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Eigenvalues from the Riccati equation

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Abstract. A non-perturbative approach for obtaining the eigenvalues of the Schrödinger equation is proposed. The method is based on the Riccati equation for the logarithmic derivative of the wavefunction. Results are shown for the anharmonic oscillator.

1. Introduction

The logarithmic perturbation theory proves to be useful in large-order calculations because it leads to closed quadrature expressions for the terms of the perturbation series (Aharonov and Au 1979, Eletsky and Popov 1980, Privman 1981 and references therein). However, in most cases these expansions are found to be asymptotic divergent and a resummation technique is required to obtain accurate eigenvalues (Seznec and Zinn-Justin 1979, Killingbeck 1981, Arteca *et al* 1984, Maluendes *et al* 1984, see also the issue 1982 *International Journal of Quantum Chemistry* **21** no 1). When the eigenvalues exhibit two asymptotic expansions (say about $\lambda = 0$ and $1/\lambda = 0$) the resummation technique is often chosen so that it matches them smoothly (Seznec and Zinn-Justin 1979, Arteca *et al* 1984, Maluendes *et al* 1984). An example of this is the anharmonic oscillator

$$H = p^2 + x^2 + \lambda x^4 \qquad p = -\mathrm{i}\mathrm{d}/\mathrm{d}x \tag{1}$$

whose eigenvalues $E(\lambda)$ obey

$$E = \sum_{j=0}^{\infty} E_j \lambda^j \tag{2}$$

$$E = \lambda^{1/3} \sum_{j=0}^{\infty} e_j \lambda^{-2j/3}. \tag{3}$$

The former series is asymptotic divergent whereas the latter has a finite convergence radius (Simon 1970).

Silva and Canuto (1982, 1984a, b) developed an interesting non-perturbative approach based on a similarity transformation proposed by Hall (1977). They showed that the Hall method compares favourably with the perturbation series (Silva and Canuto 1982) and obtained the first perturbation corrections numerically (Silva and Canuto 1984b). In fact, it is not difficult to prove that the Hall method leads to the Riccati equation from which one can actually obtain all the perturbation corrections exactly.

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Some time ago, we developed a method closely related to the logarithmic derivative algorithm in order to deal with bounded quantum mechanical systems (Fernández and Castro 1981). However, instead of solving the resulting differential equation by perturbation theory, we resorted to a systematic truncation of the Taylor series for the logarithm of the wavefunction which is similar to that performed by Silva and Canuto (1982, 1984a, b). (An interesting alternative approach was discussed by Killingbeck (1978).)

The above-mentioned procedure is further investigated in this paper. For the sake of simplicity the anharmonic oscillator (1) is considered as an illustrative example. The main equations are obtained in § 2, analytical expressions for the eigenvalues are developed in § 3 and numerical results are shown in § 4. Finally, further comments and conclusions are found in § 5.

2. The method

In this paper we restrict ourselves to the Schrödinger equation in one dimension

$$\Psi''(x) = q(x)\Psi(x) \tag{4}$$

where $q(x) = V(x) - E$. Multidimensional systems will be discussed elsewhere. If the eigenfunction $\Psi(x)$ is written $F(x)\Phi(x)$, (2) becomes

$$F'' - 2fF' + (f^2 - f')F = qF \tag{5}$$

where $f = -(\ln \Phi)'$. It is worth noticing that if $F = \Psi_0$ is an eigenfunction of a Hamiltonian operator H_0 then (5) can be rewritten as a Hall equation for $L' = f$ (Hall 1977). If all the zeroes of Ψ are taken into account in $F(x)$ then $f(x)$ is found to be a regular function.

The first two states of a model with a parity-invariant potential can be easily treated by choosing $F = x^s$, where $s = 0$ or 1 for the ground or first excited state, respectively. In this case (5) becomes

$$f' = f^2 - 2sf/x - q. \tag{6}$$

All the perturbation corrections for the anharmonic oscillator (1) can be obtained from (6) by expanding both f and E in power series of λ and then solving the resulting equations in a hierarchical manner (Aharonov and Au 1979, Eletsky and Popov 1980, Privman 1981). However, we find it more suitable to expand f in powers of x, i.e.

$$f = \sum_{j=0}^{\infty} f_j x^{2j+1}. \tag{7}$$

The Taylor coefficients f_j $(j = 0, 1, \ldots)$ obey

$$f_j = (2j + 2s + 1)^{-1}\left(\sum_{i=0}^{j-1} f_i k_{j-i-1} + E\delta_{j0} - \delta_{j1} - \lambda\delta_{j2}\right) \tag{8}$$

and are therefore found to be polynomial functions of λ and E.

If only the first $N+1$ terms in (7) are kept and $f_N > 0$, then a quadratically integrable ansatz $\Psi_0 = x^s\Phi$ is obtained which is an eigenfunction of

$$H_0 = p^2 + V_0 \tag{9}$$

with eigenvalue f_0. The potential V_0 is given by

$$V_0 = V + R \tag{10a}$$

where

$$R = \sum_{j=N}^{2N} r_j x^{2j+2} \qquad N = 1, 2, \ldots \tag{10b}$$

and

$$r_j = \sum_{k=j-N}^{N} f_k f_{j-k} - \lambda \delta_{j1}. \tag{10c}$$

The coefficients f_j ($j = 1, 2, \ldots$) are given by (8) as functions of f_0 and λ.

It follows immediately that

$$f_0 - E = R_0 \tag{11}$$

where $R_0 = \langle \Psi | R\Psi_0 \rangle / \langle \Psi | \Psi_0 \rangle$ depends on f_0. Obviously, f_0 will be an upper (lower) bound to E provided R_0 is positive (negative). The closest approach is obtained when f_0 leads to the smallest R_0^2 value. Although we cannot calculate R_0, we can reasonably estimate its sign as follows. Since $\Psi\Psi_0$ tends to zero quite quickly as $|x|$ increases we assume that the sign of R_0 is determined by the behaviour of R near the origin which is approximately given by $R \simeq (2N+2s+3) f_{N+1} x^{2N+2} + [(2N+2s+5) f_{N+2} - 2f_0 f_{N+1}] x^{2N+4}$. For this reason the roots of $f_{N+1} = 0$ are expected to be upper or lower bounds to E provided f_{N+2} is positive or negative, respectively. Since there is only one root for each N value that leads to the proper perturbation series the choice is unique. In the same way increasingly accurate lower bounds are expected from the negative minima of f_{N+1}. This assumption is confirmed in § 4.

To illustrate what was said above let us consider the first coefficients f_j:

$$\begin{aligned} &f_1 = (f_0^2 - 1)/(2s+3) \qquad f_2 = (2f_0 f_1 - \lambda)/(2s+5) \\ &f_3 = (2f_0 f_2 + f_1^2)/(2s+7). \end{aligned} \tag{12}$$

When $N = 1$ R becomes $(2s+5) f_2 x^4 + f_1^2 x^6$. Therefore, if $f_2 = 0$ then $R > 0$ for all x values and $f_0 > E$. For $N = 2$ and $f_3 = 0$ we obtain $f_2 < 0$ and $R = 2f_1 f_2 x^8 + f_2^2 x^{10} < 0$ if x is small enough. The argument above suggests that $f_0 < E$ which can be readily verified.

Rigorous upper bounds are obtained from the variation principle that leads to

$$f_0 - \langle \Psi_0 | R\Psi_0 \rangle / \langle \Psi_0 | \Psi_0 \rangle \geqslant E. \tag{13}$$

In this case f_0 is chosen so that the LHS of (13) is as small as possible. A variant of this last procedure was tried by Killingbeck (1978).

3. Analytical expressions for the eigenvalues

Let us first consider the ground state of the anharmonic oscillator. If we set $f_j = 0$ ($j = 2, 3$ and 4) in (8) we have (for the sake of simplicity we use E instead of f_0 from now on)

$$E^3 - E - 3\lambda/2 = 0 \tag{14a}$$

$$E^4 - 22E^2/17 - 18\lambda E/17 + 5/17 = 0 \tag{14b}$$

$$E^5 - 50E^3/31 - 39\lambda E^2/31 + 19E/31 + 21\lambda/31 = 0. \tag{14c}$$

On expanding E in power series of λ in these equations we obtain the actual energy perturbation series up to first, second and third order respectively. (In general there is only one root of $f_N = 0$ that leads to the $(N-1)$th-order perturbation expansion and we choose it in our calculation.) Therefore, the solutions of (14) must agree with the corresponding truncated perturbation expansions for small enough λ values. In addition to this, the approximate eigenvalues can be expanded in power series of $\lambda^{-2/3}$ as in (3). Although (14) fail to yield the actual coefficients e_i they are expected to improve the perturbation series largely because in some way they are matching both the large- and small-λ expansions. It is worth noting that the series in powers of λ for the approximate energies have finite convergence radii which is not the case of the eigenvalues of H.

As shown in table 1, (14*b*) and (*c*) yield lower and upper bounds, respectively, to the accurate eigenvalues obtained by Banerjee (1978). (Equation (14*a*) is found to lead to less accurate upper bounds.) The agreement is remarkable in the whole range of λ values. Similar accuracy is obtained for the first excited state.

Table 1. Lowest eigenvalue of the anharmonic oscillator obtained from (14*b*) and (14*c*).

λ	Equation (14*b*)	Equation (14*c*)	Exact (Banerjee 1978)
10^{-1}	1.065 00	1.065 33	1.065 286
1	1.380 8	1.396 72	1.392 352
10	2.384 0	2.478 7	2.449 174
10^2	4.821	5.082	4.999 417
10^3	10.23	10.83	10.639 789
10^4	21.98	23.27	22.861 608

When dealing with excited states this approach becomes rather cumbersome because the zeros of the wavefunction have to be taken into account explicitly (Aharonov and Au 1979). However, we can obtain analytical expressions for all the states easily from a straightforward generalisation of (14). Let us illustrate the procedure with (14*a*). We write

$$E^3 + A_1 E + A_2 \lambda = 0 \tag{15a}$$

and require that the Taylor expansion for E about $\lambda = 0$ yields the first two perturbation corrections exactly. It follows immediately that

$$A_1 = -E_0^2 \qquad A_2 = -2E_0^2 E_1 . \tag{15b}$$

In the same way (15*b*) leads to

$$E^4 + B_1 E^2 + B_2 \lambda E + B_3 = 0 \tag{16a}$$

where

$$B_1 = 2(E_0^2 E_1^2 + E_0^3 E_2)/(E_1^2 - E_0 E_2) \tag{16b}$$

$$B_2 = 8E_0^2 E_1^3/(E_0 E_2 - E_1^2) \tag{16c}$$

$$B_3 = (3E_0^4 E_1^2 + E_0^5 E_2)/(E_0 E_2 - E_1^2). \tag{16d}$$

Results for $\lambda = 0.1$ and several values of the quantum number n are shown in table 2. It is interesting that (15) and (16) yield upper and lower bounds, respectively, for all

Table 2. Eigenvalues of the anharmonic oscillator with $\lambda = 0.1$ for several values of the quantum number n obtained from (15) and (16).

n	Equations (15)	Equations (16)	Exact (Banerjee 1978)
0	1.0679	1.065 00	1.065 286
1	3.3215	3.305 11	3.306 872
2	5.782	5.743 2	5.747 959
3	8.416	8.344	8.352 678
4	11.20	11.08	11.098 596
5	14.1	13.95	13.969 926
6	17.2	16.92	16.954 795
7	20.3	20.00	20.043 863
8	23.6	23.18	23.229 552
9	26.9	26.44	26.505 555
10	30.4	29.79	29.866 525
100	523	500	504.896 937
1000	10 759	10 176	10 294.061 323

the eigenvalues of the anharmonic oscillator. As expected, the larger the quantum number the smaller the accuracy of the present formulae since the perturbation becomes more important.

Equations (15) and (16) also enable one to obtain upper and lower bounds, respectively, to the eigenvalues of the quartic oscillator ($V = x^4$). They are given by the leading coefficient of the large-λ expansion (3). A straightforward calculation shows that

$$(-B_2)^{1/3} < e_0 < (-A_2)^{1/3}. \tag{17}$$

Present results suggest a systematic way of improving the anharmonic oscillator perturbation series. We first build a function $P(\lambda, E)$ that can be factorised as $P(\lambda, E) = Q(\lambda)U(\lambda^{-2/3}, \lambda^{1/3}E)$ so that the roots of $P(\lambda, E) = 0$ can be expanded in power series of λ or $\lambda^{-2/3}$ as in (2) or (3), respectively. Then the adjustable parameters in P are set so that the former expansion agrees with the energy perturbation series up to the desired order. Owing to the nearly correct large-λ behaviour of the roots of $P = 0$ they are expected to be much more accurate than the perturbation series. This idea has recently been exploited by Fernández *et al* (1984) in order to obtain analytic expressions for the eigenvalues of the anharmonic oscillator from semiclassical considerations.

4. Large-order calculations

A question now arises about the convergence of the method just described. Since it is closely related to perturbation theory, as argued above, one expects it to be asymptotic divergent. Our numerical results confirm this assumption. We have calculated the first two energy levels of the anharmonic oscillator for several λ values, finding the same behaviour in all cases. When $\lambda = 1$, for instance, the chosen root of $f_N = 0$ oscillates about the actual eigenvalue as N increases from $N = 3$ to $N = 20$ giving rise to upper and lower bounds when N is even or odd, respectively (table 3). The amplitude of the oscillation decreases, reaches a minimum value and then increases. When $N > 20$

Table 3. Root of $f_N = 0$ for the ground state of the anharmonic oscillator with $\lambda = 1$.

N	E	N	E	N	E
3	1.381	9	1.3919	15	1.3919
4	1.397	10	1.3927	16	1.3927
5	1.390	11	1.3920	17	1.3922
6	1.394	12	1.3927	18	1.3927
7	1.3916	13	1.3920	19	1.3926
8	1.3929	14	1.3927	20	1.3927
				21	1.3843
				22	1.3864
				23	1.3878

Table 4. Root of $\partial f_N / \partial E = 0$ for the ground state of the anharmonic oscillator with $\lambda = 1$ and $\lambda = 10$.

$\lambda = 1$		$\lambda = 10$	
N	E	N	E
25	1.392 343	18	2.4484
26	1.392 346	19	2.4488
27	1.392 348	20	2.4488
28	1.392 349	21	2.4491
29	1.392 350	22	2.4490
30	1.392 351	23	2.4492
31	1.392 351	24	2.4490
		25	2.4493
		26	2.4490
Exact (Banerjee 1978)	1.392 352		2.449 174

random results are obtained though they remain quite close to the true eigenvalue. Although divergent the present method is still useful because it certainly improves the perturbation series largely matching the exact series in powers of λ with an approximate large-λ expansion. The most accurate result is obtained from the N value corresponding to the smallest oscillation amplitude.

Table 4 shows that there is a root of $\partial f_N / \partial E = 0$ that approaches the exact eigenvalue from below as discussed in § 2. It is clear from the results for $\lambda = 10$ that the procedure becomes oscillatory divergent for large enough N values. However, the root for the largest N value before the oscillation takes place is a quite accurate estimate of the eigenvalue. Such an accuracy cannot be obtained from the perturbation series.

5. Further comments and conclusions

We have shown that the eigenvalues of quantum mechanical systems can be approximately obtained from the Riccati equation for the logarithmic derivative of the wavefunction. Rigorous upper and lower bounds are obtained provided the sign of

R_0 can be determined which does not seem to be at present possible. Approximate eigenvalues come from the roots of $f_N = 0$ and $\partial f_N / \partial E = 0$.

As argued before, the present method can also be applied to excited states. For instance, in order to deal with the second excited state of the anharmonic oscillator one can choose $F = x^2 - a^2$ in (5). In this way the wavefunction will have two zeros at $x = \pm a$. As a result the coefficients f_j will depend on both a and E and two independent conditions will be necessary to determine them. A reasonable choice is $f_{N-1} = f_N = 0$.

A similar situation is found in the case of potentials which are not parity invariant. For example, when $V = x^2 + \alpha x^3 + \beta x^4$ the coefficient f_0 ($f = f_0 + f_1 x + f_2 x^2 + \ldots$) remains undetermined and an additional condition is required to calculate it.

The strategy discussed in § 3 to obtain analytical expressions for all the eigenvalues from the corresponding ground-state formula can be developed further. Let us illustrate this point by means of the Zeeman effect in hydrogen. The part of the Hamiltonian operator in atomic units that is relevant to our discussion is (Garstang 1977)

$$H = -\tfrac{1}{2}\Delta - 1/r + \tfrac{1}{8}B^2(x^2 + y^2). \tag{18}$$

It is obviously much simpler to deal with the Riccati equation for the spherical model

$$H = -\tfrac{1}{2}\Delta - 1/r + \tfrac{1}{8}B^2 r^2. \tag{19}$$

The analytical expressions for the eigenvalues of (19) can be used in approaching those of (18) by introducing appropriate adjustable parameters which lead to the proper perturbation series as discussed in § 3.

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