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A Rapid Numerical Solution to the Radial Schroedinger Equation in the Oscillatory Region

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The solution to the radial Schroedinger equation in the oscillatory region is expressed in terms of the amplitude and phase. We present a rapidly converging iterative method for numerically solving the corresponding nonlinear differential equation for the amplitude. This method is faster than the straightforward integration of the Schroedinger equation because the more slowly varing amplitude permits a much larger step size. The phase is obtained by matching with the solution from the exponential region. The method considers the departure from the WKB solution and therefore is progressively more advantageous for increasing relative energy. We also point out the generalization of this method for inhomogenious equations having the same homogenious form as the Schroedinger equation. This has relevance for special treatments of scattering problems.

1. INTRODUCTION

Explicit computation of wave functions is sometimes necessary for calculation of matrix elements. For example, the calculation of the pressure-induced monochromatic absorption coefficient of H_2 [1] cannot be accomplished by trace techniques, as can the integrated absorption coefficient [2], nor by phase-shift theories. For application to cold planetary atmospheres, the expansion either of the wavefunction of H_2 or its absorption coefficient in powers of $\hbar$ is sufficiently divergent to require the quantum mechanical calculation of the radial wave functions of the two molecules [3].

The oscillatory behavior of the solution $S(x)$ to the radial Schroedinger equation describing a particle in a potential field $V(x)$ severely limits the step size used by any conventional numerical integration scheme. For example, a relative error of 10^{-6} per step requires taking 40 steps per cycle when using the Runge–Kutta method. Because many cycles of integration are often required before the WKB approximation or a series representation accurately describes the solution, conventional numerical techniques require much computation. The limitation is particularly evident when two families of solutions must be computed for different values of t and the orbital angular momentum L.

A better approach is to integrate a function which varies much more slowly than $S(x)$. Gordon [4] does this by approximating the potential function by a polynomial over the step and achieves a result in which the step size is essentially independent of wavelength. This paper presents a method which converges most rapidly in the quasiclassical limit, i.e., for smaller wavelengths, and yet is sufficient to provide a very rapid numerical solution to the radial Schroedinger equation in the oscillatory region after the wavefunction has made a couple of oscillations. This method chooses the slowly varying amplitude $A(x)$ rather than the rapidly varying $S(x)$ to be the dependent variable. The phase variation can be expressed as an integral function of the amplitude so that specification of $A(x)$ with the appropriate boundary conditions leads to a complete specification of the solution (see, e.g., Teddington [5]). The slower variation of $A(x)$ permits a much larger step size than is possible by using $S(x)$.

2. Method

The dimensionless form of the radial Schroedinger equation can be written

$$\frac{d^2S}{dx^2} + D(x)\, S = 0, \tag{1}$$

$$D(x) = t^2 - V(x) - L(L+1)/x^2, \tag{2}$$

where x, t, and $V(x)$ are now dimensionless quantities and $D(x) > 0$ in the oscillatory region of the solutions. The method of this paper can be applied to any equation of the type (1), where $D(x) > 0$ provided x is not too close to a zero of $D(x)$.

We write

$$S(x) = A(x) \exp\left(i \int_c^x p(x)\, dx\right), \tag{3}$$

where the integral is the phase difference between c and x. When we substitute this equation into (1) and separate the real and imaginary parts, we obtain two simultaneous differential equations. One of these can be integrated directly giving $p(x) = K/A(x)^2$, where K is the constant of integration. Substituting this in the remaining equation gives the "amplitude equation"

$$A'' + D(x)\, A - K^2/A^3 = 0 \tag{4}$$

a nonlinear differential equation involving only the amplitude as the unknown and differing from the radial equation only by the last term. The solution is then

$$S(x) = A(x) \sin \left[K \int_c^x \frac{dx}{A(x)^2} + P(c)\right], \tag{5}$$

where c is an arbitrary point on the x-axis, less than x but in the region where $D(x) > 0$ and $P(c)$ is the phase at that point. For vanishing $V(x)$ at large x, (1) and (4) show that A'' will vanish at large x, or $K = tA(\infty)^2$. For unit normalization of the wavefunctions in a sphere whose radius goes to infinity, $A(\infty) = 2^{1/2}$ so that $K = 2t$ for the unbound particle.

We may perform the numerical integration of Eq. (1) up to c using, for example, the Gordon technique [4] and then match the value and slope to (5) after solving Eq. (4) for $A(x)$. This matching provides $P(c)$ and the normalization factor of $S(x)$. We find at $x = c$ that

$$P(c) = \tan^{-1}\left[\frac{2t}{A^2S'/S - (A^2)'/2}\right], \tag{6}$$

where

$$0 \leqslant P(c) \leqslant \pi, \qquad \text{if} \quad S(c) \geqslant 0,$$
$$\pi \leqslant P(c) \leqslant 2\pi, \qquad \text{if} \quad S(c) < 0$$

resolve the ambiguity of the branch of the arctangent and

$$F = \frac{A}{S} \sin P(c), \tag{7}$$

where $F \cdot S$ is the normalized solution for $x < c$.

The solution for $A(x)$ in the oscillatory region is fixed by the boundary condition at infinity and may be extended analytically by a WKB solution or by a power series solution of Eq. (4) down to a value of $x = x_f$, where the series begins to fail and then extended from $x = x_f$ to $x = c$ by the numerical solution of Eq. (4).

3. Numerical Solution of the Amplitude Equation

Conventional attempts at numerically solving Eq. (4) fail because they are unstable. For example, if we try to solve the amplitude equation by the Runge–Kutta technique, the solution blows up regardless of the direction of integration. This is partially because an extraneous oscillatory solution exists with a very short period for high t values which requires a very small step size. This can be overcome

by transforming (4) into an integral equation because the boundary conditions are then included implicitly and the extraneous solution is therefore excluded. However, the solution is still unstable because $A''(x)$ is a small quantity and is given by the difference of two large and nearly equal terms so that most of the significant figures are lost. In the WKB approximation, $A''(x)$ is identically zero and $A(x) = K^{1/2}/D(x)^{1/4}$.

We propose the following iterative method to obtain a numerical solution of Eq. (4) which converges rapidly and satisfactorily for large step sizes. Multiplying Eq. (4) through by $2A'$ and rearranging terms, we obtain

$$\left[\frac{((A^2)'/2K)^2 + 1}{A^2}\right]' + (A^2)'\, D/K^2 = 0. \tag{8}$$

Now let

$$\begin{aligned} y &= A^2, \\ s &= (y'/2K)^2, \\ B &= D/K^2, \end{aligned} \tag{9}$$

then

$$\left(\frac{1+s}{y}\right)' + y'B = 0. \tag{10}$$

If the term labeled $s(x)$ were absent, the WKB solution would be obtained: $y = B^{-1/2}$. This motivates the following rearrangement:

$$y = \left[\frac{1+s}{B + 2s'/(y^2)'}\right]^{1/2}. \tag{11}$$

We could insert the definition of s in this formula and solve for y by iteration. It is preferable, however, if we do not work too close to the zero of $D(x)$, to define the more slowly varying and dimensionless variable $f = yB^{1/2}$, which is identically 1 in the WKB approximation. Letting $R = B'/B = D'/D$, we now obtain the desired equation

$$f = \left[\frac{1 + (f' - fR/2)^2/4D}{1 + (2f''/f - 2Rf'/f + 3R^2/2 - D''/D)/4D}\right]^{1/2} \tag{12}$$

where we may choose the WKB solution as the starting point of the iteration:

$$f_1 = \left[\frac{1 + R^2/16D}{1 + (6R^2 - 4D''/D)/16D}\right]^{1/2} \tag{13}$$

From this equation, we compute f' and f'' by N-point numerical differentiation formulas using a step size considerably larger than allowed by the conventional

techniques. We then substitute this in (12) to derive f_2. We iterate in this fashion each point on a grid of points spaced between c and x_f and compare each result with the previous one. When the difference becomes less than the tolerance, we terminate the iteration for that point. Considerations which limit the step size are given in the next section. Programming the iteration of (12) by standard FORTRAN methods is easy. Following convergence, we then have

$$A(x) = (Kf(x))^{1/2}/D(x)^{1/4}. \tag{14}$$

We have applied this technique successfully to the computation of the pressure-induced absorption coefficient of H_2 [1] using a tolerance of 5×10^{-5}. For this unbound system, the largest-x points were always the first to converge. The interval under treatment shrank with each iteration cycle giving a rapid convergence with a minimum of calculations. The last point to converge was always the matching point, c and more than two iterations were seldom required.

The number of iterations depends on the value of c, which must not be chosen too near a zero of $D(x)$. It is sufficient to choose it at a value of x for which the wavefunction has already made a couple of oscillations so that the third and fifth derivatives of f are not so large that the error terms in the numerical differentiation formulas prevent accurate matching and convergence when using a reasonably large step size. Closer than about two oscillations from the zero of $D(x)$, y becomes more slowly varying than f so that iterating (11) would be more appropriate than (12).

We now present an error analysis in order to provide information useful for the application of this method.

4. Convergence Rate and Error

This method iterates the function $f = F(f, f', f'')$ by approximating f' and f'' numerically by N-point formulas operating on the n-th iteration $f^{(n)}$ and by approximating the argument f by $f^{(n)}$ and using this function to define $f^{(n+1)}$. We expand F in a Taylor series about f, f', and f'' and subtract F to obtain a difference equation in the error, $v^{(n)} = f^{(n)} - f$. For 3-point formulas this equation is, for step size Δ,

$$v_m^{(n+1)} = cv_m^{(n)} + d\left[-T_1 + \frac{1}{2\Delta}\left(v_{m-2}^{(n)} - 4v_{m-1}^{(n)} + 3v_m^{(n)}\right)\right]$$

$$+ e\left[-T_2 + \frac{1}{\Delta^2}\left(v_{m-2}^{(n)} - 2v_{m-1}^{(n)} + v_m^{(n)}\right)\right], \tag{15}$$

where

$$c \equiv \frac{\partial F}{\partial f} = e\left(\frac{3D'f'}{2Df} - \left(\frac{D'}{2D}\right)^2 - \frac{f''}{f}\right), \tag{16a}$$

$$d \equiv \frac{\partial F}{\partial f'} = -e\left(\frac{f'}{f} + \frac{D'}{2D}\right), \tag{16b}$$

$$e \equiv \frac{\partial F}{\partial f''} = \frac{-f^2}{4D + (f' - fD'/2D)^2} < 0 \tag{16c}$$

are evaluated at x_m and

$$T_1 = \frac{\Delta^2}{3} f'''(\xi_m),$$

$$T_2 = \Delta f'''(\xi_m).$$

The subscript m denotes the m-th solution point and ξ_m is some value of x in the m-th interval. T_1 and T_2 are the truncation errors in approximating the exact solution derivatives f' and f'' by 3-point formulas in the m-th interval. We illustrate the procedure for 3-point formulas but its generalization to higher-point formulas, where the error varies with a higher power of Δ, is clear.

Multiplying each term of (15) by z^m and defining the generating function $g(z) = \sum_m v_m z^m$, we collect terms to obtain the difference equation

$$g^{(n+1)}(z) = Kg^{(n)}(z) - b(z), \tag{17}$$

where

$$K \equiv c + \frac{d}{2\Delta}(z^2 - 4z + 3) + \frac{e}{\Delta^2}(z^2 - 2z + 1)$$

and

$$b(z) \equiv \sum_{m=0}^{\infty} (dT_1 + eT_2) z^m.$$

The solution of this difference equation converges in the limit $n \to \infty$ to

$$g(z) = -\frac{b(z)}{1 - K} \equiv \sum_{v=1}^{2} \frac{-C_v b(z)}{z - \lambda_v}, \tag{18}$$

provided $|K| < 1$, which is certainly the case for values of z within about Δ of unity if c, d, and e have sufficiently small absolute values (For $|z| < 1$, $b(z)$ and $g(z)$ are bounded in the domain of interest.) This equation defines the C_v and

the λ_v. Because z is arbitrary in some interval, we may equate coefficients of z^m to obtain

$$v_m = \sum_{v=1}^{2} \frac{C_v}{\lambda_v} \left(\frac{\beta_0}{\lambda_v^m} + \frac{\beta_1}{\lambda_v^{m-1}} + \cdots + \frac{\beta_m}{\lambda_v^0} \right). \tag{19}$$

We find that

$$C_1 = -C_2 = \frac{-h}{2(1-c)(1-k+h)^{1/2}} \tag{20}$$

and

$$\lambda_{1,2} = \frac{k - 3h + h^2}{k - 2h \pm h(1-k+h)^{1/2}}, \tag{21}$$

where

$$\begin{aligned} k &\equiv -4e(1-c)/d^2, \\ h &\equiv 2\Delta(1-c)/d. \end{aligned} \tag{22}$$

The condition for universal convergence is that $|\lambda_v| > 1$. This is the case when $|c| < 1$ and $h < 0$. It is also the case when either $2 < h < k - 1$ or $h \geqslant k - 1$ and $k > 4$. These do not exhaust the possibilities but they are sufficient for our purpose. Because e is negative, we have universal convergence when $|c| < 1$ and $d < 0$. For inward derivatives of the Schroedinger equation, d is negative, at least for x sufficiently far from the zero of $D(x)$. This follows because both terms in (16b) are then negative for an ingoing development of the solution. Inward derivatives f' and D' are observed to be negative for H_2 at all x, at least for $L > 4$. If $d > 0$ occurs, we must see that h satisfies the above conditions. These conditions assure a stable solution having universal convergence in the sense that the error lies within a given bound for an arbitrarily large number of steps when we develop the oscillatory solution inwards towards $x = 0$.

The tolerance is given by

$$|v_m| \leqslant \beta_{\max} \sum_{v=1}^{2} |C_v| \frac{1}{|\lambda_v| - 1} \equiv \frac{\beta_{\max}}{1-c} G(h,k), \tag{23}$$

where $\beta_{\max}$ is the maximum over all integers less than or equal to m of

$$|(d/3)\Delta + e|\,|f'''(\xi_m)|\,\Delta$$

and where $G(h, k)$ is a quantity having, in practice, a value near unity. For example, $G(h, k) = 1$ when all β_m are equal, $G(h, k) = (k+1)/(k-4)$ for $h = k > 4$, $G(h, k) \approx \sqrt{k}$ for small $|h|$, and $G(h, k) \approx \sqrt{k}/h$ for $k \gg |h| > 2$ illustrate some limiting cases. Near the WKB neighborhood, k is large and d is small so that

uniform convergence to a small tolerance is easily obtained. For a step size equal to one wavelength, $\Delta = 2\pi/t$, $G(h, k)$ is approximately unity so that the tolerance is, approximately

$$| v_m | \lesssim \frac{| f''' |}{1 - c} \frac{2\pi}{t^3} \tag{24}$$

(here the term quadratic in Δ is negligible in comparison with the linear term). Note the rapid decline with increasing t. We observe $| f''' |$ to diminish with t for fixed x at smaller t but it goes rapidly to zero at large t where the WKB approximation becomes good. Convergence to a given tolerance is therefore limited to t above a minimum value or x larger than a minimum value. Closer to the matching point and at smaller t we must use a reduced step size. In practice, we find that we can set the matching point at about two oscillations of the solution and still realize a significant gain in step size over conventional techniques.

The use of a 4-point formulas for approximating f'' significantly improves the permitted step size and makes the tolerance vary as Δ^2. Higher-point formulas provide a correspondingly greater power of Δ in the expression for the tolerance. Because f''' goes rapidly to zero with increasing x, 3-point formulas are sufficient at all but the lowest x values and lower t values.

5. Generalization to the Inhomogenious Case

This technique can be generalized to handle the inhomogenious form of (1). The integrodifferential equations of atomic scattering theory can sometimes be expressed in a form where the homogenious part is like (1) and the inhomogenious part, $g(x)$, is an integral function of the solution [6]. One approach to solving this type of equation is to iterate, using the previous iteration to evaluate $g(x)$. We point out that the general solution of this equation at any given iteration stage is the above homogeneous solution (5) plus the particular solution

$$\begin{aligned} S_p = {} & A \sin\left(\int \frac{K dx}{A^2}\right) \cdot \int \frac{A}{K} g \cos\left(\int \frac{K dx}{A^2}\right) dx \\ & - A \cos\left(\int \frac{K dx}{A^2}\right) \cdot \int \frac{A}{K} g \sin\left(\int \frac{K dx}{A^2}\right) dx \end{aligned} \tag{25}$$

obtained from the variation of parameters. $A(x)$ is still the solution of (4) so that the method of this paper, at least in principle, may be applied to certain atomic scattering problems.

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