Multichannel variational expressions of scattering theory

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We have compared variational functionals for multichannel scattering. The functionals considered were Schwinger-type functionals based on the close-coupling equations, the Schwinger-type variational functionals of Takatsuka and McKoy [Phys. Rev. A **24**, 2473 (1981)], and a Kohn-type variational functional. The results for a simple Huck-model potential containing both open and closed channels indicate that the Schwinger-type variational functionals yielded very similar results and that all the methods considered converged at a similar rate with respect to the closed-channel expansion. To obtain good convergence with any of these methods it was essential to include separate trial functions outside the range of the Huck square-well potential in the channels where a correct asymptotic form of the wave function was required, those being only the closed channels for the Schwinger-type functionals and both open and closed channels for the Kohn-type functionals. These asymptotic functions were needed to reproduce the discontinuity in the second derivative of the wave function due to the discontinuities in the model potential. Convergence characteristics of these methods with respect to target-state expansions were also considered.

I. INTRODUCTION

Variational methods have been extremely efficient in the computation of electron-molecule scattering wave functions.[1] At the static-exchange level, a variety of approaches have been used including the Kohn method,[2] and various methods related to the Schwinger variational expression.[3–5] Additionally, several extensions of these approaches have been studied for multichannel scattering. Of these methods, the extensions of the Schwinger method proposed by Takatsuka and McKoy[6,7] have been most widely applied to molecular problems.

In the present paper, we will discuss the application of the $\tilde{C}$ functional proposed by Takatsuka and McKoy[4] to the usual close-coupling equations. We show how the resulting variational expression can also be obtained from the Kohn variational expression with the appropriate variational basis set. The $\tilde{C}$ functional approach is known to be rapidly convergent even in the case where long-range forces,[8] such as those found in electron-molecule scattering, are present. This method should also have great utility in the multichannel case.[7]

We have compared a number of variational methods for a modified version of the Huck potential problem,[9] which includes closed channels.[10] The methods employed were the restricted interpolated anomaly-free (RIAF) method of Nesbet,[11] the two Schwinger-type variational methods of Takatsuka and McKoy,[6,7] and the direct application of the Schwinger[12] and $\tilde{C}$ functional methods to the close-coupling equations. One question which we have resolved here is why the RIAF and the other methods based directly on the Kohn method seemed to perform so poorly on the original Huck potential in comparison to the Schwinger-type variational methods.[13] The poor convergence properties of the Kohn-type methods on the Huck potential is in contrast to the relatively good performance found when these methods were applied to a single channel exponential scattering potential.[14,15] For rapid convergence the Kohn methods require basis functions which are outside the range of the interaction potential in the Huck problem in order to reproduce the discontinuity in the second derivative of the scattering wave function which occurs at the radius where the interaction potential has a discontinuity.[16] When such functions, which were not included in the Kohn calculations of Nesbet,[11] are included in the scattering basis, we found the RIAF method to have much better convergence properties, although the Schwinger-type approaches still exhibit much better convergence characteristics.

The various methods were applied to a modified Huck potential which contained a closed channel.[10] In this case, we found that when the open-channel basis sets were near convergence, the rate of convergence with respect to the closed-channel basis sets were identical for all of the methods which we employed. It was also found that the RIAF method[11] gave adequate but clearly inferior convergence with respect to the open-channel basis set compared to that obtained in the Schwinger-type methods. The Schwinger methods of Takatsuka and McKoy[6,7] were found to be nearly identical to the methods obtained from the direct application of the Schwinger variational expression to the close-coupling equations. Although it was expected that the Takatsuka and McKoy approach would be very similar to the close-coupling approach for the model system used here we did not anticipate that the numerical differences between the methods would be as small as two orders of magnitude less than the differences between the variational and exact results, as we have found.

Finally, we have also examined the effect of having approximate target states in the variational expressions. As was shown by Demkov,[17] the Kohn variational methods are variationally stable with respect to errors in the target state as long as a given target state is orthogonal to the exact states corresponding to the other target states used in the expansion of the wave function. Here we will show that as long as the target states are obtained from a linear

variational calculation, the overlaps between the approximate target states and the exact target states is a second-order quantity and thus the expressions used are variationally stable with respect to first-order variation in the approximate target states.

II. THE MODIFIED HUCK MODEL

We will compare the results of multichannel variational principals for a modified Huck-model potential. The original Huck model[9] has been used as a prototypical problem for multichannel scattering calculations.[11,13] Here we have used the extended model[10] to examine both the dependence on the accuracy of the target states and to compare the treatment of closed channels in various methods. In the modified Huck model[10] there are two distinguishable particles interacting through a spherically symmetric interaction potential. Furthermore, we will only include s-wave scattering. The radial Hamiltonian is then

$$H(r_1,r_2)=-\frac{1}{2}\frac{d^2}{dr_1^2}-\frac{1}{2}\frac{d^2}{dr_2^2}+V_1(r_1)+V_{12}(r_1,r_2)\ . \tag{2.1}$$

The first particle is confined by a particle in a box potential

$$V_1(r_1)=\begin{cases}0, & r_1<a_1\\ \infty, & r_1>a_1\end{cases} \tag{2.2}$$

and the interparticle interaction potential is

$$V_{12}(r_1,r_2)=\sum_{\substack{i=1\\ j=1}}^{\infty}|\theta_i(r_1)\rangle V_{ij}(r_2)\langle\theta_j(r_1)|\ . \tag{2.3}$$

The θ_i's are the exact target states, and $V_{ij}(r_2)$ is a square-well potential

$$V_{ij}(r_2)=\begin{cases}C_{ij}, & r_2<a_2\\ 0, & r_2>a_2.\end{cases} \tag{2.4}$$

We have considered two versions of this potential, the original Huck potential[9] where all coupling elements were zero except $C_{12}=C_{21}=(\frac{5}{2})^{1/2}$, and the modified Huck potential[10] where the nonzero coupling elements were $C_{12}=C_{21}=(\frac{5}{2})^{1/2}$, $C_{13}=C_{31}=0.1$, $C_{23}=C_{32}=0.2$, $C_{33}=-2.0$. For both models the radial parameters were $a_1=2\pi$ and $a_2=1.0$. The modified Huck potential has a resonant state in the third channel, which in the absence of interchannel coupling would lie at a total energy of 0.921 449 3.

III. MULTICHANNEL $\tilde{C}$ FUNCTIONAL

The multichannel $\tilde{C}$ functional can be derived in a fashion identical to that used by Maleki and Macek to derive the multichannel Schwinger functional.[12] For the purpose of clarity, we will present the scattering equations in a form applicable to the Huck-model potential problem. The most general scattering wave function for this model is of the form

$$\Psi_m(r_1,r_2)=\sum_{\mu}C_{\mu}^{m}\Phi_{\mu}(r_1,r_2)+\underline{\theta}^T(r_1)\underline{\psi}_m(r_2)\ , \tag{3.1}$$

where $\underline{\theta}$ is a vector of open target states θ_i, $\underline{\psi}_m$ is a vector of corresponding channel scattering functions $\psi_{i,m}$ and Φ_μ is a closed-channel state. The closed-channel state Φ_μ can, in turn, be defined by

$$\Phi_{\mu}(r_1,r_2)=\theta_{i(\mu)}(r_1)f_{\alpha(\mu)}(r_2)\ , \tag{3.2}$$

where $\theta_{i(\mu)}$ is a closed-channel target state and $f_{\alpha(\mu)}$ is an L^2 basis function. The open-channel scattering functions asymptotically are given by

$$\psi_{i,m}(r_2)\sim S_i(r_2)\delta_{i,m}+C_i(r_2)K_{i,m}\quad\text{as } r_2\to\infty\ , \tag{3.3}$$

where

$$S_i(r_2)=\left[\frac{2}{k_i}\right]^{1/2}\sin(k_ir_2) \tag{3.4a}$$

and

$$C_i(r_2)=\left[\frac{2}{k_i}\right]^{1/2}\cos(k_ir_2)\ . \tag{3.4b}$$

Using the Kohn variational expression,[18,19] the effects of the closed-channel contributions on the scattering wave function, i.e., correlation and polarization, can be included as a matrix optical potential,

$$\mathbf{V}^P=\sum_{\mu,\nu}\langle\underline{\theta}\,|\,H-E\,|\,\Phi_\mu\rangle_{r_1}(H-E)^{-1}_{\mu\nu}\langle\Phi_\nu\,|\,H-E\,|\,\underline{\theta}^T\rangle_{r_i}\ , \tag{3.5}$$

where H is the total Hamiltonian given in (2.1) for the system and E is the total energy. Defining the direct potential as

$$\mathbf{V}^D=\langle\underline{\theta}\,|\,H-E\,|\,\underline{\theta}^T\rangle_{r_1}+\frac{1}{2}\left[\frac{d^2}{dr^2}+\mathbf{k}^2\right]\ , \tag{3.6}$$

where $(\mathbf{k}^2)_{ij}=\delta_{ij}k_i$, the scattering problem is reduced to

$$-\frac{1}{2}\left[\frac{d^2}{dr^2}+\mathbf{k}^2\right]\underline{\psi}_m+(\mathbf{V}^D+\mathbf{V}^P)\underline{\psi}_m=0\ . \tag{3.7}$$

Rewriting Eq. (3.7) as an integral equation leads to

$$\underline{\psi}_m=\underline{S}_m+\mathbf{G}\mathbf{V}^{DP}\underline{\psi}_m\ , \tag{3.8}$$

where $\mathbf{V}^{DP}=\mathbf{V}^D+\mathbf{V}^P$, $(\underline{S}_m)_i=\delta_{im}S_i$, and $\mathbf{G}$ is the Green's function whose kernel is

$$(\mathbf{G})_{ij}=-\delta_{ij}S_i(r_<)C_i(r_>)\ . \tag{3.9}$$

Expanding $\underline{\psi}_m$ in a basis set $\underline{f}_\lambda$, the $\tilde{C}$ functional of Takatsuka and McKoy[4] for the $\bar{K}$ matrix is given by

$$\begin{aligned}-K_{mn}=&\langle S_m\,|\,\mathbf{V}^{DP}\,|\,S_n\rangle+\langle S_m\,|\,\mathbf{V}^{DP}\mathbf{G}\mathbf{V}^{DP}\,|\,S_n\rangle\\&+\sum_{\lambda,\mu}\langle S_m\,|\,\mathbf{V}^{DP}\mathbf{G}\mathbf{V}^{DP}\,|\,\underline{f}_\lambda\rangle\\&\times U^{-1}_{\lambda\mu}\langle\underline{f}_\mu\,|\,\mathbf{V}^{DP}\mathbf{G}\mathbf{V}^{DP}\,|\,S_n\rangle\ ,\end{aligned} \tag{3.10}$$

where $U^{-1}_{\lambda\mu}$ are elements of the matrix inverse of $U_{\lambda\mu}$ defined by

$$U_{\lambda\mu}=\langle \underline{f}_\lambda \mid \mathbf{V}^{DP}-\mathbf{V}^{DP}\mathbf{G}\mathbf{V}^{DP} \mid \underline{f}_\mu \rangle \ . \tag{3.11}$$

As shown by Takatsuka *et al.* for the single channel case,[15] the $\tilde{C}$ functional given in Eq. (3.10) can also be obtained by directly from the Kohn variational principle for the K matrix

$$[K_{nm}]=K^t_{nm}-\langle \Psi^t_n \mid H-E \mid \Psi^t_m \rangle \tag{3.12}$$

by using trial functions

$$\Psi^t_n=\sum_\mu C^n_\mu \Phi_\mu+\underline{\theta}^T\underline{S}_n+\sum_\alpha \underline{\theta}^T\underline{f}_\alpha C^n_\alpha \tag{3.13}$$

and

$$\Psi^t_m=\sum_\mu C^m_\mu \Phi_\mu+\underline{\theta}^T\underline{S}_m+\underline{\theta}^T\mathbf{G}\mathbf{V}^{DP}\underline{S}_m + \sum_\alpha \underline{\theta}^T\mathbf{G}\mathbf{V}^{DP}\underline{f}_\alpha C^m_\alpha \ . \tag{3.14}$$

K^t_{nm} is then the asymptotic K matrix of Ψ^t_m

$$K^t_{nm}=-\langle \underline{S}_n \mid \mathbf{V}^{DP} \mid \underline{S}_m \rangle-\sum_\alpha \langle \underline{S}_n \mid \mathbf{V}^{DP} \mid \underline{f}_\alpha \rangle C^m_\alpha \ . \tag{3.15}$$

IV. DEPENDENCE ON TARGET STATES

As has been discussed by Demkov,[17,18] the Kohn variational principle is stable with respect to variations in both the scattering functions, $\psi_{i,m}$, and in the target states, θ_i, as long as the scattering momenta satisfy

$$\langle \theta^t_i \mid H_T \mid \theta^t_i \rangle+\frac{k_i^2}{2}=E \ , \tag{4.1}$$

where θ^t_i is the trial target function and H_T is the target Hamiltonian. When the trial function is expressed as $\theta^t_i=\theta_i+\delta\theta_i$, then the first-order terms containing $\delta\theta_i$ in the expansion of $\langle \Psi^t_n \mid H-E \mid \Psi^t_m \rangle$ in the Kohn variational expression, Eq. (3.12), are products of $\langle \theta_i \mid \delta\theta_j \rangle$ and surface integrals. When $i=j$, these surface integrals can be shown to be zero. However, when $i\neq j$, these terms are, in general, not zero. Thus, for the Kohn variational expression to be valid we have to require that $\langle \theta_i \mid \delta\theta_j \rangle=0$ for $i\neq j$. Alternatively, if the θ^t_i are obtained from a linear variational expression such that

$$\langle \theta^t_i \mid \theta^t_j \rangle=\delta_{ij} \tag{4.2}$$

and

$$\langle \theta^t_i \mid H_T \mid \theta^t_j \rangle=\delta_{ij}E_j \tag{4.3}$$

then it follows that $\langle \theta_i \mid \delta\theta_j \rangle$ is actually a second-order quantity since

$$\langle \theta_i \mid \delta\theta_j \rangle=\frac{\langle \delta\theta_i \mid H_T \mid \delta\theta_j \rangle-E_j\langle \delta\theta_i \mid \delta\theta_i \rangle}{E_j-E_i} \ . \tag{4.4}$$

As long as $E_i\neq E_j$, all terms in the expansion of $\langle \Psi^t_n \mid H-E \mid \Psi^t_m \rangle$ involving the error in the target states are then of second order. Thus we can conclude that the Kohn variational expression is stable with respect to variations in both the scattering functions and target states as long as Eqs. (4.2) and (4.3) are satisfied.

V. COMPARISONS OF MULTICHANNEL METHODS

Here we will examine the convergence properties of the multichannel $\tilde{C}$ functional (MCC) discussed in Sec. III along with the multichannel Schwinger functional (MCS) discussed by Maleki and Macheck,[12] the Schwinger and $\tilde{C}$ functional multichannel functions of Takatsuka and McKoy[6,7] (TMS and TMC) and the RIAF multichannel method of Nesbet.[11]

The basis set used for the open- and closed-channel scattering functions were

$$f_{i,\lambda}=\theta_i(r_1)r_2^\lambda e^{-pr_2}, \quad \lambda=1,2,\ldots,N_0 \text{ or } N_c \tag{5.1}$$

where N_0 was the member of basis functions used in the open channels and N_c was the number of basis functions used in the closed channels. We also considered the importance of functions beyond the range of the potential (i.e., $r>a_2$), asymptotic functions, which were of the form

$$g_{i,\lambda}=\begin{cases} 0, & r_2<a_2 \\ \theta_i(r_1)(r_2-a_2)^{\lambda+1}e^{-p(r_2-a_2)}, & \end{cases} \tag{5.2}$$

$$r_2>a_2 \text{ and } \lambda=1,2,\ldots,M_0 \text{ or } M_c \ .$$

Including functions of this form in the wave functions allowed the trial function to exhibit the same discontinuities in the second derivative as would be found in the exact solution.[16]

To illustrate the importance of the asymptotic functions, consider the results for the original Huck potential problem presented in Table I. First, note that the asymp-

TABLE I. Importance of asymptotic functions in the RIAF method for the convergence of eigenphase sums for scattering by the original Huck-model potential with $E=0.625$.[a]

N_0	MCS,TMS δ_{sum} (rad)	MCC,TMC δ_{sum} (rad)	RIAF ($M_0=0$) δ_{sum} (rad)	RIAF ($M_0=N_0$) δ_{sum} (rad)
2	1.245 770	1.239 807	1.227 187	1.209 311
4	1.239 537	1.239 524	1.227 370	1.237 250
6	1.239 534	1.239 534	1.233 214	1.239 532
8	1.239 534	1.239 534	1.235 135	1.239 534

[a]Exact eigenphase sum is 1.239 534. The energy scale has been shifted up by 0.125 compared to that found in earlier applications to the Huck problem, so that the energy used here is equivalent to $E=0.5$ found in Refs. 9, 11, and 13.

TABLE II. Rates of convergence of eigenphase sums with respect to the open-channel basis set for scattering by the modified Huck-model potential with $E=0.625$.[a]

N_0,M_0,N_c,M_c	MCS δ_{sum} (rad)	TMS δ_{sum} (rad)	MCC δ_{sum} (rad)	TMC δ_{sum} (rad)	RIAF δ_{sum} (rad)
1,1,8,8	1.111 549	1.112 621	1.138 454	1.139 175	1.132 493
2,2,8,8	1.263 720	1.263 730	1.257 533	1.257 536	1.227 192
4,4,8,8	1.257 267	1.257 267	1.257 254	1.257 254	1.254 993
6,6,8,8	1.257 265	1.257 265	1.257 265	1.257 265	1.257 262
8,8,8,8	1.257 265	1.257 265	1.257 265	1.257 265	1.257 265

[a]Exact eigenphase sum is 1.257 265.

totic functions are not needed for the Schwinger or $\tilde{C}$ functionals since the trial function need only extend as far as the range of the interaction potential in the open channels. Additionally, the multichannel variational principles of Takatsuka and McKoy[6,7] are identically equivalent to the standard Schwinger and $\tilde{C}$ functionals when there are no closed channels for model potentials of this type. Table I shows that the inclusion of the asymptotic functions substantially improves the convergence properties of the RIAF method. The importance of the asymptotic functions explains why a comparison between previous results obtained using Kohn-type functionals, such as in the RIAF method,[11] and results using the Schwinger method,[13] would lead to the misleading conclusion that the Kohn methods have relatively bad convergence characteristics. This same basis set effect is clearly evident in the comparison of convergence rates of resonance energies and widths for the modified Huck potential using the R-matrix method[20] which does not require asymptotic functions and the Siegert method[21] which does require them.

The results presented here indicate that the RIAF method still converges somewhat more slowly than the Schwinger-type methods when the asymptotic functions are included, in agreement with a comparison of these methods on an exponential potential.[14,15] Also Table I shows that the $\tilde{C}$ functional methods converge somewhat faster than do the Schwinger functional methods even for the short-ranged scattering potential of the Huck model.

Next we consider the results obtained for the modified Huck model. In Table II, we present the results obtained when N_0 and M_0 were varied while N_c and M_c were both 8, which is a sufficient number of functions to assure convergence in the closed-channel part of the problem at $E=0.625$. It was found that all five methods required asymptotic functions in the closed channel for good convergence. The same pattern emerges here as was found in Table I. The methods based on the $\tilde{C}$ functional converged most rapidly, followed by those based on the Schwinger functional, and then finally the RIAF procedure. Additionally, the difference between the method based on the standard close coupling equations, MCS and MCC, and the method ot Takatsuka and McKoy,[6,7] are two orders of magnitude smaller than the errors in the variational estimates. Thus, the rates of convergence of the two approaches are effectively the same with respect to the number of open-channel functions.

We also considered the rates of convergence with respect to the closed-channel basis set. We found that when N_0 and M_0 were both 8, that all five methods yielded results identical to seven significant figures, irrespective of the values of N_c and M_c. In Table III, we see that the rate of convergence with respect to N_c and M_c is similar to that with respect to N_0 and M_0 found in Table II.

The effects of using an approximate target state are shown in Table IV. The approximate target states were linear expansions of the basis functions

$$u_n(r_1)=\left[\left[r_1-\frac{a_1}{2}\right]^2-\frac{a_1^2}{4}\right]\left[r_1-\frac{a_1}{2}\right]^{n-1},$$

$$n=1,2,\ldots,N_T\ . \quad (5.3)$$

TABLE III. Rates of convergence of eigenphase sums with respect to the closed-channel basis set for scattering by the modified Huck-model potential with $E=0.625$.[a]

N_0,M_0,N_c,M_c	MCS,TMS,MCC,TMC,RIAF δ_{sum} (rad)
8,8,1,1	1.243 110
8,8,2,2	1.256 001
8,8,4,4	1.257 121
8,8,6,6	1.257 265
8,8,8,8	1.257 265

[a]Exact eigenphase sum is 1.257 265.

TABLE IV. Convergence properties of the scattering equations with respect to the target basis set.[a]

N_T	$E_3^t-E_3$[b]	$\langle\theta_1\mid\theta_3^t\rangle$	$\delta_{sum}^t-\delta_{sum}$[c]
4	0.168	0.433×10^{-3}	0.122
6	0.439×10^{-2}	0.122×10^{-5}	0.293×10^{-2}
8	0.384×10^{-4}	0.105×10^{-8}	0.307×10^{-4}
10	0.124×10^{-6}	0.560×10^{-11}	0.106×10^{-6}

[a]Scattering for the modified Huck potential with $E=1.625$.
[b]Error in the energy of the third target state with $E_3=1.125$.
[c]Error in the eigenphase sum for any of the methods MCS, TMS, MCC, TMC, or RIAF with $N_0=M_0=8$, and $\delta_{sum}=-1.217\,114$.

The scattering energy was $E=1.625$ which is above the threshold for exciting the third state which has $E_3=1.125$. The scattering wave function then has three open channels and no closed channels. With $N_0=M_0=8$, all five scattering methods give eigenphase sums which agree to seven significant figures. As can be seen in Table IV, the error in the variation energy of the third state, $\langle\theta_1\,|\,\theta_3^t\rangle$, and the error in the eigenphase sum all converge at about the same rate. This is numerical evidence of the fact that all of these quantities are second order with respect to errors in the target trial function, θ_3^t, as was discussed in Sec. IV.

VI. CONCLUSIONS

We have compared three multichannel variational methods, the Schwinger-type methods based on the close-coupling equations,[12] the formulations of Takatsuka and McKoy,[6,7] and the standard Kohn-type variational methods,[11] using a simple model potential which contains both open and closed channels. For this problem, we have found no substantial difference between the Schwinger-type close-coupling methods and the variational methods of Takatsuka and McKoy.[6,7] Both of these methods were found to converge somewhat more rapidly than did the Kohn-type methods for the open-channel part of the problem. This comparison does not include the effects of particle indistinguishability which is an important facet of electron-molecule scattering, for which these variational methods are of particular interest. However, we expect that the relative rates of convergence will be similar in the electron-molecule scattering problem to those found here.

We have also established that methods obtained from the Kohn variational expression, such as the multichannel $\tilde{C}$ functional method suggested here, are variationally stable with respect to errors in the target states, as long as the trial target states satisfy the relationships given in Eqs. (4.2) and (4.3). The variational stability of the Kohn method can also be shown for the case of electron-molecule scattering.

Applications of the multichannel $\tilde{C}$ functional to molecular systems are in progress.

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[1]See, for example, N. F. Lane, Rev. Mod. Phys. **52**, 29 (1980); R. K. Nesbet, in *Electron-Atom and Electron-Molecule Collisions*, edited by J. Hinze (Plenum, New York, 1983), p. 21.
[2]L. A. Collins and W. D. Robb, J. Phys. B **13**, 1637 (1980).
[3]R. R. Lucchese, D. K. Watson, and V. McKoy, Phys. Rev. A **22**, 421 (1980).
[4]K. Takatsuka and V. McKoy, Phys. Rev. A **23**, 2352 (1981).
[5]R. R. Lucchese and V. McKoy, Phys. Rev. A **28**, 1382 (1983).
[6]K. Takatsuka and V. McKoy, Phys. Rev. A **24**, 2473 (1981).
[7]K. Takatsuka and V. McKoy, Phys. Rev. A **30**, 1734 (1984).
[8]M.-T. Lee, K. Takatsuka, and V. McKoy, J. Phys. B **14**, 4115 (1981).
[9]R. J. Huck, Proc. Phys. Soc. London A **70**, 369 (1957).
[10]M. Fels and A. Hazi, Phys. Rev. A **5**, 1236 (1972).
[11]R. K. Nesbet, Phys. Rev. A **18**, 955 (1978).
[12]N. Maleki and J. Macek, Phys. Rev. A **21**, 1403 (1980).
[13]K. Takatsuka and V. McKoy, Phys. Rev. Lett. **45**, 1396 (1980).
[14]D. Thirumalai and D. G. Truhlar, Chem. Phys. Lett. **70**, 330 (1980).
[15]K. Takatsuka, R. R. Lucchese, and V. McKoy, Phys. Rev. A **24**, 1812 (1981).
[16]J. A. Hendry and M. A. Hennell, J. Phys. A **9**, 11 (1976).
[17]Yu.N. Demkov, *Variational Principles in the Theory of Collisions* (MacMillan, New York, 1963), p. 27.
[18]A good general discussion of variational principles is given by E. Gerjuoy, A. R. P. Rau, and L. Spruch, Rev. Mod. Phys. **55**, 725 (1983).
[19]A detailed discussion of variationl expressions used in electron scattering is given by R. K. Nesbet, *Variational Methods in Electron-Atom Scattering Theory* (Plenum, New York, 1980).
[20]B. I. Schneider, Phys. Rev. A **24**, 1 (1981).
[21]C. W. McCurdy and T. N. Rescigno, Phys. Rev. A **20**, 2346 (1979).