

Development of a confined variational method for elastic scattering

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It is shown that the discrete energies of a scattering Hamiltonian calculated under the influence of an artificial confining potential can be used to determine its phase shifts. Two potentials that have the same energy under the influence of the confining potential have exactly the same phase shift at that energy when the confining potential is removed. Thus the phase shifts of a complicated many-body problem can be extracted by solving the Schrödinger equation under the influence of the confining potential, and then making reference to the energies and phase shifts of a much simpler model potential calculated in the same confining potential. Calculations on real systems gave very precise phase shifts for the e^- -H and e^- -He systems.

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I. INTRODUCTION

A common theme in the quantum theory of scattering is the development of procedures that take advantage of bound state methods based on square integrable (L^2) wave functions. One reason for this is the desire to adapt existing bound state program packages to the calculation of continuum states. As a general rule, a much greater degree of precision has been achieved for bound states as opposed to continuum state solutions of the Schrodinger equation. For example, the energy of the helium ground state (in a nonrelativistic model) has been determined to an almost unbelievable precision of more than 40 significant digits [1]. However, the low energy elastic scattering phase shifts for electron-hydrogen scattering are only known to an accuracy of about 10^{-4} rad (about 4 significant digits) [2,3].

Some of the bound state methods applied to scattering problems include the many different types of R -matrix methods [4–8], stabilization approaches [9,10], and the application of a complex absorbing potential (CAP) outside the scattering region [11].

Most recently, the use of real-valued as opposed to complex artificial confining potentials has been investigated. Guerout *et al.* [12,13] had used a real confining potential to determine the solution of the Schrödinger equation for the internal region wave function within a multichannel quantum defect theory formalism. More recently, a confining potential was added to a scattering system [14] so that the stochastic variational method (SVM) [14–17] could be used to optimize a basis of explicitly correlated Gaussians (ECGs) to describe the interaction region. The ECG basis was then used as a foundation for a stabilization calculation.

The present paper applies a recently developed method to calculate low energy elastic scattering phase shifts [18]. The basic idea is to add an artificial confining potential to the scattering Hamiltonian and determine the discrete energies of this modified system. The phase shifts are then extracted by

comparing the energies with the energies of a simple model potential calculated with the same confining Hamiltonian. This confined variational method (CVM) [18] has similarities with the box-variational method [8]. In its simplest form, the box-variational method requires the wave function, and thus the basis functions, to have a zero at the boundary (note, the logarithmic derivative at the box boundary can, in principle, be set to any value). The $\ell=0$ phase shifts for the n th positive energy state with energy E_n inside a cavity of radius R are then given by the identity $\delta_n = n\pi - R\sqrt{2E_n}$ [8]. The quantum Monte Carlo method for scattering can be formulated in terms of the box-variational method [19–21].

In the CVM the confining potential increases steadily from zero past some critical radius [18]. This has the advantage that the basis functions can then be almost any square integrable function. A numerical calculation is then needed to extract the phase shift from the energy of the confined state. However, this additional calculation is quite straightforward.

The present paper discusses the justification and application of the CVM to low energy scattering. The actual solution of the Schrodinger equation for the confined system is performed with the SVM [15–17] which exploits the very convenient properties of a basis consisting of ECGs. Precise phase shifts are computed for electron scattering from hydrogen in the $^1S^3$, $^3S^e$, $^3P^o$ symmetries and electron scattering from helium in the $^2S^e$ symmetry at energies below 1 eV.

II. DESCRIPTION OF METHOD**A. Formal result**

The problem is to solve the Schrödinger equation

$$\left(-\frac{\nabla^2}{2} + V(r)\right)\Psi(r) = E\Psi(r), \quad (1)$$

for $E > 0$. The central potential $V(r)$ will be assumed to be zero beyond some finite radius, say R_0 . Now consider the related equation

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$$\left(-\frac{\nabla^2}{2} + V(r) + W_{\text{CP}}(r)\right)\Psi(r) = E\Psi(r), \quad (2)$$

where W_{CP} is a confining potential and E is defined relative to $V(r \rightarrow \infty)$. This potential has the property that $W_{\text{CP}} \geq E_0$ as $r \rightarrow \infty$. It is also permissible that $W_{\text{CP}} \approx O(r^n)$ as $r \rightarrow \infty$. The potential $W_{\text{CP}}(r)$ should have two properties. It should have an analytic form which has easy to evaluate matrix elements for the basis functions used to represent $\Psi(r)$. Secondly, $W_{\text{CP}}(r)$ should be negligible for $r < R_0$. If these conditions are met, then it can be shown that the discrete energies E_i of the solution of Eq. (2) can be used to uniquely determine the phase shifts of Eq. (1) at those energies, irrespective of the specific functional form of $V(r)$.

Consider a potential $V_0(r)$ for which Eq. (2) has an eigenvalue E_0 . When $r > R_0$, the solution of Eq. (2) will be an exponentially decreasing solution, $B\phi_0(r)$. While the amplitude B may depend on the specifics of $V_0(r)$, the actual radial dependence of $\phi_0(r)$ does not depend on the form of $V_0(r)$. Now, consider the behavior of the wave function for $r < R_0$. One simply integrates the Schrödinger equation outward from the origin, and since $W_{\text{CP}}(r)$ is negligible here, the functional form of the inner wave function, $\Phi_0(r)$, will not be influenced by the form of $W_{\text{CP}}(r)$. The eigenstate will then be

$$\begin{aligned} \Psi(r) &= A\Phi_0(r), & r < R_0, \\ \Psi(r) &= B\phi_0(r), & r > R_0. \end{aligned} \quad (3)$$

The logarithmic derivatives of $\phi_0(r)$ and $\Phi_0(r)$ will agree at the matching radius. The constants A and B are chosen so that the overall normalization of $\Psi(r)$ is unity and that it is continuous at $r=R_0$.

Now consider the solution of Eq. (1) at $E=E_0$. When $r < R_0$, this will simply be $C\Phi_0(r)$ since the boundary condition at the origin only depends on E_0 . At the boundary $r=R_0$, the phase shift δ is determined from the logarithmic derivative Γ ,

$$\Gamma_\psi(r) = \frac{1}{\psi(r)} \frac{d\psi}{dr}. \quad (4)$$

There is a general functional relation between Γ_ψ and δ that can be expressed formally as

$$\delta(E_0) = f(\Gamma_\psi(R_0)). \quad (5)$$

However, the logarithmic derivative of $\phi_0(r)$ is exactly the same as $\Phi_0(r)$. The logarithmic derivative of $\phi_0(r)$ at $r=R_0$ is determined by E_0 , and its functional dependence $g(E_0)$ does not depend on $V_0(r)$. So

$$\Gamma_\psi(R_0) = \Gamma_\phi(R_0) = g(E_0). \quad (6)$$

Combining Eqs. (5) and (6), one can establish a functional relation between the energy E_0 and the phase shift, i.e.,

$$\delta(E_0) = f(g(E_0)). \quad (7)$$

The most useful consequence of Eq. (7) lies in the fact that Eq. (6) has no explicit functional dependence on the specifics of $V_0(r)$. While $g(E_0)$ depends on R_0 , E_0 , and the form of $W_{\text{CP}}(r)$, it does not depend on $V_0(r)$. Therefore, if

two potentials, V_0 and V_1 in Eq. (2) have the same eigenenergy E_0 , then their phase shifts (modulo π) will be the *same* at E_0 . From one point of view this result is not surprising. Provided the two wave functions have the same logarithmic derivative at $r=R_0$, it should not matter whether bound or continuum boundary conditions are imposed.

The immediate consequence of this result is the ability to determine the phase shift of a complicated many-body problem directly from the energy of a bound state calculation. The determination of the phase shift for a projectile scattering from a few-body system can thus be reduced to the calculation of its binding energy in a confining potential.

There are a number of ways the result obtained in this section can be exploited. These are detailed later.

B. Choice of confining potential

The most general form for the confining potential that obeys the required conditions would seem to be a function of the form

$$V(r) = \Theta(r - R_0)g(r - R_0). \quad (8)$$

The Heaviside function $\Theta(r - R_0)$ is defined,

$$\begin{aligned} \Theta(x) &= 0, & x < 0, \\ \Theta(x) &= \frac{1}{2}, & x = 0, \\ \Theta(x) &= 1, & x > 0. \end{aligned} \quad (9)$$

The confining function $g(x)$ should be zero at $x=0$. The function $g(x)$ should increase monotonically as x increases. The function $g(x)$ should go to a sufficiently large positive value to bind the scattering particles together. If the scattering energy is E_{scatt} , then the confining potential must obey the condition $\lim_{r \rightarrow \infty} g(r) > E_{\text{scatt}}$. The potential can also diverge to infinity as $O(r^n)$ when $r \rightarrow \infty$. In the present work we choose $g(r - R_0) = G(r - R_0)^2$ for reasons discussed later.

Potentials based on the Heaviside form similar to this have been adopted in a few previous works [12,13,22]. These works were mainly concerned with molecular systems.

C. Use of SVM to solve a confined Schrödinger equation

The potential given by Eq. (8) is in the form of a one dimensional central potential. Therefore, it is relatively straightforward to use with ECGs [23,24] since the matrix elements of a potential of this type are easily expressed in terms of a Laplace transform of the potential [16,25,26].

While the principles involved in the CVM are very general, its application to real physical systems in the present work has been in conjunction with the SVM. The SVM [15–17], and variants [27–31] constitute a very powerful tool for studying few-body systems. The success of the method is based on the analytic properties of the ECG basis [17,23,24,27] which have the analytic form

$$G_k = \exp\left(-\frac{1}{2} \sum A_{ij}^k \mathbf{x}_i \cdot \mathbf{x}_j\right), \quad (10)$$

where \mathbf{x}_i is the coordinate of the i th particle. The ECG basis functions have the property that the multicenter integrals that

occur with correlated basis sets are surprisingly easy to evaluate. It is feasible to use a stochastic search to optimize the nonlinear parameters of the basis because the Hamiltonian matrix elements can be evaluated very quickly.

The use of a Gaussian basis did impose some practical constraints on the shape of $W_{\text{CP}}(r)$. One problem is that the elements of a Gaussian basis set are linearly dependent and the fundamental equation to be solved is a generalized eigenvalue problem. The potential problem lurking in the background is that of linear dependence degrading the accuracy of the results or even causing catastrophic failure in the numerical solution of the generalized eigenvalue problem. While the problem of linear dependence can, in principle, be controlled by the technique of singular value decomposition, this additional level of complexity was not used in the present work.

Some practical experimentation by diagonalizing the potential $V=0$ revealed that the radial dependence of the confining potential should not be made too abrupt. Solving the Schrödinger equation with a Gaussian basis became increasingly difficult as the confining potential increasingly resembled a hard wall. For example, it was not possible to construct a Gaussian basis that could give an energy that was accurate to better than three significant digits for the potential $W_{\text{CP}}(r)=10^{-2}(r-16)^{10}$.

D. Phase shift from wave function at boundary

The simplest way to compute the phase shift is to use the behavior of the wave function at $r=R_0$. The logarithmic derivative of the wave function at the boundary and the phase shift are related by the expression

$$\cot(kR_0 + \delta) = \Gamma_{\psi}(R_0) = \frac{1}{\psi(R_0)} \left(\frac{d\psi}{dr} \right)_{r=R_0}, \quad (11)$$

where $k=\sqrt{2E}$. The logarithmic derivative is computed at $r=R_0$, and the phase shift at the boundary is extracted from Eq. (11). Alternatively, it is possible to extract the phase shift by computing the wave function at two points near the boundary. This approach has the advantage that both the phase shift and absolute normalization of the wave function are determined and will be termed the boundary condition method (BCM).

The scattering information of the artificial well potential method of Guerout *et al.* [12,13] are derived with an approach similar to the BCM. The internal region wave functions are essentially spliced onto the appropriate asymptotic form.

E. Stabilization approach for SVM

Another alternative that is useful when the interaction region wave function is determined with the SVM is to perform a stabilization calculation using established procedures [10,14,32]. The present analysis means that the basis should be capable of describing the interaction region very well provided the energy of the confined system is close to convergence.

The first SVM calculations using a confining potential were based on intuitive ideas before the present results were established. The confining potential adopted was of the form $V(r)=\lambda r^n$, where $\lambda \approx 10^{-19}$ was small and $n=12$ was large [14]. These potentials did not exactly satisfy the condition that W_{CP} should be exactly zero within some critical radius. However, the condition was approximately satisfied with $W_{\text{CP}} \approx 10^{-6}$ at $r=12a_0$. And as mentioned earlier, the purpose of the SVM calculation was not to directly compute the phase shift, but rather to generate an interaction region basis that could be used in a stabilization calculation. This particular approach will not be discussed further in the present paper since it has been investigated at length elsewhere [14] and to a certain extent it has been superseded by developments reported in the present paper.

F. Converting the energy into a phase shift

The following ansatz can be used. First choose a confining potential $W_{\text{CP}}(r)$ and then choose an auxiliary potential $\lambda v(r)$. The auxiliary potential $v(r)$ is chosen to have a simple form so that it is straightforward to determine the phase shifts at any energy by direct numerical solution of the Schrodinger equation or some other technique.

The full many-body problem for the exact Hamiltonian H [exact] under the influence of W_{CP} is first solved to generate a set of discrete eigenenergies E_i satisfying

$$(H[\text{exact}] + W_{\text{CP}})\Psi_i = E_i\Psi_i. \quad (12)$$

Then the energies of the potential $\lambda v(r)$ under the influence of $W_{\text{CP}}(r)$ are determined. The parameter λ is then adjusted until the i th eigenenergy of $H[v]$ exactly corresponds to the i th eigenenergy of H [exact], i.e., E_i .

$$\left(-\frac{\nabla^2}{2} + \lambda_i v(r) + W_{\text{CP}}(r) \right) \Psi_i'(r) = E_i \Psi_i'(r). \quad (13)$$

Finally, the continuum Schrödinger equation is solved for the potential $\lambda_i v(r)$ and the phase shift δ_i is obtained. The phase shift δ_i will be equal to the phase shift of the H [exact] at a continuum energy of $E=E_i$. This approach will be referred to as the confined variational method (CVM).

G. Long-range potentials

All atomic collision systems have potentials that have long-range components. In the case of charged particle scattering from atoms, there is the polarization potential

$$V_{\text{pol}}(r) \sim -\frac{\alpha_d}{2r^4}. \quad (14)$$

In this expression, α_d is the dipole polarizability. In the case of an electrically neutral object scattering from atoms, there is the dispersion potential

$$V_{\text{disp}}(r) \sim -\frac{C_6}{r^6}. \quad (15)$$

The parameter C_6 is the lowest-order dispersion coefficient. Other long-range terms exist, but the terms listed above are the dominant ones.

While the derivation from Eq. (1) to Eq. (7) is reliant on the fact that $W_{\text{CP}}(r)$ is zero at some finite radius, the exact potential $V_{\text{exact}}(r)$ can have a long-range component. However, this long-range component should permit easy integration beyond R_0 . Provided this is true, polarization effects can be incorporated into the calculation by simply including a component with the same asymptotic form as Eqs. (14) or (15) into the tuning potential.

H. Normalization of the wave function

One problem with the CVM concerns the overall normalization of the continuum wave function. The conversion of the confined energy into a phase shift does not directly use any information on the overall normalization of the wave function. This is not a problem when the only result wanted is the elastic cross section, but it is an issue when other scattering observables, such as a photoionization cross section, or an annihilation cross section for positron impact is wanted. It is of course possible to utilize the phase shift and then use the value of the wave function at the boundary to determine the overall normalization. However, this would lead to a decrease in the accuracy since local properties of variational wave functions are generally less accurate than their global properties [33]. The stabilization approach also automatically gives the asymptotic normalization.

Another possibility lies in evaluating the expectation value of W_{CP} ,

$$\langle W_{\text{CP}} \rangle = \int_{R_0}^{\infty} dr |\Phi_0(r)|^2 W_{\text{CP}}(r). \quad (16)$$

Two potentials which give the same energy, will not necessarily give the same value of $\langle W_{\text{CP}} \rangle$. The modeling potential $\lambda v(r)$ can be made more flexible by the inclusion of a parameter to change its shape, e.g., choose $\lambda v(r) = \lambda \exp(-\beta r)$. Then, both λ and β are adjusted until E_i and $\langle W_{\text{CP}} \rangle$ are the same for both H [exact] and $H[v]$. Equality of the energies means that the phase shifts are the same; equality of $\langle W_{\text{CP}} \rangle$ ensures that the normalization conditions at the boundaries are the same. Using $\langle W_{\text{CP}} \rangle$ to determine the overall wave function normalization should lead to accurate results. It is part of the Hamiltonian and the total energy is stable against first-order variations in the trial wave function.

III. RESULTS

Numerical verification

The first test is to verify whether the primary proposition, namely, two short-range potentials with the same energy having the phase shift, can be achieved in a practical numerical calculation. The convergence properties are also studied.

For this test, we choose

$$V(r) = -\exp(-1.40r), \quad (17)$$

$$\lambda v(r) = \lambda[\exp(-r^2) + r \exp(-2r)]. \quad (18)$$

The potential $V(r)$ represents the potential for some complicated many-body system and it will not always be possible to

determine its eigenenergies to infinite precision. The confining potential is defined

$$W_{\text{CP}}(r) = 0, \quad r < 16, \quad (19)$$

$$W_{\text{CP}}(r) = G(r-16)^2, \quad r > 16, \quad (20)$$

where $G = 3 \times 10^{-4}$. The energies of $(V + W_{\text{CP}})$ are then determined by diagonalization in a basis of Laguerre-type orbitals (LTOs). The LTOs are defined [34,35]

$$\chi_{\alpha}(r) = N_{\alpha} r^{\ell+1} \exp(-\lambda_{\alpha} r) L_{n_{\alpha}-\ell-1}^{(2\ell+2)}(2\lambda_{\alpha} r), \quad (21)$$

where the normalization constant is

$$N_{\alpha} = \sqrt{\frac{(2\lambda_{\alpha})^{2\ell+3} (n_{\alpha} - \ell - 1)!}{(\ell + n_{\alpha} + 1)!}}. \quad (22)$$

The function $L_{n_{\alpha}-\ell-1}^{(2\ell+2)}(2\lambda_{\alpha} r)$ is an associated Laguerre polynomial that can be defined in terms of a confluent hypergeometric function [36] as

$$L_{n_{\alpha}-\ell-1}^{(2\ell+2)}(2\lambda_{\alpha} r) = \frac{(n_{\alpha} + \ell + 1)!}{(n_{\alpha} - \ell - 1)!(2\ell + 2)!} \times M(-(n_{\alpha} - \ell - 1), 2\ell + 3, 2\lambda_{\alpha} r). \quad (23)$$

The exponent in Eq. (21) was set to 2.0 and the basis dimension increased in steps of 5. The results of the diagonalization for the two lowest energies are listed in Table I. The energy for the i th eigenstate for a basis of dimension N is denoted $E_{i,N}$. The exact energy of the i th eigenstate is for all practical purposes given by $E_{\text{exact},i} = E_{i,50}$.

Two columns of Table I give the exact phase shift [obtained by numerical integration of $V(r)$ using the Numerov method] at the energies of the pseudostate. The pseudostate energy decreases as the LTO basis is enlarged. The phase shifts are denoted as $\delta_{\text{exact},i,N}$.

The phase shift obtained from the BCM for the two lowest states are given in the two columns labeled $\delta_{\text{BCM},1,N}$ and $\delta_{\text{BCM},2,N}$. This phase shift was computed by evaluating the logarithmic derivative at the $r=16$ boundary. Part of the variation in $\delta_{\text{BCM},i,N}$ is due to the fact that the energy of the pseudostate changes as the basis dimension is changed. The other part of the variation is related to the ability of the LTO basis to adequately represent the wave function. The respective influence of these two factors in causing the variation in the phase shift can be estimated by reference to the $\delta_{\text{exact},i,N}$ column. It would appear that the inability to represent the scattering wave function at the boundary is the main source of error for $N \geq 30$.

The CVM phase shifts $\delta_{\text{CVM},i,N}$ are listed in Table I. The energies of the potential $[\lambda v(r) + W_{\text{CP}}(r)]$ were obtained from a calculation that gave functionally exact energies. The parameter λ was adjusted until the energy was exactly equal to either $E_{1,N}$ or $E_{2,N}$ (note, slightly different values of λ were needed for $E_{1,N}$ and $E_{2,N}$). The continuum Schrodinger equation was then integrated using the previously obtained value of λ with the continuum energy set to $E_{i,N}$. The energies at which the phase shifts are obtained are undergoing continual changes since the $E_{i,N}$ change as the dimension of the LTO basis, N , is increased.

TABLE I. The convergence of the energy and derived phase shift with respect to increasing the size of the LTO basis set. The column entries are discussed in the text. The numbers in the square brackets denote powers of ten. Energies are given in atomic units.

N	$E_{1,N}$	$\delta_{\text{exact},1,N}$	$\delta_{\text{BCM},1,N}$	$\delta_{\text{CVM},1,N}$	$E_{2,N}$	$\delta_{\text{exact},2,N}$	$\delta_{\text{BCM},2,N}$	$\delta_{\text{CVM},2,N}$
20	8.10592466029[-3]	0.4773965	0.5309627	0.4773945	3.63192796364[-2]	0.6673184	0.7805095	0.6673155
25	6.04569190259[-3]	0.4310864	0.4931422	0.4310858	2.57208169952[-2]	0.6375783	0.7339627	0.6375769
30	5.62992416864[-3]	0.4199395	0.4147941	0.4199395	2.28586364743[-2]	0.6248517	0.6215669	0.6248515
35	5.60792046301[-3]	0.4193291	0.4169931	0.4193291	2.25933186044[-2]	0.6235284	0.6185374	0.6235284
40	5.60770145958[-3]	0.4193230	0.4194748	0.4193230	2.25887828201[-2]	0.6235056	0.6237640	0.6235056
45	5.60770114269[-3]	0.4193230	0.4193651	0.4193230	2.25887729654[-2]	0.6235055	0.6235204	0.6235055
50	5.60770114218[-3]	0.4193230	0.4193572	0.4193230	2.25887729644[-2]	0.6235055	0.6235192	0.6235055

Casual examination of Table I reveals the clear superiority of $\delta_{\text{CVM},i,N}$ with respect to $\delta_{\text{BCM},i,N}$. At large values of N , $\delta_{\text{CVM},i,N}$ is the same as $\delta_{\text{exact},i,N}$ to all quoted digits while $\delta_{\text{BCM},i,N}$ only achieves four digit accuracy even when $N=50$. Even in the worst cases, $\delta_{\text{CVM},i,N}$ reproduces $\delta_{\text{exact},i,N}$ to five digits. One of the most striking features of Table I is the extreme accuracy of $\delta_{\text{CVM},i,N}$ even in those cases where the LTO basis is overestimating the actual energy of the confined state by 20%.

One reason for the accuracy of $\delta_{\text{CVM},i,N}$ is that the CVM converts a variational energy into a phase shift. The energy obtained in a variational calculation is stationary to order $(\delta\Psi)^2$ with respect to wave function variations [17]. The number of digits to which the phase shift is accurate is roughly equal to the number of digits to which the energy has converged.

The convergence of $\delta_{\text{CVM},i,N}$ in Table I is also seen to be monotonic. This is merely a reflection of the monotonic convergence of the energy in the underlying variational calculation.

The lower accuracy of $\delta_{\text{BCM},i,N}$ at high N is due to the fact it is obtained from the local properties of the wave function. While the energy may obey, $\delta E \sim (\delta\Psi)^2$, there is no formal result that any other properties should be this accurate. The local properties of the wave function cannot be guaranteed to have the same level of accuracy as the energy [33] and the four significant digits achieved by $\delta_{\text{BCM},i,50}$ is the best that can reasonably be expected. The BCM phase shifts in Table I indicate that the relative energy needs to be computed to an overall accuracy of 10^{-9} [this tolerance will depend on the specific definition of $W_{\text{CP}}(r)$ for the error in the phase shift to approach 0.001 rad.

The actual choice of the tuning potential has no impact on the computed value of the CVM phase shift. This is guaranteed by the fundamental theorem underlying the CVM, but some calculations with alternate forms for the tuning potential have been done and the overall quality of the CVM phase shifts are identical to that displayed in Table I.

IV. RESULTS ON REAL PHYSICAL SYSTEMS

A. Electron-hydrogen scattering in the $^1S^e$ channel

The e^- -H system in the singlet channel possesses a bound state, the H^- ion. The energy of the state is $-0.527\,751\,016\,5$

hartree [39]. The SVM was used to solve the Schrödinger equation under the influence of the confining potential, $W_{\text{CP}}(r)=G(r-19)^2$, where $G=6.390\,783\,3 \times 10^{-5}$. The confining potential acts upon both electrons. The actual energy being optimized was the average of the three lowest energies, i.e., $E_{\text{opt}}=(E_0+E_1+E_2)/3$. One advantage of having a bound state is that the energy difference of E_1 and the exact H^- energy is an indicator of the convergence of the basis. The value of G was not fixed during the optimization process. The value of G underwent continual small adjustments to keep the energy of the third eigenstate, i.e., E_2 , as close to -0.480 hartree as possible while the optimization was in progress. This corresponds to $k=0.2a_0^{-1}$ and made it easier to compare with previous calculations of the phase shift [2,3]. All the energies given in Table II were computed with the final value of G adopted for the largest calculation (this was done with $N=340$ as discussed later).

The imposition of the confining potential had an insignificant impact on the hydrogen ground state. The energy change was about 10^{-15} hartree. This is not surprising given that the hydrogen ground state wave function is 5×10^{-9} smaller at $R_0=19a_0$ than it is at the origin. The energy shift of the more diffuse H^- ground state was larger, being about 1.8×10^{-7} hartree. When the confining potential is turned off, the $N=300$ basis gives a H^- energy of $-0.527\,750\,982$ hartree, about 3×10^{-8} hartree larger than the exact H^- energy.

The electron-hydrogen potential has a long-range polarization potential with a dipole polarizability of 4.5 a.u. The phase shift obtained from the CVM processes is the phase shift at R_0 . The value of $V_{\text{pol}}(r=R_0)$ is 1.7×10^{-5} hartree. The potential is small, but it can effect the derived phase shift at $k \approx 0.2a_0^{-1}$ at the 0.1% level. The potential that was used to extract the phase shift was

$$V_{\text{H}}(r) = \lambda \exp(-\gamma r) - \frac{\alpha_d}{2r^4} [1 - \exp(-r^6/\rho^6)], \quad (24)$$

where ρ was set to $\rho=3a_0^3$ and γ was set to $2a_0^{-1}$.

Table II gives the energies of the three lowest states at various stages of the optimization procedure. The k values are related to the energies by the identity $k=\sqrt{2(-E-0.5)}$ and tabulated as $k_{i,N}$. The lowest-energy state is the H^- bound state. In order to generate the phase shifts, the parameter λ was adjusted until the continuum energy was equal to $(E_{i,N}$

TABLE II. The confined energies and phase shifts of the e^- -H $^1S^e$ system as a function of the number of ECGs, N . Phase shifts from some other calculations are given. Numbers in parentheses are the estimated uncertainties. Energies and k are given in atomic units.

N	$E_{0,N}$	$E_{1,N}$	$E_{2,N}$	$k_{1,N}$	$k_{2,N}$	$\delta_{\text{CVM},1,N}$	$\delta_{\text{CVM},2,N}$
SVM basis							
50	-0.52770403	-0.49368121	-0.47991805	0.11241698	0.20040932	2.47390	2.04791
100	-0.52774706	-0.49372494	-0.47999589	0.11202730	0.20002056	2.48794	2.06604
150	-0.52774993	-0.49372700	-0.47999912	0.11200894	0.20000439	2.48860	2.06679
200	-0.52775058	-0.49372721	-0.47999981	0.11200704	0.20000097	2.48867	2.06695
250	-0.52775076	-0.49372727	-0.47999994	0.11200656	0.20000030	2.48869	2.06698
300	-0.52775080	-0.49372728	-0.47999999	0.11200643	0.20000007	2.48869	2.06699
Augmented SVM basis							
50+40	-0.52772835	-0.49372047	-0.47998502	0.11206722	0.20007490	2.48650	2.06350
100+40	-0.52774797	-0.49372677	-0.47999847	0.11201094	0.20000765	2.48853	2.06664
150+40	-0.52775004	-0.49372716	-0.47999966	0.11200752	0.20000169	2.48865	2.06691
200+40	-0.52775061	-0.49372726	-0.47999990	0.11200664	0.20000051	2.48869	2.06697
250+40	-0.52775078	-0.49372728	-0.47999997	0.11200644	0.20000014	2.48869	2.06699
300+40	-0.52775081	-0.49372729	-0.48000000	0.11200637	0.20000000	2.48870	2.06699
Complex Kohn [3]					0.200		2.06678(20)
Kohn [2]					0.200		2.0673(9)
Finite element [37]					0.200		2.066
Finite difference [38]					0.200		2.0666

+0.50). The 0.50 is added to remove the energy of the H ground state. Then the continuum Schrödinger equation was integrated to $500a_0$ to give the phase shift which is listed in the columns $\delta_{\text{CVM},2,N}$. The $N=300$ basis gave a $k=0.2a_0^{-1}$ phase shift of 2.066 99 rad.

1. Addition of basis functions to represent asymptotic wave function

One inefficiency in the present approach is the use of the SVM procedure to represent the wave function in the asymptotic region. For example, the asymptotic wave function for e^- -H scattering takes the simple product form (with implied antisymmetrization), i.e.,

$$\Psi = \phi_{\text{H}}(\mathbf{r}_1)\phi(\mathbf{r}_2). \quad (25)$$

While the SVM process constructs a basis to represent the interparticle correlations, it also constructs a basis to represent a wave function with a very simple structure.

The residual errors in the confined energies given in Table II arise from two sources. One part is due to an incomplete description of interparticle correlations and the other part arises due to an incomplete description of the asymptotic wave function given by Eq. (25). One aspect of the incompleteness can be eradicated by the expedient of adding basis functions to represent the asymptotic wave function as done in the stabilization SVM [14], e.g.,

$$\Psi_{i,\text{out}} = \psi_{\text{H}}(\mathbf{r}_1)\psi_i(\mathbf{r}_2), \quad (26)$$

$$\psi_{\text{H}}(\mathbf{r}_1) = \sum_k d_k \exp(-\beta_k r_1^2), \quad (27)$$

$$\psi_i(\mathbf{r}_2) = \exp(-\alpha_i r_2^2). \quad (28)$$

The target wave function is represented as a linear combination of ECGs and the α_i are chosen to form an even tempered set with $\alpha_i = \alpha_1 / T^{i-1}$.

Table II shows the improvement this makes in the energy and phase shift for the e^- -H $^1S^e$ system. The hydrogen ground state is represented as a linear combination of 20 Gaussians with an energy of $-0.499\,999\,999\,43$ hartree. The scattering orbital is represented with a set of 40 Gaussians with $\alpha_1 = 19.45$. The largest calculation with the $N=340$ basis functions gave a phase shift of 2.066 99 rad.

One surprising aspect of the augmented basis was that the energy improvement was sensitive to the choice of α_1 . Our original expectation was that the use of a large even tempered basis would result in an energy improvement that did not vary much as α_1 was changed. However, it was found that the net energy improvement could be increased by as much as 50% by manual tuning of α_1 .

The $N=340$ basis gave a H $^-$ energy of $-0.527\,750\,987$ hartree when the confining potential was turned off. The convergence of $E_{2,N}$ versus N seems slightly quicker than $E_{0,N}$ at the larger values of N . Therefore it is reasonable to assert that the $E_{2,340}$ is converged to better than 3×10^{-8} hartree. It is possible that further increase in the

TABLE III. The confined energies and phase shifts of the e^- -H $^3S^e$ system as a function of the number of ECGs, N . The phase shifts from some other calculations at $k=0.20a_0^{-1}$ are given. Numbers in parentheses are the estimated uncertainties. Energies and k are given in atomic units.

N	$E_{1,N}$	$E_{2,N}$	$k_{1,N}$	$k_{2,N}$	$\delta_{\text{CVM},1,N}$	$\delta_{\text{CVM},2,N}$
100	-0.49426194	-0.47999481	0.1071266	0.2000519	-0.21902	-0.42514
120	-0.49426312	-0.47999828	0.1071156	0.2000172	-0.21866	-0.42444
140	-0.49426333	-0.47999918	0.1071137	0.2000082	-0.21860	-0.42425
165	-0.49426344	-0.47999968	0.1071126	0.2000032	-0.21856	-0.42415
190	-0.49426349	-0.47999990	0.1071122	0.2000010	-0.21855	-0.42411
215	-0.49426351	-0.47999997	0.1071120	0.2000003	-0.21854	-0.42409
240	-0.49426351	-0.48000000	0.1071120	0.2000000	-0.21854	-0.42409
Complex Kohn [3]				0.200		-0.42418(20)
Kohn [2]				0.200		-0.4245(5)
Finite element [37]				0.200		-0.4246
Finite difference [38]				0.200		-0.4245

basis dimension could result in a phase shift of 2.067 00 rad. A reasonably conservative estimate of the $k=0.2a_0^{-1}$ phase shift would be 2.066 99(2) rad.

A precise electron-H phase shift can also be extracted from the second lowest eigenstate. In this case we get a phase shift of 2.488 70(2) rad at $k=0.112\ 006\ 37a_0^{-1}$.

2. Comparison with previous calculations

Previously, the most accurate phase shifts so far published have come from Kohn variational calculations using correlated basis functions [2,3]. At $k=0.20a_0^{-1}$, the seminal calculation of Schwartz gave 2.0673(9) rad [2] while the more recent complex Kohn calculation of Bhatia and Temkin gave 2.066 78(20) rad [3]. The value of Schwartz was deduced by estimating the infinite basis limit of a sequence of calculations. The complex Kohn phase shifts are lower bounds [3] and the uncertainty gives an estimate of the maximum possible increase in the phase shift.

The CVM phase shift at $k=0.2a_0^{-1}$, namely, 2.066 99(2) rad can be regarded as the best estimate of the phase shift so far determined. One source of uncertainty would be the usage of a long-range polarization potential that is based on second-order perturbation theory. The effect of the polarization potential for $r > R_0$ was to increase the phase shift by about 0.000 37 rad. This correction should be reliable to better than 0.000 01 rad since the r^{-6} term in the polarization expansion involving the quadrupole (15 a.u.) and nonadiabatic dipole polarizability (5.375 a.u.) is less than 1% of the magnitude of the dipole polarizability at $r = 19a_0$.

B. Electron-hydrogen scattering in the $^3S^e$ channel

The confining potential in the SVM calculation of the e^- -H $^3S^e$ system was tuned so that the second lowest state had an energy of -0.480 000 00 hartree. The actual energy that was optimized was the average of the two lowest energies, i.e., $E_{\text{opt}}=(E_1+E_2)/2$. The energies given in

Table III were computed with the basis augmented by an additional 40 functions as defined by Eq. (28). The value of α_1 was 17.0. The final confining potential was $W_{\text{CP}}(r)=9.160\ 038\ 70 \times 10^{-5}(r-18)^2$.

The procedure used to convert the confined energy into a phase shift was exactly the same as for the singlet case. The functional form of the model potential used was that given by Eq. (24). The final phase shift at $k=0.2a_0^{-1}$ was -0.424 09 rad. The contribution of the polarization potential for $r > R_0$ was to increase the phase shift by about 0.000 56 rad.

The $k=0.2a_0^{-1}$ phase shift of -0.424 09 rad is consistent with the Kohn phase shifts of Schwartz, namely, -0.4245(5) rad [2] and that of Bhatia and Temkin, namely, -0.424 18(20) rad [3] when the limitations of the basis sets of these two earlier calculations are taken into consideration. The uncertainty of 2×10^{-4} rad quoted by Bhatia and Temkin is an estimate of the further increase in the phase shift to be expected from a calculation that was variationally complete. The CVM triplet phase shifts can be regarded as the best variational estimate of this phase shift so far determined.

One limitation of the present calculations concerned linear dependency issues. It was not possible to increase the dimension of the augmented basis beyond $N=240$. When this was attempted the energy of the lowest states started to experience big jumps as the inherent linear dependence of the ECG basis resulted in large round-off errors.

C. Use of a tuning potential with a different functional form

The actual potential between the projectile and the hydrogen atom has an attractive integrable singularity at the origin. This will influence the boundary conditions of the exact scattering wave function at the origin. An alternate parametrization based on the static potential of the atomic hydrogen ground state was also used to determine the phase shifts. This potential was

TABLE IV. Energies and phase shifts of the lowest energies of the e^- -H $1,3S^e$ systems for the wider confining potentials. The number of ECGs in the basis is given by N . The energy of the bound H $^-$ ground state is denoted by E_0 . Energies and k are given in atomic units.

N	$E_{0,N}$	$E_{1,N}$	$E_{2,N}$	$E_{3,N}$	$k_{1,N}$	$k_{2,N}$	$k_{3,N}$	$\delta_{\text{CVM},1,N}$	$\delta_{\text{CVM},2,N}$	$\delta_{\text{CVM},3,N}$
$1S^e$ symmetry										
140	-0.52774652	-0.49645290	-0.48867807	-0.47999690	0.0842271	0.1504788	0.2000155	2.64134	2.29150	2.06583
240	-0.52775055	-0.49645361	-0.48868002	-0.47999985	0.0842187	0.1504658	0.2000008	2.64173	2.29229	2.06692
340	-0.52775092	-0.49645362	-0.48868010	-0.47999996	0.0842185	0.1504653	0.2000002	2.64174	2.29232	2.06697
390	-0.52775099	-0.49645363	-0.48868011	-0.47999998	0.0842184	0.1504652	0.2000001	2.64174	2.29233	2.06697
440	-0.52775100	-0.49645363	-0.48868012	-0.48000000	0.0842184	0.1504651	0.2000000	2.64175	2.29233	2.06698
$3S^e$ symmetry										
140		-0.49676883	-0.48904093	-0.47999921	0.08038865	0.1480477	0.2000040	-0.16075	-0.30900	-0.42438
190		-0.49676908	-0.48904134	-0.47999987	0.08038647	0.1480450	0.2000006	-0.16066	-0.30885	-0.42415
240		-0.49676903	-0.48904139	-0.47999995	0.08038625	0.1480447	0.2000003	-0.16065	-0.30883	-0.42413
265		-0.49676903	-0.48904140	-0.47999997	0.08038620	0.1480446	0.2000001	-0.16065	-0.30882	-0.42412
290		-0.49676903	-0.48904141	-0.48000000	0.08038617	0.1480446	0.2000000	-0.16065	-0.30882	-0.42411

$$V_H(r) = \left(\lambda - \frac{1}{r} \right) \exp(-2r) - \frac{\alpha_d}{2r^4} [1 - \exp(-r^6/\rho^6)]. \quad (29)$$

Using this alternate form of the tuning potential led to no change in the phase shifts at the reporting precision of 10^{-5} rad.

D. Test of the BCM

The BCM was also used to extract the phase shifts for this symmetry. The outgoing wave function was extracted by multiplying the two-electron wave function by the hydrogen atom ground state (written as a linear combination of ECGs) and then integrating over one of the electron coordinates [14]. The logarithmic derivative was computed at $r=R_0$ and a correction then applied to take into account the long-range polarization potential.

The phase shifts were less accurate and were more susceptible to small changes in the calculation. For example, the $N=240$ basis for the e^- -H $3S^e$ system gave a phase shift of -0.42460 rad at $k=0.2a_0^{-1}$. When α_1 was changed to 19.45 there was a change in $E_{2,240}$ of 3.0×10^{-8} hartree. However, the phase shift changed by 1.4×10^{-4} rad. This is at least ten times larger than the change in the phase shift coming from a CVM analysis. The BCM phase shifts rely on the local value of the wave function and are therefore not able to reach the same precision as the CVM.

E. Use of a wider confining potential

Some additional calculations in a wider confining potential were done to verify that the phase shifts were independent of the choice of the confining potential radius. Calculations were done for both the $1S^e$ and $3S^e$ symmetries.

The singlet confining potential was $W_{\text{CP}}(r) = 1.88834930 \times 10^{-5}(r-23)^2$. This choice leads to the fourth confined eigenstate having a momentum of $k=0.2a_0^{-1}$. The energy being optimized was the average of the four lowest

energies, i.e., $E_{\text{opt}}=(E_0+E_1+E_2+E_3)/4$. This wider confining potential had less impact upon the energy of the H $^-$ ground state. Imposition of the confining potential raised the energy of the ground state by 0.87×10^{-8} a.u.

The energies of the lowest states at various stages of the optimization are listed in Table IV. The best energy of the H $^-$ ground state was -0.527750995 hartree; this is 1×10^{-8} hartree from convergence when the confining potential is taken into account. The biggest calculation gave a phase shift of 2.06698 rad at $k=0.20a_0^{-1}$. This is only 1×10^{-5} rad smaller than the phase shift obtained from the narrower confining potential. The effects of round-off error prevented extending the basis beyond the present size, but examination of the convergence pattern of the $k=0.20a_0^{-1}$ phase shifts suggests a converged phase shift of 2.06699 rad.

The wider confining potential for the calculations upon the e^- -H $3S^e$ system was $W_{\text{CP}}(r)=2.27232050 \times 10^{-5}(r-22)^2$. This choice resulted in the third confined eigenstate having a momentum of $k=0.2a_0^{-1}$. The energy optimized was the average of the three lowest energies, i.e., $E_{\text{opt}}=(E_1+E_2+E_3)/3$.

The influence of round-off errors due to the nonorthogonal basis had a more severe impact upon $3S^e$ phase shifts. The largest possible basis was limited to $N=290$ and attempting to go beyond this dimension led to a failure in the diagonalization procedure. The actual sequence of successive energy increments from $190 \rightarrow 240 \rightarrow 265 \rightarrow 290$ did not show a pattern that permitted an extrapolation to the $N \rightarrow \infty$ limit. The only conclusion that can be made is that the two $3S^e$ calculations gave phase shifts which agreed to 2×10^{-5} rad, i.e., the two confining potentials gave the same phase shift to within the uncertainties of the respective calculations.

F. Electron-helium scattering in the $2S^e$ channel

The CVM was applied to the s -wave scattering of electrons from the helium ground state. The SVM was used to

TABLE V. Confined energies and phase shifts for the $^2S^e$ e -He system as a function of the number of ECGs, N . The phase shifts from some other calculations at $k=0.20a_0^{-1}$ are listed. Energies and k are given in atomic units.

N	$E_{1,N}$	$E_{2,N}$	$k_{1,N}$	$k_{2,N}$	$\delta_{\text{CVM},1,N}$	$\delta_{\text{CVM},2,N}$
SVM basis						
600	-2.89806984	-2.88371635	0.1063442	0.20004016	-0.13752	-0.26660
800	-2.89807164	-2.88372084	0.1063272	0.20001766	-0.13698	-0.26572
1000	-2.89807222	-2.88372247	0.1063217	0.20000956	-0.13681	-0.26540
1200	-2.89807245	-2.88372319	0.1063196	0.20000596	-0.13674	-0.26526
1400	-2.89807260	-2.88372366	0.1063181	0.20000357	-0.13669	-0.26517
1600	-2.89807267	-2.88372384	0.1063175	0.20000267	-0.13667	-0.26513
Augmented SVM basis						
640	-2.89807236	-2.88372329	0.1063204	0.20000545	-0.13676	-0.26524
840	-2.89807263	-2.88372393	0.1063179	0.20000224	-0.13668	-0.26512
1040	-2.89807272	-2.88372415	0.1063171	0.20000114	-0.13666	-0.26508
1240	-2.89807275	-2.88372424	0.1063167	0.20000070	-0.13665	-0.26506
1440	-2.89807278	-2.88372429	0.1063165	0.20000042	-0.13664	-0.26505
1640	-2.89807279	-2.88372432	0.1063164	0.20000028	-0.13663	-0.26504
KV [40]			0.1063162	0.20	-0.1368	-0.2655
MCHF [41]				0.20		-0.2630
RM [42]				0.20		-0.265
RMPS [43]				0.20		-0.2607

optimize the average energy of the lowest two states. The confining potential used was the potential $W_{\text{CP}}(r)=1.059\,950\times 10^{-4}(r-18)^2$. This potential was adopted to give an energy close to $-2.883\,724\,377\,0$ hartree for the second confined state (this is exactly 0.02 hartree above the He ground state energy of $-2.903\,724\,377\,0$ hartree [1,39,44]). The confining potential had an insignificant effect on the energy of the helium ground state. The energy increase when the confining potential was added was less than 10^{-15} hartree.

Table V gives the energies of the two lowest states at various stages of the SVM optimization procedure. A casual inspection of the sequence of energies suggests that the overall level of convergence of the confined energy is between 10^{-6} and 10^{-7} hartree. This level of convergence is somewhat worse than the convergence of a purely bound system. For example, a SVM calculation of the Li ground state energy was performed. An ECG basis of dimension 1000 gave an energy of $-7.478\,060\,274$ hartree. This is only 5×10^{-8} hartree above the energy of Pachucki [45], namely, $-7.478\,060\,324$ hartree.

Convergence was accelerated by augmenting the basis with functions designed to represent an electron moving in the static potential of the He ground state. These additional basis functions were

$$\Psi_{\text{out}}^i = \psi^{\text{He}}(\mathbf{r}_1, \mathbf{r}_2) \exp(-\alpha_i r_3^2), \quad (30)$$

$$\psi_{\text{He}}(\mathbf{r}_1, \mathbf{r}_2) = \sum_k d_k F_k^{\text{He}}(\mathbf{r}_1, \mathbf{r}_2). \quad (31)$$

The He ground wave function $\psi_{\text{He}}(\mathbf{r}_1, \mathbf{r}_2)$ was written as a linear combination of 90 ECGs (F_k^{He}). This basis gave

$-2.903\,724\,33$ a.u. for the He ground state energy. A total of 40 electron Gaussians, defined by the relation $\alpha_i=17.0/1.45^{i-1}$, multiplying the He ground state wave function were included. The value of $\alpha_1=17.0$ is slightly different from the value adopted in Ref. [18]. This choice of α_1 resulted in the augmented basis energy improvement for the $N=1200$ basis being 5×10^{-8} hartree larger than that achieved when the choice of $\alpha_1=19.45$ was made [18]. The energies $E'_{i,N}$ and derived phase shifts ($\delta'_{\text{CVM},i,N}$) for the augmented basis are given in Table V. The potential of Eq. (24) was used for phase shift reconstruction with the helium dipole polarizability set to 1.3832 a.u. [46]. The contribution to the phase shift from the long-range part of the potential (i.e., $r>18a_0$) was only 0.000 19 rad at $k=0.20a_0^{-1}$.

The advantage of the augmented basis is readily apparent in Table V. The smallest calculation with the augmented basis with $N=640$ gives better phase shifts than the nonaugmented basis of dimension 1200. The improvement is also evident in Fig. 1 which shows the $\delta_{\text{CVM},2}$ and $\delta'_{\text{CVM},2}$ phase shifts for different sized basis sets plotted against the energy difference $\Delta E=|E'_{2,N}-E_{2,N}|$. This difference, ΔE will tend to zero as the basis size increases. Continuation of the series of calculations would result in $\delta_{\text{CVM},2}$ and $\delta'_{\text{CVM},2}$ tending to a common intercept. The limiting value of the phase shift at $k=0.20a_0^{-1}$ was $-0.265\,03$ rad.

As far as we know there have been no large scale calculations of electron scattering from helium using a correlated basis. The Kohn-variational (KV) calculations of Nesbet [40] used a basis of single particle orbitals centered on the nucleus to represent both that target and scattering electrons. This is also true of the multiconfiguration Hartree-Fock (MCHF) calculations of Saha [41]. Another notable calculation is the R matrix with pseudostates (RMPS) calculation by

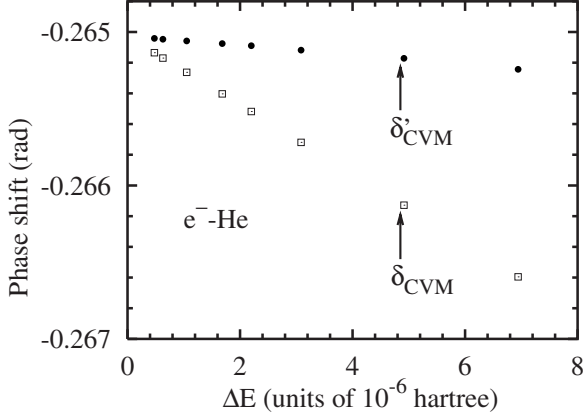


FIG. 1. The s -wave phase shifts for e^- -He scattering at $k \approx 0.2a_0^{-1}$ plotted as a function of ΔE for different sized basis sets. The phase shifts derived directly from the SVM calculation, $\delta_{\text{CVM},2,N}$, and that derived with the augmented basis, $\delta_{\text{CVM},2,N}^s$ are included.

Hudson *et al.* [43]. The RMPS calculation was not aimed specifically at low energy elastic scattering and the resulting phase shifts are not regarded as having the same accuracy as the KV. The KV helium elastic cross section of Nesbet is often adopted as a theoretical benchmark cross section [47,48].

The CVM phase shift at $k=0.2a_0^{-1}$ is slightly more positive by 0.0005 rad than the KV phase shift. But this is within the uncertainty estimate of 0.0005 rad attached to the KV phase shift. The MCHF phase shift of Saha is 0.002 rad more positive than the CVM phase shift at this momentum. We conclude that the MCHF calculation suffers from some small systematic error that leads it to overestimate the phase shifts by about 1%.

G. Electron-hydrogen scattering in the $^3P^o$ channel

So far all the examples are systems with a total orbital angular momentum of $L=0$. It is also possible to apply the SVM to systems with nonzero angular momentum [17]. The particular formulation adopted in the present work is that of the global vector method [17,25]. In this approach the total angular momentum is introduced using a global function. For a two-electron system the basis functions are

$$\Psi_{LS}(\mathbf{r}) = \mathcal{A} |u_1 \mathbf{r}_1 + u_2 \mathbf{r}_2\rangle^K Y_{LM}(u_1 \mathbf{r}_1 + u_2 \mathbf{r}_2) \chi_{SM_S} \times \prod_{i=1}^N \exp[-\beta_i r_i^2] \prod_{i<j} \exp(-\alpha_{ij}(\mathbf{r}_j - \mathbf{r}_i)^2), \tag{32}$$

where \mathcal{A} is an antisymmetrizer and χ_{SM_S} is the spin function of the particles. The nonlinear variational parameters β_i and α_{ij} are selected by the usual stochastic procedure. Full details are given in Refs. [17,25]. The spherical part of the ECG basis functions effectively allows internal angular momentum to be distributed between the different parts of the systems. Accordingly, Eq. (32) implicitly includes all possible internal symmetries that can make a contribution to the energy. This has been verified with test calculations.

The procedure to extract the phase shifts is transparently similar to the procedure for s -wave scattering. The basis functions do have additional variational flexibility in that the parameters of the global vector, $u_1 \mathbf{r}_1 + u_2 \mathbf{r}_2$, i.e., u_1 and u_2 can be adjusted and treated as additional parameters in the stochastic search. This additional degree of flexibility was not utilized and the choice $(u_1, u_2) = (0, 1)$ was adopted for all the basis functions. The augmented basis functions to represent a product of a continuum electron and the hydrogen ground state had the form

$$\Psi_{LS}(\mathbf{r}) = \mathcal{A} |\mathbf{r}_2\rangle^K Y_{LM}(\mathbf{r}_2) \chi_{SM_S} \times \phi_H(r_1) \exp(-\beta_i r_1^2), \tag{33}$$

where $\phi_H(r_1)$ is the Gaussian representation of the H ground state and the β_i are chosen as an even tempered set. The final confining potential parameters for the $^3P^o$ calculation were $G=4.397\,948\,294 \times 10^{-5}$ and $R_0=18a_0$.

Table VI records the phase shifts obtained from the CVM calculation of the $^3P^o$ symmetry. Phase shifts from some previous high accuracy calculations [49–51] are listed. Phase shifts computed with the perturbation theory expression [52,53]

$$\tan(\delta_l) \approx \frac{\pi \alpha_d k^2}{(2l-1)(2l+1)(2l+3)}, \quad l > 0, \tag{34}$$

are also given. The perturbation theory expression gives phase shifts which are some 10–20 % smaller than those of the more exact calculations.

TABLE VI. The lowest two energies of the confined $^3P^o$ e^- -H system as a function of the number of ECGs, N . The phase shifts from some other calculations at $k=0.20a_0^{-1}$ are given. Energies and k are given in atomic units.

N	$E_{1,N}$	$E_{2,N}$	$k_{1,N}$	$k_{2,N}$	$\delta_{\text{CVM},1,N}$	$\delta_{\text{CVM},2,N}$
140	-0.49174236	-0.47999981	0.1285118	0.2000010	0.017611	0.045288
190	-0.49174240	-0.47999997	0.1285115	0.2000002	0.017624	0.045328
240	-0.49174241	-0.48000000	0.1285114	0.2000000	0.017626	0.045336
Correlated optical potential [49]				0.200		0.045345
Kohn [50]				0.200		0.0450
Finite element [51]				0.200		0.0452
MERT			0.1285114	0.200	0.01556	0.03768

The CVM phase shift at $k=0.20a_0^{-1}$ was 0.423 36 rad. The contribution to this phase shift from the long-range polarization potential for $r > 18a_0$ was about 1%. The CVM phase shift compares well with the recent value of 0.042 345 rad of Bhatia that was computed with an optical potential derived from a correlated basis (COP) [49]. The present CVM calculation was not driven to convergence. All calculations with $L=0$ were performed with a mature program that was consequently efficient and reliable. The computations for the ${}^3P^o$ symmetry were performed with a completely new SVM program. Evaluation of the matrix elements was slower due to their additional complexity [17,25]. Further, the most efficient search strategies for determining the optimal ECGs basis set were developed during the course of the calculation (this would distort any attempt to deduce the variational limit from the energies listed in Table VI). So the results presented in Table VI should be regarded more as a proof of principle as opposed to the ultimate solution. Even with this caveat, the CVM ${}^3P^o$ phase shift at $k=0.20a_0^{-1}$ is still within 1×10^{-5} rad of the best phase shift ever reported.

V. SUMMARY AND PERSPECTIVES

A method of obtaining phase shifts by adding a confining potential to the scattering Hamiltonian is developed. First it was shown that two scattering Hamiltonians with the same energies in the confining potential must have the same phase shifts at that energy. This provides a mechanism for adapting practically any method for solving the bound Schrödinger equation into a procedure that can also give scattering phase shifts. One advantage of the CVM is that the initial calculation of the energy is governed by the variational principle for

bound states. The energy is therefore insensitive to first-order variations of the wave function from the exact wave function.

In the present work the SVM has been used as the numerical engine to determine the energies of the confined Hamiltonian. The use of a nonorthogonal Gaussian-type basis does impose some restrictions on the functional form of the confining potential, but these are not so severe as to effect the utility of the method. Indeed, the CVM S -wave phase shifts presented here for hydrogen and helium are very accurate.

The main source of uncertainty is the representation of the wave function at large distances where the dominant factor is the polarization potential. However, there was no detectable change in the e^- -H phase shift for scattering calculations utilizing a wider confining potential. The calculations on the ${}^1S^e$ state suggest the possible variation of the phase due to the use of a finite R_0 would be about 10^{-5} rad or less.

One application of the CVM would be to study low energy elastic scattering for physical systems that are not accessible by standard approaches. An interesting class of system worth investigating would be the e^\pm -H₂ systems. There have been no definitive first principles calculations of the scattering length or low energy phase shifts for these two systems and it has been shown that ECG basis sets can give very accurate energies for molecular systems [27,54–56]. It would first be necessary to generalize the present procedure to treat nonspherical systems.

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