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COMMENT

Variational and norm criteria in high-order perturbative–variational wavefunctions

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Abstract. The behaviour of high-order perturbative-variational wavefunctions, with one or more free parameters, is studied. A variational criterion, and a criterion based upon variation of the norm of the perturbative approximation function with order, are used for fixing free parameters. For the quartic anharmonic oscillator, both criteria seem to be equivalent. The obtained energies, not only for ground state but also for excited states, are in excellent agreement with previous results, although when we go to higher excited states we lose precision because of the worsening of the perturbative-variational wavefunctions.

1. Introduction

In monodimensional quantum problems, non-degenerate perturbation theory is, of course, one of the most used approximation techniques for broaching eigenvalue problems, which cannot be exactly solved. The most important problem with this technique is that, in many cases and even for small perturbations, the perturbation series for eigenvalues and eigenvectors are divergent (in an asymptotic way). Perhaps the longest studied example with this kind of behaviour is the eigenvalue problem for the quartic anharmonic oscillator, QAO ($H = p^2 + x^2 + \lambda x^4$). In this case, the obtained series, for every eigenvalue and taking $H_0 = p^2 + x^2$ as auxiliary Hamiltonian, are asymptotically divergent for every λ (Bender and Wu 1969, Reed and Simon 1978).

Different resummation techniques have been proposed to compensate for this behaviour. For the QAO, such techniques as Padé approximants (Simon 1970, Pascual 1979), continued fractions (Reid 1967) and the Borel summability method (Graffi *et al* 1970, Marciani 1984) have been applied, getting improved results for $\lambda < 1$ but encountering big problems for larger λ.

Another procedure, which gives excellent results and also has perturbation theory as support, is that due to Killingbeck (1981). The key feature of this method is the inclusion of one or more free parameters in the auxiliary Hamiltonian. Once we have obtained perturbation series for the chosen eigenvalue, these parameters are used to control the series convergence. Returning to the QAO, this is obtained by using, as auxiliary Hamiltonian, a harmonic oscillator with free strength α ($H_0 = p^2 + \alpha^4 x^2$). Killingbeck's criterion for fixing free parameters is related, as we shall see, to the eigenvalue power expansion and gives very good results, as we have already mentioned.

In this comment we investigate high-order perturbative wavefunctions following the basic procedure of Killingbeck. First, we shall discuss a criterion, very similar to Killingbeck's, for perturbative wavefunctions. Second, and due to the characteristics of perturbative wavefunctions, we shall propose the use of the standard variational

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criterion for fixing the free parameters, and we shall see that both criteria lead to the same results.

2. Killingbeck's criterion and the variational criterion

In a general case, the solution of our problem is posed in the following terms. We write H for our problem Hamiltonian and $H_0(\alpha)$ for the auxiliary Hamiltonian, where α denotes all free parameters. First, we use the identity

$$H = H_0(\alpha) + (H - H_0(\alpha)) \tag{1}$$

we shall write $\varepsilon_i(\alpha)$ and $|\phi_i(\alpha)\rangle$, $i = 1, 2, \ldots$, for the eigenvalues and eigenvectors, respectively, of $H_0(\alpha)$, which are analytically known for every α, and E_i and $|\psi_i\rangle$, $i = 1, 2, \ldots$, for the eigenvalues and eigenvectors of H. Then non-degenerate perturbation theory allows us to express (Galindo and Pascual 1978) the eigenvalues and eigenvectors of H as functions of those of $H_0(\alpha)$ and of the perturbation operator $H_1(\alpha)$ $(H_1(\alpha) = H - H_0(\alpha))$. Thus

$$E_i = \varepsilon_i(\alpha) + \sum_{k=1}^{\infty} E_i^{(k)}(\alpha) = \varepsilon_i(\alpha) + \sum_{k=1}^{\infty} \langle \phi_i(\alpha)|H_1(\alpha)|\psi_i^{(k-1)}(\alpha)\rangle \tag{2}$$

$$|\psi_i\rangle = |\phi_i(\alpha)\rangle + \sum_{k=1}^{\infty} |\psi_i^{(k)}(\alpha)\rangle \tag{3}$$

where

$$|\psi_i^{(n)}\rangle = \sum_{i \neq j} \frac{1}{\varepsilon_i - \varepsilon_j}\left(\langle \phi_j|H_1|\psi_i^{(k-1)}\rangle - \sum_{k=1}^{n-1} E_i^{(k)}\langle \phi_j|\psi_i^{(n-k)}\rangle(1 - \delta_{n1})\right)|\phi_j\rangle \tag{4}$$

where for simplicity we have not written the dependence on α. It must be noticed that neither E_i nor $|\psi_i\rangle$ are functions of α; however, when we truncate perturbative series (2) or (3) at some N value (Nth-order approximation), the approximations for eigenvalues $E_{i,N}$ and eigenvectors $|\psi_i\rangle_N$ are dependent on α. As we are not able to sum these series exactly, we shall have to take $E_{i,N}(\alpha)$ and $|\psi_i(\alpha)\rangle_N$, for some N and α, as the solution for our eigenvalue problem. We therefore need an adequate criterion for selecting these values.

Killingbeck has suggested fixing free parameters (α and N) in such a way that the variation of $E_{i,N}$ is equal to zero, i.e. to choose those values that make the perturbative correction $E_i^{(N)}(\alpha)$ vanish. With this condition and working in single precision, the obtained results are, for every eigenvalue and λ, equal in all (eight) figures to those of Banerjee (1978), which we shall hereafter consider exact. For the ground state and $\lambda = 1$, typical values $\alpha = 1.46$ and $N = 12$. When we work in double precision, we also get coincidence in all meaningful figures (fifteen, in this case) with the exact values, although for slightly different values, $\alpha = 1.80$ and $N = 40$ for the mentioned case.

In view of the good results for eigenvalues, we may ask what is the matter with the corresponding wavefunctions. That is, we want to know if $|\psi_i(\alpha)\rangle_N$, with α and N given by the Killingbeck criterion, is a good approximation to the exact eigenvector $|\psi_i\rangle$. This question cannot be answered precisely because we do not know exact solutions.

One possibility is to follow a similar procedure to that followed with eigenvalues. Then we try to see if the Nth-order perturbation contribution to the wavefunction is zero. We do this by studying the norm of the successive contributions to wavefunctions, $|\psi_i^{(N)}(\alpha)\rangle$. In figure 1, we represent the number of exact figures in the perturbative estimation of the eigenvalue, N_p, and the wavefunction, $-\log_{10}\langle\psi_i^{(N)}(\alpha)|\psi_i^{(N)}(\alpha)\rangle$ denoted WF, for the QAO with $\lambda = 1$, over a wide range of N for different states $i = 1$, 5, 15 and 21, and choosing an optimum α for each state. From this we find that both criteria are not at all equivalent. Moreover, we see for lower states, $i = 1$ and 5, the minimum contributions to the wavefunctions appear for lower N than those which make a perturbative contribution to the energy minimum. However, this behaviour turns upside down when we study higher excited states, $i = 15$ and 21.

Obviously, the fact that the perturbative contribution to the wavefunction is small for the optimum parameters does not necessarily imply that we have got a good approximation to the exact wavefunction. Now then, if the approximations are good, it is clear that the expectation values of our Hamiltonian between those functions

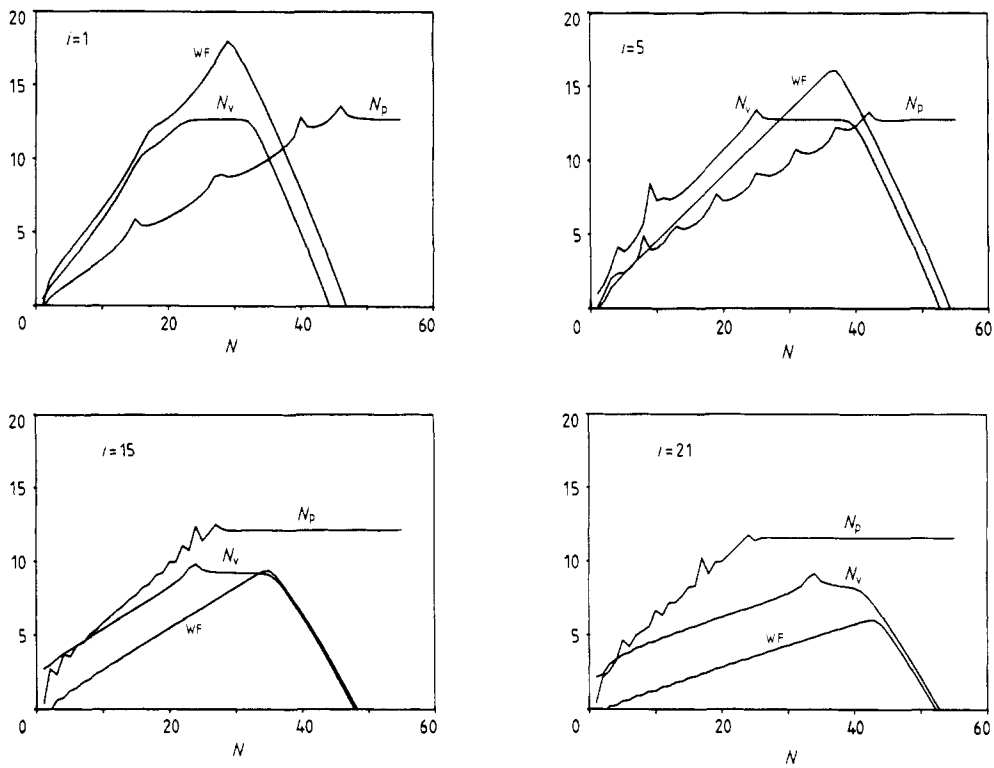

Figure 1. Representation of the numbers of figures N_v and N_p, as given by Banerjee (1978), when taking variational and perturbative results, respectively (we have reduced the number of figures in order to see the stability zones better), and representation of the wavefunction $-\log_{10}\langle\psi_i^{(N)}|\psi_i^{(N)}\rangle$ (denoted by WF). Curves are shown for the ground state $i = 1$ (taking $\lambda = 1$ and values of α from table 1) and for excited states $i = 5$, 15 and 21 (taking $\lambda = 1$ and values of α from table 2). The equivalence between the variational method and the criterion over the perturbative contributions to the wavefunctions is clear for states $i = 1$ and $i = 5$. For higher excited states, we find a loss of precision of the variational calculation in comparison with the perturbative calculation.

(properly normalised) must give good estimates for the corresponding eigenvalues. Therefore, expectation values may be taken as an additional criterion which allows us to gauge how approximate these wavefunctions are to the exact ones. When we make this, we are only using the basic piece of the standard variational criterion, for fixing free parameters, over these perturbative functions.

This last statement leads us to the second criterion that we want to study, i.e. the possibility of taking the successive perturbative approximations to the wavefunctions as trial wavefunctions for a variational calculation. Obviously, α and N are free parameters of these perturbative-variational functions. An important question will be whether the application of the variational criterion, with this kind of function, leads to similar parameter values as those given by Killingbeck's criterion, equally well over eigenvalues and eigenvectors.

The application of standard variational criterion is fine for the ground state because, in this case, we always obtain strict upper bounds to the ground-state energy. However, when we apply it to the excited states, we do not obtain upper bounds unless the trial wavefunctions are orthogonal to the subspace containing all eigenvalues lower than the one we are studying. This enables us to distinguish the ground state from the excited states.

We shall now analyse results obtained with the QAO.

3. Ground state of the QAO

The behaviour of the expectation value

$$E_i(\alpha, N) = \frac{{}_N\langle\psi_i(\alpha)|H|\psi_i(\alpha)\rangle_N}{{}_N\langle\psi_i(\alpha)|\psi_i(\alpha)\rangle_N} \qquad i = 1 \tag{5}$$

for the QAO is quite similar, when we change α and N, to that observed for the perturbative series. Calculating in double precision and, in general, up to $N = 40$, we see that from an α value, we obtain the same energy value, equal in all its figures to the exact value, from an N value ($N_<$) to another ($N_>$). That is, we obtain a stability zone or plateau quite useful for practical purposes. For N greater than $N_>$, the expectation value increases quickly.

In figure 1, for the ground state $i = 1$, we can see this behaviour of N_v, the number of exact figures in the variational estimation of the eigenvalue, for $\lambda = 1$. It is very interesting to note, in this case, that the variational plateau coincides with those orders which make the perturbative contribution to the wavefunction a minimum. This shows that there is an equivalence between variational and Killingbeck's criteria when we apply them over the wavefunction. Moreover, it is evident if we calculate with more precision (quadruple precision); we are able to find only one N that makes the energy a minimum.

In table 1, we give the best upper bounds obtained with quadruple precision. These results are exactly equal, in all figures, to those obtained in other works (Marciani 1984, Banerjee 1978), for every λ.

4. Excited states of the QAO

When we study equation (5), for QAO and $i = 3, 5, \ldots$ (even partity states; we can obtain similar results with odd parity states) we find, in a certain way, a similar

Table 1. Ground-state energies obtained with perturbative-variational wavefunctions for different values of λ. We also give the values of the free parameter α and of the order for which we get the best upper bound. For all cases, we obtain all the figures given in other works.

λ	α	N	Ground-state energy
10^{-2}	1.10	23	1.007 373 672 081 382 460 533 843 905 9828
10^{-1}	1.33	36	1.065 285 509 543 717 688 857 091 629 2238
10^{0}	1.85	35	1.392 351 641 530 291 858 981 126 741 3262
10^{1}	2.70	36	2.449 174 072 118 387 580 466 484 579 2390
10^{2}	3.95	36	4.999 417 545 137 592 083 303 562 721 2092
10^{3}	5.80	36	10.639 788 711 328 057 722 395 045 173 445
10^{4}	8.55	38	22.861 608 870 272 486 236 810 423 457 297

behaviour to that found for the ground state. So, once α is fixed, we obtain, in general, that the first orders for variational energy are lower than the exact values. However, for higher orders, there exists a stability zone, as for the ground state, where we obtain for first excited states, $i < 10$, the exact values given by Banerjee with all their figures; however, for $i > 10$ the precision decreases and for $i = 21$ we obtain coincidence only in the first nine figures. Again, out of stability zone, the variational estimation for energy increases quickly.

In table 2, we give the best variational estimates for some excited states and for different λ values; we also indicate α and N values for each case. On the other hand, we find, again, that the stability zone happens for those orders which make the perturbative correction to the wavefunction a minimum. This confirms the equivalence

Table 2. Variational energies for different excited states and values of λ. It can be seen that we lose precision when studying higher excited states, but not when we make λ bigger. It is important to note that the Killingbeck criterion continues to give good results, with the same precision, for all the cases studied here (see figure 1).

State	λ	α	N	E_ν
	10^{-1}	1.30	15	5.747 959 268 83356
3	1	1.85	30	8.655 049 957 75931
	10^{3}	5.85	31	74.681 404 200 164
	10^{-1}	1.30	15	11.098 595 622 6330
5	1	1.90	31	18.057 557 436 3033
	10^{3}	5.91	32	162.802 374 196 97
	10^{-1}	1.30	15	16.954 794 686 1442
7	1	1.90	31	28.835 338 459 5042
	10^{3}	6.01	32	265.519 951 678 2
	10^{-1}	1.40	26	44.076 208 925 2941
15	1	1.95	30	81.243 505 050
	10^{3}	6.17	28	773.133 614
	10^{-1}	1.40	24	51.594 517 194 7501
17	1	2.00	30	96.129 642 04
	10^{3}	6.23	28	918.418 407
	10^{-1}	1.43	27	67.359 251 896 5495
21	1	2.05	33	127.617 777
	10^{3}	6.33	26	1226.552 29

between the variational and Killingbeck criteria when the last one is made over the wavefunction for this kind of trial function.

Up to now, we have not worried about the orthogonality, to the subspace which contains all states with lower energy, necessary for the application of the variational criterion to the excited states to give strict upper bounds on the energy of these states. Nevertheless, it is evident if our set of trial wavefunctions contains in its domain the exact functions (or good approximations to them) then our optimum functions will be orthogonal (or almost orthogonal) to each other. A calculation of overlaps between our optimum functions for the ground and some excited states (contained in table 2, see table 3) shows that these overlaps are very small. These are, in all cases, about 10^5 times smaller than the overlaps between the best approximations when we use only one oscillator function, and always less than 10^{-7}. These comparisons show, in a certain way, that the orthogonality condition is well satisfied. This confirms that, at least for the first excited states, we have very good approximations to the exact wavefunctions. However, the increasing overlap, when we study higher and higher excited states, leads to a worsening for the expectation value. Similarly, the norm values of the perturbative contributions to the wavefunction also increase in the corresponding plateau, as shown by the progression $i = 1, 5, 15, 21$ in figure 1.

Table 3. Overlap between some states used in the calculations of tables 1 and 2. Results show that orthogonality is almost satisfied, although this is lost when we study higher and higher excited states. Results are again independent of λ. Values in brackets are the overlaps between the best variational approximations when we use only one oscillator function, with free strength.

Overlap	$\lambda = 10^{-1}$	$\lambda = 1$	$\lambda = 10^3$
$\lvert\langle 1\rvert 3\rangle\rvert$	1.8×10^{-7} $(4.3=10^{-2})$	7.3×10^{-9} (8.8×10^{-2})	2.4×10^{-7} (1.1×10^{-1})
$\lvert\langle 1\rvert 5\rangle\rvert$	3.1×10^{-1} (7.4×10^{-3})	2.6×10^{-8} (2.5×10^{-2})	1.3×10^{-7} (3.7×10^{-2})
$\lvert\langle 1\rvert 15\rangle\rvert$	9.7×10^{-13} (2.1×10^{-5})	2.7×10^{-10} (4.0×10^{-3})	5.4×10^{-10} (9.7×10^{-4})
$\lvert\langle 1\rvert 21\rangle\rvert$	1.9×10^{-13} (1.3×10^{-2})	3.4×10^{-10} (5.9×10^{-5})	1.6×10^{-9} (1.8×10^{-4})
$\lvert\langle 3\rvert 5\rangle\rvert$	6.4×10^{-8} (8.7×10^{-2})	6.8×10^{-8} (1.4×10^{-1})	2.2×10^{-7} (1.6×10^{-1})
$\lvert\langle 3\rvert 15\rangle\rvert$	1.1×10^{-10} (1.6×10^{-4})	5.3×10^{-9} (1.1×10^{-3})	4.9×10^{-9} (1.9×10^{-3})
$\lvert\langle 3\rvert 21\rangle\rvert$	2.2×10^{-12} (8.7×10^{-6})	3.1×10^{-9} (1.2×10^{-4})	1.4×10^{-8} (2.4×10^{-4})
$\lvert\langle 5\rvert 15\rangle\rvert$	6.9×10^{-10} (6.3×10^{4})	3.6×10^{-10} (2.5×10^{-3})	1.3×10^{-8} (3.6×10^{-3})
$\lvert\langle 5\rvert 21\rangle\rvert$	4.0×10^{-11} (2.9×10^{-5})	5.2×10^{-9} (2.0×10^{-4})	6.2×10^{-8} (3.5×10^{-4})
$\lvert\langle 15\rvert 21\rangle\rvert$	1.4×10^{-7} (1.0×10^{-2})	3.7×10^{-5} (1.7×10^{-2})	2.2×10^{-5} (2.0×10^{-2})

5. Conclusions

We want to remark on several important aspects of our findings. Firstly, the inclusion of adequate free parameters in perturbative theory enables us to obtain not only good estimates for the eigenvalues but also a set of excellent trial wavefunctions, which can be fitted by the variational method. It is important to point out that these functions not only give good values for the energy but they also have other properties which, at least for the QAO, seem to indicate that they are very good approximations for the wavefunctions of ground and first excited states.

Second, we should like to emphasise, apart from the parallelism found between the variational method and the criterion over the perturbative contributions to wavefunctions, the behaviour of these criteria compared with the results from the Killingbeck criterion. For ground and first excited states, we obtain the same results for eigenvalues although the variational method gives them for lower orders than does the Killingbeck criterion. This behaviour changes for higher excited states. However, for all cases, approximations to wavefunctions given by the criterion over the norm are better than those from the Killingbeck criterion, because they give better expectation values. It is important to note that the Killingbeck criterion over the eigenvalues gives better results for energy than the others when we go to higher excited states, as seen in figure 1.

In conclusion, we remark that it is evident that this treatment cannot easily be applied to any kind of Hamiltonian because, to obtain good results, we need to take into account very high orders and to calculate many expectation values. For this we need an analytical procedure for evaluating these expectation values. Therefore perturbative-variational functions are useful only for the potentials which admit analytical treatments for their matrix elements. The practical realisation of the calculation will depend not only on the potential but also on the auxiliary Hamiltonian that is used. In the same way, the accuracy of the approximation that is used will depend on the relation between the auxiliary Hamiltonian and the problem Hamiltonian. This makes more difficult the practical application of the method.

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