Variational *lower* bound on the scattering length*

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The scattering length A characterizes the zero-energy scattering of one system by another. It was shown some time ago that a variational upper bound on A could be obtained using methods, of the Rayleigh-Ritz type, which are commonly employed to obtain upper bounds on energy eigenvalues. Here we formulate a method for obtaining a variational *lower* bound on A. Once again the essential idea is to express the scattering length as a variational estimate plus an error term and then to reduce the problem of bounding the error term to one involving bounds on energy eigenvalues. In particular, the variational lower bound on A is rigorously established provided a certain modified Hamiltonian can be shown to have no discrete states lying below the level of the continuum threshold. It is unfortunately true that necessary conditions for the existence of bound states are not available for multiparticle systems in general. However, in the case of positron-atom scattering the adiabatic approximation can be introduced as an (essentially) solvable comparison problem to rigorously establish the nonexistence of bound states of the modified Hamiltonian. It has recently been shown how the validity of the variational upper bound on A can be maintained when the target ground-state wave function is imprecisely known. Similar methods can be used to maintain the variational lower bound on A. Since the bound is variational, the error in the calculated scattering length will be of second order in the error in the wave function. The use of the adiabatic approximation in the present context places no limitation in principle on the accuracy achievable.

I. INTRODUCTION

A. Variational upper bounds

The techniques involved in the determination of a variational lower bound on the scattering length which we here seek to establish bear many analogies to those involved in the simpler and better known variational upper bound on the scattering length, and we will therefore begin with some discussion of the latter.

A variational *upper* bound on the scattering length A which characterizes the scattering at zero incident kinetic energy of one system by another was obtained some time ago.[1] From some points of view, the results are applicable to a very wide class of problems—the interaction can include tensor forces or long-ranged repulsive Coulomb interactions, the two scattering systems can form composite bound states,[2] the relative orbital angular momentum of the two systems is unrestricted, and the various particles of the two systems can be distinguishable or indistinguishable. On the other hand, the original result was valid only under the very severe restriction that the ground-state wave functions and energies of the isolated systems had to be known exactly. The results could therefore be applied only to relatively simple but still quite interesting cases, including the (singlet or triplet) scattering of electrons and the scattering of positrons by H, He, Li^+, ..., and, for an assumed nucleon-nucleon potential, with the deuteron ground-state wave function and energy taken to be calculable, numerically if necessary, to doublet and quartet neutron-deuteron and proton-deuteron scattering. A number of applications were made. The calculations are really no more difficult than, and are often identical to, variational principle calculations,[3,4] but the variational bound results are, of course, much more incisive; we know not only that the error in our estimate of A is of second order in some weighted average of the error in the trial scattering wave function Ψ_t, but of well-defined sign.

After a hiatus of some fifteen years, the upper variational bound on A was recently extended to include the very much broader class of problems for which the ground-state target functions and energies are only imprecisely known.[5,6] Unfortunately if not unexpectedly, the extension is at the price of requiring more elaborate calculations. (We note that slightly different treatments must be used for a positron[5] and for an electron[6] incident on an atom, the difference arising from the indistinguishability of the incident electron and the subsequent need to bound the associated exchange integrals that have no counterpart for an incident positron.) The approach for imprecisely known target ground-state wave functions has as its starting point the variational bound for precisely known target ground-state wave functions. These are of the form $A \leq K(\Psi_t)$, with $K(\Psi_t)$ a specified functional of the trial scattering function Ψ_t. The target ground-state wave function ψ_{T0} appears in $K(\Psi_t)$ in the specification of the appropriate boundary conditions to be satisfied by Ψ_t. For ψ_{T0} imprecisely

known, we express Ψ_t formally in terms of ψ_{T0}, effectively integrate over the coordinates of the incident particle, and thereby reduce $A \leq K(\Psi_t)$ to $A \leq L(\psi_{T0})$, where L is again a specified functional. At this stage, the calculation no longer retains any scattering problem aspects; the determination of a variational upper bound on the scattering length A has been reduced to the determination of a variational upper bound on $L(\psi_{T0})$, which requires a variational bound on *bound*-state matrix elements involving the well-defined but imprecisely known ψ_{T0}, and its associated energy E_{T0}. But this is a problem that has been solved.[5,7] The variational upper bound on $L(\psi_{T0})$ involves matrix elements of H_T^2 as well as of H_T, where H_T is the target Hamiltonian, and thus far only a few very preliminary results have been obtained. There is every reason to assume, however, that not merely useful but definitive results could be obtained at least for relatively simple cases such as the scattering of positrons and electrons by helium atoms.

B. Lower bounds and variational lower bounds

We now turn to the problem at hand, the development of a variational lower bound on A. The development of the upper variational bound on A proceeds along the lines of the Rayleigh-Ritz principle, being based on the fact that A characterizes the state of lowest energy (or at least the continuum state of lowest energy), and it is to be expected that a lower variational bound on A will be much more difficult to develop than an upper one. We will temporarily assume that ψ_{T0} and E_{T0} are known, and begin with a brief review of earlier work touching on this problem. (Though of no concern to us here, we note that *when applicable* the methods reviewed in the following two paragraphs provide bounds not only on A but on the phase shift as well.)

It was shown[8] that a lower (nonvariational) bound on A can sometimes be obtained by the replacement of the energy denominator of the exact, if only formally known, optical potential by an appropriately chosen energy value; the "sometimes" relates to the fact that it is not always possible to find an energy value satisfying the necessary requirements. The result was extended somewhat by Hahn.[9] Sugar and Blankenbecler went further.[10] They also started with the optical potential but obtained a variational lower bound on A; again, however, a lower bound on an energy eigenvalue had to be obtained, and this can sometimes be very difficult. Additional results, largely formal and along much the same lines, were obtained by Hahn and Spruch,[11] and some numerical applications have been reported.[12] Very recently, a modification of this approach has been developed for positron-atom scattering which preserves the variational lower bound on A when the target wave function is not known precisely.[13] It is well known[10] that for potential scattering by a non-negative potential V, it is trivial to obtain a separable potential V_{sep} which satisfies the operator inequality $V \geq V_{\text{sep}}(\chi) \geq 0$, where the χ in the functional $V_{\text{sep}}(\chi)$ can be interpreted as a trial scattering function Ψ_t. The merit of the inequality lies in the fact that a potential scattering problem with a separable potential is easily solvable. Let A_{sep} be the scattering length associated with V_{sep}. The monotonicity theorem and the inequality $V \geq V_{\text{sep}}$ then guarantee that $A \geq A_{\text{sep}}$. Since $V - V_{\text{sep}}$ is of second order in $\delta\Psi \equiv \Psi_t - \Psi$, where Ψ is the exact scattering wave function, A_{sep} is a variational lower bound on A for this very special case. The A_{sep} that follows from V_{sep} also follows on using the Schwinger integral variational principle with $\Psi_t = \chi$, and the variational lower bound is therefore sometimes referred to as the Schwinger bound. The validity of the Schwinger bound was first recognized by Kato[14] who showed that it followed from a variational bound procedure[15] based on the introduction of an "associated potential-strength eigenvalue problem."

Clearly, the methods referred to above for obtaining lower bounds on A are of limited applicability. Results valid only for potential scattering, particularly if the potentials are required to be of well-defined sign, are of themselves of little interest. The results based on the optical potential, a potential specifically constructed to account for the effects of internal degrees of freedom, can be limited by the requirement that one find a bound on an energy eigenvalue. The Kato method is useful only if one can obtain some appropriate bounds on the potential-strength eigenvalues. This method, originally introduced in the study of potential scattering problems, was straightforwardly extended to a number of problems involving the scattering of electromagnetic waves by obstacles in wave guides, with simple geometries[16]; these problems are the analogs of one-dimensional quantum-mechanical scattering by targets with very simple internal degrees of freedom. We note, incidentally, that essentially *all* of the quantum-mechanical methods noted above can be rather easily carried over to many wave-guide problems.[17] Some further remarks on the Kato approach are contained in Appendix A.

Of particular interest to us for the purposes of the present paper is the fact that one can use the adiabatic approximation to obtain a (nonvariational) lower bound on A for the scattering of a positron by an atom if the adiabatic potential, $V_{\text{ad}}(r)$, is known and if the one-body Hamiltonian $T(R) + V_{\text{ad}}(r)$

cannot support a bound state.[18] (V_{ad} is the potential obtained on fixing the atomic nucleus and the positron, allowing only the electrons to move.) The lower bound on A for e^+-He scattering that was obtained using the adiabatic approximation was surprisingly good. While unpublished work by Hahn and Spruch suggests that it should be possible to extend the method to e^--atom scattering, and to promote the lower bound to a variational lower bound, the results can be expected to be very difficult to apply. The approach of this paper, which is restricted to e^+-atom scattering, will be to start with a formal identity of the form $A = A_{var} - (m/2\pi\hbar^2)S$ where A_{var} is a functional of Ψ_t and can be calculated, while S is a second-order term which can be bounded by using the adiabatic approximation as a comparison problem. As Ψ_t becomes better and better, S becomes smaller and smaller, and the use of the adiabatic approximation to bound S—*not* to obtain a direct bound on A—therefore places no limitation whatever on the accuracy achievable.

II. A FORMAL BOUND ON THE SECOND-ORDER TERM, S

A. Preliminaries

We consider the scattering of a distinguishable particle incident with zero kinetic energy on a target with internal degrees of freedom. Though the analysis is applicable to a somewhat wider class of problems, we will, for clarity of presentation and because it is the most obvious application, give the analysis in the context of e^+-atom scattering. To further simplify the discussion, we will make a number of assumptions, some of which will later be shown to be unnecessary. The assumptions are the following.

(i) The target is infinitely massive and electrically neutral, and is initially in its ground state which we take to be spherically symmetric.

(ii) The interaction between the incident positron and the target is spin independent.

(iii) The lowest energy of the system e^+ + atom is E_{T0}, the ground-state energy of the isolated atom. (More precisely, we assume that the positron and atom cannot form a composite bound state with energy less than E_{T0} *or* equal to E_{T0}, and that, at zero incident kinetic energy, pickup is energetically impossible.) Ignoring the small possibility of e^+-e^- annihilation, it follows that for zero incident kinetic energy, elastic scattering of the positron is the only possible scattering process.

(iv) The incident particle has an initial relative orbital angular momentum $l=0$. (The case $l>0$ is not of comparable interest, since for sufficiently low energy the scattering is then completely determined by the electric-dipole polarizability.)

(v) The (normalized) fully antisymmetrized target ground-state wave function, $\psi_{T0}(\vec{\mathbf{r}})$, where $\vec{\mathbf{r}}$ represents the totality of target space and spin coordinates, and the target ground-state energy E_{T0}, are known.

The starting point for the derivation of a variational lower bound on A is the easily derived formal identity[1]

$$A = A_{var} - (m/2\pi\hbar^2)S\,, \tag{2.1a}$$

where m is the positron mass, and where

$$A_{var} \equiv A_t + (m/2\pi\hbar^2)\int \Psi_t(H - E_{T0})\Psi_t\, d\vec{\mathbf{r}}\, d\vec{\mathbf{R}} \tag{2.1b}$$

is the explicit and calculable variational estimate, and

$$S \equiv (\delta\Psi, (H - E_{T0})\delta\Psi) \tag{2.1c}$$

is a purely formal expression, which cannot be evaluated, proportional to the second-order error difference between the exact scattering length A and A_{var}. $\vec{\mathbf{R}}$ is the positron coordinate,

$$H = H(\vec{\mathbf{r}}, \vec{\mathbf{R}}) = H_T(\vec{\mathbf{r}}) + T_{\vec{\mathbf{R}}} + V(\vec{\mathbf{r}}, \vec{\mathbf{R}}) \tag{2.2}$$

is the full Hamiltonian, $H_T(\vec{\mathbf{R}})$ is the target Hamiltonian, $T_{\vec{\mathbf{R}}}$ is the kinetic-energy operator of the incident positron, and $V(\vec{\mathbf{r}}, \vec{\mathbf{R}})$ is the positron-atom interaction. The exact scattering wave function $\Psi(\vec{\mathbf{r}}, \vec{\mathbf{R}})$ satisfies

$$(H - E_{T0})\Psi = 0\,, \tag{2.3}$$

and the boundary conditions that it be finite everywhere and that

$$\begin{aligned} &\Psi(\vec{\mathbf{r}}, \vec{\mathbf{R}}) \sim 0\,, \quad r \sim \infty\,, \\ &\Psi(\vec{\mathbf{r}}, \vec{\mathbf{R}}) \sim \psi_{T0}(\vec{\mathbf{r}})(R - A)/R\,, \quad R \sim \infty\,. \end{aligned} \tag{2.4}$$

The trial function Ψ_t is everywhere finite and satisfies the boundary conditions

$$\begin{aligned} &\Psi_t(\vec{\mathbf{r}}, \vec{\mathbf{R}}) \sim 0, \quad r \sim \infty\,, \\ &\Psi_t(r, R) \sim \psi_{T0}(\vec{\mathbf{r}})(R - A_t)/R, \quad R \sim \infty\,, \end{aligned} \tag{2.5}$$

but is otherwise arbitrary; A_t is the trial scattering length. The error function $\delta\Psi$, which is formally of first order, is defined by

$$\delta\Psi(\vec{\mathbf{r}}, \vec{\mathbf{R}}) = \Psi_t(\vec{\mathbf{r}}, \vec{\mathbf{R}}) - \Psi(\vec{\mathbf{r}}, \vec{\mathbf{R}})\,. \tag{2.6}$$

It follows that $\delta\Psi$ is everywhere finite and that

$$\begin{aligned} &\delta\Psi(\vec{\mathbf{r}}, \vec{\mathbf{R}}) \sim 0, \quad r \sim \infty\,, \\ &\delta\Psi(\vec{\mathbf{r}}, \vec{\mathbf{R}}) \sim \text{const} \times \psi_{T0}(\vec{\mathbf{r}})R^{-1}, \quad R \sim \infty\,, \end{aligned} \tag{2.7}$$

where the constant is $A - A_t$. The target wave functions $\psi_{Tn}(\vec{\mathbf{r}})$ are orthonormal and satisfy

$$(H_T - E_{Tn})\psi_{Tn}(\vec{\mathbf{r}}) = 0\,. \tag{2.8}$$

ψ_{T0} is the ground-state wave function. By assumption (iii), we have

$$H - E_{T0} \geq 0 \tag{2.9}$$

in the space of functions which are quadratically integrable or[1] approach const$\times \psi_{T0}(\vec{r})R^{-1}$ as $R \sim \infty$. We will refer to the latter class of functions as asymptotically constant functions, and note that $\delta\Psi$ is such a function. It follows immediately that $S \geq 0$ and therefore that $A \leq A_{\text{var}}$; this is the original upper variational bound.[1] To obtain the lower variational bound on A that is our present interest, it will be necessary to bound S from above by an expression that is itself of second order. (Since we are seeking a variational bound on A and since S is already of second order, we do not need a variational bound on S; we merely need a "simple" bound on S, that is, one which is of the same order as S.)

B. A formal bound on S

We consider some Hermitian operator C which has a left and right inverse, that is,

$$CC^{-1} = C^{-1}C = 1, \tag{2.10}$$

and such that the various expressions below in which it appears are finite, but which is otherwise arbitrary. It is then trivial to check that S as given by Eq. (2.1c) can be rewritten as

$$\begin{aligned} S = &(\!(H - E_{T0})\delta\Psi, C^{-1}(H - E_{T0})\delta\Psi\!) \\ &-(\!(\delta\Psi, (H - E_{T0} - C)\delta\Psi\!) \\ &-(\!(H - E_{T0} - C)\delta\Psi, C^{-1}(H - E_{T0} - C)\delta\Psi\!). \end{aligned} \tag{2.11}$$

Let us now make the further assumption that

$$H - E_{T0} - C \geq 0 \tag{2.12}$$

and

$$C \geq 0, \tag{2.13}$$

where both inequalities are in the space of asymptotically constant functions. Including the minus signs in front, the second and third terms in Eq. (2.11) are therefore nonpositive and we have

$$S \leq (\!(H - E_{T0})\delta\Psi, C^{-1}(H - E_{T0})\delta\Psi\!). \tag{2.14}$$

Note that each of the $\delta\Psi$'s in (2.14) is preceded by $H - E_{T0}$. That is the point of obtaining the inequality in the form (2.14), for it is an immediate consequence of Eqs. (2.6) and (2.3) that

$$(H - E_{T0})\delta\Psi = (H - E_{T0})\Psi_t. \tag{2.15}$$

We can therefore rewrite (2.14) as

$$S \leq (\!(H - E_{T0})\Psi_t, C^{-1}(H - E_{T0})\Psi_t\!). \tag{2.16}$$

In this form, the unknown function $\delta\Psi$ no longer appears, and we will be able to bound S from above if we can find a C which satisfies (2.10), (2.12), and (2.13). If we can produce such a C, we will have the variational lower bound

$$A \geq A_{\text{var}} - (m/2\pi\hbar^2)(\!(H - E_{T0})\Psi_t, C^{-1}(H - E_{T0})\Psi_t\!). \tag{2.17}$$

The validity of the replacement of the definition (2.1c) of S by (2.11) is trivially verified, but the step is scarcely well motivated. A more obvious if more circuitous route can be based on the discussion in Appendix B, where S will be expressed in terms of the full Green's function G of the system. Since we can bound S from above, it is not therefore surprising that we can bound G from above.

III. ADIABATIC APPROXIMATION AND A CHOICE OF C

We seek a lower bound C on $H - E_{T0}(\geq 0)$ in the space of asymptotically constant functions, where C must itself be non-negative. The procedure we will follow is based on the realization[18] that the adiabatic approximation provides a lower bound on H, and the fact that the adiabatic potential can actually be calculated nowadays for at least some light atoms. Thus, fix the positron at the distance R, and let $\mathcal{E}_0(R)$ be the lowest of the eigenvalues $\mathcal{E}_n(R)$ of $H_T + V$, defined by

$$[H_T(\vec{r}) + V(\vec{r};\vec{R}) - \mathcal{E}_n(\vec{R})]\phi_n(\vec{r};\vec{R}) = 0, \tag{3.1}$$

where R is treated as a parameter,

$$\int |\phi_n(\vec{r};\vec{R})|^2 d\vec{r} = 1, \quad \text{for all } R, \tag{3.2}$$

and

$$\phi_n(\vec{r};\vec{R}) \sim \psi_{Tn}(\vec{r}), \quad R \sim \infty. \tag{3.3}$$

By construction, we then have

$$H_T(\vec{r}) + V(\vec{r};\vec{R}) \geq \mathcal{E}_0(R) \tag{3.4}$$

in the space of asymptotically constant functions. Introducing the adiabatic potential V_{ad} defined by

$$V_{\text{ad}}(R) \equiv \mathcal{E}_0(R) - E_{T0}, \tag{3.5}$$

we then have

$$H(\vec{r},\vec{R}) - E_{T0} \geq T_{\vec{R}} + V_{\text{ad}}(R). \tag{3.6}$$

Since $V_{\text{ad}}(R) \sim 0$ as $R \sim \infty$, the lower bound on $H - E_{T0}$ provided by (3.6) represents a simple one-body Hamiltonian. Furthermore, as noted above, $V_{\text{ad}}(R)$ can often be calculated quite easily. Thus, molecular chemists and molecular physicists can calculate the ground-state energy $\mathcal{E}_0(R)$ of a fixed proton and a light atom, and a fixed positron gives exactly the same energy as a fixed proton. The $V_{\text{ad}}(R)$ thereby arrived at will not be exact, but the error could be at least roughly estimated and one could choose a $V_{\text{ad}}(R)$ more or less guaranteed to satisfy (3.6); we are concerned with a second-

order term S, and a considerable safety margin could be tolerated in the choice of V_{ad} without a serious effect on the accuracy of our variational lower bound on A.

By assumption (iii), we have $H - E_{T0} \geq 0$. It clearly does *not* follow that $T + V_{ad}$ (which is bounded from above by $H - E_{T0}$) is non-negative, but $T + V_{ad}$ is a one-body Hamiltonian, and it is a simple matter to determine whether or not it is non-negative. For positrons on helium atoms, for example, the use of the rather accurately known adiabatic interaction for protons and helium atoms[19] enables one to show[18] rather simply that there is no composite bound state of $e^+ + \mathrm{He}$ in the adiabatic approximation (nor, therefore, for the true problem). If $T + V_{ad}$ can support one or more bound states, the adiabatic approximation will not as it stands serve our purpose. [One can consider an improved adiabatic approximation. Thus, a positron and a hydrogen atom can form a composite bound state in the usual adiabatic approximation in which one fixes the $\vec{R}$ value of the positron; if, however, one first projects onto the subspace of zero total orbital angular momentum and then freezes the R value of the positron, so that the position is not fixed but has the (restricted) freedom to move on the surface of a sphere of radius R, one can show[20] that a positron cannot be bound to a hydrogen atom. Calculations in the improved adiabatic approximation are, of course, more difficult than those in the usual adiabatic approximation.] If $T + V_{ad}$ cannot support any bound states, as we will assume from now on, we have

$$H(\vec{r}, \vec{R}) - E_{T0} \geq T_{\vec{R}} + V_{ad}(R) > 0 . \tag{3.7}$$

We are now within one step of our goal. Since $T + V_{ad}$ cannot support a bound state, it will be possible by choosing λ positive but sufficiently small to introduce an artificial non-negative potential

$$V_{art}(R) = \lambda v_{art}(R) \geq 0 , \tag{3.8}$$

such that

$$T_{\vec{R}} + V_{ad}(R) - V_{art}(R) \geq 0 . \tag{3.9}$$

We then have

$$H(\vec{r}, \vec{R}) - E_{T0} - V_{art}(R) \geq T_{\vec{R}} + V_{ad}(R) - V_{art}(R) \geq 0 , \tag{3.10}$$

or, equivalently, but much more to the point,

$$H(\vec{r}, \vec{R}) - E_{T0} \geq V_{art}(R) . \tag{3.11}$$

It follows that one possible choice for C is

$$C = V_{art}(R) . \tag{3.12}$$

Equation (2.16) then becomes

$$S \leq \int V_{art}^{-1}(R) |[H(\vec{r}, \vec{R}) - E_{T0}] \Psi_t(\vec{r}, \vec{R})|^2 \, d\vec{r} \, d\vec{R} . \tag{3.13}$$

We turn now to the choice of $V_{art}(R)$.

IV. THE CHOICE OF $V_{art}(R)$

We must choose V_{art} such that the inequality (3.9) is valid and such that the integral in (3.13) exists. The first condition demands that V_{art} not fall off too slowly, while the second condition demands that V_{art} not fall off too rapidly. We are thereby very limited in our possible choices of V_{art}.

We choose the slowest falloff allowed by (3.9),

$$V_{art}(R) \sim \lambda / R^2 , \quad R \sim \infty . \tag{4.1}$$

If the integral in (3.13) is to exist, we must then choose Ψ_t sufficiently accurately such that

$$R^{5/2}(H - E_{T0}) \Psi_t(\vec{r}, \vec{R}) \sim 0 , \quad R \sim \infty . \tag{4.2}$$

We know that

$$\Psi(\vec{r}, \vec{R}) \sim \psi_{T0}(R - A)/R + O(1/R^2) , \quad R \sim \infty . \tag{4.3}$$

Unless one builds in the term of order $1/R^2$ correctly in Ψ_t, one finds

$$(H - E_{T0}) \Psi_t \sim \psi_{T0}(\vec{r}) [V_{as}(R - A_t)/R + O(R^{-3})] ,$$

where V_{as}, the asymptotic form of V, is given, with Z the nuclear charge, by

$$V_{as} = - e^2 \sum_{i=1}^{Z} (\vec{r}_i \cdot \hat{R})/R^2 , \tag{4.4}$$

with $\vec{r}_i$ the position of the ith electron and with $\hat{R} \equiv \vec{R}/R$. Equation (4.2) is therefore not satisfied. Let us therefore write, for all $\vec{R}$,

$$\Psi_t = \psi_{T0}(\vec{r}) f(\vec{R}) + M(\vec{r}, \vec{R}) , \tag{4.5}$$

where $f(\vec{R})$ and $M(\vec{r}, \vec{R})$ are to be chosen such that (4.2) is satisfied, and where

$$f(\vec{R}) \sim (R - A_t)/R, \quad R \sim \infty . \tag{4.6}$$

Since it is a long-range effect which must be accounted for, it is natural to use pseudostates.[21] We write

$$M = \psi_{ps}(\vec{r}; \vec{R}) g(\vec{R}) + N(\vec{r}, \vec{R}) , \tag{4.7}$$

where $g(\vec{R}) - 1$ is a short-range function, N is a short-range correlation term, and the pseudostate wave function is defined by

$$[H_T(\vec{r}) - E_{T0}] \psi_{ps}(\vec{r}; \vec{R}) = - V(\vec{r}, \vec{R}) \psi_{T0}(\vec{r}) . \tag{4.8}$$

For our purposes, it will suffice to replace $V(\vec{r}, \vec{R})$ by V_{as} for large R; to avoid difficulties at small R, we write, for all R, as an approximation to (4.8)

$$(H_T - E_{T0})\psi_{ps} = e^2 p(R) \sum_{i=1}^{Z} (\hat{R}\cdot\vec{r}_i)\psi_{T0}\,, \tag{4.9}$$

where $p(R) \sim 1/R^2$ as $R \sim \infty$. We could, for example, choose $p(R) = (R^2 + d^2)^{-1}$. We then have

$$(H - E_{T0})M \sim -V_{as}\psi_{T0}\,, \tag{4.10}$$

and, therefore, since $-(A_t/R)\psi_{T0}V_{as} = O(R^{-3})$,

$$(H - E_{T0})\Psi_t \sim O(R^{-3})\,,$$

so that (4.2) is now satisfied.

In practice, of course, neither ψ_{T0} nor ψ_{ps} is known exactly. Since some of the integrals which appear in the expression for the variational bound fail to exist if inexact functions are used, we must adopt a modified procedure similar to that discussed in Ref. 5. That is, we initially assume that both ψ_{T0} and ψ_{ps} are known exactly and perform all of the integrals over $\vec{R}$. To do this we first make the $\vec{R}$ dependence explicit by writing

$$\psi_{ps} = e^2 p(R)\frac{4\pi}{3}\sum_{m=-1}^{1} Y_1^{m*}(\hat{R})D_m(\vec{r})\,, \tag{4.11}$$

where D_m satisfies

$$(H_T - E_{T0})D_m(\vec{r}) = \sum_{i=1}^{Z} r_i\, Y_1^m(\hat{r}_1)\psi_{T0}(\vec{r})\,, \tag{4.12}$$

and is orthogonal to ψ_{T0}. After integrating over $\vec{R}$ we are left with integrations involving known functions of $\vec{r}$ and the unknown target functions $\psi_{T0}(\vec{r})$ and $D_m(\vec{r})$. If at this stage the target functions are approximated by trial functions the integrals remain finite. The accuracy of these trial functions can be systematically improved with the aid of subsidiary minimum principles of the Rayleigh-Ritz type.[22] To preserve the rigor of the bound on the scattering length, rigorous error bounds are required for the integrals over the target functions (and for the target energy E_{T0} as well). Methods for obtaining such error bounds have been described previously.[5-7] However, we would expect that in practice one would prefer, at the expense of complete rigor, to invest one's effort in the improvement of the trial target functions. It seems very likely that, for scattering by light atoms at least, the errors introduced by the use of inexact target functions could be made sufficiently small so that the additional effort required to obtain bounds on these errors would not be necessary.

We close with some brief comments on the assumptions listed near the beginning of Sec. II. The assumption (v) that ψ_{T0} and E_{T0} are known has just been discussed. With regard to (i), we note that for a positron incident on a positive ion with which it cannot form a composite bound state, the entire discussion goes through as above; one need merely change the boundary conditions on Ψ and Ψ_t to those appropriate to zero-energy Coulomb wave functions. We can also drop assumption (ii) and allow the positron to have spin-dependent interactions. If the total angular momentum of the target J_T is zero, no change in the formalism is required. For $J_T \neq 0$, one must study separately scattering in states with total angular momentum $J = J_T \pm \frac{1}{2}$. (We are considering $l = 0$.) We can also eliminate the assumption that the target ground state be spherically symmetric; formally, this would simply entail the replacement of $V_{ad}(R)$ by $V_{ad}(\vec{R})$.

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APPENDIX A: COMPARISON WITH SOME PREVIOUS RESULTS

Some time ago[2,23] the problem of determining upper and lower variational bounds on scattering lengths was studied within the framework of the method originally introduced by Kato for potential-scattering problems.[15] The Kato method is based on the use of an auxiliary potential-strength eigenvalue problem, and requires for its application a knowledge of (or rather appropriate bounds on) the positive and negative eigenvalues of smallest absolute magnitude. We pointed out that for the zero-energy potential-scattering problem the Kato method, which was applicable at all energies, assumed a particularly useful form; at zero incident energy it could be implemented by invoking Levinson's theorem[24] which states that the phase shift at zero energy is $n\pi$ where n is the number of bound states supported by the scattering potential. With regard to the upper bound on A, this method was completely superseded by that[1,2] based directly on the spectrum of the Hamiltonian; the latter method is very much more practical since it does not involve matrix elements of H^2, and it has a wider domain of applicability. On the other hand, a new and useful lower bound on the scattering length was obtained[2,23] by applying necessary conditions for the existence of bound states[25] to obtain the required lower bound on the smallest positive potential-strength eigenvalue. The formal result has recently been independently rediscovered by Arthurs.[26] [Actually, Arthurs's discussion is incomplete since it provides no method for obtaining the potential-strength eigenvalues. Further, in our language, Arthurs allows himself no freedom in his choice of V_{art}, choosing $V_{art} = V$ for scattering potential $V(r) \geq 0$ for all r and $V_{art} = -V$

for $V(r) \leq 0$ for all r; his approach is therefore restricted unnecessarily to scattering potentials which are of definite sign and which, in addition, cannot support bound states.]

In attempting to generalize the lower variational bound result to the problem of zero-energy scattering by a compound system, one runs into the difficulty that an extension of Levinson's theorem to this problem in a form which would be useful for our purposes is not available. One way of describing the accomplishment of the present paper is to say that it bypasses the need to generalize Levinson's theorem. At the same time, the derivation leading to the basic inequality (2.17) has been simplified enormously by the elimination of the formal machinery required in the Kato approach. (We note again that we are restricting ourselves to zero incident kinetic energy.) In addition, and perhaps most importantly, we have recognized the suitability of the adiabatic approximation as an (essentially) solvable comparison problem from which a bound on $H - E_{T0}$ can be obtained which is of a form that makes it possible to bound the second-order error term S. The result, Eq. (2.17), is precisely that which would be obtained from the Kato method along with the assumption of the validity of Levinson's theorem, in the form stated above, for scattering by compound targets.

APPENDIX B: UPPER BOUND ON THE GREEN'S FUNCTION

Under our assumption (iii) that the incident particle and the target cannot form a composite bound state, it follows that

$$H - E_{T0} \geq 0 \tag{B1}$$

with respect to asymptotically constant functions, and therefore that the full Green's function G for the energy E_{T0}, which is, roughly speaking, the reciprocal of $H - E_{T0}$, satisfies

$$G \geq 0 \tag{B2}$$

with respect to asymptotically constant functions. Using a separable form, we can replace the lower bound 0 by a lower variational bound. These results are well known. We point out here that the basic inequality, (2.16), represents the other bound on G, at the energy E_{T0}, for a class of diagonal matrix elements. Thus, G is defined as the solution of

$$(H - E_{T0})G(\vec{r}, \vec{R}; \vec{r}', \vec{R}') = \delta(\vec{r} - \vec{r}')\delta(\vec{r} - \vec{R}') \tag{B3}$$

which falls off as R^{-1} for large R. The second-order error term S, defined by Eq. (2.1c), can be expressed in terms of the Green's function, as we now show. Let us first insert a factor unity in the form $(H - E_{T0})G$ in the integrand on the right-hand side of Eq. (2.1c). The expression for S then becomes

$$S = (\delta\Psi, (H - E_{T0})G(H - E_{T0})\delta\Psi) \ . \tag{B4}$$

Application of Green's theorem gives

$$S = ((H - E_{T0})\delta\Psi, G(H - E_{T0})\delta\Psi) \ . \tag{B5}$$

The absence of a surface term is a consequence of the fact that $\delta\Psi$ and G both fall off as R^{-1} for large R. Finally we may use Eq. (2.15) to write

$$S = ((H - E_{T0})\Psi_t, G(H - E_{T0})\Psi_t) \ . \tag{B6}$$

[This expression for S was obtained and studied in some unpublished work by M. Kelly and one of us[27] (L.S.), and perhaps by others.] The form (B6) for S has the merit of being formally exact, the only unknown being the well-defined G. Thus Eq. (2.16) represents an upper bound not only on S but also on the expectation value of G with respect to $(H - E_{T0})\Psi_t$, where Ψ_t must satisfy the boundary conditions given by (2.5).

One often finds that the Green's function formalism is suggestive of approximation procedures through the use of simple operator algebra. This is a virtue of the formalism, even though the final result can usually be rederived without introducing Green's functions. In fact we first arrived at the identity (2.11) by starting with Eq. (B6) and then using the standard identity

$$\frac{1}{B} = \frac{1}{C} + \frac{1}{B}(C - B)\frac{1}{C} \ . \tag{B7}$$

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