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Exchange perturbation theory for electron scattering. Elastic scattering from hydrogen atoms

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We present a new perturbation treatment of electron scattering. It is based on determining a primitive wave function which is nonsymmetric with respect to electron exchange. The theory is developed specifically for elastic scattering from atomic hydrogen but appears generalizable to many-electron atoms and to inelastic processes as well. From the first-order wave function, which can be made square-integrable, one obtains the phase shifts through third order. Calculations with a crude spherical-well initial approximation are carried out for illustrative purposes.

I. INTRODUCTION

A number of different approaches to the electron-scattering problem are currently available. They include algebraic variation, close-coupling, channel radius, square-integrable basis functions, perturbation theory, etc. Algebraic variation methods were thoroughly reviewed by Truhlar *et al.*[1] in 1974. In this review close-coupling is considered as a separate technique since the coupled channel integro-differential equations are usually solved by numerical integration rather than basis set expansion. A detailed description of the numerical methods employed has been given by Burke and Seaton.[2]

There is one further algebraic variation method that has become prominent more recently.[3] It is a procedure based on Schwinger's[4] variational principle. When put in algebraic form this procedure requires a relatively small expansion basis although a price must be paid in terms of more difficult integral evaluation. The same trade-off of advantages is associated with channel radius methods as compared to conventional algebraic variation. Of the former, the most popular is the R-matrix[5] technique which has been reviewed by Burke and Robb.[6]

Because of the simplification in computing integrals, a variety of procedures which utilize only square-integrable basis functions (over all space) have been developed. Among these are the Fredholm determinant method of Reinhardt and coworkers,[7] a truncated potential technique due to Heller and Yamani,[8] Stieltjes-Tchebycheff moment theory,[9] and the method of complex rotated coordinates.[10]

Perturbation theory methods are the oldest and, along with close-coupling, the most commonly used. This category contains, among others, the distorted-wave Born approximation,[11] the polarized-orbital[12] technique, and perturbation expansion of the Green's function.[13] In recent years more attention has been devoted towards the development of variational approaches, particularly those related to bound-state procedures. However, it is now just being recognized that for bound-state calculations, perturbation theory can be an attractive alternative. Some of its potential advantages[14] include size consistency, efficiencies resulting from diagrammatic techniques, application of coupled-cluster approximations, simple interpretation in terms of electron pairs and, in conjunction with the valence-bond model,[15] reduced computation times. Our goal, then, is to reformulate the electron scattering problem in a way that utilizes these features.

The particular treatment developed here is based on a form of exchange perturbation theory.[16] The latter is, perhaps, best known as a method for calculating long- and intermediate-range intermolecular interaction energies. However, it is not limited to such applications. A general treatment, valid at all internuclear separations was presented[17] some time ago. More recently a valence-bond perturbation theory[15] which utilizes the same general formalism has been developed.

Valence-bond perturbation theory is so named because the zeroth-order wave function is given by the (self-consistent) valence-bond orbital model.[18] In this model each of the orbitals is an eigenfunction of a different one-electron Hamiltonian. The exchange perturbation technique is introduced as a way of dealing with such an initial approximation. Since a like circumstance occurs in scattering, one is led to the same line of attack.

Of course, the scattering wave functions are not square-integrable and, as a result, the theory must be modified. However, there is an exact correspondence between the two problems provided the phase shift in (elastic) scattering is regarded as the analog of the bound-state energy. In either event the exact wave function may be obtained from from a nonsymmetric primitive function ϕ by applying a suitable electron exchange symmetry projector. The primitive function is not unique but can be made so by requiring its deviation from the initial approximation to be minimal.[19]

Although the functional $\tilde{J}=\langle\tilde{\Psi}\,|\,(H-E)\Psi\rangle$ will vanish if $\tilde{\Psi}$ is exact, it will not do so for an arbitrary approximation such as the perturbed wave function. However, one can always vary the phase shift to satisfy the above requirement. In the linear approximation the change in the phase shift is simply proportional to $\tilde{J}$. Thus, by adding successively higher-order perturbation corrections to $\tilde{\Psi}$ one obtains successively higher-order corrections to the phase shift. A comparison of our expressions with those of potential scattering shows that the wave function through order n gives the perturbed phase shifts through order $2n+1$.

The first-order phase shift, in particular, vanishes if the initial approximation is chosen so that $\tilde{J}=0$. Such is the case when the Hulthén variational method[20] is used to determine the zeroth-order parameters. This choice has the virtue of making the first-order perturbed wave function square integrable.

Our theoretical treatment is described in Sec. II. Then, in Sec. III we illustrate the procedure in detail by carrying out a calculation with atomic hydrogen as the target and a crude spherical-well initial approximation for the scattering potential.

II. THEORY

In this Section we develop an exchange perturbation theory for elastic scattering of electrons by atomic hydrogen. Although some aspects of the treatment are peculiar to this particular problem, there are no obvious difficulties that would prevent the extension to many-electron atoms and to inelastic scattering as well.

We begin with the partial-wave expansion of the exact wave function and then develop the perturbation method for each partial wave. The Hamiltonian for the two-electron system H + e is (in a.u.)

$$H=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-r_1^{-1}-r_2^{-1}+r_{12}^{-1}\,. \tag{1}$$

In order to determine the scattering amplitude, one must solve the Schrödinger equation

$$(H-E)\Psi=0 \tag{2}$$

in which

$$E=\tfrac{1}{2}k^2+E_{1s} \tag{3}$$

is the sum of the energies of the incident electron ($\frac{1}{2}k^2$) and the ground-state hydrogen atom ($E_{1s}=-\frac{1}{2}$).

For two electrons the spin dependence in Ψ will factor, leaving a pure spatial wave function that is either symmetric (singlet) or antisymmetric (triplet) with respect to electron exchange. Henceforth, we use Ψ to represent just the spatial part of the wave function. In the asymptotic limit as r_1 or r_2 approaches infinity, Ψ separates into the product of a free-electron wave function F times a $1s$ orbital for the second electron. Thus,

$$\lim_{r_1\to\infty}\Psi(\vec{r}_1,\vec{r}_2)=F(\vec{r}_1)u_{1s}(r_2) \tag{4a}$$

and

$$\lim_{r_2\to\infty}\Psi(\vec{r}_1,\vec{r}_2)=\pm F(\vec{r}_2)u_{1s}(r_1)\,, \tag{4b}$$

where (+) refers to the singlet state and (−) to the triplet. If z is the direction of the incident electron, then

$$F(\vec{r})=e^{ikz}+f(\theta)r^{-1}e^{ikr}\,, \tag{5}$$

with $f(\theta)$ being equal to the scattering amplitude. Due to the cylindrical symmetry f depends only on the polar angle θ.

The scattering amplitude is related to the differential cross section σ by

$$\sigma(\theta)=|f(\theta)|^2\,. \tag{6}$$

In the expression for $F(\vec{r})$ both e^{ikz} and $f(\theta)$ may be expanded as a sum over the Legendre polynomials $P_l(\cos\theta)$. By combining terms in the usual fashion one finds that

$$F(\vec{r})=(kr)^{-1}\sum_{l=0}^{\infty}(2l+1)i^l e^{i\eta_l}\times\sin(kr-\tfrac{1}{2}l\pi+\eta_l)P_l(\cos\theta)\,, \tag{7}$$

and

$$f(\theta)=k^{-1}\sum_{l=0}^{\infty}(2l+1)e^{i\eta_l}\sin\eta_l P_l(\cos\theta)\,. \tag{8}$$

Since H commutes with L^2 the complete wave function Ψ can also be written as the partial-wave expansion

$$\Psi(\vec{r}_1,\vec{r}_2)=2\sum_{l=0}^{\infty}(2l+1)i^l e^{i\eta_l}\psi_l(\vec{r}_1,\vec{r}_2)\,. \tag{9}$$

Equation (9) constitutes a definition of the lth partial wave $\psi_l(\vec{r}_1,\vec{r}_2)$ with ψ_l an eigenfunction of L^2. The asymptotic behavior of ψ_l is determined by Eqs. (4), (7), and (9), which give

$$\lim_{r_1\to\infty}\psi_l(\vec{r}_1,\vec{r}_2)=(2kr_1)^{-1}\sin(kr_1-\tfrac{1}{2}l\pi+\eta_l)\times P_l(\cos\theta_1)u_{1s}(\vec{r}_2) \tag{10a}$$

and

$$\lim_{r_2\to\infty} \psi_l(\vec{r}_1,\vec{r}_2) = \pm(2kr_2)^{-1}\sin(kr_2 - \tfrac{1}{2}l\pi + \eta_l) \times P_l(\cos\theta_2) u_{1s}(\vec{r}_1) \,. \tag{10b}$$

As an approximation to ψ_l one may utilize, for example, the static (one-state) exchange function

$$\psi_l \approx \tfrac{1}{2}[G_l(1)u_{1s}(2) \pm u_{1s}(1)G_l(2)] \,, \tag{11}$$

with G_l constrained so as to obey the boundary conditions (10). By multiplying ψ_l on the left by $u_{1s}(2)(H-E)$ and integrating over the coordinates of electron 2, an integro-differential equation for G_l is obtained. This equation may then be solved iteratively using either numerical or basis set expansion techniques. Obviously, other choices for G_l could also be used as the initial approximation.

In order to achieve more than semiquantitative accuracy, however, one must go beyond the static-exchange approximation. For reasons mentioned in the Introduction, we wish to proceed by means of perturbation theory. In doing so, one important aspect that must be taken into account from the beginning is the fact that G_l and the 1s orbital will, normally, be eigenfunctions of two different one-electron Hamiltonians. Consequently, the zeroth-order Hamiltonian for the symmetrized wave function cannot be written as a sum of one-electron terms, nor is it expressible in any obvious local form. By using exchange perturbation theory this difficulty is easily circumvented.

In exchange perturbation theory[16] the exact symmetrized eigenfunction ${}^\nu\psi_l$ is generated from a nonsymmetric primitive function ϕ_l by applying a suitable exchange projection operator ${}^\nu A$; i.e.,

$${}^\nu\psi_l \propto {}^\nu A_l \,. \tag{12}$$

For two identical particles (electrons) there are two such projection operators—a singlet and a triplet given by, respectively,

$${}^S A = \tfrac{1}{2}(1+P_{12}); \; {}^T A = \tfrac{1}{2}(1-P_{12}) \,. \tag{13}$$

These operators are Hermitian and have the properties

$${}^\mu A\, {}^\nu A = \delta_{\mu\nu} \quad (\mu,\nu = S, A) \tag{14a}$$

and

$$\sum_{\mu=S,T} {}^\mu A = 1 \,. \tag{14b}$$

If the zeroth-order $\phi_l (= \phi_l^0)$ is taken to be $G_l(1)u_{1s}(2)$, then the corresponding approximation to ${}^\nu\psi_l$ will be the static-exchange function of Eq. (11). Note that Eqs. (9) and (10) refer to the symmetrized wave functions; the left-hand superscript is understood in these equations but will be displayed explicitly from now on.

Consider the primitive function $\phi_l(\nu)$ which yields the solution of symmetry ν ($\nu = S$ or T). The exact partial wave of that symmetry may be written as

$${}^\nu\psi_l = [a_l(\nu)]^{-1}\, {}^\nu A \phi_l(\nu) \,, \tag{15}$$

where $a_l(\nu)$ is a proportionality constant. Since $\phi_l(\nu)$ is otherwise unrestricted,

$$\phi_l(\nu) = a_l(\nu)\, {}^\nu\psi_l + (1 - {}^\nu A)\chi_l(\nu) \,, \tag{16}$$

where $\chi_l(\nu)$ is a completely arbitrary function. The coefficient $a_l(\nu)$ is also arbitrary; it determines the relative normalization of ϕ_l and ${}^\nu\psi_l$.

Some external criterion is necessary in order to specify $a_l(\nu)$ and $(1 - {}^\nu A)\chi_l(\nu)$. Chipman has suggested a "maximum localization" condition[19] according to which the spatial deviation between ϕ_l and ϕ_l^0 is minimized. This choice should lead to a rapidly convergent perturbation series because it makes the zeroth-order primitive function as close as possible to the exact one. For the $(1 - {}^\nu A)$ projection the deviation can be made to vanish by requiring[21]

$$(1 - {}^\nu A)\chi_l(\nu) = (1 - {}^\nu A)\phi_l^0(\nu) \,. \tag{17}$$

This leaves just the coefficient $a_l(\nu)$ to be determined. Again, in order to make ϕ_l and ϕ_l^0 as similar as possible, we insist that the perturbed primitive function have the same asymptotic normalization as ϕ_l^0. In Sec. III the asymptotic boundary conditions for ϕ_l^0 are given as

$$\lim_{r_1\to\infty} \phi_l^0 = \sin(kr_1 - \tfrac{1}{2}l\pi + \eta_l^0) \times (kr_1)^{-1} P_l(\cos\theta_1) u_{1s}(r_2) \tag{18a}$$

and

$$\lim_{r_2\to\infty} \phi_l^0 = 0 \,. \tag{18b}$$

Hence, the limiting form of ϕ_l in the direct channel ($r_1 \sim \infty$) is taken to be

$$\lim_{r_1\to\infty} \phi_l = \sin(kr_1 - \tfrac{1}{2}l\pi + \eta_l) \times (kr_1)^{-1} P_l(\cos\theta_1) u_{1s}(r_2) \,. \tag{19}$$

It is important to realize here that η_l (the phase shift in the direct channel) is not necessarily equal to the symmetrized phase shift ${}^\nu\eta_l$ except in zeroth order. They would be the same if ϕ_l were to vanish asymptotically in the exchange channel ($r_2 \sim \infty$). In general, however, the only requirement is

$$\lim_{r_1\to\infty} \phi_l \pm P_{12} \lim_{r_2\to\infty} \phi_l = \sin(kr_1 - \tfrac{1}{2}l\pi + {}^\nu\eta_l) \times (kr_1)^{-1} P_l(\cos\theta_1) u_{1s}(r_2) \,, \tag{20}$$

where (+) and (−) refer to the singlet and triplet, respectively. Substitution of the above expression into Eq. (15) followed by a comparison with Eq. (10a) yields

$$a_l(\nu) = 1\,. \tag{21}$$

The sole means whereby $a_l(\nu)$ enters into our treatment is through the boundary conditions. Operating on both sides of Eq. (16) with $H-E$ eliminates this coefficient, and one obtains

$$(H-E)\phi_l(\nu) = (1-{}^\nu A)(H-E)\phi_l^0(\nu)\,. \tag{22}$$

Since the formal theory is identical for both S and T states the symmetry designation ν will, henceforth, often be suppressed for notational convenience. To get the perturbation equations we expand ϕ_l as

$$\phi_l = \phi_l^0 + \phi_l^1 + \phi_l^2 + \cdots\,, \tag{23}$$

and write

$$H = H^0 + V\,, \tag{24}$$

where H^0 is the zeroth-order Hamiltonian that has ϕ_l^0 as its eigenfunction and V is the (first-order) perturbation. Equating terms of like order

$$(H^0 - E)\phi_l^0 = 0\,, \tag{25a}$$

$$(H^0 - E)\phi_l^1 + {}^\nu A V \phi_l^0 = 0\,, \tag{25b}$$

$$(H^0 - E)\phi_l^2 + V\phi_l^1 = 0\,, \tag{25c}$$

$$(H^0 - E)\phi_l^3 + V\phi_l^2 = 0\,, \tag{25d}$$

etc.

The consistency requirement obtained by operating on the left of each equation with $\langle\phi_l^0|$ determines the phase shifts in the direct channel. Since the kinetic energy operator is non-Hermitian with respect to unbound functions, the terms $\langle\phi_l^0| H^0 - E)\phi_l^i\rangle$ do not vanish. They can be evaluated in the usual manner, which involves a partial integration over the radial coordinates to get

$$\begin{aligned}\langle\phi_l^0|(H^0-E)\phi_l^i\rangle &= -\tfrac{1}{2}\left(\langle\phi_l^0|\nabla_1^2\phi_l^i\rangle - \langle\phi_l^i|\nabla_1^2\phi_l^0\rangle^*\right)\\ &= -\tfrac{1}{2}\int d\tau_2 \int d\Omega_1 \lim_{r_1\to\infty}\left((r_1\phi_l^0)^*\frac{\partial}{\partial r_1}(r_1\phi_l^i) - (r_1\phi_l^i)\frac{\partial}{\partial r_1}(r_1\phi_l^0)^*\right),\end{aligned} \tag{26}$$

in which $d\tau_2$ is the total volume element for electron 2 and $d\Omega_1$ the angular volume element for electron 1. We now write the total direct-channel phase shift of Eq. (19) as

$$\eta_l = \eta_l^0 + \eta_l^1 + \eta_l^2 + \eta_l^3 + \cdots\,. \tag{27}$$

Then the corresponding expansion of $\sin(kr_1 - \tfrac{1}{2}l\pi + \eta_l) \equiv S_l(r)$ is

$$\begin{aligned}S_l(r) = {}& S_l^0(r) + \eta_l^1 C_l^0(r)\\ &+ [\eta_l^2 C_l^0(r) - \tfrac{1}{2}(\eta_l^1)^2 S_l^0(r)]\\ &+ \{[\eta_l^3 - \tfrac{1}{6}(\eta_l^1)^3]C_l^0(r) - \eta_l^1\eta_l^2 S_l^0(r)\}\\ &+ \cdots\,,\end{aligned} \tag{28}$$

where $C_l \equiv \cos(kr - \tfrac{1}{2}l\pi + \eta_l)$ and the superscript ^{0} indicates that η_l is replaced by η_l^0. The boundary conditions on the perturbed wave functions thus become

$$\lim_{r_1\to\infty}\phi_l^1 = \eta_l^1 C_l^0(r_1)(kr_1)^{-1}P_l(\cos\theta_1)u_{1s}(2)\,, \tag{29a}$$

$$\lim_{r_1\to\infty}\phi_l^2 = [\eta_l^2 C_l^0(r_1) - \tfrac{1}{2}(\eta_l^1)^2 S_l^0(r_1)] \times (kr_1)^{-1}P_l(\cos\theta_1)u_{1s}(2)\,, \tag{29b}$$

$$\lim_{r_1\to\infty}\phi_l^3 = \{[\eta_l^3 - \tfrac{1}{6}(\eta_l^1)^3]C_l^0(r_1) - \eta_l^1\eta_l^2 S_l^0(r_1)\} \times (kr_1)^{-1}P_l(\cos\theta_1)\,u_{1s}(2)\,, \tag{29c}$$

etc. Taking into account Eqs. (26) and (29), the consistency requirement leads to

$$\eta_l^1 = -(2\pi)^{-1}k(2l+1)\langle\phi_l^0|{}^\nu A V\phi_l^0\rangle\,, \tag{30a}$$

$$\eta_l^2 = -(2\pi)^{-1}k(2l+1)\langle\phi_l^0|V\phi_l^1\rangle\,, \tag{30b}$$

$$\eta_l^3 = -(2\pi)^{-1}k(2l+1)\langle\phi_l^0|V\phi_l^2\rangle + \tfrac{1}{6}(\eta_l^1)^3\,, \tag{30c}$$

etc.

Although the phase shifts in the direct channel are given by Eqs. (30), the asymptotic behavior in the exchange channel is arbitrary[22] at this point. Such arbitrariness is a characteristic of exchange perturbation theory. We resolve it here in the following manner. The functional

$${}^\nu\tilde{J}_l \equiv \langle{}^\nu\tilde{\psi}_l|(H-E){}^\nu\tilde{\psi}_l\rangle \tag{31}$$

will be zero, in general, only if ${}^\nu\tilde{\psi}_l$ is exact. (In this expression and elsewhere, an overhead tilde is used to denote a function or functional which depends upon variable parameters.) In the case of an approximate wave function one can always make ${}^\nu\tilde{J}_l$ vanish by varying the phase shift. For the exact wave function a variation in the phase shift by $\delta({}^\nu\eta_l)$ causes the functional to change an amount

$$\delta({}^\nu\tilde{J}_l) = \pi[k(2l+1)]^{-1}\delta({}^\nu\eta_l) + \cdots\,, \tag{32}$$

with the missing terms being at least quadratic in $\delta({}^\nu\eta_l)$. This result follows directly[23] from Eq. (31) and the boundary conditions (10a) and (10b). Thus, in the linear approximation, the phase-shift correction we seek is

$$\delta({}^\nu\eta_l) = -(\pi)^{-1}k(2l+1){}^\nu\tilde{J}_l\,, \tag{33}$$

assuming the proportionality constant of Eq. (32) is valid for the approximate wave function as well. The above expression is employed also in the Percival[24] variation method to determine the phase shift.

Setting ${}^\nu\tilde{\psi}_l = {}^\nu A\phi_l^0$ in Eq. (33) yields

$$ {}^\nu\tilde{\eta}_l - {}^\nu\eta_l^0 = -(\pi)^{-1}\, k(2l+1)\langle\phi_l^0|{}^\nu AV\phi_l^0\rangle . \tag{34}$$

We regard the phase-shift correction ${}^\nu\eta_l - {}^\nu\eta_l^0$ as first order and, hence [cf. Eq. (30a)],

$$ {}^\nu\eta_l^1 = 2\eta_l^1 . \tag{35}$$

This definition of order is supported by considering the analogous treatment of potential scattering (${}^\nu A \rightarrow 1$) in which case[25] $\eta_l - \eta_l^0$ reduces to the first-order phase shift when $({}^\nu\tilde{\psi}_l \rightarrow)\tilde{\phi}_l$ is taken to be ϕ_l^0.

Evidently, from Eq. (35), both channels (exchange and direct) contribute equally to ${}^\nu\eta_l^1$. Thus, the boundary condition on ϕ_l^1 in the exchange channel is

$$ \lim_{r_2\rightarrow\infty} \phi_l^1 = \pm\eta_l^1 C_l^0(r_2)(kr_2)^{-1}P_l(\cos\theta_2)u_{1s}(r_1) , \tag{36}$$

which leads to

$$ \lim_{r_1\rightarrow\infty} (1 \pm P_{12})\phi_l^1 = {}^\nu\eta_l^1 C_l^0(r_1)(kr_1)^{-1} \times P_l(\cos\theta_1)u_{1s}(r_2) \tag{37}$$

when combined with Eq. (29a). The last expression agrees exactly, as it must, with what is obtained by expanding ${}^\nu\eta_l$ as

$$ {}^\nu\eta_l = {}^\nu\eta_l^0 + {}^\nu\eta_l^1 + {}^\nu\eta_l^2 + \cdots \tag{38}$$

in Eq. (20). Note that if $\eta_l^1 = 0$, both ϕ_l^1 and $(1 \pm P_{12})\ \phi_l^1$ will be square-integrable functions.

As the next approximation we take ${}^\nu\tilde{\psi}_l = {}^\nu A(\phi_l^0 + \phi_l^1)$. The corresponding correction to the phase shift is found by substituting this wave function into Eq. (33) with the result

$$ {}^\nu\eta_l - ({}^\nu\eta_l^0 + {}^\nu\eta_l^1) = -(\pi)^{-1}k(2l+1) \times (\langle\phi_l^0|{}^\nu AV\phi_l^1\rangle + \langle\phi_l^1|{}^\nu AV\phi_l^1\rangle) . \tag{39}$$

To simplify Eq. (39) we have taken advantage of the first-order perturbation equation (25b). Again, by comparison with the analogous treatment of potential scattering, the right-hand side is defined as the sum of the second- and third-order perturbation corrections with

$$ {}^\nu\eta^2{}_l = -(\pi)^{-1}k(2l+1)\langle\phi_l^0|{}^\nu AV\phi_l^1\rangle \tag{40}$$

and

$$ {}^\nu\eta_l^3 = -(\pi)^{-1}k(2l+1)\langle\phi_l^1|{}^\nu AV\phi_l^1\rangle . \tag{41}$$

There are other ways to partition the phase shift into second- and third-order contributions, but the one we have given is the most obvious. Note that the wave function through first order determines the phase shift through third order. Finally, this procedure can be extended in a straightforward manner to higher orders although we hope it will be unnecessary to do so except in rare instances.

III. ILLUSTRATIVE CALCULATION OF LOW-ENERGY S-WAVE SCATTERING

For sake of illustration we now apply our exchange perturbation theory to the problem of low-energy elastic s-wave scattering from atomic hydrogen. Since $l = 0$ throughout, the angular-momentum index will be suppressed henceforth. For a one-state initial approximation the asymptotic boundary conditions require the zeroth-order primitive function to be of the form

$$ \phi^0 = G^0(1)u_{1s}(2) , \tag{42}$$

where

$$ \lim_{r_1\rightarrow\infty} G^0 = (kr_1)^{-1}\sin(kr_1 + \eta^0) . \tag{43}$$

This zeroth-order wave function will satisfy a Schrödinger equation

$$ (H^0 - E)\phi^0 = 0 \tag{44}$$

in which H^0 has the general form

$$ H^0 = -\tfrac{1}{2}\nabla_1^2 + U_0(r_1) - \tfrac{1}{2}\nabla_2^2 - r_2^{-1} , \tag{45}$$

and U_0 is the zeroth-order potential for the free electron. The perturbation, of course, is $V = H - H^0$ with H being the total Hamiltonian of Eq. (1).

As indicated earlier, a reasonable choice for U_0 may be found by solving the one-state (static) exchange equation

$$ \int d\tau_2\, u_{1s}(2)(H - E){}^\nu A\phi^0 = [-\tfrac{1}{2}\nabla_1^2 + U_0(1) - \tfrac{1}{2}k^2]G^0(1) = 0 . \tag{46}$$

Even though U_0 is an optimal one-state potential, we decided to use something simpler for illustrative purposes—namely, the attractive spherical well defined by

$$ U_0 = \begin{cases} -D & r \leq r_0 \\ 0 & r > r_0 . \end{cases} \tag{47}$$

This choice for U_0 has the correct general behavior desired, but as we shall see, it turns out to be too crude to give very high accuracy through third order.

The solutions of the spherical-well Schrödinger equation are well known.[26] Applying the boundary conditions at the asymptote and at the origin (where the wave function must be finite) one obtains

$$ kr_1G^0(r_1) = \begin{cases} N\sin(Kr_1) & r_1 \leq r_0 \\ \sin(kr_1 + \eta^0) & r_1 > r_0 , \end{cases} \tag{48}$$

with $K^2 = k^2 + 2D$,

$$N = \sin(kr_0 + \eta^0)/\sin(Kr_0)\,, \tag{49a}$$

and

$$\eta^0 = \tan^{-1}[(k/K)\tan(Kr_0)] - kr_0\,. \tag{49b}$$

The phase shift η^0 depends upon the parameters K and r_0 which can be optimized by any of several variational methods whose advantages and disadvantages have been discussed elsewhere.[1,27] We employ Hulthén's procedure[20] here because the resulting first-order wave function is square-integrable, which simplifies the calculations. Accordingly, the functional

$${}^\nu\tilde{J} = \langle {}^\nu A\tilde{\phi}^0 | (H - E){}^\nu A\tilde{\phi}^0\rangle = \langle {}^\nu A\tilde{\phi}^0 | V\tilde{\phi}^0\rangle \tag{50}$$

is made stationary with respect to the spherical-well parameters while ${}^\nu\eta^0$ is held constant. Then the phase shift is obtained by setting ${}^\nu\tilde{J}$ equal to zero. The left superscript has been added to η^0 at this point to indicate that the zeroth-order phase shift will depend upon the symmetry of the wave function. For each r_0 there is a value of K that will keep ${}^\nu\eta^0$ fixed and vice versa. If r_0 is taken as the free variable the Hulthén stationary condition becomes

$$(\partial{}^\nu\tilde{J}/\partial r_0)_K = (\partial{}^\nu\tilde{J}/\partial K)_{r_0}(\partial{}^\nu\eta^0/\partial K)^{-1}_{r_0}(\partial{}^\nu\eta^0/\partial r_0)_K\,. \tag{51}$$

Equation (51) together with the requirement

$${}^\nu\tilde{J} = \langle {}^\nu A\tilde{\phi}^0 | V\tilde{\phi}^0\rangle = 0 \tag{52}$$

yields two relations that determine K and r_0. Note that Eq. (52) immediately makes the first-order phase shift ${}^\nu\eta^1 = 0$ [cf. Eq. (34)]. Finally, the optimum parameters were solved for by Newton-Raphson iteration[28] with the results shown in Table I.

TABLE I. Optimum spherical-well parameters[a] and phase shifts for s-wave scattering from atomic hydrogen.

			Phase shift		
k	r_0	K	Spherical well	Static exchange[b]	"Exact"[c]
			Singlet		
0.8	0.856	1.754	0.734	0.651	0.886
0.7	1.048	1.484	0.806	0.744	0.930
0.6	1.507	1.127	0.901	0.869	1.041
0.5	2.214	0.870	1.036	1.031	1.202
0.4	2.849	0.728	1.219	1.239	1.415
0.3	3.388	0.627	1.467	1.508	1.696
0.2	3.767	0.552	1.813	1.871	2.067
0.1	3.968	0.505	2.338	2.396	2.553
			Triplet		
0.8	0.975	1.983	1.547	1.614	1.643
0.7	1.016	1.912	1.676	1.749	1.780
0.6	1.055	1.847	1.822	1.901	1.933
0.5	1.091	1.790	1.989	2.070	2.105
0.4	1.122	1.743	2.176	2.257	2.294
0.3	1.146	1.706	2.387	2.461	2.500
0.2	1.162	1.680	2.620	2.679	2.717
0.1	1.170	1.665	2.874	2.908	2.939

[a] The width r_0 and depth D of the well are defined in Eq. (47); the energy of the free electron is $\frac{1}{2}k^2$, and $K^2 = k^2 + 2D$. All parameter values are in a.u.; phase shifts are in rad.

[b] See N. F. Mott and H. S. W. Massey, Ref. 4, p. 530 for the values reported here and the original references.

[c] The extensive variational results of Ref. 29 are taken to be "exact."

Our zeroth-order phase shifts (Table I) are, typically, in error by 10–15% for the singlet and 2–6% for the triplet as compared to Schwartz's[29] extensive variational calculations. Because there is no minimum condition on the error, a small value for this quantity does not necessarily imply an accurate initial approximation. Indeed, for the singlet, at energies above $k \simeq 0.5$ a.u. the static-exchange phase shifts are worse than those calculated for the spherical-well approximation.

The first-order wave function was obtained from a variational equivalent of Eq. (25b):

$$\delta\tilde{J}^1_\phi = \delta(\langle\tilde{\phi}^1 | (H^0 - E)\tilde{\phi}^1\rangle + 2\langle\tilde{\phi}^1 | {}^\nu AV\phi^0\rangle) = 0\,. \tag{53}$$

For $\tilde{\phi}^1$ we chose a Hylleraas-type linear trial function

$$\tilde{\phi}^1 = e^{-Pr_1}e^{-Qr_2}\sum_{j=1}^{N} a_j r_1^{K_j} r_2^{L_j} r_{12}^{M_j} \tag{54}$$

of the sort employed by Schwartz[29] and others[30] in electron-scattering calculations. The exponential constants P and Q may be selected arbitrarily. We set $Q = 1.0$ to reproduce the 1s state of hydrogen. Then in order to partially optimize P, a series of computations with 7–9 term trial functions[31] was carried out. From these we found $P = 0.8$ (singlet) and 1.2 (triplet) as values where the phase shift is relatively stationary over the entire energy range from $k = 0.1$ to 0.7 a.u. Of course, as the basis set is increased in size, P becomes a redundant parameter.[32]

Considerable exploration was undertaken to establish which values of (K_j, L_j, M_j) should be included in the trial function. A sensitive test of basis set completeness utilizing an alternative formula for ${}^\nu\eta^2$ was developed (see Appendix A) for this purpose. The two formulas give the same result if the first-order wave function is exact but differ for approximate wave functions. At first ($N = 7$–9) there were farily large discrepancies but, eventually, we were able to get both formulas to agree to within 0.5% at all energies. Our final basis sets for the singlet and triplet are listed in Table II. A greater number of correla-

TABLE II. Basis set for variational calculation of first-order wave function. Each basis function is of the form $e^{-Pr_1}e^{-Qr_2}r_1^{K_j}r_2^{L_j}r_{12}^{M_j}$ with P and Q fixed at the values given in the text below Eq. (54).

Singlet[a]	Triplet
$r_1^0r_2^0r_{12}^0+\cdots+r_1^6r_2^0r_{12}^0$	$r_1^0r_2^0r_{12}^0+\cdots+r_1^{11}r_2^0r_{12}^0$
$r_1^0r_2^0r_{12}^1+r_1^0r_2^0r_{12}^2$	$r_1^0r_2^0r_{12}^1+r_1^0r_2^0r_{12}^2$
$r_1^0r_2^1r_{12}^0+\cdots+r_1^0r_2^6r_{12}^0$	$r_1^0r_2^1r_{12}^0+\cdots+r_1^0r_2^6r_{12}^0$
$r_1^1r_2^0r_{12}^1+r_1^0r_2^1r_{12}^1+r_1^1r_2^1r_{12}^0$	
$r_1^1r_2^1r_{12}^1+r_1^2r_2^0r_{12}^1+r_1^2r_2^1r_{12}^1$	
$r_1^1r_2^0r_{12}^2+r_1^0r_2^1r_{12}^2$	

[a] Just the first 18 terms were used for $k=0.3$, 0.5, and 0.7. The 23-term function was necessary only for $k=0.1$.

tion terms containing $r_{12}^{M_j}$ with $M_j>0$ were required for the singlet, whereas more free-electron distortion terms of the form $r_1^{K_j}r_2^0r_{12}^0$ were necessary for the triplet.

The perturbed phase shifts determined from Eqs. (40) and (41) are reported in Table III. Our values for the singlet are quite satisfactory considering the initial approximation. Through third order the residual error is 3–6% (down from the original 10–15%). For the triplet, the residual error is less but the perturbation treatment provides only a modest improvement of the zeroth-order values. The perturbation corrections obtained here would be the right order of magnitude if ${}^{\nu}A\phi^0$ were chosen as the static-exchange function. Thus, it appears likely that an improved starting point will give much better triplet phase shifts through third order, although the explanation for this is not obvious.

As a further test of the spherical-well initial approximation (in contrast with the electron exchange aspects of our treatment) a calculation of scattering due to the static potential of atomic hydrogen was carried out. In other words, we solved the one-electron Schrödinger equation $(h-\frac{1}{2}k^2)G=0$ in which

$$h-\tfrac{1}{2}\nabla^2-\frac{1}{r}+\int\frac{[u_{1s}(r_2)]^2}{|\vec{r}-\vec{r}_2|}\,d\tau_2 \tag{55}$$

using perturbation theory. Of course, there is no electron exchange in this problem. It turns out that the first-order wave function can be determined analytically (see Appendix B). Thus, the second- and third-order phase shifts listed in Table IV contain no basis set error.

The low-order perturbation expansion of the phase shift for the static potential is similar to that of the singlet (which includes exchange) in several respects. In both cases the total correction averages ~8–10%; the ratio η^2/η^3 is, typically, −0.2 to −0.3; and the mean residual error in the total third-order phase shift is about 4–5%. It is clear that the spherical well is too crude an approximation to the static potential to give high accuracy (say 1–2%) through third order. Furthermore, the errors in the total phase shifts through third order have the right order of magnitude to account for most of the difference between our exchange perturbation theory results and the exact values.

The preliminary results presented here indicate the desirability of further investigation. Obviously, test calculations based on the static-exchange potential as the initial approximation are of top priority. One should also recognize that ϕ^0 is not

TABLE III. Exchange perturbation theory phase shifts[a] for s-wave scattering by atomic hydrogen calculated from Eqs. (40) and (41).

k(a.u.)	${}^{\nu}\eta^0$	${}^{\nu}\eta^2$	${}^{\nu}\eta^3$	Total through third-order	Static[b] exchange	"Exact"[c]
			(A) Singlet			
0.1	2.338	0.156	−0.022	2.472	2.396	2.553
0.3	1.467	0.154	−0.026	1.596	1.508	1.696
0.5	1.036	0.151	−0.039	1.148	1.031	1.202
0.7	0.806	0.121	−0.054	0.873	0.744	0.930
			(B) Triplet			
0.1	2.874	0.006	0.000	2.881	2.908	2.939
0.3	2.387	0.016	0.001	2.403	2.461	2.500
0.5	1.989	0.019	0.000	2.008	2.070	2.105
0.7	1.676	0.019	0.001	1.695	1.749	1.780

[a] In radians.

[b] See N. F. Mott and H. S. W. Massey, Ref. 4, p. 530 for the values reported here and the original references.

[c] The extensive variational results of Ref. 29 are taken to be "exact."

TABLE IV. Perturbed phase shifts [a] for s-wave scattering by the static potential of atomic hydrogen.

k(a.u.)	η^0	η^2	η^3	Total through third-order	"Exact" [b]
0.1	0.515	0.185	−0.066	0.634	0.721
0.2	0.785	0.191	−0.068	0.909	0.973
0.3	0.900	0.166	−0.055	1.011	1.046
0.4	0.942	0.119	−0.043	1.019	1.057
0.5	0.951	0.105	−0.034	1.022	1.045
0.6	0.943	0.087	−0.027	1.004	1.021
0.7	0.927	0.074	−0.021	0.980	0.993
0.8	0.906	0.061	−0.017	0.951	0.963

[a] In radians.

[b] See N. F. Mott and H. S. W. Massey, Ref. 4, p. 530 for the values reported here and the original references.

restricted to be a one-state function; our theory is easily generalized to include a multistate initial approximation.[33] The best approach, therefore, could turn out to be some combination of a limited close-coupling calculation followed by an exchange perturbation treatment.

APPENDIX A

We derive here an alternative "mixed" expression for η^2 in terms of ϕ^1 and a first-order wave function X^1 determined from the polarization equation[34]

$$(H^0 - E)X^1 + V\phi^0 = 0 . \tag{A1}$$

As noted in Sec. III, this mixed expression provides a sensitive test of completeness for the basis set employed to expand ϕ^1. Multiplication of Eq. (A1) on the left by $\langle\phi^1|$ yields

$$\langle\phi^0|V\phi^1\rangle = -\langle\phi^1|(H^0 - E)X^1\rangle . \tag{A2}$$

Since ϕ^1 is bound, $\langle\phi^1|(H^0-E)X^1\rangle = \langle X^1|(H^0-E)\phi^1\rangle$, and, therefore, the perturbation equation for ϕ^1 [Eq. (25b)] can be postmultiplied by $\langle X^1|$ to obtain

$$\langle\phi^0|V\phi^1\rangle = \langle X^1|{}^\nu A V\phi^0\rangle = -\pi^\nu \eta^2 k^{-1}(2l+1)^{-1} . \tag{A3}$$

From the derivation just given one can see that the above relation holds, in general, only for the exact ϕ^1 and X^1 which is why it serves as a check of the first-order wave function.

Note that Eq. (A3) is valid regardless of the boundary conditions on X^1. We arbitrarily chose

$$\lim_{r_1\to\infty} X^1 = -(2\pi)^{-1}\langle\phi^0|V\phi^0\rangle r_1^{-1}C_0^0(r_1)u_{1s}(2) , \tag{A4}$$

and

$$\lim_{r_2\to\infty} X^1 = -(2\pi)^{-1}\langle\phi^0|P_{12}V\phi^0\rangle r_2^{-1}C_0^0(r_2)u_{1s}(1) , \tag{A5}$$

where $C_0^0(r) = \cos(kr + \eta^0)$. In order to satisfy these boundary conditions the variational function $\tilde{X}^1$ was taken to have the form

$$\tilde{X}^1 = e^{-Pr_1}e^{-Qr_2}\sum_{j=1}^{N} b_j r_1^{K_j} r_2^{L_j} r_{12}^{M_j} + Y(r_1,r_2) + Z(r_1,r_2) , \tag{A6}$$

in which

$$Y(r_1,r_2) = -[1-\exp(-\rho r_1)](2\pi)^{-1}\langle\phi^0|V\phi^0\rangle \times r_1^{-1}C_0^0(r_1)u_{1s}(2) \tag{A7}$$

$$Z(r_1,r_2) = -[1-\exp(-\rho r_2)](2\pi)^{-1} \times\langle\phi^0|P_{12}V\phi^0\rangle r_2^{-1}C_0^0(r_2)u_{1s}(2) . \tag{A8}$$

The first term on the r.h.s. of Eq. (A6) is the same one that was used for $\tilde{\phi}^1$ except the coefficients are now changed from a_j to b_j. There is an arbitrary exponential constant ρ in the expressions for $Y(r_1,r_2)$ and $Z(r_1,r_2)$ which was set equal to 15.0.

Since the only variational parameters in $\tilde{X}^1$ are the coefficients of the bound functions, Eq. (1) is equivalent to the Euler condition

$$\delta\tilde{J}_X^1 = \delta(\langle\tilde{X}^1|(H^0-E)\tilde{X}^1\rangle + 2\langle\tilde{X}^1|V\phi^0\rangle) = 0 . \tag{A9}$$

For small basis sets the variationally optimized ϕ^1 and X^1 gave substantial discrepancies between the two sides of Eq. (A3). In the singlet state, for example, the nine-term function consisting of the first two lines in Table II led to differences as large as 10%. As noted in the text, we continued adding functions to the basis until this last figure was reduced to less than 0.5% in all cases. Most of the initial deviation was due to X^1 rather than ϕ^1.

APPENDIX B

In this Appendix our perturbation calculation of electron scattering by the static potential of a hydrogen atom is briefly described. The appropriate equations may be derived from those of exchange perturbation theory by the following substitutions:

$${}^\nu A \to 1 , \tag{B1}$$

and

$$\phi^i \to G^i(1)u_{1s}(2) . \tag{B2}$$

It has been assumed here that the wave function ψ_l in Eqs. (9), (10a), and (11) is now defined without the factor of 2 which was introduced to account for the exchange symmetry. After substituting (B2) and postmultiplying with $\langle u_{1s}(2)|$, the perturbation equations become

$$(h^0 - \tfrac{1}{2}k^2)G^i + vG^{i-1} = 0 , \tag{B3}$$

where h^0 is the spherical-well Hamiltonian,

$$v = h - h^0 = -(r^{-1} + 1)\exp(-2r) - U_0\,, \tag{B4}$$

and the wave function G^0 is given in Eq. (48). The same derivation that previously led to Eqs. (30) now yields the perturbed phase shifts

$$\eta^1 = -(k/2\pi)\langle G^0 | vG^0\rangle\,, \tag{B5}$$

$$\eta^2 = -(k/2\pi)\langle G^0 | vG^1\rangle\,, \tag{B6}$$

and

$$\eta^3 = -(k/2\pi)\langle G^0 | vG^2\rangle + \tfrac{1}{6}(\eta^1)^3\,. \tag{B7}$$

If the optimum depth and width of the spherical well are determined by the Hulthén condition, then η^1 vanishes, causing the first-order wave function to be bound. By manipulating the perturbation equations in the same way as for bound states one can obtain an alternate expression for the third-order phase shift

$$\eta^3 = -(k/2\pi)\langle G^1 | vG^1\rangle \tag{B8}$$

which requires only the first-order wave function.

An analytical solution for G^1 has been obtained by Knudson.[35] In the outer region ($r > r_0$) this solution is

$$\begin{aligned} rG^1(r) = -k^{-1}\{&\tfrac{1}{2}k(1+k^2)^{-1}\exp(-2r)[\sin(kr+\eta^0) + k\cos(kr+\eta^0)] \\ &+[E_1(2r) - \cos 2\eta^0\,\mathrm{Re}E_1(2r+2ikr) - \sin 2\eta^0\,\mathrm{Im}E_1(2r+2ikr)]\cos(kr+\eta^0) \\ &-[\sin 2\eta^0\,\mathrm{Re}E_1(2r+2ikr) - \cos 2\eta^0\,\mathrm{Im}E_1(2r+2ikr)]\sin(kr+\eta^0)\}\,; \end{aligned} \tag{B9}$$

in the inner region ($r \leq r_0$) it is

$$\begin{aligned} rG^1(r) = 2Nk^{-1}(&[c - \tfrac{1}{2}\mathrm{Im}E_1(2r+2iKr) - \tfrac{1}{4}K(1+K^2)^{-1}\exp(-2r)] \\ &\times \sin Kr + \{\tfrac{1}{2}\ln(1+K^2)^{1/2} - E_1(2r) + \mathrm{Re}E_1(2r+2iKr) \\ &- Dr + \tfrac{1}{2}K^2(1+K^2)^{-1}[1-\exp(-2r)]\}\cos Kr)\,, \end{aligned} \tag{B10}$$

where c is the constant that makes the function continuous at $r = r_0$. The parameters N, D, K, and r_0 in the above expression are defined in Eqs. (47)–(49a); and $E_1(z)$ is the exponential integral function

$$E_1(z) = \int_{-\infty}^{z} e^t/t\,dt \tag{B11}$$

which has the real and imaginary parts $\mathrm{Re}E_1(z)$ and $\mathrm{Im}E_1(z)$. Finally, the phase shifts reported in Table IV were obtained by numerical integration of Eqs. (B5), (B6), and (B8).

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