Group theoretical analysis of a quantum-mechanical three-dimensional quartic anharmonic oscillator

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Abstract

This paper illustrates the application of group theory to a quantum-mechanical three-dimensional quartic anharmonic oscillator with O_h symmetry. It is shown that group theory predicts the degeneracy of the energy levels and facilitates the application of perturbation theory and the Rayleigh-Ritz variational method as well as the interpretation of the results in terms of the symmetry of the solutions . We show how to obtain suitable symmetry-adapted basis sets.

Keywords: Group theory, anharmonic oscillator, O_h point group, perturbation theory, variational method, symmetry-adapted basis set

1. Introduction

Quantum-mechanical anharmonic oscillators have proved useful for the analysis of the vibration-rotation spectra of polyatomic molecules[1–3]. Several aspects of such spectra as well as other molecular properties have been modelled by means of simple coupled oscillators mainly with cubic and quar-

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tic anharmonicities[4–20]. These and other applications of the ubiquitous quantum-mechanical anharmonic oscillators motivated their study and the development of suitable methods for the treatment of the corresponding eigenvalue equations[21–70]. The list of papers just mentioned is far from being exhaustive and its purpose is merely to give an idea of the interest aroused by the anharmonic oscillators along the years.

Some authors have taken into account the symmetry of the anharmonic oscillators in order to simplify their treatment[59, 60, 68] and others resorted to the more formal point group symmetry (PGS) to classify the vibrational states[15, 36, 37, 49, 59, 61]. Despite the great amount of information provided by PGS none of those papers exhibits a full application of such mathematical tool, except the analysis of two-dimensional cubic and quartic oscillators by Pullen and Edmonds[41, 42]. These papers motivated a recent application of PGS to a variety of Hermitian[71–74] and non-Hermitian anharmonic oscillators with space-time symmetry[75–79]. In the latter case PGS proved suitable for determining the conditions that complex anharmonic potentials should satisfy in order to support real eigenvalues.

The aim of this paper is to reinforce the idea that PGS is most important in the study of quantum-mechanical anharmonic oscillators because we deem that such technique has been surprisingly overlooked or disregarded (except for the few works already mentioned above[41, 42, 71–79]).

In Section 2 we introduce the model, a quartic anharmonic oscillator with considerably large symmetry described by the point group O_h. This problem was treated before by means of perturbation theory and a less formal approach to symmetry based on parity and coordinate-permutation

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operations[59]. Here we classify the eigenstates of the unperturbed Hamiltonian according to the irreducible representations (irreps) of that point group and predict the rupture of the degeneracy by the quartic perturbation. In Section 3 we apply perturbation theory through second order to verify the splitting of the eigenspaces predicted in the preceding section. In Section 4 we discuss the application of the Rayleigh-Ritz variational method with basis sets adapted to the symmetry of the problem. In three consecutive subsections we discuss the harmonic oscillator basis set, the Krylov space and a non-orthogonal basis set. We show results illustrating the splitting of the unperturbed eigenspaces due to the quartic perturbation that breaks the symmetry of the system. In Section 5 we summarize the main results of the paper and draw conclusions. Finally, in the Appendix A we outline the main features of group theory that are necessary for the analysis of the present problem.

2. Model

Among the many models mentioned above we have chosen a three-dimensional quartic anharmonic oscillator already studied earlier by Turbiner[59]

$$
\begin{aligned}
H &= p_x^2 + p_y^2 + p_z^2 + x^2 + y^2 + z^2 + \lambda \left[\beta \left(x^4 + y^4 + z^4 \right) + x^2 y^2 + x^2 z^2 + y^2 z^2 \right], \\
&\quad \lambda > 0, \ \beta > 0,
\end{aligned}
\tag{1}
$$

who recognized that it exhibits the symmetry of a cube. The author stated that his classification based on parity and permutation operators was incomplete. In this paper we describe the symmetry properties of this model by means of the point group O_h[80–82]. In other words, this Hamiltonian

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operator is invariant with respect to the symmetry operations indicated in the table of characters shown in Table 1 described in the Appendix A. A detailed discussion of the construction of the matrix representation of the symmetry operations for the O_h point group is available elsewhere[73].

The eigenvalues $E_{kmn}^{(0)}$ and eigenfunctions $\varphi_{kmn}(x, y, z)$ of $H_0 = H(\lambda = 0)$ are

$$
\begin{aligned}
E_{kmn}^{(0)} &= 2(k + m + n) + 3 \\
\varphi_{kmn}(x, y, z) &= \phi_k(x)\phi_m(y)\phi_n(z), \ \ k, m, n = 0, 1, \ldots, \qquad (2)
\end{aligned}
$$

where $\phi_j(q)$ is an eigenfunction of the one-dimensional harmonic oscillator $H_{HO} = p_q^2 + q^2$. Every energy level is $\frac{(\nu+1)(\nu+2)}{2}$-fold degenerate, where $\nu = k + m + n$.

Throughout this paper we resort to the following notation for the permutation of a set of three real numbers

$$
\begin{aligned}
\{a, a, a\}_P &= \{a, a, a\} \\
\{a, b, b\}_P &= \{\{a, b, b\}, \{b, a, b\}, \{b, b, a\}\} \\
\{a, b, c\}_P &= \{\{a, b, c\}, \{c, a, b\}, \{b, c, a\}, \{b, a, c\}, \{c, b, a\}, \{a, c, b\}\}, \quad (3)
\end{aligned}
$$

where it is assumed that $a \neq b$, $a \neq c$, and $b \neq c$. It enables us to express

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the symmetry of the unperturbed eigenfunctions ($\lambda = 0$) as

$$
\begin{aligned}
&\{2n, 2n, 2n\} && A_{1g} \\
&\{2n + 1, 2n + 1, 2n + 1\} && A_{2u} \\
&\{2n + 1, 2n + 1, 2m\}_P && T_{2g} \\
&\{2n, 2n, 2m + 1\}_P && T_{1u} \\
&\{2n, 2n, 2m\}_P && A_{1g}, E_g \\
&\{2n + 1, 2n + 1, 2m + 1\}_P && A_{2u}, E_u \\
&\{2n, 2m, 2k\}_P && A_{1g}, A_{2g}, E_g, E_g \\
&\{2n + 1, 2m + 1, 2k + 1\}_P && A_{1u}, A_{2u}, E_u, E_u \\
&\{2n, 2m, 2k + 1\}_P && T_{1u}, T_{2u} \\
&\{2n + 1, 2m + 1, 2k\}_P && T_{1g}, T_{2g}
\end{aligned}
\tag{4}
$$

The anharmonic part of the potential reduces the symmetry of the system and the degeneracy of the energy levels is consequently diminished when $\lambda > 0$ causing a splitting of the energy levels. For the lowest ones this splitting is given by

$$
\begin{aligned}
\nu &= 0 \rightarrow A_{1g} \\
\nu &= 1 \rightarrow T_{1u} \\
\nu &= 2 \rightarrow A_{1g}, E_g, T_{2g} \\
\nu &= 3 \rightarrow A_{2u}, T_{1u}, T_{1u}, T_{2u} \\
\nu &= 4 \rightarrow A_{1g}, A_{1g}, E_g, E_g, T_{1g}, T_{2g}, T_{2g}.
\end{aligned}
\tag{5}
$$

This equation tells us that the lowest energy level is nondegenerate, the first excited energy level remains three-fold degenerate, the second excited energy level splits into a singlet a doublet and a triplet, the third excited energy level

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splits into a singlet and three triples (two of them of the same symmetry T_{1u}), etc. Note the alternating parity (either g or u) given by $(-1)^\nu$.

For simplicity, in this paper we restrict ourselves to the case $\beta = 0$. This choice reduces the number of parameters in the potential-energy function but alters neither the symmetry of the problem nor the main conclusions drawn from it.

3. Perturbation theory

The purpose of this section is merely to carry out a simple calculation based on perturbation theory in order to verify the splitting of the energy levels outlined by equation (5). There are several strategies for obtaining the perturbation corrections when H_0 exhibits degenerate states. Here we simply obtain the first two perturbation corrections by inserting the truncated expansion $E = E^{(0)} + E^{(1)}\lambda + E^{(2)}\lambda^2$ into the characteristic polynomial given by the secular determinant $|H - EI| = 0$ and then solving the resulting equation for $E^{(1)}$ and $E^{(2)}$. This apparently impractical brute-force approach is sufficient for present purposes; the only subtlety being that each irrep is treated separately as discussed in section 4 (in particular with the basis set of subsection 4.3). For the first energy levels we obtain the following results

$$E_{1A_{1g}} = 3 + \frac{3}{4}\lambda - \frac{15}{32}\lambda^2 + O(\lambda^3), \tag{6}$$

$$E_{1T_{1u}} = 5 + \frac{7}{4}\lambda - \frac{51}{32}\lambda^2 + O(\lambda^3), \tag{7}$$

$$E_{1E_g} = 7 + \frac{9}{4}\lambda - \frac{9}{4}\lambda^2 + O(\lambda^3),$$

$$E_{2A_{1g}} = 7 + \frac{15}{4}\lambda - \frac{171}{32}\lambda^2 + O(\lambda^3),$$

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$$E_{1T_{2g}} \;=\; 7 + \frac{15}{4}\lambda - \frac{147}{32}\lambda^2 + O(\lambda^3), \tag{8}$$

$$E_{2T_{1u}} \;=\; 9 + \frac{13}{4}\lambda - \frac{225}{56}\lambda^2 + O(\lambda^3),$$

$$E_{1T_{2u}} \;=\; 9 + \frac{21}{4}\lambda - \frac{57}{8}\lambda^2 + O(\lambda^3),$$

$$E_{3T_{1u}} \;=\; 9 + \frac{27}{4}\lambda - \frac{2649}{224}\lambda^2 + O(\lambda^3),$$

$$E_{1A_{2u}} \;=\; 9 + \frac{27}{4}\lambda - \frac{351}{32}\lambda^2 + O(\lambda^3), \tag{9}$$

which are consistent with the prediction of group theory shown in equation (5). It is worth noting that the degeneracy of the pairs of energy levels $(E_{2A_{1g}}, E_{1T_{2g}})$ and $(E_{1A_{2u}}, E_{3T_{1u}})$ breaks at second order (the correction of first order being identical). However, such states offer no difficulty because we can treat each member of the pair separate from the other because they belong to different symmetry species. This strategy is one of the advantages of a possible systematic application of group theory to perturbation theory.

4. Rayleigh-Ritz variational method

This approach is based on a variational ansatz given by a finite linear combination of functions of a basis set $B = \{f_0, f_1, \ldots\}$:

$$\psi = \sum_{i=0}^{N-1} c_i f_i. \tag{10}$$

The variational coefficients c_i are chosen so that the variational integral

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}, \tag{11}$$

is a minimum. The condition $\partial E / \partial c_j = 0$ leads to the secular equations

$$\langle f_j | H - E | \psi \rangle = 0, \; j = 0, 1, \ldots, N-1, \tag{12}$$

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from which we obtain the coefficients c_i and approximate energies $E_j(N)$, $j = 0, 1, \ldots, N - 1$. This result is valid for orthogonal as well as non-orthogonal basis functions f_j, provided that in the latter case the functions are linearly independent. This approach always yields increasingly tighter upper bounds because $E_j(N) > E_j(N + 1)$[83].

If the system exhibits symmetry it is convenient to choose a suitable basis set $B^S = \left\{ f_0^S, f_1^S, \ldots \right\}$ for each irrep S. In order to obtain it we apply the projection operator P^S (see the Appendix A for more details) to every $f_i \in B$ and then remove the linearly dependent functions from the resulting set $\left\{ P^S f_i, \ i = 0, 1, \ldots \right\}$. One advantage of using the basis sets B^S is that the dimension of the secular equations for a given accuracy is considerably smaller. Thus, instead of equations (10) and (12) we have

$$\psi^S = \sum_{i=0}^{N_S-1} c_i^S f_i^S, \tag{13}$$

and

$$\left\langle f_j^S \middle| H - E^S \middle| \psi^S \right\rangle = 0, \ j = 0, 1, \ldots, N_S - 1, \tag{14}$$

for each irrep S. In this case we obtain upper bounds for each irrep exactly in the same way as before: $E_j^S(N_S) > E_j^S(N_S + 1)$.

4.1. Basis set of eigenfunctions of H_0

One of the most convenient basis sets consists of linear combinations of eigenfunctions of H_0 adapted to the symmetry of H. In this case the variational method reduces to diagonalizing the matrix representation of the Hamiltonian $\mathbf{H}^S$ in each orthonormal basis set $B^S = \left\{ \varphi_{kmn}^S \right\}$ adapted to the corresponding symmetry species S. We thus obtain approximate eigenvalues

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E^S and eigenfunctions ψ^S that are linear combinations of the form

$$\psi^S = \sum_{k,m,n} c^S_{k\,m\,n} \varphi^S_{k\,m\,n}.$$ (15)

The coefficients $c^S_{k\,m\,n}$ and the approximate eigenvalues E^S are given by the eigenvectors and eigenvalues of $\mathbf{H}^S$, respectively, and are also solutions of a secular equation similar to (14). The projection operators enable us to construct the symmetry-adapted basis sets B^S in the following way

$$P^S \varphi_{k\,m\,n} = \sum_{k',m',n'} u^{k'\,m'\,n'}_{k\,m\,n} \varphi_{k'\,m'\,n'}.$$ (16)

Since $[H_0, P^S] = 0$ then $u^{k'\,m'\,n'}_{k\,m\,n} = 0$ unless $k + m + n = k' + m' + n' = \nu$.

After removing the linearly dependent functions and orthonormalizing the remaining ones the basis sets adapted to the symmetry of the Hamiltonian operator (1) result to be

A_{1g} :

$$\varphi_{2n\,2n\,2n}$$
$$\frac{1}{\sqrt{3}} \left(\varphi_{2n\,2m\,2m} + \varphi_{2m\,2n\,2m} + \varphi_{2m\,2m\,2n} \right)$$
$$\frac{1}{\sqrt{6}} \left(\varphi_{2k\,2m\,2n} + \varphi_{2n\,2k\,2m} + \varphi_{2m\,2n\,2k} + \varphi_{2m\,2k\,2n} + \varphi_{2n\,2m\,2k} \right.$$
$$\left. + \varphi_{2k\,2n\,2m} \right),$$ (17)

A_{2g} :

$$\frac{1}{\sqrt{6}} \left(\varphi_{2k\,2m\,2n} + \varphi_{2n\,2k\,2m} + \varphi_{2m\,2n\,2k} - \varphi_{2m\,2k\,2n} - \varphi_{2n\,2m\,2k} \right.$$
$$\left. - \varphi_{2k\,2n\,2m} \right),$$ (18)

E_g :

$$\left\{ \frac{1}{\sqrt{6}} \left(2\varphi_{2n\,2m\,2m} - \varphi_{2m\,2n\,2m} - \varphi_{2m\,2m\,2n} \right), \frac{1}{\sqrt{2}} \left(\varphi_{2m\,2n\,2m} - \varphi_{2m\,2m\,2n} \right) \right\}$$

$$\left\{ \frac{1}{\sqrt{6}} \left(2\varphi_{2k\,2m\,2n} - \varphi_{2n\,2k\,2m} - \varphi_{2m\,2n\,2k} \right), \frac{1}{\sqrt{2}} \left(\varphi_{2n\,2k\,2m} - \varphi_{2m\,2n\,2k} \right) \right\}$$

$$\left\{ \frac{1}{\sqrt{6}} \left(2\varphi_{2m\,2k\,2n} - \varphi_{2n\,2m\,2k} - \varphi_{2k\,2n\,2m} \right), \frac{1}{\sqrt{2}} \left(\varphi_{2n\,2m\,2k} - \varphi_{2k\,2n\,2m} \right) \right\} \tag{19}$$

T_{1g} :

$$\left\{ \frac{1}{\sqrt{2}} \left(\varphi_{2k\,2m+1\,2n+1} - \varphi_{2k\,2n+1\,2m+1} \right), \frac{1}{\sqrt{2}} \left(\varphi_{2m+1\,2k\,2n+1} - \varphi_{2n+1\,2k\,2m+1} \right), \right.$$
$$\left. \frac{1}{\sqrt{2}} \left(\varphi_{2m+1\,2n+1\,2k} - \varphi_{2n+1\,2m+1\,2k} \right) \right\}, \tag{20}$$

T_{2g} :

$$\left\{ \varphi_{2k\,2m+1\,2m+1}, \varphi_{2m+1\,2k\,2m+1}, \varphi_{2m+1\,2m+1\,2k} \right\}$$
$$\left\{ \frac{1}{\sqrt{2}} \left(\varphi_{2k\,2m+1\,2n+1} + \varphi_{2k\,2n+1\,2m+1} \right), \frac{1}{\sqrt{2}} \left(\varphi_{2m+1\,2k\,2n+1} + \varphi_{2n+1\,2k\,2m+1} \right), \right.$$
$$\left. \frac{1}{\sqrt{2}} \left(\varphi_{2m+1\,2n+1\,2k} + \varphi_{2n+1\,2m+1\,2k} \right) \right\}, \tag{21}$$

A_{1u} :

$$\frac{1}{\sqrt{6}} \left(\varphi_{2k+1\,2m+1\,2n+1} + \varphi_{2n+1\,2k+1\,2m+1} + \varphi_{2m+1\,2n+1\,2k+1} - \varphi_{2m+1\,2k+1\,2n+1} \right.$$
$$\left. -\varphi_{2n+1\,2m+1\,2k+1} - \varphi_{2k+1\,2n+1\,2m+1} \right), \tag{22}$$

A_{2u} :

$$\varphi_{2n+1\,2n+1\,2n+1}$$
$$\frac{1}{\sqrt{6}} \left(\varphi_{2k+1\,2m+1\,2n+1} + \varphi_{2n+1\,2k+1\,2m+1} + \varphi_{2m+1\,2n+1\,2k+1} + \varphi_{2m+1\,2k+1\,2n+1} \right.$$
$$\left. +\varphi_{2n+1\,2m+1\,2k+1} + \varphi_{2k+1\,2n+1\,2m+1} \right), \tag{23}$$

E_u :

$$\left\{\frac{1}{\sqrt{6}}\left(2\varphi_{2n+1\,2m+1\,2m+1} - \varphi_{2m+1\,2n+1\,2m+1} - \varphi_{2m+1\,2m+1\,2n+1}\right),\right.$$

$$\left.\frac{1}{\sqrt{2}}\left(\varphi_{2m+1\,2n+1\,2m+1} - \varphi_{2m+1\,2m+1\,2n+1}\right)\right\}$$

$$\left\{\frac{1}{\sqrt{6}}\left(2\varphi_{2k+1\,2m+1\,2n+1} - \varphi_{2n+1\,2k+1\,2m+1} - \varphi_{2m+1\,2n+1\,2k+1}\right),\right.$$

$$\left.\frac{1}{\sqrt{2}}\left(\varphi_{2n+1\,2k+1\,2m+1} - \varphi_{2m+1\,2n+1\,2k+1}\right)\right\},$$

$$\left\{\frac{1}{\sqrt{6}}\left(2\varphi_{2m+1\,2k+1\,2n+1} - \varphi_{2n+1\,2m+1\,2k+1} - \varphi_{2k+1\,2n+1\,2m+1}\right),\right.$$

$$\left.\frac{1}{\sqrt{2}}\left(\varphi_{2n+1\,2m+1\,2k+1} - \varphi_{2k+1\,2n+1\,2m+1}\right)\right\}, \tag{24}$$

T_{1u} :

$$\left\{\varphi_{2k+1\,2m\,2m}, \varphi_{2m\,2k+1\,2m}, \varphi_{2m\,2m\,2k+1}\right\}$$

$$\left\{\frac{1}{\sqrt{2}}\left(\varphi_{2k+1\,2m\,2n} + \varphi_{2k+1\,2n\,2m}\right), \frac{1}{\sqrt{2}}\left(\varphi_{2m\,2k+1\,2n} + \varphi_{2n\,2k+1\,2m}\right),\right.$$

$$\left.\frac{1}{\sqrt{2}}\left(\varphi_{2m\,2n\,2k+1} + \varphi_{2n\,2m\,2k+1}\right)\right\} \tag{25}$$

T_{2u} :

$$\left\{\frac{1}{\sqrt{2}}\left(\varphi_{2k+1\,2m\,2n} - \varphi_{2k+1\,2n\,2m}\right), \frac{1}{\sqrt{2}}\left(\varphi_{2m\,2k+1\,2n} - \varphi_{2n\,2k+1\,2m}\right),\right.$$

$$\left.\frac{1}{\sqrt{2}}\left(\varphi_{2m\,2n\,2k+1} - \varphi_{2n\,2m\,2k+1}\right)\right\}. \tag{26}$$

By convention φ_{ijk} means that all the subscripts are different, equal subscripts are indicated explicitly as, for example, in φ_{ijj}.

4.2. Krylov space

A particular basis set that spans what is commonly called the Krylov space is given by $f_i = H^i f$, where f is a suitably chosen function. If follows

from the properties of the projection operators discussed in the Appendix A that $P^S f_i = H^i P^S f = H^i f^S$ so that by simply choosing a seed function f^S with the correct symmetry then the resulting basis set is automatically adapted to the corresponding irrep. We thus have $B^S = \{f_i^S = H^i f^S, \ i = 0, 1, \dots\}$ for each irrep S and solve secular equations similar to (14).

Suitable seed functions are

$$f^{A_{1g}} = \exp\left[-a\left(x^2 + y^2 + z^2\right)\right], \tag{27}$$

$$f^{A_{2g}} = \left(x^4 y^2 - x^4 z^2 - x^2 y^4 + x^2 z^4 + y^4 z^2 - y^2 z^4\right) \exp\left[-a\left(x^2 + y^2 + z^2\right)\right], \tag{28}$$

$$f^{E_g} = \begin{cases} \left(2z^2 - x^2 - y^2\right) \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \\ \left(x^2 - y^2\right) \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \end{cases}, \tag{29}$$

$$f^{T_{1g}} = \begin{cases} \left(xy^3 - x^3 y\right) \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \\ \left(xz^3 - x^3 z\right) \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \\ \left(yz^3 - y^3 z\right) \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \end{cases}, \tag{30}$$

$$f^{T_{2g}} = \begin{cases} xy \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \\ xz \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \\ yz \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \end{cases}, \tag{31}$$

$$f^{A_{1u}} = \left(x^5 yz^3 - x^5 y^3 z + x^3 y^5 z - x^3 yz^5 - xy^5 z^3 + xy^3 z^5\right) \exp\left[-a\left(x^2 + y^2 + z^2\right)\right], \tag{32}$$

$$f^{A_{2u}} = xyz \exp\left[-a\left(x^2 + y^2 + z^2\right)\right], \tag{33}$$

$$f^{E_u} = \begin{cases} xyz\left(2z^2 - x^2 - y^2\right) \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \\ xyz\left(x^2 - y^2\right) \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \end{cases}, \tag{34}$$

$$f^{T_{1u}} = \begin{cases} x \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \\ y \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \\ z \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \end{cases}, \tag{35}$$

$$f^{T_{2u}} = \begin{cases} x\left(y^2 - z^2\right) \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \\ y\left(z^2 - x^2\right) \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \\ z\left(x^2 - y^2\right) \exp\left[-a\left(x^2 + y^2 + z^2\right)\right] \end{cases}, \tag{36}$$

where $a > 0$ is a nonlinear variational parameter that enables us to improve the accuracy of the results.

We carried out a set of calculations with $a = 1$ and encountered a most surprising difficulty. For some reason (unknown to us at present) the Rayleigh-Ritz variational method in the Krylov space yields only one of the two T_{1u} state triplets stemming from $E(\lambda = 0) = 7$ and only one of the T_{2g} state triplets stemming from $E(\lambda = 0) = 11$. We do not investigate this fact any further in this paper and just mention it in passing. This fact is surprising because we applied this approach in the past to other anharmonic oscillators and faced no such problem[71, 72].

4.3. Non-orthogonal basis set

In addition to the orthonormal basis set (17-26) we can also try a closely related symmetry-adapted non-orthogonal basis set given by

$$B^S = \left\{ P^S x^k y^m z^n \exp\left[-a\left(x^2 + y^2 + z^2\right)\right], \ k, m, n = 0, 1, \ldots \right\}, \tag{37}$$

where a is a variational parameter that we set equal to unity for simplicity. In order to obtain a suitable basis set B^S it is necessary to remove all the

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linearly dependent functions produced by the application of the projection operator. Since this approach is quite straightforward for programming we chose it for present calculations of basis set dimensions $N_{A_{1g}} = 41$, $N_{E_g} = 54$, $N_{T_{1g}} = 66$, $N_{T_{2g}} = 102$, $N_{A_{2u}} = 16$, $N_{T_{1u}} = 23$, $N_{T_{2u}} = 39$. The first energy levels are shown in Figure 1 for $0 \leq \lambda \leq 1$. Present numerical results are accurate enough for the purpose of illustrating the splitting of the degenerate energy levels of the harmonic oscillator as λ increases. They are consistent with both the splitting predicted by PGS (5) and the analytical perturbation results (6-9). In fact, we obtained those perturbation results from the secular determinants obtained with the symmetry-adapted basis sets (37) with $a = 1/2$ that is the exact value of this parameter for $\lambda = 0$. This strategy was already described in Section 3.

5. Conclusions

Throughout this paper we have tried to illustrate the application of group theory to a quartic anharmonic oscillator with the symmetry O_h of the cube. We chose this particular example because of its great symmetry and also because it was treated before by means of a simpler symmetry-based approach consisting only of parity and coordinate-permutation operators[59]. The present application of group theory resorts to the 48 symmetry operations shown in the table of characters in Table 1 and enables a systematic classification of the states of the oscillator in terms of the corresponding irreps.

Group theory enables us to predict the splitting of the energy levels of the harmonic oscillator as the perturbation parameter λ increases. This predic-

Table 1: Character table for group O_h

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xz, yz, xy)	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

tion is verified by the actual calculation of the perturbation corrections. An advantage of the application of group theory is that we treat each symmetry subspace independently of the others. In this way both the calculation effort as well as the undesirably effect of the degeneracy are considerably reduced. Note, for example that the degenerate energy levels with $\nu = 1$ and $\nu = 2$ can be treated as nondegenerate when one considers every symmetry species separately.

Group theory also enables us to reduce the dimension of the secular equations in the application of the Rayleigh-Ritz variational method. In addition to it, one obtains the eigenfunctions ψ_n^S that are bases for the irreps. This fact facilitates, for example, the calculation of matrix elements of the form $O_{nm}^{SS'} = \left\langle \psi_n^S \middle| O \middle| \psi_m^{S'} \right\rangle$ for any observable O. Given the symmetry of O one knows beforehand whether the matrix element $O_{nm}^{SS'}$ is zero[80–82]. This analysis leads, for example, to the selection rules for molecular spectra[80–82].
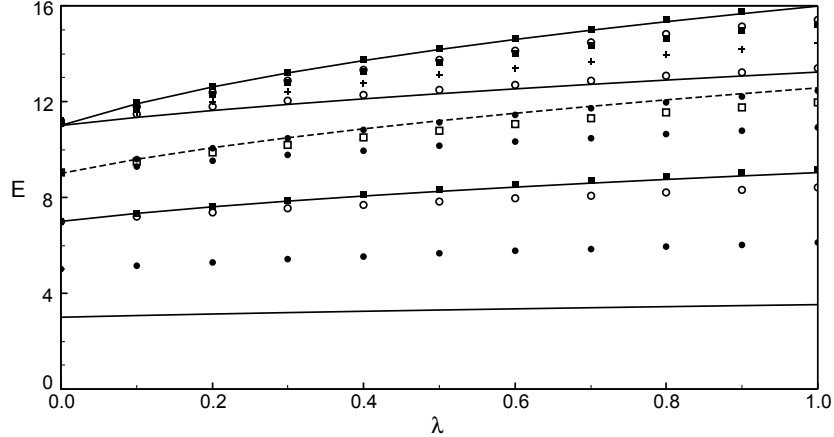
Figure 1: First eigenvalues of the Hamiltonian operator $H = p_x^2 + p_y^2 + p_z^2 + x^2 + y^2 + z^2 + \lambda \left(x^2 y^2 + x^2 z^2 + y^2 z^2 \right)$ with symmetry A_{1g} (solid line), T_{1u} (filled circles), E_g (empty circles), T_{2g} (filled squares), A_{2u} (dashed line), T_{2u} (empty squares), T_{1g} (crosses).

Appendix A. Simplified outline of Group Theory

In what follows we develop a simplified and abbreviated version of some of the elements of group theory that are necessary for the present paper. A rigorous account of group theory is available in any of the books on the subject[80–82].

Here we are interested in the analysis of the symmetry properties of a physical system that are related to all the unitary operators $X_i^\dagger = X_i^{-1}$ that leave the Hamiltonian operator H invariant

$$X_i H X_i^\dagger = H, \tag{A.1}$$

and assume that this set is finite

$$G = \{X_1, X_2, \ldots, X_h\}. \tag{A.2}$$

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The product (composition) of these unitary operators is associative: $(X_iX_j)X_k = X_i(X_jX_k)$. The identity operator X_1, which satisfies

$$X_1X_i = X_iX_1 = X_i, \tag{A.3}$$

leaves the Hamiltonian invariant and, consequently, belongs to G. It follows from (A.1) that if X_i belongs to G then X_i^{-1} belongs to G too. The product of two operators also belongs to G as follows from

$$X_iX_jH(X_iX_j)^\dagger = X_iX_jHX_j^\dagger X_i^\dagger = X_iHX_i^\dagger = H. \tag{A.4}$$

Because of all these mathematical properties the set G is a finite group.

Two such operators (or group elements) X_j and X_k are said to be conjugate if

$$X_iX_jX_i^\dagger = X_k, \tag{A.5}$$

for some $X_i \in G$. If X_l and X_k are conjugate to X_j then they are conjugate to each other. All the mutually conjugated elements of a group are collected into a class.

We can construct a matrix representation $\mathbf{X}_i$ of every operator X_i in terms of a basis

$$B = \{f_1, f_2, \ldots\}, \tag{A.6}$$

in the usual way

$$X_if_j = \sum_k (\mathbf{X}_i)_{kj} f_k, \ i = 1, 2, \ldots, h. \tag{A.7}$$

Of particular interest are the irreducible representations (irreps) obtained in terms of suitable basis sets

$$B^\alpha = \left\{ f_1^\alpha, f_2^\alpha, \ldots, f_{l_\alpha}^\alpha \right\}, \ \alpha = 1, 2, \ldots, m, \tag{A.8}$$

such that

$$X_i f_j^\alpha = \sum_{k=1}^{l_\alpha} \left(\mathbf{X}_i^\alpha\right)_{kj} f_k^\alpha, \; j = 1, 2, \ldots, l_\alpha, \; i = 1, 2, \ldots, h, \; \alpha = 1, 2, \ldots, m.$$
(A.9)

The characters of the irreps are the traces of the corresponding matrix representations

$$\chi_i^\alpha = tr\left(\mathbf{X}_i^\alpha\right).$$
(A.10)

It can be proved that the number m of irreps equals the number of classes of group elements.

In order to obtain a basis function f^α for a given irrep we apply the corresponding projection operator

$$P^\alpha = \frac{l_\alpha}{h} \sum_{i=1}^{h} \left(\chi_i^\alpha\right)^* X_i,$$
(A.11)

to an arbitrary function f: $f^\alpha = P^\alpha f$. A projection operator P satisfies the following properties: $P^\dagger = P$ and $P^2 = P$; more precisely, any operator that satisfies these two properties is a projection operator. It follows from these properties that $\langle P^\alpha f | \, P^\alpha f \rangle = \langle f | \, P^\alpha f \rangle \le \langle f | \, f \rangle$.

In order to apply the equations above we should know how to express the effect of a group operator X_i on a function $f(\mathbf{x})$ of the cartesian coordinates $\mathbf{x} = (x, y, z)$. Rotations, reflections, etc can be expressed in matrix form as $\mathbf{x}' = \mathbf{M}\mathbf{x}$ so that there is a one to one correspondence between the operators X_i and the corresponding transformation matrices $\mathbf{M}_i$. If we write

$$X_i f(\mathbf{x}) = f\left(\mathbf{M}_i^{-1}\mathbf{x}\right),$$
(A.12)

then we have the mappings

$$(X_i, X_j) \;\; \rightarrow \;\; (\mathbf{M}_i, \mathbf{M}_j)$$

$$X_i X_j \quad \rightarrow \quad \mathbf{M}_i \mathbf{M}_j. \tag{A.13}$$

It follows from (A.1) that $[H, X_i] = 0$ and, according to (A.11), we conclude that $[H, P^\alpha] = 0$.

In some cases it may be necessary to carry out an equivalent transformation of the Hamiltonian of the system

$$UHU^\dagger = \tilde{H}, \ U^\dagger = U^{-1}. \tag{A.14}$$

The point group $\tilde{G}$ for $\tilde{H}$

$$\tilde{G} = \left\{ \tilde{X}_1, \tilde{X}_2, \ldots, \tilde{X}_h \right\}, \ \tilde{X}_i = U X_i U^\dagger, \tag{A.15}$$

is isomorphic with G as follows from

$$\tilde{X}_i \tilde{X}_j = U X_i U^\dagger U X_j U^\dagger = U X_i X_j U^\dagger = \widetilde{X_i X_j}. \tag{A.16}$$

Table 1 shows the character table of the point group O_h. The first row shows the symmetry operations grouped into classes. E is the identity operation, C_n denotes a rotation by an angle $2\pi/n$, i is the inversion operation, S_n denotes a rotation by an angle $2\pi/n$ followed by a reflection with respect to a plane perpendicular to the rotation axis and σ indicates a reflection plane. The first column displays the irreps; those labelled by A, E, and T are one-, two- and three-dimensional (that is to say, $l_\alpha = 1, 2, 3$), respectively. The numbers are the characters χ_i^α and the last two columns show some basis functions for the irreps. This table summarizes some of the relevant ingredients for the construction of the projection operators P^α shown in equation (A.11). The matrix representation of the elements of this group, which is necessary for the construction of the symmetry operations (A.12) and projection operators (A.11), is available elsewhere[73].

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