Finite-basis-set expansion methods for scattering problems

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A wide variety of finite-basis-set expansion methods is applied to electron–hydrogen-atom scattering in the static-exchange approximation. All these methods are based on the Lippmann-Schwinger formalism. A careful analysis of the numerical results is presented with the aim of selecting efficient approaches to the solution of realistic electron-atom (and electron-molecule) scattering problems. The results show that the efficiency of the expansion methods may depend sensitively on the characteristics of the interaction terms. Some difficulties of the simple method of moments are pointed out. A particular least-squares method is proposed to avoid the spurious singularities encountered in applications of the Schwinger variational method to singlet scattering processes.

I. INTRODUCTION

Over the last decade, increasing interest has been devoted to the solution of quantum-mechanical scattering problems at low energies. The investigations include electron-atom and electron-molecule collisions,[1-5] photoionization processes,[3,6] and chemical reaction probabilities.[7] Promising finite-basis-set expansion methods have been suggested by using a great variety of variational functionals[1,3,8] based on the multichannel extensions of the Lippmann-Schwinger integral equation.

The best known variational principle based on the Lippmann-Schwinger equation is the stationary Schwinger variational principle[9] which becomes a maximum (or minimum) principle for the reactance matrix elements if we consider a particular class of scattering potentials.[8-10] However, there are many exceptions. An illustrative example is electron-hydrogen-atom singlet scattering in the static-exchange approximation. In this case, the numerical results of our previous paper[11] clearly show the presence of spurious singularities in the reactance matrix elements computed by the Schwinger variational method.

Since the variational results are not necessarily bounded from above (or below), it may be convenient to replace the stationary principles by a stability requirement along the lines discussed in Refs. 12 and 13. In fact, simple nonvariational expansion methods may also yield stable results in a fairly large region of the nonlinear scale parameters characterizing the basis functions (i.e., in that region the computed reactance matrix elements are almost independent of the choice of the nonlinear scale parameters). Of course, the results of a practical expansion method must show a convincing stability at relatively small sizes of the basis set.

In this paper we shall apply both variational and non-variational expansion methods to the approximate solution of the Lippmann-Schwinger integral equation. These procedures will be classified within the framework of the general method of moments (cf. Ref. 14). As a particular case, we shall discuss how the least-squares variational method suggested in Refs. 13 and 15 can be extended to the Lippmann-Schwinger formalism. A careful analysis of the numerical results will be presented for the s-wave electron–hydrogen-atom scattering in the simple static-exchange approximation. These results may be useful in selecting the most promising expansion methods for the solution of complicated scattering problems. We expect that the static-exchange approximation provides a more efficient comparative test than the s-wave scattering by a local exponential potential which has already been used to explore some virtues (or drawbacks) of 35 different expansion methods.[16]

The outline of this paper is as follows. In Sec. II we discuss the theoretical background. Section III is devoted to the least-squares variational methods that are based on the Lippmann-Schwinger equation. Numerical results computed by various finite-basis-set expansion methods are presented in Sec. IV. Some comments and remarks are left for Sec. V.

II. THEORETICAL BACKGROUND

A. Lippmann-Schwinger equation

We consider the s-wave ($l=0$) elastic scattering of an electron at energy ε. This process can be described by a stationary-state radial wave function $f(r)$ which satisfies the Schrödinger equation

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + U - \varepsilon \right] f = 0 , \qquad (2.1)$$

where atomic units (a.u.) are used, and U denotes the central scattering potential (or operator). Moreover, we shall consider only short-range interaction terms U. In this case, the general asymptotic form of the radial wave function $f(r)$ is the following:

$$f(r) = \tilde{a}_{-1}[\tilde{S}(r) + K\tilde{C}(r)] \quad \text{if } r \to \infty \ . \tag{2.2}$$

Here the coefficient $\tilde{a}_{-1}$ is different from zero and independent of r, otherwise arbitrary, and K is the reactance matrix element which can be expressed as

$$K = \tan\delta \ , \tag{2.3}$$

where δ is the phase shift. In addition, we have

$$\tilde{S}(r) = k^{-1/2}\sin(kr) \ , \tag{2.4}$$

$$\tilde{C}(r) = k^{-1/2}\cos(kr) \ , \tag{2.5}$$

and

$$k = (2\varepsilon)^{1/2} \ . \tag{2.6}$$

If the value of the coefficient $\tilde{a}_{-1}$ is fixed at $\tilde{a}_{-1} = 1$, then the solution of Eq. (2.1) will be denoted by f_1. The radial wave function $f_1(r)$ satisfies the Lippmann-Schwinger integral equation[17]

$$(1 - GU)f_1 - \tilde{S} = 0 \ , \tag{2.7}$$

where the *principal-value* free-particle Green's function G is given by

$$GUf_1 = \int_0^\infty dr' g(r,r')U(r')f_1(r') \ , \tag{2.8}$$

with

$$g(r,r') = -2\tilde{S}(r_<)\tilde{C}(r_>) \ . \tag{2.9}$$

(The symbols $r_>$ and $r_<$ denote, respectively, the greater and lesser of r,r'.) The reactance matrix element K becomes

$$K = -2\langle \tilde{S} | U | f_1 \rangle \ . \tag{2.10}$$

Here, and in the following part of this paper, we use the obvious notation

$$\langle \psi_i | \psi_j \rangle = \int_0^\infty \psi_i^*(r)\psi_j(r)dr \ , \tag{2.11}$$

and the matrix elements of an operator F (involving r) will be defined by

$$\langle \psi_i | F | \psi_j \rangle = \int_0^\infty \psi_i^*(r)F\psi_j(r)dr \ . \tag{2.12}$$

B. General method of moments

The reactance matrix element K can be computed by using a great variety of the finite-basis-set expansion methods that are based on the Lippmann-Schwinger integral equation. We shall employ the numbers ω, Q, and q ($\omega, Q, q = 0, 1, 2, \ldots$) to label a particular expansion procedure which will be called the $M_{Q,q}^{(\omega)}$ method. As a first step, we consider the expansion of the radial wave function $f_1(r)$ in terms of a convenient set of basis functions $\tilde{\varphi}_j(M_{Q,q}^{(0)};r)$. The truncated version of this expansion can be written as

$$f_1'(M_{Q,q}^{(\omega)};r) = \sum_{j=1}^N \tilde{a}_j(M_{Q,q}^{(\omega)})\tilde{\varphi}_j(M_{Q,q}^{(0)};r) \ . \tag{2.13}$$

By substituting $f_1'(M_{Q,q}^{(\omega)};r)$ into the Lippmann-Schwinger equation (2.7), we have

$$(1 - GU)f_1'(M_{Q,q}^{(\omega)}) - \tilde{S} = \tilde{\Delta}(M_{Q,q}^{(\omega)};r) \ , \tag{2.14}$$

where the deviation $\tilde{\Delta}(M_{Q,q}^{(\omega)};r)$ is related to the error of the approximate radial wave function $f_1'(M_{Q,q}^{(\omega)};r)$.

We now introduce a convenient set of test functions $\tilde{\chi}_i(M_{Q,q}^{(\omega)};r)$. As a next step, let us fix N projections of the deviation vector $\tilde{\Delta}(M_{Q,q}^{(\omega)})$ at zero:

$$\langle \tilde{\chi}_i(M_{Q,q}^{(\omega)}) | \tilde{\Delta}(M_{Q,q}^{(\omega)}) \rangle = 0, \quad i = 1, \ldots, N \ . \tag{2.15}$$

These equations can be expressed as

$$\sum_{j=1}^N L_{ij}(M_{Q,q}^{(\omega)})\tilde{a}_j(M_{Q,q}^{(\omega)}) = \langle \tilde{\chi}_i(M_{Q,q}^{(\omega)}) | \tilde{S} \rangle \ , \tag{2.16}$$

where $i = 1, \ldots, N$, and

$$L_{ij}(M_{Q,q}^{(\omega)}) = \langle \tilde{\chi}_i(M_{Q,q}^{(\omega)}) | (1 - GU) | \tilde{\varphi}_j(M_{Q,q}^{(0)}) \rangle \ . \tag{2.17}$$

Equation (2.16) is a system of linear inhomogeneous algebraic equations which determine the coefficients $\tilde{a}_j(M_{Q,q}^{(\omega)})$ according to the general method of moments.

The approximate reactance matrix element $K(M_{Q,q}^{(\omega)})$ can be calculated by substituting Eq. (2.13) into Eq. (2.10). One obtains

$$K(M_{Q,q}^{(\omega)}) = -2\sum_{j=1}^N \langle \tilde{S} | U | \tilde{\varphi}_j(M_{Q,q}^{(0)}) \rangle \tilde{a}_j(M_{Q,q}^{(\omega)}) \ . \tag{2.18}$$

Equations (2.16) and (2.18) imply

$$K(M_{Q,q}^{(\omega)}) = -2\sum_{i,j=1}^N \langle \tilde{S} | U | \tilde{\varphi}_i(M_{Q,q}^{(0)}) \rangle$$
$$\times L_{ij}^{-1}(M_{Q,q}^{(\omega)})\langle \tilde{\chi}_j(M_{Q,q}^{(\omega)}) | \tilde{S} \rangle \ , \tag{2.19}$$

where L_{ij}^{-1} is defined by

$$\sum_{i'=1}^N L_{ii'}(M_{Q,q}^{(\omega)})L_{i'j}^{-1}(M_{Q,q}^{(\omega)}) = \delta_{ij} \ . \tag{2.20}$$

Of course, the general method of moments is only a formal framework without a judicious selection of the basis functions and test functions. These functions must be specified carefully by taking into account the significant properties of the interaction term U which governs the scattering process.

C. Static-exchange approximation of the electron–hydrogen-atom scattering

We next apply $M_{Q,q}^{(\omega)}$ methods to the s-wave ($l = 0$) elastic scattering of an electron by a hydrogen atom and, as a test case, we shall use the simple static-exchange approximation suggested by Erskine and Massey.[18] Thus, we have

$$\varepsilon = E - E_1 \ , \tag{2.21}$$

where E is the total energy of the electron–hydrogen-atom system, and E_1 denotes the ground-state energy of the hydrogen atom ($E_1 = -0.5$ a.u.). The static-exchange approximation of the interaction terms U becomes

$$U = V(r) + W , \tag{2.22}$$

where

$$V(r) = -\left[\frac{1}{r} + 1\right]e^{-2r} , \tag{2.23}$$

$$Wf_1 = -\int_0^\infty rw(r,r')r'f_1(r')dr' , \tag{2.24}$$

and

$$w(r,r') = 4(-1)^S e^{-r}(E - 2E_1 - r_>^{-1})e^{-r'} . \tag{2.25}$$

Here we have $S = 0$ for singlet scattering processes, and the triplet scattering states are characterized by $S = 1$. Equation (2.3) may be written as

$$K^{(S)}(M_{Q,q}^{(\omega)}) = \tan\delta^{(S)}(M_{Q,q}^{(\omega)}), \quad S = 0, 1 \tag{2.26}$$

where $K^{(0)}(M_{Q,q}^{(\omega)})$ and $K^{(1)}(M_{Q,q}^{(\omega)})$ are, respectively, the approximate singlet and triplet reactance matrix elements computed by the $M_{Q,q}^{(\omega)}$ method.

D. Basis functions and test functions

In the present study we make use of a set of (nonorthogonal) square-integrable Slater-type functions $\varphi_j(r)$. According to the short-distance behavior of the exact solution $f_1(r)$, the functions $\varphi_j(r)$ will be taken as

$$\varphi_j(r) = A_j r^j e^{-\alpha r}, \quad j = 1, 2, \ldots \tag{2.27}$$

where α is a (real) nonlinear scale parameter characterizing the basis, and the normalization factors are denoted by A_j.

We now apply the general method of moments to a classification of some particular $M_{Q,q}^{(\omega)}$ methods by choosing various sets of basis functions $\widetilde{\varphi}_j(M_{Q,q}^{(0)};r)$ and test functions $\widetilde{\chi}_i(M_{Q,q}^{(\omega)};r)$. As a first possibility, we consider

$$\widetilde{\varphi}_j(M_{0,0}^{(0)};r) = \varphi_j(r) , \tag{2.28a}$$

$$\widetilde{\chi}_i(M_{0,0}^{(0)};r) = \varphi_i(r) , \tag{2.28b}$$

with Eq. (2.27). By substituting Eqs. (2.28a) and (2.28b) into Eqs. (2.16)–(2.19), we obtain the $M_{0,0}^{(0)}$ method. This is the *simple* nonvariational method of moments[19,20] that is called the ψM method in a recent work of Staszewska and Truhlar.[16]

Let us turn to the nonvariational method of moments for the amplitude density Uf_1 (called ζM method in Ref. 16) which will be referred to as the $M_{1,1}^{(0)}$ method. This method is given by Eqs. (2.16)–(2.19) with

$$\widetilde{\varphi}_j(M_{1,1}^{(0)};r) = U^{-1}\varphi_j(r) , \tag{2.29a}$$

$$\widetilde{\chi}_i(M_{1,1}^{(0)};r) = U\varphi_i(r) . \tag{2.29b}$$

Equations (2.19), (2.28a), (2.28b), (2.29a), and (2.29b), imply[16]

$$K^{(S)}(M_{0,0}^{(0)}) = K^{(S)}(M_{1,1}^{(0)}), \quad S = 0, 1 . \tag{2.30}$$

Notice that the approximate radial wave function $f_1'(M_{0,0}^{(0)};r)$ is different from $f_1'(M_{1,1}^{(0)};r)$.

It is immediately obvious that Eqs. (2.16)–(2.19) result in the Schwinger variational method by choosing

$$\widetilde{\varphi}_j(M_{2,0}^{(0)};r) = \varphi_j(r) , \tag{2.31a}$$

$$\widetilde{\chi}_i(M_{2,0}^{(0)};r) = U\varphi_i(r) . \tag{2.31b}$$

Thus, according to our classification, the Schwinger variational method may be called the $M_{2,0}^{(0)}$ method. We emphasize that the $M_{2,0}^{(0)}$ method is based on the classical Schwinger variational principle. Therefore, the Schwinger variational method is intrinsically superior to the $M_{0,0}^{(0)}$ and $M_{1,1}^{(0)}$ procedures.

The Schwinger variational method may be simplified by using the nonvariational $M_{0,q}^{(0)}$ methods (cf. Ref. 16) which are defined by Eqs. (2.16)–(2.19) with

$$\widetilde{\varphi}_j(M_{0,q}^{(0)};r) = \varphi_j(r) , \tag{2.32a}$$

$$\widetilde{\chi}_i(M_{0,q}^{(0)};r) = \widetilde{V}(q;r)\varphi_i(r), \quad q = 1, 2, \ldots , \tag{2.32b}$$

where the local *positive-definite* test potentials $\widetilde{V}(q;r)$ are designed to imitate some significant properties of the interaction term U as given by Eqs. (2.22)–(2.25). We shall choose

$$\widetilde{V}(q;r) = \frac{e^{-\gamma_q r}}{r}, \quad q = 1, 2, \ldots . \tag{2.33}$$

Section IV includes some illustrative results of the $M_{0,1}^{(0)}$ method in which the parameter γ_q will be taken as

$$\gamma_q = 1 \quad \text{for } q = 1 . \tag{2.34}$$

All these methods can be applied to the approximate solution of the Takatsuka-McKoy integral equation[21] which involves the subtracted radial wave function C_1 defined by

$$f_1 = C_1 + \widetilde{S} . \tag{2.35}$$

Although the Takatsuka-McKoy equation will not be considered in the present paper, we would like to mention that the standard expansions of C_1 (using the basis functions $\widetilde{\varphi}_j$) imply the appearance of the basis function $\widetilde{S}$ in the expansion of the radial wave function f_1.

In summary, the general method of moments is well suited to a systematic classification of various finite-basis-set expansion methods. This simple and important fact has been emphasized by Abdel-Raouf.[8] Moreover, the bound-state calculations of Szondy and co-workers[22–24] show that the evaluation of the matrix elements can be greatly simplified by choosing convenient test functions.

The success of a particular $M_{Q,q}^{(\omega)}$ method (e.g., the convergence of the results) may depend on the choice of the nonlinear scale parameter α in Eq. (2.27). It will be convenient to introduce the following notation:

$$K^{(S)}(M_{Q,q}^{(\omega)}) = K^{(S)}(M_{Q,q}^{(\omega)};N;k,\alpha) , \tag{2.36}$$

where N refers to the size of the basis set, and k is the wave number in atomic units. We shall prefer those $M_{Q,q}^{(\omega)}$ methods which can give reliable results by using relatively small basis-set sizes N in a fairly large region of the nonlinear scale parameter α. Of course, this region becomes larger if the basis-set size N is increased. To get some additional insight into the stability and convergence

characteristics of the finite-basis-set expansion procedures, we next apply several least-squares variational methods[13,15] to the approximate solution of the Lippmann-Schwinger integral equation.

III. LEAST-SQUARES VARIATIONAL METHODS

We make use of the integral equation equivalent to the Schrödinger equation (2.1), plus the boundary condition for large r as given by Eq. (2.2). This integral equation becomes

$$(1-GU)f - \tilde{a}_{-1}\tilde{S} = 0 \ . \tag{3.1}$$

The radial wave function $f(r)$ will be expanded in terms of the basis functions $\tilde{\varphi}_j(M_{Q,q}^{(0)})$ discussed in Sec. II. The truncated version of this expansion is

$$f'(M_{Q,q}^{(\omega)};r) = \sum_{j=1}^{N} \tilde{a}_j(M_{Q,q}^{(\omega)})\tilde{\varphi}_j(M_{Q,q}^{(0)};r), \quad \omega=1,2,\dots \ . \tag{3.2}$$

By substituting the approximate radial wave function $f'(M_{Q,q}^{(\omega)};r)$ into Eq. (3.1), we may write

$$(1-GU)f'(M_{Q,q}^{(\omega)}) - \tilde{a}_{-1}\tilde{S} = \Delta(M_{Q,q}^{(\omega)};r) \ , \tag{3.3}$$

where the deviation $\Delta(M_{Q,q}^{(\omega)};r)$ depends on the linear parameters $\tilde{a}_{-1}$ and $\tilde{a}_j(M_{Q,q}^{(\omega)})$, $j=1,\dots,N$.

We next turn to a definition of the measure of the error of the approximate radial wave function $f'(M_{Q,q}^{(\omega)};r)$ in a sufficiently large $(N+p$-dimensional) subspace spanned by the test functions $\tilde{\chi}_i(M_{Q,q}^{(0)})$ which are listed in Sec. II. This definition can be expressed as

$$\lambda[f'(M_{Q,q}^{(\omega)})] = \frac{\Lambda[f'(M_{Q,q}^{(\omega)}]}{\tilde{a}_{-1}^*\tilde{a}_{-1}} \ , \tag{3.4}$$

in which

$$\Lambda[f'(M_{Q,q}^{(\omega)}] = \sum_{h,h'=1}^{N+p} \langle \Delta(M_{Q,q}^{(\omega)}) | \tilde{\chi}_h(M_{Q,q}^{(0)}) \rangle$$

$$\times w_{hh'}(\omega)\langle \tilde{\chi}_{h'}(M_{Q,q}^{(0)}) | \Delta(M_{Q,q}^{(\omega)}) \rangle \ , \tag{3.5}$$

with

$$p \geq 2 \ . \tag{3.6}$$

Here the weight matrix $w(\omega)$ is real, symmetric and all the eigenvalues of $w(\omega)$ are larger than zero. For simplicity, we shall choose

$$w_{hh'}(\omega) = \delta_{hh'} \quad \text{for } \omega = 1 \ . \tag{3.7}$$

The variational functional $\lambda[f'(M_{Q,q}^{(\omega)})]$ is positive semidefinite by construction, and we have

$$\lambda[f] = 0 \ . \tag{3.8}$$

Let us mention that, in general, $\lambda[f']$ is larger than zero if $f \neq f'$, because equation $\lambda[f'] = 0$ would imply

$$\langle \tilde{\chi}_{h'}(M_{Q,q}^{(0)}) | \Delta(M_{Q,q}^{(\omega)}) \rangle = 0 \quad \text{for } h'=1,\dots,N+p \ , \tag{3.9}$$

which yields $N+p$ $(p \geq 2)$ linear algebraic equations for the coefficients $\tilde{a}_{-1}, \tilde{a}_1(M_{Q,q}^{(\omega)}), \dots, \tilde{a}_N(M_{Q,q}^{(\omega)})$. Consequently, the equation $\lambda[f'] = 0$ $(f \neq f')$ might be satisfied only by accident.

By variation of $\lambda[f'(M_{Q,q}^{(\omega)})]$ with respect to the linear parameters $\tilde{a}_{-1}$ and $\tilde{a}_j(M_{Q,q}^{(\omega)})$, $j=1,\dots,N$, we obtain a simple eigenvalue problem. As a next step, we normalize the eigenvector by setting

$$\tilde{a}_{-1} = 1 \ . \tag{3.10}$$

The final result is the system of linear inhomogeneous algebraic equations for the coefficients $\tilde{a}_j(M_{Q,q}^{(\omega)})$, $j=1,\dots,N$. These equations can be written in the form given by Eqs. (2.16) and (2.17), where

$$\tilde{\chi}_i(M_{Q,q}^{(\omega)}) = \sum_{h,h'=1}^{N+p} \langle \tilde{\varphi}_i(M_{Q,q}^{(0)}) | (1-UG) | \tilde{\chi}_h(M_{Q,q}^{(0)}) \rangle$$

$$\times w_{hh'}(\omega)\tilde{\chi}_{h'}(M_{Q,q}^{(0)}), \quad \omega=1,2,\dots \ . \tag{3.11}$$

In addition, the formula of the eigenvalue $\lambda = \lambda^{(S)}(M_{Q,q}^{(\omega)})$ becomes

$$\lambda^{(S)}(M_{Q,q}^{(\omega)}) = \sum_{h,h'=1}^{N+p} \langle \tilde{S} | \tilde{\chi}_h(M_{Q,q}^{(0)}) \rangle w_{hh'}(\omega)$$

$$\times [\langle \tilde{\chi}_{h'}(M_{Q,q}^{(0)}) | \tilde{S} \rangle - d_{h'}^{(S)}(M_{Q,q}^{(\omega)})] \ , \tag{3.12}$$

where $S = 0, 1$, and

$$d_h^{(S)}(M_{Q,q}^{(\omega)}) = \sum_{j=1}^{N} \langle \tilde{\chi}_h(M_{Q,q}^{(0)}) | (1-GU) | \tilde{\varphi}_j(M_{Q,q}^{(0)}) \rangle$$

$$\times \tilde{a}_j(M_{Q,q}^{(\omega)}) \ . \tag{3.13}$$

We now observe that the least-squares variational procedure leads to a particular class of the method of moments which will be referred to as the $M_{Q,q}^{(\omega)}$ $(\omega \geq 1)$ methods. For example, the $M_{Q,q}^{(1)}$ methods are defined by Eqs. (2.16)–(2.19) and (3.11), where the functions $\tilde{\varphi}_i(M_{Q,q}^{(0)})$ and $\tilde{\chi}_h(M_{Q,q}^{(0)})$ are listed in Sec. II, and the weight matrix $w(\omega=1)$ is given by Eq. (3.7). [Other weight matrices $w(\omega)$ may also lead to practical computational procedures which may be called the $M_{Q,q}^{(\omega)}$ $(\omega=2,3,\dots)$ methods.] Let us mention that the $M_{Q,q}^{(\omega)}$ $(\omega=1,2,\dots)$ methods are more simple than the quadratic variational methods,[8] and the iteration-variation methods discussed by Rayski[25] and Staszewska and Truhlar.[16] (For related methods see, e.g., Refs. 4, 26, and 27.)

In summary, the least-squares variational method provides a rationale for choosing the test functions $\tilde{\chi}_i(M_{Q,q}^{(\omega)})$, $\omega=1,2,\dots$, as defined by Eq. (3.11). Moreover, the eigenvalue $\lambda^{(S)}(M_{Q,q}^{(\omega)})$ [see Eqs. (3.12) and (3.13)] may offer a useful measure of the error of the approximate wave function within the $N+p$-dimensional subspace spanned by the test functions $\tilde{\chi}_i(M_{Q,q}^{(0)})$, $i=1,\dots,N+p$ $(p \geq 2)$.

Our numerical calculations will be carried out by choosing

$$p = 5 . \tag{3.14}$$

Since the value of p is fixed, it follows from Eq. (3.11) that the matrix elements $L_{ij}(M_{Q,q}^{(\omega)})$ are not absolutely independent of N for $\omega \geq 1$. Therefore, in general, we should not expect that the sequence of the approximate eigenvalues $\lambda^{(S)}(M_{Q,q}^{(\omega)})$ *monotonically* approaches the true eigenvalue $\lambda^{(S)} = 0$ as the basis-set size N is increased.[13]

IV. RESULTS AND DISCUSSION

A. Singlet scattering ($S = 0$)

We first compare some illustrative results of the Schwinger $(M_{2,0}^{(0)})$ variational method with those of the $M_{2,0}^{(1)}$ least-squares method defined in Sec. III. The approximate reactance matrix elements $K^{(0)}(M_{2,0}^{(0)};N;k,\alpha)$ and $K^{(0)}(M_{2,0}^{(1)};N;k,\alpha)$ were calculated at many values of the nonlinear scale parameter α. Figure 1 shows the results at $N = 5$ and $k = 0.5$ a.u. ($S = 0$). In this case both methods are capable of giving continuous and fairly accurate reactance matrix elements $K^{(0)}$ within the large region $0.15 < \alpha < 0.90$ omitted from the plot. However, the plateaus of the function $K^{(0)}(M_{2,0}^{(0)};5;0.5,\alpha)$ are broken by steep spurious branches which clearly show the presence of anomalous poles in singlet scattering processes.[11] These anomalies of the Schwinger formula can be avoided by using the $M_{2,0}^{(1)}$ least-squares variational method. Notice that the reactance matrix elements $K^{(0)}(M_{2,0}^{(1)};5;0.5,\alpha)$ presented in Fig. 1 vary continuously with respect to the nonlinear scale parameter α and, indeed, the results of the $M_{2,0}^{(1)}$ method are less sensitive to the choice of α than the reactance matrix elements $K^{(0)}(M_{2,0}^{(0)};5;0.5,\alpha)$ computed by the Schwinger variational method. These Schwinger results become very unstable in the region $\alpha > 2.5$, since an unpleasant spurious singularity is encountered at $\alpha \approx 2.7$ according to Fig. 2 of Ref. 11. On the other hand, the reactance matrix elements $K^{(0)}(M_{2,0}^{(1)};5;0.5,\alpha)$ computed by the $M_{2,0}^{(1)}$ least-squares variational method achieve a remarkable accuracy (1–2 %) also in the region $2.75 < \alpha < 5$ which is not included in Fig. 1.
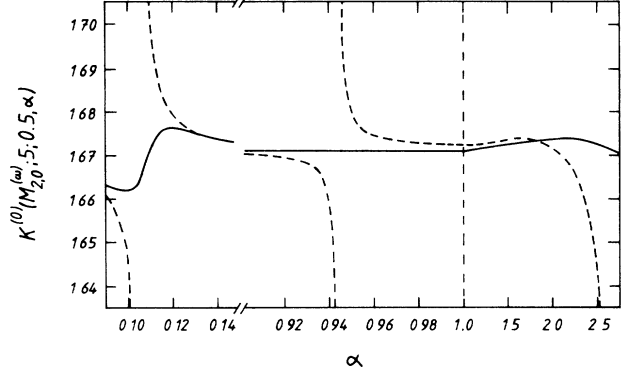

FIG. 1. Computed values of the singlet reactance matrix elements $K^{(0)}(M_{2,0}^{(\omega)};N;k,\alpha)$ vs the scale parameter α for $\omega = 0$ (dashed curves) and $\omega = 1$ (solid curve). Results were obtained by using $M_{2,0}^{(\omega)}$ ($\omega = 0,1$) expansion methods defined in text. The basis-set size N and the wave number k are fixed at $N = 5$ and $k = 0.5$ a.u. The curves are continuous and almost constant in the region omitted from the plot. The dashed-dotted vertical line indicates the change of the scale at $\alpha = 1.0$.

Since the simple $M_{0,0}^{(0)}$ method gives excellent phase shifts for the s-wave scattering by an exponential potential,[16] we have tried to apply this method to the static-exchange approximation along the lines discussed in Sec. II. This attempt was *not* successful in the singlet case. (We find that both the stability and the convergence of the results of the $M_{0,0}^{(0)}$ method are unsatisfactory also for the s-wave scattering by a Yukawa potential.)

A remarkable improvement is provided by the $M_{0,1}^{(\omega)}$ ($\omega = 0,1$) methods which make use of the test potential $\bar{V}(1;r)$ as given by Eqs. (2.33) and (2.34). Figure 2 compares the reactance matrix elements for $S = 0$, $N = 5$, and $k = 0.5$ a.u. No anomalous branches of the function $K^{(0)}(M_{0,1}^{(0)};5;0.5,\alpha)$ can be observed on the plot. However, the acceptable results of the $M_{0,1}^{(\omega)}$ methods are seen to be located in a significantly smaller region of the scale parameter α than those of the $M_{2,0}^{(\omega)}$ methods (cf. Fig. 1).

In Table I we present a finer comparison of the results

TABLE I. Singlet reactance matrix elements $K^{(0)}(M_{Q,q}^{(\omega)})$ and the eigenvalues $\lambda^{(0)}(M_{Q,q}^{(1)})$ computed by $M_{Q,q}^{(\omega)}$ methods at several basis-set sizes N. The nonlinear scale parameter α and the wave number k are fixed at $\alpha = 0.5$ and $k = 0.5$ a.u. The $M_{Q,q}^{(\omega)}$ methods and the eigenvalues $\lambda^{(0)}(M_{Q,q}^{(1)})$ are defined in text.

| N	$K^{(0)}(M_{0,1}^{(0)})$	$K^{(0)}(M_{0,1}^{(1)})$	$\lambda^{(0)}(M_{0,1}^{(1)})$	$K^{(0)}(M_{2,0}^{(0)})$	$K^{(0)}(M_{2,0}^{(1)})$	$\lambda^{(0)}(M_{2,0}^{(1)})$
1	3.782 22	3.562 19	3.6×10^{-4}	1.728 7807	1.732 3098	9.5×10^{-5}
2	2.277 64	2.208 10	2.3×10^{-6}	1.730 1330	1.734 7925	9.4×10^{-5}
3	1.820 20	1.755 70	5.2×10^{-8}	1.667 3086	1.667 7738	4.2×10^{-9}
4	1.643 36	1.654 70	3.7×10^{-10}	1.671 8326	1.670 8462	1.6×10^{-9}
5	1.668 73	1.699 63	7.2×10^{-13}	1.670 9069	1.670 9000	1.7×10^{-14}
6	1.670 01	1.670 69	4.2×10^{-14}	1.670 8560	1.670 8959	5.2×10^{-15}
7	1.671 08	1.670 97	5.0×10^{-16}	1.670 9112	1.670 9113	2.5×10^{-19}
8	1.670 93	1.670 92	3.0×10^{-18}	1.670 9112	1.670 9112	1.0×10^{-21}
9	1.670 91	1.670 91	6.1×10^{-21}	1.670 9112	1.670 9112	1.8×10^{-25}
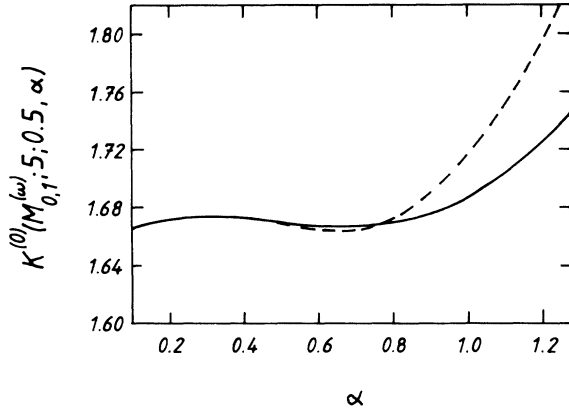
FIG. 2. Computed values of the singlet reactance matrix elements $K^{(0)}(M_{0,1}^{(\omega)};N;k,\alpha)$ vs the scale parameter α for $\omega=0$ (dashed curve) and $\omega=1$ (solid curve). Results were obtained by using $M_{0,1}^{(\omega)}$ ($\omega=0,1$) expansion methods defined in text. The basis-set size N and the wave number k are fixed at $N=5$ and $k=0.5$ a.u.
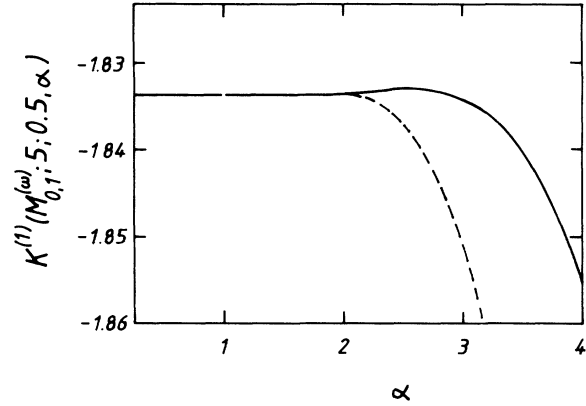
FIG. 3. Computed values of the triplet reactance matrix elements $K^{(1)}(M_{0,1}^{(\omega)};N;k,\alpha)$ vs the scale parameter α for $\omega=0$ (dashed curve) and $\omega=1$ (solid curve). The basis-set size N and the wave number k are fixed at $N=5$ and $k=0.5$ a.u. Results are omitted near $\alpha=1$.

for singlet scattering at $k=0.5$ a.u. The scale parameter was fixed at $\alpha=0.5$. The reactance matrix elements $K^{(0)}(M_{Q,q}^{(\omega)})$ were computed by using the $M_{0,1}^{(\omega)}$ and $M_{2,0}^{(\omega)}$ methods ($\omega=0,1$) at increasing basis-set sizes N. We show also the eigenvalues $\lambda^{(0)}(M_{0,1}^{(1)})$ and $\lambda^{(0)}(M_{2,0}^{(1)})$ defined by Eqs. (3.12) and (3.13). These eigenvalues are, of course, not directly related to the error of the approximate reactance matrix elements $K^{(0)}$. The sequences of the approximations $K^{(0)}(M_{2,0}^{(0)})$ and $K^{(0)}(M_{2,0}^{(1)})$ display rapid (but not monotonic) convergence up to eight digits. Although the $M_{0,1}^{(0)}$ and $M_{0,1}^{(1)}$ results show poorer convergence, useful approximations are obtained at fairly small basis-set sizes N. Notice that one might draw quite a false conclusion about the superiority of a particular expansion method by comparing the results calculated only at one fixed value of α, since the convergence characteristics depend on the choice of the nonlinear scale parameter characterizing the basis functions (cf. Ref. 10).

B. Triplet scattering ($S=1$)

In triplet scattering calculations the $M_{Q,q}^{(\omega)}$ methods may work very well except for a narrow region around $\alpha=1$. Here we encounter the well-known spurious singularity inherent in the simple static-exchange approximation at $S=1$. Of course, this triplet anomaly cannot be regarded as a defect of the $M_{Q,q}^{(\omega)}$ methods involving Slater-type functions as given by Eq. (2.27). (For a discussion see, e.g., Ref. 11.)

Figure 3 shows the triplet reactance matrix elements $K^{(1)}(M_{0,1}^{(0)};N;k,\alpha)$ and $K^{(1)}(M_{0,1}^{(1)};N;k,\alpha)$ at $N=5$ and $k=0.5$ a.u., plotting $K^{(1)}$ as a function of the scale parameter α. Results are omitted near $\alpha=1$ in order to avoid the triplet anomalies. Apart from this region, the functions $K^{(1)}(M_{0,1}^{(0)};5;0.5,\alpha)$ and $K^{(1)}(M_{0,1}^{(1)};5;0.5,\alpha)$ are seen to be almost constant up to $\alpha\approx2.2$ and $\alpha\approx3.2$, respectively.

TABLE II. Triplet reactance matrix elements $K^{(1)}(M_{Q,q}^{(\omega)})$ computed by $M_{Q,q}^{(\omega)}$ methods at several basis-set sizes N. The wave number is fixed at $k=0.5$ a.u. Both $K^{(1)}(M_{0,0}^{(0)})$ and $K^{(1)}(M_{0,0}^{(1)})$ were obtained with scale parameter $\alpha=1.8$; all other results used $\alpha=0.5$. The $M_{Q,q}^{(\omega)}$ methods are defined in text.

N	$K^{(1)}(M_{0,0}^{(0)})$	$K^{(1)}(M_{0,0}^{(1)})$	$K^{(1)}(M_{0,1}^{(0)})$	$K^{(1)}(M_{0,1}^{(1)})$	$K^{(1)}(M_{2,0}^{(0)})$	$K^{(1)}(M_{2,0}^{(1)})$
1	−1.159	−1.521	−1.787 0305	−1.748 2892	−2.088 448 797	−1.952 974 600
2	−1.106	−1.546	−1.831 6882	−1.831 7178	−1.834 814 064	−1.833 264 557
3	−1.671	−1.847	−1.831 6673	−1.831 3507	−1.834 046 436	−1.834 015 122
4	−1.789	−1.824	−1.833 7333	−1.833 8770	−1.833 723 300	−1.833 685 731
5	−1.835	−1.831	−1.833 6671	−1.833 6716	−1.833 666 857	−1.833 666 248
6	−1.840	−1.837	−1.833 6724	−1.833 6732	−1.833 666 673	−1.833 666 640
7	−1.837	−1.833	−1.833 6657	−1.833 6651	−1.833 666 652	−1.833 666 646
8	−1.835	−1.834	−1.833 6666	−1.833 6665	−1.833 666 622	−1.833 666 622
9	−1.834	−1.834	−1.833 6666	−1.833 6667	−1.833 666 622	−1.833 666 622

Similar calculations have been carried out by using the Schwinger $(M_{2,0}^{(0)})$ variational method and the $M_{2,0}^{(1)}$ least-squares method. The reactance matrix elements $K^{(1)}(M_{2,0}^{(0)})$ and $K^{(1)}(M_{2,0}^{(1)})$ show spectacular stability properties at $N=5$ and $k=0.5$ a.u. Less impressive (but still useful) results were obtained in applications of the $M_{0,0}^{(\omega)}(\omega=0,1)$ methods to the triplet scattering. (The singlet reactance matrix elements computed by the $M_{0,0}^{(\omega)}$ methods are notoriously unreliable for $N\leq9$.)

Table II illustrates how the results of various $M_{Q,q}^{(\omega)}$ methods converge at $k=0.5$ (a.u.) as the basis-set size N is increased $(S=1)$. The reactance matrix elements $K^{(1)}(M_{0,0}^{(0)})$ and $K^{(1)}(M_{0,0}^{(1)})$ were computed with $\alpha=1.8$; all other results used the scale parameter $\alpha=0.5$. The sequences of the approximations $K^{(1)}(M_{2,0}^{(0)})$ and $K^{(1)}(M_{2,0}^{(1)})$ show excellent convergence properties. (If $N\geq9$, then the results agree up to ten digits.) Moreover, the Schwinger $(M_{2,0}^{(0)})$ variational method yields monotonically convergent results at $S=1$. Remarkable accuracy is achieved also with the $M_{0,1}^{(0)}$ and $M_{0,1}^{(1)}$ methods. Finally, we mention that the simple $M_{0,0}^{(0)}$ method is capable of giving surprisingly good convergence in the narrow region $1.3<\alpha<1.6$ $(S=1)$. However, the convergence characteristics of the results computed by the $M_{0,0}^{(\omega)}$ methods are more sensitive to the choice of the nonlinear scale parameter α than those of the $M_{0,1}^{(\omega)}$ methods $(\omega=0,1)$.

V. COMMENTS

In this paper we have used the simple static-exchange approximation of the electron–hydrogen-atom scattering to probe the efficiency of various $M_{Q,q}^{(\omega)}$ methods based on the Lippmann-Schwinger integral equation. Both the Schwinger $(M_{2,0}^{(0)})$ variational method and the $M_{2,0}^{(1)}$ least-squares method give excellent results for triplet scattering processes. However, the singlet reactance matrix elements computed by the Schwinger variational method are not free of anomalies according to the results of Ref. 11. Figure 1 shows how these anomalies can be avoided by using the $M_{2,0}^{(1)}$ method presented in Sec. III. For practical use in electron-atom and electron-molecule scattering theory, the $M_{2,0}^{(\omega)}$ $(\omega=0,1)$ methods must be generalized to a multichannel formalism along the lines discussed by Nesbet[1] and Lucchese, Takatsuka, and McKoy.[3]

The calculation of the reactance matrix elements $K^{(S)}$ is greatly simplified in the $M_{0,1}^{(\omega)}$ $(\omega=0,1)$ methods which involve the test potential $\tilde{V}(1;r)$ defined in Sec. II. However, the generalization of $\tilde{V}$ to multichannel scattering is not a trivial problem. Therefore, care must be taken in applications of the $M_{0,1}^{(\omega)}$-type methods to complicated scattering processes.

The simple $M_{0,0}^{(\omega)}$ $(\omega=0,1)$ methods give fairly accurate reactance matrix elements for triplet scattering (see Table II). However, no reliable $M_{0,0}^{(\omega)}$ results were found for $S=0$ and $N\leq9$. This fact indicates that the $M_{0,0}^{(\omega)}$ methods might not be very useful in scattering calculations involving complex quantum-mechanical systems. In summary, the stability and convergence characteristics of the results computed by a particular finite-basis-set expansion method may sensitively depend on the interaction term U which governs the scattering process.

ACKNOWLEDGMENT

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

[2]J. Callaway, Adv. Phys. **29**, 771 (1980).

[3]R. R. Lucchese, K. Takatsuka, and V. McKoy, Phys. Rep. **131**, 147 (1986).

[4]B. I. Schneider and L. A. Collins, Phys. Rev. A **33**, 2970 (1986).

[5]For a review see, e.g., *Electron-Molecule Collisions*, edited by I. Shimamura and K. Takayanagi (Plenum, New York, 1984).

[6]C. W. McCurdy and T. N. Rescigno, Phys. Rev. A **35**, 657 (1987).

[7]K. Haug, D. W. Schwenke, Y. Shima, D. G. Truhlar, J. Zhang, and D. J. Kouri, J. Phys. Chem. **90**, 6757 (1986).

[8]M. A. Abdel-Raouf, Phys. Rep. **108**, 1 (1984).

[9]J. Schwinger, Phys. Rev. **72**, 742 (1947).

[10]C. Schwartz, Phys. Rev. **141**, 1468 (1966).

[11]B. Apagyi, P. Lévay, and K. Ladányi, Phys. Rev. A **37**, 4577 (1988).

[12]B. Gazdy and K. Ladányi, J. Chem. Phys. **80**, 4333 (1984).

[13]B. Apagyi and K. Ladányi, Phys. Rev. A **33**, 182 (1986).

[14]J. A. Shohat and J. D. Tamarkin, *The Problem of Moments* (American Mathematical Society, New York, 1943).

[15]K. Ladányi and T. Szondy, Nuovo Cimento B **5**, 70 (1971).

[16]G. Staszewska and D. G. Truhlar, J. Chem. Phys. **86**, 2793 (1987).

[17]B. A. Lippmann and J. Schwinger, Phys. Rev. **79**, 469 (1950).

[18]G. A. Erskine and H. S. W. Massey, Proc. R. Soc. London, Ser. A **212**, 521 (1952).

[19]I. H. Sloan and T. J. Brady, Phys. Rev. C **6**, 701 (1972).

[20]Y. Shima, D. J. Kouri, and M. Baer, J. Chem. Phys. **78**, 6666 (1983).

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

[22]T. Szondy, Acta Phys. Hung. **17**, 303 (1964).

[23]E. Szondy and T. Szondy, Acta Phys. Hung. **20**, 253 (1966).

[24]M. G. Hegyi, M. Mezei, and T. Szondy, Theor. Chim. Acta **15**, 283 (1969); **21**, 168 (1971).

[25]J. Rayski, Acta Phys. Pol. B **5**, 631 (1974).

[26]E. W. Schmid and K. H. Hoffmann, Nucl. Phys. A **175**, 443 (1971).

[27]K. Ladányi, Nuovo Cimento A **61**, 173 (1969).