Application of a variational principle for the scattering length for the target wave function imprecisely known

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In the past, variational calculations of the scattering length for scattering by a target system whose ground-state wave function is imprecisely known have suffered from numerical instabilities which severely limit their utility. The problem has recently been analyzed and the difficulty removed by the introduction of a minimum principle, not for the true scattering length, but for that of a closely connected problem. Here we report on numerical tests of this new calculational procedure. We have studied the scattering of positrons and electrons by atomic hydrogen with a trial hydrogenic ground-state wave function which is allowed to differ from the correct function. As predicted, no instability difficulties whatsoever are encountered as the trial scattering wave function and the trial target wave function are improved; apart from at most one jump for each composite bound state, the estimate of the scattering length converges monotonically.

I. INTRODUCTION

A very significant problem in theoretical physics is the accurate estimation of cross sections for a specified incident energy, and a very significant incident energy value is the value zero. The cross section can then often be characterized by a scattering length A. The variational principle is one natural tool one might attempt to use to estimate A. We will be concerned with the use of variational principles to estimate A for scattering by targets for which the ground-state wave function ϕ_T and ground-state energy E_T are only imprecisely known. In atomic and molecular physics that covers almost all targets with spatial internal degrees of freedom but the hydrogen atom and hydrogenlike ions. To go from precisely to imprecisely known target wave functions and energies is to introduce entirely new difficulties. We begin with some general remarks on variational principles.

There are of course vast areas in which variational principles have been very successful, but there are also areas in which these principles may appear to be of very limited usefulness. In fact, for at least two important situations, discussed below, the limitations are not limitations of variational principles as such. Rather, difficulties appear in the course of applications because the so-called variational principles are only *formally* variational; they give an error of second order in the error of the input trial functions, but if, as in the normal procedure, the trial functions contain variational parameters, and if these parameters are varied to find the stationary value of the so-called variational principle for the entity to be estimated, the error in the trial function and therefore the error in the estimate can be arbitrarily large even for—and sometimes especially for—a trial function of reasonable form. (We will be more concrete shortly.) Such "variational principles" are of course useful if there is available from elsewhere some reasonable trial function; one then simply inserts the trial function into the variational principle. One cannot always use the variational principle itself to estimate the trial function, and one thereby loses one of the most desirable properties of true variational principles.

The conceptual difficulties might be eased somewhat if more care were taken in the terminology used—we cast no stones, having been as imprecise in language as others—and, more precisely, if the term stationary principle were used for an estimate good to second order in the error in the trial function, and the term variational

principle were reserved for a stationary principle which can be used to good effect to determine the variational parameters contained in the trial function. In this language, singular situations arise for stationary principles which can give very poor results for trial wave functions of a reasonable form. Such stationary principles can be variational for all but small ranges of the nonlinear variational parameters and we will use the term "singular variational principles" to describe them.

To be concrete in our discussion of singular variational principles, we begin by discussing briefly the analysis of a bound-state matrix element of an arbitrary operator. A number of authors[1] gave expressions which are normally referred to as variational expressions for these matrix elements but which are, in reality, singular variational expressions. (Notwithstanding, these principles can be and have been of considerable use,[1,2] though the accuracy attainable is limited. The bound-state trial functions used must be very restricted in form—Hartree products, for example.) The variational principle for the bound-state matrix element requires not only an estimate ϕ_{Tt} of ϕ_T but an estimate L_t of a function L, an associated undetermined Lagrange multiplier, and the error in L_t for almost all ϕ_{Tt} will be *inversely* proportional to the error in ϕ_{Tt}, whereas the variational property presumes that the error in L_t is small. (We use the subscript T in the present discussion, even though we need not here be discussing a scattering problem, simply because the bound state under consideration will be the bound state of the target in later considerations.)

It was recently shown[3] that one could do much better for this important class of matrix elements than work with a singular variational principle; one could construct and use a true variational principle. The singular variational principle for $(\phi_{Tn}, W\phi_{Tm})$, where W is an arbitrary operator and ϕ_{Tn} and ϕ_{Tm} are bound-state eigenfunctions of a target Hamiltonian H_T with associated eigenvalues E_{Tn} and E_{Tm}, involves matrix elements of $H_T - E_{Tnt}$ and $H_T - E_{Tmt}$, where E_{Tnt} and E_{Tmt} are estimates of E_{Tn} and E_{Tm}, respectively; the evaluation of variational parameters in the trial functions ϕ_{Tnt} and ϕ_{Tmt} involves the inversion of the operators $H - E_{Tnt}$ and $H - E_{Tmt}$, operations which become more nearly singular as the number of basis functions used in the expansions of ϕ_{Tnt} and ϕ_{Tmt} is increased. To obtain a true variational principle, one recasts the singular variational principle into a form which involves $H_{Tmod,t} - E_{Tit}$, for $i = m$ and n, where $H_{Tmod,t}$ is a modification of H_T such that $H_{Tmod,t} - E_{Tit}$ is a positive definite operator with, therefore, a nonsingular inverse. The variational principle obtained has the very

nice property that the hard part of the calculation, the determination of the parameters contained in the trial undetermined multiplier function L_t, proceeds by finding the stationary value of a functional which has an extremum property; all possible near singularities, with their associated numerical instabilities, are thereby avoided. The estimate of the matrix element of interest does not, unfortunately, converge monotonically, but there are no limitations on the accuracy obtainable and the extremum property of the functional has important computational and conceptual advantages. The variational principle was applied to both diagonal[4] and off-diagonal[5] matrix element cases.

A second example of a singular variational principle, the subject of this paper, arises in the estimation of the scattering length A for the target ground-state wave function ϕ_T and target ground-state energy E_T only imprecisely known. (For ϕ_T and E_T known exactly, the Kohn variational principle[6] provides a variational principle for A; there is then available the even stronger variational bound[7,8] on A.) The Kohn principle involves a matrix element of H, where H is the Hamiltonian for the entire system, target and incident particle. The singular variational principle for A, for ϕ_T and E_T imprecisely known, is obtained[9] from the Kohn principle by simply replacing ϕ_T by ϕ_{Tt} and E_T by

$$E_{Tt} \equiv (\phi_{Tt}, H_T \phi_{Tt}).$$

(That the result generated by this simple replacement is indeed stationary is by no means obvious. That it is a singular variational principle, and that it could be converted to a true variational principle, was the content of Ref. 10.) If one includes variational parameters c_n in the trial scattering wave function Ψ_t, and attempts to determine the c_n by using the stationarity of the singular variational principle for A, one must invert $H - E_{Tt}$. Now whereas E_T is at the bottom edge of the continuous spectrum of H, E_{Tt} is greater than E_T and is embedded therefore in the continuous spectrum of H. The inversion of $H - E_{Tt}$ is consequently a singular operation, and, for a given ϕ_{Tt}, the error in Ψ_t can become arbitrarily large, whereas for a true variational principle one requires the error in Ψ_t to be small. It should therefore not have been surprising that attempts to use the singular variational principle as a variational principle would lead to severe numerical instabilities.

In order to study the effectivness of the singular variational principle for A in a relatively simple context, a number of authors analyzed the scattering of electrons and positrons by a model hydrogen atom, with ϕ_T and E_T for the hydrogen atom assumed to be only imprecisely known.[11-13] The

results, as expected on the basis of the above remarks, contained singularities, and while the presence of singularities does not exclude the possibility of extracting useful results, it is a complicating feature, and none of the authors made any great claims for the results obtained. (Indeed, though the authors did not use that language, they were clearly well aware that at least some of the published figures, representing the estimate of A as a function of the error introduced in ϕ_T and of the number of variational parameters, can begin to remind one of figures which arise in discussions of the ergodic theorem.) In fact, a variational principle for A—more precisely, for an approximation $\tilde{A}$ to A—is now available.[10] The starting point in its development is the replacement of E_T not by the upper variational bound E_{Tt} but by $\bar{E}$, a *lower* variational bound on E_T. Since $\bar{E}$ is not embedded in the continuous spectrum, $H - \bar{E}$ can be inverted without difficulty. An apparent difficulty arises in that the integrals are divergent, but if one notes that the appropriate boundary condition for a wave function associated with an energy below E_T involves an exponentially decaying function, one need merely introduce a convergence factor to avoid the presence of divergent integrals; the complexity of the calculation is thereby only minimally increased. One obtains an extremum principle not for the estimation of A itself but for the estimation of $\tilde{A}$, where $\tilde{A}$ is defined by replacing ϕ_T in an identity for A by ϕ_{Tt}, and $\tilde{A}$ approaches A smoothly as ϕ_{Tt} approaches ϕ_T. Since good estimates of ϕ_T are normally available, $\tilde{A}$ can usually be quite close to A. The fact that the variational estimation of $\tilde{A}$ proceeds by the use of an extremum principle (a variational upper bound) guarantees that no singularities will arise in the course of the analysis.

The variational principle for A, for ϕ_T and E_T only imprecisely known, has not previously been tested. In the same spirit as in the investigations of the singular variational principle, we analyze the variational principle in the *relatively* simple context of scattering by our model hydrogen atom, that is, with ϕ_T and E_T assumed to be only imprecisely known. We consider three cases, the scattering of positrons, the scattering of electrons in the triplet state, and the scattering of electrons in the singlet state. Each case has a distinctive characteristic. In the positron case, the Pauli principle is of course of no relevance, and it is known[14] that no composite bound state exists. In the electron case, there is one and only one composite (H$^-$) bound state[15] that can couple to the scattering states of interest, and that is a singlet state. (The other composite bound states[16] have quantum numbers which differ from those of the

scattering states.) Thus, for the electron in the triplet state, one must account for the indistinguishability of the electrons, while for the singlet state one must account for both the indistinguishability and for the composite bound state.

II. POSITRON-HYDROGEN SCATTERING

A. Preliminaries

Having assumed that the hydrogenic ground-state wave function ϕ_T and ground-state energy E_T are only imprecisely known, we choose as the normalized trial function

$$\phi_t(r_2) = (Z^3/\pi a_0^3)^{1/2} \exp(-Zr_2/a_0), \qquad (2.1)$$

where we drop the subscript T, and where a_0 is the Bohr radius and Z is an arbitrary parameter; ϕ_t clearly reduces to ϕ_T for $Z = 1$. We define E_t—again dropping the subscript T—by

$$E_t = (\phi_t, H_T \phi_t),$$

where, with T_2 the kinetic-energy operator of the electron,

$$H_T = T_2 - e^2/r_2 \qquad (2.2)$$

is the target Hamiltonian, and find

$$E_t = (Z^2 - 2Z)e^2/2a_0 . \qquad (2.3)$$

Our lower variational bound $\bar{E}$ on E_T is obtained from

$$\bar{E} = E_t - [(\langle H_T^2 \rangle - E_t^2)/(E_1 - E_t)], \qquad (2.4)$$

where

$$\langle H_T^2 \rangle \equiv (\phi_t, H_T^2 \phi_t) = Z^2(5Z^2 - 12Z + 8)(e^2/2a_0)^2 .$$

In a realistic problem the energy E_1 of the first excited state would have to be replaced by an upper variational bound, but the estimate of $\bar{E}$ is relatively insensitive to the estimate of E_1 since $E_1 - E_t$ is relatively large, and the insights to be gained from the analysis will be no less if we choose E_1 to be its true value, namely, $E_1 = -e^2/8a_0$. We then have

$$\frac{\bar{E}}{e^2/2a_0} = \frac{20Z^4 - 48Z^3 + 33Z^2 - 2Z}{4Z^2 - 8Z + 1} . \qquad (2.5)$$

[The form for ϕ_t given in Eq. (2.1) and the estimates of E_t, Eq. (2.3), and of $\bar{E}$, Eq. (2.5), will be used for both e^+ and e^- scattering.]

(While the variational principle for $\tilde{A}$ of Ref. 10 is in principle applicable to any atom, the primary domain of applicability, at least for the near future, will clearly be light atoms. For the helium atom, for example, one would determine E_t as above, but one would use experimental data to obtain a bound on E_1 and one could then determine $\bar{E}$ as above. For slightly heavier atoms, such as

carbon, nitrogen, or oxygen, E_t would be evaluated as above, but one would not want to evaluate $\bar{E}$ as above since one would not want to evaluate matrix elements of H^2; one would obtain $\bar{E}$ from experimental data, using the lower limit of the range of values of the ground-state energy allowed by the data. For still heavier atoms, the calculations become more and more difficult. It may even become difficult to choose a ϕ_t good enough to give E_t below E_1, since heavy atoms can have very low-lying excited states. κ, defined by Eq. (2.13) below, might not be sufficiently small to give a reasonable Ψ_t. Questions of heavy atoms are perhaps best left alone until after the method has been applied to helium and some slightly heavier atoms.)

It will be useful while establishing a notation to give a brief summary of the method to be used. The proofs have been given[10] and will be omitted. For positron scattering, we have the identity

$$2\pi(\hbar^2/m)A = (\phi, V\phi) + (\phi, VG(E_T)V\phi) , \qquad (2.6)$$

where

$$V = e^2/r_1 - e^2/r_{12} \qquad (2.7)$$

is the interaction of the positron with the hydrogen atom, and where $G(E) \equiv (E - H)^{-1}$. $G(E_T)$ is perfectly well defined once one imposes appropriate boundary conditions but cannot of course be obtained explicitly. The replacement of ϕ by ϕ_t in Eq. (2.6) defines $\tilde{A} \equiv \tilde{A}(E_T)$; we have

$$2\pi(\hbar^2/m)\tilde{A} = (\phi_t, V\phi_t) + (\phi_t, VG(E_T)V\phi_t) . \qquad (2.8)$$

$\tilde{A}$ clearly reduces to A for $\phi_t = \phi$ and is a good approximation to A if ϕ_t is a good approximation to ϕ. We now introduce $\tilde{A}(\bar{E})$, defined by Eq. (2.8) with E_T replaced by $\bar{E}$. [Though we will not use the fact here, it follows from the monotonicity of $G(E)$ with E for E negative, since $\bar{E} < E_T$, that $G(E_T) < G(\bar{E})$, and therefore that $\tilde{A} \leqslant \tilde{A}(\bar{E})$.] The extremum principle, which is for $\tilde{A}(\bar{E})$ rather than for A, is given by

$$A \approx \tilde{A} \equiv \tilde{A}(E_T) \leqslant \tilde{A}(\bar{E}) \leqslant \tilde{A}_{no}^{(+)} , \qquad (2.9)$$

where

$$2\pi(\hbar^2/m)\tilde{A}_{no}^{(+)} = (\phi_t, V\phi_t) + 2(\phi_t, VF_t)$$
$$+ (F_t, (H - \bar{E})F_t) . \qquad (2.10)$$

The subscript "no" denotes the absence of composite bound states, while F_t is the trial scattered component, an approximation to F, defined by

$$\Psi = \phi + F ,$$

where Ψ is the full wave function describing the scattering process. We emphasize the appearance of $\bar{E}$, rather than of E_T or E_t, in Eq. (2.10). F_t and F satisfy slightly different boundary conditions.

Formally, we have $F_t = G_t(\bar{E})V\phi_t$, where $G_t(\bar{E})$ is an approximation to $G(\bar{E}) = (\bar{E} - H)^{-1}$.

In practice, we will assume a specific form for F_t and determine the linear parameters contained in the chosen form by minimizing $\tilde{A}_{no}^{(+)}$. For the moment, we proceed formally and observe that if, in Eq. (2.10), we vary F_t as an entity, the best possible choice for F_t is defined by

$$V\phi_t + (H - \bar{E})F_t^{best} = 0 ,$$

that is, the best choice is

$$F_t^{best} = G(\bar{E})V\phi_t .$$

The extremum (minimum) value of $\tilde{A}_{no}^{(+)}$ for this choice is readily found to be $\tilde{A}(\bar{E})$.

Looking back at Eq. (2.9), we can now say in summary that $\tilde{A} \equiv \tilde{A}(E_T)$ differs from A because of the replacement of ϕ_T by ϕ_t, while $\tilde{A}(\bar{E})$ differs from $\tilde{A}(E_T)$ because of the replacement of E_T by $\bar{E}$. The expression for $\tilde{A}(\bar{E})$ involves neither ϕ_T nor E_T; the only unknown in the expression is the scattering component $F_t^{best} = G(\bar{E})V\phi_t$. The determination of $\tilde{A}(\bar{E})$ is therefore a problem which is rather similar to a scattering problem for which the properties of the target are precisely known, and we can therefore obtain a variational upper bound on $\tilde{A}(\bar{E})$. If there are no bound states, as in the present case, the upper variational bound is $\tilde{A}_{no}^{(+)}$, a functional of F_t. Since we have an upper variational bound, the numerical upper bound on $\tilde{A}(\bar{E})$—and on $\tilde{A}(E_T)$—will converge monotonically toward $\tilde{A}(\bar{E})$ as the number of basis functions in F_t is increased; there will be no singular behavior and no numerical instability.

B. Calculation

Turning now to the actual calculation, we choose F_t to be of the form

$$F_t(r_1, r_2, r_{12}) = -\tilde{A}_t f_0(r_1, r_2)$$
$$+ \sum_{lmn} c_{lmn} f_{lmn}(r_1, r_2, r_{12}) , \qquad (2.11)$$

where $\tilde{A}_t$ is the trial scattering length and

$$f_0 = \phi_t(r_2)e^{-\kappa r_1}(1 - e^{-\delta r_1})/r_1 . \qquad (2.12)$$

The factor in parentheses is a standard one; it is introduced since f_0 must be finite at the origin. The factor $\exp(-\kappa r_1)$ is unusual; it is required to give convergence at infinity. The nonlinear parameters δ and κ can be adjusted or chosen arbitrarily. In line with the discussion in Ref. 10, we choose κ to be defined by

$$\hbar^2\kappa^2/(2m) = E_t - \bar{E} . \qquad (2.13)$$

r_1 and r_2 are the coordinates of the incident positron and the atomic electron, respectively, rela-

tive to the (infinitely massive) proton, and r_{12} = $|\vec{r}_1 - \vec{r}_2|$. The c_{lmn} are linear variational parameters and the f_{lmn} are short-range correlation terms of the form

$$f_{lm} = r_1^l r_2^m r_{12}^n \exp(-\alpha r_1 - \beta r_2),\qquad (2.14)$$

where l, m, and n are non-negative integers which satisfy $l + m + n \leq \nu$. The maximum value of ν which we will consider is $\nu = 5$. The number N of correlation terms associated with $\nu = 0$ through 5 is N = 1, 4, 10, 20, 35, and 56, respectively.[17] The asymptotic form of the trial scattering wave function,

$$\Psi_t = \phi_t + F_t,\qquad (2.15)$$

is given by

$$\Psi_t \sim \phi_t(r_2)(r_1 - \tilde{A}_t e^{-\kappa r_1})/r_1.\qquad (2.16)$$

The positron-atom interaction potential is given by Eq. (2.7), and the full Hamiltonian is

$$H = H_T + T_1 + V.\qquad (2.17)$$

As Z approaches 1, κ approaches zero and our variational principle reduces, analytically, to the usual Kohn variational principle. Numerically, however, because of the presence of κ in the denominator, we cannot insert the value $Z = 1$, but there are no instabilities even for $Z = 0.999999$, for example. Any values we quote for $Z = 1$ are taken from Kohn-type calculations.

In order to compare our results with the results of previous calculations[11,18] we use

$$\alpha = 0.28 a_0^{-1},\quad \beta = 0.8 a_0^{-1},\quad \delta = 0.3 a_0^{-1}.$$

With only a trivial increase in the complexity of the calculation, that due to the presence of the decay factor $\exp(-\kappa r_1)$, we avoid the numerical

TABLE I. Upper variational bound $\tilde{A}^{(+)}$ on the model problem positron-hydrogen scattering length $\tilde{A}$, as a function of Z, for 20 correlation terms. The nonlinear parameters were fixed at $\alpha = 0.28 a_0^{-1}$, $\beta = 0.8 a_0^{-1}$, and $\delta = 0.3 a_0^{-1}$. The "exact" value of A is $A/a_0 = -2.10$.

Z	$\tilde{A}^{(+)}/a_0$
0.80	−1.93
0.85	−1.87
0.90	−1.81
0.95	−1.76
0.9999	−1.78
1.00 [a]	−1.78
1.05	−1.40
1.10	−1.12
1.15	−0.87
1.20	−0.64

[a] See Ref. 18.

TABLE II. Upper variational bound $\tilde{A}^{(+)}$ on the model problem positron-hydrogen scattering length $\tilde{A}$ as a function of N, the number of correlation terms, for $Z = 0.9999$. The nonlinear parameters were fixed at the values given in Table I. Note the monotonic decrease with N. The "exact" value of A is $A/a_0 = -2.10$.

N	$\tilde{A}^{(+)}/a_0$
0	0.70
1	0.62
4	−1.04
10	−1.42
20	−1.78
35	−1.89
56	−1.97

singularities which have been so troublesome in the past. This can be seen from the results of Tables I and II. In the tables, we drop the subscript no on $\tilde{A}^{(+)}$ since we will use the same functional whether or not composite bound states exist; the effect of the bound states will be taken into account by the form of the trial function chosen, as discussed later. Table I gives the upper variational bound on $\tilde{A}^{(+)}/a_0$ as a function of Z, for $N = 20$, while Table II gives the upper variational bound on $\tilde{A}^{(+)}/a_0$ as a function of N, for $Z = 0.9999$. The upper variational bound exhibits a smooth behavior as a function of Z for fixed N and as a function of N for fixed Z. The values given in Table II, for $N = 4$, 10, 20, and 35 agree with the values obtained in Ref. 18. The results show the predicted monotonic decrease of $\tilde{A}^{(+)}/a_0$ as the number of correlation terms is increased. A very accurate estimate[19] of A is $A/a_0 = -2.10$.

III. ELECTRON-HYDROGEN SCATTERING

We turn now to a study of the scattering length for electrons incident on hydrogen atoms. The identity for A differs from that given in Eq. (2.6) only by the insertion of the space symmetrization or space antisymmetrization operator at appropriate points. As opposed to the analysis of the scattering of electrons by helium, the example considered (formally) in Ref. 10, we need not introduce spin functions, but need merely consider spatially antisymmetric and symmetric functions for the triplet and singlet cases, respectively. (If spin functions are introduced, their inner product is unity for both cases.) The expression for A analogous to that which appears two equations above Eq. (2.11a) of Ref. 10 in the study of $e^- -$ He scattering is

$$2\pi(\hbar^2/m)A = (\mathfrak{A} V\phi, \mathfrak{A}\phi) + (\mathfrak{A} V\phi, G(E_T)\mathfrak{A} V\phi),$$

$$(3.1)$$

where, for $Q(\vec{r}_1, \vec{r}_2)$ an arbitrary function,

$$\mathfrak{A} Q(\vec{r}_1, \vec{r}_2) = 2^{-1/2}[Q(\vec{r}_1, \vec{r}_2) \pm Q(\vec{r}_2, \vec{r}_1)] ;$$

the + and − signs are to be used for the singlet and triplet cases, respectively. V differs from the expression given in Eq. (2.7) by an overall sign. Replacing ϕ by ϕ_t in Eq. (3.1) gives an approximation $A \equiv \tilde{A}(E_T)$ to A. The approximation of $G(E_T)$ by $G(E)$ in Eq. (3.1) gives an upper bound $\tilde{A}(E)$ on $\tilde{A}$. We now consider triplet and singlet scattering separately.

A. Triplet scattering

There is no composite bound state of H⁻ in the triplet state, and we therefore have, for the upper variational bound $\tilde{A}_{no}^{(+)}$ on $\tilde{A}(E)$, as in Eq. (2.11) of Ref. 10, and similar to Eq. (2.10),

$$2\pi(\hbar^2/m)\tilde{A}_{no}^{(+)} = (\mathfrak{A} V\phi_t, \mathfrak{A}\phi_t) + 2(\mathfrak{A} V\phi_t, F_t)$$
$$+ (F_t, (H - \bar{E})F_t), \qquad (3.2)$$

where, formally,

$$F_t = G_t(\bar{E})\mathfrak{A} V\phi_t. \qquad (3.3)$$

In practice, the trial function F_t will be taken to be the antisymmetrized version of the form given in Eq. (2.11). In terms of the number of different forms, this is equivalent to imposing the condition $l > m$, and the number N of (different) correlation terms associated with $\nu = 1$ through 6 is now $N = 1$, 3, 7, 13, 22, and 34, respectively.[17] Table III shows the smooth variation of $\tilde{A}^{(+)}/a_0$ as a function of Z and the smooth monotonic variation as a function of N. The values of $\tilde{A}^{(+)}/a_0$ for $Z = 0.999\,999$ and $\alpha = \beta = \delta = 0.4a_0^{-1}$ agree, for any value of N, with those given by Schwartz.[19] Table IV shows, for $Z = 0.999\,999$, the smooth monotonic convergence of $\tilde{A}^{(+)}/a_0$ as a function of N for dif-

TABLE III. Upper variational bound $\tilde{A}^{(+)}$ on the model problem triplet electron-hydrogen scattering length $\tilde{A}$ in the Born approximation [$F_t = 0$ in Eq. (3.2)] and as a function of N for different values of Z for $\alpha = \beta = \delta = 0.4a_0^{-1}$. Note the monotonic decrease with N for any given value of Z. The "exact" value of A is $A/a_0 = 1.7$.

	$\tilde{A}^{(+)}/a_0$				
N	$Z = 0.9$	$Z = 0.95$	$Z = 0.999\,999$	$Z = 1.05$	$Z = 1.1$
Born	6.17	5.54	5.00	4.54	4.13
0	3.51	2.92	2.38	2.81	2.96
1	3.47	2.88	2.38	2.79	2.94
3	2.97	2.45	2.10	2.44	2.58
7	2.91	2.42	2.04	2.37	2.51
13	2.80	2.31	1.96	2.28	2.42
22	2.74	2.29	1.93	2.25	2.39
34	2.71		1.90		

TABLE IV. Upper variational bound $\tilde{A}^{(+)}$ on the model problem triplet electron-hydrogen scattering length $\tilde{A}$ as a function of N for different values of the parameter $\rho \equiv \alpha a_0 = \beta a_0 = \delta a_0$. Z is fixed at $Z = 0.999\,999$. Note the monotonic decrease with N for any given value of ρ. The "exact" value of A is $A/a_0 = 1.77$.

	$\tilde{A}^{(+)}/a_0$			
N	$\rho = 0.3$	$\rho = 0.4$	$\rho = 0.5$	$\rho = 0.6$
0	2.43	2.38	2.36	2.35
1	2.43	2.38	2.35	2.35
3	2.22	2.10	2.10	2.20
7	2.13	2.04	2.04	2.07
13	2.01	1.96	1.98	2.02
22	1.95	1.93	1.95	1.98

ferent values of the nonlinear parameters. The variation of $\tilde{A}^{(+)}$ for different values of these nonlinear parameters is not very great—as usual, the linear variational parameters "adjust" to the choice of the nonlinear parameters. More significant is the absence of any numerical instability. A very accurate estimate[19] of A is $A/a_0 = 1.77$.

B. Singlet scattering

For singlet scattering, we choose F_t to be the symmetrized version of the form given in Eq. (2.11). In terms of the number of different forms, this is equivalent to imposing the condition $l \geqslant m$, and the number N of different correlation terms, for $\nu = 0$ through 5, is now $N = 1$, 3, 7, 13, 22, and 34, respectively.[17]

A significant difference between singlet $e^- - $H scattering and both $e^+ - $H and triplet $e^- - $H scattering is the existence of a singlet bound state. Its calculated energy is

$$\mathcal{E}_1(\text{H}^-) = -0.527\,739\,e^2/a_0.$$

One must extract the effects of the composite bound state if one is to obtain a variational upper bound, denoted by $\tilde{A}_{one}^{(+)}$, on $\tilde{A}(\bar{E})$. One finds [see Eq. (3.5b) of Ref. 10]

$$2\pi(\hbar^2/m)(\tilde{A}_{one}^{(+)} - \tilde{A}_{no}^{(+)}) = \frac{|(\Phi_{1t}, (H - \bar{E})F_t + \mathfrak{A} V\phi_t)|^2}{\bar{E} - \mathcal{E}_{1t}},$$
$$(3.4)$$

where Φ_{1t} is a normalized trial composite bound-state wave function good enough to give an assoicated trial bound-state energy,

$$\mathcal{E}_{1t} = (\Phi_{1t}, H\Phi_{1t}),$$

which satisfies

$$\mathcal{E}_{1t} < \bar{E},$$

and $\tilde{A}_{no}^{(+)}$ is given by Eq. (3.2). Equation (3.4) is a perfectly good starting point for the calculation, but a slightly simpler procedure is suggested by the following discussion; we will, at the same time, gain some further insight into the significance of $\tilde{A}_{one}^{(+)}$. Thus, we go back to Eq. (3.2) for $\tilde{A}_{no}^{(+)}$ but use a modified form for F_t. (This procedure was not discussed in Ref. 10, but is quite similar to procedures discussed in the case for which ϕ_T and E_T were known and there was one composite bound state.[8]) We choose F_t in Eq. (3.2) to be of the form

$$F_t = F_t' + c_1 \Phi_{1t}. \tag{3.5}$$

Setting the variation of $\tilde{A}_{no}^{(+)}$ with respect to c_1 equal to zero, one finds

$$c_1 = \frac{(\Phi_{1t}, (H - \bar{E})F_t' + \alpha V \phi_t)}{\bar{E} - \mathcal{E}_{1t}}.$$

With this value of c_1, the expression for $\tilde{A}_{no}^{(+)}$ that contains F_t' reduces to the expression for $\tilde{A}_{one}^{(+)}$ that contains F_t. In summary, rather than explicitly extracting the effects of the bound-state wave-function component of our trial scattering wave function, as in the original derivation[10] of $\tilde{A}_{one}^{(+)}$, we have allowed the variational principle to do the work for us.

Having seen that a connection exists between the formal and variational derivation of $\tilde{A}_{one}^{(+)}$, we consider (formally) one other form for F_t. Choosing K basis functions, we construct a $K \times K$ matrix of H, which we diagonalize. We thereby obtain the functions Φ_{nt}, $n = 1$ to K, which satisfy

$$(\Phi_{nt}, \Phi_{mt}) = \delta_{nm},$$

$$(\Phi_{nt}, H\Phi_{mt}) = \mathcal{E}_{nt}\delta_{nm}.$$

We assume that $\bar{E}$ is close enough to E_T and that our choice of basis functions is good enough to generate one eigenvalue below $\bar{E}$; we label this eigenvalue $\mathcal{E}_{1t}$. Clearly, since H⁻ has only one (singlet) composite bound state, there cannot be more than one eigenvalue which lies below $\bar{E}$. If $\bar{E}$ is so poorly chosen that $\bar{E}$ lies below $\mathcal{E}_1$, it will not be possible with any basis functions to obtain any eigenvalue below $\bar{E}$. (We will discuss this case below.) We now write

$$F_t = -\tilde{A}_t f_0 + \sum c_n \Phi_{nt}, \tag{3.6}$$

where f_0 is defined by Eq. (2.12), and insert this expression into Eq. (3.2) for $\tilde{A}_{no}^{(+)}$. Varying with respect to c_n and equating the result to zero gives

$$c_n = \frac{(\Phi_{nt}, (H - \bar{E})(-\tilde{A}_t f_0) + \alpha V \phi_t)}{\bar{E} - \mathcal{E}_{nt}},$$

and we then have

$$2\pi(\hbar^2/m)\tilde{A}_{no}^{(+)} = (\alpha V \phi_t, \alpha \phi_t) - 2\tilde{A}_t(\alpha V \phi_t, f_0)$$
$$+ \tilde{A}_t^2(f_0, (H - \bar{E})f_0)$$
$$+ \sum_{n=1}^{K} \frac{|(\Phi_{nt}, \alpha V \phi_t + (H - \bar{E})(-\tilde{A}_t f_0))|^2}{\bar{E} - \mathcal{E}_{nt}}.$$
$$\tag{3.7}$$

The interesting aspect of this last expression is the demonstration that as one improves F_t by including additional terms, as in Eq. (3.6), one contribution, that associated with Φ_{1t}, is positive, while all others cause the estimate to decrease monotonically. The discussion above suggests, but does not prove, that if one improves F_t not by adding terms as in Eq. (3.6) but, for example, as in Eq. (2.11), there will be at most one upward jump. (A formal proof can be constructed along the lines of the proof given for the case for which ϕ_T and E_T are known.[20])

We now return to the actual calculation. We use $\tilde{A}_{no}^{(+)}$ as given by Eq. (3.2), rather than $\tilde{A}_{one}^{(+)}$, and expect at most one upward jump if we fix Z and increase N. With the choice $Z = 0.999\,999$ our singlet results agree with those of Schwartz.[19] We now consider different choices of Z. From Eq. (2.5) we have

$$\bar{E}(Z = 1.15) = -0.570\,554\, e^2/a_0 < \mathcal{E}_1,$$

but the value of $\tilde{E}(Z = 1.10)$ lies (just) below $\mathcal{E}_1$,

$$\bar{E}(Z = 1.10) = -0.527\,702\, e^2/a_0 > \mathcal{E}_1.$$

The values of $\bar{E}$ for $Z = 0.90$, $0.999\,999$, and 1.05 also lie above $\mathcal{E}_1$. It follows that $\tilde{A}^{(+)}$ for $Z = 1.15$ will converge monotonically to the value $\tilde{A}(\bar{E})$, obtained from Eq. (3.1) by replacing E_T with $\bar{E}$. [If $\tilde{E}(Z)$ lies immediately below $\mathcal{E}_1$ we can expect a *very large* negative estimate. In Eq. (3.1), we approximate ϕ by ϕ_t and E_T by $\bar{E}$ and obtain $\tilde{A}(\bar{E})$. For $\bar{E}$ sufficiently close to $\mathcal{E}_1$ and therefore for a good Φ_{1t} to $\mathcal{E}_{1t}$, we can drop the Born term and approximate $G(\bar{E})$ by

$$G(\bar{E}) \approx \frac{|\Phi_{1t}\rangle\langle\Phi_{1t}|}{\bar{E} - \mathcal{E}_{1t}}$$

to obtain

$$2\pi(\hbar^2/m)\tilde{A}(\bar{E}) \approx -|(\alpha V \phi_t, \Phi_{1t})|^2/(\mathcal{E}_{1t} - \bar{E}).]$$

There will be no upward jumps since there are no composite bound states which lie below $\bar{E}(Z = 1.15)$. These expectations are borne out by the numerical results given in Table V. For $Z = 0.9$ $\tilde{A}_{no}^{(+)}$ will undergo at most one upward jump as N is increased. In fact, as seen in Table V, there is one upward jump, indicating that neither of the trial functions for $N = 0$ and $N = 1$ contain components which represent the composite bound state with sufficient accuracy for this value of Z, and that

TABLE V. Upper variational bound $\bar{A}^{(+)}$ on the model problem singlet electron-hydrogen scattering length $\bar{A}$ in the Born approximation [$F_t = 0$ in Eq. (3.2)] and as a function of N for different values of Z for $\alpha = \beta = \delta = 0.5a_0^{-1}$. Note that for the four values of Z from 0.9 to 1.10, each of which generates an $\bar{E}$ which lies above $\mathcal{E}_1$, there is one and only one jump; for $Z = 1.15$, for which $\bar{E}$ lies (just) below $\mathcal{E}_1$, there is no jump, and the estimate becomes very large and negative. The "exact" value of A is $A/a_0 = 5.95$. $Z = Z^*$ represents $Z = 0.999\,999$.

| | | | $\bar{A}^{(+)}/a_0$ | | |
N	$Z = 0.9$	$Z = Z^*$	$Z = 1.05$	$Z = 1.10$	$Z = 1.15$
Born	−8.64	−7.00	−6.35	−6	−5.3
0	−40.58	8.30	35.74	−19	−9.1
1	−56.83	8.19	34.87	−20	−9.5
3	213.38	6.91	16.78	−57	−14.1
7	68.19	6.35	13.69	−209	−16.1
13	58.07	6.22	13.06	−789	−17.1
22	55.66	6.15	12.85	−3 708	−17.4
34	55.09	6.12	12.75	−36 512	−17.5
40				+25 844	

the trial function for $N = 3$ has such a component. A very accurate estimate[19] of A is $A/a_0 = 5.95$.

The single upward jump for $Z = 0.999\,999$ and 1.05 occurs in passing from the Born approximation ($F_t = 0$) to the trial function corresponding to $N = 0$.[17] This latter function is now sufficiently accurate for these values of Z while it was not for $Z = 0.9$. That is, since $\bar{E}$ lies closer to E_T in these cases the condition on the trial composite bound-state function is less stringent and is satisfied even in the absence of correlation terms. For $Z = 1.10$, for which $\bar{E}$ lies just above $\mathcal{E}_1$, the single jump does not occur until

$N = 40!$ It might at first be somewhat disappointing that the estimate for $Z = 0.9$ is so bad even for $N = 34$, but ϕ_t for $Z = 0.9$ is in some ways a rather bad trial function; although the overlap of ϕ_t ($Z = 0.9$) with ϕ_T is close to unity, $\bar{E}(Z = 0.9)$ lies closer to $\mathcal{E}_1$ than to E_T. The hydrogen atom may be extremely simple compared to other atoms, but the existence of a very weakly bound composite state with an electron is a complicating feature for the study of singlet scattering.

Though the variational principle of Demkov[9] is singular, it is stationary with respect to errors in the trial ground-state wave function ϕ_t, that is, if one has a good trial scattering function Ψ_t, the error in the estimate of A is of second order in all errors in Ψ_t, including errors in ϕ_t. On the other hand, while the variational principle of Ref. 10, on which the present paper is based, is nonsingular, it is stationary with respect to all errors in Ψ_t other than errors in ϕ_t; it is a nonsingular variational principle for an approximation $\bar{A}$ to A. Both procedures therefore have a weakness. However, it is possible to avoid both difficulties. A nonsingular variational principle for the true scattering length has very recently been obtained[21]; it has difficulties of its own, which we hope can be eliminated.

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