

New state dependent uncertainty principle and design of objective function for optimisation: utility of kinetic and potential energy uncertainties

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Received: 16 December 2011 / Accepted: 22 May 2012 / Published online: 5 June 2012
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Abstract In this work a new state dependent Uncertainty Principle between kinetic and potential energy is formulated using Time independent Schrödinger Equation and Correspondence Principle. Validity of the above said Uncertainty Principle is also demonstrated by linear variational calculation of a one-dimensional model potential. An objective function is also been designed, to support excited state non-linear variational description of bound stationary state of any type of system. This newly designed function will serve as an alternative of ΔH in excited state nonlinear variational purpose. The utility of these objective functions is demonstrated by already evolved non-linear variational technique by using a one-dimensional model potential where crux of the problem lies on the determination of the node of excited states.

Keywords Uncertainty principle · Objective function · Kinetic energy · Potential energy

1 Introduction

The Heisenberg Uncertainty Principle is, one of the most important characteristics of Quantum Mechanics. For all quantum mechanical systems $\Delta x \Delta p_x \geq \frac{\hbar}{2}$. It gives the lower bound of the uncertainty product of position and momentum. Moreover this uncertainty relation indicates that simultaneous measurement of both the quantity in same precession is not possible. If one is good another must be bad. This is the special characteristics of this relation. Now, whether same conclusion is true for measurement of the uncertainties of \hat{T} , \hat{V} .

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Actually, it is known to all that any two operators say, \hat{A} , \hat{B} if do not commute, that is if $[\hat{A}, \hat{B}] \neq 0$ then both of them cannot be measured simultaneously with accuracy. That means there is an uncertainty relation between them. Schwarz's Inequality [1] helps us in this purpose. Schwarz's Inequality

$$\langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle \geq |\langle \phi_1 | \phi_2 \rangle|^2$$

Here, equality holds when ϕ_1 and ϕ_2 are linearly dependent.

if, $\phi_1 = (A - \langle A \rangle) \theta$ and $\phi_2 = (B - \langle B \rangle) \theta$

also, if \hat{A} , \hat{B} both Hermitian then, $\Delta A^2 \Delta B^2 \geq \frac{|\langle [\hat{A}, \hat{B}] \rangle|^2}{4} + \left| \left(\frac{\langle [\hat{A}, \hat{B}]_+ \rangle}{2} - \langle A \rangle \langle B \rangle \right) \right|^2$

as $\hat{T}(p_x)$, $\hat{V}(x)$ both Hermitian then,

$$\Delta T^2 \Delta V^2 \geq \frac{|\langle [\hat{T}, \hat{V}] \rangle|^2}{4} + \left| \left(\frac{\langle [\hat{T}, \hat{V}]_+ \rangle}{2} - \langle T \rangle \langle V \rangle \right) \right|^2$$

But, here the main objective is to formulate an uncertainty relation using the Correspondence Principle. In this context, derivation of uncertainty relation between $\hat{T}(p_x)$, $\hat{V}(x)$ is more physical as their measurements related to energy of the states of the system.

$$\langle T \rangle_n + \langle V \rangle_n = \langle E \rangle_n$$

For, stationary state, $\langle E \rangle_n = E_n$.

The Rayleigh–Ritz variation method (minimisation of Rayleigh Quotient (RQ)) lies in 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) [2,3] 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. Even 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. 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.

The linear variation method provides a way out. It says that [4,5] if one chooses a suitable set of states $\{\theta_i\}$ with gradually increasing energies to meet the conditions

(i) $\langle \theta_i | \theta_k \rangle = 0$ and (ii) $\langle \theta_i | H | \theta_k \rangle$, for $i = 0, 1, 2, \dots, k-1$, $k > i$, then the average energy of state θ_k will be an upper bound to the true one. Hence, θ_k becomes a representative of the state sought. In practice, therefore, nonlinear variations for excited states must involve a number of orthogonality and decoupling constraints [6–9].

Another way out, is to minimise ΔH^2 [10–12] for excited state in place of RQ.

This is a necessary as well as sufficient condition optimisation of trial state.

$$\Delta H^2 = \Delta T^2 + \Delta V^2 + (\langle TV \rangle + \langle VT \rangle - 2 \langle T \rangle \langle V \rangle) \quad (1)$$

For stationary state,

$$\Delta H^2 = 0 \quad (1a)$$

In this case optimisation can be carried out without concerning about the nodes of the excited states. Thus it is notable that one can consider nodes as pre-exponential parameter in non-linear minimisation of ΔH^2 . Moreover the minimisation step can be executed without any restriction. But this type of minimisation never guarantees upper bound results. Main problem of handling ΔH^2 is technical. According to Eq. (1), during minimisation using ΔH^2 , one have to perform 4th order differentiation of trial state which is a tedious and complicated job. This makes the least square minimisation as an unwelcoming method for optimisation [13].

One of the main concern of this work, is to formulate new objective function using Time independent Schrödinger equation, Virial Theorem [14] and use it for minimisation instead of ΔH^2 . The generality of these new objective functions are remarkable and synonymous to ΔH^2 , can be used in any optimisation step without any restriction. More over one can bypass the technical problem related to ΔH^2 .

The organization is as follows. In Sect. 2, the formulation will completely discussed. Section 3, will concentrate on strategy and trial states. Pilot calculations to demonstrate the basic methods with its various variants will concern us in Sect. 4. Section 5, contains summarization of the major conclusions of these formulation.

2 Formulation

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 $\langle [T, V] \rangle_n = 0$

This relation is also true for any time independent trial state.

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

thus,

$$\Delta T_n^2 = \Delta V_n^2 = \langle T \rangle_n \langle V \rangle_n - \langle TV \rangle_n \quad (2)$$

This equation is the Master Equation in both the formulation.

Again, this equation is true for the Systems obeying Classical Mechanics

$$\Delta T^2 = \Delta V^2 = \langle T \rangle \langle V \rangle - \langle TV \rangle \quad (2a)$$

These two equations tells that this is a property of both quantum and classical systems. We will now use this formulation in deriving a state dependent uncertainty principle and also in optimisation purpose.

2.1 Formulation of state dependent uncertainty principle between \hat{T}, \hat{V}

According to Correspondence Principle [15], for, large quantum limit ($n \rightarrow \infty$)

$$\frac{\Delta T_n^2 \Delta V_n^2}{\langle T \rangle_n^2 \langle V \rangle_n^2} = \frac{\Delta T_c^2 \Delta V_c^2}{\langle T \rangle_c^2 \langle V \rangle_c^2} \text{ of all bound stationary states.}$$

where c in suffix stands for classical mechanics values.

$$\text{Let, } \frac{\Delta T_c^2 \Delta V_c^2}{\langle T \rangle_c^2 \langle V \rangle_c^2} = k^2$$

As, with increase of quantum number (n) $\frac{\Delta T_n^2}{\langle T \rangle_n^2}, \frac{\Delta V_n^2}{\langle V \rangle_n^2}$ both decreases, thus it can be written that, for all bound states

$$\Delta T_n^2 \Delta V_n^2 \geq k^2 \langle T \rangle_n^2 \langle V \rangle_n^2 \quad (3)$$

Thus, here a new potential as well as state dependent uncertainty principle is derived, only using the concept of correspondence principle. Additionally from Eqs. (2) and (3) this concludes that at the stationary states of a conservative system, both must be measured in same accuracy.

2.2 Formulation of objective functions for optimisation

Now, obeying Eq. (2) and using Schwarz's Inequality, it can be written for bound stationary state that,

$$\Delta T_n^2 \Delta V_n^2 = |\langle TV \rangle_n - \langle T \rangle_n \langle V \rangle_n|^2 \quad (4)$$

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

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

Now, concentrating on Eqs. (3) and (4) 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

$$(T - \langle T \rangle) \psi = \alpha (V - \langle V \rangle) \psi \tag{6}$$

Thus, by mathematical description equality holds for any value of α .

If, $\alpha = -1$ then Eq. (5) 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. (1) 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.

$$2 \langle T \rangle = \left\langle x \frac{\partial V}{\partial x} \right\rangle \tag{7}$$

Now, combining the above said conditions Eqs. (2) and (7) for bound stationary states it is clear,

- (i) $\left| \frac{\Delta T^2}{\Delta V^2} - 1 \right| + \left| \frac{2\langle T \rangle}{\left\langle x \frac{\partial V}{\partial x} \right\rangle} - 1 \right| = 0$
- (ii) $\left| \frac{(\langle T^2 \rangle - \langle T \rangle^2)}{(\langle V^2 \rangle - \langle V \rangle^2)} - 1 \right| + \left| \frac{2\langle T \rangle}{\left\langle x \frac{\partial V}{\partial x} \right\rangle} - 1 \right| = 0$
- (iii) $\left| \frac{\Delta T^2}{(\langle T \rangle \langle V \rangle - \langle TV \rangle)} - 1 \right| + \left| \frac{2\langle T \rangle}{\left\langle x \frac{\partial V}{\partial x} \right\rangle} - 1 \right| = 0$
- (iv) $\left| \frac{\Delta V^2}{(\langle T \rangle \langle V \rangle - \langle TV \rangle)} - 1 \right| + \left| \frac{2\langle T \rangle}{\left\langle x \frac{\partial V}{\partial x} \right\rangle} - 1 \right| = 0$
- (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. (2) 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. (1) in excited state non-linear optimisation scheme.

3 Choice of trial states

3.1 Choice of basis to demonstrate uncertainty principle

Here to demonstrate the newly formulated Uncertainty Principle for a symmetric potential, linear variation scheme was adopted. We choose to employ the symmetry-adapted cosine and sine functions that are the energy eigenfunctions of the particle-in-a-box problems in $(-L, L)$. These bases have already been found to be quite convenient in several types of variational calculations. They possess nice convergence properties as well. Specially, we write for the even and odd states [16–20], respectively,

$$\Psi_n^e = \sum_{j=1}^N a_{nj} \cos \frac{(2j-1)\pi x}{2L} \quad (8)$$

and,

$$\Psi_n^o = \sum_{j=1}^N b_{nj} \sin \frac{j\pi x}{L} \quad (9)$$

The virtues of using such basis functions are, in brief, as follows. First, integrals involved in H are quite easy to evaluate. Second, existence of the nonlinear variational parameter L allows one to adopt a coupled variational scheme that is far more powerful than purely linear variations. Third, convergence of the process as a function of N is ensured. Note that the basis set leads ultimately to a secular equation at each L . But, we also realize that the kinetic energy part becomes infinitely large as $L \rightarrow 0$. At the other extreme, when $L \rightarrow \infty$, the potential energy part behaves in a similar fashion. Thus, qualitatively, the uncertainty principle guarantees the existence of an optimal choice for L . So, the practice is to adopt the following scheme. Choose a trial value for L , construct the H matrix and diagonalize it, optimize the coefficients such that the lowest energy is minimized, continue the same process at other L -values, and finally pick out the minimum of all such minima, corresponding to the optimal L value. The states and energies are then assigned according to the usual practice of linear variations. Then we calculate the desired properties using that state, and see how quickly those properties converge to the classical value.

3.2 Choice of trial state for non-linear optimisation

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

behaviour of the potential at $x \rightarrow 0$ and $x \rightarrow \infty$ the trial state is chosen for ground state. As here demonstration is restricted to one dimensional model potential then for excited state just consideration of the pre-exponential part for nodal information will serve the purpose. Thus for the trial excited states will look like,

$$\tilde{\Psi}_n = \prod_{j=1}^n (x - \alpha_j) \tilde{\phi}_0$$

where, nodal positions of Ψ_i defined by terms α_i in the above expression. $\tilde{\phi}_0$ stands for a node less function with embedded non-linear parameters that are to be varied. As here there are both pre-exponential and exponential variables so to get reasonable variational result one should opt At least three parameter exponential function.

3.2.1 Role of parity in choosing trial states

In situations where the parent potential V_0 is symmetric, one can extract some advantages of choosing trial states because the odd states are known to have a node fixed at the origin, and both even and odd states have all other nodes, if any, symmetrically distributed around the origin. Thus one can choose the even and odd states in the following way,

$$\begin{aligned} \text{Even parity states} \quad \tilde{\Psi}_n^e &= \prod_{k=1}^{n/2} (x^2 - \alpha_k^2) \phi_k, \quad n \geq 2 \\ \text{Odd parity states} \quad \tilde{\Psi}_{n+1}^o &= \prod_{k=1}^{n/2} x(x^2 - \alpha_k^2) \phi_k \end{aligned}$$

3.3 Variational floor and bound

It is a well known fact that Schrödinger Equation of most of the quantum mechanical system can't be solved exactly. Thus one has to adopt either variation method or perturbative method for calculation of energy. From that information of optimised stationary state, respective properties are calculated. Here, same is done to demonstrate the newly formed uncertainty principle. Moreover convergence of value the energy and property is shown with gradually increasing the value of N .

In linear variation method, the energy obtain, is always upper bound to the exact energy. This confirms that with gradual increase of N , will increases the accuracy of the results. Moreover in linear variation the result obeys the condition (i) and condition (ii) automatically. In case of non-linear variation if optimisation is performed obeying the two conditions, someone will definitely achieve upper bound results. But, the tusk becomes gradually tougher as someone proceeds to higher excited state ($n \geq 4$). Recently an idea of unconstrained variation of excited states knowing the nodal structure of the respective states [21] produces appreciated results, where upper-bound property of those state is not is not guaranteed. Here, also the optimisation using the newly formulated properties (i–v) doesn't guarantee upper-bound character, but easier to handle, and as a result higher state can be calculated as ease. Among all those

objective functions, function (iv) is most easy to use as it contains only one operator related to kinetic energy.

4 Results and discussion

Potential $V(x) = x^4$ is considered for this study.

The classical mechanics results obtain for this potential are as follows:

$$\langle T \rangle = \frac{2}{3}\beta a^4 \quad (10a)$$

$$\langle V \rangle = \frac{1}{3}\beta a^4 \quad (10b)$$

$$\langle T^2 \rangle = \frac{12}{21}\beta^2 a^4 \quad (10c)$$

$$\langle V^2 \rangle = \frac{5}{21}\beta^2 a^4 \quad (10d)$$

$$\Delta T^2 = \frac{8}{63}\beta^2 a^4 \quad (10e)$$

$$\Delta V^2 = \frac{8}{63}\beta^2 a^4 \quad (10f)$$

$$\langle TV \rangle = \frac{2}{21}\beta^2 a^4 \quad (10g)$$

$$\langle T \rangle \langle V \rangle - \langle TV \rangle = \frac{8}{63}\beta^2 a^4 \quad (10h)$$

$$\frac{\Delta T^2}{\langle T \rangle^2} = \frac{2}{7} = 0.285714285 \quad (10i)$$

$$\frac{\Delta V^2}{\langle V \rangle^2} = \frac{8}{7} = 1.142857143 \quad (10j)$$

$$\frac{\Delta T^2 \Delta V^2}{\langle T \rangle^2 \langle V \rangle^2} = \frac{16}{49} = 0.326530612 \quad (10k)$$

where, β is the force constant which is 1 here. a is the amplitude.

Equations (10e), (10f), (10h) demonstrates the truth of Eqs. (2) and (2a). Thus this calculation is true for both classical as well as quantum mechanics. Just like Virial Theorem.

Now, switch the Quantum Mechanical calculations. $V(x) = x^4$ is a well known AO model commonly known as Quartic Oscillator model. Let us initiate the discussion by checking the convergence of the various results. This would ensure the gradually betterment of the expectation values of the desire properties and leads to conclusion. Actually as Schrödinger Equation of most of the quantum mechanical system can't be solved exactly then, here employment of this variational scheme will serve the desire purpose. In Table 1 displays the variational results achieved by routinely increasing the size N (5, 8, 10, 15, 20) of the H matrix. Convergence of the calculated results of energy for $n = 9$ state is upto 10-digits, so property calculated is correct upto 3–4

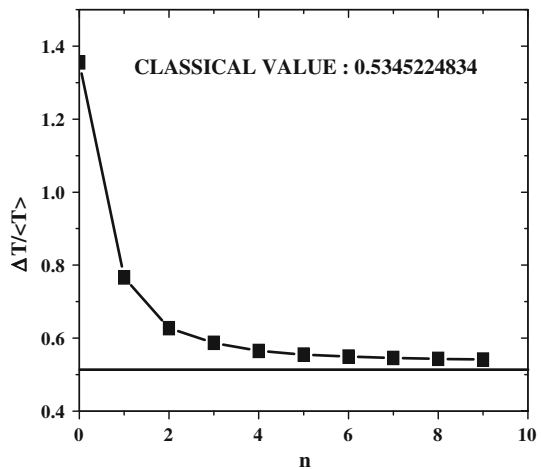
Table 1 Convergence of energies (\bar{E}_n) and convergence of properties ($\frac{\Delta T_n}{\langle T \rangle_n}, \frac{\Delta V_n}{\langle V \rangle_n}, \frac{\Delta T_n \Delta V_n}{\langle T \rangle_n \langle V \rangle_n}$) w.r.t state, obtain by linear variation scheme employing Eqs. (8), (9) for potential $V(x) = x^4$

n	N	\bar{E}_n	$\frac{\Delta T_n^2}{\langle T \rangle_n^2}$	$\frac{\Delta V_n^2}{\langle V \rangle_n^2}$	$\frac{\Delta T_n \Delta V_n}{\langle T \rangle_n \langle V \rangle_n}$
0	5	1.060 362	1.838 28	7.353 3	13.517 6
	8	1.060 362 090	1.838 112 5	7.352 450	13.514 63
	10	1.060 362 090 48	1.838 112 355	7.352 449 4	13.514 628 1
	15	1.060 362 090 484 182	1.838 123 532 435	7.352 449 412 974 0	13.514 628 092 585
	20	1.060 362 090 484 182 899	1.838 112 353 243 505	7.352 449 412 974 0231	13.514 628 092 585 51
1	5	3.799 67	0.5868	2.3475	1.3776
	8	3.799 673 0	0.5868069	2.3472276	1.377369
	10	3.799 673 029 80	0.58680684877	2.347227395	1.37736911
	15	3.799 673 029 801 3941	0.58680684811902	2.34722739247609	1.3773691079975
	20	3.799 673 029 801 3941 68	0.58680684811902175	2.3472273924760870	1.377369107997522
2	5	7.4557	0.3940	1.5765	0.6211
	8	7.455 697 9	0.393676	1.574706	0.619924
	10	7.45569793	0.393675749	1.5747030	0.61992238
	15	7.455697937986738	0.39367574463752	1.57470297855	0.6199223676636
	20	7.45569793798673839	0.3936757446374988	1.57470297854999	0.6199223676635566
3	5	11.6448	0.3414	1.3662	0.4664
	8	11.6447455	0.341108	1.364433	0.465419
	10	11.644745511	0.34110767	1.36443069	0.46541777
	15	11.64474551137816	0.3411076667429	1.3644306669719	0.46541776124349
	20	11.6447455113781620	0.341107666742961	1.36443066697184	0.465417761243309
4	5	16.264	0.3235	1.2977	0.4199
	8	16.26182	0.319297	1.27719	0.4078061
	10	16.2618260	0.3192907	1.277163	0.4077864
	15	16.2618260188502	0.31929072033	1.277162881337	0.407786256366
	20	16.261826018850226	0.3192907203338	1.2771628813352	0.4077862563651
5	5	21.2422	0.3128	1.2550	0.3926
	8	21.23837	0.30822	1.23289	0.38000
	10	21.23837294	0.30821463	1.232858586	0.3799850
	15	21.23837291823	0.308214546432	1.2328581857	0.3799848265
	20	21.238372918235940	0.3082145464316	1.232858185726	0.379984826528
6	5	26.5706	0.3201	1.2993	0.41600
	8	26.5285	0.30190	1.20767	0.364606
	10	26.5284717	0.301834	1.207339	0.3644168
	15	26.52847118368	0.30183367401	1.20733469606	0.3644142670
	20	26.52847118368251	0.3018336740028	1.207334696011	0.3644142670482
7	5	32.1576	0.3174	1.2880 0.4089	0.4089
	8	32.09868	0.29791	1.191730	0.3550
	10	32.0985985	0.297827	1.1913114	0.354805
	15	32.0985977109	0.29782634	1.191305395	0.3548021
	20	32.0985977109683	0.2978263650	1.19130539505	0.3548021554

Table 1 continued

n	N	\bar{E}_n	$\frac{\Delta T_n^2}{\langle T \rangle_n^2}$	$\frac{\Delta V_n^2}{\langle V \rangle_n^2}$	$\frac{\Delta T_n^2 \Delta V_n^2}{\langle T \rangle_n^2 \langle V \rangle_n^2}$
8	5	38.4903	0.353	1.502	0.531
	8	37.9243	0.2958	1.1838	0.35017
	10	37.923017	0.29516	1.180670	0.3484928
	15	37.92300102713	0.2951465	1.1805860	0.348445826
	20	37.9230010270339	0.295146499	1.180585999	0.3484458256
9	5	44.6770	0.3539	1.496	0.529
	8	43.9831	0.2940	1.1768	0.3460
	10	43.981183	0.293290	1.1731726	0.344080
	15	43.981158097	0.2932666373	1.1730665495	0.344021282
	20	43.9811580972897	0.29326663700	1.17306654802	0.34402128152

Fig. 1 To show the convergence of $\frac{\Delta T_n}{\langle T \rangle_n}$ (using $N = 20$ basis) towards classical value for potential $V(x) = x^4$



digits for that particular state. Because from variation Theorem, when there is error in energy value in second order, then there is error in first order in property values. Thus, property calculated using Eqs. (8) and (9) are at least accurate upto 3–4 digits. Here Table 1 (last three columns) and Figs. (1–3) explains that with increase of quantum number, those properties decreases and approaches to classical value. Actually it is expected that within finite n the convergence of desire properties is observed. Thus this demonstration proves the above said uncertainty relation in a convincing way.

Here concentration is on the family of anharmonic oscillators defined by for non-linear calculation:

$$H = -\frac{d}{dx^2} + \lambda x^4 \quad (11)$$

These oscillators have attracted considerable attention over the years (see, e.g., Refs. [20,21] and references quoted therein) as benchmark to assess the quality of any new

Fig. 2 To show the convergence of $\frac{\Delta V_n}{\langle V \rangle_n}$ (using $N = 20$ basis) towards classical value for potential $V(x) = x^4$

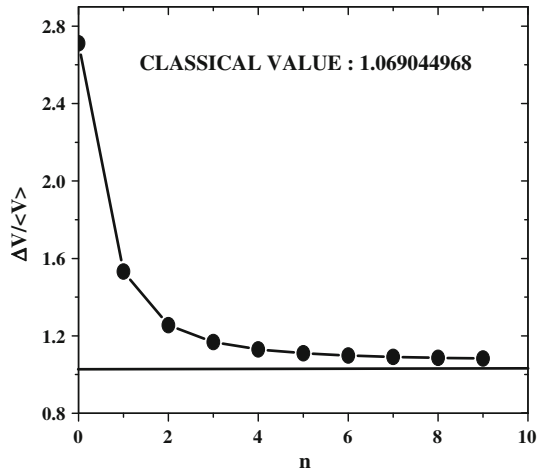
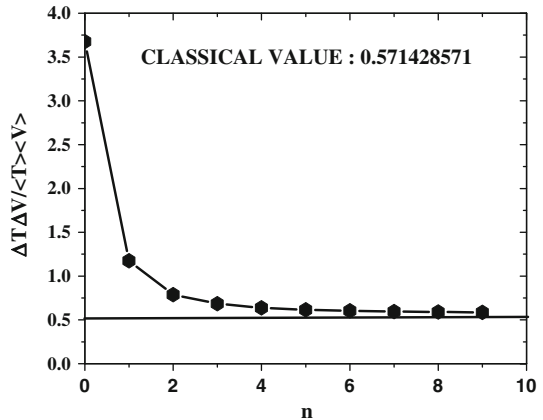


Fig. 3 To show the convergence of $\frac{\Delta T_n \Delta V_n}{\langle T \rangle_n \langle V \rangle_n}$ (using $N = 20$ basis) towards classical value for potential $V(x) = x^4$



recipe. This is primarily because of the simplicity of H in (11) and hence the availability of results by numerous methods of varying accuracy and sophistication. Here, results presented for $\lambda = 1$. In view of the small- and large- x behaviours of stationary wave functions of (11), we use:

$$\tilde{\psi}_0 = \exp \left[-ax^2 \left(1 + bx^2 + cx^4 \right)^{\frac{1}{4}} \right] \tag{12}$$

We first summarize our chief findings in Table 2, displaying average energies of the lowest 6 states of (11) at $\lambda = 1$ and some properties. Once again, here point is that errors incurred are only marginal in the overall process (compare to Table 1) also how nodal positions and the VR are affected as the increase of the states. It is found that the errors slowly increase as proceed to higher states. This is obviously due to increasing constraints of the excited states. It is expected that if the flexibility of the trial state chosen is more then accuracy will automatically increase. Similar reason is responsible

Table 2 Average energies and some properties of the first six approximate states of (11) at $\lambda = 1$

n	Nodal position	\bar{E}_n	VR	Objective function-(P4)
0	–	1.060 362 09	0.999 999 60	0.000 000 48
1	–	3.799 673 0	0.999 999 25	0.000 000 98
2	$\pm 0.575 449 19$	7.455 697 96	1.000 001 23	0.000 005 71
3	$0, \pm 0.923 923 88$	11.644 745 25	0.999 996 06	0.000 002 72
4	$\pm 0.389 536 23,$ $\pm 1.179 679 31$	16.261 826 72	0.999 977 96	0.000 009 65
5	$0, \pm 0.682 090 10,$ $\pm 1.384 572 35$	21.238 372 68	0.999 983 54	0.000 008 59

Table 3 Overlap values $\langle \tilde{\psi}_i | \tilde{\psi}_j \rangle$ of the stationary states of (11) for $i, j = 0, 1, \dots, 5$

i	j					
	0	1	2	3	4	5
0	1	0	0.000 084 51	0	0.000 925 97	0
1	0	1	0	0.000 013 67	0	0.000 037 75
2	0.000 084 51	0	1	0	0.003 282 99	0
3	0	0.000 013 67	0	1	0	0.000 916 23
4	0.000 925 97	0	0.003 282 99	0	1	0
5	0	0.000 037 75	0	0.000 916 23	0	1

Table 4 Hamiltonian coupling values $\langle \tilde{\psi}_i | H | \tilde{\psi}_j \rangle$ of the stationary states of (11) for $i, j = 0, 1, \dots, 5$

i	j					
	0	1	2	3	4	5
0	1.060 362 09	0	0.000 050 76	0	0.000 993 34	0
1	0	3.799 673 0	0	0.000 512 43	0	0.000 164 84
2	0.000 050 76	0	7.455 697 9	0	0.024 503 40	0
3	0	0.000 512 43	0	11.644 745 5	0	0.001 997 37
4	0.000 993 34	0	0.024 503 40	0	16.261 82	0
5	0	0.000 164 84	0	0.001 997 37	0	21.238 37

for the observed trends in values of $\langle \tilde{\psi}_i | \tilde{\psi}_j \rangle$ that are displayed in Table 3, The behaviour is comparable with the data presented in Table 4 of the estimates of the integrals $\langle \tilde{\psi}_i | H | \tilde{\psi}_j \rangle$. All such integrals should ideally vanish for $i \neq j$. But the tables reveal that the off-diagonal elements roughly increase with increasing (i, j) . This is again due to increasing accumulation of errors, in general, for higher excited states, since larger number of constraints is involved. In cases, however, there may be observe slight disagreements, and these are certainly because of accidental cancellations of errors.

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 the this property dependent variation method. Keeping in mind that here used a mere three-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 Conclusion

In summary, a new state dependent uncertainty relation is formulated. This relation indirectly tells the lower bound nature of uncertainties of kinetic and potential energy, as the minimum value of $\frac{\Delta T_n^2 \Delta V_n^2}{\langle T_n^2 \rangle \langle V_n^2 \rangle}$ is known for a particular potential. The motivation is to get at least some information regarding the uncertainty product of $\Delta T_n^2 \Delta V_n^2$ for a particular potential.

I have put forward a scheme of 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. Let then emphasize here that although the linear variational method stands usually as a handy tool for excited-state calculations in many critical circumstances, and particularly work using coupled variations, with one nonlinear parameter, has proved to be rewarding too [22, 23] even recently, there are 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. Real problems of excited-state calculations become apparent only in such situations. A clear case in this context is the study of supersingular spiked oscillators [24] given by the potential $x^2 + \frac{\lambda}{x^\alpha}$, with $\lambda > 0$ and $\alpha \geq 3$. There 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 circumvented in this methodology by importing this variation directly. Although 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 endeavor 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 (11) 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 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.

Acknowledgments NM is grateful to CSIR (India) for research fellowship.

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