Subsidiary minimum principles for scattering parameters

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(Received 25 March 1974)

We denote as a "primary minimum principle" one in which a quantity B of physical interest is represented as the minimum value with respect to variations in a trial function ψ_t of a functional $F(\psi_t)$; F then provides a variational upper bound on B. (The Rayleigh-Ritz principle for the ground-state energy of a system is a familiar example.) If F is quadratic in ψ_t, the variational property of F enables one to determine the linear parameters relatively easily, but the minimum property is required if the nonlinear parameters are to be determined in a way which allows for systematic improvement of ψ_t. We show here that for a wide class of problems for which primary minimum principles do not exist, useful and rigorous secondary or "subsidiary minimum principles" are available. That is, we construct a functional $F'(\psi_t)$ whose minimum value is reached for ψ_t equal to some function ψ of dynamical interest. (The Rayleigh-Ritz method provides a subsidiary minimum principle for the approximate determination of the ground-state wave function of a system.) If $B = B(\psi)$, then a study of $F'(\psi_t)$ provides a powerful tool for the estimation of ψ and therefore B, though $B(\psi_t)$ is not normally a variational bound on $B(\psi)$. Subsidiary minimum principles have recently been obtained for the approximation of the auxiliary functions that appear in the variational principle for the matrix element $(\chi_n, W\chi_m)$, where χ_n and χ_m are bound-state wave functions and W is an arbitrary operator. Here we extend the method to the estimation of matrix elements of the Green's function $g(\epsilon)$ of a bound system with ϵ below the continuum threshold energy. The response of the system to an external perturbation can be represented by matrix elements of this type. While no new results on the bound-state problem are obtained, our formulation is a convenient starting point for the further extension of the method to continuum problems. The new result obtained here is the derivation of a subsidiary minimum principle for the problem of scattering of a projectile by a target whose bound-state wave function is only imprecisely known. The subsidiary minimum principle allows for systematic improvement of the closed-channel component of the trial scattering wave function that appears in a Kohn-type variational calculation of the scattering amplitude.

I. INTRODUCTION

The power and simplicity of the Rayleigh-Ritz method for the estimation of the ground-state energy of a system is widely recognized. The energy estimate obtained represents a rigorous variational upper bound. Just on the basis of its stationary (or variational) aspect, it becomes possible, rather easily, to determine sensibly any linear variational parameters c_j contained in the trial ground-state wave function χ_{1t}. Nonlinear variational parameters, which we will denote by γ_l, are not so readily obtained from a variational principle; it is a matter of practice that the stationary point in the space of the c_j *and* the γ_l is not too easily located.[1] The minimum-principle aspect, as opposed to simply the variational aspect, introduces two advantageous features. First, not only the c_j but now also the γ_l can be determined rather readily to within a good approximation. As one goes to more complicated systems, it becomes more and more important to introduce the γ_l as well as the c_j, lest the number of c_j required for given accuracy get completely out of hand.[2] Second, one has a simple and objective criterion for determining which of two results, obtained using different χ_{1t}'s, is better.

The extension from the Rayleigh-Ritz variational upper bound on the ground-state energy to variational upper bounds on excited-state energies is provided by the Hylleraas-Undheim theorem.[3] It is natural to attempt to find analogs of the Rayleigh-Ritz and Hylleraas-Undheim methods for the estimation of other quantities of interest. These include, for example, the response functions which describe the response of a bound system to external perturbations, and the scattering parameters which characterize the scattering of a projectile by a bound system. While minimum principles have been obtained for a number of such problems, they remain purely formal and are therefore of limited value for all but the simplest bound systems if, as is usually the case, they require precise knowledge of the wave function χ_1 and energy ϵ_1 of the ground state of the bound system. One may ask whether, for χ_1 and ϵ_1 not precisely known, there exists a practical computational scheme which enjoys the benefits of the Rayleigh-Ritz method. This question can be answered affirmatively at the present time only for a very limited number of cases, including scattering lengths for positron-atom scattering.[4] The next question which arises is what one can do when one cannot construct a "primary minimum principle,"

that is, a rigorous variational upper (or lower[5]) bound on the quantity of interest. Do any computational schemes then exist which at least approach the power and simplicity of the Rayleigh-Ritz method? We will show that for a very broad class of problems there does exist a rigorous minimum principle of a secondary or subsidiary nature which can be used as a (powerful) calculational aid in the systematic approximation of the various wave functions (and other functions) that are well defined but not exactly obtainable and that are required for the evaluation (or variational estimation) of the quantity of interest. We do not then have a variational bound on the quantity of interest, but the relative ease with which the various functions can be approximated, including in particular the possibility of estimating γ_l's contained in the trial functions, makes it much simpler to obtain reliable estimates of the quantity of interest.

The present approach to the problem represents a systematic development and extension of methods introduced earlier in the problem of obtaining upper bounds on scattering lengths when composite bound states exist.[6] Such states must be "subtracted out" in order to preserve the bound. To be practical as well as rigorous this subtraction procedure need not require the composite bound-state functions to be precisely known. An effective procedure was developed based on a corollary of the Hylleraas-Undheim theorem. Recently variants of this method were applied to the problems of constructing trial functions in a variational principle for bound-state matrix elements[7] and to the variational construction of the effective potential in scattering theory.[8,9] In the latter problem the scattering parameters must be determined by numerical solution of an effective two-body integral equation. When the target bound-state function is precisely known this procedure provides a rigorous bound on an arbitrary diagonal element of the K matrix, as does the closely related technique[10] which utilizes the Feshbach projection-operator formalism.[11] Since the primary minimum principle is lost in the general case where the target consists of more than two particles, we are motivated to look for an alternative calculationally simpler procedure which does not require the numerical solution of integral equations, but which is based on a rigorous subsidiary minimum principle. Such a method has been developed and will be discussed in the following sections.

Our approach is based on the introduction of a modified Hamiltonian from which the effects of certain low-lying states have been subtracted out; the Rayleigh-Ritz method is applied to the calculation of matrix elements of the modified Hamiltonian.

Before we go into the details of the approach, it is worthwhile to continue our attempt to discuss in broad terms what we hope to accomplish. Given a bound-state system, it is possible in principle and almost always possible in practice to express the quantity of interest in terms of matrix elements of the form

$$\langle J_f | g(\epsilon) | J_i \rangle , \tag{1.1}$$

where J_f and J_i are specified functions. For the bound system in the presence of an external perturbation which is incapable of breaking up the system, $g(\epsilon)$ is the Green's function of the system at an energy which is below the threshold continuum but which can otherwise be arbitrary, with ϵ normally not one of the energy eigenvalues ϵ_n of the system. For an isolated bound system ϵ will be one of the discrete eigenvalues, say, the nth, and $g(\epsilon_n)$ will be a "modified Green's function," for the singularity must be removed. $g(\epsilon_n)$ might be the normal Green's function expressed in bilinear form, but with the (infinite) contribution of the nth term omitted.

For ϵ below the continuum threshold but not an eigenvalue, the approach of the present paper has the virtues discussed above, namely, one can proceed in a systematic fashion, employing, for example, γ_l's. For $\epsilon = \epsilon_n$, the situation is rather different, because of the difficulty of obtaining a good approximation to $g(\epsilon_n)$ if one does not know χ_n and ϵ_n. Reference 7 gives a completely general and we believe very powerful prescription for obtaining increasingly close approximations to $g(\epsilon_n)$. Thus, for $\epsilon = \epsilon_n$, the approach of Ref. 7 is not only useful, in the sense that it is useful for $\epsilon \neq \epsilon_n$, but is virtually necessary, since it makes possible the effective extraction of only formally known singularities.

The scattering of a projectile by a target is completely determined by matrix elements of the form of (1.1), but with $g(\epsilon)$ replaced by $G(E)$, where $G(E)$ is the Green's function of the projectile plus target and E is the sum of the projectile and target energies and therefore lies in the continuum. The fact that E is an eigenvalue introduces certain difficulties into the approximate evaluation of $G(E)$. The exact Green's function $G(E)$ is of course well defined, the singularity being formally eliminated in the usual way by the replacement of E by $E + i\eta$, with η a positive infinitesimal number. $G(E)$ is then a smooth function of E, as opposed to the dependence of $g(\epsilon)$ upon ϵ in the neighborhood of ϵ_n. Nevertheless, not surprisingly, one often runs across infinities in numerical studies of scattering problems.[12] [These infinities can be viewed as

having their origins in the replacement of the exact nonsingular $G(E)$ by singular approximations.] Procedures have been developed which normally make it possible in a concrete case to avoid such singularities,[13] but it is preferable to have available a method in which infinities simply cannot arise. The procedure of Ref. 7, which has exactly that virtue for $\epsilon = \epsilon_n$, will be extended in this paper to E in the continuum. With the scattering wave function decomposed into open-channel and closed-channel (decaying) components, the decaying function can be estimated by a subsidiary minimum principle, with all its attendant power, without the possibility of infinities arising. Infinities can arise in the evaluation of the open-channel component, but the determination of the open-channel component is equivalent to a one-body problem, a problem that is relatively simple and for which, therefore, the possible appearance of infinities is not nearly so worrisome.

We note that for the single-channel scattering problem a continuum of states, associated with the unbounded relative motion of target and projectile, must be subtracted out. We will show how this can be done in the context of a Kohn variational approximation.[14]

To conclude our general introductory remarks we observe that matrix elements of the form (1.1) are not only of interest in their own right, but arise in essentially all variational principles; it was, indeed, in the context of variational principles that Ref. 7 was written. More precisely, such matrix elements appear as first-order correction terms, with J_i and J_f containing (known) trial wave functions.

Section II contains a description of the method in the relatively simple context of bound-state calculations. All of the results on bound states are known,[15] but have been rederived in a slightly different form. The modified form more readily suggests the approach to be used in extending these results to the continuum problem. We have formulated the continuum results in terms of Kohn-type variational principles rather than variational principles that utilize Green's functions. We believe that this provides a calculationally simpler procedure, as discussed at the beginning of Sec. III B. In addition to serving a heuristic purpose the method developed in Sec. II has been utilized directly in Sec. III D to carry out the effective subtraction of discrete closed-channel states. Our treatment of the continuum problem in Sec. III is restricted for simplicity to the case of single-channel scattering. Level-shift calculations, which can be treated by similar methods, and multichannel generalizations will be discussed at a later date.

II. RESPONSE FUNCTIONS

Consider a system described by a Hamiltonian h. The eigenvalue problem

$$h\,|\chi_n\rangle = \epsilon_n\,|\chi_n\rangle \tag{2.1}$$

can be solved approximately for the discrete energies ϵ_n and the normalized wave functions χ_n using the Rayleigh-Ritz (or Hylleraas-Undheim) method. In addition, one is often interested in determining the response of the bound system to external perturbations. Computations of this type ultimately reduce to the problem of evaluating matrix elements of the form

$$\mathfrak{M}_{fi} = \langle J_f\,|g(\epsilon)\,|J_i\rangle\,, \tag{2.2}$$

where the Green's function $g(\epsilon)$ is defined by

$$g(\epsilon) = (\epsilon - h)^{-1}\,, \tag{2.3}$$

along with appropriate boundary conditions. We assume that the perturbation has been decomposed into harmonics with ϵ representing the energy of the system after it has absorbed or emitted a quantum of definite frequency ω. [Consider the scattering of a photon by an atom in state χ_n. The required (second-order) matrix element is then a linear combination of matrix elements of the form (2.2), with $\epsilon = \epsilon_n \pm \hbar\omega$.] For simplicity we confine the present discussion to the case where ϵ lies below the threshold of the continuous spectrum of h; the more general case is taken up in the following sections, in the context of the scattering problem. With this restriction $g(\epsilon)$, in configuration space, will vanish asymptotically. We shall be concerned here with variational methods for evaluating matrix elements of the type shown in Eq. (2.2), with J_i and J_f assumed to be known quadratically integrable functions. Actually, in most cases of interest, J_i and J_f involve the imprecisely known eigenfunctions and/or the eigenvalues of the bound system. Appropriate approximations for these functions can be introduced at a later stage.

Since we are interested in variational methods of the Rayleigh-Ritz type we express the matrix element $\mathfrak{M}_{fi}$ in terms of an ordinary function rather than a Green's function. That is, we write

$$\mathfrak{M}_{fi} = \langle J_f\,|\,L_i\rangle\,, \tag{2.4}$$

where the function L_i satisfies the inhomogeneous differential equation

$$(h - \epsilon)\,|\,L_i\rangle = -\,|J_i\rangle\,; \tag{2.5}$$

L_i will be quadratically integrable since J_i is and since ϵ lies below the continuum threshold. Alternatively, we have

$$\mathfrak{M}_{fi} = \langle L_f | J_i \rangle , \tag{2.6}$$

where

$$(h - \epsilon) | L_f \rangle = - | J_f \rangle . \tag{2.7}$$

If ϵ coincides with one of the eigenvalues of h, $g(\epsilon)$ in Eq. (2.2) must be replaced by a modified (nonsingular) Green's function.[16] This is equivalent to specifying unique solutions to Eqs. (2.5) and (2.7), whose homogeneous versions possess nontrivial solutions for $\epsilon = \epsilon_n$. A particularly convenient procedure to be followed in such cases has been developed previously,[7] and will be reviewed below. The approach of the present section may be seen as a straightforward generalization of the results of Ref. 7 to the case where ϵ lies below the continuum threshold but is not an eigenvalue of h. (The extension to the continuum domain is given in Sec. III.)

A variational approximation to $\mathfrak{M}_{fi}$ is given, as can be verified directly, by

$$\mathfrak{M}_{fiv} = \langle J_f | L_{it} \rangle + \langle L_{ft} | J_i \rangle + \langle L_{ft} | h - \epsilon | L_{it} \rangle . \tag{2.8}$$

Our primary concern here is with the problem of determining quadratically integrable trial functions L_{it} and L_{ft} which are close approximations to the solutions of Eqs. (2.5) and (2.7), respectively. In particular we look for subsidiary minimum principles to provide a method for systematic improvement of these trial functions. Such minimum principles can be set up if eigenstates of h with energies below ϵ can be effectively subtracted out.

A. $\epsilon < \epsilon_1$

The subtraction problem increases in complexity as ϵ increases. Starting with the simplest case we take $\epsilon < \epsilon_1$. (This is done for clarity of presentation; no subtractions are needed for $\epsilon < \epsilon_1$.) The off-diagonal case involves two approximations to two well-defined but imprecisely known functions, L_i and L_f. It will be convenient to develop independent subsidiary conditions for the two functions. To obtain the subsidiary condition for L_i we begin by observing that the use of Eqs. (2.4)–(2.8) enables us to express the diagonal matrix element $\mathfrak{M}_{ii}$ (which is not the matrix element under consideration) as a variational approximation plus an error:

$$\mathfrak{M}_{ii} = \mathfrak{M}_{iiv} - \langle \Delta L_i | h - \epsilon | \Delta L_i \rangle , \tag{2.9}$$

with $\mathfrak{M}_{iiv}$ defined by Eq. (2.8) with f replaced by i. We have defined

$$| \Delta L_i \rangle = | L_{it} \rangle - | L_i \rangle . \tag{2.10}$$

$h - \epsilon$ is a positive definite operator with respect to quadratically integrable functions since ϵ lies below the minimum expectation value of h. Since L_i is quadratically integrable, the choice of L_{it} can be made with the aid of the subsidiary minimum principle

$$\mathfrak{M}_{ii} \leq \mathfrak{M}_{iiv} . \tag{2.10a}$$

Similarly, the inequality

$$\mathfrak{M}_{ff} \leq \mathfrak{M}_{ffv} \tag{2.10b}$$

can be used as a subsidiary minimum principle for the approximate evaluation of L_{ft}. In particular, as in the Rayleigh-Ritz method, the trial functions may be expanded in a set of basis functions which contain linear and nonlinear variational parameters. The parameters contained in L_{it} and L_{ft} can be determined by searching for the sets which minimize the functionals $\mathfrak{M}_{iiv}$ and $\mathfrak{M}_{ffv}$, respectively. It is considerably easier to program a computer to search for an extremum than for a saddlepoint. If considered worth the effort, one can treat the nonlinear parameters as fixed by the above approach, but treat the linear parameters as open parameters that are to be recalculated, as can easily be done, to make the original functional $\mathfrak{M}_{fiv}$ stationary.

The procedure is somewhat simpler if the matrix element of interest is diagonal ($i = f$). (The diagonal matrix elements that appeared above arose as calculational tools in the analysis of off-diagonal matrix elements.) Moreover, $\mathfrak{M}_{iiv}$ then provides a variational bound on the matrix element of interest, that is, a primary minimum principle, if J_i is known.

Note that the existence of a bound state of energy ϵ_1 played no particular role in the above analysis, since we were concerned with $\epsilon < \epsilon_1$. In the following subsections we will be concerned with $\epsilon = \epsilon_1$ and $\epsilon_2 > \epsilon > \epsilon_1$. Since we will then have a bound state at or below the energy under consideration, it will be possible to obtain a subsidiary minimum principle only if we can extract the effects of that bound state; the extraction will have to be performed in the face of an imprecise knowledge of χ_1 and ϵ_1. It is trivial to extend the results to the case $\epsilon > \epsilon_n$ for $n > 1$.

B. $\epsilon = \epsilon_1$

The computational strategy outlined above must be modified when ϵ lies at or above the minimum eigenvalue of h [setting aside the case where ΔL_i in Eq. (2.9) is known by symmetry considerations to be orthogonal to the ground-state wave function]. The case where ϵ coincides with ϵ_1 arises in the computation of the zero-frequency response function (e.g., the static polarizability), in time-independent perturbation theory, and in the construction of auxiliary trial functions for the varia-

tional calculation of matrix elements $\langle\chi_1|W|\chi_1\rangle$, where W is a given operator. An equation of the form (2.5) is consistent for $\epsilon=\epsilon_1$ only if the inhomogeneous term is orthogonal to the ground-state function χ_1. For $\epsilon=\epsilon_1$ the appropriate modification of Eq. (2.5) that defines L is

$$(h-\epsilon_1)|L\rangle=-|J\rangle+|\chi_1\rangle\langle\chi_1|J\rangle, \tag{2.11}$$

where the subscript i or f is dropped to simplify the notation. A subsidiary minimum principle for the determination of approximate solutions of Eq. (2.11) was described previously.[7] We briefly review that discussion here since it provides the basis for the generalizations treated subsequently.

We shall first demonstrate that the solution to Eq. (2.11) can be represented in the form

$$|L\rangle=|M\rangle+b|\chi_1\rangle, \tag{2.12}$$

where b is a parameter to be determined and $|M\rangle$ is uniquely defined as the solution of

$$(\hat{h}-\epsilon_1)|M\rangle=-|J\rangle. \tag{2.13}$$

Here we have introduced the modified Hamiltonian

$$\hat{h}=h-\epsilon_1|\chi_1\rangle\langle\chi_1|. \tag{2.14}$$

Note that the eigenfunctions χ_n of h are all also eigenfunctions of $\hat{h}$. Furthermore, with the exception of ϵ_1, all of the eigenvalues of h are eigenvalues of $\hat{h}$; the eigenvalue ϵ_1 of h is replaced, for $\hat{h}$, by the eigenvalue 0. It follows that $\hat{h}-\epsilon_1$ has no null eigenvector, that there are therefore no solutions of the homogeneous equation associated with (2.13), and, finally, that the solution of (2.13) is indeed unique. To check if $|L\rangle$, in the form shown in Eq. (2.12), satisfies Eq. (2.11) we compute

$$\begin{aligned}(h-\epsilon_1)|L\rangle&=(h-\epsilon_1)|M\rangle+b(h-\epsilon_1)|\chi_1\rangle\\&=(\hat{h}-\epsilon_1)|M\rangle+\epsilon_1|\chi_1\rangle\langle\chi_1|M\rangle\\&=-|J\rangle+\epsilon_1|\chi_1\rangle\langle\chi_1|M\rangle.\end{aligned} \tag{2.15}$$

To determine $\langle\chi_1|M\rangle$ we project Eq. (2.13) onto $\langle\chi_1|$ and obtain

$$\langle\chi_1|(h-\epsilon_1-\epsilon_1|\chi_1\rangle\langle\chi_1|)|M\rangle=-\langle\chi_1|J\rangle, \tag{2.16}$$

which immediately yields

$$\langle\chi_1|M\rangle=(1/\epsilon_1)\langle\chi_1|J\rangle. \tag{2.17}$$

Then the last member of Eq. (2.15) becomes

$$-|J\rangle+\epsilon_1|\chi_1\rangle\langle\chi_1|M\rangle=-|J\rangle+|\chi_1\rangle\langle\chi_1|J\rangle, \tag{2.18}$$

thus verifying the solution. The parameter b is undetermined by the above considerations, which are restricted to the determination of the general form of the solution of (2.11), since χ_1 is a solution of the homogeneous equation associated with (2.11). In the application considered in Ref. 7 the component $\langle\chi_1|L\rangle$ was of no significance since it made no contribution to the variational expression considered there. Hence the simplest choice $b=0$ sufficed. If the component $\langle\chi_1|L\rangle$ is specified in advance and denoted by λ (one often requires the condition $\lambda=0$, for example), we may project Eq. (2.12) onto $\langle\chi_1|$ and use (2.17) to obtain

$$b=\langle\chi_1|L\rangle-\langle\chi_1|M\rangle=\lambda-(1/\epsilon_1)\langle\chi_1|J\rangle. \tag{2.19}$$

Equation (2.8), the variational principle for $\mathfrak{M}_{fi}$ defined by (2.2), involves L_{ft} and L_{it}, approximations to L_f and L_i. The functions L_f and L_i are defined to within a multiple of χ_1 by (2.11) (in which the appropriate subscript, f or i, is to be inserted). Unfortunately, however, it can be exceedingly difficult to obtain approximations to L_f and L_i for $\epsilon=\epsilon_1$, much more so than for $\epsilon<\epsilon_1$; for $\epsilon=\epsilon_1$, the most obvious equation approximating (2.11) (that in which the unknown χ_1 and ϵ_1 are replaced by estimates χ_{1t} and ϵ_{1t}) has very troublesome near-singularities, as discussed in detail in Ref. 7. The power of the technique introduced in Ref. 7, a slightly modified version of which we are now discussing, originates in the introduction of a subsidiary minimum principle for the approximate determination of M_i and M_f, and therefore, via (2.12) and (2.19), of L_i and L_f. More precisely, $\hat{h}-\epsilon_1$ is a positive operator so that a trial function $|M_{it}\rangle$ can be systematically improved by minimization of the form

$$\hat{\mathfrak{M}}_{iiv}=\langle J_i|M_{it}\rangle+\langle M_{it}|J_i\rangle+\langle M_{it}|\hat{h}-\epsilon_1|M_{it}\rangle, \tag{2.20}$$

in analogy with the earlier discussion leading to Eq. (2.10a). $|M_{ft}\rangle$ can be systematically improved in an analogous fashion. In other words, by working with the modified Hamiltonian $\hat{h}$ rather than with the physical Hamiltonian h, the case $\epsilon=\epsilon_1$ has been reduced, at least formally, to the simpler case $\epsilon<\epsilon_1$, the role of the positive-definite operator previously played by $h-\epsilon$ now being played by $\hat{h}-\epsilon_1$. We say formally because neither the eigenvalue ϵ_1 nor the eigenfunction χ_1 in the expression for $\hat{h}$ is precisely known in general. However, we may replace $\hat{h}-\epsilon_1$ in the functional $\hat{\mathfrak{M}}_{iiv}$ by $\hat{h}_t-\epsilon_{1t}$ where we have introduced a normalized trial function χ_{1t} and have defined

$$\epsilon_{1t}=\langle\chi_{1t}|h|\chi_{1t}\rangle, \tag{2.21}$$

and

$$\hat{h}_t=h-\frac{h|\chi_{1t}\rangle\langle\chi_{1t}|h}{\langle\chi_{1t}|h|\chi_{1t}\rangle}. \tag{2.22}$$

We assume throughout that χ_{1t} is good enough to generate an ϵ_{1t} with a negative value. Clearly $\hat{h}_t\to\hat{h}$ and $\epsilon_{1t}\to\epsilon_1$ for $\chi_{1t}\to\chi_1$. Furthermore, as

shown previously,[7] $\hat{h}_t - \epsilon_{1t}$ will be positive for χ_{1t} sufficiently accurate; the precise conditions will be quoted below. Thus the subsidiary minimum principle is preserved; the subtraction procedure is effective even when the wave function and the energy of the state to be subtracted are not precisely known. This essential feature of our method will be utilized repeatedly below.

In summary, a variational principle for $\mathfrak{M}_{fi}$ of (2.2), with $\epsilon = \epsilon_1$ and J_i and J_f known, is provided by (2.8), with $\epsilon = \epsilon_1$ replaced by its variational estimate ϵ_{1t}, defined by (2.21), and where, in line with (2.12) and (2.19), we write

$$|L_{it}\rangle = |M_{it}\rangle + [\lambda_i - (1/\epsilon_{1t})\langle\chi_{1t}|J_i\rangle]\,|\chi_{1t}\rangle$$

and a similar equation for L_{ft}. M_{it} is obtained by minimization of the form

$$\mathfrak{M}\hat{}_{iivt} = \langle J_i|M_{it}\rangle + \langle M_{it}|J_i\rangle + \langle M_{it}|\hat{h}_t - \epsilon_{1t}|M_{it}\rangle\,, \tag{2.20'}$$

with $\hat{h}_t$ defined by (2.22). M_{ft} is obtained by minimization of the analogous form, with i replaced by f.

C. $\epsilon_1 < \epsilon < \epsilon_2$

We progress now to the next most difficult case, where $\epsilon_1 < \epsilon < \epsilon_2$, with ϵ_2 representing either the energy of the first excited state, or, if no excited states exist, the continuum threshold energy. Proceeding as above we look for a solution of

$$(h - \epsilon)\,|L\rangle = -|J\rangle \tag{2.23}$$

in the form

$$|L\rangle = |M\rangle + b\,|\chi_1\rangle\,, \tag{2.24}$$

with $|M\rangle$ defined by

$$(\hat{h} - \epsilon)\,|M\rangle = -|J\rangle\,. \tag{2.25}$$

To see if b can be chosen such that $|M\rangle + b\,|\chi_1\rangle$ is in fact a solution we evaluate

$$\begin{aligned}(h - \epsilon)\,|L\rangle &= (h - \epsilon)\,|M\rangle + b\,(h - \epsilon)\,|\chi_1\rangle \\ &= -|J\rangle + \epsilon_1\,|\chi_1\rangle\langle\chi_1|M\rangle + b(\epsilon_1 - \epsilon)\,|\chi_1\rangle\,.\end{aligned} \tag{2.26}$$

This reduces to $-|J\rangle$ as required if we choose

$$b = \frac{\epsilon_1}{\epsilon - \epsilon_1}\,\langle\chi_1|M\rangle\,. \tag{2.27}$$

Starting from (2.25), we can determine $\langle\chi_1|M\rangle$ from

$$\langle\chi_1|\,(h - \epsilon - \epsilon_1\,|\chi_1\rangle\langle\chi_1|)\,|M\rangle = -\langle\chi_1|J\rangle\,, \tag{2.28}$$

which gives

$$\langle\chi_1|M\rangle = (1/\epsilon)\langle\chi_1|J\rangle\,. \tag{2.29}$$

Then b is determined as

$$b = \left(\frac{1}{\epsilon - \epsilon_1} - \frac{1}{\epsilon}\right)\langle\chi_1|J\rangle\,. \tag{2.30}$$

The variational calculation would proceed as follows. A normalized trial bound-state wave function χ_{1t} is chosen using, e.g., the Rayleigh-Ritz method. The trial functions L_{it} and L_{ft} which appear in the variational expression Eq. (2.8) are chosen in the form

$$|L_{it}\rangle = |M_{it}\rangle + b_{it}\,|\chi_{1t}\rangle\,, \tag{2.31}$$

$$|L_{ft}\rangle = |M_{ft}\rangle + b_{ft}\,|\chi_{1t}\rangle\,. \tag{2.32}$$

The variational parameters in M_{it} are determined by minimizing

$$\mathfrak{M}\hat{}_{iivt} = \langle J_i|M_{it}\rangle + \langle M_{it}|J_i\rangle + \langle M_{it}|\hat{h}_t - \epsilon\,|M_{it}\rangle\,. \tag{2.33}$$

The minimum principle is valid for values of ϵ which lie below the minimum eigenvalue of $\hat{h}_t$. We have shown[7,8] that for any normalizable function ψ the inequality

$$\frac{\langle\psi|\hat{h}_t|\psi\rangle}{\langle\psi|\psi\rangle} \geq \left(\frac{\epsilon_1}{\epsilon_{1t}}\right)\epsilon_2 \tag{2.34}$$

is satisfied. Then from a knowledge of lower bounds on ϵ_1 and ϵ_2 we may suppose that an energy $\bar{\epsilon}_2$ has been found such that

$$(\epsilon_1/\epsilon_{1t})\epsilon_2 \geq \bar{\epsilon}_2\,. \tag{2.35}$$

Thus the minimum principle holds for $\epsilon \leq \bar{\epsilon}_2$. A similar principle holds for M_{ft}.

We turn now to the evaluation of the linear variational parameters b_{it} and b_{ft}. Note that, as opposed to the case $\epsilon = \epsilon_1$ of Sec. IIB, where the differential equation defining L_t played no role in the determination of b_i and b_f, these linear parameters are here defined by the differential equations (2.23) and (2.25) and were in fact given, if only formally, in Eq. (2.30). To obtain estimates b_{it} and b_{ft} of b_i and b_f we require

$$\frac{\partial}{\partial b_{it}}\,\mathfrak{M}_{fiv} = 0\,, \tag{2.36}$$

$$\frac{\partial}{\partial b_{ft}}\,\mathfrak{M}_{fiv} = 0\,. \tag{2.37}$$

This leads to the values

$$b_{ft} = -\frac{\langle\xi_{ft}|\chi_{1t}\rangle}{\epsilon_{1t} - \epsilon}\,, \tag{2.38}$$

$$b_{it} = -\frac{\langle\chi_{1t}|\xi_{it}\rangle}{\epsilon_{1t} - \epsilon}\,, \tag{2.39}$$

with

$$|\xi_{ft}\rangle = |J_f\rangle + (h - \epsilon)\,|M_{ft}\rangle\,, \tag{2.40}$$

$$|\xi_{it}\rangle = |J_i\rangle + (h-\epsilon)|M_{it}\rangle . \tag{2.41}$$

[It can readily be checked that for the various trial functions replaced by exact functions the above results reduce to the results of (2.30).] With this choice of parameters the variational expression becomes

$$\mathfrak{M}_{fiv} = \langle J_f|M_{it}\rangle + \langle M_{ft}|J_i\rangle + \langle M_{ft}|h-\epsilon|M_{it}\rangle - \frac{\langle \xi_{ft}|\chi_{1t}\rangle\langle\chi_{1t}|\xi_{it}\rangle}{\epsilon_{1t}-\epsilon} . \tag{2.42}$$

In considering the diagonal case $i=f$, we might anticipate the simplifying feature that the original functional $\mathfrak{M}_{ii}$ itself satisfies a minimum principle. To verify this we examine the error term in Eq. (2.9), which we write as

$$-\langle \Delta L_i|h-\epsilon|\Delta L_i\rangle = -\langle \Delta L_i|h-\epsilon-(h-\epsilon)_{sep}|\Delta L_i\rangle - \langle \Delta L_i|(h-\epsilon)_{sep}|\Delta L_i\rangle , \tag{2.43a}$$

where we have introduced the operator

$$(h-\epsilon)_{sep} \equiv \frac{(h-\epsilon)|\chi_{1t}\rangle\langle\chi_{1t}|(h-\epsilon)}{\langle\chi_{1t}|h-\epsilon|\chi_{1t}\rangle} . \tag{2.43b}$$

The first term may be shown to be negative if $\epsilon_{1t}-\epsilon<0$. (This is a simple adaptation of the basic theorem of Ref. 6.) The second term vanishes if L_{it} is chosen according to the above prescription, namely, $|L_{it}\rangle = |M_{it}\rangle + b_{it}|\chi_{it}\rangle$ with b_{it} determined variationally. An analogous minimum principle for the scattering length when one and only one composite bound state exists was proved some time ago.[6] In fact, that earlier result is easily recovered from the approach adopted here by studying the limit, assuming that here too h supports one and only one bound state, as ϵ approaches the continuum threshold ϵ_{thr} from below, of the Kohn variational expression for the scattering length. In other words, the earlier result corresponds to the special case $\epsilon=\epsilon_{thr}$ of the present result.

The subtraction procedure described above can be extended in a straightforward way to the case where a known finite number of bound-state levels lie below ϵ. It is clear, however, that modifications are required in order to preserve the subsidiary minimum principle if the energy lies above the continuum threshold. This is the subject of Sec. III.

III. SINGLE-CHANNEL SCATTERING

A. Formal development

We shall be concerned here with variational approximations, along with subsidiary minimum principles, for matrix elements of the type

$$\lim_{\eta\to 0+}\langle J_f|G(E+i\eta)|J_i\rangle , \tag{3.1}$$

where

$$G(z) = (z-H)^{-1} \tag{3.2}$$

and where E lies above the continuum threshold of the Hamiltonian H. For definiteness, we discuss the problem in the context of scattering theory, by far the most important example in which matrix elements of the form (3.1) arise. We confine our attention here to the case of single-channel scattering of a particle from a bound system. We suppress spin degrees of freedom of the projectile and assume the projectile to be distinguishable from the particles in the target. Generalizations will be taken up later.

The Hamiltonian is of the form

$$H = \mathcal{K} + V + h , \tag{3.3}$$

where, in the center-of-mass frame, $\mathcal{K}$ is the kinetic-energy operator describing the relative motion of projectile and target. The interaction between projectile and target is given by the potential V; we assume V to be short ranged here, with Coulomb effects considered in Sec. III C. The target-system Hamiltonian is represented by h. The scattering amplitude is defined as

$$T(\vec{k}_f,\vec{k}_i) = \langle\phi_f|V|\phi_i\rangle + \lim_{\eta\to 0+}\langle J_f|G(E+i\eta)|J_i\rangle , \tag{3.4}$$

with

$$|\phi_i\rangle = |\chi,\vec{k}_i\rangle , \tag{3.5}$$

$$|J_i\rangle = V|\phi_i\rangle . \tag{3.6}$$

Note that $|\chi,\vec{k}_i\rangle$ can be factored into $|\chi\rangle|\vec{k}_i\rangle$, with $|\vec{k}_i\rangle$ denoting the incident plane wave of relative motion. We have dropped the subscript on the target ground-state function χ, but will retain the subscript on ϵ. Since χ satisfies

$$h|\chi\rangle = \epsilon_1|\chi\rangle \tag{3.7}$$

and since $|\vec{k}_i\rangle$ satisfies

$$\mathcal{K}|\vec{k}_i\rangle = E'|\vec{k}_i\rangle , \tag{3.8}$$

where, with $k_i=k_f\equiv k$ and with μ the reduced mass, we have

$$E' = \hbar^2k^2/2\mu ,$$

it follows that

$$(H-E)|\phi_i\rangle = V|\phi_i\rangle , \tag{3.9a}$$

with

$$E = \epsilon_1 + E' . \tag{3.9b}$$

Relations (3.5), (3.6), (3.8), and (3.9a) remain valid for i replaced by f. Throughout the formal

development in this subsection χ will be assumed to be precisely known. A practical computational procedure is described in Sec. III B. In place of the outgoing-wave boundary condition implied by the limiting procedure in Eq. (3.4) we could have adopted standing-wave conditions, and/or we could have worked with states of definite angular momentum.[17] The following discussion would not be changed in any essential way.

In analogy with Eq. (2.9) the scattering amplitude can be expressed as a variational estimate plus an explicit error term. We shall not concern ourselves here with obtaining bounds on the error term. The variational expression, derived some time ago by Kohn,[18] is of the form

$$T_v(\vec{k}_f, \vec{k}_i) = T_t(\vec{k}_f, \vec{k}_i) + \langle \Psi_{ft}^{(-)} | H - E | \Psi_{it}^{(+)} \rangle , \quad (3.10)$$

where the zeroth-order estimate T_t is determined by the asymptotic form of the initial trial function, and where the matrix element of $H - E$ is a first-order correction. In the following discussion of the trial functions we shall consider $\Psi_{it}^{(+)}$. Similar remarks hold for $\Psi_{ft}^{(-)}$ with $i \to f$ and incoming waves used in place of outgoing waves in the asymptotic form. We shall write

$$|\Psi_{it}^{(+)}\rangle = |\phi_i\rangle + |L_{it}^{(+)}\rangle . \quad (3.11)$$

Then with E below the inelastic threshold we have the configuration-space asymptotic form

$$L_{it}^{(+)}(\vec{r}, \vec{\rho}) \sim -\frac{1}{4\pi}\frac{2\mu}{\hbar^2} T_t(k\hat{\rho}, \vec{k}_i)\chi(\vec{r})\frac{e^{ik\rho}}{\rho} , \quad (3.12)$$

where $\hat{\rho} \equiv \vec{\rho}/\rho$, in the limit as ρ, the separation between the projectile and the center of mass of the target, becomes infinite. (The collection of space and spin coordinates describing the target system is represented by $\vec{r}$.) Since $|\Psi_{it}^{(+)}\rangle$ must be an approximation to the solution of

$$(H - E)|\Psi_i^{(+)}\rangle = 0 , \quad (3.13)$$

$|L_{it}^{(+)}\rangle$ must be an approximation to the solution of

$$(H - E)|L_i^{(+)}\rangle = -|J_i\rangle . \quad (3.14)$$

In close analogy with the procedure described in Sec. II we look for a formal decomposition of $|L_i^{(+)}\rangle$ into open- and closed-channel components and we shall seek a subsidiary minimum principle to help determine the closed-channel component. Dropping the subscript i and superscript (+) temporarily, we write

$$|\Psi\rangle = |\chi, f\rangle + |M\rangle , \quad (3.15a)$$

where

$$|f\rangle = |\vec{k}\rangle + |\tilde{f}\rangle . \quad (3.15b)$$

By (3.11), we then have

$$|L\rangle = |\chi, \tilde{f}\rangle + |M\rangle . \quad (3.16)$$

Associated with the state vector $|\tilde{f}\rangle$ is the single-particle function $\tilde{f}(\vec{\rho})$ which represents the outgoing wave component associated with the incident particle; in accordance with Eq. (3.11) the incident plane wave is not included in the function $\tilde{f}$. $f(\vec{\rho})$ represents the complete effective single-particle wave function. Note that

$$|\chi, f\rangle = |\chi\rangle|f\rangle , \quad |\chi, \tilde{f}\rangle = |\chi\rangle|\tilde{f}\rangle .$$

Since $\chi\tilde{f}$ carries the correct asymptotic form of L the function M will be decaying at infinity. Of course the decomposition shown in Eq. (3.15a) is not unique since an arbitrary decaying component can be added to $|\chi, f\rangle$ and subtracted from $|M\rangle$. We may take advantage of this lack of uniqueness to define M in a way which admits a minimum principle as a method of approximation. We define

$$\hat{H} = H - \epsilon_1 |\chi\rangle\langle\chi| \quad (3.17)$$

or, equivalently,

$$\hat{H} = \mathcal{K} + V + \hat{h} , \quad (3.18)$$

where $\hat{h}$ is the modified target Hamiltonian defined in Eq. (2.14). Since the first excited state of h represents the ground state of $\hat{h}$, the ground state having been raised in energy from ϵ_1 to 0 in going from h to $\hat{h}$, it follows that the component of the continuous spectrum of H associated with the target in its ground state has been raised by an amount ϵ_1 in the spectrum of $\hat{H}$. In particular, then, as opposed to the spectrum of H, the spectrum of $\hat{H}$ has no continuum between ϵ_1 and the inelastic threshold of H at ϵ_2. Then $\hat{H} - E$ will be positive if E lies below the inelastic threshold, provided $\hat{H}$ has no discrete states; such states, if they exist, can effectively be subtracted out, even though the discrete-state wave functions and eigenvalues will be imprecisely known. The full implication of these remarks will be discussed later. For the moment they serve to motivate the defining relation which we adopt for M, namely,

$$(\hat{H} - E)|M\rangle = -|\tilde{J}\rangle , \quad (3.19)$$

in which the positive definite operator $\hat{H} - E$ appears. Our task now is to verify that the "source term" $\tilde{J}$, which we require to be quadratically integrable, can be chosen in such a way that a solution to Eq. (3.14) exists in the form shown in Eq. (3.16). As a by-product of this demonstration we will find a defining equation for the function f which serves as an Euler-Lagrange equation associated with the present version of the Kohn variational principle. Thus, inserting (3.16) into (3.14) and using (3.19), (3.17), (3.3), and (3.9b), we obtain

$$
\begin{aligned}
(H-E)\,|L\rangle &= (H-E)(|\chi,\tilde{f}\rangle + |M\rangle) \\
&= (H-E)\,|\chi,\tilde{f}\rangle + (\hat{H}-E)\,|M\rangle \\
&\quad + \epsilon_1\,|\chi\rangle\langle\chi\,|M\rangle \\
&= V\,|\chi,\tilde{f}\rangle + (\mathcal{K}-E')\,|\chi,\tilde{f}\rangle - |\tilde{J}\rangle \\
&\quad + \epsilon_1\,|\chi\rangle\langle\chi\,|M\rangle \\
&= -\,|J\rangle\,.
\end{aligned}
$$

Since

$$
(\mathcal{K}-E')\,|\chi,\tilde{f}\rangle = |\chi\rangle(\mathcal{K}-E')\,|\tilde{f}\rangle\,,
$$

and since $\langle\chi\,|M\rangle$ is a state vector in ρ space, it must be possible to find a function $w = w(\vec{\rho})$ such that

$$
V\,|\chi,\tilde{f}\rangle - |\tilde{J}\rangle + |J\rangle = -\,|\chi\rangle\,|w\rangle\,. \tag{3.20}
$$

(Since V, $\tilde{J}$, and J are quadratically integrable, w will have the same property.) It follows that $\tilde{f}$ must be defined as the solution of

$$
(\mathcal{K}-E')\,|\tilde{f}\rangle = -\epsilon_1\langle\chi\,|M\rangle + |w\rangle\,. \tag{3.21a}
$$

On inserting the value of $\tilde{J}$ obtained from (3.20) into (3.19), and using (3.6), (3.5), and (3.15b), we obtain

$$
(\hat{H}-E)\,|M\rangle = -\,V\,|\chi,f\rangle - |\chi,w\rangle\,. \tag{3.21b}
$$

With w having been arbitrarily chosen, f and M are defined by the coupled equations (3.21a) and (3.21b). The functions $\tilde{f}$ and M depend on the specific choice of w. However, as shown in the Appendix, the dependence is such that the sum $L = \chi\tilde{f} + M$ is independent of w. In the following we shall set $w = 0$. Thus, the defining relation for M is taken as

$$
(\hat{H}-E)\,|M\rangle = -V\,|\chi,f\rangle\,. \tag{3.22}
$$

The projection of M on χ required to evaluate the right-hand side of Eq. (3.21a) can be determined formally in terms of the Green's function

$$
\hat{G}(E) = (E-\hat{H})^{-1}\,. \tag{3.23}
$$

Here and in the following it will be understood that E and E' contain a small positive imaginary part which approaches zero after all integrals are performed. The formal solution to Eq. (3.22) may be written as

$$
|M\rangle = \hat{G}(E)V\,|\chi,f\rangle\,, \tag{3.24}
$$

so that Eq. (3.21a) becomes (with $w = 0$)

$$
(\mathcal{K}-E')\,|\tilde{f}\rangle = -\epsilon_1\langle\chi\,|\hat{G}(E)V\,|\chi,f\rangle\,. \tag{3.25}
$$

To carry the analysis a step further we observe that $\hat{G}$ satisfies the resolvent identity

$$
\hat{G} = \hat{G}_0 + \hat{G}_0 V\hat{G}\,, \tag{3.26}
$$

where

$$
\hat{G}_0(E) = (E-\hat{h}-\mathcal{K})^{-1}\,. \tag{3.27}
$$

Since χ is an eigenfunction of $\hat{h}$ with eigenvalue zero we conclude that

$$
\langle\chi\,|\hat{G}_0(E) = (E-\mathcal{K})^{-1}\langle\chi\,|\,, \tag{3.28a}
$$

so that, from Eq. (3.26),

$$
\langle\chi\,|\hat{G} = (E-\mathcal{K})^{-1}\langle\chi\,|\,(1+V\hat{G})\,. \tag{3.28b}
$$

We can now rewrite Eq. (3.25) as

$$
(\mathcal{K}-E')\,|\tilde{f}\rangle = -\epsilon_1(E-\mathcal{K})^{-1}\langle\chi\,|\,V + V\hat{G}V\,|\chi,f\rangle\,. \tag{3.29}
$$

If then we define an effective single-particle propagator

$$
\mathcal{G} = \frac{\epsilon_1}{(E'-\mathcal{K})(E-\mathcal{K})} = \frac{1}{E'-\mathcal{K}} - \frac{1}{E-\mathcal{K}} \tag{3.30}
$$

and an effective-potential operator

$$
\mathcal{U} = \langle\chi\,|\,V + V\hat{G}V\,|\chi\rangle\,, \tag{3.31}
$$

Eq. (3.29) takes the form

$$
|\tilde{f}\rangle = \mathcal{G}\mathcal{U}\,|f\rangle\,. \tag{3.32}
$$

That is, f satisfies the single-particle Lippmann-Schwinger-like equation

$$
|f\rangle = |\vec{k}\rangle + \mathcal{G}\mathcal{U}\,|f\rangle\,. \tag{3.33}
$$

The interpretation of $\mathcal{U}$ as the effective single-particle (energy-dependent nonlocal) potential is confirmed by the relation

$$
\begin{aligned}
\langle\vec{k}_f\,|\mathcal{U}\,|f\rangle &= \langle\vec{k}_f,\chi\,|\,V\,|[\,|\chi,f\rangle + |M\rangle] \\
&= \langle\vec{k}_f,\chi\,|\,V\,|\Psi_i^{(+)}\rangle = T(\vec{k}_f,\vec{k}_i)\,,
\end{aligned} \tag{3.34}
$$

which follows directly from the definition, Eq. (3.31), on using (3.24), (3.15a), and, in the last step, Eqs. (3.4)–(3.6). The effective potential of Eq. (3.31) (as well as its multichannel generalization) was introduced previously in Ref. 9 in an approach based on integral equations for the scattering matrix.

The effective potential is of course not unique. We may, for example, introduce a transformed effective potential

$$
\mathcal{U}_T = \left(\frac{\epsilon_1}{E-\mathcal{K}}\right)^{1/2}\mathcal{U}\left(\frac{\epsilon_1}{E-\mathcal{K}}\right)^{1/2}\,,
$$

which preserves the Hermiticity property of the effective potential in the energy region where only single-channel scattering can occur. According to Eq. (3.33) the transformed single-particle function

$$
|f_T\rangle \equiv \left(\frac{\epsilon_1}{E-\mathcal{K}}\right)^{-1/2}|f\rangle
$$

satisfies the usual Lippmann-Schwinger equation

$$|f_T\rangle = |\vec{k}\rangle + \frac{1}{E' - \mathcal{K}}\, v_T |f_T\rangle .$$

We have used the relation

$$\left(\frac{\epsilon_1}{E - \mathcal{K}}\right)^{-1/2} |\vec{k}\rangle = |\vec{k}\rangle ,$$

with the positive root chosen as a matter of definition. One easily sees that the scattering amplitude is unchanged by the transformation, i.e.,

$$\langle \vec{k}_f | v_T | f_T \rangle = \langle \vec{k}_f | v | f \rangle .$$

B. Choice of trial functions

If the target function χ were known exactly a variational bound on the effective-potential operator would lead, after numerical solution of the effective single-particle integral equation for a given partial wave, to a variational lower bound on the phase shift.[8-10] The phase-shift bound is lost if, as we shall assume in the following, χ is imprecisely known. A subsidiary minimum principle remains for the construction of the effective potential, as described previously.[9] The procedure we now describe, based on a closely related minimum principle, should be considerably simpler from the calculational point of view since it does not require the exact solution of an integral equation. That step is replaced here by a variational determination of the single-particle wave function f, with the closed-channel component M constructed separately using a subsidiary minimum principle. Experience shows that accurate variational estimates of the phase shift (or K matrix) for single-particle scattering can be obtained without difficulty. The full many-body complexity of the problem is shifted to the determination of M for which methods of the Rayleigh-Ritz type have just been presented. Use of a Kohn-type principle has another advantage when χ is imprecisely known since the calculation is known to be variational with respect to errors in χ,[19] i.e., it introduces an error of order $(\chi - \chi_t)^2$ provided the energy $E = \epsilon_1 + E'$ is replaced by the variational approximation

$$E_t \equiv E' + \epsilon_{1t} , \tag{3.35}$$

with $\epsilon_{1t} = \langle \chi_t | h | \chi_t \rangle$ and $\langle \chi_t | \chi_t \rangle = 1$. As a final general remark we observe that when long-ranged Coulomb forces are present the effective-potential approach[20] involves exact Coulomb propagators and wave functions while the Kohn method requires only that the asymptotic form of the Coulomb functions be given correctly. We return to this point below.

To describe the variational procedure in more specific terms we introduce a trial function of the form

$$|\Psi_t\rangle = |\chi_t, f_t\rangle + |M_t\rangle , \tag{3.36}$$

where, as $\rho \to \infty$, f_t approaches a plane wave plus an outgoing wave and M_t vanishes. There are three functions to be determined: χ_t, f_t, and M_t. The linear and nonlinear parameters contained in χ_t can be obtained from the Rayleigh-Ritz method. f_t and M_t are approximations to f and M, defined by the coupled equations (3.22) and

$$(\mathcal{K} - E')|f\rangle = -\epsilon_1 \langle \chi | M \rangle , \tag{3.37}$$

arrived at from (3.21a) by recalling that we have chosen $w = 0$ and using $(\mathcal{K} - E')|\vec{k}_i\rangle = 0$. Assume that we have in any fashion arrived at a particular choice of f_t. Perhaps the most natural way to obtain such an estimate would be to use the variational principle (3.10), with E replaced by E_t, defined in Eq. (3.35). We would introduce a trial function $\Psi_t = \chi_t f_t + M_t$ with f_t containing few if any nonlinear parameters. M_t would contain linear and nonlinear parameters, but the nonlinear parameters would, temporarily, be given arbitrary numerical values. (We are here using a variational principle and want to avoid the determination of nonlinear parameters.) With the parameters in χ_t determined by means of the Rayleigh-Ritz theorem and with the parameters in f_t (and M_t) determined from (3.10), we would obtain an improved set of values of the coefficients in M_t by considering the functional

$$\hat{\mathfrak{M}}_v = \langle \chi_t, f_t | V | M_t \rangle + \langle M_t | V | \chi_t, f_t \rangle + \langle M_t | \hat{H}_t - E_t | M_t \rangle , \tag{3.38}$$

where, using Eqs. (2.22) and (3.3),

$$\hat{H}_t \equiv \mathcal{K} + V + \hat{h}_t = H - \frac{h|\chi_t\rangle\langle\chi_t|h}{\langle\chi_t|h|\chi_t\rangle} . \tag{3.39}$$

The continuum threshold of $\hat{H}_t$ is given by the minimum eigenvalue of $\hat{h}_t$, for which we have a lower bound, Eq. (2.34). We shall assume here that $\hat{H}_t$ supports no discrete states; if a finite number of such states exist they may be subtracted out as described in Sec. III D. Then for $E_t < \bar{\epsilon}_2$, where $\bar{\epsilon}_2$ is an energy determined such that the inequality (2.35) is satisfied, the operator $\hat{H}_t - E_t$ is positive in the space of quadratically integrable functions. It follows that the function M_t which minimizes $\hat{\mathfrak{M}}_v$ provides a solution of

$$(\hat{H}_t - E_t)|\bar{M}_t\rangle = -V|\chi_t, f_t\rangle . \tag{3.40}$$

Thus, for χ_t and f_t fixed, the variational parameters in M_t can be determined by minimizing the functional $\hat{\mathfrak{M}}_v$. In particular, a search for the nonlinear parameters in M_t, as well as for the linear parameters, can be made systematically.

With the improved version of M_{it} and M_{ft}, and with the same version of χ_t, we can obtain an im-

proved form for f_{it} and f_{ft}, and at the same time an improved variational estimate of $T(\vec{k}_f, \vec{k}_i)$, by again using (3.10). The f_t's might have many linear parameters, but they would contain very few if any nonlinear parameters. With χ_t and the M_t's fixed, integration over all but the coordinate $\vec{\rho}$ reduces (3.10) to the form of a variational principle for single-particle scattering, for which spurious calculational singularities can arise which can be relatively easily avoided. Alternatively, if it seemed desirable, the linear (but not the nonlinear) parameters in the improved version of M_t, determined as described just above, could be treated as linear variational parameters in the study of (3.10). The same could be done even for the linear parameters in χ_t. Having obtained an improved f_t, one could go back and improve M_t by the use of a subsidiary minimum principle, then improve f_t further, etc. The merit of the approach, as opposed to the direct use of (3.10) once, with no use of (3.38), is that the nonlinear parameters in the closed-channel component M_t of Ψ_t can be readily evaluated. The approach would, of course, involve additional labor, since it begins at the point at which one has already obtained a variational estimate of $T(\vec{k}_f, \vec{k}_i)$ by means of (3.10). Since the use of (3.10) will presumably give a reasonable starting point for the Ψ_t's, we expect that very few iterations will be needed.

Many alternative procedures are possible. One might insert the Born approximation $|f_t\rangle = |\vec{k}\rangle$ into (3.38), as a starting point. Instead of using the subsidiary minimum principle as an aid in constructing trial functions in a Kohn variational calculation one might use it as a link in a successive approximation procedure based on the coupled equations (3.22) and (3.37). That is, rather than solving Eq. (3.22) with f replaced by an approximation f_t one may determine M_t by minimizing the functional in Eq. (3.38). An improved f_t may then be obtained from

$$(\mathcal{K} - E')|f_t\rangle = -\epsilon_{1t}\langle\chi_t|M_t\rangle . \tag{3.41}$$

Using the well-known one-body Green's function $(E' - \mathcal{K})^{-1}$, Eq. (3.41) may be solved to give

$$|f_t\rangle = |\vec{k}\rangle + \epsilon_{1t}(E' - \mathcal{K})^{-1}\langle\chi_t|M_t\rangle , \tag{3.42}$$

with the last term obtained by numerical quadrature. At each stage of the successive approximation procedure an approximate scattering amplitude may be determined from the asymptotic form of Eq. (3.42) in configuration space. We have (reinserting subscripts i and f)

$$f_{it}(\vec{\rho}) \sim (2\pi)^{-3/2} e^{i\vec{k}_i \cdot \vec{\rho}} - (1/4\pi)(2\mu/\hbar^2) T_t(k\hat{\rho}, \vec{k}_i) e^{ik\rho}/\rho , \tag{3.43}$$

with T_t given by

$$T_t(\vec{k}_f, \vec{k}_i) = \epsilon_{1t}\langle\chi_t, \vec{k}_f|M_{it}\rangle . \tag{3.44}$$

This last result also follows from (3.41) on interpreting $\epsilon_{1t}\langle\chi_t|M_t\rangle$ as an effective potential operating on $|f_t\rangle$, and using the usual definition of transition amplitude.

Few of the many possibilities for the estimation of $T(\vec{k}_f, \vec{k}_i)$ will provide variational estimates. Thus, while (3.42), for example, may be useful in intermediate steps in the iteration process, the final calculation would normally be one that uses the normal Kohn principle (3.10) in the full many-body form.

C. Effects of monopole and multipole moments

Modifications of the preceding discussion are necessary when both projectile and target are charged. These modifications can be summarized as follows. Let us define the "monopole" Coulomb interaction v_c as the Coulomb interaction between projectile and target which would exist if the charge of the target system were concentrated at its center of mass. We now reinterpret the single-particle operator $\mathcal{K}$ in Eq. (3.3) as the kinetic-energy operator plus the pure Coulomb interaction v_c. Accordingly, the operator V in Eq. (3.3) now has the monopole component removed. Equation (3.8) is retained with the state $|\vec{k}_i\rangle$ now representing a Coulomb wave function satisfying the appropriate boundary conditions. The scattering amplitude defined in Eq. (3.4) now represents the difference between the full amplitude and the pure Coulomb amplitude. The variational expression for this amplitude is given by Eq. (3.10) with the asymptotic form of Eq. (3.12) suitably modified by the inclusion of the logarithmic phase factor in the outgoing wave.[20] Thus, as mentioned above, the exact single-particle Coulomb wave functions are not required in actual applications. Coulomb distortions enter into the asymptotic form of the trial function f_t of Eq. (3.36). The functional to be minimized in the construction of the component M_t is once again of the form shown in Eq. (3.38).

In constructing trial functions for the scattering of two systems each with a net charge, one may have to take into account not only the effect of the monopole component on the asymptotic form of f, but modifications of the asymptotic form of M due to multipole components. In particular, M falls off not exponentially but as a power of $1/\rho$.[21] The effect on M is also present in the scattering of a charged particle by a neutral but electrically polarizable system, for which the interaction has no monopole moment but does have higher moments. (For zero energy, even the asymptotic form of f is affected.) To see how the effects of the higher

moments arise in the present approach consider the form of the interaction V for electron-atom scattering. (We have assumed that the incident particle is distinguishable from the target particles, but this restriction can be removed; furthermore, we are for the moment primarily concerned with large ρ, for which distinguishability plays no role.) For an electron incident on an atom of nuclear charge Z with N electrons, we have, the monopole moment having been removed (for $N \neq Z$),

$$V = \sum_{i=1}^{N} \frac{e^2}{|\vec{\rho} - \vec{r}_i|} - \frac{Ne^2}{\rho} . \tag{3.45}$$

For ρ very large compared to atomic dimensions V is approximated by its dipole term,

$$V \sim \frac{e^2}{\rho^2} \sum_{i=1}^{N} \hat{\rho} \cdot \vec{r}_i . \tag{3.46}$$

The asymptotic form of M can be deduced from (3.24) by using the identity

$$\hat{G} = \hat{g} + \hat{G}[\mathfrak{K} - E' + V]\hat{g} , \tag{3.47}$$

where we used (3.23) and (3.18) and introduced

$$\hat{g} \equiv \hat{g}(\epsilon_1) = (\epsilon_1 - \hat{h})^{-1} ; \tag{3.48}$$

$\hat{g}$ is well defined since ϵ_1 is not an eigenvalue of $\hat{h}$. Since $(\mathfrak{K} - E')Vf$ vanishes more rapidly than ρ^{-2} we see that to leading order we can replace $\hat{G}$ by $\hat{g}$ in Eq. (3.24). Equivalently we see that for ρ fixed and large, M satisfies

$$(\hat{h} - \epsilon)|M\rangle = -\frac{e^2}{\rho^2} \left(\sum_{i=1}^{N} \hat{\rho} \cdot \vec{r}_i \right) |\chi, f\rangle . \tag{3.49}$$

Associated with this equation is a subsidiary minimum principle described earlier in connection with the determination of the zero-frequency response function [see Eq. (2.13)]. Clearly, Eq. (3.49) describes the perturbation of the target in a uniform external field of strength e/ρ^2. Physical arguments of this type form the basis of "adiabatic" approximation schemes which are often used in low-energy electron-atom scattering problems.[22] Such methods may now be subjected to systematic study using the rigorous subsidiary minimum principle which involves the function M throughout all of space, not only in the asymptotic domain.

D. Closed-channel bound states

The minimum principle which can be used to obtain an approximate solution to Eq. (3.22) must be modified when $\hat{H}$ has bound states below E. The procedure for subtracting out such discrete states is essentially identical to the one described earlier in connection with Eq. (2.23). To summarize this briefly in the present context let us assume for simplicity that $\hat{H}$ has only one bound state:

$$\hat{H}|a\rangle = E_a|a\rangle ,$$

where we take $|a\rangle$ to be normalized. The solution to Eq. (3.22) may be written as

$$|M\rangle = |N\rangle + b|a\rangle , \tag{3.50}$$

where $|N\rangle$ satisfies

$$(\hat{H}_a - E)|N\rangle = -V|\chi, f\rangle . \tag{3.51}$$

We have defined

$$\hat{H}_a = \hat{H} - E_a|a\rangle\langle a| = \hat{H} - \frac{\hat{H}|a\rangle\langle a|\hat{H}}{\langle a|\hat{H}|a\rangle} . \tag{3.52}$$

In practice, when approximate normalized states $|a_t\rangle$ are employed, the replacement of $|a\rangle$ by $|a_t\rangle$ must be made in the second form of Eq. (3.52) if we are to preserve the positivity of $\hat{H}_a - E$. [Similarly, it is $\hat{H}_t$, Eq. (3.39), which is to be used rather than $\hat{H}$ in practice.] Thus, we have subsidiary minimum principles available to construct approximations to the states $|N\rangle$ and $|a\rangle$. The Kohn trial function would be taken in the form

$$|\Psi_t\rangle = |\Psi_t'\rangle + b|a_t\rangle , \tag{3.53}$$

with

$$|\Psi_t'\rangle = |\chi_t, f_t\rangle + |N_t\rangle . \tag{3.54}$$

When the parameter b is determined variationally, the Kohn functional becomes

$$T_v(\vec{k}_f, \vec{k}_i) = T_t(\vec{k}_f, \vec{k}_i) + \langle \Psi_{ft}^{(-)\prime} | H - E | \Psi_{it}^{(+)\prime} \rangle - \frac{\langle \Psi_{ft}^{(-)\prime} | H - E | a_t \rangle \langle a_t | H - E | \Psi_{it}^{(+)\prime} \rangle}{\langle a_t | H - E | a_t \rangle} . \tag{3.55}$$

As mentioned in Sec. II the subtraction procedure is easily generalized to the case where a finite number of discrete states must be subtracted out. Since we are interested primarily in atomic applications we must inquire how the existence of infinitely many discrete states, arising from attractive long-range Coulomb interactions, affects the applicability of our method. We remark first that the states to be subtracted out are those of the modified Hamiltonian $\hat{H}$, rather than H. States present in the spectrum of H may vanish into the continuum when modified by the addition of the repulsive interaction $-\epsilon_1|\chi\rangle\langle\chi| = \hat{H} - H$. It is easy to see that this does indeed occur. For example, let the Hamiltonian H refer to the neutral helium atom and let E lie in the region corresponding to low energy electron scattering by He^+ in its ground state. In addition to the continuum of states above the He ionization threshold there is an infinite number of bound states below, accumulating at this threshold

(each corresponding to an electron weakly bound to the He^+ ion). However, in the spectrum of $\hat{H}$ the He^+ ground state has been subtracted out (or, more precisely, displaced upward). This removes *both* the continuum *and* discrete states associated with the He^+ ground state. Similar remarks hold for heavier atoms, although the He system is distinguished by the fact that the He^+ states are known exactly so that rigorous variational lower bounds on low-energy electron-He^+ phase shifts can be obtained using either the effective-potential formalism or the projection-operator method. (The required Feshbach projection operators are known for the two-electron system.[10])

APPENDIX: INVARIANCE UNDER CHANGES IN w

The analysis of Eqs. (3.21a) and (3.21b) given in the text was based on the choice $w=0$. Here we show that the wave function Ψ, given by Eq. (3.15a), is in fact independent of the choice of w. This demonstration is necessary to establish the self-consistency of our analysis and to justify the simple choice $w=0$. Let us represent the solutions of the coupled equations (3.21) as f_w and M_w to indicate explicitly the dependence on the function w. The solutions corresponding to the choice $w=0$ will be denoted as f_0 and M_0. We shall show here that

$$|\chi, f_w\rangle + |M_w\rangle = |\chi, f_0\rangle + |M_0\rangle . \tag{A1}$$

Our analysis of Eqs. (3.21) follows that in the text, but with $w \neq 0$. Thus, in place of (3.24) we have

$$|M_w\rangle = \hat{G}(E)V|\chi, f_w\rangle + \hat{G}(E)|\chi, w\rangle . \tag{A2}$$

With the aid of Eqs. (3.28b) and (3.31) we find

$$\epsilon_1\langle\chi|M_w\rangle = \frac{\epsilon_1}{E-\mathcal{K}}\,v|f_w\rangle + \frac{\epsilon_1}{E-\mathcal{K}}\langle\chi|1+V\hat{G}|\chi, w\rangle . \tag{A3}$$

As in the derivation of (3.28b) we can show that

$$\hat{G}|\chi\rangle = (1+\hat{G}V)|\chi\rangle\frac{1}{E-\mathcal{K}} . \tag{A4}$$

We then have

$$\langle\chi|V\hat{G}|\chi\rangle = v\frac{1}{E-\mathcal{K}} , \tag{A5}$$

which, when combined with (A3) gives

$$\epsilon_1\langle\chi|M_w\rangle = \frac{\epsilon_1}{E-\mathcal{K}}\,v|f_w\rangle + \frac{\epsilon_1}{E-\mathcal{K}}\left(1+v\frac{1}{E-\mathcal{K}}\right)|w\rangle . \tag{A6}$$

With this result Eq. (3.21a) becomes

$$(\mathcal{K}-E')|\tilde{f}_w\rangle = -\frac{\epsilon_1}{E-\mathcal{K}}\,v|f_w\rangle - \frac{\epsilon_1}{E-\mathcal{K}}\left(1+v\frac{1}{E-\mathcal{K}}\right)|w\rangle + |w\rangle . \tag{A7}$$

The solution can be written, using the definition (3.30) in both forms, and adding $|\tilde{k}\rangle$ to each side,

$$|f_w\rangle + \frac{1}{E-\mathcal{K}}|w\rangle = |\tilde{k}\rangle + \mathcal{G}v\left(|f_w\rangle + \frac{1}{E-\mathcal{K}}|w\rangle\right) . \tag{A8}$$

By comparison with the integral equation satisfied by f_0 [Eq. (3.33)] we conclude that

$$|f_0\rangle = |f_w\rangle + \frac{1}{E-\mathcal{K}}|w\rangle . \tag{A9}$$

This result, when combined with (A2), gives

$$|M_w\rangle = \hat{G}(E)V|\chi, f_0\rangle - \hat{G}(E)V\frac{1}{E-\mathcal{K}}|\chi, w\rangle + \hat{G}(E)|\chi, w\rangle . \tag{A10}$$

If we use (A4), along with the relation

$$|M_0\rangle = \hat{G}(E)V|\chi, f_0\rangle , \tag{A11}$$

we can rewrite (A10) as

$$|M_w\rangle = |M_0\rangle + \frac{1}{E-\mathcal{K}}|\chi, w\rangle . \tag{A12}$$

The desired result (A1) follows directly from Eqs. (A9) and (A12).

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*Supported by the National Science Foundation.
†Work supported by the U. S. Army Research Office, Durham, under Grant No. DA-ARO-D-31-124-72-G92 and by the Office of Naval Research under Grant No. N00014-67-A-0467-0007.

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[15]The earliest related extremum principle is the bound on the second-order contribution to the energy in perturbation theory obtained by E. A. Hylleraas [Z. Phys. 65, 209 (1930)]. Some variational bounds were obtained by M. Karplus and H. J. Kolker [J. Chem. Phys. 39, 1493 (1963)]. A Green's-function operator inequality that provides a concise derivation of variational bounds was introduced by R. Sugar and R. Blankenbecler [Phys. Rev. 136, 472 (1964)]; when there exist discrete eigenvalues below the actual energy of the system, a modified inequality was obtained with the aid of the Hylleraas-Undheim theorem of Ref. 3, in the manner introduced in Ref. 6. A useful general review is given by J. O. Hirschfelder, W. B. Brown, and S. T. Epstein [Adv. Quantum Chem. 1, 255 (1964)]. For a recent calculation in this area, and for further references, see, for example, J. S. Sims and J. R. Rumble, Jr., Phys. Rev. A 8, 2231 (1973).

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[17]The variational bounds that have been developed in scattering theory normally require a partial-wave analysis, largely because it is simpler to bound the real quantities, such as the phase shifts that arise in partial-wave studies, than the complex quantities, such as the scattering amplitudes that arise in studies of the full wave function. In the present study of closed channels via subsidiary minimum principles patterned after the Rayleigh-Ritz theorem, there is no particular need to perform a partial-wave decomposition.

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