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By means of SBS shift measurements and of the ultrasonic values of the absorption and velocity in  $\text{CCl}_4$  in the entire temperature range between the melting and the boiling point, we deduced "experimental" values of the relative dispersion  $(v_\infty - v_0)/v_0$ .

Then assuming the validity of the single-relaxation theory we calculate "theoretical" values of  $(v_\infty - v_0)/v_0$  in the three cases in which different groups of vibrational modes of  $\text{CCl}_4$  molecules participate in the energy exchange: (1) the case in which vibrations 1, 2, and 3 participate; (2) the case in which vibrations 1, 2, and 4 participate; (3) the case in which all the vibrations 1, 2, 3, 4, participate to the exchange.

The comparison between the "experimental" and the "theoretical" behavior of  $(v_\infty - v_0)/v_0$  in  $\text{CCl}_4$  in the temperature range between the melting and the boiling point shows that: (1) only near the melting point, the boiling point, and at room temperature could a single relaxation time theory be correct; (2) at all the other

temperatures within the range the comparison between theoretical and experimental data must be based on a multiple-relaxation-times theory in which different times refer to different groups of vibrational levels; (3) only about room temperature do all the vibrations seem to participate with the same relaxation time in the energy exchange, while near the melting point and the boiling point only three vibrations seem to participate with the same relaxation time in the exchange process, one being frozen (the fourth and the third respectively).

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### New Method for Constructing Wavefunctions for Bound States and Scattering\*

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A new method is developed for integrating coupled differential equations arising in bound state and scattering problems in quantum mechanics. The wavefunctions are easily constructed in piecewise analytic form, to any prescribed accuracy.

#### I. INTRODUCTION

Many problems in quantum mechanics are conveniently formulated in terms of coupled differential, or sometimes integrodifferential, equations. Electronic structure of atoms and molecules, molecular vibrations, perturbation theory, scattering of molecules, electrons, nuclei, etc., have often been treated from this wave-mechanical point of view. However, there is no completely satisfactory method for solving such sets of coupled differential equations. This fact is apparent from the large number of methods proposed recently for solving such systems of equations.<sup>1-7</sup>

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<sup>1</sup> L. L. Barnes, N. J. Lane, and C. C. Lin, *Phys. Rev.* **137**, A388 (1965).

<sup>2</sup> B. R. Johnson and D. Secrest, *J. Math. Phys.* **7**, 2187 (1966).

<sup>3</sup> W. A. Lester, Jr., and R. B. Bernstein, *Chem. Phys. Letters* **1**, 207, 347 (1967).

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<sup>5</sup> D. J. Diestler and V. McKoy, *J. Chem. Phys.* **48**, 2941 (1968).

<sup>6</sup> S. K. Chan, J. C. Light, and J. L. Lin, *J. Chem. Phys.* **49**, 86 (1968).

<sup>7</sup> J. Riehl, J. L. Kinsey, and J. S. Waugh, *J. Chem. Phys.* **49**, 5269 (1968).

In the present paper we develop a new method for solving systems of coupled linear second-order differential equations. The range of integration is divided into intervals which are sufficiently small that the *potential energy* for the problem may be approximated to any desired accuracy by a polynomial in each interval. The wavefunctions for these polynomial approximations to the potential are constructed analytically to prescribed accuracy. By suitably matching these wavefunctions at the boundaries between the intervals, the wavefunction for the entire range is constructed, subject to bound-state or scattering boundary conditions at the ends of the range.

The wavefunction is thus obtained as a piecewise analytic function. It is easy to use this form of wavefunction to evaluate analytically various matrix elements of interest over the wavefunction.

The accuracy of the wavefunction may be controlled automatically at any desired level. Furthermore, the calculations are designed to avoid the usual numerical instabilities associated with components of the wavefunction in their classically forbidden regions.

The method is much more efficient than those currently used. For example, 16 coupled equations have

been solved for scattering wavefunctions with about 1% of the computational effort required by other recent methods.

Many features of our method may be developed for a one-dimensional Schrödinger equation, so this simple case is examined first in Sec. II. The appropriate generalizations to the general case of many coupled radial equations are given in Sec. III. The methods of solution developed in Secs. II and III are independent of the boundary conditions which are imposed at the ends of the range. Section IV presents an iterative, but necessarily convergent, scheme by which one may satisfy the boundary conditions for the existence of a bound state, and thereby evaluate energy eigenvalues. Scattering solutions are constructed in Sec. V. In Sec. VI a transformation is constructed which guarantees the numerical stability of the solutions. Test calculations, discussed in Sec. VII, demonstrate the accuracy, reliability, and efficiency of these methods.

## II. METHOD OF SOLUTION FOR A SINGLE RADIAL EQUATION

A one-dimensional Schrödinger equation may be written

$$[d^2\psi(R)/dR^2] + [\epsilon - U(R)]\psi(R) = 0, \quad (2.1)$$

where the reduced energy  $\epsilon$  and reduced potential energy  $U(R)$  are given by

$$\epsilon = 2\mu E/\hbar^2, \quad (2.2)$$

$$U(R) = 2\mu V(R)/\hbar^2, \quad (2.3)$$

in terms of the energy  $E$ , potential energy  $V(R)$ , reduced mass  $\mu$ , and Planck's constant  $2\pi\hbar$ . We wish to solve this linear, second-order, differential equation over some specified range of  $R$ . To carry out this solution, we divide up the total range into a number of intervals whose size will be determined by conditions derived later in this section. Within each of these elementary intervals, we choose a "reference potential"  $U_0(R)$  which approximates the true potential  $U(R)$  over that interval. However, the reference potential must be chosen to be sufficiently simple so that we may easily construct two linearly independent exact solutions  $A(R)$  and  $B(R)$  to the reference, or unperturbed, wave equations:

$$[d^2A(R)/dR^2] + [\epsilon - U_0(R)]A(R) = 0, \quad (2.4)$$

$$[d^2B(R)/dR^2] + [\epsilon - U_0(R)]B(R) = 0. \quad (2.5)$$

For example, we may take this reference potential to be a linear function of  $R$ , fit to the exact potential and its derivative, at the center of the interval,  $\bar{R}$ :

$$U_0(R) = U(\bar{R}) + (R - \bar{R})[dU(R)/dR]|_{R=\bar{R}}. \quad (2.6)$$

For this choice of reference potential, linearly independent solutions may be written in terms of the Airy

integrals<sup>8</sup> or with Bessel functions of order  $\frac{1}{3}$ .<sup>9</sup> In Appendix A we derive a new method for generating these solutions easily and with known accuracy, by solving an integral equation.

A more accurate reference potential could be constructed from a quadratic approximation to the correct potential. The exact solutions for that case are parabolic cylinder functions.<sup>10</sup> A less accurate reference potential would be simply a constant,  $U(\bar{R})$ , with simple trigonometric solutions. The most useful reference potential for any given problem should be a suitable compromise between accuracy and convenience. In the applications which we have made, the linear approximation (2.6) has been selected. However, the following developments in this section are formally independent of the actual choice of reference Hamiltonian.

The Wronskian  $W$  of the reference solutions  $A$  and  $B$  is defined to be

$$W \equiv A(R)B'(R) - A'(R)B(R), \quad (2.7)$$

where the prime denotes differentiation with respect to  $R$ . It is well known that the Wronskian is independent of  $R$ . This is readily proved by differentiating the definition (2.7) to give

$$\begin{aligned} W' &= AB'' - A''B \\ &= -A[\epsilon - U_0(R)]B + [\epsilon - U_0(R)]AB \\ &= 0, \end{aligned} \quad (2.8)$$

where we have used Eqs. (2.4) and (2.5) to eliminate the second-derivative terms.

We now consider the properties of a "mixed" Wronskian  $b(R)$  formed by substituting  $\psi$  for  $B$  in Eq. (7):

$$b(R) \equiv W^{-1}(A\psi' - A'\psi). \quad (2.9)$$

(The Wronskian  $W^{-1}$  is added to give a normalization which is convenient later.) Since  $\psi$  and  $B$  satisfy similar, but not quite identical, wave equations, we expect  $b(R)$  to be "nearly" constant. This is demonstrated clearly by differentiating the definition of the Wronskian  $b(R)$ :

$$\begin{aligned} b'(R) &= W^{-1}(A\psi'' - A''\psi) \\ &= W^{-1}A[U(R) - U_0(R)]\psi, \end{aligned} \quad (2.10)$$

where we have used the wave equations (2.1) and (2.4) to simplify the right-hand side. Thus, the more nearly the reference potential  $U_0(R)$  approximates the true potential  $U(R)$ , the smaller the radial derivative  $b'(R)$  is, and thus the more nearly constant  $b(R)$  is.

Another nearly constant "mixed" Wronskian may be

<sup>8</sup> M. Abramowitz and I. A. Stegun (Eds.), *Natl. Bur. Std. (U.S.), Appl. Math. Ser. 55*, 446 (1965).

<sup>9</sup> G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, Cambridge, England, 1962), p. 97.

<sup>10</sup> W. Magnus, F. Oberhettinger, and R. P. Soni, *Formulas and Theorems for the Special Functions of Mathematical Physics* (Springer-Verlag, New York, 1966), p. 323. See also Ref. 8, p. 686.

constructed in a similar way to  $b(R)$ , substituting  $\psi$  for  $A$  in (2.7):

$$a(R) \equiv W^{-1}(B'\psi - B\psi'). \quad (2.11)$$

The derivative of  $a(R)$  is formed, as in (10), using the equations of motion (2.1) and (2.5):

$$a'(R) = -W^{-1}B[U(R) - U_0(R)]\psi. \quad (2.12)$$

Thus  $a(R)$  is also a slowly varying function of  $R$ .

Equations (2.9) and (2.11) define these slowly varying functions  $a(R)$  and  $b(R)$  in terms of the exact wavefunction  $\psi(R)$  and its derivative  $\psi'(R)$ . Since the equations are linear in  $\psi$  and  $\psi'$ , they are easily solved to yield

$$\psi = Aa + Bb, \quad (2.13)$$

$$\psi' = A'a + B'b. \quad (2.14)$$

This identifies the “mixed” Wronskian functions  $a(R)$  and  $b(R)$  as simply the expansion coefficients by which one may express the exact wavefunction  $\psi$  in terms of the solutions  $A$  and  $B$  for the reference potential. However, the derivative expression (14) may appear somewhat surprising since direct differentiation of (13) yields

$$\psi' = A'a + B'b + Aa' + Bb', \quad (2.15)$$

which contains two additional terms beyond those in Eq. (2.14). Nevertheless, Eq. (2.14) is an exact consequence of the previous equations, and the two additional terms in Eq. (2.15) must exactly cancel each other. Thus, the exact wavefunction and its derivative are fully determined by the coefficients  $a(R)$  and  $b(R)$ .

Using Eq. (2.13) for the wavefunction  $\psi$ , we may now write the differential Eqs. (2.10) and (2.12) for the expansion coefficients:

$$a'(R) = -W^{-1}B[U(R) - U_0(R)](Aa + Bb), \quad (2.16)$$

$$b'(R) = W^{-1}A[U(R) - U_0(R)](Aa + Bb). \quad (2.17)$$

Equations (2.16) and (2.17) together form a closed pair of coupled, linear, first-order differential equations for the coefficients  $a(R)$  and  $b(R)$ . Together with (2.7), (2.9), and (2.11), they are *exactly* equivalent, mathematically, to the original Schrödinger Eq. (2.1). However, in terms of ease of numerical solution, Eqs. (2.16) and (2.17) are far more convenient. The original Schrödinger equation has rapidly oscillating wavelike solutions which are difficult to represent numerically. In contrast, the  $a(R)$  and  $b(R)$  are slowly varying functions since their derivatives (2.16) and (2.17) *vanish* at the center of the interval, and remain small as long as the reference potential is a good approximation to the true potential. Thus the coefficients  $a$  and  $b$  do not change much over an interval.

We can make a simple estimate of how much the coefficients  $a(R)$  and  $b(R)$  do change over an interval, by a perturbation solution for the changes. To first order, we may neglect the small variation of  $a(R)$

and  $b(R)$  in the right-hand sides of (2.16) and (2.17). Then the average values of the derivatives over the interval  $R_l$  to  $R_r$  are

$$\left\langle \frac{da}{dR} \right\rangle_{Av} \simeq -\frac{1}{W(R_r - R_l)} \int_{R_l}^{R_r} B(R)[U(R) - U_0(R)] \times [A(R)a(R_l) + B(R)b(R_l)] dR, \quad (2.18)$$

$$\left\langle \frac{db}{dR} \right\rangle_{Av} \simeq \frac{1}{W(R_r - R_l)} \int_{R_l}^{R_r} A(R)[U(R) - U_0(R)] \times [A(R)a(R_l) + B(R)b(R_l)] dR. \quad (2.19)$$

These perturbation integrals may be evaluated analytically by expanding  $U(R) - U_0(R)$  in a power series in  $R - \bar{R}$  (see Appendix B). For a linear slope reference Hamiltonian, this series begins with the quadratic term and usually need not be carried further for numerical purposes. The first-order solutions at the right-hand side of the interval are then

$$a(R_r) \simeq a(R_l) + (R_r - R_l) \langle da/dR \rangle_{Av}, \quad (2.20)$$

$$b(R_r) \simeq b(R_l) + (R_r - R_l) \langle db/dR \rangle_{Av}. \quad (2.21)$$

To evaluate these equations, we need the values of the coefficients at the left-hand side of the interval  $R_l$ . Assuming that we have already integrated the wave equation from the left up to  $R_l$ , these initial conditions for this interval are readily calculated from the wavefunction  $\psi(R_l)$  and its derivative  $\psi'(R_l)$ , using Eqs. (2.9) and (2.11). Using these values of  $a(R_l)$  and  $b(R_l)$ , Eqs. (2.18)–(2.21) yield the first-order estimates of  $a(R_r)$  and  $b(R_r)$ . Finally, we obtain the wavefunction  $\psi(R_r)$  and its derivative  $\psi'(R_r)$  by substituting the coefficients  $a(R_r)$  and  $b(R_r)$  into Eqs. (2.13) and (2.14).

It may seem unnecessary to convert back to the wavefunction and its derivative, at each boundary between intervals, since we will next convert to  $a$  and  $b$  coefficients for the new interval in order to carry the integration another step to the right. However, this conversion is essential, since the reference potential for the next interval, and hence the new reference wavefunctions, will have different functional forms from the ones in previous intervals. Thus, the new  $a(R_l)$  will differ from the old  $a(R_r)$  even though they both refer to the same radius value.

The calculated perturbation changes in the coefficients  $a$  and  $b$  furnish a very convenient guide to suitable choice of step size. We require that the interval be small enough so that perturbation changes are sufficiently small, say 1%, of the unperturbed coefficients. By making the interval size as small as necessary, we can calculate the wavefunction to any desired degree of accuracy.

This convergence to the correct solution is quite rapid. For example, with the linear slope reference Hamiltonian (2.6), the first neglected correction term is of fourth order in the step size for small step sizes.

Thus we expect about an order of magnitude increase in precision upon halving the step size, and this seems to be observed in practice.

A typical subdivision into intervals, for a linear slope reference potential approximating a Lennard-Jones 6-12 potential, is plotted in Fig. 1. The reference and exact potentials match in magnitude and slope at the dots indicated on the lines. Even with this fairly coarse step size, the calculated perturbation changes in typical calculations have proved to be at most a few percent, and the actual accuracy of the wavefunctions still better.

To maintain comparable accuracy in successive intervals, one must vary the step sizes. In practice, the required step sizes vary rather smoothly from step to step. Thus the appropriate step size  $(\Delta R)_{n+1}$  for the next step may be estimated from the step size  $(\Delta R)_n$  for the step just completed, by the formula

$$(\Delta R)_{n+1} = (\Delta R)_n \{ \delta (|a| + |b|) / \max(|\Delta a|, |\Delta b|) \}^{1/3}. \quad (2.22)$$

Here  $\delta$  is the desired relative accuracy of the wavefunction. The cube root is appropriate to the case of the linear slope reference Hamiltonian, for which the perturbation corrections vary approximately as the cube of the step size. In practice, this simple method of estimating the successive step sizes has been very

successful. It keeps the perturbation corrections within a factor of about 2 of the nominal accuracy  $\delta$ , even though the step size often increases by two orders of magnitude over the range of integration. Occasionally, near a point of inflection of the potential, the perturbation changes were particularly small, causing the estimate of the next step size to be too large. This difficulty was avoided simply by not allowing the step size to increase by more than a factor of 2 at any single step.

We have assumed in the above discussion that the interaction potential is known as accurately as necessary and that we wish to construct a wavefunction to some given accuracy. However, in other situations the potential itself may only be known to a certain accuracy.<sup>11</sup> Then it is only necessary to make the step sizes small enough so that the reference Hamiltonian lies within this range of uncertainty of the true Hamiltonian.

In summary, the method developed in this section allows us to approximate the wavefunction, which is a solution to the Schrödinger Eq. (2.1), by a piecewise analytic function of  $R$ . The solution may be constructed to any predetermined accuracy which may be desired.

### III. METHOD OF SOLUTION FOR COUPLED RADIAL EQUATIONS

Multidimensional problems in quantum mechanics may be solved by generalization of the method presented in Sec. II for one-dimensional problems. Let us choose as a "radial" coordinate  $R$  the one in which the wavefunction shows its most oscillatory or "classical" behavior. We will treat this radial coordinate in a manner similar to the one coordinate treated in Sec. II.

To describe the other coordinates  $\Omega$  in the many-dimensional problem, we chose some appropriate set of "global" basis functions  $\phi_n(\Omega)$ . These functions will be taken, for convenience, to be orthonormal over the domain of interest

$$\int \phi_m(\Omega) \phi_n(\Omega) d\Omega = \delta_{mn} \quad (3.1)$$

and to be sufficiently complete so that the wavefunction may be written as

$$\Psi = \sum_{n=1}^N \psi_n(R) \phi_n(\Omega) \quad (3.2)$$

(exchange of identical particles is not considered here).

The original Schrödinger equation, a partial differential equation for  $\psi$ , then reduces to a set of coupled ordinary differential equations

$$\sum_{n=1}^N [\delta_{mn} (d^2/dR^2) + \epsilon \delta_{mn} - U_{mn}(R)] \psi_n(R) = 0 \quad (3.3)$$

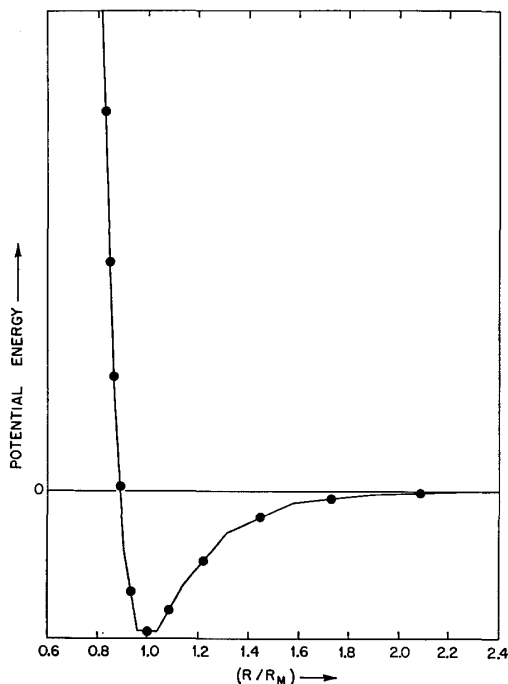


FIG. 1. A piecewise linear reference potential for a Lennard-Jones potential function.

<sup>11</sup> R. G. Gordon, J. Chem. Phys. **48**, 3929 (1968).

for  $m=1, 2, \dots, N$ . Here  $U_{mn}(R)$  is the reduced matrix element of the Hamiltonian (leaving out the kinetic energy term in the coordinate  $R$ ) taken over all the variables except  $R$ :

$$U_{mn}(R) \equiv \frac{2\mu}{\hbar^2} \int \phi_m(\Omega) H(R, \Omega) \phi_n(\Omega) d\Omega. \quad (3.4)$$

It should be noted that in the special case of no interaction, the diagonal elements  $U_{mm}$ , as defined in (3.4), are the excitation energies corresponding to the basis functions  $\phi_m$  rather than zero as sometimes defined.

It is convenient to write this in matrix notation. We consider the set of functions  $\psi_n(R)$  ("channel wavefunctions") to be the components of an  $N$ -dimensional vector function  $\psi(R)$ . The coupled differential Eq. (3.3) may then be written

$$[1(d^2/dR^2) + 1\epsilon - \mathbf{U}]\psi = 0, \quad (3.5)$$

where  $1$  is a unit matrix and  $\mathbf{U}$  is the Hamiltonian matrix whose elements are given by Eq. (3.4). The main advantage of this matrix notation is that essentially all the derivations of Sec. III may be applied to the multidimensional case simply by interpreting them as matrix equations. With this generalization in mind, all the equations in Sec. II have been written with the factors in the proper order required by matrix multiplication, so that we need not rewrite most of them here.

In choosing a *reference* Hamiltonian for the many-dimensional case, it is ordinarily convenient to take it to be a *diagonal* matrix. Then the reference Schrödinger equations become  $N$  *uncoupled* equations, each of the same form as in the one-dimensional case, and each can be solved *separately*. For example, Eq. (2.6) becomes

$$(\mathbf{U}_0)_{mn} = \delta_{mn} \{ U_{mm}(\bar{R}) + (R - \bar{R}) [dU_{mm}(R)/dR]_{R=\bar{R}} \}. \quad (3.6)$$

We will denote the  $2N$  solutions to these  $N$  uncoupled reference wave equations as  $A_{nn}(R)$  and  $B_{nn}(R)$ , the diagonal elements (and only nonzero elements) of matrices  $\mathbf{A}$  and  $\mathbf{B}$ , respectively. The Wronskian matrix  $\mathbf{W}$  of the reference solutions is likewise diagonal, with diagonal elements defined to be

$$W_{nn} = A_{nn}(R) B_{nn}'(R) - A_{nn}'(R) B_{nn}(R). \quad (3.7)$$

In terms of these reference solution matrices  $\mathbf{A}$  and  $\mathbf{B}$ , the solution vector  $\psi$  is written

$$\psi = \mathbf{A}\mathbf{a} + \mathbf{B}\mathbf{b} \quad (3.8)$$

in terms of coefficient vectors  $\mathbf{a}$  and  $\mathbf{b}$ .

Because it is so convenient to use a diagonal reference Hamiltonian, we should like the actual Hamiltonian to be as nearly diagonal as possible. We still have considerable flexibility in how we represent the actual Hamiltonian since the basis functions  $\phi_n$  can be replaced

by any linear combinations  $\tilde{\phi}_n$ ,

$$\tilde{\phi}_n = \sum_{n'} M_{nn'} \phi_{n'}. \quad (3.9)$$

If this coefficient matrix  $\mathbf{M}$  is chosen to be unitary, the new functions  $\tilde{\phi}_n$  will also be orthonormal. Therefore, for each interval in which we choose a new reference Hamiltonian, we choose  $\mathbf{M}$  in such a way that the actual Hamiltonian, in the  $\tilde{\phi}_n$  basis, is *diagonal* at the center  $\bar{R}$  of that interval in  $R$ . This choice guarantees that the perturbation terms on the right-hand sides of the coupled differential equations [analogous to Eqs. (2.16) and (2.17)], *vanish* at the center of each interval. Thus these perturbation terms should remain small within the intervals, provided we interpret the reference Hamiltonian defined by Eq. (3.6) to also be evaluated in the basis  $\tilde{\phi}_n$ . (One should note that this basis  $\tilde{\phi}_n$  is *not* equivalent to the often-discussed "adiabatic" basis, in which  $\phi_n$  are chosen to diagonalize  $\mathbf{U}$  at every value of  $R$ . Only at the center of each interval does our basis correspond to this adiabatic basis.)

If it happens that two or more eigenvalues of  $\mathbf{U}(\bar{R})$  are equal (degenerate), then the basis  $\tilde{\phi}_n$  is still not uniquely defined. In such cases we may perform an arbitrary unitary transformation within this degenerate subspace and  $\mathbf{U}(\bar{R})$  will remain diagonal. We can use this additional freedom to transform to zero the off-diagonal elements of  $d\mathbf{U}/dR|_{R=\bar{R}}$  connecting the degenerate eigenvalues of  $\mathbf{U}(\bar{R})$ . If the transformed values of the corresponding diagonal elements of  $d\tilde{\mathbf{U}}/dR|_{R=\bar{R}}$  are distinct, then the basis  $\tilde{\phi}_n$  is fully specified. The perturbation Hamiltonian is now expanded as

$$\begin{aligned} \tilde{U}(R) - \tilde{U}_0(R) &\simeq (R - \bar{R}) \\ &\times \{ \mathbf{M}(d\mathbf{U}/dR)|_{R=\bar{R}} \mathbf{M}^{-1} \} \text{ (off-diagonal elements)} \\ &+ \frac{1}{2} (R - \bar{R})^2 \{ \mathbf{M}(d^2\mathbf{U}/dR^2)|_{R=\bar{R}} \mathbf{M}^{-1} \} \text{ (diagonal elements)}. \end{aligned} \quad (3.10)$$

The perturbations produced by the off-diagonal quadratic terms, as well as all cubic and higher-order terms, have been found to be negligible in cases of interest.

The propagation of a solution vector  $\psi$  within a single interval now follows just the same pattern as in the one-dimensional case. The only addition restriction which we have found convenient is to approximate the diagonal slopes  $d\tilde{U}/dR|_{R=\bar{R}}$  as all equal to their average value. This additional approximation allows us to calculate analytically the off-diagonal perturbation changes analogous to Eqs. (2.18)–(2.21) using the last result of Appendix B. Since the main use of these perturbation corrections is in choosing the step sizes, no significant error can be introduced by this approximate evaluation of the off-diagonal perturbation integrals. As proof of this, we note that no significant changes are

observed in the solutions if we take all of the diagonal slopes to be equal to their largest or smallest value, rather than their average. Furthermore, we note that the correct values of the diagonal slopes can be used analytically for the *diagonal* perturbation changes, using the integral (B9) in Appendix B. Also, the zeroth-order uncoupled solutions for the reference Schrödinger equations are constructed with the proper slopes; this allows us to omit the diagonal elements linear in  $(R-\bar{R})$  in Eq. (3.10).

The basis functions  $\phi_n$ , selected according to the above considerations, do indeed produce only small perturbation changes within an interval. However, each interval will in general require different basis functions  $\phi_n$ . Thus, after propagating a solution through one interval, one must change to the basis appropriate to the next interval, before continuing the propagation through the next interval. Mathematically, this transformation means that the solution vector  $\psi$  and its derivative  $\psi'$ , must be multiplied on the left by a unitary transformation matrix  $T^{(k)}$ :

$$T^{(k)} \equiv M^{(k+1)\dagger} M^{(k)}, \quad (3.11)$$

where  $M^{(k)}$  and  $M^{(k+1)}$  are the unitary matrices in Eq. (3.9), for the  $k$ th and  $(k+1)$ th intervals, respectively, and  $\dagger$  signifies the Hermitian conjugate matrix.

The full method of solving the coupled differential equations then consists of alternating these transformations with the perturbation solutions within the intervals. At the beginning of an interval, the wavefunction is specified by giving  $\psi$  and  $\psi'$  in the basis for that interval. The uncoupled reference Schrödinger equations are then solved and used to derive the zeroth-order coefficient vectors  $\mathbf{a}$  and  $\mathbf{b}$ , using the matrix analogs of Eqs. (2.9) and (2.11). Then the perturbation changes in  $\mathbf{a}$  and  $\mathbf{b}$  are found from Eqs. (2.18)–(2.21) and used to construct  $\psi$  and  $\psi'$  at the end of the interval from Eqs. (2.13) and (2.14). The largest perturbation correction is then used to estimate the next interval size, from Eq. (2.22). Finally, the transformation  $T$  is constructed and used to form  $\psi$  and  $\psi'$  at the beginning of the next interval.

About half of the computation at each step is required to diagonalize the Hamiltonian  $U$ , to transform  $dU/dR$  into this basis, and to form the transformation  $T^{(k)}$ . Since all of these results are independent of the energy, it is convenient to compute these matrices once and then to store them for use in computing wavefunctions at other energies. This means that the same step sizes must be used at all the energies, but in practice this is no disadvantage since the automatic choice of step size from the perturbation changes results in step sizes almost independent of energy. Unless high accuracy is desired, it is also convenient to omit the evaluation of the perturbation changes, except at the first energy when they are used to establish the step size.

#### IV. BOUND-STATE EIGENVALUES AND WAVEFUNCTIONS

The usual boundary conditions for a quantum-mechanical eigenvalue problem require that the wavefunction vanish at both ends of a range of  $R$ . Only for special energies, the eigenvalues, can both these boundary conditions be satisfied, and usually these eigenvalues can only be located by some kind of iterative process. However, the method developed in the previous sections does not construct a wavefunction with given values at two points. Rather, it solves an "initial value" problem: given a wavefunction and its first derivative at one end of a range, it propagates that wavefunction away from that end of the range.

For the simple case of a single radial Schrödinger equation, this presents no difficulty. We simply pick a trial value for the energy, take the initial wavefunction to be zero, and its derivative to be some arbitrary constant, and propagate the wavefunction to the other end of the range. If for two neighboring trial values of energy the corresponding final values of the wavefunction differ in sign, we know that one (or perhaps some other odd number) of eigenvalues lie between these two trial energies. The initial derivative chosen for the wavefunction is arbitrary, since the wave equation is linear, and this initial derivative merely alters the wavefunction by a scale factor.

For a system of  $N$  coupled wave equations we should have to guess not only trial values of the energy but also  $N-1$  values of the initial derivatives (one of the derivatives could still be taken to be some arbitrary constant). Such a direct search for eigenvalues would then be in  $N$  variables, rather than in energy alone, and would be much more difficult. As a further difficulty, the final wavefunction is not simply characterized as positive or negative, but each of its  $N$  components can be positive or negative, and it is not obvious how changes in the initial derivatives would influence the final values. In an effort to overcome these difficulties, Cohen and Coulson<sup>12</sup> used an elaborate scheme developed by Fox for varying the initial derivatives. However, we have found a much simpler method which avoids entirely the problem of searching for the correct values of the initial derivatives.

Our method is based on the well-known superposition principle for linear differential equations: if we have several solutions, any linear combination of these solutions also is a solution to the linear differential equations. Therefore, instead of starting only one solution vector at the left end of the range, we start  $N$  solutions with any arbitrary linearly independent set of initial derivative vectors, and, of course, zero initial values for the wavefunctions themselves. (The most

<sup>12</sup> M. Cohen and C. A. Coulson, Proc. Cambridge Phil. Soc. **57**, 96 (1961). See also L. Fox, in *Boundary Value Problems and Differential Equations*, R. E. Langer, Ed. (University of Wisconsin Press, Madison, Wisc., 1960), pp. 243–256.

appropriate linearly independent set will be discussed in Sec. VI.)

Because these solutions are chosen to be linearly independent, they must span the  $N$ -dimensional space of all possible initial derivatives. Thus, we know that the correct wavefunction must always be expressible as some (unknown) linear combination of these left-hand solutions  $\psi_l$ . In matrix notation this linear combination is

$$\psi = \psi_l \cdot \mathbf{l}, \quad (4.1)$$

where  $\mathbf{l}$  is a vector of these unknown coefficients.

Now suppose that we have also propagated an arbitrary complete set of solutions  $\psi_r$ , starting from any linearly independent derivatives and values of zero at the *right*-hand side of the range. The correct wavefunction will then be some (generally different) linear combination of these right-hand functions:

$$\psi = \psi_r \cdot \mathbf{r} \quad (4.2)$$

with unknown coefficient vector  $\mathbf{r}$ .

If we have chosen the trial energy to be some correct eigenvalue, then these two expressions for the wavefunction, which are, respectively, zero at the left and right ends of the range, must match at any point  $\bar{R}$  in the range:

$$\psi_l(\bar{R}) \cdot \mathbf{l} = \psi_r(\bar{R}) \cdot \mathbf{r}. \quad (4.3)$$

Similarly, their first derivatives must also match there:

$$\psi_l'(\bar{R}) \cdot \mathbf{l} = \psi_r'(\bar{R}) \cdot \mathbf{r}. \quad (4.4)$$

These two matching conditions may be combined in super-matrix notation:

$$\begin{pmatrix} \psi_l(\bar{R}) & \psi_r(\bar{R}) \\ \psi_l'(\bar{R}) & \psi_r'(\bar{R}) \end{pmatrix} \begin{pmatrix} \mathbf{l} \\ \mathbf{r} \end{pmatrix} = 0. \quad (4.5)$$

This is a set of  $2N$  homogenous linear equations for the  $2N$  unknown coefficients  $\mathbf{l}$  and  $\mathbf{r}$ . The well-known condition that such equations have nonzero solutions is that the determinant of the coefficients vanish:

$$\det \begin{vmatrix} \psi_l(\bar{R}) & \psi_r(\bar{R}) \\ \psi_l'(\bar{R}) & \psi_r'(\bar{R}) \end{vmatrix} = 0. \quad (4.6)$$

Thus, as we vary the trial energy, this determinant will vanish at each of the eigenvalues. This approach reduces the eigenvalue problem to a simple one-dimensional search over energy for the zeroes of a function, even for the case of  $N$  coupled radial equations.

This search for a zero determinant can be carried out by any standard one-dimensional method. For example, if two trial energies can be found for which the determinants differ in sign, then the interval between them contains an eigenvalue. These two trial energies then form upper and lower bounds to a true eigenvalue. These bounds can be narrowed, by picking some intermediate energy, say by linear interpolation of the

values of the determinant, or simply by taking the midpoint of the interval. The sign of the new determinant calculated at this interpolated energy then determines in which of the two parts of the divided interval the eigenvalue lies. This process can be repeated in that subinterval, etc., and the upper and lower bounds to the eigenvalue can be made to converge to whatever accuracy is desired.

This method avoids searching for the correct initial derivatives of the wavefunction, and this is its chief advantage. However, once an eigenvalue has been located, one may want to know the corresponding eigenfunction. To construct this eigenfunction, one must then return to the linear Eqs. (4.5), with  $\psi_l$  and  $\psi_r$  evaluated at the energy eigenvalue. If some arbitrary value is assigned to one of the components of the vectors  $\mathbf{l}$  or  $\mathbf{r}$ , then we can solve Eqs. (4.5) for the remaining  $2N-1$  unknown coefficients of the eigenfunction.

## V. CONSTRUCTION OF SCATTERING WAVEFUNCTIONS

For any energy larger than the smallest dissociation energy of a system a scattering wavefunction can be constructed. These scattering states are subject to two-point boundary conditions. At the origin ( $R=0$ ) the wavefunction vanishes. At large distance ( $R \rightarrow \infty$ ), the wavefunctions must approach the asymptotic forms<sup>13</sup>

$$\psi \rightarrow \mathbf{J} - \mathbf{N}k^{-1/2}\mathbf{R}k^{1/2}, \quad (5.1)$$

where  $\mathbf{J}$  and  $\mathbf{N}$  are diagonal matrices containing as diagonal elements the regular and irregular (spherical Bessel and Neumann) functions for the various basis functions (channels).  $\mathbf{k}$  is a diagonal matrix having as its diagonal elements the wave vectors of the channels:

$$k_{ii} = [\epsilon - U_{ii}(R \rightarrow \infty)]^{1/2}. \quad (5.2)$$

$\mathbf{R}$  is the "reactance" or "tangent" matrix which we wish to determine. The usual approach is to integrate  $N$  solution vectors from zero value near the origin, with any  $N$  linearly independent initial derivative vectors. When these solutions  $\psi_0$  have been integrated out into the asymptotic region at large  $R$ , they will have the general form

$$\psi_0 = \mathbf{J}\mathbf{X} - \mathbf{N}\mathbf{Y} \quad (5.3)$$

with some matrices of constants  $\mathbf{X}$  and  $\mathbf{Y}$  rather than the proper boundary conditions (5.1). These coefficient matrices  $\mathbf{X}$  and  $\mathbf{Y}$  are determined by matching the wavefunction and derivative at large radius to the Bessel solutions  $\mathbf{J}$  and  $\mathbf{N}$  for constant wave vectors  $\mathbf{k}$ ,

<sup>13</sup> See, for example, N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, Oxford, England, 1965), Chap. 14.



through the equations

$$\mathbf{X} = (\mathbf{J}\mathbf{N}' - \mathbf{N}\mathbf{J}')^{-1}(\mathbf{N}'\psi_0 - \mathbf{N}\psi_0'), \quad (5.4)$$

$$\mathbf{Y} = (\mathbf{J}\mathbf{N}' - \mathbf{N}\mathbf{J}')^{-1}(\mathbf{J}'\psi_0 - \mathbf{J}\psi_0'). \quad (5.5)$$

However, the correct solutions can be written as linear combinations of the computed ones by multiplying (5.3) on the right by  $\mathbf{X}^{-1}$ :

$$\psi_0\mathbf{X}^{-1} = \mathbf{J} - \mathbf{N}\mathbf{Y}\mathbf{X}^{-1}. \quad (5.6)$$

Comparing (5.1) and (5.6) shows that the real symmetric reactance matrix  $\mathbf{R}$  is the solution to the linear equations

$$(\mathbf{k}^{1/2}\mathbf{X})^T\mathbf{R} = (\mathbf{k}^{1/2}\mathbf{Y})^T, \quad (5.7)$$

where  $T$  denotes the transpose of a matrix.

The usual scattering matrix  $\mathbf{S}$  is then determined from the  $\mathbf{R}$  matrix by<sup>13</sup>

$$\begin{aligned} \mathbf{S} &\equiv \mathbf{S}_r + i\mathbf{S}_i \\ &= (1 + i\mathbf{R})(1 - i\mathbf{R})^{-1}. \end{aligned} \quad (5.8)$$

Rather than directly solving these complex equations, it is more convenient to solve the equivalent real linear equations

$$(1 + \mathbf{R}^2)\mathbf{S}_i = 2\mathbf{R}. \quad (5.9)$$

In this form, the coefficient matrix  $1 + \mathbf{R}^2$  is symmetric and positive-definite, so that the very stable and efficient Cholesky algorithm<sup>14</sup> may be used to evaluate  $\mathbf{S}_i$  from (5.9). Finally, the real part of the  $\mathbf{S}$  matrix may be determined simultaneously with  $\mathbf{S}_i$  from

$$(1 + \mathbf{R}^2)\mathbf{S}_r = 1 - \mathbf{R}^2. \quad (5.10)$$

Alternately,  $\mathbf{S}_r$  may be derived from  $\mathbf{S}_i$  by

$$\mathbf{S}_r = 1 - \mathbf{R}\mathbf{S}_i. \quad (5.11)$$

The  $\mathbf{S}$  matrix has extracted all information needed from the scattering wavefunctions, to predict the result of any scattering experiment.

## VI. THE STABILIZING TRANSFORMATION

Any choice of linearly independent initial derivative vectors should lead to the same bound-state or scattering wavefunctions after appropriate linear combinations have been formed according to the methods discussed in Secs. IV and V. In practice, however, it is known that initially linearly independent solutions tend to become dependent as one integrates through a classically forbidden region. This happens because the components of the solutions with the most negative radial kinetic energy (most forbidden classically) grow the fastest. Thus each solution vector tends to have only one large component, that one with the lowest radial kinetic energy. Since all the supposedly different

solutions are tending toward this same solution vector, as the integration continues, the solutions are becoming linearly dependent. If the small components become insignificant (on the scale of the relative accuracy of the calculation) compared to the large component, then the solutions are all essentially the same, and are useless for constructing the proper solutions by taking linear combinations.

In the classically allowed region, this uneven growth of the components does not occur, since the components are mainly oscillating rather than growing. However, the problem is still a serious one, since all problems involve integrating through at least one classically forbidden region, and the loss of accuracy from developing nearly dependent solutions is often severe. Since this difficulty arises from the natural properties of the solutions rather than from any particular method for constructing the solutions, it has been ascribed sometimes to an intrinsic instability in the Schrödinger equation itself. However, we show here that this apparent instability can be completely eliminated by appropriate transformations of the solutions.

Our strategy is as follows. Suppose we label the components of our solutions in such a way that the most rapidly growing components are the furthest down the solution vector. We seek to form new linear combinations of the solution vectors such that all components which are *below the diagonal* in the solution matrix *tend toward zero* as we propagate the solutions through a classically forbidden region. Then the natural growth of the elements on and above the diagonal of the solution matrix will tend to make the diagonal elements largest. Since the column vectors making up a nearly *diagonal* solution matrix are nicely independent, we would then have turned the tide of the natural growth toward maintaining linear independence, rather than destroying it.

To carry out this strategy, we first need a quantitative measure for the rate of growth of a solution component in its classically forbidden region. For example, if we use the linear slope Hamiltonian, then aside from the small perturbation corrections (2.18)–(2.21), the  $k$ th component of the  $l$ th solution  $\psi_{kl}$  is given by

$$\psi_{kl}(R) = A_i[\alpha_k(R + \beta_k)]a_{kl} + B_i[\alpha_k(R + \beta_k)]b_{kl}, \quad (6.1)$$

where

$$\alpha_k = [(d\tilde{U}_{kk}/dR)|_{R=\tilde{R}}]^{1/3} \quad (6.2)$$

and

$$\beta_k = \frac{\tilde{U}_{kk}(\tilde{R}) - \epsilon}{(d\tilde{U}_{kk}/dR)|_{R=\tilde{R}}}. \quad (6.3)$$

We consider, for the sake of definiteness, the case in which the slope  $\alpha_k$  is positive. Then as  $R$  increases, the  $B_i$  term is rapidly growing while the  $A_i$  term is rapidly decreasing. (If the slope  $\alpha_k$  is negative, the roles are reversed, with  $A_i$  growing as  $R$  increases, and  $B_i$  decaying toward zero.)

<sup>14</sup> J. H. Wilkinson, *The Algebraic Eigenvalue Problem* (Oxford University Press, Oxford, England, 1965), p. 244.

Our strategy will thus be to take linear combinations of the solutions in such a way that the coefficients  $b_{kl}$  of the growing term are zero for  $k > l$  (i.e., for elements below the diagonal in the matrix of solutions). In matrix notation this means that we must find a coefficient matrix  $\mathbf{C}$  such that

$$\mathbf{b}\mathbf{C}=\mathbf{T}, \quad (6.4)$$

where  $\mathbf{T}$  has zeroes for all its matrix elements below the diagonal ( $\mathbf{T}$  is called an upper triangular matrix). If we can construct such a matrix  $\mathbf{C}$ , then the stable wavefunctions  $\psi$  are given by

$$\psi = \psi_0 \mathbf{C} \quad (6.5)$$

in terms of the original wavefunctions  $\psi_0$ .

The coefficient matrix  $\mathbf{C}$  is not uniquely defined by Eq. (6.4) since many different triangular matrices  $\mathbf{T}$  could be obtained with different  $\mathbf{C}$  matrices. Some of these possible  $\mathbf{C}$  matrices might be very poor choices. For example, if a  $\mathbf{C}$  matrix satisfying Eq. (6.4) had two columns identical to each other, the transformed wavefunctions would immediately lose their linear independence, even without any propagation through a nonclassical region. Such a poor choice of  $\mathbf{C}$  would thus defeat the whole purpose of the transformation, which was supposed to maintain the linear independence of the solutions. Therefore, out of the class of  $\mathbf{C}$  matrices satisfying Eq. (6.4) we wish to choose that one which best maintains the linear independence of the solutions.

To find this "best" coefficient matrix we need a quantitative measure for the linear independence of the solutions. Since two solutions are linearly independent if their Wronskian is nonzero, it seems appropriate to use the squares of the Wronskians between the various solutions, as a measure  $I$  of linear independence:

$$I_k \equiv \sum_{l,m} (\psi_{kl}\psi'_{km} - \psi_{kl}'\psi_{km})^2 / \sum_l (\psi_{kl})^2 \sum_m (\psi'_{km})^2. \quad (6.6)$$

The sum over  $l$  and  $m$  in the numerator ranges over all pairs of radial solutions for the  $k$ th basis function. The denominator is present simply to provide appropriate normalization, so that this measure of linear independence is not changed by any scale factor multiplying the wavefunction.

It is straightforward to show that this measure of linear independence is not changed in value when the wavefunction is transformed by Eq. (6.5), provided the coefficient matrix  $\mathbf{C}$  is taken to be any *unitary* matrix. That is, if the coefficient matrix has an inverse  $\mathbf{C}^{-1}$  equal to its Hermitian conjugate matrix  $\mathbf{C}^\dagger$ ,

$$\mathbf{C}^{-1} = \mathbf{C}^\dagger, \quad (6.7)$$

then the degree of linear dependence is invariant under the transformation (6.5). Thus we can safely transform

with unitary  $\mathbf{C}$  matrices without fear that linear independence will be lost in the transformation.

The unitary condition in fact determines  $\mathbf{C}$  uniquely, since there is only *one* unitary matrix which satisfies Eq. (6.4). We can prove the existence and uniqueness of this unitary  $\mathbf{C}$  matrix by starting with the fact<sup>15</sup> that any matrix  $\mathbf{b}$  can be decomposed into a product

$$\mathbf{b} = \mathbf{T}\mathbf{Q}, \quad (6.8)$$

where  $\mathbf{T}$  is an upper triangular matrix and  $\mathbf{Q}$  is a unitary matrix. Comparing Eqs. (6.4), (6.7), and (6.8), we see that the required unitary  $\mathbf{C}$  matrix is given by

$$\mathbf{C} = \mathbf{Q}^\dagger. \quad (6.9)$$

Furthermore, the decomposition (6.8) is unique if  $\mathbf{b}$  is nonsingular and if the diagonal elements of  $\mathbf{T}$  are required to be real and positive.<sup>15</sup> However, we can also require real and positive diagonal elements for  $\mathbf{T}$ , without any loss of generality. In the physical wavefunctions, this merely fixes a particular choice of the arbitrary over-all phase factor for each solution vector.

Actually constructing the unitary solution to Eq. (6.4) is most conveniently accomplished by a product of Householder's "elementary Hermitian" matrices:

$$\mathbf{C} = (1 - 2\mathbf{W}_N\mathbf{W}_N^T)(1 - 2\mathbf{W}_{N-1}\mathbf{W}_{N-1}^T) \cdots (1 - 2\mathbf{W}_2\mathbf{W}_2^T), \quad (6.10)$$

where the unit vectors  $\mathbf{W}_N, \mathbf{W}_{N-1}, \dots, \mathbf{W}_2$  can be constructed by methods analogous to those of Wilkinson.<sup>16</sup> The resulting algorithm uses the constants

$$S_k \equiv \text{sgn}\left\{\left(\sum_{l=1}^k b_{kl}^2\right)^{1/2}, b_{kk}\right\}, \quad (6.11)$$

$$2K_k^2 \equiv S_k^2 + b_{kk}S_k. \quad (6.12)$$

Then the  $l$ th component of the  $k$ th unit vector is given by

$$\begin{aligned} (\mathbf{W}_k)_l &= b_{kl}/2K_k, & \text{if } l < k \\ &= (b_{kk} + S_k)/2K_k, & \text{if } l = k \\ &= 0, & \text{if } l > k. \end{aligned} \quad (6.13)$$

Each of the factors in this product form of  $\mathbf{C}$  stabilizes a particular row of components in the matrix,  $\psi$ , whose columns are the solution vectors. For components in the classically allowed region, the corresponding factor in  $\mathbf{C}$  may be omitted. When all components are classical no stabilizing transformation is needed at all.

Since the stable linear combinations change as the Hamiltonian changes with  $R$ , the appropriate stabilizing transformation should be made in each interval for which there are any components tunneling outside their classical region. In practice, these stabilizing

<sup>15</sup> Reference 14, p. 241.

<sup>16</sup> Reference 14, p. 233.

transformations have been very successful in increasing the accuracy and reliability of computed wavefunctions.

## VII. TEST CALCULATIONS

The methods developed in this paper have been programmed in FORTRAN IV, and a number of test calculations have been carried out to verify the accuracy, reliability and efficiency of the methods.

A number of eigenvalues for one-dimensional potentials have been calculated using the methods of Secs. II and IV and checked against exact eigenvalues. The perturbation changes (2.20) and (2.21) were reliable indicators of the accuracy of the wavefunctions, and the step sizes estimated by Eq. (2.22) maintained consistent accuracy throughout the range of integration.

The multichannel scattering methods of Secs. III, V, and VI were tested by comparison with recent calculations of rotationally inelastic scattering between an atom and a molecule. Accuracy of about  $10^{-3}$  in the squares of the  $S$  matrix elements is obtained by keeping the maximum perturbation changes less than one percent.

For the 16-channel scattering calculation,<sup>17</sup> the present method is about two orders of magnitude faster than the previous methods in terms of actual computer time required. Most of this remarkable advantage in efficiency comes from the small number of radial steps required: typically, 20–30 steps with the present method, compared to several thousand steps in typical numerical methods.<sup>17</sup>

The reason that such large steps may be taken with the present method is that the step size is determined by the accuracy of a polynomial approximation to the interaction potential. Thus, the step size is essentially independent of the *wavelength* of the wavefunctions. In fact, steps containing ten or more oscillations of the wavefunctions are often obtained in the automatic choice of step size. In contrast, other numerical methods are based on polynomial approximation to the wavefunction, and the step sizes must usually be kept below about  $\frac{1}{10}$  of a wavelength. Thus the advantages of the present method are more pronounced at higher energies.

Classical mechanics is usually considered to provide an approximate description of scattering which is easier to handle than the full quantum-mechanical description. However, for less than about 50 channels, it is now actually easier to solve the rigorous equations for quantum scattering than to solve the classical equations of motion.

## APPENDIX A: EVALUATION OF AIRY FUNCTIONS

The Airy functions are the reference wavefunctions for a linear slope Hamiltonian. In this Appendix, we

outline a new method for evaluating them accurately and easily.

The two Airy functions  $Ai(z)$  and  $Bi(z)$  are defined<sup>8</sup> to be real, linearly independent solutions to the differential equation

$$Ai''(z) = zAi(z), \quad (A1)$$

$$Bi''(z) = zBi(z), \quad (A2)$$

subject to the boundary conditions, as  $z \rightarrow \infty$ :

$$Ai(z) = 0, \quad (A3)$$

$$Bi(z) \rightarrow \infty, \quad (A4)$$

and as  $z \rightarrow -\infty$ :

$$Ai(z) \rightarrow \pi^{-1/2} |z|^{-1/4} \cos(\frac{2}{3}|z|^{3/2} - \frac{1}{4}\pi), \quad (A5)$$

$$Bi(z) \rightarrow -\pi^{-1/2} |z|^{-1/4} \sin(\frac{2}{3}|z|^{3/2} - \frac{1}{4}\pi). \quad (A6)$$

For small  $z$ , we can evaluate these functions from their well-known power series.<sup>8</sup>

For large  $|z|$ , these series are slowly convergent, and cannot be used for numerical evaluation. The usual approach is to use asymptotic series<sup>18</sup> at large  $|z|$ . However, these asymptotic series do not give sufficiently accurate functions and derivatives for our purposes, especially for use with the integrals in Appendix B. Instead, we base our evaluations at large positive  $z$  on the integral expressions

$$Ai(z) = \frac{1}{2}\pi^{-1/2} z^{-1/4} \exp(-\frac{2}{3}z^{3/2}) \int_0^\infty \frac{\rho(x) dx}{1 + (3x/2z^{3/2})}, \quad (A7)$$

$$Bi(z) = \pi^{-1/2} z^{-1/4} \exp(+\frac{2}{3}z^{3/2}) \int_0^\infty \frac{\rho(x) dx}{1 - (3x/2z^{3/2})}, \quad (A8)$$

where

$$\rho(x) \equiv \pi^{-1/2} 2^{-11/6} 3^{-2/3} x^{-2/3} e^{-x} Ai[(\frac{2}{3}x)^{2/3}]. \quad (A9)$$

These integral representations follow from one<sup>19</sup> for the Bessel function  $K_\nu(z)$ , along with the expressions relating the Airy functions to Bessel functions of order  $\frac{1}{3}$ .<sup>8,9</sup> If one expands these integrands for large  $|z|$ , one regains the usual asymptotic series. Instead, we note the fact that the weight function  $\rho(x)$  in these integrals is *positive* over the range of integration, and that its moments  $\mu_k$ ,

$$\begin{aligned} \mu_k &\equiv \int_0^\infty x^k \rho(x) dx \\ &= \Gamma(3k + \frac{1}{2}) / 54^k k! \Gamma(k + \frac{1}{2}), \end{aligned} \quad (A10)$$

can be explicitly evaluated<sup>20</sup> as in Eq. (A10). These properties allow us to evaluate the integrals (A7) and (A8) by the method of generalized Gaussian quadra-

<sup>18</sup> Reference 8, p. 448.

<sup>17</sup> B. R. Johnson, D. Secrest, W. A. Lester, Jr., and R. B. Bernstein, Chem. Phys. Letters 1, 396 (1967); B. R. Johnson, Wisc. Theoret. Chem. Inst. Tech. Rept. WIS-312, 1968.

<sup>19</sup> I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series and Products* (Academic Press Inc., New York, 1965), Formula 6.627, p. 715.

<sup>20</sup> Reference 19, Formula 6.621.3, p. 712.

TABLE I. Positions  $x_i$  and weights  $w_i$  for the Gaussian integration of Airy functions.

$i$	$x_i$	$w_i$
1	1.4083081072180964D+01	3.1542515762964787D-14
2	1.0214885479197331D+01	6.6394210819584921D-11
3	7.4416018450450930D+00	1.7583889061345669D-08
4	5.3070943061781927D+00	1.3712392370435815D-06
5	3.6340135029132462D+00	4.4350966639284350D-05
6	2.3310652303052450D+00	7.1555010917718255D-04
7	1.3447970824609268D+00	6.4889566103335381D-03
8	6.4188858369567296D-01	3.6440415875773282D-02
9	2.0100345998121046D-01	1.4399792418590999D-01
10	8.0594359172052833D-03	8.1231141336261486D-01

ture.<sup>21</sup> The integrals are approximated as sums

$$Ai(z) \simeq \frac{1}{2} \pi^{-1/2} z^{-1/4} \exp(-\frac{2}{3} z^{3/2}) \sum_{i=1}^n \left( \frac{w_i}{1 + (3x_i/2z^{3/2})} \right), \quad (A11)$$

$$Bi(z) \simeq \pi^{-1/2} z^{-1/4} \exp(+\frac{2}{3} z^{3/2}) \sum_{i=1}^n \left( \frac{w_i}{1 - (3x_i/2z^{3/2})} \right). \quad (A12)$$

Here the  $n$  weights  $w_i$  and  $n$  positions  $x_i$  are solutions to the  $2n$  equations

$$\mu_k = \sum_{i=1}^n x_i^k w_i, \quad k=0, 1, 2, \dots, 2n-1. \quad (A13)$$

These equations may be solved conveniently by an algorithm given previously.<sup>22</sup> Values of these positions and weights for  $n=10$  are given in Table I.

For large negative arguments of the Airy functions, we may develop similar improved asymptotic expressions. These may be derived by expressing the Airy functions in terms of Bessel functions of pure imaginary argument:

$$Ai(-z) = (\frac{2}{3})^{1/2} (1/\pi i) [K_{1/3}(-i\zeta) - K_{1/3}(+i\zeta)], \quad (A14)$$

$$Bi(-z) = (\frac{2}{3})^{1/2} (1/\pi) [K_{1/3}(-i\zeta) + K_{1/3}(i\zeta)], \quad (A15)$$

in which  $\zeta = \frac{2}{3} z^{3/2}$ . Substituting into these expressions an integral equation<sup>19</sup> for the Bessel functions gives

$$Ai(-z) = (\pi^{1/2} z^{1/4})^{-1} \times \int_0^\infty \frac{\cos(\zeta - \frac{1}{4}\pi) + (x/\zeta) \sin(\zeta - \frac{1}{4}\pi)}{1 + (x/\zeta)^2} \rho(x) dx, \quad (A16)$$

$$Bi(-z) = (\pi^{1/2} z^{1/4})^{-1} \times \int_0^\infty \frac{(x/\zeta) \cos(\zeta - \frac{1}{4}\pi) - \sin(\zeta - \frac{1}{4}\pi)}{1 + (x/\zeta)^2} \rho(x) dx, \quad (A17)$$

<sup>21</sup> J. A. Shohat and J. D. Tamarkin, *The Problem of Moments* (American Mathematical Society, Providence, R.I., 1950), Chap. 4.

<sup>22</sup> R. G. Gordon, *J. Math. Phys.* 9, 655 (1968).

in which  $\rho(x)$  is the same weight function (A9). Thus the same generalized Gaussian quadrature may be applied to these integrals, giving

$$Ai(-z) \simeq (\pi^{1/2} z^{1/4})^{-1} \times \sum_{i=1}^n w_i \frac{\cos(\zeta - \frac{1}{4}\pi) + (x_i/\zeta) \sin(\zeta - \frac{1}{4}\pi)}{1 + (x_i/\zeta)^2}, \quad (A18)$$

$$Bi(-z) \simeq (\pi^{1/2} z^{1/4})^{-1} \times \sum_{i=1}^n w_i \frac{(x_i/\zeta) \cos(\zeta - \frac{1}{4}\pi) - \sin(\zeta - \frac{1}{4}\pi)}{1 + (x_i/\zeta)^2}, \quad (A19)$$

in which the weights  $w_i$  and positions  $x_i$  are the same solutions to the moment equations (A13) which are used in evaluating (A11) and (A12).

Since the weight function  $\rho(x)$  decreases faster than exponentially at large  $x$ , we conclude from general theorems<sup>23</sup> that all these approximations must converge to the exact functions as  $n \rightarrow \infty$ . Furthermore, at any finite  $n$  we may construct<sup>22,24</sup> error bounds giving the maximum amount by which the approximate sum differs from the true integral. At about  $n=10$ , the sums differ from the integrals by less than one part in  $10^{14}$  for all  $z$  which are too large for the power series to be summed to that accuracy (using 16-digit arithmetic). The actual ranges of  $z$  over which the quadrature method and series method are used are summarized in Table II.

Accurate values of the first derivatives of the Airy functions may be evaluated by differentiating the appropriate approximate functions constructed above.

## APPENDIX B: INTEGRALS OVER AIRY FUNCTIONS

We consider here integrals of the form

$$\int R^n A[\alpha(R+\beta_1)] B[\alpha(R+\beta_2)] dR, \quad (B1)$$

where  $A(x)$  and  $B(x)$  are any linear combinations of

TABLE II. Ranges for methods of evaluating Airy functions. "Series" refers to the power series.<sup>23</sup> "Integration" means the generalized Gaussian integration formulas of the indicated equation number,  $n=10$ . With this combination of methods, 16-digit arithmetic will give at least 14 significant figures in the functions in the classically forbidden region, and an accuracy of better than one part in  $10^{14}$  of the local amplitude, in the oscillating classical region.

$z$	$Ai(z)$	$Bi(z)$
$z < -5.0$	Integration (A18)	Integration (A19)
$-5.0 < z < 3.7$	Series	Series
$3.7 < z < 8.0$	Integration (A11)	Series
$8.0 < z$	Integration (A11)	Integration (A12)

<sup>23</sup> Reference 21, p. 20.

<sup>24</sup> R. G. Gordon, *J. Math. Phys.* 9, 1087 (1968).

Airy functions  $Ai(x)$  and  $Bi(x)$ ,

$$A(x) = Ai(x)a + Bi(x)b, \quad (B2)$$

$$B(x) = Ai(x)a' + Bi(x)b', \quad (B3)$$

and  $a, b, a'$ , and  $b'$  are arbitrary constants.

Integrals of this form are needed for evaluating perturbation corrections, as in Eqs. (2.18) and (2.19), and also in calculating any matrix elements of interest over the wavefunction.

The only properties of the functions which we use are the differential equations

$$A''(x) = xA(x) \quad (B4)$$

and

$$B''(x) = xB(x). \quad (B5)$$

These allow us to eliminate second or higher derivatives in favor of the functions themselves or their first derivatives. As a simple example of how these properties allow us to evaluate integrals (B1), we consider the case  $n=0, \beta_1=\beta_2$ :

$$\int A[\alpha(R+\beta)]B[\alpha(R+\beta)]dR = (R+\beta)A[\alpha(R+\beta)] \times B[\alpha(R+\beta)] - A'[\alpha(R+\beta)]B'[\alpha(R+\beta)]/\alpha. \quad (B6)$$

To verify this result, we differentiate the right-hand side once with respect to  $R$ , obtaining

$$\begin{aligned} & A[\alpha(R+\beta)]B[\alpha(R+\beta)] + \alpha(R+\beta)\{A'[\alpha(R+\beta)]B[\alpha(R+\beta)] + A[\alpha(R+\beta)]B'[\alpha(R+\beta)]\} \\ & - \{A''[\alpha(R+\beta)]B[\alpha(R+\beta)] + A'[\alpha(R+\beta)]B'[\alpha(R+\beta)]\} \\ & = A[\alpha(R+\beta)]B[\alpha(R+\beta)] + \alpha(R+\beta)\{A'[\alpha(R+\beta)]B[\alpha(R+\beta)] + A[\alpha(R+\beta)]B'[\alpha(R+\beta)]\} \\ & - \{\alpha(R+\beta)A[\alpha(R+\beta)]B'[\alpha(R+\beta)] + A'[\alpha(R+\beta)]\alpha(R+\beta)B[\alpha(R+\beta)]\} \\ & = A[\alpha(R+\beta)]B[\alpha(R+\beta)], \end{aligned} \quad (B7)$$

which is the desired integrand in (B6). In a similar way, one can derive the following integrals:

$$\begin{aligned} \int RA[\alpha(R+\beta)]B[\alpha(R+\beta)]dR &= \frac{1}{3}(R^2 - R\beta - 2\beta^2)A[\alpha(R+\beta)]B[\alpha(R+\beta)] \\ &+ (1/6\alpha^2)\{A'[\alpha(R+\beta)]B[\alpha(R+\beta)] + A[\alpha(R+\beta)]B'[\alpha(R+\beta)]\} + (1/3\alpha)(2\beta - R)A'[\alpha(R+\beta)]B'[\alpha(R+\beta)], \end{aligned} \quad (B8)$$

$$\begin{aligned} \int R^2A[\alpha(R+\beta)]B[\alpha(R+\beta)]dR &= (1/15)(3R^3 - R^2\beta + 4R\beta^2 + 8\beta^3 - 3\alpha^{-3})A[\alpha(R+\beta)]B[\alpha(R+\beta)] \\ &+ (1/15\alpha^2)(3R - 2\beta)\{A'[\alpha(R+\beta)]B[\alpha(R+\beta)] + A[\alpha(R+\beta)]B'[\alpha(R+\beta)]\} \\ &+ (1/15\alpha)(-3R^2 + 4R\beta - 8\beta^2)A'[\alpha(R+\beta)]B'[\alpha(R+\beta)]. \end{aligned} \quad (B9)$$

These results may also be obtained with the aid of a third-order differential equation<sup>18</sup> satisfied by products of Airy functions.

Similar integrals may be derived using the differential Eqs. (B4) and (B5), for the case in which the two functions have different origins ( $\beta_1 \neq \beta_2$ ):

$$\begin{aligned} \int A[\alpha(R+\beta_1)]B[\alpha(R+\beta_2)]dR &= [\alpha^2(\beta_1 - \beta_2)]^{-1}\{A'[\alpha(R+\beta_1)]B[\alpha(R+\beta_2)] - A[\alpha(R+\beta_1)]B'[\alpha(R+\beta_2)]\}, \quad (B10) \\ \int RA[\alpha(R+\beta_1)]B[\alpha(R+\beta_2)]dR &= [- (\beta_1 + \beta_2 + 2R)/\alpha^3(\beta_1 - \beta_2)^2]A[\alpha(R+\beta_1)]B[\alpha(R+\beta_2)] \\ &+ \{[R/\alpha^2(\beta_1 - \beta_2)] + [2/\alpha^3(\beta_1 - \beta_2)^3]\}\{A'[\alpha(R+\beta_1)]B[\alpha(R+\beta_2)] - A[\alpha(R+\beta_1)]B'[\alpha(R+\beta_2)]\} \\ &+ [2/\alpha^4(\beta_1 - \beta_2)^2]A'[\alpha(R+\beta_1)]B'[\alpha(R+\beta_2)]. \end{aligned} \quad (B11)$$

Integrals involving  $R^n$ ,  $n > 1$  may be derived, for  $\beta_1 \neq \beta_2$ , by differentiating Eq. (B11) with respect to  $\beta_1$  or  $\beta_2$ .

All the integrals evaluated in this Appendix are exact results. However, in numerical evaluation of the right-

hand sides, loss of accuracy due to near-cancellation of large terms sometimes occurs. Then it is necessary to use accurate values of the Airy functions, as evaluated in Appendix A, in order to obtain reliable values of these integrals.