Atomic Multiplets lecture 3

Repetition: $\hat{H}_{tot} = \hat{H}_{ion} + \hat{H}_{SOC} + \hat{H}_{CF} + \hat{H}_{coulomb}^{e^- - e^-}$ → largest energy scale in TM 3d shell

$$V_{CF}(r,\Omega) = \sum_{\lambda=0}^{\infty}{}^{(**)} \sum_{k=-\lambda}^{\lambda} \sqrt{\frac{4\pi}{2\lambda+1}}\, A_{\lambda k}\, r^{\lambda}\, Y_{\lambda}^{k}(\Omega)$$ multipole expansion

↓

Determined by point group: $V_{CF}^{cubic} = \sqrt{11}\cdot 14 \cdot D_q(r)\left(Y_4^0 + \sqrt{\frac{5}{14}}\left(Y_4^4 + Y_4^{-4}\right)\right)$

$$\hat{H}_{CF} = \sum_{\lambda,\alpha,\beta} \tilde{A}_{\lambda(m_\alpha - m_\beta)}\, C_i(\lambda, l_\alpha, m_\alpha, l_\beta, m_\beta)\, \delta_{\alpha\sigma\beta}\, c_\alpha^\dagger c_\beta$$

$$C_i(..) = \int d\Omega\, Y_{l_\alpha}^{*m_\alpha}(\Omega)\, Y_\lambda^{(m_\alpha - m_\beta)}(\Omega)\, Y_{l_\beta}^{m_\beta}(\Omega)$$

$\begin{cases} 0 \text{ if } l_\alpha + l_\beta < \lambda \\ 0 \text{ if } (\lambda + l_\alpha + l_\beta) \text{ odd} \end{cases}$ (**)

point group symmetry (O_h) ⇌ QN: irreps (e_g, t_{2g})

Γ_3, Γ_5

If it were only for the CF operator, the energy of n-electron configurations would be given by counting occupation of irrep. labeled states!

d^1: e_g^1 (4x), t_{2g}^1 (6x) → d^2: e_g^2 (6x), t_{2g}^2 (15x), $e_g^1 t_{2g}^1$ (24x)

$4\mathcal{E}_{e_g}$ $6\mathcal{E}_{t_{2g}}$ $2\cdot\mathcal{E}_{e_g}$ $2\cdot\mathcal{E}_{t_{2g}}$ $\mathcal{E}_{e_g}+\mathcal{E}_{t_{2g}}$

But we must not forget about $\hat{H}^{e^- - e^-}_{Coulomb}$: distinguish strong/weak CF

i) strong CF:

example d^2

$$\begin{pmatrix} e_g^2 & & \\ & t_{2g}^2 & \\ & & e_g^1 t_{2g}^1 \end{pmatrix} = \hat{H}^{e^- - e^-}_{Coulomb}$$

in CF eigenbasis off-diags $\ll \Delta CF$

⇒ consider matrix elements within CF subspaces:

gs: t_{2g}^2 (dim = 15) previously we have argued that Coulomb-interaction cannot split states within a "term" $^{2S+1}N(L)$ but now?

instead of conserving total angular momentum (which is quenched) the spherical $(|r-r'|)^{-1}$ operator conserves the irreps. of each n-electron configuration!

So far we only considered irreps. on single particle Hilbert spaces: (d-shell, cubic)

$\mathcal{H}^1 = \text{span}(\mathcal{G}_i)$ i: irrep. dim = 10

$\mathcal{H}^2 = \mathcal{H}^1 \otimes \mathcal{H}^1 = \text{span}(\mathcal{G}_i \times \mathcal{G}_j)$ i,j: irreps. dim = 45

BUT $\mathcal{G}_i \cdot \mathcal{G}_j$ does not have to belong to an irrep. on $\mathcal{H}^2$

in O_h the product of two t_{2g} subspaces contains four irreps.

$$\underbrace{t_{2g} \times t_{2g}}_{\text{ground state for our octahedron}} = {}^1A_1 + {}^1E + {}^3T_1 + {}^1T_2$$

1× 2× 3·3 = 9× 3× ⇒ dim 15

(Like ang. mom. terms we use Capitals for "total"-irrep. term $2S+1\mathcal{N}$(irrep.))

let's do the other subspaces:

$$e_g \times e_g = {}^1A_1 + {}^3A_2 + {}^1E \qquad \dim = 6$$

$$e_g \times t_{2g} = {}^1T_1 + {}^3T_1 + {}^1T_2 + {}^3T_2 \qquad \dim = 24$$

$\Rightarrow$ in between CF subspaces Coulomb-int. can only mix equivalent terms!

ii) **weak CF**:

example d^2

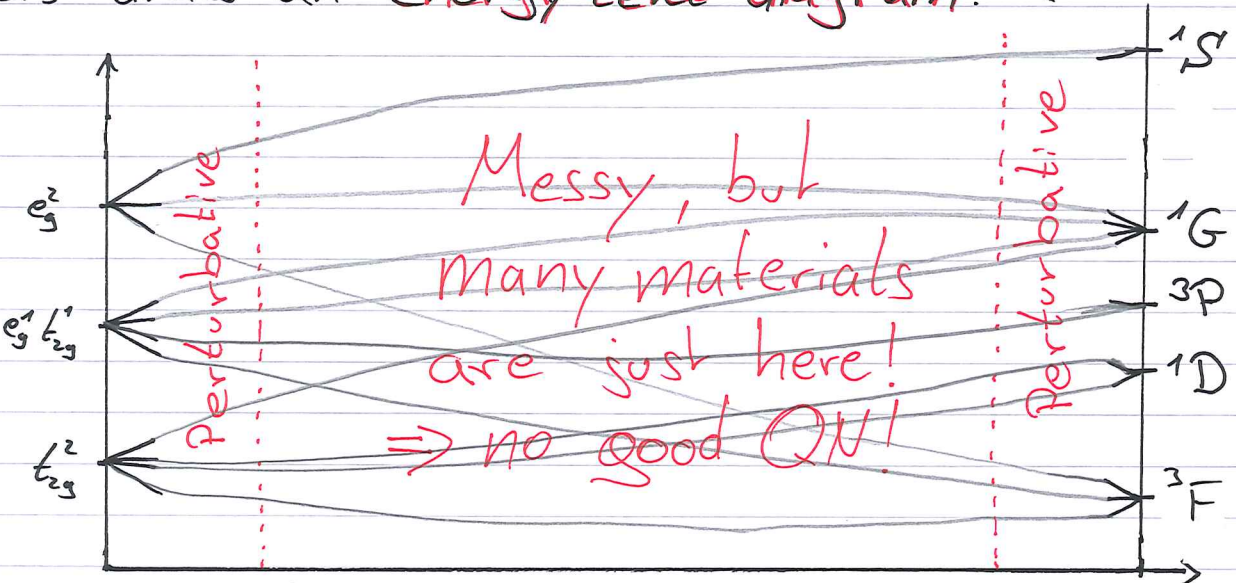
$$\begin{pmatrix} {}^3F & & & & \\ & {}^3P & & & \\ & & {}^1G & & \\ & & & {}^1D & \\ & & & & {}^1S \end{pmatrix} = \hat{H}_{CF}$$

Easy for us! Which irreps. are contained within each term subspace?

O_h:

$S \rightarrow A_1$; $P \rightarrow T_1$; $D \rightarrow E + T_2$; $F \rightarrow A_2 + T_1 + T_2$; $G \rightarrow A_1 + E + T_1 + T_2$

Let's draw an energy-level diagram: (Tanabe-Sugano)



⇓

for finite size systems: - exact diagonalization
- numerical methods like Lanczos

Susceptibility of free Ions

$\underline{B}$ field couples linearly to $\underline{M} = \underline{L} + 2\underline{S}$

$$H = H_{loc} - \frac{eh}{2m_e c}(\underline{L} + 2\underline{S})\cdot \underline{B}$$

μ_B $\underline{M}$

(pay Attention to the fact that $\underline{M} \neq \underline{J} = \underline{L} + \underline{S}$)

here we omitted already the diamagnetic "Lamor" term. (small for magn. ions)

Free energy: $\beta = \frac{1}{k_B T}$

$$f = -\frac{1}{\beta} \ln Tr\left(e^{-\beta(H_{loc} - M\cdot B)}\right)$$

for χ we need $\chi = -\frac{\partial^2 f}{\partial B^2}$

watch out $[H_{loc}, M] \neq 0$

use Eigenbasis of $(H_{loc} - MB)$

$$m = -\partial_B f = Tr\left(M \cdot e^{-\beta(H_{loc} - M\cdot B)}\right) \Big/ Tr\left(e^{-\beta(H_{loc} - M\cdot B)}\right) = \langle M \rangle_{H_{loc} - MB}$$

$$\chi_{static} = \partial_B m\Big|_{B=0} = \int_0^\beta d\tau \, \langle M(\tau) M \rangle_{H_{loc}}$$

$$M(\tau) = e^{\tau H_{loc}} M e^{-\tau H_{loc}}$$

use Eigenbasis of H_{loc} without B!

many body states

$\Rightarrow$ assume we can calculate Eigenvectors/values of H_{loc} so that:

$$H_{loc}|n\rangle = E_n|n\rangle \quad \text{with} \quad \sum_n |n\rangle\langle n| = \mathbb{1}$$

partition fct.

$$\Rightarrow Z = \mathrm{Tr}\left(e^{-\beta H_{loc}}\right) = \sum_n e^{-\beta E_n} \quad \text{and} \quad \chi_{static} = \frac{1}{Z}\sum_{n,m} |\langle m|M|n\rangle|^2 \frac{e^{-\beta E_m} - e^{-\beta E_n}}{E_n - E_m}$$

for $n=m$ quotient is taken as limit $E_m \to E_n$ $\Rightarrow \beta e^{-\beta E_n}$

Typically we distinguish $E_n = E_m$ and $E_n \neq E_m$ contributions (very different low T behaviour!)

Curie part: $\chi_c := \frac{\beta}{Z} \sum_{m,n}^{E_n = E_n} |\langle m|M|n\rangle|^2 e^{-\beta E_n}$

van Vleck part: $\chi_{vV} := \frac{1}{Z} \sum_{m,n}^{E_m \neq E_n} |\langle m|M|n\rangle|^2 \frac{e^{-\beta E_m} - e^{-\beta E_n}}{E_n - E_m}$