

4. Angular momentum

In the following we consider general and exact approaches, such as *angular momentum algebra* and *group theory*, and later, methods for approximations, such as *perturbation theory*, in applications of quantum mechanics.

Consider first the angular momentum (liikemäärämomentti, kulmaliikemäärä, pyörimismäärä) and derivation of its quantization from commutation relation, only.

Angular momentum operators

These operators can be written in terms of position and momentum operators q and p_q , whose commutation relations are

$$[q, p_{q'}] = i\hbar\delta_{qq'} \tag{4.1}$$

where $q, q' = x, y$ or z .

4.1. Operators and their commutation relations

Classically angular momentum is defined as

$$\ell = \mathbf{r} \times \mathbf{p} = \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = (y p_z - z p_y) \hat{\mathbf{i}} + (z p_x - x p_z) \hat{\mathbf{j}} + (x p_y - y p_x) \hat{\mathbf{k}}, \tag{4.2}$$

and thus, its components are

$$\ell_x = y p_z - z p_y, \ell_y = z p_x - x p_z \text{ and } \ell_z = x p_y - y p_x. \tag{4.3}$$

Classically $\ell = \bar{\mathbf{I}} \cdot \boldsymbol{\omega}$ ja $E = \ell^2 / 2I = \frac{1}{2} I \omega^2$) and

$$\ell^2 = \ell_x^2 + \ell_y^2 + \ell_z^2 \tag{4.4}$$

Now, as in quantum mechanics

$$\left(p_x \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x} \right), \quad \left(p_y \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial y} \right) \text{ and } \left(p_z \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial z} \right),$$

it follows that the angular momentum components take the form

$$\begin{aligned} \ell_x &= \frac{\hbar}{i} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \\ \ell_y &= \frac{\hbar}{i} \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), \text{ and} \\ \ell_z &= \frac{\hbar}{i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \end{aligned} \tag{4.5}$$

Let us find commutators:

$$[\ell_x, \ell_y] =$$

$$\tag{4.6}$$

Similarly, the other two, and thus,

$$[\ell_x, \ell_y] = i\hbar \ell_z, \quad [\ell_y, \ell_z] = i\hbar \ell_x \text{ ja } [\ell_z, \ell_x] = i\hbar \ell_y, \tag{4.7}$$

which are the basic commutation rules of angular momentum in quantum mechanics.

As above, it can be shown that

$$[\ell^2, \ell_q] = 0. \tag{4.8}$$

4.2. Angular momentum observables

In a compact form (4.7) can be written as

$$\mathbf{l} \times \mathbf{l} = i\hbar\mathbf{l}, \tag{4.9}$$

because

$$\mathbf{l} \times \mathbf{l} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ l_x & l_y & l_z \\ l_x & l_y & l_z \end{vmatrix} =$$

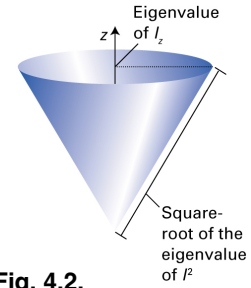


Fig. 4.2.

4.3. Shift operators

Let us define *raising* and *lowering operator*, which are also called *shift or ladder operators* (nostava and laskeva operaattori, tikapuuoperaattorit)

$$l_+ = l_x + il_y \quad \text{and} \quad l_- = l_x - il_y \tag{4.10}$$

with inverse relations

$$l_x = (l_+ + l_-) / 2 \quad \text{and} \quad l_y = (l_+ - l_-) / 2i. \tag{4.11}$$

It is easy to show that

$$[l_+, l_z] = -\hbar l_+, \quad [l_-, l_z] = -\hbar l_-, \quad \text{ja} \quad [l_+, l_-] = 2\hbar l_z, \tag{4.12}$$

and that l^2 commutes with ladder operators

$$[l^2, l_{\pm}] = 0.$$

Note that **shift operators are not hermitian**, but complex conjugates of each other.

$$\tag{4.13}$$

Definition of states

Next, we will find the angular momentum states by using the commutation relations.

4.4. Effect of shift operators

Because l^2 and l_z commute, (4.8), they have the same eigenfunctions. Thus, from (3.33) and (3.37) we have the eigenvalue equations

$$\begin{aligned} l^2 |l, m_l\rangle &= \hbar^2 l(l+1) |l, m_l\rangle \quad \text{and} \\ l_z |l, m_l\rangle &= \hbar m_l |l, m_l\rangle, \end{aligned} \tag{4.14-15}$$

where $l = 0, 1, 2, 3, \dots$ and $m_l = l, l-1, l-2, \dots, -l$. Let us find next $l_+ |l, m_l\rangle$. From (4.12)

$$\begin{aligned} l_+ l_z - l_z l_+ &= -\hbar l_+, \quad \text{thus} \quad l_z l_+ |l, m_l\rangle = (l_+ l_z + \hbar l_+) |l, m_l\rangle \\ &= l_+ \hbar m_l |l, m_l\rangle + \hbar l_+ |l, m_l\rangle = \hbar(m_l + 1) l_+ |l, m_l\rangle. \end{aligned}$$

Therefore, $l_+ |l, m_l\rangle$ is an eigenfunction of l_z with the eigenvalue $\hbar(m_l + 1)$. So,

$$l_+ |l, m_l\rangle = \text{constant} \times |l, m_l + 1\rangle \tag{4.17a}$$

and similarly

$$l_- |l, m_l\rangle = \text{constant} \times |l, m_l - 1\rangle \tag{4.17b}$$

These equations hold, if $m_l < l$ and $m_l > -l$, and for $l_+ |l, l\rangle = 0$ and $l_- |l, -l\rangle = 0$. For this reason l_+ and l_- are called raising and lowering operators.

4.5. Eigenvalues of angular momentum

As discussed in sec. 3, operators l^2 and l_z correspond the "rotational states" of electrons on atomic orbitals, when $l = 0, 1, 2, 3, \dots$. Then, quantization follows from the uniqueness of the wavefunction.

More generally, starting from the commutation relations (4.7), only, one can choose to accept half-integral quantum numbers, too. Then, the angular momentum can assume "half-integral" values, as well. For example, the spin of an electron or proton are half-integral angular momenta.

Let us denote the common eigenfunctions of general angular momentum j and its z -component with $|j, m_j\rangle$. Then, we can write the eigenvalue equations as

$$\begin{aligned} j^2 |j, m_j\rangle &= \hbar^2 j(j+1) |j, m_j\rangle ; j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots \quad \text{and} \\ j_z |j, m_j\rangle &= \hbar m_j |j, m_j\rangle ; m_j = j, j-1, \dots, -j . \end{aligned} \quad (4.22)$$

4.6. Matrix elements of shift operators

The matrix elements of angular momentum can be obtained by using relations (4.10) and (4.11). Therefore, let us find $j_{\pm} |j, m_j\rangle = c_{\pm} |j, m_j \pm 1\rangle$. So,

$$j_- j_+ =$$

Now, $(j_+ |j, m_j\rangle)^* = \langle j, m_j | j_-$, and thus,

$$j_+ |j, m_j\rangle = \hbar (j(j+1) - m_j(m_j+1))^{1/2} |j, m_j+1\rangle \quad (4.29a)$$

Similarly, we can derive

$$j_- |j, m_j\rangle = \hbar (j(j+1) - m_j(m_j-1))^{1/2} |j, m_j-1\rangle \quad (4.29b)$$

4.7. Orbital angular momentum eigenfunctions

As an example, let us consider **orbital angular momentum** ℓ , whose eigenfunctions are the **spherical harmonics**, in sec. 3 these results were found directly from the Schrödinger equation. **Now, let us find these results from the general properties of angular momentum.**

In polar coordinates the angular momentum operators are

$$\begin{aligned} \ell_x &= -\frac{\hbar}{i} \left(\sin\theta \frac{\partial}{\partial\theta} + \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right) \\ \ell_y &= \frac{\hbar}{i} \left(\cos\theta \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right) \\ \ell_z &= \frac{\hbar}{i} \frac{\partial}{\partial\phi} \end{aligned} \quad (4.30)$$

and

$$\ell^+ = \ell_x + i \ell_y = \hbar e^{i\phi} \left(\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right). \quad (4.31)$$

Thus, for the eigenfunctions of the state state $m_\ell = \ell$ we can write $\ell^+ |l, \ell\rangle = 0$ or

$$\ell^+ = \ell_x + i \ell_y = \hbar e^{i\phi} \left(\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right). \quad \text{whose solutions are the spherical harmonics, for } m_\ell = \ell$$

$$\psi_{\ell\ell}(\theta, \phi) = Y_{\ell\ell}(\theta, \phi) = N \sin^\ell\theta e^{i\ell\phi} \quad (4.32)$$

because

Now, the eigenfunctions for the other values of m_ℓ are easily obtained by using ℓ_- .

4.8. Spin

In 1925 Uhlenbeck and Goudsmit suggested **an internal angular momentum of the electron, its spin, and its only quantum number 1/2**, to simplify interpretation of atomic spectra. Later, Dirac "found" the half-integer quantum numbers and the electron spin, in particular, from his relativistic extension of quantum mechanics.

So, the electron spin is 1/2 and denoted as $s = 1/2$. Therefore, its z-component is $m_s = \pm 1/2$ (up or down). The corresponding eigenstates are $|s, m_s\rangle$, usually written as

$$\alpha = | \frac{1}{2}, \frac{1}{2} \rangle \text{ and } \beta = | \frac{1}{2}, -\frac{1}{2} \rangle .$$

Eigenvalue equations are

$$\begin{aligned} s_z \alpha &= \frac{1}{2} \hbar \alpha , & s_z \beta &= -\frac{1}{2} \hbar \beta , \\ s^2 \alpha &= \frac{3}{4} \hbar^2 \alpha \text{ and } s^2 \beta &= \frac{3}{4} \hbar^2 \beta \end{aligned} \tag{4.33}$$

and by using the ladder operators, we obtain

$$\begin{aligned} s^+ \alpha &= 0 , & s^+ \beta &= \hbar \alpha , \\ s^- \alpha &= \hbar \beta \text{ and } s^- \beta &= 0 \end{aligned} \tag{4.34}$$

and thus, the non-zero matrix elements are

$$\langle \alpha | s^+ | \beta \rangle = \hbar \text{ and } \langle \beta | s^- | \alpha \rangle = \hbar . \tag{4.35}$$

Coupling of angular momenta in composite systems

Next, consider a system formed by two angular momenta, e.g. orbital angular momenta of two electrons ℓ , or the orbital angular momentum ℓ and spin s of a single electron.

4.9. Uncoupled and coupled states

The state of two angular momenta can be defined by "listing the quantum numbers" in ket vector $| j_1, m_{j1} ; j_2, m_{j2} \rangle$. It can be done so, because

j_1^2, j_{1z}, j_2^2 and j_{2z} all commute.

For finding the total angular momentum "vector" j , the two vectors j_1 and j_2 are "summed componentwise", and the sum can be written as $| j_1, j_2 ; j, m_j \rangle$, because

j_1^2, j_2^2, j^2 and j_z all commute. This is called *coupling* of j_1 and j_2 .

However, generally

$$[j_{1z}, j^2] \neq 0 \text{ and } [j_{2z}, j^2] \neq 0 , \tag{4.37}$$

and therefore, m_{j1} and m_{j2} can not be used to describe the state simultaneously with j .

Later we will see, that depending on the case it is better to use the *uncoupled representation* $| j_1, m_{j1} ; j_2, m_{j2} \rangle$ or the *coupled representation* $| j_1, j_2 ; j, m_j \rangle$.

Exercise: Find out, if $j = j_1 + j_2$ is an angular momentum?

4.10. Permitted values of total angular momentum

Let us find the permitted values of j and m_j . Because

$$\begin{aligned} j_z |j_1, m_{j_1}; j_2, m_{j_2}\rangle &= (j_{z1} + j_{z2}) |j_1, m_{j_1}; j_2, m_{j_2}\rangle \\ &= \hbar (m_{j_1} + m_{j_2}) |j_1, m_{j_1}; j_2, m_{j_2}\rangle \end{aligned}$$

and $j_z |j_1, j_2; j, m_j\rangle = \hbar m_j |j_1, j_2; j, m_j\rangle$, we get

$$m_j = m_{j_1} + m_{j_2}. \tag{4.41}$$

As the maximum value of m_j is $j_1 + j_2$, j is allowed to assume values from "Clebsch–Gordan series"

$$j = j_1 + j_2, j_1 + j_2 - 1, \dots, |j_1 - j_2|. \tag{4.42}$$

The lower limit of Clebsch–Gordan series $|j_1 - j_2|$ is defined by the condition, that the **coupled presentation has to contain the same number of states as the uncoupled one does**. This can be formulated as sc. "triangle condition".

Example Coupling of orbital angular momentum and spin of a p-electron $\ell = 1$ and $s = 1/2$ in hydrogen atom.

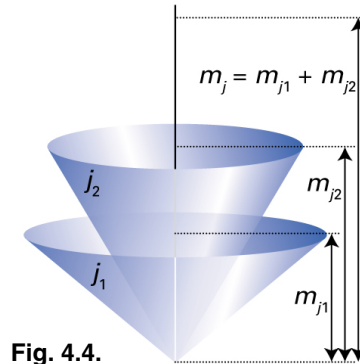


Fig. 4.4.

4.11. Vector model of coupled angular momenta

Coupling of two angular momenta can also be graphically illustrated. It should fulfil the following conditions:

1. $|j| = \sqrt{j(j+1)}$, where j is one of the permitted values in Clebsch–Gordan series.
2. For the \mathbf{j} -vector only the z -component is given, but not the x and $y \Rightarrow$ cone description.
3. For \mathbf{j}_1 and \mathbf{j}_2 :
 $|\mathbf{j}_1| = \sqrt{j_1(j_1+1)}$ and
 $|\mathbf{j}_2| = \sqrt{j_2(j_2+1)}$
 \Rightarrow cone description.
4. The z -components m_{j_1} and m_{j_2} of \mathbf{j}_1 and \mathbf{j}_2 are shown in uncoupled representation.

The z -component m_j of \mathbf{j} is given in the coupled representation.

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Figs. 4.6–7.



Next, let us couple two spins $s_1 = 1/2$ and $s_2 = 1/2$. Uncoupled presentation consists of **four possible states** $|s_1 m_{s1}; s_2 m_{s2}\rangle$ as

$$\begin{aligned}
 \left| \frac{1}{2} \frac{1}{2}; \frac{1}{2} \frac{1}{2} \right\rangle &= \alpha_1 \alpha_2 & \left| \frac{1}{2} \frac{1}{2}; \frac{1}{2} -\frac{1}{2} \right\rangle &= \alpha_1 \beta_2 \\
 \left| \frac{1}{2} -\frac{1}{2}; \frac{1}{2} \frac{1}{2} \right\rangle &= \beta_1 \alpha_2 & \left| \frac{1}{2} -\frac{1}{2}; \frac{1}{2} -\frac{1}{2} \right\rangle &= \beta_1 \beta_2
 \end{aligned}$$

In coupling, the total angular momentum becomes $S = s_1 + s_2, \dots, |s_1 - s_2| = 1, 0$ and the state $S = 1$ is called *triplet*, because $M_s = 1, 0, -1$; and the state $S = 0$ and $M_s = 0$ is called *singlet*, correspondingly. Thus, the couple representation also has four states

$$|s_1 s_1; S M_S\rangle \equiv \left| \frac{1}{2} \frac{1}{2}; S M_S \right\rangle \equiv |S M_S\rangle \text{ as}$$

$$\begin{aligned}
 &|1, 1\rangle \\
 &|0, 0\rangle \quad |1, 0\rangle \\
 &|1, -1\rangle
 \end{aligned}$$

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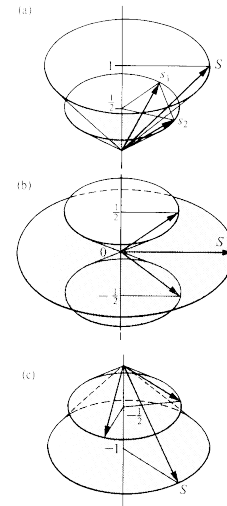
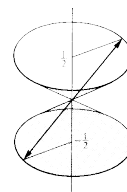


Fig. 4.8.

Fig. 4.9–10.

4.12. Clebsh–Gordan coefficients

The coupled state wavefunction $|j_1 j_2; j m_j\rangle$ can be presented with those of uncoupled ones $|j_1 m_{j1}; j_2 m_{j2}\rangle$

$$|j_1 j_2; j m_j\rangle = \sum_{\substack{m_{j1} m_{j2} \\ m_j = m_{j1} + m_{j2}}} c_{m_{j1} m_{j2}} |j_1 m_{j1}; j_2 m_{j2}\rangle, \tag{4.43}$$

where $c_{mj_1 mj_2}$ are *Clebsh–Gordan coefficients (or Wigner coefficients)*. Note, $m_j = m_{j1} + m_{j2}$.

Now, let us determine the **coupling constants** in case of two spins, as

$$|S M_S\rangle = \sum_{\substack{m_{s1} m_{s2} \\ M_S = m_{s1} + m_{s2}}} c_{m_{s1} m_{s2}} |m_{s1} m_{s2}\rangle.$$

Obviously,

$$|1 1\rangle = \alpha_1 \alpha_2, \tag{4.45}$$

thus $c_{\alpha\alpha} = 1$. Now, by using the lowering operator $S^- = s_1^- + s_2^-$, Eq. (4.30)

$$S^- |S, M_S\rangle = \hbar \sqrt{S(S+1) - M_S(M_S-1)} |S, M_S-1\rangle, \tag{4.46}$$

we get from left hand side $S^- |1 1\rangle = \hbar \sqrt{2} |1 0\rangle$.

From the right we get $(s_1^- + s_2^-) \alpha_1 \alpha_2 = s_1^- \alpha_1 \alpha_2 + s_2^- \alpha_1 \alpha_2$

$$= \hbar (\beta_1 \alpha_2 + \alpha_1 \beta_2), \text{ thus } \hbar \sqrt{2} |1 0\rangle = \hbar (\alpha_1 \beta_2 + \beta_1 \alpha_2)$$

which means

$$|1 0\rangle = \frac{1}{\sqrt{2}} (\alpha_1 \beta_2 + \beta_1 \alpha_2). \tag{4.47}$$

Further operation with $S^- = s_1^- + s_2^-$ gives

$$|1 -1\rangle = \beta_1 \beta_2. \tag{4.48}$$



The state $|0\ 0\rangle = a\ \alpha_1\ \beta_2 + b\ \beta_1\ \alpha_2$ is found from the orthogonality condition $\langle 0\ 0|1\ 0\rangle = 0$, which together with normalization gives

$$|0\ 0\rangle = \frac{1}{\sqrt{2}} (\alpha_1\ \beta_2 - \beta_1\ \alpha_2). \tag{4.49}$$

Table of the coupling coefficients for two spins $s_1 = 1/2$ and $s_2 = 1/2$:

m_{s1}	m_{s2}	$ 1\ 1\rangle$	$ 1\ 0\rangle$	$ 0\ 0\rangle$	$ 1\ -1\rangle$
α	α	1	0	0	0
α	β	0	$(1/2)^{1/2}$	$(1/2)^{1/2}$	0
β	α	0	$(1/2)^{1/2}$	$-(1/2)^{1/2}$	0
β	β	0	0	0	1

4.13. Coupling of several angular momenta

Coupling three or more angular momenta can be carried out pairwise, e.g., first two of those, and then, adding a third one, then fourth, and so on.

Example 4.2 Coupling three of the hydrogen atom p-orbitals $\ell_{1,2,3} = 1$.



5. Group theory

Use of the symmetry properties of the system usually helps in finding the solutions to the Schrödinger equation. It simplifies calculations particularly in cases, where **qualitative information** is sufficient, *e.g.*, showing if some quantities are equal or zero. Examples of these are the matrix elements (integrals) $\langle n|Q|n\rangle$ and $\langle n|Q|m\rangle$ and degeneracy. Also, group theory usually defines the most fundamental and natural (symmetry related) quantum numbers, like those of atomic orbitals: s, p, d, f, g, . . .

Example What are the conditions for ℓ^2 or ℓ_z to commute with the Hamiltonian (and therefore, to give good quantum numbers for the energy eigenstates) ?

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V \quad \text{and} \quad \ell_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}, \quad \text{thus}$$

$$[H, \ell_z] =$$

Symmetries of objects

Systematic inspection of symmetry properties is based on the relevant symmetry operations and the group they form. Then the **group theory** immediately classifies the system and its basic properties.

5.1. Symmetry operations and elements

Symmetry operation is an act of doing something to the system, which remains apparently unchanged, *e.g.*, after changing positions of identical parts of the system. The more the system, *e.g.* a molecule, has symmetry operations the higher is its symmetry. Usual **symmetry operations are rotation, translation, reflection and inversion**, which happen with respect to a **symmetry element (axis, direction, plane or point)**.

The symmetry operations of molecules and atoms form sc. **point groups** (pisteryhmä), which do not include **translations** as do the more general **space groups** (avaruusryhmä).

Symmetry operations of point groups always leave one point (center of the molecule) unchanged.

Point groups incorporate **five different operations**:

E, **identity** or unit operator (yksikkö- tai ykkösoperaattori), which does nothing.

C_n , **n-fold rotation** (n-lukuinen rotaatio) is a rotation by an angle $360^\circ/n$ wrt. **symmetry axis**. The clockwise (seen from below) rotation is C_n^+ and counterclockwise C_n^- . Note, that $C_2^+ = C_2^-$. If the object has several rotation axes, the one with largest value of n is called **principal axis** (pääakseli).

σ , **reflection** (heijastus) wrt *mirror plane* (heijastustaso). If the principal axis is in the plane, it is called **vertical plane** and the operation is denoted by σ_v , and if it is perpendicular to the plane, it is called **horizontal plane** and the operation is σ_h . **Dihedral plane** σ_d (and reflection) is a special case of vertical reflection plane, where it bisects the angle between two C_2 -axes, which are perpendicular to the principal axis.

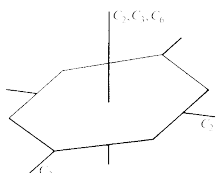
i , **inversion** (inversio) wrt **center of symmetry**. In inversion wrt origin each point of the object at (x, y, z) becomes projected to the opposite side with same distance, *i.e.* to $(-x, -y, -z)$.

S_n , **improper rotation** or rotary–reflection (kiertoheijastus) wrt rotation axis. Improper rotation is a composite operation consisting of an n -fold rotation and horizontal reflection. Note that $S_1 = \sigma_h$ and $S_2 = i$.

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Fig. 5.3.



5.2. Classification of molecules

The list of all symmetry operations of a molecule defines its point group. Molecules with the same point group have several common properties. This is an incomplete list of most important symmetry operations:

C_1 contains only identity E or 1 .

C_s : E and one reflection σ or m .

C_i : E and inversion i or $1.$

C_n : E and n -fold rotation C_n or n .

C_{nv} : E , C_n and n vertical reflections σ_v .

C_{nh} : E , C_n and σ_h .

D_n : E , C_n and n two-fold rotations C_2 perpendicular to C_n .

D_{nh} : All operations in group D_n added by σ_h .

D_{nd} : All operations in group D_n and n reflections σ_d .

S_n : E and S_n . Note, for odd n $S_n = C_{nh}$.

Note that some combinations of symmetry operations produce new ones, *e.g.*, point group C_{2h} has inversion $i = \sigma_h C_2$.

Groups T and O are sc. cubic point groups without principal axis. They contain several axes of highest n , similarly as the icosahedral group I .

T : E , 3 C_2 , 4 C_3 and 4 C_3' .

T_d : " T " + 6 σ_d and 6 S_4
(group of regular tetrahedron).

T_h : $T_d + i$ (inversion).

O : E , 8 C_3 , 3 $C_2 = 3 C_4^2$,
6 C_2' and 6 C_4 .

O_h : O + reflections of octahedron
(group of regular octahedron).

I : Group of icosahedron.

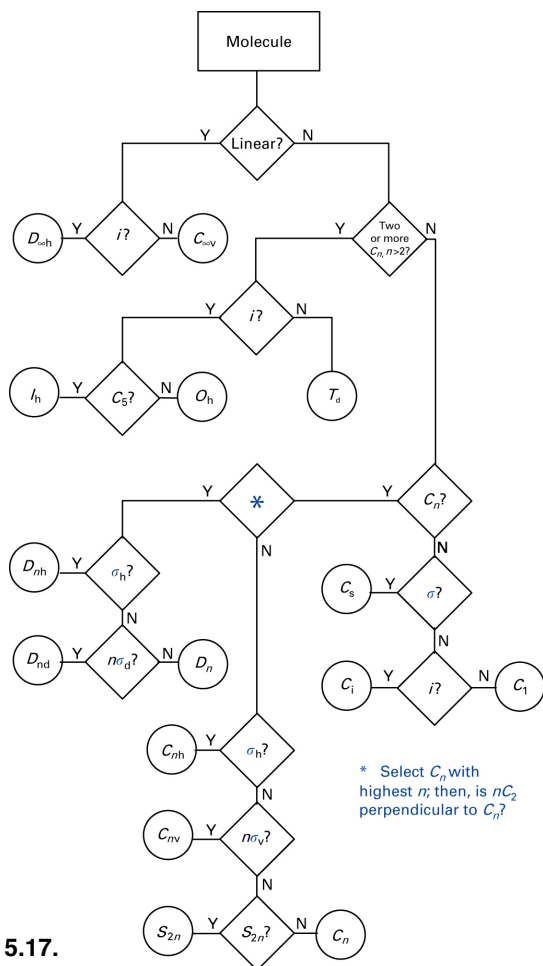


Fig. 5.17.

$n =$	2	3	4	5	6	∞
C_n						
D_n						
C_{nv}						
C_{nh}						
D_{nh}						
D_{nd}						
S_{2n}						

Fig. 5.18.

Above, we have used sc. *Schoenflies* notation/names for the point groups. There is another notation, which lists the symmetry elements, which is sc. *Herman-Mauguin* or International notation, in this table:

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The point group of atoms is R_3 , the point group of the sphere, the full spherical symmetry. Naturally, none of the molecules belong to this point group. Properties of R_3 are the ones of angular momentum.



Calculus of symmetry

5.3. Definition of group

A set of *elements* with "multiplication"

$$RS = T,$$

where, R, S and T belong to this set, form a group, if

- (1) identity E belongs to this set,
- (2) multiplication is associative, which means that $T(SR) = (TS)R$,
- (3) the "product" of two elements also belongs to this set, and
- (4) each element R has its "inverse" R^{-1} , which also belongs to this set.

Note! The product needs not to be commutative, $TS \neq ST$.

Note!

$$R R^{-1} = R^{-1} R = E.$$

It is easy to inspect and find, that the **symmetry operations of "point groups" form a groups.**

5.4. Group multiplication tables

Consider next the *representation* (esitys) of a point group by matrices, which allows calculation of a "product" $i = \sigma_h C_2$ by the usual rules of matrix multiplication.

Let us first find multiplication table of one specific group, independent of matrices, as an example.

Consider point group C_{3v} as an example. Now, the *symmetry elements* of C_{3v} are rotation axis C_3 and 3 reflection planes σ_v , and *symmetry operations* are E, C_3^+ , C_3^- , σ_v , σ_v' and σ_v'' . Number of elements in the group is 6, which is called *order of the group*, h.

The multiplication table is (shown as R = ST)

Table 5.2.

S=\T=	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
E	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
C_3^+	C_3^+	C_3^-	E	σ_v'	σ_v''	σ_v
C_3^-	C_3^-	E	C_3^+	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^-	C_3^+
σ_v'	σ_v'	σ_v	σ_v''	C_3^+	E	C_3^-
σ_v''	σ_v''	σ_v'	σ_v	C_3^-	C_3^+	E

Fig. 5.19.

5.5. Matrix representations

Matrices, which obey this multiplication table can be chosen in many (∞) different ways. The choice is defined by sc. *basis*, which we now choose as shown in the figure. The picture shows, e.g. 1s-orbitals of the atoms in NH_3 molecule.

Fig. 5.23.

Dimension of this basis is 4, i.e. the number of basis functions. The basis can be given as a "vector" $f = (s_N, s_A, s_B, s_C)$, and the effect of symmetry operations can be written as $\sigma_v (s_N, s_A, s_B, s_C) = (s_N, s_A, s_C, s_B)$. This can be written as a matrix multiplication

$$\sigma_v (s_N, s_A, s_B, s_C) = (s_N, s_A, s_B, s_C) \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} = (s_N, s_A, s_C, s_B) \tag{5.3}$$

This matrix is called a *representation* (esitys) of σ_v and it is denoted by $D(\sigma_v)$, whose components can be written as $D_{ji}(\sigma_v)$. One should note, that multiplication by a matrix only means that

$$\sigma_v s_N = s_N, \quad \sigma_v s_A = s_A, \\ \sigma_v s_B = s_C \quad \sigma_v s_C = s_B.$$

Generally for any basis function f_i and operation R, we can write

$$R f_i = \sum_j f_j D_{ji}(R) \tag{5.4}$$

Similarly for C_3^+

$$C_3^+ (s_N, s_A, s_B, s_C) = (s_N, s_A, s_B, s_C) \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} = (s_N, s_B, s_C, s_A) \quad \text{or} \quad C_3^+ f_i = \sum_j f_j D_{ji}(C_3^+),$$

for any f_i . The representations of all operations in group C_{3v} are given in basis (s_N, s_A, s_B, s_C) in the Table 5.3, on next page.

Consider now two consequent operations or "product", e.g. $\sigma_v C_3^+ = \sigma_v''$ with matrices.

$$D(\sigma_v) D(C_3^+) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} = D(\sigma_v'')$$

This means that the "product" of operations can be found by matrix multiplication. In general, if R and S are symmetry operations of a group, then

$$D(R) D(S) = D(RS) \tag{5.5}$$

Table 5.3. Matrix representations of C_{3v} in the basis (s_N, s_A, s_B, s_C) .

$D(E)$	$D(C_3^+)$	$D(C_3^-)$
$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{bmatrix}$
$\chi(E) = 4$	$\chi(C_3^+) = 1$	$\chi(C_3^-) = 1$
	ja	
$D(\sigma_v)$	$D(\sigma_v')$	$D(\sigma_v'')$
$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$
$\chi(\sigma_v) = 2$	$\chi(\sigma_v') = 2$	$\chi(\sigma_v'') = 2$

If the multiplication table of two groups is the same, the groups are called *homomorphic*.

Note, that notations are

$$(RS) f = f D(RS) \\ = f [D(R) D(S)] \\ = [f D(R)] D(S),$$

though

$$(RS) f = R (S f);$$

and

$$D(R^{-1}) = D(R)^{-1} \tag{5.6}$$

5.6. Properties of matrix representations

Let us consider another basis $f' = (s_N, s_1, s_2, s_3)$, which is defined by $f = (s_N, s_A, s_B, s_C)$ such, that $s_1 = s_A + s_B + s_C$, $s_2 = 2s_A - s_B - s_C$ and $s_3 = s_B - s_C$.

The transformation can be written as

$$f'_i = \sum_j f_j c_{ji}$$

or

$$f' = f c, \tag{*}$$

where

$$c = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 2 & 0 \\ 0 & 1 & -1 & 1 \\ 0 & 1 & -1 & -1 \end{bmatrix}$$

Equation (5.4) can be written in compact form

$$R f = f D(R) \tag{**}$$

and correspondingly, in basis f' ,

$$R f' = f' D'(R).$$

With substitution of (*), we get $R f c = f c D'(R)$ and with multiplication from right by c^{-1} , follows $R f = f c D'(R) c^{-1}$. Comparison with (**) allows us to write sc. *similarity transformation*

$$D(R) = c D'(R) c^{-1} \tag{5.7a}$$

and

$$D'(R) = c^{-1} D(R) c. \tag{5.7b}$$

As

$$c^{-1} = \begin{bmatrix} 6 & 0 & 0 & 0 \\ 0 & 2 & 2 & 2 \\ 0 & 2 & -1 & -1 \\ 0 & 0 & 3 & -3 \end{bmatrix} / 6,$$

the matrix representation of C_{3v} in basis f' can be calculated.

Table 5.4. Matrix representation of C_{3v} in basis (s_N, s_1, s_2, s_3) .

$D'(E)$ $\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$ $\chi(E) = 4$	$D'(C_3^+)$ $\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1/2 & -1/2 \\ 0 & 0 & 3/2 & -1/2 \end{bmatrix}$ $\chi(C_3^+) = 1$	$D'(C_3^-)$ $\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1/2 & 1/2 \\ 0 & 0 & -3/2 & -1/2 \end{bmatrix}$ $\chi(C_3^-) = 1$
ja		
$D'(\sigma_v)$ $\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$ $\chi(\sigma_v) = 2$	$D'(\sigma'_v)$ $\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1/2 & 1/2 \\ 0 & 0 & 3/2 & 1/2 \end{bmatrix}$ $\chi(\sigma'_v) = 2$	$D'(\sigma''_v)$ $\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1/2 & -1/2 \\ 0 & 0 & -3/2 & 1/2 \end{bmatrix}$ $\chi(\sigma''_v) = 2$

In Tables 5.3 and 5.4 it is also given the *trace* (jälki, German Spur) of the matrices, which is the **sum of diagonal elements**. Compare!

5.7. Characters of representations

The trace of the matrix (sum of the diagonal elements) is its *character* (karakteeri)

$$\chi(\mathbf{R}) = \sum_i D_{ii}(\mathbf{R}) = \text{Tr } \mathbf{D}(\mathbf{R}). \tag{5.8}$$

We note, that the characters of symmetry operations remain in similarity transformations. This is easy to generalise, because

$$\text{Tr } \mathbf{ABC} = \text{Tr } \mathbf{BCA} = \text{Tr } \mathbf{CAB}. \tag{5.9}$$

Thus, in general

$$\chi(\mathbf{R}) = \chi'(\mathbf{R}).$$

5.8. Characters and classes

In addition we note, that **different types of operations have different and similar ones have the same characters**. Now, for C_{3v} we have: $\chi(\mathbf{E}) = 4$, $\chi(\text{rotation}) = 1$ and $\chi(\text{reflection}) = 2$. Thus, we see that the character characterizes or classifies the elements of the group, and therefore, we define the concept *class* (luokka):

The elements R_1 and R_2 belong to the same class, if such element S belongs to the group, that

$$R_1 = S^{-1} R_2 S. \tag{5.10}$$

However, depending on the representation it may accidentally happen that operations belonging to different classes have the same character. As an example, consider the one dimensional representation consisting of 1×1 matrices [1], only.

5.9. Irreducible representations

If the matrix representation of the group is or can be transformed to *block-diagonal form*, like the matrices in Table 5.3, the representation can be *reduced* to two (or more) representations. Thus, the 4-dimensional representation in Table 5.3 can be reduced to 1- and 3-dimensional representations, as $\mathbb{D}^{(4)} = \mathbb{D}^{(1)} \oplus \mathbb{D}^{(3)}$, (direct sum). The 1-dimensional representation consists of six 1×1 matrices [1], which obey the multiplication table of C_{3v} , Table 5.2.

After transformation to another basis the reduction can be continued, as seen in Table 5.4. We obtain $\mathbb{D}^{(4)} = 2 \mathbb{D}^{(1)} \oplus \mathbb{D}^{(2)}$. The reduction can not be continued further, and therefore, these are the *irreducible representations* of the point group C_{3v} (redusoitumaton esitys). From now on let us use a short form "*irrep*".

Let us make a look at the basis sets of irreps. We see that the functions s_N and s_1 have the same *symmetry species* (symmetrialaji) in group C_{3v} and they *span* (virittää) or form the bases for the two 1-dimensional irreps. Functions s_2 and s_3 are of different symmetry (species) and span the 2-dim irrep.

Thus, we learn that "different" basis functions span different irreps, and therefore, **irreps can be used to "describe symmetry properties"**.

Let us name the irreps or symmetry species. The 1-dim irrep with characters (1, 1, 1, 1, 1, 1) is called Γ_1 and 2-dim irrep with characters (2, -1, -1, 0, 0, 0) is called Γ_3 . The more usual notations for these are A_1 and E . Note that incidentally the identity operation is denoted by E , too.

Figs. 5.24.

5.10. Orthogonality theorems

For **irreducible representations** we have the **great orthogonality theorem (GOT)**:

$$\sum_{\mathbf{R}} D_{ij}^{(\ell)}(\mathbf{R})^* D_{i'j'}^{(\ell')}(\mathbf{R}) = \frac{h}{d_\ell} \delta_{\ell\ell'} \delta_{ii'} \delta_{jj'}, \tag{5.12}$$

where h is the *order of the group*, ℓ refers to the irrep Γ_ℓ and d_ℓ is the *dimension of the irrep*.

For **irreps** we also have the **little orthogonality theorem (LOT)**:

$$\sum_{\mathbf{R}} \chi^{(\ell)}(\mathbf{R})^* \chi^{(\ell')}(\mathbf{R}) = h \delta_{\ell\ell'}, \quad \text{or} \quad \sum_c g(c) \chi^{(\ell)}(c)^* \chi^{(\ell')}(c) = h \delta_{\ell\ell'}, \tag{5.13, 5.14}$$

where c refers to the classes and $g(c)$ is the number of symmetry operations in class c .

The GOT implies that

number of symmetry species = number classes

and

$$\sum_\ell d_\ell^2 = h. \tag{5.18}$$

Consider C_{3v} , which consists 3 classes. Then we have 3 symmetry species (and irreps), of which we know two, Γ_1 and Γ_3 or A_1 and E , already. Let us name the third one as Γ_2 or A_2 . Now, with (5.18) we can write $1^2 + d_2^2 + 2^2 = 6$, which gives $d_2 = 1$. By using the LOT (5.14) we can now fill the missing row in the *character table* of C_{3v} , Table 5.5.

Table 5.5.
Character table of group C_{3v} .

C_{3v} ,	E	2 C_3	3 σ_v
A_1	1	1	1
A_2			
E	2	-1	0

Note! Also the columns are orthogonal to each other.

Reduced representations

Let us find out how to identify the symmetry species, which are spanned by a given basis.

5.11.Reduction of representations

To identify the irreps, which the basis functions span, we need to reduce the matrix rep

$$\mathbb{D}(\mathbf{R}) = \sum_\ell a_\ell \mathbb{D}^{(\ell)}(\mathbf{R}), \tag{5.19}$$

corresponding the symmetry elements Γ_ℓ

$$\Gamma = \sum_\ell a_\ell \Gamma_\ell. \tag{5.20}$$

E.g., for the basis (s_N, s_A, s_B, s_C) and C_{3v} group we found $\Gamma = 2 A_1 + E$.

Thus, in general, we need to find the "reduction coefficients" a_ℓ .

Similarity transformation preserves the trace of matrices, and therefore,

$$\chi(\mathbf{R}) = \sum_\ell a_\ell \chi^{(\ell)}(\mathbf{R}), \tag{5.21}$$

which together with the LOT implies

$$a_\ell = \frac{1}{h} \sum_{\mathbf{R}} \chi^{(\ell)}(\mathbf{R})^* \chi(\mathbf{R}) \tag{5.22}$$

and/or

$$a_\ell = \frac{1}{h} \sum_c g(c) \chi^{(\ell)}(c)^* \chi(c). \tag{5.23}$$

Often, for finding the symmetry species it is sufficient to inspect the character tables, only.



Example 5.8. What symmetry species do the s-orbitals of atoms in CH₄ molecule span?

	<i>E</i>	8 <i>C</i> ₃	3 <i>C</i> ₂	6 <i>S</i> ₄	6σ _d
A ₁	1	1	1	1	1
A ₂	1	1	1	-1	-1
E	2	-1	2	0	0
T ₁	3	0	-1	1	-1
T ₂	3	0	-1	-1	1

5.12. Symmetry-adapted bases

Next, a method is described for projecting out from a given basis f a new one sc. *symmetry-adapted basis* f' , which spans the irreps of given symmetry species.

A *projection operator*

$$P_{ij}^{(\ell)} = \frac{d_\ell}{h} \sum_R D_{ij}^{(\ell)}(R)^* R \tag{5.24}$$

has the property

$$P_{ij}^{(\ell)} f_j^{(\ell)} = f_i^{(\ell)} \delta_{\ell\ell'} \delta_{ij'} \tag{5.25}$$

thus, it projects from the irrep ℓ function $f_j^{(\ell)}$ another function $f_i^{(\ell)}$ belonging to the same irrep.

A *projection operator*

$$P^{(\ell)} = \sum_i P_{ii}^{(\ell)} = \frac{d_\ell}{h} \sum_R \chi^{(\ell)}(R)^* R \tag{5.29-30}$$

has the property

$$P^{(\ell)} f_j = \sum_i f_i^{(\ell)} \tag{5.31}$$

in words, it **projects from function f_j a sum of all functions belonging to ℓ .**

Example 5.9. Construct the symmetry-adapted bases from basis (s_A, s_B, s_C) for group C_{3v} .

Symmetry properties of functions

5.13. Transformation of p-orbitals

Consider the p-orbitals of N in NH_3 molecule as a basis for symmetry species in group C_{3v} . The real p-orbitals are

$$\begin{aligned} p_x &= r \sin\theta \cos\phi f(r) = x f(r), \\ p_y &= r \sin\theta \sin\phi f(r) = y f(r) \quad \text{and} \\ p_z &= r \cos\theta f(r) = z f(r), \end{aligned}$$

where $f(r)$ is the spherically symmetric radial part. Thus, the symmetry properties are the same as those of the basis $\mathbf{f} = (x, y, z)$, whose transformations for the operations in C_{3v} are shown in Fig. 5.28. Thus, we can write, e.g.

$$\sigma_v(x, y, z) = (-x, y, z) = (x, y, z) \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

and

$$C_3^+(x, y, z) = \left(-\frac{1}{2}x + \frac{1}{2}\sqrt{3}y, -\frac{1}{2}\sqrt{3}x - \frac{1}{2}y, z\right) = (x, y, z) \begin{bmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

etc. Representation of group C_{3v} in basis (x, y, z) is given in Table 5.7.

Because the matrices are in block-diagonal form, we see, that z spans the species A_1 and functions (x, y) span the species E . Note, that the sum of characters add up correctly

$$(3, 0, 1) = (1, 1, 1) + (2, -1, 0).$$

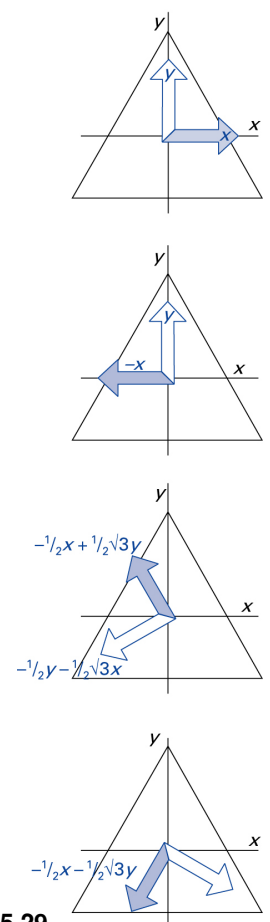


Fig. 5.29.

5.14. Direct-product bases and atomic d-orbitals

A product of two bases with dimensions d_1 and d_2 form a sc. *direct-product basis*, whose dimension is $d = d_1 d_2$. For a direct product of two bases, which span Γ_ℓ and $\Gamma_{\ell'}$, it can be shown that

$$\chi(R) = \chi^{(\ell)}(R) \chi^{(\ell')}(R) \quad (5.32)$$

Direct-product of basis (x, y, z) with itself is $(x, y, z) \times (x, y, z) = (x^2, xy, xz, yx, y^2, yz, zx, zy, z^2)$. Basis (x, y, z) spans species A_1 and E, and its characters are 3, 0 and 1, see Table 5.7. Now, eq. (5.32) implies characters 9, 0 and 1, and by inspecting the character table of C_{3v} we find, that these numbers can be found from the direct-sum $2 A_1 + A_2 + 3 E$, only. Further inspection leads to conclusions, that

$$\begin{aligned} (z) \times (x, y) &= (xz, yz) \quad \rightarrow \quad A_1 \times E = E \\ (x, y) \times (x, y) &= (x^2, xy, yx, y^2) \quad \rightarrow \quad E \times E = A_1 + A_2 + E. \end{aligned}$$

Direct-products of symmetry species are tabulated, Appendix 1. Further analysis shows, that the symmetry-adapted x^2+y^2 spans A_1 , $(x^2-y^2, xy+yx=2xy)$ span E and $(xy-yx=0)$ corresponds A_2 . Also these can be found in tables in Appendix 1.

This is a direct (and easy) way to find atomic d-orbitals $(xy, yz, zx, x^2-y^2, 3z^2-r^2)$ and the symmetry species they span.

Table 5.7

$D(E)$	$D(C_3^+)$	$D(C_3^-)$
$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1/2 & -1/2\sqrt{3} & 0 \\ 1/2\sqrt{3} & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1/2 & 1/2\sqrt{3} & 0 \\ -1/2\sqrt{3} & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$
$\chi(E) = 3$	$\chi(C_3^+) = 0$	$\chi(C_3^-) = 0$
$D(\sigma_v)$	$D(\sigma_v')$	$D(\sigma_v'')$
$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1/2 & -1/2\sqrt{3} & 0 \\ -1/2\sqrt{3} & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1/2 & 1/2\sqrt{3} & 0 \\ 1/2\sqrt{3} & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$
$\chi(\sigma_v) = 1$	$\chi(\sigma_v') = 1$	$\chi(\sigma_v'') = 1$

5.15. Direct-product groups

Consider two groups G and G' of the order h and h', whose only common element is E and whose elements R_i and R_j' commute, for $i = 1, 2, \dots, h$ and $j = 1, 2, \dots, h'$. Symmetry operations $R_i R_j'$ form the direct-product group of groups G and G' and it is denoted by $G'' = G \otimes G'$. For the characters it holds that

$$\chi(RR') = \chi(R) \chi(R'), \quad (5.37)$$

$h'' = hh'$ and similarly for the number of classes: $\#(\text{classes})'' = \#(\text{classes}) \times \#(\text{classes})'$.

Example 5.11. Construct the character table of direct-product group $D_{3h} = C_{3v} \otimes C_s$ using (5.37)

C_{3v} (3m)	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
$C_s=C_h$ (m)	E	σ_h	
A'	1	1	
A''	1	-1	

Similarly for groups $D_{6h} = D_6 \otimes C_i$ and $O_h = O \otimes C_i$.

5.16. Vanishing integrals

Let us consider evaluation of an integral over a range for an odd function $f: f(-x) = -f(x)$ and an even function $g: g(-x) = g(x)$ in range $-a < x < a$. It is easy to see that the integral for the odd function vanishes identically, whereas for the even function it does not, necessarily. However, incidentally the latter one can vanish, as well.

Symmetry analysis of the range $(-a, a)$ leads to the same result, as follows. The symmetry operations are E and σ_h , and thus, it belongs to the group C_s . Functions g and f span symmetry species A' and A'' , in this order. Now, based on the possible symmetry of the integrand, we can conclude, that

an integral of an integrand with certain symmetry over a symmetric range vanishes, except if the symmetry species of the integrand is highest possible, sc. full symmetry, usually A_1 .

This result can be generalized and used in evaluation of matrix elements, *e.g.*, for expectation values and transition probabilities, *etc.* It is often called as "matrix element rule".

Fig. 5.32.

In case the integrand is a product of several functions and/or operators, its symmetry species is found as a direct-product of its factors. If it is other than the highest (usually A_1), the integral vanishes, otherwise not necessarily.

An alternative way of finding the same conclusion can be carried out based on the orthogonality analysis

$$\int_{\tau} f_i^{(\ell)*} f_j^{(\ell')} d\tau \propto \delta_{\ell\ell'} \delta_{ij}. \tag{5.38}$$

Example 5.12. Find those orbitals of N atom in NH_3 molecule, which may have nonzero *overlap integral* (peittointegraali) with the 1s orbitals of H, *i.e.*, s_1, s_2 and s_3 .

5.17. Symmetry and degeneracy

Hamiltonian of a system has to be **invariant** (remain unchanged) in all symmetry operations. Therefore, the **hamiltonian has the full symmetry** and it commutes with all other symmetry operations. This implies, that ψ and $R\psi$ are both eigenfunctions of the Schrödinger equation $H\psi = E\psi$ corresponding to the same eigenenergy E . Thus, **the eigenfunctions of the same symmetry species are degenerate with the same eigenenergy** and all eigenfunctions of that species can be found by using symmetry operators (or projection operators). Therefore, the **degree of degeneration is the dimension of irrep**, $\chi(E)$.

Full rotation group

5.18. Generators of rotations

The point group of heteronuclear diatomic or linear molecule is $C_{\infty v}$ and that of homonuclear diatomic is $D_{\infty h}$. Properties of $C_{\infty v}$ **allows derivation of the properties of the z-component of angular momentum, i.e., operator l_z** . This follows from the fact that rotation by any angle ϕ with respect to a fixed axis is one of the symmetry operations of the group.

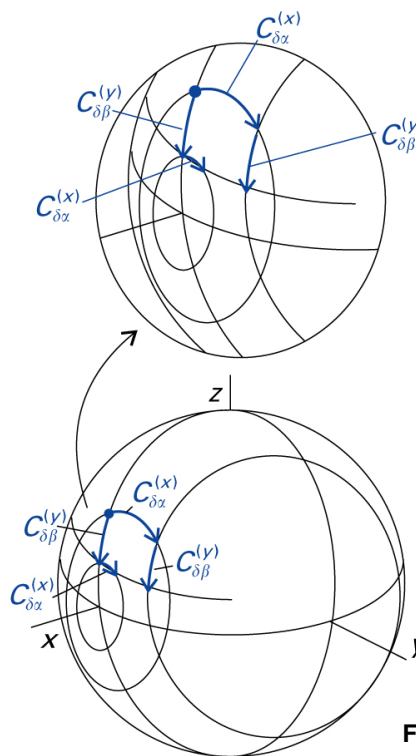


Fig. 5.35.

5.19. Point group of sphere

The point group of spherical atoms is R_3 and it gives the properties of angular momentum l^2 including the commutation rules. Coupling of two angular momenta can be done by reducing the direct-product of species spanned by the irreps of those two.

Writing the representation of rotation $C_a^{(z)}$ in a basis of spherical harmonics $\{Y_{\ell\ell}, Y_{\ell\ell-1}, \dots, Y_{\ell-\ell}\}$ it can be seen that its character is

$$\chi(C_\alpha) = \frac{\sin[(\ell + \frac{1}{2})\alpha]}{\sin[\frac{1}{2}\alpha]} \tag{5.47b}$$

6. Perturbation theory and variation theorem

In practical calculations, after possibly utilizing group theory, **approximate methods are needed for finding the numerical values.** Next, we will consider the two most applied ones: *perturbation theory* and *variation theorem*, and later, also the iteration algorithm.

Semiclassical WKB approximation

Let us start from the total energy in classical mechanics, $E = p^2/2m + V$, and one-dimensional time-independent S-equation

$$\hbar^2 \frac{d^2\psi}{dx^2} + p^2\psi = 0, \tag{6.1a}$$

where now

$$p(x) = \{2m [E - V(x)]\}^{1/2}. \tag{6.1b}$$

For a free particle $V(x) = \text{constant}$, and then, the solutions to (6.1) are trivially

$$\psi_{\pm}(x) = \exp(\pm ikx) = \exp(\pm ipx/\hbar).$$

For a slowly varying potential function $V(x)$ we now try a solution

$$\psi(x) = c_+ \psi_+(x) + c_- \psi_-(x). \tag{6.2}$$

This is sc. *Wentzel–Kramers–Brillouin (WKB) approximation.*

Next, let us make a substitution

$$\pm px = S_{\pm}(x) = S_{\pm}^{(0)} + \hbar S_{\pm}^{(1)}(x).$$

This leads to a solution (see the text book)

$$\psi(x) = \left(\frac{1}{p(x)}\right)^{1/2} \left\{ c_+ \exp\left[\frac{i}{\hbar} \int_0^x p(x) dx\right] + c_- \exp\left[-\frac{i}{\hbar} \int_0^x p(x) dx\right] \right\} \tag{6.5b}$$

The probability density of $\psi(x)$ in Eq. (6.5b) is proportional to $1/p$. This is the same as the "classical probability density" $1/v$.

For the classically allowed region, $E > V$, where p is real, the solution (6.5b) takes the form

$$\psi(x) = \frac{C}{p^{1/2}(x)} \sin\left\{\frac{1}{\hbar} \int_0^x p(x) dx + \delta\right\}, \tag{6.6}$$

where $C \sin \delta = (c_+ + c_-)$. In this region WKB approximation is good, see the Fig. 6.1.

At $E = V$ WKB diverges at $p = 0$, and in classically forbidden region p is imaginary. In the latter case the solution to (6.5) is a linear combination of exponentially decaying and exponentially growing functions.

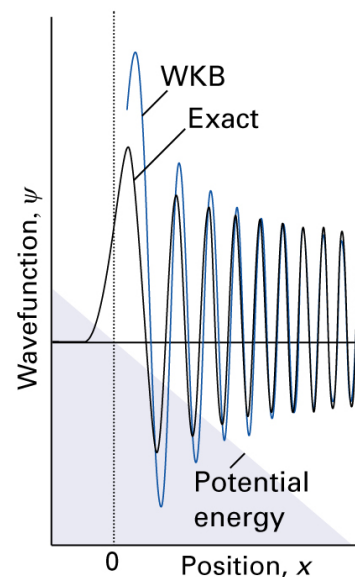


Fig. 6.1.

Time-independent perturbation theory

Consider a system, whose hamiltonian H is almost the same as the one of the known "reference system" $H^{(0)}$. Let us denote the deviation or **perturbation as $H^{(1)}$** . Thus,

$$H = H^{(0)} + H^{(1)}. \tag{6.10}$$

Here we assume that both of the hamiltonians are time-independent.

6.1. Perturbation of two-level system

Assume we know solutions of the reference system, i.e., solutions to the equation

$$H^{(0)} \psi^{(0)}_m = E^{(0)}_m \psi^{(0)}_m. \tag{6.11a}$$

Let us further assume a reference system of two states, only: $\psi^{(0)}_m$; $m = 1, 2$; in bracket notation, normalized levels $|1\rangle$ and $|2\rangle$. Now, we search for solutions of the perturbed system

$$H \psi = E \psi \tag{6.11b}$$

by using a trial wave function

$$\psi = a_1 \psi^{(0)}_1 + a_2 \psi^{(0)}_2 = a_1 |1\rangle + a_2 |2\rangle. \tag{6.12}$$

Thus, we need to find a_1 and a_2 .

Substitution of (6.12) to (6.11b) gives

$$H (a_1 |1\rangle + a_2 |2\rangle) = E (a_1 |1\rangle + a_2 |2\rangle)$$

and multiplication by both $\langle 1|$ and $\langle 2|$ gives

$$\begin{aligned} a_1 \langle 1|H|1\rangle + a_2 \langle 1|H|2\rangle &= E a_1 & a_1 H_{11} + a_2 H_{12} &= E a_1 \\ a_1 \langle 2|H|1\rangle + a_2 \langle 2|H|2\rangle &= E a_2 & a_1 H_{21} + a_2 H_{22} &= E a_2 \end{aligned} \quad \text{or}$$

as $\langle ij| = \delta_{ij}$. This is a pair of coupled equations for the unknown factors a_1 and a_2

$$\begin{aligned} (H_{11}-E) a_1 + H_{12} a_2 &= 0 \\ H_{21} a_1 + (H_{22}-E) a_2 &= 0, \end{aligned} \tag{6.13}$$

which has **non-trivial solutions only if**

$$\begin{vmatrix} H_{11}-E & H_{12} \\ H_{21} & H_{22}-E \end{vmatrix} = 0. \tag{6.14a}$$

This implies, that

$$(H_{11}-E) (H_{22}-E) - H_{12} H_{21} = 0, \tag{6.14b}$$

with solutions

$$E_{\pm} = 1/2 (H_{11}+H_{22}) \pm 1/2 \{ (H_{22}-H_{11})^2 + 4 H_{12} H_{21} \}^{1/2}. \tag{6.14c}$$

Now, consider a **special case**, where $H_{mm} = H^{(0)}_{mm} + H^{(1)}_{mm} = H^{(0)}_{mm} = E^{(0)}_m$, **i.e., $H^{(1)}_{mm} = 0$** . As for the nondiagonals we have $H_{12} = H^{(0)}_{12} + H^{(1)}_{12} = H^{(1)}_{12}$ and similarly $H_{21} = H^{(1)}_{21}$, it follows

$$E_{\pm} = 1/2 (E^{(0)}_1+E^{(0)}_2) \pm 1/2 \{ (E^{(0)}_2-E^{(0)}_1)^2 + 4 \epsilon^2 \}^{1/2}, \tag{6.15}$$

where $\epsilon^2 = H^{(1)}_{12} H^{(1)}_{21}$. Furthermore, $\epsilon^2 = |H^{(1)}_{12}|^2$, because H is hermitian.

Fig 6.4 shows how the "perturbation" ϵ and $\Delta E = E^{(0)}_2 - E^{(0)}_1$ cause increasing separation of the levels $E^{(0)}_1$ and $E^{(0)}_2$.

If $\epsilon/\Delta E \ll 1$, by using $(1+x)^{1/2} \approx 1 + 1/2 x$, where $x \ll 1$, we obtain

$$E_+ \approx E^{(0)}_2 + \epsilon^2/\Delta E^{(0)} \quad (6.16)$$

and $E_- \approx E^{(0)}_1 - \epsilon^2/\Delta E^{(0)}$.

Let us find wave functions by using trial functions (6.17a)

$$\psi_- = \cos\beta \psi^{(0)}_1 + \sin\beta \psi^{(0)}_2 \quad \text{and} \quad \psi_+ = -\sin\beta \psi^{(0)}_1 + \cos\beta \psi^{(0)}_2.$$

These are "already orthonormalized", if $|1\rangle = \psi_1$ and $|2\rangle = \psi_2$ are, because $\langle + | + \rangle = \langle - | - \rangle = \sin^2\beta + \cos^2\beta = 1$ and $\langle + | - \rangle = \sin\beta \cos\beta - \sin\beta \cos\beta = 0$. Let us find β by substituting $| - \rangle = \psi_-$ into the Schrödinger equation and using the orthogonality condition Figs. 6.3 and 6.4.

$$0 = \langle + | H | - \rangle = -\sin\beta \cos\beta H_{11} + \cos^2\beta H_{12} - \sin^2\beta H_{21} + \sin\beta \cos\beta H_{22},$$

which implies $(E^{(0)}_1 - E^{(0)}_2) \sin\beta \cos\beta = \cos^2\beta H^{(1)}_{12} - \sin^2\beta H^{(1)}_{21}$. If $H^{(1)}_{12} = H^{(1)}_{21}$, it follows

$$\tan 2\beta = 2 |H^{(1)}_{12}| / (E^{(0)}_2 - E^{(0)}_1). \quad (6.17b)$$

In case of degeneracy, $(E^{(0)}_1 - E^{(0)}_2) = 0$, this leads to $\tan 2\beta = \infty$ or $\sin\beta = \cos\beta = 1/\sqrt{2}$ and

$$\psi_- = 1/\sqrt{2} (\psi_1 + \psi_2) \quad \text{and} \quad \psi_+ = 1/\sqrt{2} (-\psi_1 + \psi_2).$$

In case of small perturbation, $H^{(1)}_{12} / \Delta E \ll 1$, we have $\tan 2\beta = 2 H^{(1)}_{12} / (E_2 - E_1) \approx 2 \beta \ll 1$, and $\sin\beta \approx \beta$ and $\cos\beta \approx 1$. Thus,

$$\psi_- \approx \psi^{(0)}_1 + (H^{(1)}_{12} / \Delta E^{(0)}) \psi^{(0)}_2 \quad \text{and} \quad \psi_+ \approx \psi^{(0)}_2 - (H^{(1)}_{12} / \Delta E^{(0)}) \psi^{(0)}_1. \quad (6.18)$$

6.2. Many-level systems

Consider a general case, where the (unperturbed) reference system is

$$H^{(0)} |n\rangle = E_n^{(0)} |n\rangle; n = 0, 1, \dots \quad (6.19)$$

and number of states is not restricted, but we assume the states are **not degenerate**. Now, we write

$$H = H^{(0)} + H^{(1)} + H^{(2)} + \dots$$

Let us define λ (strength of perturbation) to keep track of the order of perturbation, as

$$H = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \dots \quad (6.20a)$$

At the end we set $\lambda = 1$. Similarly, we write the wave function

$$\psi = \psi_0^{(0)} + \lambda \psi_0^{(1)} + \lambda^2 \psi_0^{(2)} + \dots \quad (6.20b)$$

and eigenenergy

$$E_0 = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \dots \quad (6.20c)$$

Substitution to

$$H \psi = E \psi$$

gives

$$\lambda^0 \{ H^{(0)} \psi_0^{(0)} - E_0^{(0)} \psi_0^{(0)} \} + \lambda \{ H^{(0)} \psi_0^{(1)} + H^{(1)} \psi_0^{(0)} - E_0^{(0)} \psi_0^{(1)} - E_0^{(1)} \psi_0^{(0)} \} + \lambda^2 \{ H^{(0)} \psi_0^{(2)} + H^{(1)} \psi_0^{(1)} + H^{(2)} \psi_0^{(0)} - E_0^{(0)} \psi_0^{(2)} - E_0^{(1)} \psi_0^{(1)} - E_0^{(2)} \psi_0^{(0)} \} + \dots = 0.$$

Considering λ as arbitrary, each of the orders must vanish separately, and thus,

$$H^{(0)} \psi_0^{(0)} = E_0^{(0)} \psi_0^{(0)} \quad (6.21a)$$

$$(H^{(0)} - E_0^{(0)}) \psi_0^{(1)} = (E_0^{(1)} - H^{(1)}) \psi_0^{(0)} \quad (6.21b)$$

$$(H^{(0)} - E_0^{(0)}) \psi_0^{(2)} = (E_0^{(2)} - H^{(2)}) \psi_0^{(0)} + (E_0^{(1)} - H^{(1)}) \psi_0^{(1)}. \quad (6.21c)$$

The first order correction to energy

Eq. (6.21a) is simply for the ground state ($n = 0$) of Eq. (6.19). Note that similar expansions are valid for other states ($n > 0$), as well.

Let us search for the first order correction to the ground state $\psi_0^{(0)}$ with a trial expansion

$$\psi_0^{(1)} = \sum_n a_n \psi_n^{(0)} = \sum_n a_n |n\rangle, \tag{6.22}$$

substituted to (6.21b). This gives

$$\sum_n a_n (E_n^{(0)} - E_0^{(0)}) |n\rangle = (E_0^{(1)} - H^{(1)}) |0\rangle \tag{6.23}$$

Multiplying by $\langle 0|$ from the left we obtain $0 = E_0^{(1)} - \langle 0|H^{(1)}|0\rangle$, which gives the **first order correction to the energy**

$$E_0^{(1)} = \langle 0|H^{(1)}|0\rangle. \tag{6.24}$$

The first order correction to wavefunction

Multiplying (6.23) from the left by $\langle k|$, for $k \neq 0$, we get

$$a_k (E_k^{(0)} - E_0^{(0)}) = -H^{(1)}_{k0}$$

and

$$a_k = H^{(1)}_{k0} / (E_0^{(0)} - E_k^{(0)}). \tag{6.26}$$

Thus, the **first order wavefunction** is

$$\psi_0 = \psi_0^{(0)} + \psi_0^{(1)} = \psi_0^{(0)} + \sum_{k \neq 0} \{ H^{(1)}_{k0} / (E_0^{(0)} - E_k^{(0)}) \} \psi_k^{(0)}. \tag{6.27}$$

The second order correction to energy

Let us use the same technique for finding the second order correction to the energy, So,

$$\psi^{(2)}_0 = \sum_n b_n \psi_n^{(0)} = \sum_n b_n |n\rangle, \tag{6.28}$$

which we substitute into (6.21c). Similarly as above, we get for the **second order correction**

$$E_0^{(2)} = H_{00}^{(2)} + \sum_n' \left(\frac{H_{0n}^{(1)} H_{n0}^{(1)}}{E_0 - E_n} \right). \tag{6.30}$$

6.3. Comments on perturbation expressions

It can be shown, that the wavefunction of order n is sufficient to give the energy of order $2n+1$.

The main factor effecting on the convergence of the PT expansion **is the strength of the perturbation**. Another significant factor is the possible disappearance of matrix elements

$$H^{(1)}_{0n} = \langle 0|H^{(1)}|n\rangle \tag{6.31}$$

because of symmetry, *i.e.*, as "vanishing integrals".

The closure approximation

In case the denominator in (6.30) can be approximated as $E_0 - E_n \approx -\Delta E$,

$$E_0^{(2)} \approx H_{00}^{(2)} - \{ \sum_n H_{0n}^{(1)} H_{n0}^{(1)} - H_{00}^{(1)} H_{00}^{(1)} \} / \Delta E \tag{6.32}$$

and denoting the numerator as

$$\epsilon^2 = \langle 0 | H^{(1)2} | 0 \rangle - \langle 0 | H^{(1)} | 0 \rangle^2, \tag{6.33a}$$

we can write

$$E_0^{(2)} \approx H_{00}^{(2)} - \epsilon^2 / \Delta E. \tag{6.33b}$$

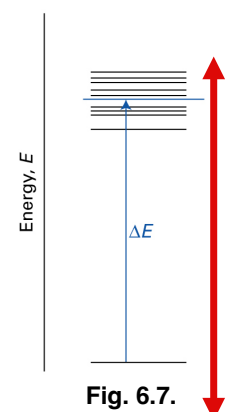


Fig. 6.7.

6.4. Perturbation theory for degenerate states

The above perturbation theory does not apply for degenerate states, because of divergent denominators in the expressions of wavefunctions and energies. A modification is needed.

Consider **r-fold degenerate eigenenergy** E_0 from the reference system equation

$$H^{(0)} |0, \ell\rangle = E^{(0)}_0 |0, \ell\rangle; \ell = 1, 2, \dots, r \tag{6.35}$$

where $|0, \ell\rangle$ are the linearly independent states. And as before, we have $H = H^{(0)} + H^{(1)}$.

It is useful to choose such linear combinations of $|0, \ell\rangle$ which fit to the symmetry of the perturbation. Therefore, we write

$$\varphi^{(0)}_{0i} = \sum_{\ell} d_{\ell i} |0, \ell\rangle = \sum_{\ell} d_{\ell i} \psi^{(0)}_{\ell i} \tag{6.36}$$

which should diagonalize $H^{(1)}$, i.e., $\langle \varphi^{(0)}_{0i} | H^{(1)} | \varphi^{(0)}_{0j} \rangle = 0$, if $i \neq j$. Now, let us find the coefficients $d_{\ell i}$ doing that.

As before, we start with

$$\varphi_i = \psi^{(0)}_{0i} + \lambda \psi^{(1)}_{0i} + \dots$$

and

$$E_i = E^{(0)}_{0i} + \lambda E^{(1)}_{0i} + \dots,$$

substitute these into $H \psi_i = E_i \psi_i$ and obtain

$$H^{(0)} \varphi^{(0)}_{0i} = E^{(0)}_0 \varphi^{(0)}_{0i} \tag{6.37a}$$

$$(H^{(0)} - E^{(0)}_0) \psi^{(1)}_{0i} = (E^{(1)}_{0i} - H^{(1)}) \varphi^{(0)}_{0i}, \tag{6.37b}$$

as Eqs. (6.21) above.

Now, let us write the first order correction as

$$\psi^{(1)}_{0i} = \sum_{\ell} c_{\ell} \psi^{(0)}_{0\ell} + \sum_{n \neq 0} c_n \psi^{(0)}_n \tag{6.38}$$

where the former sum is over the degenerate states $\psi^{(0)}_{0\ell}$ and the latter is over all others. With notation $\psi^{(0)}_{\ell} = |0 \ell\rangle$ and substitution with Eq. (6.36) $\varphi^{(0)}_{0i} = \sum_r d_{\ell i} |0, \ell\rangle$ into (6.37b) we get

$$\sum_{\ell} c_{\ell} (E^{(0)}_0 - E^{(0)}_0) |0 \ell\rangle + \sum_{n \neq 0} c_n (E^{(0)}_n - E^{(0)}_0) |n\rangle = \sum_{\ell} d_{\ell i} (E^{(1)}_{0i} - H^{(1)}) |0 \ell\rangle. \tag{6.39a}$$

Multiplying this from left by $\langle 0 k |$, which is one (possibly linear combination) of functions $\langle 0 \ell |$ such that $\langle 0 k | n \rangle = 0$ and $\langle 0 k | 0 \ell \rangle = S_{k\ell} \neq 0$, we get sc. **secular equations**

$$0 = \sum_{\ell} d_{\ell i} \{ E^{(1)}_{0i} S_{k\ell} - \langle 0 k | H^{(1)} | 0 \ell \rangle \} \tag{6.39b}$$

or

$$\sum_{\ell} d_{\ell i} (E^{(1)}_{0i} S_{k\ell} - H^{(1)}_{k\ell}) = 0, \tag{6.41}$$

where

$$S_{k\ell} = \langle 0 k | 0 \ell \rangle \tag{6.40a}$$

and

$$H^{(1)}_{k\ell} = \langle 0 k | H^{(1)} | 0 \ell \rangle. \tag{6.40b}$$

This group of equations, $i = 1, 2, \dots, r$; (or matrix equation) for coefficients $d_{\ell i}$ ($\ell = 1, 2, \dots, r$), has nontrivial solutions, if the **secular determinant** vanishes, i.e.,

$$\det [H^{(1)}_{k\ell} - E^{(1)}_{0i} S_{k\ell}]_{i\ell} = 0. \tag{6.42}$$

The first order energy corrections $E^{(1)}_{0i}$ ($i = 1, 2, \dots, r$) are found from matrix diagonalization. The, the coefficients $d_{\ell i}$ corresponding to each $E^{(1)}_{0i}$ are found from Eq. (6.41).

Note, if we choose $S_{k\ell} = \delta_{k\ell}$ and $r = 2$, the Eq. (6.42) returns the earlier two-level case, Eq. (6.14c).

Variation theory

Another approach to find or estimate the solution to the Schrödinger equation is to use a trial wavefunction ψ_{trial} . It can be written by using a proper functional form (educated guess) with parameters, which will be fitted or "optimized" to make ψ_{trial} the best approximate to the exact wavefunction.

6.5. Variation theorem

Define *Rayleigh ratio*

$$\mathcal{E} = \langle \psi_{\text{trial}} | H | \psi_{\text{trial}} \rangle / \langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle. \tag{6.43a}$$

Then, we can use the *variation theorem*

$$\mathcal{E} \geq E_0 \text{ for any } \psi_{\text{trial}}, \tag{6.43b}$$

where E_0 is the ground state energy of the hamiltonian H . **The equality $\mathcal{E} = E_0$ holds only, if the trial function is identical with the exact wavefunction, $\psi_{\text{trial}} = \psi_0$.**

Let us prove the variation theorem by writing $\psi_{\text{trial}} = \sum_n c_n \psi_n = \sum_n c_n |n\rangle$, where $\{\psi_n\}$ is the complete set of solutions to $H \psi_n = E_n \psi_n$. Because

$$\begin{aligned} \langle \psi_{\text{trial}} | (H - E_0) | \psi_{\text{trial}} \rangle &= \sum_{n,m} c_n^* c_m \langle n | (H - E_0) | m \rangle \\ &= \sum_{n,m} c_n^* c_m (E_m - E_0) \langle n | m \rangle = \sum_n |c_n|^2 (E_n - E_0) \geq 0, \end{aligned}$$

we obtain $\langle \psi_{\text{trial}} | H | \psi_{\text{trial}} \rangle \geq E_0 \langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle$, which proves the theorem.

Optimization of the parameters $\{p_n\}$ is done the "usual way" from the conditions

$$(\partial \mathcal{E} / \partial p_1) = 0, (\partial \mathcal{E} / \partial p_2) = 0, \dots ;$$

i.e., **from the extremum of the gradient of \mathcal{E} in the parameter space $\{p_n\}$.**

Example 6.8. Use the trial $\psi_{\text{trial}}(r) = e^{-kr}$ for the ground state of hydrogen like one-electron atoms with nuclear charge Ze . Find the parameter k and the corresponding eigenenergy.

$$\int_0^\infty r^n e^{-\alpha r} dr = \frac{n!}{\alpha^{n+1}}$$



6.6. Rayleigh-Ritz method

The *Rayleigh-Ritz method* is based on a trial wavefunction

$$\psi_{\text{trial}} = \sum_i c_i \psi_i = \sum_i c_i |i\rangle, \tag{6.44}$$

where the **parameters c_i are to be optimized**. Functions $\{\psi_i\}_{i=0}^{N-1}$ are called as **basis set**.

Now, the Rayleigh ratio is

$$\mathcal{E} = \langle \psi_{\text{trial}} | H | \psi_{\text{trial}} \rangle / \langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle = \{ \sum_{ij} c_i^* c_j \langle i | H | j \rangle \} / \{ \sum_{ij} c_i^* c_j \langle i | j \rangle \} = \{ \sum_{ij} c_i^* c_j H_{ij} \} / \{ \sum_{ij} c_i^* c_j S_{ij} \}.$$

Allowing real coefficients c_i , only, minimization condition for \mathcal{E} is (6.45)

$$\frac{d\mathcal{E}}{dc_k} = \frac{\left(\sum_j c_j H_{kj} + \sum_i c_i H_{ik} \right) \sum_{ij} c_i c_j S_{ij} - \left(\sum_j c_j S_{kj} + \sum_i c_i S_{ik} \right) \sum_{ij} c_i c_j H_{ij}}{\left(\sum_{ij} c_i c_j S_{ij} \right)^2} =$$

$$= \frac{\sum_j c_j (H_{kj} - E S_{kj}) + \sum_i c_i (H_{ik} - E S_{ik})}{\sum_{ij} c_i c_j S_{ij}} = 0.$$

This implies, that for all k

$$\sum_i c_i (H_{ik} - E S_{ik}) = 0,$$

and thus, non-trivial solutions exist, if

$$\det (H_{ik} - E S_{ik}) = 0. \tag{6.46}$$

This leads to N equations and

N roots, i.e., N eigenenergies \mathcal{E}_i , where N is the number of basis functions in (6.44). The lowest one, \mathcal{E}_0 , is the ground state energy. For all energies the coefficients are obtained from (6.46) and the wavefunction from (6.44).

Hellmann–Feynman theorem

For a system of quantum particles (atoms, molecules, nanostructures) the structure and external interactions are described in the hamiltonian. In the following we inspect **how the total energy of the system is changed, when the hamiltonian is changed**.

Consider hamiltonian with a parameter P (e.g. a bond length or an external field, etc.). Then, both the wavefunction ψ and the energy $E(P) = \langle \psi | H | \psi \rangle$ depend on P. Assume the wavefunction is normalized $\langle \psi | \psi \rangle = 1$. **Now, the change of energy as a function of P is**

$$\begin{aligned} dE/dP &= d/dP \langle \psi | H | \psi \rangle = \langle d\psi/dP | H | \psi \rangle + \langle \psi | dH/dP | \psi \rangle + \langle \psi | H | d\psi/dP \rangle \\ &= E d/dP \langle \psi | \psi \rangle + \langle \psi | dH/dP | \psi \rangle = \langle dH/dP \rangle. \end{aligned}$$

H. Hellmann, *Einführung in die Quantenchemie* (1937).
R.P. Feynman, PR56, 340 (1939).

Thus, we have proved the *Hellmann–Feynman theorem*:

$$\boxed{\frac{dE}{dP} = \left\langle \frac{dH}{dP} \right\rangle}. \tag{6.48}$$

This is a practical method for calculation of forces in molecular dynamics simulations. For practical accuracy, **the wavefunction should be known accurately, enough**.

Example Find the molecular energy as a function of the external electric field \mathcal{E} , when

$$H = H^{(0)} - \mu_z \mathcal{E}$$

Time-dependent perturbation theory

6.7. Time-dependence of two-level system

Time-dependent perturbation theory is needed to consider the system response to **turning the perturbation "on" or "off"**, and also, if the **perturbation operator explicitly depends on time**,

$$H(t) = H^{(0)} + H^{(1)}(t). \quad (6.49)$$

A usual time-dependent perturbation is the electromagnetic field

$$H^{(1)}(t) = H^{(1)} 2 \cos(\omega t). \quad (6.50)$$

Let us find the time-dependent solution $\Psi(t)$ of the Schrödinger equation

$$H \Psi = i\hbar (\partial\Psi/\partial t). \quad (6.51)$$

Let us first restrict us to a two-level system (as we did in sec. 6.1), where the eigenenergies E_1 and E_2 correspond to eigenstates ψ_1 and ψ_2 of the stationary state reference system

$$H^{(0)} \psi_n = E_n \psi_n ; n = 1, 2; \quad \text{with} \quad \Psi_n(t) = \psi_n e^{-iE_n t/\hbar} \quad (6.52)$$

from Eq. (1.38). Let us choose a trial wavefunction

$$\Psi(t) = c_1(t) \Psi_1(t) + c_2(t) \Psi_2(t), \quad (6.53)$$

where also the **coefficients $c_i(t)$ depend on time**. With substitution to (6.51) we obtain

$$c_1 H^{(0)} \Psi_1 + c_1 H^{(1)} \Psi_1 + c_2 H^{(0)} \Psi_2 + c_2 H^{(1)} \Psi_2 = i\hbar (\partial c_1/\partial t \Psi_1 + c_1 \partial \Psi_1/\partial t + \partial c_2/\partial t \Psi_2 + c_2 \partial \Psi_2/\partial t)$$

and by using $H^{(0)} \Psi_n = i\hbar (\partial \Psi_n/\partial t)$

$$\text{we get} \quad c_1 H^{(1)}(t) \Psi_1 + c_2 H^{(1)}(t) \Psi_2 = i\hbar \dot{c}_1 \Psi_1 + i\hbar \dot{c}_2 \Psi_2, \quad (6.54)$$

where we denote $\dot{c} = dc/dt$.

With substitution of (6.52), we get

$$c_1 H^{(1)}(t) \psi_1 e^{-iE_1 t/\hbar} + c_2 H^{(1)}(t) \psi_2 e^{-iE_2 t/\hbar} = i\hbar \dot{c}_1 \psi_1 e^{-iE_1 t/\hbar} + i\hbar \dot{c}_2 \psi_2 e^{-iE_2 t/\hbar}, \quad (6.55a)$$

and further, multiplying by ψ_1^* and integrating ($\int \psi_1^* \psi_2 d\tau = 0$), we get

$$c_1 H^{(1)}_{11}(t) e^{-iE_1 t/\hbar} + c_2 H^{(1)}_{12}(t) e^{-iE_2 t/\hbar} = i\hbar \dot{c}_1 e^{-iE_1 t/\hbar}, \quad (6.55b)$$

where

$$H^{(1)}_{ij}(t) = \int \psi_i^* H^{(1)}(t) \psi_j d\tau = \langle \psi_i | H^{(1)}(t) | \psi_j \rangle.$$

Now, let us write for the difference $E_2 - E_1 = \hbar\omega_{21}$ and **assume that $H^{(1)}_{11}(t) = H^{(1)}_{22}(t) = 0$** , again. This is valid for the usual perturbations, like electromagnetic field. Then, we find

$$\dot{c}_1 = (1/i\hbar) c_2 H^{(1)}_{12}(t) e^{-i\omega_{21}t} \quad (6.57a)$$

and similarly

$$\dot{c}_2 = (1/i\hbar) c_1 H^{(1)}_{21}(t) e^{i\omega_{21}t}. \quad (6.57b)$$

Now, let us discuss two cases:

(i) The perturbation is "off" or absent. Then $\dot{c}_1 = \dot{c}_2 = 0$, $c_1 = c_1(0) = \text{constant}$, $c_2 = c_2(0) = \text{constant}$ and

$$\Psi(t) = c_1(0) \psi_1 e^{-iE_1 t/\hbar} + c_2(0) \psi_2 e^{-iE_2 t/\hbar}. \quad (6.58)$$

Now, $|c_1(0) e^{-iE_1 t/\hbar}|^2 = |c_1(0)|^2$ is a constant, whose **interpretation is the probability that the system occupies the state ψ_1** . The other constant, $|c_2(0)|^2$, is the probability for occupation of the state ψ_2 .

(ii) Assume the perturbation is "on" with a **constant strength**, i.e., $H^{(1)}_{12}(t) = \hbar V$ and $H^{(1)}_{21}(t) = \hbar V^*$ are constants. Then, solution to the pair of equations (6.57)

$$\begin{aligned}\dot{c}_1 &= (1/i\hbar) c_2 H^{(1)}_{12} e^{-i\omega_{21}t} \\ \dot{c}_2 &= (1/i\hbar) c_1 H^{(1)}_{21} e^{i\omega_{21}t}.\end{aligned}$$

will be found from

$$\begin{aligned}\ddot{c}_2 &= (1/i\hbar) \dot{c}_1 H^{(1)}_{21} e^{i\omega_{21}t} + i\omega_{21} (1/i\hbar) c_1 H^{(1)}_{21} e^{i\omega_{21}t} \\ &= (1/i\hbar)^2 c_2 H^{(1)}_{12} H^{(1)}_{21} + i\omega_{21} \dot{c}_2 \\ &= -|V|^2 c_2 + i\omega_{21} \dot{c}_2,\end{aligned}\tag{6.60}$$

with the notation $H^{(1)}_{12} H^{(1)}_{21} = \hbar^2 V^2$. Solution to this is

$$c_2(t) = (A e^{i\Omega t} + B e^{-i\Omega t}) e^{i\omega_{21}t/2}; \quad \Omega = 1/2 (\omega_{21}^2 + 4|V|^2)^{1/2},\tag{6.61}$$

where A and B are given by the initial conditions. Similar expression is found for c_1 , and if the initial conditions are $c_1(0) = 1$ and $c_2(0) = 0$, then

$$c_1(t) = \{ \cos(\Omega t) + i (\omega_{21}/2\Omega) \sin(\Omega t) \} e^{-i\omega_{21}t/2}\tag{6.62}$$

and

$$c_2(t) = -i (|V|/\Omega) \sin(\Omega t) e^{i\omega_{21}t/2}.$$

These are **exact solutions in case of two levels**.

Rabi oscillations

Consider the probabilities of finding the system in state 1 or 2. Let us denote these as P_1 and P_2 . $P_1 + P_2 = 1$, as there are no other states. Thus, $P_2(t) = 1 - P_1(t)$ with the time dependence called **Rabi oscillations**

$$P_2 = |c_2|^2 = \frac{4|V|^2}{\omega_{21}^2 + 4V^2} \sin^2 \frac{(\omega_{21}^2 + 4V^2)^{1/2}}{2} t.\tag{6.63}$$

Now, let us consider two common cases:

(i) A **degenerate system**, where $E_1 = E_2$, and thus, $\omega_{21} = 0$. Then

$$P_2(t) = \sin^2(|V|t),\tag{6.64}$$

shown in Fig. 6.12. We see, that **the larger the perturbation, the faster the oscillation**; but on the other hand, **no matter how weak the perturbation is, it is always sufficient for the "transition"**.

(ii) The other extreme $(E_2 - E_1)/\hbar \gg V$, whence

$$P_2(t) \approx (2|V|/\omega_{21})^2 \sin^2(1/2 \omega_{21}t).\tag{6.65}$$

This is illustrated in Fig. 6.13. Now, we see that **oscillation frequency is given by the level spacing and the amplitude by the perturbation strength with respect to level spacing**. Occupation probability of level 2 is always lower than 1.

6.8. Many-level systems

The order of the differential equations grows together with the number of levels, and therefore, general solutions cannot be found similarly to the two-level case.

For book keeping of the "virtual transitions" between the levels in many-level case, one can use the sc. **Feynman diagrams**.

6.9. Fermi's golden rule

Consider a transition in a many-level system from the initial state E_i to the final state E_f . Denote $E_f - E_i = \hbar\omega_{fi}$. Assume interaction with the electromagnetic radiation

$$H^{(1)}(t) = H^{(1)} 2 \cos \omega t = H^{(1)} (e^{i\omega t} + e^{-i\omega t}). \quad (6.75)$$

Then, it can be shown that occupation probability of the final state f , if i is initially unoccupied, is

$$P_{fi}(t) = \frac{4V_{fi}^2}{(\omega_{fi} - \omega)^2} \sin^2 \frac{\omega_{fi} - \omega}{2} t \quad (6.77)$$

where $V_{fi}^2 = H^{(1)}_{if} H^{(1)}_{fi} / \hbar^2 = V_{if}^2 = V^2$. Compare with the two-level system, Eq. (6.65). We see, that **occupation probability of state f strongly increases while approaching the resonance $\omega_{fi} - \omega = 0$.**

In case of several closely spaced final states we denote the *density of states* (DOS) by $\rho(E_f)$, at about E_f . Then, it can be shown that

$$P_{fi}(t) = 2\pi\hbar V_{fi}^2 \rho(E_f) t \quad (6.82)$$

and by defining the *transition rate* (spectral line intensity) as

$$W_{if} = dP_{fi}/dt, \quad (6.83)$$

we arrive at the *Fermi's golden rule*

$$\underline{W_{if} = 2\pi\hbar V_{fi}^2 \rho(E_f) = 2\pi/\hbar |H^{(1)}_{fi}|^2 \rho(E_f)}. \quad (6.84)$$

6.10. Einstein transition probabilities (A and B coefficients)

Transition probability is proportional also to the intensity of the electromagnetic field $\rho(\nu)$ (number of photons / units of time and space), at the transition frequency. Thus, the rate (or probability) of the *stimulated absorption* can be written as

$$W_{if} = B_{if} \rho, \quad (6.86)$$

where B_{if} is sc. **Einstein B coefficient** for stimulated absorption. Correspondingly, the transition rate (or probability) of *stimulated emission* can be written as

$$W_{fi} = B_{fi} \rho, \quad (6.87)$$

where B_{fi} is sc. **Einstein B coefficient** for stimulated emission. As $|H^{(1)}_{fi}|^2 = |H^{(1)}_{if}|^2$, $B_{if} = B_{fi}$.

In thermal equilibrium the occupation of energy levels obey the **Boltzmann distribution**, *i.e.*, $N_f / N_i = \exp(-h\nu / kT)$. Now, because $W_{if} = W_{fi}$, for an equilibrium, there has to be one more transition mechanism. This is the *spontaneous emission*, for which

$$W_{fi} = A_{fi}. \quad (6.90)$$

In equilibrium $N_i W_{if} = N_f W_{fi}$, whence $N_i B \rho = N_f (B \rho + A)$, where $A = A_{fi}$ and $B = B_{if} = B_{fi}$. From comparison with the Boltzmann distribution we get

$$N_f / N_i = B \rho / (B \rho + A) = \exp(-h\nu/kT),$$

and further

$$\rho = (A/B) / \{\exp(h\nu/kT) - 1\}. \quad (6.92a)$$

Now, comparison with the Planck distribution of black body radiation, Eq. (0.5)

$$\rho(\nu) = (8\pi h\nu^3/c^3) / \{\exp(h\nu/kT) - 1\} \quad (6.92b)$$

gives

$$A/B = 8\pi h(\nu/c)^3. \quad (6.93)$$

Thus, the proportion of spontaneous emission to stimulated emission increases as the cube of transition frequency (or level spacing).

6.11. Lifetime and spectral linewidth (energy uncertainty)

Some unspecified time after excitation, the excited state will decay to some lower state, e.g., the ground state, through spontaneous emission. All such transitions contribute to the *lifetime of the excited state*.

The stationary state with an eigenenergy E , is described by the wavefunction (6.52) $\Psi(t) = \psi e^{-iEt/\hbar}$ and $|\Psi|^2 = |\psi|^2$, but for a decaying state

$$|\Psi|^2 = |\psi|^2 e^{-t/\tau} \quad (6.94)$$

and therefore,

$$\Psi = \psi e^{-iEt/\hbar - t/2\tau} \quad (6.95)$$

where τ is the *lifetime* of the state.

This kind of decaying wavefunction is a superposition of "several" wavefunctions with energies close to E . This superposition wavefunction is

$$e^{-iEt/\hbar - t/2\tau} = \int g(E') e^{-iE't/\hbar} dE', \quad (6.96a)$$

i.e., a Fourier transform of the spectral line (spectral density function)

$$g(E') = \frac{\hbar/\tau}{(E - E')^2 + (\hbar/2\tau)^2}. \quad (6.96b)$$

This is sc. Lorentz line shape of spontaneous emission of photons carrying away the energy of transition, i.e., $\Delta E = E_i - E_f = \hbar\omega_{if}$.

Thus, the function $g(E')$ describes the energy spectrum of contributing frequencies or wavelengths. So, if the state is metastable, its energy is not discrete, but a distribution with Lorentzian shape and a *half width* δE , an *uncertainty of the excited state energy*, broadening of the spectral line.

Fourier analysis gives for the half width $\delta E = \hbar/\tau$.

Thus, it is customary to present this as an "uncertainty relation of time and energy"

$$\tau \delta E \approx \hbar. \quad (6.97)$$

This can be used to determine the lifetimes of quantum states from experimental line widths.