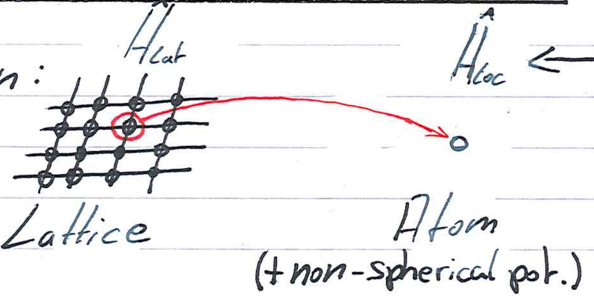
Atomic Multiplets lecture 2 (From Coulomb to Crystal Fields)

Repetition:



$\hat{H}_{Loc}$ ← rich structure for partially filled shells!
Essential for understanding "Local probes" of materials

$$\text{Components of } \hat{H}_{Loc} = \overbrace{\hat{H}_{ion}^{sph.} + \hat{H}_{CF} + \hat{H}_{SOC}}^{\text{single particle op}} + \overset{\text{two part. op.}}{\hat{H}_{Coulomb}^{e^- - e^-}}$$

intra-shell const. $\hat{H}_{ion}^{sph.}$: constant within a partially filled shell (offset)

$\hat{H}_{CF}$: crystal-field potential (violates conservation of L) L "quenched"

$\hat{H}_{SOC}$: spin-orbit coupling (only $J = L + S$ conserved)

$\hat{H}_{Coulomb.}^{e^- - e^-}$: conseves total $L = \sum_i l_i$ and $S = \sum_i s_i$

$$[H_{Coulomb}^{e^- e^-}, L^2] = [H_C, L_z] = 0$$

. relevant for 3d shell

Let's concentrate on $\hat{H}_{CF}$ and $\hat{H}_{coulomb}$ (dominant for 3d shell)

Just by conservation laws / symmery we have learnt that $\hat{H}^{e^- - e^-}_{coulomb}$ lifts degeneracies by splitting terms

in 2^{nd} quantization: (intra-shell, i.e. nl fixed ⇝ e.g. intra 3d for TMOs)

$$\hat{H}^{e^- - e^-}_{coulomb} = \frac{1}{2} \sum_{\substack{m_1 m_2 m_3 m_4 \\ \sigma \bar{\sigma}}} V^{nl}_{m_1 m_2 m_3 m_4} \, c^{+}_{m_1\sigma} \, c^{+}_{m_2\bar{\sigma}} \, c_{m_3\bar{\sigma}} \, c_{m_4\sigma}$$

with matrix element

$$V^{nl}_{m_1 m_2 m_3 m_4} = \int d^3r \, d^3r' \, f^{*}_{nl\,m_1}(r) \, f^{*}_{nl\,m_2}(r') \frac{e^2}{|r - r'|} f_{nl\,m_3}(r') \, f_{nl\,m_4}(r)$$

in principle in the shell nl we get $(2l+1)^4$ matrix elements

(d-shell: 625)

for intra-shell scattering

reducible to $l+1$ independent parameters! $\varphi_{nlm}(r,\Omega) = R_{nl}(r) \cdot Y_{lm}(\Omega)$

↑ spherical harmonics

$$V^{nl}_{m_1 m_2 m_3 m_4} = \sum_{\lambda=0}^{l} \frac{F^{2\lambda}}{4\lambda+1} \sum_{\kappa=-2\lambda}^{2\lambda} G(l,\lambda,m_1,m_2,m_3,m_4,\kappa)$$

$$\text{with } G(\ldots) = \int d\Omega \, Y^*_{lm_1}(\Omega)\, Y^*_{\lambda\kappa}(\Omega)\, Y_{lm_4}(\Omega) \cdot \int d\bar{\Omega}\, Y^*_{lm_2}(\bar{\Omega})\, Y_{\lambda\kappa}(\bar{\Omega})\, Y_{lm_3}(\bar{\Omega})$$

Strong selection rules: even $\lambda \leq 2l$

$m_1 + m_2 = m_3 + m_4$

$$\text{and } F^{\lambda} := e^2 \int dr\, dr' \frac{r_<^{\lambda}}{r_>^{\lambda+1}} R^2_{nl}(r)\, R^2_{nl}(r')$$

↑ Slater integrals

$R_{nl}(r)$ not known analytical in general

↳ Hydrogen WF

↳ Hartree-Fock WF

↳ Wannier-fct. from DFT

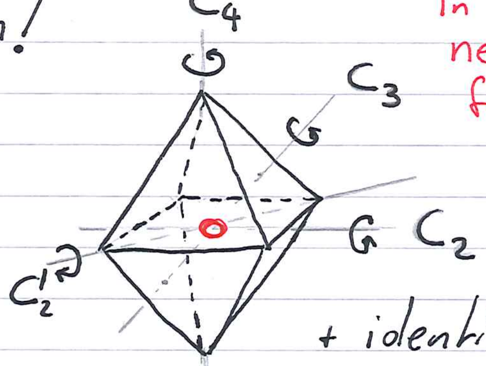
Now for the crystal field operator H_{CF} (simpler because single particle pot.)

Before writing the operator explicitly, consider its symmetry / conservation laws.

$$[H_{CF}, L^2] \neq 0$$

H_{CF} breaks spherical symmetry but retains discrete symmetry transformation!

In a simple cub. Lattice nearest neighbours form an octahedron:



+ identity E, inversion, etc.

1. **Conclusion** (symmetry)

All symmetry operations* of the crystal must bring H_{CF} back to H_{CF}

$$R_{CF}^{+} H_{CF} R_{CF} = H_{CF}$$

* proper or improper rotations

2. Conclusion (conserved quantum numbers)

Any wave functions that are related by symmery transformations

$R^{+}_{CF}\,\psi_1 = \psi_2$ must have the same CF energy $\varepsilon_1^{CF} = \varepsilon_2^{CF}$

this extends to linear combination of wave functions

$$R^{+}_{CF}(a\cdot\psi_1 + b\,\psi_2) = \psi_1 \Rightarrow \varepsilon_1^{CF} = \varepsilon_2^{CF}$$

cubic

Example: $3z^2 - r^2$, x^2-y^2 , xy , xz , yz (cubic harmonics in cartesian coordinates)

rotations by $\frac{\pi}{2}$: $xy \xrightarrow{y\to z} xz \xrightarrow{x\to y} yz$ ✓

$$\Rightarrow \varepsilon_{xy} = \varepsilon_{xz} = \varepsilon_{yz}$$

$$\frac{1}{2}(x^2-y^2) + \frac{1}{2}(3z^2-r^2) = z^2-y^2 \xrightarrow{z\to x} x^2-y^2$$

$$\Rightarrow \varepsilon_{x^2-y^2} = \varepsilon_{3z^2-r^2}$$

We found two subspaces in the d-shell which are invariant under cubic symmetry transformations!

Like H_{Coulomb} can't split states wit equiv. ∠

⇒ H_{CF} can't lift degeneracies of invariant subspaces!

Questions: 1. What is the associated quantum number ?
2. How to find invariant subspaces systematically ?

Looking back, we can actually define H_{CF} by its symmetries!

Symmetries ⇝ R_{CF} = matrices in a chosen basis

⇝ taken together, these matrices (and their algebra) form a "representation" of a mathematical group $\xrightarrow[\text{no transl.}]{\text{only local}}$ "point group"

(closure*, associativity, identity, inversion)

*e.g. in our octahedron $C_2' \cdot C_2 = C_4$

$$C_4 \cdot C_4 \cdot C_4 \cdot C_4 = E$$

: and many more ..

for one point group we can find several "representations"

↳ e.g. all "point groups" can be represented by setting all matrices to be 1x1 and 1

$$R_{CF} = (1)$$

this is the so called a_{1g} representation (or Γ_1)

↳ a n-dimensional representation is said to be reducible when it can be reduced to a block form by linear transformation:

$$\begin{pmatrix} r_{11} & \cdots & r_{1n} \\ \vdots & \ddots & \vdots \\ r_{n1} & \cdots & r_{nn} \end{pmatrix} \longrightarrow \begin{pmatrix} \begin{matrix} \tilde{r}_{11} & \cdots & \tilde{r}_{1m} \\ \vdots & \ddots & \vdots \\ \tilde{r}_{m1} & \cdots & \tilde{r}_{mm} \end{matrix} & 0 \\ 0 & \begin{matrix} \tilde{r}_{m+1\,m+1} & \cdots & \tilde{r}_{m+1\,n} \\ \vdots & \ddots & \vdots \\ \tilde{r}_{n\,m+1} & \cdots & \tilde{r}_{nn} \end{matrix} \end{pmatrix}$$

⇒ a_{1g} is irreducible (each point-group has a finite # of irreps.)

our single particle wave-functions form a basis for a representation (e.g. d-shell)

$$\underbrace{\begin{pmatrix} & & \\ & R^{3d}_{CF} & \\ & & \end{pmatrix}}_{\text{5 dim rep.}} \begin{pmatrix} x^2-y^2 \\ 3z^2-r^2 \\ xy \\ xz \\ yz \end{pmatrix} = \tilde{f}$$

$\Longrightarrow$ from our very first arguments we have seen that in cubic symmetry (point group O_h) it is impossible to mix

$$x^2-y^2, 3z^2-r^2 \quad \text{with} \quad xy, xz, yz$$

with $$R^{3d}_{Oh} = \begin{pmatrix} R_{e_g} & 0 \\ 0 & R_{t_{2g}} \end{pmatrix}$$

R^{3d}_{Oh} contains two different irreps.

$\hat{H}_{CF}$ can only split degenerate wave-functions that belong to different irreps. QN are irrep labels!

Explicit form of $\hat{H}_{CF}$ (H_{CF} conserves spin)

Expand the potential on spherical harmonics:

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

Like for the Coulomb interaction $\varphi = R(r) \cdot Y(\theta,\phi)$

matrix elements for the operator separate into an analytical angular part and a non-analytical radial part:

$$\hat{H}_{CF} = \sum_{\alpha\beta} \sum_{\lambda} \underbrace{\tilde{A}_{\lambda(m_\alpha - m_\beta)}}_{\text{radial}}\, \underbrace{G(\lambda, l_\alpha m_\alpha, l_\beta m_\beta)}_{\text{analytical gives selection rule}}\, \delta_{\sigma_\alpha \sigma_\beta}\, c_\alpha^\dagger c_\beta$$

$\lambda \leq 2l$ (for d-shell $\lambda \leq 4$)

the rest depends on the point group! E.g. O_h for d-shell:

inversion symmetry $\Rightarrow \lambda$ even $\rightsquigarrow$ no mixing of odd and even shells: counter-example C in graphene

mixing of s- and p-shell to sp^2 hybrids

$\Downarrow$

$$A_{\lambda k} = A_{\lambda -k}$$

$$\left(R_{O_h}^{+} H_{CF} R_{O_h} \overset{!}{=} H_{CF}\right)$$

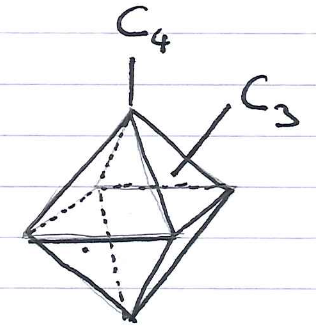
upon C_4 only Y_4^0, Y_4^4, Y_4^{-4} remain!

so
$$V_{O_h} = A_{40} Y_4^0 + A_{44}\left(Y_4^4 + Y_4^{-4}\right)$$

after requesting identity upon application of C_3 we remain actually with only one parameter

$$V_{O_h} = \sqrt{\pi}\,14\,Dq\left(Y_4^0 + \sqrt{\frac{5}{14}}\left(Y_4^4 + Y_4^{-4}\right)\right)$$

$Dq \rightsquigarrow$ historic notation $\varepsilon_{e_g} - \varepsilon_{t_{2g}} =: 10\,Dq$



we have started with the C_4 axis,

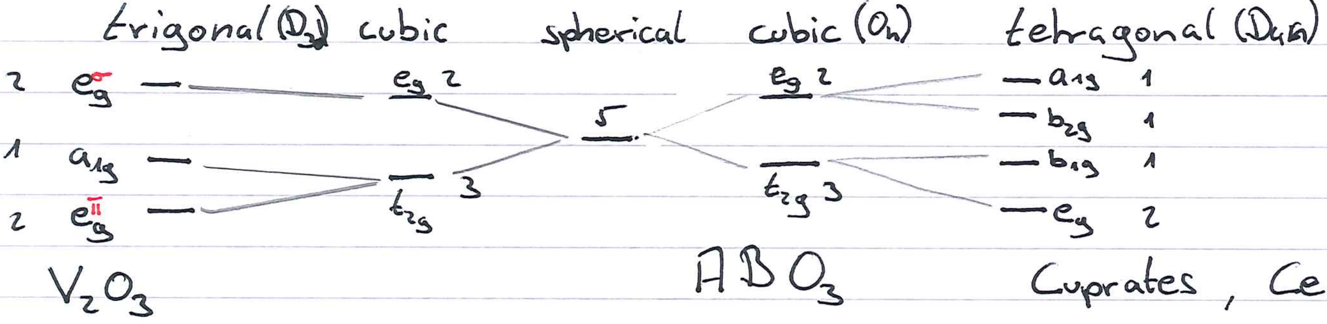
would we have started with C_3,

we would have arrived at

$$V_{O_h} = \sqrt{\pi}\,14\,Dq \cdot \left(Y_4^0 + \sqrt{\tfrac{10}{7}} \left(Y_4^3 - Y_4^{-3} \right) \right)$$

just a rotation of $\hat{z}$ from C_4 to C_3

Both are usefull!..



$$V_{D_{4h}} = a \cdot Y_2^0 + b\, Y_4^0 + c\left(Y_4^4 + Y_4^{-4}\right)$$ Distort along C_4

$$V_{D_3} = a\, Y_2^0 + b\, Y_4^0 + c\left(Y_4^3 - Y_4^{-3}\right)$$ Distort along C_3

Final remark:

$\hat{H}_{CF}$ is single particle operator ⇝ it counts occupations of CF-levels:

$3d^1$ (10)	$3d^2$ (45)	…
$4 \times \varepsilon_{e_g}$	$6 \times 2 \cdot \varepsilon_{e_g}$	
$6 \times \varepsilon_{t_{2g}}$	$15 \times 2\varepsilon_{t_{2g}}$	
	$24 \times (\varepsilon_{e_g} + \varepsilon_{t_{2g}})$	

Outlook:

i) use atomic H to predict spectra of local probes XAS

ii) embed atom into a bath
Anderson Impurity Model
↳ Dynamical Mean-Field Theory