

4. Groups Theory and Quantum Mechanics4.1 Functions as basis for the representation of a group

So far we have considered the action of symmetry operations on the coordinates of points. In analogy we can define the action of the symmetry operation \hat{R} on a function f :

$$\hat{R}f(\vec{r}) = f(\hat{R}^{-1}\vec{r}).$$

Now we can use a set of n functions f_1, f_2, \dots, f_n . The set forms a basis for a representation of the group if the following holds:

$$\hat{R} \begin{pmatrix} f_1 \\ f_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} f_1' \\ f_2' \\ \vdots \end{pmatrix} = \Gamma(R) \begin{pmatrix} f_1 \\ f_2 \\ \vdots \end{pmatrix}$$

$\Gamma(R)$ is a representation of the symmetry group in the n -dimensional basis f_1, f_2, \dots, f_n . We say: f_1, f_2, \dots, f_n span a basis for a n -dimensional representation of the group.

(4.1 Example: effect of symmetry operations on functions and atomic orbitals as basis sets).

4.2 Wave functions as basis for irreducible representations

We are interested in the symmetry properties of a wave function ψ , which is solution of the Schrödinger equation

$$\hat{H}\psi = E\psi.$$

We consider a symmetry operation \hat{R} of the system. As the symmetry operation transform the system into an physically equivalent state, we expect that Hamilton operator \hat{H} should be invariant with respect to the transformation into a new basis:

$$\hat{H} = \hat{R}^{-1}\hat{H}\hat{R} \quad \text{or} \quad \hat{R}\hat{H} = \hat{H}\hat{R},$$

i.e. \hat{H} and \hat{R} commute.

(4.2: Detailed consideration of commutability).

This has important implications for the eigenfunctions of \hat{H} :

- Case 1: non-degenerate eigenfunctions:

Schrödinger equation: $\hat{H}\psi_i = E_i\psi_i$

symmetry operation: $\hat{R}\hat{H}\psi_i = \hat{R}E_i\psi_i$

$$\hat{H}(\hat{R}\psi_i) = E_i(\hat{R}\psi_i)$$

$\hat{R}\psi_i$ is eigenfunction of \hat{H} with eigenvalue E_i . As the system is non-degenerate (by definition), it follows: $\hat{R}\psi_i = \pm\psi_i$, i.e. non-degenerate eigenfunctions of \hat{H} belong to a 1-dimensional irrep of the group.

- Case 2: degenerate eigenfunction:

Schrödinger equation: $\hat{H}\psi_{il} = E_i\psi_{il} \quad \forall \psi_{i,1..k}$

symmetry operation: $\hat{H}(\hat{R}\psi_{il}) = E_i(\hat{R}\psi_{il})$

$\hat{R}\psi_i$ is eigenfunction of \hat{H} with eigenvalue E_i . As the system is k-fold degenerate, $\hat{R}\psi_i$

can be a linear combination of the eigenfunctions $\psi_{i,1..k}$: $\hat{R}\psi_{il} = \sum_{j=1}^k r_{jl}\psi_j$, i.e. a set of k

degenerate eigenfunctions of \hat{H} belongs to a k-dimensional irrep of the group (note: (1) any linear combination of eigenfunctions of degenerate levels is eigenfunction of the system as well; (2) if the representation was reducible, the functions would not have to be transformed into each other. In this case the eigenvalues would not have to be identical as well).

(4.3: Example, 2p orbitals of NH₃).

4.3 Direct product of functions

We assume two sets of functions

$$X_1, X_2, \dots, X_m \quad \text{and} \quad Y_1, Y_2, \dots, Y_n,$$

which form a basis for a representation of the group (for example two sets of wavefunctions).

What is the symmetry of the product functions $X_i Y_j$ (extremely important question, a product function occur often in quantum mechanics)?

We consider the application of symmetry operation \hat{R} :

$$\hat{R}X_i = \sum_{j=1}^m x_{ij} X_j \quad \text{and} \quad \hat{R}Y_i = \sum_{j=1}^n y_{ij} Y_j .$$

Application to product:

$$\hat{R}X_i Y_k = \sum_{j=1}^m x_{ij} X_j \hat{R}Y_k = \sum_{j=1}^m \sum_{l=1}^n \underbrace{x_{ij} y_{lk}}_{z_{ji,kl}} X_j Y_l .$$

$z_{ij,kl}$ is a matrix of dimension $(nm) \times (nm)$.

The functions $X_i Y_j$ with $i = 1, 2, \dots, n; j = 1, 2, \dots, m$ are called the direct product of X_i and Y_j ($X \otimes Y$). They span a basis for a representation of the group of dimension $m \times n$.

For the characters of the direct product we obtain:

$$\chi_z(R) = \sum_{j,l} z_{jl,jl} = \sum_j \sum_l x_{jj} y_{ll} = \chi_x(R) \chi_y(R)$$

i.e. the characters of the representation spanned by the direct product of two sets of functions are the products of the characters of the original representations.

Note: With section 3.13 we can immediately determine, which irreps are contained in the direct product!

4.4 Nonzero matrix elements

Why are direct products do important? In quantum mechanics we are often interested in matrix elements of an operator, e.g. if we would like to determine the expectations value of an observable. These matrix elements are of the type, i.e. they contain direct products of functions (and operators):

$$\int f_A^* f_B d\tau \text{ or } \langle f_A | f_B \rangle$$

$$\int f_A^* \hat{O} f_B d\tau \text{ or } \langle f_A | \hat{O} | f_B \rangle.$$

Such matrix elements can only be nonzero, if the function over which we integrate is completely symmetric or contains a completely symmetric part.

(4.4: Example: integration over odd or even function).

Important: The representation of a direct product contains the totally symmetric representation only if the representations of the product functions are of identical symmetry (or at least contain a part with identical symmetry).

Proof:

We consider two sets of functions $A \otimes B$. The characters of the direct products are χ_{AB} . For an arbitrary irrep of the group i we obtain (compare section 3.13)

$$a_i = \frac{1}{h} \sum_R \chi_i(R) \chi_{AB}(R)$$

for the number of irreps of symmetry type i , contained in $A \otimes B$. For the totally symmetric irrep:

$$a_i = \frac{1}{h} \sum_R \chi_{AB}(R) = \frac{1}{h} \sum_R \chi_A(R) \chi_B(R) = \delta_{AB} \text{ (compare section 3.12)}$$

Consequently, A and B must be of identical symmetry in order to contain the totally symmetric representation.

(4.5: Example: direct products in C_{3v}).

4.5 Examples for matrix elements

4.5.1 Hamilton operator: $\langle A | \hat{H} | B \rangle$

As discussed before, \hat{H} is totally symmetric with respect to the symmetry operations of the system, i.e. $\Gamma_{\hat{H}} = A_1$. Therefore:

$$\Gamma_{\langle f_A | \hat{H} | f_B \rangle} = \Gamma_i \otimes \Gamma_{\hat{H}} \otimes \Gamma_f = \Gamma_i \otimes \Gamma_f$$

Hamilton matrix elements of wave function of different symmetry are zero.

4.5.2 Dipole operator: $\langle A | \hat{\mu} | B \rangle$

Electric dipole operator: $\hat{\mu} = \sum_i q_i x_i + \sum_i q_i y_i + \sum_i q_i z_i$ (q_i, \vec{r}_i : charge, position of particle i)

$$\underbrace{\sum_i q_i x_i}_{\hat{\mu}_x} + \underbrace{\sum_i q_i y_i}_{\hat{\mu}_y} + \underbrace{\sum_i q_i z_i}_{\hat{\mu}_z}$$

The parts of the dipole operator have the symmetry of the functions x, y, z.

Case A: Permanent dipole moment $\langle A | \hat{\mu} | A \rangle$

$$\Gamma_{\hat{\mu}_x} = \Gamma_A \otimes \Gamma_A \otimes \Gamma_x$$

$$\Gamma_{\hat{\mu}_y} = \Gamma_A \otimes \Gamma_A \otimes \Gamma_y$$

$$\Gamma_{\hat{\mu}_z} = \underbrace{\Gamma_A \otimes \Gamma_A}_{\Gamma_A^2} \otimes \Gamma_z$$

A permanent dipole moment exists if the symmetry of x, y or z is contained in Γ_A^2 . Note: Γ_A^2

always contains the totally symmetric representation.

Case B: Transition dipole moment $\langle f | \hat{\mu} | i \rangle$

A nonzero transition dipole moment requires that at least one of the components

$$\Gamma_{\hat{\mu}_x} = \Gamma_i \otimes \Gamma_f \otimes \Gamma_x$$

$$\Gamma_{\hat{\mu}_y} = \Gamma_i \otimes \Gamma_f \otimes \Gamma_y$$

$$\Gamma_{\hat{\mu}_z} = \Gamma_i \otimes \Gamma_f \otimes \Gamma_z$$

contains the totally symmetric representation (IR, VIS, UV spectroscopy).

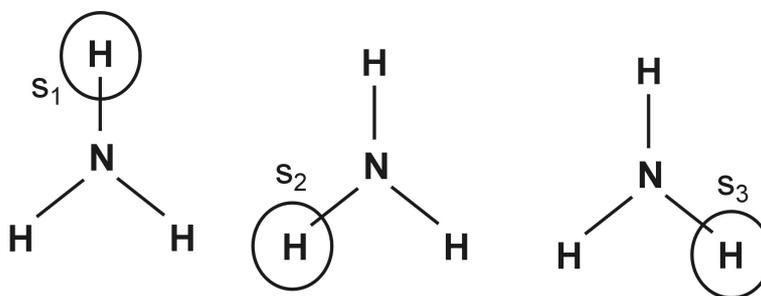
(4.6: Example: permanent dipole moments in ammonia).

4.6 Projection operators

The last section demonstrates that it is useful to construct wavefunctions, which represent a basis for the irreps of the symmetry group. If this is the case, we can easily decide which integrals are zero and which can be nonzero. How are these functions constructed in a general fashion?

Example:

We consider a set of atomic wave functions, i.e. the three 1s function located at the H atoms of a NH_3 molecule:



- (1) These functions span a basis for a three dimensional representation of the group C_{3V} (i.e. the symmetry operations of the group transform the wave functions into linear combinations of each other).
- (2) The representation is reducible (as there are only 1 and 2 dimensional representations in C_{3V}).

We have to perform a transformation to a new basis, which transforms the representation into a set of irreps of C_{3V} (i.e. blockdiagonalizes the transformation matrices). This new symmetry adapted basis is constructed applying a set of projection operators:

We consider a set of l_i functions $\varphi_1^i, \varphi_2^i, \dots, \varphi_{l_i}^i$, which correspond to the i -th irrep of the group which has dimension l_i . Now we apply an operation of the group R to one function φ_s^i :

$$\hat{R}\varphi_s^i = \sum_s \Gamma_{st}^i(\hat{R})\varphi_s^i \quad (\text{definition of the representation}).$$

By left-multiplication with / summation over operations of the group $\sum_R \Gamma_{s't'}^j(\hat{R})^*$:

$$\begin{aligned} \sum_R \Gamma_{s't'}^j(\hat{R})^* \hat{R} \varphi_t^i &= \sum_R \sum_s \Gamma_{s't'}^j(\hat{R})^* \Gamma_{st}^i(\hat{R}) \varphi_s^i \\ &= \sum_s \varphi_s^i \underbrace{\sum_R \Gamma_{st}^i(\hat{R}) \Gamma_{s't'}^j(\hat{R})^*}_{\text{GOT (section 3.12)}} \\ &= \frac{h}{\sqrt{11_j}} \delta_{ij} \delta_{ss'} \delta_{tt'} \end{aligned}$$

$$\Rightarrow \underbrace{\frac{l_j}{h} \sum_R \Gamma_{s't'}^j(\hat{R})^* \hat{R}}_{\hat{P}_{s't'}^j} \varphi_t^i = \delta_{ij} \delta_{tt'} \varphi_s^i$$

Interpretation: $\hat{P}_{s't'}^j$ acts on some function φ_t^i . Only if this function contains a component which belongs to the irrep j and within this irrep exactly to the function t', the operation will yield the s'-th function if irrep j.

Most important case:

$$\hat{P}_{t't}^j \varphi_t^i = \varphi_t^i \delta_{ij} \delta_{tt'}$$

The operator acts on a function φ_t^i . Only if this function contains the t'-th function of irrep j the operation yields $\varphi_{t'}^j$ (i.e. the t'-th function of irrep j). In other words: the operator “projects” the component of desired symmetry out of the starting function.

Consequently, we can generate the desired set of symmetry adapted functions by applying all projection operators to the full set of function spanning the representation. The drawback: we need the full representation matrices, but all we have are the characters (from the character table).

Therefore we construct a simplified projection operator:

$$\hat{P}_{t't}^j = \frac{l_j}{h} \sum_R \Gamma_{t't}^j(\hat{R})^* \hat{R}$$

By summing over the functions contained in irrep j:

$$\begin{aligned}
\hat{P}_j &= \sum_{i'} \hat{P}_{i'j} \\
&= \frac{l_j}{h} \sum_{i'} \sum_R \Gamma_{i'j}^j(\hat{R})^* \hat{R} \\
&= \frac{l_j}{h} \sum_R \underbrace{\sum_{i'} \Gamma_{i'j}^j(\hat{R})^*}_{\chi^j(\hat{R})} \hat{R} \\
\Rightarrow & \boxed{\hat{P}_j = \frac{l_j}{h} \sum_R \chi^j(\hat{R}) \hat{R}}
\end{aligned}$$

Note: the functions generated by the simplified operator are not orthogonal. They have to be orthogonalized “manually”.

(4.7: NH₃: generation of symmetry adapted H-s functions).