Extension of the Schwinger variational principle beyond the static-exchange approximation

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We propose a new variational principle for scattering theory which extends the Schwinger variational principle beyond the static-exchange approximation and to inelastic scattering. Application of this formulation to the scattering of electrons by hydrogen atoms at energies below $k^2 = 0.64$ demonstrates the rapid convergence of the phase shift with respect to the number of basis functions for both the open- and closed-channel orbitals. Furthermore, we show that the convergence of the phase shift with respect to the number of expansion functions (exact states or pseudostates) is also fast. In our theory, the resulting phase shifts can be more accurate than those of the close-coupling method even if the same expansion basis is used. The phase shifts in our $1s$-$\overline{2s}$-$\overline{2p}$ calculation are comparable to those of $1s$-$2s$-$2p$-$\overline{3p}$-$\overline{3d}$ calculation of Matese and Oberoi [Phys. Rev. A **4**, 569 (1971)], which are very close to the exact values. Several aspects of the convergence characteristics are also discussed.

I. INTRODUCTION

The Schwinger variational principle[1] has been successfully applied to the elastic scattering of electrons by molecules in the static-exchange approximation.[2] In a simple two-channel model system, we also found[3] that the convergence of the K matrix in the Schwinger principle was superior to that of the other standard variational principles[4] such as the Kohn method.[5] The mathematical basis for the different convergence characteristics of these variational methods has recently been discussed.[6] The results of these recent applications of the Schwinger principle suggest that the Schwinger principle should be extended to take account of polarization and short-range correlation effects and to include inelastic scattering.

In a general scattering system the application of the Schwinger principle beyond the static-exchange approximation is not unique. An obvious approach[7,8] would be to apply the Schwinger principle to the close-coupling equations as an alternative to the numerical integration procedure. A slightly more general method has been discussed by Nesbet,[9] in which the Schwinger principle is applied to the so-called generalized close-coupling equations.[9,10] In the latter case, the configurations for the closed-channel components can be selected more flexibly so that the configuration interaction technique, for example, can be used through the optical-potential formalism.[10] In both methods, the Schwinger principle should converge faster[6] to the exact close-coupling results than the Kohn-type methods if applied to the same coupled equations. So far, neither of the above Schwinger methods has been applied to an actual system.

In this paper we develop another approach to the extension of the Schwinger variational principle beyond the static-exchange approximation. Our formulation is not based on any coupled equations, indicating that the equation is defined for the total wave function and not for the scattering orbitals from the outset. Consequently, the configurations for the closed-channel components can be selected freely without the use of an optical potential. A more important feature is that the K matrix given by our method can be more accurate than that of the close-coupling approximation, even if the same expansion basis (hereafter referred to simply as pseudostates[4]) or trial functions are used for the closed channels. For the same reasons, the convergence with a given set of pseudostates is quite fast with respect to the size of the basis set both for the open-channel orbitals and for the closed-channel orbitals. Therefore we can expect that our new variational principle can provide K matrices close to the exact values with small sets of trial functions.

In Sec. II, the general formulation will be presented. To demonstrate the important characteristics of our method, we apply the theory to the elastic scattering of electrons by H atom in Sec. III. To our knowledge this is the first application of the Schwinger-type variational principle beyond the static-exchange approximation. Section IV presents a discussion of the encouraging convergence characteristics of our theory.

II. THEORY

A. Preliminary

We begin our discussion with a very simple formulation of the Schwinger principle on which our new formulation will be based. The Schrödinger equation for the $(N+1)$ particle system is

$$(E - H)\Psi_m = 0, \quad m = 1, 2, \ldots, N_0, \tag{2.1}$$

where N_0 is the number of open channels, and the Hamiltonian H is

$$H = H_{N+1} = H_N + T_{N+1} + \sum_{i=1}^{N} \frac{1}{r_{i,N+1}}$$
$$+ \sum_{\alpha} \frac{Z_\alpha}{r_{\alpha,N+1}} , \qquad (2.2)$$

with H_N defined as the total Hamiltonian of the target system. T_{N+1} is the kinetic-energy operator of $(N+1)$th particle and the third and fourth terms in Eq. (2.2) are the electron-electron and electron-nucleus interactions, respectively. These interactions are referred to collectively as V hereafter.

Identifying $H_N + T_{N+1}$ as a zeroth-order (unperturbed) Hamiltonian H_0, one easily converts the Schrödinger equation to the Lippmann-Schwinger equation of the form

$$\Psi_m = S_m + G_0 V \Psi_m , \qquad (2.3)$$

where G_0 is the standing-wave Green's function associated with $E - H_0$ and S_m is the regular solution of $E - H_0$. Based on this equation it is quite easy to construct the Schwinger variational functional for the K matrix, as

$$-\tfrac{1}{2} K_{mn} = \frac{\langle \Psi_m | V | S_n \rangle \langle S_m | V | \Psi_n \rangle}{\langle \Psi_m | V - V G_0 V | \Psi_n \rangle} . \qquad (2.4)$$

Formally this variational principle is complete and has no major draw-back at least for the collisions of nonidentical particles. However, as pointed out by Geltman,[11] it is essential to include the *continuum* states of the target atom (molecule) in the total Green's function G_0, in order that the wave function on the left-hand side of Eq. (2.3) should be antisymmetric. This certainly suggests that it would be very difficult to construct and treat the Green's function exactly in the collision of identical particles. For this reason Eq. (2.3) is normally avoided and instead the Schwinger principle is applied to the coupled equations which are much more manageable.[7,8,9]

Apart from the above difficulty, it is worthwhile to consider the theoretical merit of Eqs. (2.3) and (2.4). As we have already described elsewhere, the K matrix resulting from Eq. (2.4) should be one rank closer to the exact one than that given by the Schrödinger equation formalism.[6] For example, insertion of the total wave function of the close-coupling approximation into the right-hand side of Eq. (2.3) yields a wave function on the left-hand side which is one iteration higher. This indicates that we can obtain a better K matrix through the Schwinger procedure than the close-coupling approach even if the same pseudostates are employed for both methods. In what follows, we will develop a more feasible Schwinger variational principle which is based on the Lippmann-Schwinger equation, Eq. (2.3).

B. Formulation

Let $\Phi_m(1, 2, \ldots, N)$ $(m = 1, 2, \ldots, N_0)$ be the eigenfunctions of H_N with the energy E_m which are open in the collision. The projection operator P,

$$P = \sum_{m=1}^{N_0} |\Phi_m\rangle\langle\Phi_m| , \qquad (2.5)$$

defines the open-channel space. Note that this is different from the P operator in Feshbach formalism[12] and is defined uniquely on an N-body space. To remove the continuum component from the Green's function G_0, we apply P to Eq. (2.3), which yields

$$P\Psi_m = S_m + G_0^P V \Psi_m , \qquad (2.6)$$

where

$$S_m = \Phi_m s_m , \qquad (2.7)$$

with s_m being the regular solution of $E - E_m - T_{N+1}$. We assume the normalization for s_m to be

$$s_m(r) \underset{r \to \infty}{\sim} k_m^{-1/2} \sin\left(k_m r - \frac{l_m}{2}\pi\right). \qquad (2.8)$$

G_0^P is explicitly defined by

$$G_0^P = \sum_m |\Phi_m\rangle g_m(r_{N+1}, r'_{N+1})\langle\Phi_m| , \qquad (2.9)$$

and $g_m(r_{N+1}, r'_{N+1})$ is the standing-wave Green's function defined by

$$(E - E_m - T_{N+1}) g_m(r_{N+1}, r'_{N+1}) = \delta(r_{N+1}, r'_{N+1}) . \qquad (2.10)$$

Multiplication by V from the left in Eq. (2.6) leads to

$$(VP - V G_0^P V)\Psi_m = V S_m . \qquad (2.11)$$

Since the operator in the parentheses in Eq. (2.11) is not Hermitian, Eq. (2.11) cannot be directly transformed into a variational principle.

To recover the unprojected component of G_0, i.e., $G_0 - G_0^P$, we consider the following Schrödinger equations:

$$P\hat{H}P\Psi_m = PV(1 - P)\Psi_m \qquad (2.12)$$

and

$$(1 - aP)\hat{H}(1 - aP)\Psi_m = -a(1 - aP)\hat{H}P\Psi_m , \qquad (2.13)$$

where $\hat{H} = E - H$. With some simple manipulation the latter equation can be written as

$$[\hat{H} - a(P\hat{H} + \hat{H}P) + aP\hat{H}P]\Psi_m = a(VP - PVP)\Psi_m . \qquad (2.14)$$

In Eqs. (2.12) and (2.14), we made use of $P\hat{H}_0 = \hat{H}_0 P$ with $\hat{H}_0 = E - H_0$ and $P^2 = P$. The terms $P\hat{H}P$ and PVP can be eliminated from Eqs. (2.12) and

(2.14),

$$[\hat{H} - a(P\hat{H} + \hat{H}P)]\Psi_m = a(VP - PV)\Psi_m . \qquad (2.15)$$

Here a is an arbitrary parameter which will be determined later. Multiplying Eq. (2.15) by $1/a$ and adding this to Eq. (2.11) gives

$$\left(\tfrac{1}{2}(PV + VP) - VG_0^P V + \frac{1}{2a}[\hat{H} - a(P\hat{H} + \hat{H}P)]\right)\Psi_m = VS_m . \qquad (2.16)$$

Now we have to determine the parameter a. In variational principles with fractional functionals, such as the Schwinger principle, the Hermiticity of the operator is essential to ensure the stationary property.[13] Otherwise the resulting K matrix will include first-order errors. Hence the parameter a should be determined so that the operator in the square bracket in Eq. (2.16) will be Hermitian. The total wave function is written in a somewhat general form,

$$\Psi_m = A\Phi_m \bar{s}_m + \sum_n A\Phi_n \bar{c}_n K_{nm} + \psi , \qquad (2.17)$$

where $\bar{s}_m$ and $\bar{c}_m$ asymptotically correspond to the Bessel and Neumann functions, respectively. Without loss of generality we assume that both $\bar{s}_m$ and $\bar{c}_m$ are orthogonalized to all short-range orbitals which constitute Φ_n, viz.,

$$\int \Phi_n \bar{s}_m (1) d\tau_1 = \int \Phi_n \bar{c}_m (1) d\tau_1 = 0 . \qquad (2.18)$$

The nonorthogonal part of the open-channel orbi-

tals are contained implicitly in ψ. Its functional form need not be specified here. The antisymmetrizer A is defined by

$$A = (N + 1)A_{N+1} , \qquad (2.19a)$$

with

$$A_{N+1} = \frac{1}{(N+1)!} \sum \epsilon_q Q , \qquad (2.19b)$$

where Q is the permutation operator and ϵ_q is its parity. The coefficient $N+1$ in Eq. (2.19a) is chosen so that

$$P|A\Phi_m \mu_m\rangle = |\Phi_m \mu_m\rangle , \quad \mu_m = \bar{s}_m \text{ or } \bar{c}_m . \qquad (2.20)$$

The key condition for a is

$$\langle A\Phi_m \bar{s}_m |[\hat{H} - a(P\hat{H} + \hat{H}P)]|A\Phi_m \bar{c}_m\rangle$$
$$= \langle A\Phi_m \bar{c}_m |[\hat{H} - a(P\hat{H} + \hat{H}P)]|A\Phi_m \bar{s}_m\rangle . \qquad (2.21)$$

By selecting

$$a = \frac{N+1}{2} , \qquad (2.22)$$

we see that both terms in Eq. (2.21) vanish, i.e.,

$$\langle A\Phi_m \mu_m |\hat{H} - \frac{N+1}{2}(P\hat{H} + \hat{H}P)|A\Phi_m \nu_m\rangle = 0 ,$$
$$\mu_m, \nu_m = \bar{s}_m, \bar{c}_m . \qquad (2.23)$$

Thus this choice of a ensures that the operator in Eq. (2.16) is Hermitian.

We can now construct the variational functional on the basis of Eq. (2.16)

$$-\tfrac{1}{2}K_{mn} = \frac{\langle \Psi_m |V|S_n\rangle\langle S_m |V|\Psi_n\rangle}{\left\langle \Psi_m \left|\left[\tfrac{1}{2}(PV + VP) - VG_0^P V + \frac{1}{N+1}\left(\hat{H} - \frac{N+1}{2}(P\hat{H} + \hat{H}P)\right)\right]\right|\Psi_n\right\rangle} , \qquad (2.24)$$

which is stationary with respect to variations about the exact wave functions Ψ_m and Ψ_n. $\delta K_{mn} = 0$ yields Eq. (2.16) and its conjugate. Expansion of Ψ_m and Ψ_n in the basis functions ψ_i and variation of Eq. (2.24) gives

$$-\tfrac{1}{2}K_{mn} = \sum_{ij} \langle S_m |V|\psi_i\rangle (\Delta^{-1})_{ij}\langle \psi_j |V|S_n\rangle , \qquad (2.25)$$

with

$$\Delta_{ij} = \left\langle \psi_i \left|\left[\tfrac{1}{2}(PV + VP) - VG_0^P V + \frac{1}{N+1}\left(\hat{H} - \frac{N+1}{2}(P\hat{H} + \hat{H}P)\right)\right]\right|\psi_j\right\rangle . \qquad (2.26)$$

Although the newly introduced term $\hat{H} - \tfrac{1}{2}(N+1)(P\hat{H} + \hat{H}P)$ may seem difficult to evaluate, we note that the most tedious matrix elements, Eq. (2.21), vanish. Hence the term $\hat{H} - \tfrac{1}{2}(N+1)(PH + HP)$ is not difficult to evaluate. Further, we would like to point out that the operator in Eqs. (2.24) and (2.26) can be rewritten in simpler forms for evaluation,

$$\tfrac{1}{2}(PV + VP) - VG_0^P V + \frac{1}{N+1}\hat{H} - \tfrac{1}{2}(P\hat{H} + \hat{H}P) = \frac{1}{N+1}\hat{H} + (VP - P\hat{H}) - VG_0^P V \qquad (2.27a)$$

$$= \frac{1}{N+1}\hat{H} + (PV - \hat{H}P) - VG_0^P V . \qquad (2.27b)$$

III. ELASTIC SCATTERING OF ELECTRON BY HYDROGEN ATOM

In the preceding section, we have transformed the original Schwinger variational principle to the much more tractable form. This has been accomplished by expressing $(G_0 - G_0^P)V$ in terms of elements involving the Hamiltonian. This was performed by introducing the partial Schrödinger equations, Eqs. (2.12) and (2.14). It is clearly important to assess the theoretical merits of our new formulation. For example, what are its convergence characteristics? To answer these questions we apply our formulation to the elastic scattering of electrons by H atom including the effect of polarization. These calculations were done for energies up to $k^2 = 0.64$ a.u. and for $L = 0$. Our primary concern in this paper is to present a theory of a new variational principle and to check its convergence property. The choice of the most efficient pseudostates is a distinct matter.[14]

A. Computational detail

To compare our results with those of close-coupling calculations (and its expansion technique variants), we choose our trial functions to be of the same form as in the close-coupling approach, although our variational principle does not necessarily require this. The basis functions are

$$A\phi_{1s}\bar{s}\theta_{1,3} \quad \text{and} \quad A\phi_{1s}\bar{c}\theta_{1,3} , \tag{3.1a}$$

$$A\phi_{1s}\phi_{1s}\theta_1 , \tag{3.1b}$$

$$A\phi_{1s}g_i\theta_{1,3} \quad (i = 1, 2, \ldots, M) \tag{3.1c}$$

and

$$A\phi_t g_j\theta_{1,3} \quad (j = 1, 2, \ldots, N_t) \tag{3.1d}$$

where ϕ_{1s} is the $1s$ state of the hydrogen atom, and ϕ_t's are the exact states or pseudostates used to represent the closed channels. The functions $\bar{s}$ and $\bar{c}$ represent the functions $(1 - e^{-r})j_0$ and $(1 - e^{-r})n_0$ after orthogonalization to ϕ_{1s}. The j_l and n_l are lth Bessel and Neumann functions, respectively, and are normalized as in Eq. (2.8). The functions g_i and g_j are the Slater functions $r^n e^{-\alpha r}Y_{lm}(\alpha = 2.5)$ again suitably orthogonalized to ϕ_{1s}. Finally, θ_1 and θ_3 denote the singlet and triplet spin eigenfunctions, respectively. The importance of the configuration $A\phi_{1s}\phi_{1s}\theta_1$ has been stressed by Rescigno.[15]

Due to the selection of the a parameter in Eq. (2.16), and the orthogonality constraints on $\bar{s}$, $\bar{c}$, and g_i's, many matrix elements of $\hat{H} - a(P\hat{H} + \hat{H}P)$ vanish. In fact, the matrix element of the kinetic-energy operator arising from the Hamiltonian terms is only nonzero within the block of functions of Eq. (3.1b) and also within the block of the func-

tions of Eq. (3.1d).

All the integrations for the long-range functions, including the Green's function, are treated numerically by Gauss–Legendre quadrature. However, in order to give more flexibility to the quadrature process, the radial coordinate is divided into sections of variable length. In each section a 32-point Gaussian quadrature is used. The numerical representation of potential terms are generated in each integration section and stored if advantageous. The value at each quadrature point contributing to the integrals is accumulated to make up the matrix elements.

B. Convergence; $1s$-$2p$ and $1s$-$\overline{2p}$ calculation

We have shown previously that the convergence of the Schwinger method with respect to the number of basis functions required in the expansion of the open-channel function is extremely good.[3,6] In fact, at the static-exchange level in these studies of the e-H system, one to two short-range functions plus two long-range functions already provide quite accurate phase shifts. This behavior is due to the inclusion of the open-channel Green's function G_0^P in our theory. However, for the closed channels our present scheme does not include the Green's function. This difference can affect the convergence of the procedure.

In Table I, we show the convergence of the phase shift of a $1s$-$2p$ calculation for e-H atom at $k^2 = 0.55$. For this energy, the $1s$-$2p$ close-coupling calculation of Burke and Shey[16] and the very accurate value by Schwartz[17] are available for comparison. Two conclusions can be drawn from Table I: (1) The convergence, even for the closed channel is considerably fast. Only 3-5 basis functions are required to give reasonably

TABLE I. The convergence of the singlet (δ_s) and triplet (δ_t) phase shifts in $1s$-$2p$ calculation[a] at $k^2 = 0.55$.

N_{2p}[b]	δ_s	δ_t
0[c]	0.701	1.691
1	0.704	1.691
2	0.716	1.697
3	0.733	1.706
4	0.739	1.709
5	0.739	1.709
6	0.740	1.710
7	0.742	1.713

[a] The close-coupling result of a $1s$-$2p$ calculation (Ref. 16) is $\delta_s = 0.734$. Schwartz's exact value (Ref. 17) is $\delta_s = 0.908$.

[b] The number of basis functions for the closed channel. For the open-channel orbital $M = 2$ [See Eq. (3.1c)].

[c] The static-exchange value by the close-coupling method (Ref. 20) is $\delta_s = 0.700$.

converged phase shifts in Table I. (2) Our phase shift can be better than that of the corresponding close-coupling method, even if the same pseudostate expansion is used. In fact, this is true for all calculations we have carried out here except at $k^2 = 0.64$. We will return to this second point in the next subsection.

Although the calculated phase shift becomes stable with expansions of 3–4 functions, the final result still differs from Schwartz's accurate value.[17] This is of course due to the fact that the physical $2p$ state is a poor representation of the actual "polarization" effect. As an example, we have shown in the first column of Table II the convergence of a $1s$-$\overline{2p}$ calculation at the same energy, where the pseudostate $\overline{2p}$ is a simple $2p$ orbital with exponent roughly optimized to 1.1. With this $\overline{2p}$ pseudostate, the phase shift converged at $N = 6$ to the better value ($\delta_s = 0.845$) than that ($\delta_s \simeq 0.742$) of the $1s$-$2p$ calculation. With this improvement the calculated phase shift is already better than that of the $1s$-$2s$-$2p$-$3s$-$3p$ close-coupling result ($\delta_s = 0.7975$) of Burke and Shey.[16] The convergence of the singlet phase shift at $k^2 = 0.01$ in Table II is another encouraging example of very fast convergence. With one to two functions in the closed channel the phase shift is already very close to the converged value. Incidentally, our phase shift $\delta_s = 2.548$ is surprisingly close to the "exact" value. We note that the extensive calculations by Matese and Oberoi[20] using $1s$-$2s$-$2p$-$\overline{3s}$-$\overline{3p}$-$\overline{3d}$ states expansion gave a value $\delta_s = 2.545$. We note, however, that at $k^2 = 0.64$ our $1s$-$\overline{2p}$ calculation with an exponent of 1.5 gave a value of $\delta_s = 0.784$, while Schwartz's value is $\delta_s = 0.886$ and Matese-Oberoi's value is

$\delta_s = 0.873$. Our phase shift was slightly better than that of the $1s$-$2s$-$2p$ value ($\delta_s = 0.773$). This behavior shows that in low energy regions, angular correlation effects should be dominant.

C. Accuracy; $1s$-$\overline{2p}$ and $1s$-$\overline{2s}$-$\overline{2p}$ calculations

In this section we will test the capability of our method with a small number of trial functions for the energy range $k^2 = 0.01$–0.64. The poor behavior of the $1s$-$\overline{2p}$ calculation at $k^2 = 0.64$ suggests that in the relatively higher energy range s-type excitation configurations (the radial correlation) should be included in addition to p-type ones (the angular correlation). Hence we now apply our theory at the $1s$-$2s$-$\overline{2p}$ level. We also replace the simple $\overline{2p}$ pseudostate with a more elaborate one which was propsed by Damburg and Karule[21] to take full account of the atomic dipole polarizability. The latter $\overline{2p}$ pseudostate which is denoted here as $\overline{2p}_{DK}(q)$ has a radial part of $r^2(1 + 0.5r)$ e^{-qr}. The original Damburg-Karule state is defined with $q = 1.0$.

In Tables III(a) and III(b) we show our phase shifts for the $1s$-$2s$-$\overline{2p}_{DK}(q = 1.0)$ calculation. The close-coupling results with the same state expansion and also with the $1s$-$2s$-$2p$-$\overline{2p}$ expansion by Burke et al.[22] are also listed for comparison. The number of the basis functions are $M = N_{2s} = 3$ for s orbitals and $N_{\overline{2p}} = 4$ for p orbitals [see Eq. (3.1)]. Except for $k^2 = 0.64$, our singlet phase shifts are closer to the exact value than those of the $1s$-$2s$-$\overline{2p}_{DK}$ (1.0) calculation from the close-coupling method. Furthermore, our phase shifts are again better than those of the $1s$-$2s$-$2p$-$\overline{2p}$ calculation except for $k^2 = 0.64$. The somewhat poor result at $k^2 = 0.64$ is probably due to an inadequate basis set. In fact, an additional p-type basis function ($N_{\overline{2p}} = 5$) gives $\delta_s = 0.821$ which is closer to the close-coupling value. This also occurs for the triplet phase shifts, since the triplet-scattering wave function has a smaller set of basis functions than the singlet scattering by the number of doubly occupied configurations.

Our $1s$-$2s$-$\overline{2p}_{DK}$ (1.0) calculation clearly gives a sufficiently accurate result with this small basis. To further evaluate our method, however, we changed the exponent q to 1.3 and replaced the $2s$ function by $r^2 e^{-ur}$ with $u = 0.9$. These exponents were chosen through a rough optimization with a small basis set at $k^2 = 0.64$. For the basis functions in the $1s$-$\overline{2s}$-$\overline{2p}_{DK}$ (1.3) calculation we have added another p-type function to the basis set in the $1s$-$2s$-$\overline{2p}_{DK}$ ($q = 1.0$) calculation. The phase shifts are shown in Table III. The singlet phase shifts are now close to the exact value at any energy. As seen from Table III, the calculated re-

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TABLE II. The convergence of the singlet phase shifts in $1s$-$\overline{2p}$ calculation.

$N_{\overline{2p}}$[a]	$1s$-$\overline{2p}(1.1)$ $k^2 = 0.55$[b]	$1s$-$\overline{2p}(1.5)$ $k^2 = 0.01$[c]
0	0.701	2.396[d]
1	0.769	2.534
2	0.784	2.544
3	0.811	2.547
4	0.830	2.548
5	0.841	2.548
6	0.845	2.548
7	0.845	

[a] The basis set for the closed-channel orbital. For the open channel $M = 2$. [See Eq. (3.1c)].

[b] The exact value of Schwartz (Ref. 17) is $\delta_s = 0.908$. The close coupling with $1s$-$2s$-$2p$-$3s$-$3p$ expansion (Ref. 16) gives $\delta_s = 0.798$.

[c] The exact value is $\delta_s = 2.553$ (Refs. 17 and 19) $\delta_s = 2.556$ (Ref. 18).

[d] The static-exchange value (Ref. 22) is also $\delta_s = 2.396$.

TABLE III. Phase shifts for the $1s$-$2s$-$\overline{2p}_{DK}(q=1.0)$ calculation.

Methods	$k^2=$	(a) Singlet phase shifts by various methods.				
		0.01	0.09	0.25	0.49	0.64
Static-exchange,CC[a,b]		2.396	1.508	1.031	0.744	0.651
$1s$-$2s$-$\overline{2p}$, CC		2.529	1.657	1.155	0.875	0.823
$1s$-$2s$-$2p$-$\overline{2p}$, CC		2.532	1.663	1.162	0.881	0.832
$1s$-$2s$-$\overline{2p}$ (this work)		2.550	1.684	1.179	0.895	0.818[c]
$1s$-$2s$-$2p$-$\overline{3s}$-$\overline{3p}$-$\overline{3d}$ [d]		2.545	1.683	1.187	0.917	0.873
$1s$-$\overline{2s}$-$\overline{2p}$ (this work)		2.565	1.715	1.217	0.945	0.878
exact		2.556	1.696	1.201	0.930	0.887

		(b) Triplet phase shift in various methods.[e]				
Static-exchange, CC		2.908	2.461	2.070	1.749	1.614
$1s$-$2s$-$\overline{2p}$, CC		2.937	2.498	2.102	1.777	1.641
$1s$-$2s$-$2p$-$\overline{2p}$, CC		2.937	2.498	2.102	1.777	1.642
$1s$-$2s$-$\overline{2p}$ (this work)		2.930	2.496	2.111	1.783	1.644
$1s$-$2s$-$2p$-$\overline{3s}$-$\overline{3p}$-$\overline{3d}$		2.937	2.498	2.102	1.777	1.641
$1s$-$\overline{2s}$-$\overline{2p}$ (this work)		2.926	2.503	2.113	1.778	1.648
exact		2.939	2.500	2.105	1.780	1.644

[a] CC denotes the close-coupling calculation.
[b] Burke, Gallaher, and Geltman, Ref. 22.
[c] $\delta_s = 0.821$ if another p-type basis function is added.
[d] Matese and Oberoi, Ref. 20.
[e] Shimamura, Ref. 18; Schwartz, Ref. 17; Abdel-Raouf, Ref. 19.
[f] The structure of (b) is similar to that of Table III (a).

sults are comparable to those of $1s$-$2s$-$2p$-$\overline{3s}$-$\overline{3p}$-$\overline{3d}$ calculation by Matese and Oberoi.[20] The maximum deviation from the exact phase shift is 1.61% in our method, while the maximum error in the static-exchange calculation amounted to 26.6%. Our triplet phase shift at $k^2=0.01$ could be improved, since the pseudostates used here are optimized for the singlet scattering. However, its error is only 0.44%. These numerical results show that our method is very promising.

The results in Table III show that it is possible for our calculated phase shifts to be larger than the exact values. As is well known, the phase shifts from the close-coupling methods cannot exceed the exact values at these energies for this system.[23] Since our theory is not based on the close-coupling equations this condition is no longer valid. Most methods generally do not provide a maximum or minimum principle for the phase shift at arbitrary energies. In other words, most of the established variational principles, including the Kohn and Schwinger principles, are merely stationary principles unless they are used under certain conditions. The development of stationary principles which are also maximum or minimum principles is one of the crucial problems in this field.

In these circumstances it is encouraging for a method to provide reasonably accurate values of the phase shifts even though these values may be larger or smaller than the exact values. The results in Table III are very encouraging in this regard since these values, which can be seen to be converged from the results of Tables I and II, are always very close to the exact values for all energies in this calculation. Furthermore, we will discuss some theoretical reasons in the next section why the Schwinger principle is expected to give accurate results with adequate basis sets. We also note that any variational principle with a functional of fractional form can make use of the pole-shifting techniques[13] which yields a quasi-minimum (or quasi-maximum) principle quite simply. We did not apply this technique in the present work but it will be used in selecting the most reasonable basis sets for future studies of electron-molecule scattering.

IV. DISCUSSION

There are clearly two convergence characteristics of importance in these applications. One is the convergence for the closed-channel orbitals as well as open-channel orbitals for a given pseudostate expansion. Another is the convergence with respect to the number of pseudostates. Both of these convergence properties of our method have been investigated. Although we have substituted $G_0 - G_0^P$ with Hamiltonian components, Eq. (2.6) still retains the important role of the integral

equation.[6] The left-hand side of Eq. (2.6), $P\Psi_m$, in which the most important scattering information is involved is contributed to by both open- and closed-channel wave functions through the open-channel Green's function G_0^P. Ψ_m is conceptually divided into two parts

$$\Psi_m = \Psi_m^o + \Psi_m^c ,\qquad (4.1)$$

where Ψ_m^o and Ψ_m^c are open-channel and closed-channel components of Ψ_m, respectively. By the definition of P, Eq. (2.6) can be written as

$$P\Psi_m^o = S_m + G_0^P V(\Psi_m^o + \Psi_m^c) .\qquad (4.2)$$

As mentioned in Sec. II A, Ψ_m^o on the left-hand side of Eq. (4.2) is of one rank higher than Ψ_m^o contained on the right-hand side. Therefore Ψ_m^o of the left-hand side is inherently of higher accuracy than the Ψ_m^o in the Hamiltonian (differential equation) formalism. Thus we expect that our new method can give better results than the close-coupling formalism with the same state expansion and that it should converge rapidly.

As mentioned in the Introduction and Sec. II A, the application of the Schwinger principle to a system in the nonstatic-exchange approximation may be formulated in different ways. One is based on the Lippmann-Schwinger equation for the total wave function, Eq. (2.3), and another is applied to the Lippmann-Schwinger equation derived from the close-coupling equation.[7-9] The application of the Schwinger principle directly to the close-coupling equations should show a faster convergence to the exact close-coupling values (not the exact value) than the Kohn-type principles[6] when applied to the same coupled equations. Naturally, both methods will only approach the numerical close-coupling values in accuracy.[24] If, on the other hand, the Schwinger principle is applied to the total wave function, Eq. (2.6), the resulting value can approach the *exact* value faster than the close-coupling method itself. Therefore our new Schwinger principle can lead to a better K matrix than the other Schwinger principles[7,8,9] which are applied directly to the close-coupling equations. Also, for the same reason stated above, we predict that our Schwinger principle will give accurate phase shifts with fewer basis functions than the Kohn principle which was applied by Schwartz[17] and Shimamura[18] using 50 and more Hylleraas-type trial functions.

Before closing this section, we comment on some technical issues which are relevant to our theory. For long-range potential scattering such as the Coulomb scattering, we may want to make use of the two potential formula.[25] In such a case, writing the Hamiltonian of Eq. (2.2) as

$$H = (H_N + T_{N+1} + \nu_{N+1}) + (V - \nu_{N+1})$$
$$= \tilde{H}_0 + \tilde{V} ,\qquad (4.3)$$

we can reformulate our variational principle, where ν_{N+1} indicates the long-range potential and $\tilde{V}$ is the residual short-range potential. S_m and G_0^P should be redefined for the new zeroth-order Hamiltonian $\tilde{H}_0$ in this case.

One of the important characteristics of the Schwinger principle is that an L^2 approach[26] is possible.[1,2] In potential scattering—including the static-exchange approximation—the scattering orbital is always associated with the potential, and this is the basis of the L^2 approach. Seemingly, the wave function in our functional, Eq. (2.24) is not necessarily associated with the potential, since it includes the Hamiltonian. However, due to the property of Eq. (2.23), the long-range functions are free from the operation of the kinetic operator and are always associated with the potential. Therefore an L^2 approach is always possible in our variational principle.

V. CONCLUDING REMARKS

We have proposed a new variational principle to extend the Schwinger method beyond the static-exchange approximation. In the theory the selection of the basis functions is very flexible. The configuration interaction technique can be applied to define the projection operator P and the closed-channel component of the wave function. Since our equation is defined for the total wave function, the use of the optical-potential formalism is avoided. Furthermore, the K matrix given in our formalism can be more accurate than the numerical close-coupling method even if the same state expansions are used. Our theory does not require the close-coupling expansion of the wave function. Also, we have shown that our K matrix (or phase shift) converges quite fast with respect to the size of the basis for both the open- and closed-channel orbitals. Due to these convergence properties our K matrix approaches the exact value with a small set of trial functions. In fact, we have obtained very accurate phase shifts for the elastic collision between e^- and H atom using $1s$-$2s$-$\overline{2p}$ state expansion and small numbers of basis functions (4 – 5) for each scattering (both open and closed) orbital. We found that these results are of comparable accuracy to those of the $1s$-$2s$-$2p$-$\overline{3s}$-$\overline{3p}$-$\overline{3d}$ close-coupling calculation.[20] Therefore our new method is very encouraging for further application to electron-molecule collisions.

Finally, we would like to point out that the fractional form of the K matrix in Eq. (2.24) should have a close bearing to the resonance formula for

the K matrix proposed by Feshbach.[27] This aspect will be discussed in our future paper.

[1]J. M. Blatt and J. D. Jackson, Phys. Rev. 76, 18 (1949).

[2]R. R. Lucchese and V. McKoy, J. Phys. B 12, L421 (1979); Phys. Rev. A 21, 112 (1980); D. K. Watson, R. R. Lucchese, V. McKoy, and T. N. Rescigno, ibid. 21, 738 (1980); R. R. Lucchese, D. K. Watson, and V. McKoy, ibid. 22, 421 (1980).

[3]K. Takatsuka and V. McKoy, Phys. Rev. Lett. 45, 1396 (1980).

[4]For a review article, see J. Callaway, Phys. Rep. 45, 89 (1978).

[5]W. Kohn, Phys. Rev. 74, 1763 (1948).

[6]K. Takatsuka, R. R. Lucchese, and V. McKoy, Phys. Rev. A (in press). In connection with this paper, see also, D. Thirumalai and D. G. Truhlar, Chem. Phys. Lett. 70, 330 (1980); J. Callaway, Phys. Lett. 77A, 137 (1980).

[7]A. L. Zubarev, Fiz. Elem. Chastits At. Yadra 9, 453 (1979) [Sov. J. Part. Nucl. 9, 188 (1978)].

[8]N. Maleki and J. Macek, Phys. Rev. 21, 1403 (1980).

[9]R. K. Nesbet, Variational Methods in Electron-Atomic Scattering Theory (Plenum, New York, 1980).

[10]R. K. Nesbet, Adv. Quantum Chem. 9, 215 (1975); Adv. At. Mol. Phys. 13, 315 (1977).

[11]S. Geltman, Topics in Atomic Collision Theory (Academic, New York, 1969), p. 99.

[12]H. Feshbach, Ann. Phys. (N.Y.) 19, 287 (1962).

[13]K. Takatsuka and V. McKoy, Phys. Rev. A 23, 2352 (1981).

[14]For a recent attempt to determine the pseudostates for e^--H collision, see P. W. Coulter, Phys. Rev. A 22, 372 (1980), and references therein.

[15]T. N. Rescigno, J. Chem. Phys. 66, 5255 (1977).

[16]P. G. Burke and H. M. Shey, Phys. Rev. 126, 147 (1962).

[17]C. Schwartz, Phys. Rev. 124, 1468 (1961).

[18]I. Shimamura, J. Phys. Soc. Jpn. 30, 1702 (1971).

[19]M. A. Abdel-Raouf and D. Belschner, J. Phys. B 11, 3677 (1978).

[20]J. J. Matese and R. S. Oberoi, Phys. Rev. A 4, 569 (1971).

[21]R. Damburg and E. Karule, Proc. Phys. Soc. London 90, 637 (1967).

[22]P. G. Burke, D. F. Gallaher, and S. Geltman, J. Phys. B 2, 1142 (1969).

[23]Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. 128, 932 (1962); 130, 381 (1963).

[24]This is the distinct issue from the computational effort.

[25]For example, L. S. Rodberg and R. M. Thaler, Introduction to the Quantum Theory of Scattering (Academic, New York, 1967).

[26]T. N. Rescigno, V. McKoy, and B. Schneider, Electron-Molecule and Photon-Molecule Collisions (Plenum, New York, 1979); P. G. Burke, Adv. At. Mol. Phys. 15, 471 (1979); K. Takatsuka and V. McKoy, Phys. Rev. A 23, 2359 (1981).

[27]H. Feshbach, Ann. Phys. (N.Y.) 43, 410 (1967).