commun.* **6**, 265 (1973).

¹³R. J. Drachman, *Phys. Rev.* **138**, A1582 (1965).

- ¹⁴R. S. Oberoi and J. Callaway, *Phys. Rev. A* **1**, 45 (1970).
- ¹⁵D. M. Schrader, *Phys. Rev.* **A1**, 1070 (1970).
- ¹⁶D. M. Schrader and J. C. Simpson (unpublished).
- ¹⁷A. Dalgarno, *Adv. Phys.* **11**, 281 (1962).
- ¹⁸E.g., E. Clementi, *IBM J. Res. Dev.* **9**, 2 (1965).
- ¹⁹H. Eissa, U. Opik, *Proc. Phys. Soc. Lond.* **92**, 556 (1967).
- ²⁰S. P. Khare and P. Shobha, *J. Phys. B* **4**, 208 (1971).
- ²¹R. S. Mulliken, *J. Chim. Phys.* **46**, 675 (1949).
- ²²E.g., F. E. Harris and H. H. Michels, *Adv. Chem. Phys.* **13**, 205 (1967).
- ²³P. Empedocles, *Theoret. Chim. Acta* **13**, 139 (1969).
- ²⁴H. Reeh, *Z. Naturforsch.* **15A**, 377 (1960).
- ²⁵R. Bulirsch and J. Stoer, *Numer. Math.* **8**, 1 (1966).
- ²⁶A. Temkin, *Phys. Rev.* **116**, 358 (1959).
- ²⁷A. Dalgarno and N. Lynn, *Proc. Phys. Soc. Lond. A* **70**, 223 (1957).
- ²⁸R. W. LaBahn and J. Callaway, *Phys. Rev.* **147**, 28 (1966).
- ²⁹R. P. McEachran, D. L. Morgan, A. G. Ryman, and A. D. Stauffer, *J. Phys. B* **10**, 663 (1977).
- ³⁰R. R. Teachout and R. T. Pack, *At. Data* **3**, 195 (1971).
- ³¹A. Dalgarno and A. L. Stewart, *Proc. R. Soc. Lond. A* **238**, 269 (1956).
- ³²For example, F. T. Smith, *Phys. Rev.* **179**, 111 (1969); V. Sidis and H. Lefebvre-Brion, *J. Phys. B* **4**, 1040 (1971); S. A. Evans, J. S. Cohen, and N. F. Lane, *Phys. Rev. A* **4**, 2235 (1971).
- ³³M. Mittleman, *Ann. Phys. (N.Y.)* **14**, 94 (1961).
- ³⁴A. Dalgarno, G. W. F. Drake, and G. A. Victor, *Phys. Rev.* **176**, 194 (1968).
- ³⁵C. J. Kleinman, Y. Hahn, and L. Spruch, *Phys. Rev.* **165**, 53 (1968).
- ³⁶A. V. Shtoff, *Vest. Len. Univ., Fiz.-Khim.* **10**, 22 (1968).
- ³⁷J. Callaway, R. W. LaBahn, R. T. Pu, W. M. Duxler, *Phys. Rev.* **168**, 12 (1968).
- ³⁸A. V. Shtoff, *Vest. Len. Univ., Fiz.-Khim.* **22**, 36 (1969).
- ³⁹B. S. Yarlagadda, G. Csanak, H. S. Taylor, B. Schneider, and R. Yaris, *Phys. Rev. A* **7**, 146 (1973).
- ⁴⁰G. Csanak and H. S. Taylor, *Phys. Rev. A* **6**, 1843 (1972).
- ⁴¹M. Ya. Amusia, N. A. Cherepkov, L. V. Chernysheva, and S. G. Shapiro, *J. Phys. B* **9**, L531 (1976).
- ⁴²G. Hunter, M. Kuriyan, *Proc. R. Soc. Lond. A* **341**, 491 (1975).
- ⁴³W. R. Garrett, *Phys. Rev.* **178**, 210 (1969).
- ⁴⁴R. H. Young, W. J. Deal, *Int. J. Quantum Chem.* **9**, 835 (1975).
- ⁴⁵T. K. Rebane and E. P. Smirnov, *Opt. Spektrosk.* **34**, 1037 (1973) [*Opt. Spectrosc.* **34**, 601 (1973)].
- ⁴⁶B. L. Jhanwar, S. P. Khare, and P. Shobha, *J. Phys. B* **8**, 1228 (1975).
- ⁴⁷I. H. Sloan, *Proc. R. Soc. Lond. A* **281**, 151 (1964).
- ⁴⁸R. J. Drachman, *Phys. Rev.* **144**, 25 (1966).
- ⁴⁹N. R. Kestner, J. Jortner, M. H. Cohen, and S. A. Rice, *Phys. Rev.* **140**, A56 (1965).
- ⁵⁰R. J. Drachman, *Phys. Rev.* **173**, 190 (1968).
- ⁵¹T. C. Caves and A. Dalgarno, *J. Quant. Spectrosc. Radiat. Transfer* **12**, 1539 (1972).
- ⁵²A. Dalgarno, C. Bottcher, and G. A. Victor, *Chem. Phys. Lett.* **7**, 265 (1970).
- ⁵³A. K. Bhatia, A. Temkin, H. Eiserike, *Phys. Rev.* **9**, 219 (1974).