On the symmetry of the quantum-mechanical particle in a cubic box

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In this paper we show that the point-group (geometrical) symmetry is insufficient to account for the degeneracy of the energy levels of the particle in a cubic box. The discrepancy is due to hidden (dynamical symmetry). We obtain the operators that commute with the Hamiltonian one and connect eigenfunctions of different symmetries. We also show that the addition of a suitable potential inside the box breaks the dynamical symmetry but preserves the geometrical one. The resulting degeneracy is that predicted by point-group symmetry.

PACS numbers: 03.65.Ge, 02.20.-a, 03.65.Fd

I. INTRODUCTION

The particle in a one-dimensional box with impenetrable walls is one of the first models discussed in most introductory books on quantum mechanics and quantum chemistry. It is suitable for showing how energy quantization appears as a result of certain boundary conditions. Once we have the eigenvalues and eigenfunctions for this model one can proceed to two-dimensional boxes and discuss the conditions that render the Schrödinger equation separable. The particular case of a square box is suitable for discussing the concept of degeneracy. The next step is the discussion of a particle in a three-dimensional box and in particular the cubic box as a representative of a quantum-mechanical model with high symmetry. This model is also suitable for discussing the perfect gas in statistical mechanics. The spherical box is also of great pedagogical value because it enables us to discuss the conservation of the angular momentum of the particle.

In two enlightening articles Leyvraz et al and lemus et al discussed the accidental degeneracy and hidden symmetry of the particle in square and rectangular wells, respectively. They showed that point group (geometrical) symmetry is insufficient to account for the degree of degeneracy of those quantum-mechanical models and then proceeded to find the operator that commutes with the Hamiltonian one and connects eigenfunctions of different symmetry. In this way they constructed a larger symmetry group that accounts for the full degeneracy of the square well.

Leyvraz et al briefly commented on the problem of a particle in a cubic box with impenetrable walls. They mentioned that the suitable symmetry point group is $O_h$ and that in this case there should be two additional dynamical symmetries. The purpose of this paper is to pursue the study of this quantum-mechanical model much in the same way those authors did in the case of the two-dimensional wells.

In Sec. II we summarize the well known results of the Schrödinger equation for the cubic box and discuss the degeneracy of the energy levels. In Sec. III we analyze the problem from the point of view of its point-group symmetry and show the accidental degeneracies that cannot be explained by the geometrical symmetry of the cube. We extend the analysis of Leyvraz et al to the three dimensional case and derive three operators that commute with the Hamiltonian of the system and connect functions belonging to different irreducible representations. To this end, we make extensive use of the group projection operators. In Sec. IV we add a perturbation potential that is invariant...
under the symmetry operations of the $O_h$ point group and show that it breaks the dynamical symmetry of the system while conserving the geometrical one. We also discuss another perturbation that conserves both types of symmetry. Finally, in Sec. V we summarize the main results and draw conclusions.

II. THE PARTICLE IN A CUBIC BOX

In order to simplify the discussion of the Schrödinger equation for the particle in a cubic box with impenetrable walls we choose the following units:

\[
\begin{align*}
\text{length} & \quad \frac{L}{2} \\
\text{energy} & \quad \frac{2\hbar^2}{mL^2} \\
\text{momentum} & \quad \frac{2\hbar}{L}
\end{align*}
\]

where $m$ is the mass of the particle and $L$ the length of the box edges. In this way the Schrödinger equation becomes

\[H\psi = E\psi,
\]

\[H = p_x^2 + p_y^2 + p_z^2
\]

\[p_q = -i\frac{\partial}{\partial q}
\]

\[\psi(\pm 1, y, z) = \psi(x, \pm 1, z) = \psi(x, y, \pm 1) = 0.
\]

The dimensionless eigenvalues and eigenfunctions are:

\[E_{n_1n_2n_3} = \frac{1}{4}(n_1^2 + n_2^2 + n_3^2)
\]

\[\psi_{n_1n_2n_3}(x, y, z) = \sin \frac{n_1\pi(x + 1)}{2} \sin \frac{n_2\pi(y + 1)}{2} \sin \frac{n_3\pi(z + 1)}{2},
\]

where origin of the system of coordinates has been placed at the center of the box. Note that $\psi_{n_1n_2n_3}(-x, y, z) = (-1)^{n_1+1}\psi_{n_1n_2n_3}(x, y, z)$ (and similar relationships for the other two coordinates).

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

\[\{a, b, c\}_P = \{\{a, b, b\}, \{b, a, b\}, \{b, b, a\}\}
\]

\[\{a, b, c\}_P = \{\{a, b, c\}, \{c, a, b\}, \{b, c, a\}, \{b, a, c\}, \{c, b, a\}, \{a, c, b\}\}.
\]

Thus, the set of quantum numbers $\{n, m, m\}_P$ leads to a three-fold degenerate energy level; that is to say, three linearly independent eigenfunctions with the same energy $E_{nmm}$ (provided that $m \neq n$). Analogously, three different quantum numbers $\{n_1, n_2, n_3\}_P$ give rise to a six-fold degenerate energy level.

III. POINT-GROUP SYMMETRY

The suitable point group for describing the symmetry of the particle is a cubic box is $O_h$ with irreducible representations $\{A_{1g}, A_{2g}, E_g, T_{1g}, T_{2g}, A_{1u}, A_{2u}, E_u, T_{1u}, T_{2u}\}$. It predicts two-fold ($E_g, E_u$) and three-fold ($T_{1g}, T_{2g}, T_{1u}, T_{2u}$) degenerate energy levels. It is clear that the geometrical symmetry of the cube is insufficient to account for the degeneracy already described in the preceding section. Therefore, as in the case of the particle in a square box
there must be a hidden dynamical symmetry. In order to discuss this point in more detail we should first classify the eigenfunctions according to their point-group symmetry.

Such classification is greatly facilitated by the projection operators\textsuperscript{7,8}

\[ P^j = \frac{l_j}{h} \sum_R \chi(R)^j R \]

where \( l_j \) is the dimension of the irreducible representation \( j \), \( h \) the order of the group, \( \chi(R)^j \) the character of the group operation \( R \) for the irreducible representation \( j \), and the sum is over all the operations \( R \) of the group. The appendix outlines how to obtain the projection operators.

The first energy levels are

\[
\begin{align*}
\{1,1,1\} & \quad A_{1g} \\
\{1,1,2\} & \quad T_{1u} \\
\{1,2,2\} & \quad T_{2g} \\
\{1,1,3\} & \quad E_g, A_{1g} \\
\{2,2,2\} & \quad A_{2u} \\
\{1,2,3\} & \quad T_{1u}, T_{2u}
\end{align*}
\]

(6)

and the sets of degenerate eigenfunctions produced by the projection operators are:

\[
\begin{align*}
1A_{1g} & \quad \psi_{111} \\
1T_{1u} & \quad \{\psi_{211}, \psi_{121}, \psi_{112}\} \\
1T_{2g} & \quad \{\psi_{122}, \psi_{212}, \psi_{221}\} \\
1E_g & \quad \left\{ \frac{1}{3} (2\psi_{311} - \psi_{131} - \psi_{113}), \frac{1}{3} (\psi_{311} - 2\psi_{131} + \psi_{113}) \right\} \\
2A_{1g} & \quad \left\{ \frac{1}{3} (\psi_{311} + \psi_{131} + \psi_{113}) \right\} \\
2T_{1u} & \quad \left\{ \frac{1}{3} (\psi_{123} + \psi_{321}), \frac{1}{3} (\psi_{312} + \psi_{132}), \frac{1}{3} (\psi_{231} + \psi_{213}) \right\} \\
1T_{2u} & \quad \left\{ \frac{1}{3} (\psi_{123} - \psi_{321}), \frac{1}{3} (\psi_{312} - \psi_{132}), \frac{1}{3} (\psi_{231} - \psi_{213}) \right\}
\end{align*}
\]

(7)

The two eigenfunctions \( E_g \) are linearly independent but not orthogonal. One can easily obtain two orthogonal functions by appropriate linear combinations. We have just left them as they come from the application of the projection operator \( P^{E_g} \). Exactly the same situation takes place in the case of the degenerate eigenfunctions \( 2T_{1u} \) and \( 1T_{2u} \). Functions of different symmetry are obviously orthogonal. The magnitude of the energy increases from top to bottom in Eq. (7). The three-fold degenerate level given by \( \{1,1,3\} \) with eigenfunctions \( 1E_g \) and \( 2A_{1g} \) and the sixth-fold one \( \{1,2,3\} \) with eigenfunctions \( 2T_{1u} \) and \( 1T_{2u} \) cannot be explained by point-group symmetry. In general
we have

\[
\begin{align*}
\{2n - 1, 2n - 1, 2n - 1\} & \quad A_{1g} \\
\{2n, 2n, 2n\} & \quad A_{2u} \\
\{2n, 2n, 2m - 1\}_p & \quad T_{2g} \\
\{2n - 1, 2n - 1, 2m\}_p & \quad T_{1u} \\
\{2n - 1, 2n - 1, 2m - 1\}_p & \quad A_{1g}, E_g \\
\{2n, 2n, 2m\}_p & \quad A_{2u}, E_u \\
\{2n - 1, 2m - 1, 2k - 1\}_p & \quad A_{1g}, A_{2g}, E_g, E_g \\
\{2n, 2m, 2k\}_p & \quad A_{1u}, A_{2u}, E_u, E_u \\
\{2n - 1, 2m - 1, 2k\}_p & \quad T_{1u}, T_{2u} \\
\{2n, 2m, 2k - 1\}_p & \quad T_{1g}, T_{2g}
\end{align*}
\]

(8)

In order to understand such degeneracy of the energy levels suppose that there is an operator \( D \) that commutes with \( H \) and preserves the boundary conditions. If \( \psi \) is eigenfunction of \( H \) with eigenvalue \( E \) then \( D\psi \) is eigenfunction of \( H \) with the same eigenvalue: \( HD\psi = ED\psi \). If it happens that \( D \) connects functions of different symmetry \( S \) and \( S' \) \( D\psi^S = \psi^{S'} \) then the degree of degeneracy is greater than the one predicted by point-group symmetry. The accidental degeneracy of the energy levels of the particle in a cubic box can be explained by a couple of operators of symmetry \( E_g \) as shown by the products

\[
\begin{align*}
E_g \times A_{1g} & = E_g \\
E_g \times A_{2g} & = E_g \\
E_g \times E_g & = A_{1g} + A_{2g} + E_g \\
E_g \times T_{1g} & = T_{1g} + T_{2g} \\
E_g \times T_{2g} & = T_{1g} + T_{2g} \\
E_g \times A_{1u} & = E_u \\
E_g \times A_{2u} & = E_u \\
E_g \times E_u & = A_{1u} + A_{2u} + E_u \\
E_g \times T_{1u} & = T_{1u} + T_{2u} \\
E_g \times T_{2u} & = T_{1u} + T_{2u}.
\end{align*}
\]

(9)

Application of the projection operator \( P_{E_g} \) to \( x^2 \) and \( y^2 \)

\[
\begin{align*}
P_{E_g} x^2 & = \frac{1}{3} \left( 2x^2 - y^2 - z^2 \right) \\
P_{E_g} y^2 & = \frac{1}{3} \left( 2y^2 - x^2 - z^2 \right)
\end{align*}
\]

(10)

shows that two suitable operators are

\[
\begin{align*}
D_{E_g}(1) & = 2p_x^2 - p_y^2 - p_z^2 \\
D_{E_g}(2) & = 2p_y^2 - p_x^2 - p_z^2.
\end{align*}
\]

(11)
These are probably the two additional dynamical symmetries mentioned by Leyvraz et al.\[2\] We illustrate the effect of these operators on the particular case \{1, 3, 5\}_P. The functions of symmetry \(E_g\) are

\[
\begin{align*}
\psi^{[1]}_{E_g} &= 2\psi_{135} - \psi_{513} - \psi_{351}, \\
\psi^{[2]}_{E_g} &= \psi_{135} - 2\psi_{513} + \psi_{351}, \\
\psi^{[3]}_{E_g} &= 2\psi_{315} - \psi_{531} - \psi_{153}, \\
\psi^{[4]}_{E_g} &= \psi_{315} - 2\psi_{531} + \psi_{153}.
\end{align*}
\]  

(12)

The first pair is orthogonal to the second one, but each pair is not orthogonal as argued above. The application of the operators \(D_{E_g}\) yields

\[
\begin{align*}
P^{A_1g} D_{E_g}(1)\psi^{[1]}_{E_g} &= 4\pi^2 \left(\psi_{135} + \psi_{513} + \psi_{351} + \psi_{315} + \psi_{531} + \psi_{153}\right), \\
P^{A_2g} D_{E_g}(1)\psi^{[1]}_{E_g} &= 4\pi^2 \left(\psi_{135} + \psi_{513} + \psi_{351} - \psi_{315} - \psi_{531} - \psi_{153}\right), \\
P^{A_1g} D_{E_g}(1)\psi^{[3]}_{E_g} &= \pi^2 \left(\psi_{135} + \psi_{513} + \psi_{351} + \psi_{315} + \psi_{531} + \psi_{153}\right), \\
P^{A_2g} D_{E_g}(1)\psi^{[3]}_{E_g} &= -\pi^2 \left(\psi_{135} + \psi_{513} + \psi_{351} - \psi_{315} - \psi_{531} - \psi_{153}\right).
\end{align*}
\]  

(13)

We clearly see that the operators \(D_{E_g}\) already connect the functions of symmetry \(A_{1g}\) and \(A_{2g}\) with the two pairs of functions of symmetry \(E_g\) and thus account for the six-fold degenerate energy level with quantum numbers \(n_1 = 1\), \(n_2 = 3\), \(n_3 = 5\). Note that we have chosen only one member of each pair \(\{\psi^{[1]}_{E_g}, \psi^{[3]}_{E_g}\}\) as an illustrative example. We can prove the other accidental degeneracies in Eq. (5) exactly in the same way.

We can build other operators that commute with \(H\) and connect functions of different symmetry. For example,

\[
D_{A_{2g}} = \left(p_x^2 - p_y^2\right) \left(p_x^2 - p_z^2\right) \left(p_y^2 - p_z^2\right),
\]  

(14)

accounts for the degeneracy of the pairs \(\{A_{1g}, A_{2g}\}\), \(\{T_{1g}, T_{2g}\}\), \(\{A_{1u}, A_{2u}\}\), and \(\{T_{1u}, T_{2u}\}\).

In this paper we do not try to explain the degeneracy that comes from Pythagorean relations of the form \(n_1^2 + n_2^2 + n_3^2 = m_1^2 + m_2^2 + m_3^2\) that have been already discussed for the square box.\[2\] However, in what follows show the first cases in increasing energy order

\[
\begin{align*}
\{3, 3, 3\}, \{1, 1, 5\}_P & \quad A_{1g}, A_{1g}, E_g \\
\{1, 4, 4\}_P, \{2, 2, 5\}_P & \quad T_{2g}, T_{2g} \\
\{1, 1, 6\}_P, \{2, 3, 5\}_P & \quad T_{1u}, T_{1u}, T_{2u} \\
\{1, 2, 6\}_P, \{3, 4, 4\}_P & \quad T_{1g}, T_{2g}, T_{2g} \\
\{1, 5, 5\}_P, \{1, 1, 7\}_P & \quad A_{1g}, E_g, A_{1g}, E_g \\
\{2, 5, 5\}_P, \{3, 3, 6\}_P, \{1, 2, 7\}_P & \quad T_{1u}, T_{1u}, T_{1u}, T_{2u}
\end{align*}
\]  

(15)

IV. PERTURBATION THEORY

Suppose that we add a potential \(V(x, y, z)\) inside the box and obtain

\[
H = H_0 + V,
\]  

(16)
where $H_0$ is given by Eq. (2). In particular we are interested in the polynomial potential

$$V(x, y, z) = x^2 y^2 + x^2 z^2 + y^2 z^2,$$

that is invariant under the operations of the group $O_h$ (note, for example, that $P A_1 g V(x, y, z) = V(x, y, z)$). Since $H$ does not commute with the operators $D$ discussed in the preceding section, then we expect that the dynamical symmetry is broken and the accidental degeneracy removed. On the other hand, the point-group symmetry remains unbroken and the degeneracy of the energy levels is that given by the geometrical symmetry.

Perturbation theory\(^{1,2,10}\) is probably the simplest way of verifying those conclusions. We write $H = H_0 + \lambda V$ and expand the energy in a $\lambda$-power series $E = E^{(0)} + E^{(1)} \lambda + \ldots$. Straightforward application of this approach yields

$$E_{1A_1g} = \frac{3}{4} + \lambda \frac{(\pi^2 - 6)^2}{3\pi^4} + \ldots$$

$$E_{1T_1u} = \frac{3}{2} + \lambda \frac{(\pi^2 - 3)(\pi^2 - 6)}{3\pi^4} + \ldots$$

$$E_{1T_2g} = \frac{9}{4} + \lambda \frac{(2\pi^2 - 3)(2\pi^2 - 9)}{12\pi^4} + \ldots$$

$$E_{1E_g} = \frac{11}{4} + \lambda \frac{36\pi^4 - 304\pi^2 + 285}{108\pi^4} + \ldots$$

$$E_{2A_1g} = \frac{11}{4} + \lambda \frac{18\pi^4 - 152\pi^2 + 507}{54\pi^4} + \ldots$$

$$E_{1A_2u} = 3 + \lambda \frac{(2\pi^2 - 3)^2}{12\pi^4} + \ldots$$

$$E_{2T_2u} = \frac{7}{2} + \lambda \frac{36\pi^4 - 196\pi^2 - 75}{108\pi^4} + \ldots$$

$$E_{2T_1u} = \frac{7}{2} + \lambda \frac{36\pi^4 - 196\pi^2 + 411}{108\pi^4} + \ldots,$$

for the lowest eigenvalues. We clearly see that the accidental degeneracy of the pairs of irreducible representations $(E_g, A_1g)$ and $(T_1u, T_2u)$ was already broken by the perturbation as argued above. One can easily carry out the same calculation on the higher states.

Another interesting perturbation potential is

$$V_{HO}(x, y, z) = x^2 + y^2 + z^2.$$  

In this case the resulting Schrödinger equation is separable in three one-dimensional equations of the form

$$(p_x^2 + p_y^2) \varphi_n(q) = \epsilon_n \varphi_n(q), \ n = 1, 2, \ldots$$

$$\varphi_n(\pm 1) = 0,$$

and the eigenfunctions and eigenvalues of the whole system are given by

$$\psi_{mnk}(x, y, z) = \varphi_m(x) \varphi_n(y) \varphi_k(z)$$

$$E_{mnk} = \epsilon_m + \epsilon_n + \epsilon_k.$$  

Equation \(^{20}\) cannot be solved exactly but we can obtain accurate results by means of perturbation theory\(^{10}\) or any other approximate method. For the present purposes it is sufficient to know that such solution already exists and that $\varphi_n(-q) = (-1)^{n+1} \varphi_n(q)$. 


It is not difficult to convince oneself that the accidental degeneracy was not broken by this perturbation, although the Hamiltonian operator does not commute with the operators $D$ discussed in the preceding section. The explanation is that any function of the operators $p_q^2 + q^2$, $q = x, y, z$, commute with $H$ and we can therefore construct operators $D$ by simply substituting $p_q^2 + q^2$ for $p_q^2$ in the expressions derived in the preceding section. Note that the symmetry of the new operators is exactly the same.

The discussion of the three-dimensional oscillator in a cubic box suggests a straightforward generalization. If we have a Hamiltonian operator of the form

$$H = \sum_{j=1}^{M} H_j,$$

where $[H_j, H_k] = 0$, then we can construct $M - 1$ operators of the form

$$D_k = \sum_{j=1}^{M-1} d_{kj} H_j, \quad k = 1, 2, \ldots, M - 1,$$

that are linearly independent and commute with $H$. It may be possible that a judicious choice of the coefficients $d_{kj}$ leads to operators that connect functions of different symmetry. The number of operators that we can obtain in this way is enormous because any function of the operators $H_j$ will commute with $H$ and we expect some kind of dynamical symmetry emerging from it. We have already seen some examples in the preceding section.

V. CONCLUSIONS

We have shown that the point-group symmetry is insufficient to account for the degree of degeneracy of the energy levels of the particle in a cubic box. The additional degeneracy is due to a dynamical symmetry given by operators that commute with the Hamiltonian one. We have shown how to derive such operators by means of the projection operators of the group $O_h$. The next step would be to build a larger group that embodies both the point-group operations as well as the dynamical operators. We do not do it here because we want to keep this paper as simple as possible. It is clear that the particle in two and three-dimensional boxes are suitable exactly solvable problems for teaching the occurrence of both geometrical and dynamical types of symmetry.

The cubic box is somewhat more complicated than the square one. In the case of the square box one can obtain the linear combinations of eigenfunctions that are bases for the irreducible representations by inspection. In the case of the cubic box it is preferable to resort to a more systematic approach based on projection operators. This procedure is straightforward but rather cumbersome for hand calculation and it is therefore convenient to resort to computer algebra to speed it. For this reason, the particle in a cubic box is a suitable example to encourage the students to get some skills in group theory as well as in computer algebra. In the appendix we outline how to construct the matrix representation of the group operations as well as the projection operators.

Appendix A: Symmetry operations, matrix representation and projection operators

The analysis of the particle in a cubic box presented in Sec. III is greatly facilitated by the application of projection operators [5]. For this purpose we need to know the effect of the symmetry operations on the cartesian coordinates.
\( \mathbf{x} \) that we express in matrix form as \( \mathbf{x}' = \mathbf{Mx} \), where \( \mathbf{M} \) is a \( 3 \times 3 \) unitary matrix and \( \mathbf{x} \) and \( \mathbf{x}' \) are \( 3 \times 1 \) column matrices. Once we have the matrix representation \( \mathbf{M} \) for a given symmetry operation \( R \) then we easily derive the effect of the latter on a function \( f(\mathbf{x}) \) as

\[
Rf(x) = f\left(\mathbf{M}^{-1}\mathbf{x}\right).
\]  

(A1)

Taking into account equations (5) and (A1) the application of the projection operator \( P^j \) on \( f(\mathbf{x}) \) is straightforward.

The symmetry elements of the group \( O_h \) are summarized in most books on group theory.\(^8\) The matrix representation of the 48 symmetry operations is given explicitly in a recent paper by Delibas et al.\(^11\) For the present study of the particle in a cubic box we built the matrices without locating all the symmetry elements of the cube explicitly. We resorted to a rather more algebraic procedure that we describe in what follows because it may be useful for those who prefer a less geometrical approach.

To begin with we obtain the 48 matrices for the following coordinate transformations (note that each line embodies 6 transformations)

\[
\begin{align*}
\{x, y, z\} & \rightarrow \{x, y, z\}_p \\
\{x, y, z\} & \rightarrow \{-x, y, z\}_p \\
\{x, y, z\} & \rightarrow \{x, -y, z\}_p \\
\{x, y, z\} & \rightarrow \{x, y, -z\}_p \\
\{x, y, z\} & \rightarrow \{-x, -y, z\}_p \\
\{x, y, z\} & \rightarrow \{-x, y, -z\}_p \\
\{x, y, z\} & \rightarrow \{x, -y, -z\}_p \\
\{x, y, z\} & \rightarrow \{-x, -y, -z\}_p.
\end{align*}
\]  

(A2)

The next step is to identify the symmetry operation associated to each matrix. First, note that the traces of these matrices are the characters for the \( T_{1u} \) irreducible representation. Second, take into account that the determinant of a rotation \( C_n \) is unity and the determinants of a reflection \( \sigma \) and the improper rotation \( S_n \) are minus one. Third, remember that the order \( n \) of a symmetry operation \( a \) is the smallest positive integer such that \( a^n = E \) (the identity operation). For example, \( \det \mathbf{M}(S_6) = -1 \) and \( \mathbf{M}(S_6)^6 = \mathbf{I} \) (the identity matrix). We can thus group all the matrices derived above in the corresponding group classes, except \( 6C_2 \) and \( 3C_2(= C_4^2) \) that share the same trace, determinant, and order. The identification of the matrices for the three rotations by an angle \( \pi \) about the coordinate axes \((C_2 = C_4^2)\) is straightforward and the remaining six matrices represent the rotations \( C_2 \) about axes that bisect opposite edges of the cube.

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