LETTER TO THE EDITOR

A pocket calculator determination of energy eigenvalues

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Abstract. The radial Schrödinger equation is converted to a recursive equation which can be treated satisfactorily by a programmable pocket calculator. Specimen calculations show that the eigenvalue error varies very smoothly with the integration step width h. The method is applied to a problem for which the traditional energy perturbation series is apparently divergent asymptotic.

1. Introduction

The determination of the eigenvalues of the Schrödinger equation is most often carried out using variational methods, which involve the calculation of matrix elements and also the choice of suitable basis functions. If only the eigenvalues and certain expectation values are required, it may be easier to use a direct numerical method which replaces the Schrödinger differential equation by one or more finite difference equations. Hawk and Hardcastle (1976) have recently achieved good results for the helium atom using such an approach, but considerable computer capacity is needed to handle such a problem. In the present letter we deal with a much more simple case, the Schrödinger equation for one particle in a central field, and show that it is possible to attack the problem in such a way that useful eigenvalue estimates can be made using some of the less expensive types of programmable pocket calculator. The basic theory is developed in § 2, and an example is given to show the characteristic features of the method. Section 3 uses the method to investigate a problem of interest in perturbation theory, and § 4 briefly discusses possible extensions of the work which allow the calculation of expectation values.

2. Basic theory

We start from the Schrödinger equation in atomic units,

$$-\tfrac{1}{2}\nabla^2\psi + V\psi = E\psi \tag{1}$$

where V is some central potential. We assume ψ to take the form $\mathscr{Y}_l\phi(r)$ where $\mathscr{Y}_l$ is a *solid* harmonic of degree l (e.g. x or xy). Making this substitution in (1), and multiplying throughout by r, leads to an equation for the function ϕ:

$$2r(V-E)\phi = r\mathrm{D}^2\phi + (2l+2)\mathrm{D}\phi \tag{2}$$

(we adopt the usual notation $\mathrm{D} = \mathrm{d}/\mathrm{d}r$). The next step is the introduction of the finite

difference approximation, which we accomplish by means of the simple replacements of 'first principles' calculus,

$$h^2 D^2 \phi \to \phi(r+h) + \phi(r-h) - 2\phi(r) \tag{3}$$

$$2h D \phi \to \phi(r+h) - \phi(r-h). \tag{4}$$

The resulting difference equation will, of course, only simulate (1) exactly in the limit $h \to 0$, but we shall see that surprisingly good results for E can be obtained without approaching the limit too closely. The step which is crucial to our method is the final one, the introduction of a ratio variable $R(r)$, defined by the equation

$$\phi(r+h) = R(r)\phi(r). \tag{5}$$

With the substitutions (3), (4) and (5), the differential equation (1) is converted to a recursive equation for the calculation of the values of $R(r)$:

$$2r[1 + h^2(V-E)] = R(r)[r + h(l+1)] + [r - h(l+1)](R(r-h))^{-1}. \tag{6}$$

Equation (6) has an obvious advantage in that only one calculated number, $R(r-h)$, needs to be stored (together with the r value) in order to proceed to $R(r)$. This simplification means that the method described here will work on a programmable calculator with quite limited memory capacity. For the special case of a one-dimensional Schrödinger equation the equation analogous to (6) is the equation

$$2[1 + h^2(V-E)] = R(x) + (R(x-h))^{-1} \tag{7}$$

and this equation has been applied to the study of a perturbed harmonic oscillator (Killingbeck 1977a). Inspection of equation (6) shows that it has a further remarkable feature; if the starting point is chosen at $r = h(l+1)$, then $R(hl)$ can be assigned any finite value without disturbing the calculation at larger r values. This simplification is presumably related to our initial postulated form for ψ, and would merit further investigation; however, if we just accept it as a bonus and proceed with the calculation, it leads to satisfactory results, as we see in our following examples.

To determine the ground state eigenvalue for the states with angular momentum l, we use some initial estimate of E in the equation (6), with any non-zero value for $R(hl)$, and with some small h value. The value of $R(r)$ as r increases will either become negative (at *one* r value) or pass through unity from below. The first occurrence shows a node in the approximate ψ, and indicates that the E estimate was too high; the second occurrence shows that ψ is increasing with r, which suggests that E was too low. Trying various E values leads to a 'sandwiching' of the energy value between upper and lower bounds, finally giving some energy estimate $E(h)$. Changing h will change $E(h)$ until it approaches the required true eigenvalue in the limit $h \to 0$. Table 1 shows the way in which the energy estimate varies for the particular case of the Hamiltonian (1) with the potential $V = \lambda r - r^{-1}$; the $E(h)$ values were determined to four decimal places at each h value. As an interesting practical detail, we note that the two requirements $R < 0$ or $R > 1$ can be written as the single requirement $R^2 - R > 0$ which needs only one conditional jump instruction in the calculator program. The calculations were carried out on a Casio fx-201 calculator. This calculator can be programmed to make step-like changes in the trial E values automatically if desired. Such a facility is not essential, of course, and the method was also tested successfully on the less powerful Prinztronic Program calculator.

Table 1. Specimen $E(h)$ values for $V = \lambda r - r^{-1}$.

State	λ	h 0·4	0·2	0·1	0·05	0
1s	0	−0·4815	−0·4951	−0·4988	−0·4997	−0·5000
	1	0·6055	0·5841	0·5794	0·5782	0·5778
2s	0	−0·1238	−0·1247	−0·1249	−0·1250	−0·1250
	1	2·3961	2·4359	2·4465	2·4492	2·4501
2p	0	−0·1238	−0·1247	−0·1249	−0·1250	−0·1250
	1	2·0072	1·9815	1·9759	1·9746	1·9742
3d	0	−0·0553	−0·0555	−0·5555	−0·5556	−0·0556
	1	2·9283	2·8778	2·8666	2·8639	2·8630

In general we would expect the eigenvalue estimate to approach its limiting value in a manner described by a power series in h^2, and a study of table 1 shows that the error is proportional to h^2 up to surprisingly large h values. If there is also an h^4 term in the error, then the following extrapolation formula holds:

$$E_0 = \tfrac{1}{45}(64E_1 - 20E_2 + E_4). \tag{8}$$

Here E_N denotes $E(Nh)$. In the h^2 region the simpler extrapolation formula

$$E_0 = \tfrac{1}{3}(4E_1 - E_2) \tag{9}$$

holds. Since the time taken to perform each traverse along the r axis varies as h^{-1}, it is clearly useful to be able to find E_0 accurately while using only fairly large h values. Even the use of (9) with $h = 0·2$ gives a good estimate of E_0 in our example. (The same feature also appeared in a trial calculation of the 1s eigenvalue for the potential $V = -r^{-1} \exp(-r)$, for which the eigenvalue $-0·0103$ was obtained.) Table 1 includes results for the 2s state, i.e. the first excited s state. These were obtained by applying the criteria explained above only after ψ had already passed through one node, thus exploiting the traditional theorems about the increase in the number of nodes with the increase in the energy eigenvalue. Higher eigenvalues could be obtained by looking for functions with greater numbers of nodes. For the 2s state the $E(h)$ values at $\lambda = 1$ are lower bounds, whereas for the other states treated they are upper bounds.

3. An application to perturbation theory

The Hamiltonian (1) with $V = \lambda r - r^{-1}$ describes the influence of the perturbation λr on the hydrogen atom. For real positive λ the 1s and other bound states are well defined, whereas for real negative λ they are not. Such problems usually lead to divergent asymptotic series if traditional Rayleigh–Schrödinger perturbation theory is used to find the energy (Killingbeck 1977b). By using the method of § 2, we have calculated the 1s state eigenvalue for several λ values in the range $0 < \lambda < 0·3$, and these are given in table 2. If the series for the eigenvalue is written in the form

$$E = -\tfrac{1}{2} + \sum_{n=1}^{\infty} \epsilon_n \lambda^n \tag{10}$$

Table 2. λ depencence of the lowest eigenvalue.

λ	Numerical	Series (12)	Series (13)
0·05	−0·4281	−0·4283	−0·4285
0·10	−0·3610	−0·3616	−0·3610
0·15	−0·2971	−0·2974	−0·2969
0·20	−0·2357	−0·2330	−0·2357
0·25	−0·1765	−0·1660	−0·1767
0·30	−0·1193	−0·0939	−0·1193

then the Rayleigh–Schrödinger theory gives

$$\epsilon_1 = -\epsilon_2 = 1\cdot500; \qquad \epsilon_3 = 6\cdot750; \qquad \epsilon_4 = -49\cdot6875. \tag{11}$$

The weak perturbation region is the region $0 < \lambda \leqslant 0\cdot05$ for this problem. For $\lambda \geqslant 0\cdot1$ the smallest term in the Rayleigh–Schrödinger series is the λ^3 term or a preceding one, and the 'best estimate' obtained by truncating at this term is not very close to our numerical results. We show instead in table 2 the average of the second- and third-order estimates, i.e. the result obtained with the choice

$$\epsilon_1 = -\epsilon_2 = 1\cdot500; \qquad \epsilon_3 = 3\cdot375; \qquad \epsilon_n = 0 \quad (n > 3). \tag{12}$$

This choice is suggested by the averaging process for asymptotic series as discussed by Morse and Feshbach (1953), and seems to give fair results. The results for the series with coefficients

$$\epsilon_1 = 1\cdot4745; \qquad \epsilon_2 = -0\cdot925; \qquad \epsilon_3 = 0\cdot800; \qquad \epsilon_n = 0 \quad (n > 3) \tag{13}$$

are also shown, and are even better. The latter series is obtained by fitting a third-order polynomial to our exact energy values at $\lambda = 0\cdot1, 0\cdot2, 0\cdot3$, but it also works well at the other λ values which are tabulated. The point to be noted here is that the 'best' polynomial in λ for the energy may be quite different from that suggested by the formal perturbation series when the latter is asymptotic, particularly if the fit is required over a fairly wide range of λ values. This feature is perhaps not always appreciated by workers who discuss the recovery of perturbation coefficients from numerical data.

4. Discussion

The method described in this letter is essentially a refined mathematical version of the kind of arguments (based on the curvature of the wavefunction) which are used in quantum mechanics textbooks to explain the existence of discrete bound state energies. Our use of the ratio variable $R(r)$ renders the method simple to apply, even to serious problems such as the perturbation problem studied in § 3, while the results of § 2 indicate that the error in the energy varies as h^2 over an extended range of h values. Although in principle $\psi(r)$ can be constructed from the sequence of $R(r)$ values when E has been determined accurately, it is clear that the method is best suited to the determination of energy eigenvalues. One way of finding expectation values from

energy calculations is to use the prescription

$$\langle A \rangle_\lambda = \frac{1}{2\Delta}(E(\lambda + \Delta A) - E(\lambda - \Delta A)) \tag{14}$$

which yields correct values in the limit $\Delta \to 0$. For our calculations, which have been taken to only four decimal places, we might hope to get expectation values correct to two places if we use the small value $\Delta = 0 \cdot 01$. A trial calculation for the Hamiltonian of § 3 actually gave $\langle r \rangle = 1 \cdot 50$ (the correct hydrogenic value) at $\lambda = 0$ and $\langle r \rangle = 0 \cdot 90$ at $\lambda = 1$. Empirically it was noted that $\partial E / \partial \lambda$ depends only very weakly on h; table 1 illustrates this for the large change $0 \to 1$ of λ.

For problems involving simple r^n-type perturbations of the hydrogen atom (or the harmonic oscillator) it is not too difficult to be confident about the number of nodes and the number of turning points which the exact wavefunction should have, and this knowledge can be used in the criteria for deciding whether the postulated $E(h)$ value is too high or too low. It would be interesting to investigate whether the simple criteria which suffice in this letter will work as easily for an arbitrary smooth potential; presumably the methods of Protter and Weinberger (1967) would be relevant in a formal approach to the problem.

References

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