

A simple and effective technique to locate quasi-degeneracy in a symmetric double well potential

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Abstract Perturbation theory based model can be used to locate the quasi-degeneracy in an arbitrary double well potential. This method, extensively explain the effect of the coupling term on pair of states called quasi-degenerate. This model helps us to calculate the energy of the pair of quasi-degenerate states using appreciably small basis. Dispersion equation corresponding to the split energy levels are presented in a very explicit form. Numerical calculation shows that the proposed method can give extremely accurate results for symmetric double-well potentials.

Keywords Symmetric double well potential · Quasi-degeneracy · Perturbation model · Kinetic energy uncertainty

1 Introduction

The phenomena of quantum tunneling in the double well potential is

$$V(x) = \alpha x^4 - \beta x^2$$

a long-standing and well-known problem in quantum mechanics. The interest in this problem ranges from various branches of physics to chemistry. Several methods have been proposed to calculate the energy splitting. The instanton method [1,2] is helpful to understand the physical insight of the quantum tunneling. However, the validity of this method is restricted in case of large separation between the two potential minima. The WKB approximation [3,4] is widely used for its simple mathematical form. But the approximated results are known to be inaccurate due to inherent defect in

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connection formula. Quadratic connection formula instead of Airy function had been used to modify the WKB results at the ground state [1, 5]. Some refinements have been developed to improve the accuracy of WKB approximation by changing the phase loss at the classical turning points [6–9]. The anharmonicity is also taken into consideration in case of small separation [7]. Using numerical methods [4, 10, 11], one can get the solution up to the desired accuracy but a considerable deal of physical insight is lost in such methodologies. Time dependent perturbation theory [12] and variation principle based method with periodic boundary conditions [13] can be applied to calculate the separation between these two pair of quasi-degenerate states. Till date none of such approximations have provided the perfect results. In chemistry, this type of potential corresponds to two equilibrium positions or molecular configurations. The periodic inversion of ammonia (NH_3) is a well known example of quantum tunnelling. The internal rotation in the CH_3CH_3 molecule from one configuration to another is a good example of a symmetric double-well potential. On the other hand, the asymmetric H_2O_2 hindered rotor or beryllium dicyclopentadienyl represent asymmetric double well potentials. Ammonia (NH_3), cyanamide (NH_2CN), PH_3 , and AsH_3 are chemical examples of symmetrical double-well potentials where atoms can tunnel through the barrier [13].

In this paper, it has been tried to design a method by using Relaiigh-Schrödinger perturbation theory based approach. Taking in to account the barrier height and barrier area of a given symmetric double well potential, a pair of equations have been designed. The energy separation between the pair of states can be calculated applying these equations just knowing the coupling terms. The sole requirement of this calculation is to know the higher energy state of the pair. Concept of scaling of Hamiltonian has also been employed for the desired calculation. The problem of calculating the lower energy state of the quasi-degenerate pair can be bypassed. Thus, neither the matrix diagonalisation nor other variational techniques are required to know the ground state. The phenomena of quantum tunneling as well as the effect of barrier height and barrier area on the pair of states can explicitly be analysed and discussed by these equations.

2 Theory

In the present calculation, the potential have been divided into two parts. The parent one is the unperturbed potential and the other is perturbing potential. With gradual increase of the strength of the coupling term of the perturbing potential both barrier area and barrier height increases. The primary step is to study the effect of the increase of coupling term of the perturbing potential on the parent one. In this context, I have focused on the kinetic energy. With the increase of the coupling strength, well depth increases and the particle gradually gets trapped in it. In such cases, momentum of the particle increases as well as its kinetic energy. Thus one needs to calculate the change of kinetic energy with respect to the unperturbed potential. To study this effect we have designed the parameter,

$$P_1 = \left(\frac{\hbar^2 (\Delta T_n^2 - \Delta T_{n-1}^2)_{\text{perturbed}}}{A (\Delta T_n^2 - \Delta T_{n-1}^2)_{\text{unperturbed}}} \right) \quad (1)$$

where, h and A are the barrier height and barrier area respectively.

For potential,

$$V(x) = \alpha x^{2m} - \beta x^{2n} \quad (m > n) \quad (2)$$

α, β are coupling terms
here,

$$h = \left(\frac{\beta^m}{\alpha^n} \right)^{\frac{1}{(m-n)}} \left(\left(\frac{n}{m} \right)^{\frac{n}{(m-n)}} - \left(\frac{n}{m} \right)^{\frac{m}{(m-n)}} \right) \quad (3)$$

$$A = 4 \left(\frac{\beta^{2m+1}}{\alpha^{2n+1}} \right)^{\frac{1}{2(m-n)}} \left[\left(\frac{n}{2n+1} \right) \left(\frac{n}{m} \right)^{\frac{(2n+1)}{2(m-n)}} - \left(\frac{m}{2m+1} \right) \left(\frac{n}{m} \right)^{\frac{(2m+1)}{2(m-n)}} \right] \quad (4)$$

$$\frac{h^2}{A} = \left(\frac{\beta^{2m-1}}{\alpha^{2n-1}} \right)^{\frac{1}{2(m-n)}} \frac{\left[\left(\left(\frac{n}{m} \right)^{\frac{n}{(m-n)}} - \left(\frac{n}{m} \right)^{\frac{m}{(m-n)}} \right) \right]}{4 \left[\left(\frac{n}{2n+1} \right) \left(\frac{n}{m} \right)^{\frac{(2n+1)}{2(m-n)}} - \left(\frac{m}{2m+1} \right) \left(\frac{n}{m} \right)^{\frac{(2m+1)}{2(m-n)}} \right]} \quad (5)$$

The flexibility of this parameter is noted. First of all this parameter is unit less. Secondly, it can explain the whole of the increasing and the decreasing effects of the coupling terms in the entire range. $\frac{h^2}{A}$ is completely taking care of the effect of the coupling terms on the barrier. The denominator $\left((\Delta T_n^2 - \Delta T_{n-1}^2)_{unperturbed} \right)$ is to compare the effect of the perturbing potential to that of the parent potential. Thus, the study of this parameter will extensively explain the entire phenomena. Qualitatively this parameter P_1 is potential independent also. The nature of variation of this parameter with respect to the coupling terms is same for double-well potentials. The calculation of ΔT_n^2 is not difficult. In fact, for stationary state

$$\Delta T_n^2 = \Delta V_n^2 \quad (6)$$

Thus, calculation of ΔV_n^2 will also serve the purpose.

Similarly, for energy calculation, another parameter is designed obeying the same principle.

$$P = \left(\frac{h^2 \left((E_n + h)^2 - (E_{n-1} + h)^2 \right)_{perturbed}}{A \left(E_n^2 - E_{n-1}^2 \right)_{unperturbed}} \right) \quad (7)$$

These two parameters will extensively explain the entire effect of the coupling terms on the pair of states. For unperturbed potential ($\beta = 0$) both P and P_1 are zero. The objective now is to derive relations between the parameters P and β , P_1 and β at a fixed α . This completely depends on the value of m and n .

Now, we need to derive equations between the parameters and β for a fixed m and n . Then we have to use scaling of Hamiltonian concept,

$$H(\alpha, \beta) = \alpha^{\frac{1}{(m+1)}} \left[-\frac{d^2}{dx^2} + x^{2m} - \frac{\beta}{\alpha^{\frac{2}{(m+1)}}} x^{2n} \right] \tag{8}$$

$$V(\alpha, \beta) = [\alpha y^{2m} - \beta y^{2n}] = \alpha^{\frac{1}{(m+1)}} \left[x^{2m} - \frac{\beta}{\alpha^{\frac{2}{(m+1)}}} x^{2n} \right] \tag{9}$$

where, $y = \mu x$, μ is a constant.

Thus, one pair of equation is sufficient to explain the entire phenomena for a set of potential of fixed m and n . Second step is to calculate the energy and the property difference between the states from the modeled equations and then variationally calculate the energy or property of the excited state of the pair. Then automatically we will obtain the lower energy state of the pair. Thus, without extensive calculation of variation or perturbation theory one obtains the lower energy state of the pair. This will reduce the computational cost as well as time of calculation. Secondly, the energies of this pair of states can be calculated with any arbitrary basis set. The N value will also be less. Thus, the problem of using higher number of basis in this type of calculation is removed. Even $N=10$ can easily serve the purpose.

3 Result and discussion

In order to illustrate the method, we apply it to a typical example of a symmetric double well potential, which has potential form as,

$$V(x) = \alpha x^4 - \beta x^2 \tag{10}$$

Here, we set the particle mass $m = \frac{1}{2}$, $\hbar = 1$. Now, for $\alpha = 1$ we calculate P and P_1 as a function of β .

We obtain the following pair of equations,

$$P_1 = \beta^4 (4.100592 - \beta) \left(0.976055\beta^2 - 3.812077\beta + 5.335754 \right) \exp \left[-0.084414 (\beta + 5.377108)^2 \right] \tag{11}$$

$$P = \beta^2 \left(0.183198\beta^2 - 0.496256\beta + 0.9554502 \right) \exp \left[-0.113803 (\beta + 2.065982)^2 \right] \tag{12}$$

We calculate the energy eigenvalues for the ground state using Eq. (12) and ΔT_0^2 , ΔV_0^2 , using Eq. (11) and compare them with the exact value. Tables 1 and 2 show the details. Now, using Eqs. (8) and (12) we calculate the energy eigenvalues for the ground state of potential having value other than 1. Table 3 shows the result of the calculation. It is clear that numerically calculated results are in excellent agreement with the exact results. The absolute errors $|E_{calculated} - E_{exact}|$ are only about 10^{-14} . More accurate results can be expected through increasing N . Compared with other numerical methods such as the Numerov method [10] and the simplistic

Table 1 Eigenvalues of the ground state in the double well potential $V(x) = x^4 - \beta x^2$

β	E_0^{Exact}	$E_0^{Calculated}$
0	1.060 362 090 484 166 64	–
1.0	0.657 653 005 180 697 5820	0.657 653 005 180 697 5875
6.0	–5.748 190 520 667 182 40	–5.748 190 520 667 182 15
10.0	–20.633 576 702 947 905 80	–20.633 576 702 947 905 55
15.0	–50.841 387 284 381 954 36	–50.841 387 284 381 946 51
20.0	–93.726 370 917 860 558 56	–93.726 370 917 860 558 45

Table 2 ΔT_0^2 value estimated for the ground state in the double well potential $V(x) = x^4 - \beta x^2$

β	$\Delta T_0^2 (Exact)$	$\Delta T_0^2 (Calculated)$
0	0.918 539 677 618 401 0480	–
1.0	0.703 643 366 949 075 7086	0.703 643 366 949 075 6846
6.0	5.431 645 607 542 611 9473	5.431 645 607 542 611 9876
10.0	9.421 383 874 005 184 6794	9.421 383 874 005 184 6891
15.0	14.534 530 912 799 435 4527	14.534 530 912 799 435 4278
20.0	19.599 719 422 146 019 5576	19.599 719 422 146 019 5654

Table 3 Eigenvalues of the ground states in the double well potential $V(x) = \alpha x^4 - \beta x^2$ at different α, β – value

α	β	E_0^{Exact}	$E_0^{Calculated}$
1.0	18.0	–75.056 769 717 647 8006	–75.056 769 717 632 5468
0.01	0.70	–11.081 483 215 537 9772	–11.081 483 215 531 694 186
0.10	3.23	–23.572 461 292 275 6976	–23.572 461 292 184 320
5.0	43.86	–86.936 411 504 183 6954	–86.936 411 503 853 6660
10.0	69.60	–109.453 569 880 046 6560	–109.453 569 879 623 671 195

scheme-shooting method [11]. The present method is extremely effective. We are now able to calculate the quasi-degenerate energy pair with ease, even using N=10 basis. We need not require calculating the ground state variationally. Figure 1, explains how increase of coupling terms affect the pair of states. Initially, with increase of β value P_1 increase and attains maxima (point A). It is the point after which ground state starts observing the effect of the presence of the double well in the potential. That means the particle in the ground state starts getting trapped inside the well. Just after point B the effect of coupling term is greater for ground state than the first excited state. Point C is the point after which first excited state starts getting trapped inside the well. Point D is the situation where quasi-degeneracy arises. After point B the effect of coupling terms is on ground state is always higher than the first excited state. Quasi-degeneracy is the situation where both of the states are in almost identical environment. Point B will shift to the right for higher α -value (greater than 1) and will shift to the left for

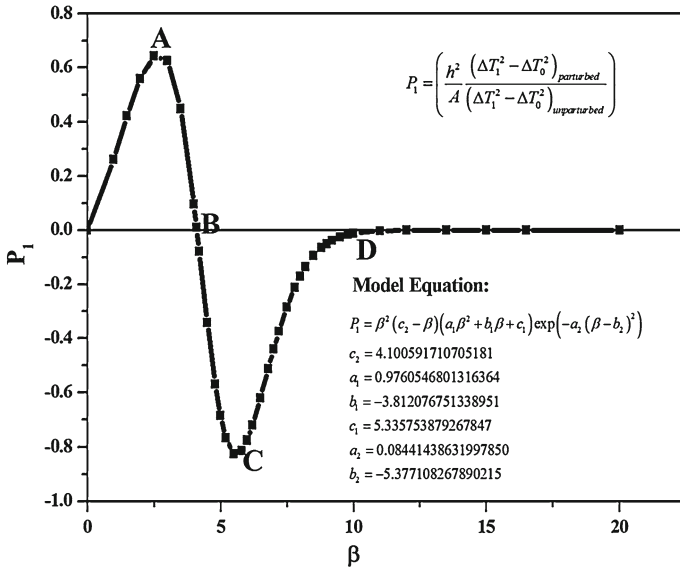


Fig. 1 Parameter P_1 is plotted against β for double well potential $V(x) = x^4 - \beta x^2$

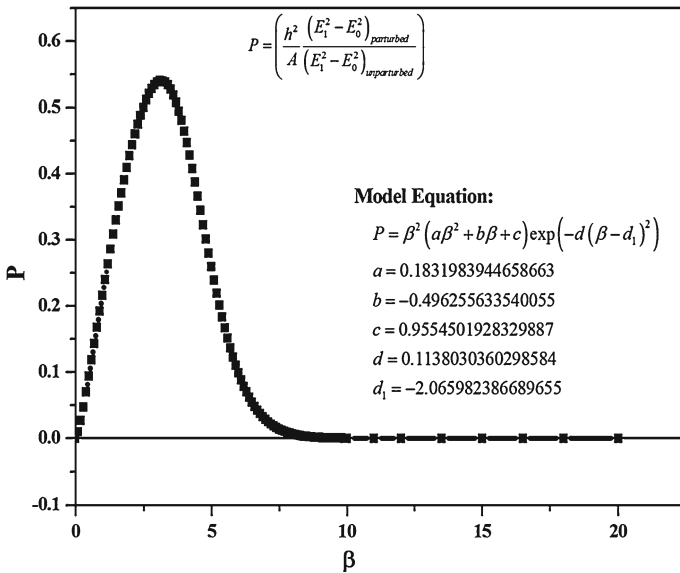


Fig. 2 Parameter P is plotted against β for double well potential $V(x) = x^4 - \beta x^2$

lower α -value (less than 1). For, all symmetric double well potential the nature of the plot is qualitatively identical. Nature of the plot of P_1 against β is same for all types of symmetric double well potential.

Figure 2 shows the variation of P with respect to β . The asymptotic decay nature of both the curve explains that for higher β -value there is quasi-degeneracy.

Finally, in a simple and elegant way a pair of equations has been derived which are able to explain whole of the phenomena of quasi-degeneracy. Such general method can be applied to any other symmetric double well potential.

4 Summary

A pair of equations has been derived to calculate energy splitting of symmetric double well potentials by the perturbation based model. These equations are able to explain the whole phenomena of quasi-degeneracy in a symmetric double well potential. The effect of coupling terms on the pair of quasi-degenerate state has also been explained. Even these pair of equations extensively explains the localization of a particle inside the double well. This method will reduce the computational cost and time for the energy calculation in a symmetric double well potential.

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