Scattering formulation based on an amplitude-independent variational principle

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In this paper we reply to the preceding Comment by Abdel-Raouf concerning several features of an amplitude-independent variational principle which we have recently proposed. The most substantive discussion concerns the nature of the singularities which can arise in one of these variational principles. The specific variational principle involved contains the Hamiltonian and not the Green's-function operator.

The complexities of low-energy electron-molecule collisions have stimulated much interest in several approaches to the scattering problem.[1] In this context, we have recently discussed a series of amplitude-independent variational principles.[2-4] Basically our discussion was concerned with elucidating the relationship between the Schwinger- and Kohn-type variational principles and with extending the Schwinger principle so as to obtain additional variational functionals which could be of some utility in electron-molecule collisions.

In this paper we reply to the Comment of Abdel-Raouf[5] concerning the originality of our development of these variational principles and to his criticism of some features which we attributed to one of these variational functionals. A summary of our response is that while we agree with some of his comments we disagree with others. We will also clarify some aspects of our formulation.

We begin with Schrödinger's equation for the scattering problem in the form

$$(E-H)\phi = \hat{H}\phi = 0 \ . \tag{1}$$

As usual H is divided into a collision-free part H_0 and an interaction potential V. We note, however, that $\hat{H}$ is defined as $E-H$ in Eq. (1). The scattering wave function can be written as

$$\phi = S + \tilde{C} \tag{2}$$

which $\tilde{C}$ expanded in the form

$$\tilde{C} = C\tan\delta + \sum_i a_i \chi_i \ . \tag{3}$$

In these equations, S is a regular solution of H_0 at energy E, and C is a regularized version of the irregular solution. In Eq. (3), χ_i is a square-integrable (L^2) function and δ is the phase shift. For convenience we consider the simple case of potential scattering. The function $\tilde{C}$ satisfies the Schrödinger equation

$$\hat{H}\tilde{C} = VS \tag{4}$$

and the corresponding Lippmann-Schwinger equation

$$(V - VG_0V)\tilde{C} = VG_0VS \ , \tag{5}$$

where G_0 is the Green's function for $H_0 - E$ with the appropriate boundary condition. Obviously more general variants of Eq. (6) may be obtained by working with the iterated version of the Lippmann-Schwinger equation.

For the inhomogeneous equation

$$Ay = b \ , \tag{6}$$

where A is an operator and y is a function to be determined, it is well known that the associated variational functional for the quantity $\langle y|A|y\rangle$ is given by

$$[Y] = \frac{\langle y|b\rangle\langle b|y\rangle}{\langle y|A|y\rangle} \ . \tag{7}$$

In Eq. (7), y is treated as a trial function. The conditions under which $[Y]$ is unique and variationally stable are known and have recently been discussed.[6] Equations (4) and (5) immediately lead to the following functionals:

$$F_1 = \frac{\langle\tilde{C}|V|S\rangle\langle S|V|\tilde{C}\rangle}{\langle\tilde{C}|\hat{H}|\tilde{C}\rangle} \tag{8}$$

and

$$[X] = \frac{\langle\tilde{C}|VG_0V|S\rangle\langle S|VG_0V|\tilde{C}\rangle}{\langle\tilde{C}|(V-VG_0V)|\tilde{C}\rangle} \ . \tag{9}$$

At the time we wrote our paper in which we obtained Eqs. (8) and (9), we were unfortunately unaware of the earlier work of Moe and Saxon[7] [in which Eq. (8) had been obtained] and that of Kolsrud[8] [in which both Eqs. (8) and (9) had been derived]. Abdel-Raouf correctly points this out in his paper.[5] Kolsrud did, however, draw our attention to his previous publication[8] and we were able to add a note in proof to a later paper[9] in which we presented results of our application of the functional of Eq. (9).

A few comments on the relevance of Eqs. (8) and (9) to our work at that time are in order. First, unlike the Schwinger and its related variational principles which all contain the Green's function, Eq. (8) is an amplitude-independent functional in which only the Hamiltonian appears. This can be a substantial advantage in applications to electron-molecule collisions since much more powerful computational procedures are available for handling matrix elements of the Hamiltonian than of the Green's function for such systems. Applications of Eq. (8) to a two-channel model problem showed convergence characteristics very similar to those of the Schwinger principle which is known to be of higher order than the usual Kohn method.[4,10] We also noted, on theoretical grounds,[10] that the functional of

Eq. (9) should directly provide K matrices of the quality of those obtained after one iteration in the iterative Schwinger method.[11] This is an important feature since substantial improvement normally occurs after one iteration in this procedure[11] and, moreover, such iterations can be quite time consuming for the more difficult or larger molecular targets. These observations were confirmed in actual applications to the polar systems LiH and CO^+.[9] We believe that these developments have helped to put this functional, referred to by us as the $\tilde{C}$ functional, in a very useful perspective.

We now turn to Abdel-Raouf's comments concerning several features of the variational functional F_1 of Eq. (8) which we discussed in Ref. 3 and 4. Abdel-Raouf[5] claims that we stated that the trial functions used in F_1 need not satisfy the appropriate scattering boundary conditions. In our paper,[4] however, we stated that no specific *asymptotic form* is required of the function $\tilde{C}$ used in this functional. We note that the term *asymptotic form* has been replaced by *boundary condition* in his criticism of an important feature of this functional. In the ordinary Kohn-type variational principles, the coefficient of the asymptotic function $\tilde{C}$ in Eq. (3) is determined algebraically. On the other hand, such a computational constraint is not necessarily required of F_1, suggesting that an L^2 approach can be used to F_1. Of course, if one specifically introduces the asymptotic function $\tilde{C}$ into the scattering basis, just as in Eq. (3), F_1 reduces exactly to the Kohn principle.[3] What we stated was that F_1 does not require the correct asymptotic function in the trial function. However, we never stated that F_1 does not require any *boundary conditions* when applied in an L^2 form. In the application of this method to a model two-channel problem, we explicitly stated that boundary conditions had to be imposed on the basis functions.[4] In fact, we actually defined a boundary as in the R-matrix theory, and applied the F_1 functional inside the boundary by using only L^2 functions on which certain boundary conditions were imposed at this boundary.[4] We showed that the wave function ϕ could consequently be smooth everywhere. This follows from the fact that the logarithmic derivatives at the boundary are imposed on $\tilde{C}$ rather than on the total wave function ϕ. It can be shown that the logarithmic derivative of $\tilde{C}$ does not depend on $\tan\delta$, while that of ϕ does.[4] These and other details are discussed in Ref. 4. The results of these applications illustrated the excellent convergence characteristics of the functional.

In Ref. 3 we argued that by working with a slightly modified Schrödinger equation, the anomalous singularities which arise in many standard variational principles could be avoided in the functional of Eq. (8). In his model calculations, Abdel-Raouf[5] finds an anomalous singularity in our supposedly anomalous-singularity-free modification of Eq. (8). This result does show that anomalous singularities cannot be avoided in this modified functional as we originally stated. However, we will show that with appropriate modifications and approximations, the procedure remains very useful and can provide meaningful insight into the nature of these resonances. It should be noted that a number of methods for avoiding these anomalous singularities have been developed.[12]

The procedure we discussed in Ref. 3 for avoiding these anomalous singularities begins with the slightly modified Schrödinger equation

$$(\hat{H} - tX)|\tilde{C}_t\rangle = V|S\rangle \quad , \tag{10}$$

where

$$X = V|S\rangle\langle S|V \quad , \tag{11}$$

and t is an arbitrary parameter. This inhomogeneous equation leads to the functional

$$F_1^t = \frac{\langle \tilde{C}_t|V|S\rangle\langle S|V|\tilde{C}_t\rangle}{\langle \tilde{C}_t|(\hat{H} - tX)|\tilde{C}_t\rangle} \quad , \tag{12}$$

which can provide the phase shift through the relation

$$-\tfrac{1}{2}\tan\delta = \langle S|V|S\rangle + \frac{F_1^t}{1 + tF_1^t} \tag{13a}$$

$$= \langle S|V|S\rangle + \frac{\langle \tilde{C}_t|V|S\rangle\langle S|V|\tilde{C}_t\rangle}{\langle \tilde{C}_t|\hat{H}|\tilde{C}_t\rangle} \quad . \tag{13b}$$

We first consider the proportionality between $|\tilde{C}_t\rangle$ and $|\tilde{C}\rangle$. We define $\underline{\hat{H}}_c$ to be the matrix representation of $\hat{H}$ in a basis $B = \{C, \chi_i, i = 1, 2, \ldots, N\}$. In what follows we assume that this basis is used both in the Kohn method and F_1^t functional but not in the R-matrix approach to F_1^t which we discussed above. We apply $\underline{\hat{H}}_c^{-1}$, if it exists, to Eq. (10). This is written symbolically (in a matrix sense) as

$$[1 - t\underline{\hat{H}}_c^{-1}V|S\rangle\langle S|V]|\tilde{C}_t\rangle = \underline{\hat{H}}_c^{-1}V|S\rangle \quad . \tag{14}$$

On the other hand,

$$|\tilde{C}\rangle = \underline{\hat{H}}_c^{-1}V|S\rangle \tag{15}$$

holds in the implicit matrix representation of the Kohn principle [see Eq. (4)]. Hence, we have

$$|\tilde{C}_t\rangle = \{t\langle S|V|\tilde{C}_t\rangle + 1\}|\tilde{C}\rangle \quad . \tag{16}$$

Hence, if $\underline{\hat{H}}_c^{-1}$ exists, i.e., Eq. (16) has a nondivergent solution within a given basis, and if Eq. (10) is solved in a manner similar to the ordinary Kohn method, the phase shift of Eq. (13) must be independent of t and thus must coincide with that of the usual Kohn method. Abdel-Raouf's results of Table I are therefore to be expected.[5] These functionals are still, however, quite useful. First, they can be applied with considerable flexibility as we showed in our calculations.[4] Secondly, if $\det(\underline{\hat{H}}_c)$ is zero and hence the usual Kohn method has a divergence, we can analyze the situation in greater detail,

Consider the case where $\det(\underline{\hat{H}}_c) = 0$ and $|\tilde{C}\rangle$ diverges. Even in this case, the pole-shifting operator can be used to keep $|\tilde{C}_t\rangle$ finite by adjusting t. This is illustrated numerically in Fig. 1 of Abdel-Raouf.[5] Generally as $\det(\underline{\hat{H}}_c)$ approaches zero, $|\tilde{C}\rangle$ of Eqs. (15) and (16) begins to diverge. On the other hand $|\tilde{C}_t\rangle$ remains finite throughout. The coefficient x_t of Eq. (16), i.e.,

$$x_t = t\langle S|V|\tilde{C}_t\rangle + 1 \tag{17}$$

must approach zero as $\det(\underline{\hat{H}}_c)$ approaches zero as a function of the incident energy or of the size of the basis set.

If x_t of Eq. (17) is zero, Eq. (10) can then be written as

$$\underline{\hat{H}}_c|\tilde{C}_t\rangle = V|S\rangle\{t\langle S|V|\tilde{C}_t\rangle + 1\} = 0 \tag{18}$$

again in a matrix sense. Thus, within the basis set B, $|\tilde{C}_t\rangle$ belongs to the zero eigenvalue of $\hat{H}$, or

$$\langle \mu_j|\hat{H}|\tilde{C}_t\rangle = 0 \quad , \tag{19}$$

where μ_j belongs to the basis B. Thus, as pointed out by

Abdel-Raouf in Fig. 2,[5] Eq. (13b) has a singularity when $\underline{\hat{H}}_c^{-1}$ is singular. Nevertheless, as we will show below, we can still make use of the fact that $|\tilde{C}_t\rangle$ is still finite.

We note that $-\frac{1}{2}\tan\delta$ of Eq. (13) can also be written as

$$-\tfrac{1}{2}\tan\delta = \langle S|V|S\rangle + \frac{1}{x_t}\langle S|V|\tilde{C}_t\rangle \quad , \tag{20}$$

which shows the divergence due to $x_t = 0$. That x_t is zero follows from Eq. (19). We also note that only $\underline{\hat{H}}_c$ is used in Eq. (19). Thus, another approximation for x_t in Eq. (20) is to use

$$\langle S|\hat{H}|\tilde{C}_t\rangle = x_t^s\langle S|V|S\rangle \quad . \tag{21}$$

If x_t^s is not zero, $-\frac{1}{2}\tan\delta$ can then be approximated by

$$-\tfrac{1}{2}\tan\delta = \langle S|V|S\rangle + \frac{1}{x_t^s}\langle S|V|\tilde{C}_t\rangle \quad . \tag{22}$$

It is easy to see that $\tan\delta$ of Eq. (22) is equivalent to the value given by Kato's identity[13]

$$[\lambda] = \frac{1}{x_t^s}\lambda_t + 2\left\langle S + \frac{1}{x_t^s}\tilde{C}_t\middle|H\middle|S + \frac{1}{x_t^s}\tilde{C}_t\right\rangle \quad , \tag{23}$$

where λ denotes $\tan\delta$ and λ_t is the coefficient of C in $\tilde{C}_t$.

We next consider the case

$$\langle S|\hat{H}|\tilde{C}_t\rangle = 0 \tag{24}$$

possibly occurring in Eq. (21) and leading to $x_t^s = 0$ unless $\langle S|V|S\rangle = 0$. Equations (19) and (24) then lead to another type of singularity in Eq. (22). Thus, there are two kinds of singularities. (i) A singularity of the first kind. This is solely due to Eq. (19) and inherent in the Kohn principle. This singularity is spurious and avoidable[14] in various ways[14–16] including the use of Eq. (22). (ii) A singularity of the second kind. When both Eqs. (19) and (24) hold, this singularity occurs. These conditions simply imply that $|\tilde{C}_t\rangle$ is the solution of the projected Schrödinger equation

$$(E - H)|\tilde{C}_t\rangle = 0 \tag{25}$$

within the basis $\{S, C, \chi_i | i = 1, \ldots, N\}$. With a given basis, this singularity cannot be avoided by a change of method. It is also impossible to mathematically identify whether this singularity is spurious or physically meaningful, the latter case being possibly connected with a resonance. To our knowledge, little is known about the properties of Eq. (23). For example, can the singularity disappear completely from this energy region as the basis set is augmented? Such questions are still open and important for a deeper understanding of resonance phenomena.

In Ref. 3 we also showed that a *maximum* principle could be developed for $(F_1^t)^{-1}$. The argument is as follows.[3] Kato[17] showed that for a variational functional

$$J(V) = \frac{\langle V|A|V\rangle}{\langle V|f\rangle\langle f|V\rangle} \tag{26}$$

one has a *minimum* principle if the operator $A + C|f\rangle\langle f|$ is *positive* for some fixed constant C. In our expression for $-(F_1^t)^{-1}$,

$$-(F_1^t)^{-1} = \frac{\langle \tilde{C}_t| - (\hat{H} - tX)|\tilde{C}_t\rangle}{\langle \tilde{C}_t|VS\rangle\langle VS|\tilde{C}_t\rangle} \quad , \tag{27}$$

we have $A = -(\hat{H} - tX)$, $|f\rangle = |VS\rangle$, and $|\tilde{C}_t\rangle = V$. Since $\hat{H}$ is $E - H$, the $-\hat{H}$ of electron-molecule collision systems has a lower bound. Moreover, X of Eq. (11) is positive definite. Therefore we can generally find t which makes $-(H - tX) + cV|S\rangle\langle S|V$ positive for some constant c. This can also be stated by saying that $(\hat{H} - tX) + c'V|S\rangle\langle S|V$ can be negative for some constant c' by choosing t sufficiently large. We thus have a *minimum principle for* $-(F_1^t)^{-1}$ or, equivalently, a *maximum* principle for $(F_1^t)^{-1}$. Of course, if the H under study has eigenvalues at negative infinity, this maximum principle does not hold.

In the paper of Abdel-Raouf,[5] our claim that the *negativeness* of $\hat{H} - tX + c'V|S\rangle\langle S|V$ for some c' and t leads to a *maximum* principle for $(F_1^t)^{-1}$ has been replaced by the statement that the *positiveness* of $\hat{H} - tX + c'V|S\rangle\langle S|V$ for some c', and t leads to a *minimum* principle for $(F_1^t)^{-1}$. Obviously this latter statement does not make sense, since for any reasonable Hamiltonian of interest $\hat{H}$ does not have a lower bound. Note that with our definition of $\hat{H}$ as $E - H$, $\hat{H}$ can be negative infinity.

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