Dirichlet and von Neumann Basis Set for Quantum Mechanical Anharmonic Oscillators

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It is shown that accurate upper and lower bounds to the eigenvalues of anharmonic oscillators can be obtained by means of the Rayleigh-Ritz variational method and two trigonometric basis sets of functions which satisfy Dirichlet and Von Neumann boundary conditions. Numerical results show that the Dirichlet basis set is more appropriate than the harmonic oscillator one for calculating eigenvalues and the value of eigenfunctions at the origin.

1. Introduction

The anharmonic oscillators

$$H(\omega, \lambda, k) = -(1/2)\,(\mathrm{d}^2/\mathrm{d}x^2) + \omega^2 x^2/2 + \lambda\, x^{2k}, \qquad (1)$$

have been widely studied during the last years due to their great usefulness in many branches of Physics and Chemistry [1], [2] (and references cited therein). Several methods were proposed to obtain their eigenfunctions ψ_i and their associated eigenvalues E_i. One of them, which we are going to discuss here, is the Rayleigh-Ritz (RR) variational method. As is well-known, it consists in approximating the eigenfunctions ψ_i by means of a linear combination ψ_i

$$\psi_i = \sum_{j=1}^{N} c_{ji}\, \varphi_j\,; \quad i = 1, 2, \ldots, N\,, \qquad (2)$$

where $\{\varphi_j\}$ is some given basis set. The coefficients c_{ji} and the approximate eigenvalues ε_i are provided by solving the secular equations

$$\sum_{j=1}^{N} (\langle \varphi_i | H\, \varphi_j \rangle - \varepsilon_i \langle \varphi_i | \varphi_j \rangle)\, c_{ji} = 0\,; \quad i = 1, 2, \ldots, N\,. \qquad (3)$$

These RR eigenvalues are upper bounds to the exact ones [3], [4].

The natural basis set for the problem (1) seems to be the set of harmonic oscillator (HO) eingenfunctions, but we shall show here that this is not the best choice.

In Sect. 2 we discuss some useful properties of two sets of trigonometric functions which obey Dirichlet (D) and Von Neumann (VN) boundary conditions. The RR eigenvalues provided by these basis sets are, under certain conditions, upper and lower bounds to the exact eigenenergies, respectively.

Further in Sect. 3, we show that these basis sets are more suitable than the harmonic oscillator eigenfunctions to calculate the eigenvalues of problem (1), especially when k is large enough. Besides, the convergence rate provided by the trigonometric functions when calculating $\Psi_i(0)$ is higher than the showed by the harmonic oscillator basis set.

Finally in Sect. 4, we discuss briefly the importance of the results obtained in previous sections as well as the possibility of applying the proposed procedure to more complex models which are of great interest in many areas of Physics and Chemistry.

2. Dirichlet and Von Neumann basis sets

When $\omega = 0$ and $k \to \infty$, the Hamiltonian (1) describes a particle of unit mass ($\hbar = 1$) moving inside a box of length $L = 2$ bounded with impenetrable walls. This fact suggests that the set of functions.

$$\varphi_i^{\mathrm{D}} = b^{-1/2} \sin \left\{ \frac{i+1}{2} \left(\frac{x}{b} - 1 \right) \right\}; \quad i = 0, 1, 2, \ldots, \qquad (4)$$

could be appropriate for studying the problem (1) when k is large. The superscript D means that φ_i^{D} satisfies Dirichlet boundary conditions i.e.

$$\varphi_i^{\mathrm{D}}(-b) = \varphi_i^{\mathrm{D}}(b) = 0\,. \qquad (5)$$

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It is clear that φ_i^{D} is the ith eigenstate of a particle in a box of length $L = 2b$.

If $\{\psi_i^{\mathrm{D}}\}$ and $\{\varepsilon_i^{\mathrm{D}}\}$ ($i = 1, 2, \ldots, N$) are the approximate eigenfunctions and eigenvalues, respectively, obtained from the RR variational method, it can be demonstrated that [5]

$$\varepsilon_i^{\mathrm{D}}(b) \geqq E_i\,; \quad \lim_{N, b \to \infty} \varepsilon_i^{\mathrm{D}}(b) = E_i\,. \tag{6}$$

Thus, if we use (4) to obtain the eigenvalues and eigenfunctions of (1) we are sure from (6) that the greater the N- and b-values are, the more accurate the results are.

A very good test of accuracy of the results is the well-known virial theorem [5–7]

$$\lim_{N, b \to \infty} (\langle \psi_i^{\mathrm{D}} \mid \mathrm{d}^2 \psi_i^{\mathrm{D}}/\mathrm{d}x^2 \rangle + \omega^2 \langle \psi_i^{\mathrm{D}} \mid x^2 \psi_i^{\mathrm{D}} \rangle + 2k\,\lambda\,\langle \psi_i^{\mathrm{D}} \mid x^{2k} \psi_i^{\mathrm{D}} \rangle) = 0\,. \tag{7}$$

By means of the RR variational method we can obtain lower bounds too, if we use the basis set

$$\varphi_i^{\mathrm{VN}} = \{b^{-1/2} + \delta_{i0}((2b)^{-1/2} - b^{-1/2})\} \cdot \cos\left\{\frac{i\,\pi}{2}\left(\frac{x}{b} - 1\right)\right\}, \quad i = 0, 1, 2, \ldots. \tag{8}$$

Here the superscript VN means that φ_i^{VN} satisfies Von Neumann boundary conditions

$$(\mathrm{d}\varphi_i^{\mathrm{VN}}/\mathrm{d}x)\,(-b) = (\mathrm{d}\varphi_i^{\mathrm{VN}}/\mathrm{d}x)\,(b) = 0\,. \tag{9}$$

If $\{\varepsilon_i^{\mathrm{VN}}\}$ and $\{\psi_i^{\mathrm{VN}}\}$ are the eigenvalues and eigenfunctions obtained from the secular equations (3), it follows that ψ_i^{VN} will satisfy (9) for all N- and b-values and [8, 9]

$$\lim_{N \to \infty} \varepsilon_0^{\mathrm{VN}}(b) \leqq E_0\,, \tag{10a}$$

$$\lim_{N \to \infty} \varepsilon_i^{\mathrm{VN}}(b) \leqq E_i; \quad i \neq 0 \quad \text{if} \quad b \geqq b_0\,, \tag{10b}$$

$$\lim_{N \to \infty} (\partial \varepsilon_i^{\mathrm{VN}}/\partial b)\,(b_0) = 0\,, \tag{10c}$$

$$\lim_{N, b \to \infty} \varepsilon_i^{\mathrm{VN}}(b) = E_i\,. \tag{10d}$$

The larger the N- and b-values are, the closer is $\varepsilon_i^{\mathrm{VN}}$ to E_i. Also in this case the exactness of the results can be tested by means of the virial theorem (7) [8, 9].

The aforementioned properties of the basis sets (4) and (8) lead to an efficient procedure to calculate the eigenvalues of problem (1). It consists in solving the secular equations (3) for the two basis sets and increasing the values of N and b till both the virial theorem (7) and the equality $\varepsilon_i^{\mathrm{D}} = \varepsilon_i^{\mathrm{VN}}$ are fulfilled up to the desired degree of accuracy. To avoid large matrices one can work with even and odd functions separately.

3. Results and Discussion

Tables I and II show the first five eigenvalues of H (1, 1/2, 3) and H (1, 1/2, 4), respectively, obtained with $N = 30$ basis functions in each case. Numerical results confirm the theoretical conclusions obtained in the previous section. In fact we can see that $\varepsilon_i^{\mathrm{D}} \geqq E_i$ for all b-values and that $\varepsilon_i^{\mathrm{VN}} \leqq E_i$ whenever $b \geqq b_0$ (the exact b_0-value is of no relevance for us).

In general, and as we can see in Tables I and II, the b-value for which convergence is reached becomes smaller while increasing k. Thus, the kinetic energy ($\propto b^{-2}$) counterbalances the potential one ($\propto b^{2k}$). The numerical calculations show clearly that the larger the k value, the better are the eigenvalues obtained with the trigonometric functions. On the contrary, results obtained by means of the harmonic oscillator basis set become worse as k increases. This is due to the fact that for larger k-values the potential function of (1) resembles the particle-in-a-box potential more than the harmonic oscillator one.

Although our RR eigenfunctions and eigenvalues satisfy both the virial theorem (7) and the equality $\varepsilon_i^{\mathrm{D}} = \varepsilon_i^{\mathrm{VN}}$, we have added, as another test of accuracy, the eigenvalues obtained by Hioe et al. [1] at the bottom of each table.

The results obtained with the trigonometric basis sets are better than those yielded by the harmonic oscillator eigenfunctions also when calculating quantities other than eigenvalues. In what follows, we discuss the success of the aforesaid basis sets in calculating $\Psi_i(0)$ because these quantities possess an actual physical interest [10, 11] (and references cited therein).

In Table III we show the $\psi_i(0)$-values for the first six even states of the harmonic oscillator obtained with $N = 30$ Dirichlet basis functions and $b = 7.5$ (convergence up to the last decimal place). The results are in total agreement with the exact values

$$\Psi_{2i}^2(0) = \pi^{-1/2}\,2^{-2i}(i!)^{-2}(2i)!\,. \tag{11}$$

In order to show that the Dirichlet basis set is better than the harmonic oscillator one for computing $\Psi_i(0)$, we have calculated $\psi_i^{\mathrm{D}}(0)$ ($N = 30$) and $\psi_i^{\mathrm{HO}}(0)$ ($N = 30, 40$). Results are shown in Table IV together with those provided by a scaled harmonic

Table 1. First five eigenvalue of H (1, 1/2, 3).

b		ε_0	ε_1	ε_2	ε_3	ε_4
1.0	D	1.3070738	5.1030984	11.303292	19.954390	31.065538
	VN	0.22693699	1.6296045	5.2491295	11.382887	20.002129
1.5	D	0.76515291	2.7728591	5.7551064	9.7411668	14.758629
	VN	0.64294024	2.1392182	4.0888988	6.7203952	10.360785
2.0	D	0.71799710	2.5180649	4.9894518	8.0162851	11.518351
	VN	0.71758975	2.5150216	4.9755631	7.9664074	11.3678898
2.5	D	0.71781231	2.5166980	4.9833111	7.9947208	11.455092
	VN	0.71781231	2.5166980	4.9833109	7.9947200	11.455089
3.0	D	0.71781231	2.5166980	4.9833110	7.9947204	11.455090
	VN	0.71781231	2.5166980	4.9833110	7.9947204	11.455090
Ref. [2]		0.717812	2.51670	4.98331	7.99472	11.4551

Table 2. First five eigenvalue of H (1, 1/2, 4).

b		ε_0	ε_1	ε_2	ε_3	ε_4
1.0	D	1.3029469	5.0909555	11.285952	19.935748	31.047131
	VN	0.21253827	1.6028376	5.2285775	11.368002	19.988794
1.5	D	0.77068027	2.8159475	5.8870654	9.9876133	15.107257
	VN	0.70403540	2.4648615	4.8750315	7.8767762	11.599279
2.0	D	0.74551143	2.6843987	5.4969080	9.0956827	13.372125
	VN	0.74550827	2.6843780	5.4968237	9.0953974	13.371260
2.5	D	0.74550995	2.6843890	5.4968687	9.0955500	13.371724
	VN	0.74550995	2.6843890	5.4968687	9.0955500	13.371724
Ref. [2]		0.74551	2.6844	5.4969	9.0956	

Table 3. $\psi_i^2(0)$-values for the harmonic oscillator calculated with Dirichlet basis set ($N = 30$).

b	$i = 0$	$i = 1$	$i = 2$	$i = 3$	$i = 4$	$i = 5$
1	1.0144710	0.99360984	0.99743597	0.99865682	0.99917895	0.99944748
2	0.60315426	0.46047994	0.48028993	0.48939111	0.49347123	0.49559533
3	0.56478435	0.29847515	0.28181385	0.29969981	0.31184280	0.31867252
4	0.56419050	0.28221725	0.21453949	0.19576527	0.20404717	0.21644838
5	0.56418958	0.28209485	0.21157667	0.17648077	0.15639688	0.14987448
6	0.56418958	0.28209479	0.21157109	0.17630930	0.15427298	0.13889425
7	0.56418958	0.28209479	0.21157109	0.17630924	0.15427059	0.13884353
7.5	0.56418958	0.18109479	0.21157109	0.17630924	0.15427059	0.13884353
Exact	0.564189583	0.181094791	0.211571093	0.176309244	0.154270589	0.138843530

Table 4. $\psi_i(0)^2$-values of H (0, 1, 2) calculated with Dirichlet basis set ($\psi_i^{\mathrm{D}}(0)^2$, $b = 4.5$), harmonic oscillator basis set ($\psi_i^{\mathrm{HO}}(0)^2$ and scaled harmonic oscillator basis set ($\psi_i^{\mathrm{HO}}(a, 0)^2$).

N		$i = 0$	$i = 1$	$i = 2$	$i = 3$	$i = 4$	$i = 5$
30	$\psi_i^{\mathrm{D}}(0)^2$	0.70574955	0.51690397	0.42587718	0.37703201	0.34489029	0.32148467
	$\psi_i^{\mathrm{HO}}(0)^2$	0.70574948	0.51690328	0.42589481	0.37695145	0.34435124	0.32583023
	$\psi_i^{\mathrm{HO}}(a, 0)^2$	0.70574955	0.51690397	0.42587718	0.37703208	0.34489004	0.32148279
40	$\psi_i^{\mathrm{HO}}(0)^2$	0.70574955	0.51690401	0.42587663	0.37703423	0.34490999	0.32131407
	$\psi_i^{\mathrm{HO}}(a, 0)^2$	0.70574955	0.51690397	0.42587718	0.37703201	0.34489029	0.32148468

Table 5. $\psi_i(0)^2$-values of H (0, 1, 3), H (0, 1, 4), H (1, 1/2, 2), H (1, 1/2, 3), H (1, 1/2, 4) calculated with Dirichlet basis set ($N = 30$ and b large enough to reach convergence).

(ω, λ, k, b)	$i = 0$	$i = 1$	$i = 2$	$i = 3$	$i = 4$	$i = 5$
(0, 1, 3, 3.5)	0.72835218	0.61632430	0.53613215	0.48994576	0.45848716	0.43504380
(0, 1, 4, 3)	0.74727649	0.67619636	0.61084310	0.56907233	0.53991504	0.51783861
(1, 1/2, 2, 4.5)	0.69674030	0.46148967	0.38016065	0.33637338	0.30758944	0.28664996
(1, 1/2, 3, 3.5)	0.72071051	0.55527623	0.48728547	0.44652154	0.41844861	0.39740430
(1, 1/2, 4, 3)	0.7419875	0.61826615	0.56701340	0.52787023	0.50163655	0.48158158

oscillator basis set $\{\varphi_i^{HO}(a, x) = a^{1/2}\, \varphi_i^{HO}(a\, x)\}$ ($N = 30, 40$) where the scale parameter a was determined in such a way that $\langle \varphi_0^{HO}(a, x) \mid H\, \varphi_0^{HO}(a, x)\rangle$ reaches its minimum value. Table IV shows, beyond any doubt, that $\psi_i^D(0)$ converges more quickly to the exact value than $\psi_i^{HO}(0)$ and $\psi_i^{HO}(a, 0)$, when N increases. In fact, when passing from $N = 30$ to $N = 40$ the first eleven (we only show six in Table IV) $\psi_i^D(0)$-values (i even) remain unchanged, but only three $\psi_i^{HO}(a, 0)$ and one $\psi_i^{HO}(0)$ are stable.

From the previous discussions we can conclude that Dirichlet basis set will be even more appropriate than the other ones for the remaining oscillators ($k > 2$).

In Table V we report the $\Psi_i(0)$-values for several oscillators of the form (1). In each case the N- and b-values were chosen in order to achieve stability in the last figure. The conclusions obtained before allow us to assure that the results of Table V must be accurate up to the last decimal place reported. Once more, we see that the b value, beyond which results are stable, decreases when k increases. As far as we know, the $\Psi_i(0)$-values shown in Table V have not been reported previously.

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