

Minimum-variance approach to electron-scattering calculations: Elimination of anomalies and Monte Carlo implementation

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It is demonstrated, in calculations on one- and two-electron systems, that K -matrix (real-valued) boundary conditions in the trial wave function in the minimum-variance method can give anomalies at certain energies, while T -matrix (complex) boundary conditions do not. A Monte Carlo procedure is proposed for computing scattering amplitudes in a many-electron system that uses the minimum-variance approach to treat incident and target electrons on the same footing. Successful exploratory calculations on e^- -H scattering in the radial limit suggest that this approach may provide a path to direct Monte Carlo scattering calculations on many-fermion systems.

There has been substantial interest in recent years in developing methods which reduce the quantum scattering problem to some variety of the Monte Carlo integration procedure.^{1,2} The principal barrier to the development of such approaches is the same as that encountered in Monte Carlo calculations on bound states of many-particle systems,³⁻⁵ namely, that when the wave function is not of one sign, Monte Carlo integration of functions which are not positive definite is required.^{6,7} In a scattering problem this difficulty is especially severe because the asymptotic form of the wave function is oscillatory, and, in electron-atom or electron-molecule scattering in particular, the antisymmetry of the many-electron wave function further complicates matters. The approach we would like to explore here is based on a simple—and old—idea for optimizing a trial scattering wave function but retains the spirit of more sophisticated Monte Carlo methods in that it treats the many-particle problem directly and involves sampling from an N -electron distribution.

In the context of Monte Carlo calculations of bound-state energies, Umrigar, Wilson, and Wilkens⁸ pointed out that minimization of the variance sum

$$\sigma^2 = \sum_i w(i) [H\Psi(i)/\Psi(i) - E_g]^2 / \sum_i w(i) \quad (1)$$

provides a method for optimizing a trial function Ψ with a much smaller number of points than would be required to successfully quadrature matrix elements of the Hamiltonian. The sum in this equation is over configurations (points in the N -particle coordinate space); E_g is the current guess for the energy of the state in question, and $w(i)$ is a weight function. The argument for why this approach should require many fewer points than a numerical integration of matrix elements of H is fairly straightforward. If, for example, the trial function Ψ , has n parameters and is capable of representing the exact wave function, then n points in the sum are sufficient to deter-

mine the n parameters exactly.

The application of this idea in a scattering calculation starts with the variance sum in the form

$$\sigma^2 = \sum_i |(H - E)\Psi_i(i)|^2 w(i), \quad (2)$$

where Ψ_i is a trial function satisfying scattering boundary conditions. This idea is an old one, especially in the form where the quantity minimized is the variance integral

$$\sigma_i^2 = \int |(H - E)\Psi_i(\tau)|^2 w(\tau) d\tau. \quad (3)$$

Scattering problems are generally formulated by expanding the total wave function (target plus projectile) in terms of a finite set of target states and then explicitly projecting out these states by integrating over the coordinates of the target. This produces a set of coupled, one-body equations that describe the motion of the projectile. In this context, the use of the variance sum, as given in Eq. (2), has been investigated by Bardsley, Gerjuoy, and Sukumar⁹ in a one-channel case and by Mertz and Collins¹⁰ in a coupled-channel radial problem. Both of these studies yielded the encouraging result that accurate scattering amplitudes could be calculated with a modest number of terms (fewer than 15 for one channel and fewer than 50 in the five-channel case) in the sum in Eq. (2). However, in spite of its occasional resurrection in the literature, this idea has not emerged as a generally reliable approach to scattering calculations.

We wish to examine the idea of using the minimum-variance principle to solve the full (unprojected) Schrödinger equation. However, before investigating the possibility of applying the minimum-variance idea directly to a many-electron scattering problem, we would like to point out a serious deficiency in the way this procedure has been formulated in the past. That deficiency is that the method can suffer from a problem which appears to be reminiscent of the anomalies (spurious singularities) appearing in applications of the Kohn variational princi-

ple¹¹ and, less seriously, in applications of the Schwinger variational principle.¹² With the minimum-variance method, however, the anomalies appear predictably—near energies where the phase shift or scattering eigenphases approach particular values. Fortunately, a simple modification of the formalism eliminates those spurious resonances in the present case.

Using a single-channel, *s*-wave potential scattering problem as an example, for which the Hamiltonian is $H = -\frac{1}{2}d^2/dr^2 + V(r)$, the usual approach to scattering calculations via minimizing the variance can be summarized as follows. Let ϕ_0 and ϕ_1 be continuum functions of the form

$$\phi_0 = \sin(kr), \quad (4a)$$

$$\phi_1 = g(r)\cos(kr), \quad (4b)$$

where $g(r)$ is a cutoff function which is unity for large r and goes to zero at least as fast as r for small r . Choose a trial function which has *K*-matrix scattering boundary conditions,

$$\Psi_t^K = \sum_{n=2}^N c_n \phi_n + \phi_0 + K \phi_1, \quad (5)$$

where the functions $\phi_n(r)$, for $n \geq 2$, are square-integrable basis functions and *K* denotes the *K* matrix which, in this case, is just the tangent of the phase shift, $\tan \delta$. All the quantities in Ψ_t are real, so substituting Eq. (5) in Eq. (2) and setting the derivatives of σ^2 with respect to c_n and *K* gives the working equation

$$\underline{A} \mathbf{c} = \mathbf{b}, \quad (6)$$

where the elements of the matrix \underline{A} and the vector \mathbf{b} are defined by

$$A_{nm} = \sum_i (H - E) \phi_n(i) (H - E) \phi_m(i), \quad (7a)$$

$$b_n = \sum_i (H - E) \phi_n(i) (H - E) \phi_0, \quad (7b)$$

and the first element of the solution vector c_1 denotes *K*.

It has been alleged that the minimum-variance method in this form is free of the false resonances which occur in the Kohn and Hulthen variational principles.¹³ In a sense that is true because the functional in Eq. (2) is positive definite. However, at an energy where the phase shift δ is equal to $\pi/2$, the *K* matrix is infinite and therefore one of the elements of the solution vector in Eq. (6) becomes infinite. Since Ψ_t^K is not capable of reproducing the exact wave function, the variance will be infinite at such an energy, as can be seen by substituting Eq. (5) into Eq. (2) and letting *K* go to infinity. We speculate that it is a property of the minimum-variance method that, near such energies, σ^2 is minimized by optimizing the coefficients c_n at the expense of producing accurate values of *K*. The end effect is that a numerical implementation of the minimum-variance method as outlined above displays anomalies. These are apparently narrow in most one-dimensional problems, and to our knowledge have not been observed previously. In Fig. 1 we present calculations of the *s*-wave phase shift for the potential

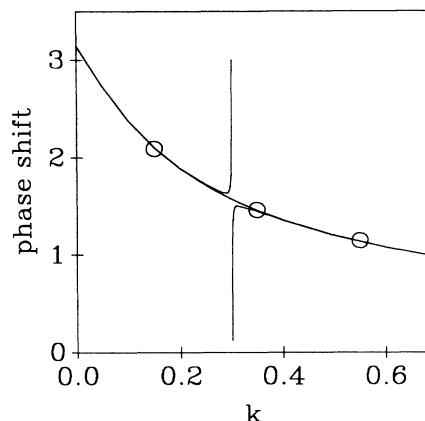


FIG. 1. *s*-wave phase shift for the potential $-\exp(-r)$ from calculations with basis functions of the form $r \exp(-\xi r)$ with exponents $=5/1.5^n$ with $n=0,1,2,3$. Solid line with false resonance: *K*-matrix boundary conditions; continuous solid line: *T*-matrix boundary conditions; circles: exact values.

$V(r) = -e^{-r}$ in a basis of our functions of the form $r \exp(-\xi_n r)$ with exponents chosen according to $\xi_n = 5/1.5^n$. In Fig. 2 we show how the anomaly near the energy where $\delta = \pi/2$ becomes narrower as the basis is improved, which is the qualitative behavior observed in calculations employing the Kohn principle. There are 64 radial points in the variance sum in these calculations with weights equal to Gauss-Laguerre quadrature weights, and the cutoff function $g(r)$ is chosen as $1 - \exp(-r)$.

The observation of anomalies of this limited type in the minimum-variance method would not be of much interest if the problem were as benign for multidimensional problems as it is for one-dimensional ones. That is not the case, and we demonstrate below that even in a two-dimensional problem of these anomalous features can be

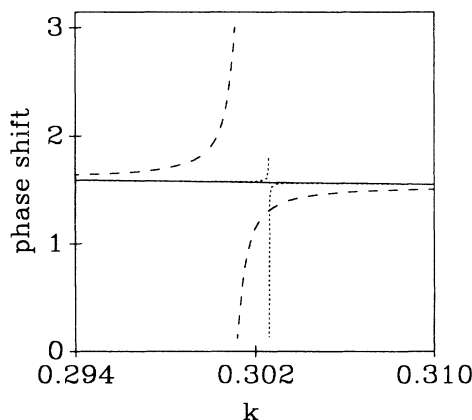


FIG. 2. Basis set dependence of calculations in Fig. 1. Solid line: *T*-matrix boundary conditions (both basis sets); dashed line: *K*-matrix calculation with four basis functions as in Fig. 1; dotted line: *K*-matrix calculation with one additional basis function with $\xi = 5/1.5^4$.

quite wide and persist even for large basis sets.

Fortunately there is a way to avoid this problem. It is essentially the same remedy which solves the difficulty of anomalies in the Kohn variational principle.¹⁴ If we choose the trial function to have T -matrix boundary conditions

$$\Psi_t^T = \sum_{n=2}^N c_n \phi_n + \phi_0 + T \phi_1, \quad (8)$$

with ϕ_0 and ϕ_n defined as in Eq. (4), but with ϕ_1 defined as an outgoing wave

$$\phi_1(r) = g(r) e^{ikr}. \quad (9)$$

Now the matrix elements in Eq. (5) have the form

$$A_{nm} = \sum_i [(H-E)\phi_n(i)]^* (H-E)\phi_m(i), \quad (10a)$$

$$b_n = \sum_i [(H-E)\phi_n(i)]^* (H-E)\phi_0. \quad (10b)$$

The T matrix is not singular at real energies in the continuum [$T = e^{i\delta} \sin(\delta)$ in the s -wave example], and Eq. (6) does not become ill conditioned at any energy. An essential point to note here is that, in using T -matrix boundary conditions, one is allowing the variational principle to determine both the magnitude and phase of an unknown quantity, whereas K -matrix boundary conditions force all the basis set error into the phase of the scattering matrix. Calculations using T -matrix boundary conditions for the one-dimensional example are shown in Figs. 1 and 2.

The use of T -matrix (or S -matrix) boundary conditions in the complex Kohn variational method leads to a complex symmetric matrix representation of $H-E$ in the working equations, and this feature has been credited with being at the heart of the elimination of spurious singularities in the Kohn method.¹⁴ This observation suggests that using the complex trial function Ψ_t^T in a calculation which extremizes the "complex" variance σ_c^2 defined without complex conjugation,

$$\sigma_c^2 = \sum_i [(H-E)\Psi_t^T(i)]^2 w(i) \quad (11)$$

provides an alternative which performs still better numerically. For the one-dimensional case Eq. (11) gives results which are essentially indistinguishable from those from Eq. (2), but for the two-dimensional case Eq. (11) gives a slight improvement, as we demonstrate below.

Having eliminated the false resonances in the usual formulation of the minimum-variance method, we propose to solve electron-atom or electron-molecule problems by applying the minimum-variance technique directly to the N -electron system. The trial function in Eq. (2) or Eq. (11) must therefore be able to include the effects of electron correlation, but since no matrix elements are required, it may be chosen in a sophisticated and flexible way. As in bound-state Monte Carlo calculations we may make explicit use of interelectronic coordinates or Jastrow factors¹⁵ to enforce the two-electron cusp condition. We also propose to use Monte Carlo methods to sample the many-electron coordinate space to provide points for the variance sum, as did Umrigar, Wilson, and Wilkens⁸

in their bound-state calculations.

To perform a preliminary test of this idea we have chosen the radial limit of a two-electron system, electron-hydrogen-atom scattering with singlet spin coupling. For this problem the Hamiltonian is

$$H = -\frac{1}{2} \frac{d^2}{dr_1^2} - \frac{1}{2} \frac{d^2}{dr_2^2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_>}, \quad (12)$$

where r_1 and r_2 are the distances of the two electrons from the nucleus and $r_>$ is the greater of r_1 and r_2 . This is a legitimate two-electron problem in which only the $l=0$ angular momentum component of the interelectronic repulsion is retained. In this example we consider only elastic scattering, and the two-electron trial function is

$$\Psi_t = (\chi_1, \phi_0) + c_1 (\chi_1 \phi_1) + \sum_{\alpha=2}^N c_\alpha (\chi_{n_\alpha}, \chi_{m_\alpha}), \quad (13)$$

where c_1 denotes the T -matrix element for elastic scattering. The notation (χ_i, χ_j) denotes the symmetrized product

$$(\chi_i, \chi_j) = [\chi_i(r_1)\chi_j(r_2) + \chi_j(r_1)\chi_i(r_2)]/\sqrt{2}, \quad (14)$$

ϕ_0 and ϕ_1 are continuum functions defined as in Eqs. (4a) and (9), χ_1 , χ_2 , and χ_3 are the hydrogenic 1s, 2s, and 3s functions, and the remaining basis functions are Laguerre functions of the form

$$\chi_{n+4}(r) = \{\lambda^3 / [(n+1)(n+2)]\}^{1/2} r L_n^{(2)}(\lambda r) e^{-\lambda r/2} \quad (15)$$

with $\lambda=6$. We used functions with $n=0$ to 7 in Eq. (15) to yield a total of 11 square-integrable basis functions and 66 correlating terms in Ψ_t^T . The trial function chosen in Eq. (13) is clearly restricted to elastic scattering below the $n=2$ threshold, since continuum functions only appear in connection with the 1s target state. Equation (13) can be suitably modified to treat inelastic processes.

The points in the variance sum are chosen by sampling a distribution which allows a high probability for one

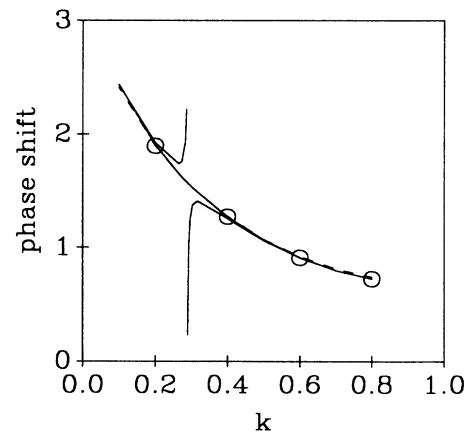


FIG. 3. Phase shifts for the radial limit e^- -H scattering problem. Continuous solid line: "complex" variance method [Eq. (11)] with T -matrix boundary conditions; solid line with false resonance: K -matrix boundary conditions; dashed line: minimum-variance method [Eq. (2)] with T -matrix boundary conditions.

TABLE I. Comparison of calculations for singlet e^- -H scattering phase shifts in the radial limit.

k	K matrix	T matrix		Ref. 17
		Eq. (2)	Eq. (11)	
0.2	1.9248	1.8989	1.9044	1.8973
0.4	1.2535	1.2723	1.2690	1.2696
0.6	0.9080	0.9193	0.9109	0.9105
0.8	0.7268	0.7404	0.7254	0.7261

electron to be distant from the atom while the other one remains near the nucleus. In these calculations we chose points by Metropolis¹⁶ sampling the particular distribution

$$\rho(x_1, x_2) = \frac{(e^{-\alpha_1|x_1|} e^{-\alpha_2|x_2|} + e^{-\alpha_1|x_2|} e^{-\alpha_2|x_1|})^2}{2/(\alpha_1\alpha_2) + 8/(\alpha_1 + \alpha_2)^2} \quad (16)$$

on the interval $(-\infty, \infty)$ for both variables and defining $r_1 = |x_1|$ and $r_2 = |x_2|$. We then chose the weight function in Eq. (2) or (11) to be

$$w(r_1, r_2) = r_1 r_2 / \rho(r_1, r_2) \quad (17)$$

to further weight the large- r region. The exponents in the distribution function are $\alpha_1 = 0.1$ and $\alpha_2 = 0.05$. With these choices of distribution and weight functions the variance sum approaches a particular variance integral as the number of Monte Carlo points M is increased:

$$\sigma^2 = \sum_{i=1}^M |(H-E)\Psi_i(i)|^2 w(i) \rightarrow \int_0^\infty dr_1 \int_0^\infty dr_2 |(H-E)\Psi_i(r_1, r_2)|^2 r_1 r_2 \quad (18)$$

The results of calculations with 2000 Monte Carlo points are given in Fig. 3, which shows calculations using T -matrix boundary conditions in Eq. (2) and in Eq. (11) as well as the results of calculations using K -matrix boundary conditions. Even with the flexible trial function we used in these calculations, the false resonance which appears in the K -matrix results is quite broad and is even broader with other weight functions of the form $(r_1 r_2)^m$ with $0 \leq m \leq 3$ which we investigated. T -matrix boundary conditions give accurate values for the phase shift using both forms of the variance sum, with the "complex" variance approach in Eq. (11) generally giving slightly better results. Numerical comparison with the results of Adelman and Reinhardt¹⁷ are given in Table I.

These results suggest that the proposed approach to electron-scattering calculations may provide a practical method for solving the problem including electron corre-

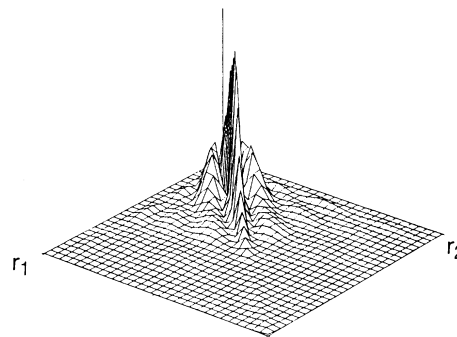


FIG. 4. Local variance, $|(H-E)\Psi_i(r_1, r_2)|^2 r_1 r_2$, from a minimum-variance calculation with 66 correlating configurations using 11 Laguerre functions with $\lambda = 2.0$ (so $n=0$ is hydrogenic 1s) at $k = 0.6$.

lation and target response. The key to such calculations is the construction of a flexible trial function capable of an accurate representation of the correlated wave function. Since the minimum-variance technique is a fitting method, it is important that the trial function be efficient in the sense that it contain as few variational parameters as possible. It is clear from bound-state Monte Carlo calculations, and in particular from the work of Umrigar, Wilson, and Wilens,⁸ that enforcement of the cusp condition on the wave function is critical to effectively minimizing the local variance. In Fig. 4 we show the value of the variance function, $|(H-E)\Psi_i(r_1, r_2)|^2 r_1 r_2$, from a minimum-variance calculation on the radial limit problem. The variance peaks along the line $r_1 = r_2$, reflecting the fact that the trial function we have used in these calculations does not explicitly enforce the cusp condition for the radial limit problem. Clearly, it will be important to employ Jastrow factors¹⁵ in the general case.

Calculations using these methods on inelastic processes and on systems of higher dimensionality are underway. The critical question, which remains open at this time, is whether the Monte Carlo minimum-variance method proposed here performs well in higher-dimensional systems—as the success of similar methods in optimizing trial functions in the electronic bound-state problem suggests it might.

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