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Phys 342 Final Project

Symmetry as the root of degeneracy: Applications of the theory of finite point groups to energy spectra and selection rules in quantum mechanics

I. Abstract

First proposed by Wigner in 1926 [5], the theory of groups can provide useful insights for understanding quantum mechanical situations, including useful applications with regard to eigenvalue problems. In particular, by thinking of the collection of symmetry operations under which the Hamiltonian of a system of interest is invariant as a group, the formalism of group theory provides powerful techniques for determining the existence and extent of degeneracy in the eigenenergy spectrum, perturbations that can be applied to remove those degeneracies, and even to predict the selection rules governing transitions between stationary states. The primary goal of the present work is to provide a brief introduction to those concepts and constructs of group theory necessary to make use of character tables for finite point groups in assessing degeneracies and calculating matrix elements corresponding to electric dipole transitions in quantum mechanics. Space permitting, these techniques will then be applied to a small number of very general example situations.

II. Introduction

Before diving into definitions and the terminology of group theory, it is useful to first take a closer look at what it is that group theory can help us to understand. Given a physical system of interest described by a Hamiltonian $\boldsymbol{H}$, much of quantum mechanics deals with the determination of the allowed states describing the system, the energies corresponding to those states, and their time-evolution. As we learn in undergraduate school, the allowed stationary states $|\psi_n\rangle$ with energy eigenvalues E_n are those satisfying the time-independent Schrödinger equation

$$\hat{\boldsymbol{H}}|\psi_n\rangle = E_n|\psi_n\rangle \tag{1}$$

where $\hat{\boldsymbol{H}}$ is the Hermitian operator representing the Hamiltonian $\boldsymbol{H}$. While there exist far more physically interesting Hamiltonians for which Eq. (1) is not exactly solvable than there are for which it is, there are still several physical systems for which exact solutions of the Schrödinger equation are well know, such as the harmonic oscillator or hydrogen atom. In comparing the states and eigenenergy spectra for a few of these solved systems, it becomes immediately evident that the eigenvalues of the stationary states are not always unique. That is, in certain systems there are multiple stationary states that share the same energy eigenvalue. Such states are said to be degenerate. In the case of the unperturbed[1] hydrogen atom, for instance, there are n^2 degenerate stationary states $|\psi_{nlm}\rangle$ ($2l+1$ for each $l = 0,1,2,...,n-1$) corresponding to each eigenenergy

[1] That is, the hydrogen atom given by the Hamiltonian $\boldsymbol{H} = \frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \frac{Ze^2}{r}$, without incorporating the relativistic correction for the electron momentum, ***L*-*S*** coupling, etc.

$$E_n = \frac{-Z^2 e^2}{2a_0 n^2} \tag{2}$$

where

$$a_0 = \frac{\hbar^2}{m_e e^2} \tag{3}$$

is the Bohr radius [1]. Thus every excited state is degenerate! This is in contrast to the energy spectra of the 1D harmonic oscillator, whose energies $E_n = \hbar\omega\left(n+\frac{1}{2}\right)$ are well-known to be evenly spaced and non-degenerate [1–2]. What is the source of this degeneracy, one might rightly wonder? As we shall soon show, apart from "accidental degeneracies"[2], degeneracies in the energy spectrum of the solution space of Eq. (1) arise from symmetries of the Hamiltonian.

Now consider an arbitrary symmetry transformation $\boldsymbol{T}$ with operator $\hat{\boldsymbol{T}}$, such as a rotation about a fixed axis, or a space inversion. We say that $\boldsymbol{T}$ is a symmetry of the system if $\hat{\boldsymbol{T}}$ commutes with $\hat{\boldsymbol{H}}$, i.e. if $\hat{\boldsymbol{T}}\hat{\boldsymbol{H}} = \hat{\boldsymbol{H}}\hat{\boldsymbol{T}}$. Equivalently[3], we can say that the Hamiltonian is invariant under $\boldsymbol{T}$. If $\boldsymbol{T}$ is a symmetry of the system, then by Eq. (1) we have that

$$E_n\left(\hat{\boldsymbol{T}}\left|\psi_n\right\rangle\right) = \hat{\boldsymbol{T}}E_n\left|\psi_n\right\rangle = \hat{\boldsymbol{T}}\hat{\boldsymbol{H}}\left|\psi_n\right\rangle = \hat{\boldsymbol{H}}\left(\hat{\boldsymbol{T}}\left|\psi_n\right\rangle\right) \tag{4}$$

Thus if $\left|\psi_n\right\rangle$ is an eigenstate of $\boldsymbol{H}$ with eigenvalue E_n and $\boldsymbol{H}$ is invariant under $\boldsymbol{T}$, then $\hat{\boldsymbol{T}}\left|\psi_n\right\rangle$, which is in general different from $\left|\psi_n\right\rangle$, is another eigenstate of $\boldsymbol{H}$ with the *same* energy eigenvalue E_n. It is therefore clear that if $\boldsymbol{H}$ is invariant under each member of a set of m transformations $\boldsymbol{T}_1, \boldsymbol{T}_2, ..., \boldsymbol{T}_m$, then the potential exists for each energy level to be up to $m+1$ times degenerate (though it is also possible that two or more of the $\boldsymbol{T}_i$ transform $\left|\psi_n\right\rangle$ into the same final state). We shall now introduce the finite group theory framework necessary to identify the maximal set of transformations $\boldsymbol{T}_i$ under which $\boldsymbol{H}$ is invariant as the symmetry group G_S of $\boldsymbol{H}$ and the set of eigenstates belonging to the same eigenenergy as a basis for an irreducible representation of G_S [2–3].

III. An introduction to the theory of finite point groups

III.1 Definitions

Quite generally, an abstract *group G* is defined as a set of objects, called elements of the group *G*, along with an operation of composition (•) which together satisfy the following four conditions [3]:

1. *closure*: for all elements *a* and *b* of *G*, the element $a \bullet b \equiv ab$ is also an element of *G*.
2. *associativity*: the composition operation is associative, i.e. $a(bc) = (ab)c$.
3. *identity*: there must exist an element *e* in the set *G* such that for every element *a* in *G*, $ea = ae = a$.

[2] Accidental degeneracies are those degeneracies which correspond to special choices of the parameter values in *H* such that sets of basis functions belonging to different irreducible representations of the symmetry group of *H* coincide in energy [3].

[3] This equivalence follows from the observation that if the Hamiltonian is invariant under a transformation $\boldsymbol{T}$, then we have that $\hat{\boldsymbol{T}}\hat{\boldsymbol{H}}\hat{\boldsymbol{T}}^{-1} = \hat{\boldsymbol{H}}$, which implies that $\hat{\boldsymbol{T}}\hat{\boldsymbol{H}} = \hat{\boldsymbol{T}}\hat{\boldsymbol{H}}\hat{\boldsymbol{E}} = \hat{\boldsymbol{T}}\hat{\boldsymbol{H}}\hat{\boldsymbol{T}}^{-1}\hat{\boldsymbol{T}} = \hat{\boldsymbol{H}}\hat{\boldsymbol{T}}$, and hence commutivity.

4. *invertability*: every element *a* of *G* have an inverse a^{-1} that is also an element of *G*. That is, $\forall a \in G,\ \exists\, a^{-1} \in G:\ aa^{-1} = a^{-1}a = e$.

A group with *g* elements is said to be a group of *order g*. While there are many examples of infinite groups (such as the set of all integers under addition, or the set of all rotations about an axis under addition), we will restrict ourselves here to the discussion of *finite groups*, i.e. groups of finite order.

An example of a finite group is the *cyclic group* of order 4, denoted by C_4. The elements of C_4 are the first four powers of a generating element *a* and can be denoted by $a, aa \equiv a^2, aa^2 \equiv a^3, aa^3 \equiv e$. It is easy to verify by inspection that the elements of C_4 satisfy conditions 1–4 above for being a group. A special property of C_4 is that all of its member elements commute with one another. While all cyclic groups have this property, it is not shared by all groups in general. Groups whose elements commute are referred to as *Abelian* groups. Several, though not all, of the point groups we shall be examining and using later are Abelian. Finally, if a subset of the elements of a group *G* satisfy the requirements of a group under the same composition operation, then they are termed a *subgroup G'* of *G*. The group C_2 with elements $a^2, a^2a^2 \equiv e$, is therefore an example of a subgroup of C_4.

Another important concept that we shall make extensive use of is the notion of *conjugate elements* and *conjugate classes* (hereafter simply *classes*). Two elements *a* and *b* of a group *G* are said to be conjugate to one another if there exists an element *u* also in *G* such that [3]

$$uau^{-1} = b \tag{5}$$

Strictly speaking, Eq. (5) states that the element *b* is conjugate to *a*. But application of $u = \left(u^{-1}\right)^{-1}$ on the right and u^{-1} on the left of both sides yields

$$u^{-1}uau^{-1}\left(u^{-1}\right)^{-1} = u^{-1}b\left(u^{-1}\right)^{-1}$$

$$\left(u^{-1}u\right)a\left(u^{-1}\left(u^{-1}\right)^{-1}\right) = u^{-1}b\left(u^{-1}\right)^{-1}$$

$$eae = u^{-1}b\left(u^{-1}\right)^{-1}$$

$$a = u^{-1}b\left(u^{-1}\right)^{-1}$$

showing that if *b* is conjugate to *a*, then *a* is also conjugate to *b*. We see that the conjugacy of group elements is therefore reflexive. It can similarly be shown that conjugacy is transitive [3], and by simply letting $u = e$ and $b = a$ in Eq. (5), we can see that conjugacy is also symmetric. Conjugacy therefore satisfies the three properties of an equivalence relation[4]. This is useful because an equivalence relation can be used to partition a set into distinct classes [3]. In this case, two elements are in the same conjugate class if they are conjugate to each other, and thus a conjugate class consists of all those elements of the group that are conjugate to each other. It is worth noting that for Abelian groups, each element forms a class by itself, since for any *u* we

[4] That is, a relation $\leftrightarrow$ is denoted an equivalence relation if it is:

1. symmetric, such that $a \leftrightarrow a$
2. reflexive, such that if $a \leftrightarrow b$, then $b \leftrightarrow a$
3. transitive, such that if $a \leftrightarrow b$ and $b \leftrightarrow c$, then $a \leftrightarrow c$

have that $uau^{-1} = auu^{-1} = ae = a$, so that each element of an Abelian group is conjugate to only itself. For Abelian groups, then, the number of classes *r*, is equal to the order of the group.

III.2 Finite point groups

As alluded to in section II, we are interested in symmetry transformations under which the physical system of interest is invariant. *Symmetry transformations* refer to those *isometric* (i.e. distance-preserving) transformations which bring the system into coincidence with itself [3], and the collection of all such symmetry transformations forms the symmetry group G_S of the system. There are three primary types of geometric transformations from which all isometric transformations, and thus all symmetry transformations, can be constructed [3]. These are:

1. Rotation about some fixed axis through a definite (i.e. non-infinitesimal) angle
2. Reflection in a plane
3. Space translation

It should be noted that each of these three classes of transformation constitute symmetry transformations in there own right. A fourth class of symmetry transformation is space inversion (i.e. $(x, y, z) \to (-x, -y, -z)$ in Euclidian 3-space), and it can be constructed by combining a rotation through an angle of π about some axis (such as the z-axis) with a reflection in a plane perpendicular to that axis (in this case, the xy-plane). From this description it is clear that a space inversion transformation is equivalent to the more commonly referred to parity transformation. Inversion symmetry is really just a special case of a class of symmetries called *rotation-reflection* symmetries. An *n*-fold rotation-reflection (sometimes also called rotary reflection [2]) transformation $\boldsymbol{S}_n$ is defined to be equivalent to a rotation transformation $\boldsymbol{C}_n$ through an angle $2\pi / n$ combined with a reflection transformation $\boldsymbol{\sigma}_h$ about the plane perpendicular to the axis of rotation[5] [3]. That is, $\boldsymbol{S}_n \equiv \boldsymbol{C}_n \boldsymbol{\sigma}_h = \boldsymbol{\sigma}_h \boldsymbol{C}_n$, where we have shown explicitly that rotation transformations commute with reflections about planes perpendicular to the axis of rotation.

Note that under a rotary reflection, the point of intersection between the axis of rotation and the plane of reflection (in the case of an inversion in Euclidian 3-space, the origin $(0,0,0)$) is left unaltered. For a rotation, those points along the axis of rotation remain fixed, as do all points in the plane of reflection under a reflection transformation. A symmetry group with the property that each of its transformation elements leaves at least one point of the system fixed is called a *point group*. Since a space translation by definition results in a constant shift in the position of each point in the system, a point group cannot contain any elements which correspond to simple translation transformations. Note, however, that only a system which extends infinitely in at least one spatial dimension, such as an infinite crystal lattice, can be invariant under a space translation transformation. Space translations therefore cannot be elements of the symmetry group for any finite system, and from this it follows that the symmetry groups of all spatially-finite systems are point groups [2-3].

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[5] The subscript *h* on the reflection transformation denotes that, if the axis of rotation is taken to be vertical, then the plane of reflection perpendicular to that axis is horizontal. Similarly, $\boldsymbol{\sigma}_v$ represents a reflection about a vertical plane containing the axis of rotational symmetry. When no rotation axis is specified, a reflection transformation is denoted by $\boldsymbol{\sigma}$, without a subscript.

We will now enumerate and briefly describe several, though not all, common, physically relevant[6] point groups, starting with those corresponding to cyclic symmetry groups consisting of only rotations about a single axis. If an object is symmetric, that is, brought into coincidence with itself, under a rotation through an angle of $2\pi/n$, then that axis is termed an *n*-fold rotation axis, or an axis of the *n*th order. Being cyclic, the symmetry group of rotations about an *n*-fold axis, C_n, is generated by taking powers of the unit rotation transformation for the group, denoted[7] $\boldsymbol{C}_n$. With the identification $(\boldsymbol{C}_n)^n \equiv \boldsymbol{E}$, the identity transformation, it is clear that the point group C_n is of order *n*. Since application of the unit rotation transformation $\boldsymbol{C}_n$ results physically in a rotation by $2\pi/n$, $\boldsymbol{C}_n\boldsymbol{C}_n = (\boldsymbol{C}_n)^2 \equiv \boldsymbol{C}_n^2$ corresponds to two sequential $2\pi/n$ rotations about the same axis, or, equivalently, a single rotation by $2(2\pi/n)$. In this light, the earlier identification of $(\boldsymbol{C}_n)^n$ with the identity transformation makes intuitive sense, as we see that $(\boldsymbol{C}_n)^n$ is equivalent to a rotation by $n(2\pi/n) = 2\pi$ which returns the system to its original orientation.

Another cyclic point group is S_{2n}, the symmetry group containing rotation-reflections about a single 2*n*-fold rotary-reflection axis [2]. All elements of this point group can be written as powers of $\boldsymbol{S}_{2n}$, so the order of the group is therefore *2n*, where $(\boldsymbol{S}_{2n})^{2n} \equiv \boldsymbol{E}$, as with all cyclic groups. For $n=1$ we have the point group S_2, which has only the two elements: $\boldsymbol{E}$ and $\boldsymbol{S}_2 = \boldsymbol{C}_2\boldsymbol{\sigma}_h \equiv \boldsymbol{I}$, the latter of which is the definition of the inversion transformation introduced earlier. Because the only non-identity element of S_2 is $\boldsymbol{I}$, S_2 is also commonly referred to as C_i, where the subscript *i* refers to inversion. The presence of the inversion transformation $\boldsymbol{I}$ among the elements of an object's symmetry group indicates that the object has a center of symmetry [2].

By adding to the group C_n the reflection transformation $\boldsymbol{\sigma}_h$ about a plane perpendicular to the *n*-fold rotation axis, we can form the point group C_{nh} [2–3]. For the group to be closed, we see that it must contain *2n* elements: *n* corresponding to the powers of $(\boldsymbol{C}_n)^k$, $k = 1, 2, ..., n$, and another *n* corresponding to the products $(\boldsymbol{C}_n)^k\boldsymbol{\sigma}_h$, $k = 1, 2, ..., n$. Though not a cyclic group, C_{nh} is still Abelian because each of it contains only rotations, perpendicular reflections, and their products. Note also that since both C_n and S_n are subgroups of C_{nh}, C_{nh} represents a higher level of symmetry than either C_n or S_n.

Things get more interesting when we start looking at the symmetry groups of objects or systems with more than a single axis of rotational symmetry. If an object has a 2-fold rotational axis perpendicular to an *n*-fold rotational symmetry axis, then it must also have $(n-1)$ additional *2*-fold rotational axes in the plane perpendicular to the *n*-fold axis for a total of *n 2*-fold axes, each separated by an angle of $2\pi/n$. This can be seen by following the orientation of the initial *2*-fold axis under *n* successive applications of the transformation $\boldsymbol{C}_n$. Figure 1 provides an example of this procedure for the case $n=3$. The symmetry group consisting of rotations about these *n 2*-fold axes and 1 *n*-fold axis is called the dihedral point group D_n [2–3]. D_n is of order

[6] While rotation-only point groups containing only finite rotations about an n-fold axis, with $n > 6$, are indeed point groups, they have scant applications in physics, since molecules and potentials with this type of symmetry arise relatively rarely.

[7] I will use boldface to distinguish point group elements from the point groups themselves.

2n, with the rotation transformations in C_n accounting for half the elements, and a single rotation through an angle of π, denoted by $\boldsymbol{U}_2^{(k)}$, $k = 1, 2, ..., n$, specific to each of the n *2*-fold horizontal[8] axes making up the other half of the elements. It is worth noting that the only Abelian dihedral point group is D_2; all other dihedral groups contain non-commuting transformations. We shall see why this is important momentarily.

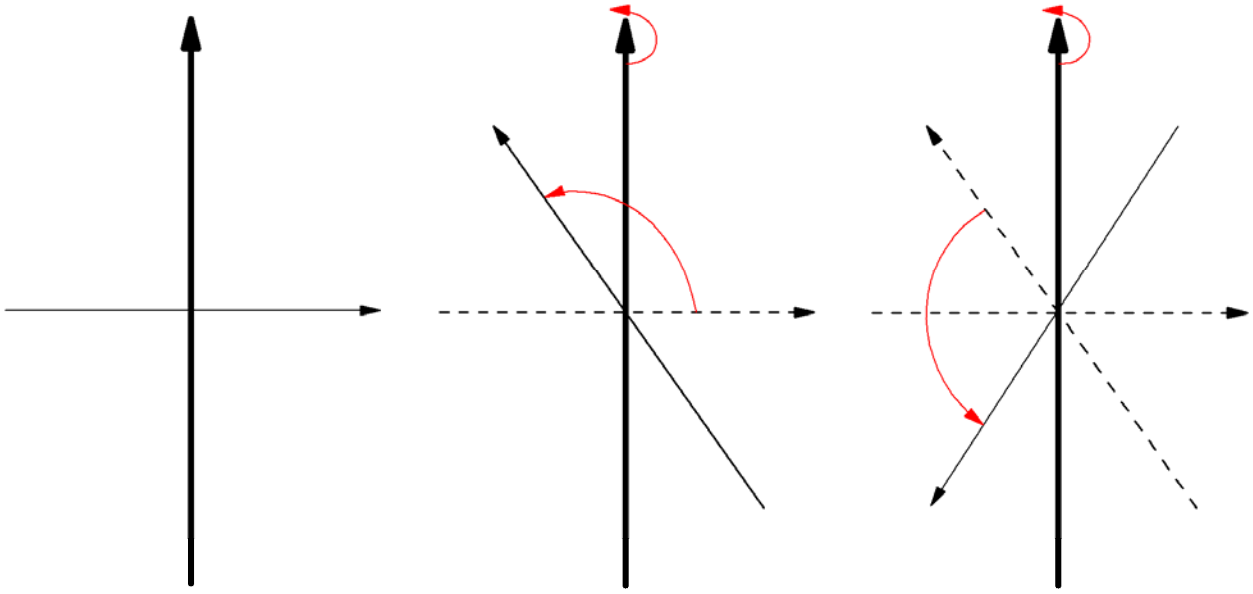

Figure 1. Diagram showing the generation of the dihedral point group D_3 through consecutive rotations of the horizontal *2*-fold axis rotational axis through angles of $2\pi/3$ radians about the vertical *3*-fold rotational axis

It is important at this point to pause to discuss *equivalent axes* and transformation classes. Up to now, each of the symmetry transformation elements of each of the point groups discussed (C_n, S_{2n}, and C_i, and C_{nh}), have formed their own class within their respective point groups. To see why, we recall that each of these point groups is Abelian, and that, as was mentioned in section III.1, the elements of Abelian groups form classes by themselves. With the incorporation of additional, *non-equivalent* axes of rotational symmetry in the dihedral groups with $n > 2$, non-commuting transformations were introduced to the symmetry group, allowing for non-singleton conjugate classes. "All axes (or planes) of symmetry which can be brought into coincidence under some transformation in the symmetry group are said to be *equivalent axes* (or *equivalent planes*)" [3]. This is essentially a restatement of Eq. (5) in words, with the axes taking the place of the group elements *a* and *b*. Thus, transformations in the group representing rotations (or rotary reflections) through the same angle about equivalent axes are conjugate elements of the symmetry group, and are therefore in the same class [3]. The number of classes into which a

[8] It is typical to orient that axis permitting the greatest number of rotations, i.e. the greatest rotational symmetry axis, if there is only one, in the vertical direction. For dihedral groups, then, all of the *2*-fold axes are in the horizontal plane, perpendicular to the vertically oriented *n*-fold axis.

group can be partitioned, *r*, along with the number of elements in each class, are convenient for describing the structure of the group and will prove useful later, as these characteristics are specific to the group in question, and independent of any particular representation of the group.

III.3 Representations of groups

We will now introduce the notion of group representations and quote (with references, but for the most part without proof, due to space limitations) a few useful results from the theory of finite groups. Our treatment will follow closely that of Landau [2]. Let G_S be the symmetry group[9] of order g of a physical system of interest and ϕ_1 a single-valued function of the coordinates describing the system. Upon the application of each of the g symmetry transformations $\boldsymbol{G}^{(k)}$, $k = 1, 2, ..., g$, in G_S to ϕ_0, ϕ_0 is transformed into g different functions $\phi_1, \phi_2, ..., \phi_g$ [2]. It is in general possible that not all of these g functions are linearly independent, but can instead can all be represented as linear combinations of the f functions $\psi_1, \psi_2, ..., \psi_f$, where[10]

$$f \le g . \tag{6}$$

Since this is generally true from any single-valued ϕ_0, then it should also be true for $\phi_0 = \psi_i$ for all $i = 1, 2, ..., f$. Put another way, each transformation $\boldsymbol{G}^{(k)}$ in G_S maps each function ψ_i into a linear combination of the f ψ_i functions. Thinking of $\boldsymbol{G}^{(k)}$ as the operator $\hat{\boldsymbol{G}}^{(k)}$, this can be expressed symbolically as

$$\hat{\boldsymbol{G}}^{(k)}\psi_i = \sum_{n=1}^{f} G_{ni}^{(k)}\psi_n \tag{7}$$

where the $G_{ni}^{(k)}$ are a set of f constants particular to the transformation $\boldsymbol{G}^{(k)}$ and the function ψ_i [2]. We note that the ψ_i can always be chosen to be orthonormal [2], and that identifying them as a set of basis functions allows for the interpretation of the f^2 constants $G_{ni}^{(k)}$ (f constants for each of the f functions) as the elements of a matrix representation of the transformation operator $\hat{\boldsymbol{G}}^{(k)}$ with respect to this ψ_i basis. In this manner, we can construct matrices for each of the g symmetry transformation operators $\hat{\boldsymbol{G}}^{(k)}$ in G_S. Taken together, a set containing a matrix for each element of a group is referred to as a *representation* of the group [2]. More precisely, a representation of a group is a homomorphic mapping of that group onto a group of operators that are represented by matrices in the vector space L in which the functions ψ_i are defined [3]. The *dimension* of the representation is equal to f, the number of functions ψ_i with respect to which the matrices were generated and which are called the *basis* of the representation of the group [2]. Additionally, we note that when the basis functions are chosen to be orthonormal, the matrices for the symmetry transformations can be shown to be unitary [2–3], indicating that the operators

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[9] Although we use a particular group here (the symmetry group), the definitions and results of this section hold for groups generally, unless specified otherwise.

[10] Equality occurs only in the case that the ϕ_i are all linearly independent, in which case $\phi_i = \psi_i$ for all $i = 1, 2, ..., g$.

themselves are unitary[11]. This is reassuring, as we're already familiar with both the utility and prevalence of unitary operators in quantum mechanics. From this point forward we will assume that sets of basis functions are orthonormal and that matrices are unitary.

It should be immediately clear that since a representation of a group is given with respect to a basis, then a different choice of basis functions ψ_i' can lead to a "different" representation of the group. Here, "different" refers to least some of the matrices in the representation with basis functions ψ_i being distinguishable from those matrices corresponding to the same operators in a second representation with basis ψ_i'. In many cases, however, this "difference" is only superficial. Two group representations of the same dimension are said to be *equivalent representations* if the basis functions ψ_i of the first representation can be mapped onto the basis functions ψ_i' of the second representation by a unitary linear transformation. That is, equivalent representations are those for which

$$\psi_i' = \hat{\boldsymbol{S}}\psi_i \tag{8}$$

for all $i = 1, 2, ..., f$, where $\hat{\boldsymbol{S}}$ is a linear unitary operator [2]. The matrix for the operator $\hat{\boldsymbol{G}}^{(k)}$ in the transformed (primed) representation is then equal to the matrix of

$$\hat{\boldsymbol{G}}^{(k)\prime} = \hat{\boldsymbol{S}}^{-1}\hat{\boldsymbol{G}}^{(k)}\hat{\boldsymbol{S}} \tag{9}$$

in the untransformed (unprimed) representation [2].

Equivalent representations are called such because, despite distinguishable differences in their constituent matrices, there is a quantity calculable from the matrix for each operator, called the *character* of that element of the symmetry group, which is the same in equivalent representations [2–4]. The character of an element $\boldsymbol{G}^{(k)}$ of G_S in a particular representation is defined as [2–3]

$$\chi\left(\boldsymbol{G}^{(k)}\right) = Tr\left(G_{nm}^{(k)}\right) = \sum_{i=1}^{f} G_{ii}^{(k)} . \tag{10}$$

Two representations of a group are thus considered to be truly different only if the characters of matrices that correspond to the same group element are different.

Now, note the similarity between Eq. (9) and Eq. (5). If we interpret $\hat{\boldsymbol{S}}$ in Eq. (9) as the operator for that symmetry transformation in G_S which takes the element $\boldsymbol{G}^{(k)}$ to its conjugate element, denoted here as $\boldsymbol{G}^{(k)\prime}$, then we see that, in any representation, the characters of matrices for elements in the same class (i.e. conjugate symmetry transformations) are the same [2–3]. Letting K_i, $i = 1, 2, ..., r$ denote the classes of G_S and a superscript μ indicate a particular representation basis, we write that if two symmetry transformations $\boldsymbol{G}^{(m)}$ and $\boldsymbol{G}^{(n)}$ belong to the same class K_i, then

$$\chi^{(\mu)}\left(\boldsymbol{G}^{(m)}\right) = \chi^{(\mu)}\left(\boldsymbol{G}^{(n)}\right) = \chi_i^{(\mu)} \tag{11}$$

and that for any two representations μ and ν of the same dimension,

$$\chi_i^{(\mu)} = \chi_i^{(\nu)} \tag{12}$$

This implies that if we were to calculate or otherwise know the character of just one matrix from each class in the group for a certain representation, then we'd know the characters of all of the

[11] While this is not generally true for groups of infinite order, it is true for finite groups.

elements of the group in that representation, and thus be able to distinguish that representation from other, potentially non-equivalent representations.

Before discussing non-equivalent representations further, let us first motivate our interest in them by returning to the quantum mechanical eigenvalue problem of Eq. (1). We saw already in Eq. (4) that a symmetry of the Hamiltonian gives rise to degeneracy, and that if the symmetry group G_S of the Hamiltonian contains g transformations, then there can be up to g solutions to Eq. (1) corresponding to the same eigenvalue, of which some f are linearly independent. Identifying $\hat{\boldsymbol{T}} \to \hat{\boldsymbol{G}}^{(k)}$ and $\hat{\boldsymbol{G}}^{(k)}|\psi_n\rangle \to \psi_i$ in Eq. (4), Eq. (7) shows that the application of a symmetry transformation in G_S upon each of those f linearly independent eigenfunctions can be expressed as a linear combination of those same eigenfunctions. Applying each of the symmetry transformations under which the Hamiltonian is invariant to this set of f linearly independent energy eigenfunctions then gives us an f-dimensional representation of the symmetry group in which the eigenfunctions are the basis [3]. Distinguishing the types of possible representations of a symmetry group should then help us to classify the eigenfunctions on the basis of symmetry alone.

We begin by looking at the matrix elements $G_{ni}^{(k)}$, defined in Eq. (7) with respect to a set of f basis functions ψ_i. Suppose that instead of transforming each ψ_i into a linear combination of all f of the basis functions, that a symmetry transformation operator $\hat{\boldsymbol{G}}^{(k)}$ mapped each member of a subset of the ψ_i back into that subset, i.e. into linear combinations of only members of the subset. For convenience, we will let $\psi_1, \psi_2, ..., \psi_a$ populate this subset[12]. Then Eq. (7) says that for $i \le a$, $G_{ni}^{(k)} = 0$ for all $n > a$, and the f-by-f matrix for $\hat{\boldsymbol{G}}^{(k)}$ with respect to the entire basis is of the form

$$G_{ni}^{(k)} = \begin{bmatrix} G_{11}^{(k)} & G_{12}^{(k)} & \cdots & G_{1a}^{(k)} & G_{1,a+1}^{(k)} & \cdots & G_{1f}^{(k)} \\ G_{21}^{(k)} & G_{22}^{(k)} & \cdots & G_{2a}^{(k)} & G_{2,a+1}^{(k)} & \cdots & G_{2f}^{(k)} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \cdots & \vdots \\ G_{a1}^{(k)} & G_{a2}^{(k)} & \cdots & G_{a,a}^{(k)} & G_{a,a+1}^{(k)} & \cdots & G_{a,f}^{(k)} \\ 0 & 0 & \cdots & 0 & G_{a+1,a+1}^{(k)} & \cdots & G_{a+1,f}^{(k)} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 0 & G_{f,a+1}^{(k)} & \cdots & G_{f,f}^{(k)} \end{bmatrix}. \tag{13}$$

This matrix may be divided into sub-matrices, as is represented diagrammatically in Figure 2a, where the expression in brackets gives the dimensions of the sub-matrix. If the matrix for another operator $\hat{\boldsymbol{G}}^{(l)}$ in G_S can be written in the same form as (13), then its matrix may similarly be divided into sub-matrices, as in Figure 2b. According to the usual rules for matrix multiplication, the operator $\hat{\boldsymbol{G}}^{(k)}\hat{\boldsymbol{G}}^{(l)}$ will have a matrix of the form given diagrammatically in Figure 2c. What is remarkable here is that the sub-matrices along the diagonal behave the same way under multiplication as the full matrices. In the case that the set of f basis vectors can be

[12] While in principle any of the ψ_i could be in this subset that gets mapped into itself under $\hat{\boldsymbol{G}}^{(k)}$, it is always possible to renumber the basis functions so that the subset contains the first a functions.

transformed such that each matrix for all of the element in G_S is of the same form as Eq. (13), then that *f*-dimensional representation is said to be *reducible*. Since they behave precisely analogously to the full matrices under combination, the set of sub-matrices $D^a(k)$ for each $k = 1, 2, ..., g$ form a *reduced a*-dimensional representation of the group. Similarly, the set of sub-matrices $D^{f-a}(k)$ form an *f-a*-dimensional representation.

$D^a(k)$ [*a,a*]	*A(k)* [*a,f-a*]
0 [*f-a,a*]	$D^{f-a}(k)$ [*f-a,f-a*]

(a)

$D^a(l)$ [*a,a*]	*A(l)* [*a,f-a*]
0 [*f-a,a*]	$D^{f-a}(l)$ [*f-a,f-a*]

(b)

$D^a(k)D^a(l)$ [*a,a*]	$D^a(k)A(l) + A(k)\,D^{f-a}(l)$ [*a,f-a*]
0 [*f-a,a*]	$D^{f-a}(k)D^{f-a}(l)$ [*f-a,f-a*]

(c)

Figure 2. Diagrammatic representations of two matrices (a–b) as well as the product of those matrices (c)

It is often possible to continue this process by identifying smaller and subsets of the basis functions that transform only among themselves under the symmetry transformations of the group, though not indefinitely. The representation of a group with respect to a set of basis functions which cannot be further partitioned into subsets as above is called an *irreducible* representation [2–3]. It can be shown [3] that since the full *f*-dimensional representation consists of unitary matrices[13], that $A(k) = 0$ for all *k*, indicating that the subsets of functions that transform among themselves are actually subspaces L_j of *L*, the vector space in which they are defined. In this case, we say that the *f*-dimensional representation with which we started is *fully reducible*. Since a unitary representation[14] can always be found for finite point groups, we have that any reducible, *f*-dimensional representation D^f can always be decomposed into the direct sum of a finite number of irreducible representations as

$$D^f = D_1^\alpha + D_2^\beta + D_3^\gamma + ... + D_h^\eta \tag{14}$$

where $\alpha + \beta + ... + \eta = f$. It is customary to write the decomposition of D^f in terms of unique irreducible representations, so in the event that two or more of these irreducible representations are equivalent, we would rewrite Eq. (14) with integral coefficients c_i affixed to each unique representation on the left-hand side denoting the number of times it is contained in the reducible representation. If, for instance, D_1^α is equivalent to D_2^β, we would write the sum as

$$D^f = 2D_1^\alpha + D_3^\gamma + ... + D_h^\eta \tag{15}$$

[13] We're assuming here that the basis functions are orthonormal and that the matrices are therefore unitary, but have mentioned previously that this is always possible for representations of finite point groups.
[14] A unitary representation is one in which all of the matrices are unitary.

where coefficients equal to one have been suppressed. We say that the $c_i\lambda$ basis functions with respect to which a unique, λ-dimensional irreducible representation D^λ contained c_i times in the fully reduced *f*-dimensional representation belong to that irreducible representation. As alluded to earlier in this section, the symmetry properties of basis functions belonging to an irreducible representation D^λ are determined by the form of D^λ.

The final piece of information we need before discussing character tables is a major theorem proven elsewhere [2–4]: the number of unique irreducible representations of a group, *h*, is equal to the number of classes in the group, *r*. That is, using our current notation

$$h = r \tag{16}$$

III.4 Irreducible representations and character tables

Much useful information about a symmetry point group is displayed succinctly in its *character table*, an example of which is given in Figure 3 for the dihedral point group of order 3. In the present work, we shall not concern ourselves with the construction of character tables (i.e. how to make them), but rather with their interpretation (i.e. how to use them). The interested reader is directed to chapter 4 of Hamermesh's book [3] for a systematic approach to acquiring the data for a character table. To that end, we begin by describing the organization and then identifying the contents of the table.

The first thing to note is that character tables are typically broken up into four quadrants, each of which contains information of a different type. Starting in the upper left hand quadrant and proceeding clockwise, we shall label the quadrants I-IV, as in Figure 4. Quadrant I contains the name of the point group *G* to which the table refers. Quadrant II consists of *r* columns, one for each of the *r* conjugate classes into which the elements of *G* may be partitioned. Each column is labeled by an element of the conjugate class represented by that column, with the first column always representing the identity transformation *E*. Following the column label is, in parenthesis, the number of elements in the conjugate class. If no number is given, as is always the case for the first column, then the conjugate class is to be understood to include only the element listed (i.e. it is a singleton class). From Figure 3, we see that there are six distinct symmetry transformations in D_3 which form a total of three classes: one class containing just the identity transformation as well as two non-trivial classes, containing two and three transformations, respectively.

D_3:	E	$C_3(3)$	$U_2(3)$
A_1	1	1	1
A_2; z	1	1	–1
E; x, y	2	–1	0

Figure 3. A character table for the dihedral point group D_3

Quadrant IV consists of *r* rows, one for each of the irreducible representations of the group[15]. It is customary for denote 1-dimensional representations[16] by the letters *A* and *B*. Basis

[15] Recall that the number of distinct irreducible representations of a group is equal to the number of distinct classes in the group.

[16] For one-dimensional representations, the matrices contain only a single entry, and so each matrix is itself equal to its character χ.

functions belonging to *A* (*B*) are *symmetric* (*antisymmetric*) with respect to rotation about the *n*-fold principle axis, which is always to be taken along the *z*-direction [2–3]. Symmetry and antisymmetry with respect to inversion is denoted by the subscripts *g* and *u*, respectively[17]. In a similar manner, the basis functions are indicated as being symmetric (antisymmetric) with respect to reflection about a plane perpendicular to the primary axis by a prime (two primes). In this manner, we see that the symmetry properties of basis functions are indeed classified by the irreducible representation to which they belong. Two-dimensional representations are denoted by *E* (not to be confused with the identity transformation, also denoted by the overworked letter *E*), and 3-dimensional representations are represented by *F*. Numerical subscripts are used to distinguish between unique irreducible representations of the same dimension. The coordinates (x, y, or z) which appear beside certain representations identify the representations by which the coordinates themselves are transformed and are useful for determining selection rules for electric dipole transitions [3]. Finally, Quadrant III is filled by an *r*-by-*r* array containing the character for each irreducible representation of each class. A glance at Figure 3 now tells us that the dihedral point group D_3 has two 1-dimensional representations, the basis functions belonging to which are all symmetric with respect to rotation about the *z*-axis, and one 2-dimensional representation.

Quad I	Quad II
Quad IV	Quad III

Figure 4. Schematic showing the labeling scheme used in the present work to identify the different quadrants of a character table

IV. Applications to quantum mechanics

IV.1. Assessing degeneracy

Now that we are familiar with the contents of character tables, we may put them to use in the context of quantum mechanics. We saw in sections III.3–4 that "a symmetry property of a linear operator, [such as the Hamiltonian operator $\hat{\boldsymbol{H}}$], leads to a classification of the eigenfunctions of that operator according to the same symmetry" [3]. We have also seen how applying transformations from the symmetry group of the Hamiltonian to solutions of Schrödinger's equation, Eq. (1), yields a set of energy eigenfunctions, i.e. degenerate states, corresponding to the same energy which can be used to form an irreducible representation of the symmetry group. Thus, for each energy eigenvalue E_n, there is a corresponding irreducible representation of the symmetry group G_S [2], and it the dimension of this representation which determines the number of degenerate states of energy E_n. An energy level can therefore not degeneracy unless the symmetry group has an irreducible representation of dimension two or greater[18].

[17] The *g* comes from the German word *gerade*, which, in a mathematical context only, means *even*. The *u* comes from the antonym of gerade, *ungerade*, which is understood to mean *odd* in a mathematical setting.

[18] An important caveat here is that, because the Hamiltonian is invariant under time reversal (at least in the absence of magnetic or otherwise explicitly time-dependent fields), there is an additional operation under which the Hamiltonian is invariant which connects base functions with their complex conjugates. Two irreducible unit-representations (i.e. 1-dimensional representations) with characters that are complex conjugates are then said to form a two-dimensional representation, since their basis functions both correspond to a doubly degenerate energy level.

As a direct consequence of this fact, the energy level spectrum of any Hamiltonian whose symmetry group is Abelian is necessarily non-degenerate. This is because the number of classes, *r*, in an Abelian group, and therefore the number of unique irreducible representations of the group, is equal to the number of elements in the group, *g*. This means that the basis vectors used to construct a fully reducible representation of the group can be decomposed into *g* subspaces, and since there were at most *g* basis functions to begin with by Eq. (6), we have that there is only one basis function per subspace, or, equivalently, that each of the *g* irreducible representations are 1-dimensional, allowing for no degeneracies.

IV.2. Removing degeneracy via perturbation

Suppose now that the symmetry group for a Hamiltonian H_0 of interest is non-Abelian, so that some degeneracies exist. If we apply a perturbing potential *V* to the system, then the symmetry group for the full Hamiltonian $H = H_0 + V$ is given by the intersection of the symmetry group for the unperturbed Hamiltonian, G_S, and the symmetry group of the perturbing potential, G_S'. If G_S is a subset of G_S', then the symmetry of the perturbation is greater than that of the original Hamiltonian, and degeneracies cannot by alleviated by the perturbation. In the other extreme, if the intersection is empty, then the full Hamiltonian is entirely unsymmetrical, and all degeneracies are removed. If, however, G_S' is a subset of G_S, then the full Hamiltonian will be of lower symmetry than was the unperturbed Hamiltonian, allowing for the possible removal of specific degeneracies [2–3].

V. References

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