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Minimum-Variance Method for Potential Scattering

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In variational solutions of differential or integral equations the variance integral and variance sum provide measures of the inadequacy of the trial function. For certain potential-scattering problems the variance integral can be used to derive rigorous upper and lower bounds to the phase shift. In more general scattering problems, the study of the variance sum or integral gives a check on the convergence of the standard variational calculations, and an alternative criterion for choosing the best trial function. Results are shown for an attractive exponential potential.

I. INTRODUCTION

The standard variational principles[1] for scattering are the extensions of the Rayleigh-Ritz principle by Hulthén,[2] Kohn,[3] and Rubinow.[4] Similar methods have been suggested more recently by Harris and Michels.[5] These methods share several unsatisfactory features.

(a) Convergence of the results can be misleading. As the number of variational parameters is increased, the results obtained by the standard techniques may converge rapidly to a common value, but there is no guarantee that this is the correct value. It is easy to construct an example of a calculation where convergence to the wrong value is achieved. For example, in studying e-H collisions at an energy of 0.005 a.u. (0.14 eV), we obtained the results shown in Table I. For each of the three standard techniques, the phase shift is given for trial functions with three, six, and 12 parameters. In each case the convergence is fast, and the three answers for the 12-term function agree to eight significant figures. However, the correct value for the phase shift, as given by Schwartz, is 2.551, in contrast to the value of 2.396 obtained by each of these methods. The explanation for this discrepancy is that the trial wave functions were constrained so that no matter how many adjustable parameters were introduced, one of the two indistinguishable electrons was always in the 1s hydrogenic state. Thus the result should converge to the one-state-exchange approximation value, as indeed it does.

In performing this calculation we deliberately restricted the trial wave functions so that they do not span the whole function space. In more serious calculations, of course, one tries to ensure that the trial functions span the whole space as best one can. However, the standard techniques are unable to indicate whether this desired spanning of the function space actually has been achieved. Hopefully, the variational theorem ensures that we have chosen the best possible wave function within the space spanned by the trial function, but the variational theorem assuredly does not tell us how important the rest of the function space may be.

(b) The standard methods do not give upper and lower bounds on the phase shift. This difficulty clearly is related to difficulty (a); the problem of obtaining rigorous bounds will be discussed in Sec. III.

(c) The wave functions obtained by these methods may be relatively poor for other purposes, such as photoionization studies, even though they give good phase shifts.

(d) The application of the standard theories to systems with many electrons and several open

TABLE I. Phase shifts of e-H scattering at $k = 0.1$ a.u.

No. of parameters	Hulthén	Kohn	Rubinow
3	2.365 97	2.355 72	2.341 94
6	2.395 64	2.395 66	2.395 64
9	2.395 789	2.395 788	2.395 792
12	2.395 818 2	2.395 818 2	2.395 818 2

channels involves very large computations. Most of the applications to date have been to e-H or e-He collisions.

(e) The Hulthén method does not always lead to real solutions, and the Kohn and Rubinow methods have singularities at certain energies.[6] The problem of the singularities can be overcome in various ways, as will be discussed in Sec. V.

In this paper, we will present the minimum-variance method as a possible technique for tackling these problems. This method has also been called the least-squares or local-energy method. Before we introduce the method, we will recall some features of the standard variational procedures. We will consider potential scattering, and for simplicity will discuss only the s wave (generalization to nonzero angular momentum is trivial). The Schrödinger equation will be written

$$\mathfrak{L}\Psi \equiv \left(\frac{d^2}{dr^2} + k^2 - \frac{2m}{\hbar^2} V(r)\right)\Psi(r) = 0. \tag{1}$$

The basis of the standard variational methods is the Kato identity.[7,8] Suppose we are searching for a wave function $\Psi(r)$, exactly solving (1), which asymptotically behaves as

$$\Psi(r) \approx \cos(kr+\theta) + \cot(\eta-\theta)\sin(kr+\theta). \tag{2}$$

η is the scattering phase shift and θ is an arbitrary phase factor, which is often taken to be zero or $-\frac{1}{2}\pi$. Let $\Psi_t(r)$ be a trial function with the corresponding phase shift η_t. Then η and η_t are related through the Kato identity,

$$\cot(\eta-\theta) = \cot(\eta_t-\theta) - (1/k)\int \Psi(r)\mathfrak{L}\Psi_t(r)dr. \tag{3}$$

If we write $\Psi_t(r) = \Psi(r) + \delta\Psi(r)$, this identity becomes

$$\cot(\eta-\theta) = \cot(\eta_t-\theta) - (1/k)\int \Psi_t(r)\mathfrak{L}\Psi_t(r)\,dr + (1/k)\int \delta\Psi(r)\mathfrak{L}\delta\Psi(r)\,dr. \tag{4}$$

The last term on the right-hand side of this expression is of second order in the error function $\delta\Psi(r)$, and the first two terms are defined by the trial function. Thus, as is well known, the Kato identity leads directly to the aforementioned variational principles,[2-4] which then provide a second-order estimate for the phase shift for any trial function $\Psi_t(r)$,

$$\cot(\eta-\theta) \approx \cot(\eta_t-\theta) - (1/k)\int \Psi_t(r)\mathfrak{L}\Psi_t(r)\,dr. \tag{5}$$

The Kato identity is also used in the selection of the best trial function, that is in the determination of variable parameters within the trial function. For example, in the Kohn and Rubinow methods the sole criterion is that the right-hand side of (5) should be stationary with respect to changes of all the trial-function parameters, including η_t.

When $\delta\Psi(r)$ is small, the use of (5) often leads to very accurate values for the phase shift. However, in the standard methods we cannot check whether or not $\delta\Psi(r)$ is indeed small. In the minimum-variance method we seek an estimate or, if possible, a rigorous bound on the error inherent in a variational calculation. This can be achieved by a study of the integral $\int \Psi\mathfrak{L}\Psi_t$ which appears on the right-hand side of Eq. (3). In Sec. III we show how this integral can be bounded in terms of the variance integral, which is a function of Ψ_t alone and is introduced in Sec. II.

II. MINIMUM-VARIANCE METHOD

Consider the following integral, henceforth to be called the variance integral,

$$U[\Psi_t] = \int |\, w(r)\mathfrak{L}\Psi_t(r)\,|^2 dr. \tag{6}$$

The function $\omega(r)$ is an arbitrary weight function. This integral is non-negative and is zero only for the exact wave function. Thus the value of this integral gives a measure of the accuracy of any trial function and the minimization of this value provides an alternative criterion for the choice of trial-function parameters.

The integral $U[\Psi_t]$ was introduced into the scattering problem by Kato.[7] He showed that formal bounds on the phase shift could be obtained in terms of the value of $U[\Psi_t]$ and the eigenvalues of an auxiliary equation. In general, it is difficult to obtain bounds on these values, but Kato has shown that for potentials of a definite sign these bounds can be obtained by the comparison-potential method. Delves[8] and Shimamura[9] have extended Kato's ideas and discussed the application to more complex problems. In Sec. III we will show how upper and lower bounds can be obtained on the phase shift without the introduction of an auxiliary equation. The condition that the potential does not change sign is not required, but it is replaced by a condition on the strength of the potential.

For many-body problems the evaluation of the variance integral would be extremely tedious. This leads us to also consider the variance sum

$$X[\Psi_t] = \sum_i |\, \omega(r_i)\mathfrak{L}\Psi_t(r_i)\,|^2. \tag{7}$$

If the sum includes a large number of points which are well distributed in configuration space, the value of the sum provides a useful criterion for the assessment of trial functions.

The minimization of the variance sum has been applied to the determination of energies and wave functions of bound states[10] and autoionizing states[11] but to the best of our knowledge it has not been applied directly to scattering problems. In Sec. IV, we will demonstrate the power of this version of the method in the context of potential scattering.

III. UPPER AND LOWER BOUNDS ON PHASE SHIFT

By applying the Schwarz inequality to the Kato identity, we find

$$k\left|\cot(\eta-\theta)-\cot(\eta_t-\theta)\right| = \left|\int \frac{\Psi(r)}{\omega(r)}\omega(r)\mathfrak{L}\Psi_t(r)\,dr\right|$$

$$\leq\left[\int\left|\frac{\Psi(r)}{\omega(r)}\right|^2 dr\int\left|\omega(r)\mathfrak{L}\Psi_t(r)\right|^2 dr\right]^{1/2}$$

$$\leq \Psi_{\max}(W\,U[\Psi_t])^{1/2}, \quad (8)$$

where

$$W=\int\left[1/\left|\omega(r)\right|^2\right]dr, \quad (9)$$

and $\Psi_{\max}$ is the maximum value of $|\Psi(r)|$. On the right-hand side of this inequality the integral $U(\Psi_t)$ is determined by the trial functions, and can be made arbitrarily small. The integral W is also known, and the weight function must be chosen so that W is finite. The only unknown quantity is $\Psi_{\max}$. This inequality was presented recently by Miller,[12] who suggested that $\Psi_{\max}$ should be replaced by an upper bound to the trial wave function. This procedure should in general lead to a reasonable estimate of the error in the trial function, as was demonstrated by Miller, but by this replacement the rigorous nature of the bounds is lost. However, we can show that for certain potentials one can obtain a rigorous upper bound on $\Psi_{\max}$.

Consider the Lippmann-Schwinger equation for $\Psi(r)$,

$$\Psi(r)=\Psi_0(r)+\int G_0(r,\,r')V(r')\Psi(r')\,dr, \quad (10)$$

$G_0(r,r')$ is the free-space Green's function and $\Psi_0(r)$ is the undistorted wave, i.e., in the s-wave potential-scattering problem under present consideration

$$\Psi_0(r)=\sin kr,$$
$$G_0(r,\,r')=\frac{2m}{\hbar^2 k}\sin kr_<\cos kr_>, \quad (11)$$

where $r_<$ and $r_>$ refer to the smaller and greater of r and r'. For simplicity, we will take the phase factor θ, introduced in Eq. (2), to be $-\frac{1}{2}\pi$, so that the same normalization is used in Eqs. (2) and (10).

Let $r_{\max}$ be the position at which $\Psi(r)$ has its maximum amplitude. By applying the Lippmann-Schwinger equation at $r_{\max}$, we find

$$\Psi_{\max}=\left|\Psi(r_{\max})\right| \leq 1+\left|\int G_0(r_{\max},\,r')V(r')\Psi(r')\,dr'\right|$$

$$\leq 1+\Psi_{\max}\int\left|G_0(r_{\max},\,r')V(r')\,dr'\right|$$

$$\leq 1+y_{\max}\Psi_{\max}, \quad (12)$$

where

$$y(r)=\int\left|G_0(r,\,r')V(r')\right|dr' \quad (13)$$

and $y_{\max}$ is the maximum value of $y(r)$. Then provided that $y_{\max}<1$, we have

$$\Psi_{\max}\leq 1/(1-y_{\max}). \quad (14)$$

From the Schwarz inequality (8), we then find

$$\tfrac{1}{2}k\left|\tan\eta-\tan\eta_t\right| \leq \frac{1}{1-y_{\max}}(W\,U[\Psi_t])^{1/2}. \quad (15)$$

Thus we have rigorous upper and lower bounds on $\tan\eta$, provided that the potential $V(r)$ is sufficiently weak that $y(r)$, as defined in Eq. (13), is always less than one. Note that there is no restriction on the sign of the potential.

As an illustration of this technique, consider the potential

$$V(r)=-\lambda e^{-\beta r}. \quad (16)$$

Since $|G_0(r,\,r')|<2m/\hbar^2 k$, we see immediately that

$$y_{\max}\leq\frac{2m}{\hbar^2 k}\int_0^\infty\left|V(r')\right|dr'=\frac{2m}{\hbar^2 k}\,\frac{\lambda}{\beta}. \quad (17)$$

This bound would be particularly useful at high energies. For example, we can obtain limits on the error of the first Born approximation[13] by taking $\Psi_t(r)=\sin kr$. For small k, a better bound can be found by using the inequality

$$G_0(r,\,r')\leq\frac{2m}{\hbar^2 k}kr_<=\frac{2m}{\hbar^2}r_< \quad (18)$$

from which we obtain

$$y(r)\leq\frac{2m}{\hbar^2}\left(\int_0^r\left|V(r')\right|r'\,dr'+r\int_r^\infty\left|V(r')\right|dr'\right). \quad (19)$$

With the exponential potential,

$$y(r)\leq\frac{2m\lambda}{\hbar^2\beta^2}(1-e^{-\beta r}),$$

so that

$$y_{\max}\leq 2m\lambda/\hbar^2\beta^2. \quad (20)$$

We now present some numerical results obtained for this potential with $\lambda=1$, $\beta=2$, and $k=0.5$. For these values of the parameters, the smaller limit on $y_{\max}$ is given by inequality (20). Following the example, and personal advice, of Miller,[12] we used as a trial wave function,

$$\Psi_t(r)=\sin kr+\tan\eta_t\cos kr\,(1-e^{-\alpha r})+\sum_{n=1}^{N}c_n r^n e^{-\beta r}. \quad (21)$$

In a brief preliminary calculation we compared the bounds obtained with several values of α, and found the tightest limits with $\alpha=1.5$. The exponen-

TABLE II. Phase-shift values for the expoential potential with varying weight functions: $\lambda=1$, $\beta=2$, $k=0.5$, $p=2.4$, $N=6$.

Weight function parameter γ	Lower bound $\eta_{\min}$	Upper bound $\eta_{\max}$	First-order estimate η_1	Second-order estimate η_2	Minimum variance integral $U_{\min}$
0			0.255 373 4	0.255 373 11	5.9×10^{-10}
0.1	0.255 219	0.255 526	0.255 372 6	0.255 373 11	6.8×10^{-10}
0.5	0.255 286	0.255 457	0.255 371 9	0.255 373 11	1.1×10^{-9}
0.75	0.255 291	0.255 453	0.255 372 3	0.255 373 11	1.6×10^{-9}
1.0	0.255 279	0.255 466	0.255 372 6	0.255 373 11	2.9×10^{-9}
1.5	0.254 916	0.255 830	0.255 372 8	0.255 373 11	1.1×10^{-7}

tial parameter p was also varied in order to produce the smallest possible difference between the upper and lower bounds. The number of short-range terms, N, was varied from two to 16. The optimum value of p varies with N, and we present results for the value of 2.4 which is most appropriate for $N=6$.

In choosing the weight function, the constraint that $1/\omega(r)$ must be integrable, from 0 to ∞, led us to use an exponential $e^{\gamma r}$, with γ positive. While this function increases with γ and so weights the outer region more than the inner, this effect could be minimized by taking a very small value for γ.

Having fixed the nonlinear parameters and the weight function, the calculation was carried out as follows. For each value of the trial phase shift η_t, the linear coefficients c_n were chosen to give lowest value of the variance integral, $U[\Psi_t]$. Upper and lower bounds on $\tan\eta$ were then found from inequalities (15) and (20). By varying η_t, the least upper bound and greatest lower bound on $\tan\eta$ were determined. These limits are shown in Tables II and III. The value of η_t for which the variance integral is least is denoted by η_1, and the minimum value of that integral is $U_{\min}$. A second-order estimate of the phase shift, η_2, was obtained by substitution in Eq. (5), i.e.,

$$\tan\eta_2=\tan\eta_1+(1/k)\int\Psi_t(r)\mathcal{L}\Psi_t(r)\,dr. \tag{22}$$

It should be noted that the right-hand side of this equation is not stationary with respect to the variation of any of the parameters in the trial wave function, since the projection of $(H-E)\Psi_t$ onto any of the basis functions will not be zero, accept perhaps by accident. In this respect our method is very different from the standard variational techniques.

In Table II we show the results of variations in the exponent γ of the weight function. The lowest value for $U_{\min}$ was obtained with $\gamma=0$; however, no bounds can be obtained with this value, since W is infinite. The best bounds are obtained with a relatively large value 0.75 for γ; this is primarily because W, being equal to $1/\gamma$, decreases with increasing γ. It is also interesting that the first-order estimate is not optimum at $\gamma=0.75$. However, the variation in η_1 is slight and the second-order estimate is exact to at least eight significant figures for all values of γ.

In Table III we show the effect of varying the number of short-range terms between two and 16. Since the value of the parameter p was fixed at 2.4, these results could be improved by the variation of p, at all values of N other than six.

In Sec. IV we will demonstrate the use of the variance sum for the same example.

IV. VARIANCE SUM

The variance sum $X[\Psi_t]$ was evaluated using the points and weights appropriate to Gauss-Laguerre integration. The quadrature points and weights must be defined in terms of a dimensionless variable. This was taken to be r/r_0, where r_0 is a scale length. Our procedure was first to deter-

TABLE III. Phase shifts for the exponential potential, with varying numbers of short-range functions: $\lambda=1$, $\beta=2$, $k=0.5$, $p=2.4$, $\gamma=0.75$.

No. short-range functions N	Lower bound $\eta_{\min}$	Upper bound $\eta_{\max}$	First-order estimate η_1	Second-order estimate η_2	Minimum variance integral $U_{\min}$
2	0.247 403	0.264 417	0.255 932	0.255 371 31	1.7×10^{-5}
4	0.253 123	0.257 599	0.255 363	0.255 373 10	1.2×10^{-6}
6	0.255 291	0.255 453	0.255 372	0.255 373 11	1.6×10^{-9}
8	0.255 322	0.255 421	0.255 371	0.255 373 11	5.8×10^{-10}
12	0.255 3720	0.255 3744	0.255 373 11	0.255 373 11	3.7×10^{-13}
16	0.255 3729	0.255 3733	0.255 373 11	0.255 373 11	6.7×10^{-14}

TABLE IV. Phase shifts obtained by minimization of the variance sum with 12 summation points: $\lambda=1$, $\beta=2$, $k=0.5$, $p=2.4$, $N=6$, $\gamma=0.75$.

Scale length (r_0) (a.u.)	Phase shifts	
	First-order (η_1)	Second-order (η_2)
1	0.255 938 6	0.255 938 3
$\frac{1}{2}$	0.255 373 7	0.255 373 0
$\frac{1}{3}$	0.255 380 5	0.255 373 1
$\frac{1}{4}$	0.255 400 1	0.255 373 2
$\frac{1}{5}$	0.255 400 3	0.255 372 5

mine the value of the phase shift η_1 of the trial function which leads to the minimum value of the variance sum. A second-order estimate was then obtained from Eq. (22). The integral in this equation was obtained by numerical quadrature using the same summation points.

We first used 48 summation points and obtained results identical to those presented above, to at least eight significant figures. We, therefore, reduced the number of points to 12. The results with six short-range functions are shown in Table IV. The second-order phase shift obtained in this way is accurate to six significant figures for each value of the scale length except 1. We cannot obtain bounds with such a small number of points, and can see no rigorous mathematical way of choosing the best value for the scaling length r_0.

V. SINGULARITIES IN KOHN AND RUBINOW METHODS

It has been realized for many years that the Kohn and Rubinow methods lead to singularities at certain energies. Nesbet[6] has suggested that these can be avoided by a judicious choice between the two techniques. He has given a criterion for choosing the method which is more reliable at a particular energy. This leads to discontinuities in the phase shift as a function of energy, but then discontinuities are usually very small. Harris and Michels[5] have suggested an alternative technique, which they call the minimum-norm method, which gives in a sense an interpolation between the Kohn and Rubinow results.

The minimum-variance method gives an alternative technique for avoiding these singularities within the framework of the standard theories. The best trial functions can be obtained using the Kohn and Rubinow criteria and the variance integral, or sum, calculated for arbitrary linear combinations of these two functions. The linear combination which leads to the lowest variance integral is then used in Eq. (22) to generate the second-order estimate for the phase shift. This method is superficially similar to that of Harris and Michels,[5] but it is not equivalent, and has the advantage that the minimum value of the variance integral gives a measure of the accuracy of the trial function.

In the standard technique one sometimes encounters difficulties due to the singularities of the operator $(H-E)^{-1}$ within the space of the short-range functions. In the minimum-variance method, as described in Sec. II, these problems are completely avoided, since the operator $(H-E)^{-2}$ cannot have a singularity within any space spanned by square-integrable functions.

VI. DISCUSSION AND CONCLUSIONS

We have demonstrated that the minimization of the variance integral provides a variational principle which may be superior to the standard techniques in several ways. In regard to the specific points discussed in Sec. I we can make the following comments.

(i) Spurious convergence can be immediately recognized. If, as the number of terms in the trial function is increased, the variance integral converges to a nonzero value, the convergence may be misleading. When the addition of more terms of a particular type leads to an insignificant decrease in the variance integral, one should look for alternative ways to extend the trial function. Similar conclusions can be drawn when using the variance sum, provided that the number of summation points is large compared to the number of variational parameters and that it is well distributed in configuration space.

(ii) Rigorous upper and lower bounds on the phase shift can be obtained for some potential-scattering problems, and confidence limits can be set in more general problems. These confidence limits would be obtained in the manner suggested by Miller,[12] that is, from inequality (8) by replacing Ψ_{max} by the maximum value of the trial wave function. Probably, this replacement would lead to serious error only near energies at which resonant scattering occurs. For narrow resonances the wave function can become extremely large, and it is extremely difficult to obtain meaningful bounds on the phase shift.

(iii) If specific features of the wave function are required, other than the phase shifts, these requirements can be taken into account in the selection of the weight function $\omega(r)$. For example, in calculating dipole-length matrix elements the long-range region should be given greater weight than the short-range region. In calculating bound-free transition probabilities it might be useful to incorporate the bound-state wave function into the weight function. We have not yet examined the utility of this idea, nor can we suggest a criterion for choosing the best weight function in this context.

(iv) Analytic evaluation of the variance integral is extremely difficult in most nontrivial problems.

However, the use of the variance sum involves no analytic integrations or solutions of differential equations. The crucial factor is of course the number of summation points. We are presently investigating e-H scattering to determine how many points are needed. It is clear that the explicit inclusion of more than three electrons would involve excessive computation, unless reliable Monte Carlo methods could be developed. However, with the use of model potentials or pseudopotentials the scope for applications is still considerable, for both electron-atom and electron-molecule collisions.

In summary, we wish to suggest that the study of the variance sum or integral could be useful in two respects. First, when used in conjunction with Kohn and Rubinow methods, as described in Sec. V it apparently avoids the singularities, gives an estimate of the possible error, and provides a check on the convergence of the results. Second, the minimization of the variance sum or integral provides an alternative criterion for choosing the best trial function.

We recognize, of course, that the results we have obtained thus far are very limited in scope, and that the merits of the minimum-variance method in actual collision problems, especially many-particle problems, remain to be established.

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