

Analytic accurate formulae for eigenenergies of a strongly anharmonic oscillator and an oscillator with a double-well potential

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1984 J. Phys. A: Math. Gen. 17 1461

(<http://iopscience.iop.org/0305-4470/17/7/013>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 31/05/2010 at 08:31

Please note that [terms and conditions apply](#).

Analytic accurate formulae for eigenenergies of a strongly anharmonic oscillator and an oscillator with a double-well potential

J Makarewicz

Institute of Chemistry, A Mickiewicz University, 60-780 Poznan, Poland

Received 13 July 1983

Abstract. Analytical formulae are presented of the first- to fifth-order renormalised perturbation theory (RPT), allowing highly accurate calculation of energy levels of a strongly anharmonic oscillator (AO) and an oscillator with a double-well potential (DWP).

1. Introduction

The anharmonic oscillator with a potential $V = \frac{1}{2}ax^2 + bx^{2M}$ ($a \geq 0$) has been the subject of many extensive studies. The literature provides exhaustive numerical tables and many approximate formulae of a limited range of application (Bazley and Fox 1961, Chan and Stelman 1963, Krieger *et al* 1967, Biswas *et al* 1971, 1973, Lakshmanan and Prabhakaran 1973, Hioe and Montroll 1975, Hioe *et al* 1976, 1978, Benerjee *et al* 1978, Benerjee 1978, Caswell 1979, Halliday and Suranyi 1980, Killingbeck 1981, Mathews *et al* 1981, 1982).

In contradiction to the case when $a \geq 0$, the approximate methods found almost no application in the calculation of energy levels of DWP ($a < 0$), in spite of the fact that this potential is widely used in description of ring-puckering and inversion vibrations in molecules (Lister *et al* 1978).

Recently Caswell (1979) reported results of his calculations for AO and DWP obtained with his 20th-order RPT applied. However, the calculations of this kind require computer aid. Killingbeck (1981) also studied this problem and proposed a direct method of calculation of the renormalised perturbation series.

In this paper we give, applying the results of our previous paper (Makarewicz 1984, hereafter referred to as I), analytical formulae allowing highly accurate calculation of energy levels of a general one-dimensional AO with the potential

$$V = \sum_{k=0}^M \lambda^k V_k x^{2(k+1)} \quad (\text{the formal perturbation parameter } \lambda \text{ we further take: } \lambda = 1).$$

We are interested in the case when $V_k \geq 0$ (then V has one minimum) and when $V_0 < 0$, $V_1 > 0$, $V_k \geq 0$ (then V has two minima).

2. Formulae for mean values of x^{2m} and energy eigenvalues

2.1. Renormalised perturbation series for the mean values of x^{2m} and energy eigenvalues

It is well known that although the AO Hamiltonian

$$H = -(\hbar^2/2m) d^2/dx^2 + V(x) \quad (1)$$

includes $M+2$ parameters (m and $\{V_k\}_{k=0}^M$), the energy E depends on $M+1$ parameters, as the transformation

$$x = (m\omega_0/\hbar)^{-1/2} r$$

where

$$\omega_0 = (2|V_0|/m)^{1/2}$$

gives the Hamiltonian:

$$H = \hbar\omega_0 h(\{v_k\}), \quad (2)$$

$$h(\{v_k\}) = -\frac{1}{2} d^2/dr^2 + \frac{1}{2} sr^2 + \sum_{k=1}^M v_k r^{2(k+1)}$$

where

$$v_k = (\hbar/m\omega_0)^{(k+1)} V_k / \omega_0 \hbar,$$

$$s = \text{sgn } V_0.$$

The energy of AO depends linearly on ω_0

$$E = \hbar\omega_0 \mathcal{E}(\{v_k\})$$

so, it is sufficient to find the eigenvalues $\mathcal{E}(\{v_k\})$ depending on M parameters.

According to the perturbation theory the mean values $\langle r^{2m} \rangle$ and eigenenergies \mathcal{E} are expanded as follows:

$$\langle r^{2m} \rangle = \sum_n \mathcal{R}_n(2m) v_1^{n_1} v_2^{n_2} \dots v_M^{n_M}, \quad (3)$$

$$\mathcal{E} = \sum_n \mathcal{E}_n v_1^{n_1} v_2^{n_2} \dots v_M^{n_M}, \quad (4)$$

where

$$n \equiv (n_1 n_2 \dots n_M) \quad \text{and} \quad (n_1 n_2 \dots n_k 0 \dots 0) \equiv (n_1 n_2 \dots n_k).$$

For one-dimensional AO ($s=1$) the $\mathcal{R}_n(2m)$ and \mathcal{E}_n coefficients calculated from equations (6)–(8) of I have the polynomial forms:

$$\mathcal{R}_n(2m) = M_n(2m) \sum_k r_k(2m; n) \varepsilon^k, \quad (5)$$

$$\mathcal{E}_n = N_n \sum_k e_k(n) \varepsilon^k, \quad (6)$$

where

$$\varepsilon \equiv 2\mathcal{E}_0 = 2n + 1.$$

The coefficients $M_n(2m)$ and $r_k(2m; n)$ for the first indices n are included in table 1.

Table 1. The $M_n(2m)$ and the $r_k(2m; n)$ coefficients defining the polynomials $\mathcal{R}_n(2m) = M_n(2m) \sum_k r_k(2m; n) \varepsilon^k$.

n	m	$M_n(2m)$	$k =$	0	1	2	3	4	5	6
0	1	$\frac{1}{2}$			1					
	2	$\frac{3}{8}$		1		1				
	3	$\frac{5}{16}$			5		1			
	4	$\frac{35}{128}$		9		14		1		
	5	$\frac{63}{256}$			89		30		1	
	6	$\frac{231}{1024}$		225		439		55		1
1	1	$-\frac{3}{4}$		1		1				
	2	$-\frac{1}{16}$			67		17			
	3	$-\frac{15}{128}$		63		118		11		
	4	$-\frac{21}{128}$			501		210		9	
	5	$-\frac{195}{256}$		495		1 126		175		4
2	1	$\frac{5}{32}$			67		17			
	2	$\frac{9}{256}$		513		1 138		125		
	3	$\frac{512}{7}$			117 281		59 110		3 129	
	4	$\frac{4096}{7}$		451 001		809 285		107 179		1 495
01	1	$-\frac{15}{16}$			5		1			
	2	$-\frac{15}{128}$		63		118		11		
	3	$-\frac{1}{256}$			19 277		8 290		393	
	4	$-\frac{7}{512}$		12 825		29 253		4 835		127
3	1	$-\frac{7}{32}$		513		1 138		125		
	2	$-\frac{1}{512}$			305 141		178 330		10 689	
	3	$-\frac{1}{12288}$		23 391 809		8 632 571		48 261 305		230 475
11	3	$\frac{3}{512}$		179 550		463 623		91 060		2 807
4	2	$\frac{15}{4096}$		971 046		3 105 983		783 020		29 183
101	2	$\frac{7}{256}$		41 715		108 432		20 395		578

The remaining coefficients needed are determined from the following relations

$$\begin{aligned}
 \mathcal{R}_{11}(2) &= -6\mathcal{R}_1(6), & \mathcal{R}_4(2) &= \frac{1}{4}\mathcal{R}_3(4), & \mathcal{R}_{02}(2) &= -\frac{7}{2}\mathcal{R}_{01}(6), \\
 \mathcal{R}_{11}(4) &= 2\mathcal{R}_2(6), & \mathcal{R}_{21}(2) &= -9\mathcal{R}_2(6), & \mathcal{R}_{02}(4) &= \frac{1}{2}\mathcal{R}_{11}(6), \\
 \mathcal{R}_{001}(2) &= -4\mathcal{R}_0(8), & \mathcal{R}_{21}(4) &= 3\mathcal{R}_3(6), & \mathcal{R}_{0001}(2) &= -5\mathcal{R}_0(10), \\
 \mathcal{R}_{001}(4) &= \mathcal{R}_1(8), & \mathcal{R}_{101}(2) &= -7\mathcal{R}_1(8), & \mathcal{R}_{0001}(4) &= \mathcal{R}_1(10), \\
 \mathcal{R}_{001}(6) &= \mathcal{R}_{01}(8).
 \end{aligned}$$

The coefficients N_n and $e_k(n)$ are included in table 2. The above equations allow us to calculate \mathcal{E} with the accuracy of fifth-order perturbation theory. They hold only for $s = 1$ and for the case when the anharmonic constants values v_k are sufficiently low.

Knowing the perturbation series (3) and (4), we will now construct the renormalised series which give good results also for $s = -1$ and for high values of v_k .

For this purpose we introduce the renormalisation parameters β_k and calculate the parameter ω from

$$\omega^2 = s + \sum_{k=1}^M \beta_k v_k \omega^{-k}. \tag{7}$$

This equation gives a positive value of ω which means that the zero-order Hamiltonian for RPT:

$$h_0(\omega) = T + \frac{1}{2}(\omega r)^2$$

Table 2. The N_n and the $e_k(n)$ coefficients defining the polynomials $\mathcal{E}_n = N_n \sum_k e_k(n) \varepsilon^k$.

m	N_n	$k =$	0	1	2	3	4	5	6
0	$\frac{1}{2}$			1					
1	$\frac{3}{8}$		1		1				
2	$-\frac{1}{32}$			67		17			
01	$\frac{5}{16}$			5		1			
3	$\frac{3}{256}$		513		1 138		125		
11	$-\frac{15}{128}$		63		118		11		
001	$\frac{35}{128}$		9		14		1		
4	$-\frac{1}{2048}$		305 141		178 330		10 689		
21	$\frac{1}{512}$		117 281		59 110		3 129		
02	$-\frac{1}{512}$		19 277		8 290		393		
101	$-\frac{63}{128}$		167		70		3		
0001	$\frac{63}{256}$		89		30		1		
5	$\frac{3}{4096}$		971 046		3 105 983		783 020		29 183
31	$-\frac{1}{12288}$		23 391 809		48 261 305		8 632 571		230 475
12	$\frac{3}{1024}$		179 550		463 623		91 060		2 807
201	$\frac{7}{20480}$		2 020 443		4 162 767		647 857		13 733
011	$-\frac{57}{128}$		12 825		29 253		4 835		127
1001	$-\frac{105}{256}$		495		1 126		175		4
00001	$\frac{231}{1024}$		225		439		55		1

which we extract from the total Hamiltonian

$$h = T + \frac{1}{2}sr^2 + \sum_{k=1}^M v_k r^{2(k+1)} = h_0 + \frac{1}{2}(s - \omega^2)r^2 + \sum_{k=1}^M v_k r^{2(k+1)}$$

has bound states (in contrast to the ordinary zero-order Hamiltonian $h_0(s)$ for which bound states do not exist if $s = -1$). So, the RPT allows us to calculate eigenenergies also for $s = -1$ (DWP). The renormalised perturbation series for $\langle r^{2m} \rangle$ and \mathcal{E} in terms of $w_k \equiv v_k \omega^{-k}$ are of the forms

$$\langle r^{2m} \rangle = \omega^{-m} \sum_n \mathcal{R}'_n w_1^{n_1} w_2^{n_2} \dots w_M^{n_M}, \tag{8}$$

$$\mathcal{E} = \omega \sum_n \mathcal{E}'_n w_1^{n_1} w_2^{n_2} \dots w_M^{n_M}, \tag{9}$$

where the new coefficients $\mathcal{R}'_n \equiv \mathcal{R}'_n(2m)$ and \mathcal{E}'_n are related to the old $\mathcal{R}_n \equiv \mathcal{R}_n(2m)$ and \mathcal{E}_n by equations

$$\mathcal{R}'_n = \sum_K p_{n,n'}(m; K) \mathcal{R}_n \beta_1^{k_1} \beta_2^{k_2} \dots \beta_M^{k_M}, \tag{10}$$

$$\mathcal{E}'_n = \sum_K f_{n,n'}(K) \mathcal{E}_n \beta_1^{k_1} \beta_2^{k_2} \dots \beta_M^{k_M}, \tag{11}$$

where

$$K = (k_1 k_2 \dots k_M)$$

and indices n' are determined by the condition

$$(1n'_1 2n'_2 \dots Mn'_M) = (1n_1 2n_2 \dots Mn_M) - (1k_1 2k_2 \dots Mk_M).$$

The coefficients $p_{n,n'}(m; K)$ are tabulated in table 3 and the $f_{n,n'}(K)$ we obtain from

the relation

$$f_{n,n'}(K) = p_{n,n'}(-1; K).$$

For $N = 1n_1 + 2n_2 + \dots + Mn_M = 5$ they are included in table 4.

2.2. Determination of the renormalisation parameters

The β_k constants depend on the quantum number n and the order N of RPT i.e. if the highest power at w_k is N_k , then in calculating the energies the values $\beta_k(N_k)$ are taken. We determine the $\beta_k(N_k)$ from equations

$$\lim_{v_k \rightarrow \infty} (v_k^{-1/(k+1)} \mathcal{E}(\{v_1\}))_{v_1 = v_k \delta_{l,k}} \equiv \tilde{E}^{(N_k)} = E(2k+2) \tag{12}$$

where $E(2k+2)$ is the energy of AO with the potential $V = x^{2k+2}$. These equations are of the general form:

$$W_{N_k}(x_k) x_k^{-1/(k+1)} = E(2k+2): x_k = (\beta_k(N_k))^{-1} \tag{13}$$

where $W_{N_k}(x_k)$ are polynomials.

For $k = 1$ the polynomials $W_1(x_1)$ are the following:

$$W_{N_1}(x_1) = \sum_{n=0}^{N_1} A_n x_1^n \mathcal{E}_n,$$

where

$$A_0 = 1 - \sum_{i=1}^{N_1} a_i, \quad a_i = (i! 2^i)^{-1},$$

$$A_n = 1 + \sum_{i=1}^{N_1-n} a_i \prod_{j=0}^{i-1} (3n+2j-1), \quad n = 1, 2, \dots, N_1.$$

For $k > 1$ the polynomials $W_{N_k}(x_k)$ are:

$$W_{N_k}(x_k) = \frac{1}{2} \mathcal{E}_0 + x_k \underbrace{\mathcal{E}_{0\dots 1}}_k,$$

where

$$N_k = 1.$$

Numerical values of $\beta_k(N_k)$ for the first ten states are given in table 5. However it does not include the values of $\beta_k(2)$ as second-order RPT does not give more accurate results than first-order RPT.

We also do not give the values of $\beta_k(N_k)$ for $k > 3$ since in order to calculate them, the values of energy levels $E_n(2k+2)$ not so far reported in the literature must be known (numerical values of $E_n(4)$ are taken after Benerjee (1978), and $E_n(6)$ and $E_n(8)$ are taken from the paper of Krieger *et al* (1967)). In general, anharmonic constants v_k rapidly decrease with increasing k and so their renormalisation is not necessary. Let us notice that for $n \gg 1$ the values of $\beta_k(N_k)$ increase almost linearly with increasing n , which means that the expansion for the energy of RPT gives, for high states, the results of the same accuracy as the WKB method (see paper I).

This fact is illustrated by the results of table 6 where we compare the energies of quadratic-quartic AO calculated with our fifth-order RPT with the five-term WKB method (Kesarwani and Varshni 1981) and those calculated numerically by Hioe and

Table 5. The values of the renormalisation parameters $\beta_k(N_k)$.

n	$\beta_1^{(1)}$	$\beta_2^{(1)}$	$\beta_3^{(1)}$	$\beta_1^{(3)}$	$\beta_1^{(4)}$	$\beta_1^{(5)}$
0	6.000	22.5	105	10.3034	12.628 37	12.779 836
1	10.000	52.5	315	14.1488	16.243 77	18.803 042
2	13.437	112.5	861	16.6285	19.454 74	20.605 647
3	16.999	149.9	1 635	24.4383	22.859 86	25.471 550
4	21.106	217.5	2 423	33.6324	28.244 91	31.136 899
5	25.370	305.8	3 847	42.4774	34.403 02	33.935 285
6	29.703	413.5	5 885	51.0430	41.251 27	38.958 229
7	34.074	539.7	8 626	59.4686	48.420 53	44.363 665
8	38.470	682.8	12 172	67.8148	55.572 50	50.048 038
9	42.881	844.9	16 630	76.1113	62.646 80	55.994 542
10	47.302	1025.6	22 100	84.3745	69.657 73	62.172 898

Montroll (1975). It follows from this comparison that for high states the results obtained by our method are in very good agreement with the WKBJ results, with the accuracy to at least six significant digits. For high v_1 and low n , RPT yields the results with the same accuracy while the WKBJ method fails.

2.3. Correcting coefficients

For some of the lowest states, equations (12) have no solutions. Then we calculate β_k from the equation

$$d\tilde{E}^{(N_k)}/d\beta_k = 0.$$

The energies of these states are charged with much greater errors than the energies of the other states. In order to reduce these errors, let us modify the equation for the energy of these states. In formula (9) we replace the $\mathcal{E}'_{0\dots 0N_k}$ coefficients

$$\mathcal{E}'_{0\dots 0N_k} = \sum_{l=0}^{N_k} c_l^{(k)} \beta_k^l \mathcal{E}'_{0\dots 0(N_k-l)}$$

by the modified coefficients

$$\tilde{\mathcal{E}}'_{0\dots 0N_k} = \mathcal{E}'_{0\dots 0N_k} + (a_{N_k}^{(k)} - 1)c_{N_k}^{(k)} \beta_k^{N_k} \mathcal{E}'_0.$$

We have found empirically that $a_{N_k}^{(k)}$ of a general form

$$a_{N_k}^{(k)} = A_{N_k}^{(k)} \exp(b_{N_k}^{(k)}/\sqrt{v_k})$$

gives good results for $N_k \leq 3$.

Such correcting coefficients also improve energies of the lowest states for $N_1 = 4, 5$ although the $\beta_1(4)$ and $\beta_1(5)$ values are determined from equation (12). The values of the $A_{N_k}^{(k)}$ and $b_{N_k}^{(k)}$ for $N_k \leq 3$ ($s = \pm 1$) and for $N_1 = 4$ ($s = 1$) are included in table 7. If $v_k < v_k^{\min} = (b_{N_k}^{(k)}/\ln A_{N_k}^{(k)})^2$ we take $a_{N_k}^{(k)} = 1$. For $N_1 = 4$ and $s = -1$ the $a_4^{(1)}$ have the same form as for $s = 1$, but the $b_4^{(1)}$ coefficients are different. They are for the quantum number $n = 0, 1, 2$ as follows:

$$b_4^{(1)}(0) = -0.0002, \quad b_4^{(1)}(1) = -0.00015, \quad b_4^{(1)}(2) = -0.0007.$$

Table 6. Eigenenergies of the quadratic-quartic AO calculated with five-term WKB method by Kesarwani and Varshni (1981) (the first line), with our fifth-order RPT (the second line) and those calculated numerically by Hioe and Montroll (1975) (the numbers in parentheses).

v_1	$n=0$	1	2	4	6	8
0.01	0.507 256 204 (20)	1.535 648 28 (8)	2.590 845 80 (0)	4.774 913 12 (2)	7.048 326 88 (8)	9.402 692 31 (1)
0.1	0.558 760 543 (33)	1.769 514 79 (64)	3.138 624 03 (31)	6.220 300 90 (0.90)	9.657 839 99 (39.99)	13.382 474 8 (79.969 8)†
1	0.774 649 833 (0.65)	2.739 744 61 (2.27)	5.179 204 54 (1.69)	10.963 582 9 (83.1)	17.634 049 1 (49.2)	24.994 936 4 (45.7)
200	3.539 330 65 (34)	14.089 928 8 (8)	27.549 802 1 (7)	60.033 989 1 (3.1)	97.891 331 5 (1.5)	139.900 396 (400)
1000	6.014 574 21 (0.85)	24.025 754 4 (6.1)	47.014 483 4 (7)	102.516 150 (57)	167.212 258 (8)	239.011 578 (80)

† This value as was shown by Kesarwani is inaccurate.

Table 7. The correcting coefficients for $N_k \leq 4$.

N_k	$N_1=1$		$N_2=1$		$N_3=1$		$N_1=3$		$N_1=4$	
	A	b	A	b	A	b	A	b	A	b
0	1.0296	-0.0055	1.0830	-0.010	1.140	-0.010	1.0042	-0.0007	0.9996	0
1	1.0187	-0.003	1.0555	-0.005	1.097	-0.004	—	—	0.9987	0
2	—	—	1.0082	0	1.032	0	—	—	0.9952	0.0005

For $n = 3$ and $s = -1$, $a_4^{(1)}(3) = 1.000\ 25$. In the case $N_1 = 5$ ($s = \pm 1$) we take

$$A_5^{(1)}(n) = 1 \text{ except for } n = 3 \text{ when}$$

$$A_5^{(1)}(3) = \begin{cases} 1.002\ 33 & \text{for } s = +1, \\ 1.002\ 43 & \text{for } s = -1. \end{cases}$$

For $N_1 = 5$ and $s = -1$ we take:

$a_5^{(1)}(n) = A_5^{(1)}(n) \exp(b_5^{(1)}/v_1)$ except for $n = 2$ when $a_5^{(1)}(2) = \exp(b_5^{(1)}/v_1^3)$. The values of $b_5^{(1)}$ for $s = \pm 1$ for $n = 0, 1, \dots, 5$ are included in table 8. If $v_1 < 0.01$ we take $a_5^{(1)} = 1$.

Table 8. The values of the $b_5^{(1)}$ coefficients.

n	$s = +1$	$s = -1$
0	0.000 08	-0.000 125
1	0	0.000 021
2	0.000 02	0.000 001
3	-0.000 25	0.000 145
4	0.000 06	-0.000 07
5	0.000 04	-0.000 03

2.4. The accuracy of energy formulae

The proposed method of determination of renormalisation parameters is very effective. In the first-order RPT calculated eigenenergies of the quadratic–quartic, quadratic–sextic and quadratic–octic AO ($s = 1$) are charged with the errors $d = (|E^{\text{RPT}} - E^{\text{Exact}}|/E^{\text{Exact}}) \times 100\%$; less than 0.06%, 0.2%, 0.6% respectively.

For the most important case of quadratic–quartic AO ($s = 1$) these errors for arbitrary values of the quantum number n and anharmonic constants v_1 are as follows (the maximum errors are given in %):

$$\begin{aligned} \text{for } N_1 = 3 & \quad d = 0.005, \\ \text{for } N_1 = 4 & \quad d = 0.0007, \\ \text{for } N_1 = 5 & \quad d = 0.000\ 05. \end{aligned}$$

The errors in eigenvalues for quadratic–quartic DWP grow quickly with increasing height of the barrier $V_b = (16v_1)^{-1}$. For low barriers the accuracy of eigenenergies is rather high and equals:

for $N_1 = 3$

$$\begin{aligned} d &= 0.005 \text{ for } v_1 \geq 1 \text{ except for } n = 0, 2 \text{ when} \\ d &\cong 0.01 \text{ for } 10 \geq v_1 \geq 1, \end{aligned}$$

for $N_1 = 4$

$$\begin{aligned} d &= 0.0005 \text{ for } v_1 \geq 1 \text{ except for } n = 3 \text{ when} \\ d &\cong 0.001 \text{ for } v_1 \geq 100, \end{aligned}$$

Table 9. Eigenenergies of the quadratic-quartic AO ($s = 1$) calculated with the fifth-order RPT.

v_1	$n = 0$	$n = 1$	$n = 2$	$n = 3$
0.005	1.007 373 672 0810 (4)	3.036 525 304 492 (513)	5.093 939 132 748 (2)	7.178 573 1815 (07)
0.05	1.065 285 548 (09)	3.306 871 99 (2 01)	5.747 959 36 (27)	8.352 677 58 (83)
0.5	1.392 351 637 (42)	4.648 811 7 (2 7)	8.655 051 04 (49 96)	13.156 802 3 (39 9)
5	2.449 173 78 (4 07)	8.599 002 0 (3 5)	16.635 920 4 (1 5)	25.806 288 (76)
50	4.999 416 7 (7 5)	17.830 191 9 (2 7)	34.873 982 1 (4 3)	54.385 295 2 (1 6)
500	10.639 787 7 (8 7)	38.086 833 04 (46)	74.681 401 8 (4 2)	116.603 161 (99)
5000	22.861 608 05 (87)	81.903 316 74 (95)	160.685 912 6 (09 8)	250.950 61 (74)
v_1	$n = 4$	$n = 6$	$n = 8$	$n = 10$
0.005	9.289 479 8169 (3)	13.586 715 8010 (6)	17.979 510 5829 (37)	22.462 605 532 (42)
0.05	11.093 594 4 (5 6)	16.954 796 6 (4 7)	23.229 551 0 (2 2)	29.866 520 7 (5 2)
0.5	18.057 558 1 (7 4)	28.835 348 (38)	40.690 379 8 (86 1)	53.449 085 (102)
5	35.885 167 (71)	58.241 307 (299)	83.003 861 8 (7 0)	109.772 554 (70)
50	75.876 995 (7 004)	123.640 702 (698)	176.628 653 2 (6 0)	233.966 207 (25)
500	162.802 365 (74)	265.519 953 6 (1 7)	379.511 310 0 (1 2)	502.886 368 (99)
5000	350.435 888 (96)	571.647 792 5 (1 6)	817.156 874 5 (5 0)	1082.888 46 (52)

for $N_1 = 5$

$d = 0.0005$ for $v_1 \geq 0.2$ except for $n = 3$ when

$d \cong 0.001$ for $v_1 \geq 100$.

In tables 9, 10 the values of energies of quadratic–quartic AO and DWP calculated from formulae presented above are compared with the more accurate data computed for $s = 1$ by Benerjee (1978) and for $s = -1, v_1 \geq 1$ by Caswell (1979) and for $s = -1, 1 > v_1 \geq 0.2$ by us (the calculations are performed using the numerical method of Noomerov–Cooley (Cooley 1961) with accuracy to ten significant digits). As can be seen from the data presented, the accuracy of our results (which is a few orders greater than that of Caswell (1979) and Killingbeck (1981) for the same N) increases with increasing anharmonic constant v_1 . This fact arises from the way the renormalisation parameters were determined.

Table 10. Eigen energies of the DWP ($s = -1$) calculated with the RPT of the fifth order.

v_1	$n = 0$	$n = 1$	$n = 2$	$n = 3$
0.2	0.397 504 (6)	1.013 473 (1)	2.156 669 (4)	3.484 123 (7)
0.3	0.404 312 (0)	1.220 951 (2)	2.575 564 3 (3 7)	4.155 105 (94)
0.5	0.453 827 53 (0)	1.542 267 3 (8 1)	3.206 948 (51)	5.144 332 (23)
1	0.577 280 0 (4)	2.083 052 0 (1)	4.253 568 (71)	6.768 018 (20)
10	1.377 816 0 (8)	4.995 666 9 (5)	9.894 741 (2)	15.522 40 (25)
100	3.070 102 9 (34)	11.033 705 3 (6 0)	21.694 678 9 (9 7)	33.916 61 (75)
v_1	$n = 4$	$n = 6$	$n = 8$	$n = 10$
0.2	4.993 204 (0)	8.428 89 (94)	12.314 46 (4)	16.569 50 (45)
0.3	5.934 3819 (20)	9.961 148 (80)	14.493 56 (4)	19.442 55 (1)
0.5	7.311 198 (203)	12.189 017 (38)	17.656 089 (74)	23.610 008 (609 984)
1	9.564 081 (90)	15.828 823 (36)	22.824 184 (76)	30.424 798 (84)
10	21.736 532 (40)	35.576 346 (50)	50.956 266 (3)	67.616 682 (0)
100	47.392 915 (20)	77.369 059 (61)	110.647 488 (7)	146.673 751 (6)

3. Conclusions

The analytical formulae for energy eigenvalues and for mean values r^{2m} of AO $s = \pm 1$ derived in this work provide a high accuracy of results which is sufficient for practical purposes if the barrier of DWP $s = -1$ is not too high; for example, for fifth-order RPT

the errors in the eigenenergies of the quadratic-quartic AO are less than 0.000 05% for $s = 1$ and less than 0.0005% for $s = -1$ for arbitrary values of quantum number n and anharmonic constant v_1 , $v_1 \geq 0.2$ if $s = -1$. The formulae for $\langle r^{2m} \rangle$ allow us to derive the effective rotational constants of molecules and other molecular constants depending on the mean values of vibrational coordinates.

Acknowledgment

I would like to thank Dr J Koput for performing numerical calculations of the energy levels of DWP.

References

- Bazley N and Fox D 1961 *Phys. Rev.* **124** 483
Benerjee K 1978 *Proc. R. Soc. A* **364** 265
Benerjee K, Bhatnagar S P, Chounry V and Kanwal S S 1978 *Proc. R. Soc. A* **360** 575
Biswas S N, Datta K, Saxena R P, Srivatsava P K and Varma V S 1971 *Phys. Rev. D* **4** 3617
— 1973 *J. Math. Phys.* **14** 1190
Caswell W E 1979 *Ann. Phys., NY* **123** 153
Chan S I and Stelman D 1963 *J. Mol. Spectrosc.* **10** 278
Cooley J W 1961 *Math. Comp.* **15** 363
Halliday I G and Suranyi P 1980 *Phys. Rev. D* **21** 1521
Hioe F T, MacMillen D and Montroll E W 1976 *J. Math. Phys.* **17** 1320
— 1978 *Phys. Rev. C* **43** 305
Hioe F T and Montroll E W 1975 *J. Math. Phys.* **16** 1945
Kesarwani R N and Varshni J P 1981 *J. Math. Phys.* **22** 1983
Killingbeck J 1981 *J. Phys. A: Math. Gen.* **14** 1005
Krieger J B, Lewis M L and Rosenzweig C 1967 *J. Chem. Phys.* **47** 2942
Lakshmanan M and Prabhakaran J 1973 *Lett. Nuovo Cimento* **7** 689
Lister D G, MacDonald J N and Owen N L 1978 *Internal Rotation and Inversion* (London: Academic)
Makarewicz J 1984 *J. Phys. A: Math. Gen.* **17** 1461
Mathews P M and Raghavan S 1982 *J. Phys. A: Math. Gen.* **15** 103
Mathews P M, Seetharaman M, Raghavan S and Bhargava V T A 1981 *Phys. Lett. A* **83** 118