Journal of Mathematical Chemistry 18 (1995) 349–357

Asymptotic series for the quantum quartic anharmonic oscillator

N. Aquino

Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, Apdo. Postal 55-534, México, D.F. 09340, México

Received 6 April 1995; revised 7 September 1995

We propose a numerical method to find solutions of the one-dimensional Schrödinger equation when the potential is symmetric and can be expanded in a polynomial form. We used a non-perturbative method, in which we include explicitly the correct asymptotic behavior of the wave function computed by the WKB method. The numerical convergence is very fast and allows to compute the energy eigenvalues and eigenfunctions simultaneously. The method is applied to the quartic anharmonic oscillator with one and two wells, we compute the energy eigenvalues for the ground state and for the first six excited states, the results obtained are in agreement with those reported previously in the literature.

1. Introduction

There exists a great interest in finding analytic or numerical solutions for anharmonic oscillators in several fields of physics, for example in field theory and atomic and molecular physics. In the latter, the anharmonic potentials are used to study molecular vibrations of some diatomic molecules [1], or in small rings of compounds like trimethylene oxide [2–4], cyclopentane [5], cyclobutane [6] and, in addition, in the study of NH_3 inversion [7,8].

From a mathematical point of view, some authors [9,10] have made a complete study about the analytic properties of the energy levels for the Hamiltonian $H = \frac{1}{2}(p^2 + x^2) + \lambda x^4$ as a function of the anharmonic parameter λ. They showed that the problem cannot be solved by using perturbation theory, because the perturbative series for the energy in terms of the anharmonic parameter λ diverges for any value of λ positive.

In their second paper, Bender and Wu [9] were able to show the complicated analytic structure of the energy $E(\lambda)$ as a function of the anharmonic parameter λ, while studying the wave function in the WKB approximation at first order in λ. Simon [10] and after Loeffel and Martin [11] gave a formal demonstration of the conjectures of Bender–Wu, using Hilbert-space methods. The singular behavior of

$E(\lambda)$ for the anharmonic oscillator opens the opportunity to propose new methods to determine both the eigenvalues and the eigenfunctions for this problem. Loeffel et al. [12] proved the Stieltjes property of Rayleigh–Schrödinger (RS) series and discussed the convergence of any diagonal sequence of Padé aproximants. Also they determined ground state energy eigenvalues for $\lambda \leqslant 0.5$ using continued fractions with the quotient difference algorithm; Čížek and Vrscay [13] extended these results for $\lambda \leqslant 1000$. The Borel summability of the anharmonic oscillator RS series was established by Graffi et al. [14], and they reported ground state energy calculations for $\lambda \leqslant 7.0$; additional discussions on the Borel summability were done by Caswell [15] and Zinn–Justin [16]. After Lipantov [17] introduced the functional-integral equivalent to WKB approximation, Brézin et al. [18] used this idea to rederive the leading terms of Bender–Wu. Halliday and Suranyi [19] using the Lipantov's idea developed an alternative perturbation series that converges, unlike the conventional RS perturbation theory. Fanelli and Struzynski [20] proposed the inclusion of an adjustable parameter into the perturbing and unperturbed terms of the Hamiltonian; after this they used RS perturbation theory. They obtained better values than the standard perturbation theory for small values of λ, and were able to extend the range of applicability of this method to values of $\lambda \leqslant 20000.0$; following the method of Fanelli and Struzinski, Aquino et al. [21] computed the energy eigenvalues for the anharmonic oscillator with double well. Iraxu [22] proposed the use of a piecewise perturbation technique in which the unperturbed potential is adjusted instead of the use of $x^2/2$ as a reference potential and λx^4 as the perturbation. In 1985, Berk [23] published a paper where he showed that the perturbation problem is reduced significantly if the asymptotic WKB wave function of zero order is employed as the zero-order wave function. In the same year Silverston et al. [24] obtained the RS perturbation theory energy coefficients using high-order perturbation theory. Vinette and Čížek [25] established upper and lower bounds of the ground state energy of anharmonic oscillators using the so-called "renormalized inner projection technique" that is a combination of renormalization and Löwdin's inner projection. This technique was successfully applied to quartic, sextic and octic anharmonic oscillators.

A wide variety of non-perturbative methods have been used to calculate accurate energy eigenvalues for the anharmonic oscillator: for example, the variational method [26–28], the power series method [32–35], the Hill determinant method [29–31,40], high order WKB calculations [42], and phase integrals [43]. The inconvenience of the methods based on a matrix diagonalization is the great amount of time necessary to obtain high quality precision for the energy eigenvalues. In addition, we cannot select only one particular energy level, because with the matrix method one cannot avoid obtaining the lower levels too. On the other hand, with the methods based on power series we can compute each energy level independently of the others. The time consumed in these calculations is very low and the convergence of the energy eigenvalues is very fast.

2. The method

In this section we will calculate the energy eigenvalues for the quartic anharmonic oscillator without using perturbation theory. The corresponding Hamiltonian is given, in atomic units, by

$$H = \tfrac{1}{2}(p^2 + x^2) + \lambda x^4, \quad \lambda > 0, \tag{1}$$

but in order to simplify our discussion, it will be written as

$$H = \tfrac{1}{2}(p^2 + x^2) + \tfrac{1}{2}\mu^2 x^4,$$

where $\mu^2 = 2\lambda$. The Schrödinger equation for this system is, therefore,

$$\frac{d^2\Psi}{dx^2} + [E' - x^2 - \mu^2 x^4]\Psi = 0, \tag{2}$$

with $E' = 2E$, E being the eigenvalue of (1). Defining

$$x = \mu^{-1/3} y,$$

eq. (2) reduces to

$$\frac{d^2\Psi}{dy^2} + [\epsilon - \mu^{-4/3} y^2 - y^4]\Psi = 0, \tag{3}$$

where $\epsilon = \mu^{-2/3} E'$.

If we assume a solution of the form

$$\phi(y) = \sum_{n=0}^{\infty} a_n y^n, \tag{4}$$

then the coefficients a_n must be determined. It is easily found that for both the *even* solution ($\phi(0) = 1$, $\phi'(0) = 0$ or, equivalently $a_0 = 1$, $a_1 = 0$) and the *odd* solution ($\phi(0) = 0$, $\phi'(0) = 1$ or, equivalently $a_0 = 0$, $a_1 = 1$), the recurrence relation for the coefficients is

$$a_{n+2} = \frac{a_{n-4} - \mu^{-4/3} a_{n-2} - \epsilon a_n}{(n+1)(n+2)}. \tag{5}$$

However, as y increases it is necessary to take a large number of terms in order to assure convergence. It is, hence, convenient to try another function with the correct asymptotic behavior. For large values of y we may take the asymptotic behavior of the wavefunction from a WKB calculation as follows: It is well known that the wave function in WKB approximation [37] is given by

$$\psi_{\mathrm{WKB}}(y) = \phi(y) \exp\left(\pm i \int^{y} p(y)dy\right),$$

where $\phi(y)$ is a slowly varying function and $p(y) = \sqrt{\epsilon - V(y)}$, for our case $V(y) = \mu^{-4/3}y^2 + y^4$. Then, as y is larger than ϵ, we can develop $p(y)$ through the binomial theorem, and then approximate it as $p(y) = i(y^2 + \mu^{-4/3})$. After doing the integration and taking the minus sign (to assure convergence when $y \to +\infty$), the exponential part of ψ_{WKB} is $\exp(-y^3/3 - \mu^{-4/3}y/2)$. Since we want the solution of eq. (3) to be valid not only for large values of y, we propose the function

$$\psi(y) = A \exp\left(\frac{-y^3}{3} - \frac{\mu^{-4/3}y}{2}\right) \sum_{m=1}^{\infty} b_m y^{-m}, \tag{6}$$

where A is a constant.

When (6) is substituted into (3), the following recurrence relation is obtained:

$$b_1 = 1,$$

$$b_2 = -(\epsilon + \tfrac{1}{4}\mu^{-8/3})b_1/2,$$

$$b_{m+1} = -\frac{1}{2m}[(m-2)(m-1)b_{m-2} - \mu^{-4/3}(m-1)b_{m-1} + (\epsilon + \tfrac{1}{4}\mu^{-8/3})b_m], \quad m > 2. \tag{7}$$

If the two solutions (4) and (6) are compatible for any value of $y \neq 0$, the following equations must hold:

$$\phi(y) = \psi(y) \quad \text{and} \quad \phi'(y) = \psi'(y)$$

or

$$\phi'(y)/\phi(y) = \psi'(y)/\psi(y)$$

for every y where $\phi(y) \neq 0$ and $\psi(y) \neq 0$.

In order to compute the energy eigenvalues we consider the function

$$f(\epsilon, y) = \phi'(\epsilon, y)/\phi(\epsilon, y) - \psi'(\epsilon, y)/\psi(\epsilon, y) \tag{8}$$

defined for values of ϵ and y such that ϕ and ψ do not vanish.

The function thus defined is identically zero for the exact value of the energy (independently of the value of y), but it is non-zero for other values of ϵ. Therefore, it only remains to find the roots of eq. (8) in order to determine the energy eigenvalues. We may begin by choosing the initial value of y as the classical turning point, while the initial energy ϵ_0 must be estimated *a priori*.

Once the value of y is chosen (represented by y^*), it is kept fixed and the energy eigenvalues are calculated by the Newton–Raphson method:

$$\epsilon_{n+1} = \epsilon_n - f(\epsilon_n, y^*)/f'(\epsilon_n, y^*), \tag{9}$$

where the prime indicates derivative with respect to the energy.

2.1. NUMERICAL RESULTS

With this method we compute the ground state and the first six excited states for the anharmonic oscillator; in table 1 we show the results. The values obtained are exact up to the ninth decimal figure. These results can be compared with those of refs. [30,32,35,38,39]. The eigenvalues in columns 2–4 are the same as those obtained by Palma and Campoy [32,35] with a different method, whereas the result of the last column is reported only by Banerjee [30].

To obtain the precision shown in table 1, the number of terms used in each series were about 40 for eq. (4) and about 60 for eq. (6), using $y^* =$ classical turning point.

The choice of y^* equal to or greater than the turning point is for convenience, because the oscillations of wave functions in the permitted classical region could produce points where $\phi(y)$ or $\psi(y)$ is equal to zero and then we cannot use eq. (8) to obtain the energy eigenvalues. On the other hand, in the classically prohibited region the wave functions are very smooth and the probability of finding points y^* where eq. (8) is not defined decreases. In practice we did not have trouble with any of our calculations using this fact. Another remark of computational importance is the following: when y^* is smaller than the classical turning point we need a large number of terms to assure the convergence of function ψ, the opposite fact occurs when y^* is greater than the classical turning point, then ϕ converge very slowly; the best choice of y^* then is near the classical turning point.

3. The anharmonic oscillator with double well

The Hamiltonian for the quartic anharmonic oscillator with double well is

$$H = \tfrac{1}{2}(p^2 - x^2) + \lambda x^4 . \tag{10}$$

The main feature of this problem is that the lower energy eigenvalues are very clo-

Table 1
Energy eigenvalues for the anharmonic oscillator eq. (1) as a function of the anharmonic parameter λ. The eigenvalues were obtained using eq. (9) taking $y^* =$ classical turning point. These values are in complete agreement with those reported previously in refs. [30,32,35,38,39].

n	$\lambda = 0.1$	$\lambda = 0.25$	$\lambda = 1.0$	$\lambda = 100$	$\lambda = 5000$
0	0.559146327	0.620927029	0.803770651	3.131384164	11.430804350
1	1.769502644	2.025966164	2.737892268	11.187254251	40.951658476
2	3.138624308	3.698450319	5.179291687	21.906898149	80.342956305
3	4.628828089	5.557577138	7.942403984	34.182524112	125.475371945
4	6.220300900	7.568422873	10.963583094	47.707205851	175.217948105
5	7.899767227	9.709147876	14.203139104	62.281237969	228.832287501
6	9.657839992	11.964543620	17.634049116	77.770770599	285.823895809

sely (almost degenerate) bunched in pairs when the wells are very far. The most interesting quantity to compute is the splitting between these pairs of energy levels when $\lambda \to 0$ because the separation distance between the two wells follows $\lambda^{-1/2}$. This problem cannot be solved with the use of perturbation theory. This can be qualitatively understood by observing that the term λx^4 transforms the continuous spectrum $\frac{1}{2}(p^2 - x^2)$ into a completely discrete spectrum. The alternative perturbation expansion in parameter λ takes $H_0 = \frac{1}{2}p^2 + x^4$ as the non-perturbed Hamiltonian (assuming that this spectrum is known), but this alternative does not work, because the perturbation becomes too large for small λ, which is the regime of interest.

The Schrödinger equation for the anharmonic oscillator with double well is

$$d^2\Psi/dy^2 + [E' + \mu^{-4/3}y^2 - y^4]\Psi = 0\,, \tag{11}$$

where μ, y and E' were defined in section 2. We may use the method described in section 2 to solve eq. (11) without important modifications. The solution near the origin is, as before, given by eq. (4), whereas the far solution that includes the asymptotic behavior is

$$\psi(y) = \exp\left(\frac{-y^3}{3} + \frac{\mu^{-4/3}y}{2}\right)\sum_{m=1}^{\infty} b_m y^{-m}\,. \tag{12}$$

Substitution of solutions (4) and (12) into eq. (11) gives a recurrence relation for the coefficients a_n and b_n. To compute the energy eigenvalues it is necessary to find the zeros of function f defined by eq. (8). To do this we need to evaluate both f and f' in a point y^* whose value must be greater than or equal to the maximum of the classical turning points. The classical turning points are determined by the equation

$$y^4 - \mu^{-4/3}y^2 - E' = 0\,.$$

3.1. NUMERICAL RESULTS

The energy eigenvalues obtained using this method are given in table 2. In addition to the quantum number n we include the spectroscopic notation where the superindex s means the symmetric state and a denotes the antisymmetric one. The

Table 2
Energy eigenvalues for the anharmonic oscillator with double well as a function of parameter λ.

n	State	$\lambda = 0.005$	$\lambda = 0.01$	$\lambda = 0.02$	$\lambda = 0.05$	$\lambda = 0.10$
0	O^s	−11.797975697	−5.553236207	−2.439438881	−0.632746418	−0.154124828
1	O^a	−11.797975697	−5.553236206	−2.439345769	−0.576529565	0.142765102
2	1^s	−10.414903197	−4.203985943	−1.174320024	0.254744272	1.010188900
3	1^a	−10.414903197	−4.203985695	−1.165868331	0.771773019	1.949137370

values showed in table 2 were also obtained by Banerjee [40] by using a different method; another approach to solve this problem based on the variational method can be found in refs. [27,28]. These values were obtained using about 100 terms in the wave functions (about 40 for eq. (4) and about 60 in eq. (12)).

The remarks about the selection of y^* discussed in the previous section are valid for this problem too.

4. Pure quartic oscillator

As a final example, we consider the pure quartic potential

$$V(x) = x^4 .$$

Using the method of previous sections, we first obtain the recurrence relations for the coefficients a_n and b_n:

even states:

$$a_0 = 1 , \quad a_2 = -E/2 , \quad a_4 = -Ea_2/12 ;$$

odd states:

$$a_1 = 1 , \quad a_3 = -E/6 , \quad a_5 = -Ea_3/20 . \tag{21}$$

In general we have

$$a_{n+2} = \frac{a_{n-4} - Ea_n}{(n+1)(n+2)} \quad \text{for } n \geqslant 4 .$$

Whereas for the asymptotic solution, we have

$$b_1 = 1 , \quad b_2 = -E/2 , \quad b_3 = -Eb_2/4$$

and

$$b_{n+1} = -\frac{Eb_n + (n-1)(n-2)b_{n-2}}{2n} \quad \text{for } n \geqslant 3 .$$

The energy eigenvalues for this problem are reported in table 3, they are compared

Table 3
Energy eigenvalues for potential $V(x) = x^4$.

n	Present work	Exact ref. [31,41]
0	1.0603620904	1.06036209048
1	3.7996730298	3.79967302980
2	7.4556979379	7.45569793798
3	11.644745511	11.6447455113

with those obtained by the method of refs. [31,41]. We can see that our calculations are in agreement with previous calculations.

5. Conclusions

The method proposed in this paper allows to compute every energy level independently of the others. To do this it is necessary to initialize the process by giving an initial value for the energy eigenvalue ϵ_0 and the point y^* is usually taken as the classical turning point or greater. Sometimes, when y^* is too small the function ϕ (eq. (4)) converges very fast, but the function ψ (eq. (6) or (11)) converges very slow (or does not converge); in this case it is convenient to increase the value of y^* to assure the convergence of both functions.

The convergence of our method is better than those mentioned in this paper because we are including the asymptotic behavior explicitly in the wave function. We can use this method without modifications for the anharmonic oscillator with one and two wells, whereas the Biswas [29] and Saxena [36] methods cannot be used for both problems.

As we showed, the method is used without modifications for quite different values of the anharmonic parameter λ given the same precision for the eigenvalues. If we want to know the explicit form of the wave function, it can be calculated from eqs. (4) and (6).

Acknowledgements

The author would like to thank M. Berrondo, A. Palma and R. Rodríguez for his useful commentaries. The author also wishes to thank the referee for his useful comments on the introduction of this work and ref. [24].

References

[1] H.W. Kroto, *Molecular Rotation Spectra* (Wiley, 1975).
[2] J. Fernandez, R.J. Meyers and W.D. Gwinn, J. Chem. Phys. 23 (1955) 758.
[3] S.I. Chan, J. Zinn, J. Fernandez and G.W. Gwinn, J. Chem. Phys. 33 (1960) 1643.
[4] S.I. Chan, T.R. Borges, J. Russell, H.L. Strauss and W.D. Gwinn, J. Chem. Phys. 44 (1966) 1103.
[5] G.W. Rathjens, J. Chem. Phys. 36 (1962) 2401.
[6] G.W. Rathjens, N.K. Freeman, W.D. Gwinn and K.S. Pitzer, J. Am. Chem. Soc. 75 (1953) 5634.
[7] G. Campoy, A. Palma and L. Sandoval, Int. J. Quantum Chem.: Quantum Chem. Symp. 23 (1989) 355.
[8] N. Aquino, M.Sc. Thesis, UNAM, México (1992), unpublished;
N. Aquino, A. Palma, J.L. López and M.A. Rosales, Pramana J. Phys. 54 (1995) 75.

[9] C.M. Bender and T.T. Wu, Phys. Rev. Lett. 21 (1968) 406; Phys. Rev. 184 (1969) 1231; Phys. Rev. Lett. 27 (1971) 461; Phys. Rev. D7 (1972) 1620.
[10] B. Simon, Ann. Phys. 58 (1970) 76.
[11] J. Loffel and A. Martin, *Proc. R.C. Programe 25 Conf.*, Strasbourg, 1970, unpublished.
[12] J. Loffel, A. Martin, B. Simon and A. Wightman, Phys. Lett. B30 (1969) 656.
[13] J. Čížek and E.R. Vrscay, Int. J. Quantum Chem. 11 (1981) 27.
[14] S. Graffi, V. Grecchi and B. Simon, Phys. Lett. B32 (1970) 631.
[15] W.E. Caswell, Ann. Phys. (N.Y.) 123 (1979) 153.
[16] J. Zinn-Justin, Phys. Rep. 70 (1981) 109.
[17] L. Lipantov, Pis'ma Zh. Eksp. Teor. Fiz. 25 (1977) 116 [JEPT Lett. 25 (1977) 104].
[18] E. Brézin, J.C. Le Gillou and J. Zinn-Justin, Phys. Rev. D15 (1977) 1544.
[19] I.G. Halliday and P. Suranyi, Phys. Rev. D21 (1980) 1529.
[20] R. Fanelli and R.E. Struzynski, Am. J. Phys. 51 (1983) 561.
[21] N. Aquino, J.L. López-Bonilla and M.A. Rosales, Rev. Mex. Fís. 40 (1994) 946.
[22] L.Gr. Ixaru, Phys. Rev. D25 (1982) 1557.
[23] A. Berk, Phys. Rev. A31 (1985) 1241.
[24] H.J. Silverstone, J.G. Harris, J. Čížek and J. Paldus, Phys. Rev. A32 (1985) 1965.
[25] F. Vinette and J. Čížek, J. Math. Phys. 32 (1991) 3392.
[26] C.E. Reid, J. Mol. Spectrosc. 36 (1970) 183.
[27] R. Balsa, M. Plo, J.G. Esteve and A.F. Pacheco, Phys. Rev. D28 (1983) 1945.
[28] R.M. Quick and H.G. Miller, Phys. Rev. D31 (1985) 2682.
[29] S.N. Biswas, K. Datta, R.P. Saxena, P.K. Srivastava and V.S. Varna, J. Math. Phys. 14 (1973) 1190.
[30] K. Banerjee, Proc. Roy. Soc. Lond. A364 (1978) 265.
[31] K. Banerjee, S.P. Bhatnager, V. Choudhury and S.S. Kanwal, Proc. Roy. Soc. Lond. A360 (1978) 575.
[32] G. Campoy and A. Palma, Act. Méx. Cien. y Tec. 11 (1984) 47.
[33] R.N. Chaudhury and B. Mukherjee, J. Phys. A: Math. Gen. 17 (1984) 277.
[34] F.M. Fernández, J.F. Oglivie and R.H. Tipping, J. Chem. Phys. 85 (1986) 5850.
[35] A. Palma and G. Campoy, Phys. Lett. A121 (1987) 221.
[36] R. Saxena and V.S. Varma, J. Phys. A: Math. Gen. 15 (1982) L149.
[37] L.I. Shiff, *Quantum Mechanics* (McGraw-Hill, New York, 1955) pp. 269–279.
[38] J. Récamier and R. Jáuregi, Int. J. Quantum Chem.: Quantum Chem. Symp. 26 (1992) 153.
[39] R. Jáuregi and J. Récamier, Phys. Rev. A46 (1992) 2240.
[40] K. Banerjee and S.P. Bhatnager, Phys. Rev. D18 (1978) 4767.
[41] F.M. Fernández, Q. Ma and R.H. Tipping, Phys. Rev. A39 (1989) 1605;
F.M. Fernández, A.M. Meson and E.A. Castro, J. Phys. A18 (1985) 1389.
[42] R.N. Kesarwani and Y.P. Varshni, J. Math. Phys. 22 (1981) 1983.
[43] S.B. Yuste, Phys. Rev. A48 (1993) 3478.