

## Variational Approach to the Feshbach Equations for Scattering

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A variational method is constructed for the Feshbach equations for scattering. An example is carried out on the *S*-wave electron-hydrogen system. It is shown that fast convergence of the phase shift can be obtained throughout the energy range of interest including the resonance region. No anomalous singularities have been encountered.

In atomic and molecular problems, the Rayleigh-Ritz variational method is extremely useful in treating bound-state problems. Its counterpart in scattering problems, namely, Kohn's variational method,<sup>1</sup> has, however, been relatively less successful. This results partly from the difficulties in handling the anomalous singularities and partly from treating resonances that one often encounters in actual applications. These difficulties are illustrated in the well-known work of Schwartz<sup>2</sup> for elastic scattering of electrons by hydrogen atoms. Recently, several alternative variational methods have been developed to remedy these difficulties.<sup>3-5</sup> In this Letter, we propose an alternative version of Kohn's variational method which is free of the above difficulties, and we show that this new method is capable of providing high accuracy, using electron-hydrogen scattering as an example.

The fundamental difference of the present approach from other recently proposed methods lies in the fact that we start with the Feshbach equation<sup>6</sup> instead of the Schrödinger equation. The Feshbach equation is, of course, formally equivalent to the Schrödinger equation. By construction, the Feshbach equation, however, has the resonance structure built into its effective Hamiltonian. It is this feature which removes

the difficulties encountered in the conventional Kohn variational method and permits a simple description of resonances.

For convenience we now specifically consider the scattering of an electron by atoms. The state function for the scattering system may be separated into the open- and closed-channel components. If *P* and *Q* are the projection operators which project onto the open- and closed-channel subspaces, respectively, the Schrödinger equation may be written as<sup>6</sup>

$$(PHP - E)P\Psi = -PHQ\Psi, \quad (1a)$$

$$(QHQ - E)Q\Psi = -QHP\Psi, \quad (1b)$$

where *H* is the Hamiltonian. Equations (1a) and (1b) can be solved to give the Feshbach equation,

$$\left( PHP + PHQ \frac{1}{E - QHQ} QHP - E \right) P\Psi = 0. \quad (2)$$

By construction of *P* we have

$$P\Psi_{\vec{r} \rightarrow \infty} \rightarrow \Psi,$$

where  $\vec{r}$  denotes the coordinates of the outgoing electron.

Now, on applying Kohn's variational principle to the Feshbach equation, we obtain the variational functional

$$\delta \left( k \tan \frac{1}{2} \theta - \left\langle P\Psi \left| PHP + PHQ \frac{1}{E - QHQ} QHP - E \right| P\Psi \right\rangle \right) = 0, \quad (3)$$

where *k* is the momentum of the outgoing electron and the normalization of  $\Psi$  is taken such that the outgoing electron wave function approaches

$$[\sin(kr + \frac{1}{2}l\pi) + \tan\theta \cos(kr + \frac{1}{2}l\pi)]/r \quad (4)$$

asymptotically.

A functional can be constructed for Eq. (1b), namely,

$$\delta (\langle Q\Psi | QHQ - E | Q\Psi \rangle + \langle Q\Psi | QHP | P\Psi \rangle + \langle P\Psi | PHQ | Q\Psi \rangle) = 0. \quad (5)$$

Hence if we assume  $Q\Psi = \sum_n C_n \varphi_n$ , where  $\varphi_n$  is a set of basis functions, with the  $C_n$  as undetermined coefficients, Eq. (2) can be rewritten as

$$\delta(k \tan \frac{1}{2}\theta - \langle P\Psi | PHP + \sum_{n,m} PHQ | \varphi_n \rangle A_{nm}^{-1} \langle \varphi_m | QHP - E | P\Psi \rangle) = 0, \quad (6)$$

where  $A_{nm}^{-1}$  is the element of the inverse of the matrix  $\langle \varphi_n | QHQ - E | \varphi_m \rangle$ . Although this is mathematically equivalent to both the conventional Kohn method and various modified Kohn methods, in the present formulation the orthogonality between the  $P$  space and the  $Q$  space is preserved. A trial basis function used in the present formulation should therefore be either in  $Q$  space or in  $P$  space. This will help to remove the anomalous singularity. The closed-channel resonances arise naturally when  $E$  approaches one of the eigenvalues of  $QHQ$ . In an earlier work,<sup>7</sup> we used for  $Q\Psi$  the eigenfunction of  $QHQ$ . This is different from the  $Q\Psi$  calculated from Eq. (5). The present method gives faster convergence for phase-shift calculations.

A numerical example is carried out for electron-hydrogen S-wave scattering. We assume

$$Q\Psi = Q \sum C_i \{ r_1^{n_i} r_2^{m_i} \exp[-(\alpha r_1 + \beta r_2)] \pm r_1^{m_i} r_2^{n_i} \exp[-(\alpha r_2 + \beta r_1)] \} P_l(\cos \theta_{12}), \quad (7)$$

$$P\Psi = \varphi(r_2) e^{-r_1/\sqrt{\pi}} \pm \varphi(r_1) e^{-r_2/\sqrt{\pi}}, \quad (8)$$

where

$$P = |\psi_{1s}(1)\rangle \langle \psi_{1s}(1)| + |\psi_{1s}(2)\rangle \langle \psi_{1s}(2)| - |\psi_{1s}(1)\psi_{1s}(2)\rangle \langle \psi_{1s}(1)\psi_{1s}(2)|,$$

and  $Q = 1 - P$ . The function  $\varphi(r_2)$  assumes the form

$$\varphi(r) = \sum_{j=0} d_j r^j e^{-tr} + \frac{(1 - e^{-tr})}{r} [\sin(kr) + \tan \theta \cos(kr)], \quad (9)$$

where  $t$ ,  $\alpha$ , and  $\beta$  are the nonlinear parameters; and  $\psi$  is the ground state for hydrogen. Equation (7) is similar to those used by O'Malley and Geltman,<sup>8</sup> but here we use fewer nonlinear parameters and our eigenvalues for  $QHQ$  are considerably lower.

In computation, several interesting features are observed:

(a) With a suitable choice of  $t$ ,  $\theta$  usually converges to three or four significant figures by us-

ing five terms of  $d_j$ 's. If ten terms are included,  $\theta$  usually converges to five significant figures. More terms are needed near the resonance. The phase shift does converge in this energy region.

(b) Although only separable wave functions are used for the closed-channel component, the convergence is very impressive. This suggests the effectiveness of the variational method. For example, at  $k=0.1$  a.u. with an arbitrary choice of

TABLE I. S-state phase shift for elastic electron-hydrogen scattering.

$k^2/\theta$	Schwartz <sup>a</sup>	<sup>1</sup> S	This work	Schwartz <sup>a</sup>	<sup>3</sup> S	This work
		$1s-2s-2p^b$			$1s-2s-2p^b$	
0.01	2.553	2.492	2.550	2.9388	2.9355	2.9383
0.04	2.067		2.060	2.7171	2.7153	2.7172
0.09	1.696	1.596	1.690	2.4996		2.4994
0.16	1.415		1.408	2.2938		2.2937
0.25	1.202	1.093	1.192	2.1046	2.0956	2.1042
0.36	1.041		1.032	1.9329		1.9323
0.49	0.930	0.817	0.921	1.7797	1.767	1.7787
0.64	0.886	0.773	0.877	1.643	1.633	1.6431
		$1s-2s-2p + \text{corr}^c$			$1s-2s-2p + \text{corr}^c$	
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

<sup>a</sup>See Ref. 2.

<sup>b</sup>See Ref. 9.

<sup>c</sup>See Ref. 10.

TABLE II. Resonance  $S$  states for elastic electron-hydrogen scattering.  $\epsilon_n$  is the eigenvalue of  $QHQ$ ,  $E_n$  is the resonance position, and  $\Delta = E_n - \epsilon_n$ .

State	$n$	$\epsilon_n$ (Ry)	$E_n$ (Ry)	$\Delta$ (Ry)	Width (eV)
$^1S$	1	-0.148 766	-0.148 894	$-1.28 \times 10^{-4}$	$4.11 \times 10^{-2}$
		-0.148 779 <sup>a</sup>	-0.148 65 <sup>b</sup>		$4.75 \times 10^{-2}$ <sup>b</sup>
	2	-0.125 992 4	-0.126 002 3	$-0.99 \times 10^{-5}$	$0.043 \pm 0.006$ <sup>c</sup>
		-0.126 008 3 <sup>a</sup>	-9.125 95 <sup>b</sup>		$2.65 \times 10^{-3}$
		-0.125 018 6	-0.125 019 4	$-8.0 \times 10^{-7}$	$6.22 \times 10^{-5}$
		-0.127 107 7	-0.127 102 9	$+4.8 \times 10^{-6}$	$3.1 \times 10^{-5}$
$^3S$	1	-0.127 108 <sup>a</sup>	-0.126 992 3 <sup>b</sup>		$2.06 \times 10^{-5}$ <sup>b</sup>
		-0.125 110 1	-0.125 108 9	$+3 \times 10^{-8}$	$2.4 \times 10^{-6}$
	2	-0.125 092 <sup>a</sup>			
		-0.125 000 6	-0.125 000 6	$< 10^{-8}$	$2.4 \times 10^{-8}$

<sup>a</sup>See Ref. 14.<sup>b</sup>See Ref. 10.<sup>c</sup>See Ref. 15.

$\alpha = 0.6$ ,  $\beta = (-2E - \alpha^2)^{1/2}$ , we obtain  $\theta = 2.539$  rad by using a four-term  $s$ -wave, nine-term  $p$ -wave trial function. This is a 77% improvement over the  $1s-2s-2p$  close-coupling calculation.<sup>9,10</sup> The latter consumes much more computer time.

When the  $d$  wave as well as more terms are included in  $Q\Psi$ , we are able to improve the  $1s-2s-2p$  close-coupling result by 90–96% for the singlet  $S$  state. For the triplet  $S$  state our results differ, usually in the fifth place, from the most accurate results of Schwartz (see Table I).

(c) We have used Eq. (7) to calculate the eigenvalues of  $QHQ$ . In both the singlet and the triplet cases, we found at least three resonances below the  $n=2$  threshold. The existence of these series of resonances has been discussed in the literature.<sup>11,12</sup> It is interesting to note that for the singlet case the shift (see Table II) is negative and for the triplet case the shift is positive, and it decreases rapidly with increasing width. Furthermore, in the triplet case we also obtained lower eigenvalues<sup>13,14</sup> than those of Bhatia, Temkin, and Perkins.<sup>14</sup> Although the differences are very small, it is perhaps sufficient to demonstrate that for these resonances the inclusion of  $r_{12}$  in the trial function will not improve the results significantly. From the singlet scattering calculation, it appears that to include Hylleraas coordinates in the trial function may improve the convergence slightly, but the improvement is considerably less than one would usually assume. The

full details of this calculation will be presented in a forthcoming paper.

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