Contents

Elements of group theory

Pun intended.

Keypoints:

- A discrete group consist of a finite number of elements
- The solutions to the Schrodinger Equation are uniquely determined by the set of symmetry operations of the problem

1.1 Introduction

The theory of quantum mechanics relies heavily on concepts from group theory. One can find solutions to problems simply by looking at their symmetries. It has endless applications in both chemistry and physics. Unfortunately, the topic is enormous and we will only be able to cover a small fraction of it. Here, I follow the book by Bradley and Cracknell and the text by Eva Pavarini [1]

[1] *C.J. Bradley and A.P. Cracknell, The mathematical theory of symmetry in solids, Oxford University Press, 1972. E. Pavarini et al., Correlated electrons: from models to Materials, ISBN 978-3-89336-796-2. The chapter by Pavarini can also be found on Canvas.*

1.2 Groups: a first look.

The abstract definition of a group is given as follows:

Definition 1.1. *A* **group** *G is a set of* **elements** *(for example A, B ...) together with a product such that:*

- *the product of two elements gives another element in the group. Mathematically: if* $A, B \in G$ *then* $AB \in G$.
- *the product is associative:* $(AB)C = A(BC)$ *for all* $A, B, C \in G$.
- *there exists a unique identity E such that* $EA = AE = A$ *for all* $A \in G$.
- *every element has an inverse:* $AA^{-1} = A^{-1}A = E$ *for all* $A \in G$. *E is the identity .*

Here we will consider **finite groups**, which consist of a finite number of elements. The abstract definition may not be very illuminating, so let's take an example. We will consider a simple object, an equilateral triangle, and ask: "what are the symmetries and how do we make a group out of this?". Figure 1.1 shows such a triangle. Also indicated are three lines (the red, blue and green medians) that are for visual aid only. There are two symmetry operations that will turn the triangle back to itself. The first is the clock-wise or anti-clockwise rotation by 120° around the intersection of the three medians and the second is the reflection in any one of the medians. Together with the defining bullet points, we can use these two operations (reflection and rotation) to make a group. The symmetry operations are called **generators**. Let's call them P (rotation) and Q (reflection). Note that P and Q can be multiplied to create other elements of our group.

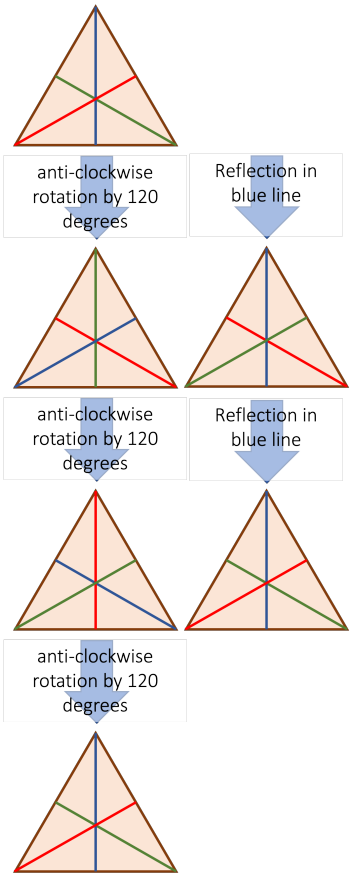

Figure 1.1: The two symmetry operations for the equilateral triangle.

Let's take another look at Fig. 1.1. We note that if we apply P three times consecutively, we return to the original triangle (with the color of the medians in the bottom triangle equivalent to the one on top). This allows us to define a so-called **generating relation**: $P^3 = E$. In words: multiplying the element P three times is equal to an identity operation. The idea is that the identity (unity) leaves everything the same (**invariant**). Similarly, we find that reflecting the triangle in a median twice also returns us to the original state: $Q^2 = E$. You can check for yourself that there is another generating relation: $QP = P^2Q$ (see exercise 1).

Taken together, we thus have two elements and three defining relations and together they fulfill the conditions set out above. The group of possible symmetry operations that leave the equilateral triangle invariant is called G_6^2 (here G simply stands for group, 2 indicates the number of generators and 6 is the order of the group; see below). Groups are often represented by their multiplication table. Such a table can be obtained once the generators and defining relations are given.

$\otimes$	E	P	P^2	Q	PQ	P^2Q
E	E	P	P^2	Q	PQ	P^2Q
P	P	P^2	E	PQ	P^2Q	Q
P^2	P^2	E	P	P^2Q	Q	PQ
Q	Q	P^2Q	PQ	E	P^2	P
PQ	PQ	Q	P^2Q	P	E	P^2
P^2Q	P^2Q	PQ	Q	P^2	P	E

Table 1.1: Multiplication table for G_6^2. To obtain the correct result always multiply the row element by the column element.

The choice of generators and generating relations is not unique. In the example above, I could also have chosen clockwise rotations or a reflection in the red or green line. Any combination of these rotations and reflections would have resulted in a multiplication table similar to the one above. We conclude this section with a few more definitions.

Definition 1.2. *The* **order** *of a group G is simply the number of elements in the group.*

The multiplication table above shows that our group, G_6^2, has six elements (including the identity) and is thus of order 6.

Definition 1.3. *The order of an element is the smallest integer, n, such that* $A^n = E$.

The generating relations show that the order of the element P in our example is three, while Q is of order two.

1.3 Morphisms and subgroups

A morphism is an operation that transforms the elements of a group from one representation to another.

Definition 1.4. *Given a mapping F that transforms the group G onto G', the mapping is a* **homomorphism** *if the multiplication of elements is preserved.*

Therefore, for a homomorphic mapping F we have $F(G_1)F(G_2) = F(G_1G_2)$.

Definition 1.5. *a mapping is called an* **isomorphism** *when each element of G maps onto a unique element of G'.*

Let's go back to the example of the previous section. We have the group G_6^2 and want to define a mapping onto the group $G' = G_2^1$. The latter has two elements, E and P'. The generating relation of G_2^1 is $P'^2 = E$. The multiplication table is simple to derive and puts constraints on the mapping. A homomorphic mapping F from one group to the other would then require relations linking their elements. For example[2]:

$$F(E) = E,\ F(P) = E,\ F(P^2) = E,\ F(Q) = P',\ F(PQ) = P',\ F(P^2Q) = P' \tag{1.1}$$

define such a homomorphic mapping.

Definition 1.6. *The relations*

$$F(E) = E,\ F(P) = E,\ F(P^2) = E \tag{1.2}$$

are called the **kernel** *of the mapping, F. The kernel is the set of elements in G that map onto the identiy in G'.*

Finally, if a mapping is defined such that all elements of G are transformed and reproduce the complete set of elements of G, the mapping is called an **automorphism**. A good way of thinking about automorphisms is in terms of matrix representations and we'll get back to this in the next sections.

Definition 1.7. *A* **subgroup** *of G is a set of elements of G that together define a group with the same binary composition (multiplication) as in G.*

The group G_6^2 has 6 subgroups. A trivial subgroup is G_1^1 consisting of the element E. the full group, G_6^2 is also called a subgroup. These two groups are called **improper subgroups** and every group has at least two of them (the identity and the group itself). Then there are three groups that are representations of G_2^1 defined above. Each group has the identity element the other element is Q, PQ and P^2Q respectively. We'll take the last one as an example. The multiplication table reads (see table 1.1):

$\otimes$	E	P^2Q
E	E	P^2Q
P^2Q	P^2Q	E

which is indeed isomorphic to G_2^1 under the mapping $F(P^2Q) = P'$. The last subgroup of G_6^2 is the group consisting of the elements E, P and P^2, which is thus labelled G_3^1. The multiplication table is easily found and has an interesting property[3] If you take any two elements of G_3^1, you can verify that $G_aG_b = G_bG_a$. A group for which this holds is called an **Abelian group**. We also need **conjugate pairs**.

Definition 1.8. *two elements* G_a *and* G_b *are conjugate pairs if there is another element A in G such that* $G_a = AG_bA^{-1}$

Show that..

the multiplication table for G_2^1 has the form:

$\otimes$	E	P'
E	E	P'
P'	P'	E

[2] *try to explain why this is not an isomorphism.*

[3]

$\otimes$	E	P	P^2
E	E	P	P^2
P	P	P^2	E
P^2	P^2	E	P

[4] *Given that for any element A in G the last point of definition 1.1 holds, we have* $AEA^{-1} = AA^{-1} = E$

The identity matrix is conjugate to itself[4]. A group G can be subdivided in **conjugacy classes** or classes in short. Such a class consists of all mutually conjugate elements of the group. For example, the group G_6^2 has three classes:

$$C_1 = \{E\}\,,\ C_2 = \left\{P,\ P^2\right\}\,,\ C_3 = \left\{Q,\ PQ,\ P^2Q\right\} \tag{1.3}$$

To conclude this section, we define the outer direct product of G and the semi-direct product.

Definition 1.9. *The* **outer direct product** $G = H \otimes K$ *is a group such that,*

- *if* $h \in H$ *and* $k \in K$*, then* $hk = kh$ *where H and K are subgroups of G.*
- *all elements g of G are of the form* $g = hk$*.*
- *the only element that is in both H and K is the identity.*

Definition 1.10. *The* **semi-direct product** $G = H \wedge K$ *is a group such that,*

- *if* $h \in H$*, then* $hK = Kh$ *where H and K are subgroups of G.*
- *all elements g of G are of the form* $g = hk$*.*
- *the only element that is in both H and K is the identity.*

The important difference between the outer product and semi-direct product is that the latter is not commutative ($H \wedge K \neq K \wedge H$).

1.4 Group representations

The previous sections are quite abstract, so let's try to make it a bit more concrete. Molecules and crystals have symmetries and it is these symmetries that determine their properties. When we solve a problem in quantum mechanics, we are looking for a solution to the Schrödinger equation,

$$H\psi(\vec{r}) = E\psi(\vec{r}) \tag{1.4}$$

in 1st year quantum mechanics, you probably worked through the atomic hydrogen problem and found that the solutions could be written in the form:

$$\psi_{nlm}(\vec{r}) = R_{nl}(\varrho)Y_m^l(\vartheta, \phi) \tag{1.5}$$

where $(\varrho,\ \vartheta,\ \phi)$ are spherical coordinates. In more complicated problems (e.g. molecules and crystals), it is easier to think of the Schrödinger equation as a matrix equation,

$$\hat{H}\,|\psi\rangle = E\,|\psi\rangle \tag{1.6}$$

where $\hat{H}$ is a matrix and $|\psi\rangle$ is a vector in **Hilbert space**. The state vector $|\psi\rangle$ *i* is made up of the atomic orbitals. For example,

$$|\psi\rangle = \sum_{i=1}^{n} c_i \psi_{i,lm} \tag{1.7}$$

Starting from a single atom, we can construct new Hilbert spaces for molecules and crystals by taking the outer product or **tensor product** of the basis states of the atom. These new Hilbert spaces can become large very quickly. For example, if we take a system of N qubits, each described by a 2 dimensional Hilbert space (e.g. spin-up and spin-down), the dimension of Hilbert space grows as 2^N.

In the early years of the development of quantum mechanics, it was realised that this matrix representation offered deep connections to linear algebra. When we solve the Scrödinger equation, we are trying so solve an equation of the form:

$$\begin{bmatrix} H_1 & H_{12} & \cdots & H_{1N} \\ H_{21} & H_2 & \cdots & H_{2N} \\ \vdots & & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_N \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix} \tag{1.8}$$

[5] *The Hamiltonian is a differential operator and the problem to solve is non-linear and as such corresponds to a generalized eigenvalue problem. This is more complicated as described here, but does not change the logic behind the approach.*

where the H_i represent sub-blocks of Hilbert space corresponding to simple units (an atom, an electron shell etc.). and the H_{ij} represent couplings between the different blocks. Under certain conditions[5] this problem must be solvable by a basis transformation. In other words, there must exist a matrix *S*, such that,

$$\lambda = SHS^{-1} \tag{1.9}$$

with λ a diagonal matrix[6]. This relation is also known as a similarity transformation and the matrix S thus represents a transformation of the vector (Hilbert) space. This has important connections with the abstract structure of group theory developed above and requires **representation theory** to understand.

The idea behind representation theory is that one can define homomorphisms that map abstract elements of a group to a group of square matrices. This mapping by definition preserves multiplication and the matrices represent transformations of a vector space.

Definition 1.11. *The matrix representation of a group G is defined by the homomorphism that maps elements of G to square matrices* Γ*. The matrix multiplication preserves the group multiplication table. The representation is unitary when all i matrices of the group satisfy* $\Gamma_i \Gamma_i^\dagger = E$

In the following we will always deal with unitary representations[7]. An example of a matrix representation is that of the group G_6^2. The elements P and Q can be represented by:

$$P = \begin{bmatrix} -0.5 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -0.5 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \; Q = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{1.10}$$

and from this we can define the other elements of the group described above. Representations are not unique. For a given representation Γ of of a group G, it is possible to define a non-singular matrix S such that

$$\Gamma' = S\Gamma S^{-1} \tag{1.11}$$

where the Γ' is also a representation of G. The two representations are said to be **similar**. The similarity transformation is important and allows us to define **reducible representations** and **irreducible representations**.

Definition 1.12. *A matrix representation,* Γ*, is said to be reducible if a similarity transformation exists such that*[8]

$$S\Gamma S^{-1} = \begin{bmatrix} H_1 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & H_N \end{bmatrix} \tag{1.12}$$

i.e. it can be brought in block diagonal form.

On the other hand, the representation is said to be irreducible if this transformation does not exist. Note that the matrices $H_{1...N}$ appearing in the reducible representation are themselves *irreducible* representations of elements of the group. The importance of this is that Γ' defined above is a complete representation of the group. Every reducible representation can thus be transformed to a block diagonal form, where the blocks are irreducible representations. This is often expressed in a **Clebsch-Gordan sum**:

$$\Gamma' = \Gamma^1 \bigoplus \Gamma^2 \bigoplus ... \Gamma^N \tag{1.13}$$

This is an important statement: it tells us that the problem of finding the representations of any group reduces to finding the non-equivalent unitary, irreducible representations of the group[9].

An essential ingredients of representation theory is the orthogonality theorem, based on the two lemma's of Schur[10].

Definition 1.13. *If we consider a group G with elements T, then for two unitary, irreducible representations* Γ^p *and* Γ^q *of G we have,*

$$\sum_{g \in G} \Gamma^p_{\mu,\omega} \left[\Gamma^q_{\mu',\omega'} \right]^\star = \frac{h}{l_p} \delta_{p,q} \delta_{\mu,\mu'} \delta_{\omega,\omega'} \tag{1.14}$$

where h is the order of the group G and l_p the dimension of the representation matrix. The importance of this theorem is that it is a statement of 'preservation of length'. Consequently, it tells us something about the properties of the matrices representing a group. To arrive at this insight, we need to introduce the **character** of reducible representations.

Definition 1.14. *The character of a matrix* Γ *is the defined as the trace*[11] *of the matrix:*

$$\chi = Tr(\Gamma) = \sum_{i=1}^{l} \Gamma_{i,i} \tag{1.15}$$

[6] *Remember definition 1.8*

[7] *This is a consequence of a basic axiom in quantum mechanics that states that the time evolution of a system is unitary.*

[8] *the* $H_{1...N}$ *are matrices that are not diagonal.*

[9] *The term unitary, irreducible representations is often abbreviated to irrep*

[10] *Proofs of the theorem are easily found online...*

[11] *the trace of a matrix is the sum of its diagonal elements*

One can proof that the elements of the group G belonging to the same class (see below definition 1.8) all have the same character. By definition, the elements in a class are conjugate pairs for which $G_a = AG_bA^{-1}$. Since A belongs to G, there exists a matrix representation where,

$$\Gamma_a = \Gamma_A \Gamma_b \Gamma_A^{-1} \tag{1.16}$$

from this it follows that

$$Tr(\Gamma_a) = Tr(\Gamma_A \Gamma_b \Gamma_A^{-1}) = Tr(\Gamma_b) \tag{1.17}$$

where in the last step we have used that Γ_A and Γ_b commute (this is due to one of two lemma's by Schur). We can now combine the orthogonality theorem (def. 1.13) with the characters of the irreducible representations: For the characters χ^p and χ^q of two irreducible representations, the following relation holds:

$$\sum_{g \in G} \chi^p(g) [\chi^q(g)]^\star = h\delta_{p,q} \tag{1.18}$$

where h is the order (number of elements) of the group. This orthogonality relation of the characters has a number of important consequences. It allows us to determine whether a representation is reducible or not. After all, only irreducible representations obey the orthogonality relation.

Groups can be completely specified by the characters. One can show that the characters of a reducible representation can be given by a linear combination of the characters of irreducible representations:

$$\chi(g_i) = \sum_j a_j \chi^p(g_j) \tag{1.19}$$

It must therefore be possible to write any reducible matrix representation that transforms according to the group relations in the following form:

$$\Gamma' = a_1\Gamma^1 \bigoplus a_2\Gamma^2 \bigoplus ...a_N\Gamma^N \tag{1.20}$$

or,

$$\begin{bmatrix} a_1\Gamma^1 & & \mathcal{O} \\ \vdots & \ddots & \vdots \\ \mathcal{O} & \cdots & a_N\Gamma^N \end{bmatrix} \tag{1.21}$$

where the matrices $\Gamma^1 ... \Gamma^N$ are irreducible matrices. From the orthogonality relations one can show that,

$$a_j = \frac{1}{h} \sum_k N_k \chi^{\Gamma^k}(g_k) \chi^{\Gamma'}(g_k) \tag{1.22}$$

In words: the coefficients appearing in Eq. 1.20 can be calculated if we know the characters of the reducible and irreducible representation. N_k counts the number of times an element appears in the group. Any given group consists of a number of classes and this is also the number of inequivalent irreducible representations. The elements within a class all have the same character and so, we can define a group by the characters of the different classes. The collection of characters is often represented in a so-called **character table**. The character table is represented as a table with the classes on the horizontal direction and the irreducible representations along the vertical direction. The entries of the character table can be determined using the above definition of Γ'. We will not work out how to do this in detail, but instead we will focus on how to apply the character tables in quantum mechanics problems.

Show that..

the determinant of the matrix for which $r' = Rr$ holds, equals 1.

1.5 Point groups

A Point group is the set of symmetry operations that act on a point in space O and leave distances and angles invariant. In physics and chemistry, we will therefore almost always be concerned with 3 dimensional point groups. The point group with all possible rotations is called the proper rotations group, indicated by $SO(3)$, and it can be represented by all orthogonal matrices with determinant 1. When combined with the inversion operator, the group is known as $O(3)$: the 3 dimensional rotation group[12]. It consists of all orthogonal matrices (with determinant plus and minus one). The matrices with determinant -1 are known as improper rotations and consist of a rotation and an inversion. In addition to (improper) rotations O(3) also includes reflections.

In solids and molecules only subsets of $O(3)$ are used, in combination with the identity and inversion operator. The subset for a particular molecule reflects the

[12] *For d dimensions, the group O(d) is also known as the orthogonal group*

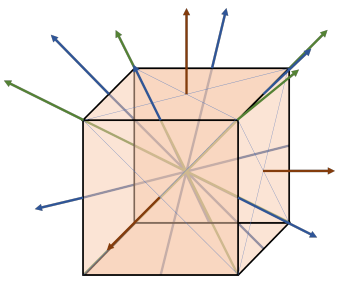

Figure 1.2: Symmetry operations of a cube. Orange indicate the three 4-fold axes, green indicate the four 3-fold axes and blue the 6 two-fold axes.

symmetry of the molecule. The triangle in section 1.2 could represent an ammonia molecule for which the group consists of only 2 rotations and three reflections. When discussing molecules the following groups can be used to cover all possible symmetries in 3 space dimensions:

1 : C_n, C_{nh}, C_{nv}, S_{2n}, D_n, D_{nd}, D_{nh}

2 : T, T_d, T_h, O, O_h, I, I_h

The groups listed under 1 are known as axial groups, while the groups listed under 2 are known as polyhedral groups. The former consists of proper rotation groups (C) improper rotation groups (S). The sub-labels h and v indicate that the group includes a reflection perpendicular to the axis of rotation (C_{nh}; horizontal plane assuming rotation around z) or n reflections that contain the rotation axis (C_{nv}; vertical plane assuming rotation around z). The improper rotation group S_{2n} contains an even-fold rotation reflection axis (odd-fold rotation-reflection is the same as C_{nh}). The D groups are known as dihedral groups and consist of the rotation groups and n two-fold axes[13] perpendicular to the rotation axis. The sub-label d indicates it has a diagonal element. The groups listed under 2 are the tetrahedral group (T), octahedral group (O; not to be confused with O(d)) and the icosahedral group (I). They are composed of the set of elements that leave the tetrahedron, cube and dodecahedron invariant. As an example, O has three 4-fold axes, four 3-fold axes and 6 diagonal 2-fold axis (see Fig. 1.2).

In crystals it is only possible to use subsets of these groups. For example, the group C_n in crystals only comes with the values $n = 2, 3, 4, 6$. Other values of n simply are not compatible with the formation of an infinite crystal[14]. This leads to the definition of exactly 32 **crystallographic point groups**. As discussed in the previous section, these point groups can be completely specified by their character tables. We will not list them here, as they are tabulated and can be easily found (for example, on wikipedia).

[13] *A two-fold axis is a 180 degree rotation about a line*

[14] *If you are interested in this, have a look at the work of Johann F.C. Hessel.*

1.6 Space groups

In addition to the 32 point groups, crystals are characterized by an additional group: the translation group. The translation group is the set of lattice translations $\mathbf{R} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$. The translation group is both unitary and Abelian. The unit vectors can also be thought of as operators. Applying the operator $\hat{R}$ shifts the vector $\mathbf{r}$ to $\mathbf{r} + \mathbf{R}$. It is easy to convince yourself that operators $\hat{R}_1$ and $\hat{R}_2$ commute.

In three dimensions we can define three distinct operators $\hat{\tau}_{i=x,y,z}$ for the independent directions in space, each forming an infinite cyclic subgroup[15]. Elements in the group are often indicated as:

$$\{\mathbf{R}_\alpha|\tau\} \tag{1.23}$$

where $\mathbf{R}_\alpha$ is some vector belonging to the translation group.The irreducible representations of these Abelian groups are 1 dimensional. Since a 1-dimensional matrix consists of a single number, the character of the representation is at the same time also a representation! The generator G of the cyclic group has to satisfy the relation $G^L = 1$, with L the order of the group. Given this relation, the character can be written as:

$$\gamma_{k_1}(\hat{\tau}_x) = e^{ik_1 n_1 x} \tag{1.24}$$

where the numbers k_1 have to satisfy the condition $k_1 = 2\pi m_1/L$ with $m_1 = 0, 1, 2....$ For a crystal, L is the length of the crystal assuming periodic boundary conditions. Note that we have as many characters as we have k-values and each character is an irreducible representation of the translation group.

The translation group can be used to quickly derive Bloch's theorem. Assume that the potential of a crystal is periodic, $V(\mathbf{r}+\mathbf{R}) = V(\mathbf{r})$ or, in our new language, $\{\mathbf{R}_\alpha|\tau\}\, V(r) = V(r)$. Since the kinetic energy is also invariant under translations, the wavefunctions must satisfy the condition:

$$\{\mathbf{R}_\alpha|\tau\}\, \psi(\mathbf{r}) = \psi(\mathbf{r}+\mathbf{R}) = e^{ik_1 n_1 x}\psi(\mathbf{r}) \tag{1.25}$$

where we have used in the first step that the action of a translation is to shift the coordinates of the wave functions, while in the second step we have used that the irreducible representations of the translation group are given by their characters.

When we make composite groups of the crystallographic point groups and translation groups, we end up with so-called **space groups**. The combination of point groups and (fractional) translations give rise to two additional symmetry operations that can leave a crystal invariant: the screw axis and the glide plane. The screw axis is a rotation followed by a fractional translation, while the glide plane is a reflection followed by a fractional translation. By combining the 32 point groups with translations, screw axes and glide planes, in total 230 distinct space groups can be generated. If a group contains a glide plane or screw axis, it is said to be **non-symmorphic**, while it is called **symmorphic** without these elements.

Show that..

the two operations $\hat{R}_1 = \hat{x}$ and $\hat{R}_2 = \hat{y}$ commute

[15] *Cyclic groups are generated by a single element.*

1.7 Basis functions of irreducible representations.

The final ingredient of group theory that we will discuss are the **basis functions** corresponding to irreducible representations. Basis functions can be used to generate the matrices representing the symmetry elements because they form a complete, orthonormal set that satisfies the following orthogonality condition:

$$\left\langle \Gamma^n i | \Gamma^{n'} j \right\rangle = \delta_{n,n'}\delta_{i,j'} \tag{1.26}$$

Here Γ^n is a representation of a symmetry element of a group and j labels the basis function corresponding to the representation (also called partner function). The number of basis functions equals the dimension of the representation. The basis functions connect abstract symmetry operators with their matrix representations according to:

$$\hat{P}_g \left| \Gamma^n i \right\rangle = \sum_j M_{i,j}^{\Gamma^n}(g) \left| \Gamma^{n'} j \right\rangle \tag{1.27}$$

where $M_{i,j}^{\Gamma^n}(g)$ is the matrix corresponding to element g of the representation Γ^n of the group G[16]. The combination of Eq. 1.26 and Eq. 1.27 leads to,

$$\left\langle \Gamma^{n'} j | \hat{P}_g | \Gamma^n i \right\rangle = \sum_j M_{i,j}^{\Gamma^n}(g) \left\langle \Gamma^{n'} j | \Gamma^n \right\rangle = M_{i,j}^{\Gamma^n}(g)\delta_{n,n'} \tag{1.28}$$

showing that the matrix elements are diagonal in each irreducible representation. This relation can be used to generate the matrix elements of the matrix representations.

The basis functions defined above are completely abstract, so it probably helps to provide you with a concrete example. Let's return to our example of the triangle in Fig. 1.1. As we discussed in section 1.3, this triangle has three classes and therefore there are three irreducible representations. The basis functions in this case are conveniently expressed in terms of function $f(x, y, z)$. Note that we need the orthogonality of the basis vectors, so these are functions of the basis vectors $\hat{x}$, $\hat{y}$ and $\hat{z}$ of unit length. The first step now is to find the action of the symmetry operator on the $\hat{x}$, $\hat{y}$ and $\hat{z}$ vectors. The action of our 6 elements on the $\hat{z}$ vector are easiest. The action of E, P and P^2 (corresponding to no action and rotation about the z-axis) leave the z-axis invariant. The action of Q (reflection), PQ and P^2Q (reflection followed by rotations) also leave the z-axis invariant.

How about the $\hat{x}$ and $\hat{y}$ vectors? Of course, they are also invariant under the identity operator. It is not difficult to show (using simple geometry) that the vector $\hat{x}$ transforms to $0.5(-\hat{x} + \sqrt{3}\hat{y})$ under the action of the operator P. This gives the following relation:

$$\hat{P}_P \left| x \right\rangle = \frac{1}{2}(- \left| x \right\rangle + \sqrt{3} \left| y \right\rangle) \tag{1.29}$$

Similar transformations can be obtained for the action of the other elements on $\hat{x}$ and $\hat{y}$. These relations are summarized in the following table:

	$\hat{x}$	$\hat{y}$	$\hat{z}$
E	$\hat{x}$	$\hat{y}$	$\hat{z}$
P	$0.5(-\hat{x} + \sqrt{3}\hat{y})$	$0.5(-\hat{x} - \sqrt{3}\hat{y})$	$\hat{z}$
P^2	$0.5(-\hat{x} - \sqrt{3}\hat{y})$	$0.5(\sqrt{3}\hat{x} + \hat{y})$	$\hat{z}$
Q	$-\hat{x}$	$\hat{y}$	$\hat{z}$
PQ	$0.5(\sqrt{3}\hat{x} - \hat{y})$	$0.5(-\hat{x} - \sqrt{3}\hat{y})$	$\hat{z}$
P^2Q	$0.5(\sqrt{3}\hat{x} + \hat{y})$	$0.5(\sqrt{3}\hat{x} - \hat{y})$	$\hat{z}$

From this table one can generate the matrix representation of the group. For example if we want to generate a matrix describing the two-dimensional irreducible representation of a reflection followed by a rotation (i.e. PQ) in the basis $|x\rangle$ and $|y\rangle$, we find,

$$\left[|x\rangle \ |y\rangle \right] \hat{P}_P \hat{P}_Q \begin{bmatrix} |x\rangle \\ |y\rangle \end{bmatrix} = \begin{bmatrix} \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ -\frac{1}{2} & -\frac{\sqrt{3}}{2} \end{bmatrix} \tag{1.30}$$

The table above can be used to generate the matrices for other operators as well and once we have the matrices, we can generate the character table for our class. As with the representations, the basis functions are not unique. We could have chosen an arbitrary function of x,, y and z as basis function, but that would likely have generated a

[16] *Sorry. You may not to read this sentence three times...*

reducible representation. Basis functions that generate irreducible representations are often listed together with the character table. We are now in the position to completely specify our group (which is in fact better known as the group C_{3v}):

C_{3v}	E	$2C_3(z)$	$3\sigma_v$	linear	quadratic	cubic
A^1	1	1	1	z	$x^2+y^2,\ z^2$	z^3 $x(x^2-3y^2)$ $z(x^2+y^2)$
A^2	1	1	–1	R_z	-	$y(3x^2-y^2)$
E	2	-1	0	$(x,y),(R_x, R_y)$	$(x^2+y^2,xy),(xz,yz)$	(xz^2,yz^2) $[xyz,\ z(x^2+y^2)]$ $[x(x^2+y^2),\ y(x^2+y^2)]$

Table 1.2: character table for the group C3v. The numbers appearing in front of the labels C_i and σ_v indicate the number of elements in the class. The order of the group is 6 and it has three irreducible representations (indicated here by their Mulliken symbol).

where also quadratic and cubic basis functions are given. The labels A indicate a singly degenerate representation (in other words, a one-dimensional representation) while E indicates a doubly degenerate representation. We will also encounter representations that are labeled T, which means it is a triply degenerate representation. These symbols are known as Mulliken symbols. In the next section we'll consider an important set of basis functions: the wavefunctions of a molecule or solid.

As mentioned, basis functions are not unique. Once we know how simple basis functions transform under the operations of the group, we can define arbitrary basis functions. This is achieved using projection operators. The orthogonality theorem for characters combined with the matrix representation given above can be shown to lead to the following definition:

Definition 1.15. *If one knows the characters of the irreducible representations of a group, the projection operator:*

$$\hat{P}^{\Gamma_n} = \frac{l_n}{h}\sum_R \chi^{\Gamma n}(R)^* \hat{P}_R \tag{1.31}$$

where l_n is the dimension of Γ_n, h is the order of the group. By acting with this operator on an arbitrary function, one can obtain the basis functions of the irreducible representations.

As an example, we will consider the Ammonia molecule in the next section and in Excercise 2 the basis states of an hypothetical AB_4 molecule.

1.8 The molecular orbitals of Ammonia

We now put our new-gained insight in group theory to use by analyzing the molecular orbital structure of an ammonia (NH_3) molecule. By inspection of Fig. 1.3 we see that the ammonia molecule has a three-fold rotation axis around the vertical axis and three reflection planes. Since the nitrogen is above the plane of the three hydrogen atoms, there is no horizontal reflection plane, nor a horizontal rotation axis. This leads us to the point group C_{3v}, the character table of which is shown above in table 1.2. The character table has three irreducible representations (A_1, A_2 and E) and therefore we can expect the molecular orbitals of NH_3 to fall in one of these three types. The easiest is to start with the orbitals on the nitrogen atom. They are at the center of the point group and we can easily estimate how the atomic orbitals transform under the action of the point group[17]. The 1s, 2s orbitals are radial and transform according to $x^2+y^2+z^2$. Looking at the character table 1.2, we see that they belong to the A_1 representation. Similarly, the p_x, p_y and p_z orbitals transform according to x, y and z respectively. From the character table we see that p_z transforms according to the A_1 representation, while p_x and p_y transform according to the 2 dimensional E representation (the character of the identity operation is 2 according according to the table. The trace of a 2x2 identity matrix is 2; ergo, the dimension of the matrix representation is 2). This makes sense: rotating the p_x orbital by 120 degrees about z does not leave it invariant. It is easy to show that the orbital transforms from p_x in our original frame of reference to a superposition of $p_{x'}$ and $p_{y'}$ orbitals in the rotated frame of reference according to $p_{x'} \to -0.5p_x + \sqrt{3}/2p_y$. Such a transformation is indeed described by the 2x2 rotation matrix of Eq. 1.30 and corresponds to a C_3 rotation.
Next, we investigate how the hydrogen 1s orbitals transform under the C_{3v} group. This is a bit more subtle, because the orbitals change position in space under the action of the group elements. For example, under an anti-clockwise rotation the orbital labelled "1", appears in position 2. It is in this simple case not difficult to write down a matrix representation for the group. Starting from the state vector constructed out of the

[17] *Since the nitrogen atom coincides with the rotations axis, they remain in the same spatial position in space under the operation of the elements.*

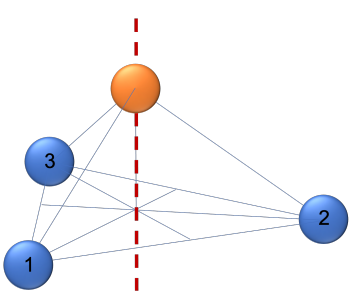

Figure 1.3: The NH_3 molecule. It features a 3-fold rotation axis (dashed red line) and vertical reflection planes indicated by the three lines bisection the base lines of the triangle.

3 1*s* orbitals, one can write down a matrix relation describing a specific action. For example, the anti-clockwise rotation can be found from the matrix equation:

$$\begin{bmatrix} a & b & c \\ d & e & f \\ g & h & j \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{bmatrix} = \begin{bmatrix} \psi_2 \\ \psi_3 \\ \psi_1 \end{bmatrix} \tag{1.32}$$

from which it follows that,

$$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \tag{1.33}$$

The matrix in Eq. 1.33 is a representation of C_3. It is also easy to see that it is part of a *reducible* representation: the character table for the group C_{3v} does not contain a three dimensional irreducible representation. One can write down the 6 matrices corresponding to all elements of C_{3v}:

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, C_3^+ = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}, C_3^- = \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \tag{1.34}$$

$$\sigma_v^1 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}, \sigma_v^2 = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix}, \sigma_v^2 = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{1.35}$$

From this overview we can write down the characters of the representation:

C_{3v}	E	$2C_3(z)$	$3\sigma_v$
$\Gamma=A_1+E$	3	0	1
A^1	1	1	1
E	2	-1	0

The top row describes the characters for the reducible representation of the 1*s* orbitals. We could have similarly arrive at this result by counting the number of atomic sites that remain invariant under a symmetry operation. This is the case, because this is the only way in which you can get an entry on the diagonal of the matrix representation. The identity operation leaves all sites invariant and so you find the entry 3. A rotation transforms any atom into another atom (nothing is invariant), so it has character 0. A reflection interchanges two sites, but leaves one invariant. It therefore has character 1. From Eq. 1.22, we know that it should be possible to reconstruct this from the characters of the irreducible representation of C_{3v}. Since the character $\chi(E)=3$, we know that one of the components is the E representation. The only other possibility that results in the characters of Γ is to add A_1 and E. These considerations imply that one should be able to construct basis functions (molecular orbitals, MO) from the hydrogen 1*s* orbitals that transform according to these irreducible representations. There will be one MO transforming according to A_1 and 2 (degenerate) MO's transforming according to E. To construct these basis functions, we make use of the projection operator defined in Eq. 1.31. This works as follows. For each of the irreducible representations (here A_1 and E), we consider the action of $\hat{P}^{\Gamma^n}$ on an original state. We start with the A_1 representation. The order of the group $h=6$ and $l_{A_1}=1$. Remember: by acting with this operator on an arbitrary function, we project out the basis functions of the irreducible representation. Therefore, if we take the 1*s* orbital of atom 1 as arbitrary function, we find:

$$\hat{P}^{A_1}\psi_1 = \frac{1}{6}\left[1\psi_1^E + 1\psi_2^{C_3^+} + 1\psi_3^{C_3^-} + 1\psi_1^{\sigma_v^1} + 1\psi_3^{\sigma_v^2} + 1\psi_2^{\sigma_v^3}\right] \tag{1.36}$$

where the superscripts are only there to help you understand where the state is coming from. The numbers in front of the basis-functions are the characters that appear in the projection operator. The basis function that transforms according to A_1 is thus:

$$\psi_{A_1} = \frac{1}{3}\left[\psi_1 + \psi_2 + \psi_3\right] \tag{1.37}$$

We can do the same with the E representation. We find:

$$\hat{P}^E\psi_1 = \frac{2}{6}\left[2\psi_1^E - 1\psi_2^{C_3^+} - 1\psi_3^{C_3^-} + 0\psi_1^{\sigma_v^1} + 0\psi_3^{\sigma_v^2} + 0\psi_2^{\sigma_v^3}\right] \tag{1.38}$$

and therefore:

$$\psi_E^1 = \frac{1}{3}\left[2\psi_1 - \psi_2 - \psi_3\right] \tag{1.39}$$

However, this is only one of the two basis functions of E (E is a 2 dimensional representation). There are different methods to determine the last basis state. For example, we could make use of orthogonality (find the vector that is orthogonal to both ψ_{A_1} and ψ_E^1). A more general approach is to keep using the projection operator. For example,

$$\hat{P}^E\psi_2 = \frac{2}{6}\left[2\psi_2^E - 1\psi_3^{C_3^+} - 1\psi_1^{C_3^-}\right] \tag{1.40}$$

and

$$\hat{P}^E\psi_3 = \frac{2}{6}\left[2\psi_3^E - 1\psi_1^{C_3^+} - 1\psi_2^{C_3^-}\right] \tag{1.41}$$

The last basis function can be found by taking the difference of two states:

$$\psi_E^2 = \hat{P}^E\psi_2 - \hat{P}^E\psi_3 = [\psi_2 - \psi_3] \tag{1.42}$$

1.9 The group of the Hamiltonian

We are now ready to eat the main dish: the connection between group theory and quantum mechanics. As mentioned earlier, the goal of solving a quantum mechanical problem is to find the energies (eigenvalues) and wavefunctions (eigenfunctions) for a given Hamiltonian with a number of symmetries. An alternative statement is that we are looking for the eigenfunctions of a Hamiltonian that is invariant under a group of symmetries. The meaning of this statement is that the solutions of the Schrödinger equation do not change under a symmetry operation. Symbolically we mean that if we transform the system under the action of a projector P,

$$P : |\psi\rangle \rightarrow |\psi'\rangle \tag{1.43}$$

the states $|\psi'\rangle$ and $|\psi'\rangle$ really are the same state. Instead of acting on the state, we can also let P act on the operators in the Hamiltonian. This is where matrix representations come in handy. Let's take,

$$|\psi'\rangle = \hat{P}\,|\psi\rangle \tag{1.44}$$

then,

$$\langle\psi'|\,\hat{H}\,|\psi'\rangle = \langle\psi|\,\hat{P}^\dagger\hat{H}\hat{P}\,|\psi\rangle \tag{1.45}$$

Under the assumption that the operator $\hat{P}$ is unitary[18], we find that,

$$\hat{H} = \hat{P}^\dagger H\hat{P} \tag{1.46}$$

which is the statement that H is invariant under the symmetry operation. It follows that $\hat{H}$ and $\hat{P}$ commute:

$$\left[H, \hat{P}\right] = 0 \tag{1.47}$$

The group of symmetry operations, $\hat{P}_R$, for which:

$$\left[H, \hat{P}_R\right] = 0 \tag{1.48}$$

defines the group of the Hamiltonian. One can show that,

- The elements $\hat{P}_R$ form a group.
- If the wavefunction, ψ_n is an eigenfunction of the Hamiltonian (with eigenvalue E_n), then (because of Eq. 1.48) $\hat{P}_R\psi_n$ is an eigenfunction with the same eigenvalue.
- If an eigenvalue is d-fold degenerate, the dimension of irreducible representation of the operator $\hat{P}_R$ is d.
- If one has a complete set of eigenfunctions, we can use Eq. 1.27 to make a matrix representation of the element R.

The essence of the combination of group theory and quantum mechanics is that we can apply the knowledge (documented character tables for all point and space groups) to determine the eigenfunctions and their degeneracies. An example was discussed in section 1.6: the translation group. Because this is a subgroup of the Hamiltonian, the k distinct irreducible representations of the translation group, can be used to label the corresponding basis functions (Bloch waves) and to each basis function corresponds a unique eigenvalue (E_k). Note that group theory does not tell us anything about the details of the eigenvalues. These need to be obtained from further calculation. Similarly, the projection operator Eq. 1.31 allows us to determine linear combinations of atomic orbitals that are invariant (eigenfunctions)under symmetry operations of the point group. By definition, we now know that they are also eigenfunctions of the Hamiltonian.

[18] *This means that the following condition is met: $\hat{P}^\dagger\hat{P} = \hat{P}\hat{P}^\dagger = I$. It follows from this that $\hat{P}^\dagger = \hat{P}^{-1}$*

Exercises I

Elements of group theory

In the following set of exercises we will discuss some elementary exercises.

1 The multiplication table of G_6^2

In this exercise we will check some of the statements presented in this chapter 1.2.

$\mathcal{A}$ In the text it is claimed that there is a defining relation $QP = P^2Q$. Show that this equality indeed holds and explain in words what it means.

$\mathcal{B}$ Check that the matrix representation of G_6^2 (Eq. 1.10) is unitary[19].

$\mathcal{C}$ Check that the matrix representation of G_6^2 (Eq. 1.10) indeed satisfies the multiplication table. It suffices to choose a few interesting entries.

[19] *Remember that this means $U^\dagger U = E$ and that † involves complex conjugation and transposition*

2 $PtCl_4$ orbital symmetry (after Atkins 2006 [1])

In figure 1.4 the Cl ligand orbitals are schematically indicated. They form a square planar array and belong to point group D4h. Find the character table online and identify the symmetry type of the combination $\psi_A - \psi_B + \psi_C - \psi_D$.

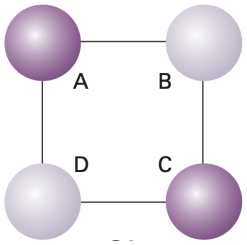

Figure 1.4: Cl ligands of a $PtCl_4$ molecule

3 AB_4 molecules

Consider a molecule of the form given in Fig. 1.5.

$\mathcal{A}$ List all possible symmetry operations for this molecule that transform it back onto itself.

$\mathcal{B}$ Make a list of subgroups that together form the group of AB4.

$\mathcal{C}$ Make a list of the classes.

$\mathcal{D}$ Find the 2D irreducible matrix representations for the elements of this group.

$\mathcal{E}$ Verify that your results fulfill condition Eq. 1.18.

$\mathcal{F}$ Look up the group C4v online and verify that this is indeed the point group describing this molecule.

$\mathcal{G}$ For the H atoms we consider only the 1s orbitals. Using the character table of C4v, find the 4 basis functions that describe the molecular orbitals of the H atoms.

$\mathcal{H}$ Verify that your basis functions are orthogonal, given that:

$$\int \psi_i^\star \psi_j = 1 \tag{E1.1}$$

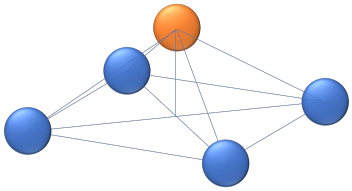

Figure 1.5: An AB4 molecule

SOME APPLICATIONS OF GROUPS IN PHYSICS AND CHEMISTRY

We may as well cut out group theory. That is a subject that will never be of any use in physics. - James Jean

KEYPOINTS:

- Group theory predicts lifting of degeneracy in crystal fields-
  The finiteness of overlap integrals can be determined from GTSelection rules for optical properties follow the symmetry groups.

2.1 Introduction

In this chapter we will touch upon a number of applications of group theory. We start by exploring the lifting of degeneracies due to the crystal field effect. This is followed by a discussion of overlap integrals and their finiteness. The same arguments are then applied to study the selection rules underlying optical processes.

2.2 The full rotation group O(3)

To understand the hierarchy of eigenvalues in solids or molecules and the relation with symmetry, we return to the most symmetric case: the hydrogen atom. In this simplest example, we have a single proton as nucleus and the long range Coulomb potential with which the electron interacts. Since the Coulomb potential is spherically symmetric (the potential only depends on the coordinate $\vec{r}$, which is the distance of electron to the nucleus), we can separate the wavefunction in radial and angular components as,

$$\psi_{n,l,m} = R_{n,l} Y_l^m(\vartheta, \phi). \tag{2.1}$$

In introductory quantum mechanics courses, you learned that the energy levels are given by

$$E_n = -\frac{\hbar^2}{2ma_0^2}\frac{1}{n^2} \tag{2.2}$$

Since this only depends on the quantum number n, the orbital angular momentum states with different m for a particular value of l are degenerate in energy. We will see in this first application that lowering of symmetry results in the lifting of those degeneracies.

We start with a first look at the radial eigenfunctions:

$$Y_l^m(\vartheta, \phi) = (-1)^m \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}} P_l^m(\cos[\vartheta]) e^{im\phi} \tag{2.3}$$

[20] *I will ignore here all details associated with the two components of O(3). The interested reader can find all info on wikipedia.*

These functions are in fact basis functions for the **full rotation group**, O(3)[20]. This is important, because it tells us that it must be possible to obtain the characters of $O(3)$ by making use of representation theory. Without further proof, we note that it must be possible to define a rotation operator, $\hat{P}_\alpha$ that rotates an object by an angle α in terms of a matrix $D(\alpha)$ according to:

$$\hat{P}_\alpha Y_l^m(\vartheta', \phi') = \sum_{m'} D^l_{m,m'} Y^l_{m'}(\vartheta, \phi) \tag{2.4}$$

For a specific rotation where we take the z-axis as rotation axis, the action of the operator on a basisfunction for a particular quantum number l is,

$$\hat{P}_\alpha Y_l^m(\vartheta', \phi') = Y_l^m(\vartheta, \phi - \alpha) = e^{im\alpha} Y_l^m(\vartheta, \phi) \tag{2.5}$$

where in the last step we made use of Eq. 2.3. This states that indeed the $Y_l^m(\vartheta, \phi - \alpha)$ are eigenfunctions of the operator $\hat{P}$. Combining this with Eq. 2.4, we find that the matrix $D(\alpha)$ is given by:

$$D^l(\alpha) = \begin{bmatrix} e^{-il\alpha} & \dots & 0 \\ \vdots & e^{-i(l-1)\alpha} & \\ & & \ddots \\ 0 & \dots & e^{il\alpha} \end{bmatrix} \tag{2.6}$$

The trace of this matrix is the character for rotations of the group O(3) and is given by:

$$\chi^l(\alpha) = \sum_{m=-l}^{l} e^{-im\alpha} = \frac{\sin\left(l+1/2\right)\alpha}{\sin\frac{\alpha}{2}} \tag{2.7}$$

Similar expressions can be found for the other characters of O(3): and with these

Table 2.3: character table for the group O(3). I stands for inversion and S for rotations followed by an inversion.

$O(3)$	E	$C(\alpha)$	I	$S(\alpha)$	σ
Γ^l	2l+1	$\frac{\sin\left(l+1/2\right)\alpha}{\sin\frac{\alpha}{2}}$	$(-1)^l(2l+1)$	$(-1)^l\frac{\sin\left(l+1/2\right)(\alpha+\pi)}{\sin\frac{(\alpha+\pi)}{2}}$	$(-1)^l$

characters, we can work out how the degeneracies are lifted if we lower the symmetry.

2.3 Crystal field splitting

We are now in the position to see what happens when an atom is placed in a periodic arrangement with other atoms. What happens in words is that the symmetry of the full rotation group is lowered. In a crystal, the potential is no longer just radially dependent. Instead, the crystal is only invariant under sub-group of these rotations. Group theory is the ideal tool to predict what happens to the energy levels of the original atom. The recipe is as follows:

- First determine the point group corresponding to the crystal.
- Compute the O(3) characters of orbitals with a particular value of the quantum number l.
- Determine to which irreducible representations these orbitals belong in the lower symmetry group.

The first step is non-trivial, but we will assume the structure is known. To compute the characters in O(3) is also easy. Finally, we need to determine the irreps for the orbitals with particular orbital angular momentum l. This can be done by making use of Eq. 1.22 of the previous chapter. To illustrate the procedure, we will work through a concrete example: cubic crystal field splitting in ABO_3 oxides.

The crystal structure of ABO_3 is shown in figure 2.6 and consists of a central atom surrounded by 8 oxygen atoms. It is not difficult to see that this cube has the same set of symmetry operations as the cube of figure 1.2 of the previous chapter. The actual group of this structure is O_h, but for simplicity we will first consider that the group of symmetry operations describing this cubic unit cell is O[21]. The character table for the group O is as follows:

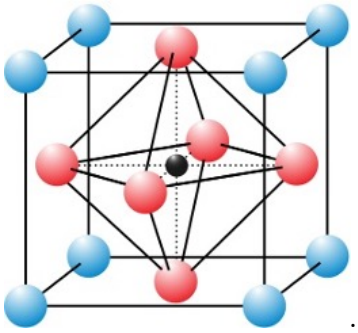

Figure 2.6: Unit cell for ABO_3. The cell is cubic, with the A atom (black) in the centre of the cell. The central atom is surrounded by an octahedron of oxygen atoms(red). The B atoms are located at the corners of the unit cell (blue).

[21] *The difference between O and O_h is the addition of a center of inversion in the latter. We could start with O_h, but the exercise becomes a lot more tedious. Instead, we ignore inversion for the moment and will work out the correct irreps at the end.*

O	E	$8C_3$	$6C_2'$	$6C_4$	$3C_2$
A_1	1	1	1	1	1
A_2	1	1	–1	-1	1
E	2	-1	0	0	2
T_1	3	0	-1	1	-1
T_2	3	0	1	-1	-1
Γ^2	5	-1	1	-1	1

This group has 5 classes and each class consists of a sub-group of a particular rotation. The first step is to write down the characters for the representations of these elements in the full rotation group for particular values of l. In our example, we will consider the effect of the crystal field potential on a central transition metal atom (for example Ti or Cu). In this case, the outer occupied shell of the free atom is the 3d shell. We therefore consider the case $l = 2$. The characters for this representation are indicated in the table by the Γ^2 representation (to compute these numbers we used $l = 2$ and $\alpha = 2\pi/3, \pi, \pi/4$ and π for the individual columns).

How to read this result? Since the character of the identity operator is 5, we know this is a 5 dimensional representation. This makes sense: the 3d-orbitals in a free atom are all degenerate and the quantum number $l = 2$ implies that there are $m = -2, -1, 0, 1, 2$, i.e. five orbitals. We also know the characters for the specific elements in $O(3)$ that make up the group O. However, if we look back to the character table for O, we see that we have a problem. There is no five dimensional irreducible representation in O! This tells us without further calculation that the degeneracy of the 3d-orbitals must be lifted. The trick is that we have to find the direct sum of irreducible representations of O that give us the correct representation in O. In other words, we need to determine,

$$\Gamma^2 = a_1\Gamma^{A_1} \bigoplus a_2\Gamma^{A_1} \bigoplus ...a_N\Gamma^{T_2} \tag{2.8}$$

such that we obtain the characters of the Γ^2 representation. This can be done with trial and error b y adding the characters of different representations, but there is a more systematic approach that makes use of the orthogonality relations through Eq. 1.22:

$$a_j = \frac{1}{h}\sum_k N_k \chi^{\Gamma^k}(g_k)\chi^{\Gamma'}(g_k) \tag{2.9}$$

This states that the coefficient of a particular irrep j can be computed if the characters of the full representation and those of the irreducible represenation are known. We can now use this to our advantage. We find:

- $a_{A_1} = \frac{1}{24}[1\cdot 1\cdot 5 + 8\cdot 1\cdot -1 + 6\cdot 1\cdot 1 + 6\cdot 1\cdot -1 + 3\cdot 1\cdot 1] = 0$

- $a_{A_2} = \frac{1}{24}[1\cdot 1\cdot 5 + 8\cdot 1\cdot -1 + 6\cdot -1\cdot 1 + 6\cdot -1\cdot -1 + 3\cdot 1\cdot 1] = 0$
- $a_E = \frac{1}{24}[1\cdot 2\cdot 5 + 8\cdot -1\cdot -1 + 6\cdot 0\cdot 1 + 6\cdot 0\cdot -1 + 3\cdot 2\cdot 1] = 1$
- $a_{T_1} = \frac{1}{24}[1\cdot 3\cdot 5 + 8\cdot 0\cdot -1 + 6\cdot -1\cdot 1 + 6\cdot 1\cdot -1 + 3\cdot -1\cdot 1] = 0$
- $a_{T_2} = \frac{1}{24}[1\cdot 3\cdot 5 + 8\cdot 0\cdot -1 + 6\cdot 1\cdot 1 + 6\cdot -1\cdot -1 + 3\cdot -1\cdot 1] = 1$

Note that $h = 24$ is the total number of elements in O. and each term is of the form $N_k \chi^{\Gamma^k} \chi^{\Gamma'}$ where the first χ is the character of the element in the O group and the second is the character of the Γ^2 representation of that element. The only coefficients that are finite are a_E and a_{T_2} and this tells us that the reducible Γ^2 representation in O can be written as:

$$\Gamma^2 = E \oplus T_2 \tag{2.10}$$

From the character table we now see that the E representation is two dimensional and the T_2 representation is three dimensional. Therefore, the degeneracy of the five orbitals is lifted and we are left with a two-fold degenerate state and a three fold degenerate state. What remains to be determined is how these orbitals transform under the symmetry operations so that we can determine to which representation they belong. This can be done by looking up the full character for O online or by realizing that only the $3d_{xy,xz,yz}$ can transform in an invariant way under four-fold rotations[22] We conclude that the $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ orbitals form a triplet, while the $3d_{x^2-y^2}$ and $3d_{z^2-r^2}$ form a doublet. These degeneracies can be further lifted if additional symmetries are broken. An example can be found in exercise 1.

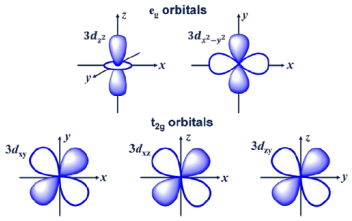

Figure 2.7: The five 3*d*-orbitals.

[22] *The $3d_{x^2-y^2}$ orbital is an eigenfunction of the four-fold rotation $C_4(z)$, but is not invariant under any $C_4(x)$ or $C_4(y)$.*

To conclude this section, we return to the fact that the ABO_3 crystal structure also ha an inversion center. This is easy to see if we refer back to Fig. 2.6: if we take the central atom as the center of inversion and invert all axes, we retrieve the same crystal. By looking at how the 3*d* orbitals transform under inversion (Fig. 2.7), we see that they also do not change sign. This tells us that the character of inversions for this case is $\chi = 1$. The character table for the group O_h can be found online. This group has a number of additional classes that are combinations of rotations and inversions. Since we know that the character for inversion is 1, we only have to focus on the first 5 rows of the character table. We immediately recognize that the characters of the rotations are identical to those of O. The only difference is that there are now irreps with an additional label (g or u from the german for even (gerade) and odd (ungerade)). The correct decomposition of Γ^2 is thus,

$$\Gamma^2 = E_g \oplus T_{2g} \tag{2.11}$$

2.4 Symmetry and expectation values

The second application we will discuss is the impact of symmetries on observable quantities. Very generally speaking, anything that we observe in quantum mechanics requires the measurement of an observable of the form:

$$\langle \psi | \hat{O} | \phi \rangle \tag{2.12}$$

where the initial ($|\phi\rangle$) and final ($|\psi\rangle$) state wavefunctions may or may not be the same. Another example is the rate of transitions from an initial to a final state due to a weak perturbation, $\hat{H}'$, that are given by Fermi's golden rule:

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar} \left| \langle \psi_f | \hat{H}' | \psi_i \rangle \right|^2 \rho(E_F) \tag{2.13}$$

Yet other examples are the selection rules for an infrared optical transition, or matrix element for a photoemission process where an electron is ejected from a solid to a vacuum state, both of which are of the form,

$$\langle \psi_f | e^{i\vec{q}\cdot\vec{r}} \hat{p} | \psi_i \rangle \tag{2.14}$$

or the $\alpha\beta$ and χ integrals involved in the tight-binding approach discussed in Chapter **??**.

Each of these expressions involves evaluating complex integrals and group theory is of little help in the actual evaluation of these integrals. What group theory can do is to provide a quick insight into *when* these integrals are zero by symmetry.

Theorem 2.1. *A product of the form*

$$\langle \psi | \hat{O} | \phi \rangle \tag{2.15}$$

is finite when it transforms under the A_1 representation of the symmetry group of the Hamiltonian.

We will not worry about the proof[23]. Instead, we'll focus on what it means. We recognize that Eq. 2.28 is an expectation value and must therefore be a real number. The product has to transform under any of the group's symmetry operations according to a positive number. If this where not the case, we would symbolically find that

$$\hat{P}\left(\langle\psi|\,\hat{O}\,|\phi\rangle\right) = -\langle\psi'|\,|\phi'\rangle \tag{2.16}$$

which implies that the expectation value is zero ($\left(\langle\psi|\,\hat{O}\,|\phi\rangle\right)$ is not supposed to change under a symmetry operation). From this observation we thus find that the expectation value is finite only if it transforms according to the A_1 irreducible representation, for only under this representation the characters of a group are all equal to 1.

To make use of theorem 2.3 we need a few ingredients. Firstly, we will assume that we have already determined the eigenfunctions of the physical problem at hand (i.e. the molecular orbitals of a molecule; the Bloch functions of a crystal etc.). Second we need to define the direct product of two representations in order to determine the characters of the representation according to which Eq. 2.3 transforms.

Since we choose eigenfunctions of the (unperturbed) Hamiltonian, they form a complete and orthogonal set of basisfunctions of the representation of the group of the Hamiltonian. We thus have,

$$\hat{H}_0\left|\psi^i_\alpha\right\rangle = E^i_\alpha\left|\psi^i_\alpha\right\rangle \tag{2.17}$$

where the index α refers to one of the basis functions that spans the i'th representation of the full group. To make it more concrete, for an atom we have irreducible representations that are labelled by the quantum number l. For $l = 2$, we thus have five basis functions that span the i'th representation (see table 2.3): $\left|\psi^l_\alpha\right\rangle$ and $\alpha = 3d_{xy}...3d_{z^2-r^2}$ and we know that these $3d$ states are mutually orthogonal.

Suppose now that we have two sets of basis functions corresponding to two different representations, then the matrix element,

$$\left\langle\phi^j_\beta\right|\hat{H}_0\left|\psi^i_\alpha\right\rangle = E^i_\alpha\left\langle\phi^j_\beta|\psi^i_\alpha\right\rangle = \delta_{\alpha,\beta}\delta_{i,j} \tag{2.18}$$

2.5 Direct product groups and their representations

The second ingredient necessary to evaluate matrix elements is the notion of the direct product group. Such groups are defined as the 'composite' group consisting of elements that are products of the individual elements of the two groups. For two groups G_1 and G_2, the direct product group is:

$$G = G_1 \otimes G_2 \tag{2.19}$$

We already encountered an example of a product group in section 2.3. The group O_h is the direct product group of the orthogonal group O with the inversion group $C_i = \{I, i\}$ where i is the inversion operator. The direct product group contains ten elements (5 elements of O combined with 2 elements of C_i).

The notion of direct product groups becomes useful when we consider the representations of these groups. In practical applications, we define the symmetry operations as matrices that multiply our basis functions. For each element, we can define a matrix for one of the irreducible representations of the group and a corresponding character.

Theorem 2.2. *The direct product of (irreducible) representations of two groups forms a (irreducible) representation of the direct product group*

We will again not worry so much about the proof, but make use of the consequences of this statement: the characters of the direct product group can be simply expressed as products of the characters of the two original groups.

Definition 2.1. • *The character of an irreducible representation of a direct product group $G_1 \otimes G_2$ is obtained from:*

$$\chi^{G_1\otimes G_2}(R_1P_2) = \chi^{G_1}(R_1)\chi^{G_2}(P_2) \tag{2.20}$$

- *The character of a representation of a direct product between two representations of the same group $\Gamma^1 \otimes \Gamma^2$ is obtained from:*

$$\chi^{\Gamma^1\otimes\Gamma^2}(R) = \chi^{\Gamma^1}(R)\chi^{\Gamma^2}(R) \tag{2.21}$$

[23] *see Chapter 6 of Hamermesh, Group theory and its application to to physical problems (1962)*

To see this for yourself, consider the following matrix product:

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix} \otimes \begin{bmatrix} e & f & g \\ h & i & j \\ k & l & m \end{bmatrix} \tag{2.22}$$

The characters (trace or sum of the diagonal elements) of these two matrices are $a+d$ and $e+i+m$ respectively. To obtain the matrix product, we need to multiply each element of the second matrix with the entire first matrix (A_1):

$$\begin{bmatrix} eA_1 & fA_1 & gA_1 \\ hA_1 & iA_1 & jA_1 \\ kA_1 & lA_1 & mA_1 \end{bmatrix} \tag{2.23}$$

The trace of this new (6 by 6!) matrix is $e\mathrm{Tr}(A_1)+i\mathrm{Tr}(A_1)+m\mathrm{Tr}(A_1) = ea+ed+ia+id+ma+md$. This is indeed equivalent to $(a+d)(e+i+m)$ or the product of the characters of the two individual matrices.

We will however mostly be interested in the direct product of irreducible representations of the *same* group. The resulting product representation is in general reducible. In this case, the character is:

$$\chi^{\Gamma^i \otimes \Gamma^j}(R) = \chi^{\Gamma^i}(R)\chi^{\Gamma^j}(R) = \sum_{\Gamma^k} a_{ijk}\chi^{\Gamma^k}(R) \tag{2.24}$$

Making use of Eq. 1.22, we can compute the coefficients a_{ijk} according to,

$$a_{ijk} = \frac{1}{h}\sum_{\alpha} N_\alpha \chi^{\Gamma^k}(R_\alpha)\left[\chi^{\Gamma^i}(R_\alpha)\chi^{\Gamma^j}(R_\alpha)\right] \tag{2.25}$$

or equivalently,

$$a_{ijk} = \frac{1}{h}\sum_{\alpha} N_\alpha \chi^{\Gamma^k}(R_\alpha)\chi^{\Gamma^i \otimes \Gamma^j}(R_\alpha) \tag{2.26}$$

2.6 Matrix elements

We are now in a position to consider the effect of perturbations. As mentioned above, we consider wavefunctions to be eigenfunctions of some Hamiltonian, $\hat{H}_0$. We would like to know under what conditions a matrix element of the form,

$$\left\langle \phi_\alpha^i \right| \hat{H}' \left| \phi_\beta^j \right\rangle \neq 0 \tag{2.27}$$

We can now cast theorem 2.3 in the following form:

Theorem 2.3. *A product of the form*

$$\phi_\alpha^{(i)} \otimes \hat{H}_\chi'^{(k)} \otimes \phi_\beta^j \tag{2.28}$$

is finite when it transforms as the irreducible A_1 representation.

The α,β and χ indicate orbitals or block diagonal parts of H' that transform according to a specific symmetry element, while i, j and k label irreps. This allows us to make use of Eq. 2.26 in evaluating expectation values. Let's consider a concrete example. We take an electron in a $3p$ orbital of the central Ti atom in $SrTiO_3$ (Fig. 2.6). As before, we determine to which irreducible representation these orbitals belong and find that they transform according to the T_1 representation. We now ask the question if we can make an optical excitation between this state and and a vacuum level state (which transforms according to the A_1 representation). To do this, we need an expression for the interaction. As you may (but don't have to) know, the interaction between electrons and light is given by,

$$\hat{H}' = -\frac{e}{mc}\hat{p}\cdot\vec{A} \tag{2.29}$$

One can show that $\vec{A}$ commutes with the Hamiltonian, but $\hat{p}$ does not. We therefore need to determine how the components of $\hat{p}$ transform under the symmetry operations of the group of the Hamiltonian. Since the components (p_x, p_y, p_z) are linear in x,y and z they also transform according to the T_1 representation. From the above, we find that the direct product,

$$\psi_{3s}^{A_1} \otimes \hat{H}_p'^{T1} \otimes \phi_{3p}^{T_1} \tag{2.30}$$

From which we find (making use of Eq. 2.21),

O	E	$8C_3$	$6C_2'$	$6C_4$	$3C_2$
$T^1 \otimes T^1$	9	0	1	1	1
$A_1 \otimes (T^1 \otimes T^1)$	9	0	1	1	1

We have thus found the characters of the reducible representation of the matrix element[24]. We now use the decomposition formula Eq. 2.26 to find the irreducible representations that make up the product $A_1 \otimes (T^1 \otimes T^1)$. It works similar to before

- $a_{A_1} = \frac{1}{24}[1\cdot 1\cdot 9 + 8\cdot 1\cdot 0 + 6\cdot 1\cdot 1 + 6\cdot 1\cdot 1 + 3\cdot 1\cdot 1] = 1$
- $a_{A_2} = \frac{1}{24}[1\cdot 1\cdot 9 + 8\cdot 1\cdot 0 + 6\cdot -1\cdot 1 + 6\cdot -1\cdot 1 + 3\cdot 1\cdot 1] = 0$
- $a_E = \frac{1}{24}[1\cdot 2\cdot 9 + 8\cdot -1\cdot 0 + 6\cdot 0\cdot 1 + 6\cdot 0\cdot 1 + 3\cdot 2\cdot 1] = 1$
- $a_{T_1} = \frac{1}{24}[1\cdot 3\cdot 9 + 8\cdot 0\cdot 0 + 6\cdot -1\cdot 1 + 6\cdot 1\cdot 1 + 3\cdot -1\cdot 1] = 1$
- $a_{T_2} = \frac{1}{24}[1\cdot 3\cdot 9 + 8\cdot 0\cdot 0 + 6\cdot 1\cdot 1 + 6\cdot -1\cdot 1 + 3\cdot -1\cdot 1] = 1$

and we therefore find that the product can be decomposed as:

$$\psi_{vac}^{A_1} \otimes \hat{H}_p'^{T^1} \otimes \phi_{3p}^{T^1} = A_1 + E + T_1 + T_2 \tag{2.31}$$

Since this contains the A_1 representation, the expectation value,

$$\langle \phi_{vac} | \hat{p} \cdot \vec{\hat{A}} | \phi_{3p} \rangle \neq 0 \tag{2.32}$$

It would have actually been sufficient to take a look at,

$$\hat{H}_p'^{T^1} \otimes \phi_{3p}^{T^1} \tag{2.33}$$

and,

O	E	$8C_3$	$6C_2'$	$6C_4$	$3C_2$
$T^1 \otimes T^1$	9	0	1	1	1

The same decomposition as above now gives,

$$\hat{H}_p'^{T^1} \otimes \phi_{3p}^{T^1} = A_1 + E + T_1 + T_2 \tag{2.34}$$

This tells us how $\hat{H}|\phi\rangle$ transforms and it is possible to show[25] that a matrix element will be finite if the closing bra $\langle\psi|$ transforms according to the A_1, E, T_1 or T_2 representations.

[24] *The identity operator has character 9, so its dimensionality is 9. The octahedral group only has representations with dimension 1, 2 and 3.*

[25] *I think it is sufficient to show that the direct product of an irrep with itself always has the A_1 irrep in its decomposition.*

2.7 Molecular Vibrations

One of the valuable applications is that it allows us to predict infrared and Raman active vibrational modes for molecules and crystals[26]. You can work your way through the quantum problem if you are interested[27], but here we will simply focus on the group theory approach.

The essential thing you need to know about the quantum problem is that the vibrations are described by a problem of the form:

$$H|f_K\rangle = E_{ph}(K)|f_K\rangle \tag{2.35}$$

where the $|f_K\rangle$ are the vibrational modes and $E_{ph}(K)$ is the corresponding energy. There is a bit of a subtlety with the label K. For molecules, K just labels the different vibrational modes. For example, H_2O has three different vibration modes and K=1,2,3. In crystals you have a near-infinite number of modes and the label K can be interpreted as the momentum of propagating vibrations (a.k.a. a phonon). Because of periodicity, we can construct similar diagrams for phonon modes as we did for electrons. An example is shown in Fig. 2.8. This problem is very similar to the problem of constructing molecular orbitals. In that case, we have

$$H|\psi_\alpha\rangle = E_\alpha^{M.O.}|\psi_\alpha\rangle \tag{2.36}$$

and we were looking for the molecular orbitals $|\psi_\alpha\rangle$ that were expressed in terms of the atomic wavefunctions of the individual atoms. The difference is that here, each atom has three degrees of freedom (it can move in the x,y and z directions) and we need to take that into account in our analysis. This problem would be equivalent to the problem of finding M.O's of an ammonia molecule (section 1.8 where the 1s-orbitals on the hydrogen is replaced by three 2p orbitals. This is a more complicated situation: the symmetry operations do not necessarily map the $2p_x$ orbitals from one hydrogen atom onto the $2p_x$ orbital of the next atom. Instead, you could imagine that these

[26] *In a molecule you also have rotational and mixed modes. The same arguments apply.*

[27] *In short, motion of the atoms is described as coupled quantum harmonic oscillators and you need to find the normal modes of the problem. This can be found in basic solid state textbooks[27] or physical chemistry textbooks[28]*

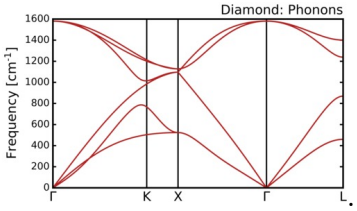

Figure 2.8: Phonon spectrum of Diamond

three orbitals form a 'vector'. The problem now is to find how that vector transforms under group operations.

The same principles for molecular orbitals, also apply to the case of finding vibrations. First, we identify the point group of our molecule. Second, we find the characters for the reducible representation describing the invariant atoms and then decompose this in irreducible representations (similar to what we did in section 1.8 below Eq. 1.34). The key difference is that the movement of each atom is described by three components and we and we can thus represent this movement by a vector. To include this, we need to compute the direct product of the reducible representation of the atomic sites with the irreducible representations for the vector:

$$\Gamma_{vib} = \Gamma_{a.s} \otimes \Gamma_{vec} \tag{2.37}$$

The rest of the procedure is then similar to before. There is however one small caveat: Eq. 2.37 also contains the motion and rotation of the molecule as a whole (absolute motion/rotation of cenre of mass). Since we are only interested in the vibrations of the molecule (relative motion/rotation of atoms), we need to subtract these from our reducible representation:

$$\Gamma_{vib} = (\Gamma_{a.s} \otimes \Gamma_{vec}) - \Gamma_{tr} - \Gamma_{rot} \tag{2.38}$$

In this expression, Γ_{tr} are the characters of the irreducible representations for the (x,y,z) components of the vector. We haven't made use of the basisfunctions for Γ_{rot} yet. As you may have already realized, rotations of a molecule correspond to higher angular momentum states (as the molecule starts to rotate, its angular momentum increases). Angular momentum is described by $\vec{L} = \vec{r} \times \vec{p}$ and you may remember that this vector is perpendicular to the two vectors making up the product. It therefore transforms differently under symmetry operations compared to the (x,y,z) components. The irreducible representations of the angular momentum vector are indicated in the character tables by the (R_x, R_y, R_z) basis functions.

Once we have determined Γ_{vib}, we can analyze the symmetry of the vibrational (or phonon) modes by looking at how Γ_{vib} decomposes into irreducible representations. From this we can then construct the normal modes of the molecule and by making use of the same arguments of section 2.6, we can also determine whether a mode is infrared active or not. Finding the normal modes follows a procedure that involves projection operators similar to finding the molecular orbitals. Let's go to a concrete example

2.8 Vibrations of H_2O

A simple, but insightful example is the set of vibrational modes of hydrogen. Unfortunately (for me), we have not yet considered the point group of hydrogen, which is C_{2v}. The character table is:

C_{2v}	E	C_2	σ_v	σ_v'	lin.	quad.
A^1	1	1	1	1	z	x^2,y^2,z^2
A^2	1	1	–1	–1	R_z	xy
B^1	1	-1	1	–1	R_y, x	xz
B^2	1	-1	–1	1	R_x, y	yz
$\Gamma_{a.s.}$	3	1	3	1		

The σ_v reflection plane is *in the plane* of the molecule because it contains the C_2 rotation, while σ_v' is perpendicular to the molecule. In contrast to before, we are now interested in the motion of atoms in space. The choice of the frame of reference therefore matters. Looking at the character table, we see that the z-component transforms as the A_1 representation, so we must choose our z-axis along the C_2 rotation axis. The x-component transforms according to B_1 and is left invariant by σ_v. The x-axis of our reference frame must therefore also lie in the plane of the molecule.

We can now write down the characters of the atomic site representation using the same counting procedure discussed below Eq. 1.34 in section 1.8. Under the identity operation, all three atoms stay in their own place so we add three times 1 together to get the character of the identity operation. Under the action of C_2, only the central oxygen remains in the same location. The character is therefore 1. When the molecule is reflected in the vertical plane, all atoms remain in the same position and we again obtain the character three. Finally, the reflection in the plane perpendicular to the paper (going through the z-axis) only leaves the oxygen invariant and we again find character 1[32].

This is a reducible representation as is easily seen by looking at the character table. There are no two or three dimensional irreps, so $\Gamma_{a.s.}$ needs to be constructed from

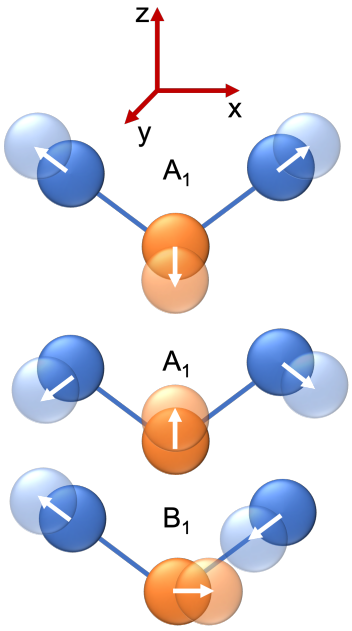

Figure 2.9: Three vibrational modes of H_2O. Also indicated are the irreps to which they belong.

[32] *Note that we are dealing with movement of atoms. we do not have to worry about positive and negative lobes of wave functions here*

three irreps of C_{2v}. This is done using the same method as used in section 2.3 by making use of Eq. 2.9. We find:

- $a_{A_1} = \frac{1}{4}[1\cdot 1\cdot 3 + 1\cdot 1\cdot 1 + 1\cdot 1\cdot 3 + 1\cdot 1\cdot 1] = 2$
- $a_{B_1} = \frac{1}{4}[1\cdot 1\cdot 3 + 1\cdot -1\cdot 1 + 1\cdot 1\cdot 3 + 1\cdot -1\cdot 1] = 1$

while all other coefficients are equal to zero and so,

$$\Gamma_{a.s} = 2A_1 + B_1 \tag{2.39}$$

According to Eq. 2.42, we need to know the characters of the representation of the radial (x, y, z) vector. The character table tells us that it can be composed out of irreducible representations according to:

$$\Gamma_{vec} = A_1 + B_1 + B_2 \tag{2.40}$$

and this is also the representation of Γ_{tr} since it has the same components. We'll also need the representation of the angular momentum:

$$\Gamma_{rot} = A_2 + B_1 + B_2 \tag{2.41}$$

We can now compute the direct product:

$$\begin{aligned}
(\Gamma_{a.s} \otimes \Gamma_{vec}) &= (2A_1 + B_1) \otimes (A_1 + B_1 + B_2) && (2.42)\\
&= 2A_1\cdot A_1 + 2A_1\cdot B_1 + 2A_1\cdot B_2 + B_1\cdot A_1 + B_1\cdot B_1 + B_1\cdot B_2 && (2.43)\\
&= 2A_1 + 2B_1 + 2B_2 + B_1 + A_1 + A_2 && (2.44)\\
&= 3A_1 + 3B_1 + 2B_2 + A_2 && (2.45)
\end{aligned}$$

where in going from line 2.43 to 2.44, we have made use of the character table. Subtracting of Γ_{tr} and Γ_{rot}, we finally find:

$$\Gamma_{vib} = 2A_1 + B_1 \tag{2.46}$$

Our symmetry analysis thus tells us that H_2O will have three vibrational modes, two with A_1 symmetry and one mode with B_1 symmetry. What this 'means' is that the molecule has two vibrations that leave the symmetry of the molecule intact. In this simple case you can see that bond stretching or band angle changing vibrations leave all symmetries intact.

We won't bother with determining the actual motions of the atoms corresponding to these modes (they are however indicated in Fig. 2.9).

2.9 Infrared and Raman active modes

In this section we combine the knowledge of sections 2.6 and 2.7 to determine the optically allowed transitions between molecular vibrations. We'll assume that our molecule is initially in its ground state with no excited vibrations. We'll call this state $|f_i\rangle$ and it must have A_1 symmetry. When we let the molecule interact with the electric field of the photon, a dipole moment will be created due to the displacement of atoms. Similar to Eq. 2.29, we have,

$$\hat{H}' = -\vec{E}\cdot\vec{u} \tag{2.47}$$

where $\vec{E}$ is the photon electric field and $\vec{u}$ is the dipole moment. Similar to the motion of the atoms, $\vec{u}$ transforms according to a vector (e.g. as Γ_{vec}). The only components of $\vec{u}$ that are important are those that have overlap with the $\vec{E}$ field (i.e. if the field is polarized along the x direction, we only need to consider the dipole moment $(u_x, 0, 0)$. To determine whether a molecule is infrared active, we need to determine whether the matrix element for the transition is finite:

$$\langle f_f|\,\hat{H}'\,|f_i\rangle \neq 0 \tag{2.48}$$

where $|f_f\rangle$ is one of the vibrational modes of the molecule. This can be done using the same procedure as in section 2.6 and so we need to ask whether the product $\Gamma_{vec} \otimes \Gamma_i$ is finite or not. If the molecule is originally in its groundstate, then $\Gamma_{vec} \otimes A_1 = \Gamma_{vec}$.

We can now compare the irreps of Γ_{vib} with those of Γ_{vec}. All modes in Γ_{vib} that also appear in Γ_{vec} are optically active. It is possible to consider more complicated cases. For example, in a 2-photon process where the first photon excites the molecule. The interaction with a second photon now has a different matrix element, because we start from an already excited state that does not necessarily has the A_1 representation. Also note that not all vibrational modes need be optically active.

We can also consider the Raman effect where a photon is scattered, rather then absorbed. We will not go into the details here, but the difference in process is reflected in the perturbation. One can show that $\hat{H}'$ transforms as a second rank tensor (and not as a vector). This is especially important when the point group of the molecule or solid has inversion symmetry. It turns out that in the absorption process the dipole moment couples states that have opposite parity (i.e. odd or even under inversion). In Raman processes, only states with the same parity couple and the two experiments combined provide us with a complete picture of the optically active modes. Without inversion symmetry, one can have vibrations that don't couple in either process.

2.10 Lattice vibrations.

A proper discussion of phonon modes in crystals would require us to now delve into the representations of space groups. Perhaps this will one day be part of this course. For now, i'll leave a few remarks. The analysis of phonon modes in solids follows quite closely that of molecular vibrations. The key difference is that vibrations in solids are *propagating* and this means that there is an additional vector (the phonon momentum) that has to transform according to the space group symmetry. However, at a special point in the Brillouin zone ($\vec{k} = 0$), this distinction disappears and the approach is in fact similar to that of the molecular vibrations above.

At the zone center, one can apply the formalism of section 2.7 and determine the phonon modes of the crystal accordingly. There is one big difference. In the molecular case, the total number of vibrations depends on the number of atoms in the molecule and is at most $3M$ (three degrees of freedom, M atoms in the molecule). Symmetry considerations may lower the number of independent modes.

In a solid we have N unit cells and one might therefore expect $3N$ phonon modes. This is however not the case. Instead, we will find a number of **phonon branches** that is equal to $3K$, where K counts the number of distinctly different atoms per unit cell. Each branch consists of $3N$ modes and each mode has a different momentum.

Exercises II

Applications of group theory

One exercise corresponding to each paragraph.

Crystal field splitting

1

In this exercise, we will look at the degeneracy of $3d$ orbitals in non-cubic geometry.

$\mathcal{A}$

Molecular vibrations of NH_3

2

In this exercise, we will look at the molecular vibrations of NH_3. The ammonia molecule is shown in Fig. 2.10 and as you may remember has point group C_{3v}.

$\mathcal{A}$ Look up the character table for the C_{3v} point group and determine the characters of the $\Gamma_{a.s.}$ representation.

$\mathcal{B}$ Find the decomposition of the $\Gamma_{a.s.}$ representation.

$\mathcal{C}$ Compute

$$\Gamma_{vib} = (\Gamma_{a.s} \otimes \Gamma_{vec}) - \Gamma_{tr} - \Gamma_{rot} \tag{E2.1}$$

You can use the online decomposition tool.

$\mathcal{D}$ Which of these modes are infrared active?

$\mathcal{E}$ Can you indicate with arrows how the atoms are moving for a vibration with A_1 symmetry?

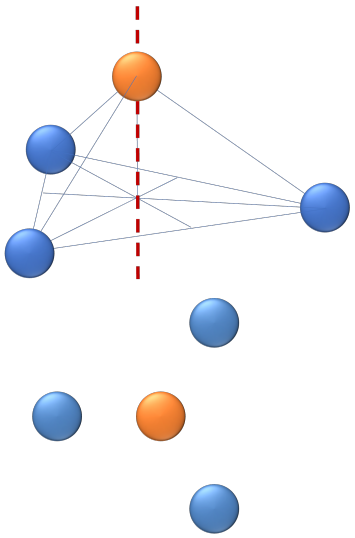

Figure 2.10: NH_3 molecule in 3D and viewed from above.

Further reading

[1] OCLC: 66528976

[1] **P. W. Atkins and J. De Paula, Atkins' Physical chemistry, en, 8th ed, New York: W.H. Freeman, 2006, ISBN: 978-0-7167-8759-4.**

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[3] Wikipedia, *Crystal structure*. [Online]. Available: `https://en.wikipedia.org/wiki/Crystal_structure`.

Index