Interrelation between variational principles for scattering amplitudes and generalized R-matrix theory

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We establish a connection between the Kohn variational principle, with (complex) outgoing-wave boundary conditions, and the Kapur-Peierls form of the R-matrix theory. We show that the complex Kohn method, unlike the usual Kohn method, does not suffer from the problem of spurious singularities. We also discuss a generalization that allows the calculation of scattering cross sections over a continuous range of energies from a single diagonalization of the Hamiltonian. Several numerical examples are presented.

I. INTRODUCTION

In recent years electron-molecule and electron-atom scattering calculations have taken, broadly speaking, two major computational paths. The first of these, which involves the use of finite sets of basis functions, has been the use of variational principles based on either the differential or integral form of the scattering equations. The other approach has been to numerically solve the integro-differential equations resulting from a close-coupling expansion in target eigenstates. In the literature one finds descriptions of a large number of apparently different basis-set approaches based on variational principles, such as the Kohn and the Schwinger principles in their various implementations[1] as well as complex basis function or complex coordinate methods.[2] Recently, Miller and Jansen op de Haar[3] have clarified some important connections between the Kohn variational method and complex basis function approaches in the context of atom-molecule scattering.

In this paper we further explore the connections between the Kohn variational principle, a variational principle suggested by Nuttall and Cohen,[4] and the basis function R-matrix method.[5] Our principal interest here is in the use of these methods for electron scattering. In such problems the wavelength of the scattered particle is typically of the size of the target (of the order of a_0), but a critical point is the need for rapid convergence with respect to increasing the size of the basis when the potential behaves as r^{-n} asymptotically. This is the case if any target electronic polarization is included in the calculation or when the target has a permanent dipole or higher multipole moment.

The outline of the paper is as follows. In Sec. II we briefly discuss the equivalence, already established by Miller and Jansen op de Haar, of the Kohn variational principle and the variational principle suggested by Nuttall and Cohen for the T matrix for a particular choice of trial function. In addition, we show that using the identical trial function in the Kapur-Peierls form of R-matrix theory[6] leads to equivalent numerical accuracy to the variational forms. Finally, we explore an extension, in the spirit of complex basis function techniques, which allows the computation of the scattering amplitude for a range of energies from a single trial function. Section III presents the results of numerical calculations on short-range $[-\exp(-r)]$ and long-range (asymptotically r^{-3}) potentials. Section IV discusses the outlook for large-scale applications of these ideas to electron-molecule collisions.

II. THEORY

The Kohn variational principle[7] for the lth partial wave may be written as

$$\lambda^l = \lambda_t^l - \frac{2}{k} \int_0^\infty u_t^l(r) \left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V(r) - k^2/2 \right] u_t^l(r) dr , \quad (1)$$

where we employ atomic units throughout. Conventionally the trial function $u_t^l(r)$ is chosen with principal value boundary conditions:

$$u_t^l(r) = j_l(kr) + \lambda_t^l g(r) n_l(kr) + \sum_i c_i \varphi_i(r) . \quad (2)$$

Here, $j_l(kr)$ $[n_l(kr)]$ is the regular (irregular) Ricatti-Bessel function and $g(r)$ is a cutoff function which approaches zero for small r at least as fast as r^{l+1} and goes to one as r approaches infinity. With this choice of trial function λ^l and λ_t^l denote the tangent of the phase shift and its trial value, respectively. The φ_i are a set of

square-integrable (L^2) basis functions. It is with this form of the trial function that the well-known singularities of the Kohn method are associated.[8] If, on the other hand, we write the trial function with outgoing-wave boundary conditions,

$$u_t^l(r) = j_l(kr) + \lambda_{tt}^l g(r) h_l^+(kr) + \sum_i c_i \varphi_i(r) , \qquad (3)$$

where $h_l^+(kr)$ denotes the outgoing Ricatti-Hankel function, then λ_l and λ_t^l refer to the partial-wave scattering amplitude. This seemingly trivial change in boundary conditions will be seen to have profound consequences with regard to the spurious singularities of the Kohn variational principle.

To obtain the working equations, first insert the trial function into Eq. (1) and then set the derivatives with respect to the linear parameters to zero,

$$\frac{\partial \lambda}{\partial c_i} = 0, \quad \frac{\partial \lambda}{\partial \lambda_t} = 0 , \qquad (4)$$

thereby defining trial values for λ_t and the set of c_i. In the following we will suppress the partial wave index l. Performing the variations indicated in Eq. (4) gives, after an integration by parts of the matrix element involving $j(kr)$ and $h^+(kr)$ [or $n(kr)$] and some rearrangement,

$$\mathbf{c} = -\underline{M}^{-1}\mathbf{s} . \qquad (5)$$

To define the terms in this equation we first relabel the basis functions so that φ_0 refers to $g(r)h^+(kr)$ or $g(r)n(kr)$ depending on whether the trial function of Eq. (2) or Eq. (3) is used, and φ_1 through φ_N refer to the square-integrable functions. Then the vector $\mathbf{c}$ denotes the linear parameters $(\lambda_t, c_1, \ldots, c_N)$. The elements of $\mathbf{s}$ are $\langle \varphi_i^* | (E - H) | j \rangle$, and the elements of the matrix $\underline{M}$ are $\langle \varphi_i^* | (E - H) | \varphi_j \rangle$.

Using the trial values given by Eq. (5) in Eq. (1), we obtain the working equation for the final stationary result:

$$\lambda = -2/k (\langle j | V | j \rangle + \mathbf{s}\underline{M}^{-1}\mathbf{s}) . \qquad (6)$$

Writing the final expression in this form transparently reveals the origin of the spurious singularities encountered in the Kohn method when the trial function in Eq. (2) is used. In that case (if the basis of φ_i is a set of real-valued functions), $\underline{M}$ is a real symmetric matrix and has zero determinant at the values of E corresponding to the eigenvalues of H in the basis of φ_i plus $g(r)n(kr)$. On the other hand, if the trial function in Eq. (3) is used, $\underline{M}$ is a complex symmetric matrix, and its zeros are at complex values of E (except at E equal to a bound-state energy of H). We will establish below that in this case $\underline{M}$ can have no zeros at real values of E in the continuum, and that all the continuum eigenvalues of H in this basis are in the lower half E plane. As an example, we show, in Fig. 1, the spectrum obtained for the case of s-wave scattering by an attractive exponential potential. In this case, the square-integrable basis consisted of 14 Slater-type functions. Other basis-set parameters are as described in Sec. III.

Nuttall and Cohen[4] suggested another approach also leading to a complex symmetric matrix representation of
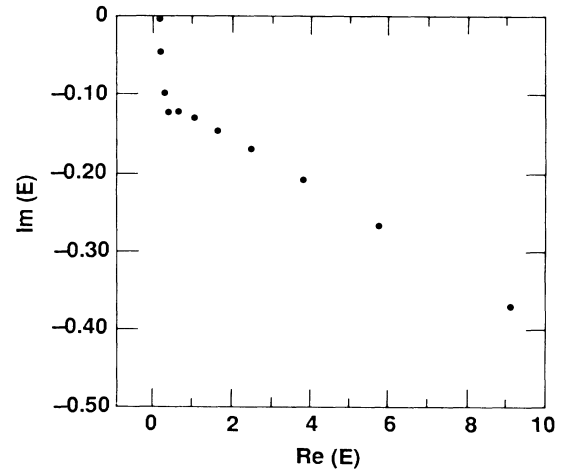

FIG. 1. Complex spectrum for s-wave exponential potential problem. Basis consists of 14 Slater-type functions and a cutoff Hankel function with $k = 0.55$.

$E-H$ in the working equations, which they proposed in the context of complex coordinate calculations, and which has been used extensively in complex basis function calculations. This approach begins with a stationary expression for the T matrix:

$$[T] = \langle j | V | j \rangle + \langle j | V | \chi \rangle + \langle \tilde{\chi} | V | j \rangle - \langle \tilde{\chi} | V | \chi \rangle . \qquad (7)$$

Miller and Jansen op de Haar[3] have pointed out that the trial functions χ and $\tilde{\chi}$ in this variational principle should have purely outgoing and incoming boundary conditions, respectively. Thus the trial functions corresponding to Eq. (3) above are

$$| \chi \rangle = c_0 g(r)e^{ikr} + \sum_i c_i \varphi_i(r) ,$$

$$| \tilde{\chi} \rangle = c_0^* g(r)e^{-ikr} + \sum_i c_i^* \varphi_i^*(r) . \qquad (8)$$

Inserting these trial functions into Eq. (7) and setting the derivatives of $[T]$ with respect to the linear parameters c_i to zero leads ultimately to the same expression for T as given for λ in Eq. (6) (except for an overall factor of $-2/k$). It can, in fact, be shown that the bilinear form given in Eq. (7) is equivalent to the Kohn variational expression of Eq. (1) for the case of a trial function of the form of Eq. (1) or (2).[9]

It is appropriate at this point to note that Eq. (6) appears to be nothing more than the exact expression for the T matrix:

$$T = \langle k | V | k \rangle + \langle k | VGV | k \rangle \qquad (9)$$

in which the Green's function G is approximated by the inverse of the matrix representation of $(E - H)$ in a basis consisting of a set of square-integrable functions plus a single continuum function of the form $g(r)h^+(kr)$:

$$G \simeq \sum_{i,j} | \varphi_i \rangle [\langle \varphi_i^* | (E - H) | \varphi_j \rangle]^{-1} \langle \varphi_j^* | . \qquad (10)$$

A remarkable fact, as pointed out by Lane and Robson,[10] is that the Kapur-Peierls form of R-matrix theory,[6] which imposes outgoing-wave boundary conditions on the wave function at finite r, can be put into precisely this form, except that the range of integration is over the finite interval $[0,a]$. The conventional formulation of Kapur-Peierls theory involves surface integrals, which when converted to integrals over a finite volume, yields the following expression for the T matrix:[10]

$$T = \langle k \mid V \mid k \rangle + \langle k \mid V(E - H - L)^{-1} V \mid k \rangle \ . \quad (11)$$

In this equation the Bloch operator[11] L is given by

$$L = \delta(r - a)(\partial/\partial r - ik) \ . \quad (12)$$

It is important to realize that the operator $(H + L)$ is not Hermitian. Thus to construct a spectral representation of the Green's function $(E - H - L)^{-1}$, it is necessary to use a biorthogonal set of eigenfunctions.[11] This property leads to a complex symmetric representation of the matrix when we realize that the dual eigenvector is the complex conjugate of the direct state. Thus Eq. (11) shares this important property with Eq. (6) which arose from the application of variational principles, even though Eq. (11) is not itself derived from a variational principle. However, since Eq. (11) and Eq. (6) are identical in the limit $a \rightarrow \infty$ or if the potential V vanishes outside of $r = a$, one might expect that trial functions like those in Eq. (8) would yield results of comparable accuracy to those obtained from the variational approaches.

Bloch[11] has shown that the Kapur-Peierls eigenvalues, that is, the eigenvalues of the equation

$$(H + L - E)\psi = 0 \quad (13)$$

lie in the lower half of the complex energy plane. This fact, along with the formal equivalence of the Kapur-Peierls expression for T and that arising from the complex variational principle in the limit $a \rightarrow \infty$, supports our earlier statement that the complex symmetric representation of H in the basis of φ_i plus $g(r)h^+(kr)$ has no eigenvalues at real values of E in the continuum. Thus, the complex version of the Kohn method will not suffer from the occurrence of spurious singularities.

Whether we approach this problem via the Kapur-Peierls method in Eq. (11) or via the variational methods in Eq. (6), the working equations bear a striking resemblance to complex basis function calculations of Green's-function matrix elements.[12] In such calculations, arbitrary complex basis sets are used with only the criterion that the discretized continuum eigenvalues of H remain in the lower half E plane. The similarity between the two approaches suggests the possibility of generalizing the present approach by employing several complex continuum functions, like $g(r)h^+(kr)$, with different values of k. In essence, such a procedure represents a quadrature of the continuous spectrum of the Hamiltonian together with an interpolation between those values of k by the square-integrable portion of the basis.

Under these conditions, a single trial function might be able to produce accurate results for a range of energies spanned by the values of k represented in the basis. This approach recovers, for either of the methods described above, a highly desirable property generally associated with R-matrix theory, namely, that a single diagonalization of the Hamiltonian gives results for a range of energies. There is a subtlety in this procedure for the variational approach which requires some clarification.

Consider the free-free matrix elements of the Hamiltonian which appear in the matrix M:

$$\int_0^\infty g(r)h^+(kr)[E + (\tfrac{1}{2}d^2/dr^2) - l(l+1)/2r^2 - V(r)]$$

$$\times g(r)h^+(k'r)dr \ .$$

If, in this integral $k = k'$, then E minus the kinetic energy operator acts on the function $g(r)h^+(kr)$ to give zero as r approaches infinity. This is the point Miller and Jansen op de Haar[3] make about the simple definition of the matrix elements in the procedure which makes use of only one value of k. When more than one k value is employed, so that k does not equal k', for example, this integral does not converge as written. Thus to evaluate this matrix element we must use its analytic continuation from the upper half k plane. If the kinetic energy matrix elements are given by analytic formulas, as they generally will be for simple choices of $g(r)$, the analytic continuation from $\text{Im}(k) > 0$ is given simply by those formulas. A trivial example of this sort of continuation is given by the integral

$$\int_0^\infty e^{ikr}dr = -1/ik \ . \quad (14)$$

This integral does not formally converge for real values of

TABLE I. Ratio of tangent of phase shift to accurate value (accurate value is $-1.744\,939\,3$) at $k = 0.15$ for s-wave scattering by an exponential potential. N refers to number of L^2 functions used in expanding trial wave function. See text for definition of various methods reported (AF, OAF, and $L2$-SVP taken from Ref. 15. SVP taken from Ref. 16.)

N	AF	OAF	$L2$-SVP	SVP	R-matrix	KP	CK
2	1.0005	1.0009	−0.6463	1.0000		0.9969	0.9937
4	1.0006	1.0004	1.2585	1.0000	−1.0235	1.0004	0.9991
6	1.0001	1.0000	1.0163		1.1364	1.0000	0.9999
8	1.0000		1.0016		1.0003		1.0000
10			1.0013		1.0000		
12			1.0009				
14			1.0004				

TABLE II. As in Table I, for $k=0.35$ (accurate value is 9.091 809 5).

N	AF	OAF	$L2$-SVP	SVP	R-matrix	KP	CK
2	0.9879	0.9858	0.1676	0.9999		1.1105	1.0963
4	0.9980	0.9978	0.7987	1.0000	0.1221	1.0021	1.0049
6	0.9983	0.9999	0.9261		0.5243	0.9977	1.0001
8	1.0000	0.9999	0.9382		0.9986	1.0000	1.0000
10		1.0000	0.9711		0.9998		
12			0.9916		1.0000		
14			0.9984				

k, but the formula gives the correct analytic continuation to real values of k from the upper half k plane. If we did not have the formula, the analytic continuation could be carried out by doing the integration numerically along a ray in r given by $re^{i\theta}$, $0 < \theta < \pi/2$, and leaving k real. The latter procedure can generally be used in cases where the analytic formulas are not available.[13] Thus the approach of continuum basis functions with more than one value of k is related to methods which analytically continue the Hamiltonian by one technique or another, while the use of only an "on-shell" trial function is not. In Sec. III we explore the convergence properties of these procedures and the performance of basis sets which contain continuum functions with more than one value of k.

III. COMPUTATIONAL EXPERIMENTS

The first example we consider is s-wave scattering of electrons by the potential

$$V(r) = -e^{-r} , \tag{15}$$

since this problem has been the subject of a systematic comparison of a number of different methods.[14-16] To facilitate comparison with previous work, the square-integrable basis functions in our calculations were chosen either as simple Slater functions,

$$\varphi_n(r) = r^n e^{-\lambda r} , \tag{16}$$

or (the unitarily equivalent) Laguerre functions,

$$b_n(r) = \frac{(2\lambda)^{3/2}}{\sqrt{(n+1)(n+2)}} re^{-\lambda r} L_n^2(2\lambda r) . \tag{17}$$

The latter choice reduces problems caused by numerical linear dependence of the basis functions. The cutoff function is taken to be

$$g(r) = (1 - e^{-\alpha r}) . \tag{18}$$

Tables I–III compare the results of various methods at three different energies for increasing numbers of square-integrable $(L2)$ functions. With a trial function of the form given by Eq. (3), we performed calculations using the complex Kohn (CK) and Kapur-Peierls (KP) methods. We also performed R-matrix calculations in which only the square-integrable functions were used in the trial function. The radius was chosen as $15a_0$ for the KP and R-matrix methods. The R-matrix results were obtained with $\alpha = 1.0$ and $\lambda = 0.5$; all other results used $\lambda = 2.5$. The results quoted for the anomaly-free (AF) and optimized anomaly-free (OAF) adaptations of the Kohn method were taken from Ref. 15. These both use real trial functions of the form of Eq. (2). The tables also show results of the Schwinger variational method both with (SVP)[16] and without $(L2$-SVP$)$[15] continuum functions in the basis. All the methods which include continuum functions in the basis display rapid convergence. The $L2$-SVP and R-matrix results, on the other hand, which do not use continuum functions, show much poorer convergence. We also carried out CK calculations over a fine energy grid and found no evidence of any instabilities or spurious singularities.

The second example we considered was s-wave scattering from a long-range potential

$$V(r) = \frac{(1 - e^{-r})^2}{r^3} , \tag{19}$$

using the same form for the basis as we did in the previous example. Table IV shows how the results of the CK and KP methods converge at three different energies as the number of Laguerre basis functions is increased. These results were obtained with $\alpha = \lambda = 1.0$. Note that

TABLE III. As in Table I, for $k=0.55$ (accurate value is 2.200 382 7).

N	AF	OAF	$L2$-SVP	SVP	R-matrix	KP	CK
2	0.9968	0.9940	0.6063	0.9999		0.9820	1.0356
4	0.9999	0.9970	0.9264	1.0000	-0.2668	1.0025	1.0003
6	1.0000	0.9999	0.9369		0.3420	1.0000	1.0000
8		1.0000	0.9775		0.9932		
10			0.9969		0.9992		
12			0.9997		0.9999		
14			0.9997		1.0000		

TABLE IV. s-wave phase shifts for long-range potential discussed in text.

N	k=0.15		k=0.35		k=0.55	
	KP	CK	KP	CK	KP	CK
5	2.468 45	2.471 93	1.881 66	1.880 05	1.564 28	1.562 32
10	2.468 86	2.473 57	1.880 86	1.882 61	1.563 95	1.564 99
15	2.468 86	2.473 53	1.880 93	1.882 60	1.563 96	1.565 00
20	2.468 86	2.473 53	1.880 93	1.882 60	1.563 96	1.565 00

the rates of convergence for both methods are comparable, but that the KP method seems to converge to values slightly different from those obtained with the CK procedure. For this long-range potential, the KP results are weakly dependent on the finite value of the box radius used in the calculations ($30a_0$ here). Not surprisingly, we found that R-matrix calculations (not shown) in which only the discrete basis functions were retained converged very slowly. Takatsuka et al.[16] also found that the accuracy of Schwinger calculations employing solely L^2 functions were strongly affected by the range of the potential.

We also carried out calculations with the generalized CK method in which more than one continuum function was included in the basis. Table V shows the results of a calculation employing 20 Laguerre functions and three continuum functions. The accuracy of the results is of course highest when the physical value of k coincides with that of one of the continuum functions. The method is, however, capable of interpolating between the continuum basis-set k values with an accuracy of better than 0.1%. With only one continuum function in the expansion, the CK method is capable of producing accurate results only in a narrow region centered around the value of k used. This behavior is displayed in Fig. 2 and contrasted with the results of the generalized CK method.

IV. CONCLUSION

The principal points of this paper have been to show (1) that with a trial function containing outgoing waves

$[h_l^+(kr)]$ the Kohn variational principle has no spurious singularities, (2) that a transparent connection exists between Kapur-Peierls theory and the complex Kohn variational principle for a particular choice of trial function, and (3) that a substantially more general form of the trial function, using continuum basis functions with more than one energy, leads to a computational approach which allows calculation of the cross section over a range of energies from one diagonalization of the Hamiltonian. Particularly in the latter approach, these ideas hold considerable promise for application to electron-molecule collisions.

In electron scattering calculations the limiting factor, particularly for molecular targets, is the computation of two-electron interaction integrals. Using the more general trial function we have employed here allows the efficient calculation of cross sections with minimal recomputation at each energy of a large subset of the integrals involved. No matter which of the procedures discussed here is used, only a few partial waves (of the order of 10) are needed asymptotically in electron-molecule scattering at energies less than 10 eV. Thus the prescription of expanding the wave function in the interaction region in square-integrable basis functions, which may be centered on atomic centers, while using only a few functions of the form $Y_{lm}(\Theta)h_l^+(kr)$ asymptotically represents an optimum description of the physics of the situation.
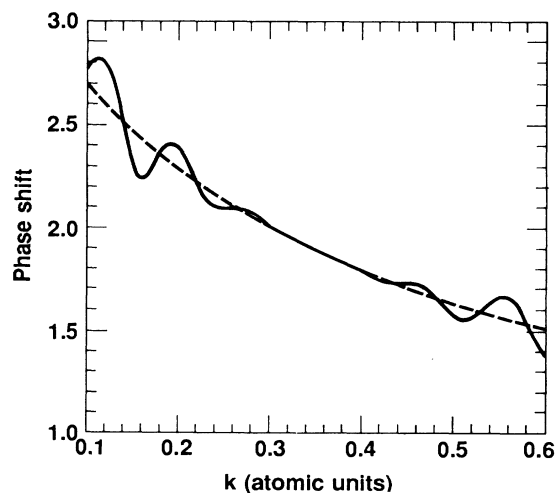
TABLE V. s-wave phase shifts for long-range potential with multiple continuum functions in basis. (Expansion basis consisted of 20 Laguerre functions plus three cutoff Hankel functions with k values of 0.15, 0.35, and 0.55.)

k	CK	Exact
0.1	2.697 89	2.694 33
0.15	2.473 53	2.473 53
0.2	2.284 36	2.285 63
0.25	2.126 61	2.127 76
0.3	1.994 39	1.995 04
0.35	1.882 61	1.882 60
0.40	1.785 54	1.786 25
0.45	1.702 02	1.702 80
0.5	1.628 98	1.629 68
0.55	1.565 00	1.565 00
0.6	1.506 64	1.507 25

FIG. 2. Energy dependence of s-wave phase shifts for long-range potential computed using CK method with one ($k=0.35$, solid curve) and three continuum functions, respectively.

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