On the Variational Treatment of a Class of Double-Well Oscillators

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Article

On the Variational Treatment of a Class of Double-Well Oscillators

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Abstract: We compare the well known Rayleigh-Ritz variational method (RRVM) with a recently proposed approach based on supersymmetric quantum mechanics and the Gram-Schmidt orthogonalization method (SSQMGS). We apply both procedures to a particular class of double-well harmonic oscillators that had been conveniently chosen for the application of the latter approach. The RRVM eigenvalues converge smoothly from above providing much more accurate results with less computational effort. Present results show that the unproved SSQMGS upper bounds do not hold.

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1. Introduction

There has been some interest in the calculation of the eigenvalues and eigenfunctions of rather simple one-dimensional Hamiltonians with double-well potentials because they are supposed to be useful for the calculation of the probability density for the one-dimensional Fokker-Planck equation[1, 2]. In a paper appeared recently, Batael and Drigo Filho[3] proposed a variational method that is supposed to yield upper bounds to all the eigenvalues of the Hamiltonian. They constructed the variational wavefunctions by means of supersymmetric quantum mechanics (SSQM) and the Gram-Schmidt (GM) orthogonalization method but did not provide a plausible proof for those bounds. From now, on we will refer to this approach as SSQMGS.

The well known Rayleigh-Ritz variational method (RRVM), discussed in most textbooks on quantum chemistry[4,5], is known to provide upper bounds to all the eigenvalues of a given Hamiltonian operator[6] (see also a recent simpler proof of the RRVM upper bounds[7]). In our opinion, it is interesting to compare the SSQMGS and the RRVM because they apparently exhibit somewhat similar features.

In section 2 we discuss the one-dimensional quantum-mechanical models and the approximate method used for obtaining their eigenvalues. In section 3 we compare and discuss the eigenvalues provided by SSQMGS and RRVM.

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2. Models and methods

Batael and Drigo Filho[3] obtained some eigenvalues of a particular class of simple quantum-mechanical models of the form

$$H = -\frac{d^2}{dx^2} + V(x),\ V(x) = \sum_{j=0}^{2K-1} A_{2j} x^{2j},\ K = 2, 3, \tag{1}$$

that are amenable for the application of SSQM. We can provide an alternative sound reason for this choice without resorting to SSQM.

From a square-integrable exponential function

$$\psi_0(x) = e^{-F(x)}, \tag{2}$$

we can obtain a reference potential $V_0(x)$ as follows

$$\frac{\psi_0''}{\psi_0} = F'^2 - F'' = V_0 - E_0,\ F(x) = \sum_{j=0}^{K} F_j x^{2j},\ F_K > 0. \tag{3}$$

For some particular values of the coefficients A_j we can choose F_j so that $V_0(x) = V(x)$. In this case both $\psi_0(x)$ and E_0 are exact and the SSQMGS is expected to yield the most accurate results.

For example, when $K = 2$ the requirement for $V_0(x) = V(x)$ is that the coefficients A_j satisfy

$$4a_2a_6 - a_4^2 + 12a_6^{3/2} = 0, \tag{4}$$

while for $K = 3$ we have two restrictive conditions

$$\begin{aligned} 4a_{10}a_6a_8 - 40a_{10}^{5/2} - 8a_{10}^2a_4 - a_8^3 &= 0, \\ 16a_{10}^2a_6^2 - 64a_{10}^3a_2 - 96a_8a_{10}^{5/2} - 8a_{10}a_6a_8^2 + a_8^4 &= 0. \end{aligned} \tag{5}$$

The role of A_0 is irrelevant because it is just a shift of E_0.

Since the potential $V(x)$ is parity invariant, then the eigenfunctions of H have definite parity (they are either even or odd). This fact enables us to apply the approximate methods to each symmetry thus reducing considerably the computation time.

The RRVM is based on trial functions of the form

$$\varphi^{[N]} = \sum_{j=0}^{N-1} c_j f_j, \tag{6}$$

where $B = \{f_0, f_1, \ldots\}$ is a complete set of basis functions. The variational principle leads to a secular equation of the form

$$(\mathbf{H} - E\mathbf{S})\,\mathbf{c}, \tag{7}$$

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where the $N \times N$ matrices $\mathbf{H}$ and $\mathbf{S}$ have elements $H_{ij} = \langle f_i | H | f_j \rangle$ and $S_{ij} = \langle f_i | f_j \rangle$, respectively, and $\mathbf{c}$ is a column vector of the expansion coefficients c_j[4,5]. The approximate eigenvalues $E_i^{[N]}$, $i = 0, 1, \ldots, N-1$, are roots of the secular determinant $|\mathbf{H} - E\mathbf{S}|$ that yields the characteristic polynomial $p(E)$. It can be proved that $E_n^{[N-1]} > E_n^{[N]} > E_n$, where E_n is an exact eigenvalue of H[6,7]. For each $E_n^{[N]}$ we obtain $\varphi_n^{[N]}$ and it can be proved that $\left\langle \varphi_i^{[N]} \middle| \varphi_j^{[N]} \right\rangle = 0$ if $E_i^{[N]} \neq E_j^{[N]}$. Obviously, in the case of present one-dimensional toy models there are no degenerate states and $\left\langle \varphi_i^{[N]} \middle| \varphi_j^{[N]} \right\rangle = 0$ if $i \neq j$. In particular, when the basis set B is orthonormal then $\mathbf{S} = \mathbf{I}$ (the $N \times N$ identity matrix).

It follows from $\left\langle \varphi_i^{[N]} \middle| H \middle| \varphi_j^{[N]} \right\rangle = \left\langle \varphi_i^{[N]} \middle| \varphi_j^{[N]} \right\rangle E_i^{[N]}$[7] that

$$E_i^{[N]} = \frac{\left\langle \varphi_i^{[N]} \middle| H \middle| \varphi_i^{[N]} \right\rangle}{\left\langle \varphi_i^{[N]} \middle| \varphi_i^{[N]} \right\rangle} > E_i, \tag{8}$$

that resembles the SSQMGS expression (equation (8)) reported by Batael and Drigo Filho[3] without proof. More precisely, one can prove rigorously that the bounds proposed by these authors apply to the ground state and first-excited state that have the smallest energy for each symmetry (provided, of course, that the trial functions have the appropriate symmetry). However, as far as we know, there is no proof for the remaining states (as in the case of the RRVM[6,7]). The outcome of upper bounds and orthogonal approximate wavefunctions make the RRVM and the SSQMGS look similar, with the difference that in the latter case the upper bounds have not been rigorously proved, except in the two cases just mentioned.

When the potential is parity invariant, we can apply the RRVM to each kind of symmetry thus reducing the dimension of the matrices involved in the calculation.

The simplest basis set is given by the eigenfunctions of the Harmonic oscillator

$$H_{HO} = -\frac{d^2}{dx^2} + \omega^2 x^2. \tag{9}$$

Although the asymptotic behaviour of the eigenfunctions of H_{HO} is quite different from that of the problems discussed here, such eigenfunctions exhibit two advantages. First, we already know that this orthonormal basis set is complete and, second, the matrix elements H_{ij} can be calculated exactly without difficulty.

In principle, we can resort to a set of basis functions with suitable asymptotic behaviour[8] but it is not necessary for present discussion.

There are many ways of obtaining a suitable value of ω; here we arbitrarily resort to the condition

$$\frac{d}{d\omega} \sum_{j=0}^{M} H_{jj}(\omega) = 0, \; M \leq N. \tag{10}$$

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3. Results and discussion

We first consider the example with $K = 2$, $A_0 = 1$, $A_2 = A_4 = -2$ and $A_6 = 1$ that allows an exact ground state ψ_0 with $E_0 = 0$. The ansatz used by Batael and Drigo Filho[3] is a curious linear combination of functions with no definite parity which is not convenient for a parity-invariant Hamiltonian operator. They chose the nonlinear parameter $c_0 = 0$ that leads to the exact ground-state eigenfunction ψ_0 (of even parity) but it is not clear why they kept the nonlinear parameter c_n in the exponential factors of the other trial functions ψ_n. Although Batael and Drigo Filho mentioned the advantage of the separate treatment of even and odd states, their ansätze do not reflect this fact. Another curious feature of their approach is the choice of Legendre Polynomials that are known to be orthogonal in the interval $[-1, 1]$ when in the present case the variable interval is $(-\infty, \infty)$.

Tables 1 and 2 show the convergence of the lowest RRVM eigenvalues towards results that are supposed to be accurate up to the last digit. We estimated ω from equation (10) with $M = 10$ and arbitrarily chose an integer value close to the real root. Although the rate of convergence depends on ω, the choice of an optimal value of this adjustable parameter is not that relevant. As expected, the RRVM eigenvalues converge from above[4–7]. Note that Batael and Drigo Filho[3] did not report the eigenvalues E_n of this model but $\lambda_n = E_n/2$ as in reference[1]. Although the RRVM requires about 25 basis functions for a ten-digit accuracy, the calculation is extremely simple because it only requires the diagonalization of matrices $\mathbf{H}$ with elements H_{ij} that can be obtained analytically. On the other hand, the SSQMGS is considerably cumbersome because it requires the numerical calculation of all the integrals and minimization of the approximate energy that is a function of nonlinear parameters. Besides, the accuracy of these results cannot be improved any further.

In the second example we also have $K = 2$, but since $A_0 = 0$, $A_2 = -26$, $A_4 = 6$ and $A_6 = 1$ then there is no exact ground state. Tables 3 and 4 show the the convergence of the lowest RRVM eigenvalues towards results that are also supposed to be accurate up to the last digit. We estimated ω as in the previous example. In this case, we appreciate that the SSQMGS eigenvalues E_4 and E_6 do not provide upper bounds which suggests that the equation (8) of Batael and Drigo Filho[3] does not hold. This fact is not surprising because, as stated above, such bounds were not proved rigorously.

The last example is given by $K = 3$, $A_0 = 0$, $A_2 = 3/2$, $A_4 = -5/2$, $A_6 = 1/4$, $A_8 = -1/2$ and $A_{10} = 1/4$. In this case there is an exact ground state ψ_0 with $E_0 = 0$. The RRVM eigenvalues are shown in Tables 5 and 6 together with those of Batael and Drigo Filho.

It is worth comparing the performances of the RRVM and the SSQMGS. The former approach provides eigenvalues of unlimited accuracy (depending only on hardware and software facilities) that converge towards the exact energies from above. On the other hand, the accuracy of the SSQMGS eigenvalues is determined by the accuracy of the initial ansatz ψ_0. Batael and Drigo Filho chose a particular class of potentials for which one can obtain the exact ψ_0 or at least a sufficiently accurate trial function with the appropriate asymptotic behaviour. Such models are of the form illustrated in section 2. Batael and Drigo Filho reported more digits than the actual accuracy of their results. Present RRVM eigenvalues are even more accurate than those used by Batael and Drigo Filho as benchmark.

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While it has already been proved that the RRVM provides upper bounds to the energies of all the states[6,7] such proof is lacking in the case of the SSQMGS and we have already pointed out two cases in which the latter approach fails to provide such bounds. As is well known, one counterexample is sufficient to prove an statement false.

Table 1. RRVM even-state eigenvalues for $A_0 = 1$, $A_2 = A_4 = -2$, $A_6 = 1$ with $\omega = 4$

N	E_0	E_2	E_4	E_6
5	0.02	4.677918651	14.53469054	28.3757404
10	6.6×10^{-6}	4.62986462	14.35154075	27.52416887
15	1.5×10^{-8}	4.629826578	14.3509522	27.51712162
20	8.6×10^{-11}	4.629826494	14.35095078	27.51709995
25	9.7×10^{-13}	4.629826493	14.35095078	27.5170999
30	2.5×10^{-15}	4.629826493	14.35095078	27.5170999
$E_n/2$		2.314913246	7.17547539	13.75854995
Ref.[3]	0	2.31799	7.18145	13.7670

Table 2. RRVM odd-state eigenvalues for $A_0 = 1$, $A_2 = A_4 = -2$, $A_6 = 1$ with $\omega = 4$

N	E_1	E_3	E_5	E_7
5	0.8655650394	9.111949632	20.98289274	36.23196314
10	0.8459004855	9.007614525	20.55620684	35.17488491
15	0.8458893236	9.007557826	20.55577168	35.16841201
20	0.845889291	9.007557632	20.55577029	35.16839427
25	0.8458892907	9.00755763	20.55577028	35.16839416
30	0.8458892907	9.00755763	20.55577028	35.16839416
$E_n/2$	0.4229446453	4.503778815	10.27788514	17.58419708
Ref.[3]	0.42388	4.50813	10.2852	17.5941

Table 3. RRVM even-state eigenvalues for $A_0 = 0$, $A_2 = -26$, $A_4 = 6$, $A_6 = 1$ with $\omega = 5$

N	E_0	E_2	E_4	E_6
5	−14.39416156	−2.418081882	6.897731829	23.83165889
10	−14.47163202	−2.523730405	6.599680377	21.61724028
15	−14.47165595	−2.523911539	6.59851881	21.60602543
20	−14.47165597	−2.523911704	6.598517525	21.60600654
25	−14.47165597	−2.523911705	6.598517524	21.60600652
30	−14.47165597	−2.523911705	6.598517524	21.60600652
Ref.[3].	−14.4483	−2.42763	6.596869	21.56765

Table 4. RRVM odd-state eigenvalues for $A_0 = 0$, $A_2 = -26$, $A_4 = 6$, $A_6 = 1$ with $\omega = 5$

N	E_1	E_3	E_5	E_7
5	−14.3640557	−0.4515691057	13.89792265	32.55127969
10	−14.42792517	−0.6900912613	13.35318022	30.73875482
15	−14.42794579	−0.690175821	13.3524621	30.7269972
20	−14.42794583	−0.6901759943	13.3524612	30.72698225
25	−14.42794583	−0.6901759952	13.35246119	30.72698222
30	−14.42794583	−0.6901759952	13.35246119	30.72698222
Ref.[3].	−14.4135	−0.65821	13.36402	

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Table 5. RRVM even-state eigenvalues for $A_0 = 0$, $A_2 = 3/2$, $A_4 = -5/2$, $A_6 = 1/4$, $A_8 = -1/2$, $A_{10} = 1/4$ with $\omega = 5$

N	E_0	E_2	E_4	E_6
5	0.09	4.573017185	16.36066839	34.15352004
10	0.002	4.32310851	15.61645666	31.68651075
15	6.1×10^{-5}	4.315907553	15.58461237	31.54805825
20	1.8×10^{-6}	4.315700166	15.58363087	31.54320834
25	$2.1 \times 10^{-}7$	4.31569472	15.58360629	31.54308125
30	7.6×10^{-10}	4.315694041	15.58360331	31.54306785
35	1.0×10^{-9}	4.315694019	15.58360321	31.54306732
40	1.1×10^{-10}	4.315694016	15.58360319	31.54306723
45	8.5×10^{-12}	4.315694015	15.58360319	31.54306722
50	7.6×10^{-13}	4.315694015	15.58360319	31.54306722
Ref.[3].	0	4.31612	15.5851	31.5460

Table 6. RRVM odd-state eigenvalues for $A_0 = 0$, $A_2 = 3/2$, $A_4 = -5/2$, $A_6 = 1/4$, $A_8 = -1/2$, $A_{10} = 1/4$ with $\omega = 5$

N	E_1	E_3	E_5	E_7
5	1.256573678	9.855150686	24.44520554	44.68121271
10	1.048870482	9.357073321	23.02789536	41.29594435
15	1.046988529	9.351398959	23.00064258	41.16116412
20	1.046927491	9.351217587	22.9997951	41.15687172
25	1.046922323	9.351202299	22.99972988	41.15661593
30	1.046922115	9.351201593	22.99972602	41.15659472
35	1.046922092	9.351201522	22.99972569	41.15659332
40	1.046922091	9.351201519	22.99972568	41.15659324
45	1.046922091	9.351201519	22.99972568	41.15659323
50	1.046922091	9.351201519	22.99972568	41.15659323
Ref.[3].	1.04703			

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