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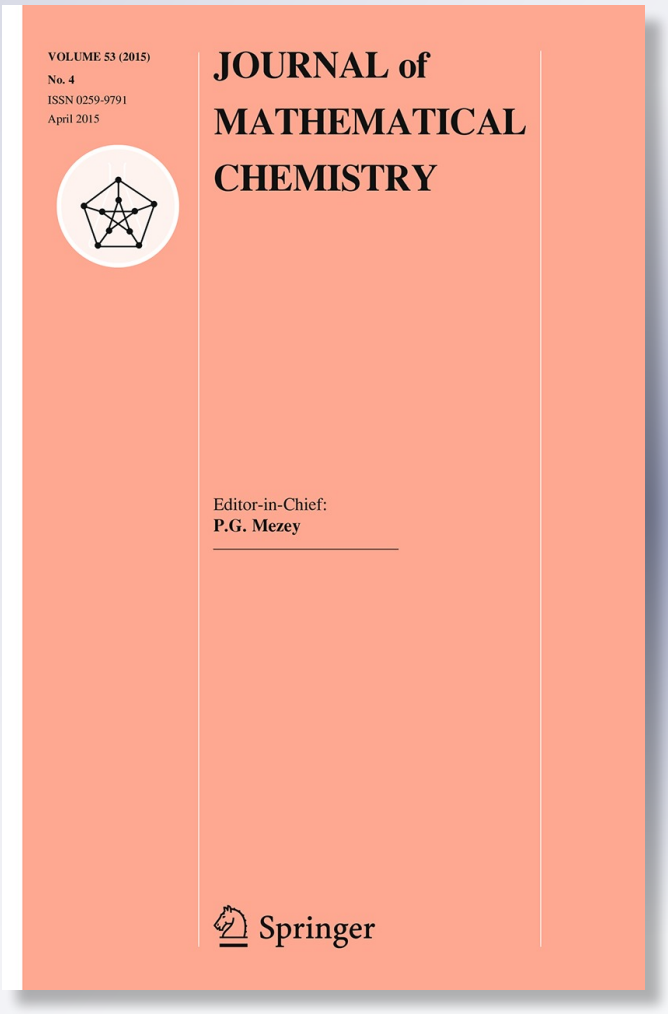

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ORIGINAL PAPER

Perturbation theory by the moment method and point-group symmetry

Francisco M. Fernández

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Abstract We analyze earlier applications of perturbation theory by the moment method (also called inner product method) to anharmonic oscillators. For concreteness we focus on two-dimensional models with symmetry C_{4v} and C_{2v} and reveal the reason why some of those earlier treatments proved unsuitable for the calculation of the perturbation corrections for some excited states. Point-group symmetry enables one to predict which states require special treatment.

1 Introduction

Many years ago there was great interest in perturbation theory without wavefunction. Fernández and Castro [1] developed an approach for multidimensional nonseparable problems that was based on the recurrence relations of the moments of the wavefunction instead of the wavefunction itself. They applied it to the Zeeman effect in Hydrogen and to the Hydrogen molecular ion. Austin [2] resorted to this approach in order to obtain the coefficients of the renormalized perturbation series for the lowest states of the Zeeman effect in Hydrogen and Arteca et al. [3] carried out a similar calculation by means of an order-dependent mapping. Fernández and Castro [4] also applied this moment perturbation theory (MPT) to the Hydrogen in parallel magnetic and electric fields and outlined its application to multidimensional anharmonic oscillators.

Sometime later Killingbeck et al. [5] rediscovered the approach and baptized it inner-product method. They applied it to one-dimensional anharmonic oscillators and later Killingbeck and Jones [6] to two dimensional ones. Fernández et al. [7] developed

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the MPT in a more general way and showed the general conditions that the recurrence relations for the moments should satisfy in order to be suitable for a successful perturbation calculation.

After that, there has been many applications of the MPT to a variety of quantum-mechanical models [8–23] and Fernández [24] reviewed some of them in a comprehensive way. It is worth noting that after so many years of application of the MPT [5,6,8–12,17–20,23] some authors never acknowledged the existence of the seminal articles that first introduced the MPT [1] and its combination with the renormalized series [2,3].

The simplest two-dimensional model first treated by Killingbeck and Jones [6] and Witwit [9] is $H = p_x^2 + p_y^2 + x^2 + y^2 + \lambda\left(ax^4 + by^4 + 2cx^2y^2\right)$. Their calculations were restricted to $a = b$ because "The potential is non-separable but shows a high symmetry; this cuts down the amount of computation required, although the more general anisotropic case can also be treated by the method" [6] and "The inner product method deals with more general parameter values, but still requires $a = b$ since the equations used exploits this symmetry to reduce computation" [9]. Fernández and Ogilvie [16] showed that the application of the MPT to the case $a \neq b$ is not that trivial because the moments of order zero for some pairs of states coupled by the perturbation satisfy quadratic, instead of linear, equations (see also Fernández [24]). This is the reason why Killingbeck and Jones [6] and Witwit [9] were unable to apply the perturbation approach to such non-symmetric anharmonic interactions. In fact, Fernández and Morales [15] had previously overcome a similar difficulty in the treatment of the Zeeman effect in Hydrogen.

Most of the applications of the MPT to anharmonic oscillators took into account the symmetry of the eigenfunctions (see, for example, [6,9,21,22]). However, such treatments of symmetry look rather rudimentary when compared with the more rigorous approach carried out, for example, by Pullen and Edmonds [25,26]. Those enlightening papers motivated the application of point-group symmetry (PGS) to several multidimensional non-Hermitean anharmonic oscillators that led to most interesting conclusions [27–30].

The purpose of this paper is to show why the simple symmetry arguments invoked by Killingbeck and Jones [6] and Witwit [9] were insufficient to solve the Schrödinger equation for the multidimensional anharmonic oscillators by means of the MPT, except for some particular states. For simplicity we focus on the two-dimensional anharmonic oscillator shown above but the same ideas apply to all the other models studied so far.

In Sect. 2 we outline the main ideas of PGS [31,32] that we use in Sect. 3 to classify the different cases given by general choices of potential parameters. In Sect. 4 we analyze the symmetry of the eigenfunctions for the case $a = b$ and discuss the effect of the symmetry of the anharmonic interaction on the perturbation corrections to the eigenvalues. We also outline the effect of symmetry on the behaviour of the moments of the wavefunction. We calculate the energy eigenvalues for a particular model and compare our results with those of Killingbeck and Jones [6] and Witwit [9]. In Sect. 5 we carry out a similar analysis for the case $a \neq b$. Finally, in Sect. 6 we summarize the main results of the paper and generalize the conclusions drawn in the preceding sections.

2 Point-group symmetry

In what follows we summarize a few results of group theory that will be useful throughout this paper.

The set of unitary transformations U_i, $i = 1, 2, \ldots, h$ that leave a given Hamiltonian operator H invariant $U_i H U_i^\dagger = H$ form a group with respect to the composition $U_i U_j$ [31,32]. The invariance is obviously equivalent to $[H, U_i] = 0$. Clearly, if ψ is an eigenfunction of H with eigenvalue E then $U_i\psi$ is also eigenfunction with the same eigenvalue as follows from $HU_i\psi = U_i H\psi = EU_i\psi$.

The eigenfunctions of H are bases for the irreducible representations (irreps) of the point group G of H and can therefore be classified according to them [31,32]. Group theory gives us projection operators P^S such that for any arbitrary function f $P^S f$ is basis for the irreducible representation S unless $P^S f = 0$. The projection operators are given by

$$P^S = \frac{l_S}{h} \sum_{i=1}^{h} \chi^S(U_i)^* U_i, \tag{1}$$

where l_S is the dimension of the irreducible representation S, h is the order of the group and $\chi^S(U_i)$ is the character of the operation U_i for the irrep S [31,32].

It is well known that there is a one-to-one correspondence between the unitary operators U_i and unitary matrices $\mathbf{M}_i$ such that [31]

$$U_i f(\mathbf{x}) = f(\mathbf{M}_i^\dagger \mathbf{x}). \tag{2}$$

Any projection operator P is self-adjoint $P^\dagger = P$ and idempotent $P^2 = P$. If ψ^S is an eigenfunction of H and is basis for the irrep S then

$$\left\langle F \middle| \psi^S \right\rangle = \left\langle F \middle| P^S \psi^S \right\rangle = \left\langle P^S F \middle| \psi^S \right\rangle. \tag{3}$$

This brief introduction to group theory will prove sufficient for all the discussions in the subsequent sections.

3 Symmetry of the two-dimensional oscillator

As indicated in the introduction we will discuss the application of the MPT to the two-dimensional anharmonic oscillator

$$H = p_x^2 + p_y^2 + x^2 + y^2 + \lambda\left(ax^4 + by^4 + 2cx^2y^2\right), \tag{4}$$

where $p_q = -i\frac{d}{dq}$. We have the following cases:

Case 0: $c = 0$. This problem is separable in cartesian coordinates and was chosen by Killingbeck and Jones [6] to test their algorithms. It is not relevant for present discussion.

Case 1: $a = b = c$. The potential depends only on $r^2 = x^2+y^2$ and the Schrödinger equation is therefore separable in spherical coordinates. This case was also a benchmark for Killingbeck and Jones [6] but it is of no interest for present purposes.

Case 2: $a = b \neq c$. This case was studied by both Killingbeck and Jones [6] and Witwit [9] by means of the MPT. We will discuss it in the present paper. A suitable point group is C_{4v} with the following unitary operations

$$\begin{aligned} E &: (x, y) \rightarrow (x, y) \\ C_4 &: (x, y) \rightarrow (y, -x) \\ C_4^3 &: (x, y) \rightarrow (-y, x) \\ C_2 &: (x, y) \rightarrow (-x, -y) \\ \sigma_{v1} &: (x, y) \rightarrow (x, -y) \\ \sigma_{v2} &: (x, y) \rightarrow (-x, y) \\ \sigma_{d1} &: (x, y) \rightarrow (y, x) \\ \sigma_{d2} &: (x, y) \rightarrow (-y, -x) \end{aligned} \tag{5}$$

where C_n is a rotation by an angle $2\pi/n$ and σ denotes a reflection [31,32]. The irreps are A_1, A_2, B_1, B_2 and E; the first four ones one-dimensional and the last one two-dimensional.

Case 3: $a \neq b$. This case was treated by Fernández and Ogilvie [16] and Radicioni et al. [21,22] and was avoided by Killingbeck and Jones [6] and Witwit [9]. The point group is C_{2v} with operations

$$\begin{aligned} E &: (x, y) \rightarrow (x, y) \\ C_2 &: (x, y) \rightarrow (-x, -y) \\ \sigma_{v1} &: (x, y) \rightarrow (x, -y) \\ \sigma_{v2} &: (x, y) \rightarrow (-x, y) \end{aligned} \tag{6}$$

and only one-dimensional irreps A_1, A_2, B_1 and B_2. It is an Abelian group.

4 Perturbation theory for Case 2

The eigenfunctions and eigenvalues of the unperturbed oscillator $H_0 = H(\lambda = 0)$ are

$$\begin{aligned} H_0\varphi_{m,N-m} &= E_N^{(0)}\varphi_{m,N-m}, \ m = 0, 1, \ldots, N \\ E_N^{(0)} &= 2(N + 1), \ N = 0, 1, \ldots, \end{aligned} \tag{7}$$

where

$$\varphi_{m,n}(x, y) = \phi_m(x)\phi_n(y), \tag{8}$$

and $\phi_m(q)$ is an eigenfunction of $H_{HO} = p_q^2 + q^2$. The N -th unperturbed eigenvalue is $(N + 1)$-fold degenerate and the perturbation reduces this degeneracy because the symmetry of H is smaller than that of H_0.

The perturbation splits the set of degenerate eigenfunctions of H_0 with eigenvalue $E^{(0)}_{2K}$, $K = 0, 1, \ldots$, into sets of eigenfunctions of H of symmetry A_1, B_1, A_2 and B_2 and those with eigenvalue $E^{(0)}_{2K+1}$ into sets of eigenfunctions of symmetry E. As a result, the eigenfunctions of H can be written as linear combinations of the complete set of eigenfunctions of H_0 in the following way:

$$\begin{aligned}
\psi^{A_1} &= \sum_{m=0}^{\infty}\sum_{n=m}^{\infty} c^{A_1}_{mn}\varphi^{+}_{2m,2n}\\
\psi^{B_1} &= \sum_{m=0}^{\infty}\sum_{n=m+1}^{\infty} c^{B_1}_{mn}\varphi^{-}_{2m,2n}\\
\psi^{A_2} &= \sum_{m=0}^{\infty}\sum_{n=m+1}^{\infty} c^{A_2}_{mn}\varphi^{-}_{2m+1,2n+1}\\
\psi^{B_2} &= \sum_{m=0}^{\infty}\sum_{n=m}^{\infty} c^{B_2}_{mn}\varphi^{+}_{2m+1,2n+1}\\
\psi^{E}_{eo} &= \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} c^{E}_{mn}\varphi_{2m,2n+1}\\
\psi^{E}_{oe} &= \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} c^{E}_{nm}\varphi_{2m+1,2n},
\end{aligned} \tag{9}$$

where

$$\varphi^{+}_{m,n} = \frac{\sqrt{2-\delta_{mn}}}{2}\left(\varphi_{m,n}+\varphi_{n,m}\right),\ \varphi^{-}_{m,n} = \frac{1}{\sqrt{2}}\left(\varphi_{m,n}-\varphi_{n,m}\right). \tag{10}$$

The subscripts o and e stand for even and odd, respectively and refer to the behaviour of ψ^E_{eo} and ψ^E_{oe} with respect to the reflection planes σ_{v1} and σ_{v2}. The derivation of these symmetry-adapted basis functions by means of the projection operators (1) is straightforward. With respect to the coefficients of the eigenfunctions of symmetry E note that if ψ^E_{eo} is an eigenfunction of H then $\sigma_{d1}\psi^E_{eo} = \psi^E_{oe}$ is also a linearly independent eigenfunction with the same eigenvalue; therefore, $\{\psi^E_{eo}, \psi^E_{oe}\}$ is a basis for this irrep.

The MPT is based on recurrence relations for the moments

$$I_{m,n} = \langle f_{m,n}\,|\psi\rangle,\ f_{m,n} = x^m y^n e^{-\alpha(x^2+y^2)},\ m,n = 0,1,\ldots, \tag{11}$$

where ψ is an eigenfunction of H. Therefore, according to (3) we have

$$I_{m,n} = \left\langle f_{m,n}\,\middle|\,\psi^S\right\rangle = \left\langle P^S f_{m,n}\,\middle|\,\psi^S\right\rangle, \tag{12}$$

for the irrep S. Obviously, $I_{m,n} = 0$ if $f_{m,n}$ does not have the proper symmetry. A straightforward calculation shows that

$$
\begin{aligned}
I^{A_1}_{2m,2n} &= \frac{1}{2}\left\langle \left(f_{2m,2n} + f_{2n,2m}\right) \middle| \psi^{A_1} \right\rangle \\
I^{B_1}_{2m,2n} &= \frac{1}{2}\left\langle \left(f_{2m,2n} - f_{2n,2m}\right) \middle| \psi^{B_1} \right\rangle \\
I^{A_2}_{2m+1,2n+1} &= \frac{1}{2}\left\langle \left(f_{2m+1,2n+1} - f_{2n+1,2m+1}\right) \middle| \psi^{A_2} \right\rangle \\
I^{B_2}_{2m+1,2n+1} &= \frac{1}{2}\left\langle \left(f_{2m+1,2n+1} + f_{2n+1,2m+1}\right) \middle| \psi^{B_2} \right\rangle \\
I^{E}_{2m,2n+1} &= \left\langle f_{2m,2n+1} \middle| \psi^{E}_{eo} \right\rangle \\
I^{E}_{2m+1,2n} &= \left\langle f_{2m+1,2n} \middle| \psi^{E}_{oe} \right\rangle .
\end{aligned} \tag{13}
$$

We appreciate that $I^{A_1}_{2m,2n} = I^{A_1}_{2n,2m}$, $I^{B_1}_{2m,2n} = -I^{B_1}_{2n,2m}$, etc. is the kind of boundary conditions taken into account in earlier MPT treatments of the anharmonic oscillators (see, for example, [6,9,21,22]).

In order to illustrate the effect of the symmetry of the perturbation on the corrections of first order to the energy we simply diagonalize the matrix representation of the perturbation $\mathbf{H}'$ in the basis set of degenerate eigenfunctions of H_0. Obviously, since functions of different symmetry do not mix it is preferable (and advisable) to diagonalize the matrices $\mathbf{H}'(S)$ for every one of the irreps S.

The case $N = 0$ is trivial but we include it here for completeness. There is only one function and the correction of first order is

$$
\left\langle \varphi_{00} \left| H' \right| \varphi_{00} \right\rangle = \frac{3a + c}{2}. \tag{14}
$$

When $N = 1$ we have two functions of symmetry E that lead to a diagonal matrix:

$$
\mathbf{H}'(E) = \begin{pmatrix} \frac{3(3a+c)}{2} & 0 \\ 0 & \frac{3(3a+c)}{2} \end{pmatrix}, \tag{15}
$$

because $\varphi_{0,1}$ and $\varphi_{1,0}$ have different eigenvalues with respect to the operators σ_{v1} and σ_{v2}.

When $N = 2$ the function φ_{11} is B_2 and the functions $\{\varphi_{20}, \varphi_{02}\}$ are linear combinations of functions of symmetry A_1 and B_1. We have

$$
\left\langle \varphi_{11} \left| H' \right| \varphi_{11} \right\rangle = \frac{3\,(5a + 3c)}{2}, \tag{16}
$$

for the former and

$$
\mathbf{H}' = \begin{pmatrix} \frac{21a+5c}{2} & c \\ c & \frac{21a+5c}{2} \end{pmatrix}, \tag{17}
$$

for the latter. This matrix is not diagonal; however if we use the symmetry-adapted functions $\{\varphi^{+}_{20}, \varphi^{-}_{20}\}$ we obtain a diagonal one:

$$\mathbf{H}' = \begin{pmatrix} \frac{7(3a+c)}{2} & 0 \\ 0 & \frac{3(7a+c)}{2} \end{pmatrix} \tag{18}$$

A different situation arises for $N = 3$ because the four degenerate unperturbed eigenfunctions can be grouped into two pairs of symmetry E: $\{\varphi_{3,0}, \varphi_{1,2}\}$ and $\{\varphi_{0,3}, \varphi_{2,1}\}$. Both lead to identical matrix representations of the perturbation:

$$\mathbf{H}'(E) = \begin{pmatrix} \frac{39a+7c}{2} & \sqrt{3}c \\ \sqrt{3}c & \frac{3(9a+5c)}{2} \end{pmatrix} \tag{19}$$

with eigenvalues

$$E^{(1)} = \frac{11\,(3a+c) \pm 2\sqrt{9a^2 - 12ac + 7c^2}}{2}. \tag{20}$$

We cannot make this matrix diagonal by means of symmetry operations; therefore the inner product method as applied by Killingbeck and Jones [6] and Witwit [9] is expected to fail, and in fact they entirely omitted the treatment of these energy levels. By a judicious manipulation of the moment recurrence relations one can derive a quadratic equation for one of the moments of order zero in order to obtain the corrections to the energy [16,21,22,24].

From the results above we conclude that the first energy levels corrected to first order are given by

$$\begin{aligned}
E_{1A_1} &= 2 + \frac{3a+c}{2}\lambda + \ldots \\
E_{1E} &= 4 + \frac{3\,(3a+c)}{2}\lambda + \ldots \\
E_{1B_2} &= 6 + \frac{3(5a+3c)}{2}\lambda + \ldots \\
E_{2A_1} &= 6 + \frac{7\,(3a+c)}{2}\lambda + \ldots \\
E_{1B_1} &= 6 + \frac{3\,(7a+c)}{2}\lambda + \ldots \\
E_{2E} &= 8 + \frac{11\,(3a+c) - 2\sqrt{9a^2 - 12ac + 7c^2}}{2}\lambda + \ldots \\
E_{3E} &= 8 + \frac{11\,(3a+c) + 2\sqrt{9a^2 - 12ac + 7c^2}}{2}\lambda + \ldots
\end{aligned} \tag{21}$$

where the subscript jS indicates that the symmetry S appears for the j-th time. The level order may change with the relative magnitudes of the potential parameters.

Killingbeck and Jones [6] and Witwit [9] calculated some of the eigenvalues corresponding to $N = 0, 1, 2, 4$, respectively. Note that they omitted the four states that stem from $N = 3$ and three of the five states that come from $N = 4$ [which do not appear in equation (21)]. The reason is that their mathematical treatment of the moment recurrence relations did not enable them to obtain suitable working equations

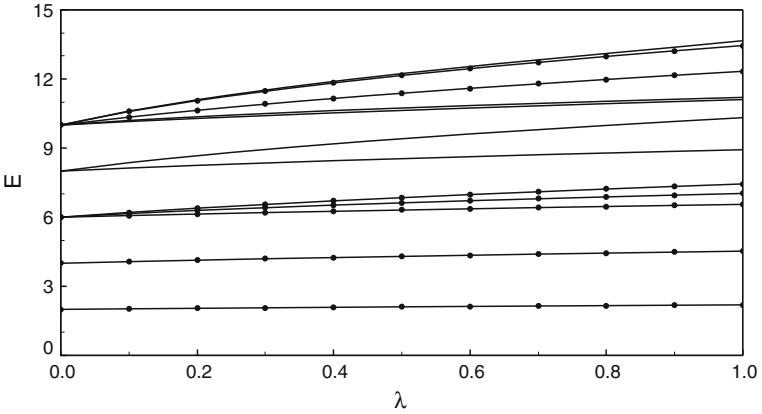

Fig. 1 First eigenvalues of the anharmonic oscillator (4) (Case 2). Solid lines and points indicate present and Witwit's results [9], respectively

for such cases. They chose examples where the perturbation corrections of first order are linear functions of the potential parameters, while for $N = 3$, for example, they are nonlinear as shown above. In the case $N = 3$ one expects quadratic equations for the moments of order zero as shown by Fernández and Ogilvie [16] and Radicioni et al. [21,22] (see also Fernández [24]) for the Case 3 discussed in the following section.

In order to illustrate the omission of states mentioned above we calculated the eigenvalues of the anharmonic oscillator with $a = b = 0$, $c = 1$ and $0 \leq \lambda \leq 1$ and compared them with those reported by Witwit [9] (Killingbeck and Jones [6] also showed some results). Figure 1 clearly shows that those authors omitted 7 of the 15 states that come from $N = 0, 1, 2, 3, 4$. In order to obtain the eigenvalues displayed in that figure we resorted to the Rayleigh–Ritz variational method in the Krylov space spanned by the set of non-orthogonal functions $\Omega_n^S = H^n \Omega^S$ for each irrep S. For the present problem suitable reference functions Ω^S are given by

$$\begin{aligned}
\Omega^{A_1} &= e^{-\alpha(x^2+y^2)} \\
\Omega^{B_1} &= (x^2 - y^2) e^{-\alpha(x^2+y^2)} \\
\Omega^{A_2} &= (xy^3 - x^3 y) e^{-\alpha(x^2+y^2)} \\
\Omega^{B_2} &= xy e^{-\alpha(x^2+y^2)} \\
\Omega_{oe}^{E} &= x e^{-\alpha(x^2+y^2)} \\
\Omega_{eo}^{E} &= y e^{-\alpha(x^2+y^2)},
\end{aligned} \tag{22}$$

where $\alpha > 0$ can be chosen in order to get the greatest rate of convergence. Here we simply chose $\alpha = 1$ and matrices of dimension 20×20 because great accuracy is not required.

In order to facilitate the comparison of the results and the interpretation of Fig. 1 in what follows we list the labels used in the present paper and in the ones of those authors:

$$
\begin{aligned}
&N = 0 \rightarrow 1A_1 \rightarrow (0, 0, e)\\
&N = 1 \rightarrow 1E \rightarrow (0, 1, \text{mixed}),\ (1, 0, \text{mixed})\\
&N = 2 \rightarrow \begin{cases} 1B_1 \rightarrow (0, 2, \text{o})\\ 2A_1 \rightarrow (0, 2, \text{e})\\ 1B_2 \rightarrow (1, 1, \text{e}) \end{cases}\\
&N = 3 \rightarrow \begin{cases} 2E \rightarrow \text{omitted}\\ 3E \rightarrow \text{omitted} \end{cases}\\
&N = 4 \rightarrow \begin{cases} 3A_1 \rightarrow \text{omitted}\\ 2B_1 \rightarrow \text{omitted}\\ 1A_2 \rightarrow (1, 3, \text{o})\ .\\ 2B_2 \rightarrow (1, 3, \text{e})\\ 4A_1 \rightarrow \text{omitted} \end{cases}
\end{aligned} \tag{23}
$$

Killingbeck and Jones [6] mentioned problems with some excited states. They briefly referred to the coupling of the states $\varphi_{1,2}$ and $\varphi_{3,0}$ but did not show any equation that could overcome the difficulty. On the other hand, Witwit [9] never considered this situation at all.

5 Perturbation theory for Case 3

When $a \neq b$ the perturbation splits the set of degenerate eigenfunctions of H_0 with eigenvalue $E^{(0)}_{2K}$, $K = 0, 1, \ldots$, into sets of eigenfunctions of H of symmetry A_1, and A_2 and those with eigenvalue $E^{(0)}_{2K+1}$ into sets of eigenfunctions of symmetry B_1 and B_2. The eigenfunctions of H can be written as linear combinations of the unperturbed eigenfunctions in the following way:

$$
\begin{aligned}
\psi^{A_1} &= \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} c^{A_1}_{mn}\varphi_{2m,2n}\\
\psi^{A_2} &= \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} c^{A_2}_{mn}\varphi_{2m+1,2n+1}\\
\psi^{B_1} &= \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} c^{B_1}_{mn}\varphi_{2m+1,2n}\\
\psi^{B_2} &= \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} c^{B_2}_{mn}\varphi_{2m,2n+1}.
\end{aligned} \tag{24}
$$

As in the preceding case we apply straightforward perturbation theory of first order beginning with the trivial case $N = 0$:

$$
\langle \varphi_{00} \left| H' \right| \varphi_{00} \rangle = \frac{3a + 3b + 2c}{4}. \tag{25}
$$

When $N = 1$ the two functions exhibit symmetry B_1 and B_2 and the perturbation matrix is diagonal

$$\mathbf{H}' = \begin{pmatrix} \frac{3(5a+b+2c)}{4} & 0 \\ 0 & \frac{3(a+5b+2c)}{4} \end{pmatrix}. \tag{26}$$

Of the three functions for $N = 2$ two exhibit symmetry A_1 and the remaining one symmetry A_2. The matrix for the former is not diagonal

$$\mathbf{H}'(A_1) = \begin{pmatrix} \frac{3a+39b+10c}{4} & c \\ c & \frac{39a+3b+10c}{4} \end{pmatrix}, \tag{27}$$

and has eigenvalues

$$E^{(1)} = \frac{21a + 21b + 10c \pm 2\sqrt{81a^2 - 162ab + 81b^2 + 4c^2}}{4}. \tag{28}$$

This matrix cannot be brought into a diagonal form by means of symmetry operations. On the other hand, for the symmetry A_2 we simply have

$$\langle \varphi_{11} | H' | \varphi_{11} \rangle = \frac{3\,(5a + 5b + 6c)}{4} \tag{29}$$

Thus, the first eigenvalues corrected to first order are:

$$\begin{aligned}
E_{1A_1} &= 2 + \frac{3a + 3b + 2c}{4}\lambda + \ldots \\
E_{1B_1} &= 4 + \frac{3\,(5a + b + 2c)}{4}\lambda + \ldots \\
E_{1B_2} &= 4 + \frac{3\,(a + 5b + 2c)}{4}\lambda + \ldots \\
E_{2A_1} &= 6 + \frac{21a + 21b + 10c - 2\sqrt{81a^2 - 162ab + 81b^2 + 4c^2}}{4}\lambda + \ldots \\
E_{3A_1} &= 6 + \frac{21a + 21b + 10c - 2\sqrt{81a^2 - 162ab + 81b^2 + 4c^2}}{4}\lambda + \ldots \\
E_{1A_2} &= 6 + \frac{3\,(5a + 5b + 6c)}{4}\lambda + \ldots
\end{aligned} \tag{30}$$

In this case the inner product method as applied by Killingbeck and Jones [6] and Witwit [9] begins to be unsuitable at $N = 2$ because it is not expected to yield the states A_1 (although, it is known to be successful for the remaining state A_2 [24]). In order to obtain the perturbation corrections for E_{2A_1} and E_{3A_1} one has to manipulate the moment recurrence relations and derive a quadratic expression for one of the moments of order zero as shown by Fernández and Ogilvie [16] and Radicioni et al. [21,22] (see also Fernández [24]).

6 Conclusions

The aim of this paper is the discussion of the application of the MPT (or inner product method) to anharmonic oscillators. For concreteness in the preceding sections we focused on the simple two-dimensional model (4) but other cases can be treated in the same way. We have shown that PGS is extremely useful for understanding the way in which the perturbation affects the states of the unperturbed model and the boundary and initial conditions that one should consider during the manipulation of the moment recurrence relations. In particular we were interested in the determination of the conditions under which the application of the inner product method in the way proposed by Killingbeck and Jones [6] and Witwit [9] is successful. The conclusion of our analysis is that such an approach is expected to fail for some excited states of the anharmonic oscillator (4) for the Cases 2 and 3 discussed in sects. 4 and 5, respectively. The particular results derived there can be generalized in the following way: suppose that $\chi_{n,j}$, $j = 1, 2, \ldots, \nu$ are degenerate eigenfunctions of H_0 with eigenvalue $E_n^{(0)}$ adapted to the symmetry S of the point group G of H. If the dimension l_S of S is smaller than ν then the application of the inner product approach proposed by Killingbeck and Jones [6] and Witwit [9] is expected to fail. In this case one has to manipulate the recurrence relations for the moments in order to derive a polynomial function of one of the moments of order zero. Each of the roots of this polynomial will lead to the correction to the energy of each of the states coupled by the perturbation. For example, the states stemming from $N = 3$ in Case 2 lead to two quadratic equations from which we obtain the perturbation corrections for the energy levels E_{2E} and E_{3E}. It is not difficult to verify that more complex situations appear for greater values of N. The Case 3 was not treated by Killingbeck and Jones [6] and Witwit [9] but Fernández and Ogilvie [16] and Radicioni et al. [21,22] (see also Fernández [24]) showed how to obtain quadratic polynomial equations for the two states A_1 coming from $N = 2$. PGS predicts that for $N = 3$ we should have two quadratic equations that yield the perturbation corrections for two states of symmetry B_1 and two states of symmetry B_2.

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