

## Schwinger variational principle applied to long-range potentials

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(Received 2 September 1983)

We discuss an adaptation of the Schwinger variational principle which is particularly suitable for dealing with long-range potentials. The method treats the direct interaction potential exactly by numerical integration and assumes a separable representation of the Schwinger type for the exchange potential. The method should be very effective for obtaining the electronic continuum solutions of strongly polar molecular ions. The related photoionization cross sections can be shown to be variationally stable.

### I. INTRODUCTION

In recent years several new approaches<sup>1-5</sup> have been developed for studying the collisions of low-energy electrons with molecules and the related problem of molecular photoionization. In several of these methods, the use of discrete basis functions plays an important role. Of specific interest to the developments in this paper is the Schwinger variational method in which the trial scattering wave function can, in principle, be expanded exclusively in a discrete basis. It is known that the expansion of the trial wave function, in such a basis, e.g.,  $|\tilde{\Psi}\rangle = \sum_i c_i |\alpha_i\rangle$ , in the Schwinger variational principle is equivalent to the use of a separable potential of the form

$$V^S(\vec{r}, \vec{r}') = \sum_{i,j} \langle \vec{r} | V | \alpha_i \rangle (V^{-1})_{ij} \langle \alpha_j | V | \vec{r}' \rangle \quad (1)$$

in the Lippmann-Schwinger equation.<sup>6</sup> Clearly the basis functions in Eq. (1) must span the range of the full potential in order for  $V^S$  to be an adequate representation of  $V$ . Applications to date have shown that for molecular targets with no strong long-range potentials,<sup>7</sup> e.g.,  $\text{H}_2$ ,  $\text{N}_2^+$ , and  $\text{CO}_2$ ,<sup>8-10</sup> a discrete basis set approach to the Schwinger variational principle can be very effective. However, for strongly polar systems, e.g.,  $\text{LiH}$ ,  $\text{NO}^+(2\pi^{-1})$ , and  $\text{CO}^+(5\sigma^{-1})$ ,<sup>11-13</sup> it is difficult to describe the long-range forces with only discrete basis functions and we have found that continuum functions must be included in the trial function so as to obtain the correct scattering solutions particularly at low energies. For these cases and, more generally, to have a method which can provide accurate solutions where such solutions may be required, we have developed an iterative procedure for solving the Lippmann-Schwinger equation which is based on the Schwinger variational principle.<sup>2</sup> In this iterative procedure appropriate continuum functions can be systematically incorporated into the basis set for the trial scattering function. Criteria for the convergence of this method have been developed.<sup>2</sup>

The features discussed above pertain to the Schwinger variational principle in a form in which the entire scattering potential  $V$ , including both its long- and short-range

components, is projected on a basis in the separable form of Eq. (1). The Schwinger variational principle can be expressed in a form which assumes that the direct and long-range interactions will be treated exactly, e.g., by numerical integration, and only the short-range forces such as exchange effects will be projected onto a discrete basis set as in Eq. (1).<sup>14,15</sup> If this approach could be implemented efficiently, it could be expected to be a very effective way of applying the Schwinger method to the more difficult system such as the scattering of electrons by strongly polar molecular ions which often arises in studies of molecular photoionization. In fact, Rescigno and Orel<sup>5</sup> have recently developed an approach to electron-molecule collisions in which exactly this division of the scattering potential into a long-range direct component and a short-range exchange component is made but in which the exchange component is approximated by a separable potential of the form

$$V_{\text{ex}}(\vec{r}, \vec{r}') = \sum_{i,j} \langle \vec{r} | \alpha_i \rangle \langle \alpha_i | V_{\text{ex}} | \alpha_j \rangle \langle \alpha_j | \vec{r}' \rangle. \quad (2)$$

The results of the application of this approach were impressive.<sup>5</sup> Exactly such a separation of the scattering potential and the subsequent representation of the exchange component by a basis set expansion of the form of Eq. (2) have been used extensively and successfully by Schneider and Collins.<sup>3</sup> These results certainly suggest that a similar approach within the framework of the Schwinger variational method would be very useful.

In this paper we develop an adaptation of the Schwinger variational principle for long-range potentials in which the static component of the electron-molecule interaction is treated exactly and the exchange interactions are approximated by the separable potential of the form of Eq. (1). Most importantly, we will show that the use of a separable potential of this type leads to *variationally stable* scattering matrices. The method also includes an iterative procedure for obtaining the converged scattering solutions systematically. Moreover, the related photoionization cross sections can be shown to be variationally stable. The method of solution is essentially based on the integral equations approach of Sams and Kouri<sup>5,16,17</sup> and does not

require the Green's function for the static potential.<sup>5</sup>

In the next section we formulate our adaptation of the Schwinger potential for long-range potentials and demonstrate that the photoionization cross sections obtained with these continuum solutions are variationally stable. In Sec. III we illustrate various features of our method by application to the  $e\text{-NO}^+(X^1\Sigma^+)$  and  $e\text{-H}_2$  systems. The first example is chosen as an application of the method to molecular photoionization involving a strongly polar ion while the second example has been extensively studied by several methods. The results of these applications, particularly those of the  $e\text{-NO}^+$  system, are very encouraging and show that the procedure converges rapidly.

## II. THEORY

### A. Formulation

The Schrödinger equation for electron-molecule scattering in the static-exchange approximation is

$$(\nabla^2 - U + k^2)\psi_{\vec{k}}(\vec{r}) = 0, \quad (3)$$

where  $\frac{1}{2}U$  is the static-exchange potential of the target. To this equation we also add terms containing Lagrange multipliers to impose any desired orthogonality of the continuum function  $\psi_{\vec{k}}$  to occupied target orbitals. We can write Eq. (3) including the auxiliary orthogonality conditions as

$$(\nabla^2 - U + k^2)\psi_{\vec{k}}(\vec{r}) = \sum_i \lambda_i \chi_i(\vec{r}), \quad (4)$$

where, for example,  $\chi_i$  are the occupied orbitals of some closed-shell molecular target and  $\lambda_i$  are the Lagrange multipliers. These Lagrange multipliers play an important role in determining the photoelectron continuum functions in

the frozen-core approximation.<sup>9</sup> By breaking the scattering potential  $U$  into its direct and exchange components,  $U_{\text{dir}}$  and  $U_{\text{ex}}$ , respectively, Eq. (4) becomes

$$(\nabla^2 - U_{\text{dir}} + k^2)\psi_{\vec{k}} = U_{\text{ex}}\psi_{\vec{k}} + \sum_i \lambda_i \chi_i. \quad (5)$$

The solution of Eq. (5) can be written as

$$\psi_{\vec{k}} = \psi_{\vec{k}}^e + \sum_i \lambda_i \psi_{\vec{k}}^{X_i}, \quad (6)$$

where the functions  $\psi_{\vec{k}}^e$  and  $\psi_{\vec{k}}^{X_i}$  satisfy the equations

$$\psi_{\vec{k}}^e = \psi_{\vec{k}}^d + G^d U_{\text{ex}} \psi_{\vec{k}}^e \quad (7a)$$

and

$$\psi_{\vec{k}}^{X_i} = G^d \chi_i + G^d U_{\text{ex}} \psi_{\vec{k}}^{X_i}. \quad (7b)$$

In Eqs. (7)  $\psi_{\vec{k}}^d$  is the solution for the direct potential, i.e.,

$$(\nabla^2 - U_{\text{dir}} + k^2)\psi_{\vec{k}}^d = 0 \quad (8)$$

and  $G^d$  is the Green's function for the static potential, i.e.,  $(\nabla^2 - U_{\text{dir}} + k^2 \pm i\epsilon)^{-1}$ . The orthogonality of  $\psi_{\vec{k}}$  to the orbitals  $\chi_i$  requires that

$$\langle \chi_j | \psi_{\vec{k}} \rangle = \langle \chi_j | \psi_{\vec{k}}^e \rangle + \sum_i \langle \chi_j | \psi_{\vec{k}}^{X_i} \rangle \lambda_i = 0 \quad (9)$$

and, hence,

$$\lambda_i = - \sum_j (A^{-1})_{ij} \langle \chi_j | \psi_{\vec{k}}^e \rangle, \quad (10)$$

where

$$A_{ij} = \langle \chi_i | \psi_{\vec{k}}^{X_j} \rangle. \quad (11)$$

The partial-wave  $K$ -matrix element associated with solutions of Eqs. (6) and (7) is given by

$$K_{l'm} = K_{l'm}^d - \frac{1}{k} \left[ \langle \psi_{kl'm}^d | U_{\text{ex}} | \psi_{kl'm}^e \rangle + \sum_{i,j} (\langle \psi_{kl'm}^d | \chi_i \rangle + \langle \psi_{kl'm}^d | U_{\text{ex}} | \psi_{kl'm}^{X_i} \rangle) (A^{-1})_{ij} \langle \chi_j | \psi_{kl'm}^e \rangle \right], \quad (12)$$

where  $K_{l'm}^d$  is the  $K$ -matrix element for the direct potential and we have assumed the molecule is linear.

Our objective is to obtain a variationally stable expression of the Schwinger form for such  $K$ -matrix elements. We assume that we have exact values for the  $K_{l'm}^d$  and  $\langle \psi_{kl'm}^d | \chi_i \rangle$  elements which can be obtained from the solution of Eq. (8). We will discuss our method for solving this equation later. We obtain a variational estimate of  $K_{l'm}$  by constructing variational estimates of the matrix elements

$$I_{l'l}^{(1)} = \langle \psi_{l'l}^d | U_{\text{ex}} | \psi_{l'l}^e \rangle, \quad (13a)$$

$$I_{l'i}^{(2)} = \langle \psi_{l'i}^d | U_{\text{ex}} | \psi_{l'i}^{X_i} \rangle, \quad (13b)$$

$$I_{ij}^{(3)} = \langle \chi_i | \psi_{ij}^e \rangle, \quad (13c)$$

$$I_{ij}^{(4)} = A_{ij} = \langle \chi_i | \psi_{ij}^{X_j} \rangle. \quad (13d)$$

In Eqs. (13) we have abbreviated the partial-wave designa-

tion. We can use Eqs. (6) and (7) to write the following variational expressions for these four terms<sup>13,18-20</sup>

$$\begin{aligned} \tilde{I}_{l'l}^{(1)} &= \langle \psi_{l'l}^d | U_{\text{ex}} | \tilde{\psi}_{l'l}^e \rangle + \langle \tilde{\psi}_{l'l}^e | U_{\text{ex}} | \psi_{l'l}^d \rangle \\ &\quad - \langle \tilde{\psi}_{l'l}^e | U_{\text{ex}} - U_{\text{ex}} G^d U_{\text{ex}} | \tilde{\psi}_{l'l}^e \rangle, \end{aligned} \quad (14a)$$

$$\begin{aligned} \tilde{I}_{l'i}^{(2)} &= \langle \psi_{l'i}^d | U_{\text{ex}} | \tilde{\psi}_{l'i}^{X_i} \rangle + \langle \tilde{\psi}_{l'i}^e | U_{\text{ex}} G^d | \chi_i \rangle \\ &\quad - \langle \tilde{\psi}_{l'i}^e | U_{\text{ex}} - U_{\text{ex}} G^d U_{\text{ex}} | \tilde{\psi}_{l'i}^{X_i} \rangle, \end{aligned} \quad (14b)$$

$$\begin{aligned} \tilde{I}_{ij}^{(3)} &= \langle \chi_j | \psi_{ij}^d \rangle + \langle \chi_j | G^d U_{\text{ex}} | \tilde{\psi}_{ij}^e \rangle + \langle \tilde{\psi}_{ij}^{X_j} | U_{\text{ex}} | \psi_{ij}^d \rangle \\ &\quad - \langle \tilde{\psi}_{ij}^{X_j} | U_{\text{ex}} - U_{\text{ex}} G^d U_{\text{ex}} | \tilde{\psi}_{ij}^e \rangle, \end{aligned} \quad (14c)$$

$$\begin{aligned} \tilde{I}_{ij}^{(4)} &= \langle \chi_i | G^d | \chi_j \rangle + \langle \chi_i | G^d U_{\text{ex}} | \tilde{\psi}_{ij}^{X_j} \rangle \\ &\quad + \langle \tilde{\psi}_{ij}^{X_i} | U_{\text{ex}} G^d | \chi_j \rangle \\ &\quad - \langle \tilde{\psi}_{ij}^{X_i} | (U_{\text{ex}} - U_{\text{ex}} G^d U_{\text{ex}}) | \tilde{\psi}_{ij}^{X_j} \rangle. \end{aligned} \quad (14d)$$

Expansion of the trial functions  $\tilde{\psi}^e$  and  $\tilde{\psi}^x$  in a basis  $\{|\alpha_i\rangle\}$  and variation of the expansion parameters leads to the variationally stable expressions for these elements, i.e.,

$$\tilde{I}_{i'l}^{(1)} = \sum_{a,b} \langle \psi_{i'}^d | U_{\text{ex}} | \alpha_a \rangle [D^{-1}]_{ab} \langle \alpha_b | U_{\text{ex}} | \psi_l^d \rangle, \quad (15a)$$

$$\tilde{I}_{i'l}^{(2)} = \sum_{a,b} \langle \psi_{i'}^d | U_{\text{ex}} | \alpha_a \rangle [D^{-1}]_{ab} \langle \alpha_b | U_{\text{ex}} G^d | \chi_l \rangle, \quad (15b)$$

$$\tilde{I}_{il}^{(3)} = \langle \chi_i | \psi_l^d \rangle + \sum_{a,b} \langle \chi_i | G^d U_{\text{ex}} | \alpha_a \rangle [D^{-1}]_{ab} \times \langle \alpha_b | U_{\text{ex}} | \psi_l^d \rangle, \quad (15c)$$

$$\tilde{I}_{ij}^{(4)} = \langle \chi_i | G^d | \chi_j \rangle + \sum_{a,b} \langle \chi_i | G^d U_{\text{ex}} | \alpha_a \rangle [D^{-1}]_{ab} \times \langle \alpha_b | U_{\text{ex}} G^d | \chi_j \rangle, \quad (15d)$$

where  $[D^{-1}]_{ab}$  is an element of the inverse of the matrix

$$D_{ab} = \langle \alpha_a | (U_{\text{ex}} - U_{\text{ex}} G^d U_{\text{ex}}) | \alpha_b \rangle. \quad (16)$$

Use of Eq. (15) in Eq. (12) provides a variationally stable expression for the  $K$  matrix.

Finally, insertion of a separable approximation for  $U_{\text{ex}}$  of the form

$$U_{\text{ex}}^s = \sum_{a,b} U_{\text{ex}} | \alpha_a \rangle [U_{\text{ex}}^{-1}]_{ab} \langle \alpha_b | U_{\text{ex}} \quad (17)$$

in Eqs. (7) yields the wave functions

$$\psi_{kl}^{(0)e} = \psi_{kl}^d + \sum_{a,b} G^d U_{\text{ex}} | \alpha_a \rangle [D^{-1}]_{ab} \langle \alpha_b | U_{\text{ex}} | \psi_{kl}^d \rangle, \quad (18a)$$

$$\psi^{(0)\chi_i} = G^d \chi_i + \sum_{a,b} G^d U_{\text{ex}} | \alpha_a \rangle [D^{-1}]_{ab} \times \langle \alpha_b | U_{\text{ex}} G^d | \chi_i \rangle, \quad (18b)$$

which will be shown to be point-by-point variationally stable in Sec. II C. Substitution of Eqs. (18) in Eq. (6) gives a total scattering solution whose partial wave asymptotic form defines a  $K$  matrix identical to that obtained by using Eqs. (15) in Eq. (12).

### B. Iterative procedure

The functions in Eqs. (18) provide approximate solutions of Eq. (3). In several applications, it can be important to obtain the converged solutions of Eq. (3). A procedure for doing so begins by augmenting the initial basis  $\{|\alpha_i\rangle\}$  with the energy-dependent set of functions  $S^{(0)} = \{\psi_{kl_1}^{(0)}, \psi_{kl_2}^{(0)}, \dots, \psi_{kl_p}^{(0)}\}$  defined by the initial solutions of Eqs. (18). Here  $l_p$  is the maximum partial wave retained in the expansion of  $\psi_{\vec{k}}^{(0)}$ . Equations (18) are now solved again with this augmented basis providing a new, and more accurate, set of solutions  $S^{(1)} = \{\psi_{kl_1}^{(1)}, \psi_{kl_2}^{(1)}, \dots, \psi_{kl_p}^{(1)}\}$ . Repetition of this procedure with a new basis consisting of the set of functions  $\{|\alpha_i\rangle\}$  and  $S^{(1)}$  leads to a more converged set of solutions  $S^{(2)} = \{\psi_{kl_1}^{(2)}, \psi_{kl_2}^{(2)}, \dots, \psi_{kl_p}^{(2)}\}$ . These functions are the con-

verged solutions of Eq. (3) when the set of  $S^{(n+1)}$  functions is equal to the  $S^{(n)}$  set.<sup>2</sup>

### C. Variational stability of photoionization cross sections

An important objective of our work is to use these continuum solutions to obtain molecular photoionization cross sections. The relevant one-electron matrix element is given by

$$M = \langle \phi_i | \vec{\mu} | \psi_{\vec{k}} \rangle = \langle R | \psi_{\vec{k}} \rangle, \quad (19)$$

where  $\phi_i$  is the orbital from which ionization occurs,  $\psi_{\vec{k}}$  is the photoelectron continuum function, and  $\vec{\mu}$  is the dipole moment operator. We now show that our approximate continuum solutions obtained above provide vibrationally stable estimates of Eq. (19). For convenience we keep the same notation as in the preceding section, although in actual applications to photoionization one must redefine the Green's function and the scattering potential of Eq. (1) due to the presence of the Coulomb potential. From Eqs. (6), (7), (10), and (19), we obtain

$$M = \langle R | \psi_{\vec{k}}^d \rangle + \langle R | G^d U_{\text{ex}} | \psi_{\vec{k}}^e \rangle + \sum_{i,j} (\langle R | G^d | \chi_i \rangle + \langle R | G^d U_{\text{ex}} | \psi^{x_i} \rangle) \times (A^{-1})_{ij} \langle \chi_j | \psi_{\vec{k}}^e \rangle. \quad (20)$$

To obtain a variational expression for the matrix element  $M$ , we need, in addition to the variational estimates of  $I_{il}^{(3)}$  and  $I_{ij}^{(4)}$ , given by Eqs. (14), variational expressions for  $I_i^{(5)}$  and  $I_i^{(6)}$  where

$$I_i^{(5)} = \langle R | G^d U_{\text{ex}} | \psi_i^e \rangle \quad (21a)$$

and

$$I_i^{(6)} = \langle R | G^d U_{\text{ex}} | \psi^{x_i} \rangle, \quad (21b)$$

where we again use a partial-wave designation for the continuum function,  $\psi^e$ . Variational functionals for  $I_i^{(5)}$  and  $I_i^{(6)}$  can be written as

$$\tilde{I}_i^{(5)} = \langle R | G^d U_{\text{ex}} | \tilde{\psi}_i^e \rangle + \langle \tilde{\psi}^R | U_{\text{ex}} | \psi_i^d \rangle - \langle \tilde{\psi}^R | (U_{\text{ex}} - U_{\text{ex}} G^d U_{\text{ex}}) | \tilde{\psi}_i^e \rangle \quad (22a)$$

and

$$\tilde{I}_i^{(6)} = \langle R | G^d U_{\text{ex}} | \tilde{\psi}^{x_i} \rangle + \langle \tilde{\psi}^R | U_{\text{ex}} G^d | \chi_i \rangle - \langle \tilde{\psi}^R | (U_{\text{ex}} - U_{\text{ex}} G^d U_{\text{ex}}) | \tilde{\psi}^{x_i} \rangle, \quad (22b)$$

where  $\tilde{\psi}^R$  is a variational trial function for  $\psi^R$  and

$$\psi^R = G^d R + G^d U_{\text{ex}} \psi^R. \quad (23)$$

As before, we expand the trial functions  $\tilde{\psi}^R$ ,  $\tilde{\psi}^{x_i}$ , and  $\tilde{\psi}_i^e$  in the basis  $\{|\alpha_i\rangle\}$  to obtain the variational expressions for  $\tilde{I}_i^{(5)}$  and  $\tilde{I}_i^{(6)}$ , i.e.,

$$\tilde{I}_i^{(5)} = \sum_{a,b} \langle R | G^d U_{\text{ex}} | \alpha_a \rangle [D^{-1}]_{ab} \langle \alpha_b | U_{\text{ex}} | \psi_i^d \rangle \quad (24a)$$

and

$$\tilde{I}_i^{(6)} = \sum_{a,b} \langle R | G^d U_{\text{ex}} | \alpha_a \rangle [D^{-1}]_{ab} \langle \alpha_b | U_{\text{ex}} G^d | \chi_i \rangle . \quad (24b)$$

Use of Eqs. (15c), (15d), and (24) in Eq. (20) leads to a variationally stable expression for the matrix element  $M$ . However, insertion of Eqs. (18) for  $\psi_j^e$  and  $\psi_i^x$  directly into Eq. (19) gives the identical expression for this matrix element, showing that our procedure provides a variationally stable estimate of  $M$ .

Finally, we note that  $\tilde{I}_i^{(5)}$  and  $\tilde{I}_i^{(6)}$  are exactly the matrix elements found in Eqs. (18), with  $\langle R |$  replaced by  $\langle \vec{r} |$ . This indeed confirms that the wave functions we obtain are variationally stable.

#### D. Computational approach

To evaluate the variational expressions of Eqs. (15) and (24) it is necessary to solve for the partial-wave static solution,  $\psi_{klm}^d$ , and functions of the form

$$\psi^u(\vec{r}) = \langle \vec{r} | G^d | u \rangle , \quad (25)$$

where  $|u\rangle$  may be either  $U_{\text{ex}}|\alpha\rangle$  or  $|\chi_i\rangle$ . Procedures for evaluating  $U_{\text{ex}}|\alpha\rangle$  have been given elsewhere.<sup>20</sup> The functions  $\psi_{klm}^d$  and  $\psi^u$  satisfy the integral equations

$$\psi_{klm}^d = S_{klm} + G^0 U_{\text{dir}} \psi_{klm}^d \quad (26)$$

and

$$\psi^u = G^0 u + G^0 U_{\text{dir}} \psi^u , \quad (27)$$

respectively, where  $S_{klm}$  is the free-particle solution and  $G^0$  the free-particle Green's function. Partial-wave expansions are first made in Eqs. (26) and (27) and the resulting coupled equations then converted to a set of Volterra integral equations. Volterra integral equations have been used extensively in related applications<sup>5,16,17,21</sup> and techniques for their numerical solution have been discussed elsewhere.<sup>5,17,21</sup> In fact, our approach is very similar to what has been used recently by Rescigno and Orel.<sup>5</sup> First, we consider Eq. (26). The partial-wave function  $\psi_{ll'm}^d$ , defined by the expansion

$$\psi_{klm}^d(\vec{r}) = \sum_{l'} \psi_{ll'm}^d(r) Y_{l'm}(\hat{r}) , \quad (28)$$

is obtained from Eq. (29), i.e.,

$$[\psi^d] = [\phi^d][M_2^{-1}] , \quad (29)$$

where

$$(M_2)_{l'l} = \delta_{l'l} + \frac{1}{k} \sum_{l''} \int_0^\infty g_{l''} U_{ll''}^{\text{dir}} \phi_{l''l}^d dr \quad (30)$$

and  $\phi_{ll'}^d$  satisfies the Volterra integral equation

$$\begin{aligned} \phi_{ll'}^d(r) &= f_l(r) \delta_{ll'} + \frac{1}{k} \sum_{l''} f_{l''}(r) \int_0^r g_{l''}(r') U_{ll''}^{\text{dir}}(r') \phi_{l''l'}^d(r') dr' \\ &\quad - \frac{1}{k} \sum_{l''} g_{l''}(r) \int_0^r f_{l''}(r') U_{ll''}^{\text{dir}}(r) \phi_{l''l'}^d(r') dr' . \end{aligned} \quad (31)$$

In Eqs. (29) and (30)  $f_l$  and  $g_l$  are the Riccati-Bessel and Riccati-Neumann functions, respectively, and we have suppressed the subscripts  $k$  and  $m$  for convenience. It is well known that placing Eq. (30) on a quadrature mesh provides a noniterative propagation scheme for outward integration of the equations.<sup>17,21</sup> The associated  $K$  matrix, i.e.,  $[K^d]$ , is given by

$$[K^d] = [M_1][M_2^{-1}] , \quad (32)$$

where

$$(M_1)_{l'l} = -\frac{1}{k} \sum_{l''} \int_0^\infty f_{l''} U_{ll''}^{\text{dir}} \phi_{l''l}^d dr \quad (33)$$

and  $(M_2)_{l'l}$  is given in Eq. (30).

To maintain accuracy, numerical stabilization procedures had to be carried out at various grid points as the solutions were propagated outward. These procedures have been described in detail elsewhere.<sup>17,21,22</sup>

The solution of Eq. (27) is obtained in a similar way by transforming the equation for  $\psi^u$  to a Volterra-type integral equation for  $\phi^u$ . In partial-wave form, for each inhomogeneity  $u$ , we have

$$\psi_l^u = \phi_l^u + \sum_{l'} \phi_{ll'}^d C_{l'} , \quad (34)$$

where, in matrix notation

$$[C] = [M_3^{-1}][M_4] \quad (35)$$

with

$$(M_3)_{ll'} = - \left[ \delta_{ll'} + \frac{1}{k} \sum_{l''} \int_0^\infty g_{l''} U_{ll''}^{\text{dir}} \phi_{l''l}^d dr \right] \quad (36a)$$

and

$$(M_4)_l = \frac{1}{k} \sum_{l'} \int_0^\infty g_{l'} U_{ll'}^{\text{dir}} \phi_{l'}^u dr . \quad (36b)$$

The function  $\phi_{ll'}^u(r)$  satisfies the integral equation

$$\begin{aligned} \phi_{ll'}^u(r) &= -\frac{1}{k} \int_0^\infty f_l(r_<) g_l(r_>) u_l(r') dr' \\ &\quad + \frac{1}{k} \sum_{l''} f_{l''}(r) \int_0^r g_{l''} U_{ll''}^{\text{dir}} \phi_{l''l'}^u dr' \\ &\quad - \frac{1}{k} \sum_{l''} g_{l''}(r) \int_0^r f_{l''} U_{ll''}^{\text{dir}} \phi_{l''l'}^u dr' . \end{aligned} \quad (37)$$

Again the usefulness of this equation becomes apparent when it is placed on a quadrature mesh.

In the numerical integrations we used the ordinary Simpson's rule cyclically, and then used Simpson's " $\frac{3}{8}$  rule" for integrals which ended on a midpoint of an ordinary Simpson's rule quadrature. Knirk<sup>23</sup> has shown this quadrature scheme should be generally more accurate than the overlapped Simpson's rule or the trapezoidal rule.

### III. APPLICATIONS

To illustrate our procedure we first studied the photoionization cross section for the  $2\pi$  level of NO leading to the  $X^1\Sigma^+$  state of  $\text{NO}^+$ . We primarily looked at the

$2\pi \rightarrow k\sigma$  component of this cross section which is shape-resonant enhanced.<sup>12,24,25</sup> We have studied this system recently and it provides a good example of difficulties which can arise in obtaining the electronic continuum of strongly polar ions in resonance regions.

The rotationally unresolved, fixed-nuclei photoionization cross section is given by

$$\sigma(R) = \frac{4\pi^2}{3} \omega |\langle \Psi_i(\vec{r}, R) | \vec{\mu} | \Psi_f(\vec{r}, R) \rangle|^2, \quad (38)$$

where  $\vec{\mu}$  is the dipole moment operator and  $\omega$  the photon frequency. In Eq. (38)  $\Psi_i(\vec{r}, R)$  is the initial state of the molecule and  $\Psi_f$  the final ionized state. For  $\Psi_i$  we use the self-consistent field (SCF) wave function and for the  $(N-1)$  bound electrons of  $\Psi_f$  we use the ground-state SCF orbitals, i.e., the frozen-core approximation. The continuum orbital is a solution of the one-particle Schrödinger equation with the static-exchange potential of this ion. Details of the SCF basis, quadrature grids, and partial-wave expansions have been given previously.<sup>12</sup> In these studies the dipole moment of the molecular ion with respect to the center of mass of the system is  $1.27D$ .<sup>12</sup> We also assume the experimental ionization potential of 9.3 eV.

To illustrate the performance of the method and to compare it with the iterative Schwinger variational approach, we have carried out calculations with three different initial basis sets. These are given in Table I and consist of six, twelve, and eighteen Cartesian and spherical Gaussian functions defined as

$$\phi(\vec{r})^{\alpha, l, m, n} = N_c (x - A_x)^l (y - A_y)^m (z - A_z)^n e^{-\alpha |\vec{r} - \vec{A}|^2} \quad (39)$$

and

$$\phi(\vec{r})^{\alpha, l, m} = N_s |\vec{r} - \vec{A}|^l e^{-\alpha |\vec{r} - \vec{A}|^2} Y_{lm}(\Omega_{\vec{r} - \vec{A}}), \quad (40)$$

respectively. There are slight differences in the respective basis sets for the two methods. We have found that basis functions are needed at the center of mass in the iterative Schwinger method to represent the direct component of the scattering potential. However, in the present method where only the exchange potential is projected on a basis, higher-order Gaussian functions on the nuclei are more effective than those at the center of mass.

Our results are given in Table II. There we show some  $^2\Sigma$   $K$ -matrix elements, the  $k\sigma$  eigenphase sum, and the  $2\pi \rightarrow k\sigma$  photoionization cross section at a photon energy of 14 eV which corresponds to the peak of the shape resonance in this channel.<sup>12</sup> At this photon energy the photoelectron kinetic energy is 4.7 eV. We chose this example since it is generally more difficult to obtain converged  $K$  matrices and photoionization cross sections in resonant regions than at nonresonant energies. The results show that, even starting with the very small basis of six functions, the present method gives essentially the converged results after one iteration. The Schwinger method, in which the entire potential is projected onto the basis, gives much poorer results at this level. It is important to note, however, that with just six basis functions and no iterative im-

TABLE I. Starting Gaussian basis sets for the  $^2\Sigma$  continuum of the  $e\text{-NO}^+(X^1\Sigma^+)$  system.

Basis set	Center	Present method				Center	Iterative Schwinger method				
		$l$	$m$	$n$	$\alpha$		$l$	$m$	$n$	$\alpha$	
I	Nuclei <sup>a</sup>	0	0	0	4.0	Nuclei	0	0	0	4.0	
		0	0	0	0.5		0	0	0	0.5	
		0	0	1	1.0		0	0	1	1.0	
II	Nuclei	0	0	0	8.0	Nuclei	0	0	0	8.0	
		0	0	0	2.0		0	0	0	2.0	
		0	0	0	0.5		0	0	0	0.5	
		0	0	1	1.0		0	0	1	1.0	
		0	0	1	0.25		0	0	1	0.25	
		0	0	2	0.5		c.m. <sup>b</sup>	1	0		1.0
						c.m.		2	0		1.0
III	Nuclei	0	0	0	8.0	Nuclei	0	0	0	8.0	
		0	0	0	4.0		0	0	0	4.0	
		0	0	0	2.0		0	0	0	2.0	
		0	0	0	1.0		0	0	0	1.0	
		0	0	0	0.5		0	0	0	0.5	
		0	0	1	2.0		0	0	1	1.0	
		0	0	1	1.0		0	0	1	0.25	
		0	0	1	0.25		c.m.	1	0		1.0
		0	0	2	0.5			2	0		1.0
						3		0		1.0	
					4	0		1.0			

<sup>a</sup>Basis functions on the nuclei are Cartesian Gaussians.

<sup>b</sup>Center of mass. Functions here are always spherical Gaussians.

TABLE II. Comparison of the  ${}^2\Sigma$   $K$ -matrix elements,  $\sigma$  eigenphase sums, and the  $2\pi \rightarrow k\sigma$  photoionization cross sections at a photoelectron kinetic energy of 4.7 eV for the  $e$ -NO $^+$  system obtained by the present method and the iterative Schwinger method.

	Basis set I <sup>a</sup>		Basis set II		Basis set III	
	$L^2$ <sup>a</sup>	Iterated <sup>b</sup>	$L^2$	Iterated	$L^2$	Iterated
$K_{(l,l')}$	Present method					
0,0	-0.224	0.091	-0.045	0.094	0.069	0.094
0,1	0.625	-0.524	-0.439	-0.526	-0.518	-0.526
1,1	31.451	-1.585	-2.467	-1.549	-1.740	-1.546
0,2	0.884	0.534	0.564	0.535	0.536	0.535
1,2	11.006	-1.154	-1.343	-1.145	-1.177	-1.145
2,2	3.579	-0.529	-0.595	-0.525	-0.553	-0.524
$\delta_{\text{sum}}^c$	1.616	-0.498	-0.806	-0.489	-0.576	-0.488
$\sigma_i^d$	1.336	1.501	1.328	1.509	1.472	1.513
	Iterative Schwinger method					
0,0	13.346	-0.273	-0.043	0.103	-0.033	0.096
0,1	14.671	-1.285	-0.397	-0.551	-0.524	-0.534
1,1	16.582	-2.764	-2.729	-1.507	-2.471	-1.521
0,2	-2.554	-0.121	0.603	0.532	0.553	0.535
1,2	-2.901	-1.571	-1.209	-1.135	-1.122	-1.144
2,2	0.564	-0.864	-0.423	-0.524	-0.370	-0.523
$\delta_{\text{sum}}$	-1.076	-0.853	-0.869	-0.488	-0.748	-0.479
$\sigma_i$	0.798	0.524	1.239	1.342	1.277	1.524

<sup>a</sup>Discrete basis functions only. See Table I.

<sup>b</sup>One iteration only.

<sup>c</sup>In radians.

<sup>d</sup>In megabarns (1 Mb =  $10^{-18}$  cm $^2$ ).

provement, the present method provides a good estimate of the photoionization cross section. This is a consequence of the variational stability of these cross sections. At the  $L^2$  level, the differences between the two methods become smaller as the size of the basis sets increases but, as expected, the present method yields more accurate results. With these larger basis sets, the differences between these two methods become quite small once the wave functions are improved iteratively. Away from the resonant energies in the  $2\pi \rightarrow k\sigma$  channel and for the non-resonant  $2\pi \rightarrow k\pi$  and  $k\delta$  channels, the present method performs extremely well providing accurate cross sections at the  $L^2$  level with just six basis functions. For these channels and with these small basis sets, the cross sections obtained with the Schwinger method would change by as much as 40% with iteration.

As a next example we obtain some  ${}^2\Sigma_g$   $K$ -matrix elements and eigenphase sums for  $e$ -H $_2$  at  $k^2=0.25$  in the static-exchange approximation. This system is simple and has been extensively studied previously. We chose this system so as to compare the present method both with the iterative Schwinger procedure<sup>2</sup> and the method of Rescigno and Orel.<sup>5</sup> Our present method is very similar to theirs<sup>5</sup> and differs essentially only in the use of a different separable representation of the exchange potential, i.e., the use of Eq. (1) instead of Eq. (2). As we have shown earlier, the use of the separable potential of the form of Eq. (2) leads to a variationally stable formulation. For the comparison of these results for this simple system obtained by the different approaches we do not believe it is

necessary to present extensive numerical details.

For these studies of  $e$ -H $_2$  we use an SCF target wave function constructed from a  $[5s\ 2p]$  basis discussed previously.<sup>2</sup> This basis gives an SCF energy of  $-1.1330$  a.u. and a quadrupole moment of 0.452 a.u. We chose two small scattering basis sets containing two and four  $\sigma_g$  functions, respectively. The basis functions are given in Table III. The results of these calculations are given in Table IV and show that with only two basis functions the present method already provides quite accurate  $K$ -matrix elements at the  $L^2$  level. With this same basis and without any iterations the Schwinger method gives much poorer results. With four basis functions the differences between these two methods at the  $L^2$  level remain significant. However, after one iteration, the two methods give essentially the same results. The iterated results in Table

TABLE III. Starting basis sets for the  ${}^2\Sigma_g$  continuum of  $e$ -H $_2$ . All functions are centered on the nuclei. All are Cartesian Gaussian functions defined in Eq. (39).

Basis set	$l$	$m$	$n$	$\alpha$
I	0	0	0	0.5
	0	0	1	0.5
II	0	0	0	1.0
	0	0	0	0.3
	0	0	1	1.0
	0	0	1	0.3

TABLE IV. Comparison of the  ${}^2\Sigma_g$   $K$ -matrix elements and eigenphase sums for  $e\text{-H}_2$  at  $K^2=0.25$  a.u.

Basis set		Present method		Iterative Schwinger method	
		$L^2$	Iterated	$L^2$	Iterated
I	$K_{(l,l')}$				
	(0,0)	-1.721	-1.546	0.690	-1.549
	(0,2)	0.019	0.013	-0.028	-0.014
	(2,2)	0.014	0.016	0.002	0.016
	$\delta_{\text{sum}}$	-1.026	-0.976	0.606	-0.975
II	(0,0)	-1.598	-1.546	-2.079	-1.545
	(0,2)	0.016	0.013	0.004	0.013
	(2,2)	0.015	0.016	0.004	0.016
	$\delta_{\text{sum}}$	-0.992	-0.976	-1.118	-0.974

IV are almost identical to the converged  $K$  matrices at this energy. For comparison, with their choice of Eq. (2) for the separable representation of the exchange potential, Rescigno and Orel<sup>5</sup> obtained values for  $K_{00}$ ,  $K_{02}$ , and  $K_{22}$  of  $-1.490$ ,  $0.012$ , and  $0.0148$ . These calculations<sup>5</sup> used the present  $[5s\ 2p]$  SCF basis, i.e.,  $7\sigma_g$  functions, to form the separable representation of the potential. Larger basis sets in the present method without iterations and in their studies<sup>5</sup> can both provide the converged  $K$  matrices directly.

#### IV. CONCLUSIONS

We have developed an adaptation of the Schwinger variational principle which is particularly well suited for treating long-range potentials. The method treats the direct component of the interaction potential exactly by numerical procedures but assumes a separable representation of the Schwinger type for the exchange potential. The method includes an iterative procedure for systematically obtaining converged solutions of the corresponding Lippmann-Schwinger equation. The approach should be

particularly useful in obtaining continuum solutions of strongly polar ions which are required in related studies of resonant molecular photoionization cross sections. The method, moreover, provides variationally stable estimates of these photoionization cross sections. In this regard, applications of the method to the photoionization of the  $2\pi$  level of NO gave encouraging results and suggest that the approach can be quite useful in other related applications.

#### ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under Grant No. CHE-81-28166. One of us (M.E.S.) acknowledges support of a National Science Foundation (NSF) fellowship. The research reported in this paper made use of the Dreyfus-NSF Theoretical Chemistry Computer which was funded through grants from the Camille and Henry Dreyfus Foundation, the National Science Foundation (Grant No. CHE-78-20235), and the Sloan Fund of the California Institute of Technology.

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