

# A simulated annealing based study of the effect of Gaussian perturbation in quartic oscillator and quadratic double well potentials

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**Abstract** Perturbation theory based model can be used to locate the quasi-degeneracy in an arbitrary double well potential. In this work, unconstrained optimisation has been done using Simulated Annealing to calculate the energy spectrum of double well potential. Using this calculation the author has studied the effect of a Gaussian perturbation on single and double well potential. A comparative study of quartic double well potential and Gaussian double well potential has also been done on the basis of chemical and statistical point of view. The efficiency of this method is notable. Numerical calculation shows that the proposed method can give extremely accurate results for symmetric double well potentials.

**Keywords** Unconstrained optimisation · Simulated annealing · Symmetric double well potential · Gaussian perturbation · Specific heat

## 1 Introduction

The Rayleigh–Ritz variation method lies at the heart of quantum chemistry. For a given Hamiltonian  $H$ , this variation method of obtaining bound, approximate, quantum stationary states by minimizing the Rayleigh quotient (RQ)[1] applies, in general, to the ground one. At best, the methodology can be extended to encompass states that are lowest in energies of a specific symmetry, provided the trial state incorporates the right symmetry information. This factor restricts severely the applicability of the energy-minimum principle. In case of constrained variation one chooses a suitable set of states

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$\{\theta_i\}$  with gradually increasing energies to meet the conditions (i)  $\langle \theta_i | \theta_k \rangle = 0$  and (ii)  $\langle \theta_i | H | \theta_k \rangle = 0$ , for  $i = 0, 1, 2, \dots, k-1, k > i$ . Then the average energy of state  $\theta_k$  will be an upper bound to the true one [2–4]. In case of simple systems, it is notable that the crux of the problem lies in our lack of knowledge about the precise positions of nodes of excited-state wave functions [5]. Indeed, if we take a trial function with one or more variable nodal positions, it would turn out that an unconstrained minimization of energy is achieved only by placing the nodes farther beyond the classical turning points, thus getting closer and closer to the actual ground state. In other words, had the nodal positions been exactly known beforehand, one could use the said principle for approximate calculations of properties of excited states in a general manner. Thus, an unconstrained minimization of the RQ cannot be pursued to get excited bound states. Nodal position can be considered as parameter if one chooses to optimise newly designed objective function other than energy. In this work, it is shown if one chose such functions, then there is no such necessity of considering node as parameter [6]. Thus choice of function plays the vital role in calculations. In case of double well potential due to quasi degeneracy [7] this choice becomes even crucial.

Double-well (DW) potential models have been employed in a wide range of fields including physics, chemistry and biology (for a recent review on DW systems [8]). We may classify quantum DW models into three categories: exactly solvable, quasi-exactly solvable, and approximately solvable models [9]. In the exactly solvable model, we can determine the whole spectrum analytically by a finite number of algebraic steps. In contrast, we can determine a part of the whole spectrum in the quasi-exactly solvable model. In other models, eigenvalues are obtainable only by approximate analytical or numerical method.

Examples of exactly solvable models include the double square-well potential and the Manning potential [10]. The Razavy potential [11, 12] expressed by hyperbolic functions belongs to the quasi-exactly solvable models. In this paper, we pay our attention to two types of approximately solvable models with a quartic potential [13] and a quadratic potential perturbed by a Gaussian barrier [14, 15] model. These models have been commonly adopted for studies of tunneling and stochastic resonance in DW systems. In this work, the author has initially applied Simulated Annealing technique using a newly designed function to calculate the energy spectrum of double well potential and then made a comparison between the quartic and Gaussian double well potential. The objective is to see whether both double well potential represents same chemical environment, because the vibration modes, however, may have double or multiple potential minima, such as inversion, ring-puckering, large-amplitude bending, and torsional vibrations [16]. A single harmonic oscillator is unable to describe these types of motion, and a number of approaches have been proposed to construct double- or multiple-well potential surfaces. Prominent approaches include the quadratic potential perturbed by a Gaussian function barrier [17], the quartic–quadratic potential [18, 19], the hyperbolic secant functions [20] and the linear combination of cosine functions etc. It is, however, curious that studies on the effect of Gaussian perturbation on quartic double well potential. Specific heats of symmetric double-well systems at very low temperatures have the Schottky-type anomaly [21], which is rooted to a small energy gap in low-lying two-level eigenstates induced by a tunneling through the potential barrier. Whether, this type of perturbation removes such defects.

## 2 Methods

$$V(x) = \alpha x^4 \tag{1}$$

$$V_1(x) = V(x) - \beta x^2 \tag{2}$$

$$V_2(x) = V(x) + \beta_1 \exp(-ax^2) \tag{3}$$

$$V_3(x) = V_1(x) - \beta_2 \exp(-ax^2) \tag{4}$$

Here, an attractive quadratic and a repulsive Gaussian perturbation is applied to a quartic oscillator potential [(Eq. (1))] to construct double well potentials  $V_1(x)$ ,  $V_2(x)$ . We apply Simulated Annealing technique using newly designed optimisable parameter to optimise the first twenty energy states of these potentials. The increase of the strength of the quadratic perturbation increases the quasi degeneracy. Thus, it has been studied how the energy gap between first two energy levels of Gaussian double well potential changes with the increasing strength of the Gaussian term. Then, we apply Gaussian perturbation on quartic double well potential to see how it affects the energy levels of such potentials. The formula used for optimisation is as follows

Time independent Schrödinger equation

$$\begin{aligned} \hat{H}\psi_n &= E_n\psi_n \\ (\hat{T} + \hat{V})\psi_n &= E_n\psi_n \end{aligned}$$

Now, if the equation is left multiplied by  $\hat{T}$  and consider the expectation value  $\Delta T_n^2 = \langle T \rangle_n \langle V \rangle_n - \langle TV \rangle_n$

Similarly, if the equation is left multiplied by  $\hat{V}$  and consider the expectation value  $\Delta V_n^2 = \langle T \rangle_n \langle V \rangle_n - \langle VT \rangle_n$

Then from Hyper-Virial Theorem  $\langle [T, V] \rangle_n = 0$

$$\langle TV \rangle_n = \langle VT \rangle_n$$

thus,

$$\Delta T_n^2 = \Delta V_n^2 = \langle T \rangle_n \langle V \rangle_n - \langle TV \rangle_n \tag{5}$$

This equation is the master equation in both the formulation. Again, this equation is true for the Systems obeying Classical Mechanics

$$\Delta T^2 \Delta V^2 = \langle T \rangle \langle V \rangle - \langle TV \rangle \tag{5a}$$

These two equations tells that this is a property of both quantum and classical systems.

Now, obeying Eq. (1) and using Schwarz’s Inequality, it can be written for bound stationary state that,

$$\Delta T_n^2 \Delta V_n^2 = \left| \langle TV \rangle_n^2 - \langle T \rangle_n \langle V \rangle_n \right|^2 \tag{6}$$

But, as the aim is to find an objective function to support optimisation in excited non-linear variational description, so, main focus is on the approximate solution of excited state.

Thus, first it is being proved that  $\langle [T, V] \rangle = 0$  for any real/imaginary wave function. Then again from Schwarz's Inequality it can be written that

$$\Delta T_n^2 \Delta V_n^2 \geq \left| \langle TV \rangle_n^2 - \langle T \rangle_n \langle V \rangle_n \right|^2 \quad (7)$$

Now, concentrating on Eqs. (6) and (7) it is quite clear that equality holds for stationary state where as inequality for approximate cases. Now, whether there is any of the approximate state where this inequality becomes equality. This can be explored by the concept of linear dependence

$$(T - \langle T \rangle) \psi = \alpha (V - \langle V \rangle) \psi \quad (8)$$

Thus, by mathematical description equality holds for any value of  $\alpha$ .

If,  $\alpha = -1$  then Eq. (8) is reduced to time independent Schrödinger equation and thus it is clear that,

$$\alpha^2 = \frac{\langle TV \rangle \Delta T^2}{\langle VT \rangle \Delta V^2} = \frac{\Delta T^2}{\Delta V^2} = 1$$

But, here if  $\alpha = \pm 1$ ,

$$\Delta T^2 = \Delta V^2$$

Thus, Eq. (5) is necessary but not sufficient condition for bound stationary states.

Again there is another necessary condition for bound stationary states which is Virial Theorem and is true for systems obeying Quantum or Classical mechanics.

$$2 \langle T \rangle = \left\langle x \frac{\partial V}{\partial x} \right\rangle \quad (9)$$

Now, combining the above said conditions Eqs. (5) and (9) for bound stationary states it is clear,

$$\begin{aligned} \text{i)} & \left| \frac{\Delta T^2}{\Delta V^2} - 1 \right| + \left| \frac{2\langle T \rangle}{\left\langle x \frac{\partial V}{\partial x} \right\rangle} - 1 \right| = 0 \\ \text{ii)} & \left| \frac{(\langle T^2 \rangle - \langle T \rangle^2)}{(\langle V^2 \rangle - \langle V \rangle^2)} - 1 \right| + \left| \frac{2\langle T \rangle}{\left\langle x \frac{\partial V}{\partial x} \right\rangle} - 1 \right| = 0 \\ \text{iii)} & \left| \frac{\Delta T^2}{(\langle T \rangle \langle V \rangle - \langle TV \rangle)} - 1 \right| + \left| \frac{2\langle T \rangle}{\left\langle x \frac{\partial V}{\partial x} \right\rangle} - 1 \right| = 0 \\ \text{iv)} & \left| \frac{\Delta V^2}{(\langle T \rangle \langle V \rangle - \langle TV \rangle)} - 1 \right| + \left| \frac{2\langle T \rangle}{\left\langle x \frac{\partial V}{\partial x} \right\rangle} - 1 \right| = 0 \end{aligned}$$

$$v) \left| \frac{\Delta T^2 \Delta V^2}{(\langle T \rangle \langle V \rangle - \langle TV \rangle)^2} - 1 \right| + \left| \frac{2\langle T \rangle}{\left\langle x \frac{\partial V}{\partial x} \right\rangle} - 1 \right| = 0$$

These five conditions are necessary and sufficient condition for bound stationary states. Because these two conditions (Eq. (5) and Virial Theorem) are simultaneously true only in case of bound stationary states. Left hand side of condition (i)–(v) (P) will serve as objective function instead of Eq. (5) in excited state non-linear optimisation scheme. These parameters are previously used to optimise the first few excited state of a quartic oscillator potential.

### 3 Simulated annealing

Simulated Annealing (SA) [22–25] is a technique borrows its working principle from the method of annealing in which a molten melt of metals is cooled very slowly reaches the thermodynamic minimum energy state. The working of SA is based on the metropolis sampling scheme. We ascribe a temperature  $T$  to the system. In a move we see if the objective function decreases its value or not. If it does, we accept new set of  $r_{ij}$ 's as a better structure. If not, then we subject the system to the metropolis sampling test. We calculate the quantity  $\exp(-\Delta F/kT)$  where  $\Delta F$  is the change in the value of the objective function in two steps. If  $\exp(-\Delta F/kT)$  is greater than a random number  $r$  (between 0 and 1) we accept the move, as it is more probable than any random event. This makes SA a potent optimizer as during the search it might happen that in one move the system might move to a higher parameter but this higher parameter point might be a starting point for achieving a better structure. If  $T$  is kept large, the system will have large thermal fluctuations and most moves will be accepted which is necessary in the initial part of the search. As the search proceeds  $T$  is decreased by assigning an optimisation schedule and when  $T \rightarrow 0$  the system finds out the near-exact result we are looking for.

Success of non-linear variational calculation depends on the choice of trial state  $\tilde{\phi}_n$ . Because better the choice of trial state better will be the convergence of the results more over as here the main focus is on excited state optimisation.

Thus we chose

For even parity states,

$$\psi_n = \sum_i^N c_i \exp(-a_i x^2) \quad (10a)$$

For odd parity states,

$$\psi_n = x \sum_i^N c_i \exp(-a_i x^2) \quad (10b)$$

For our calculation we restrict ourselves  $N = 50$ . Here,  $c_i, a_i$  are all nonlinear parameters.

**Table 1** Variational upper bounds to energies for even and odd states of the potential  $V_1(x)$  and  $V_2(x)$ 

N	$V_1(x)$ ( $\alpha = 1 \beta = 15$ )	$V_2(x)$ ( $\alpha = 1 \beta_1 = 15 a = 5.12$ )
0	5.408612715617884	4.64709163217703036
1	5.408612715812822	5.00275447374390403
2	15.935280110095241	11.8324821016275782
3	15.935280164925373	13.5507701875245240
4	25.980542292878151	19.4671245082559460
5	25.980548994652235	23.2744169222716302
6	35.460582511313731	28.8720519603231232
7	35.461040958641405	34.0426382323892440
8	44.227982895557813	39.8898324747024448
9	44.246515323743405	45.7930195265074502
10	51.809663901638092	52.0297189016040278
11	52.204321634814164	58.4279423456971259
12	57.308511213327322	65.0520800869662423
13	59.706475307472491	71.8492500979871950
14	63.756351297416089	78.8302756099485294
15	67.806026751651256	85.9752097049294548
16	72.255023529729055	93.2820030937900811
17	76.946407586432105	100.740671073241785
18	81.874398352572673	108.346617326538122
19	87.014858449597927	116.093385141089144

Here, upper-bound property of those states is not guaranteed. Here, also the optimisation using the newly formulated properties (i-v) doesn't guarantee upper-bound character but better the trial state closure will be the results. Among all those objective functions, function (iv) is most easy to use as it contains only one operator related to kinetic energy.

#### 4 Optimisation of energy states

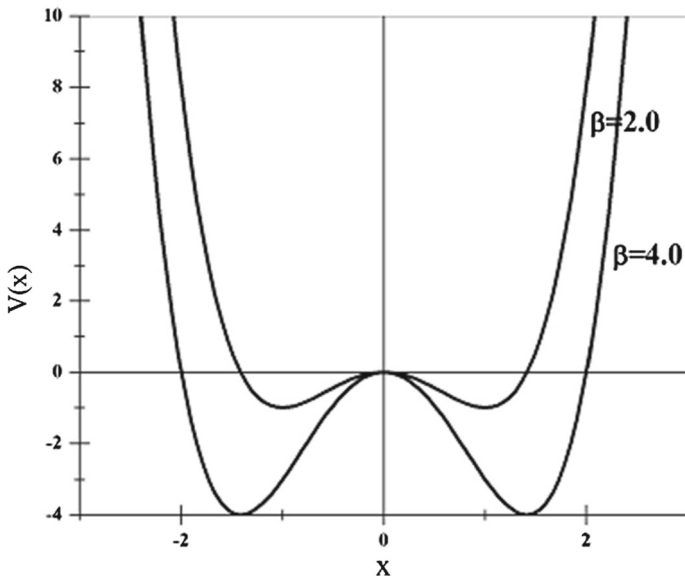
The potentials chosen for study are

$$V_1(x) = \alpha x^4 - \beta x^2$$

$$V_2(x) = \alpha x^4 + \beta_1 \exp(-ax^2)$$

The recipe is to optimise the energy states adopting Simulated Annealing technique using the newly designed function as the objective function for optimisation. We optimised first twenty energy states of both potential  $V_1(x)$  ( $\alpha = 1 \beta = 15$ ) and  $V_2(x)$  ( $\alpha = 1 \beta_1 = 15 a = 5.12$ )

Optimised energies are given in Table 1 for both the potentials. Initially we start with the trial function [Eq. (10a)] and minimise P4 for ground state of potentials  $V_1(x)$ ,  $V_2(x)$ . Then apply Eq. (10b) to minimise first excited state then continued these calculations upto  $n=19$ . In each of the optimisation we have not used orthogonality



**Fig. 1** Plot of potential  $V_1$  at different  $\beta$  values

constraints. It is quite clear from Table 1 that the method we have employed for the calculation of energies of these potentials is appreciably successful. In this calculation we restrict ourselves to  $N=50$ . Previously this newly designed parameter was used to optimise the energy states of a quartic oscillator potential with node as parameter <sup>6</sup>. In this calculation nodal position has not been used as optimisable parameter. Now, we need not require the information of the nodal position to optimise the excited quantum state in unconstrained variation. One only needs to choose a proper trial function. Particularly work using non-linear unconstrained variation is rewarding in pathological cases where choice of a suitable basis set with properties demanded by the potential is lacking.

Then, one is forced to opt for nonlinear variations. Even, this method can also be employed in calculating excited state energies of 2D and 3D potentials. In general, therefore, this example, including some stringent tests of goodness of the quality of approximate eigenstates obtained via the present recipe, point to the success of this property dependent variation method. Keeping in mind that here used hundred-parameter function to construct all the states tabulated here, this results look quite satisfactory. Surely, a more flexible trial function would have performed much better.

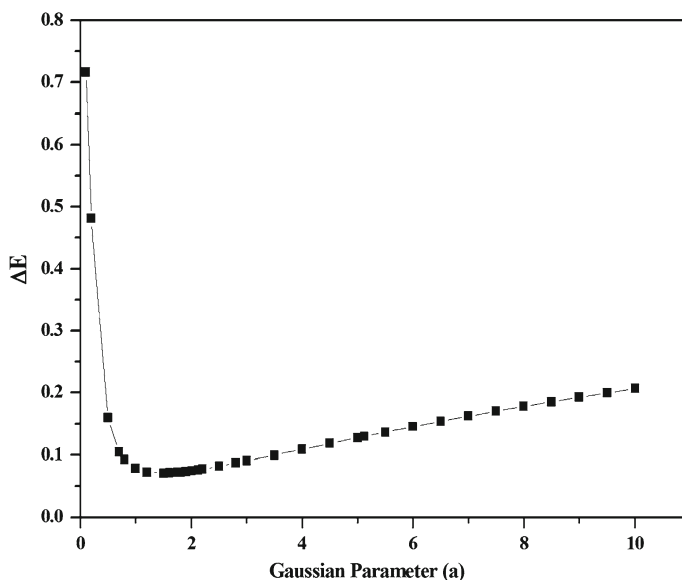
## 5 Comparative study of quartic double well potential and Gaussian double well potential

In case of potential  $V_1(x)$  with increase of  $\beta$  value the area of the barrier increases, whereas, classical boundary increases. This can easily be explained by Fig. 1. But for potential  $V_2(x)$ , barrier area depends on  $\beta_1, a$ . First of all, it has been seen that with

**Table 2** Energy difference relative to the unperturbed potential  $V(x)$  between first two energy states of potential  $V_2(x)$  at different  $\beta_1$  with varying strength (a) of the Gaussian term

$\beta_1$	$a$	2.5	7.5	15.0	25.0
5.0	0.663622939107862	0.476424241516660	0.549551202120502	0.629606540403016	0.689396632286312
15.0	0.159524989567553	0.082036500097828	0.170214707726082	0.265845202246959	0.348248000529687
40.0	0.001053232755862	0.002467963140698	0.019500998774620	0.054266935025497	0.097603143511490
75.0	0.000002067788653	0.000071212348569	0.002319575700286	0.0111549230733535	0.028396768276741
100.0	0.00000004239444	0.000009019389984	0.000680649578233	0.004768552300339	0.014088286819834
120.0	0.00000000242648	0.000002052331667	0.000283947566446	0.002542913703577	0.008575104724101





**Fig. 2** Plot of energy difference relative to the unperturbed potential between first two energy states of potential  $V_2(x)$  at  $\beta_1 = 15$  with varying strength ( $a$ ) of the Gaussian term

increase of  $\beta_1$  energy gap between the pair of states decreases. But increases of ‘ $a$ ’ does not always increase the quasi degeneracy of system. It is clear from Table 2 and Fig. 2 that with increase of  $\beta_1$  value quasi degeneracy increases. But, in case of ‘ $a$ ’, there is an optimum value for which quasi degeneracy is maximum. Any deviation from that point will also increase the energy gap between the successive pair of states. This concludes that both the double well potentials do not lead to same chemical environment. In, Table 1,

$\beta = \beta_1$  but extent of quasi degeneracy is more in case of potential  $V_1(x)$ . Thus, quartic double well potential is the model for vibrational mode of a stronger bond, where Gaussian double well potential is the model for vibrational mode of a relatively weaker bond. Because, the vibration modes, however, may have double or multiple potential minima, such as inversion, ring-puckering, large-amplitude bending, and torsional vibrations and these phenomena occurs for molecules having strong bond. Thus, for these types of molecules stronger the bond more will be quasi degeneracy in the in the vibrational modes of the molecule. For, example  $NH_3$  has umbrella rotation but  $PH_3$  does not. Because of the strength of  $N - H$  is more than  $P - H$ .

## 6 Effect of Gaussian perturbation on quartic double well potential

Now, if one applies Gaussian perturbation then the potential will have the form

$$V_3(x) = V_1 - \beta_2 \exp(-ax^2)$$

**Table 3** Energy values of first twenty energy states of potential  $V_3(x)$  at  $\beta_2 = 5.0$  with varying strength (a) of the Gaussian term to observe the effect of Gaussian perturbation on quasi-degenerate states of potential  $V_1(x)$

n	a	0.5	2.5	12.0	25.0	50.0	100.0
0	5.22899752344468990	5.40858226271004840	5.4086127145378242	5.408612715511829	5.4086127155833452	5.4086127158087578	
1	5.22899752396880050	5.4085822630050302	5.4086127147712872	5.40861271573252360	5.4086127157976094	5.4086127156011158	
2	15.5973082283046692	15.9347542623678322	15.9352799595421714	15.9352800863596968	15.9352801008952909	15.9352801050961474	
3	15.5973083863463414	15.9347543503414073	15.9352800270489822	15.9352801496375562	15.935280161550196	15.9352801639704751	
4	25.4116149996734072	25.9756720973251447	25.9805321942523939	25.9805477236174837	25.9805486749824581	25.9805416194076848	
5	25.4116355308796108	25.9756838354607301	25.9805407390093492	25.9805477236174837	25.9805411379839661	25.9805488988458144	
6	34.5588492520698124	35.420378377226518	35.4601376556984498	35.4604200901062326	35.4604952051040918	35.4605285968730576	
7	34.5603061990906858	35.428961000249675	35.4607566886567902	35.4609830554726812	35.4610246441038334	35.4610358096470576	
8	42.8178342831120257	44.0341482798698891	44.2127169983620831	44.2204818546051808	44.22350668616138296	44.2251085872903094	
9	42.8753137914297148	44.0807134169778791	44.2408142645399742	44.245059169255768	44.2460638115853815	44.2463662404323035	
10	49.3679727002424924	50.5628966165037639	51.4160810534590862	51.5783706156107584	51.6637166016122036	51.71450165872131777	
11	50.3055321052898421	51.6247059428629136	52.14919734445965105	52.1875325451047560	52.1986909474735681	52.20238969778833482	
12	54.4511841497066799	55.226354010389594	55.9388428158681159	56.3130789738177088	56.6025865011347963	56.816533415484997138	
13	57.6389757209779525	58.7243653712503519	59.5086658800619661	59.635973531844281	59.6810503482265085	59.69743178462907096	
14	61.6560488736295831	62.5584033894877942	62.9253641348677108	63.064440986281773	63.2123117888278720	63.34909354710686908	
15	65.8974562322530453	66.8292108689269658	67.4900087552406891	67.6738715884110782	67.7544164798326652	67.7869159291812178	
16	70.4287110805244296	71.3233651458221019	71.7178031845517802	71.7934475136320334	71.8740946925917204	71.9591953664599728	
17	75.1981408174365988	76.0731254301371962	76.5936217384993192	76.7759811442523948	76.8740594855641036	76.9183976871447116	
18	80.1877303265042478	81.043199933230227	81.4496278785965338	81.5157171455398029	81.569646783770288	81.6305547734802915	
19	85.38088666317004203	86.2179652317411396	86.6630393315699728	86.8241459274126548	86.9271057608886616	86.9792705139824136	

A Gaussian perturbation is applied to a Quartic Double well potential. The calculation is done for different  $\beta_2$  using a series of 'a' values. Table 3, 4 and 5 show the calculation.

Initially for  $\beta_2 = 5.0$  (Table 3) weak perturbation is applied. It is clear that; extent of quasi degeneracy is same for both  $V_1$  and  $V_3$  only some dispersion in the higher energy states. But, in case of stronger perturbation (Tables 4, 5)  $\beta_2 = 28.0$  and  $\beta_2 = 56.250$  results are different. It is clearly seen from the result that effect of this Gaussian perturbation is more on higher energy state than lower states. In case of higher strength of Gaussian, with increase of 'a' values, quasi degeneracy in higher energy pair is removed and a new pair is generated. This, observation is clearly seen in Table 5. The number of these accidental pair increases with higher 'a' values. Usually, lower state in the quasi degenerate pair is an even parity state but here the lower state in the pair is an odd parity state thus the order is reversed, this is indeed an interesting result due to extra delocalisation of the higher even parity states. Also, in first column of Table 5. quasi degeneracy is removed. It means that proper choice of perturbation can remove the quasi degeneracy of the systems.

Specific heats of symmetric double-well systems at very low temperatures have the Schottky-type anomaly, which is rooted to a small energy gap in low-lying two-level eigenstates induced by a tunnelling through the potential barrier. Here, it can be concluded from the energy spectrum that as the nature of the spectrum is almost same for low and moderate strength with the unperturbed potential, then, these type of potentials also have Schottky-type anomaly in their specific heat at very low temperature. In case of first column of Table 5 the quasi degeneracy is removed so it can be expected that for this potential there will be no Schottky-type anomaly in very low temperature specific heat [17]. Thus, one can hope that proper choice of Gaussian field can remove the Schottky-type anomaly.

## 7 Conclusion

A methodology has been put forwarded for obtaining excited quantum stationary states through an unconstrained minimization of the P4. The motivation is to derive and extend the applicability of the property (mandatory condition in stationary states) based optimisation method rather than RQ or least square minimisation method. The present route will find a distinctive edge. Work along this direction is in progress. Property minimization in excited-state calculations by using nonlinear variational trial wave functions is the key point here. The problem of an a priori knowledge of nodal positions is removed directly. Now, for this type of minimisation doesn't require any additional information of node or any special state dependent character. This minimisation is a general scheme of optimisation of any trial states, particularly in respect of electronic structure calculations.

As nonlinear variations are much more powerful than the linear ones, the endeavour has been found to be rewarding even when one chooses a three-parameter wave function to simulate some fifth excited state. Result for the Hamiltonian is a clear case in point. Thus, the kind of generality the present recipe provides is remarkable. And, this is certainly a much more desirable extension in comparison with the sacrifice made of

**Table 4** Energy values of first twenty energy states of potential  $V_3(x)$  at  $\beta_2 = 28.0$  with varying strength (a) of the Gaussian term to observe the effect of Gaussian perturbation on quasi-degenerate states of potential  $V_1(x)$

n	a	0.5	2.5	12.0	25.0	50.0	100.0
0	4.337194896963112	5.408441485312970	5.408612709173333	5.4086127149185046	5.4086127153880098	5.4086127155045958	5.4086127157893458
1	4.3371959558191194	5.4084414878640032	5.408612709775644	5.4086127153410074	5.4086127157234358	5.4086127157893458	5.4086127157893458
2	13.8038536142069503	15.9322862855593925	15.9352791397903814	15.9352799382048147	15.9352800424126712	15.935280047031651	15.935280047031651
3	13.8039033861698712	15.9322874487428834	15.9352793453917343	15.9352800730681849	15.9352801449108483	15.9352801593659805	15.9352801593659805
4	22.0594863792048485	25.9511375103457595	25.9804633837363212	25.9805210793333607	25.980532832553262	25.9805371819625179	25.9805371819625179
5	22.0709363981328224	25.9514856928233719	25.9804978608453716	25.9805411841936084	25.9805470791638413	25.980548434344179	25.980548434344179
6	27.7589084041577756	34.1609360608506769	35.454247674810798	35.4586212753457488	35.4597048231724834	35.460118970676774	35.460118970676774
7	28.5164341113513194	35.2254337565534392	35.4591527617408672	35.4606737602043828	35.460941861149159	35.461010674662475	35.461010674662475
8	31.1699025216066907	35.4706847787552988	41.1242907135828481	43.7994390747888058	44.1448215670150485	44.1942436209136868	44.1942436209136868
9	34.0482212991178876	42.0400769884604095	44.2035870006313729	44.2368237972651368	44.2437191504404979	44.2456317388052458	44.2456317388052458
10	37.2612646205795172	43.5926023801595548	44.4694897998826448	45.3770764743429796	48.0342871397439524	50.03773813442416873	50.03773813442416873
11	40.8494440481551333	46.4876721671918887	51.7169719173607287	52.0851487878225505	52.1685543146005912	52.19275830484775458	52.19275830484775458
12	44.7279291810360248	50.7050327958067255	52.7929539886750838	52.9364363519319161	53.2203277916653197	53.8503545697081143	53.8503545697081143
13	48.8669746031060415	54.2127480878168853	58.0519584422183679	59.1968088398682895	59.5427567087850105	59.65199895278243281	59.65199895278243281
14	53.2467129150161789	58.5210343193836042	61.1750190916741596	61.3789232663927535	61.5673604875950469	61.85978769774358188	61.85978769774358188
15	57.8496177856370042	62.9507880393748289	65.672209688920763	66.9023769143833054	67.4771053490387907	67.6910470279803019	67.6910470279803019
16	62.6617415160896893	67.6023871134008694	70.1653376789308804	70.4668923301076493	70.634117861702781	70.8596505790674148	70.8596505790674148
17	67.671415044842016	72.5047021347814642	74.8714991302211708	75.8592103712996214	76.4948392287716388	76.7787392176436754	76.7787392176436754
18	72.8686058869593368	77.584347906778432	79.9635248221561244	80.3524714673803828	80.5148042020315878	80.6982927812408946	80.6982927812408946
19	78.2445626958987824	82.864678572788204	85.0692688712636702	85.8609800801271846	86.4785256197401822	86.8031235560880852	86.8031235560880852

**Table 5** Energy values of first twenty energy states of potential  $V_3(x)$  at  $\beta_2 = 56.25$  with varying strength (a) of the Gaussian term to observe the effect of Gaussian perturbation on quasi-degenerate states of potential  $V_1(x)$

n	a	0.5	2.5	12.0	25.0	50.0	100.0
0	2.9810426308825555	5.40826660022556640	5.4086126998790788	5.408612713566228	5.4086127149418388	5.4086127153079388	5.4086127153079388
1	3.0074909851109055	5.40826678489010240	5.4086127029925492	5.408612714790351	5.4086127156209826	5.4086127157633886	5.4086127157633886
2	3.2636055889381624	10.1272443044855862	15.9352758260267322	15.9352793966117545	15.9352798708244449	15.9352800029987733	15.9352800029987733
3	8.4464673571860302	15.9290931418779209	15.9352783429551507	15.9352799600614076	15.9352801214390211	15.9352801531735048	15.9352801531735048
4	10.1357712347206998	15.9291714638348978	20.998801583545152	25.9801524541939343	25.980491421430294	25.9805236439941502	25.9805236439941502
5	11.1780139257024942	25.8926656810932485	25.9804255473424703	25.9805309271524223	25.9805447691760207	25.980547803140638	25.980547803140638
6	14.0499824203317729	25.9175277134268569	25.980720022349832	27.8031681375640111	34.6649164484264496	35.4577335366026354	35.4577335366026354
7	16.9735046696012261	27.7516364173069938	35.4556842878014676	35.4601441565733708	35.4608178654774448	35.4609760560181542	35.4609760560181542
8	19.9916443121801492	34.8027914441557051	35.4624674493034532	35.4651250624849616	35.491091988709897	41.0991722108555866	41.0991722108555866
9	23.4314700516846982	35.2012810354031878	44.0676522954031107	44.2205825262336365	44.2400288907887074	44.2446013409768479	44.2446013409768479
10	27.1412647741868795	39.5093612277347574	44.2624478195869936	44.2908069578212728	44.308675568681819	44.396723285255815	44.396723285255815
11	31.0877178217030696	43.1230017863488424	49.4735812853099395	51.8407063064441145	52.1178897193931379	52.17892244188577334	52.17892244188577334
12	35.2713721054104318	45.8674488099855484	52.3339759150032471	52.5195251858562604	52.5778896369338873	52.6827932395057445	52.6827932395057445
13	39.6751035893513196	50.4560905069101953	54.8429839119328553	58.1686083450737512	59.303196492008678	59.58574801172176904	59.58574801172176904
14	44.2866718114940668	54.5075156604067736	60.2051255718751444	60.7439260142069406	60.8759879189452793	61.03813318462967974	61.03813318462967974
15	49.0962531174505639	59.0318659123858032	63.4505261487573034	65.4915863101139486	67.0153303164186466	67.5518571043659808	67.5518571043659808
16	54.094699240909673	63.8131845499852091	68.812413176386162	69.6702750792661725	69.879955232982196	70.0644975650979928	70.0644975650979928
17	59.273880127775556	68.7341572917381268	73.0447920244748624	74.4884654692901869	75.902515167014201	76.5787638515450873	76.5787638515450873
18	64.6264735160666355	73.9045870799595264	78.4460525601468142	79.4702070195678481	79.7514574402971768	79.9383087699945848	79.9383087699945848
19	70.1458185448542384	79.234049927035823	83.404140476803839	84.5778598464398215	85.817335937488643	86.554921070726202	86.554921070726202

the upper bound nature of average energies that one obtains in linear variations. Hope, further studies along this line may surely explain the utility of this type of variational calculation.

Here, a comparative study of Quartic double well and Gaussian double well is done on the basis of their chemical environment and it has been found that Quartic double well potentials are model for vibrational mode of a stronger bond where Gaussian double well potentials are for relatively weaker bonds. The author has also studied the effect of Gaussian perturbation on a quartic double well potential and now can be proposed that Schottky-type anomaly can be removed by using proper Gaussian field in double well potential.

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## References

1. S.T. Epstein, *The Variational Method in Quantum Chemistry* (Academic Press, New York, 1974)
2. J. Hendekovic, Chem. Phys. Lett. **90**, 198 (1982)
3. H.G. Miller, T. Geveci, Chem. Phys. Lett. **100**, 115 (1983)
4. J. Hendekovic, J. Kucar, Chem. Phys. Lett. **100**, 117 (1983)
5. N. Mukherjee, Int. J. Quantum Chem. **112**, 960 (2012)
6. N. Mukherjee, J. Math. Chem. **50**, 2303 (2012)
7. N. Mukherjee, J. Math. Chem. **51**, 1938 (2013)
8. M. Thorwart, M. Grifoni, P. Hanggi. Annals Phys. **293**, 14 (2001)
9. B. Bagchi, A. Ganguly, J. Phys. A **36**, L161 (2003)
10. M.F. Manning, J. Chem. Phys. **3**, 136 (1935)
11. M. Razavy, Am. J. Phys. **48**, 285 (1980)
12. A.V. Turbiner, Commun. Math. Phys. **118**, 467 (1988)
13. W.E. Caswell, Ann. Phys. **123**, 153 (1979)
14. R. Balsa, M. Plo, J.G. Esteve, A.F. Pacheco, Phys. Rev. D **28**, 1945 (1983)
15. R.M. Quick, H.G. Miller, Phys. Rev. D **31**, 2682 (1985)
16. C.-K. Lin, H.-C. Chang, S.H. Lin., J. Phys. Chem. A **111**, 9347 (2007)
17. H. Hasegawa, Phys. Rev. E **86**, 061104 (2012)
18. S. Kirkpatrick, C.D. Gelatt, M.P. Vecchi, Science **220**, 671 (1983)
19. S.I. Chan, J. Zinn, J. Fernandez, W.D. Gwinn, J. Chem. Phys. **33**, 1643 (1960)
20. J.D. Swalen, J.A. Ibers, J. Chem. Phys. **36**, 1914 (1962)
21. J. Laane, R.C. Lord, J. Chem. Phys. **47**, 4941 (1967)
22. M.F. Manning, J. Chem. Phys. **3**, 136 (1935)
23. S. Kirkpatrick, J. Stat. Phys. **34**, 975 (1984)
24. P. Dutta, S.P. Bhattacharyya, Chem. Phys. Lett. **167**, 309 (1990)
25. S. Nandi, P. Chaudhury, R. Sharma, S.P. Bhattacharyya, J. Theor. Comput. Chem. **7**, 977 (2008)