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Variational Calculations of Scattering*

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It has been found that the behavior of calculated results using variational principles for scattering problems is rather different from that previously known for bound-state problems. As more and more adjustable terms are added to the trial function, the "stationary" value for the phase shift does not converge smoothly, but may on occasion turn out to be grossly inaccurate. In this paper the phenomenon is displayed and partially analyzed, but not completely understood. We seem to be stuck with the conclusion that for a given amount of computational labor, a scattering phase shift may be determined only to an accuracy an order of magnitude worse than that of the analogous eigenvalue problem.

VARIATIONAL PRINCIPLES

The expression

$$L = \int \psi^*(E - H)\psi \tag{1}$$

is stationary with respect to variations of the trial function ψ, when ψ approaches the correct solution of Schrödinger's equation. It is necessary only to require that ψ go to zero at infinity rapidly enough (for example, $\int \psi^*\psi = 1$), and we have the Rayleigh–Ritz variational principle for eigenvalues E. The standard procedure is to expand ψ in terms of some convenient set of functions χ_i,

$$\psi = \sum_{i=1}^{N} C_i \chi_i , \tag{2}$$

and variation of the constants C_i gives the well-known (finite) matrix eigenvalue problem.

$$\det \| H_{ij}^{(N)} - EN_{ij}^{(N)} \| = 0, \tag{3}$$

where $i, j = 1, \cdots, N$.

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$$H_{ij}^{(N)} = \int \chi_i^* H \chi_j ;$$

$$N_{ij}^{(N)} = \int \chi_i^* \chi_j .$$

As the set of trial functions is augmented the several lowest eigenvalues of $H_{ij}^{(N)}$ approach the several lowest eigenvalues of the complete operator H *monotonically* (*1*). Thus increased labor insures an improved answer here, although the rate of convergence is another question.

Let us turn now to the scattering problem. The wave function ψ is now not normalizable but may be given a specified asymptotic form, such as

$$(4\pi)^{1/2}\psi \xrightarrow[r\to\infty]{} (\sin kr/kr) + \tan\delta(\cos kr/kr) \tag{4}$$

for s waves; δ is a trial value for the phase shift and will be treated as a variational parameter, and $E = \hbar^2 k^2/2m$. We now have Kohn's variational principle for $\lambda = \tan\delta/k$,

$$[\lambda] = \lambda + \frac{2m}{\hbar^2}\int \psi^*(E - H)\psi \, dv. \tag{5}$$

Construct the trial function ψ as follows:

$$\psi = \varphi + \sum_{i=1}^{N} C_i \chi_i , \tag{6a}$$

where

$$\varphi = [(\sin kr/kr) + \lambda(\cos kr/r)f(r)]1/(4\pi)^{1/2} \tag{6b}$$

is the asymptotic part, and the functions χ_i die off rapidly as $r \to \infty$. The function $f(r)$ is put in to shield the $1/r$ singularity with the $\cos kr$ term at $r \to 0$, and is not now of particular interest. The distribution of factors k is such that everything is finite at $k \to 0$, λ going to minus the scattering length.

Now we look closely at the variational principle.

$$\begin{aligned}
[\lambda] &= \sum_{i,j=1}^{N} C_i C_j M_{ij} + 2\sum_{i=1}^{N} C_i R_i + B + \lambda. \\
M_{ji} &= M_{ij} = \frac{2m}{\hbar^2}\int \chi_i(E - H)\chi_j ; \\
R_i &= \frac{2m}{\hbar^2}\int \chi_i(E - H)\varphi; \\
B &= \frac{2m}{\hbar^2}\int \varphi(E - H)\varphi;
\end{aligned} \tag{7}$$

(everything may be taken as real). Variation of the constants C_i gives the set of N linear equations,

$$\sum_{j=1}^{N} M_{ij} C_j = -R_i . \tag{8}$$

At first sight one is tempted to say that scattering calculations are easier than eigenvalue problems, since it is an easier job to solve (8) than (3). However, it is the crux of this study to realize that the matrix M_{ij} may very well be *singular*, and when this happens, the entire variational procedure collapses.

Solving (8) is not the end of the problem, since we have still to vary λ; but this is easily done, since the trial function is linear in λ. We can write

$$R_i = R_i^{(0)} + \lambda R_i^{(1)},$$

and since M_{ij} is independent of λ, we have

$$C_j = C_j^{(0)} + \lambda C_j^{(1)}.$$

The result of varying the C's can then be written

$$[\lambda] = W_0 + \lambda W_1 + \lambda^2 W_2 + B_0 + \lambda B_1 + \lambda^2 B_2 + \lambda, \tag{9}$$

where

$$\begin{aligned} W_0 &= \sum_{i,j} C_i^{(0)} M_{ij} C_j^{(0)} + 2 \sum_i C_i^{(0)} R_i^{(0)}, \\ W_1 &= 2 \sum_{i,j} C_i^{(0)} M_{ij} C_j^{(1)} + 2 \sum_i C_i^{(0)} R_i^{(1)} + 2 \sum_i C_i^{(1)} R_i^{(0)}, \\ W_2 &= \sum_{i,j} C_i^{(1)} M_{ij} C_j^{(1)} + 2 \sum_i C_i^{(1)} R_i^{(1)}; \end{aligned} \tag{10}$$

and we have finally the stationary result $\lambda = -(W_1 + B_1 + 1)/2(W_2 + B_2)$ (minimizing value, "first-order" accurate), and

$$[\lambda] = W_0 + B_0 - (W_1 + B_1 + 1)^2/4(W_2 + B_2)$$

(stationary value, "second-order" accurate).

THE PROBLEM OF THE CONTINUOUS SPECTRUM

The Hamiltonian H has a continuous spectrum of eigenvalues (the scattering states) of which E is one. Thus the operator $E - H$ with which we are dealing has a continuum of eigenvalues passing through the value zero. In a calculation we represent $E - H$ by a matrix in the subspace of the complete Hilbert space of H which is spanned by our N trial functions. This finite matrix of $E - H$, which we have called $M_{ij}^{(N)}$, will have N eigenvalues, and, as N increases toward infinity, we expect to recover a complete representation of $E - H$. We should therefore not be surprised to find that occasionally the matrix $M_{ij}^{(N)}$ has an eigen-

value very close to zero. It may be correct to say that the a priori probability of having an exactly zero eigenvalue for some matrix $M_{ij}^{(N)}$ is zero; but the number of eigenvalues less than some given magnitude has a finite probability, which must *grow* as N increases.

Our problem here is analogous to finding the stationary value of the simple quadratic form

$$l = \alpha x^2 + 2\beta x + \gamma.$$

When α happens to be zero l can have an extremum only if β also is zero. However, for finite but very small α the extremum is

$$l_0 = -(\beta^2/\alpha) + \gamma,$$

which varies wildly as α varies near zero. Our many-parameter problem is similarly solved in terms of the eigenvectors of the given matrix M

$$M^{(N)} \cdot \xi^{(\alpha)} = \epsilon_\alpha \xi^{(\alpha)}. \tag{11}$$

(We have now dropped the $\sum_{i=1}^{N}$ notation in favor of a dot to signify matrix and vector multiplication.) The solution of (8) is

$$C = -\sum_\alpha \xi^{(\alpha)} (\xi^{(\alpha)} \cdot R / \epsilon_\alpha), \tag{12}$$

and the stationary value of the quadratic form $C \cdot M^{(N)} \cdot C + 2C \cdot R$ becomes

$$-\sum_\alpha [\xi^{(\alpha)} \cdot R]^2 / \epsilon_\alpha . \tag{13}$$

Now when $M^{(N)}$ has a zero eigenvalue the solution to (8) is not well defined; or when some eigenvalue ϵ_α of $M^{(N)}$ is very close to zero, one term in (13) may be exceedingly large in magnitude, and our calculated phase shift, which is supposed to be "stationary" (differing from the true value by only "second-order errors") will be grossly in error. To understand this better, we must also look at the numerator $[\xi^{(\alpha)} \cdot R]^2$ to see if perhaps it goes to zero when ϵ_α is zero and thus saves us. The statement of $\epsilon_\alpha = 0$ is

$$\sum_{j=1}^{N} M_{ij} \xi_j^{(\alpha)} = 0,$$

which when expressed in terms of our functions is

$$\int \chi_i (E - H) \left[\sum_{j=1}^{N} \xi_j^{(\alpha)} \chi_j \right] = 0, \tag{14}$$

for all $i = 1, 2, \cdots, N$, while in the numerator we have

$$\xi^{(\alpha)} \cdot R = \int \varphi (E - H) \left[\sum_{j=1}^{N} \xi_j^{(\alpha)} \chi_j \right]. \tag{15}$$

Equation (14) states that the function

$$(E - H)\left[\sum_{j=1}^{N} \xi_j^{(\alpha)} \chi_j\right]$$

is orthogonal to each of the χ_i's; φ is, however, a quite independent function and we could conclude that (15) is certainly zero only if the χ_i's were a complete set of functions, i.e., $N \to \infty$. Nevertheless as N gets larger, we may expect $\xi^{(\alpha)} \cdot R$ to get small at close to the same place where ϵ_α gets small, and we may thus hope that as the "probability" of finding poles in the answer (13) increases, the strength of these poles decreases and some sort of reasonable convergence does actually occur. We do not have any general theory of the nature of this presumed convergence; we present instead, in the next section, results of some "experimental" (numerical) studies of this process.

It is interesting to note that problems of the kind we are observing are reminiscent of, if not parallel to, earlier discussions of general scattering theory. We have in mind comparison of Eq. (13) with expressions to be found in the classic papers of Wigner (*2*) on resonance scattering; also see the description by Baker (*3*) of scattering as related to the eigenvalue problem in a large box; even the popular $i\epsilon$ added to the operator $E - H$ in the denominator of equations in "formal scattering theory" (*4*) is put there solely to remove the singularity in this operator due to the continuous spectrum. In these formal studies the limit ($\epsilon \to 0$, size of box $\to \infty$) is taken analytically and we are given the answer according to general formulas. Similarly one may use the variational principle for scattering to give a correct result (i.e., *in principle* solution) to the problem only for an infinite number of trial functions. In doing any specific calculation with a finite number of trial functions we will, however, be faced with the probable occurrence of the singularities and we must learn to live with them. It is the intent of this paper to point out and to illustrate the occurrence of this wild behavior; what is desired, but now lacking, is an analysis telling us how *best* to handle this problem.

ILLUSTRATIONS AND DISCUSSION

We have been speaking above of the matrix of $E - H$ in the basis of some chosen set of N functions χ_i as being "nearly" singular and what is now required is some more specific way of displaying this behavior and its consequences in the variational calculations. For a given set of χ_i we could vary the energy E and thus expect to map out these singularities; but we take the problem to be that of calculating the phase shift at any given energy, and so we choose instead to vary some nonlinear parameter: the scale factor κ in the trial functions[1]

$$\chi_i = \chi_i(\kappa \mathbf{r}).$$

[1] It is interesting to look at the history of the use of the scale parameter as an independent variable constant in the trial functions. In the early work of Hylleraas, with only a few

First we present a simple, solvable problem to show the occurrence of the singularities. Let us construct the matrix of the s-wave part of the operator

$$\nabla^2 + k^2$$

in the basis of functions

$$\chi_n = r^n e^{-\kappa r/2}, \qquad n = 0, 1, \cdots, N-1,$$

and ask where this matrix is singular. This is worked out in Appendix I, and we find that $M_{nn'}$ will have a zero eigenvalue whenever

$$\kappa = 2k \tan m\pi/2(N+1), \qquad m = 1, 2, \cdots, N.$$

For the case of large N we can read this result in terms of the eigenvalues k^2 of the operator ∇^2.

$$k^2 \approx [(\kappa\mu/2N)(\pi/2)]^2,$$

for $\mu = N + 1 - m \ll N$, which looks like the spectrum of levels in a spherical box of radius $R \sim 2N/\kappa$. The last trial function used here, $r^N e^{-\kappa r/2}$, has its maximum at just this point $r = R$, and so we can see some analogy between working with some finite number of functions and working in a finite box.[2]

The actual physical problem we have been studying which will be used here as illustration is s-wave elastic scattering of electrons from the ground state of hydrogen. The trial functions used here are fashioned after those used so successfully by Hylleraas and others to describe the bound states of 2-electron atoms:

$$\chi_{lmn} = e^{-\kappa(r_1+r_2)/2}\,\frac{(r_1^m r_2^n \pm r_1^n r_2^m) r_{12}^l}{4\pi\sqrt{2}}, \qquad (l, m, n \geqq 0),$$

and the asymptotic part of ψ is

$$\varphi = \frac{2e^{-r_2}}{4\pi\sqrt{2}}\left[\frac{\sin kr_1}{kr_1} + \lambda\frac{\cos kr_1}{r_1}(1 - e^{-\kappa r_1/2})\right] \pm (1 \leftrightarrow 2),$$

lengths are in units of $\hbar^2/mc^2$. Groups of trial functions χ_{lmn} are taken so that one always uses all functions with $l + m + n \leqq N$, and then we increase N.

linear trial functions, variation of κ seems to have been very important in reducing the eigenvalue of the Ritz calculation; and this procedure was followed through the relatively recent work of Kinoshita (up to 39 parameters). However, Pekeris, in carrying the work past one thousand parameters, has not tried to vary the scale parameter, saying that so many linear terms can easily compensate for it, and he has thereby reduced the amount of numerical work. At the outset of our program to calculate electron-hydrogen scattering with many trial functions, we decided to adopt Pekeris' approach; but we are now led back to varying κ for quite different reasons.

[2] One may consider other basis functions. For example $r^N e^{-\kappa^2 r^2/2}$ has its maximum at $R \sim N^{1/2}/\kappa$; thus in an effectively smaller box the eigenvalues are separated more. Whether this would be an advantage depends on the particular problem. For if the actual wavefunction has a large structure, it will take more of these Hermite functions to do the work of fewer Laguerre functions.

Thus for the triplet (space antisymmetric) state this gives 1, 3, 7, 13, 22, 34, 50, 70 as the dimensions of the matrix for $N = 1$ through 8, respectively. Figure 1 shows curves put through many points computed for W_0 at $k = 0.8$, as a function of κ. Except perhaps for $\kappa < 0.5$, we believe all the structure of these curves has been resolved, and the behavior is as predicted by (13). The relation between the number of poles and N is not simple—at lower energies fewer poles develop—but they are clearly present. If one were asked to determine the extremum value of W_0, it would appear to be a ridiculous problem. However, when we carry out the variation of λ to get the stationary value $[\lambda]$ things behave better, see Fig. 2. The poles still exist, probably the same number of them, but they become more localized; and between poles the values of $[\lambda]$ are not only relatively constant, but fairly reproducible from one interval to the next.

From a study of Fig. 2, and many other sets of data like it, we draw the following "experimental" conclusions about the results of variational calculations of scattering.

A. Any single calculation, although it is based on a variational principle and should give an approximate value of the phase shift accurate to "second order," may in fact yield a value anywhere from $-\infty$ to $+\infty$.

B. By varying some nonlinear parameter we can map out this behavior in detail and draw conclusions about the "probability" of these wild results occurring, namely:

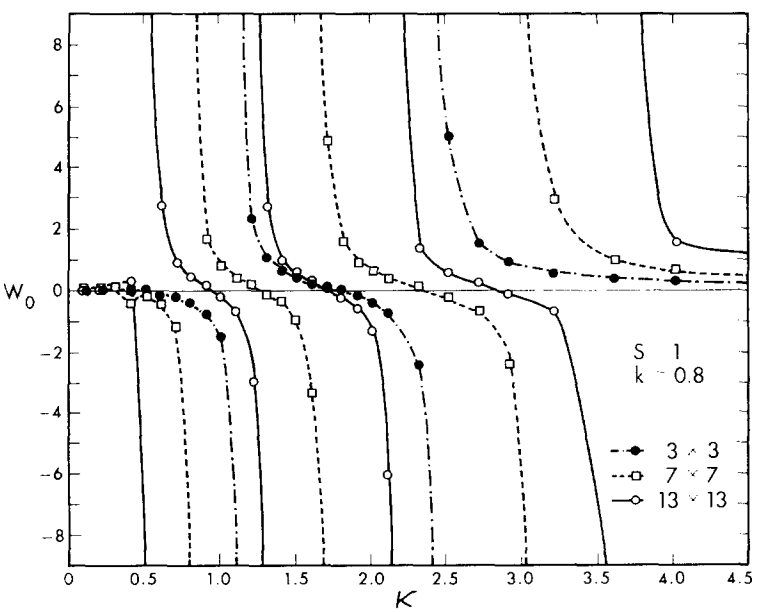

FIG. 1. Results of a varestricted riational calculation with $\delta = 0$

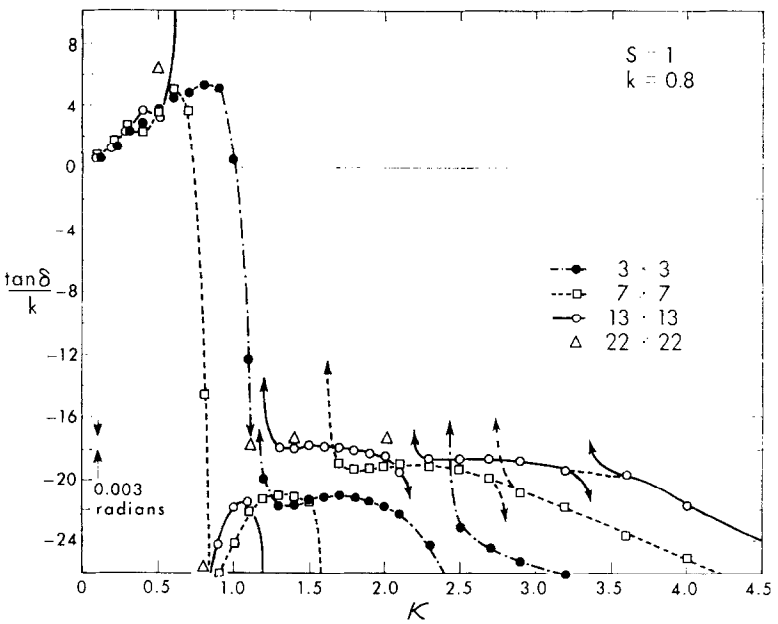

FIG. 2. Results of a complete variational calculation

C. that with a larger number of trial functions, although the number of singular points increases, they do in fact appear to become less strong; the two dashed sections in Fig. 2 indicate points where we believe poles do exist but we have not resolved them.

D. The encouraging fact is that as N increases the *average* value of the function $[\lambda]$, as observed between the singularities, appears to become not only smooth, but flat, and this is the manner in which we expect to find our convergence.

We should note that there is no particular significance to be attached to the use of κ as a variational parameter to give some "best" value of $[\lambda]$, since the curves clearly show more than one extremum. It seems that the best we can do is, for each given number of trial functions, extract from these curves an *average* value of $[\lambda]$; and we should also carry along a measure of the *fluctuations* (neglecting the poles) which measure our uncertainty in this average.

Thus from Fig. 2, the 3×3 matrix gives stationary values around $[\lambda] = -21$ or -22, but its poles are quite wide. The 7×7 matrix has extrema at $[\lambda] = -21$, -19.4, -19.0; the 13×13 has an extremum near -21 and then has a good flat region at -18.0 and -18.6. The few points for the 22 and 34 size matrices are all between -17 and -18 and one point for 50×50 is at -17.3. The convergence appears as a smooth and an upward trend. From this data we guess a final value of $[\lambda] = -17.2 \pm 0.6$. This looks very inaccurate only because for this particular

example the tangent is so large; converted into phase shift this gives $\delta = 1.642 \pm 0.003$ radians, which may be considered fairly good.

A companion problem is the rapid growth of numerical round-off errors which occurs in the solution of the linear equation (8) when the matrix is close to singular. This error may be measured simply by comparing the two terms of Eq. (10),

$$-U = \sum_i C_i R_i ,$$

and

$$V = \sum_{ij} C_i M_{ij} C_j ,$$

after the solution C_i has been obtained by standard numerical procedures. We have carried out several calculations at zero energy, where the matrix of $E - H$ cannot be singular for any finite number of trial functions (given no bound states), and we expect a smoother, monotonic convergence of the variational procedure. We do in fact get nice parabolic curves (varying κ), but the difficulty of growing numerical uncertainties is still present. Thus with 50 parameters for the triplet state at $k = 0$, we have not been able to determine the stationary value of the scattering length to better than about $\frac{1}{2}$ of one percent accuracy, while working with 8 decimal places.

From this and several other sample calculations we have devised an empirical rule that if the phase shift is not sufficiently well converged by the time one has gotten to around $N = 7$, an increased number of parameters will not improve the result because the numerical round-off errors will take over. This rule applies, of course, only to work with 8 significant figures (floating point arithmetic on IBM 704), and it could be overcome by doing double precision arithmetic; however, it not only seems indecent to have to use more than 8 figures to get an answer good to three figures, but it does become quite expensive.

This question of expense, or perhaps we should say efficiency, is really our central concern. Putting aside temporarily the question of numerical accuracy, we still have the problem, as we see from Fig. 2, of doing the calculation with any given size matrix many times over, varying κ, in order to plot out the singularities carefully. The more points we take, the smoother the curves we can draw and the greater becomes our confidence in extracting an average value. There is also clearly a point of diminishing returns: when we see the magnitude of the fluctuations in any one curve after smoothing over the singularities. What we need most, and now lack completely, is some quantitative theoretical analysis of the width of the singularities, leading to a prescription of how to get the most information from the smallest number of computations. There are some phenomena which we do not understand at all, such as the extrema in the 13×13 case in Fig. 2 near $[\lambda] = -22$, and all the points at positive values of $[\lambda]$ for $\kappa < 1.0$. In our present state of ignorance we have chosen simply to ignore these

values, mostly on the basis of their minority populations. The best rationalization we can give for this treatment is that we are looking for convergence, and we take our data where we see the best convergent behavior.

Further illustrations of curves like Fig. 2 will be given in a separate publication presenting results of variational calculation of the s-wave elastic scattering phase shifts for electrons on hydrogen atoms at several energies.

ATTEMPTS TO OVERCOME OR AVOID THE PRESENT DIFFICULTIES

We list here several ideas which were considered either through discussion or experimentation for improving the wild nature of the convergence we have discussed. None has proved curative, although some may be instructive.

I. Carry out the variation of λ first, then solve the linear equations. This is easily done and we have a new matrix,

$$\bar{M}_{ij} = M_{ij} - (1/B_2) R_i^{(1)} R_j^{(1)},$$

which, it might be hoped, is less singular. We tried this very briefly and found no worthwhile change in the results.

II. Our trial function is somewhat redundant, since the χ_i are presumably a complete set (when we take all of them), but we have also added the asymptotic function φ. We might use another basis χ_i which are all orthogonal to φ with $E - H$; this makes all $R_i = 0$, and we have to solve, instead of simultaneous linear equations (8), an eigenvalue problem:

$$\det \| \bar{\bar{M}} \| = 0,$$

where $\bar{\bar{M}}$ is a function of the trial value of λ. This looks rather like Hulthén's first variational principle. But we expect the usual difficulties to arise: for any value of λ we may be able to satisfy the above equation at suitable values of κ, for the same reason: because $E - H$ has a continuous spectrum passing through zero.

III. Consider some other variational principle, in particular Schwinger's, since it is often said that integral equations are smoother than differential equations. Aside from the greater practical difficulty of computing integrals with the Green's function as compared to the Hamiltonian, we think there is nothing to be gained here. What is involved is an operator $(E - H)/(E - H_0)$, and while in the full Hilbert space the zeros of the denominator are cancelled precisely by those of the numerator, in the finite space of some given number of trial functions this matching will not be exact, and we will have the same problem.

Variational principles based on the operator $(E - H)^2$ will be free of the problem of actual singularities. However, in addition to the greater complexity of computing matrix elements, this will probably behave no better than the

zero-energy calculations we have already described, i.e., the very small eigenvalues will hurt us numerically.

The method of Kato (referred to and discussed in Ref. 5) gives both upper and lower bounds for the phase shift of the scattering of a particle by a central potential. The recent work of Spruch and Rosenberg (5) has produced rigorous upper bounds for $-\tan/k$ at zero energy, and at finite energies in case of potentials vanishing beyond some finite distance. That approach relates to the problem of the nth discrete eigenvalue of some system; our purpose here is to learn to face the continuous spectrum squarely and to live with, not avoid, the concurrent difficulties.

IV. The formal theory of scattering overcomes the problem of the singularity of $1/(E - H)$ by adding an $i\epsilon$ in the denominator, and later letting ϵ go to zero in formal operations. We thought of similarly spreading out the energy definition in our procedure by replacing the matrix equation

$$M \cdot C = -R,$$

where M is the finite matrix of $E - H$, by

$$(M^2 + \epsilon^2) \cdot C = -M \cdot R.$$

This does prevent the occurrence of any extremely wild behavior in our answer, but the result does depend on ϵ. From a brief trial of this technique it seems that this is simply one way of getting smooth curves across the singular regions, but the fluctuations in this smooth curve are essentially the same as before. If one had some a priori prescription for choosing ϵ, this method might be useful, as one could hope to accept calculations at only one value of κ, thus saving a great deal of labor. The required condition would be that the error introduced by ϵ should be less than the error inherent in the problem given the particular set of trial functions available at the time. This is probably no more than a restatement of our general need for an understanding of the over-all convergence.

V. Consideration about numerical accuracy. The method we use for solving (8) is a good one—elimination with pivotting. This technique, as we have used it for several bound-state problems, has given solutions correct (by examining $U - V$) to six and seven figures (in our 8-figure machine) with matrices up to size 80. When we first noticed inaccuracies in the third figure of our zero-energy calculation (50×50 matrix), we tried many variations of numerical techniques to improve the solution of the linear equations; but the only thing that succeeded in decreasing $U - V$ was a complete double-precision (16-figure arithmetic) solution of the equation (by the original method). However, we then found that if the input matrix—which is computed in single precision and undoubtedly contains rounding errors of a couple of units in the eighth place—was changed (randomly) by one unit in the eighth place, the new solution, although

internally accurate to eight figures, differed from the first solution by as much as our original error in $U - V$, namely, almost one percent.[3] Thus, in order to get better than three-figure accuracy in this calculation, we have to compute the matrix to better than eight places. At this point we quit.

SUMMARY

It has been shown that the concept of "the extremum" in variational principles for scattering is not well understood when one does actual calculations with any finite number of trial functions. We understand how, because of the continuum of eigenvalues of H for positive energies, the so-called "stationary" value of the phase shift obtained from any single variational calculation may be anywhere from $-\infty$ to $+\infty$. On the basis of purely experimental (numerical) results displayed in graphs like Fig. 2, we can advise that one may overlook the rough parts and deal with the smooth parts to get an answer; and in this manner we have succeeded in obtaining some very accurate results. What we lack is a quantitative analysis of the convergence problem, which would tell us how to get the best answer, most efficiently. Without such further support, it may be necessary, in the realm of scattering problems, for "variational principles" to relinquish the popularly held title as the way to get the most output for the least input

APPENDIX I

Instead of the simple function $r^n e^{-\kappa r^2}$, we will use as our basis some Laguerre polynomials

$$u_n(r) = \text{coeff. of } s^n \text{ in } \frac{e^{-(\kappa r^2)(1+s)/(1-s)}}{(1-s)^2}. \tag{A.1}$$

The matrix is then

$$M_{nn'} = \langle n \mid \nabla^2 + k^2 \mid n' \rangle = \text{coeff. of } s^n t^{n'} \text{ in } I.$$

$$I = \frac{1}{(1-s)^2(1-t)^2} \int_0^\infty r^2\, dr\, e^{-\kappa r(1-st)/(1-s)(1-t)} \left(k^2 - \frac{\kappa^2}{4}\frac{1+s}{1-s}\frac{1+t}{1-t}\right)$$

$$= \frac{2}{\kappa^3(1-st)^3}\left[k^2(1-s)(1-t) - \frac{\kappa^2}{4}(1+s)(1+t)\right],$$

or

$$M_{nn'} = \frac{1}{\kappa^3}\left\{\delta_{nn'}\left(k^2 - \frac{\kappa^2}{4}\right)[(n+1)(n+2) + n(n+1)] - \left(k^2 + \frac{\kappa^2}{4}\right)[n(n+1)\delta_{n',n-1} + n'(n'+1)\delta_{n,n'-1}]\right\}.$$

[3] See Wilkinson (6) and other papers referred to there. An analysis is given of round-off errors in terms of finding what input matrix will give the results obtained.

In order to find when the determinant of M is zero, we solve the recursion formula

$$\left(k^2 - \frac{\kappa^2}{4}\right) 2(n+1)^2 C_n - \left(k^2 + \frac{\kappa^2}{4}\right)(n+1)[nC_{n-1} + (n+2)C_{n+1}] = 0.$$

The solution is

$$C_n = \text{const.} \frac{1}{(n+1)} \sin (n+1)\varphi,$$

where $\cos \varphi = (k^2 - \kappa^2/4)/(k^2 + \kappa^2/4)$. Applying the boundary condition $C_N = 0$, we have the eigenvalues determined,

$$(N+1)\varphi = m\pi, \qquad m = 1, 2, 3, \cdots, N,$$

or equivalently

$$\kappa^2/4k^2 = \tan^2\{[m/(N+1)](\pi/2)\}.$$

APPENDIX II

We present here a short and very preliminary attempt at discussing the convergence of variational calculations. Consider that the process of adding more trial functions serves to remove from a given trial function some of the error, which error may be described as an admixture of some of the wrong eigenfunctions. It is frequently said that the admixture of an eigenfunction ψ_x to a desired eigenfunction ψ_0 may be measured by $(E_x - E_0)^{-1}$. In bound-state problems this is a finite number, and one generally finds "good" convergence for many problems. (By "good" convergence we mean something where the nth step gives a contribution something like a^n, where a is appreciably less than unity; a "poor" convergence would be something like having the nth step contributing as n^{-2}, for example.)

For the scattering problem many $(E_x - E_0)$ will get very small, more so as the number of trial functions increases. Compensating for this is the fact that a state nearby (in energy) will have a phase shift very close to that of the state being studied. Just how these two effects compensate is what we do not understand theoretically; and we give here a model calculation which suggests that maybe things do behave quite well.

Consider Kohn's variational principle for the second Born approximation to the phase shift (i.e., expand everything in powers of the strength of the potential).

$$\begin{aligned}[\lambda^{(2)}] = {} & +\langle \chi^{(1)} \mid k^2 + \nabla^2 \mid \chi^{(1)} \rangle + 2\lambda^{(1)} \langle \chi^{(1)} \mid k^2 + \nabla^2 \mid (\cos kr/r) f \rangle \\ & - 2\langle \chi^{(1)} \mid U \mid \sin kr/kr \rangle + (\lambda^{(1)})^2 \langle (\cos kr/r) f \mid k^2 + \nabla^2 \mid (\cos kr/r) f \rangle \\ & - 2\lambda^{(1)} \langle \sin kr/kr \mid U \mid (\cos kr/r) f \rangle,\end{aligned}$$

where

$$U = (2m/\hbar^2)V(r),$$

and $\lambda^{(1)}$ is a free parameter. Let us take $f = 1 - e^{-\kappa r/2}$, as usual, then if we set $k = 0$, we will be able to have the matrix diagonal with the choice

$$\chi^{(1)} = \sum_n C_n u_n ; \qquad u_n = \text{coeff. of } s^n \text{ in } e^{-(\kappa r/2)(1+s)/(1-s)}(1-s)^2(1+s).$$

We then get

$$\langle \chi^{(1)} | k^2 + \nabla^2 | \chi^{(1)} \rangle = -\frac{1}{4\kappa} \sum_{n=0}^{N-1} (n+1)(n+2)C_n^2;$$

the terms linear in $\chi^{(1)}$ are

$$-2 \sum_{n=0}^{N-1} C_n \left[+U_n + \frac{\lambda^{(1)}}{4} (-1)^n \right],$$

where $U_n = \int_0^\infty r^2\, dr\, U(r) u_n(r)$; and the constant terms are

$$-\lambda^{(1)2} \frac{\kappa}{4} - 2\lambda^{(1)} \int_0^\infty r\, dr\, U(r)(1 - e^{-\kappa r/2}).$$

Let us take $U = \eta\mu e^{-\mu r}/r$; then

$$U_n = (\eta/4\mu)(-1)^n[1 - (n+2)\beta^{n+1} + (n+1)\beta^{n+2}],$$

where $\beta = [(\kappa/2) - \mu]/[(\kappa/2) + \mu]$, and we get, upon varying the C_n,

$$[\lambda^{(2)}] = \frac{\kappa}{4}\lambda^{(1)2} - \frac{\eta\kappa}{(\kappa/2) + \mu}\lambda^{(1)} + 4\kappa \sum_{n=0}^{N-1} \frac{1}{(n+1)(n+2)} \cdot \left\{ \frac{1}{4}\lambda^{(1)} + \frac{\eta}{4\mu}[1 - (n+2)\beta^{n+1} + (n+1)\beta^{n+2}] \right\}^2$$

$$= \lambda^{(1)2} \frac{\kappa}{4} \left(-\frac{1}{N+1} \right) + \lambda^{(1)} \frac{\eta\kappa}{2\mu} \left(\frac{-1 + \beta^{N+1}}{N+1} \right) + \frac{\eta^2}{2\mu} \left[1 - \beta^{2N+2} - \frac{\kappa}{2\mu} \frac{(1 - \beta^{N+1})^2}{N+1} \right].$$

Now, varying $\lambda^{(1)}$, we get simply

$$[\lambda^{(2)}] = (\eta^2/2\mu)[1 - \beta^{2N+2}], \tag{A.2}$$

which converges very rapidly. (If we had chosen $\kappa/2 = \mu$, the exact answer is obtained from the first term, but this makes the problem uninteresting.) Notice that if we had not varied $\lambda^{(1)}$, the error after N terms would be of order $1/N$, which is extremely slow convergence. The variation of the trial phase shift is essential in getting a good fit for the asymptotic part of the wave function, since the localized variational functions have a hard time getting out to large distances.

In this soluble model calculation we have seen that one may in principle

expect convergence as good as that found in bound-state problems. The fact of working here at $k = 0$ meant there were no explicit problems of the singularities of $E - H$ with which the body of this paper is concerned; we are not sure just how representative this special result is.

For the purposes of further comparison, we set up this problem on the computer, using the single basis,

$$r^n e^{-\kappa r^2}, \qquad (n = 0, 1, \cdots, N-1) \text{(with } \kappa/2\mu = \tfrac{1}{4}),$$

and letting the machine do the diagonalization which our Laguerre polynomial here did analytically. This is then a test of numerical accuracy: the matrix of ∇^2 will not have a zero eigenvalue for any finite N, but some eigenvalues may get quite small as N increases (presumably $\sim 1/N^2$), and we may expect increasing inaccuracy due to the finite numerical accuracy of machine operations. The quantity $[\lambda] - 1$ computed agreed well with (A.2) up to about $N = 10$; and from $N = 10$ to $N = 20$ there was essentially no increase in accuracy, the round-off errors growing to several decimal places larger than the answer itself.

In these trial calculations the difference $U - V$ stayed in the last (eighth) decimal place up to $N = 8$, then increased sharply, and from $N = 11$ to $N = 19$ this error fluctuated from less than 10^3 up as high as 10^6 in the eighth place. To compare this with a typical bound-state calculation, we repeated this calculation by replacing the matrix of ∇^2 by that of $(\nabla^2 - \epsilon^2)$ with a value of $\epsilon = 0.08$, which keeps the smallest eigenvalue of the matrix always greater than it was before at around $N = 5$. Now the error $U_2 - V_2$ was no greater than 2 in the last place with only one exception (then equal to 4) for all $N < 20$. However, the errors in $U_0 - V_0$, although better than one order of magnitude reduced from the first calculation, were still very large, growing over four and five decimal places; but this may be explained by the fact that this calculation converges in the worst possible manner (expansion of 1 in Laguerre functions).

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