Basis Functions

C734b

The group of the Hamiltonian or Schrodinger equation is the set of function operators {**A**, **B**, …, **T**,…} isomorphous with the symmetry group {A, B, …, T, .}

Eigenfunctions of the Hamiltonian form a **basis** for the group of the Hamiltonian.

Therefore, what is a basis?

If we have a set of operators that form a group, then a basis is a set of objects, each one of which, when operated on by one of the operators, is converted into a linear combination of the set of the objects.

Objects ≡ vectors, functions or quantum mechanical operators

Matrix representations form an irreducible or reducible group representation.

Let $\{\Phi_s\} \equiv$ set of n-degenerate eigenfunctions of **H** corresponding to a particular eigenvalue E

$$\Rightarrow \hat{H}\phi_s = E\phi_s \quad \mathrm{s} = 1,\ldots,\mathrm{n}$$

$$\because \left[\hat{T}, \hat{H}\right] = 0 \Rightarrow \hat{H}\hat{T}\phi_s = \hat{T}\hat{H}\phi_s = \hat{T}E\phi_s = E\hat{T}\phi_s$$

$\Rightarrow \hat{T}\phi_s$ is an eigenfunction of **H** with the same eigenvalue E

$\hat{T}\phi_s$ $\equiv$ linear combination of $\{\varphi_s\}$; that is, $\hat{T}\phi_s = \sum_{i=1}^{n} \phi_i \Gamma(T)_{is}$, $\mathrm{s} = 1,\ldots,\mathrm{n}$

In matrix form: $\hat{T}\langle \phi_1,\ldots,\phi_s,\ldots| = \langle \phi_1',\ldots,\phi_s',\ldots| = \langle \phi_1,\ldots,\phi_s,\ldots|\Gamma(T)$

or $\hat{T}\langle \phi| = \langle \phi'| = \langle \phi|\Gamma(T) \quad$ 1.)

Thus, $\{\varphi_s\}$ can be regarded as a set of basis functions in an n-dimensional vector space called **function space**.

$\therefore$ can interchange "eigenfunction" and "eigenvector".

Eq. 1.) implies that every set $\{\varphi_s\}$ that corresponds to eigenvalue E forms a basis for one of the IRs of the symmetry group G = {T}.

$\Rightarrow$ every energy level may be labeled according to its IR in G.

Question: How to construct basis function sets which form bases for particular IRs?

Answer: Use projection operators (later).

Next: consider the transformation of an operator $\hat{Q}$

Effect of **T** (no proof) is to transform an operator $\hat{Q}$ into $\hat{Q}' = \hat{T}\hat{Q}\hat{T}^{-1}$

* Operators can also form bases for the IRs of the group of the Hamiltonian.

Important question: can group theory tell us under which conditions a matrix element = 0?

Answer ≡ yes!

Neglecting spin-orbit coupling, a quantum mechanical state function ≡ **spinor** ≡ product of a spatial part (orbital) and a spin function (for electron)

$$\Rightarrow \Psi(r, m_s) = \psi(r)\chi(m_s)$$

$\hat{Q}_s^j$ acts on space (not spin)

$$\Rightarrow \langle \Psi_u^k | \hat{Q}_s^j | \Psi_q^i \rangle = \langle \psi_u^k | \hat{Q}_s^j | \psi_q^i \rangle \langle \chi_u | \chi_q \rangle \quad (1.)$$

Since χ functions are orthogonal $\Rightarrow \langle \chi_u | \chi_q \rangle = 0$

unless χ_u and χ_q have the same spin quantum number

Therefore, Eq. (1.) means ΔS = 0 ≡ spin selection rule.

Note: with spin-orbit coupling, this rule is not rigid but certainly transitions between states where ΔS ≠ 0will be weaker.

Now consider what happens to <Q> under a symmetry operator T.
It's value is unchanged.

$$\therefore \langle Q \rangle = \left\langle \Psi_u^k \middle| \hat{Q}_s^j \middle| \Psi_q^i \right\rangle = \left\langle \hat{T}\Psi_u^k \middle| \hat{T}\hat{Q}_s^j \hat{T}^{-1} \middle| \hat{T}\Psi_q^i \right\rangle \quad (2.)$$

Left-hand side of Eq. (2.) is invariant and therefore belongs to the totally symmetric representation Γ^1: A_1 or equivalent.

$\hat{Q}_s^j \left| \Psi_q^i \right\rangle$ is a function that transforms according to the direct product $\Gamma^j \otimes \Gamma^i$

The integrand in Eq. (2.) is the product of two functions: Ψ_u^{k*} and $\hat{Q}_s^j \left| \Psi_q^i \right\rangle$

It transforms as the direct product: $\Gamma^{k*} \otimes \Gamma^j \otimes \Gamma^i$

Question: What is the condition that $\Gamma^{a*} \otimes \Gamma^b$ contains Γ^1 ?

Condition is:

$$a_1 = \frac{1}{h}\sum_T \chi_1(T)\chi^{a*b}(T) = \frac{1}{h}\sum_T \chi^a(T)\chi^b(T) \neq 0$$

IR reducible

This will be true if a = b (orthogonality theorem for characters)

$\Rightarrow$ Eq. (2.) = 0 unless $\Gamma^j \otimes \Gamma^i$ contains Γ^k (by orthogonality)

or $\Gamma^i \otimes \Gamma^j \otimes \Gamma^k \subset \Gamma^1$

Conclusion: a matrix element is zero unless the direct product of any two of the representations contains the third one.

Example of Matrix Elements: Transition Probabilities

Probability of a transition being induced by interaction with electromagnetic radiation is proportional to a matrix element of the form:

$$\left\langle \psi^{k} \middle| \hat{Q}^{j} \middle| \psi^{i} \right\rangle$$

Q ≡ electric dipole operator, -e**r**, for strongest (E1) electric dipole transitions. Components of –e**r** transform like x, y, and z.

or **Q** ≡ magnetic dipole (M1) operator with components that transform as R_x, R_y, or R_z. (weaker than E1)

or **Q** ≡ electric quadrupole (E2) operator with components that transforms as binary products of x, y, and z. (weaker than E1; comparable to M1).