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Abstract. A new application of the Hellmann-Feynman theorem is shown to allow accurate calculation of expectation values along with energies for the Schrödinger equation, for variable boundary position and boundary conditions. Power series and finite difference versions of the method are developed and applied to perturbed oscillator and perturbed hydrogen atom problems.

1. Introduction

Several techniques are available for calculating the eigenvalues of the one-particle Schrödinger equation. For the one-dimensional (or radial) equation there are available power series methods and finite difference methods which give highly accurate energy values (Killingbeck 1983). These methods are very simple and avoid some of the calculation which is required by the matrix-variational approach. They obtain an energy eigenvalue E_n without producing the normalised eigenfunction ψ_n. To find a quantity such as $\langle\psi_n|f|\psi_n\rangle$ they proceed by noting that a small term εf added to the potential would give an energy shift $\varepsilon\langle\psi_n|f|\psi_n\rangle$. This reduces the problem to one involving only accurate energy differences (Killingbeck 1979). In a matrix-variational approach, the eigencolumn associated with E_n could be obtained, but the matrix elements of f for the basis set would be needed in order to find $\langle f\rangle$. The main disadvantage of the energy differencing approach is the necessity of performing several energy calculations to find one expectation value. The present work obtains expectation values directly using power series or finite difference methods, and leads to a speedy and accurate technique well suited to microcomputer calculations.

To make clear the principles involved, much of the discussion will be centred on the perturbed oscillator Schrödinger equation

$$-D^2\psi + \mu x^2\psi + \lambda x^{2M}\psi = E\psi \tag{1}$$

since comparative results using other techniques are plentiful in the literature (e.g. Simon 1970, Tipping 1976, Banerjee 1978). Section 2 explains the simple mathematics which forms the basis of the new method. Section 3 sets out the power series version of the method, with illustrative results, and points out its flexibility in handling problems with various boundary conditions. Section 4 applies the method to an effective potential approximation for the Zeeman effect. Section 5 sets out the finite difference version of the method, and shows how it can calculate unusual expectation values such as $\langle x^2(1+x^2)^{-1}\rangle$ or the ψ^2 value at a specified point. There are several comments about the best way to implement the calculations, and § 6 discusses some points in detail. The computer language notation $A(N)$ (rather than A_N) is used in recurrence relations.

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2. Basic principles

The energy E_n of each eigenfunction ψ_n will vary with μ and λ. The Hellmann-Feynman identity

$$\langle\psi_n|x^2|\psi_n\rangle = \partial E_n/\partial\mu \tag{2}$$

will hold for the bound states of the Schrödinger equation (1). By calculating each energy E_n for a sequence of μ values such as $\mu \pm \Delta$, $\mu \pm 2\Delta$, with Δ small, a good estimate of $\partial E_n/\partial\mu$ and so of $\langle x^2\rangle$ can be obtained. This is the basis of Killingbeck's earlier (1979) approach. However, it is possible to proceed further by noting that a variety of techniques (e.g. the Hill determinant method, the power series method, the finite difference method) locate an energy eigenvalue by finding a zero of some appropriate function of E. (For the methods of this paper the function used is actually the wavefunction ψ at some specified boundary.) The eigenvalue condition can thus be written in the form

$$F(E, \mu, \lambda) = 0 \tag{3}$$

for the case of the Schrödinger equation (1). From the chain rule of partial differential calculus we obtain the result

$$\langle x^2\rangle = (\partial E/\partial\mu)_\lambda = -(\partial F/\partial\mu)_E/(\partial F/\partial E)_\mu. \tag{4}$$

This is the key equation which leads to the methods of this paper. $\langle x^{2M}\rangle$ will follow from an analogous equation which uses $\partial F/\partial\lambda$ instead of $\partial F/\partial\mu$. Strictly speaking, $\partial F/\partial\mu$ should be worked out with E held at an energy eigenvalue, but it suffices to use the current energy estimate in the convergent iterative procedures developed in this work.

3. The power series method

For the case of the Schrödinger equation (1) we write the wavefunction in the form

$$\psi = \exp(-\tfrac{1}{2}\beta x^2)\sum A(N)x^{2N+P} \tag{5}$$

where P is the parity index (0 for even, 1 for odd). Substituting (5) into (1) leads to a recurrence relation for the coefficients:

$$aA(N+1) = bA(N) + cA(N-1) + \lambda A(N-M) \tag{6}$$

where

$$a = (2N+P+1)(2N+P+2) \tag{7}$$

$$b = (4N+2P+1) - E \tag{8}$$

$$c = \mu - \beta^2. \tag{9}$$

Differentiating (6) with respect to E quickly shows that to obtain $\partial\psi/\partial E$ we should use (5) with the coefficients $A(N)$ replaced by new coefficients $B(N)$ which obey the recurrence relation

$$aB(N+1) = bB(N) + cB(N-1) + \lambda B(N-M) - A(N). \tag{10}$$

Similarly, $\partial\psi/\partial\mu$ is obtained by using in (5) the coefficients $C(N)$, for which

$$aC(N+1)=bC(N)+cC(N-1)+\lambda C(N-M)+A(N-1). \tag{11}$$

The three recurrence relations (6), (10) and (11) all use the same numerical coefficients a, b and c, which leads to a compact computation. The initial conditions are that all A, B and C coefficients are zero for $N<0$, with $A(0)=1$, $B(0)=0$ and $C(0)=0$. If the boundary condition to be used is the Dirichlet condition $\psi(L)=0$, then the sums of the series for $\psi(L)$, $\partial\psi(L)/\partial E$ and $\partial\psi(L)/\partial\mu$ are computed along with the coefficients. Strictly speaking, of course, the series actually represent $\exp(\frac{1}{2}\beta L^2)\psi(L)$, etc, but by working only with the ratios of series we can ignore the exponential factor; its main role is to provide an adjustable convergence parameter β. Starting from a trial energy E, we calculate a corrected energy E^1 using the Newton's method formula

$$E^1=E-\psi(L)/(\partial\psi(L)/\partial E). \tag{12}$$

A value for $\langle x^2\rangle$ emerges at the same time by using equation (4). To calculate $\langle x^{2Q}\rangle$ for $2Q\neq 2$ it is only necessary to use $A(N-Q)$ instead of $A(N-1)$ as the last term in equation (11). (This corresponds to adding a 'dummy' term εx^{2Q} to the potential.) It should also be clear how to include extra terms in the equations when the potential is a polynomial involving several terms; our λx^{2M} term is a representative general term.

It is best to compute E^1 from (12) and $\langle x^2\rangle$ from (4) by using ratios of the relevant partial sums at each N, rather than waiting until each separate partial sum has converged. Experience shows that this procedure of using the ratios of partial sums cuts computing time by roughly an order of magnitude, while empirical adjustment of the β value speeds up convergence even further. A single 'run' ends when E^1 as computed by (12) reaches a stable value, which is used to start the next run. After a few runs the computed $\langle x^2\rangle$ and E values reach their final limits. In practice the whole calculation can be packed into a short microcomputer program (Killingbeck 1984b) which can handle a variety of circumstances. The operator inputs a trial E; the nearest eigenvalue and the associated $\langle x^2\rangle$ value (or selected $\langle x^{2Q}\rangle$ value) are computed directly in about a minute, if the eigenvalues are well separated. An attenuator subroutine (Killingbeck 1984a) will prevent jumping to other eigenvalues. The value of $A(0)$ can be adjusted to avoid overflow or underflow. Alternatively, the quantities $T(N)=A(N)L^N$ can be used as the subjects of the recurrence relation, with a corresponding slight modification of the relevant equations; this procedure is probably the best computationally.

The calculation as described above allows the investigation of the way in which energies and expectation values vary with the position of the boundaries at $x=\pm L$ (for this symmetric potential). By differentiating equation (5) with respect to x it is easy to see that to treat homogeneous Neumann boundary conditions at $x=\pm L$ it is only necessary to modify the series sums a little. In the summations each coefficient $A(N)$ or $B(N)$ or $C(N)$ is multiplied by a factor $(2NL^{-1}-\beta)$. As L is increased, the effect of the L^{-1} term diminishes, so that for $L\to\infty$ the results become asymptotically the same for homogeneous Dirichlet or Neumann conditions. In the case of homogeneous Dirichlet conditions with $L\to\infty$ the method takes an extremely simple form. Equation (6) then becomes isomorphic to the recurrence relation which would arise in a Hill determinant approach to the problem (Banerjee 1978), with $A(N)$ interpreted as the value of the determinant of an $N\times N$ truncation of the Hill determinant. The requirement that the determinant shall be zero is then implemented in the present power series approach by using (instead of the partial sums) only the

current $A(N)$, $B(N)$ and $C(N)$ coefficients when forming the various ratios. It is thus possible to work out the results for $L=\infty$ within the course of a calculation for some finite L, so exhibiting directly the effect of moving the boundaries inwards.

Table 1 gives a few illustrative results for the perturbed oscillator Schrödinger equation (1) for the case $M=2$. The results were checked by noting that the independently calculated values of E, $\langle x^2\rangle$ and $\langle x^4\rangle$ obeyed the virial theorem

$$E=2\mu\langle x^2\rangle+3\lambda\langle x^4\rangle. \tag{13}$$

Table 1. Some results for the potential $\mu x^2+\lambda x^4$, for both even and odd parity ground states. The parameter values $L=6$, $\beta=2$ were used throughout.

(μ,λ)	E	$\langle x^2\rangle$	$\langle x^4\rangle$
1, 0	1.0	0.5	0.75
0, 1	1.060 362 09	0.362 022 65	0.353 454 03
1, 1	1.392 351 64	0.305 813 65	0.260 241 45
1, 0	3.0	1.5	3.75
0, 1	3.799 673 03	0.901 605 90	1.266 5577
1, 1	4.648 812 70	0.801 250 60	1.015 4372

4. Perturbed Coulomb problems

Once the basic principles of the method of § 3 have been understood it is possible to apply them to other problems. The most obvious next step is to look at radial problems, where we cannot use the even parity of the potential since the coordinate range is from $r=0$ to $r=R$. For the case of the perturbed hydrogenic Schrödinger equation (in atomic units)

$$-\tfrac{1}{2}\nabla^2\psi-Zr^{-1}\psi+V(n)r^n\psi=E\psi \tag{14}$$

with positive integer n, we can first derive the traditional radial equation for states of angular momentum l and then write the radial function $R(r)$ in the form

$$R=r^{l+1}\exp(-\beta r)\sum A(n)r^n. \tag{15}$$

The resulting recurrence relation for the $A(n)$ is then

$$aA(N+1)=bA(N)+cA(N-1)+V(n)A(N-n-1) \tag{16}$$

where

$$a=\tfrac{1}{2}(N+1)(N+2l+2) \tag{17}$$

$$b=\beta(N+l+1)-Z \tag{18}$$

$$c=-(E+\tfrac{1}{2}\beta^2). \tag{19}$$

By differentiating (16) with respect to E or Z or any other parameter we can construct a theory analogous to that derived for the perturbed oscillator in § 3. For the case $R\to\infty$ it is not necessary to form any series sums; the $A(N)$ and other coefficients are used directly in forming the various required ratios.

In a discussion of the hydrogen atom Zeeman effect, Killingbeck (1981) showed that at low field strengths it is possible to represent the effect of a perturbing term

$\frac{1}{8}\gamma^2(x^2+y^2)$ in the hydrogenic Hamiltonian by an effective potential $A\gamma^2r^2$. The factor A is state-dependent and follows from perturbation theory and angular momentum theory. The new method of the present paper obviously makes it easy to calculate results using the effective potential. Silva and Canuto (1984) have recently used a factorised wavefunction method for this problem. Table 2 shows some typical results obtained by the new method. The virial theorem was used to check the computed numbers. Perturbation theory indicates that the $\langle r^n\rangle$ values obtained using the effective potential will be very close to those for the true potential, and they can be used to calculate the small second-order correction to the energy eigenvalue which is caused by changing from the effective potential to the true potential (Killingbeck 1981, 1983). What the present new technique does is to allow speedier calculations using the effective potential approximation. The effective potential takes care of state mixing which is diagonal in l and table 3 shows clearly how this dominant contribution varies with m. The values of the product $\langle r\rangle\langle r^{-1}\rangle$ also show that the wavefunction's radial distortion is not a simple scaling.

Table 2. Some results for the effective potential $-r^{-1}+A\gamma^2r^2$ at $\gamma=0.1$. (The linear Zeeman term $\frac{1}{2}\gamma l_z$ is omitted.)

State	(A,β)	E	$\langle r\rangle$	$\langle r^{-1}\rangle$
1s	$\frac{1}{12}$, 1	−0.497 521 65	1.489 1892	1.004 8729
2s	$\frac{1}{12}$, 1	−0.095 653 02	5.184 6442	0.294 566 76
$2p_0$	$\frac{1}{20}$, 1	−0.111 752 51	4.516 3106	0.271 520 61
$2p_{-1}$	$\frac{1}{10}$, 1	−0.100 522 03	4.256 2638	0.285 681 79
$3d_{-1}$	$\frac{1}{14}$, 2	−0.004 308 92	6.961 2074	0.161 284 53
$3d_{-2}$	$\frac{3}{28}$, 2	0.013 425 11	6.498 8556	0.172 192 65

Table 3. Perturbed oscillator results obtained by the finite difference method, with $L=6$. The (1, 0) results agree with the analytic ones for the harmonic oscillator.

(μ,λ)	$\langle x^2/(1+x^2)\rangle$	$\psi^2(1)$	$\psi^2(2)$
1, 0	0.242 1279	0.207 5538	0.010 3335
0, 1	0.204 8996	0.182 7323	0.000 8049
1, 1	0.182 6673	0.149 2132	0.000 3215
1, 0	0.515 7443	0.415 1075	0.082 6678
0, 1	0.415 5184	0.495 8498	0.005 9583
1, 1	0.389 2709	0.474 7630	0.002 9812

5. A finite difference method

The methods of the preceding sections work well for polynomial potentials and they are applicable in principle to any potential with a convergent power series expansion. They could also be applied to potentials such as $x^2(1+gx^2)^{-1}$ by incorporating a factor $(1+gx^2)$ in the ansatz (5) for ψ, as Heading (1982) did in a tridiagonal matrix formalism for such potentials. For more general potentials a finite difference approach can be used. Starting from the Schrödinger equation

$$-D^2\psi+V\psi=E\psi \tag{20}$$

and using the lowest-order finite difference representation of $D^2\psi$ we quickly obtain the recurrence relation

$$\psi(x+h) = [2+F(x)]\psi(x) - \psi(x-h) \tag{21}$$

where

$$F(x) = h^2[V(x) - E]. \tag{22}$$

To use equation (21) we assign $\psi(0)$ and $\psi(h)$ to suit the boundary condition at $x=0$ and calculate $\psi(2h)$ and so on using some trial E value. If the outer boundary is at $x=L$ then E is varied to give $\psi(L, E)=0$. Using (21) in this way gives eigenvalues which differ from the correct eigenvalues of (20) by a leading term of order h^2. Killingbeck (1979) used perturbation theory to show that the modified equation

$$\psi(x+h) = (2+F+\tfrac{1}{12}F^2)\psi(x) - \psi(x-h) \tag{23}$$

will give eigenvalue errors of order h^4 if $V(x)$ is smooth. The use of Killingbeck's correction term is particularly well suited to the methods of this paper, since it gives a procedure which is computationally more simple than that associated with the Numerov method. ψ in (23) plays the same role as A in (6) and it is clear that the values of $\partial\psi/\partial E$ will obey the recurrence relation

$$B(x+h) = (2+F+\tfrac{1}{12}F^2)B(x) - B(x-h) - h^2G(x)\psi(x) \tag{24}$$

with

$$G(x) = 1+\tfrac{1}{6}F(x) \tag{25}$$

(and with the x dependence of F in (23) and (24) being understood). To find the expectation value of some function $U(x)$ we need to have the recurrence relation analogous to that for the $C(N)$ coefficients in § 3. By adding a 'dummy term' $\mu U(x)$ to the potential and differentiating (23) with respect to μ (at $\mu=0$) we obtain the required relation:

$$C(x+h) = (2+F+\tfrac{1}{12}F^2)C(x) - C(x-h) + h^2G(x)U(x)\psi(x). \tag{26}$$

To use the preceding equations in the spirit of § 3 the procedure is as follows, for the specimen case $\psi(0)=\psi(L)=0$. The quantities $\psi(0)$, $B(0)$, $C(0)$, $B(h)$ and $C(h)$ are set equal to zero and $\psi(h)$ is set equal to 1 (or any constant value which avoids overflow problems in the computation). Some initial E is used and the corrected energy E^1 and the estimated $\langle U\rangle$ are calculated from

$$E^1 = E - \psi(L)/B(L) \tag{27}$$

$$\langle U\rangle = -B(L)/C(L). \tag{28}$$

The calculation can be made automatic, with the runs being repeated until the energy and $\langle U\rangle$ value have converged. The results refer to the state with energy nearest to the starting E, if the shift E^1-E is suitably attenuated (Killingbeck 1984a). By counting the sign changes in ψ it is possible to see which excited state has been located. To apply the Neumann condition $\partial\psi/\partial x=0$ at $x=L$ we can use the test that $\psi(L+h)-\psi(L-h)$ rather than $\psi(L)$ should be zero.

The results for E and $\langle U\rangle$ as obtained using two or more h values can be treated by Richardson extrapolation to give accurate results for the differential equation (20) (Killingbeck 1983). The use of Richardson extrapolation makes the finite difference

method slower than the power series method, but we have checked that the results of the two methods agree for a variety of problems in which both are applicable. Table 3 shows several expectation values for the perturbed oscillator problem which can be found by the finite difference approach but not by the power series approach. (To simulate an even parity state calculation the basic result $\psi(h) = \psi(-h)$ is used to deduce the initial values of the various quantities.) The local quantities $\psi^2(y)$ for $x = y$ were obtained by taking $U(x)$ in the following form (as expressed in BASIC)

$$0.5*(x > y - \tfrac{1}{2}h)*(x < y + \tfrac{1}{2}h)/h \tag{29}$$

to simulate a 'half-delta function' at $x = y$. For a radial problem, where all of the space (not half of it) is being integrated over, the factor 0.5 in (29) is replaced by 1. The expression (29), although not acceptable in traditional algebra, is evaluated as a Boolean function by most microcomputers. This is one reason why, apart from their simplicity, the methods of the present work are particularly suited to the capabilities of modern microcomputers. A Boolean function of the form $(\psi(x)/\psi(x-h) < 0)$ can be used to add one to the node count whenever ψ changes sign (Killingbeck 1984a).

6. The choice of convergence factors

Table 1 shows some results for the potential x^4 (i.e. $\mu = 0$, $\lambda = 1$). These results were obtained speedily by the method of § 3, even though the correct asymptotic form of the wavefunction as given by analysis and by numerical calculation has a dominant factor $\exp(-|x|^3/3)$ (Killingbeck 1984a). The use of a simple Gaussian convergence factor for one-dimensional problems and of a scaled hydrogenic factor for radial problems has been found to give good convergence and accuracy in a variety of calculations, with the choice of β not being very critical. The use of the simple standard convergence factors leads to near-universal algorithms and programs, whereas use of the formally 'correct' factors gives more complicated recurrence relations which vary more markedly from case to case. Further, for a method such as ours, which can use boundaries at any finite distance, the use of a mathematically exact asymptotic factor seems to be of little relevance.

We wish to point out an interesting difference between the methods of §§ 3 and 5. If the method of § 5 is used to simulate an even parity one-dimensional calculation, the choice $U(x) = x$ in equation (26) will yield $\langle |x| \rangle$, since the integration runs from 0 to ∞. However, the 'full space' $\langle x \rangle$ value is obviously zero and so would not be sought using the method of § 3. The equations of § 3 suppose all operators to be of even parity, so that the recurrence relations mention only coefficients attached to even powers of x. To handle a one-dimensional 'mixed parity' potential such as $\mu x^3 + \lambda x^4$ would require the method of § 5, with the boundary conditions $\psi(0) = \psi(2L) = 0$ and the displaced potential $\mu(x-L)^3 + \lambda(x-L)^4$.

7. Conclusion

In the last few years the use of microcomputers has made it possible to pass on to a new stage in the study of traditional model systems such as perturbed oscillators or perturbed hydrogen atoms. In the area of perturbation theory many previously inaccessible perturbation series can now be calculated automatically, so that attention can be

concentrated on the interpretation and use of the series. In the area of direct numerical computation the methods described in this paper should make it easier to pass on to problems such as: how do energies and other quantities vary as boundary positions, boundary conditions and the shape of the potential $V(x)$ vary? It might also be possible to produce a numerical method to calculate the energy perturbation series for an arbitrary perturbation $\mu U(x)$; the E_1 term is just $\langle U \rangle$ and E_2 can be obtained as $\frac{1}{2}\partial\langle U\rangle/\partial\mu$. The simple equations of § 2 and the procedures used in the later sections are probably capable of much further development, but the illustrative results presented here establish clearly the promise of these methods for a variety of calculations.

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