

Pseudospectral techniques in minimum-variance calculations of electron-scattering cross sections

T. N. Rescigno

Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94550

C. W. McCurdy

Department of Chemistry, The Ohio State University, 120 West Eighteenth Avenue, Columbus, Ohio 43210

B. I. Schneider

Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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We propose a method for calculating electron-scattering cross sections which consists of a combination of the minimum-variance approach to optimizing a trial wave function and pseudospectral techniques for evaluating exchange contributions. Tests in simple applications indicate that this hybrid approach is remarkably efficient. Only one-electron matrix elements and quantities depending on the trial function and its derivatives evaluated at grid points are required. The extension to more complex systems is discussed.

Despite the fact that sophisticated *ab initio* methods have been developed to study electron-molecule scattering,¹⁻⁴ the dynamics of those collisions for polyatomic molecules⁵ continue to be treated at a primitive level. *Ab initio* calculations including even a few open electronic channels for a molecule with more than three atoms have yet to appear. Our recent investigations of variational methods⁶ for computing scattering amplitudes as well as the studies of the *S*-matrix Kohn method by Miller and co-workers^{7,8} have shown encouraging accuracy and computational efficiency in this context. Particularly important is the fact that exchange matrix elements involving continuum functions can be avoided in these approaches.⁹ However, the application to polyatomic molecules remains a formidable task.

Fundamentally, there are only two obvious approaches to implementing these ideas for polyatomic systems: single center expansions or discretization on three-dimensional grids. Single center expansions have been successful for linear molecules. However, in the general case, there are no good angular momentum quantum numbers and the number of coupled radial equations (per electronic channel) in this approach increases as l^2 , where l is the maximum angular momentum of the spherical harmonics included in the expansion. In fact, it is not difficult to show that direct, three-dimensional numerical quadrature of the integrals involved requires roughly the same number of operations as the single center expansion of the problem. By making use of the pseudospectral techniques being investigated by Friesner,¹⁰⁻¹² or the discrete variable methods being studied by Light *et al.*,¹³ the three-dimensional quadrature idea can be made substantially more attractive. Nonetheless, the prospects are discouraging on both fronts.

In the context of Monte Carlo calculations of bound-state energies, Umrigar, Wilson, and Wilkens¹⁴ have recently 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 wave function with a much smaller number of points than it would take to successfully quadrature the matrix elements of the Hamiltonian. The sum in this equation is over configurations (points in the N -particle coordinate space), ψ denotes a trial wave function whose parameters are to be optimized, E_g is the current guess for the energy, and $w(i)$ is a weight function. Because this is a fitting procedure and not an integration, it should require a much smaller number of points than would be required to quadrature a many-electron integral of similar form. The argument that this is the case goes as follows. If, for example, the trial function has n parameters and is capable of representing the exact wave function, then n configurations (points) would be sufficient to determine the n parameters *exactly*.

This argument is not new of course,¹⁵ nor is its application to scattering problems. There have been studies in collision problems where the *integral* of the variance was minimized,¹⁶⁻¹⁸ but two in particular have used the variance *sum* in the form

$$\sigma^2 = \sum_i w(i) [(H - E)\psi_t(i)]^2 \quad (2)$$

to find the parameters in a trial function ψ_t which satisfies scattering boundary conditions. Bardsley, Gerjuoy, and Sukumar¹⁹ and Merts and Collins²⁰ have investigated this approach in one-channel and coupled-channel radial problems, respectively, and have found that the number of points required to produce accurate scattering amplitudes is remarkably small. The drawback, however, is that if one wants to escape with having used very small numbers of points (fewer than 15 in the single-channel problem and fewer than 50 in the five-

channel problem), the points and weights have to be chosen carefully.

The application of these ideas to electronic collision problems is hindered by the fact that exchange forces produce nonlocal operators in H , even in the single-channel case. At first glance it appears, therefore, that one must evaluate the action of integral operators on ψ_t in order to evaluate the terms in Eq. (2), thereby thwarting the attempt to get away without evaluating any integrals. Merts and Collins²⁰ circumvented this issue by applying the minimum-variance technique only in the intermediate radial scattering region, where the potentials are local and have simple multipolar forms. The wave function in the inner region was generated by a different technique.

Our purpose in this Brief Report is to point out that, by making use of the pseudospectral techniques being investigated by Friesner¹⁰⁻¹² in the context of molecular Hartree-Fock calculations, we can effectively evaluate exchange terms in a manner which requires only the evaluation of ψ_t at a small number of grid points in coordinate space. Thus the entire procedure can be constructed such that no two-electron integrals need be explicitly evaluated. The most attractive aspect of this approach is that it is immediately applicable to polyatomic problems, because, as Friesner has shown, the grid techniques being used are easily adaptable to three-dimensional molecular systems.

We begin by choosing all appropriate form for ψ_t which incorporates scattering boundary conditions. Our examples in this paper are single-channel s -wave problems, so we specialize to that case for convenience. The equations for three-dimensional and multichannel cases are similar. We can pick the form which appears in Kohn variational calculations,

$$\psi_t = \sum_{n=0}^N c_n \varphi_n(r) + s(r), \quad (3)$$

where φ_n for $n=1$ to N are square-integrable basis functions, $s(r) = \sin(kr)$, and the first function in the sum is

$$\varphi_0(r) = (1 - e^{-\gamma r}) \cos(kr).$$

Thus c_0 is the scattering amplitude (K -matrix element) we seek to compute. Inserting ψ_t in Eq. (2) and minimizing with respect to the linear coefficients gives the least-squares equations,

$$\underline{A} \underline{c} = \underline{b}, \quad (4)$$

where the matrix \underline{A} and the vector \underline{b} are given by

$$A_{n,m} = \sum_i (H - E) \varphi_n(i) (H - E) \varphi_m(i), \quad (5)$$

$$b_n = \sum_i (H - E) \varphi_n(i) (H - E) s(i). \quad (6)$$

The fact that \underline{A} does not display the spurious singularities associated with the Kohn variational method has been discussed elsewhere.^{19,21} Short of singularities caused by extremely injudicious choices of the grid points, there appear to be no formal problems with the method as described here.

The difficulties inherent in the electron-scattering problem are displayed by the simplest example, electron-hydrogen atom collisions in the static-exchange approximation. In this approximation the hydrogen atom is frozen in its $1s$ state and the effective Hamiltonian for s -wave triplet scattering is

$$H = -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} + J_{1s} - K_{1s}, \quad (7)$$

where the Coulomb and exchange operators are defined by

$$J_{1s} \varphi_n(r) = \varphi_n(r) \int dr' \chi_{1s}(r') \chi_{1s}(r') / r_>, \quad (8)$$

$$K_{1s} \varphi_n(r) = \chi_{1s}(r) \int dr' \chi_{1s}(r') \varphi_n(r') / r_>, \quad (9)$$

and $r_>$ denotes the greater of r and r' .

The first observation to make here is that the derivative and local potential terms ($-1/r$ and J_{1s}) present no problem in constructing the variance sum in Eq. (2). Also, for calculations on molecular (atomic) systems, we can choose the square-integrable functions φ_n to be Gaussian (Slater) basis functions. Then $K \varphi_n$ is simply a basis function multiplied by a one-electron integral that is precisely the same as a nuclear attraction integral in conventional bound-state calculations. Those terms can be calculated using well-known and efficient algorithms for which computer codes are available.

The difficult terms are $K_{1s} \varphi_0(r)$ and $K_{1s} s(r)$, but those can be evaluated with remarkable efficiency using pseudospectral techniques. We begin by expanding $\varphi_0(r)$ and $s(r)$ in the square-integrable basis,

$$s(r) = \sum a_n \varphi_n(r), \quad (10)$$

$$\varphi_0(r) = \sum b_n \varphi_n(r).$$

This expansion works extremely well to evaluate the exchange terms because the exchange operator is a short-range operator. To compute the coefficients for the expansion of $s(r)$, for example, we use least-squares improvement of the collocation method outlined by Friesner.¹¹ Define the matrix \underline{R} by

$$R_{i,n} = \varphi_n(r_i). \quad (11)$$

Then the coefficient vector \underline{a} is given by

$$\underline{a} = (\underline{R}^+ \underline{R})^{-1} \underline{R} \underline{s}, \quad (12)$$

where the vector \underline{s} is given by $s_i = s(r_i)$. The points r_i are the collocation points and can be chosen to be entirely independent of the grid points on which the variance sum is evaluated. There may be more collocation points in this procedure than there are square-integrable functions, but there may be no fewer. In the case that there are the same number of points as functions, the method is equivalent to simple collocation. After \underline{a} is computed, the value of $K_{1s} s(r)$ is then simply given by

$$K_{1s} s(r) = \sum_{n=1}^N K_{1s} \varphi_n(r) a_n, \quad (13)$$

with a similar expression for $K_{1s} \varphi_0(r)$. The entire con-

struction of σ^2 can thus be performed using the values of the basis functions and their derivatives together with one-electron integrals. No two-electron integrals or continuum matrix elements are needed.

We have performed two simple tests to demonstrate the effectiveness of the combination of pseudospectral techniques and minimization of the variance sum. The first of those is the computation of phase shifts for triplet electron-hydrogen atom collisions in the static-exchange approximation.

We have used 14 nonorthogonal functions φ_n chosen to be simple Slater functions, $\varphi_n = \exp(-\alpha_n r)$, with exponents given by $\alpha_n = 14/1.4^n$ with $n = 1, \dots, 14$. In Table I we show the convergence of the results with respect to the number of collocation points used. For that study we used 64 Gauss-Laguerre points and weights as the points and weights for evaluating the variance sum. We also chose the collocation points as Gauss-Laguerre points, but no weights were used in the pseudospectral calculation. The results show that 25 collocation points are sufficient to evaluate the exchange terms.

To investigate the rate of convergence of the method with respect to the number of points used in the variance sum we have chosen a somewhat harsher test case. To the triplet static-exchange potential we add an attractive long-range potential of the form $-1/(1+r^3)$. Table II shows the convergence properties of that calculation with respect to increasing the number of Gauss-Laguerre points and weights in the variance sum. The number of points used to approximate $K_{1s}\varphi_0(r)$ and $K_{1s}s(r)$ was 30 in all cases. It is important to show that there is nothing magic about the fact that the calculations in Table II were performed using quadrature points and weights. To demonstrate that fact we chose similar numbers of points according to $r_i = (i\Delta r)^3$ for $i = 1, \dots, M$ and used unit weights. Table II also lists those results, which show that the rate of convergence is similar for the latter procedure. The same conclusion was drawn from using the Gauss-Laguerre points with unit weights. However, we did find that choosing the points for the variance sum to be evenly spaced was much less efficient. The reader should note, however, that unless the trial wave function is capable of producing the exact solution, the solution of Eq. (2) depends on the choice of the weight function $w(i)$.

TABLE I. Values of $\tan\delta_0$ at $k=1.0$ a.u. for triplet e^- -H scattering in the static-exchange approximation as a function of the number of points used to construct $K_{1s}s$ and $K_{1s}\varphi_0$ [Eq. (12)]. See text for other details of the calculation.

n	$\tan(\delta_0)$
20	5.572
25	5.500
30	5.498
35	5.500
40	5.503
45	5.502
50	5.502
55	5.502

TABLE II. s -wave scattering from long-range potential discussed in text. The first two rows of results used N -point Gauss-Laguerre points and weights in the variance sum. For the second set of calculations, the points were spaced as $r_i = (i\Delta r)^3$, $i = 1, \dots, N$, with Δr chosen such that $r_N = 75$ a.u., and the weights were all unity.

k	N	$\tan\delta_0$			
		15	24	48	64
0.2		0.0401	-0.0636	0.0053	0.0052
1.0		-2.0678	-2.1121	-2.1186	-2.1193
0.2		0.0542	0.0051	0.0052	0.0052
1.0		-2.2374	-2.1171	-2.1113	-2.1112

This fact explains why the results in Table II seem to be converging to slightly different limits.

If it had been necessary to use specialized quadratures to evaluate the variance sum in one dimension, then to solve a three-dimensional problem the grid would have to be a product of three one-dimensional grids. As it stands, the insensitivity of the procedure to the grid used to compute the variance sum shown here and in the calculations of other workers indicates that extension of the method to three dimensions will be relatively straightforward.

From these calculations, and a large number of other computational experiments, we can draw two preliminary conclusions about the choice of grid points. First, the density of points should be higher in the interaction region than at large distances. This conclusion is more or less obvious since $(H-E)$ operating on either the square-integrable functions or on the continuum functions produces a result which vanishes as r goes to infinity. Second, it is important to sample the region where the derivative of the cutoff function for the continuum functions [in this case only $\varphi_0(r)$] is large. The cutoff function, e.g., $(1 - e^{-\gamma r})$, regularizes the continuum function at the origin. If it switches on in the asymptotic region, the coupling between it and the square-integrable functions comes from the kinetic energy and will be nonzero only in the region where the derivatives of the cutoff function are nonzero.

Although the tests reported in this Brief Report are only on simple cases, they provide encouraging evidence that the combination of minimum-variance and pseudospectral techniques is an effective approach to the electron-scattering problem. It is evident that the components of a polyatomic calculation using this approach are easy to construct—at least much easier to construct than two-electron integrals or any molecular integrals involving continuum functions. Our preliminary analysis also indicates that the computer code necessary to implement the present approach is vastly simpler than would be necessary if we were to use single center expansions for any part of the problem.

What remains to be seen is whether or not the rate of convergence with respect to the number of terms in the variance sum and in the collocation set is as rapid for molecular problems as it is in these simple test cases.

However, the results of Friesner in the bound-state problem indicate that molecular problems can be solved with remarkably small collocation grids. Furthermore, we have not used any of the more sophisticated refinements (such as aliasing functions) developed in that context. Tests are underway on molecular problems and will be reported in future publications.

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