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Practical Points Concerning the Solution of the Schrödinger Equation

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ABSTRACT

We consider the numerical solution of the one-dimensional Schrödinger equation in a potential of the type occurring in molecular spectroscopy, i.e., with both an inner and an outer classical turning point. Some practical tricks are described which, it is hoped, may prove useful to others. These involve choice of a step size, changing step size, iteration on the eigenvalue, setting upper and lower bounds on the eigenvalue, determining a useful range of x for the integration, etc. Formulas are derived for the value of the function, and of the first derivative, to be used in conjunction with the Noumerov method.

I. INTRODUCTION

In connection with a calculation of molecular energy levels of the quarkium molecule ion, it proved necessary to solve the one-dimensional (radial) Schrödinger equation many times over, for different values of the vibrational quantum number N (= number of nodes in the radial wavefunction) and of the angular momentum number L. The calculation being of an exploratory nature, we were not interested in extreme accuracy for the wavefunction, and were willing to trade accuracy against machine time. The methods described in this paper are, however, useful for any desired accuracy, the modification in the choice of parameters being obvious in each case.

We shall discuss the various problems encountered, and methods used to solve

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ponentially small in that region, due to the "repulsive core" of the potential $V(x)$. The energy E in (2.2) is an eigenvalue, to be determined so that the solution $u_N(x)$ of (2.1) is not only square-integrable (and therefore approaches zero as x approaches infinity), but has exactly N nodes (zeros) on the positive x axis.

The eigenvalues E_N in question are negative. For any E, eigenvalue or not, there are two values of x, called the classical turning points, at which

$$f(x) = 0 \quad \text{classical turning points.} \tag{2.3}$$

The desired solution $u(x)$ has increasing exponential behavior for $0 < x < x_1$, oscillatory behavior between the two turning points [where $f(x)$ is negative], and decreasing exponential behavior for $x > x_2$.

In the remainder of this Section, as well as in Section III, we shall concentrate on the problem of numerical integration of the differential equation (2.1), without worrying about the eigenvalue problem aspects; that is, we assume that $f(x)$ is a given function, which is large and positive for small x, becomes negative in the range $x_1 < x < x_2$ [where x_1 and x_2 are the solutions of (2.3)], and then becomes positive again, approaching a constant positive value as x approaches infinity.

Considered purely as a differential equation, Eq. (2.1) is linear, second-order, and self-adjoint (does not involve the first derivative explicitly). There is one "canonical" method for its numerical solution, the Noumerov method, which is so clearly superior to all other methods that no other method should be seriously considered in practice. To establish notation for later use, we review this method briefly here, and follow this with a brief reminder why this is the method of choice.

We start from the Taylor expansion of $u(x + h)$ around the point x,

$$u(x + h) = \sum_{n=0}^{\infty} \frac{h^n}{n!} u^{(n)} \tag{2.4}$$

where $u^{(n)}$ is the n'th derivative of $u(x)$ evaluated at the point x. We obtain

$$\frac{1}{2}[u(x + h) + u(x - h)] = u + \frac{1}{2} h^2 u^{(2)} + \frac{h^4}{4!} u^{(4)} + \frac{h^6}{6!} u^{(6)} + \ldots \tag{2.5}$$

and, differentiating twice,

$$\frac{1}{2}[u^{(2)}(x + h) + u^{(2)}(x - h)] = u^{(2)} + \frac{1}{2} h^2 u^{(4)} + \frac{h^4}{4!} u^{(6)} + \ldots . \tag{2.6}$$

We now multiply (2.6) by the factor $\frac{1}{12} h^2$, and subtract the result from (2.5). This eliminates the term proportional to $u^{(4)}$. We replace the second derivative

In a region of negative $f(x)$, the behavior of $u(x)$ is oscillatory, of type $\sin(kx - b)$ with $k \simeq [-f(x)]^{1/2}$. In either case, we obtain the estimate

$$u^{(6)} \sim [f(x)]^3 u(x). \tag{3.1}$$

We substitute this estimate into the error term of (2.8), and use the notation (2.7) to obtain

$$\text{Relative error per step} = \frac{\text{Error in } u(x+h)}{u(x)} \sim -\frac{72}{10}[T(x)]^3. \tag{3.2}$$

The relative error per step that we are prepared to tolerate depends on the total number of steps we anticipate having to take, and on the accuracy with which we wish to know the final wavefunction. Crudely speaking, the number of steps we shall have to take is proportional to the number of nodes N in the wavefunction, since a given accuracy in $u(x)$ decides in the main the number of steps h needed per half-wavelength of $u(x)$, and the number of half-wavelengths can be estimated as $N + \frac{1}{2}$ for our present purpose.

To give an example, suppose we anticipate having to take some 500 steps altogether, and we wish to know the function $u(x)$ to 1% accuracy. We can then tolerate relative errors of up to 2×10^{-5} per step, which by (3.2) means $|T(x)| \leq 0.01$ is a safe upper limit. Since the actual error committed is proportional to the cube of $T(x)$, we gain accuracy rapidly as $T(x)$ decreases in absolute value. Thus, we also want to avoid $T(x)$ becoming too small; otherwise, we are wasting steps. Suppose we decide to double the step size h when $|T(x)|$ falls below one fifth the value of its upper limit, i.e., below 0.002 in our example. Doubling the step size multiplies $T(x)$ [Eq. (2.7)] by 4. Thus the new value of T after the net-size doubling is 0.008, still below the upper limit 0.01. If $T(x)$ decreases steadily in absolute value as x increases (as it does in our problem until we reach the inner turning point), the sooner the net-size doubling is done, the better.

These estimates depend, of course, on integrating in such a way that the error made at a given step does not tend to perpetuate itself, with compound interest during subsequent steps. In practice, this means we must not integrate "against the grain" of the differential equation: e.g., for x larger than the outer turning point, the solution we want has decreasing exponential behavior; if we integrate in that region, every little error we make admixes to this desired solution an undesired portion proportional to an increasing exponential. After comparatively few steps, the desired solution is utterly submerged by the exponentially increasing error terms. The remedy is obvious, however. In this region of x we must integrate inwards rather than outwards. With this understood, our crude method of error estimation is adequate.

The values of $u(x)$ known to us are $u(x-h)$ and $u(x)$. We thus require an accurate formula for midpoint interpolation—accurate to the same order as the Noumerov method itself—for otherwise we lose the advantage of the Noumerov method.

Letting $x_0 = x - \frac{1}{2}h$ be the point at which we desire to know u, our problem can be restated as follows: find $u(x_0)$, given values of $u(x_0 + h')$ and $u(x_0 - h')$, and given that $u(x)$ satisfies the differential equation (2.1).

The solution, though exceedingly simple, does not, to our knowledge, appear in the literature: it consists in using the basic formula of the Noumerov method, (2.8), to solve for $u(x)$! The accuracy is then obviously the same as the accuracy of the Noumerov method. No additional function values need be stored and net-size halving is now as simple as net-size doubling. For the sake of the record, we write down the midpoint interpolation formula explicitly[2]:

$$u(x) = \frac{[1 - T(x+h)]u(x+h) + [1 - T(x-h)]u(x-h)}{2 + 10T(x)} + \frac{h^6 u^{(6)}}{480} + \cdots. \quad (3.5$$

IV. Iteration on the Eigenvalue when We Are Close; a Derivative Formula

Let $v(x)$ be a "trial function" which is sufficiently close to the true function $u(x)$. We leave the deflnition of "sufficiently close" to Section V. Then the usual "variation method" of quantum mechanics asserts that an improved value of the energy eigenvalue E can be found by quadrature over the known function $v(x)$, namely,

$$\frac{2ME}{\hbar^2} \simeq \frac{\int v(x)\{-(d^2v/dx^2) + [2MV(x)/\hbar^2]v(x)\}\,dx}{\int [v(x)]^2\,dx}. \quad (4.1)$$

Written in this form, the expression is rather awkward. However, we have seen already that, for purely numerical reasons, we must integrate outwards for small x, and inwards for large x. We now make a virtue out of this necessity: Let Q be a trial value for the energy E, hopefully close to the true value of E. Then integrate the differential equation

$$\frac{d^2v}{dx^2} = \frac{2M}{\hbar^2}[V(x) - Q]v(x) \equiv f_Q(x)v(x), \quad (4.2)$$

first outwards from some sufficiently small value of x until we reach a joining

[2] In the error term, we may replace $2 + 10T(x)$ by 2.

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Taking the second derivative on both sides, and multiplying by $\frac{1}{6}h^2$, we obtain

$$B_1 \equiv \left(\frac{h^2}{12}\right)[u''(x+h) - u''(x-h)] = \frac{h^3}{6}u^{(3)} + \frac{h^5}{36}u^{(5)} + \dots . \qquad (4.5)$$

We subtract (4.5) from (4.4) and use the differential equation to replace u'' by $f(x)u(x)$, to obtain the first derivative formula:

$$hu' = [1 - T(x+h)]u(x+h) - [1 - T(x-h)]u(x-h) + (7/360)h^5u^{(5)} + \dots \qquad (4.6)$$

Here $T(x)$ is defined by (2.7) with $f(x) = f_Q(x)$ defined by (4.2). The error term in (4.6) may be sufficiently small in some cases. It is, however, of order $h^5u^{(5)}$, poorer than the basic error of the Noumerov method.

At substantially no expense in machine time, the accuracy of the first derivative, and hence of (4.3), can be improved significantly, simply by using function values at $x + 2h$ and $x - 2h$. We define

$$A_2 = \tfrac{1}{2}[u(x+2h) - u(x-2h)] \qquad (4.7)$$

and

$$\begin{aligned} B_2 &= \tfrac{1}{12}h^2[u''(x+2h) - u''(x-2h)] \\ &= T(x+2h)u(x+2h) - T(x-2h)u(x-2h) \end{aligned} \qquad (4.8)$$

We then write down the Taylor expansions of A_1, A_2, B_1, and B_2, carrying terms up to order $h^9u^{(9)}$ inculsive. We eliminate the terms proportional to $h^ku^{(k)}$ with $k = 3, 5, 7$ and solve for hu'. The procedure is tedious but strightforward; we quote only the result which is

$$hu' = \frac{16}{21}\left(-A_1 + \frac{37}{32}A_2 - \frac{37}{5}B_1 - \frac{17}{40}B_2\right) - \frac{4016}{35}\frac{h^9u^{(9)}}{9!} + \dots . \qquad (4.9)$$

Thus, by integrating a mere two steps beyond the joining point $x = x_0$, we can determine the value of the first derivative to an accuracy substantially better than the basic accuracy of the Noumerov method. (We note that the instability problems involved in the use of higher-order schemes do *not* arise here: we wish to find u' at one point $x = x_0$, whereas instability arises only if we wish to replace a differential equation by a difference equation of higher order, and to integrate over many steps.)

We now have an iteration scheme of second order for the eigenvalue E: starting from a trial eigenvalue Q, near to E, we find an improved approximation to

of halving suffice to get us close enough to E_N so that we can use the faster, second-order iteration scheme of Section IV.

The first step to ascertain where Q lies in relation to E_N is to count the nodes of the trial function $v(x)$ generated by (4.2). As we generate $v(x)$, we count each node and accumulate. If the node count, at any stage, exceeds N, then the trial value Q was too high. Conversely, if at the end of generating $v(x)$, the node count is below N, then Q was too low. Since we generate $v(x)$ in two stages, so to speak, first by integrating out, then by integrating in, a bit of care is required to avoid double counting of nodes occurring right at the joining point x_0.

While node counting is enough to reject completely unsuitable values of Q and to decide whether such values are high or low, a correct node count by itself is not sufficient to allow us to use the procedure of Section IV. We have found the following simple scheme quite adequate to ensure convergence:

(1) Ascertain whether the number of nodes in $v(x)$ equals N; if not, proceed with halving.

(2) If the node count agrees, proceed to evaluate the second-order correction E-Q from (4.3) and (4.9); the *sign* of the correction is right, even if the magnitude is far off. Thus, if E-Q turns out to be positive, Q was too low, and we replace Q_1 by Q; if E-Q turns out to be negative, Q was too high, and we replace Q_2 by Q.

(3) Now compute the new $E = Q + (E - Q)$ predicted by the second-order iteration scheme. If this new value of E lies between Q_1 and Q_2, it is safe to use. If not, the next trial value is determined by (5.2).

In this way, we combine the safety of the halving scheme with the speed of the second-order iteration. Two cautions should be observed, however. (1) Once the correction $E - Q$ gets very small, it is not necessary to readjust Q_1 and Q_2, and it is actually safer not to, since round-off errors can then lead to trouble. (2) To avoid trouble of an unforeseen sort, it is desirable to keep a count of the number of iterations, and to go out with a failure indication once this count exceeds 50, say. This should not happen, but things which should not happen sometimes do; a simple iteration count will prevent looping of the program.

VI. Setting Upper and Lower Bounds on the Eigenvalue

The halving method of Section V requires bounds Q_1 and Q_2 on the true eigenvalue E_N. In this section, we discuss methods of setting such bounds.

The simplest case, and the one occurring most of the time, is that we alread

No matter what value of a we choose in (6.3), the right side of (4.1) is an upper limit Q_2 to the true ground-state energy E_0. The two methods can be combined by determining the parameter a in (6.3) from the oscillator-potential fitting, the function (6.3) being just of the right form for the ground-state wavefunction of an oscillator potential.

Although this method is safe, it is probably overly elaborate for the time gained. With a bit of experience, it is possible to make a reasonable guess at the zero-point energy $E_0 - \text{Min}[V(x)]$, and to set a generous upper limit Q_2 which is nonetheless far nearer to the true E_0 than the trivial choice $Q_2 = 0$, without going to all the trouble of evaluating (4.1) numerically for the function (6.3).

Once the lowest eigenvalue E_0 is known, a safe upper limit for the eigenvalue E_1 is

$$E_1 \leq Q_2 = E_0 + 3\{E_0 - \text{Min}[V(x)]\}. \tag{6.4}$$

The factor 3 is exactly right for a square-well potential, and is an overestimate (hence giving an upper bound) for all other potentials; for an oscillator potential, the correct factor would be 2, to that 3 is a perfectly safe choice for an upper limit.

Once E_0 and E_1 are known, extrapolation becomes possible with more and more accuracy as further eigenvalues are accumulated. We thus fall back on the choice (6.1) which ensures very rapid convergence.

VII. Starting the Integration: Deciding on the Range of Integration

The outwards integration must start at a value of x less than the inner turning point x_1 [the lower root of (2.3)]; the inwards integration must start at a value of x larger than the outer turning point x_2 [the higher root of (2.3)]. In this section, we discuss the choice of these starting points, and hence the choice of the total range of integration for the wavefunction. We also discuss how the integrations are started so as to get the desired solution, i.e., the exponentially increasing solution for the outwards integration, the esponentially decreasing solution for the inwards integration.

We discuss the second point first; that is, let us suppose we have chosen a starting value of x, call it $x = a$, for the outward integration. Clearly $v(a)$ can be set arbitrarily, since one multiplicative factor is free. To get going with the Noumerov method, we require an approximation to $v(a + h)$ for the exponentially increasing solution.

The first thing to realize is that quite sizeable errors are permitted here. An erroneous choice of $v(a + h)$ has the effect of admixing, to the desired exponentially

$$\int_a^{x_1} [f(x)]^{1/2}\, dx = A. \tag{7.4}$$

The integrand is zero at the upper limit, the classical turning point x_1. We again replace the integral by a trapezoidal-rule approximation, and keep going downwards through $x_1 - h$, $x_1 - 2h$, $x_1 - 3h$, ..., until the accumulated sum exceeds A. The terms in the sum are of form $[12T(x_i)]^{1/2}$ where $T(x)$ is defined by (2.7).

The uppermost value of x, $x = b$, is determined similarly, the condition being

$$\int_{x_2}^{b} [f(x)]^{1/2}\, dx = A. \tag{7.5}$$

Since $f(x) = f_Q(x)$ [Eq. (4.2)] depends on the value of the trial energy Q, the turning points x_1, x_2, as well as the cutoff points a and b, depend on the value of Q. As Q increases, the outer turning point x_2 and the outer cutoff point b move further out (increase in value), whereas the inner turning point x_1 and the inner cutoff point a move inwards (decrease in value). In principle, therefore, a and b ought to be recalculated whenever the trial energy Q changes.

This, however, is neither necessary nor desirable, except in the earliest stages of the iteration process, when the trial energy is still very poor. As soon as the upper limit Q_2 has improved to the point where it yields the right number of nodes, the values of a and b associated with this upper limit Q_2 should be retained and used throughout the remainder of the iteration. First of all, this saves time. Second, if a and b are allowed to change during the later stages of the iteration process, it is possible to get into serious trouble: the truncation errors associated with replacing the differential equation by a difference equation, as well as the errors made in the very crude starting formula (7.3), can lead to hunting of the second-order iteration procedure unless a and b are kept fixed.

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