

Discrete-basis-set approach to the minimum-variance method in electron scattering*

Deborah A. Levin, Thomas N. Rescigno,[†] and Vincent McKoy

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

(Received 3 May 1976; revised manuscript received 12 November 1976)

We show that the minimization of the variance integral provides a method for the determination of scattering wave functions which uses discrete basis functions exclusively. By using a separable representation of the scattering potential only one new class of matrix elements appears in the evaluation of the variance integral which is not already required in the diagonalization of the Hamiltonian. The choice of Gaussian basis functions for the expansion of the scattering wave function should make the method particularly applicable to electron-molecule scattering. Some advantages and limitations of the method are discussed.

I. INTRODUCTION

The use of discrete basis sets offers considerable advantages in the calculation of electron scattering processes.¹ For example, these methods require only standard matrix techniques in their applications rather than the more usual approach of numerical integration of the differential equations. Moreover these methods can be extended to the calculation of scattering amplitudes for nonspherical potentials, thus avoiding the need for single-center expansions of the nonspherical potentials or their scattering wave functions. We have recently proposed one such method which is based on the use of Gaussian-type orbitals in the direct solution of the Lippmann-Schwinger equation for the full elastic scattering amplitude.² With Gaussian basis functions being the usual choice for the multicenter molecular problem this approach can be implemented with standard bound-state integral programs. Schneider has also developed an approach to electron-molecule scattering based on the R -matrix formalism in which discrete basis functions are used to expand the scattering wave functions in the internal region.³

Although these two methods rely on the use of discrete basis functions to achieve their critical simplifications they do not avoid the continuum completely. Specifically the free-particle Green's function must be dealt with in the solution of the T -matrix equation and a numerical integration is needed in the outer region in the R -matrix approach. Two methods which use discrete basis functions exclusively have been developed and applied to electron-atom scattering. These methods are the Fredholm determinant method, its related equivalent quadrature approach of Reinhardt and coworkers⁴ and the J -matrix technique of Heller and Yamani.⁵ However these methods are restricted to systems with spherical potentials and at present do not seem rigorously applicable to

scattering by nonspherical potentials, e.g., electron molecule scattering, without resorting to a single-center expansion.

In this paper we discuss an approach to scattering problems which uses discrete basis functions entirely and which is applicable to both electron-atom and electron-molecule scattering. The method is essentially a variational approach to scattering and is based on the minimization of a variance integral, $U[\tilde{\Psi}]$, defined as

$$U[\tilde{\Psi}] = \frac{\int w(r) [(H - E)\tilde{\Psi}]^2 d\tau}{\int \tilde{\Psi} \tilde{\Psi} d\tau}, \quad (1)$$

where r represents the coordinates of all particles. The function $w(r)$ is an arbitrary but positive weight function. This variance integral is non-negative for any trial function $\tilde{\Psi}$ and is zero only for the exact wave function. Minimization of the value of this variance integral obviously provides a criterion for the determination of the parameters appearing in $\tilde{\Psi}$. The method is referred to as the minimum variance or least-squares method and has been applied to the determination of bound states⁶ and more recently to potential scattering problems.⁷ However, in this work⁷ trial functions $\tilde{\Psi}$ of the Kohn type explicitly containing continuum functions are used and hence, in this form the method would not be practical for applications to electron-molecule scattering.

In our proposed method we will use Eq. (1) to determine scattering wave functions but these functions will be expanded entirely in discrete basis functions. This procedure leads to a simple matrix equation which determines the linear parameters in the expansion of $\tilde{\Psi}$. Scattering information can then be extracted from the approximate scattering wave function which is known to be proportional to the true scattering solution over the region of space spanned by the discrete basis functions.^{8,9} Our choice of Gaussian basis functions as the discrete basis set for the expansion of $\tilde{\Psi}$

makes the method particularly applicable to molecular problems. Moreover by using a separable representation of the scattering potential, the evaluation of the variance integral, $U[\tilde{\Psi}]$ of the quadratic variational principle, leads to only one new class of matrix elements in addition to those already required in the direct diagonalization of the Hamiltonian. This is an important consideration since the method can provide approximate scattering wave functions at arbitrary energies whereas the direct diagonalization of the Hamiltonian in a discrete basis yields such wave functions only at the discrete eigenvalues. Thus in contrast to the Harris method,¹⁰ a single choice of an expansion basis can give scattering information over an arbitrary number of energies.

The outline of the paper is as follows: In Sec. II we review the minimum variance method and some previous applications of the method to scattering problems. There we will also derive the simple matrix eigenvalue equation which results from Eq. (1) if $\tilde{\Psi}$ is expanded exclusively in a discrete basis set. In Sec. III we present the results of the application to some model potentials and to *s*-wave scattering for helium in the static-exchange approximation. Finally in Sec. IV we discuss future applications of the method.

II. THEORY

The minimization of the variance integral and of the related variance sum has been used to determine the energies and wave functions of bound⁶ and autoionizing states and more recently has been applied directly to scattering problems.⁷ In these applications both Bardsley⁷ and Miller¹¹ employed trial functions, $\tilde{\Psi}$, of the Kohn type in the variance integral to obtain *s*-wave phase shifts for an attractive exponential potential and for the hydrogen atom in the static approximation with and without exchange. The trial functions $\tilde{\Psi}$ are hence of the form (for *s*-wave scattering),

$$\tilde{\Psi}(r) = \sum_{n=1}^N c_n \phi_n + S(kr) + \tan \delta C(kr), \quad (2)$$

where ϕ_n are bound-like functions and S and C behave asymptotically like sine and cosine, respectively. The minimum variance method obviously leads to integrals which do not arise in the Kohn and Hulthén variational procedures. For these simple one-dimensional problems the additional integrals are tractable. In these cases the method can offer some advantages since the positive definite character of the variance integral eliminates the occurrence of false resonances which appear in the Kohn procedures and the variance integral can be used to derive bounds to the phase shifts.

Our purpose is to exploit certain features of this

minimum variance method to develop a purely discrete basis set approach for obtaining scattering wave functions at arbitrary energies. For applications of the minimum variance method to electron-molecule scattering trial functions of the form of Eq. (1) containing continuum-like functions are clearly not practical since they lead to intractable integrals. However, a number of studies have shown that approximate scattering wave functions can be obtained by diagonalizing the Hamiltonian in a large discrete basis set since the eigenfunctions are proportional to the scattering wave functions over the region spanned by the basis.^{1,8} Unfortunately one can obtain such information only at scattering energies equal to the eigenvalues of the Hamiltonian matrix. For many applications this is a severe limitation. We can cite two obvious examples. In a distorted-wave formalism, to obtain the electronically inelastic amplitude in electron-impact excitation we would require the scattering wave functions at specific incident and final energies. Furthermore, a sum over all partial-wave amplitudes at one energy is required just to evaluate the total elastic cross section; with the phase shifts obtained only at a discrete number of points, an interpolation would be necessary since it is not in general possible to make the various partial-wave eigenvalues coincide. Such an interpolation is particularly difficult in the vicinity of a resonance. Our goal then is to use the quadratic variational principle, i.e., the minimum variance method, to generate scattering wave functions at arbitrary energies in a completely discrete basis set representation at any energy.

The formulation is straightforward. We expand $\tilde{\Psi}$ in a discrete basis set, i.e.,

$$\tilde{\Psi} = \sum_{i=1}^N c_i \varphi_i, \quad (3)$$

and substitute this expansion into Eq. (1) to obtain

$$U[\tilde{\Psi}] = \frac{\sum_{i,j} c_i c_j \int w(r) [(H-E)\varphi_i] [(H-E)\varphi_j] d\tau}{\sum_{i,j} c_i c_j \int \varphi_i \varphi_j d\tau}. \quad (4)$$

Minimization of U with respect to the linear coefficients $\{c_i\}$ leads to a set of equations which can be written in matrix form as

$$\underline{QC} = \underline{USC}, \quad (5)$$

where \underline{C} is the vector of coefficients $\{c_i\}$ and

$$Q_{ij} \equiv \int w(r) [(H-E)\varphi_i] [(H-E)\varphi_j] d\tau, \quad (6)$$

$$S_{ij} \equiv \int \varphi_i \varphi_j d\tau. \quad (7)$$

E is the scattering energy. For the exact solution the variance integral is zero. To minimize the variance we simply obtain the solution of the eigenvalue equation, Eq. (5), corresponding to the smallest eigenvalue. Writing $H = T + V$, we obtain for Q_{ij}

$$Q_{ij} = \int \omega(r) [T\varphi_i T\varphi_j + V\varphi_i V\varphi_j + T\varphi_i V\varphi_j + V\varphi_i T\varphi_j - 2E(\varphi_i T\varphi_j + \varphi_i V\varphi_j) + E^2 S_{ij}] d\tau. \quad (8)$$

The evaluation of the various terms appearing in Q_{ij} , for a many-particle Hamiltonian, will undoubtedly involve very difficult integrations. Let us assume that H is a single-particle Hamiltonian determined by an effective one-body target potential, e.g., the Hartree-Fock static-exchange or optical potential. Assuming for the moment that a convenient form can be chosen for the weighting function, $w(r)$, the last three terms in the integral, Eq. (8), correspond to elements of the kinetic energy, potential energy, and overlap matrices arising in normal variational calculations. The remaining integrals are greatly simplified if we assume a nonlocal, separable form for the potential V , i.e.,

$$V(r, r') = \sum_{\alpha, \beta=1}^N V_{\alpha\beta} \varphi_\alpha(r) \varphi_\beta(r') \quad (9)$$

and

$$V\Psi = \sum_{\alpha, \beta=1}^N V_{\alpha\beta} \varphi_\alpha(r) \int \varphi_\beta(r') \Psi(r') d^3r'. \quad (10)$$

The scattering potential is thus represented by an $N \times N$ matrix with elements $V_{\alpha\beta}$. With this form of V we have

$$\int V\varphi_i V\varphi_j d\tau = \sum_{\alpha} V_{\alpha j} V_{\alpha i}, \quad (11)$$

$$\int T\varphi_i V\varphi_j d\tau = \sum_{\alpha} V_{\alpha j} T_{\alpha i}. \quad (12)$$

These quantities again require just the potential energy and kinetic energy matrices. We emphasize that the assumption of a separable interaction has only been made with respect to the scattering potential and not the kinetic energy. However the integral containing $T\varphi_i T\varphi_j$ is a new integral not appearing in ordinary variational calculations. In the next section we will see that with φ_i and φ_j chosen as Gaussian functions this integral is very simple and can be done analytically.

Once the vector of coefficients, \underline{C} , corresponding to the minimum eigenvalue of Eq. (5) is obtained the scattering wave function $\tilde{\Psi}$ is known.

The phase shift can be extracted by examining the quantity

$$\tan \delta_l(r) = W[R_l, j_l] / W[R_l, n_l] \quad (13)$$

as a function of r until it acquires a nearly constant value. This value is obviously the phase shift. In Eq. (13) R_l is the radial function derived from $\tilde{\Psi}$, $j_l(kr)$ and $n_l(kr)$ are the Bessel and Neuman functions, respectively, and W is the Wronskian. This procedure has been discussed in recent applications to the scattering of electrons by H_2 , N_2 ,⁸ and F_2 .¹² One may also use the approach recently suggested by Dalgarno for obtaining phase shifts from these approximate scattering wave functions.¹³ In using Eq. (13), we have assumed that the analytic radial functions, R_l , are accurate in the potential-free region and can therefore be matched to Bessel and Neuman functions. Although we have not done so, one could clearly modify this procedure to match R_l to any numerically generated zeroth-order distorted wave, e.g., those generated by a quadrupole field. If there is significant off-diagonal long-range coupling, a more general matching procedure such as that involving the solution of coupled equations in the external region would have to be employed.

III. RESULTS

We have used this discrete basis set approach to the minimum variance method to study the scattering of electrons by several model potentials and by helium in the static-exchange approximation. These potentials include the attractive exponential potentials, $-e^{-r}$ and $-e^{-r^2}$, and the screened Coulomb potentials of the form e^{-r^2}/r . Although we present results for s -wave scattering only, the approach is clearly applicable to the higher partial waves. Our primary purpose is to test an approach which may have specific advantages in future applications to electron-molecule scattering.

All the results except those for the exponential, $V(r) = -e^{-r}$, were obtained using a basis set of Gaussian functions. We choose Gaussian basis functions since this choice is the most convenient for future applications. The integral containing $(-\frac{1}{2}\nabla^2\varphi_i)(-\frac{1}{2}\nabla^2\varphi_j)$, which is the only new integral appearing in this method if we assume the separable form for the potential, has a simple form. For basis functions of the form

$$\varphi_{jkl}^{\vec{A}, \alpha} = (\chi - A_x)^j (y - A_y)^k (z - A_z)^l \exp[-\alpha(\vec{r} - \vec{A})^2], \quad (14)$$

where \vec{A} is the vector locating center A and j, k, l determine the order of the Gaussian, i.e., s, p, d, \dots , we have

TABLE I. Phase-shift values for the potential $V(r) = -e^{-r}$.

k (a.u.)	U^a	δ^b	δ_{ex}^c
0.3	6.6×10^{-4}	1.56	1.57
0.4	1.8×10^{-3}	1.31	1.36
0.5	2.4×10^{-3}	1.14	1.20
0.6	5.1×10^{-3}	0.99	1.08
0.7	6.7×10^{-3}	0.91	0.98

^aValue of the variance integral defined in Eq. (4).

^bPhase shifts calculated by the minimum variance method with a basis set of nine Slater functions of the form $r^n e^{-\alpha r}$ with $\alpha = 1$.

^cExact phase shift obtained by Calogero's method. See text.

$$\int \left(-\frac{1}{2} \nabla^2 \varphi_{000}^{\vec{B}, \beta} \right) \left(-\frac{1}{2} \nabla^2 \varphi_{000}^{\vec{A}, \alpha} \right) d\tau = \frac{\alpha^2 \beta^2 \pi^{3/2}}{(\alpha + \beta)^{7/2}} e^{-\eta D} \left(\frac{4\alpha^2 \beta^2 D^2}{(\alpha + \beta)^2} - 20 \frac{D\alpha\beta}{\alpha + \beta} + 15 \right), \quad (15)$$

with $D = (\vec{A} - \vec{B})^2$ and $\eta = \alpha\beta/(\alpha + \beta)$. Integrals involving other Gaussian functions can be determined by taking the appropriate derivative of Eq. (15) with respect to the coordinates of a particular center.¹⁴

For several applications, particularly those of scattering by potentials with a Coulomb behavior at short distances, the use of an appropriate weighting function, $w(r)$, proved very helpful. Our choice of weighting function was fixed by requiring that the resulting variance integral still be evaluated by standard bound-state molecular integral programs for Gaussian basis sets. This is a reasonable choice to keep the method applicable to realistic problems. This suggests the weighting function

$$w(r) = 1 - \alpha e^{-\tau r^2}, \quad 1 \geq \alpha \geq 0, \quad \tau > 0, \quad (16)$$

which does lead to a variance integral, Eq. (4) that can be evaluated with multicenter Gaussian integral programs. This function increases from

a value of $1 - \alpha$ as $r \rightarrow 0$ to unity as r becomes large. Hence $w(r)$ weights the outer region more than the inner. This choice of weighting function yielded approximate scattering solutions which show significant amplitude in the physically significant inner regions and hence are simpler to analyze for scattering information. In this way we avoid the apparent tendency of the least-squares method to yield solutions with small amplitudes in those regions where the scattering potential is large. Since it is precisely in this inner region where one desires a solution with large amplitude, we choose a weighting function which forces a small amplitude at large r . By varying the parameters α and τ we can change the relative weights of the outer and inner regions so as to obtain a lower value for the variance integral.

Tables I and II show results for several model potentials. The phase shifts in Table I are for the attractive exponential potential $V(r) = -e^{-r}$. We used a basis set of nine Slater orbitals and did not use a weighting function, i.e., $w(r) = 1$. Comparison of the calculated phase shifts with the exact phase shifts at increasing values of k shows the obvious trend that solutions with small variances yield more accurate phase shifts. This basis set obviously cannot represent the scattering functions at larger incident momentum as well as those at lower k . For this potential we also solved the minimum variance equations without assuming a separable form for the potential. These calculated phase shifts agreed well with those derived by assuming a separable form for V indicating that this representation of the potential is adequate.

Table II gives the s -wave phase shifts for several potentials and the effect of the weighting function on the value of the variance integral and the phase shifts. Comparison of the phase shift at $k = 0.5$ demonstrates the advantage of using an adequate weighting function. In this case a basis set of 17 Gaussian functions along with a weighting function gives the same value of the phase shift and vari-

TABLE II. Phase shifts for various model potentials.

k (a.u.)	$V(r)$	U^b	$w(r)^c$	δ^d	δ_{ex}
0.287	$-e^{-r^2}$	1.45×10^{-4}	$1 - 0.79e^{-0.28r^2}$	0.62	0.65
0.287	$-e^{-r^2}$	1.03×10^{-4}	1	0.64	0.65
0.287	$-e^{-r^2}/r$	1.42×10^{-4}	$1 - 0.99e^{-0.28r^2}$	0.42	0.41
0.287	e^{-r^2}/r	1.51×10^{-4}	$1 - 0.79e^{-0.28r^2}$	-0.14	-0.14
0.500 ^a	$-2e^{-r^2}/r$	2.21×10^{-3}	1	2.64	2.65
0.500	$-2e^{-r^2}/r$	2.45×10^{-3}	$1 - 0.88e^{-0.28r^2}$	2.63	2.65

^aA set of 28 Gaussian basis functions was used in this calculation. All the other calculations were done with a set of 17 Gaussian functions.

^bValue of the variance integral.

^c $w(r)$ is the weighting function used in minimizing the variance integral.

^dThe phase shift extracted from the approximate scattering wave function. See text.

TABLE III. Phase shifts for e -He scattering in the static-exchange approximation.

k (a.u.)	U	δ^a	δ^b
0.1	4.5×10^{-6}	2.98	3.00
0.2	2.3×10^{-5}	2.84	2.88
0.3	1.1×10^{-4}	2.69	2.72
0.4	6.0×10^{-4}	2.58	2.59
0.5	2.4×10^{-3}	2.40	2.45
0.6	5.9×10^{-3}	2.33	2.33
0.7	8.7×10^{-3}	2.17	2.19
0.8	1.9×10^{-2}	2.08	2.10

^a Calculated from the minimum variance method with a basis of Gaussian basis functions and a weighting function of the form of Eq. (16) with $\tau=0.28$ and $0.79 \leq \alpha \leq 0.99$.

^b Accurate phase shifts from Ref. 15. These values are those of Ref. 15 rounded off to three significant digits.

ance integral as a basis of 28 Gaussian functions used without a weighting function.

Table III lists the phase shifts for the scattering of electrons by the static-exchange potential of helium from $k=0.1$ to $k=0.8$. These phase shifts were calculated with a basis of 17 Gaussian functions and agree well with the results of Schneider.¹⁵ In these calculations most of the matrix manipulations are independent of the impact energy so scattering solutions can be obtained at very many energies quite economically. While the matrix Eq. (5) must be solved for each energy, it is only the lowest eigenvalue and corresponding eigenvector that are required. For large matrices, this can represent a substantial savings. Finally Table IV illustrates the effect of the weighting function on the phase shift and variance integral for the e^- -helium scattering. By increasing the weighting of the outer region over the inner region the variance integral can be decreased leading subsequently to an improved value of the phase shift. We also noted that, at the same energy, the scattering wave function obtained by the minimum variance method is generally a smoother function than that given by the direct diagonalization of the Hamiltonian. It is worth noting that although the Lippmann-Schwinger equations are exactly soluble with the approximation of Eq. (9), the present approach does not require the free-particle Green's function nor the construction of any matrix inverse.

IV. CONCLUSIONS

We have shown that minimization of the variance integral provides a method for the determination of scattering wave functions which uses discrete basis functions exclusively and completely avoids

the continuum. The applications of this method to scattering by several model potentials and by the static-exchange potential of helium show that the method can provide reliable scattering wave functions economically.

The choice of Gaussian basis functions for the expansion of the scattering wave function should make the method particularly applicable to electron-molecule scattering. Moreover by using a separable representation of the scattering potential only one new class of matrix element appears in the evaluation of the variance integral which is not already required in the diagonalization of the Hamiltonian. The analysis presented here, which is appropriate for treating single-channel potential problems, would have to be modified to handle problems in which the reactance matrix is not diagonal. In such cases, no simple formula for the reactance matrix can be given which is independent of the normalization of the wave function because at any energy there may be more than one linearly independent solution. One possible method for dealing with this problem in an L^2 basis has been discussed by Hazi.¹⁶ If N linearly independent solutions are needed at a particular energy, we can simply repeat the calculations for several choices of expansion bases and use the appropriate multichannel extension of Eq. (13). A simpler, but approximate, approach would be to use a decoupling scheme (low " l spoiling") as has been done by several authors.¹⁷

There are several features of our approach to the minimum variance method which should lead to significant advantages in solving certain problems. For example, we found that the approximate scattering wave function obtained from the minimum variance method is usually a smoother function than the eigenfunction obtained by diagonalization of the Hamiltonian in the same discrete basis set. This feature can be important if one wants to use these scattering wave functions to obtain informa-

TABLE IV. Effect of the weighting function on the phase shift.

α^a	U	δ
0.7986	1.35×10^{-3}	2.593
0.8865	1.13×10^{-3}	2.587
0.9899	5.98×10^{-4}	2.580

^a The weighting function is of the form $w(r) = 1 - \alpha e^{-\tau r^2}$ with $\tau=0.28$. The phase shift is for $k=0.4$ where the accurate value is 2.58. The relative weighting of the outer region ($r=4$ a.u.) to the inner region ($r=1$ a.u.) varies from 2.5 to 3.9 for these choices of α .

tion other than the phase shifts. Such an application would be the use of these wave functions to evaluate an electronically inelastic scattering amplitude in the distorted wave approximation. For this application one may also use a weighting function so as to obtain wave functions with desirable features in the important regions of space.

ACKNOWLEDGMENTS

We want to thank Larry Yaffe and Dr. C. William McCurdy, Jr., for helpful discussions in the early stages of this work. We also thank Dr. Andrew Hazi for extensive clarification of the contents of Ref. 16.

*Supported by a grant from the National Science Foundation.

†Present address: Lawrence Livermore Laboratory, University of California, Livermore, Calif. 94550.

‡This work was performed under the auspices of the U.S. Energy Research and Development Administration under Contract No. W-7405-ENG-48.

¹See, for example, A. U. Hazi and H. S. Taylor, *Phys. Rev. A* **2**, 1109 (1970); W. P. Reinhardt, D. W. Oxtoby, and T. N. Rescigno, *Phys. Rev. Lett.* **28**, 401 (1971).

²T. N. Rescigno, C. W. McCurdy, Jr., and V. McKoy, *Phys. Rev. A* **10**, 2240 (1974).

³B. Schneider, *Chem. Phys. Lett.* **31**, 237 (1975).

⁴W. P. Reinhardt, *Computer Phys. Comm.* **6**, 303 (1973).

⁵E. J. Heller and H. A. Yamani, *Phys. Rev. A* **9**, 1201 (1974).

⁶See, for example, M. H. Lloyd and L. M. Delves, *Int. J. Quantum Chem.* **3**, 169 (1969).

⁷J. N. Bardsley, E. Gerjuoy, and C. V. Sukumar, *Phys. Rev. A* **6**, 1813 (1972); F. H. Read and J. R. Soto-Mon-

tiel, *J. Phys. B* **6**, L15 (1973).

⁸C. W. McCurdy, Jr., T. N. Rescigno, and V. McKoy, *J. Phys. B* **9**, 691 (1976).

⁹A. U. Hazi and M. Fels, *Chem. Phys. Lett.* **8**, 582 (1971).

¹⁰F. E. Harris and H. H. Michels, *Phys. Rev. Lett.* **22**, 1036 (1969).

¹¹K. J. Miller, *Phys. Rev. A* **3**, 607 (1971).

¹²T. N. Rescigno, C. F. Bender, C. W. McCurdy, and V. McKoy, *J. Phys. B* **9**, 2141 (1976).

¹³M. Oppenheimer, H. Doyle, and A. Dalgarno, *Chem. Phys. Lett.* **32**, 6 (1975).

¹⁴I. Shavitt, *Methods of Computational Physics* (Academic, New York, 1963), Vol. II, p. 30.

¹⁵B. Schneider, *Chem. Phys. Lett.* **25**, 140 (1974).

¹⁶A. U. Hazi, *Chem. Phys. Lett.* **20**, 251 (1973), and private communications.

¹⁷T. Winter and N. F. Lane, *Chem. Phys. Lett.* **30**, 363 (1975); M. A. Morrison and N. F. Lane, *Phys. Rev. A* **12**, 2361 (1975).