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

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HIGHLIGHTS

- Symmetry determines the degeneracy of a quantum-mechanical system.
- Group theory facilitates the application of variational methods.
- The key is the use of symmetry-adapted basis sets.
- A perturbation reduces the symmetry of the system.
- Group theory predicts the splitting of the energy levels.

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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.

1. Introduction

Quantum-mechanical anharmonic oscillators have proved useful for the analysis of the vibration–rotation spectra of polyatomic molecules. Several aspects of such spectra as well as other molecular

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properties have been modelled by means of simple coupled oscillators mainly with cubic and quartic anharmonicities. 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.

Some authors have taken into account the symmetry of the anharmonic oscillators in order to simplify their treatment [1] and others resorted to the more formal point group symmetry (PGS) [2,3]. The latter two papers motivated a recent application of PGS to a variety of Hermitian [4–6] and non-Hermitian anharmonic oscillators with space–time symmetry [7–11]. 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. 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 operations [1]. 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 particular, we discuss the harmonic oscillator basis set and a closely related 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 we outline the main features of group theory that are necessary for the analysis of the present problem.

2. Model

Among the many available models we have chosen a three-dimensional quartic anharmonic oscillator already studied earlier by Turbiner [1]

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

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 [12–14]. In other words, this Hamiltonian operator is invariant with respect to the symmetry operations indicated in the table of characters shown in Table 1 described in the Appendix. A detailed discussion of the construction of the matrix representation of the symmetry operations for the O_h point group is available elsewhere [15].

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

$$E_{k\,m\,n}^{(0)} = 2(k + m + n) + 3 \\ \varphi_{k\,m\,n}(x, y, z) = \phi_k(x)\phi_m(y)\phi_n(z), \quad k, m, n = 0, 1, \ldots, \tag{2}$$

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

$$\{a, a, a\}_P = \{a, a, a\} \\ \{a, b, b\}_P = \{\{a, b, b\}, \{b, a, b\}, \{b, b, a\}\} \\ \{a, b, c\}_P = \{\{a, b, c\}, \{c, a, b\}, \{b, c, a\}, \{b, a, c\}, \{c, b, a\}, \{a, c, b\}\}, \tag{3}$$