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Variational Principles for Multichannel Feshbach Equations for Scattering and Rearrangement Collisions

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Variational functionals are constructed for solving Feshbach equations for multichannel scattering and rearrangement collisions. The open-channel and closed-channel components of the state function are varied separately. This separation disentangles the violent fluctuation in the open-channel component from the closed-channel component and speeds up the convergence in the resonance energy region. Numerical illustrations are given for the elastic (e, H) scattering.

I. INTRODUCTION

The work of Feshbach[1] has made clear that it is advantageous to separate the state function Υ into the closed-channel and open-channel segments

$$\Upsilon = P\Upsilon + Q\Upsilon \qquad (1.1)$$

and to exhibit their interrelations in the form of a pair of coupled equations

$$(E - PHP)\, P\Upsilon = PHQ\Upsilon\ , \qquad (1.2a)$$

$$(E - QHQ)\, Q\Upsilon = QHP\Upsilon\ , \qquad (1.2b)$$

where H is the Hamiltonian of the system, $Q = 1 - P$ with $PQ = 0$. P is a projection operator which projects onto the open channels asymptotically,

$$P\Upsilon \to \mathcal{A} \sum_\gamma \nu_\gamma(\vec{\rho}_\gamma)\, \psi_\gamma^0(\vec{r}_\gamma) \quad \text{as } \rho \to \infty\ , \qquad (1.3)$$

where the internal coordinates $\vec{r}_\gamma$ for the asymptotic eigenfunctions ψ_γ are labeled collectively according to their associated open-channel coordinates $\vec{\rho}_\gamma$. The ν_γ's in Eq. (1.3) satisfy the appropriate boundary conditions of the collision system.

The Feshbach equation given by Eqs. (1.2) or their alternative form

$$(E - \mathcal{H})\, P\Upsilon = 0\,, \qquad (1.4)$$

with

$$\mathcal{H} = P\left(H + HQ\,\frac{1}{E - QHQ + i\eta}\,QH\right)P\,, \qquad (1.5)$$

are in a form which is most convenient for dealing with the closed-channel resonant scatterings[2–9] and rearrangement collisions.[9–15] The quantity $\eta \to 0^+$ in the effective Hamiltonian $\mathcal{H}$ is introduced for the case when the γ sum in Eq. (1.3) does not extend over all the open channels.

The projection-operator formulation of Feshbach is related to the coupled-equation formulation. In fact it puts the various coupled-equation approaches to the scattering and rearrangement collision on a firm theoretical ground. Formally, it allows a unique description of the neglected terms in the form of an optical potential for a truncated coupled-equation calculation. More important, it permits the generalization of the set of coupled equations to satisfy a variational principle with bounds for a certain class of projection operators.[16,17] This follows from the fact that if P is constructed to project onto all the open channels not only asymptotically but throughout the entire channel coordinates, then one need only solve exactly the open-channel equation given by Eq. (1.2a) for a given variationally bounded $Q\Upsilon$ to maintain the minimum principle.[16] This minimum principle contributes to the success of the close-coupling approximations.[18–20]

The rigorous-bound principle is obtained under the strong assumption that Eq. (1.2a) for the open channels can be exactly solved. In practice this is often difficult to accomplish especially for multichannel problems. The purpose of the present work is to investigate the method of solving the Feshbach equations in a new variational principle proposed by us recently.[21] In this variational principle, we make use of the advantages obtained in separating Υ into the closed- and open-channel segments by varying $P\Upsilon$ and $Q\Upsilon$ separately. This permits the fluctuations in $P\Upsilon$ to be disentangled from that of $Q\Upsilon$ in the determination of variational parameters in $Q\Upsilon$. For each chosen trial function $Q\Upsilon$, Eq. (1.2a) is then solved variationally for $P\Upsilon$. This proves to be extremely helpful in stablizing the solution for $P\Upsilon$ in the resonance region.

A variational principle of this kind was simultaneously but independently proposed by Hahn.[22] An excellent account of the formal relations between the new variational principle with both the variational principle for scattering[23-30] and the generalized variational bounds[16,17] was given there. Since Eq. (1. 2a) is now solved only variationally, the new variational principle is, therefore, no longer rigorously bounded. It is, however, of interest to note that the results we have obtained for the elastic (e, H) scattering using the new variational principle appear to be bounded by the Schwartz results.[31] In the present paper, further results of our calculation are reported.

Before presenting the variational procedures and their sample application to the (e, H) scattering, it is perhaps worthwhile to discuss the availability of the projection operators P and Q. A remarkable feature of the Feshbach equation lies in its generality in the projection operator. The only physical requirement is that P projects *asymptotically* onto the desired open channels. There are a number of ways that the projection operators may be constructed to satisfy this requirement.[1,2,9-12] For the particular case where P projects onto all the open channels, the projection operator can be easily constructed in the form[9]

$$P = 1 - Q, \tag{1.6}$$

with

$$Q = \sum_\lambda | \chi_\lambda(\vec{\rho}, \vec{r}) \rangle \langle \chi_\lambda(\vec{\rho}\,', \vec{r}\,') | \; ; \tag{1.7}$$

here the χ_λ's which may be constructed, for example, by diagonalizing the Hamiltonian in terms of a set of basis functions are square-integrable functions of the coordinates of the entire collision system. With Q given in terms of χ_λ, it is clear that asymptotically

$$Q\Upsilon \rightarrow 0 \quad \text{as} \; \rho \rightarrow \infty ; \tag{1.8}$$

consequently, $P\Upsilon$ satisfies Eq. (1. 3) with the γ-sum sums over all the open channels. With the projection operator Q constructed in this manner, $Q\Upsilon$ does not contain open-channel components only asymptotically. At small-channel coordinates $Q\Upsilon$ in general contains open-channel components. Such open-channel components at small channel coordinates can, to a large extent, be removed from $Q\Upsilon$ by apporpirate choice of the χ functions in Q. We shall therefore consider that the explicit expressions for the projection operator Q and $P = 1 - Q$, with P projecting onto all the open channels, are available.

II. MULTICHANNEL VARIATIONAL PRINCIPLE

In this section we discuss the variational principle in which the open-channel and closed-channel components of the state functions are varied separately. This separation will help to disentangle the violent fluctuation in the open-channel component from the closed-channel component and to speed up the convergence in the resonance-energy region.

We shall formulate the variational principle in terms of the reactance matrix R. Let there be N_0 open channels which are arranged in order of increasing target energy. The asymptotic function in Eq. (1. 3) may be rearranged in the form

$$\sum_\gamma \rho_\gamma^{-1} \nu_\gamma(\rho_\gamma) \psi_\gamma(r_\gamma) \mathcal{Y}_\gamma(\hat{\rho}_\gamma \cdot \hat{r}_\gamma) \; , \tag{2.1}$$

where $\mathcal{Y}_\gamma(\hat{\rho}_\gamma \cdot \hat{r}_\gamma)$ contains the angular and spin functions. We may think that channel indices are being renumbered to include the description of angular and spin states. The radial function for channel γ takes the asymptotic form

$$\nu_{\gamma\gamma'}(\rho_\gamma) \rightarrow (\mu_\gamma / k_\gamma)^{1/2} (\sin\xi_\gamma \, a_{\gamma\gamma'} + \cos\xi_\gamma \, b_{\gamma\gamma'}), \qquad \gamma = 1, \ldots, N_0 \tag{2.2}$$

with

$$\xi_\gamma = k_\gamma \rho_\gamma + \Delta z_\gamma / k_\gamma + n_\gamma \; , \tag{2.3}$$

where Δz_γ is the residual charge in the γ channel, and η_γ is an additional constant phase factor which may be chosen for convenience for inelastic and rearrangement collisions. For elastic scattering, it takes the form

$$\eta_\gamma^{(\mathrm{elastic})} = -\tfrac{1}{2} l_\gamma \pi + (\Delta z_\gamma / k_\gamma) \ln 2k_\gamma + \arg\Gamma(l_\gamma + 1 - i\Delta z_\gamma / k_\gamma) \, . \tag{2.4}$$

In Eq. (2. 2), we have introduced an additional subscript γ' with $\gamma' = 1, \ldots, N_0$ for $\nu_{\gamma\gamma'}$ to denote the initial channel. The radial channel function $\nu_{\gamma\gamma'}$ behaves like $\rho_\gamma^{l_\gamma + 1}$ in the limit $\rho_\gamma \rightarrow 0$. We have the boundary condition

$$\lim [\rho_\gamma^{-l_\gamma - 1} \nu_{\gamma\gamma'}(\rho_\gamma)] = \delta_{\gamma\gamma'} \quad \text{as} \; \rho_\gamma \rightarrow 0 \tag{2.5}$$

for γ and $\gamma' = 1, \ldots, N_0$.

For each set of initial conditions $\{a_{\gamma\gamma'}\}$, the reactance-matrix elements may be determined from the set of values $\{b_{\gamma\gamma'}\}$ by solving the linear equations

$$\sum_{j=1}^{N_0} R_{\gamma j} a_{j\gamma'} = b_{\gamma\gamma'} \, . \tag{2.6}$$

In matrix notation, we have

$$\mathcal{R} = b a^{-1} \, . \tag{2.7}$$

For standard phase convention,[32] the reactance matrix is real so that

$$\mathcal{R} = \tilde{\mathcal{R}}^* = \tilde{\mathcal{R}} = \tilde{a}^{-1} \tilde{b} \; ; \tag{2.8}$$

the S matrix can then be determined either in terms of $\mathcal{R}$ or a and b:

$$S=\frac{1+i\mathcal{R}}{1-i\mathcal{R}}=\frac{(1-\mathcal{R}^2)+2i\mathcal{R}}{1+\mathcal{R}^2} \qquad (2.9a)$$

$$=(a+ib)(\tilde{a}a+\tilde{b}b)^{-1}(\tilde{a}+i\tilde{b}) \, . \qquad (2.9b)$$

Note that in determining S-matrix elements the inversion of the complex matrix can be avoided.

The reactance-matrix elements $R_{\gamma\gamma'}$ (or the values for $b_{\gamma\gamma'}$) can be obtained by applying the variational principles for scattering to the Feshbach equation given by Eq. (1.4). The Kohn variational functional takes the form[23,24,33]

$$[J_p]=J_{pt}-\langle P\Upsilon_t|\mathcal{H}-E|P\Upsilon_t\rangle+\Delta J_p, \qquad (2.10)$$

with

$$\Delta J_p\equiv\langle P(\Upsilon-\Upsilon_t)|\mathcal{H}-E|P(\Upsilon-\Upsilon_t)\rangle, \qquad (2.11)$$

$$\mathcal{H}=P\left(H+HQ\frac{1}{E-QHQ}QH\right)P, \qquad (2.12)$$

$$J_{Pt}=\tfrac{1}{2}\hbar^2\sum_{i,j=1}^{N_0}a_{\gamma i}(R_{ij})_t a_{j\gamma'}, \qquad (2.13)$$

where the trial function $P\Upsilon_t$ should be constructed to satisfy the boundary conditions inferred by Eqs. (1.3), (2.1), (2.2), and (2.5).

The functional $[J_P]$ is stationary with respect to a small variation in $P\Upsilon_t$ and J_{pt} as well as $Q\Upsilon_t$, which is expressed in terms of the inverse operator $Q(E-QHQ)^{-1}Q$ [see Eq. (1.2b)] in the effective Hamiltonian $\mathcal{H}$ given by Eq. (2.11). The first-order variation in $[J_P]$ can be carried out with respect to $P\Upsilon_t$ and J_{pt} for each stationary $Q\Upsilon_t$ obtained from a variational functional $[J_Q]$ constructed for the closed-channel component[21]:

$$[J_Q]=\langle Q\Upsilon_t|QHQ-E|Q\Upsilon_t\rangle$$
$$+\langle Q\Upsilon_t|QHQ|P\Upsilon_t\rangle+\langle P\Upsilon_t|PHQ|Q\Upsilon_t\rangle. \qquad (2.14)$$

It can be shown that $[J_Q]$ is stationary with respect to small variations in $Q\Upsilon_t$ to give Eq. (1.2b). This is a two-step variational procedure in which a stationary $Q\Upsilon_t$ is first obtained from functional $[J_Q]$ and then the variations on the functional $[J_p]$ is carried out for each stationary $Q\Upsilon_t$.

Consider the case when the trial function for the closed-channel component is taken to be of the form

$$|Q\Upsilon_t\rangle=\textstyle\sum_i|Q\phi_i\rangle c_i, \qquad (2.15)$$

where $Q\phi_i$ are square integrable. The variations with respect to the linear parameters

$$\frac{\partial[J_Q]}{\partial c_i}=0 \qquad (2.16)$$

yield

$$\textstyle\sum_j\langle Q\phi_i|E-QHQ|Q\phi_j\rangle c_j=\langle Q\phi_i|QHQ|P\Upsilon_t\rangle. \qquad (2.17)$$

In matrix notation, we have

$$\tilde{\mathcal{H}}\mathcal{C}=\mathcal{B}, \qquad (2.18)$$

where the matrix elements for $\tilde{\mathcal{H}}$ and $\mathcal{B}$ are defined as

$$H_{ij}=\langle Q\phi_i|E-H|Q\phi_i\rangle, \qquad (2.19)$$

$$B_i=\langle Q\phi_i|H|P\Upsilon\rangle. \qquad (2.20)$$

Hence the stationary $Q\Upsilon_t$ is formally given by

$$|Q\Upsilon_t\rangle=\Big(\sum_{i,j}|Q\phi_i\rangle H^{-1}_{ij}\langle Q\phi_j|\Big)H|P\Upsilon_t\rangle, \qquad (2.21)$$

where H^{-1}_{ij} is the matrix element of inverse of $\tilde{\mathcal{H}}$. We have therefore

$$Q\frac{1}{E-QHQ}Q=\sum_{i,j}|Q\phi_i\rangle H^{-1}_{ij}\langle Q\phi_j|. \qquad (2.22)$$

The open-channel variational functional $[J_P]$ for a given stationary closed-channel function $Q\Upsilon_t$ then takes the form

$$[J_P]=J_{pt}-\langle P\Upsilon_t|H+\sum_{ij}(H|Q\phi_i\rangle H^{-1}_{ij}\langle Q\phi_j|H)$$
$$-E|P\Upsilon_t\rangle. \qquad (2.23)$$

As mentioned before, the first-order variation in $[J_p]$ can be carried out in a number of ways. In the rare case where anomalous singularities occur in the open-channel component, the violent fluctuations may be controlled by the alternative procedures proposed by Harris[28,30] and Nesbet.[25] Such anomalous singularities will not introduce any fluctuation in the closed-channel variational functional $[J_Q]$. We found it is sometimes convenient to use an alternative open-channel variational functional $[J_p']$ constructed from Eq. (1.2a):

$$[J_p']=J_{pt}-\langle P\Upsilon_t|PHP-E|P\Upsilon_t\rangle+\langle P\Upsilon_t|PHQ|Q\Upsilon_t\rangle$$
$$+\langle Q\Upsilon_t|QHP|P\Upsilon_t\rangle. \qquad (2.24)$$

This functional $[J_p']$ together with the function $[J_Q]$ form a pair of functionals which permits $P\Upsilon_t$ and $Q\Upsilon_t$ to be varied separately. For computational conveniences we have made use of both $[J_p]$ and $[J_p']$ open-channel functionals in the numerical illustration reported in Sec. III.

The variational functionals constructed in this section satisfy the stationary principle. Owing to the inequality[16]

$$Q(QHQ-E)Q>0 \qquad (2.25)$$

an estimate of the error involved in the variation procedure can be obtained from Eq. (2.11). For the case where the norm of the error in the open-channel functional is smaller than the norm of the error in the closed-channel functional, the variational functionals provide an approximate bound on the reactance-matrix elements.[22] It should be

TABLE I. s-wave phase shift for the static-exchange approximation of electron-hydrogen scattering.

	^3S		^1S	
k^2 (in a.u.)	N.I.[a]	Variational	N.I.[a]	Variational
0.01	2.908	2.90760	2.396	2.39581
0.04	2.679	2.67915	1.871	1.87017
0.09	2.461	2.46113	1.508	1.50811
0.16	2.257	2.25730	1.239	1.23951
0.25	2.070	2.07007	1.031	1.03150
0.36	1.901	1.90056	0.869	0.86906
0.49	1.749	1.74882	0.744	0.74415
0.64	1.614	1.61410	0.651	0.65127

[a] Numerical integration, see Ref. 36.

stressed that the inequality (2.25) is satisfied only for the class of Q which contains no open-channel states not only asymptotically but throughout the entire channel coordinates.

III. APPLICATION TO ELASTIC (e,H) SCATTERING

In this section we report the application of the variational procedure of Sec. II to the elastic (e, H) scattering. It is well known that in the elastic (e, H) channel there are a number of resonances for which the Kohn variational procedure does not converge. This application would serve as a good example on the convergence of the two-step variational procedure. In addition there are other theoretical calculations which may be used to assess the new variational procedure.[3–9,18–20,34,35]

The Hamiltonian for the (e, H) scattering system can be written in the center-of-mass coordinate as (in atomic units)

$$H=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{r_{12}}\,. \tag{3.1}$$

For elastic scattering, the projection operators have been found to be

$$P=1-Q\,, \tag{3.2}$$

$$Q=\left[1-|\psi_{1s}(\vec{r}_1)\rangle\langle\psi_{1s}(\vec{r}_1)|\,\right]\times\left[1-|\psi_{1s}(\vec{r}_2)\rangle\langle\psi_{1s}(\vec{r}_2)|\,\right] \tag{3.3}$$

TABLE II. The eigenvalues of QHQ for the s-state electron-hydrogen system (in a.u.).

		BTP[a]	OG[b]	CR[c]	Present
	1	−0.148779	−0.14872	−0.1479	−0.148766
^1S	2	−0.126008	−0.12596	−0.12598	−0.125992
	3				−0.125019
	1	−0.127108	−0.12701	−0.1270	−0.127108
^3S	2	−0.125092	−0.12507	−0.12517	−0.125110
	3				−0.125006

[a] Reference 4. [b] Reference 3. [c] Reference 6.

TABLE III. Fixed nonlinear parameter calculation for the s-wave phase shift for electron-hydrogen scattering (in a.u.); ($\alpha=0.5$, $\beta=0.75$).

	^1S		^3S	
k/δ	Present	$1s$-$2s$-$2p$[a]	Present	$1s$-$2s$-$2p$
0.1	2.539	2.492	2.9372	2.9355
0.2	2.047		2.7157	2.7153
0.3	1.673	1.596	2.4981	
0.4	1.389		2.2918	
0.5	1.174	1.093	2.1028	2.0956
0.6	1.013		1.9308	
0.7	0.902	0.817	1.7770	1.767
0.8	0.857	0.773	1.6406	1.633

[a] Reference 18.

with

$$\psi_{1s}(\vec{r}_1)=e^{-r_i}/\pi^{1/2}\,, \tag{3.4}$$

where we have taken the proton to be infinitely heavy in comparison with the electron and set the channel coordinates to be the electron coordinates.

We shall consider the s-wave scattering and take the open-channel trial function to be

$$P\Upsilon_t=(1-Q)[F_{1s}(\vec{r}_2)\,\psi_{1s}(\vec{r}_1)\pm F_{1s}(\vec{r}_1)\,\psi_{1s}(\vec{r}_2)], \tag{3.5}$$

with

$$F_{1s}(r_i)=r_i^{-1}(\sin kr_i+\tan\delta\,\cos kr_i)(1-e^{-\tau r_i})+\sum_{j=0} d_j r_i^j e^{-\tau r_i}\,, \tag{3.6}$$

where the ± signs denote the singlet and triplet scatterings, respectively, $\tan\delta$ is the R matrix element, and τ is a nonlinear parameter to be

TABLE IV. s-wave phase shifts for electron-hydrogen scattering (in a.u.).

	^1S		^3S	
k^2/δ	Schwartz[a]	Present	Schwartz	Present
0.01	2.533(1)	2.550	2.9388(4)	2.9383
0.04	2.0673(9)	2.060	2.717(5)	2.7172
0.09	1.6964(5)	1.690	2.4996(8)	2.4994
0.16[b]	1.4146(4)	1.408	2.2938(4)	2.2937
0.25	1.202(1)	1.192	2.1046(4)	2.1042
0.36	1.041(1)	1.032	1.9329(8)	1.9323
0.49	0.930(1)	0.921	1.7797(6)	1.7782
0.64	0.886(3)	0.877	1.643(3)	1.6431
	$1s$-$2s$-$2p$ + Corr[c]		$1s$-$2s$-$2p$ + Corr	
0.6790	0.9205	0.9161	1.6158	1.6132
0.7208	0.762	0.753	1.5828	1.5829
0.74	0.8376	0.822	1.5724	1.5701

[a] Reference 31.

[b] The rigorous lower bounds of the s-wave shifts including up to d-wave hydrogenic states have been found (Ref. 37) at $k^2=0.16$ a.u. to be $\delta=1.4112$ (singlet) and $\delta=2.29356$ (triplet).

[c] Reference 19.

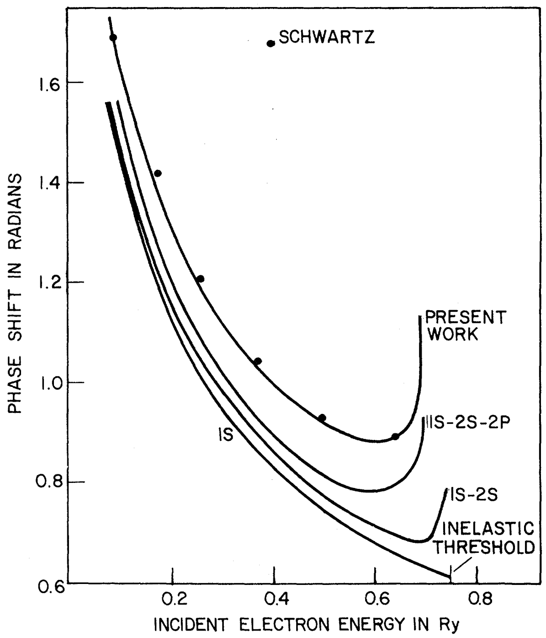

FIG. 1. Comparison of the energy dependence of the s-wave phase shift for the singlet (e, H) scattering in the present variational approximation with that in the Kohn variational approximation (Schwartz, Ref. 31) and in the various close-coupling approximations (1s, Ref. 36; 1s-2s, Ref. 18; 1s-2s-2p, Ref. 18).

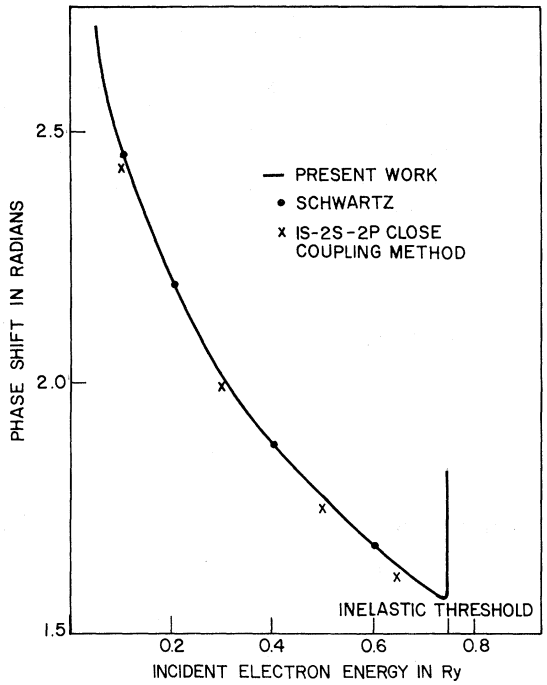

FIG. 2. Comparison of the energy dependence of the s-wave phase shift for the triplet (e, H) scattering in the present variational approximation with that in the Kohn variational approximation (Schwartz, Ref. 31) and in the 1s-2s-2p close-coupling approximation (Ref. 18).

adjusted so that $\tan\delta$ converges with increasing number of linear parameters d_j. The closed-channel trial function is chosen to be of the form given by Eq. (2.15). With $P\Upsilon_t$ given by Eqs. (3.5) and (3.6), the variational functional corresponding to Eq. (2.23) takes the form

$$[J_p]=\tfrac{1}{2}k\tan\delta-\langle P\Upsilon_t|H+\sum_{ij}\langle H|Q\phi_i\rangle H_{ij}^{-1}\langle Q\phi_j|H\rangle - E|P\Upsilon_t\rangle. \quad (3.7)$$

The stationary solutions are obtained with the variations

$$\frac{d[J_p]}{d(\tan\delta)}=0, \quad \frac{d[J_p]}{dd_j}=0 \ . \quad (3.8)$$

The functional given by Eq. (3.7) is obtained for the case in which only linear parameters are varied in the closed-channel trial function $Q\Upsilon_t$ [see Eqs. (2.16)-(2.18)]. If the nonlinear parameters in the trial function are to be varied, it is convenient to use the pair of functionals $[J_p']$ and $[J_Q]$ given, respectively, in Eqs. (2.24) and (2.14).

To investigate the convergence of the open-channel variational functional, we first consider the special case with $Q\Upsilon_t=0$, i.e.,

$$\delta(\tfrac{1}{2}k\tan\delta-\langle P\Upsilon_t|PHP-E|P\Upsilon_t\rangle)=0\,, \quad (3.9)$$

and compare the variational result with the known static-exchange result obtained by numerical differentiation (Table I).[36] It is found that the phase shift converges quickly with increasing number of linear parameters. No anomalous singularity and significant fluctuation have been found in a large number of calculations.

For the closed-channel trial function we adopt

TABLE V. Phase shifts in the neighborhood of resonances[a] (in a.u.).

^1S	k^2	0.700	0.701	0.702	0.703	0.704	0.705	0.706
	δ	1.455	1.718	2.166	2.724	3.139	0.238	0.379
^1S	k^2	0.74782	0.74798	0.74801	0.74804	0.74807		
	δ	1.641	2.142	2.448	2.731	2.957		
^3S	k^2	0.745780	0.745792	0.745794	0.745798	0.745808		
	δ	1.595(4)	1.805(2)	2.305(4)	0.991(1)	1.486(1)		

[a] Parentheses indicates the uncertainty in the last figure quoted.

TABLE VI. Resonance energies for the s-wave electron-hydrogen scattering (in a.u.).

		E_n	Δ(shift)	Width (in eV)
^1S	1	-0.148894	-1.28×10^{-4}	4.11×10^{-2}
		-0.14865^{a}		$4.75\times10^{-2\,a}$
	2	-0.126002	-0.99×10^{-5}	2.65×10^{-3}
		-0.12595^{a}		2.19×10^{-3}
	3	-0.125019	-8×10^{-7}	6.22×10^{-5}
^3S	1	-0.12703	$+4.8\times10^{-6}$	3.1×10^{-5}
		-0.126992^{a}		$2.06\times10^{-5\,a}$
	2	-0.125109	$+3.0\times10^{-8}$	2.4×10^{-6}
	3	-0.1250006	$<10^{-8}$	2.4×10^{-8}

[a] Reference 19.

the separable form

$$Q\Upsilon_t=\sum_{l\mu\nu} c_{l\mu\nu}\,Q\left(r_1^\mu r_2^\nu e^{-(\alpha r_1+\beta r_2)}\pm r_1^\nu r_2^\mu e^{-(\beta r_1+\alpha r_2)}\right)\times P_l(\cos\theta_{12})\,, \quad (3.10)$$

where $\cos\theta_{12}$ in the Legendre function is the cosine of the angle between the two electrons. The function $Q\Upsilon_t$ to be adopted should have the flexibility to account for the interactions which are not contained in an open-channel trial function. One of the important interactions in the elastic (e, H) channel is the formation of the three-body resonances which are not contained in the open-channel trial function $P\Upsilon_t$ given by Eqs. (3.5) and (3.6). Consequently one of the criteria for the $Q\Upsilon_t$ is in its ability to account for these resonances. We have therefore used this function and calculated the quasistationary approximation of the resonance by determining the eigenvalues of QHQ. The results so obtained are compared in Table II with the results obtained using other types of functions. It is seen from Table II that the separable trial function is capable of yielding as accurate values as other trial functions including the Hylleraas-type trial functions. The separable trial function has, however, certain computational advantages.

In determining the stationary solutions of the functionals, we may carry out variations with respect to the linear parameters and leave the nonlinear parameters fixed in both the open- and closed-channel trial functions. We observe that the result so obtained depends sensitively on the nonlinear parameters α and β in the close-channel trial function [see Eq. (3.10)]. The nonlinear parameter τ in the open-channel trial function [see Eq. (3.6)], on the other hand, affects the convergence of the result. In Table III, the result obtained for a set of chosen nonlinear parameters α and β is tabulated as a function of scattering energy. In this calculation, we have included in $Q\Upsilon_t$ six s-wave terms and nine p-wave terms. It is seen that the present procedure gives consistent improvement (about 75%) over the ^1S $1s$-$2s$-$2p$ close-coupling results[18]

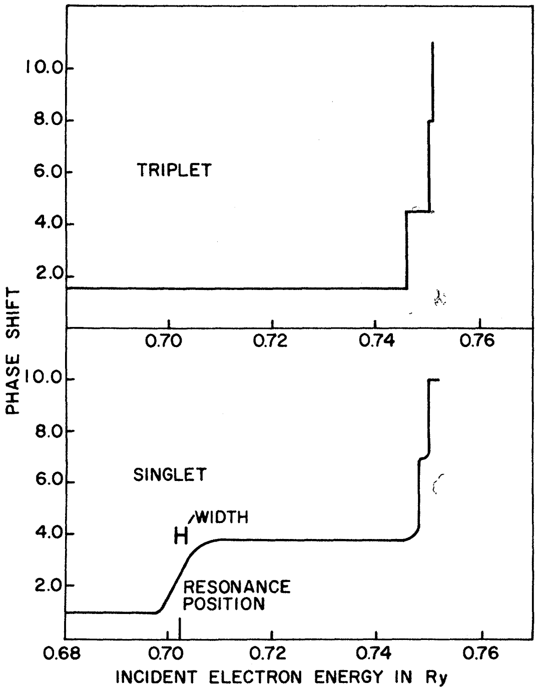

FIG. 3. Multiresonance structure of the s-wave phase shift for the singlet and triplet (e, H) scattering.

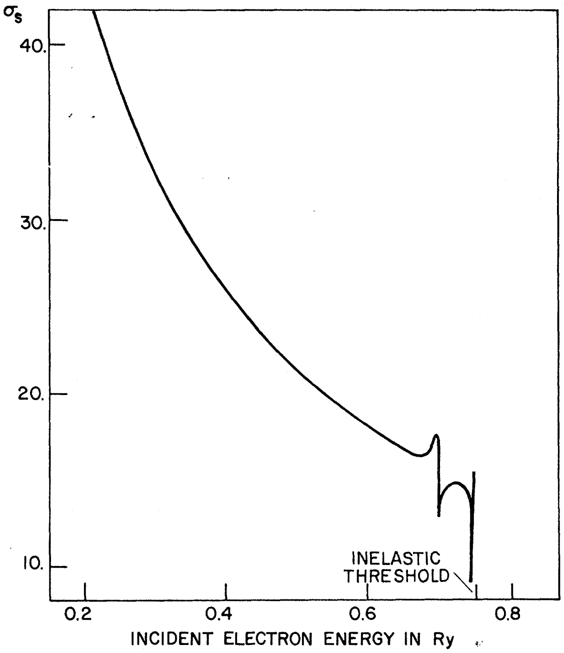

FIG. 4. Energy (Ry) dependence of the s-wave contribution to the total elastic (e, H) scattering cross section (a_0^2).

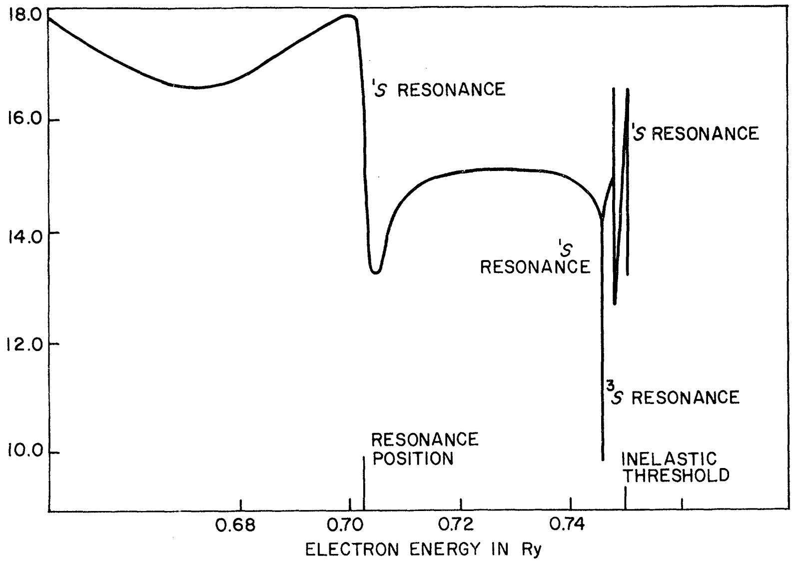

FIG. 5. Details of the energy dependence of the s-wave contribution to the total elastic (e, H) scattering cross section (a_0^2) in the resonance-energy region.

(as compared with the Schwartz result[31]) over a significant energy range ($k = 0.1-0.8$ a.u.). This implies that the nonlinear parameters once properly determined are not sensitively energy dependent. (This is, however, not the case in the resonance-energy region.) We may use fixed α and β values for a range of energies so that a significant number of integrals need not be recalculated at different energies.

More accurate phase shift are obtained if the nonlinear parameters α and β are optimized. In Table IV, the s-wave phase shift obtained with optimized α and β and 50 linear parameters including up to the d-wave terms in $Q\Upsilon_t$ are compared with other calculations. The present procedure gives in general 92–96% improvement over the $1s$-$2s$-$2p$ close-coupling calculations for singlet scattering. For triplet scattering, our result differs from the Schwartz result only in the fifth significant figure. The energy dependence of the phase shift is compared in Figs. 1 and 2 with various other calculations.

Near the elastic threshold, the ratio $(\tan\delta)/k$ gives the scattering length

$$a = (\tan\delta/k) \quad \text{as } k \to 0 . \qquad (3.11)$$

Our 50-term $Q\Upsilon_t$ computation gives $a^{(1)} = 6.15$ a.u. and $a^{(3)} = 1.88$ a.u. This is to be compared with the Schwartz value $a^{(1)} = 6.09$ a.u. and $a^{(3)} = 1.88$ a.u. obtained with a 50-term Hylleraas-type trial function. Schwartz has shown[31] that a more accurate result of $a^{(1)} = 5.97$ a.u. and $a^{(3)} = 1.77$ a.u. can be obtained by improving his asymptotic wave function which corresponds to our open-channel trial function. The effect of the long-range potential on the asymptotic wave function in relation with the scattering-length determination has been investigated by Rosenberg *et al.*[38] and by Temkin.[39]

Near the first excitation threshold, we enter the closed-channel resonance region. In this resonance region, we found that the convergence of the phase shift depends very sensitively on the nonlinear parameter τ in the open-channel trial function. This is the region where the conventional Kohn variational procedure has convergence difficulties.[31,40] In the present procedure, we adjust the τ parameter in $P\Upsilon_t$ so that the desired convergence in $P\Upsilon_t$ is achieved. The nonlinear parameters α and β in $Q\Upsilon_t$ are taken in the resonance-energy region to be the values obtained in optimizing QHQ. Table V illustrates the detailed manner in which the phase shift goes through a resonance. Our result for the resonances agrees with the close-coupling results as shown in Table VI. The multiresonance structure of the phase-shift[9,41] is shown in Fig. 3.

The s-wave contribution to the total elastic-scattering cross section can be obtained from the singlet and triplet scattering cross section:

$$\sigma = \tfrac{1}{4}\sigma^{(1)} + \tfrac{3}{4}\sigma^{(3)} . \qquad (3.12)$$

This is shown in Figs. 4 and 5. The width of higher-member triplet resonances are too narrow to be seen for the adopted scale.

Note added in proof. We have recently received a report of a paper prior to publication [D. G. Truhlar and R. L. Smith, Phys. Rev. (to be published)] from Dr. Truhlar. In this paper, an investigation of the convergence of the variational technique was carried out.

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