Revista Mexicana de Física **40**, *No. 6 (1994) 946–953*

Perturbation theory for the double-well potential

N. AQUINO

Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa
Apartado postal 55534, 09340 México, D.F., México

J.L. LÓPEZ-BONILLA

Area de Física, División de CBI
Universidad Autónoma Metropolitana-Azcapotzalco
Apartado postal 16-306, 02200 México, D.F., México

AND

M.A. ROSALES

Depto. de Física y Matemáticas, Escuela de Ciencias
Universidad de las Américas-Puebla
Apartado postal 100, Sta. Catarina Mártir, 72820 Puebla, Pue., México

Recibido el 21 de febrero de 1994; aceptado el 25 de agosto de 1994

ABSTRACT. The energy eigenvalues for the ground state and the first excited states of the quartic anharmonic oscillator (QAO) with a (symmetrical) double well potential are calculated with a procedure, based on the Rayleigh-Schrödinger (RS) perturbation theory, which introduces an adjustable parameter both in the perturbative potential and in the unperturbed hamiltonian.

RESUMEN. Se calculan los eigenvalores de la energía para el estado base y los primeros estados excitados del oscilador no armónico cuártico (QAO) con un doble pozo (simétrico) de potencial. El método empleado se basa en la teoría de perturbaciones de Rayleigh-Schrödinger, e introduce un parámetro ajustable tanto en el potencial perturbativo como en el hamiltoniano no perturbado.

PACS: 32.20.–d; 31.15.+q

1. INTRODUCTION

The double-well problem is almost as old as Quantum Mechanics, and one of the first applications of this problem was the calculation of the NH_3 inversion frequency back in 1932 [1]. Ever since the problem has been dealt with by a number of authors [2–6], but the agreement between *ab-initio* calculations [7–9] and experimental result [10] has been recently shown.

The simplest analytical form for a symmetrical double well (Fig. 1) is that given by a QAO whose potential is

$$V(x) = -\tfrac{1}{2}\omega^2 x^2 + \lambda x^4, \quad \text{with } \lambda > 0. \tag{1}$$

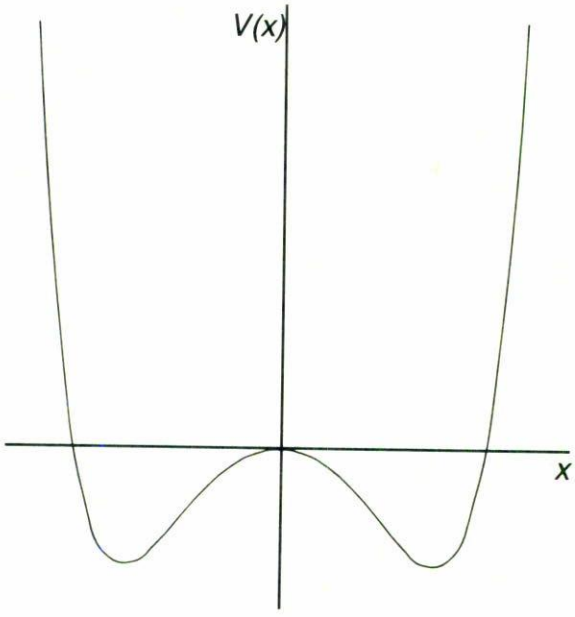

FIGURE 1. The double-well potential $V(x) = -\frac{1}{2}\omega^2 x^2 + \lambda x^4$.

One interesting feature of this problem is that the lowest eigenvalues have very close values when the two wells are sufficiently separated, *i.e.*, when $\lambda \to 0$, since the eigenvalue separation goes as $\lambda^{-1/2}$ whereas the well depth varies as $-1/\lambda$.

The solution of this problem as a perturbation of the harmonic oscillator, using standard perturbation theory [11,12] is not possible since the perturbative series for the energy eigenvalues diverges for any value of the perturbation parameter λ [13,14]. This odd fact can be qualitatively understood if we observe that the term λx^4 transforms the continuous spectrum of the operator $\frac{1}{2}(p^2 - \omega^2 x^2)$ into a totally discrete spectrum.

A possible solution would be to attempt a perturbative expansion in ω^2 (assuming the spectrum of $\frac{1}{2}p^2 + \lambda x^4$ to be known), but this alternative does not work because the perturbation becomes very large for small λ and such is, precisely, the interesting regime.

The aim of this paper is to show how the energy eigenvalues for the QAO can be computed through the use of the RS perturbation theory, successfully applied by other authors [15–19] to the problem of the anharmonic oscillator with a single well ($V(x) = \frac{1}{2}\omega^2 x^2 + \lambda x^4$, with $\lambda > 0$).

2. THE PERTURBATIVE METHOD

The hamiltonian for the QAO with a double well is given by

$$H = \tfrac{1}{2}p^2 - \tfrac{1}{2}\omega^2 x^2 + \lambda x^4, \quad \text{with } \lambda > 0, \tag{2}$$

where $m = \hbar = 1$.

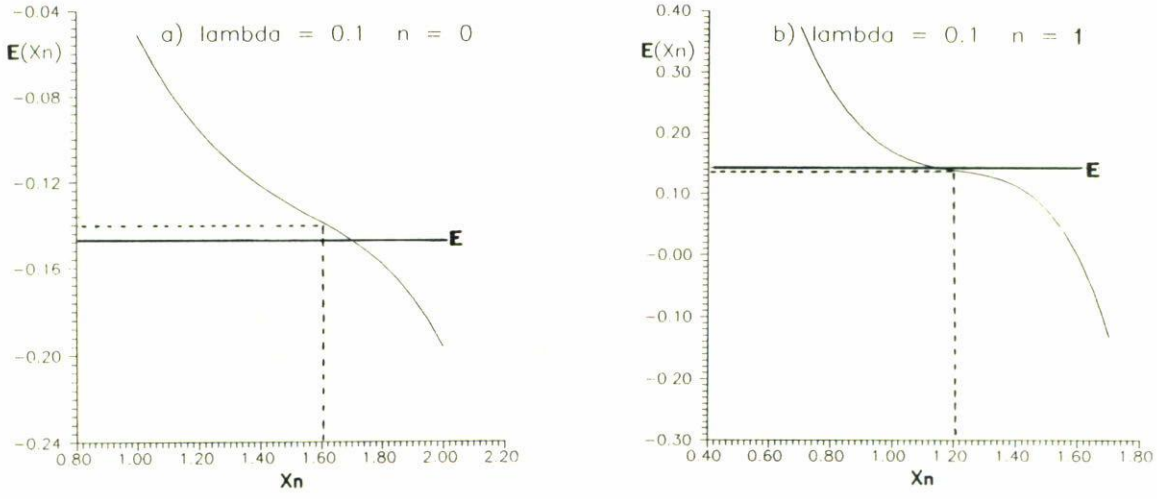

FIGURE 2. Plot of the energy E as a function of x for $n = 0$ and $n = 1$ for $\lambda = 0.1$. E represents the exact energy of the Hamiltonian (2).

In order to give this hamiltonian the usual form as an unperturbed hamiltonian plus a perturbative term *i.e.*,

$$H = H_0 + U, \tag{3}$$

we write

$$H_0 = \tfrac{1}{2}(p^2 + \omega'^2 x^2) \tag{4a}$$

and

$$U(x) = \lambda x^4 - \tfrac{1}{2}(\omega'^2 + \omega^2)x^2. \tag{4b}$$

The essential difference with the standard perturbation theory is that a new frequency ω' has been introduced into both the perturbative potential $U(x)$ and the unperturbed hamiltonian H_0. It must be noticed that the *effective* potential $U(x)$ to be used in the calculations is not the *real* potential $V(x)$ of Eq. (1). $V(x)$ does not depend on ω' whereas $U(x)$ does. The Hamiltonian (4a) has been completed so as to represent a harmonic oscillator and to be able to use perturbation theory of non-degenerated states.

The remaining problem is to solve the eigenvalue problem $H\Psi_n = E_n\Psi_n$ with standard perturbation theory with corrections to second order [11]. The eigenvalues are then expressed as

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)}, \tag{5}$$

where

$$E_n^{(0)} = \langle n|H_0|n\rangle, \quad E_n^{(1)} = \langle n|U|n\rangle \quad \text{and} \quad E_n^{(2)} = \sum_{k\neq n} \frac{|\langle n|U|k\rangle|^2}{E_n^{(0)} - E_k^{(0)}}, \tag{6}$$

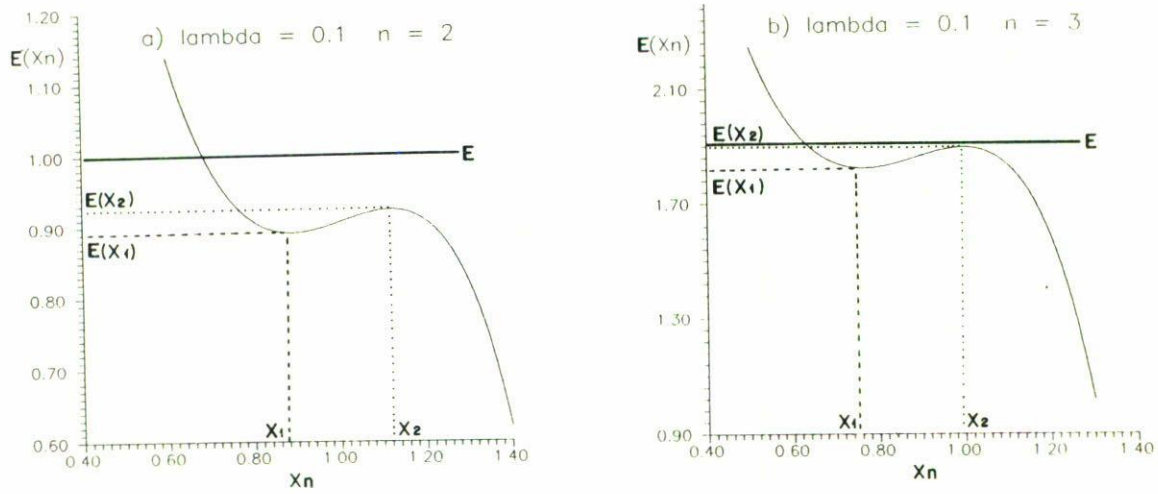

FIGURE 3. Plot of the energy for $n = 2$ and $n = 3$.

the functions $|n\rangle$ are states of the harmonic oscillator and use has been made of the equation $\langle n|U|k\rangle = \langle k|U|n\rangle$.

After computation of the corresponding matrix elements, the contributions to the energy become

$$\begin{aligned}
\frac{E_n^{(0)}}{\omega} &= \left(n + \tfrac{1}{2}\right) Y_n, \\
\frac{E_n^{(1)}}{\omega} &= \frac{3}{4Y_n^2}(2n^2 + 2n + 1)\lambda' - \frac{(1 + Y_n^2)(2n + 1)}{4Y_n}, \\
\frac{E_n^{(2)}}{\omega} &= \frac{\lambda'^2}{4Y_n^2}\big[n(n-1)(n-2)(n-3) - (n+1)(n+2)(n+3)(n+4) \\
&\quad + 8n(n-1)(2n-1)^2 - 8(n+1)(n+2)(2n+3)^2\big] \\
&\quad + \frac{\lambda'(1 + Y_n^2)}{8Y_n^4}\big[(n+1)(n+2)(2n+3) - n(n-1)(2n-1)\big] \\
&\quad + \frac{(1 + Y_n^2)^2}{32\,Y_n^3}\big[n(n-1) - (n+1)(n+2)\big],
\end{aligned} \tag{7}$$

where the following substitutions have been introduced:

$$\omega' = Y_n\omega, \quad \text{and} \quad \lambda' = \frac{\lambda}{\omega^3},$$

so that Eq. (7) will yield energies in *Hartrees*.

TABLE I.

n	λ'	x_1	x_2	$E(x_1)$	$E(x_2)$	Perturb. $E(x_A = 1)$	Exact
0	0.100	1.590	1.590	−0.137750	−0.137750	−0.05125	−0.15413
	0.085	1.740	1.740	−0.20611	−0.20611	−0.07772	−0.23171
	0.075	1.890	1.890	−0.26798	−0.26798	−0.09602	−0.30208
	0.050	2.504	2.504	−0.50684	−0.50684	−0.14406	−0.63275
	0.035	3.313	3.313	−1.00334	−1.00334	−0.17446	−1.12403
	0.025	4.404	4.404	−1.88484	−1.88484	−0.19539	−1.82079
	0.020	5.348	5.348	−2.99551	−2.99551	−0.20605	−2.43946
1	0.100	1.218	1.218	0.13785	0.13785	0.16875	0.142765
	0.085	1.338	1.338	−0.01010	−0.01010	0.05723	−0.00318
	0.075	1.440	1.440	−0.13186	−0.13186	−0.0227	−0.12279
	0.050	1.683	1.683	−0.60329	−0.60329	−0.23906	−0.57653
	0.035	2.410	2.410	−1.20429	−1.20429	−0.38152	−1.11403
	0.025	3.150	3.150	−2.13279	−2.13279	−0.48164	−1.81993
	0.020	3.800	3.800	−3.14328	−3.14328	−0.53305	−2.43935
2	0.100	0.887	1.120	0.89137	0.92348	0.90624	1.01018
	0.085	0.962	1.224	0.67866	0.71535	0.68470	0.82387
	0.075	1.022	1.314	0.51067	0.55195	0.51313	0.68350
	0.050	1.270	1.686	−0.07736	−0.01045	0.02031	0.25474
	0.035	1.571	2.163	−0.69862	−0.58053	−0.32042	−0.11461
	0.025	1.969	2.810	−1.46949	−1.23988	−0.56680	−0.62654
	0.020	2.321	3.338	−2.16655	−1.78602	−0.69575	−1.17432
3	0.100	0.753	0.990	1.83209	1.90673	1.94914	1.90625
	0.085	0.810	1.074	1.54302	1.62544	1.60883	1.35817
	0.075	0.857	1.148	1.31876	1.40884	1.33133	1.46159
	0.050	1.045	1.448	0.56577	0.69679	0.57031	0.77177
	0.035	1.266	1.821	−0.16916	0.03808	−0.02242	0.13085
	0.25	1.546	2.322	−0.99408	−0.63170	−0.46680	−0.57558
	0.20	1.788	2.769	−1.66896	−1.10681	−0.70375	−1.16586

3. NUMERICAL RESULTS

Equations (5), (6) and (7) provide the expression for the energy with corrections up to second order in terms of an adjustable (arbitrary in principle) parameter Y_n. In order to calculate the approximate energy of the hamiltonian (2) from Eqs. (5) and (7) we must recall that the exact value of the energy is independent of Y_n and, hence, the optimal energy will be the *least sensitive* to the variations in Y_n. This statement is known as the *least sensitivity principle* [18]. Therefore, the optimal energy is obtained where a local maximum of minimum, or an inflexion exists.

As they are, Eqs. (7) are useful to compute the values of the energy for $\lambda > 1$, whereas

TABLE II.

			$\lambda' = 1$			
n	Y_1	Y_2	$\varepsilon(Y_1)$	$\varepsilon(Y_2)$	Exact	Perturb. $E(Y_n = 1)$
0	1.9182	1.9182	0.5170	0.5170	0.5148	−0.6250
1	2.2594	2.2594	2.0195	2.0195	2.0206	−10.125
2	2.3944	2.8632	4.1600	4.1401	4.1911	−40.875
3	2.6142	3.2342	6.6787	6.6204	6.7055	−142.375
4	2.8241	3.5502	9.4393	9.3806	9.5010	−316.125
5	3.0900	3.8002	12.5079	12.374	12.5319	−595.625
6	3.1824	4.0303	15.7518	15.5697	15.7663	−1006.00
			$\lambda' = 100$			
n	Y_1	Y_2	$\varepsilon(Y_1)$	$\varepsilon(Y_2)$	Exact	Perturb. $E(Y_n = 1)$
0	9.7380	9.7380	3.0743	3.0743	3.0695	−26025.2
1	11.0920	11.0920	11.0300	11.0300	11.0331	−205125
2	11.6796	13.6520	21.5990	21.5309	21.6941	$-7.66E05$
3	12.6647	15.4150	33.8252	33.6144	33.9160	$-1.96E06$
4	13.5985	16.8061	47.3129	46.9429	47.3923	$-4.05E06$
5	14.4454	18.0005	61.8544	61.3161	61.9175	$-7.29E06$
6	15.2200	19.0420	77.3133	76.5995	77.3679	$-1.19E07$
			$\lambda' = 5000$			
n	Y_1	Y_2	$\varepsilon(Y_1)$	$\varepsilon(Y_2)$	Exact	Perturb. $E(Y_n = 1)$
0	35.2242	35.2242	11.4309	11.4309	11.4140	$-6.56E07$
1	40.9608	40.9608	40.8986	40.8986	40.9099	$-5.16E08$
2	43.1240	50.3880	79.9414	79.6940	80.2852	$-1.92E09$
3	46.7506	56.8345	125.0726	124.3099	125.4030	$-4.92E09$
4	50.1880	61.9780	174.8434	173.4932	174.1310	$-1.0E10$
5	53.2960	66.3800	228.4905	226.5240	228.7342	$-1.8E10$
6	56.1416	70.2150	285.5133	282.9036	285.7143	$-3.0E10$

to perform the computation for the case $\lambda < 1$ it is necessary to make the substitution $Y_n = 1/X_n$ and to find the optimal energy in terms of the new parameter X_n.

For the states $n = 0$ and $n = 1$ the plot of the energy as a function of X_n for a given $\lambda(< 1)$ is that shown in Fig. 2 where the horizontal line labeled with an E represents the exact value of the energy calculated by non-perturbative methods [8,9,20]. For these states there exist no local maxima or minima, but only an inflexion point.

The graphs corresponding to the state $n = 2$ and $n = 3$ are shown in Fig. 3, where the existence of one local minimum (at x_1) and one local maximum (at x_2) is evident. The

behavior of the energy curve for the next excited states $n > 3$ is similar, and there is the systematic finding that the exact value of the energy E is closer to $E(x_2)$.

In Tables I and II we present the energy eigenvalues for the ground state and the six first excited states of the Hamiltonian (2) for some values of λ', the corresponding values produced by the RS standard perturbation theory and the exact values.

4. CONCLUSIONS

The introduction of an adjustable parameter into the perturbed hamiltonian and into the perturbation potential yields an improvement in the approximation of the energy eigenvalues, and such an improvement is more noticeable as λ' increases. It is also interesting to notice that the technique used here allows the calculation for values of λ' as large as 5000 where the standard perturbation theory obviously fails. The results for values of λ for which Y_n or X_n are close to unity, the predicted energy value is quite similar to that obtained by the standard theory and also to the exact value (see Table I).

The method used was developed by Fanelli and Struzynski [15] for the quartic oscillator. In this work we have shown that it can also be applied to the double-well problem. Although such method cannot be classified as "highly precise" the computation of the optimal energy is so simple that correction up to a higher order might be easily included in order to get more approximate eignvalues. The calculation of the optimal energy can be done with a microcomputer, where the time and memory consumption is very small, or even with a programmable pocket calculator.

On the other hand, it must be said that for $\lambda' < 0.020$ the curve is so smooth that it is difficult to determine the optimal energy. This problem also shows that when the perturbative hamiltonian is small the perturbation theory produces incorrect values.

REFERENCES

1. M. Dennison and G.E. Uhlenbeck, *Phys. Rev.* **41** (1932) 313.
2. M.F. Manning, *J. Chem. Phys.* **3** (1935) 136.
3. F.T. Wall and G. Glockler, *J. Chem. Phys.* **5** (1937) 314.
4. R.R. Newton and L.H. Thomas, *J. Chem. Phys.* **16** (1948) 310.
5. C.C. Constain and G.B.B.M. Surtherland, *J. Chem. Phys.* **56** (1952) 321.
6. J.D. Swalen and J.A. Ibers, *J. Chem. Phys.* **36** (1962) 1914, and references therein.
7. P.R. Bunker, W.P. Kramer and V. Spirko, *Can. J. Phys.* **62** (1984) 1801.
8. G. Campoy, A. Palma, and L. Sandoval, *Int. J. Quantum Chem. Symp.* **23** (1989) 335.
9. N. Aquino, Sc. Thesis, UNAM, México (1992) (unpublished).
10. N.S. Benedict and E.K. Plyler, *Can. J. Phys.* **35** (1957) 1235.
11. L.I. Schiff, *Quantum Mechanics* 3rd. Ed, Addison-Wesley, Reading, Mass, (1965) pp. 381-390.
12. Among other mehtods used to solve this problem we can mention: WKB method: D. Park, *Introduction to Quantum Theory*, McGraw-Hill, New York (1964) Sec. 4.7; B.R. Holstein *Am. J. Phys.* **56** (1988) 338. EBK (Einstein-Brillouin-Keller) method: M.K Ali and W.P. Snider, *J. Chem. Phys.* **91** (1989) 300. Matrix variational method: R. Balsa, M. Plo, J.G. Steve and F. Pacheco, *Phys. Rev.* **D28** (1983) 1945; R.M. Quick and H.C. Miller, *Phys. Rev.* **D31** (1985) 2682.
13. C.M. Bender, and T.T. Wu, *Phys. Rev.* **184** (1969) 1231.

14. B. Simon, *Ann. Phys.* **58** (1970) 76.
15. R. Fanelli and R.E. Struzynski, *Am. J. Phys.* **51** (1983) 561.
16. W.E. Caswell, *Ann. Phys.* **123** (1979) 153.
17. R. Seznec and Justin J. Zinn, *J. Math. Phys.* **20** (1979) 1378.
18. P.M. Stevenson, *Phys. Rev.* **D23** (1981) 2916.
19. I.G. Halliday and P. Suranyi, *Phys. Rev.* **D21** (1980) 1529.
20. K. Banerjee and S.P. Bhatnagar, *Phys. Rev.* **D18** (1978) 4767.