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Variational principles for reactive collisions based on the generalized Lagrange multiplier method

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In this study is discussed a general approach to derive variational principles for physical magnitudes $Q(\phi)$ which are dependent on functions ϕ known to be solutions of physical equations [see Gerjuoy *et al.*, *Rev. Mod. Phys.* **55**, 725 (1983)]. The approach is based on Lagrange multipliers which are incorporated into the expression for calculating Q by demanding that the functions ϕ fulfill their equations. This approach is first applied to derive a general variational principle for the T -matrix elements based on the Lippmann-Schwinger equation. As special cases we obtained the bilinear forms of the Schwinger and the Newton variational principles. Next this approach is employed to derive a new Kohn-type variational principle for the S -matrix elements for reactive collisions based on the Schrödinger equation which contains complex potentials. Finally, this approach is further utilized to derive a novel variational principle for the flux function.

I. INTRODUCTION

The presentation of physical functions in terms of discrete basis sets is a very common process while solving bound-state problems, scattering problems as well as problems of similar types in other branches of Physics. As the physical system becomes more involved the number of basis sets to be included in such an expansion becomes accordingly larger and larger. Thus it is well known that the main bottleneck of every treatment of a large bound-state problem or a large scattering process is the size of the matrix of coefficients that has to be treated. This situation calls not only for very efficient methods to solve such a system of equations but also for developing efficient variational principles (VP) that will allow us to reduce the number of equations to be solved.

Variational principle is one of the most powerful and reliable methodologies in calculus and has been applied extensively not only to bound-state problems in which extremum condition is satisfied but also to scattering problems in which only stationarity is fulfilled.¹⁻³ In scattering theory, electron scattering has been the main target of applications of variational principles, especially the Kohn-type variational principle, although the applications have been mostly confined to electron-atom scattering² and scarce in the case of electron-molecule scattering.³ This is because only a small number of partial waves are needed at low collision energies thanks to the smallness of the electron mass.

It was only recently that methods based on solving coupled algebraic equations to treat reactive (exchange) processes ran into severe difficulties caused by the lack of computer core memory. This situation enforced the introduction of variationally based improvements in order to reduce the size of the encountered system of algebraic equations to be solved.

Following a very extensive study, Staszewska and Truh-

lar,⁴ who investigated 35 different algebraic methods for solving the Lippmann-Schwinger (LS) equation concluded that the Newton VP⁵ which is applied for the amplitude density function^{6,7} (and not the wave function) yields the most efficient set of algebraic equations. This method which was incorporated in one version of the Baer-Kouri-Levin-Tobocman equations^{7,8} was then successfully applied to a large series of reactions.⁹

Miller¹⁰ developed a method where the wave function is expressed as a coupled channel expansion simultaneously in all arrangements using standard Jacobi coordinates of each arrangement. Into this method Miller and co-workers¹¹ (see Ref. 12 for a similar application in nuclear physics) incorporated the Kohn VP¹³ (in such a way that it avoids the Kohn anomalies) which was then also successfully applied to a series of reactions¹⁴ as well as to photodissociation.¹⁵

Recently, Neuhauser and Baer (NB)¹⁶ proposed the use of negative imaginary potentials (NIP) for the study of reactive (exchange) processes. The idea is to decouple the one arrangement channel (AC) of interest from all the others by absorbing the fluxes leaking into the other ACs and in this way to be able to eliminate them. NIPs for this purpose have to fulfill three (somewhat contradictory) basic requirements:

(a) They have to be short range (~ 1 Å).
(b) They have to be concentrated enough to absorb all the flux they encounter.

(c) They have to be soft enough not to cause reflection.

Such potentials can be found; they are of a triangular, linear-ramp-type form and their parameters, namely, their height and width, can be safely estimated before the numerical treatment.

In actual calculations¹⁶⁻¹⁸ these potentials are added to the ordinary potential and the resulting Hamiltonian is now treated as usual. The application of the NIP was further extended by substituting them also in the asymptotic region^{16,18} of the AC under consideration. In this way Baer, Neuhauser, and Oreg (BNO)¹⁹ converted the scattering problem into a bound system problem and expanded the

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scattering wave function in terms of basis sets. This last step makes the BNO approach somewhat similar to the method of Miller^{10,11} because, like him, BNO consider the Schrödinger equation expressed in terms of Jacobi coordinates and like in his case the BNO wave function is expanded in terms of basis sets. The main difference between the two approaches is that in Miller's case all ACs are solved simultaneously whereas BNO solve for one AC at a time. This one AC is somewhat broader than the usual ones (to prevent leakages of fluxes from other ACs) but still is of much smaller size than the entire configuration space to be treated in Miller's approach. However, whereas Miller treats real potentials BNO have to treat complex potentials. This seems to be a serious disadvantage but from the experience that Neuhauser, Baer, and co-workers¹⁶⁻²⁰ as well as Child²¹ have had no essential difficulties were encountered in working with these potentials.

Since we intend to extend this method to realistic three-dimensional systems it is important to incorporate the relevant VP. The present study was motivated by this need.

Eight years ago Gerjuoy, Rau, and Spruch²² wrote a very illuminating review on the application of VP to scattering and bound-state problems and introduced a unified formulation for the construction of VP. The basic idea of their approach is that the equation which describes the process under consideration can be incorporated into a VP as constraints through the use of (generalized) Lagrange multipliers; these can be constants, scalars, vectors, or matrix functions of one or more variables, operators, etc. In a typical case the Lagrange multiplier L serves as a new function which has to be calculated and then used to construct the VP. The construction of the VP readily yields the variational identities for a given quantity Q . This approach was mentioned for the first time by Borowitz and Gerjuoy²³ but then was independently introduced by Haymaker and Blankenbecker²⁴ and by Rau and Spruch (mentioned, without reference, in Ref. 22). In Ref. 25 we listed a few of the main references on this subject.

The strange feeling about VP, when going through the literature, is that it seems like a "Black Magic" where addition and subtraction of "zeros" finally lead to a numerical stable procedure for calculating various quantities. The application of Lagrange multipliers as presented in this review yields a unified way (which also requires skill and sometimes ingenuity) to derive variationally sound equations. Also a series of cases which are important as well as instructive were worked out.

Here, in our study, we concentrated on two types of scattering problems:

(a) We applied this approach to derive a general representation of a VP for the T -matrix elements based on the LS equation from which we obtained, as special cases, the bilinear forms⁴ of the Schwinger and the Newton VPs.

(b) We employed this approach to derive VP for the case where a multiarrangement scattering problem is converted into a single AC bound system problem with the use of the NIP. This was done twice; once when the single AC was chosen to be a products AC and we derived the Kohn-type VP¹³ (which are, in fact, Kato's variational identities²⁶) for the S -matrix elements and the second time when the single AC was chosen to be the reagents AC and the aim is to calculate directly the reactive flux function. The final equations obtained for the first case are similar to those derived by Miller and co-workers¹¹ and Kamimura.¹²

II. CONSTRUCTION OF VARIATIONAL PRINCIPLES FOR THE LIPPMANN-SCHWINGER EQUATION

In this section we derive the Schwinger and the Newton variational principle with use of the Gerjuoy-Rau-Spruch's Lagrange multiplier method. This is not only instructive for understanding the basic idea of their method, but also enables us to derive a more general VP expression.

The LS equation for the potential scattering case is written in the form,

$$\psi = \phi + G_0 V \psi, \quad (1)$$

where ψ is the full solution, G_0 is the Green function of the form,

$$G_0 = (E - H_0)^{-1}. \quad (2)$$

ϕ is the solution for the unperturbed Hamiltonian H_0 and V is the perturbation potential. The coordinate representation of G_0 is

$$G_0(R^>, R^<) = -\frac{2\mu}{\hbar^2} \phi_{re}(R^<) \phi_{ir}(R^>), \quad (3)$$

where $R^<$ and $R^>$ are the lesser and the greater of two given variables R and R' , ϕ_{re} and ϕ_{ir} are the regular and the irregular solutions of the unperturbed SE and μ is the reduced mass of the system. Consequently the coordinate representation of the LS equation is

$$\begin{aligned} \psi(R) = & \phi_{ir}(R) - \frac{2\mu}{\hbar^2} \left[\phi_{re}(R) \int_0^R dR' \phi_{re}(R') V(R') \right. \\ & \left. \times \psi(R') - \phi_{re}(R) \int_R^\infty dR' \phi_{ir}(R') V(R') \psi(R') \right]. \end{aligned} \quad (4)$$

The starting point for building a VP is the expression,

$$Q_v = Q_t - \int_0^\infty dR L [\psi_t - \phi - G_0 V \psi_t], \quad (5)$$

where Q_v is a variational estimate for Q , Q_t is a trial value of Q calculated from the analytic expression $Q_t = Q(\psi_t)$, $\psi_t(R)$ is a trial solution of ψ and $L(R)$ is a Lagrange multiplier yet to be determined. In order for Eq. (5) to be stationary the following condition has to be fulfilled:

$$\begin{aligned} \delta Q = & \int_0^\infty dR \delta L (\psi - \phi - G_0 V \psi) \\ & - \int_0^\infty dR L (1 - G_0 V) \delta \psi = 0. \end{aligned} \quad (6)$$

Since the second expression is zero because ψ is a solution to the LS equation we are left with equation:

$$\delta Q - \int dR L (1 - G_0 V) \delta \psi = 0. \quad (7)$$

Thus it is now our task to determine $L(R)$ so that Eq. (7) is satisfied.

For the following we assume that Q is given in the form:

$$Q = \int dR \phi^*(R) \Gamma(R) \psi(R) + q, \quad (8)$$

where $\Gamma(R)$ is the coordinate representation of given operator Γ , and q is a constant. Consequently δQ becomes

$$\delta Q = \int dR \phi^*(R) \Gamma(R) \delta \psi(R). \quad (9)$$

To continue the treatment of Eq. (7) with δQ given in Eq. (9) we need to show that

$$\int dR L G_0 V \delta \psi = \int dR \delta \psi G_0 V L. \quad (10)$$

This is explicitly done in Appendix A using the coordinate representation of the Green function.

Substituting Eqs. (9) and (10) in Eq. (7) yields

$$\int dR \delta \psi [\phi^* \Gamma - L - V G_0 L] = 0. \quad (11)$$

Since Eq. (11) is required to be fulfilled for any $\delta \psi$ we get that L has to be a solution of the equation

$$L = \phi^* \Gamma + V G_0 L. \quad (12)$$

Next we define the function $\lambda(R)$ by the expression

$$L(R) = \Gamma(R) \lambda(R) \quad (13)$$

and consequently the equation for $\lambda(R)$ can be written formally as

$$\lambda = \phi^* + (\Gamma^{-1} V G_0 \Gamma) \lambda. \quad (14)$$

Thus λ fulfills an integral equation where the boundary conditions are given in terms of the complex conjugate solution of the unperturbed SE.

In what follows we consider the case that Q is a T -matrix element defined as

$$T = \int dR \phi^*(R) V(R) \psi(R), \quad (15)$$

and we will distinguish between two representations.

A. The noniterative representation for T

Comparing Eq. (8) with Eq. (15) it is seen that in this case $q = 0$ and that $\Gamma = V$. Assuming $V \neq 0$ we get from Eq. (14) that

$$\lambda = \phi^* + G_0 V \lambda \quad (16)$$

which is identical to the LS equation with ϕ^* as the unperturbed solution. Consequently λ is recognized as ψ^* and L becomes

$$L(R) = V(R) \psi^*(R). \quad (17)$$

Thus the new estimate of the T -matrix element in Eq. (5) (employing bra-ket notation) is

$$T = \langle \phi | V | \psi_i \rangle - \langle \psi_i | V | \psi_i \rangle + \langle \psi_i | V | \phi \rangle + \langle \psi_i | V G_0 V | \psi_i \rangle. \quad (18)$$

This expression is known as the Schwinger variational principle written in a bilinear form.⁴

B. The iterative representation for T

Considering Eq. (15) and replacing ψ by the expression given in Eq. (1) T can also be written as

$$T = \langle \phi | V | \phi \rangle + \langle \phi | V G_0 V | \psi \rangle. \quad (19)$$

Repeating the process N times yields for T , the N th-order representation for T (Born series)

$$T = \sum_{j=0}^{N-1} \langle \phi | V (G_0 V)^j | \phi \rangle + \langle \phi | V (G_0 V)^N | \psi \rangle \quad (20)$$

comparing this expression for T with the one for Q given in Eq. (8) we get

$$q = \sum_{j=0}^{N-1} \langle \phi | V (G_0 V)^j | \phi \rangle; \quad \Gamma = V (G_0 V)^N. \quad (21)$$

Substitution of Eq. (21) for Γ in Eq. (14) yields the following equation for λ :

$$\lambda = \phi^* + G_0 V \lambda \quad (22)$$

which is identical to the LS equation for ψ but where the inhomogeneous term ϕ is replaced by ϕ^* . Consequently, as before, λ is recognized as ψ^* . Replacing λ , in Eq. (13), by ψ^* and recalling Eq. (21) for Γ we find that L is given as

$$L = V (G_0 V)^N \psi^*. \quad (23)$$

Substituting Eq. (23) in Eq. (5) and replacing Q by T given in Eq. (20) a new estimate for T is obtained,

$$T = \sum_{j=0}^N \langle \phi | V (G_0 V)^j | \phi \rangle + \langle \phi | V (G_0 V)^N \psi_i \rangle - \int dR V (G_0 V)^N \psi_i^* [\psi_i - \phi - G_0 V \psi_i]. \quad (24)$$

Employing the explicit form of the Green function it can be shown that the second term in Eq. (24) becomes

$$\therefore \int dR \psi_i^* V (G_0 V)^N [\psi_i - \phi - G_0 V \psi_i]$$

and consequently Eq. (24) (in bra-ket notation) becomes

$$T = \sum_{j=0}^N \langle \phi | V (G_0 V)^j | \phi \rangle + \langle \phi | (V G_0)^N V | \psi_i \rangle - \langle \psi_i | V (G_0 V)^N | \psi_i \rangle + \langle \psi_i | V (G_0 V)^N | \phi \rangle + \langle \psi_i^* | V (G_0 V)^N G_0 V | \psi_i \rangle. \quad (25)$$

This expression can also be written in terms of amplitude density functions,

$$\xi_i = V \psi_i. \quad (26)$$

Thus,

$$T = \sum_{j=0}^N \langle \phi | V (G_0 V)^j | \phi \rangle + \langle \phi | (V G_0)^N | \xi_i \rangle - \langle \xi_i | (G_0 V)^{N-1} G_0 | \xi_i \rangle + \langle \xi_i | (G_0 V)^N | \phi \rangle + \langle \xi_i | (G_0 V)^N G_0 | \xi_i \rangle. \quad (27)$$

The case $N = 1$ is of particular interest because it yields the bilinear form of the Newton VP⁴

$$T = \langle \phi | V | \phi \rangle + \langle \phi | V G_0 | \xi_i \rangle + \langle \xi_i | G_0 V | \phi \rangle - \langle \xi_i | G_0 | \xi_i \rangle + \langle \xi_i | G_0 V G_0 | \xi_i \rangle. \quad (28)$$

This completes the treatment of the LS equation.

III. CONSTRUCTION OF A VARIATIONAL PRINCIPLE FOR THE SCHRÖDINGER EQUATION WITH NEGATIVE IMAGINARY POTENTIALS

In this chapter we consider a simple case of potential scattering to which is added a NIP at the quasiasymptotic region to absorb the flux going out from the interaction region towards the asymptotic region (see Fig. 1). The discussion of this case will not only enable us to introduce the NIP but also to show how we treat such a case employing the NIP and to construct the relevant VP. These ideas will be used to discuss reactive scattering in Sec. IV.

The unique feature of the NIP, once properly chosen, is to absorb those parts of the scattered waves which pass through it without causing any reflection. The no-reflection condition is very important because if the wave function is continuously fed by a source term its shape along the R interval $0 \leq R \leq R_I$ should not be affected by the NIP. Following a series of studies, we found that the best potentials for this purpose and which at the same time are of a reasonable short range are the triangular potentials of the form¹⁶ [see Fig. 1(b)]:

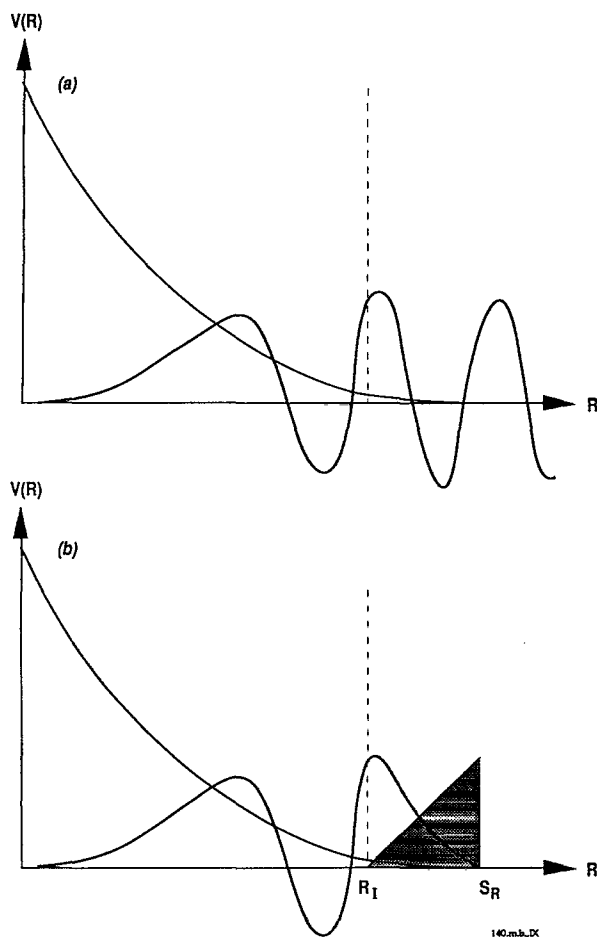


FIG. 1. A linear potential with a schematic wave function. (a) Without negative imaginary potential, (b) with negative imaginary potential (shaded area). The portion of the wave function which is affected by the negative imaginary potential is in the interval $R_I \leq R$.

$$V_I(R) = -iv_I(R) = \begin{cases} -iv_{0I} \frac{R - R_I}{\Delta R} & R_I \leq R \leq S_R, \\ 0, & \text{otherwise} \end{cases} \quad (29)$$

where

$$S_R = R_I + \Delta R. \quad (30)$$

Another important feature of these potentials is that the parameters v_{0I} and ΔR can be estimated *a priori* before doing the calculations, which guarantees that the scattering treatment is not approximate but accurate. It was established that for a given translational energy E_t and a mass m two conditions have to be fulfilled, namely,¹⁶

$$\hbar E_t^{1/2} / (\Delta R \sqrt{8m}) \ll v_{0I} \ll (\Delta R \sqrt{8m}) E_t^{3/2} / \hbar. \quad (31)$$

The condition on the lhs guarantees full absorption once the wave function passes through the NIP and the one on the rhs ensures that no reflection takes place before the wave penetrates it (these two conditions were recently significantly improved by Child²¹).

In order to solve the scattering problem we make the following definitions:^{18,19}

(a) The full Hamiltonian H is given in the form,

$$H = T + U(R). \quad (32)$$

(b) The unperturbed Hamiltonian H_0 is given in the form,

$$H_0 = T + W(R). \quad (33)$$

(c) The functions ψ_0 and ψ are the solutions of the unperturbed SE,

$$(E - H_0)\psi_0 = 0 \quad (34)$$

and the full SE,

$$(E - H)\psi = 0. \quad (35)$$

(d) Next is introduced the perturbed part of the wave function, namely,

$$\chi = \psi - \psi_0 \quad (36)$$

which can be shown to fulfill the equation,^{18,19}

$$(E - H)\chi = V\psi_0, \quad (37)$$

where $V(R)$ is the perturbation potential defined as

$$V(R) = U(R) - W(R). \quad (38)$$

In the actual calculation of $\chi(R)$, employing Eq. (37), the NIP is added to H so that now H becomes

$$H = T + U - iv_I(R). \quad (32')$$

It is important to emphasize that on the rhs of Eq. (37) the NIP [i.e., $-iv_I(R)$] is not added to $V(R)$.

Equation (37) is solved for the range $0 \leq R \leq S_R$ [see Fig. 1(b)] for which $\chi(R)$ is assumed to be $\neq 0$; however it yields the correct form for $\chi(R)$ for the interval $0 \leq R \leq R_I$ only.

The expression to be considered in order to extract the VP for some magnitude Q is

$$Q_v = Q_t - \int_0^{S_R} L [(E - H)\chi_t - V\psi_0] dR, \quad (39)$$

where S_R was introduced through Eqs. (29) and (30), L is Lagrange multiplier and $Q_t = Q(\chi_t)$. The corresponding

stationary condition leads to the expression,

$$\delta Q - \int_0^{S_R} L [(E - H)\delta\chi] dR - \int_0^{S_R} \delta L [(E - H)\chi - V\psi_0] dR = 0. \quad (40)$$

The last term on the rhs is zero because χ is expected to fulfil Eq. (37) and so we are left with an equation for L ,

$$\delta Q - \int_0^{S_R} L [(E - H)\delta\chi] dR = 0. \quad (41)$$

Our next task is to exchange the positions between $\delta\chi$ and L in the second term. To this end we have to consider the expression,

$$\begin{aligned} \int_0^{S_R} L(R) \left(\frac{d^2}{dR^2} \delta\chi(R) \right) dR \\ = \int_0^{S_R} \delta\chi(R) \left(\frac{d^2}{dR^2} L(R) \right) dR + B, \end{aligned} \quad (42)$$

where B is given in the form,

$$B = \left[L(R) \frac{d}{dR} (\delta\chi(R)) - \frac{dL(R)}{dR} \cdot \delta\chi(R) \right] \Big|_0^{S_R}. \quad (43)$$

In Appendix B it is proved that $B \equiv 0$. Consequently, Eq. (41) becomes

$$\delta Q - \int_0^{S_R} [\delta\chi(E - H)L] dR = 0. \quad (44)$$

Next we consider the case that Q is the S -matrix element

$$S = \langle \psi_0 | V | \psi \rangle = \langle \psi_0 | V | (\psi_0 + \chi) \rangle \quad (45)$$

and, therefore,

$$\delta S = \langle \psi_0 | V | \delta\chi \rangle = \int_0^{S_R} \delta\chi(R) V(R) \psi_0^*(R) dR. \quad (46)$$

Substituting Eq. (46) in Eq. (44) yields

$$\int_0^{S_R} \delta\chi [(E - H)L - V\psi_0^*] dR = 0 \quad (47)$$

which leads to the equation for $L(R)$,

$$(E - H)L = V\psi_0^*. \quad (48)$$

It is noticed that $L(R)$ satisfies a similar equation that $\chi(R)$ is satisfying except that the homogeneous term, $V\psi_0$ is replaced by $V\psi_0^*$. Since the lhs in Eq. (48) along the range $0 < R < R_f$ is real and V is real we get

$$L(R) = \chi^*(R). \quad (49)$$

Replacing in Eq. (39), $L(R)$ by $\chi^*(R)$ and Q by S given in Eq. (45), we find that the modified value for S is

$$S = \langle \psi_0 | V | (\psi_0 + \chi_i) \rangle - \langle \chi_i | E - H | \chi_i \rangle + \langle \chi_i | V | \psi_0 \rangle \quad (50)$$

or

$$\begin{aligned} S = \langle \psi_0 | V | \psi_0 \rangle + \langle \psi_0 | V | \chi_i \rangle \\ - \langle \chi_i | E - H | \chi_i \rangle + \langle \chi_i | V | \psi_0 \rangle. \end{aligned} \quad (51)$$

Equation (51) is reminiscent of the expression employed by Kamimura¹² and by Zhang, Chu, and Miller¹¹ to treat scattering processes and of the one used by Karplus and Kolker²⁷ to treat the refractive index of hydrogen.

The expression of S , in Eq. (51) is our functional to start the calculation of χ_i . Since H contains the NIP, the resulting χ_i is expected to be *nonzero* only along the interval $[0, S_R]$ and therefore can be expanded in terms of a bound basis set,

$$\chi_i = \sum_{n=1}^N a_n f_n(R), \quad (52)$$

where $f_n(R)$ is an orthogonal basis set in the $(0, S_R)$ interval.

Substituting Eq. (52) and its complex conjugate in Eq. (51) the stationary equations for a_n and a_n^* (which are considered to be independent of a_n) are obtained by demanding

$$\frac{\partial S}{\partial a_n} = 0, \quad n = 1, \dots, N \quad (53a)$$

and

$$\frac{\partial S}{\partial a_n^*} = 0, \quad n = 1, \dots, N. \quad (53b)$$

From Eq. (53b) we get the algebraic equation for \mathbf{a}

$$\mathbf{A}\mathbf{a} = \mathbf{b}, \quad (54)$$

where

$$\begin{aligned} A_{nm} &= \int_0^{S_R} dR f_n(R) (E - H) f_m(R), \\ b_n &= \int_0^{S_R} dR f_n(R) V(R) \psi_0(R). \end{aligned} \quad (55)$$

In the same way we get from Eq. (53a) the algebraic equations for \mathbf{a}^+ , the Hermitian conjugate vector to \mathbf{a} ,

$$\mathbf{a}^+ \mathbf{A} = \mathbf{b}^+. \quad (56)$$

Substituting Eq. (52) in Eq. (51) yields for S

$$\begin{aligned} S &= \int_0^{S_R} dR \psi_0(R) V(R) \psi_0^*(R) \\ &+ 2 \operatorname{Re} \sum_{n=1}^N a_n^* b_n - \sum_{nm} a_n^* A_{nm} a_m \end{aligned} \quad (57)$$

which completes our derivation.

IV. VARIATIONAL PRINCIPLES FOR REACTIVE COLLISIONS BASED ON THE NEGATIVE IMAGINARY POTENTIAL METHOD

To study reactive exchange process implies treating a multi-AC problem. All available methods^{9,14,28-37} enforce solving the SE for all coupled ACs. Consequently the difficulties in studying reactions are expected to increase nonlinearly with the number of atoms added to the system.

Here we would like to consider a different approach which is based on solving one AC at a time. This AC may be the reagents one¹⁶⁻²⁰ (as was frequently treated in the last few years) or an exchange AC¹⁸ (as has been only recently introduced). The decoupling of this one AC from all others is done by adding to the Hamiltonian a weak short range NIP of the kind described in the previous chapter. In the case of potential scattering we showed how to construct such a potential that absorbs the flux going from the interaction region out to the asymptotic region. Here these potentials are used to absorb the flux going from the one AC under

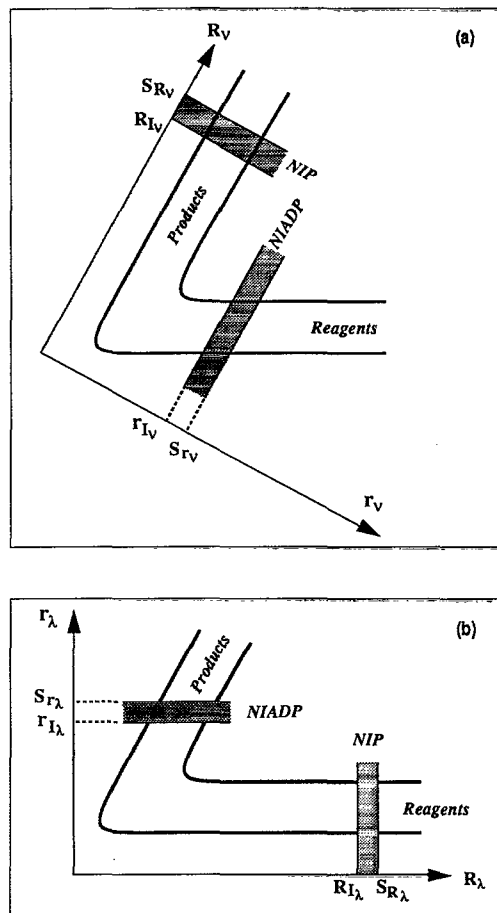


FIG. 2. A collinear potential energy surface in mass scaled coordinates with negative imaginary potentials along "borders" of arrangement channels. (a) The products arrangement channel, (b) the reagents arrangement channel. NIP stands for negative imaginary potential and NIADP stands for negative imaginary arrangement decoupling potential.

consideration to all the others. A situation of this kind is shown in Fig. 2(a) where we present the collinear potential energy surface (in mass scaled coordinates). The absorbing NIP which decouples the products AC from the reagents one is the potential located along the *products* translational coordinate R_v for a given short range of the *products* vibrational coordinate r_v . This potential was termed as the negative imaginary arrangement decoupling potential (NIADP). Having this potential and adding the NIP at the asymptotic region of this AC, the scattering problem is again converted into a bound system problem.^{18,19}

A similar situation is encountered in Fig. 2(b) where, with the help of the NIADP, we eliminated the *products* AC. To obtain the reactive probability the flux along the line $r_\lambda = r_{I\lambda}$ is calculated.

In section IV.1 we concentrate on the products AC for which the VP with respect to the reactive S matrix element is derived. In this sense our final outcome is reminiscent of the one derived for the more ordinary case.¹¹⁻¹² In section IV.2 we concentrate on the reagents AC for which a VP is constructed with respect to the reactive flux function.

A. Construction of a variational principle for the products arrangement channel: The treatment of the S -matrix element

To solve a single *products* decoupled AC case we make use of the perturbative representation of the SE where the inhomogeneous term follows from the reagents AC and serves as the link between the reagents and the products. Thus the equation to be solved is

$$(E - H)\chi_{n_{\lambda 0}} = V_\lambda \psi_{n_{\lambda 0}}, \quad (58)$$

where $n_{\lambda 0}$ is an initial state in the reagents AC and V_λ is a perturbation potential (related to the λ AC) obtained from the relation,

$$V_\lambda = U - W_\lambda. \quad (59)$$

Here U is the full potential of the three atom system and W_λ is the unperturbed potential related to the reagents.

In what follows we consider the collinear case for the sake of explaining our approach without having to deal with heavy algebra and a lot of indices. The index λ will be used to designate the reagents AC and ν the products one.

The interaction potential V is assumed to fulfill the condition,

$$\lim_{R_\lambda \rightarrow \infty} V_\lambda(R_\lambda, \dots) = 0. \quad (60)$$

As for W it is assumed to be a separable potential of the kind

$$W_\lambda(R_\lambda, r_\lambda) = v_\lambda(r_\lambda) + w_\lambda(R_\lambda), \quad (61)$$

where $v_\lambda(r_\lambda)$ is the (asymptotic) diatomic potential and $w_\lambda(R_\lambda)$ is a distortion potential which increases as R_λ decreases.

As in the previous section [see Eqs. (35) and (39)] our starting equation for deriving the VP is

$$S_{n_\nu, n_{\lambda 0}}^{(v)} = S_{n_\nu, n_{\lambda 0}}(\chi_{n_{\lambda 0}}) - \int_0^{S_{r_\nu}} \int_0^{S_{R_\nu}} dR_\nu dr_\nu L_t [(E - H)\chi_{n_{\lambda 0}} - V_\lambda \psi_{n_{\lambda 0}}]. \quad (62)$$

Here $S_{n_\nu, n_{\lambda 0}}$ is the matrix element related to the $n_{\lambda 0} \rightarrow n_\nu$ transition and S_r and S_R are r_ν and R_ν values, respectively, introduced in Eq. (29).

The first variation of $S_{n_\nu, n_{\lambda 0}}$ leads to the expression,

$$\delta S_{n_\nu, n_{\lambda 0}} - \int_0^{S_{r_\nu}} \int_0^{S_{R_\nu}} L(E - H) \delta \chi_{n_{\lambda 0}} dr_\nu dR_\nu - \int_0^{S_{r_\nu}} \int_0^{S_{R_\nu}} \delta L [(E - H)\chi_{n_{\lambda 0}} - V_\lambda \psi_{n_{\lambda 0}}] = 0. \quad (63)$$

The last term in Eq. (63) is assumed to be zero because $\chi_{n_{\lambda 0}}$ is expected to fulfill Eq. (58) so that the equation for L is

$$\delta S_{n_\nu, n_{\lambda 0}} - \int_0^{S_{r_\nu}} \int_0^{S_{R_\nu}} L(E - H) \delta \chi_{n_{\lambda 0}} dr_\nu dR_\nu = 0. \quad (64)$$

To exchange positions between L and $\delta \chi_{n_{\lambda 0}}$ we have to consider the expressions,

$$I_x = \int_0^{S_x} dx L_t \frac{\partial^2}{\partial x^2} (\delta \chi_{n_{\lambda 0}}), \quad x = r_\nu, R_\nu. \quad (65)$$

The details of the exchange were worked out in the previous section, and in Appendix B.

Consequently Eq. (64) becomes

$$\delta S_{n,n_{\lambda 0}} - \int_0^{S_{r_v}} \int_0^{S_{R_v}} \delta \chi_{n_{\lambda 0}} (E - H) L dR_v dr_v = 0. \quad (66)$$

Next we consider $\delta S_{n,n_{\lambda 0}}$ given in the form,

$$\begin{aligned} S_{n,n_{\lambda 0}} &= \langle \psi_{n_v} | V_v | \Psi_{n_{\lambda 0}} \rangle \\ &= \langle \psi_{n_v} | V_v | (\psi_{n_{\lambda 0}} + \chi_{n_{\lambda 0}}) \rangle. \end{aligned} \quad (67)$$

Here V_v is the perturbed potential and ψ_n is an unperturbed wave function both defined in the v AC. Forming the variation of $S_{n,n_{\lambda 0}}$ and substituting it into Eq. (66) we obtain

$$\int_0^{S_{r_v}} \int_0^{S_{R_v}} dR_v dr_v \delta \chi_{n_{\lambda 0}} [(E - H)L - V_v \psi_{n_v}^*] = 0. \quad (68)$$

It is well noticed that for an arbitrary $\delta \chi_{n_{\lambda 0}}$, $L(R, r)$ has to satisfy the equation,

$$(E - H)L_{n_v} = V_v \psi_{n_v}^*. \quad (69)$$

Since $\psi_{n_v}^*$ stands for an outgoing wave function the index n_v was added to L to emphasize its dependence on the final state n_v .

Considering Eq. (69) it is noticed that the homogeneous part is identical to the one fulfilled by $\chi_{n_{\lambda 0}}$ [see Eq. (58)]. As for the inhomogeneous part the potential, in case of $\chi_{n_{\lambda 0}}$ is multiplied by the unperturbed incoming wave function $\psi_{n_{\lambda 0}}$ and here in Eq. (69) it is multiplied by an unperturbed outgoing solution $\psi_{n_v}^*$. Consequently, the function L that satisfies Eq. (68) (for any $\delta \chi_{n_{\lambda 0}}$) will be designated as

$$L = L_{n_v} = \chi_{n_v}^*. \quad (70)$$

Returning now to Eq. (62) we may write

$$\begin{aligned} S_{n,n_{\lambda 0}}^{(v)} &= S_{in,n_{\lambda 0}}(\chi_{in,n_{\lambda 0}}) - \int_0^{S_{r_v}} \int_0^{S_{R_v}} \\ &\quad dR_v dr_v \chi_{in_v}^* [(E - H)\chi_{in_{\lambda 0}} - V_{\lambda} \psi_{n_{\lambda 0}}] \end{aligned} \quad (71)$$

or employing bra-ket notation we may write the modified expression for $S_{n,n_{\lambda 0}}^{(v)}$ as

$$\begin{aligned} S_{n,n_{\lambda 0}}^{(v)} &= \langle \psi_{n_v} | V_v | \psi_{n_{\lambda 0}} \rangle + \langle \psi_{n_v} | V_v | \chi_{in_{\lambda 0}} \rangle + \langle \chi_{in_v} | V_{\lambda} | \psi_{n_{\lambda 0}} \rangle \\ &\quad - \langle \chi_{in_v} | E - H | \chi_{in_{\lambda 0}} \rangle. \end{aligned} \quad (72)$$

Next we expand $\chi_{n_{\lambda 0}}$ and $\chi_{n_v}^*$ in terms of the same basis sets,

$$\chi_{in_{\lambda 0}} = \sum_{nm} a_{inmn_{\lambda 0}} f_n(R_v) g_m(r_v), \quad (73a)$$

$$\chi_{n_v}^* = \sum_{n'm'} a_{in'm'n}^* f_{n'}(R_v) g_{m'}(r_v). \quad (73b)$$

Forming the corresponding algebraic equations [see Eqs. (53)] we end up with the following expressions:

$$\mathbf{A} \mathbf{a}_{in_{\lambda 0}} = \mathbf{b}_{n_{\lambda 0}}, \quad (74a)$$

$$\mathbf{a}_{in_v}^+ \mathbf{A} = \mathbf{b}_{n_v}^+ \quad (74b)$$

where the \mathbf{A} elements are

$$A_{nmn'm'} = \langle f_n g_m | E - H | f_{n'} g_{m'} \rangle, \quad (75)$$

the $\mathbf{b}_{n_{\lambda 0}}$ elements are

$$b_{nmn_{\lambda 0}} = \langle f_n g_m | V_{\lambda} | \psi_{n_{\lambda 0}} \rangle \quad (76a)$$

and those of $\mathbf{b}_{n_v}^+$ are

$$\mathbf{b}_{nmn_v}^+ = \langle \psi_{n_v} | V_v | f_n g_m \rangle. \quad (76b)$$

If now Eqs. (73) are substituted in Eq. (72) it can be shown that $S_{n,n_{\lambda 0}}$ is given in the form,

$$\begin{aligned} S_{n,n_{\lambda 0}} &= \langle \psi_{n_v} | V_v | \psi_{n_{\lambda 0}} \rangle + \sum_{nm} b_{nmn_v}^* a_{inmn_{\lambda 0}} \\ &\quad + \sum_{nm} a_{inmn_v}^* b_{nmn_{\lambda 0}} \\ &\quad - \sum_{n'm'} a_{inmn_v}^* A_{nmn'm'} a_{in'm'n_{\lambda 0}}. \end{aligned} \quad (77)$$

It is important to emphasize again that in calculating the \mathbf{A} -matrix elements the upper limits of the integrals are S_R and S_r .

B. Construction of a variational principle for the reagents arrangement channel: The treatment of reactive flux

For the single reagents decoupled AC Eq. (58) with the perturbation given in Eq. (59) is employed. The only difference in the application of Eq. (58) for this case is that the kinetic energy operator is written here in terms of the reagents coordinates.

To calculate the reactive transition probabilities we use the flux expression [see Fig. 2(b)].

$$P_{n_{\lambda 0}} = 2 \operatorname{Im} \left[\int_0^{\infty} \psi_{n_{\lambda 0}} \frac{\partial \psi_{n_{\lambda 0}}^*}{\partial r_{\lambda}} \bigg|_{r_{\lambda}=r_{\lambda I}} dR_{\lambda} \right]. \quad (78)$$

Equation (78) can also be written as

$$P_{n_0} = 2 \operatorname{Im} \left[\int_0^{\infty} \int_0^{\infty} dR dr \delta(r - r_I) \psi_{n_0} \frac{\partial \psi_{n_0}^*}{\partial r} \right], \quad (79)$$

where $\delta(r - r_I)$ is the Dirac's δ function. Here and in what follows the index λ is deleted as the forthcoming treatment is carried out in the λ AC only.

Since Ψ_{n_0} is written as

$$\Psi_{n_0} = \chi_{n_0} + \psi_{n_0}, \quad (80)$$

where ψ_{n_0} is the unperturbed initial solution and χ_{n_0} is the perturbed one and since the flux in Eq. (78) is calculated at r values for which $\psi_{n_0}(R, r)$ is already zero, P_{n_0} can be written also as

$$P_{n_0} = 2 \operatorname{Im} \left[\int_0^{\infty} dR \int_0^{\infty} dr \delta(r - r_I) \chi_{n_0} \frac{\partial \chi_{n_0}^*}{\partial r} \right]. \quad (81)$$

Our aim is to construct a VP for the quantum flux. This case is unique because to our knowledge this is the first time in scattering theory that a VP is constructed for a physical quantity which is not linear with respect to the unknown wave function. This we do again, employing the Langrange multiplier method. Let us consider the expression,

$$\begin{aligned} Q_{n_0}^{(v)} &= \int \int dR dr \chi_{in_0} \frac{\partial \chi_{in_0}^*}{\partial r} \delta(r - r_I) \\ &\quad - \int \int dR dr L [(E - H)\chi_{in_0} - V\psi_{n_0}], \end{aligned} \quad (82)$$

where L is an unknown function. The function $Q_{n_0}^{(v)}$ is relat-

ed to $P_{n_0}^{(v)}$ in the following way:

$$P_{n_0}^{(v)} = -i(Q_{n_0}^{(v)} - Q_{n_0}^{(v)*}). \quad (83)$$

Consequently our starting point for constructing the VP is

$$P_{n_0}^{(v)} = -i \left\{ \iint dR dr \delta(r-r_I) \left[\chi_{in_0}^* \frac{\partial \chi_{in_0}^*}{\partial r} - \chi_{in_0}^* \frac{\partial \chi_{in_0}}{\partial r} \right] - \iint dR dr L [(E-H)\chi_{in_0} - V\psi_0] + \iint dR dr L^* [(E-H)\chi_{in_0}^* - V\psi_0^*] \right\}. \quad (84)$$

Like in Sec. IV A we continue by expanding both $\chi_{in_0}(R,r)$ and $L(R,r)$ in terms of the same orthonormal basis sets,

$$\chi_{in_0}(R,r) = \sum_{nm} a_{inmn_0} f_n(R) g_m(r), \quad (85a)$$

$$L_{n_0}(R,r) = \sum_{nm} c_{nmn_0} f_n(R) g_m(r). \quad (85b)$$

Next we substitute Eqs. (85) in Eq. (84) and derive the following expressions:

$$\frac{\partial P_{n_0}}{\partial a_{inmn_0}} = \frac{\partial P_{n_0}}{\partial a_{inmn_0}^*} = 0, \quad n, m = 1, \dots \quad (86a)$$

$$\frac{\partial P_{n_0}}{\partial c_{nmn_0}} = \frac{P_{n_0}}{\partial c_{nmn_0}^*} = 0, \quad n, m = 1, \dots \quad (86b)$$

From Eqs. (86b) we obtain the algebraic equations for calculating the coefficients a_{inmn} and a_{inmn}^* :

$$\mathbf{A} \mathbf{a}_{in_0} = \mathbf{b}_{n_0}, \quad (87a)$$

$$\mathbf{a}_{in_0}^+ \mathbf{A} = \mathbf{b}_{n_0}^+, \quad (87b)$$

respectively. Here the \mathbf{A} matrix is the same as the one defined in Eq. (75) and \mathbf{b}_{n_0} is the same as the one defined in Eq. (76a) ($\mathbf{b}_{n_0}^+$ is the complex conjugate of \mathbf{b}_{n_0}). The equations to be solved for c_{nmn_0} and $c_{nmn_0}^*$ are obtained from Eqs. (86b):

$$\mathbf{A} \mathbf{c}_{n_0} = \mathbf{d}_{in_0}, \quad (88a)$$

$$\mathbf{c}_{n_0}^+ \mathbf{A} = \mathbf{d}_{in_0}^+, \quad (88b)$$

where

$$d_{inmn_0} = \sum_{m'} a_{inm'n_0}^* \left(g_m \frac{dg_{m'}}{dr} - \frac{dg_m}{dr} g_{m'} \right) \Big|_{r=r_I}. \quad (89)$$

Once Eqs. (87) and (88) are solved the final expression for the flux is [see Eq. (84)]

$$P_{n_0} = 2 \operatorname{Im} \left\{ \left(\sum_{nm} a_{inmn_0} a_{inm'n_0}^* g_m \frac{dg_{m'}}{dr} \right) \Big|_{r=r_I} - \sum_{nm} c_{n'n'm'n_0}^* A_{n'm'n_0} a_{inmn_0} - \sum_{n'm'} c_{n'n'm'n_0}^* b_{n'm'n_0} \right\}. \quad (90)$$

Equation (90) can also be written in a matrix notation:

$$P_{n_0} = 2 \operatorname{Im} [Q_t - \mathbf{c}_{n_0}^+ (\mathbf{A} \mathbf{a}_{in_0} - \mathbf{b}_{n_0})], \quad (91)$$

where Q_t is the initial estimate for Q [see Eqs. (81) and (83)] given in the form,

$$Q_t = \sum_{nm} a_{inm'n_0}^* a_{inmn_0} \left(g_m \frac{dg_{m'}}{dr} \right) \Big|_{r=r_I}. \quad (92)$$

In case Eqs. (87) can be solved exactly, Eq. (92) is the final result for Q_t . Sometimes the dimensions of \mathbf{A} are so large that Eqs. (87) can only be solved approximately. The rest of the discussion in this section applies for this case.

Extracting $\mathbf{c}_{n_0}^+$ from Eq. (88b) and substituting the result in Eq. (91) yields

$$P = 2 \operatorname{Im} [Q_t - \mathbf{d}_{in_0}^+ ((\mathbf{A}^{-1})_t \mathbf{A} \mathbf{a}_{in_0} - (\mathbf{A}^{-1})_t \mathbf{b}_{n_0})] \quad (93)$$

or [see Eq. 94(a)]

$$P = 2 \operatorname{Im} [Q_t - \mathbf{d}_{in_0}^+ ((\mathbf{A}^{-1})_t \mathbf{A} - \mathbf{I}) \mathbf{a}_{in_0}], \quad (94)$$

where $(\mathbf{A}^{-1})_t$ is an estimate (only) for the inverse of \mathbf{A} . In case $(\mathbf{A}^{-1})_t$ is exactly the inverse of \mathbf{A} the value of P becomes

$$P = 2 \operatorname{Im}(Q_t). \quad (95)$$

Considering again the definition of Q_t and the elements of $\mathbf{d}_{in_0}^+$ it is well noticed that the following relation exists [for $(\mathbf{A}^{-1})_t = (\mathbf{A}^{-1})$ exact]:

$$d_{inmn_0}^* = \frac{\partial Q_t}{\partial a_{inmn_0}} = \frac{\partial Q_t^*}{\partial a_{inmn_0}^*} = 2i \frac{\partial I_m(Q)}{\partial a_{inmn_0}} \quad (96)$$

which can also be written as [see Eq. (83)]

$$d_{inmn_0}^* = i \frac{\partial P_t}{\partial a_{inmn_0}}. \quad (97)$$

Equation (97) implies that the elements of $\mathbf{d}_{in_0}^+$ are formed by differentiating the initial guess of the probability flux with respect to a_{inmn_0} . Thus if symbolically the row vector $\mathbf{d}_{in_0}^+$ is written as

$$\mathbf{d}_{in_0}^+ = i \left(\frac{\partial \tilde{P}_t}{\partial \mathbf{a}_{in_0}} \right), \quad (98)$$

then Eq. (94) becomes

$$\bar{P} = P_t - \operatorname{Im} \left[\left(\frac{\partial P_t}{\partial \mathbf{a}_{in_0}} \right) ((\mathbf{A}^{-1})_t \mathbf{A} - \mathbf{I}) \mathbf{a}_{in_0} \right] \quad (99)$$

which completes our derivation.

This type of correction to a given initial value belongs to a wide range of cases where an estimate to a magnitude Γ is obtained from a set of constants (a_1, \dots, a_n) which are known to be an approximate solution of a system of algebraic equations,

$$\mathbf{A} \mathbf{a} = \mathbf{b}. \quad (100)$$

It can be shown that the improved estimate for Γ is given in the form

$$\Gamma = \Gamma_t - \left(\frac{\partial \Gamma_t}{\partial \mathbf{a}_t} \right) [(\mathbf{A}^{-1})_t \mathbf{A} - \mathbf{I}] \mathbf{a}_t, \quad (101)$$

where $(\partial \Gamma_i / \partial a_i)$ is a row vector with the elements,

$$\left(\frac{\partial \tilde{\Gamma}_i}{\partial a_i} \right) = \left(\frac{\partial \Gamma_i}{\partial a_{i,1}}, \dots, \frac{\partial \Gamma_i}{\partial a_{i,N}} \right) = \nabla \cdot \Gamma_i. \quad (102)$$

This outcome can be extended in a straightforward way to the case that Γ is a vector.

V. DISCUSSION AND CONCLUSIONS

In this publication we concentrated on a very interesting approach to derive VP's for almost every physical magnitude $Q(\phi)$, where ϕ is known to be solution of a physical equation. This approach is based on the idea to use the equation for ϕ (for instance the SE) as a constraint for the calculation of $Q(\phi)$. The constraint is incorporated into the equation for Q via the undetermined Lagrange multiplier.²²⁻²⁵ The idea, although being simple yields most interesting and important results. The best way to understand how the incorporation of the Lagrange multiplier is done is to apply it to realistic cases. An instructive example is the calculation of an inverse for a matrix which was discussed in the review by Gerjuoy *et al.*²² for the sake of introducing this approach.

In our present study we applied the Lagrange multiplier to construct VP for five different cases related to scattering: (a), (b) Employing the LS equation we constructed the two most well-known VP's for the T -matrix elements namely the Schwinger VP (based on calculating the wave function) and the Newton VP (based on calculating the amplitude density function). In fact, more was accomplished; we derived a VP for a general case from which the Schwinger and the Newton VP's followed as special cases.

(c) While introducing the application of negative imaginary potentials (NIP) for potential scattering (by doing that a scattering problem is converted into a bound system problem) we derived the relevant VP. It was shown that the final expressions are somewhat reminiscent of those obtained by others.^{11,12}

(d) We extended the potential scattering case to reactive scattering. Here we made use of the NIPs to extract one single reactive AC and calculate for it the variationally corrected relevant S matrix element. The calculation of these matrix elements is done by solving a perturbative-type inhomogeneous SE where the source term (the inhomogeneous term) has its origin in the reagents AC. Again the final equations are reminiscence of those obtained by others^{11,12} but still different as will be explained shortly.

(e) We made use of the NIP to extract the reagents AC. The calculation of the reactive probabilities, in this case, is done by employing flux expressions without obtaining the relevant S matrix elements. In fact this case, among other things enabled us to show how to construct a VP for an uncommon physical magnitude such as quantum flux. It is important to emphasize that variationally corrected flux results will differ from the corresponding results obtained from variationally calculated S matrix elements (however they are expected to be more accurate).

This last fact leads to a more general subject. It is common to calculate cross sections (integral, differential, etc.) employing variationally corrected S matrix elements. In fact

one could obtain, directly, variationally calculated cross sections without going through the corresponding S matrix elements and in this way to obtain more accurate results. This subject will be discussed elsewhere.

As our final subject we would like again refer to the similarities and differences between the Miller¹² and the Baer-Neuhauser-Oreg¹⁹ (BNO) approaches to calculate reactive cross sections.

According to both methods one solves for the S -matrix elements employing the SE. According to both methods the calculations are done by expanding the scattering wave function in terms of bound-state functions employing Jacobi coordinates for the relevant AC and both methods end up by solving algebraic equations. But the main difference between the two approaches is that in Miller's method^{10,11} one has to solve for all the ACs in one single calculation whereas according to BNO one may treat each AC separately and carry out the calculation for this one AC only. BNO arrived at this possibility by the application of NIP's which are added to the regular potential and enabled the extraction of the one AC of interest. The addition of the NIP makes the homogeneous part of BNO matrix of coefficients \mathbf{A} complex but it's form is relatively simple; the \mathbf{A} matrix is easily written as

$$\mathbf{A} = \mathbf{B} - i\mathbf{C}, \quad (103)$$

where \mathbf{B} is a real symmetric matrix [identical to the (Direct \times Direct) part in Miller's case] and \mathbf{C} is also a real symmetric matrix of the form,

$$C_{nn'} = \langle \phi_n | v_I(r) | \phi_{n'} \rangle, \quad (104)$$

where $v_I(r)$ was introduced in Eq. (29).

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APPENDIX A

The proof for

$$\int_0^\infty dR \xi_1 G_0 \xi_2 = \int_0^\infty dR \xi_2 G_0 \xi_1.$$

We start considering the explicit representation of the lhs (deleting the various constants belonging to G_0) of the above equation:

$$\begin{aligned} I_{12} &= \int_0^\infty dR \xi_1 G_0 \xi_2 \\ &= \int_0^\infty dR \xi_1(R) \phi_{ir}(R) \int_0^R dR' \phi_{re}(R') \xi_2(R') \\ &\quad + \int_0^\infty dR \xi_1(R) \phi_{re}(R) \int_R^\infty dR' \phi_{ir}(R') \xi_2(R'). \end{aligned} \quad (A1)$$

Changing the order of integration in the first term yields

$$\therefore \int_0^\infty dR \zeta_2(R) \phi_{re}(R) \int_R^\infty dR' \zeta_1(R') \phi_{ir}(R') \quad (A2)$$

and changing it in the second term yields

$$\therefore \int_0^\infty dR \zeta_1(R) \phi_{ir}(R) \int_0^R dR' \zeta_2(R') \phi_{re}(R'). \quad (A3)$$

Combining Eqs. (A2) and (A3) yields

$$I_{12} = \int_0^\infty dR \zeta_2(R) \phi_{ir}(R) \int_0^R dR' \phi_{re}(R') \zeta_1(R') \\ + \int_0^\infty dR \zeta_2(R) \phi_{re}(R) \int_R^\infty dR' \phi_{ir}(R') \zeta_1(R') \quad (A4)$$

or

$$I_{12} = \int_0^\infty dR \zeta_2 G_0 \zeta_1 = I_{21} \quad (A5)$$

which completes our proof.

APPENDIX B: ANALYSIS OF CONTRIBUTIONS AT THE BOUNDARIES TO THE VARIATIONAL EQUATIONS

In this appendix we analyze the expression defined as

$$B = b(S_R) - b(0) \\ = \left[L(R) \frac{d}{dR} (\delta\chi(R)) - \delta\chi(R) \frac{dL}{dR} \right]_0^{S_R} \quad (B1)$$

We start by considering $b(R=0)$. At $R=0$ the total wave function, $\psi(R)$, and the unperturbed wave function $\psi_0(R)$ as well as their corresponding derivatives are equal to zero. Since $\chi(R)$ is given in the form [see Eq. (36)]

$$\chi(R) = \psi(R) - \psi_0(R) \quad (B2)$$

the same holds for $\chi(R)$ and its derivatives, namely,

$$\chi(R) = 0 \quad \text{for} \quad R = 0 \quad (B3a)$$

and

$$\frac{d^n \chi}{dR^n} = 0 \quad \text{for} \quad R = 0. \quad (B3b)$$

This implies that all possible variations of $\chi(R)$ (as well as their derivatives) are equal to zero at $R=0$ and hence $b(R=0) = 0$.

Next we consider $b(R=S_R)$. Here, since the NIP absorbs $\chi(R)$ entirely this means that $\chi(R)$ is identically zero along the whole range $S_R < R < \infty$. Therefore, not only $\chi(R)$ but also its first derivative ($d\chi/dR$) is zero for $R \geq S_R$. The same holds for $\delta\chi(R)$ so that $b(R)$ for $R = S_R$ is equal to zero.

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