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Theory of Low-Energy Scattering of Electrons by Hydrogen Atoms*

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The theory of low-energy electron–hydrogen atom scattering is reformulated to include, in any truncated coupled-channel calculation, the contribution from continuum states due to exchange effects. The existence of such a contribution has been explicitly demonstrated by Castillejo, Percival, and Seaton, although the standard treatment does not include it. Our formulation of the problem employs the expansion of the exact wave function $\Psi^{\pm}$ in terms of the complete set of hydrogenic states $\{\varphi_\alpha\}$ in the form $\Psi^{\pm}=\sum_\alpha \varphi_\alpha(1)\,\psi_\alpha^{\pm}(2)$. Although this expansion is not termwise symmetric or antisymmetric, the entire sum is made so by use of the integral equation for $\Psi^{\pm}$. The boundary conditions satisfied by the scattering coefficients $\psi_\alpha^{\pm}$ are automatically specified in this approach. Furthermore, it is now clear that the entire, exact elastic or inelastic amplitude is contained in the scattering wave function $\psi_\alpha^{\pm}$. The elastic wave function $\psi_0^{\pm}$ (and also the set of open-channel wave functions) is shown to obey both homogeneous (optical potential) and inhomogeneous equations. The equivalence of these equations with each other and with the equation found using Feshbach's projection-operator method is demonstrated. A set of homogeneous equations are found for the case where only certain chosen channels are kept and the rest are truncated. This latter set of equations is identical to those obtained by Hahn, O'Malley, and Spruch as an adjunct to calculations establishing bounds on scattering parameters. Both the exact and the approximate sets of equations for the $\psi_\alpha^{\pm}$ differ from the corresponding equations used in all previous coupled-channel calculations. Using our results, the relation between the Born-Oppenheimer amplitude and first-order exchange amplitude of Bell and Moiseiwitsch is discussed. Each is shown to be a different first-order approximation to the exact amplitude, although the Born-Oppenheimer amplitude is seen to be an approximation to the amplitude derived from the inhomogeneous equation. Some simple single-channel calculations of phase shifts and scattering lengths have been carried out. The triplet phase shifts and scattering length derived from the approximate homogeneous equation are identical to those of the standard static exchange approximation, a result expected on the basis of the antisymmetry of the Ψ^{-}. However, the singlet phase shifts and scattering length differ from those of the standard static exchange approximation. We find that for $k^2 \leq 0.09$, the singlet phase shifts are larger than those calculated in the 1*s*-2*s* strong-coupling approximation, and that the singlet scattering length is 7.85, where quantities are given in atomic units. For $k^2 > 0.09$, the singlet phase shifts are less than those of the 1*s*-2*s* case and approach those of the static exchange calculation. Reasons for this behavior are discussed.

INTRODUCTION

ALTHOUGH the scattering of electrons by hydrogen atoms is one of the simplest collision problems that includes the effects of the Pauli principle, it is still too difficult to be solved exactly, and all numerical calculations have been based on approximations of various kinds. The coupled-channels method is one of the most popular theoretical approaches on which approximations are based.[1] In this method, the exact scattering wave function $\Psi^{\pm}$ [upper (lower) signs refer to singlet (triplet) total spin functions] is expanded via the complete set of states $\{\varphi_\alpha\}$ of the H atom,

$$\Psi^{\pm}=\sum_\alpha\left[\varphi_\alpha(1)\chi_\alpha^{\pm}(2)\pm\varphi_\alpha(2)\chi_\alpha^{\pm}(1)\right], \quad (1)$$

and Eq. (1) is then substituted into the Schrödinger equation $(E-H)\Psi^{\pm}=0$. A set of coupled, integro-differential equations for the scattering coefficients $\chi_\alpha^{\pm}$ is found; these are to be solved with the boundary condition

$$\chi_\alpha^{\pm}(r)\sim\delta_{\alpha 0}\exp(i\mathbf{k}\cdot\mathbf{r})+f_{\chi_\alpha}^{\pm}(\theta)\exp(ikr)/r, \quad (2)$$

where φ_0 is the ground state.

The standard approximation consists of truncating the set of coupled equations,[1] and solving the remainder for $\chi_\alpha^{\pm}$ subject to Eq. (2). The amplitude $f_{\chi_0}^{\pm}$ is then interpreted as the elastic scattering amplitude. An identical set of equations is also found by truncating the expansion for $\Psi^{\pm}$ and using this abbreviated expansion in a variational integral.[1] With the present availability of high-speed computers, numerous calculations of this sort have been carried out in recent years. In addition, minimum principles and bounds on scattering parameters have been developed that have proved useful in assessing the accuracy of these calculations.[1]

Despite the great effort that has gone into such calculations, no one, to our knowledge, has yet included the effects of continuum hydrogenic states on the scattering. That is, $f_{\chi_0}^{\pm}$, for example, is *not* the true elastic amplitude, and would not be even if $\chi_0^{\pm}$ were determined exactly. Instead, the true elastic amplitude $f_0^{\pm}$ is obtained by examining

$$\lim_{r_2\to\infty}\langle\varphi_0(1)\,|\,\Psi^{\pm}\rangle=\lim_{r_2\to\infty}\{\chi_0^{\pm}(2)\pm\sum_\alpha \varphi_\alpha(2)\langle\varphi_0\,|\,\chi_\alpha^{\pm}\rangle\}$$
$$=\exp(i\mathbf{k}\cdot\mathbf{r}_2)+f_0^{\pm}(\theta)\exp(ikr_2)/r_2. \quad (3)$$

From (3) we see that $f_0^{\pm}$ contains $f_{\chi_0}^{\pm}$ and also contributions from those states $\varphi_k(2)$ which are in the continuum.

It might be thought that there is no contribution from the continuum states in Eq. (3), thus assuring that

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[1] Many references to the recent literature may be found in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964). See also P. G. Burke and K. Smith, Rev. Mod. Phys. 34, 458 (1962).

$\chi_0^\pm$ does yield the entire elastic amplitude. A simple example shows that this is false, for we only need to assume that electrons 1 and 2 are distinguishable and solve $(E-H)\Psi(1,2)=0$ in this case using the expansion $\Psi(1,2)=\sum_\alpha \varphi_\alpha(1)u_\alpha(2)$ [electron 2 incident]. Then $\Psi^\pm=\Psi(1,2)\pm\Psi(2,1)$ is a solution of $(E-H)\Psi^\pm=0$. The analog of $\chi_0^\pm$ is now u_0, which yields only the amplitude for distinguishable particle scattering. Hence the continuum states must make a contribution to $f_0^\pm$ in this case of $\chi_\alpha=u_\alpha$. That there is a singularity occurring in the expansion (3), the effect of which is to provide precisely the correct exchange amplitude, has been shown by Castillejo, Percival, and Seaton.[2]

The problem of attempting to include these continuum states within the framework of Eq. (1), is formidable, since it essentially requires solving the whole set of coupled equations, rather than just the truncated version. On the other hand, if only a truncated set is considered, then we ignore continuum exchange contributions to $f_0^\pm$. Hence, inclusion of more channels in the truncated set of equations for $\chi_\alpha^\pm$ will not necessarily be an improvement since the contribution of the continuum states remains undetermined.

A possible means of avoiding this problem, based on the fact that the $\chi_\alpha^\pm$ are not uniquely specified by Eq. (1), has been noted by Hahn, O'Malley, and Spruch.[3] The $\chi_\alpha^\pm$ may be redefined by requiring that $\langle\varphi_0|\chi_\alpha^\pm\rangle=0$, $\alpha\neq 0$. This then forces $f_{\chi_0}^\pm$ to be the true elastic amplitude. Unfortunately, there is a difficulty that renders this approach impractical. Namely, it would be necessary to solve the entire set of coupled equations in order to make sure that the condition $\langle\varphi_0|\chi_\alpha^\pm\rangle=0$, $\alpha\neq 0$, was, in fact, obeyed. Without such a guarantee, we would not know that $\chi_0^\pm$ was the only source of scattered waves, thus bringing us immediately back to the problem of using (1) without any restrictions on the $\chi_\alpha^\pm$. In other words, we are guaranteed that the redefined $\chi_\alpha^\pm$'s exist by the result of Castillejo, Percival, and Seaton.[2] But we do not yet know the new set of coupled equations that the redefined $\chi_\alpha^\pm$ obey. It is clear that such a new set must exist in order that only $\chi_0^\pm$ contribute to $f_0^\pm$. If the old set of coupled equations[1] is used, then in effect we are dealing with the $\chi_\alpha^\pm$ of Eq. (1). It would be necessary to solve this whole set, calculate the amplitude arising from the singularity, and add this extra amplitude to that obtained from $\chi_0^\pm$ (viz., $f_{\chi_0}^\pm$).

From the foregoing discussion, it is clear that practical methods for including continuum-state contributions are desirable. We explore several related methods in this paper. The main procedure we follow is based on previous work on the scattering of a fermion by a system of identical fermions.[4] Instead of using Eq. (1) for $\Psi^\pm$, we expand in the form

$$\Psi^\pm=\sum_\alpha \varphi_\alpha(1)\psi_\alpha^\pm(2)\,, \tag{4}$$

and require the entire sum in (4) to be antisymmetric, even though termwise it is not. The advantage of Eq. (4) over Eq. (1) is that $\psi_0^\pm$, for example, will contain the entire elastic amplitude $f_0^\pm$. Furthermore, any approximation to $\psi_0^\pm$ obtained by solving a truncated set of equations will now not neglect continuum exchange contributions to $f_0^\pm$.

In I, for the case of arbitrary targets, it was shown that $\psi_0^\pm$ obeyed an inhomogeneous differential equation, and also that the open-channel wave functions $\psi_\alpha^\pm$ ($0\leq\alpha\leq n_0=$ number of open channels) obeyed a set of coupled, inhomogeneous differential equations. All exchange effects were contained in the inhomogeneous terms. An advantage of this set of equations is the absence of the usual exchange nonlocalities. A drawback, however, is that one cannot define an optical potential from an inhomogeneous equation. However, the problem of determining an (uncoupled) optical-potential equation for $\psi_0^\pm$ was solved by Bell and Squires[5] for the case of the scattering of a fermion by a target containing an arbitrary number of fermions. Field-theoretic techniques were used by these latter authors to obtain their results. Using the methods of I, we have rederived the result of Bell and Squires for $e^-+\mathrm{H}$ elastic scattering and have extended it to include inelastic scattering as well. For the inelastic case, we find a set of coupled, homogeneous, integro-differential equations for the $\psi_\alpha^\pm$ in the open channels, thus permitting an optical-potential matrix to be determined. This latter set of coupled equations for the $\psi_\alpha^\pm$ closely resembles those for the $\chi_\alpha^\pm$, though there are important distinctions as we show later.

An alternative approach to the problems of continuum states and the optical potential has been put forward by Feshbach,[6] who used a different projection-operator method than that of I. We show that the results obtained using Feshbach's approach are identical to those obtained using our methods. Although all the equations derived for $\psi_0^\pm$ (or for the open-channel column vector wave function) by different means are thus shown to be identical, in their original forms some are seen to be more useful. This is particularly true for Feshbach's method. We show that if one wishes to ignore some or all of the closed channels, Feshbach's equations are the easiest way to obtain the coupled equations in this approximation. A derivation of the correct equations to use in a truncated coupled-channels calculation is contained in the work of Hahn, O'Malley, and Spruch,[3] although these authors made no use of it. We discuss this point in detail later.

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[2] L. Castillejo, I. Percival, and M. Seaton, Proc. Roy. Soc. (London) **A254**, 259 (1960).

[3] Y. Hahn, T. O'Malley, and L. Spruch, Phys. Rev. **128**, 932 (1962); **134**, B397 (1964). Their method is equivalent to removing the singularity exchange contributions of Ref. 2 and including it in the coefficient $\chi_0^\pm$. This method is also briefly discussed in Ref. 2.

[4] F. S. Levin, Phys. Rev. **140**, B1099 (1965). We denote this work by I, and refer to equations from it as (I-1), (I-2), etc.

[5] J. S. Bell and E. J. Squires, Phys. Rev. Letters **3**, 96 (1959).

[6] H. Feshbach, Ann. Phys. (N. Y.) **19**, 287 (1962).

Numerous calculations have been made in Born approximation and we discuss the relationship between the Born-Oppenheimer amplitude and the first-order exchange approximation amplitude of Bell and Moiseiwitsch.[7] In particular, we show that the Born-Oppenheimer result is the lowest order amplitude arising when the inhomogeneous equation for $\psi_0{}^{\pm}$ is solved, while the result of Bell and Moiseiwitsch[7] is the lowest order amplitude arising when the homogeneous equation for $\psi_0{}^{\pm}$ is solved. Both results are first-order approximations (in some sense) to the exact amplitude.

We have also carried out some simple single-channel calculations of phase shifts and scattering lengths based on the correct zero-order ("static" approximation) equations and have compared the results with previous calculations. Despite the differences in the equations obeyed by the $\chi_\alpha{}^{\pm}$ and the $\psi_\alpha{}^{\pm}$, we find that the "static" approximations for $\chi_0{}^{\pm}$ and $\psi_0{}^{\pm}$ yield nearly identical phase shifts except at very low energies where the phase shifts from the static approximation to $\psi_0{}^{\pm}$ are larger than those of the $1s$-$2s$ strong-coupling approximation to $\chi_0{}^{\pm}$. The reasons for this are discussed.

INHOMOGENEOUS EQUATIONS

We first review the results of I, using the following notation. The total Hamiltonian is H and can be expressed as (we assume an infinitely heavy proton)

$$H=H_1+H_2+v=H_0+v\,, \tag{5}$$

where

$$H_i=T_i+v_i=-(\hbar^2/2m)\nabla_i{}^2-e^2/r_i \tag{6}$$

is the Coulomb Hamiltonian for electron i, and

$$v=e^2/r_{12}$$

is the interelectronic interaction. The electrons are labeled 1 and 2, and

$$H_i\varphi_\alpha(i)=\epsilon_\alpha\varphi_\alpha(i)\,. \tag{7}$$

We also define

$$V_i=-e^2/r_i+e^2/r_{12}=v_i+v\,.$$

Finally, $\phi_k(i)=\exp(i\mathbf{k}\cdot\mathbf{r}_i)$ and φ_k is the Coulomb plane wave of momentum k satisfying (7) with $\epsilon_k=\hbar^2k^2/2m$.

From I, we know that $\Psi^{\pm}$ is given by[8]

$$\Psi^{\pm}=i\eta(E^+-H)^{-1}[\varphi_0(1)\phi_k(2)\pm\varphi_0(2)\phi_k(1)]\,, \tag{8}$$

where $E^+=E+i\eta$ and E is the total energy given by $E=\epsilon_k+\epsilon_0$. The limit $\eta\rightarrow 0$ is always assumed after relevant integrations have been done. By using the operator relation

$$(E^+-H)^{-1}=(E^+-H_1-T_2)^{-1}[1+V_2(E^+-H)^{-1}]\,,$$

Eq. (8) may be transformed to give the analog of Eq. (I-15):

$$\begin{aligned}\Psi^{\pm}=\varphi_0(1)\phi_k(2)\pm\varphi_0(2)\phi_k(1)&\\ \pm[E^+-H_1-T_2]^{-1}(V_1-V_2)\varphi_0(2)\phi_k(1)&\\ +(E^+-H_1-T_2)^{-1}V_2\Psi^{\pm}\,.&\end{aligned} \tag{9}$$

Alternatively, we may use the propagator $(E^+-H_0)^{-1}$ to expand $(E^+-H)^{-1}$, thus giving[9]

$$\Psi^{\pm}=\varphi_0(1)\varphi_k(2)\pm\varphi_0(2)\varphi_k(1)+(E^+-H_0)^{-1}v\Psi^{\pm}\,. \tag{10}$$

Our attention in this section will be mainly focused on (9); Eq. (10) is the basis for the derivation of the homogeneous equations obeyed by the $\psi_\alpha{}^{\pm}$. Note that $\psi^{\pm}$ does not contain Coulomb phase shifts, although we would have to include shielding factors into H in order to solve for $\Psi^{\pm}$ from (10) because of the φ_k.

As in I, we introduce the diagonal projection-operator matrix $P(1)$:

$$P(1)=\begin{bmatrix}P_0(1) & & & \\ & P_1(1) & & \\ & & \ddots & \\ & & & P_n(1)\end{bmatrix}=\begin{pmatrix}P_0(1) & \\ & P_I(1)\end{pmatrix},$$

where $P_\alpha(1)=|\varphi_\alpha(1)\rangle\langle\varphi_\alpha(1)|$ and n labels an arbitrary hydrogenic state.[10] Letting $\mathbf{1}$ denote the unit matrix in the space of $\{\varphi_\alpha\}$, then $Q(1)=\mathbf{1}-P(1)$. It follows from Eq. (4) that

$$P(1)\Psi^{\pm}=\begin{bmatrix}\varphi_0(1)\psi_0{}^{\pm}(2)\\ \varphi_1(1)\psi_1{}^{+}(2)\\ \cdots\\ \varphi_n(1)\psi_n{}^{\pm}(2)\end{bmatrix}.$$

Operating on (9) with $P(1)$ and $Q(1)$, eliminating $Q(1)\Psi^{\pm}$ from the $P(1)\Psi^{\pm}$ equation, and carrying out a number of operator manipulations, we obtain an uncoupled equation for $P(1)\Psi^{\pm}$ which is the analog of Eq. (I-52):

$$\begin{aligned}P(1)[E-H_1-T_2-P(1)UP(1)]&\\ \times[P(1)\Psi^{\pm}\mp P(1)\Phi_k(1)]=\pm P(1)\bar{U}\Phi_k(1)\,.&\end{aligned} \tag{11}$$

Here, $\Phi_k(i)$ is a column vector having $\varphi_0(j)\phi_k(i)$ in the first row $[j=2(1)$ as $i=1(2)]$ and zeros in the other n rows,

$$U=V_2+V_2[E^+-Q(1)HQ(1)]^{-1}Q(1)V_2\,, \tag{12}$$

and

$$\bar{U}=V_1+V_2[E^+-Q(1)HQ(1)]^{-1}Q(1)V_1\,. \tag{13}$$

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[7] K. L. Bell and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A276**, 346 (1963).

[8] We drop the normalization $2^{-1/2}$ in the source term of Eq. (8). This will lead to no error. This form of the Lippmann-Schwinger equation is given by Gell-Mann and Goldberger, Phys. Rev. **91**, 398 (1953).

[9] Both Eqs. (9) and (10) give an antisymmetric function, since $\Psi^{\pm}$ in Eq. (8) is constructed to be antisymmetric. This is obvious in the case of (10), since H_0 and v are both symmetric. Equation (9) on the other hand, is not manifestly antisymmetric, although it is seen to be so by iteration. For a scattering system containing more than three identical particles, it is not possible to write an equation analogous to (10) for the exact, antisymmetric wave function. The reason is that the rearrangement of labels due to exchange causes a binding interaction for one grouping of particles to become a perturbing interaction for another grouping of particles. Only by introducing a model Hamiltonian and using perturbation theory can this be accomplished, as implied by Bell and Squires (Ref. 6).

[10] Both open and closed channels may be included in the range $0\leq\alpha<n$.

Equation (12) will be recognized as defining the optical-potential operator for the case in which the electrons are distinguishable.[11] A formal solution to (11) is

$$P(1)\Psi^{\pm}=P(1)u\pm P(1)\Phi_k(1)\pm P(1)GP(1)\bar{U}\Phi_k(1)\,, \quad (14)$$

where $P(1)u$ is the solution to the homogeneous portion of Eq. (11) and

$$P(1)GP(1)=P(1)[E^+-H_1-T_2-P(1)UP(1)]^{-1}P(1)\,.$$

If the number of open channels is no greater than $n+1$, then the denominators in Eqs. (12) and (13) represent the effects of virtual excitations. As mentioned in the Introduction, it is not possible to solve Eq. (11) exactly. The analog for (11) of the usual truncation procedure[1] is to neglect the virtual excitations in U and $\bar{U}$. Doing this, we get a truncated set of coupled equations for the (now approximate) functions $P(1)\hat{\Psi}^{\pm}=P(1)\Psi^{\pm}\mp P(1)\Phi_k(1)$:

$$P(1)[E-H_1-T_2-P(1)V_2P(1)]P(1)\hat{\Psi}^{\pm} \\ =\pm P(1)V_1\Phi_k(1)\,, \quad (15)$$

or written in a more standard notation,

$$(E-\epsilon_\alpha-T_2)\hat{\psi}_\alpha{}^{\pm}(2)-\sum_{\beta=0}^{n}\langle\varphi_\alpha(1)|V_2|\varphi_\beta(1)\rangle\hat{\psi}_\beta{}^{\pm}(2) \\ =\pm\langle\varphi_\alpha(1)|V_1|\varphi_0(2)\phi_k(1)\rangle\,,\quad 0\leq\alpha\leq n\,, \quad (16)$$

where $\langle\varphi_\alpha(1)|P(1)\hat{\Psi}^{\pm}\rangle=\hat{\psi}_\alpha{}^{\pm}(2)$. For the purposes of computing phase shifts and cross sections, the term $P(1)\Phi_k(1)$ may be dropped, since it will not contribute asymptotically if n labels a bound state.

The set of coupled, inhomogeneous equations given by (16) may be used to calculate scattering parameters. To within the approximation of ignoring the couplings to the states in $Q(1)$, $\hat{\psi}_0{}^{\pm}$ contains all of the elastic amplitude, including the continuum contributions neglected in $\chi_0{}^{\pm}$ of Eq. (1).

The set of equations given by (16) bears a strong resemblance to the truncated set obeyed by the $\chi_\alpha{}^{\pm}$ of Eq. (1). To see this, let us consider the case $n=0$. Then we have

$$(E-\epsilon_0-T_2-\langle\varphi_0(1)|V_2|\varphi_0(2)\rangle)\hat{\psi}_0{}^{\pm} \\ =\pm\langle\varphi_0(1)|V_1|\varphi_0(2)\phi_k(1)\rangle\,. \quad (17)$$

Consider now the inhomogeneous term. We may rewrite it as

$$\langle\varphi_0(1)|V_1|\varphi_0(2)\phi_k(1)\rangle \\ =\langle\varphi_0(1)|V_1+H_2+T_1-E|\varphi_0(2)\phi_k(1)\rangle\,, \quad (18)$$

since $(H_2+T_1-E)|\varphi_0(2)\phi_k(1)\rangle=0$. Putting (18) into (17), we see that Eq. (17) is now identical with the equation obeyed by $\chi_0{}^{\pm}$ in the so-called static exchange approximation,[1,2,12] except that in Eq. (17) $\phi_k(1)$ replaces $\chi_0{}^{\pm}(1)$ in the exchange term. This replacement then changes the equation from integro-differential to inhomogeneous.

In I, we showed how the scattering phase shift δ_l could be expressed in terms of a phase shift η_l from the solution to the homogeneous equation and a phase shift $\bar{\eta}_l$ from the solution to the inhomogeneous equation:

$$e^{i\delta_l{}^{\pm}}\sin\delta_l{}^{\pm}=e^{i\eta_l}(\sin\eta_l\pm\sin\bar{\eta}_l)\,.$$

Formulas relating η_l and $\bar{\eta}_l$ to the interactions are given in I. We also defined scattering lengths a and $\bar{a}$ related to the true scattering length A:

$$A^{\pm}=a\pm\bar{a}\,.$$

Here a and $\bar{a}$ are the scattering lengths obtained from the solutions to the homogeneous and inhomogeneous equations, respectively. We now apply the formulas of I to determine the scattering lengths a, $\bar{a}$, and A for Eq. (17) as an example of a calculation involving the inhomogeneous equation. The results of more detailed computations will be discussed elsewhere.

It is, of course, unnecessary to calculate a, since that was done nearly twenty years ago by Chandrasekhar and Breen[13] and more recently by Seaton.[14] The result (in atomic units) is $a=-9.44$, where the asymptotic form of the ($k=0$) S-wave solution F_0 to the homogeneous portion of Eq. (17) is $F_0\sim(1-a/r)$. The scattering length $\bar{a}$ is found by integrating the product of the S-wave solution F_0 and the S-wave portion of the inhomogeneous term in Eq. (17) [in limit $k=0$] and then dividing by $(\hbar^2\cos\eta_0)/2m$. The final expression, easily found by using the formulas of I and the definitions of quantities in Eq. (17), is

$$\bar{a}=8[\cos\eta_0(k=0)]^{-1}\int r[e^{-r}(r-2)+e^{-2r}(r+2)]F_0(r)dr\,.$$

For F_0, we used the $X_0(r)$ of Chandrasekhar and Breen, with a normalization determined by relating the known value of a to its integral expression in terms of V_2 and F_0 (see I). The value of $\eta_0(k=0)$ was determined to be π by extrapolating the results in Table I of Burke and Smith[1] to zero energy. Numerical integration then yields $\bar{a}=-34.9$, a result whose accuracy is expected to be good to within ±1. The results for $A^{\pm}$ are found in Table III, which we discuss later.

It is straightforward to calculate the "Born approximation" T^{B} to the amplitude resulting from Eq. (17). We find

$$T^{\mathrm{B}}=\langle\phi_{k'}(2)\varphi_0(1)|V_2|\varphi_0(1)\phi_k(2)\rangle \\ -\langle\phi_{k'}(2)\varphi_0(1)|V_1|\varphi_0(2)\phi_k(1)\rangle\,. \quad (19)$$

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[11] H. Feshbach, Ann. Phys. (N. Y.) **5**, 357 (1958); Ann. Rev. Nucl. Sci. **8**, 49 (1958).

[12] In the static exchange approximation, $\chi_0{}^{\pm}$ obeys $\langle\varphi_0(1)|E-H|\varphi_0(1)\chi_0{}^{\pm}(2)\pm\varphi_0(2)\chi_0{}^{\pm}(1)\rangle=0$. We discuss this approximation, and the role of the kinetic-energy operators in the exchange term, in the next section.

[13] S. Chandrasekhar and F. M. Breen, Astrophys. J. **103**, 41 (1946).

[14] M. J. Seaton, Proc. Roy. Soc. (London) **A241**, 522 (1957).

This is just the well-known Born-Oppenheimer approximation to the amplitude.[7] We have used quotation marks above to indicate that we are not actually dealing with a simple Born series in a perturbing interaction. The V_i's can, and do, support bound states, and this causes difficulties with the Born series for rearrangement collision amplitudes.[15]

One of the seeming problems associated with (19) is that because of the rearrangement implied by the exchange terms, we no longer deal with eigenfunctions of a single unperturbed Hamiltonian and this leads to orthogonality difficulties [e.g., $\langle\varphi_0|\phi_k\rangle\neq 0$]. It has been claimed that one could thus add to V_1 a constant potential that would change the cross section.[7,16] Two methods have been proposed to get around this problem. In Mittleman's approach[17] a projection operator is used to ensure orthogonality, while Bell and Moiseiwitsch[7] attempt to remedy the problem (for the $e^-+\mathrm{H}$ case) by using the arbitrariness in the definition of the $\chi_\alpha{}^\pm$ (noted in the Introduction) to include "all" first-order terms in V_1 and V_2 in $T^{\text{“B”}}$.

Now we have already seen that the use of a truncated expansion in Eq. (1) fails to include the continuum contributions. It is thus not surprising that use of such an expansion would lead to a "Born" amplitude that seems to be unsatisfactory. On the other hand, we find from Eqs. (11) and (19) that the Born-Oppenheimer approximation actually *does* include all first-order terms in V_1 and V_2. The point is that the Born-Oppenheimer approximation is the first term not in a Born series, but in a series obtained by expanding the solution to the inhomogeneous equation in powers of V_1 and V_2. There is no guarantee that such an expansion is meaningful.[15]

As we shall see, the method of Bell and Moiseiwitsch[7] is fully equivalent to determining, in lowest order, the amplitude arising from $\psi_0{}^\pm$ of Eq. (4). The difficulty with all such approximations is that we only know that the lowest order term agrees with the exact calculation; higher order terms do not include all terms of the exact calculation. In addition to this difficulty, there is also the problem of the convergence of the "Born" series. As we show later, the result of Bell and Moiseiwitsch is an approximation to an expansion in powers of v only; v, being repulsive, can support no bound states, and so the series is very likely convergent. The *lowest* order term of this expansion in powers of v may be obtained by using Eq. (10). The analog of (17) [see Eq. (23)] is found to be

$$\begin{aligned}[E-\epsilon_0-H_2-\langle\varphi_0(1)|v|\varphi_0(1)\rangle]\psi_0{}^\pm(2)\\ =\pm\langle\varphi_0(1)|v|\varphi_0(2)\varphi_k(1)\rangle,\end{aligned}$$

with $\varphi_k(1)$ replacing $\phi_k(1)$ of (17). The "Born" amplitude T'^{B} analogous to (19) is now

$$\begin{aligned}T'^{\mathrm{B}}=T_{\mathrm{Coul}}+\langle\varphi_{k'}(2)\varphi_0(1)|v|\varphi_0(1)\varphi_k(2)\rangle\\ \pm\langle\varphi_{k'}(2)\varphi_0(1)|v|\varphi_0(2)\varphi_k(1)\rangle,\end{aligned}\qquad(20)$$

where

$$T_{\mathrm{Coul}}=\langle\phi_{k'}(2)\varphi_0(1)|v_2|\varphi_0(1)\varphi_k(2)\rangle.$$

The interaction v_2 occurs only in T_{Coul}. [The amplitude of Bell and Moiseiwitsch[7] reduces to this if their plane waves ϕ_k are everywhere replaced by Coulomb waves φ_k.] Clearly, all states appearing in (20) are eigenfunctions of the same Hamiltonian, thus resolving the nonorthogonality problem. A further discussion of the lowest order amplitudes is given in the next section.

HOMOGENEOUS EQUATIONS

We derive, in this section, the homogeneous equations obeyed by the $\psi_\alpha{}^\pm$; as we show in the Appendix, these equations, and thus the $\psi_\alpha{}^\pm$, are the same as those of the preceding section. The homogeneous equation obeyed by $\psi_0{}^\pm$ is the optical-potential equation. This potential is unique, since the function $\psi_0{}^\pm$ is unique. However, it is possible to introduce other functions $\psi_0{}'^\pm$ obeying equations with different nonlocal, energy-dependent potentials, that still yield the correct amplitude $f_0{}^\pm$, as shown for example by Mittleman.[18] This is, of course, the basis for the comment that the optical potential is not unique. In the strict sense of the optical potential being *defined* as the nonlocal operator appearing in the (unique) equation for $\psi_0{}^\pm$, then this optical potential is unique. As we shall see, the triplet optical potential of Mittleman[18] is identical to our result, which is also identical to the results of Bell and Squires[5] and Feshbach.[6]

To obtain the homogeneous equation, we use Eq. (10) and the projection-operator matrices $P(1)$ and $Q(1)$. As in I, and the derivation of Eq. (11), we apply $P(1)$ and $Q(1)$ to both sides of (10), giving

$$\begin{aligned}P(1)\Psi^\pm=\varphi_0(1)\varphi_k(2)\\ +P(1)(E^+-H_0)^{-1}v[P(1)+Q(1)]\Psi^\pm,\end{aligned}\qquad(21\text{a})$$

and

$$\begin{aligned}Q(1)\Psi^\pm=\pm\varphi_0(2)\varphi_k(1)\\ +Q(1)(E^+-H_0)^{-1}v[P(1)+Q(1)]\Psi^\pm.\end{aligned}\qquad(21\text{b})$$

At this point, we can solve Eq. (21b) for $Q(1)\Psi^\pm$, substitute the result into Eq. (21a) and obtain the following *inhomogeneous* equation for $P(1)\Psi^\pm$:

$$\begin{aligned}P(1)\Psi^\pm=\varphi_0(1)\varphi_k(2)+(E^+-H_0)^{-1}\\ \times P(1)\mathcal{V}[P(1)\Psi^\pm\pm\varphi_0(2)\varphi_k(1)].\end{aligned}\qquad(22)$$

In differential form, Eq. (22) becomes

$$P(1)[E-H_0-\mathcal{V}]P(1)\Psi^\pm=\pm P(1)\mathcal{V}\varphi_0(2)\varphi_k(1),\qquad(23)$$

where

$$\mathcal{V}=v+v(E^+-H_0-Q(1)v)^{-1}Q(1)v.\qquad(24)$$

It should be noted that state $\varphi_n(1)$ occurring in $P(1)$ is

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[15] R. Aaron, R. Amado, and B. Lee, Phys. Rev. **121**, 319 (1961).

[16] In point of fact, we could only do this by also subtracting the same constant from V_2 in order to avoid changes in H.

[17] M. H. Mittleman, Phys. Rev. **122**, 1930 (1961); **126**, 373 (1962).

[18] M. H. Mittleman, Ann. Phys. (N. Y.) 14, 94 (1961).

bound. If it is a free state $\varphi_{k'}$, then we must have $k' < k$. We compare, in the Appendix, these results with the optical-potential equations and show their equivalence.

Since we wish to derive a homogeneous equation for $P(1)\Psi^{\pm}$, it is necessary to eliminate the factor $\pm\varphi_0(2)\varphi_k(1)$ in Eq. (21b) which gives rise to the inhomogeneity. This can be done using the following trick. We apply $P(2)$ to each side of Eq. (10), which leads to the following equation for $\pm\varphi_0(2)\varphi_k(1)$:

$$\pm\varphi_0(2)\varphi_k(1) = P(2)\{\Psi^{\pm} - (E^{+}-H_0)^{-1}v[P(1)+Q(1)]\Psi^{\pm}\}.$$

Substituting this result into (21b) we find

$$Q(1)\Psi^{\pm} = P(2)\Psi^{\pm} + [Q(1)-P(2)] \times (E^{+}-H_0)^{-1}v[P(1)+Q(1)]\Psi^{\pm}. \quad (25)$$

Again we note that if n corresponds to a continuum state $\varphi_{k'}$, then we must have $k' < k$ for Eq. (25) to hold. Now,

$$Q(1)-P(2) = Q-P, \quad (26)$$

with $Q = Q(1)Q(2)$ and $P = P(1)P(2)$. Hence, on using (26) and solving (25) for $Q(1)\Psi^{\pm}$, we find, after some operator algebra,

$$Q(1)\Psi^{\pm} = P(2)\Psi^{\pm} + [E^{+}-H_0-(Q-P)v]^{-1} \times (Q-P)v[P(1)+P(2)]\Psi^{\pm}. \quad (27)$$

As a preliminary step before obtaining the desired result for $P(1)\Psi^{\pm}$, we consider $[P(1)+P(2)]\Psi^{\pm}$. From Eq. (4) and its symmetry properties we may rewrite $P(2)\Psi^{\pm}$ as $\pm P_{12}P(1)\Psi^{\pm}$, where P_{12} is the two-particle transposition operator. Hence,

$$[P(1)+P(2)]\Psi^{\pm} = (1 \pm P_{12})P(1)\Psi^{\pm}. \quad (28)$$

Using this last result and substituting Eq. (27) into Eq. (21b), we obtain the homogeneous equation for $P(1)\Psi^{\pm}$:

$$P(1)\Psi^{\pm} = \varphi_0(1)\varphi_k(2) + P(1)(E^{+}-H_0)^{-1}V_{\mathrm{opt}}^{\pm}P(1)\Psi^{\pm}. \quad (29)$$

Here,

$$V_{\mathrm{opt}}^{\pm} = V_{\mathrm{opt}}(1 \pm P_{12}) = \{v + v[E^{+}-H_0-(Q-P)v]^{-1} \times (Q-P)v\}(1 \pm P_{12}), \quad (30)$$

defining V_{opt}. Alternatively, we have

$$V_{\mathrm{opt}}^{\pm} = v^{\pm} + v^{\pm}[E^{+}-H_0-\tfrac{1}{2}(Q-P)v^{\pm}]^{-1}\tfrac{1}{2}(Q-P)v^{\pm}, \quad (31)$$

with $v^{\pm} \equiv v(1 \pm P_{12})$. Equation (30) or (31) defines the optical-potential operator for $e^{-}+\mathrm{H}$ scattering.

The differential form of Eq. (29) is given by

$$P(1)[E-H_0-V_{\mathrm{opt}}^{\pm}]P(1)\Psi^{\pm} = 0. \quad (32)$$

We see that there are no kinetic-energy operators acting on the exchange terms: The exchange effects occur solely in the optical potential. This is in apparent contrast to the results of Feshbach[6] and of Hahn, O'Malley, and Spruch,[3] who applied Feshbach's formalism to the $e^{-}+\mathrm{H}$ problem. However, as we show later, there is no contradiction: For the $e^{-}+\mathrm{H}$ problem, the kinetic-energy operators do not act on the exchange terms.[19]

We have stated earlier that $\psi_0^{\pm}$ is the elastic wave function of Bell and Squires[5] and that $V_{\mathrm{opt}}^{\pm}$ (for $n=0$) is their optical potential. As noted in I, this result follows from the uniqueness of $\psi_0^{\pm}$ and the Schrödinger equation. It can also be verified by comparing various orders of perturbation theory for the self-energy (which Bell and Squires show is the optical-potential operator) with an expansion of $V_{\mathrm{opt}}^{\pm}$ in powers of v. We have established that $V_{\mathrm{opt}}^{\pm}$ and the self-energy are identical to third order in v, as indeed they must be because of the uniqueness of $\psi_0^{\pm}$. It is evident that Eq. (30) is a closed-form expression for the self-energy operator in the case of a target containing one particle identical with the projectile.

Although it is straightforward to show that V_{opt}^{-} is the same as Mittleman's triplet optical potential,[18] we shall not demonstrate it here. However, his singlet potential[18] is not the same as V_{opt}^{+}.

Equation (32) is a compact way of writing the set of coupled equations describing the open-channel wave functions $P(1)\Psi^{\pm}$. Even if only the ground-state channel is open, (33) may be regarded as a set of coupled equations. Let us examine the equation for $\psi_0^{\pm}$, i.e., we choose $n=0$ in Q and P. Then $Q \to Q_0 = Q_0(1)Q_0(2)$ and $P \to P_0 = P_0(1)P_0(2)$, and we find that

$$V_{\mathrm{opt}}^{\pm} = v^{\pm} + v[E^{+}-H_0-(Q_0-P_0)v]^{-1}(Q_0-P_0)v^{\pm}. \quad (33)$$

If there is insufficient energy to excite the H atom, then V_{opt} is real. This follows from the fact that a singularity can occur only if in some intermediate state one electron is in φ_k and the other is in φ_0. But Q_0 allows neither electron to be in the ground state, while P_0 requires both electrons to be in the ground state. Hence there can be no singularity and we may take $\lim \eta \to 0$ in the denominator of $V_{\mathrm{opt}}^{\pm}$. Note that for V_{opt}^{-}, the factor P_0 is zero. However, for the more general case in which $n \neq 0$, P does make a contribution to V_{opt}^{-}. The reason is that P is the product of the two matrices $P(1)$ and $P(2)$, each of which operates in a different space. We shall show explicitly how P affects coupled-channels calculations later in this section.

We have investigated the behavior of Eq. (33) in the adiabatic limit and determined the long-range properties of its first- and second-order terms. The first-order term, when combined with v_2, gives the usual shielded interaction, plus an exchange term, both of which fall off exponentially. The factor P_0 also gives terms which fall off exponentially, which may be seen from Eq. (49). Only from Q_0 is there a long-range force, the polarization potential, which is obtained in the usual way.[18]

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[19] We believe that this result is true in general, and not merely for the $e^{-}+\mathrm{H}$ scattering system. Examination of Bell and Squires' work (Ref. 5) shows that this is the case for all orders of perturbation theory in a model Hamiltonian approach.

We show, in the next section, that Eq. (32) can be derived using Feshbach's projection-operator method.[6] Consequently, we may apply the theorem of Hahn, O'Malley, and Spruch[3] on lower bounds to the elastic phase shifts resulting from Eq. (32). Within the limitations discussed by these authors,[3] we thus find that the exact phase shifts $\eta^{\pm}$ are bounded from below by the phase shifts $\eta_S^{\pm}$ of the static exchange approximation,[12] and that as more channels are included in the static exchange approximation, the bounds increase in value.

The static exchange approximation[12] (or its extension to the case of coupling), is equivalent to calculating $\chi_0^{\pm}$ of Eq. (1) [or the many-channel wave function $\sum_{\alpha=0}^{n}(1\pm P_{12})\varphi_\alpha(1)\chi_\alpha^{\pm}(2)$] to first order in the interactions not included in the binding potential of the H atom. We now wish to consider the analogous approximation for Eq. (32). From Eq. (30) or (31), we see that the first-order interaction in $V_{\text{opt}}^{\pm}$ is apparently the term $v^{\pm}$. Hence the analog for Eq. (32) of the static exchange approximation would seem to be

$$P(1)[E-H_0-v^{\pm}]P(1)\Xi^{\pm}=0. \tag{34}$$

This equation, however, is *not* the proper analog. The reason is that, in addition to ignoring terms second order and higher in v, we also want to include *all* couplings to the states in $P(1)$. It is obvious from Eq. (30) that the terms containing P in the denominator of V_{opt} do involve such couplings. What is required, then, is a form for V_{opt} in which only the term Q appears in the denominator. As we show in the next section, Eq. (32) can be cast into such a form, given by Feshbach's equation for $P\Psi^{\pm}$. The result of including all coupling terms is a first-order equation of the form

$$P(1)[E-H_0-v^{\pm}+vP(2)]P(1)\Psi_P^{\pm}=0. \tag{35}$$

In addition to the nonlocality in $v^{\pm}$, this equation contains an extra nonlocality vP due to exchange effects. It is derived in the next section.

We call the solution $P(1)\Psi_P^{\pm}$ to Eq. (35) the *static approximation* to the exact solution $P(1)\Psi^{\pm}$. If it were permissible to ignore all couplings to the neglected (closed) channels, that is, if the terms with Q were small, then (35) would be a good approximation to the correct equation. On the other hand, (35) does treat all of the chosen channels, i.e., the ones in $P(1)$, correctly. In the present work, we solve Eq. (35) for the case $n=0$ and only the elastic channel open.

For $n=0$, Eq. (35) reduces to

$$\begin{aligned}\{E-\epsilon_0-H_2-\langle\varphi_0(1)|v|\varphi_0(1)\rangle\\ +\langle\varphi_0(1)|v|\varphi_0(1)\varphi_0(2)\rangle\langle\varphi_0(2)|\}\\ \times|\psi_{P,0}^{\pm}(2)\rangle\mp\langle\varphi_0(1)|v|\varphi_0(2)\psi_{P,0}^{\pm}(1)\rangle=0.\end{aligned} \tag{36}$$

We use the symbol $\psi_{P,0}^{\pm}(2)$ to denote $\langle\varphi_0(1)|\Psi_P^{\pm}\rangle$. As will become evident in the next section, the redefined $\chi_0^{\pm}$, discussed in the Introduction, would obey an uncoupled equation very similar to this. In fact, the equation is identical to (36) once it is realized that the redefined $\chi_0^{-}=\psi_0^{-}$, while the redefined $\chi_0^{+}=\psi_0^{+}-\frac{1}{2}\varphi_0\langle\varphi_0|\psi_0^{+}\rangle$.

Equation (36) differs from the more familiar equation of the static exchange approximation[12] in two ways. First, the operator $(E-\epsilon_0-H_2)$ does not act on the exchange term $\varphi_0(2)\psi_{P,0}^{\pm}(1)$ in Eq. (36). Second, Eq. (36) contains the additional exchange nonlocality $\langle\varphi_0(1)|v|\varphi_0(1)\varphi_0(2)\rangle\langle\varphi_0(2)|\psi_{P,0}^{\pm}(2)\rangle$ not present in the static exchange approximation. [The generalizations of these terms are given in Eq. (35).] Obviously, these differences are proportional to $\varphi_0(2)\langle\varphi_0|\psi_{P,0}^{\pm}\rangle$. For the case of $\psi_{P,0}^{-}$, the triplet phase shifts[20] η_P^{-} must be the same (for all partial waves L) as η_S^{-} already calculated from the static exchange approximation.[21] This is evident for $L\neq 0$, since $\varphi_0\langle\varphi_0|\psi_{P,0}^{\pm}\rangle$ picks out only the S-wave component. But even for $L=0$, there can be no change since any alteration of the wave function by a factor proportional to φ_0 is inconsequential because of the antisymmetry. However, this latter point is not true for $\psi_{P,0}^{+}$: the $L=0$ singlet phase shifts η_P^{+} will be different from those of the static exchange approximation, although the $L\neq 0$ phase shifts will be unaltered. Similar considerations apply to the scattering lengths derived from (36). We discuss the phase shifts and scattering lengths later.

These remarks are also applicable to the case of coupling, given by Eq. (35). If, for example, we were to include the 1*s*, 2*s*, and 2*p* states of hydrogen, then both $\eta_P^{\pm}$ would differ from the phase shifts determined by Burke and Schey[22] in their 1*s*-2*s*-2*p* calculations. The difference would be maintained for the $L=0$ and $L=1$ partial waves, since it is only in these partial waves that $\psi_P^{\pm}$ differs from the solutions of the 1*s*-2*s*-2*p* calculations.

We now return to the question of the first-order exchange amplitude of Bell and Moiseiwitsch.[7] Two different integral equations, leading to identical scattering amplitudes, can be written for $\psi_{P,0}^{\pm}$. These result from treating v_2 in H_2 of Eq. (36) either as a perturbation or exactly. We find, for these two different cases,

$$\begin{aligned}\psi_{P,0}^{\pm}(2)=\phi_k(2)+(E^{+}-\epsilon_0-T_\alpha)^{-1}\{v_2\psi_{P,0}^{\pm}(2)\\ +\langle\varphi_0(1)|v^{\pm}|\varphi_0(1)\psi_{P,0}(2)\rangle\\ -\langle\varphi_0(1)|v|\varphi_0(1)P_0(2)\psi_{P,0}^{\pm}(2)\rangle\},\end{aligned} \tag{37a}$$

and

$$\begin{aligned}\psi_{P,0}^{\pm}(2)=\varphi_k(2)+(E^{+}-\epsilon_0-H_2)^{-1}\\ \times\{\langle\varphi_0(1)|v^{\pm}|\varphi_0(1)\psi_{P,0}^{\pm}(2)\rangle\\ -\langle\varphi_0(1)|v|\varphi_0(1)P_0(2)\psi_{P,0}^{\pm}(2)\rangle\}.\end{aligned} \tag{37b}$$

We may now write out the exact scattering amplitudes (they are equal) arising from Eqs. (37a) and (37b). In each, we may form the "Born" terms by replacing $\psi_{P,0}^{\pm}$ by the first terms on the right-hand sides of (37a) and (37b). This leads identically to the result of Bell and

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[20] The angular momentum label L on the phase shifts is suppressed.

[21] See Burke and Smith, Ref. 1.

[22] P. G. Burke and H. M. Schey, Phys. Rev. **126**, 147 (1962).

Moiseiwitsch[7] for Eq. (37a) and to Eq. (20) for the *lowest* order amplitude arising from Eq. (37b). Bell and Moiseiwitsch's result is thus one type of first-order approximation to the exact amplitude, obtained by assuming that the state of the projectile is a plane wave, whereas Eq. (37b) assumes the state of the projectile to be a Coulomb plane wave. Bell and Moiseiwitsch were led to derive their result because of the orthogonality problem associated with the Born-Oppenheimer amplitude.[7] As we have seen, lack of orthogonality is merely a consequence of solving an inhomogeneous equation and should not be interpreted as an indication of an unsatisfactory theory. [In fact, as we shall show elsewhere, the inhomogeneous-equation method can be easily extended to derive coupled equations for rearrangement collisions.] However, the amplitude derived by Bell and Moiseiwitsch, though probably more accurate, cannot be regarded as intrinsically better than that of the Born-Oppenheimer approximation, since each is the lowest order term in a perturbation series for potentials that admit bound states. Only the amplitude from (37b) avoids this problem, although in this case, we are faced with the difficulty of evaluating matrix elements containing continuum Coulomb functions. Clearly, the simplest approach is to solve the differential equation numerically, thus obtaining the phase shifts directly.

DERIVATION USING FESHBACH'S METHOD

In this section, we derive an equation for $\psi_0^\pm$ using Feshbach's projection-operator method.[6] The equation will be of the form of Eq. (29) with $(Q-P)$ in $V_{\text{opt}}^\pm$ replaced by Q (plus other changes). We show that the new equation for $\psi_0^\pm$ reduces to (32), thus verifying the assertion of the preceding section.

For the $e^-+\text{H}$ problem, the object of Feshbach's method is to find a projection operator $\mathcal{P}$ such that

$$\mathcal{P}\Psi^\pm = \varphi_0(1)u^\pm(2) \pm \varphi_0(2)u^\pm(1)\,, \tag{38}$$

where only the elastic channel is assumed to be open. The function $u^\pm$ is required to yield the entire elastic amplitude $f_0^\pm$. Hence $u^\pm$ is the same as the redefined $\chi_0^\pm$ discussed in the Introduction. Since $u^\pm$ is to yield the entire elastic amplitude, then we must have, for either r_1 or r_2 asymptotic,

$$\Psi^\pm - \mathcal{P}\Psi^\pm = 0\,, \quad r_1 \text{ or } r_2 \to \infty\,. \tag{39}$$

A *sufficient* condition for (41) to hold is that

$$\langle \varphi_0(i) | \Psi^\pm - \mathcal{P}\Psi^\pm \rangle = 0\,, \quad i=1,2\,, \tag{40}$$

and it is with the aid of such an equation that the form of $\mathcal{P}$ is determined.[6]

Equation (40) is a relation between $\psi_0^\pm$ and $u^\pm$. Choosing $i=1$, we find

$$\psi_0^\pm(2) = u^\pm(2) + \varphi_0(2)\langle \varphi_0 | u^\pm \rangle\,. \tag{41}$$

Since $\psi_0^\pm$ is known, Eq. (41) is an integral equation for $u^\pm$. For the upper sign, we find that

$$u^+ = \psi_0^+ - \tfrac{1}{2}\varphi_0\langle \varphi_0 | \psi_0^+ \rangle\,,$$

while for the lower sign, we find

$$u^- = \psi_0^- + \varphi_0\langle \varphi_0 | u^- \rangle\,.$$

Clearly, u^- is undefined to within a multiple of φ_0. Hence, we may write

$$\begin{aligned} \mathcal{P}\Psi^+ &= \varphi_0(1)\psi_0^+(2) + \varphi_0(2)\psi_0^+(1) - \varphi_0(1)\varphi_0(2)\langle \varphi_0 | \psi_0^+ \rangle \\ &\equiv [P_0(1)+P_0(2)-P_0]\Psi^+\,, \end{aligned} \tag{42}$$

and

$$\begin{aligned} \mathcal{P}\Psi^- &= \varphi_0(1)\psi_0^-(2) - \varphi_0(2)\psi_0^-(1) \\ &= [P_0(1)+P_0(2)]\Psi^- \equiv [P_0(1)+P_0(2)-P_0]\Psi^-\,. \end{aligned} \tag{43}$$

The last line of (41) follows from the antisymmetry of Ψ^-.

Thus, for both $\Psi^\pm$, we may write $\mathcal{P}=P_0(1)+P_0(2)-P_0$. This expression for $\mathcal{P}$ is the same as that found by Hahn, O'Malley, and Spruch.[3] These authors show that $\mathcal{P}$ is indeed a projection operator, as did Feshbach[6] [$P(1)+P(2)$ is *not* a projection operator], and they also show that inelastic channels may be included by dropping the zero subscript on the P's and using the matrices $P(i)$. In this latter case, we find that $\mathcal{Q}\equiv \mathbf{1}-P$ is just the operator $Q=Q(1)Q(2)$. Thus, $\mathcal{P}+Q=\mathbf{1}$.

Before considering Feshbach's equation for $\mathcal{P}\Psi^\pm$, we wish to emphasize that it is not the quantity $u^\pm$ of Eq. (38) that is of interest, but $\psi_0^\pm$. In Feshbach's formalism, $u^\pm$ is a bridge—albeit one that maintains the symmetry of the problem—to $\psi_0^\pm$. It is $\psi_0^\pm$ that yields the exact amplitude and that is uniquely defined through $\psi_0^\pm = \langle \varphi_0 | \Psi^\pm \rangle$. The $u^\pm$ are not uniquely defined, since Eq. (40) could be replaced by Eq. (39), which could give a $u'^\pm$ differing from $u^\pm$ at small r. This is seen in the work of Hahn, O'Malley, and Spruch,[3] who note that the function $\Psi_S^\pm = \varphi_0(1)\chi_S^\pm(2) \pm \varphi_0(2)\chi_S^\pm(2)$ satisfies $\mathcal{P}\Psi_S^\pm = \Psi_S^\pm$ and so derive that the phase shifts $\eta_S^\pm$ of the static exchange approximation are lower bounds to the exact phase shifts $\eta^\pm$. However, the proof of Hahn *et al.*[3] is more general than just stated. In deriving their results, these authors did not make use of the relation between $u^\pm$ and $\psi_0^\pm$. Hence, their result is that $\eta_S^\pm$ provide lower bounds to the phase shifts for *any* function of the form of Eq. (38) that obeys the equation for $\mathcal{P}\psi^\pm$, which we write out below. However, it is not true that any function of the form of Eq. (38) will yield the proper amplitude [$f_0^\pm$ of Eq. (3)]: Only those $u^\pm$ which are related to $\psi_0^\pm$ by, for example, Eq. (39) or (40) will yield the correct amplitude. This is easily seen to be the case by considering the equation obeyed by $u^\pm$ when coupling to channels other than φ_0 is ignored. This is just the equation of the static exchange approximation, which we know does not include the continuum contributions. To find the correct "static" equation, we must relate $u^\pm$ somehow to $\psi_0^\pm$, i.e., we must solve for $\psi_0^\pm$. As noted in the preceding section, in the static approximation, $\psi_0^\pm$ does not obey the equation of the static exchange approximation.

The equation obeyed by $\mathcal{P}\Psi^\pm$ is given by Feshbach[6]:

$$\mathcal{P}\{E-H-HQ(E-QHQ)^{-1}QH\}\mathcal{P}\Psi^\pm=0. \tag{44}$$

Here, $\mathcal{P}$ is taken to be $\mathcal{P}=P(1)+P(2)-P$. Operating in both sides of (44) with $P(1)$, we find

$$P(1)\{E-H_0-v-vQ(E^+-H_0-QvQ)^{-1}Qv\}\mathcal{P}\Psi^\pm=0, \tag{45}$$

where $[H_0,Q]=0$ has been used. Since $[P(1),H_0]=0$, (45) reduces to

$$P(1)[E-H_0]P(1)\Psi^\pm-P(1)\times[v+vQ(E^+-H_0-QvQ)^{-1}Qv]\mathcal{P}\Psi^\pm=0 \tag{46}$$

or

$$P(1)\{E-H_0-[v+v(E^+-H_0-Qv)^{-1}Qv]\times(1\pm P_{12})\}P(1)\Psi^\pm+P(1)\times\{v+v(E^+-H_0-Qv)^{-1}Qv\}P\Psi^\pm=0. \tag{47}$$

The *static approximation* to Eq. (47) is obtained by dropping the terms with Q, so that there is no coupling to the channels not included in $P(1)$. The result is just Eq. (35), thus establishing the results of the preceding section.

Equation (47) is easily transformed to Eq. (32) [with $V_{\text{opt}}^\pm$ given by Eq. (30) or (31)] by the use of some operator identities and Eq. (32), which we have established independently. We proceed by transforming the factor $(E^+-H_0-Qv)^{-1}Qv$ of Eq. (47) using the operator equation $A^{-1}=B^{-1}+B^{-1}(A-B)A^{-1}$, where A and B are operators possessing inverses. First we rewrite the factor in question:

$$(E^+-H_0-Qv)^{-1}Qv=[E^+-H_0-(Q-P)v-Pv]^{-1}[(Q-P)v+Pv]. \tag{48}$$

Employing the above-mentioned operator equation in Eq. (48) and collecting terms eventually leads to

$$(E^+-H_0-Qv)^{-1}Qv=V_{\text{opt}}-v+v(E^+-H_0-Qv)^{-1}PV_{\text{opt}}, \tag{49}$$

where V_{opt} is given by Eq. (30).

Substituting (49) into (47) we find

$$P(1)[E-H_0-V_{\text{opt}}^\pm]P(1)\Psi^\pm+P(1)[v+v(E^+-H_0-Qv)^{-1}Qv]P\Psi^\pm-P(1)v(E^+-H_0-Qv)^{-1}PV_{\text{opt}}^\pm P(1)\Psi^\pm=0. \tag{50}$$

We now prove that the last two terms in Eq. (50) cancel. Operating on each side of Eq. (29) with $P(2)$ gives

$$P(2)\Psi^\pm=(E^+-H_0)^{-1}P(2)V_{\text{opt}}^\pm P(1)\Psi^\pm. \tag{51}$$

Substituting (51) into the $P\Psi^\pm$ terms in (50) then leads to

$$P(1)(E-H_0-V_{\text{opt}}^\pm)P(1)\Psi^\pm+P(1)[v(E^+-H_0)^{-1}+v(E^+-H_0-Qv)^{-1}Qv(E^+-H_0)^{-1}]PV_{\text{opt}}^\pm P(1)\Psi^\pm-P(1)v(E^+-H_0-Qv)^{-1}PV_{\text{opt}}^\pm P(1)\Psi^\pm=0. \tag{52}$$

But the term in square brackets in (52) is just $v(E^+-H_0-Qv)^{-1}$, as is shown by using the operator relation $A^{-1}=B^{-1}+A^{-1}(A-B)B^{-1}$, thus establishing the cancellation. Hence, we find

$$P(1)[E-H_0-V_{\text{opt}}^\pm]P(1)\Psi^\pm=0, \tag{32}$$

as stated above.

Equation (32) is the more compact form, but Eq. (47) is evidently more useful, since it allows one to write a simple equation for $P(1)\Psi^\pm$ in which all the states in $Q(1)$ are excluded. It is interesting that (38) does not follow from (47) directly. One first would have to hypothesize Eq. (32) and then show consistency through the cancellation proved above. However, it is worth emphasizing again that Eqs. (51), (52), and (32) only hold if the hydrogenic states in $P(1)$ do not include those $\varphi_{k'}$ with $k'\geq k$, where k is the incident wave number. Equation (47), on the other hand, is valid regardless of the states included in $P(1)$.

We close this section with a comment about the scattering amplitude. In I, we showed that Eq. (11) or (14) does give the correct elastic amplitude. Similar results can be demonstrated for Eq. (29) or (32). However, at first glance, the same does not seem to be true of Eq. (47). For example, the lowest order terms, apart from the Coulomb amplitude due to H_2, would seem to contain an extra amplitude involving the factor $vP\Psi^\pm$. This is, of course, only an apparent defect. If we express $P(1)\Psi^\pm$ of Eq. (50) in terms of $\varphi_0(1)\varphi_k(2)$ [i.e., use the integral equation for $P(1)\Psi^\pm$ analogous to Eq. (29)], so that we then have the Born terms of the amplitude, it becomes evident that the Born approximation to the factor $vP\Psi^\pm$ is zero. The higher order terms in $vP\Psi^\pm$ are nonvanishing, as is the case for the amplitude arising from Eq. (29). It is not difficult to show that the correct elastic amplitude is indeed obtained from (51), just as with the other equations.

SINGLE-CHANNEL CALCULATIONS

In this section, we discuss the results of some single-channel calculations we have carried out using the equations derived above, and we compare our phase shifts and scattering lengths with other calculations. All calculated quantities are given in atomic units.

Only scattering lengths have been calculated from the inhomogeneous equation for $\psi_0^\pm$, Eq. (17). However, both phase shifts and scattering lengths have been computed for Eq. (36), the static approximation to the elastic scattering equation. In addition to these latter quantities, we have also determined the scattering lengths and phase shifts for Eq. (34), the incorrect static equation. This was done to evaluate the effect of dropping the term $(E-2\epsilon_0)\varphi_0(2)\langle\varphi_0|\psi_0^\pm\rangle$ occurring in the static exchange approximation. Our discussion will concern only the S-wave phase shifts $\eta_P^\pm(L=0)$, since, as noted before, the equation for $\psi_{P,0}^\pm$ differs from the equation for $\chi_S^\pm$, the static exchange wave function, only in the S wave.

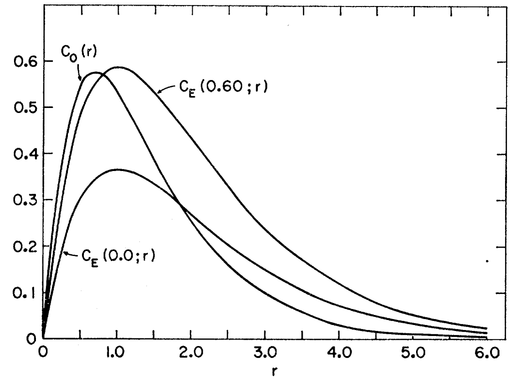

FIG. 1. Shown are the functions $C_0(r)$ and $C_E(k^2;r)$, each multiplied by $\pi^{1/2}$, for $k^2=0.0$ and $k^2=0.6$. Both k and r are given in atomic units.

Both Eqs. (34) and (36) were integrated using a noniterative method to handle the exchange nonlocalities; the method is identical to that used by Marriott.[23] All numerical integrations were carried out using the Runge-Kutta scheme. The nodal definition was used in computing phase shifts. The computer program for determining the scattering parameters was checked by computing the phase shifts and scattering lengths for the triplet case and also for the case where exchange is ignored. These results agreed with previous calculations[21]; consequently, we do not list any triplet phase shifts, since they are identical to the values obtained in the static exchange approximation. A final check on the over-all accuracy was provided by changing the mesh size of the numerical integration from 0.1 to 0.05. The results for $k=0.2$, 0.5, and 0.8 remained unchanged.

In Table I, we list the singlet S-wave phase shifts $\eta_P^+(L=0)$ derived from Eq. (36) and compare them with the results of other calculations, the values of which have been tabulated by Burke and Smith.[1] Only results for $k^2\leq 0.70$ are listed, since the singlet resonance is found to occur at slightly larger values of k^2.

The most striking aspect of this table is the fact that for $k^2<0.16$, η_P^+ is larger than the corresponding phase shift of the strong-coupling approximation, which is a coupled-channels calculation that includes the $1s$ and $2s$ states. On the other hand, for $k^2\geq 0.16$, η_P^+ is less than the strong-coupling phase shift and as k increases rapidly approaches the value of η_S^+, the phase shift of the static exchange approximation.

TABLE I. Singlet S-wave phase shifts. k is given in atomic units.

k^2	Static approx.	Static exch. approx.	Strong-coupling approx.	$1s$-$2s$-$2p$	Variational calc.
0.0001	3.063				
0.01	2.414	2.396	2.404	2.491	2.553
0.04	1.890	1.871	1.878	1.974	2.067
0.09	1.526	1.508	1.519	1.540 ($k^2=0.10$)	1.696
0.16	1.253	1.239	1.257	1.355 ($k^2=0.15$)	1.415
0.25	1.042	1.031	1.046	1.082	1.202
0.30	0.959	0.949		1.008	
0.40	0.833	0.825		0.888	1.047 ($k^2=0.36$)
0.50	0.744	0.737		0.811	0.930 ($k^2=0.49$)
0.64	0.652	0.651	0.698	0.776 ($k^2=0.65$)	0.886
0.70	0.630			1.240	

To help understand this behavior, we have plotted in Fig. 1 the radial dependence of the coefficient, from both Eq. (36) and the equation of the static exchange approximation, which multiplies the nonlocal factor $\langle\varphi_0|\psi_0^+\rangle$. For Eq. (36) this coefficient, denoted by $C_0(r)$, is

$$C_0(r)=2[1-e^{-2r}(r+1)]\varphi_0(r)\,, \tag{53}$$

while for the static exchange approximation this coefficient, denoted by $C_E(k^2;r)$, is[12]

$$C_E(k^2;r)=[(k^2+1)r]\varphi_0(r)\,. \tag{54}$$

Apart from these terms, the two equations are identical.

Two values of $C_E(k^2;r)$ are shown in Fig. 1. It is clear from these curves that $C_E(0.6;r)$ and $C_0(r)$ are quite similar, and it is thus not surprising that at the larger values of k^2, η_P^+, and η_S^+ are nearly the same. On the other hand, as k^2 approaches zero, $C_E(k^2;r)$ and $C_0(r)$ become less alike, with the extreme case of $C_E(0.0;r)$ illustrated in Fig. 1. This difference in the two coefficients is reflected in the differing values of η_P^+ and η_S^+. That $\eta_P^+\geq\eta_S^+$ can be expected from the theorem of Hahn, O'Malley, and Spruch.[3] The difference is greatest at $k=0$, as shown in the scattering lengths A_P^+ and A_S^+ of Table III, which we will discuss shortly.

We may now use this information to help explain the fact that for $k^2\leq 0.09$, $\eta_P^+>\eta_{1s\text{-}2s}^+$. In the $1s$-$2s$ strong-coupling case, there are two coupled equations. The one for χ_0^+, the coefficient of the ground state φ_0 in Eq. (1), is identical to that of the static exchange approximation, except for the additional term $(k^2+\frac{1}{4})\varphi_{2s}(r)\langle\varphi_0|\chi_{2s}^+\rangle$, in an obvious notation. For $k^2\leq 0.09$, the state χ_{2s}^+ is relatively far off the energy shell, and the overlap $\langle\varphi_0|\chi_{2s}^+\rangle$ should be small. Furthermore, the factor $(k^2+\frac{1}{4})$ is small. [Also φ_{2s} has a node at $r=2$, which should help reduce the contribution of this term when it is integrated.] Hence, the extra term $(k^2+\frac{1}{4})\varphi_{2s}(r)\langle\varphi_0|\chi_{2s}^+\rangle$ should not make a strong contribution to $\eta_{1s\text{-}2s}^+$, the main contribution coming from the terms of the static exchange approximation. As we see in Table I, the $1s$-$2s$ phase shifts are larger than η_S^+, but less than η_P^+ for $k^2\leq 0.09$. On the other hand, for $k^2\geq 0.16$, the $2s$ coupling term in the χ_0^+ equation is not as far off the energy shell and also the contribution of the χ_0^+ coupling term in the χ_{2s}^+ equation can increase $\langle\varphi_0|\chi_{2s}^+\rangle$, so that $\eta_{1s\text{-}2s}^+$ may be greater than η_P^+. Hence the fact that the $1s$-$2s$ phase shift and η_P^+ cross at some energy is not unexpected, although these qualitative arguments cannot predict the value at which the crossing takes place.

Since the term $\langle\varphi_0(1)|v|P\Psi^+\rangle$ of Eq. (36) is so similar to the kinetic-energy term $(E-2\epsilon_0)\varphi_0(2)\langle\varphi_0|\chi_0^+\rangle$ of the static exchange approximation, it is interesting to de-

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[23] R. Marriott, Proc. Phys. Soc. (London) **72**, 121 (1958).

TABLE II. Singlet S-wave phase shifts. k is given in atomic units.

k^2	Correct static approx. [Eq. (36)]	Incorrect static approx. [Eq. (34)]
0.0001	3.063	3.121
0.01	2.414	2.926
0.04	1.890	2.717
0.09	1.526	2.521
0.16	1.253	2.342
0.25	1.042	2.186
0.30	0.959	2.120
0.40	0.833	2.018
0.50	0.744	1.945
0.64	0.652	1.879
0.70	0.630	1.281
0.0000	7.85	2.16

termine the effect of ignoring these terms. If we do so, the resulting equation is (34). This equation results from using the projection operator $\mathcal{P}$ *and* the assumption that $\langle\varphi_0|\psi_0^+\rangle=0$, which is not a valid result. The singlet phase shifts and scattering length obtained from this equation are tabulated in Table II and compared with A_P^+ and η_P^+. (The triplet parameters were found to be identical to those from the static exchange approximation, as required by antisymmetry of the spatial wave function.) The effect of dropping the term $\langle\varphi_0(1)|v|P\Psi^\pm\rangle$ is clear in this table; not only are all the incorrect phase shifts greater than η_P^+, they are also larger than any phase shifts so far calculated. The importance of the extra exchange term thus is evident.

Before turning to the comparison of scattering lengths, we point out that the $1s$-$2s$ strong-coupling approximation based on Eq. (1) is not the same as the strong-coupling approximation based on Eq. (35). Qualitative arguments similar to those used above lead us to expect that the singlet $1s$-$2s$ phase shifts from Eq. (35) may be larger than the singlet $1s$-$2s$-$2p$ phase shifts of Table I for low energies, although the presence of the $1p$ state makes the application of this argument somewhat uncertain. The results for the $1s$-$2s$ S-wave phase shifts will be reported elsewhere.

The results of our scattering-length calculations are given in Table III, where we compare them with the results obtained by other methods.[21] As can be expected from the behavior of the phase shifts, the singlet scattering length of the static approximation A_P^+ is smaller than the singlet scattering lengths of the static exchange (A_S^+) and strong-coupling approximations. Furthermore, as indicated above and verified in Table III, $A_P^-=A_S^-$. The curious aspects of Table III, however, are the scattering lengths determined from the inhomogeneous equation. These results could not be expected to be accurate, since the entire distinguishable particle solution [solution to the homogeneous part of Eq. (11)] is approximated so crudely by the solution to the homogeneous portion of Eq. (17). Inclusion of some coupling reduces the "static" scattering length by nearly a factor of 2 when exchange is ignored,[24] and coupling will presumably alter $\bar{a}$, the exchange scattering length, by a large amount also (see the discussion of the Lippmann and Schey[25] calculation below). The significance of the sign of A^+ in the first row of Table III is not understood, but coupled-channels calculations should help in understanding this. The results of such calculations for the inhomogeneous equation will be discussed elsewhere.

CONCLUDING REMARKS

We first summarize the results of this paper. It has been shown that $\psi_0^\pm$ obeys an inhomogeneous equation, with all exchange effects contained in the inhomogeneous term. Scattering lengths in the "static" approximation to the exact inhomogeneous equations have been determined. We have also derived the set of optical-potential equations for the open-channel wave functions (or any chosen set of channels) in several ways. Both phase shifts and scattering lengths were calculated in the static approximation to these equations, in the limit of pure elastic scattering, i.e., one channel open. These various results have been compared with the results of other calculations. A comparison with the older forms of the theory that do not include the continuum exchange contributions has been given. Finally, we have shown how the Born-Oppenheimer and first-order exchange approximations[7] are related to the present work. We have made no comments about continuum contributions to variational calculations. None, in fact, were necessary since the forms of the variational wave functions were so chosen as to exclude these contributions.

The use of an inhomogeneous equation to represent the effects of the Pauli principle was first used by Lippmann and Schey,[25] in a heuristic approach. Their equation for $\psi_0^\pm$ may be regarded as an approximation to Eq. (11) for the case $n=0$. The inhomogeneity is approximated by the term $\lambda\varphi_0$, where λ is a constant (which is determined in the calculation). The potential $\langle\varphi_0(1)|U|\varphi_0(1)\rangle$ of Eq. (11) is approximated by the usual shielded Coulomb potential plus a polarization potential that is finite at the origin. It is difficult to assess quantitatively the accuracy of these approximations, but we can show some qualitative conclusions from the results of the calculations based on them. First,

TABLE III. Scattering lengths, in atomic units.

Calculation	A^-	A^+
Inhomogeneous equation	25.46	-44.34
Static approximation	2.35	7.85
Static exchange approximation	2.35	8.095
Strong-coupling approximation	2.33	8.05
$1s$-$2s$-$2p$	1.89	6.74
Variational calculation	1.76	5.96

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[24] See Table I of Burke and Smith, Ref. 1.

[25] B. A. Lippmann and H. Schey, Phys. Rev. **121**, 1112 (1960).

the approximation of $\langle\varphi_0(1)|U|\varphi_0(1)\rangle$ used by Lippmann and Schey is an attempt to include the effects of coupling on the solution u_0 of Eq. (14); this approximation is known to be accurate at large values of r. Thus, this solution to the homogeneous equation is obviously far more accurate than that of Chandrasekhar and Breen,[13] which we have used. Second, the approximation of the inhomogeneity by $\lambda\varphi_0$ is not expected to be good because the functional dependence of the inhomogeneity is clearly more complicated than just the dependence of φ_0 on r. On the other hand, use of the orthogonality condition[25] to determine λ probably helps to overcome this to some extent. Finally, since the relevant exchange scattering parameters are determined by integrating the product of the homogeneous solution and $\lambda\varphi_0$, the use of such a simple form as φ_0 to represent the inhomogeneity may not be too inaccurate. This last comment is borne out, of course, by the reasonableness of the phase shifts and scattering length obtained by Lippmann and Schey[25] especially when compared with the large value of the triplet scattering length obtained from our calculation using the inhomogeneous equation. The simulation of the effects of other channels by use of the polarization potential thus indicates that a coupled-channel calculation using the inhomogeneous equation may lead to greatly improved results, as noted above.

Let us now consider the homogeneous equations. With only a single channel considered, we have seen that the singlet phase shifts are increased in value over the old strong-coupling results for certain energies. This is clearly a result of including the continuum exchange contributions. The physical interpretation of this inclusion is that we are now allowing the two electrons to experience a greater correlation than was possible in the older treatment. Such a correlation is obviously introduced, in Eq. (36), through the terms $P_0\Psi^{\pm}$, which force both electrons to be in the ground state where (a) they must be near to each other and (b) they can feel the effect of v most strongly. Further correlations of this type are introduced by the operator P in the case of coupling given by Eq. (34). It is thus quite likely that, in contrast to the results of Burke and Schey,[22] inclusion of $1s$-$2s$-$2p$ couplings in Eq. (34) will give singlet phase shifts in much closer agreement with those of variational calculations.[26]

Since the structure of the $1s$-$2s$-$2p$ coupled-channels equations are quite similar to those of the older calculations, except for the addition of several extra exchange nonlocalities (recall the discussion of the $1s$-$2s$ case above), we expect to find a resonance in $1s$-$2s$-$2p$ calculations based on Eq. (35). The reason is that we would be retaining essentially the older amplitude which produced a resonance and adding to it another, and presumably nonresonant, amplitude. Calculations to test this are planned.

We have stressed the differences that may occur in the coupled-channel calculation of scattering parameters using Eq. (35) as compared to those previously calculated. This is an obvious consequence of the real difference between Eq. (35) and the coupled equations that result on using a truncated version of Eq. (1). Even though the functional dependence of the terms in Eq. (36) and in the equation of the static exchange approximations are quite similar, we must not regard these two equations as being equally valid approximations to the exact scattering equation. Their origins are based on quite different treatments of the Pauli principle. As we have remarked above, the difference between our equation and the older ones based on a truncated form of Eq. (1) is much more marked in the $1s$-$2s$ coupling case, and becomes even more pronounced as more states are included in the coupled-channels equations. In addition to possible improvements in the low-energy scattering parameters, one will also hopefully get better results at higher energies using Eq. (35) for just the $1s$-$2s$-$2p$ coupling case. Further couplings, though harder to calculate, will also be interesting to investigate.

Note added in proof. Due to an error in the computer program, the singlet phase shifts and scattering length for Eq. (36) are incorrect. They should equal, instead, the values obtained from the static exchange approximation. Furthermore, it can be shown that as long as $P(1)$ contains only bound states, then Eq. (34), for the singlet case, can be transformed into the equation obeyed by the truncated form of Eq. (1). The truncation of Eq. (1) will be such that the sum on α runs over the same states as are in $P(1)$. Hence, in this case, the singlet scattering parameters are the same as obtained in the standard type of calculation using a truncated form of Eq. (1). This is not true however, for the triplet state. While the equality of the static exchange approximation results and those obtained from Eq. (36) can be predicted, it can be shown that this equality no longer holds when coupling is introduced. Thus our conclusions remains valid for the case of triplet scattering. When all states including the continuum are considered, our method still provides a unique means of determining the scattering amplitude. The author wishes to thank Dr. R. Peterkop for pointing out the necessary existence of the error in the calculations of the singlet scattering parameters.

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APPENDIX: PROOF OF SOME EQUALITIES

In I, it was stated that the four different equations for $\psi_0^{\pm}$ were identical, an identity that follows from the

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[26] C. Schwartz, Phys. Rev. **124**, 1468 (1961).

uniqueness of Eq. (4) and thus of $\psi_0^\pm$ itself. We have already seen that Eqs. (32) and (46) are identical. We now show that Eqs. (11) and (23) are identical; the identity of (23) and (32) will complete the circle and thus establish the remark of I stated above. We shall work with the integral equations for $\psi_0^\pm$ in establishing the identity of (23) and (32). It will again be clear that P cannot contain continuum states with wave number greater than or equal to k.

The identity of (11) and (23) will be demonstrated by transforming (11) into (23). First we note that from Eqs. (12) and (13)

$$\begin{aligned}&P(1)UP(1)\\&\quad=P(1)[v+v(E^+-H_0-Q(1)v)^{-1}Q(1)v]P(1)\end{aligned}\tag{A1}$$

and

$$\begin{aligned}&P(1)\bar{U}\Phi_k(1)\\&\quad=P(1)[v+v_1+v(E^+-H_0-Q(1)v)^{-1}\\&\qquad\times Q(1)(v+v_1)]\Phi_k(1),\end{aligned}\tag{A2}$$

since $[H_0,Q(1)]=[v_2,Q(1)]=0$. Substituting Eqs. (A1) and (A2) into Eq. (11), using $P(1)(E-\epsilon_0-H_2+v_1)\Phi_k(1)=0$, and rearranging terms, we find

$$\begin{aligned}&[E-\epsilon_0-H_2-P(1)UP(1)]P(1)\Psi^\pm\\&\quad=\pm P(1)[UQ(1)\Phi_k(1)\\&\qquad+v(E^+-H_0-Q(1)v)^{-1}Q(1)v_1\Phi_k(1)].\end{aligned}\tag{A3}$$

To obtain (A3), we have also employed the relation

$$-UP(1)\Phi_k(1)+U\Phi_k(1)=UQ(1)\Phi_k(1).$$

We wish to eliminate the term $v_1\Phi_k(1)$. To do this, we observe that, by definition,

$$\varphi_k(1)=\phi_k(1)+(E^+-\epsilon_0-H_1)^{-1}v_1\phi_k(1),$$

or

$$v_1\phi_k(1)=(E^+-\epsilon_0-H_1)[\varphi_k(1)-\phi_k(1)].$$

Hence,

$$v_1\Phi_k(1)=(E^+-H_0)[\varphi_0(2)\varphi_k(1)-\Phi_k(1)].$$

Thus, the second term on the right-hand side of Eq. (A3) may be written as

$$\begin{aligned}&v(E^+-H_0-Q(1)v)^{-1}Q(1)v_1\Phi_k(1)\\&\quad=v(E^+-H_0-Q(1)v)^{-1}(E^+-H_0)Q(1)\\&\qquad\times[\varphi_0(2)\varphi_k(1)-\Phi_k(1)]\\&\quad=[v+v(E^+-H_0-Q(1)v)^{-1}Q(1)v]\\&\qquad\times[\varphi_0(2)\varphi_k(1)-Q(1)\Phi_k(1)]\\&\quad=U\varphi_0(2)\varphi_k(1)-UQ(1)\Phi_k(1).\end{aligned}\tag{A4}$$

Substituting (A4) into (A3) then leads to the cancellation of the $UQ(1)\Phi_k(1)$ terms, thus producing Eq. (23).

Next we turn to the relationship between (23) and (32), establishing the identity using the integral equations (22) and (29). We transform Eq. (29) into (22). First we rewrite the denominator of $V_{\rm opt}^\pm$:

$$\begin{aligned}&[E^+-H_0-(Q-P)v]^{-1}(Q-P)v\\&\quad=[E^+-H_0-Q(1)v]^{-1}\\&\qquad\times\{1-P(2)v[E^+-H_0-(Q-P)v]^{-1}\}(Q-P)v,\end{aligned}\tag{A5}$$

since $Q-P=Q(1)-P(2)$. Furthermore, the term $\{\ \}(Q-P)v$ in (A5) can be rewritten as

$$\{\ \}(Q-P)v=Q(1)v-P(2)V_{\rm opt}.\tag{A6}$$

Thus, substituting (A6) into (A5) and then into Eq. (29), we obtain

$$\begin{aligned}P(1)\Psi^\pm=&\ \varphi_0(1)\varphi_k(2)+(E^+-H_0)^{-1}P(1)\\&\times\{U-v[E^+-H_0-Q(1)v]^{-1}P(2)V_{\rm opt}\}\\&\times(1\pm P_{12})P(1)\Psi^\pm.\end{aligned}\tag{A7}$$

The terms $P(2)V_{\rm opt}^\pm P(1)\Psi^\pm$ may be transformed in the following way. The integral equation for $P(1)\Psi^\pm$ is equivalent to the equation obtained from (10) by projecting with $P(1)$ and equating $P(1)v\Psi^\pm$ to $P(1)V_{\rm opt}^\pm P(1)\Psi^\pm$. Similarly, projecting on (10) with $P(2)$, we find

$$\begin{aligned}\pm P(2)\Psi^\pm&=\pm\varphi_0(2)\varphi_k(1)+(E^+-H_0)^{-1}\\&\qquad\times P(2)V_{\rm opt}^\pm[\pm P(2)\Psi^\pm]\\&=\pm\varphi_0(2)\varphi_k(1)+(E^+-H_0)^{-1}\\&\qquad\times P(2)V_{\rm opt}^\pm P(1)\Psi^\pm,\end{aligned}$$

or

$$\begin{aligned}&P(2)V_{\rm opt}^\pm P(1)\Psi^\pm\\&\quad=(E^+-H_0)^{-1}[P(2)\Psi^\pm\mp\varphi_0(2)\varphi_k(1)].\end{aligned}\tag{A8}$$

Putting (A8) into (A7), we get

$$\begin{aligned}P(1)\Psi^\pm=&\ \varphi_0(1)\varphi_k(2)+(E^+-H_0)^{-1}P(1)\\&\times\{U(1\pm P_{12})P(1)\Psi^\pm+v(E^+-H_0-Q(1)v)^{-1}\\&\times(E^+-H_0)[\mp P(2)\Psi^\pm\pm\varphi_0(2)\varphi_k(1)]\}.\end{aligned}\tag{A9}$$

Since $v(E^+-H_0-Q(1)v)^{-1}(E^+-H_0)=U$, Eq. (A9) may finally be put into the form

$$\begin{aligned}P(1)\Psi^\pm=&\ \varphi_0(1)\varphi_k(2)+(E^+-H_0)^{-1}P(1)\{U(1\pm P_{12})\\&\times P(1)\Psi^\pm\mp UP(1)\Psi^\pm\pm U\varphi_0(2)\varphi_k(1)\},\end{aligned}$$

which just reduces to Eq. (22).

We have now established that the four equations derived for $\psi_0^\pm$ are identical, thus providing explicit proof that the various methods of deriving $\psi_0^\pm$ lead to identical functions.