Relative performances of the Kohn, Schwinger, and Newton variational principles in scattering theory[a)]

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Comparisons of three variational principles commonly used in scattering problems, namely those due to Kohn (KVP), Schwinger (SVP), and Newton (NVP), are presented. These comparisons are conducted by computing K-matrix elements for elastic scattering from nine different interaction potentials. We represent the KVP trial functions as expansions containing two non-L^2 terms that represent the asymptotic free wave, and a set of L^2 functions, while the SVP and the NVP trial functions are expansions containing only the L^2 terms. Three different sets of L^2 functions are used to examine the effect of changing the basis on the convergence characteristics of the three methods. We find that the rates of convergence for the Kohn, Schwinger, and Newton methods are strongly dependent on the nature of the potential and the basis set used. We also find that purely repulsive potentials are, in general, easier to converge than purely attractive potentials.

I. INTRODUCTION

There has recently been a resurgence of interest in variational methods for the calculation of S- or K-matrix elements in scattering problems,[1] including reactive collisions.[2] The variational principles that have been used in such calculations range from methods derived in the late 1940's, such as the Kohn variational principle (KVP)[3]—whose applications have been limited in the past due to the so-called Kohn anomalies[4]—and the Schwinger variational principle (SVP),[5] to more recent methods such as the Newton variational principle (NVP).[6] A number of additional variational functionals (stationary expressions) that are known today have been derived from, or are related to, these three variational principles.[1(f)] The formal relationships between these variational principles have been discussed by Takatsuka, Lucchese, and McKoy.[1(g)]

In the variational approach to the calculation of S-, T-, or K-matrix elements, one expands the scattering wave function or its amplitude density[7] in a set of basis functions. Extremization of the variational functional then leads to linear algebraic equations for the expansion coefficients. Variational methods are useful in this approach in that they improve the accuracy of the results obtained with a given number of basis functions, compared to the results of a direct solution of the integral or differential equations. This becomes an important consideration in multichannel reactive scattering problems, where the size of the basis required for an accurate solution is often the factor that limits the size of the problems that can be successfully handled, even by modern supercomputers.

In this paper, we present a comparative study of the three variational methods mentioned above. The motivation for the present study was provided by the following facts. Most previous comparisons of the various variational methods[1(c),1(f),8-12] have been conducted for potentials $V(r) = ce^{-r}$ ($c = \pm 1$) using the basis functions $|n\rangle = a_n r^n e^{-\alpha r}$. However, in the applications of variational methods to reactive scattering problems,[2] other, very different types of basis functions are usually employed. It is not clear whether the advantages or disadvantages of one variational principle, as revealed in the comparisons mentioned above, can be expected to carry over to different types of potentials and basis sets. Another, perhaps more subtle aspect of the earlier comparisons, is that trial functions for *different quantities* have often been used in the different methods. For example, in comparisons of the SVP and related methods to the NVP and related methods, often the *wave function* is expanded in terms of an L^2 basis in the former, and the *amplitude* density is expanded in the latter.[9,10] Even if the same set of L^2 functions are used in these expansions, *the quantities being expanded in the different methods are different.*

In the present work, we compare the SVP and the NVP wih an S-matrix version of the KVP recently developed by Zhang, Chu, and Miller[8] (hereafter refered to simply as the KVP). We study the convergence characteristics of the three methods by computing K-matrix elements for elastic scattering from nine one-dimensional potentials. In order to be consistent in these comparisons, we expand the same trial quantity, viz., the trial wave function, in each case. In the case of the KVP, we express the trial wave function as an expansion containing two non-L^2 terms that represent the asymptotic free wave, and a set of L^2 functions (see below). The derivation of the KVP is based on the Schrödinger (differential) equation, and hence the two non-L^2 terms are required in this case, to satisfy the boundary conditions. Derivations of both the SVP and the NVP, in contrast, make use of the Lippmann–Schwinger (integral) equation, and it is the Green function present in this equation that enforces the boundary conditions. In this sense, the presence of the Green function in the integral equation approach fulfills the role of the two non-L^2 terms in the KVP trial function. Therefore, we have chosen to express the trial functions used in the SVP

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and the NVP as expansions containing L^2 functions only. In order to study the effects of changing the basis set used to expand the trial wave function, we use three sets of L^2 functions in this study.

We present our results in terms of the percent error in K-matrix elements as a function of the number of basis functions, where the percent errors have been estimated with respect to exact results obtained by converged finite-difference calculations. We have used the KVP in exactly the same form as Zhang, Chu, and Miller[8] to compute the S-matrix elements which were then used to compute the K-matrix elements. In the case of the SVP and the NVP, we computed the T-matrix element, a quantity linearly related to the S-matrix element, and computed the K-matrix elements using the well-known relationship between them.

The remainder of this paper is organized as follows: in Sec. II, we present the variational functionals used in our calculations, provide details regarding the nine potentials and the three basis sets, and discuss the computational aspects of numerical integrations, and the evaluation of matrix elements. In Sec. III, we present and discuss the results of our comparisons. In Sec. IV, we summarize our work and make concluding remarks.

II. VARIATIONAL FUNCTIONALS, POTENTIALS, AND BASIS SETS

We compare the convergence characteristics of the three variational methods, the KVP, the SVP, and the NVP, by studying elastic scattering from nine one-dimensional potentials, using three different L^2 basis sets to expand the trial wave function in each method.

A. The Kohn variational principle

In this work, we use the S-matrix version of the KVP.[8] The stationary expression for the S-matrix element in this formulation is given by

$$S=\overline{S}+(i/\hbar)\langle\Psi(r)|(H-E)|\Psi(r)\rangle\,, \tag{1}$$

where

$$\Psi(r)=-u_0(r)+c_1u_1(r)+\sum_{n=2}^{N}c_nu_n(r)\,, \tag{2}$$

$$u_0(r)=f(r)\exp(-ikr)v^{-1/2}\,, \tag{2a}$$

$$u_1(r)=f(r)\exp(+ikr)v^{-1/2}\,, \tag{2b}$$

and where $f(r)$ is a damping factor, introduced to enforce the boundary condition $\Psi(0)=0$:

$$f(r)=[1.0-\exp(-\alpha r^m)]\,. \tag{2c}$$

In these equations, v is the asymptotic velocity, given by $v=\hbar k/\mu$. We adopt units in which $\hbar=1$, and $\hbar^2/2\mu=1$, so that $v=2k$, and $k=\sqrt{E}$, where E is, of course, the energy. The functions $\{u_n(r)\}$ for $n=2,...N$, constitute a set of L^2 functions. If $m=1$ in Eq. (2c), this expansion becomes identical to that of Zhang, Chu, and Miller.[8]

Substituting the expression for $\Psi(r)$ from Eq. (2) into Eq. (1), and extremizing the resulting expression with respect to the expansion coefficients $\{c_n\}$ leads to (in matrix notation)[8]

$$S=(i/\hbar)(\mathbf{M}_{0,0}-\mathbf{M}_0^t\mathbf{M}^{-1}\mathbf{M}_0)\,, \tag{3}$$

where

$$\mathbf{M}_{0,0}=\langle u_0|(H-E)|u_0\rangle\,,$$

$$(\mathbf{M}_0)_n=\langle u_n|(H-E)|u_0\rangle\,,$$

$$(\mathbf{M})_{n,n'}=\langle u_n|(H-E)|u_{n'}\rangle\,,$$

for $n,n'=1,...N$. Since the basis functions $u_0(r)$ and $u_1(r)$ in Eq. (2) are complex, the vectors and matrices above turn out to be complex. Adopting the convention that Miller and coworkers have found convenient, the functions in the bras are not complex conjugated unless explicitly shown. Solving Eq. (3) for S is, at this point, a straightforward operation. However, the matrix $\mathbf{M}$ whose inverse has to be found is complex, and having to invert a complex matrix becomes unattractive very rapidly, as the size of the matrix increases. This difficulty can be overcome by the application of the Löwdin–Feschbach partitioning identity to Eq. (3), which yields the following stationary expression for the S-matrix element[8]:

$$S=(B-C^2/B^*)\,, \tag{4}$$

where

$$B=\mathbf{M}_{0,0}-\mathbf{M}_0^t\mathbf{M}^{-1}\mathbf{M}_0\,,$$

$$C=\mathbf{M}_{1,0}-\mathbf{M}_1^t\mathbf{M}^{-1}\mathbf{M}_0\,,$$

and

$$(\mathbf{M}_1)_n=\langle u_n|(H-E)|u_1\rangle\,,$$

where the indices of the matrix $\mathbf{M}$ and the vectors $\mathbf{M}_0$ and $\mathbf{M}_1$ run from $n=2,...N$. This expression has the advantage that the matrix whose inverse has to be found is completely real, and involves only matrix elements of $(H-E)$ between square integrable functions. In the present work, the above expression is used to compute the S-matrix element, which is then used to compute the K-matrix element using the relationship

$$K=i(1-S)(1+S)^{-1}\,. \tag{5}$$

B. The Schwinger and Newton variational principles

In the case of elastic scattering, the Schwinger variational functional for the T-matrix element may be expressed as follows:

$$-kT=2\langle\phi|V|\Psi\rangle-\langle\Psi|V-VG^0V|\Psi\rangle\,, \tag{6}$$

where $|\phi\rangle=k^{-1/2}\sin(kr)$ is the free particle wave function in one dimension, and $G^0(r,r')$ is the kernel of the outgoing wave free particle Green function,

$$G^0(r,r')=-(1/k)\sin(kr_<)\exp(ikr_>)\,, \tag{7}$$

where $(r_<,r_>)$ are the lesser, and greater, respectively, of (r,r'). The scattering wave function $\Psi(r)$ is, of course, expressed as

$$\Psi(r)=\sum_{n=1}^{N}c_nu_n(r)\,, \tag{8}$$

where $\{u_n(r)\}$, $n=1,...,N$, constitute a set of L^2 functions.

We use the following expression of the Newton variational functional for the T-matrix element, given in terms of the wave function $\Psi(r)$:

$$-kT=K_B^I+2\langle\phi|VG^0V|\Psi\rangle-\langle\Psi|V(G^0-G^0VG^0)V|\Psi\rangle\,, \tag{9}$$

where K_B^I is given by $\langle\phi|V|\phi\rangle$, the first term in the Born expansion of the Lippmann–Schwinger equation. The scat-

tering wave function $\Psi(r)$ is of course, expressed as in Eq. (8). The above expressions are used to compute the T-matrix element using the SVP and the NVP, respectively, and the results used to compute the K-matrix elements, using the relationship

$$K = T(1 + iT)^{-1}. \tag{10}$$

In many applications of the NVP, the amplitude density $V(r)\Psi(r)$ has been expanded directly in a discrete set of L^2 functions.[9,10,13] However, since we wish to make our comparisons of the three variational principles based on the trial *wave function*, we use the above formulation of the Newton variational functional, given explicitly in terms of the scattering wave function $\Psi(r)$.

C. Potentials and basis sets

We conduct our investigations using nine different interaction potentials $V(r)$. These are listed in Table I, and labeled by numbers and letters such as 1A, 2B, and so on, for convenience. All of the potentials used are representative of the types of potentials commonly encountered in systems of interest to chemical physicists, with the possible exception of the potential used in cases 5A and 5B. It should be noted that these two cases involve the same potential, which is constructed by adding to the Morse potential 2B, a barrier that reaches its maximum at values of r where one normally expects to find the maxima of centrifugal barriers. However, compared to centrifugal barriers, the present barrier is vastly exaggerated in terms of its height [the maximum of the barrier corresponds to $V(r) = 3.21$, at $r = 4.28$], and vastly diminished in terms of the range of its influence. For this potential, the case 5A corresponds to elastic scattering at energy $E = 2.0$, which is below the maximum of the barrier, and 5B, to elastic scattering at $E = 10.0$, which is well above the barrier.

We use three L^2 basis sets in our investigations. These are also listed in Table I. Basis 1 is the distributed Gaussian basis (DGB)[14] which has been used in many applications of variational methods to scattering problems.[2] Since the Gaussians do not satisfy the boundary condition of vanishing at $r = 0$, we have multiplied them with the damping function of Eq. (2c). Basis 2, as mentioned in Sec. I, has been used in previous comparisons of variational methods,[1(c),1(f),8-12] using potentials 1A and 1B. We include these in our calculations so that connection with work that has been already published can be made. Basis 3 consists of eigenfunctions of the one-dimensional box problem, where the "inside" of the box is the interval $[0, R_{\max}]$.[15]

D. Calculations

We adopt the following convention in referring to our calculations and results: we refer to the potentials and basis sets using the labels given to them in Table I. So, for example, 2A1 refers to calculations on potential 2A, i.e., the Morse potential with $D_e = 1.0$ and $r_e = 1.0$, using basis 1, i.e., the distributed Gaussian basis, while 4B3, by the same convention, refers to calculations on the repulsive Yukawa potential with the one-dimensional box basis. For the damping function in Eq. (2c), we have set $\alpha = 1$, and used two values for m, i.e., $m = 1$ and 4. The results reported in this section are for those values of m for which we obtained faster convergence of the K-matrix elements. To check the correctness of our calculations, we have reproduced the exact K-matrix elements reported by Staszewska and Truhlar for potential 1A,[10] using the three basis sets, for each of the three variational principles used here.

TABLE I. The potentials and basis sets used in this work.

(A) Potentials

Label	$V(r)$	Parameter values
1A	$-\exp(-\alpha r)$	$\alpha = 1.0$
1B	$+\exp(-\alpha r)$	$\alpha = 1.0$
2A	$D_e[1-\exp\{-\beta(r-r_e)\}]^2 - D_e$	$D_e = 1.0,\ r_e = 1.0, \beta = 1.5$
2B	$D_e[1-\exp\{-\beta(r-r_e)\}]^2 - D_e$	$D_e = 10.0,\ r_e = 2.0,\ \beta = 1.5$
3A	$A\exp(-\alpha r)$	$A = -10.0, \alpha = 1.0$
3B	$A\exp(-\alpha r)$	$A = 10.0, \alpha = 1.0$
4A	$A\exp(-\alpha r)/r$	$A = -5.0, \alpha = 1.0$
4B	$A\exp(-\alpha r)/r$	$A = 5.0, \alpha = 1.0$
5[a]	$2B + A\exp[-(r-r_e)^2/2]$	$A = 4.0, r_e = 4.0$

(B) Basis sets

Label	Function	Remarks
1	$\lvert u_n\rangle = \exp[-\sigma_n(r-r_n)^2]$	$\sigma_n = [c/(r_{n+1} - r_n)]^2;\ c = 0.60$
2	$\lvert u_n\rangle = r^n \exp(-\alpha r)$	$\alpha = 1.0$
3	$\lvert u_n\rangle = \sin[n\pi r/R_{\max}]$	$n = 1,2,\ldots,(N-1)$.

$R_{\max} = 20$ for the results in Tables II, III, and one column of IV(A). Except for these cases and the other two columns of Table IV(A), $R_{\max} = 10$.

[a] The cases 5A and 5B use the same potential, but different energies. Case 5A corresponds to elastic scattering at $E = 2.0$, and case 5B, to that at $E = 10.0$.

All integrations are done numerically, using various high-order Newton–Cotes algorithms. However, the evaluation of matrix elements involving quantities such as G^0VG^0 [see Eq. (9)] by integrating once over each Green function is known to be very inaccurate, unless very small step sizes are used. To avoid this difficulty, we evalute these matrix elements by a method that is very similar in spirit to that of the half-integrated Green function approach of Schwenke *et al.*[16] In the present approach, we explicitly evaluate the half-integrated quantity $g_n(r)$ for the basis function $|u_n\rangle$, as follows:

$$g_n(r) = \int_0^\infty dr' G^0(r,r') u_n(r') , \tag{11}$$

so that matrix elements such as $\langle u_m|G^0VG^0|u_n\rangle$ can now be expressed as

$$\langle u_m|G^0VG^0|u_n\rangle = \langle g_m|V|g_n\rangle .$$

Apart from increasing the accuracy of these matrix elements for a given integration step size, the above approach also has the following important advantage: it reduces the effort involved in applying the NVP to a given problem to very nearly the same as that of applying the SVP, by eliminating the need to integrate a second time over the Green function $G^0(r,r')$.

In the following section, we present our results in the form of tables of percent error in K-matrix elements for a given number of variational parameters N, or figures in which the percent error is plotted against N. For many potentials, the percent error in K-matrix elements are extremely large for small basis sizes, and often the errors oscillate wildly until the basis size reaches a certain minimum. This is to be expected, since in general, none of the variational methods used for scattering calculations are true maximum or minimum principles.[17] The approach to the converged result, therefore, need not be monotonic. In order to show this nonmonotonic convergence, rather than take the absolute values of percent errors, we have chosen to retain their signs in the tables and the figures. In the figures, except for Figs. 4(a) and 4(b), we set the top and bottom limits of the ordinate to $+1\%$ and -1%, respectively, so that the scale of this axis would not obscure the behavior as convergence to the exact results are reached. In Figs. 4(a) and 4(b), the top and bottom limits of the ordinate are $+10\%$ and -10%, respectively.

III. RESULTS AND DISCUSSION

Before we discuss the results of our calculations, it is useful to establish some terminology. When we say that a certain method shows "faster convergence," we mean that it is the first to achieve a *stable* error lower than 0.1%, for a given number of basis functions. We also say that the method that shows faster convergence has a higher "rate of convergence." The choice of the cutoff point for determining the convergence as 0.1% is of course, arbitrary, but is based on the following consideration. In most applications, an accuracy of 0.1% is quite sufficient, and in many cases, it may prove to be extraordinarily expensive to reduce the error beyond this value. It should be noted that the column N in the tables refer to the number of variational parameters (expansion coefficients) in the trial wave function [Eq. (1)], and, for the KVP, is always one less than the actual number of terms in the expansion of $\Psi(r)$.

Since potentials 1A and 1B have been used in many previous investigations, we examine the results for these potentials first. The percent errors in K-matrix elements for 1A, using the three basis sets are listed in Table II. For basis 1(1A1), the NVP yields the fastest convergence, reaching a stable error of 0.1% with a single variational parameter (basis function), while the SVP reaches the same limit with $N \cong 7$. The results for the KVP converge at a much slower rate, and convergence to within 0.1% of the exact result is achieved at $N \cong 35$. Basis 2, as we mentioned in the Introduction, has been used in most of the previous comparisons of variational methods. From Table II, we see that the results using the three variational methods with basis 1(1A2) show that the KVP and NVP converge at similar rates, the latter being slightly faster. The SVP is the slowest to converge, reaching the 0.1% threshold for $N \cong 7$. Compared to the relatively poor performance of the KVP using basis 1, basis 2 indeed seems ideally suited for this method. Turning to the results for basis 3(1A3), we see that the pattern that we already encountered in the case of basis 1 is repeated. The convergence of the KVP results, while slower than those of the SVP and the NVP, are nevertheless, faster than that of the KVP results using basis 1(1A1). The results for potential 1B, presented in Table III, follow the general trends that we see in the case of 1A. For basis 1 and 3, the convergence of the KVP is much poorer for this potential than for 1A, while the other two methods show no significant difference in the rate of convergence. But here again, basis 2 seems to be the most efficient in obtaining fast convergence to the exact result, for the KVP.

In a recent paper, Zhang, Chu, and Miller[8] have claimed that the S-matrix version of the KVP converges much faster than the SVP or the NVP. This claim was supported by the results of using the KVP and basis 2, to compute S-matrix elements for potentials 1A and 1B. The percent errors in the K-matrix elements [evaluated from the S-matrix elements—see Eq. (5)] were then compared with the previously published results of Staszewska and Truhlar.[9,18] From that comparison, the S-matrix version of the KVP appeared to converge faster than the other two methods, for cases 1A2 and 1B2. However, it is important to note that the quantity expanded in the L^2 basis as the NVP trial function in Ref. 9, is the *amplitude density* $V(r)\Psi(r)$. The comparison of the KVP to the SVP and the NVP that is presented in Ref. 8, is therefore, based on using different trial quantities in the different methods. Using the *same* trial quantity, namely $\Psi(rt)$, in all three variational methods, we see here that the conclusions are somewhat different. We find that the performance of the KVP is, at best, superior to that of the SVP but not the NVP, and even then, only for basis 2. For the other two basis sets, the convergence of the KVP results are much slower than those from the SVP and the NVP.

From the results presented in Tables II and III, basis 2 is the most reliable basis for expanding scattering wave functions, in the sense that all three methods, and especially the KVP, converge rapidly if this basis is used. However, the use

TABLE II. Percent error in K-matrix elements for case 1A. $m = 1$, $E = 0.5$, $R_{max} = 20$, $K_{exact} = 0.541\,951$.

	1A1			1A2			1A3		
N	KVP	SVP	NVP	KVP	SVP	NVP	KVP	SVP	NVP
1	− 5.7053	− 22.4057	− 0.0808	− 5.7053	− 52.9557	− 1.2501	− 5.7053	− 49.3482	− 2.7857
3	− 2.6526	− 3.0102	− 0.0325	− 0.1707	− 1.4586	− 0.0419	− 9.2176	− 6.2314	− 0.0528
5	− 2.0210	− 0.2024	− 0.0004	− 0.0007	− 0.4823	0.0000	− 7.8939	− 0.4467	− 0.0042
7	− 0.7621	− 0.0240	0.0000	0.0000	− 0.0037	0.0000	− 3.9046	− 0.1041	− 0.0007
9	− 0.4155	− 0.0077	0.0000	0.0000	− 0.0013	0.0000	− 1.9496	− 0.0292	− 0.0002
11	− 0.3039	− 0.0026	0.0000	0.0000	0.0000	0.0000	− 1.0781	− 0.0092	0.0000
13	− 0.2487	− 0.0007	0.0000	0.0000	0.0000	0.0000	− 0.6521	− 0.0033	0.0000
15	− 0.2142	0.0000	0.0000	0.0000	0.0000	0.0000	− 0.4225	− 0.0013	0.0000
17	− 0.1899	0.0000	0.0000	0.0000	0.0000	0.0000	− 0.2888	− 0.0006	0.0000
19	− 0.1714	− 0.0002	0.0000	0.0000	0.0000	0.0000	− 0.2056	− 0.0002	0.0000
21	− 0.1565	− 0.0004	0.0000	0.0000	0.0000	0.0000	− 0.1511	0.0000	0.0000
23	− 0.1441	− 0.0006	0.0000	0.0000	0.0000	0.0000	− 0.1142	0.0000	0.0000
25	− 0.1336	− 0.0007	0.0000	0.0000	0.0000	0.0000	− 0.0882	0.0000	0.0000
27	− 0.1246	− 0.0009	0.0000	0.0000	0.0000	0.0000	− 0.0694	0.0000	0.0000
29	− 0.1168	− 0.0011	0.0000	0.0000	0.0000	0.0000	− 0.0554	0.0000	0.0000
31	− 0.1098	− 0.0011	0.0000	0.0000	0.0000	0.0000	− 0.0448	0.0000	0.0000
33	− 0.1037	− 0.0011	0.0000	0.0000	0.0000	0.0000	− 0.0367	0.0000	0.0000
35	− 0.0982	− 0.0011	0.0000	0.0000	0.0000	0.0000	− 0.0304	0.0000	0.0000
37	− 0.0932	− 0.0011	0.0000	0.0000	0.0000	0.0000	− 0.0253	0.0000	0.0000
39	− 0.0886	− 0.0011	0.0000	0.0000	0.0000	0.0000	− 0.0212	0.0000	0.0000

of this basis could lead to certain problems in most potentials, especially for the KVP. The reason for this becomes clear if one examines the nature of these basis functions. The functions $|n\rangle = a_n r^n \exp(-\alpha r)$ grow rapidly with r as n increases, and are only slowly damped by the exponential term for the value of $\alpha = 1.0$ used here. For small values of $n (n \leqslant 5)$, the functions are damped quickly (i.e., within $r \leqslant 20$), and the matrix elements involving them can be evaluated numerically using a reasonably small number ($\cong 1000$) of integration steps. For potentials such as 1A and 1B, where only a few functions are needed for convergence, this basis therefore yields good results. However, if a fairly large number of functions are necessary for convergence, the upper limit of integration has to be moved "out" considerably before the matrix elements can be accurately evaluated. In such cases, the number of integration steps required to accurately evaluate the integrals over such large ranges of r, renders the use of this basis highly impractical.

In order to illustrate these ideas, we present in Table IV, the results for potential 2A, and basis 2 in Table IV (2A2). In this case, the SVP and the NVP results do converge quickly. The K-matrix elements obtained by the application of the KVP not only converge slower than those from the other two methods, but as Table IV indicates, they converge to the

TABLE III. Percent error in K-matrix elements for case 1B. $m = 1$, $E = 0.5$, $R_{max} = 20$, $K_{exact} = -0.452\,247$.

	1B1			1B2			1B3		
N	KVP	SVP	NVP	KVP	SVP	NVP	KVP	SVP	NVP
1	− 2.2861	− 8.8602	0.3383	− 2.2861	− 31.6951	2.5895	− 2.2861	− 26.7993	− 0.2306
3	8.7600	− 2.8860	− 0.0004	0.4429	− 2.6114	− 0.0033	45.9846	− 0.4458	0.0117
5	10.6185	− 0.0402	0.0004	0.0018	− 0.1444	0.0011	42.8929	− 0.1802	0.0011
7	4.5360	− 0.0064	0.0000	0.0000	− 0.0336	0.0000	21.2010	− 0.0292	0.0002
9	2.4783	− 0.0013	0.0000	0.0000	− 0.0004	0.0000	10.6314	− 0.0069	0.0000
11	1.7393	− 0.0007	0.0000	0.0000	0.0000	0.0000	5.9142	− 0.0020	0.0000
13	1.3678	− 0.0004	0.0000	0.0000	0.0000	0.0000	3.5912	− 0.0007	0.0000
15	1.1425	− 0.0004	0.0000	0.0000	0.0000	0.0000	2.3319	− 0.0002	0.0000
17	0.9891	− 0.0004	0.0000	0.0000	0.0000	0.0000	1.5947	− 0.0002	0.0000
19	0.8758	− 0.0004	0.0000	0.0000	0.0000	0.0000	1.1359	0.0000	0.0000
21	0.7878	− 0.0004	0.0000	0.0000	0.0000	0.0000	0.8360	0.0000	0.0000
23	0.7171	− 0.0004	0.0000	0.0000	0.0000	0.0000	0.6320	0.0000	0.0000
25	0.6583	− 0.0004	0.0000	0.0000	0.0000	0.0000	0.4882	0.0000	0.0000
27	0.6087	− 0.0004	0.0000	0.0000	0.0000	0.0000	0.3843	0.0000	0.0000
29	0.5661	− 0.0004	0.0000	0.0000	0.0000	0.0000	0.3074	0.0000	0.0000
31	0.5291	− 0.0004	0.0000	0.0000	0.0000	0.0000	0.2490	0.0000	0.0000
33	0.4969	− 0.0004	0.0000	0.0000	0.0000	0.0000	0.2041	0.0000	0.0000
35	0.4681	− 0.0004	0.0000	0.0000	0.0000	0.0000	0.1689	0.0000	0.0000
37	0.4427	− 0.0004	0.0000	0.0000	0.0000	0.0000	0.1411	0.0000	0.0000
39	0.4197	− 0.0004	0.0000	0.0000	0.0000	0.0000	0.1185	0.0000	0.0000

wrong result! The convergence to the wrong result is the result of not moving the upper limit of integration out far enough. The results obtained from the KVP using basis 2 and setting $R_{max} = 20$, 40, and 80, are shown in Table IV(A). It is clear that increasing R_{max} certainly decreases the KVP percent error, for this basis. However, the KVP rate of convergence is nevertheless, only comparable to that of the SVP, and slower than that of the NVP. For example, for $R_{max} = 20$, the KVP requires $N \geqslant 9$ to yield a stable error $\leqslant 0.1\%$ [Table IV(A)], while for the same value of R_{max}, the SVP and NVP (not shown) require 9 and 3 variational parameters, respectively, to reach the same error limit. *Since this is clearly a problem of the basis more than that of the variational principles, we have chosen to leave out the results of using this basis for the other potentials.*

Returning to Table IV, we note that for the other two basis sets, the NVP shows the fastest convergence, followed by the SVP. The convergence of the KVP is slow compared to the other two variational methods for this potential, especially when basis 1 is used. Also, in Table IV, we notice that the SVP and the NVP results for case 2A2 converge even when R_{max} is only 10. The explanation for this can be found in the form of the variational functionals for the two methods. From Eqs. (6) and (9), respectively, we see that in the SVP and the NVP functionals, the interaction potential $V(r)$ explicitly appears in the matrix elements that have to be evaluated. Since the potential vanishes as r increases, in these cases we get additional help from $V(r)$ in converging the integrals.

The remaining potentials can be broadly classified into two categories: (1) those that have both a repulsive and an attractive part [the Morse potential 2B, and its modified version, 5], and (2) potentials that are either purely attractive [3A,4A] or purely repulsive [3B,4B]. We present the

TABLE IV. Percent error in K-matrix elements for case 2A. $m = 1$, $E = 2.0$, $R_{max} = 10$, $K_{exact} = 0.507\,756$.
(A) Percent error in K-matrix elements for case 2A2, computed using the KVP, for different values of R_{max}.

	2A1			2A2			2A3		
N	KVP	SVP	NVP	KVP	SVP	NVP	KVP	SVP	NVP
1	−3.9740	−71.9188	−7.4455	−3.9740	−86.2184	−2.4529	−3.9740	−82.9826	−11.1345
3	3.4318	18.9215	−1.9716	−5.6433	−20.5752	0.0839	−2.6574	−21.3169	−0.2107
5	2.6814	−9.7283	−0.0583	−0.5428	−32.5207	0.0004	−5.0022	1.0200	−0.1475
7	−1.6937	−0.5455	−0.0047	−1.3006	−0.0390	−0.0004	−3.5673	2.6552	−0.0461
9	−0.9757	−0.0731	−0.0006	−1.2967	0.0073	0.0000	−0.3992	−1.3201	−0.0089
11	−0.3911	−0.0102	−0.0002	−1.2967	0.0102	0.0000	−0.2572	−0.1893	−0.0018
13	−0.2194	−0.0006	0.0000	−1.2961	0.0148	0.0000	−0.2220	−0.0418	−0.0004
15	−0.2470	0.0012	0.0000	−1.2951	−0.0012	0.0000	−0.1794	−0.0091	−0.0002
17	−0.2858	0.0020	0.0000	−1.2947	−0.0035	0.0000	−0.1676	−0.0012	−0.0002
19	−0.2966	0.0030	0.0000	−1.2945	−0.0008	0.0000	−0.1672	0.0008	0.0000
21	−0.2868	0.0047	0.0000	−1.2945	0.0006	0.0000	−0.1637	0.0010	0.0000
23	−0.2675	0.0102	0.0000	−1.2945	0.0032	0.0000	−0.1542	0.0010	0.0000
25	−0.2454	−0.0213	0.0000	−1.2945	−0.0008	0.0000	−0.1410	0.0014	0.0000
27	−0.2241	−0.0033	0.0000	−1.2945	0.0201	0.0000	−0.1262	−0.0091	0.0000
29	−0.2044	−0.0010	0.0000	−1.2945	−0.0213	0.0000	−0.1117	−0.0004	0.0000
31	−0.1871	0.0000	0.0000	−1.2945	0.0165	−0.0000	−0.0981	−0.0002	0.0000
33	−0.1717	0.0006	0.0000	−1.2945	0.0144	0.0000	−0.0859	0.0000	0.0000
35	−0.1583	0.0012	0.0000	−1.2945	0.0043	0.0000	−0.0750	0.0000	0.0000
37	−0.1465	0.0014	0.0000	−1.2945	0.0014	0.0000	−0.0656	0.0000	0.0000
39	−0.1361	0.0018	0.0000	−1.2945	0.0205	0.0000	−0.0573	0.0000	0.0000

(A)	R_{max}		
N	20.0	40.0	80.0
1	−3.9942	−3.9942	−3.9942
3	−5.6523	−5.6523	−5.6523
5	−0.5359	−0.5359	−0.5359
7	−1.2228	−1.2228	−1.2228
9	−0.0654	−0.0668	−0.0668
11	0.0160	−0.0063	−0.0063
13	0.0315	−0.0047	−0.0047
15	0.0226	−0.0018	−0.0018
17	0.0226	−0.0020	−0.0020
19	0.0242	−0.0016	−0.0016
21	0.0242	−0.0014	−0.0014
23	0.0240	−0.0014	−0.0010
25	0.0238	−0.0014	−0.0010
27	0.0236	−0.0012	−0.0010
29	0.0236	−0.0012	0.0000
31	0.0236	−0.0014	−0.0008
33	0.0236	−0.0014	−0.0006

TABLE V. Exact K-matrix elements for the cases presented in the figures.

Label	Energy	m^a	R_{max}	K_{exact}
2B	10.0	4	10.0	2.311 902
3A	5.0	1	10.0	− 3.450 152
3B	5.0	1	10.0	1.321 414
4A	5.0	1	10.0	− 2.980 829
4B	5.0	1	10.0	− 3.012 463
5A	2.0	4	10.0	− 0.925 001
5B	10.0	4	10.0	− 0.443 471

[a] See Eq. (2c).

results for these cases in the form of figures, where we plot the percent error in K-matrix elements against the number of variational parameters N. These plots make it easy to see the relationships between the rates of convergences of the three variational principles in each case. The details of the calculations, such as the energy, the value of the parameter m in Eq. (2c), and the exact value of the K-matrix element, are summarized in Table V.

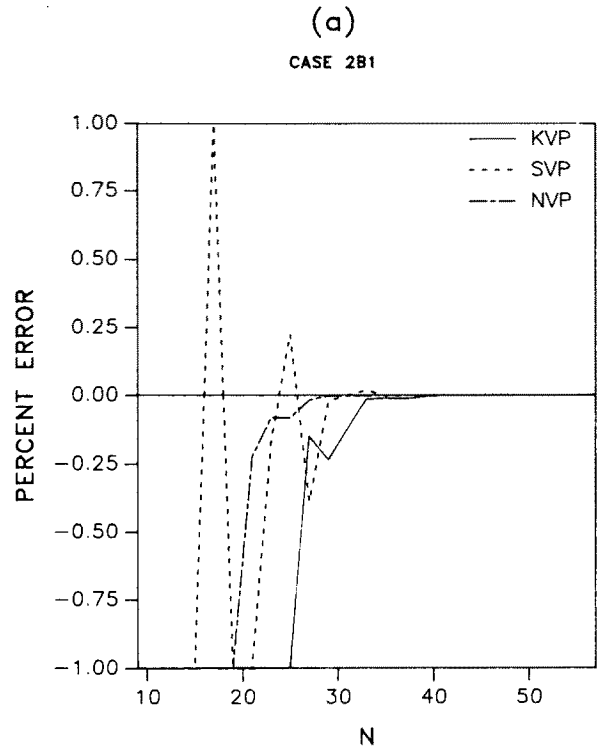
A. Category 1

We plot in Fig. 1(a), the percent error in K-matrix elements for case 2B1. For this case, the NVP shows the fastest rate of convergence, reaching a stable percent error $\leqslant 0.1\%$ for $N \geqslant 25$. The SVP results converge at a slower rate, and the KVP is the slowest of the three. The latter two methods converge to within 0.1% of the exact result with $N \geqslant 31$ and 33, respectively. The effect of changing the basis for the same potential is clearly seen by comparing this figure with Fig. 1(b), where we plot the results for case 2B3. It is seen that using basis 3 (one-dimensional box eigenfunctions), the SVP achieves slightly faster convergence for this potential than when basis 1 was used, requiring only 27 variational parameters to yield a K-matrix element that has converged to within 0.1% of the exact result. The rates of convergence for the KVP and the NVP is in contrast, slower than that in Fig. 1(a). The KVP now requires $N \geqslant 39$ to reach the 0.1% threshold, while the NVP requires $N \geqslant 27$, the same as the SVP!

For case 5A1, represented in Fig. 2, we see that the NVP converges to the 0.1% threshold at $N \cong 23$, while the SVP and the KVP require about $N \cong 25$ and 27, respectively, to reach the same threshold. For case 5A3 (not shown) the NVP ($N \cong 21$) is once again superior to the SVP ($N \cong 23$) and the KVP ($N \cong 31$). The rates of convergence of the NVP and the SVP seem to be relatively insensitive to the change of basis for this potential, at $E = 2.0$. For cases 5B1 and 5B3, we summarize the relative rates of convergence as follows: for case 5B1, NVP ($N \cong 25$) > SVP($N \cong 31$) = KVP ($N \cong 33$); and for case 5B3, NVP ($N \cong 27$) > SVP ($N \cong 29$) > KVP ($N \cong 37$). Once again, these numbers indicate that basis 3 causes the NVP and the KVP rates of convergence to decrease, with the KVP being the most sensitive to the change from basis 1 to basis 3.

B. Category 2

Category 2, as defined above, consists of cases where the interaction potentials used are either purely attractive



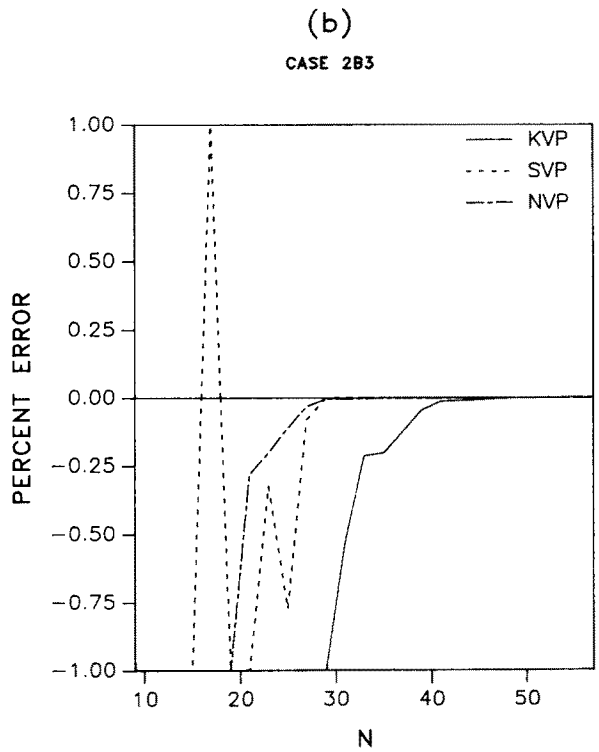


FIG. 1. Comparison of the results of using two different basis sets on the same potential: (a) the percent error in K-matrix elements vs the total number of basis functions, for case 2B1, i.e., potential 2B, basis 1; (b) same as (a), but for case 2B3.

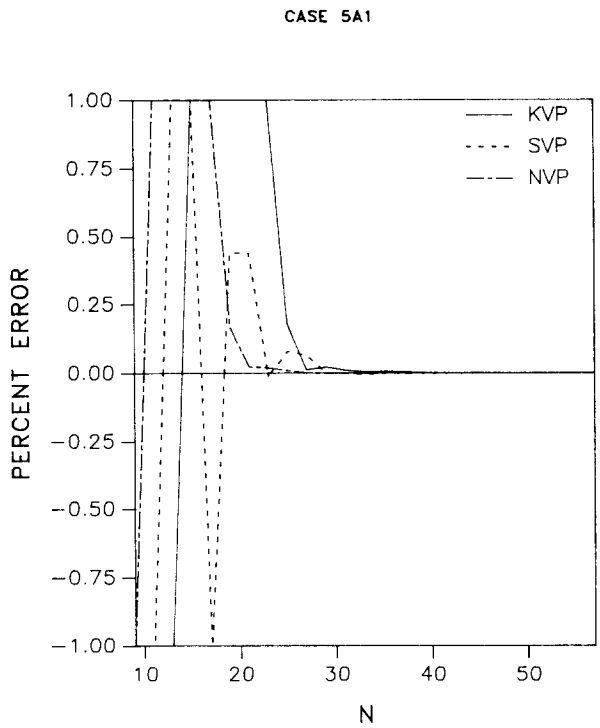
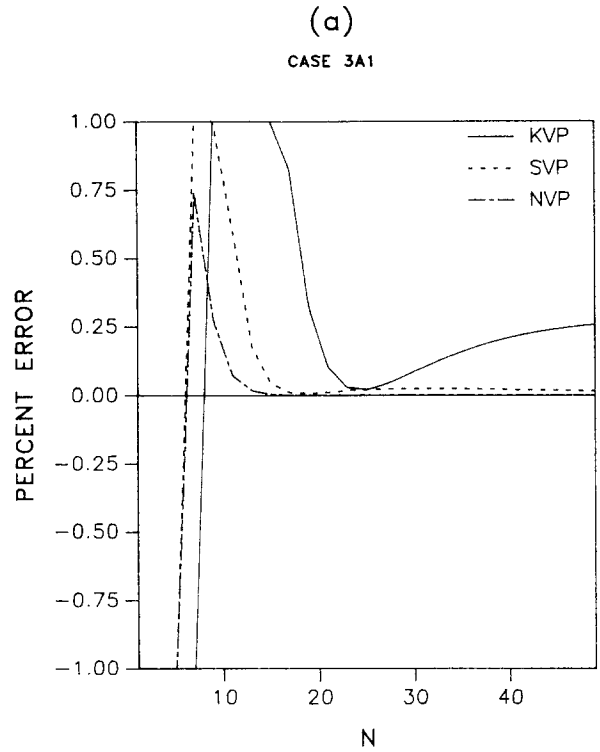


FIG. 2. The percent error in K-matrix elements vs total number of basis functions, for case 5A1.



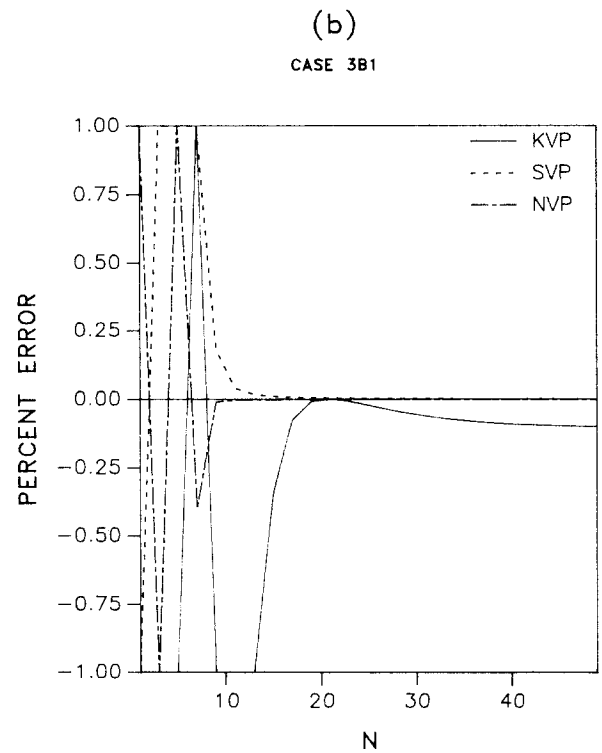


FIG. 3. Same as Fig. 2, but for the following cases: (a) 3A1; (b) 3A3.

[$V(r) \leqslant 0$, for all r]—potentials 3A, 4A—or purely repulsive [$V(r) \geqslant 0$ for all r]—potentials 3B and 4B. We represent the results for these potentials in Figs. 3 and 4.

An examination of Figs. 3(a) and 3(b) for cases 3A1 and 3B1 reveals the interesting fact that the KVP curves seem to diverge to the wrong result, reminiscent of case 2A2 (Table IV). However, for each of these cases, the percent error decreases for sufficiently large N. For case 3A1, the percent error continues to increase beyond the limit shown in Fig. 3(a), to reach 0.27% between $N = 58$ and $N = 70$, but then decreases to 0.25% at $N = 80$ and continues to decrease beyond this point. The KVP result for case 3B1 follows a similar pattern, but the percent error never exceed 0.10%. We provide an explanation for this behavior, below. The KVP results using basis 3 show none of the peculiarities mentioned above. As a consequence, for the potential 3A, basis 3 *accelerates* the convergence of the KVP compared to basis 1, in direct contrast to the behavior found in the cases of category 1 potentials. The SVP and the NVP seem to be relatively insensitive to changes in the basis, especially in the case of potential 3B. However, a careful comparison shows that both the SVP and the NVP converge *slower* if basis 3, rather than basis 1, is used.

Turning to Fig. 4, we see that the patterns seen in Fig. 3 are present here also. It is obvious that the KVP is extremely slow to converge for cases 4A1 [Fig. 4(a)] and 4A3 [Fig. 4(b)], the two cases dealing with the attractive Yukawa potential. Going beyond the range of N shown in the figures, we have found that, for these cases, the percent errors in the

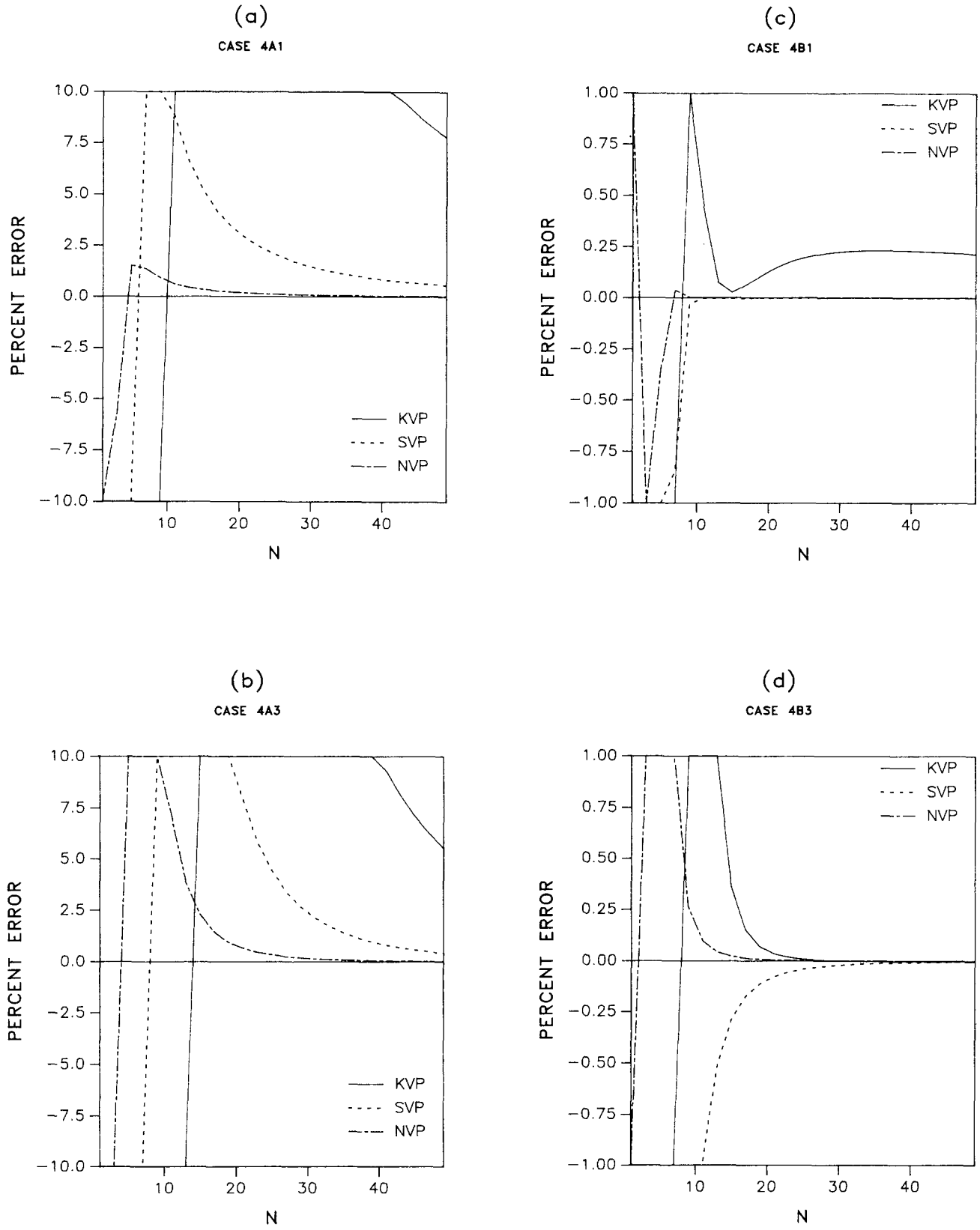


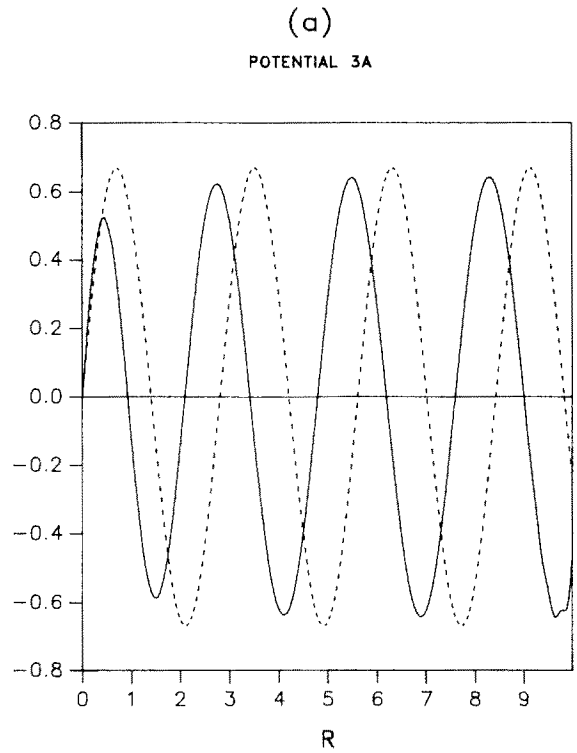
FIG. 4. Same as Fig. 3, but for the following cases: (a) 4A1; (b) 4A3; (c) 4B1; (d) 4B3.

KVP results decrease extremely slowly, with basis 3 converging slightly faster than basis 1. At $N = 160$, the case 4A1 KVP result is in error by 0.76%, whereas the case 4A3 KVP result is in error by 0.16%. This indicates once again, that basis 3 causes the KVP to converge faster, compared to basis 1. Examining the SVP and the NVP curves in Figs. 4(a) and 4(b), we also see that the opposite is true for these two methods—basis 3 converges slower than basis 1, similar to the behavior found in potential 3A. The SVP, while converging faster than the KVP for the two cases, is slower than the NVP to reach the 0.1% threshold, for both case 4A1 and case 4A3. The KVP results for case 4B1 [Fig. 4(c)] appear to converge to the wrong result, reminiscent of case 2A2 (Table IV) and of 3A1 [Fig. 3(a)] and 3B1 [Fig. 3(b)]. However, for this case also, the percent error decreases for sufficiently large N, and reaches the 0.1% threshold at $N = 112$.

The following general conclusions emerge from these comparisons: for potentials of category 1, the KVP results converge at rates that, while lower than those of the SVP and the NVP, compare favorably with them. However, for potentials of category 2, the KVP is a reliable method only for purely repulsive potentials. The KVP is the most sensitive of the three methods to the nature of the basis used to expand the trial function. Going from basis 1 to basis 3 causes the KVP rate of convergence to decrease for potentials of category 1, while it increases for potentials of category 2. Unless the upper integration limit $R_{\max}$ is carefully chosen, the use of basis 2 in the KVP can lead to completely wrong results. The SVP and the NVP are less sensitive to changes in the nature of the basis functions, but the change in the rates of convergence of these two methods generally decrease when basis 3 is used, as opposed to basis 1, for potentials of both category 1 and 2. Due to the explicit presence of the asymptotically vanishing potential $V(r)$ in the Schwinger and Newton variational functionals, the convergence of the SVP and the NVP when basis 2 is used, appears to be less crucially dependent on the choice of $R_{\max}$, from the results listed in Table IV. Among the three methods, the NVP achieves the fastest convergence in all the potentials, regardless of the nature of the basis used.

Below, we attempt to explain the tendency of the KVP curves to diverge, after reaching a fairly small percent error in the K-matrix element, that we have noticed in Figs. 3(a), 3(b), and 4(c). In each of these cases, L^2 terms in the trial wave function of Eq. (1) is represented by a set of Gaussians. The fact that the apparent tendency to converge to the wrong result is completely absent in the cases where basis 3 is used [cases 3A3, 3B3, and 4B3], indicates that this behavior could have its source in some of the characteristics of basis 1. The Gaussian basis used in this work is defined in Table I. The spacings between the centers of the Gaussians are determined by the condition that they be equally spaced in the interval $[0, R_{\max}]$. The fractional overlap between the Gaussians are kept constant as N is increased, which means that each Gaussian becomes "thinner" with increasing N.

In Fig. 5(a), we present, as a solid line, the real part of the wave function $\Psi(r)$ for case 3A, computed by the SVP, using 80 basis 3 functions. Except for the slight "kink" near



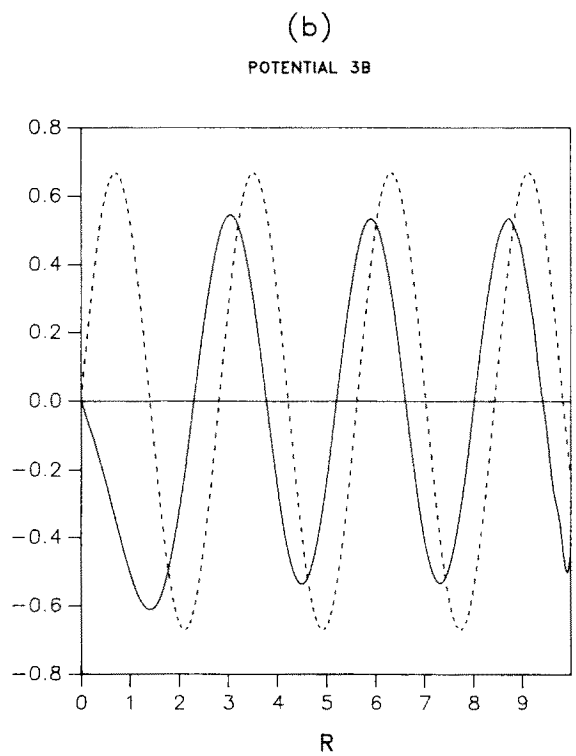


FIG. 5. The scattering wave function $\Psi(r)$ (solid line) and the asymptotic free wave $|\phi\rangle$ (dashed line) at energy $E = k^2 = 5.0$, for (a) potential 3A, (b) potential 3B.

$r = 9.8$, this wave function is well converged. To establish its relationship to the asymptotic free wave, we have also plotted, as a dashed line, the function $|\phi\rangle = k^{-1/2}\sin(kr)$. We note that the terms $u_0(r)$ and $u_1(r)$ in the expansion of $\Psi(r)$ have imaginary parts $[\sin(kr)]$ with the same phase as $|\phi\rangle$, and real parts $[\cos(kr)]$ that are out of phase with them by exactly $\pi/2$. The KVP is now entrusted with the task of building, from the functions $u_0(r)$ and $u_1(r)$, and a set of Gaussians, the function $\Psi(r)$. From Fig. 5(a), we see that the first maximum of $\Psi(r)$ occurs at $r \cong 0.40$, whereas the first maximum in $|\phi\rangle$ occurs at $r = 0.702$. It is reasonable to expect, under these circumstances, that a Gaussian centered at $r \cong 0.4$ would be very helpful in constructing the curve $\Psi(r)$ in this region. The requirement that the Gaussians be equally spaced, implies that if a Gaussian is placed at $r = 0.4$, there would be Gaussian centers at $r = 0.8$, 1.2, 1.6, and so on. Examining the $\Psi(r)$ curve in Fig. 5(a), we see that such an arrangement of Gaussians would, in fact, be quite satisfactory. The Gaussians centered at $r = 1.2$, 2.8, etc., would contribute to $\Psi(r)$ in significant ways, while those at $r = 2.0$, 3.2, etc., would serve to either modify the oscillations due to $u_0(r)$ and $u_1(r)$, or, if that proves to be unnecessary, be "turned off" ($c_n \cong 0$) by the variational method.

The important point to note above, is that the above distribution of Gaussians corresponds to approximately 25 equally spaced Gaussians between $r = 0$ and $r = R_{\max} = 10$, or in terms of the KVP variational parameters, to $N \cong 26$. Examining Fig. 3(a) reveals that the KVP curve does reach a minimum error in the range $N = 24$ to $N = 26$. As N increases beyond this value, the centers of the Gaussians are shifted away from the presumably satisfactory arrangement that was available at $N \cong 26$. More critical perhaps, is the fact that the Gaussians now become progressively "thinner". This appears to be responsible for the *increase* in the KVP percent error as N increases. As N reaches very large values (beyond $N = 80$), we obtain a dense array of very narrow Gaussians in the interval $[0, R_{\max}]$. The situation is now analogous to solving for $\Psi(r)$ on a fine grid,[19] and once again, the errors decrease.

In Fig. 5(b), we present the converged wave function $\Psi(r)$ (solid line) for case 3B, and also the asymptotic free wave $|\phi\rangle$ (dashed line). An analysis similar to the one presented above for Fig. 5(a), would reveal that $N \cong 21$ provides an arrangement of Gaussians that seems to be satisfactory for this case. As Fig. 3(b) reveals, the percent error in the KVP results do reach a minimum in the vinicity of $N \cong 21$. The situation in the case of Fig. 4(c) is analogous to these cases.

Why are the convergence characteristics of the SVP and the NVP relatively immune to the spacings of the Gaussians? We believe that the presence of the Green function in the integral equation approaches, is responsible for this. It can be shown[1(g)] that the SVP and the NVP functionals of Eqs. (6) and (9) can be obtained by using the Lippmann–Schwinger equation for $\Psi(r)$, in the KVP functional. In other words, we use

$$\Psi(r) = \phi(r) + \int_0^\infty dr' G^0(r,r') V(r') \Psi(r')$$

once, in the ket $|\Psi\rangle$ of Eq. (1), to get the SVP functional. Applying the expression above in the bra *and* the ket, we get the NVP functional. It is easy to see that using the Lippmann–Schwinger equation in this manner would amount to using the following expansion for $\Psi(r)$:

$$\Psi(r) = \phi(r) + \sum_{n=1}^{N} c_n g_n(r) ,$$

where $g_n(r)$ are the functions defined in Eq. (11). If the functions $u_n(r)$ of Eq. (11) are the Gaussians of basis 1, which are predominately localized about their centers, the corresponding functions $g_n(r)$ would be more delocalized than the Gaussians themselves, due to the integration in Eq. (11). Such delocalization of previously localized functions can be expected to decrease, to some extent, the importance of their positions in the interval $[0, R_{\max}]$. It is also interesting, in this context, that the KVP rates of convergence increase upon going from the predominately local functions of basis 1 to the nonlocal functions of basis 3, in the cases of potentials of category 2. However, the above explanation may not tell the whole story, as indicated by the facts that the KVP rates of convergence *decrease* in going from basis 1 to basis 3, for potentials of category 1.

Comparing Fig. 3(a) to 3(b), Fig. 4(a) to 4(c), and Fig. 4(b) to 4(d) reveals the interesting fact that, for a given basis, the calculations on a purely repulsive potential appear to converge faster than those on an "analogous"[20] purely attractive potential. The great contrast in the behavior of the KVP results for potentials 4A and 4B is especially striking. The results for the SVP and NVP calculations for these cases also show similar differences in behavior. Thus, for a given basis, the variational methods converge faster on a purely repulsive potential, than on the analogous[20] purely atttractive potential.

We now attempt to provide an explanation for the above observation. The curve representing $\Psi(r)$ in Fig. 5(a) suggests that in an attractive potential, the scattering wave function is "compressed" in the "interaction region" relative to the asymptotic free wave. This is to be expected, since the kinetic energy of the incoming particle increases as the potential becomes more negative. As a consequence, $\Psi(r)$ in an attractive potential would have higher frequency oscillations in this region than the asymptotic free particle wave. The higher frequency oscillations in $\Psi(r)$ imply that a larger number of Guassians (if basis 1 is used) or the high energy eigenfunctions of the one-dimensional box problem (if basis 3 is used) are required for an accurate expansion. In contrast, $\Psi(r)$ for scattering from a purely repulsive potential is "dilated" in the interaction region, as clearly seen in Fig. 5(b). This can, of course, be related to the loss of kinetic energy experienced by the incoming particle, due to the increase in the potential energy. Accordingly, the $\Psi(r)$ for this case has lower frequency oscillations in this region than the asymptotic wave. A relatively fewer number of Gaussians, or the lower energy eigenfunctions of the one-dimensional box problem, are therefore able to accurately represent this solution. (Note however, that basis 2 is an exception to this. In the case of this basis, the higher terms are functions that reach their maxima at progressively larger values of r, and

hence the *higher* terms are more suited to represent low frequency oscillations.)

IV. SUMMARY AND CONCLUSION

In this study, we have compared the relative performance of the S-matrix version of the Kohn variational principle, with T-matrix versions of the Schwinger and the Newton variational principles, using a variety of interaction potentials and a few commonly used basis sets. We have found that the rates of convergence of the variational methods are dependent on the nature of the potentials and the basis sets used to expand the scattering wave functions.

For potentials that have both a repulsive and an attractive part, the KVP results indicate that the method is capable of converging to the correct result with 5–10 more basis functions than the number required for the SVP and the NVP to converge. The ease of application of the KVP, coupled with the fact that the method developed in Ref. 8 makes it possible to avoid inverting a complex matrix to compute S-matrix elements, therefore makes the KVP a very practical method for calculations on such potentials. In contrast, for potentials that are purely attractive the Kohn method appears not to be very successful. For potentials of category 2, the KVP also suffers from the drawback that the convergence characteristics depend sensitively on the nature of the basis functions. The results presented in this paper and the discussion above indicate that the SVP and the NVP are, in general, more robust variational principles than the KVP, in the sense that they appear to converge quickly to the correct result even in situations where the KVP rate of convergence appears to be very slow. The SVP and the NVP also appear to be rather insensitive to the nature of the basis functions used to expand $\Psi(r)$.

In these studies, we have used the same trial quantity, viz., the trial wave function, for studying the relative performance of three variational principles. By taking this approach, we see that there are a few cases where the KVP results converge faster than those from the SVP (1A2,1B2), but no cases where they converge faster than those from the NVP. It is also interesting that for potentials of category 1, that have a repulsive and an attractive part, the rate of convergence of the KVP is higher if basis 1, rather than basis 3 is used. However, potential 2A, which belongs to category 1, is clearly an exception to this. For category 2 potentials, the KVP rate of convergence is increased in all cases if basis 3 is used. For the SVP and the NVP, the use of basis 3 seems to decrease the rate of convergence, in general, compared to their respective rates of convergence if basis 1 is used.

We chose to exclude the non-L^2 terms in the SVP and the NVP trial functions, because the Green function, as mentioned in Sec. I, fulfills the task of enforcing the boundary conditions for these methods. Although it is known that the presence of non-L^2 terms such as $u_0(r)$ and $u_1(r)$ of Eq. (2) accelerate the convergence of the SVP,[1(g)] at least for cases 1A2 and 1B2, the present approach seems to be a fair way to evaluate the relative merits of the three methods.[21] Moreover, the present implementation of the SVP and the NVP are closer in spirit to the existing calculations where these methods have been used.[2(a)-2(d),9-11,16]

We pointed out in the Introduction, that in the integral equation approaches, the boundary conditions are imposed by the Green function. This naturally permits a certain degree of flexibility in the choice of the trial functions for the SVP and the NVP. Including non-L^2 terms in the expansion is, as mentioned in the preceding paragraph, one option. In the case of the NVP, one also has the option of expanding the wave function *or* the amplitude density, in a set of basis functions. The question of great relevance as far as applications to complex and large calculations such as those of multidimensional reactive scattering are concerned, of course, is how fast a certain method can be made to converge, by a careful choice of the trial function. A future publication addresses these and related questions in detail.[22]

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