Crystal-field, tight-binding and Jahn-Teller

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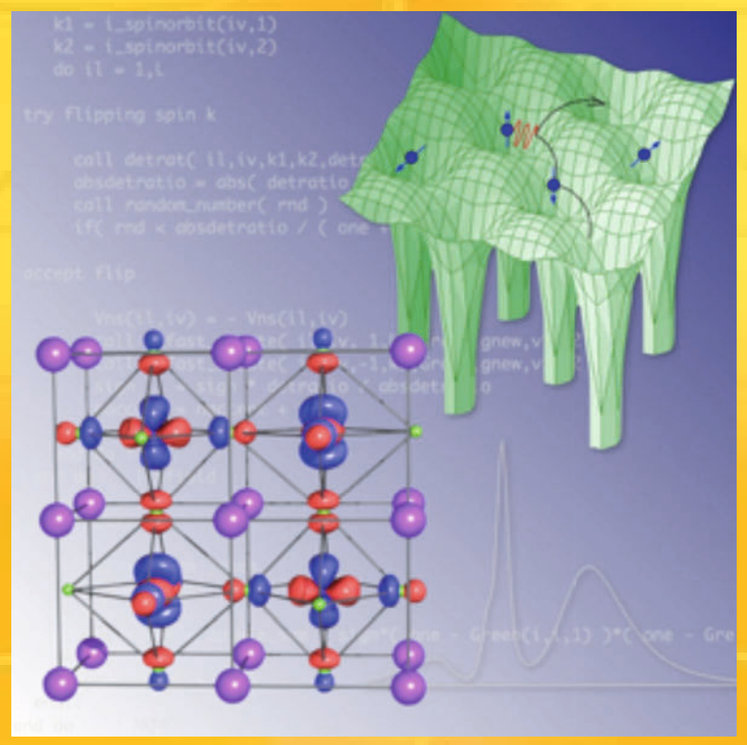

the many-body problem

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the many-body problem

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i,\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} - \sum_\alpha \frac{1}{2M_\alpha}\nabla_\alpha^2 + \frac{1}{2}\sum_{\alpha\neq\alpha'} \frac{Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|}$$

(atomic units: Appendix A)

Born-Oppenheimer Ansatz

$$\Psi(\{\mathbf{r}_i\},\{\mathbf{R}_\alpha\}) = \psi(\{\mathbf{r}_i\};\{\mathbf{R}_\alpha\})\Phi(\{\mathbf{R}_\alpha\})$$

$$\begin{cases} \hat{H}_e\psi(\{\boldsymbol{r}_i\};\{\boldsymbol{R}_\alpha\}) = \varepsilon(\{\boldsymbol{R}_\alpha\})\psi(\{\boldsymbol{r}_i\};\{\boldsymbol{R}_\alpha\}), & \text{electrons} \\ \hat{H}_n\Phi(\{\boldsymbol{R}_\alpha\}) = E\Phi(\{\boldsymbol{R}_\alpha\}), & \text{lattice} \end{cases}$$

electrons and lattice

electronic Hamiltonian

$$\begin{aligned}\hat{H}_e &= -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq i'}\frac{1}{|\mathbf{r}_i-\mathbf{r}_{i'}|} - \sum_{i\alpha}\frac{Z_\alpha}{|\mathbf{r}_i-\mathbf{R}_\alpha|} + \frac{1}{2}\sum_{\alpha\neq\alpha'}\frac{Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha-\mathbf{R}_{\alpha'}|} \\ &= \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn}\end{aligned}$$

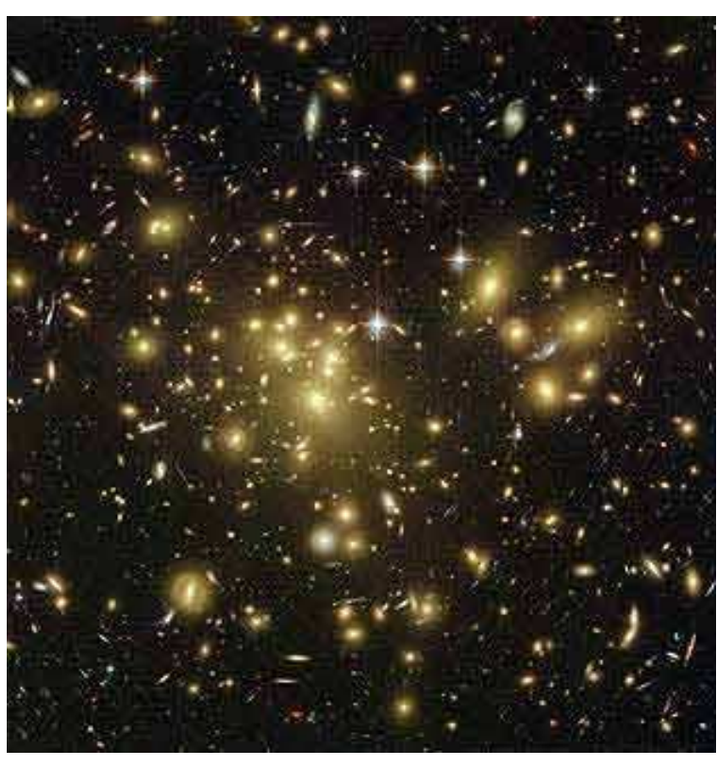
lattice Hamiltonian

$$\begin{aligned}\hat{H}_n &= -\sum_\alpha \frac{1}{2M_\alpha}\nabla_\alpha^2 + \varepsilon(\{\boldsymbol{R}_\alpha\}) \\ &= \hat{T}_n + \hat{U}_n,\end{aligned}$$

if we know the crystal structure we can concentrate on electrons

a single iron atom

26 electrons, 78 arguments, 10^{78} values
10 X 10 X 10 grid



$$\Psi_0(\mathbf{r}_1, \mathbf{r}_1, \ldots, \mathbf{r}_{26})$$

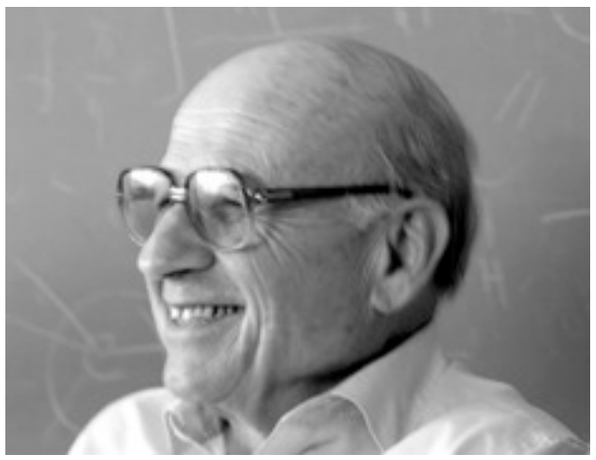
density-functional theory

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i,\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} - \sum_\alpha \frac{1}{2M_\alpha}\nabla_\alpha^2 + \frac{1}{2}\sum_{\alpha\neq\alpha'} \frac{Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|}$$

Kohn-Sham Hamiltonian

$$\hat{h}_e = \sum_i \left[-\frac{1}{2}\nabla_i^2 + v_R(\boldsymbol{r}_i)\right] = \sum_i \hat{h}_e(\boldsymbol{r}_i)$$

$$v_R(\boldsymbol{r}) = -\sum_\alpha \frac{Z_\alpha}{|\boldsymbol{r} - \boldsymbol{R}_\alpha|} + \int d\boldsymbol{r}' \frac{n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} + \frac{\delta E_{\mathrm{xc}}[n]}{\delta n} = v_{en}(\boldsymbol{r}) + v_H(\boldsymbol{r}) + v_{xc}(\boldsymbol{r})$$



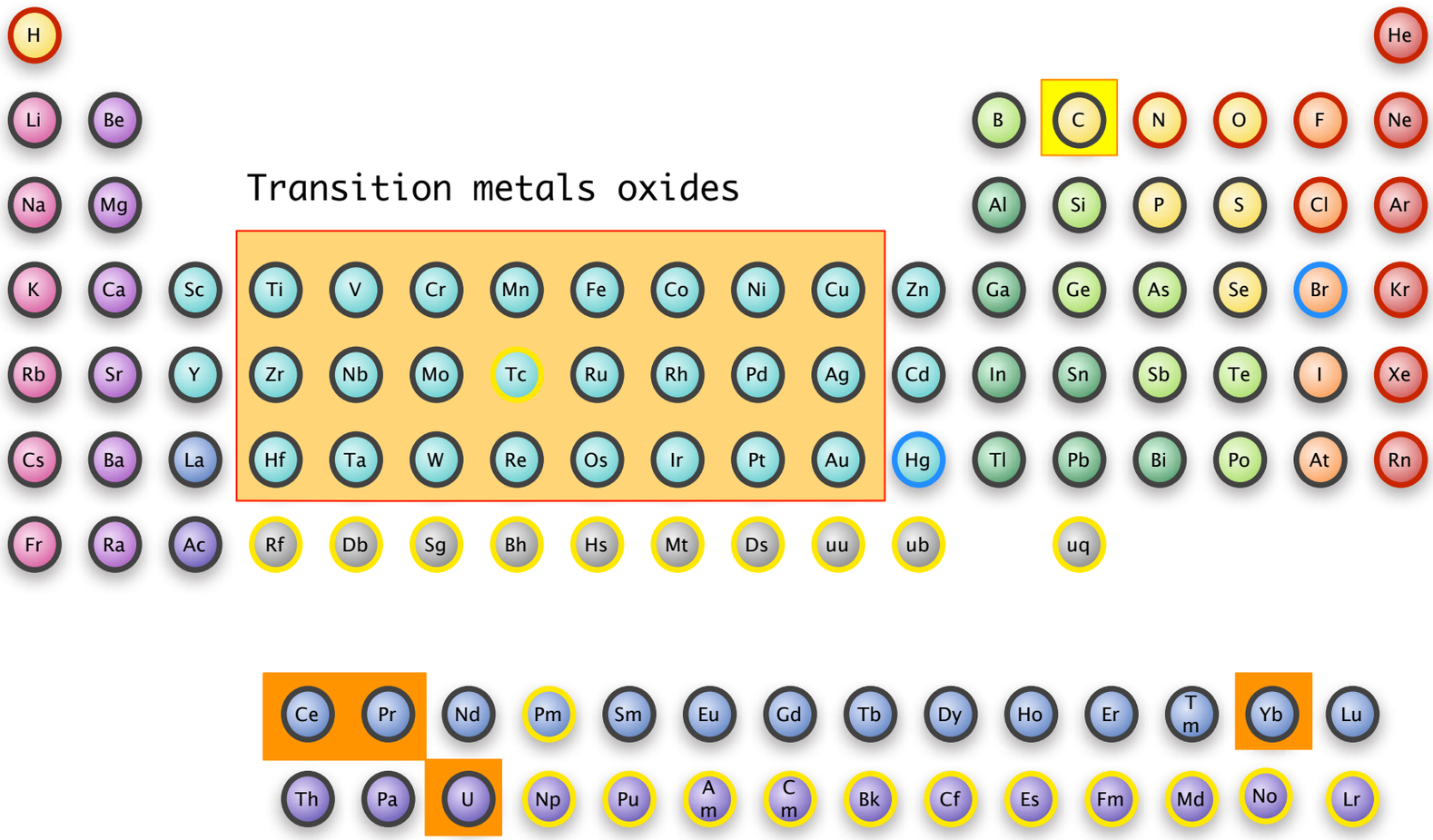
Walter Kohn

Nobel Prize in Chemistry (1998)

Kohn-Sham equations

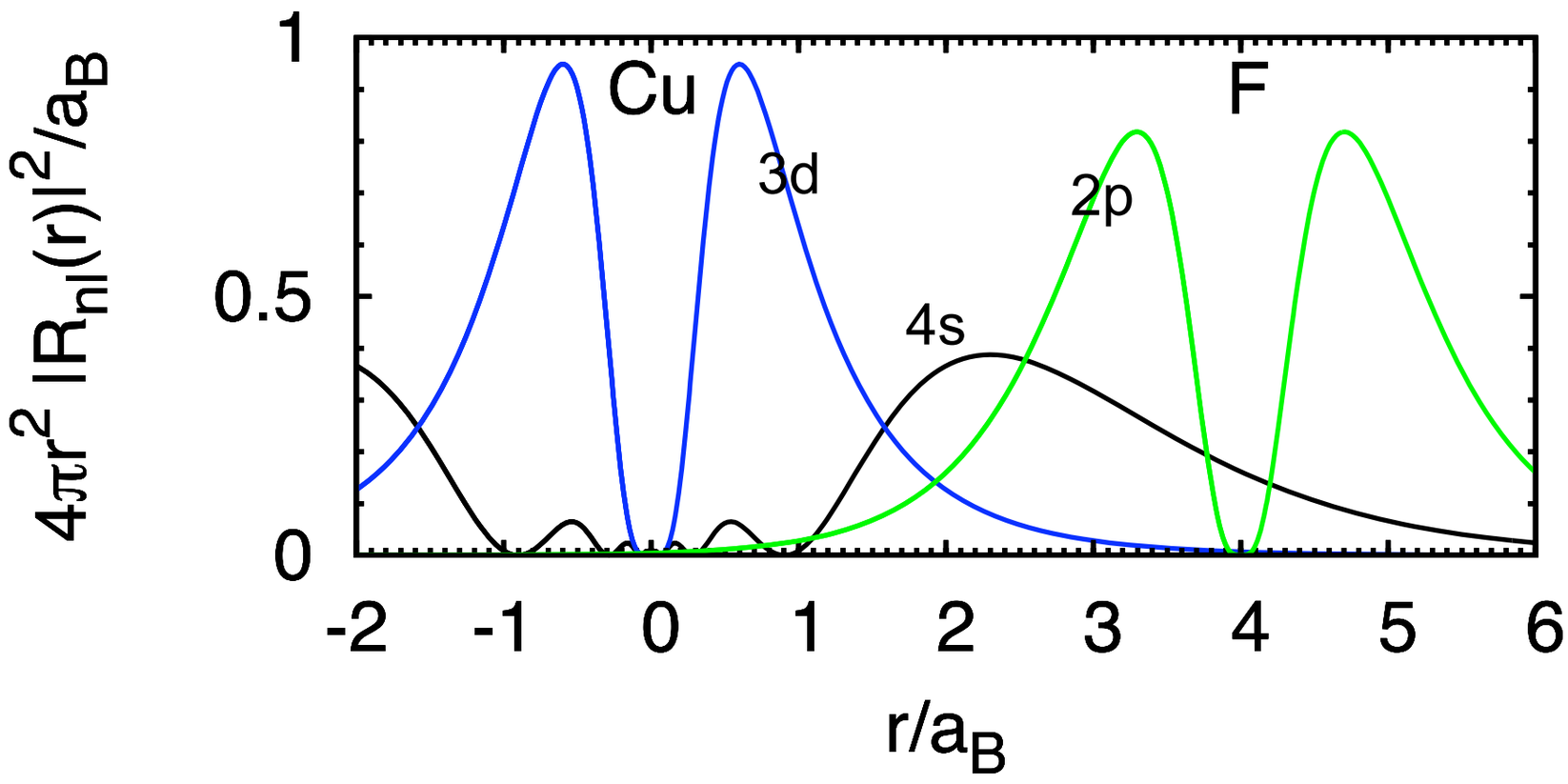
understand and predict properties of solids, molecules, biological systems, geological systems...

strongly correlated systems



example: Mott insulators metallic in LDA, GGA,..

strongly correlated systems

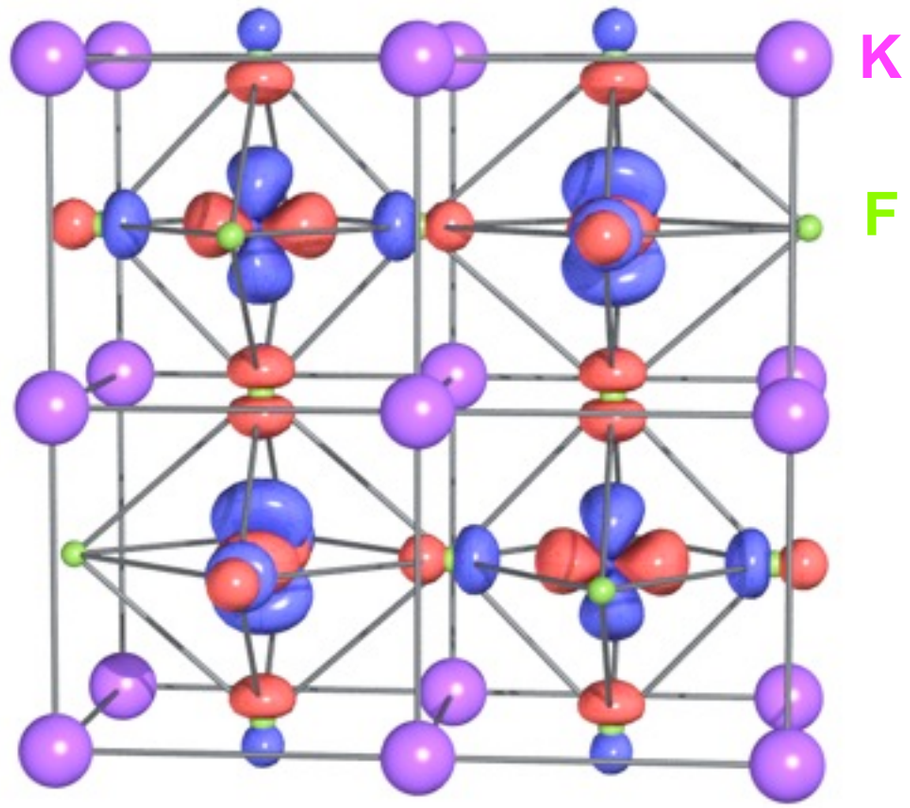


$$\psi_{nlm}(\rho,\theta,\phi) = R_{nl}(\rho)Y_l^m(\theta,\phi)$$

$$R_{nl}(\rho) = \sqrt{\left(\frac{2Z}{n}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\rho/n} \left(\frac{2\rho}{n}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2\rho}{n}\right)$$

(hydrogen-like atom: Appendix B)

an example: $KCuF_3$

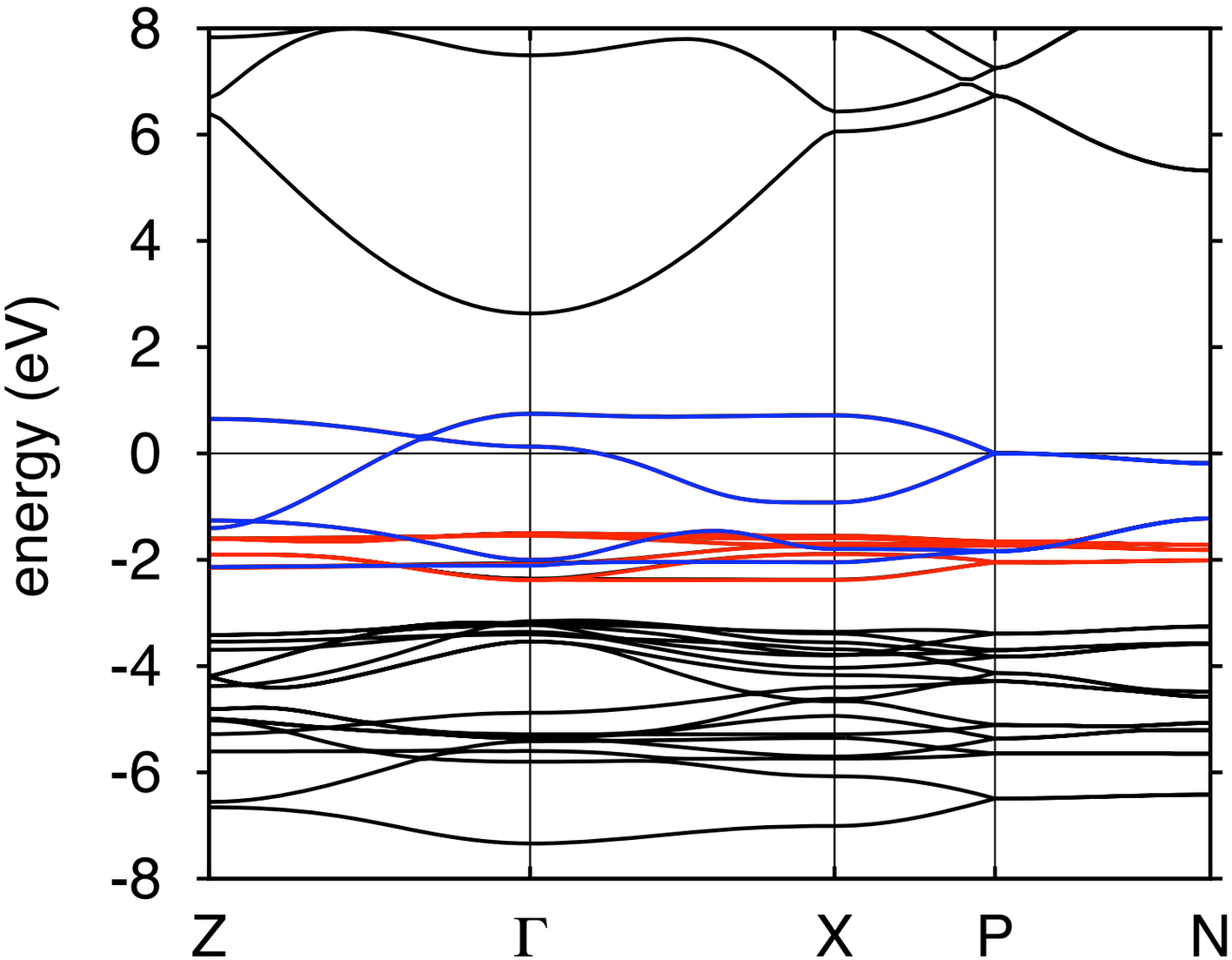


$K^+ Cu^{2+} F^-$

$K\ 4s^0\ Cu\ 3d^9\ F\ 2p^6$

odd number of electrons

LDA band structure



K *4s* Cu *4s*

Cu *3d*

F *2p*

partially filled d-like bands, metallic

LDA,GGA,...

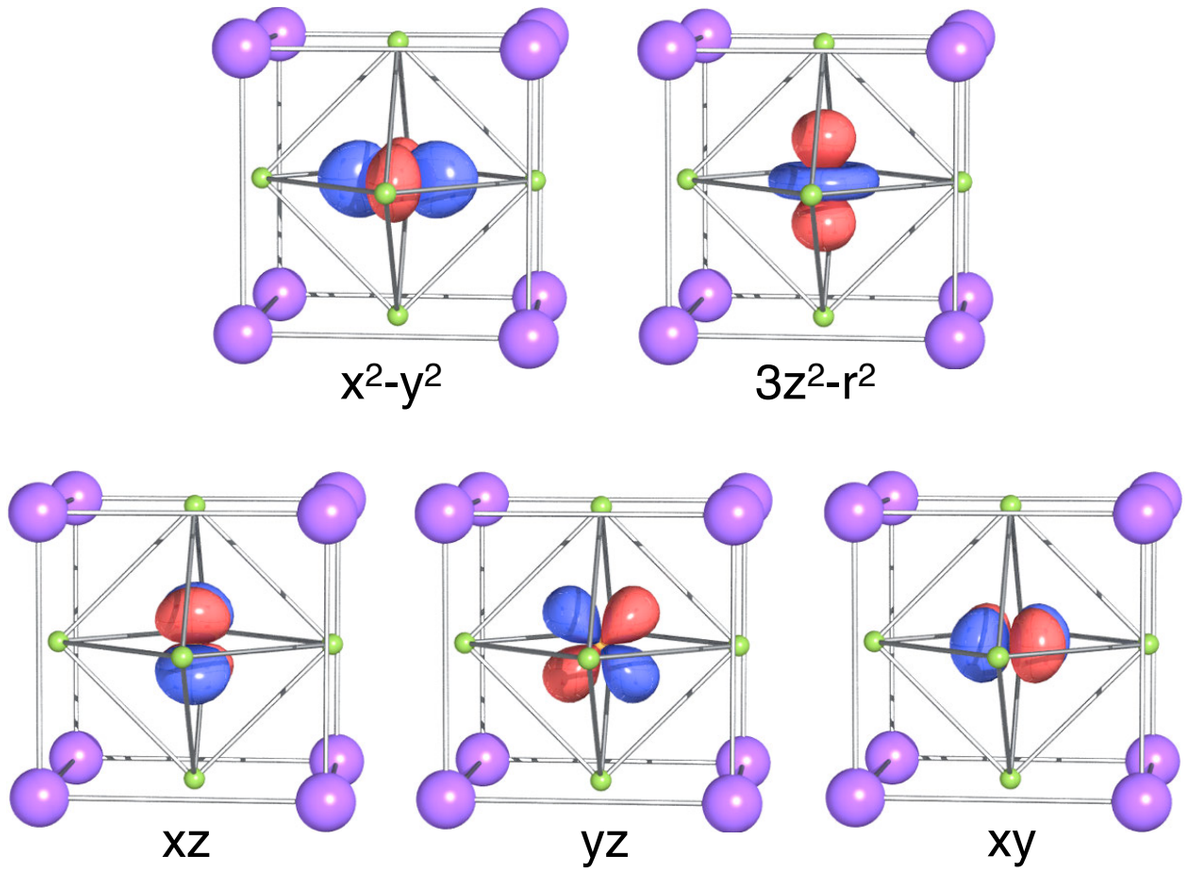
in reality: insulator, paramagnetic for T>40 K

back to the many-body problem

$$
\begin{aligned}
\hat{H}_e &= -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \frac{1}{2}\sum_{\alpha\neq\alpha'} \frac{Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|} \\
&= \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn}
\end{aligned}
$$

many-body models

$$\psi_{in\sigma}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}} e^{-i\boldsymbol{R}_i \cdot \boldsymbol{k}} \, \psi_{n\boldsymbol{k}\sigma}(\boldsymbol{r})$$



LDA localized Wannier functions

many-body models

second quantization

$$\hat{H}^{\mathrm{LDA}} = -\sum_{\sigma} \sum_{in,i'n'} t^{i,i'}_{n,n'} c^{\dagger}_{in\sigma} c_{i'n'\sigma},$$

$$t^{i,i'}_{n,n'} = -\int d\boldsymbol{r}\, \overline{\psi}_{in\sigma}(\boldsymbol{r})[-\frac{1}{2}\nabla^2 + v_{\mathrm{R}}(\boldsymbol{r})]\psi_{i'n'\sigma}(\boldsymbol{r}).$$

$$\varepsilon^{i,i}_{n,n'} = -t^{i,i}_{n,n'} = \int d\boldsymbol{r}\, \overline{\psi}_{in\sigma}(\boldsymbol{r}) \left[-\frac{1}{2}\nabla^2 + v_{\mathrm{R}}(\boldsymbol{r})\right] \psi_{in'\sigma}(\boldsymbol{r})$$

many-body models

$$\hat{H}_e = \hat{H}^{\mathrm{LDA}} + \hat{U} - \hat{H}_{\mathrm{DC}}$$

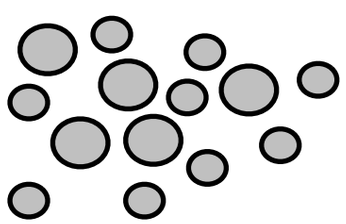
$$\hat{U} = \frac{1}{2} \sum_{ii'jj'} \sum_{\sigma\sigma'} \sum_{nn'pp'} U^{ij\ i'j'}_{np\ n'p'} c^{\dagger}_{in\sigma} c^{\dagger}_{jp\sigma'} c_{j'p'\sigma'} c_{i'n'\sigma}$$

$$U^{iji'j'}_{np\ n'p'} = \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2 \, \frac{\overline{\psi}_{in\sigma}(\boldsymbol{r}_1) \overline{\psi}_{jp\sigma'}(\boldsymbol{r}_2) \psi_{j'p'\sigma'}(\boldsymbol{r}_2) \psi_{i'n'\sigma}(\boldsymbol{r}_1)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}.$$

$\hat{H}_{\mathrm{DC}}$ long range Hartree and mean-field exchange-correlation already are well described by LDA (GGA,..)

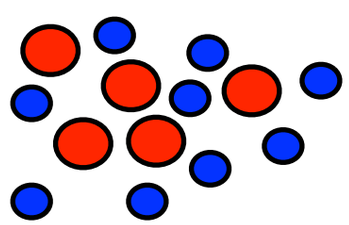
light and heavy electrons

electrons



light (weakly correlated): LDA (GGA,..)

heavy(strongly correlated): U



$$\hat{H}_e = \hat{H}^{\mathrm{LDA}} + \hat{U}^l - \hat{H}^l_{\mathrm{DC}}$$

eg. *l* shell

$$\hat{U}^l - \hat{H}^l_{\mathrm{DC}}$$

short-range correction to LDA

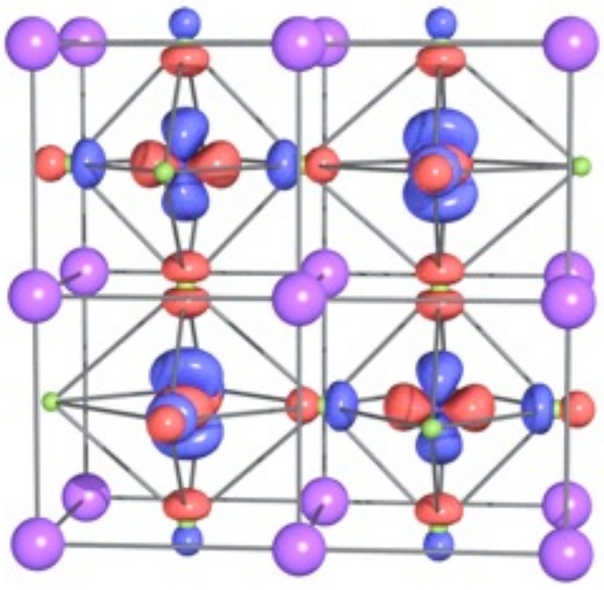
local or almost local

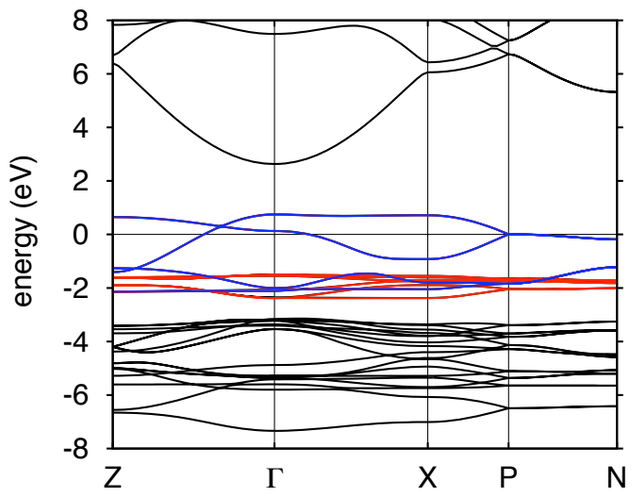
for a *l* shell, the local Coulomb interaction is

$$\hat{U}^l = \frac{1}{2}\sum_i \sum_{\sigma\sigma'} \sum_{m_\alpha m'_\alpha} \sum_{m_\beta m'_\beta} U_{m_\alpha m_\beta m'_\alpha m'_\beta} c^\dagger_{i m_\alpha \sigma} c^\dagger_{i m_\beta \sigma'} c_{i m'_\beta \sigma'} c_{i m'_\alpha \sigma}$$

screening? cRPA, cLDA

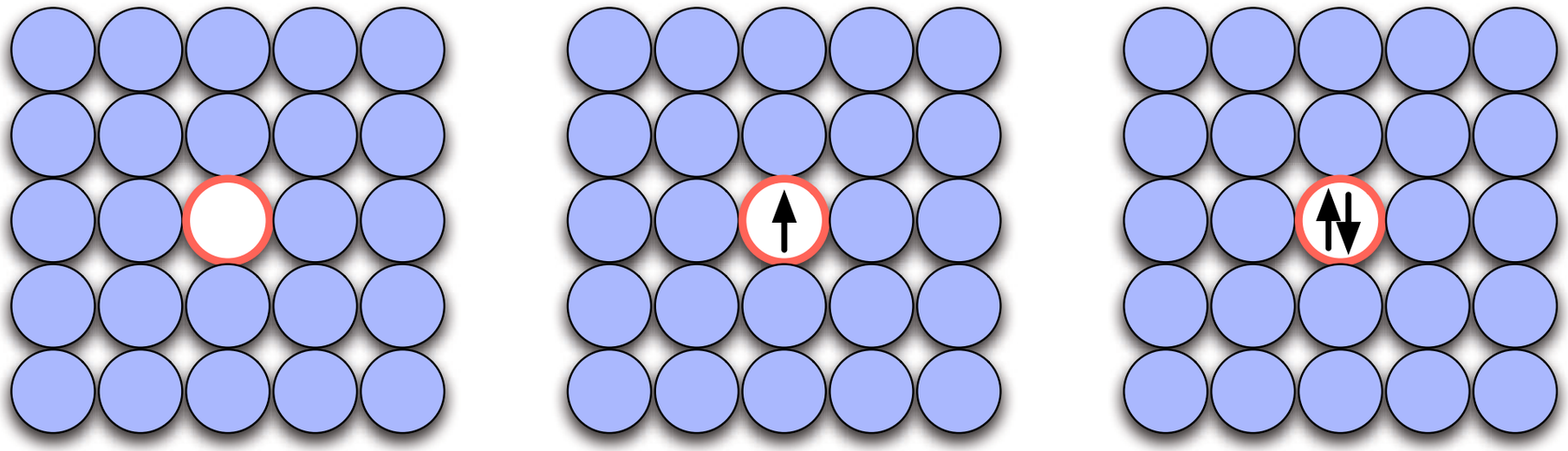
model for e_g bands





$$
\begin{aligned}
H= \quad & - \sum_{m,m',i,i',\sigma} t^{i,i'}_{mm'} c^{\dagger}_{im\sigma} c_{im'\sigma} + U \sum_{i\ m} \hat{n}_{im\uparrow} \hat{n}_{im\downarrow} \\
& + \quad \frac{1}{2} \sum_{\substack{i\sigma\sigma' \\ m\neq m'}} (U - 2J - J\delta_{\sigma,\sigma'}) \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} \\
& - \quad J \sum_{i\ m\neq m'} \left[c^{\dagger}_{im\uparrow} c^{\dagger}_{im\downarrow} c_{im'\uparrow} c_{im'\downarrow} + c^{\dagger}_{im\uparrow} c_{im\downarrow} c^{\dagger}_{im'\downarrow} c_{im'\uparrow} \right] - \hat{H}^{e_g}_{\mathrm{DC}}
\end{aligned}
$$

dynamical mean-field theory

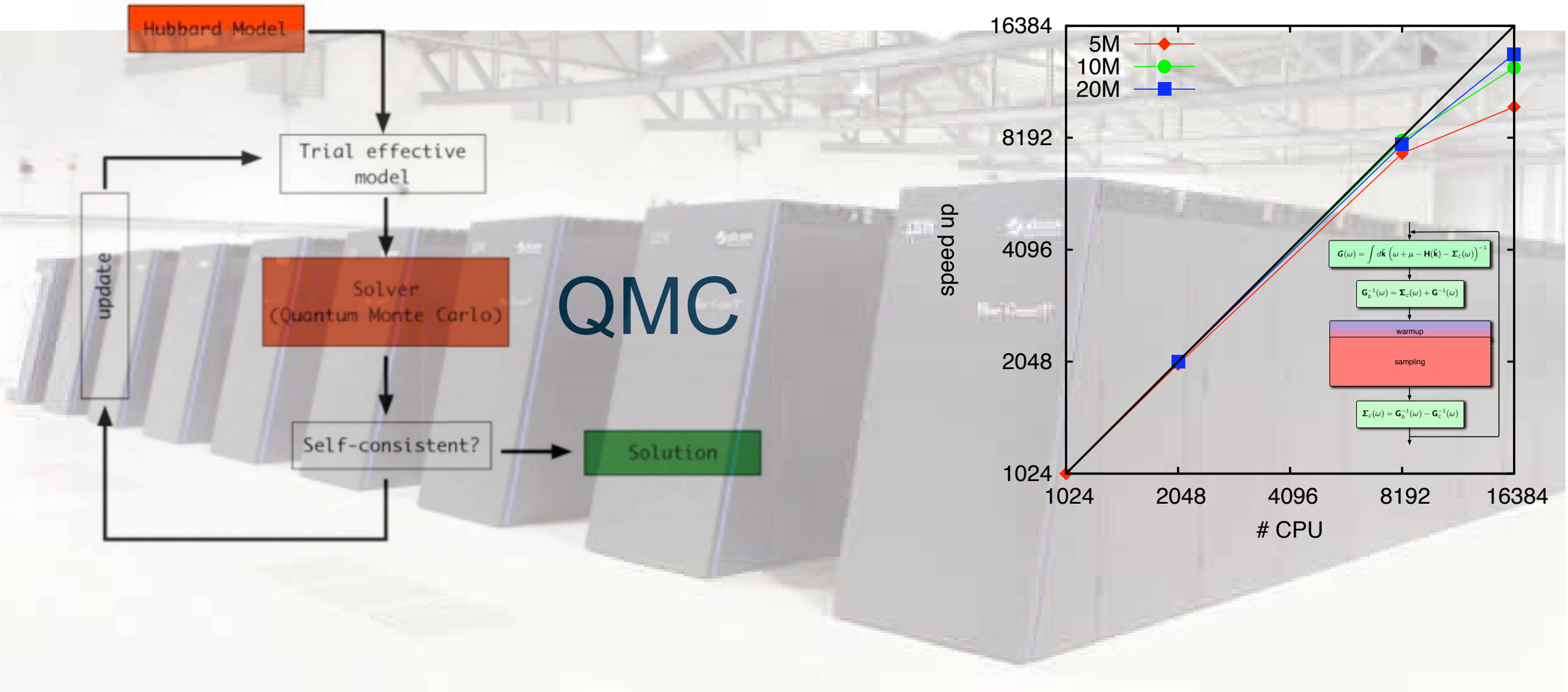


$$G_0{}^{-1} - G^{-1} = \Sigma(\omega)$$

dynamics captured self-energy local
exact in infinite dimensions

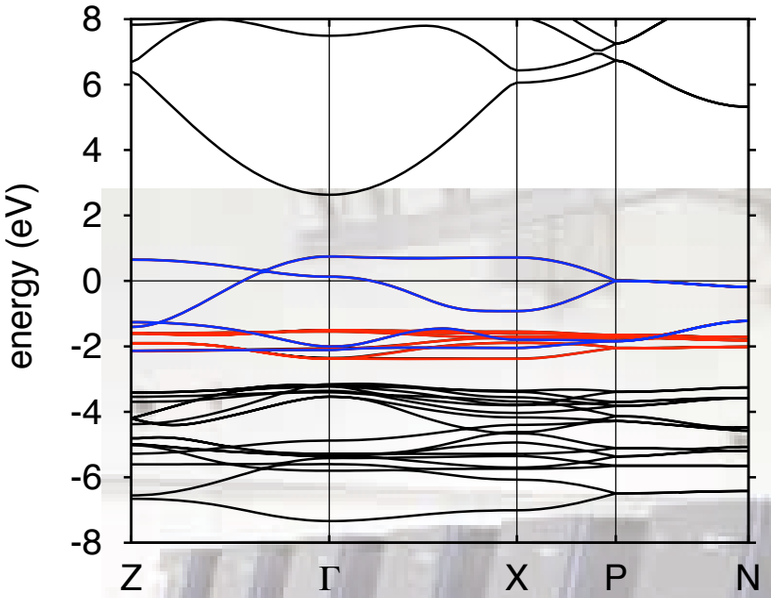
Metzner and Vollhardt, PRL **62**, 324 (1989); Georges and Kotliar, PRB **45,** 6479 (1992)

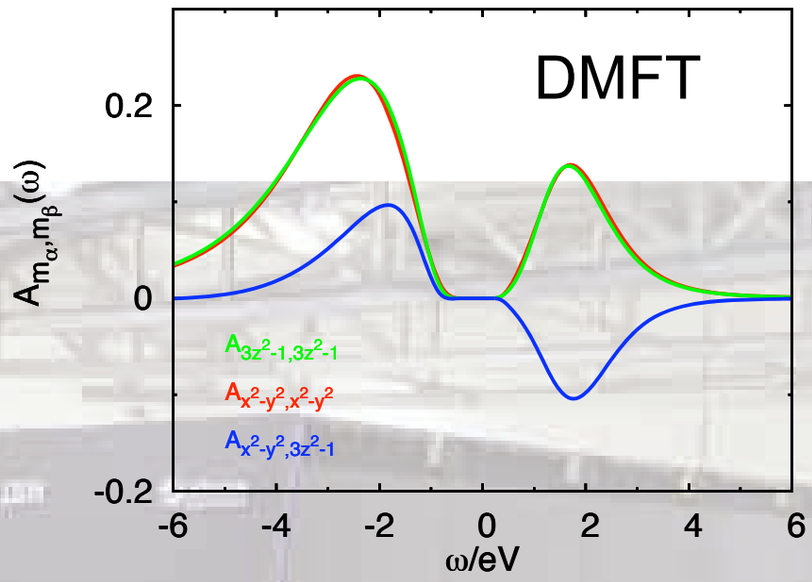
LDA+DMFT

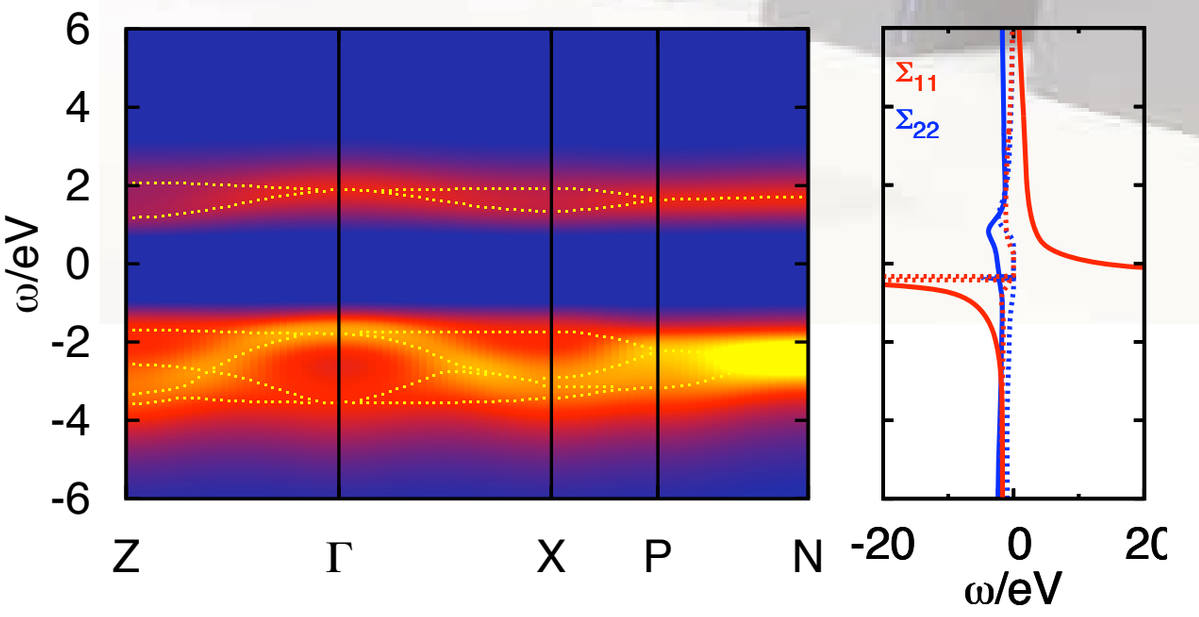


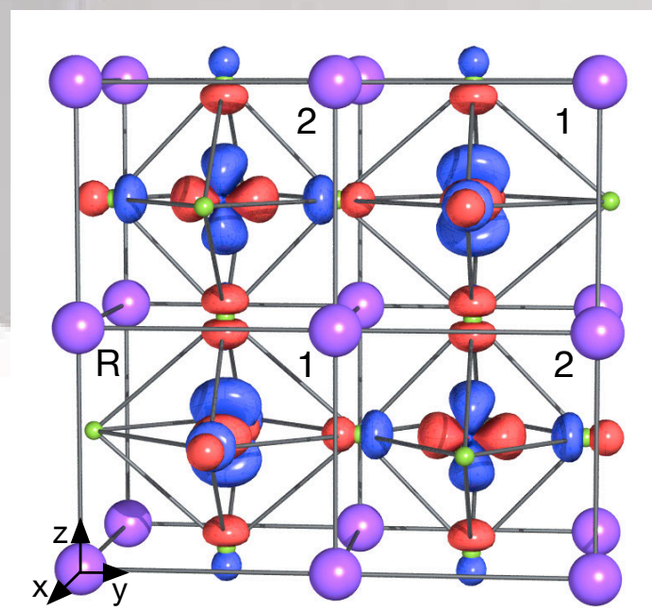
more details in chapter 6, The LDA+DMFT Approach, last year book

LDA+DMFT: $KCuF_3$

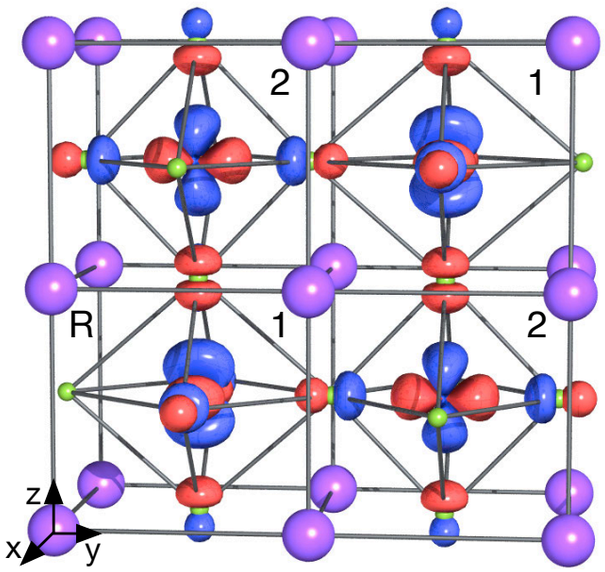








let us suppose we have no computers...



$$\hat{H}_e = \hat{H}^{\mathrm{LDA}} + \hat{U} - \hat{H}_{\mathrm{DC}}.$$

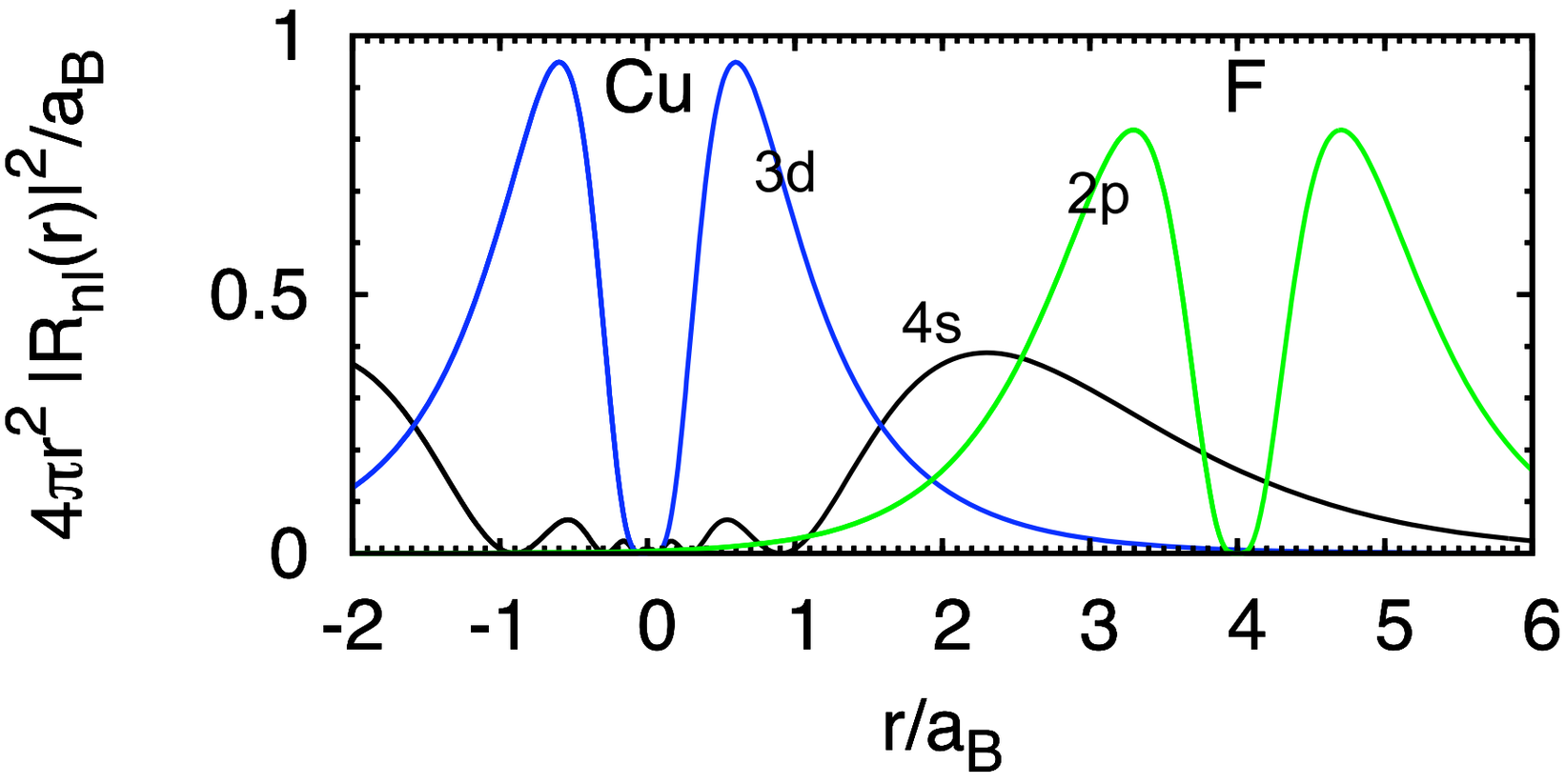
$$\hat{H}^{\mathrm{LDA}} = -\sum_{\sigma} \sum_{in,i'n'} t^{i,i'}_{n,n'} c^{\dagger}_{in\sigma} c_{i'n'\sigma},$$

$$t^{i,i'}_{n,n'} = -\int d\boldsymbol{r}\, \overline{\psi}_{in\sigma}(\boldsymbol{r})[-\frac{1}{2}\nabla^2 + v_{\mathrm{R}}(\boldsymbol{r})]\psi_{i'n'\sigma}(\boldsymbol{r}).$$

$$\varepsilon^{i,i}_{n,n'} = -t^{i,i}_{n,n'} = \int d\boldsymbol{r}\, \overline{\psi}_{in\sigma}(\boldsymbol{r}) \left[-\frac{1}{2}\nabla^2 + v_{\mathrm{R}}(\boldsymbol{r})\right] \psi_{in'\sigma}(\boldsymbol{r}).$$

the basis set

atomic functions



$$\psi_{nlm}(\rho,\theta,\phi) = R_{nl}(\rho)Y_l^m(\theta,\phi)$$

(hydrogen-like atom: Appendix B)

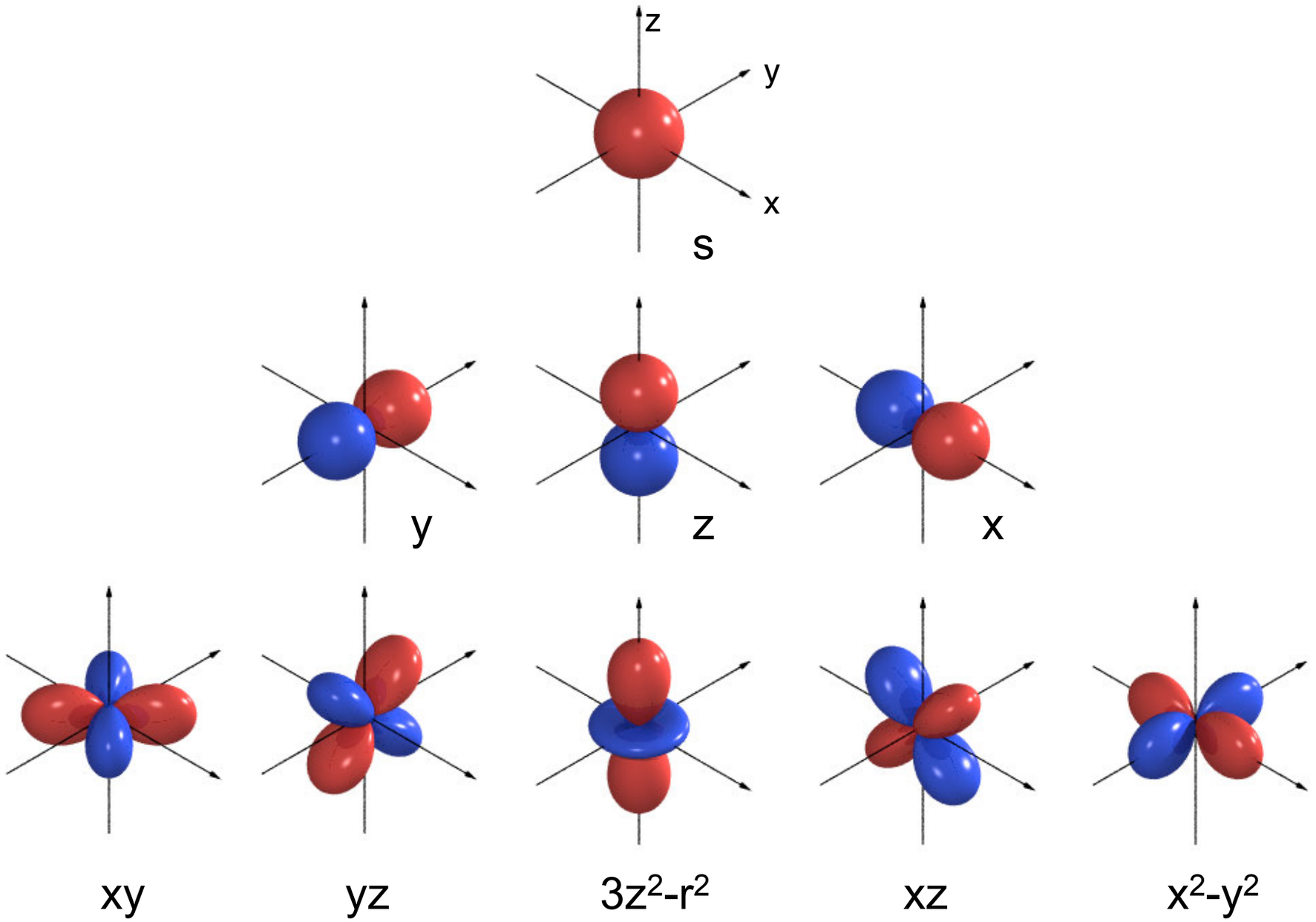
$$R_{nl}(\rho) = \sqrt{\left(\frac{2Z}{n}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\rho/n} \left(\frac{2\rho}{n}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2\rho}{n}\right)$$

Laguerre polynomials

real harmonics

$$
\begin{aligned}
s \quad &= y_{00} \quad = Y_0^0 \quad &&= \sqrt{\tfrac{1}{4\pi}} \\
p_y \quad &= y_{1-1} = \tfrac{i}{\sqrt{2}}(Y_1^1 + Y_{-1}^1) &&= \sqrt{\tfrac{3}{4\pi}} \quad y/r \\
p_z \quad &= y_{10} \quad = Y_2^0 \quad &&= \sqrt{\tfrac{3}{4\pi}} \quad z/r \\
p_x \quad &= y_{11} \quad = \tfrac{1}{\sqrt{2}}(Y_1^1 - Y_{-1}^1) &&= \sqrt{\tfrac{3}{4\pi}} \quad x/r \\
d_{xy} \quad &= y_{2-2} = \tfrac{i}{\sqrt{2}}(Y_2^2 - Y_{-2}^2) &&= \sqrt{\tfrac{15}{4\pi}} \quad xy/r^2 \\
d_{yz} \quad &= y_{2-1} = \tfrac{i}{\sqrt{2}}(Y_1^2 + Y_{-1}^2) &&= \sqrt{\tfrac{15}{4\pi}} \quad yz/r^2 \\
d_{3z^2-r^2} \quad &= y_{20} \quad = Y_2^0 \quad &&= \sqrt{\tfrac{15}{4\pi}}\tfrac{1}{2\sqrt{3}} \; (3z^2 - r^2)/r^2 \\
d_{xz} \quad &= y_{21} \quad = \tfrac{1}{\sqrt{2}}(Y_1^2 - Y_{-1}^2) &&= \sqrt{\tfrac{15}{4\pi}} \quad xz/r^2 \\
d_{x^2-y^2} \quad &= y_{22} \quad = \tfrac{1}{\sqrt{2}}(Y_2^2 + Y_{-2}^2) &&= \sqrt{\tfrac{15}{4\pi}}\tfrac{1}{2} \quad (x^2 - y^2)/r^2
\end{aligned}
$$

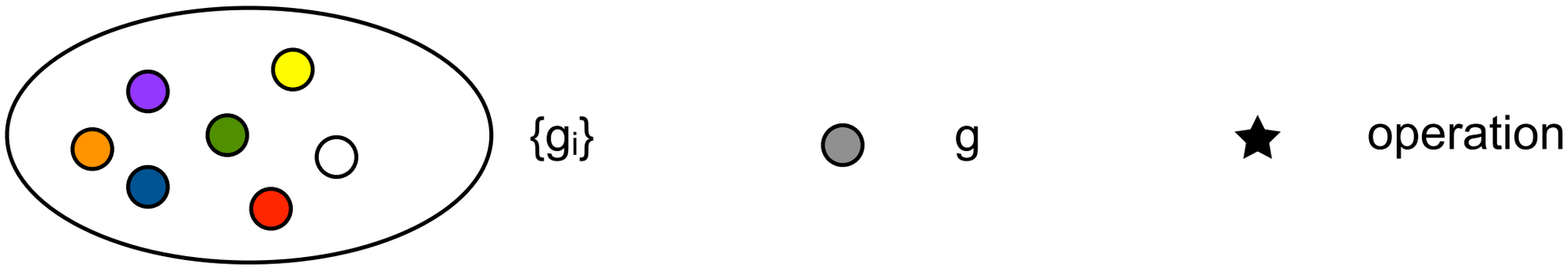
atomic functions



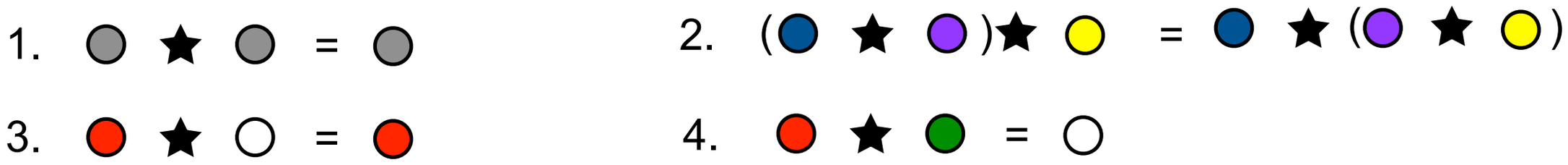
group theory

group

A *group* G is a set of elements $\{g_i\}$ plus an operation, $\star$, which satisfy the following conditions



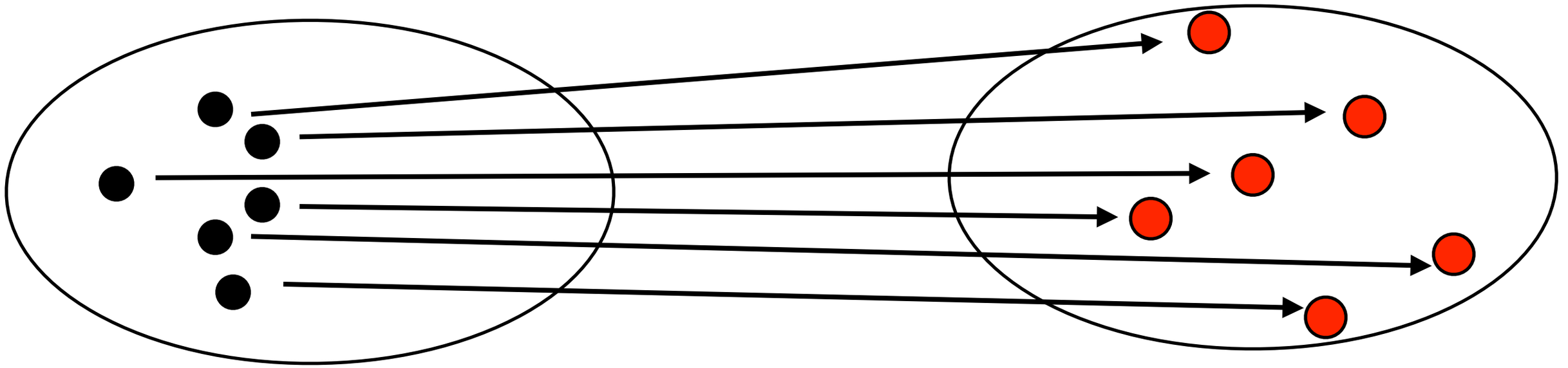
1. G is closed under group multiplication, i.e., $g_i \star g_j = g_k \in G \ \forall g_i,\ g_j \in G$
2. the *associative law* holds, i.e., $g_i \star (g_j \star g_k) = (g_i \star g_j) \star g_k \ \ \forall g_i,\ g_j,\ g_k \in G$
3. there is an *identity element* $e \in G$, such that $g_i \star e = e \star g_i = g_i \, \forall g_i \in G$
4. there is an *inverse element* $g_i^{-1} \in G$ to each $g_i \in G$, such that $g_i \star g_i^{-1} = g_i^{-1} \star g_i = e$



one-to-one correspondence

$G = \{g\}$

$G' = \{O(g)\}$



abstract group
defined by some algebra

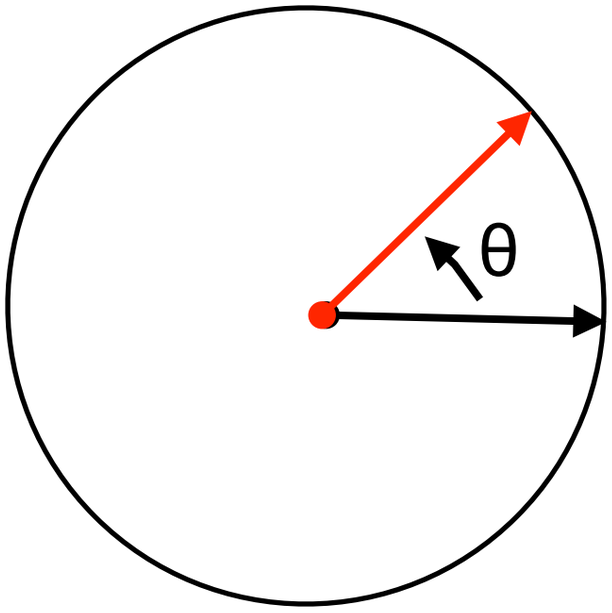
group of symmetry operators

+ linear space

representation of the
abstract group

matrix representations

example: group of rotations in 2D



$$G = \{g\}$$

$$g = R(\theta) \rightarrow M(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$$

$$\begin{aligned} x' &= x\cos\theta - y\sin\theta, \\ y' &= y\sin\theta + x\cos\theta. \end{aligned}$$

abstract group	group of matrices	linear space
SO(2)	orthogonal 2X2 with det=1	(x,y)

representations

basis transformations

$$BAB^{-1} = A'$$

character

$$\chi(g_i) = \mathrm{Tr}\ \Gamma(g_i)$$

reducible representation

$$\Gamma(g_i) = \begin{pmatrix} \Gamma_1(g_i) & 0 \\ 0 & \Gamma_2(g_i) \end{pmatrix} \quad \forall g_i \in G$$

irreducible representation

characters & orthogonality

orthogonality relations

$$\sum_i [\chi_{j_1}(g_i)]^* \chi_{j_2}(g_i) = \sum_k N_k [\chi_{j_1}(\mathcal{C}_k)]^* \chi_{j_2}(\mathcal{C}_k) = h\delta_{j_1,j_2}$$

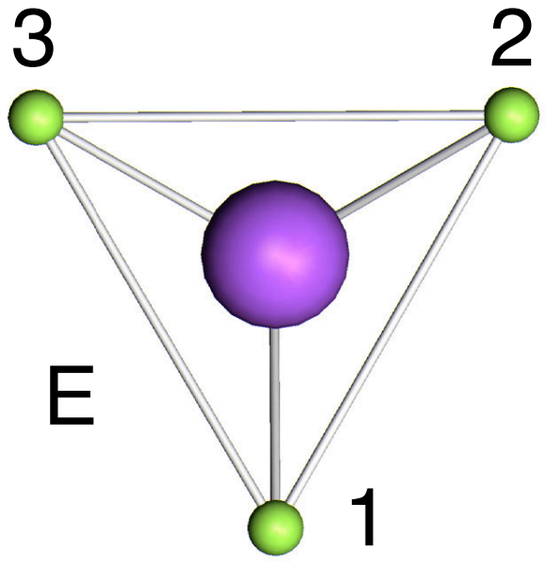
$$\sum_j [\chi_j(\mathcal{C}_k)]^* \chi_j(\mathcal{C}_l) = \frac{h}{N_k}\delta_{l,k}$$

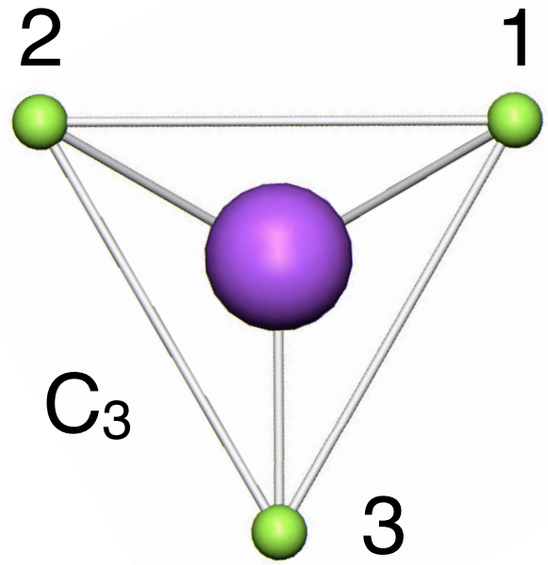
decomposition formula

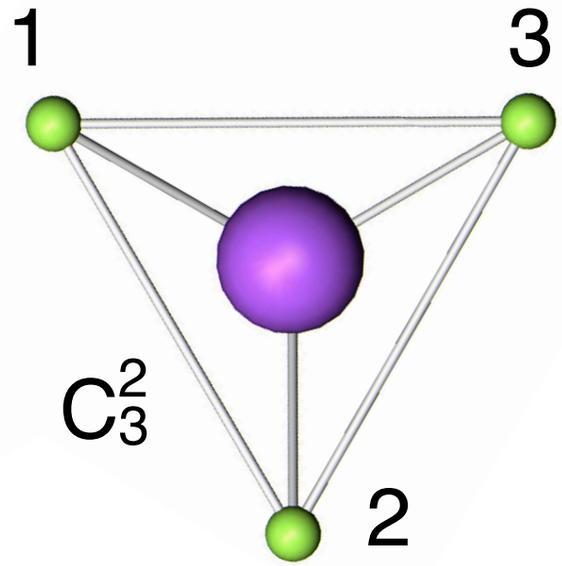
$$\chi(g_i) = \sum_j a_j \chi_j(g_i),$$

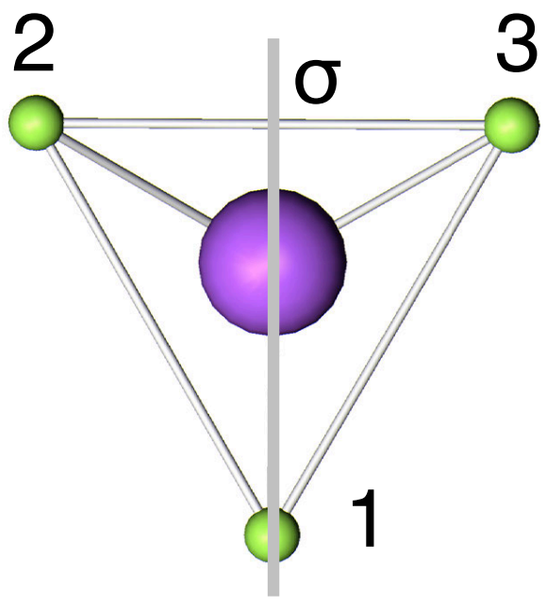
$$a_j = \frac{1}{h}\sum_k N_k [\chi_j(\mathcal{C}_k)]^* \chi(\mathcal{C}_k).$$

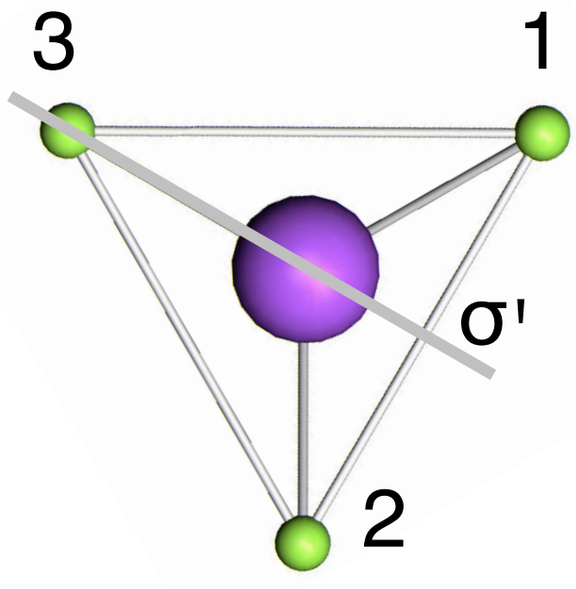
NH_3

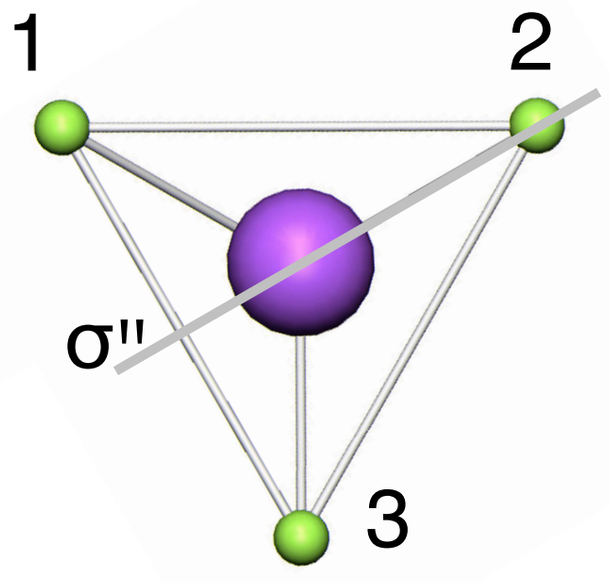






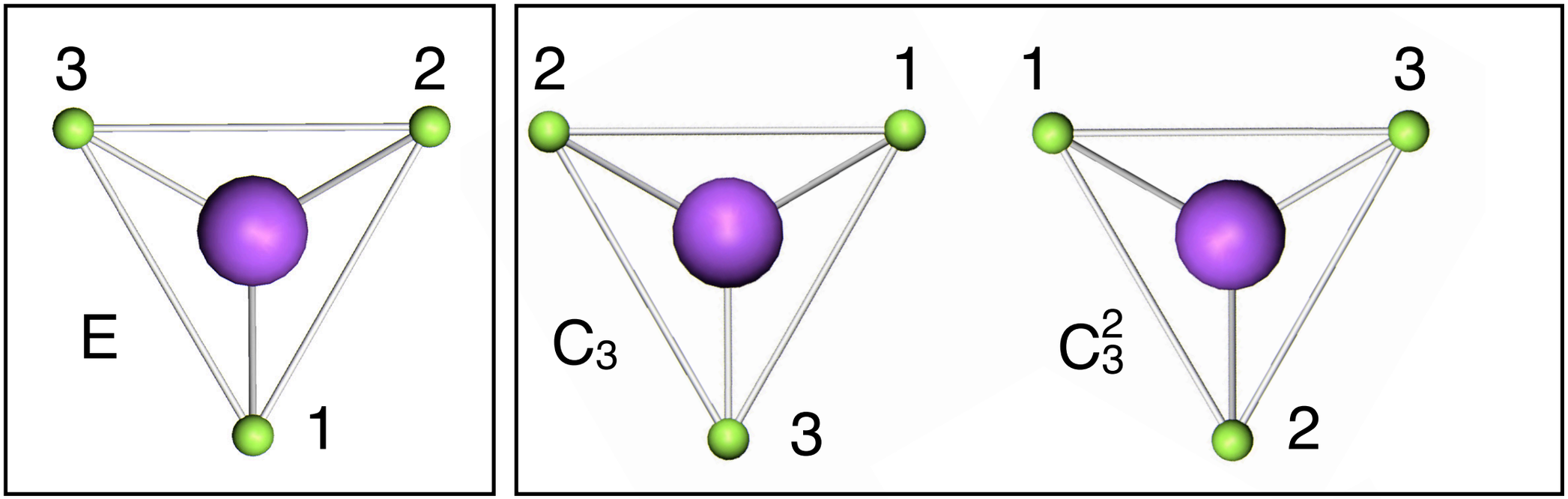






classes

$$g_i = g_X \star g_j \star g_X^{-1}$$



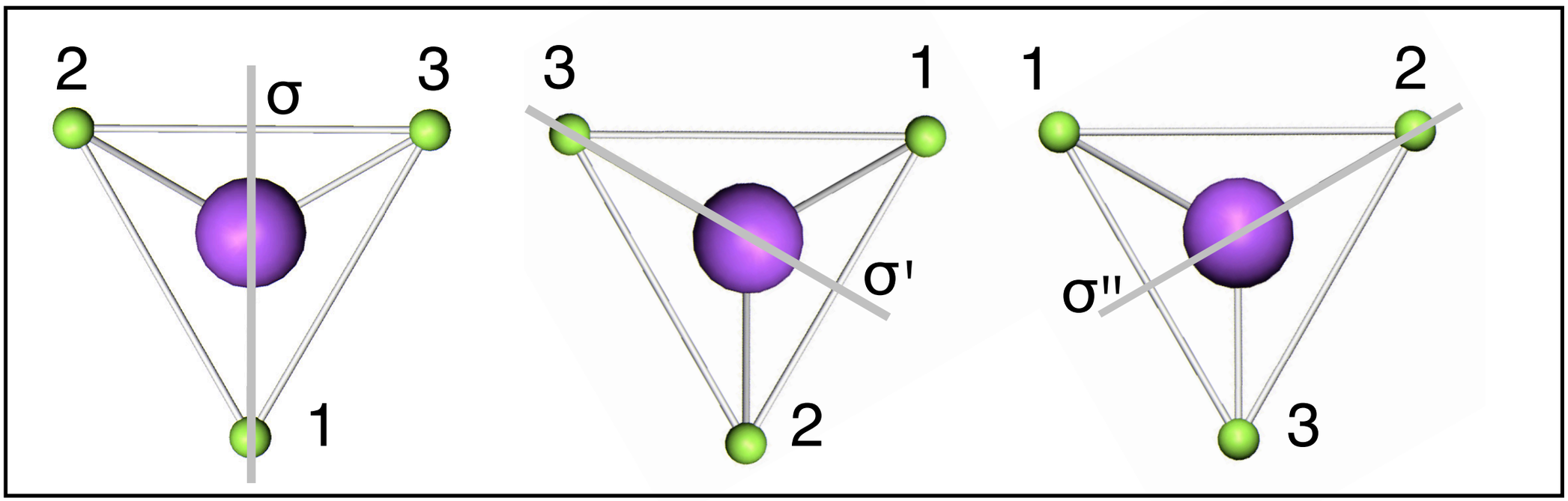
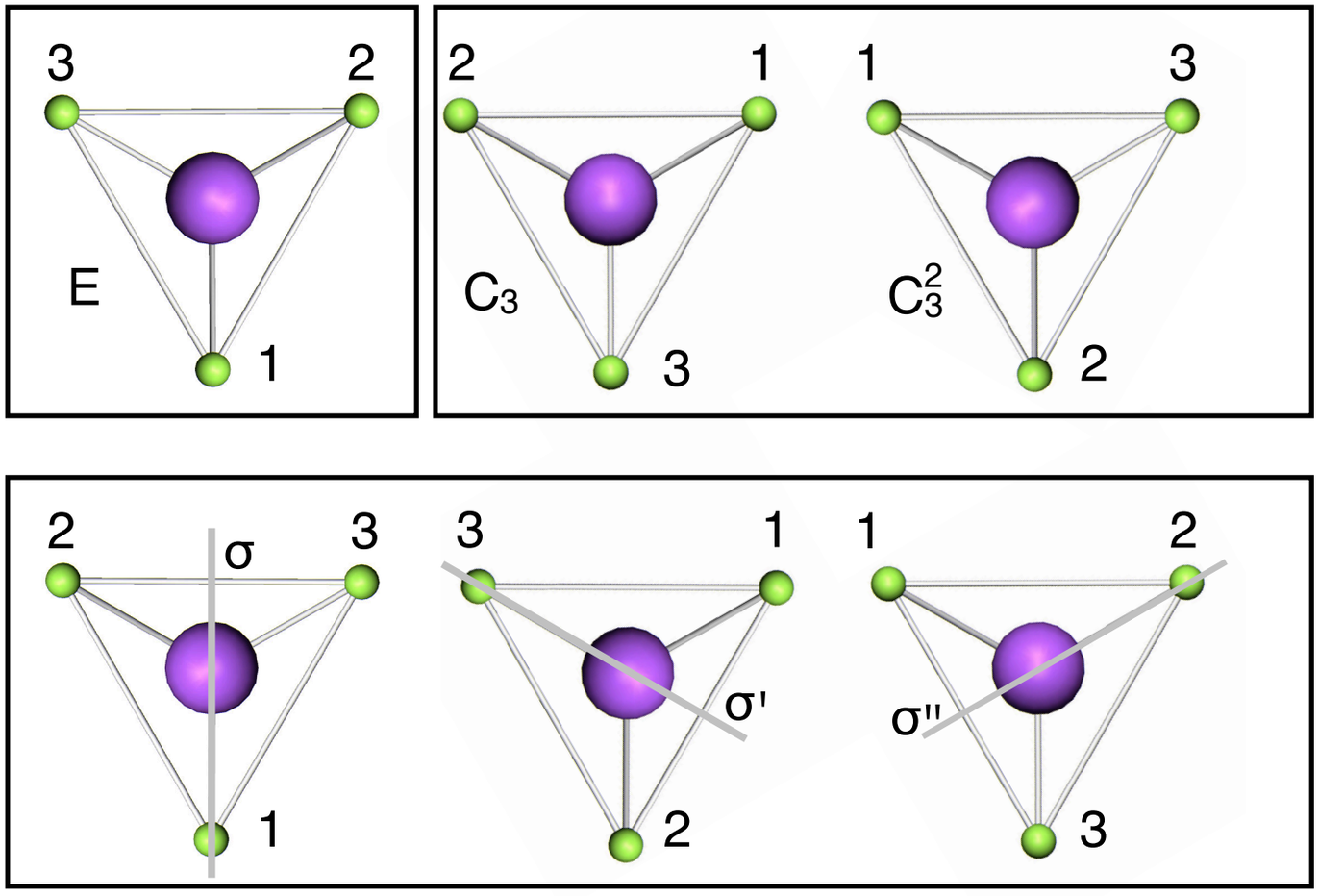


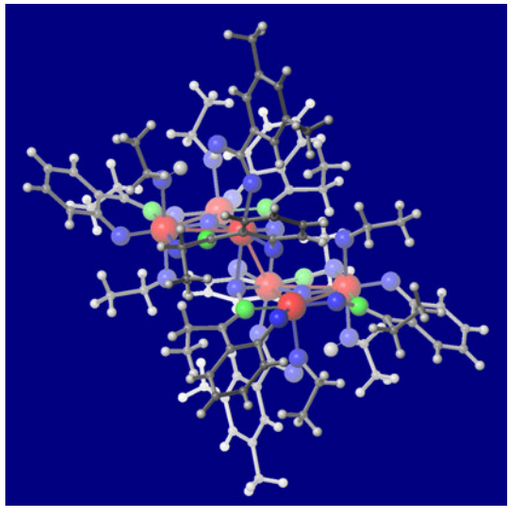
table of characters

trivial rep

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	−1
Γ_3	2	−1	0



partners for the irr reps



C_i	E	I
Γ_1	1	1
Γ_2	1	-1

s,xy,xz,yz, x^2-y^2, $3z^2$-r^2

x,y,z

$$\hat{\mathcal{P}}_j^{ii} = \frac{d_j}{h} \sum_g \left[\Gamma_j^{ii}(g)\right]^* O(g)$$

$$f_j^i(\boldsymbol{r}) = \hat{\mathcal{P}}_j^{ii} f(\boldsymbol{r})$$

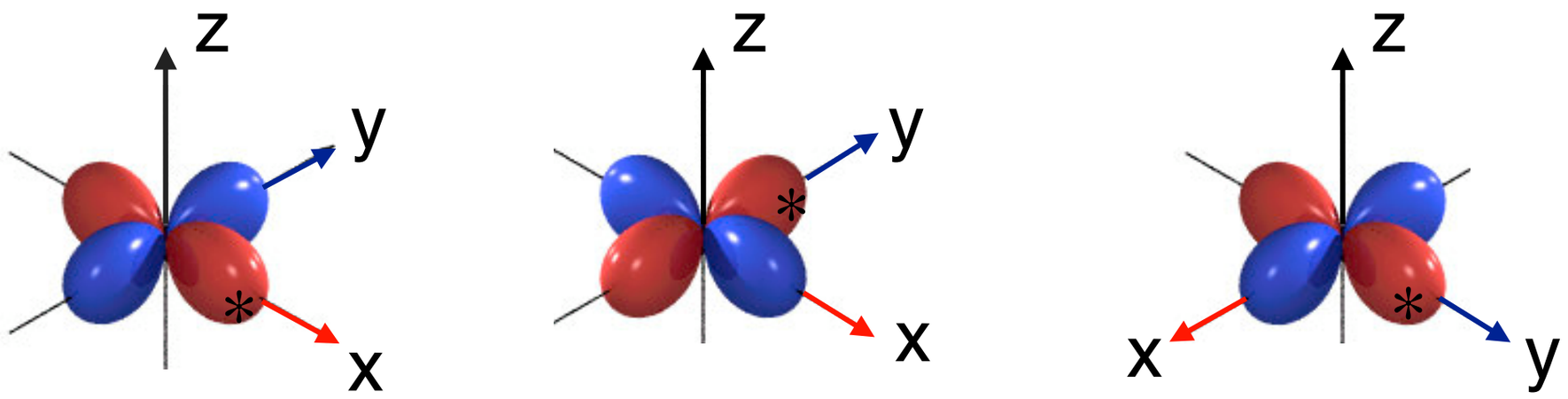
f(x) --- > [f(x)+f(-x)]/2 Γ_1

f(x) --- > [f(x)+f(-x)]/2 Γ_2

point group operations

- E, the identity
- C_n, a rotation by an angle $2\pi/n$; in a crystal, n can only take the values $n = 2, 3, 4, 6$
- σ reflection in a plane, classified as
  - σ_h, reflection through a plane perpendicular to the axis of highest rotation symmetry, called *principal axis*
  - σ_v, reflection through a plane to which the principal axis belongs
  - σ_d, reflection through a plane to which the principal axis belongs, and bisecting the angle between the two-fold axes perpendicular to the principal axis.
- $S_n = \sigma_h \otimes C_n$, improper rotation of an angle $2\pi/n$; in a crystal, n can only take the values $n = 3, 4, 6$.
- $I = S_2$, the inversion.

functions and operators



f(**r**) O(C$_4$)f(**r**) f(C$_{-4}$**r**)

$$f'(\boldsymbol{r}') = O(g)f(\boldsymbol{r}) = f(g^{-1}\boldsymbol{r}).$$

$$\hat{H}' = O(g)\hat{H}O(g^{-1}).$$

group of H

$$H = H'$$

$$O(g)\hat{H}\psi(\boldsymbol{r}) = O(g)\varepsilon_j\psi(\boldsymbol{r}) = \varepsilon_j O(g)\psi(\boldsymbol{r}) = \hat{H}O(g)\psi(\boldsymbol{r}).$$

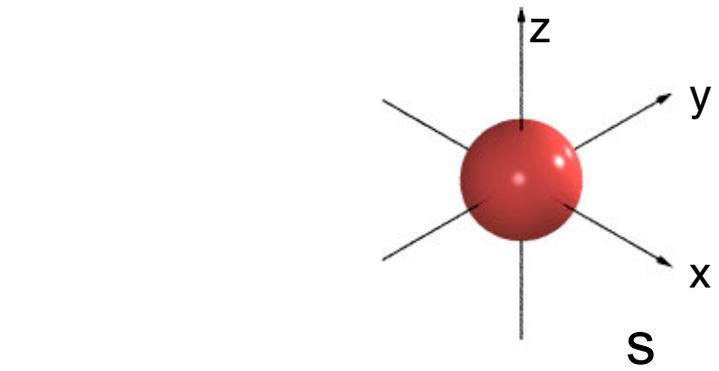
free atom

spherical potential

rotationally invariant, O(3) or more

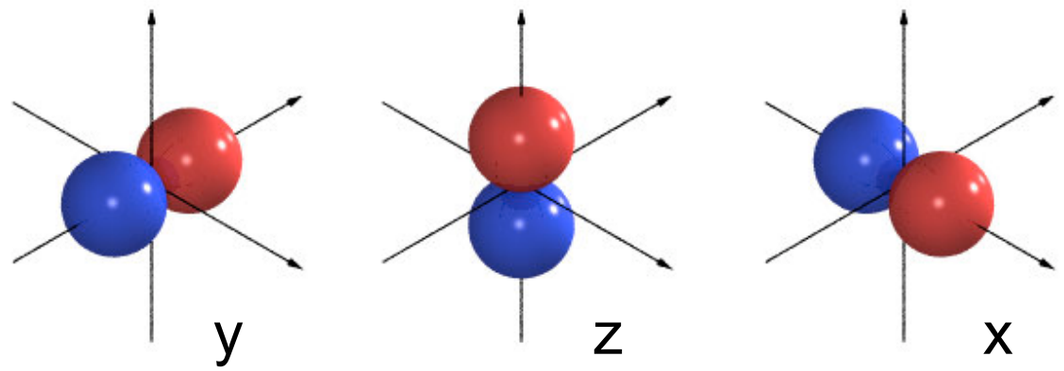
eigenvalues: n

eigenvectors: n,l,m



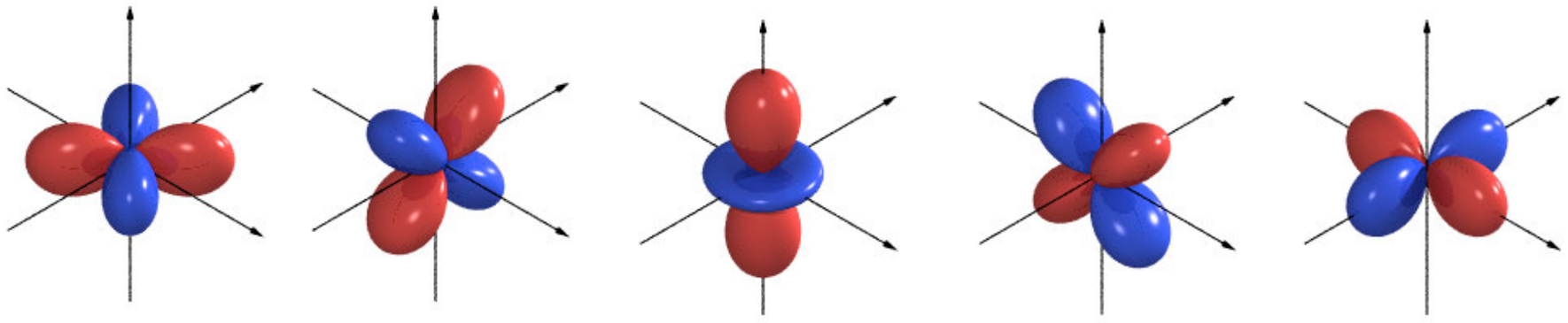
s

l=0



y z x

l=1



xy yz $3z^2-r^2$ xz x^2-y^2

l=2

2l+1-dim irr reps

basis $\psi_{nlm}(\rho,\theta,\phi) = R_{nl}(\rho)Y_m^l(\theta,\phi)$

identity E $\chi^l(E) = 2l+1$

rotation $O(C_\alpha)Y_m^l(\theta,\phi) = Y_m^l(\theta,\phi-\alpha) = e^{-im\alpha}Y_m^l(\theta,\phi).$

$$\chi^l(\alpha) = \sum_{m=-l}^{l} e^{-im\alpha} = \frac{\sin(l+\frac{1}{2})\alpha}{\sin\frac{\alpha}{2}}.$$

inversion $\chi^l(I) = (-1)^l(2l+1).$

reflection $\chi^l(\sigma_h) = (-1)^l.$

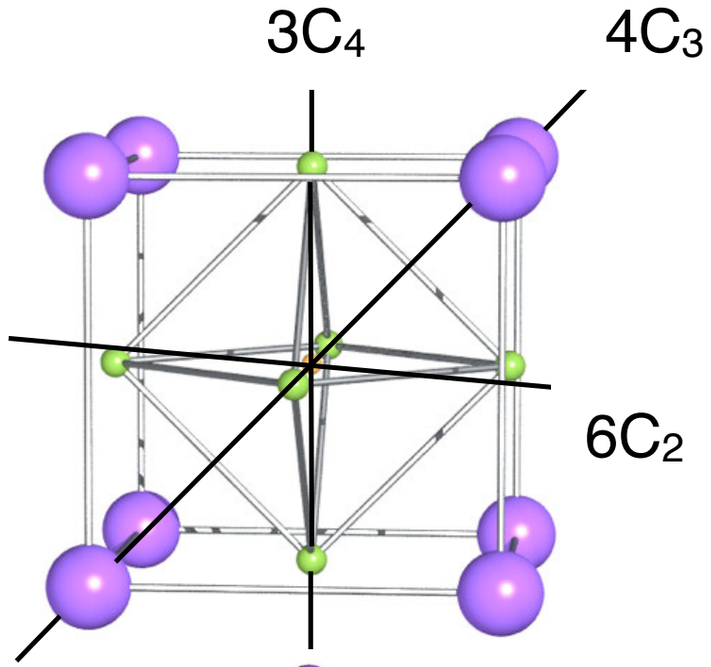
improper rotation $S_\alpha = I \otimes C_{\alpha+\pi}$ $\chi^l(S_\alpha) = (-1)^l \frac{\sin(l+\frac{1}{2})(\alpha+\pi)}{\sin\frac{\alpha+\pi}{2}}$

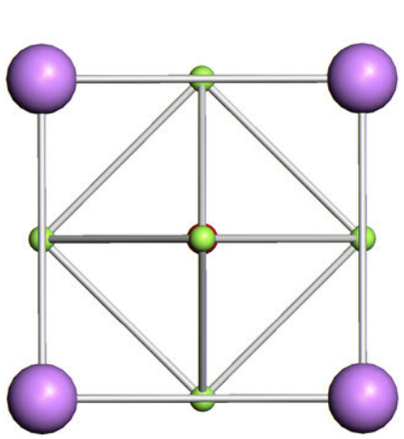
$O(3)$	E	C_α	I	S_α	σ
Γ^l	$2l+1$	$\sin(l+\frac{1}{2})\alpha/\sin\frac{\alpha}{2}$	$(-1)^l(2l+1)$	$(-1)^l\sin(l+\frac{1}{2})(\alpha+\pi)/\sin\frac{\alpha+\pi}{2}$	$(-1)^l$

from atoms to materials:
the crystal field

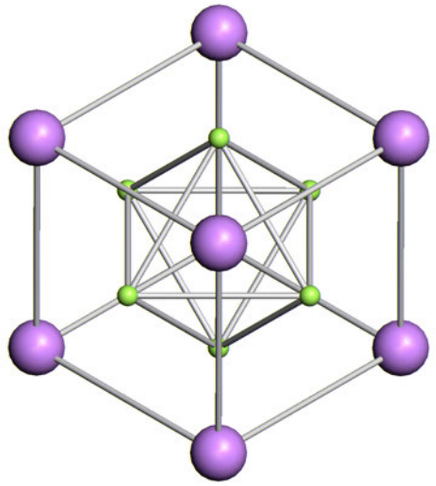
perovskite structure ABC_3

rotations (group O)

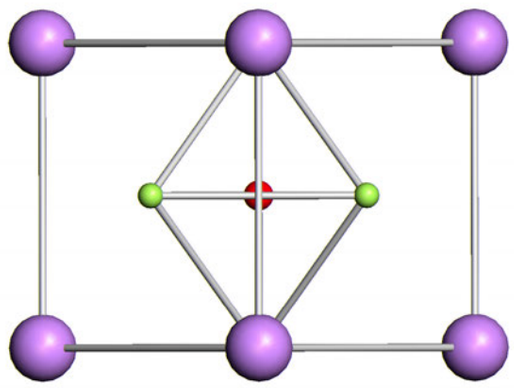




C_4



C_3



C_2

perovskite: group $O_h = O \otimes C_i$

it is the symmetry group of the cube

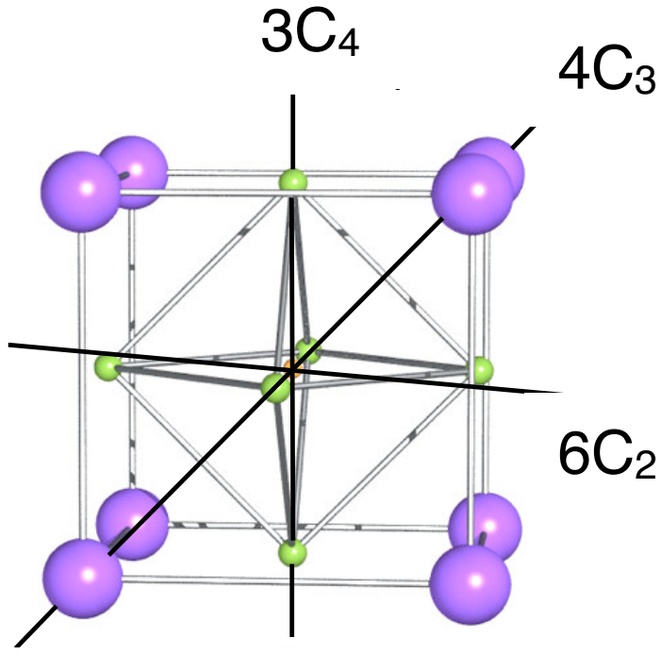
crystal-field theory

how do d levels split at the Cu site?

point charge model

$$v_{\mathrm{R}}(\boldsymbol{r}) = \sum_{\alpha} \frac{q_\alpha}{|\boldsymbol{R}_\alpha - \boldsymbol{r}|} = v_0(r) + \sum_{\alpha \neq 0} \frac{q_\alpha}{|\boldsymbol{R}_\alpha - \boldsymbol{r}|} = v_0(r) + v_c(\boldsymbol{r})$$

crystal field



cubic perovskite

point charge model: F_6 octahedron

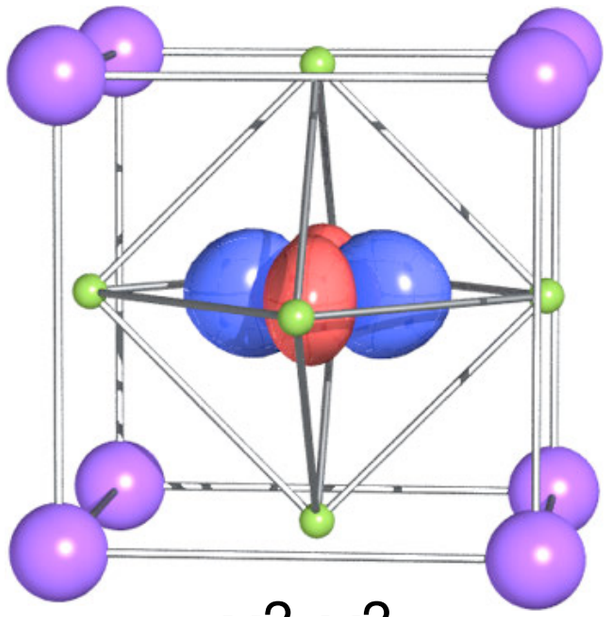
$$v_{\mathrm{oct}}(\boldsymbol{r}) = \frac{35}{4}\frac{q_C}{a^5}\left(x^4+y^4+z^4-\frac{3}{5}r^4\right) = D\left(x^4+y^4+z^4-\frac{3}{5}r^4\right).$$

$$H_{\mathrm{CF}} = \begin{array}{c} \begin{array}{ccccc} \text{m=-2} & \text{m=-1} & \text{m=0} & \text{m=1} & \text{m=2} \end{array} \\ \begin{pmatrix} Dq & 0 & 0 & 0 & 5Dq \\ 0 & -4Dq & 0 & 0 & 0 \\ 0 & 0 & 6Dq & 0 & 0 \\ 0 & 0 & 0 & -4Dq & 0 \\ 5Dq & 0 & 0 & 0 & Dq \end{pmatrix} \end{array}.$$

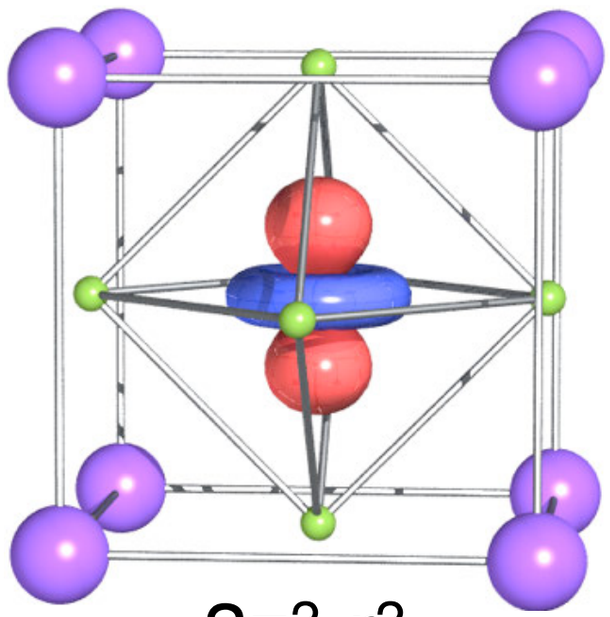
$$\psi_{nlm}(\rho,\theta,\phi) = R_{nl}(\rho)Y_l^m(\theta,\phi)$$

atomic functions

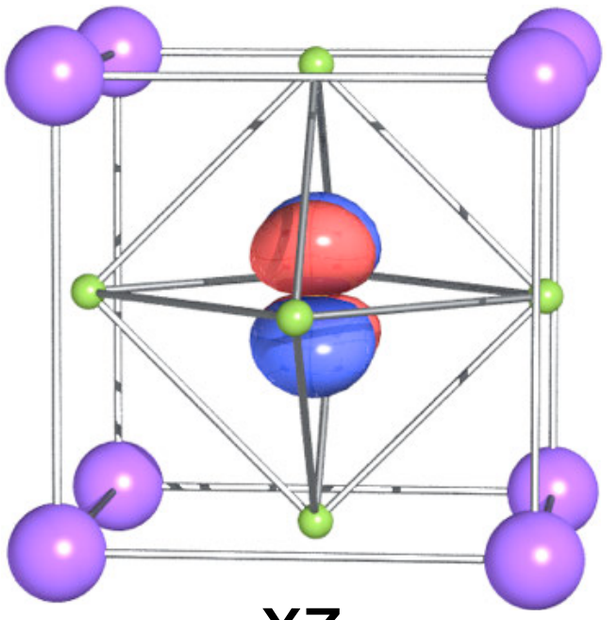
atomic d orbitals



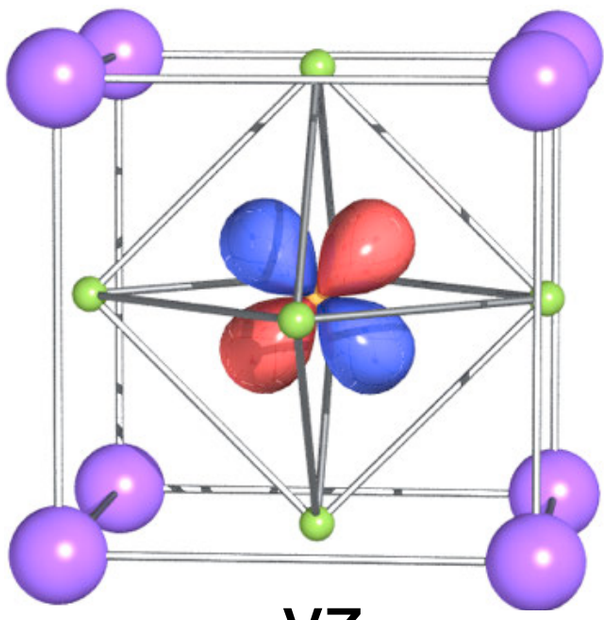
x^2-y^2



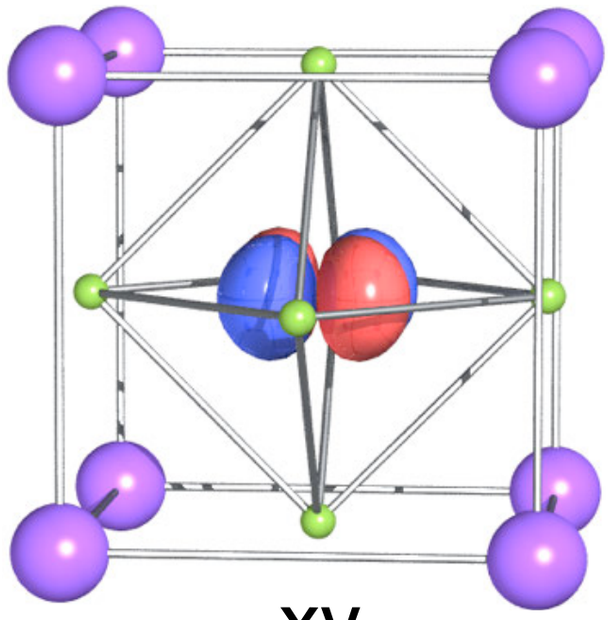
$3z^2-r^2$



xz



yz



xy

crystal field and group theory

$O(3)$	E	C_α	I	S_α	σ
Γ^l	$2l+1$	$\sin(l+\frac{1}{2})\alpha/\sin\frac{\alpha}{2}$	$(-1)^l(2l+1)$	$(-1)^l\sin(l+\frac{1}{2})(\alpha+\pi)/\sin\frac{\alpha+\pi}{2}$	$(-1)^l$

$$O_h = O \otimes C_i$$

O	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
Γ^s	1	1	1	1	1
Γ^p	3	0	-1	-1	1
Γ^d	5	-1	1	1	-1
Γ^f	7	1	-1	-1	-1

crystal field and group theory

O	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
Γ^s	1	1	1	1	1
Γ^p	3	0	−1	−1	1
Γ^d	5	−1	1	1	−1
Γ^f	7	1	−1	−1	−1

$$\chi(g_i) = \sum_j a_j \chi_j(g_i),$$

$$a_j = \frac{1}{h} \sum_k N_k [\chi_j(\mathcal{C}_k)]^* \chi(\mathcal{C}_k).$$

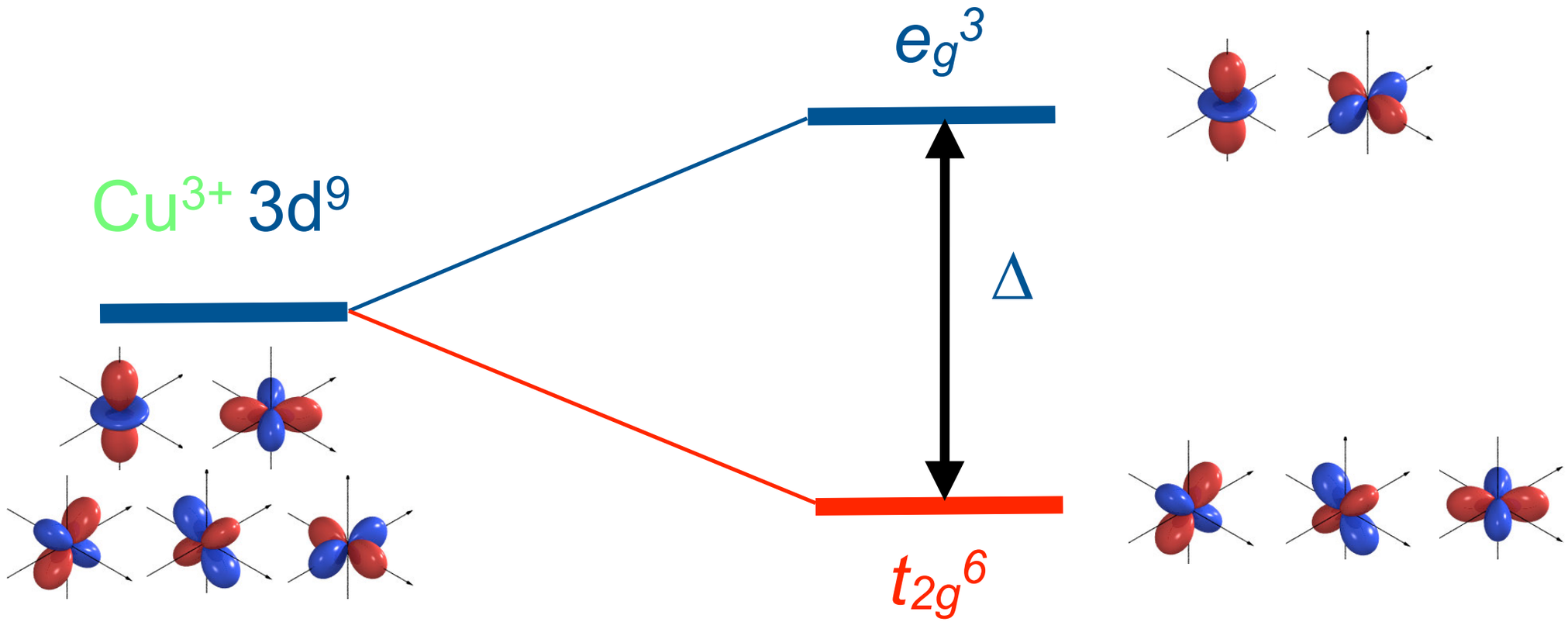
O		E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
$(x^2+y^2+z^2)$	A_1	1	1	1	1	1
	A_2	1	1	1	−1	−1
$(x^2-y^2, 3z^2-r^2)$	E	2	−1	2	0	0
(x,y,z)	T_1	3	0	−1	−1	1
(xy,xz,yz)	T_2	3	0	−1	1	−1

$$\Gamma^s = a_1$$
$$\Gamma^p = t_1$$
$$\Gamma^d = e \oplus t_2$$
$$\Gamma^f = a_2 \oplus t_1 \oplus t_2$$

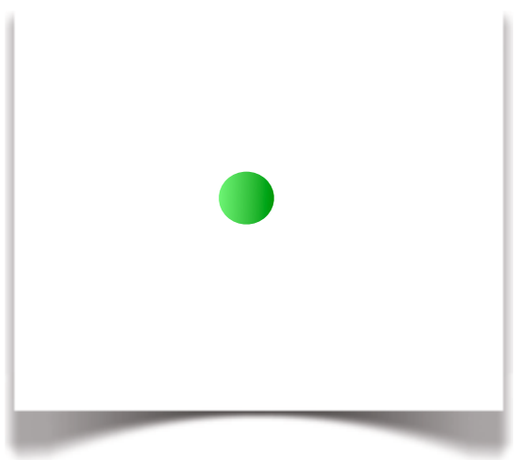
$$\hat{\mathcal{P}}_j^{ii} = \frac{d_j}{h} \sum_g \left[\Gamma_j^{ii}(g)\right]^* O(g)$$

$$f_j^i(\boldsymbol{r}) = \hat{\mathcal{P}}_j^{ii} f(\boldsymbol{r})$$

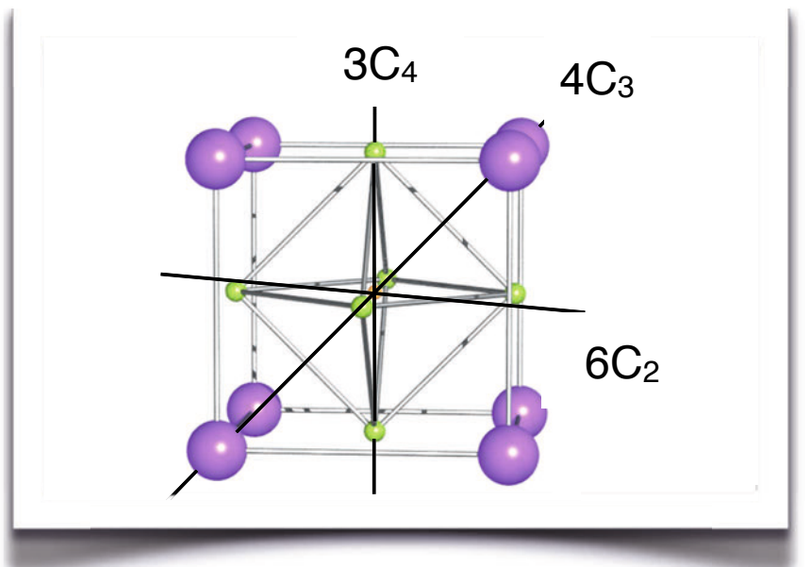
cubic crystal-field



spherical



cubic

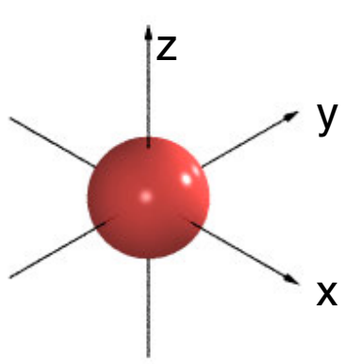


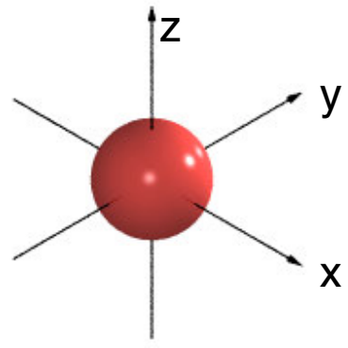
from atoms to materials:
the tight-binding method

hydrogen molecular ion

$$\hat{h}_e(\boldsymbol{r}) = -\frac{1}{2}\nabla^2 - \frac{1}{|\boldsymbol{r}-\boldsymbol{R}_1|} - \frac{1}{|\boldsymbol{r}-\boldsymbol{R}_2|} = -\frac{1}{2}\nabla^2 + v(\boldsymbol{r}-\boldsymbol{R}_1) + v(\boldsymbol{r}-\boldsymbol{R}_2) = -\frac{1}{2}\nabla^2 + v_R(\boldsymbol{r}).$$

basis: s functions



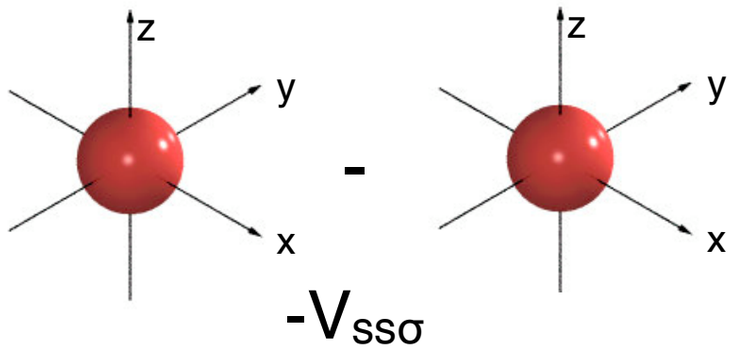


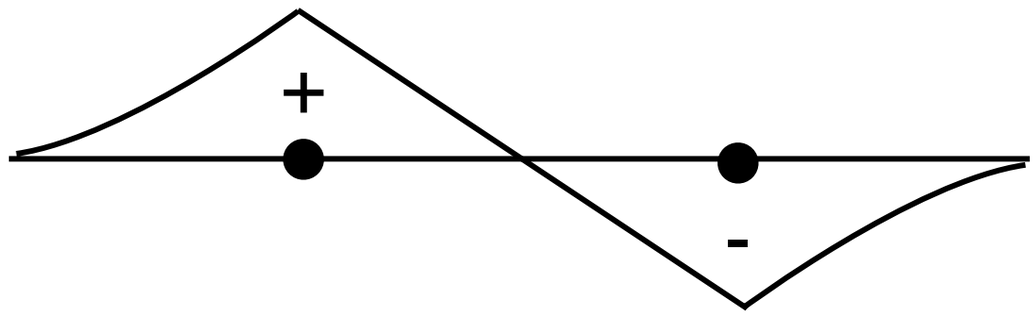
hydrogen molecular ion

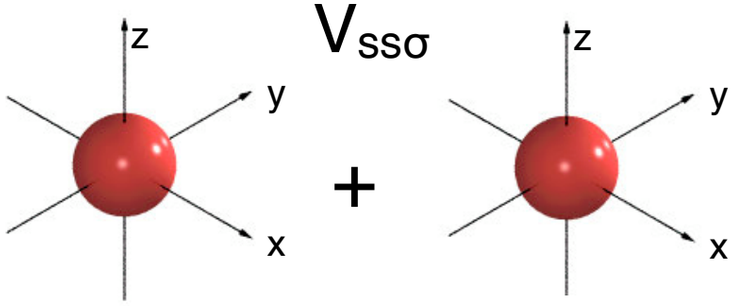
$$H = \varepsilon_{1s}^{0}\, O + \begin{pmatrix} \Delta\varepsilon_{1s} & V_{ss\sigma} \\ V_{ss\sigma} & \Delta\varepsilon_{1s} \end{pmatrix} \qquad O = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}$$

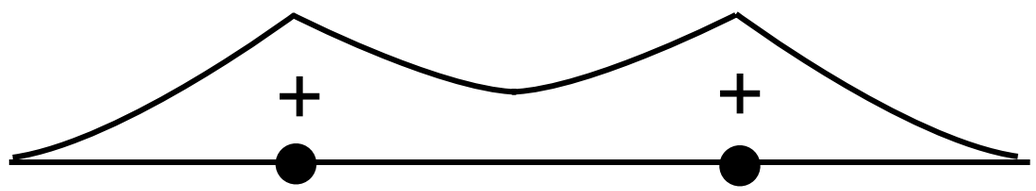
$$\begin{aligned}
\Delta\varepsilon_{1s} &= \int d\boldsymbol{r}\, \psi_{1s}(\boldsymbol{r} - \boldsymbol{R}_\alpha)\, [v_R(\boldsymbol{r}) - v(\boldsymbol{r} - \boldsymbol{R}_\alpha)]\, \psi_{1s}(\boldsymbol{r} - \boldsymbol{R}_\alpha), \quad \alpha = 1, 2 \\
V_{ss\sigma} &= \int d\boldsymbol{r}\, \psi_{1s}(\boldsymbol{r} - \boldsymbol{R}_\alpha) v(\boldsymbol{r} - \boldsymbol{R}_\alpha) \psi_{1s}(\boldsymbol{r} - \boldsymbol{R}_{\alpha'}), \quad \alpha \neq \alpha' \\
S &= \int d\boldsymbol{r}\, \psi_{1s}(\boldsymbol{r} - \boldsymbol{R}_\alpha) \psi_{1s}(\boldsymbol{r} - \boldsymbol{R}_{\alpha'}), \quad \alpha \neq \alpha'.
\end{aligned}$$

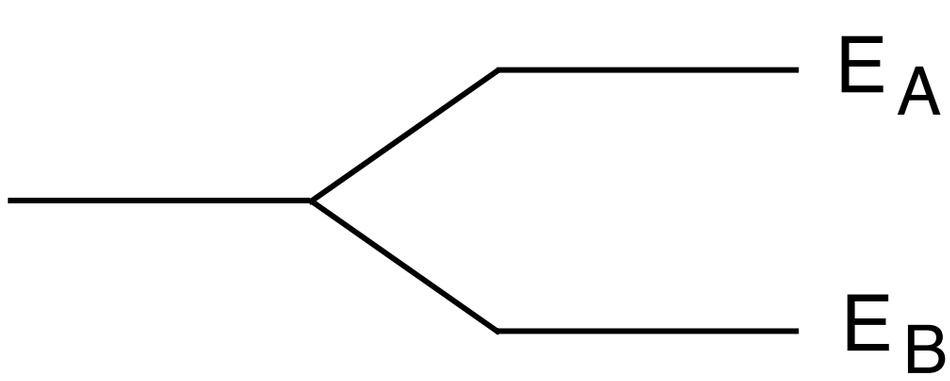
hydrogen molecular ion











$$E_A = \varepsilon_{1s}^0 + \frac{\Delta\varepsilon_{1s} - V_{ss\sigma}}{1 - S}$$

$$E_B = \varepsilon_{1s}^0 + \frac{\Delta\varepsilon_{1s} + V_{ss\sigma}}{1 + S}.$$

crystal

$$\hat{h}_e(\boldsymbol{r}) = -\frac{1}{2}\nabla^2 - \sum_{i,\alpha} \frac{Z_{i,\alpha}}{|\boldsymbol{r} - \boldsymbol{T}_i - \boldsymbol{R}_\alpha|} = -\frac{1}{2}\nabla^2 + \sum_{i,\alpha} v(\boldsymbol{r} - \boldsymbol{T}_i - \boldsymbol{R}_\alpha) = -\frac{1}{2}\nabla^2 + v_R(\boldsymbol{r}),$$

Bloch functions

$$\psi^\alpha_{lm}(\boldsymbol{k}, \boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_i e^{i\boldsymbol{T}_i \cdot \boldsymbol{k}}\ \psi_{lm}(\boldsymbol{r} - \boldsymbol{T}_i - \boldsymbol{R}_\alpha).$$

$$\begin{aligned} H^{\alpha,\alpha'}_{lm,l'm'}(\boldsymbol{k}) &= \langle \psi^\alpha_{lm}(\boldsymbol{k}) | \hat{h}_e | \psi^{\alpha'}_{l'm'}(\boldsymbol{k}) \rangle, \\ O^{\alpha,\alpha'}_{lm,l'm'}(\boldsymbol{k}) &= \langle \psi^\alpha_{lm}(\boldsymbol{k}) | \psi^{\alpha'}_{l'm'}(\boldsymbol{k}) \rangle. \end{aligned}$$

Hamiltonian

Overlap

crystal

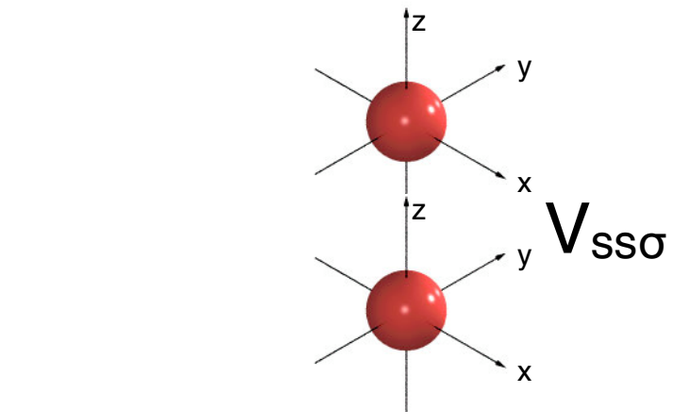
$$H^{\alpha,\alpha'}_{lm,l'm'}(\boldsymbol{k}) = \varepsilon^{0}_{l'\alpha'} O^{\alpha,\alpha'}_{lm,l'm'}(\boldsymbol{k}) + \Delta\varepsilon^{\alpha}_{lm,l'm'}\delta_{\alpha,\alpha'} - \frac{1}{N}\sum_{i\alpha\neq i'\alpha'} e^{i(\boldsymbol{T}_{i'}-\boldsymbol{T}_i)\cdot\boldsymbol{k}}\; t^{i\alpha,i'\alpha'}_{lm,l'm'}.$$

$$\Delta\varepsilon^{\alpha}_{lm,l'm'} = \int d\boldsymbol{r}\, \overline{\psi}_{lm}(\boldsymbol{r}-\boldsymbol{R}_\alpha)[v_R(\boldsymbol{r}) - v(\boldsymbol{r}-\boldsymbol{R}_\alpha)]\psi_{l'm'}(\boldsymbol{r}-\boldsymbol{R}_\alpha),$$

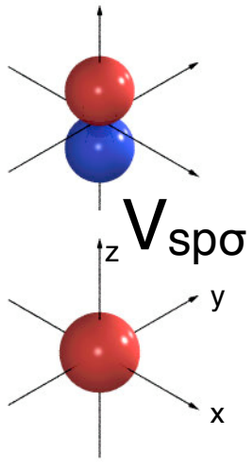
$$t^{i\alpha,i'\alpha'}_{lm,l'm'} = -\int d\boldsymbol{r}\, \overline{\psi}_{lm}(\boldsymbol{r}-\boldsymbol{R}_\alpha-\boldsymbol{T}_i)[v_R(\boldsymbol{r}) - v(\boldsymbol{r}-\boldsymbol{R}_{\alpha'}-\boldsymbol{T}_{i'})]\psi_{l'm'}(\boldsymbol{r}-\boldsymbol{R}_{\alpha'}-\boldsymbol{T}_{i'}).$$

$$V^{i\alpha,i'\alpha'}_{lm,l'm'} = \int d\boldsymbol{r}\, \overline{\psi}_{lm}(\boldsymbol{r}-\boldsymbol{R}_\alpha-\boldsymbol{T}_i) v(\boldsymbol{r}-\boldsymbol{R}_\alpha-\boldsymbol{T}_i)\psi_{l'm'}(\boldsymbol{r}-\boldsymbol{R}_{\alpha'}-\boldsymbol{T}_{i'})$$

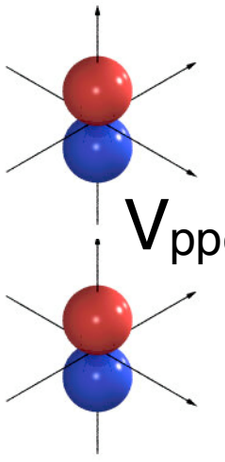
two-center integrals



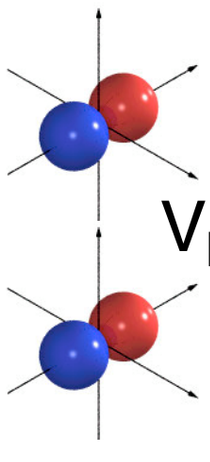
$V_{ss\sigma}$



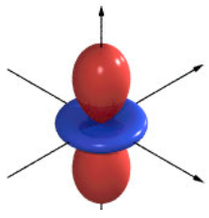
$V_{sp\sigma}$



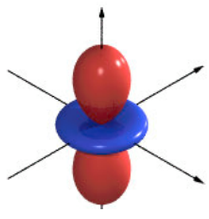
$V_{pp\sigma}$



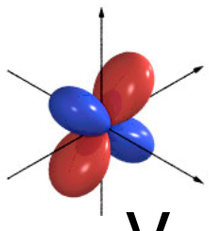
$V_{pp\pi}$



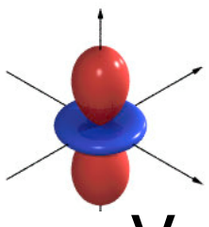
$V_{sd\sigma}$



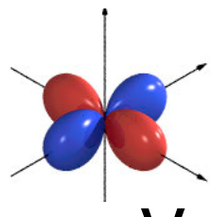
$V_{pd\sigma}$



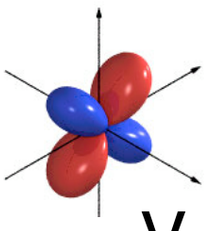
$V_{pd\pi}$



$V_{dd\sigma}$

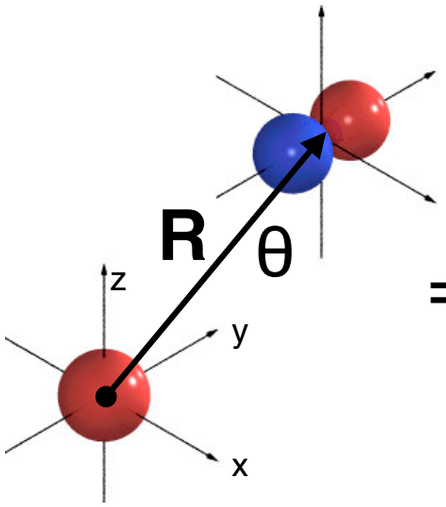


$V_{dd\delta}$

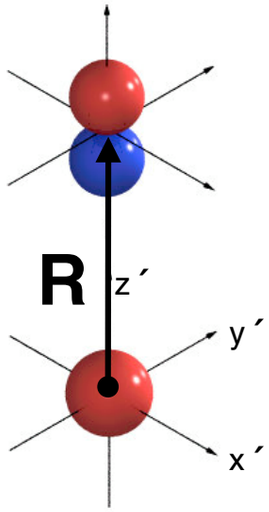


$V_{dd\pi}$

two-center integrals

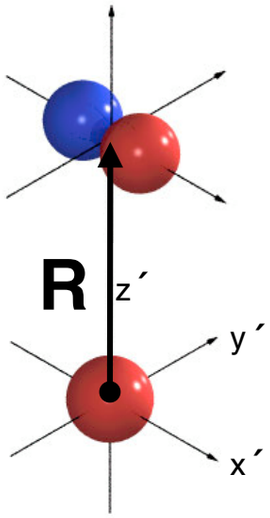


$= \cos\theta$



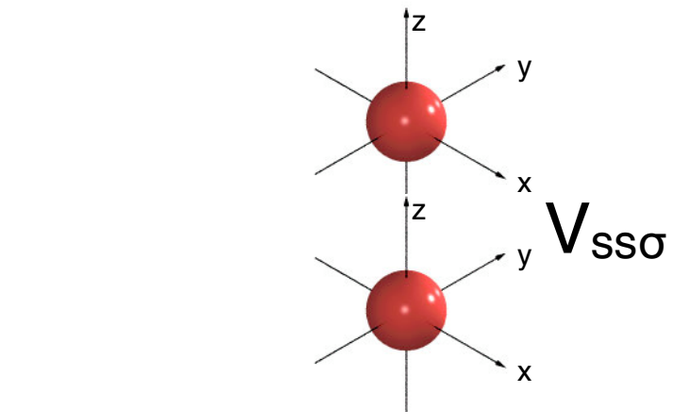
$V_{sp\sigma}$

$+ \sin\theta$

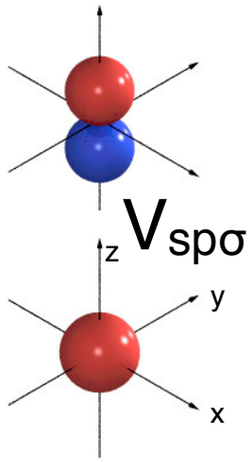


0

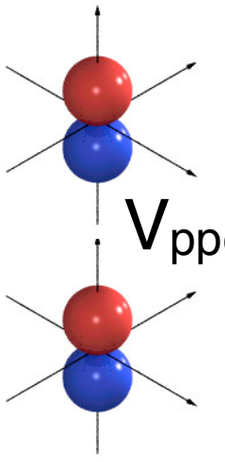
two-center integrals



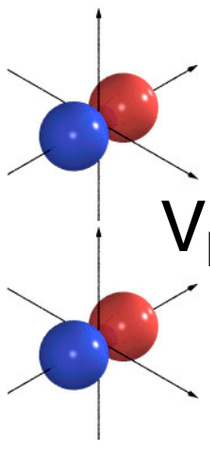
$V_{ss\sigma}$



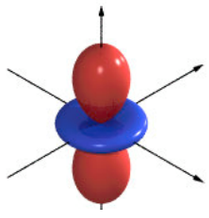
$V_{sp\sigma}$



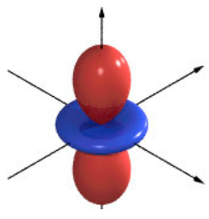
$V_{pp\sigma}$



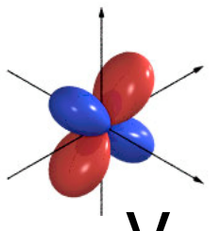
$V_{pp\pi}$



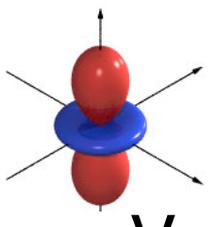
$V_{sd\sigma}$



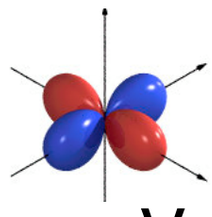
$V_{pd\sigma}$



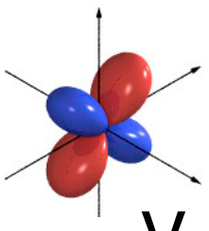
$V_{pd\pi}$



$V_{dd\sigma}$

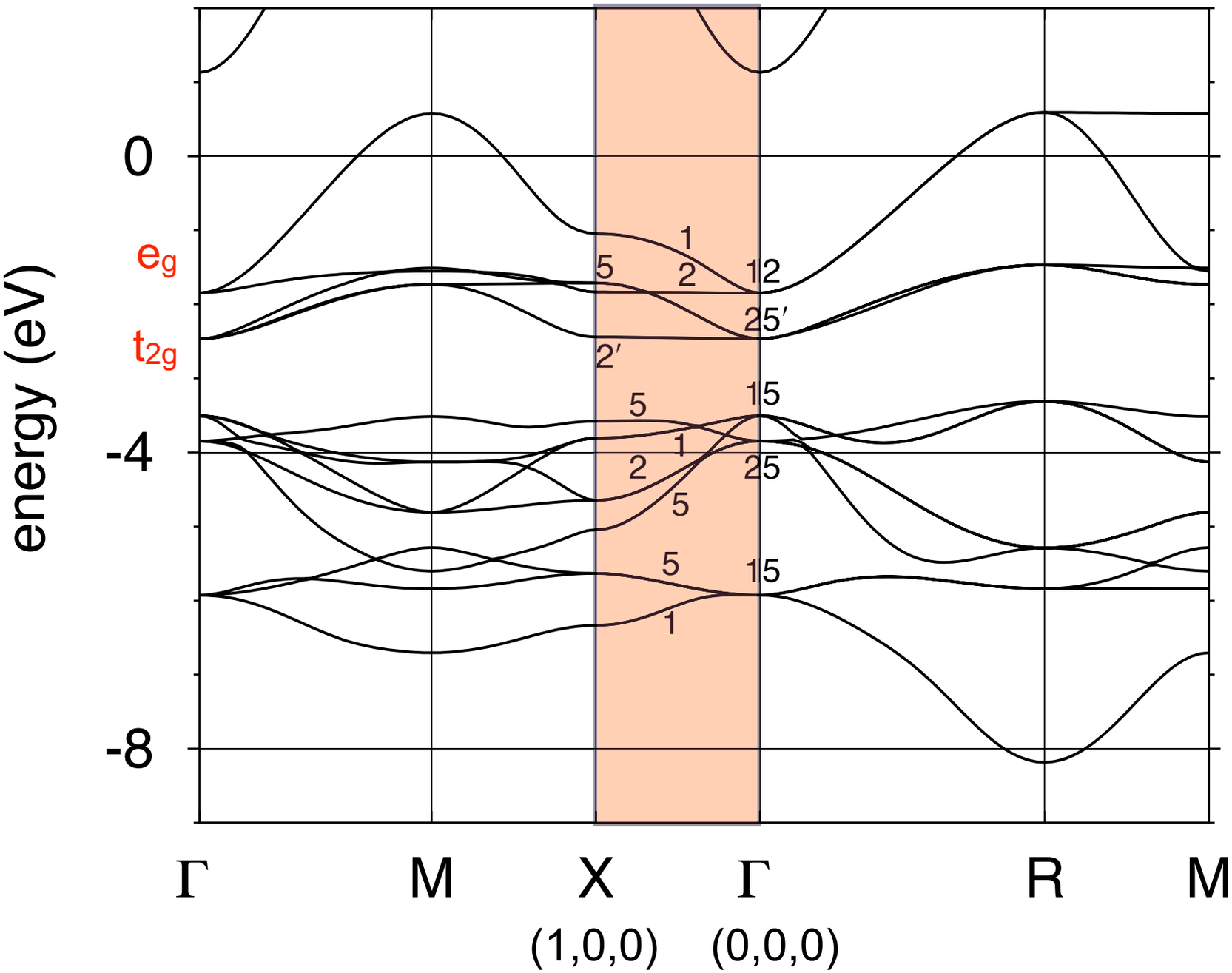


$V_{dd\delta}$



$V_{dd\pi}$

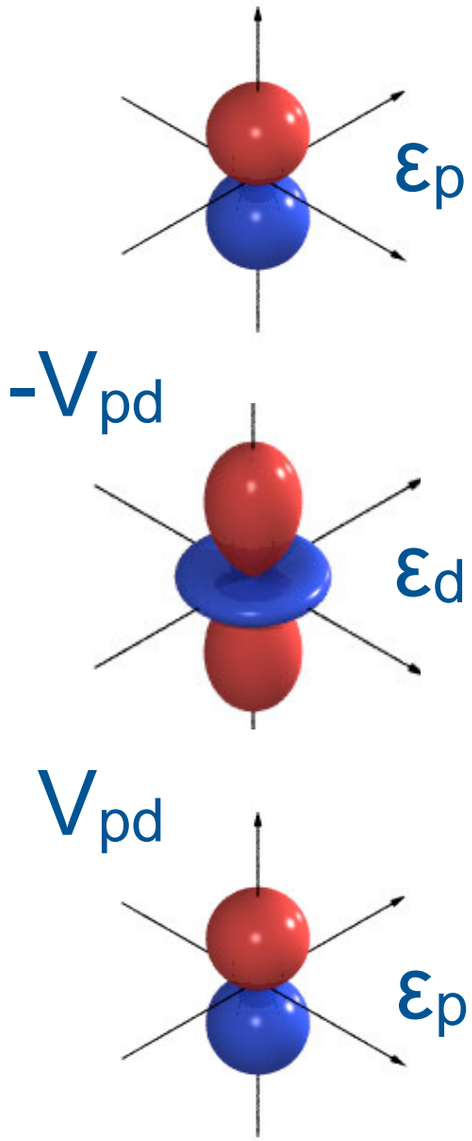
cubic perovskite



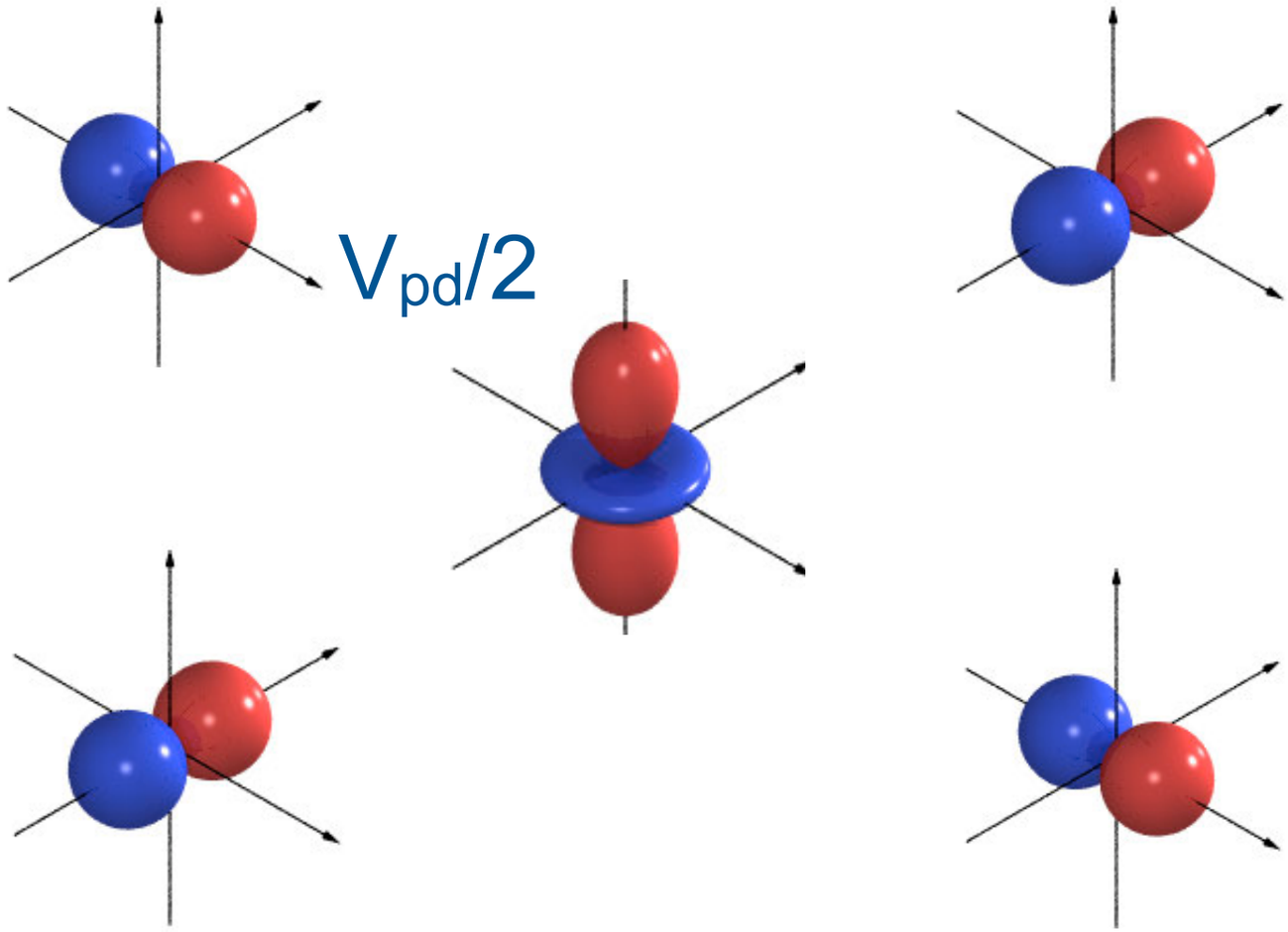
Cu d bands

F p bands

tight-binding model

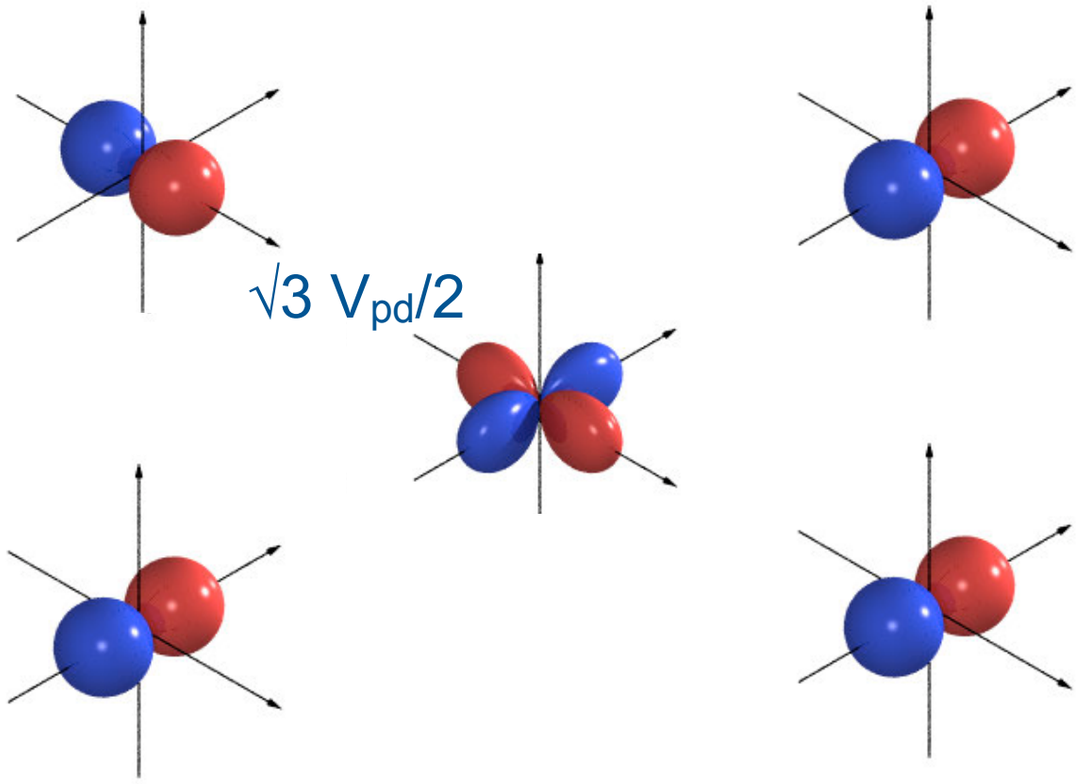


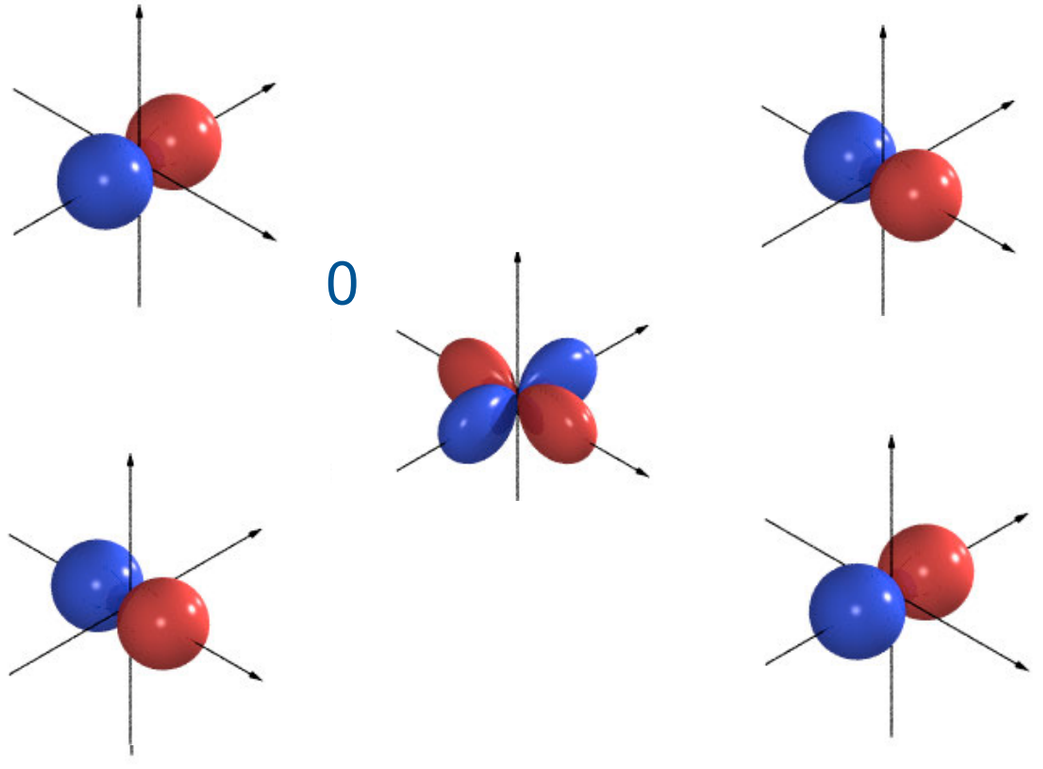
$V_{pd} < 0$



Slater integrals: Appendix B

tight-binding model





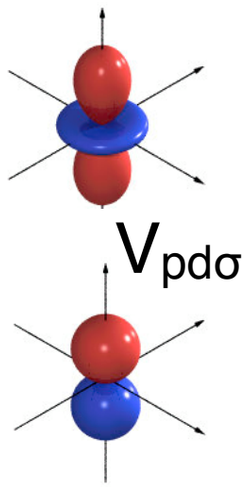
cubic perovskite, e_g bands

$H^{\mathrm{TB}}_{e_g}$	$\lvert \boldsymbol{k}\ z^c\rangle$	$\lvert \boldsymbol{k}\ x^a\rangle$	$\lvert \boldsymbol{k}\ y^b\rangle$	$\lvert \boldsymbol{k}\ 3z^2-r^2\rangle$	$\lvert \boldsymbol{k}\ x^2-y^2\rangle$
$\lvert \boldsymbol{k}\ z^c\rangle$	ε_p	0	0	$-2V_{pd\sigma}s_z$	0
$\lvert \boldsymbol{k}\ x^a\rangle$	0	ε_p	0	$V_{pd\sigma}s_x$	$-\sqrt{3}V_{pd\sigma}s_x$
$\lvert \boldsymbol{k}\ y^b\rangle$	0	0	ε_p	$V_{pd\sigma}s_y$	$\sqrt{3}V_{pd\sigma}s_y$
$\lvert \boldsymbol{k}\ 3z^2-r^2\rangle$	$-2V_{pd\sigma}\overline{s}_z$	$V_{pd\sigma}\overline{s}_x$	$V_{pd\sigma}\overline{s}_y$	ε_d	0
$\lvert \boldsymbol{k}\ x^2-y^2\rangle$	0	$-\sqrt{3}V_{pd\sigma}\overline{s}_x$	$\sqrt{3}V_{pd\sigma}\overline{s}_y$	0	ε_d

Γ-X

$$
\begin{aligned}
\varepsilon_2(\boldsymbol{k}) &= \varepsilon_d \\
\varepsilon_1(\boldsymbol{k}) &= \varepsilon_p + \frac{\Delta_{pd}}{2} + \frac{\sqrt{\Delta_{pd}^2 + 16V_{pd\sigma}^2|s_x|^2}}{2} \\
&\sim \varepsilon_d + 2t - 2t\cos k_x a
\end{aligned}
$$

$$t = V_{pd\sigma}^2/\Delta_{pd}$$



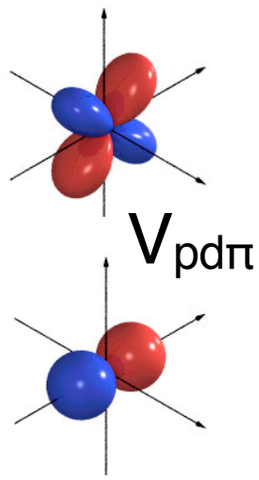
cubic perovskite, t_{2g} bands

$H^{\mathrm{TB}}_{t_{2g}}$	$\lvert \boldsymbol{k}\ y^a \rangle$	$\lvert \boldsymbol{k}\ x^b \rangle$	$\lvert \boldsymbol{k}\ xy \rangle$
$\lvert \boldsymbol{k}\ y^a \rangle$	ε_p	0	$2V_{pd\pi} s_x$
$\lvert \boldsymbol{k}\ x^b \rangle$	0	ε_p	$2V_{pd\pi} s_y$
$\lvert \boldsymbol{k}\ xy \rangle$	$2V_{pd\pi} \overline{s}_x$	$2V_{pd\pi} \overline{s}_y$	ε_d

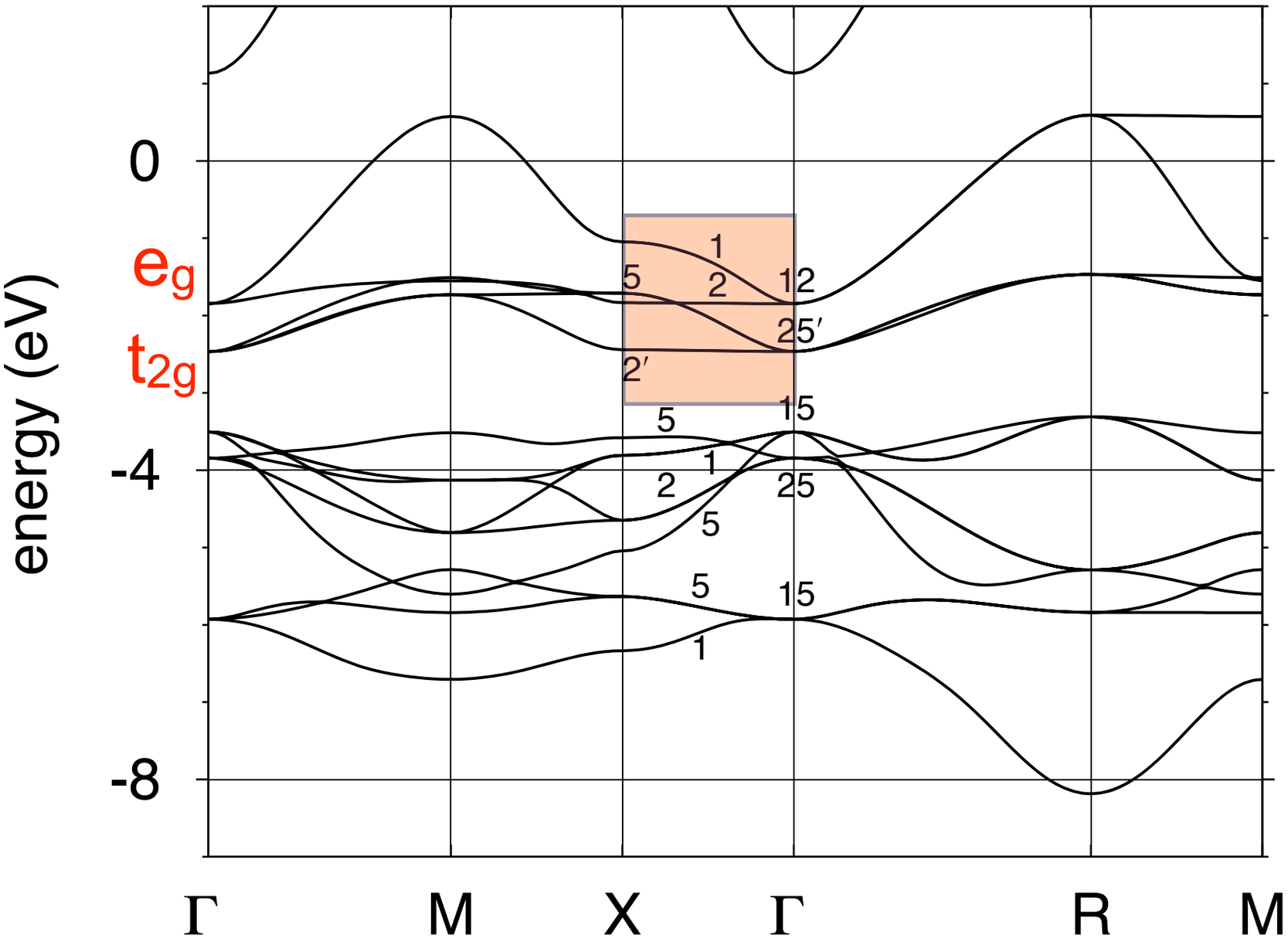
Γ-X

$$
\begin{aligned}
\varepsilon_{2'}(\boldsymbol{k}) &= \varepsilon_d \\
\varepsilon_5(\boldsymbol{k}) &= \varepsilon_p + \frac{\Delta_{pd}}{2} + \frac{\sqrt{\Delta_{pd}^2 + 16 V_{pd\pi}^2 |s_x|^2}}{2} \\
&\sim \varepsilon_d + 2t - 2t \cos k_x a
\end{aligned}
$$

$$t = V_{pd\pi}^2 / \Delta_{pd}$$



cubic perovskite



group theory and periodic systems

- lattice translations $\boldsymbol{T} = n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c}$, where n_i are integers and $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ the primitive translations that define the unit cell.

- glide planes and screw axes, which are made by a point group operation R and a translation of a vector $\boldsymbol{f}$ which is a fraction of a lattice vector.

point group + translations = space groups

group of k point

effect of point group operations

$$O(R)\psi_{\boldsymbol{k}}(\boldsymbol{r}) = O(R)u_{\boldsymbol{k}}(r)e^{i\boldsymbol{r}\cdot\boldsymbol{k}} = u_{\boldsymbol{k}}(R^{-1}\boldsymbol{r})e^{i\boldsymbol{r}\cdot R\boldsymbol{k}} = u'_{R\boldsymbol{k}}(\boldsymbol{r})e^{i\boldsymbol{r}\cdot R\boldsymbol{k}} = \psi_{R\boldsymbol{k}}(\boldsymbol{r}).$$

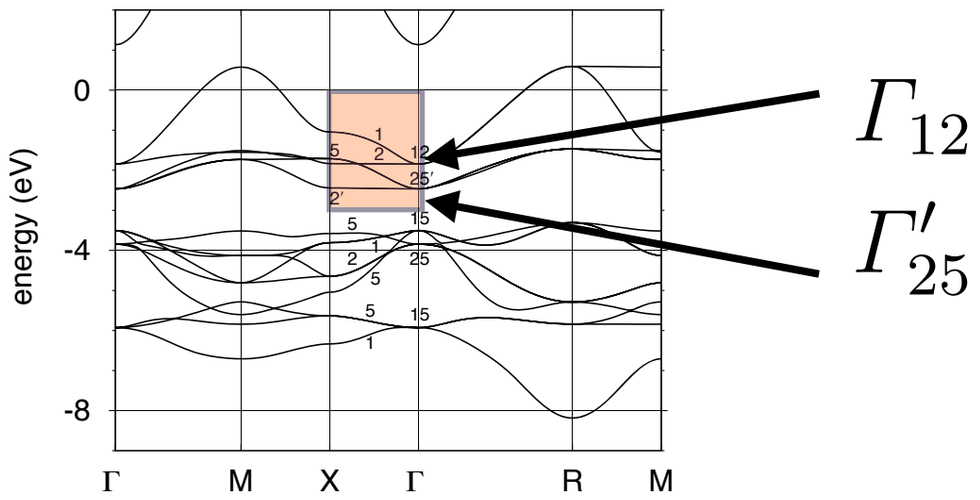
$$\boldsymbol{r}\cdot R\boldsymbol{k} = R^{-1}\boldsymbol{r}\cdot\boldsymbol{k}.$$

group of k

$$R\boldsymbol{k} = \boldsymbol{k} + \boldsymbol{G}$$

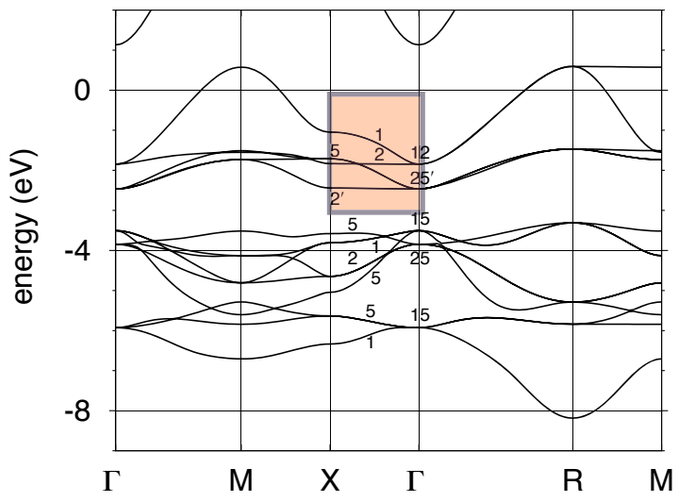
(same phase)

Γ point



	O_h	E	$3C_4^2$	$6C_4$	$6C_2'$	$8C_3$	I	$3IC_4^2$	$6IC_4$	$6IC_2'$	$8IC_3$
	$\Gamma_1(g)$	1	1	1	1	1	1	1	1	1	1
	$\Gamma_2(g)$	1	1	−1	−1	1	1	1	−1	−1	1
$(x^2-y^2, 3z^2-r^2)$	$\Gamma_{12}(g)$	2	2	0	0	−1	2	2	0	0	−1
(x, y, z)	$\Gamma_{15}(u)$	3	−1	1	−1	0	−3	1	−1	1	0
	$\Gamma_{25}(u)$	3	−1	−1	1	0	−3	1	1	−1	0
	$\Gamma_1'(u)$	1	1	1	1	1	−1	−1	−1	−1	−1
	$\Gamma_2'(u)$	1	1	−1	−1	1	−1	−1	1	1	−1
	$\Gamma_{12}'(u)$	2	2	0	0	−1	−2	−2	0	0	1
	$\Gamma_{15}'(g)$	3	−3	1	−1	0	3	−3	1	−1	0
(xy, xz, yz)	$\Gamma_{25}'(g)$	3	−3	−1	−1	0	3	−3	−1	−1	0

Γ-X or Δ direction



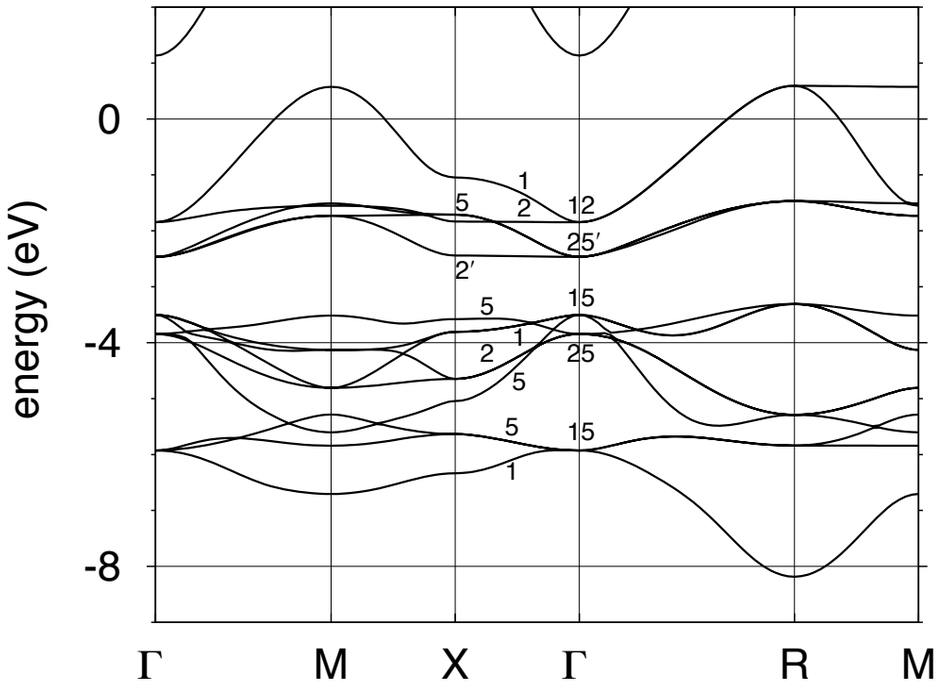
	C_{4v}	E	C_4^2	$2C_4$	$2IC_4^2$	$2IC_2'$
$1, x, 3x^2 - r^2$	Δ_1	1	1	1	1	1
$y^2 - z^2$	Δ_2	1	1	−1	1	−1
yz	Δ_2'	1	1	−1	−1	1
$yz(y^2 - z^2)$	Δ_1'	1	1	1	−1	−1
$y, z; xy, xz$	Δ_5	2	−2	0	0	0

$$\Gamma_{12} \quad \rightarrow \Delta_1 \oplus \Delta_2$$
$$\Gamma_{25}' \quad \rightarrow \Delta_2' \oplus \Delta_5$$

p bands

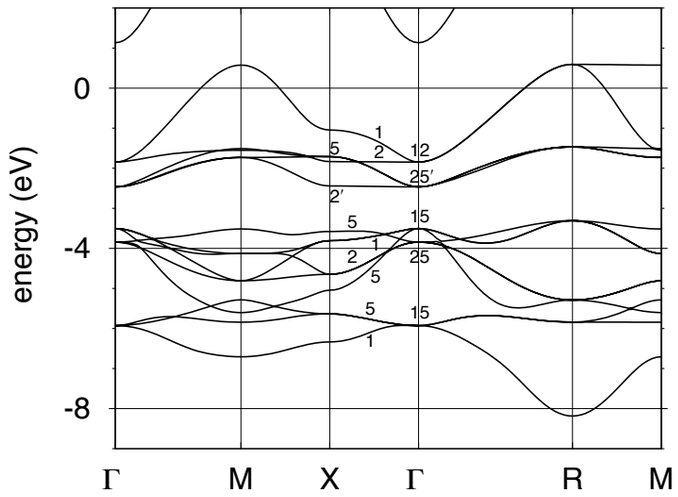
9X9 reducible representation

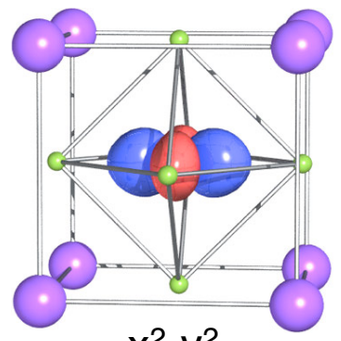
	E	$3C_4^2$	$6C_4$	$6C_2'$	$8C_3$	I	$3IC_4^2$	$6IC_4$	$6IC_2'$	$8IC_3$
Γ^F	9	-3	1	-1	0	-9	3	-1	1	0

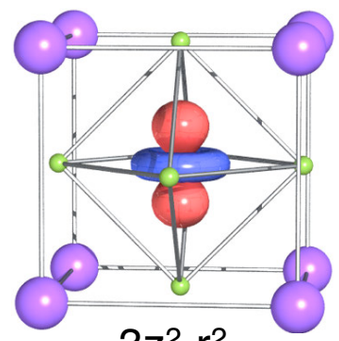


The Γ^F representation can be decomposed in irreducible representations of the group O_h as $\Gamma^F = 2\Gamma_{15} \oplus \Gamma_{25}$. Along Γ-X the decomposition is $2\Delta_1 \oplus \Delta_2 \oplus 3\Delta_5$.

crystal field and covalency

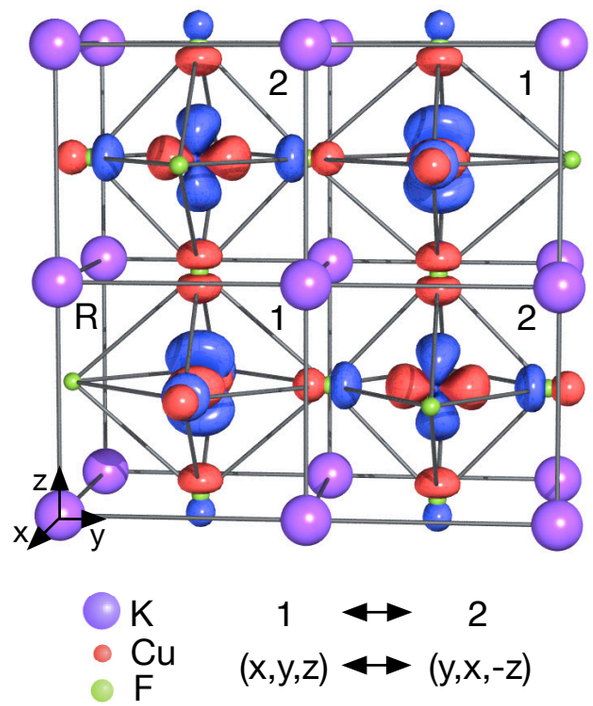






M point

$$
\begin{aligned}
|M\psi_{x^2-y^2}\rangle &= c_{1d}|M\ x^2-y^2\rangle + c_{1p}\left[|M\ x^a\rangle - |M\ y^b\rangle\right], \\
|M\psi_{xy}\rangle &= c_{2d}|M\ xy\rangle - c_{2p}\left[|M\ y^a\rangle + |M\ x^b\rangle\right],
\end{aligned}
$$



Wt_{2g}-We_g

the Jahn-Teller effect

the many-body problem

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i,\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} - \sum_\alpha \frac{1}{2M_\alpha}\nabla_\alpha^2 + \frac{1}{2}\sum_{\alpha\neq\alpha'} \frac{Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|}$$

(atomic units: Appendix A)

Born-Oppenheimer Ansatz

$$\Psi(\{\mathbf{r}_i\},\{\mathbf{R}_\alpha\}) = \psi(\{\mathbf{r}_i\};\{\mathbf{R}_\alpha\})\Phi(\{\mathbf{R}_\alpha\})$$

$$\begin{cases} \hat{H}_e\psi(\{\boldsymbol{r}_i\};\{\boldsymbol{R}_\alpha\}) = \varepsilon(\{\boldsymbol{R}_\alpha\})\psi(\{\boldsymbol{r}_i\};\{\boldsymbol{R}_\alpha\}), & \text{electrons} \\ \hat{H}_n\Phi(\{\boldsymbol{R}_\alpha\}) = E\Phi(\{\boldsymbol{R}_\alpha\}), & \text{lattice} \end{cases}$$

$$\hat{H}_n = \hat{T}_n + \varepsilon(\{\boldsymbol{R}_\alpha\})$$

BO surface

lattice equation

$$\hat{H}_n = \hat{T}_n + \varepsilon(\{\boldsymbol{R}^0_\alpha\}) + \sum_{\alpha\mu}\left[\frac{\partial \hat{U}_n}{\partial u_{\alpha\mu}}\right]_{\{\boldsymbol{R}^0_\alpha\}} u_{\alpha\mu} + \frac{1}{2}\sum_{\alpha\mu,\alpha'\mu'}\left[\frac{\partial^2 \hat{U}_n}{\partial_{\alpha\mu}\partial_{\alpha'\mu'}}\right]_{\{\boldsymbol{R}^0_\alpha\}} u_{\alpha\mu}u_{\alpha'\mu'} + \ldots,$$

minimum BO surface

linear term

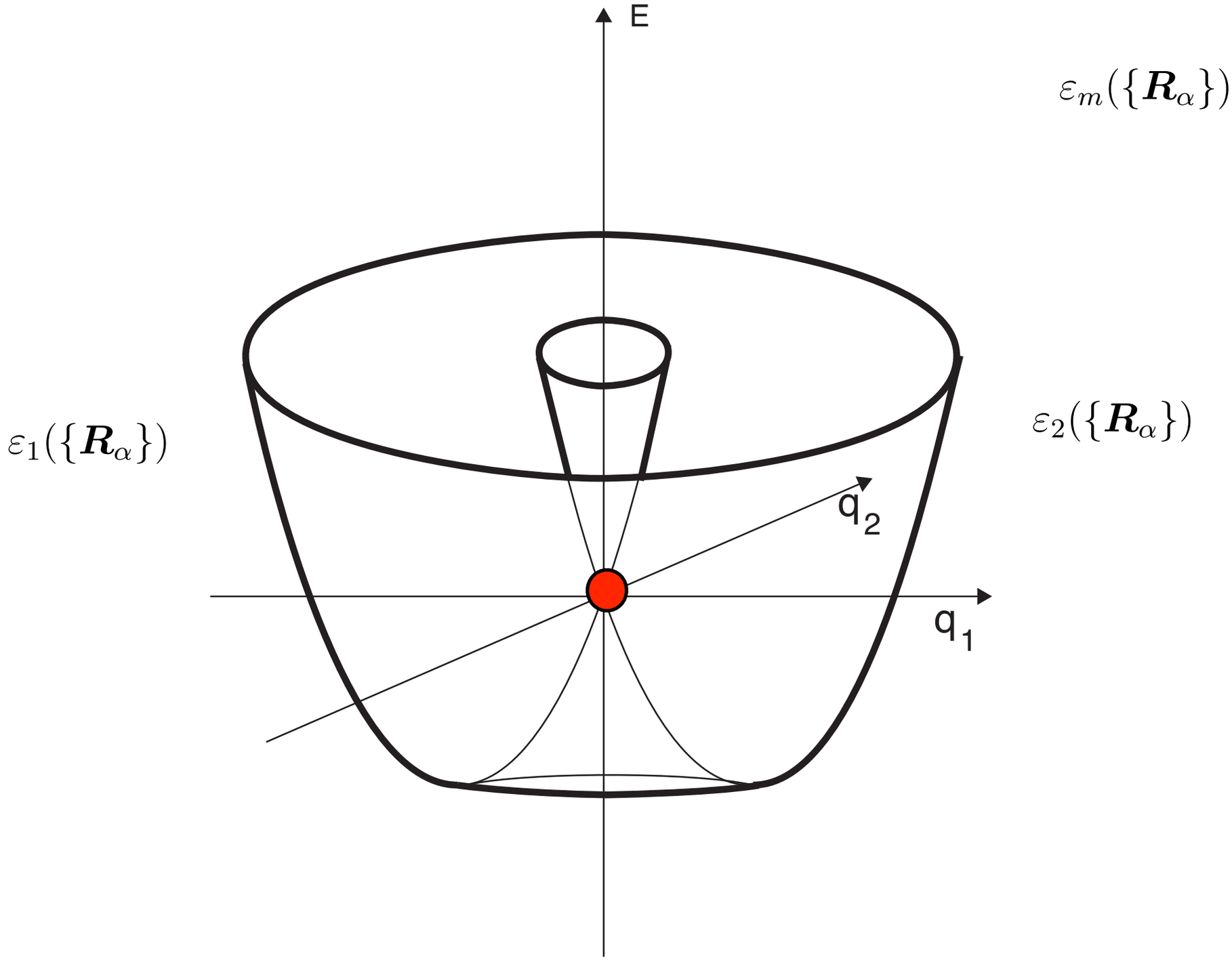
phonons

$$\hat{H}_n \sim \hat{T}_n + \frac{1}{2}\sum_{\alpha\mu,\alpha'\mu'}\left[\frac{\partial^2 \hat{U}_n}{\partial_{\alpha\mu}\partial_{\alpha'\mu'}}\right]_{\{\boldsymbol{R}^0_\alpha\}} u_{\alpha\mu}u_{\alpha'\mu'} + \cdots = \hat{T}_n + \hat{U}^{\mathrm{PH}}_n(\{\boldsymbol{R}^0_\alpha\}) + \ldots,$$

$$\hat{H}_n \sim \frac{1}{2}\sum_{\beta\nu}(P^2_{\beta\nu} + \omega^2_{\beta\nu}Q^2_{\beta\nu}).$$

normal modes

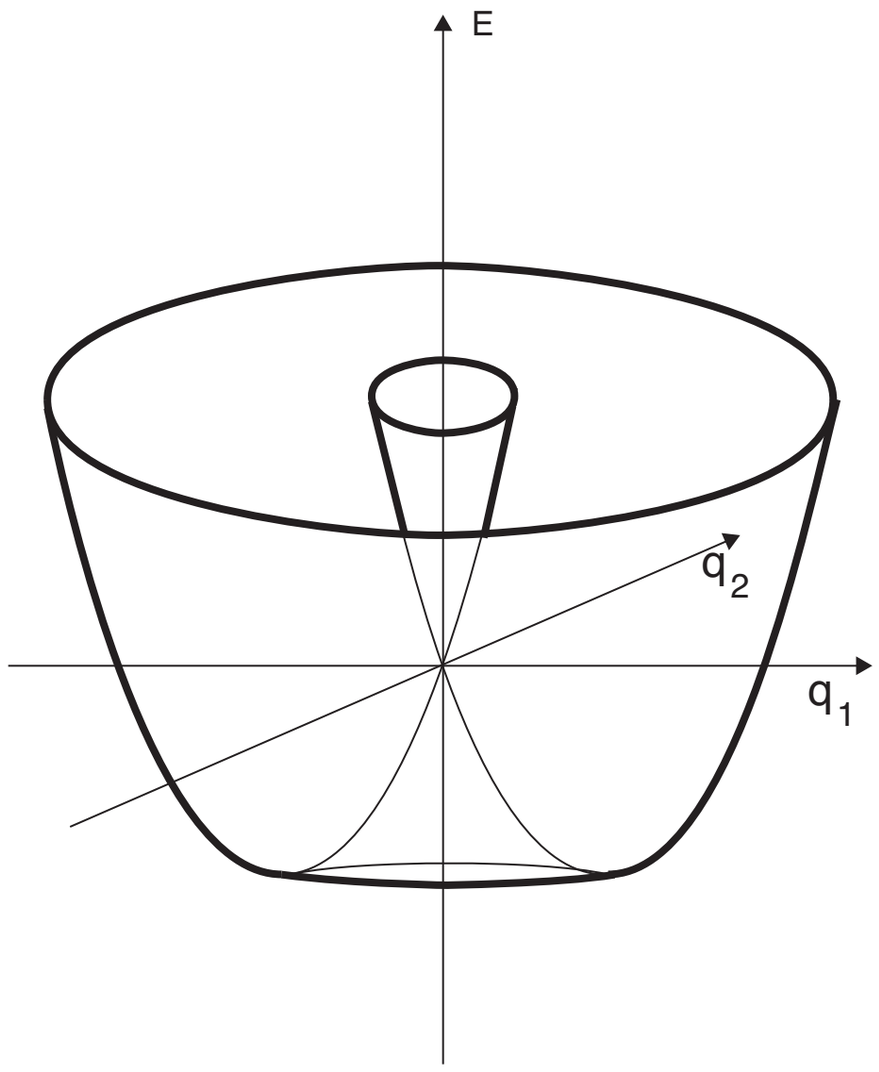
degenerate BO surfaces



mexican hat

Jahn-Teller theorem

The Jahn-Teller theorem states that any electronically degenerate system can lower its energy under some structural distortions, and therefore is unstable. The only exceptions are linear molecules and Kramers degeneracy.



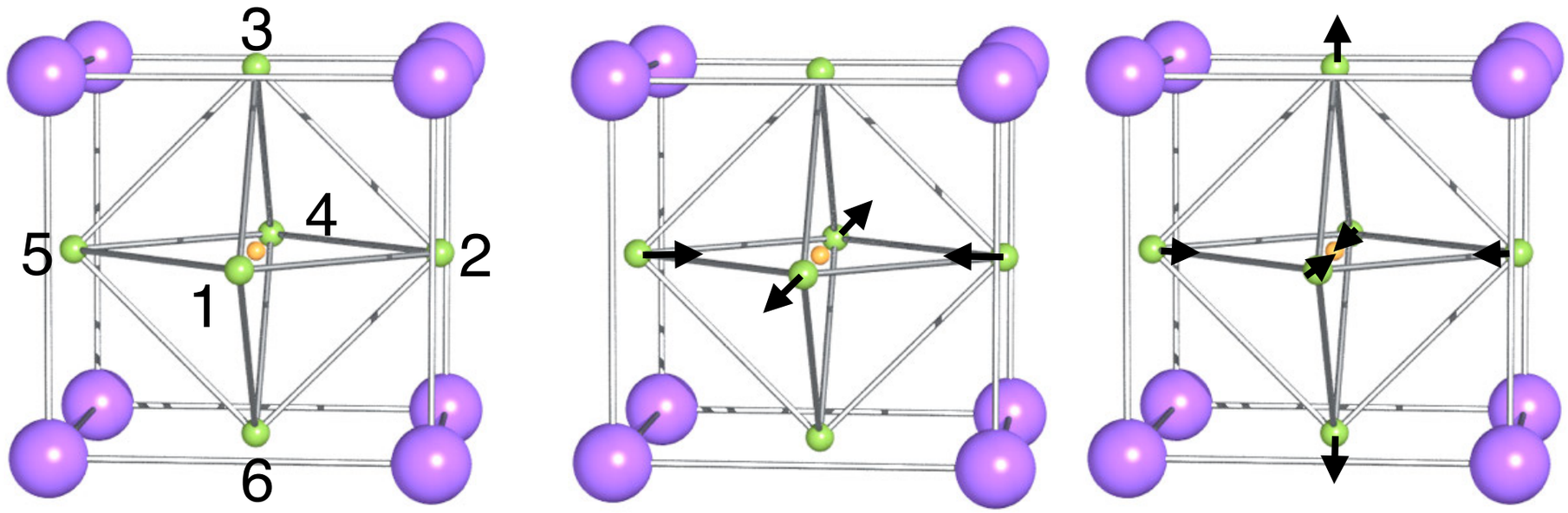
generalized BO Ansatz

$$\Psi(\{\boldsymbol{r}_i\},\{\boldsymbol{R}_\alpha\}) \;=\; \sum_m \psi_m(\{\boldsymbol{r}_i\};\{\boldsymbol{R}_\alpha\})\Phi_m(\{\boldsymbol{R}_\alpha\}).$$

$$\hat{H}_n\Phi_m(\{\boldsymbol{R}_\alpha\}) = [\hat{T}_n + \hat{U}_n^{\rm PH}]\Phi_m(\{\boldsymbol{R}_\alpha\}) + \sum_{m,m'} U^{\rm JT}_{m,m'}\Phi_{m'}(\{\boldsymbol{R}_\alpha\}) = E\Phi_m(\{\boldsymbol{R}_\alpha\}).$$

$$\begin{aligned}\langle\psi_m|\hat{H}_e(\{\boldsymbol{R}_\alpha\})|\psi_{m'}\rangle &= \varepsilon(\{\boldsymbol{R}^0_\alpha\}) + \sum_{\alpha\mu}\langle\psi_m|\left[\frac{\partial\hat{H}_e}{\partial u_{\alpha\mu}}\right]_{\{\boldsymbol{R}^0_\alpha\}}|\psi_{m'}\rangle u_{\alpha\mu} + \ldots \\ &= \varepsilon(\{\boldsymbol{R}^0_\alpha\}) + \hat{U}^{\rm JT}_{m,m'} + \ldots.\end{aligned}$$

cubic perovskite, degenerate e_g levels



Q1 Q2

$$
\begin{aligned}
\boldsymbol{Q}_1 &= [\boldsymbol{u}_1(q_1) - \boldsymbol{u}_4(q_1) - \boldsymbol{u}_2(q_1) + \boldsymbol{u}_5(q_1)], \\
\boldsymbol{Q}_2 &= [\boldsymbol{u}_3(q_2) - \boldsymbol{u}_6(q_2) - \boldsymbol{u}_1(q_2) + \boldsymbol{u}_4(q_2) - \boldsymbol{u}_2(q_2) + \boldsymbol{u}_5(q_2)],
\end{aligned}
$$

$$
\begin{aligned}
\boldsymbol{u}_1(q_1) &= \tfrac{1}{\sqrt{2}} q_1 (1,0,0) & \boldsymbol{u}_1(q_2) &= -\tfrac{1}{\sqrt{6}} q_2 (1,0,0) \\
\boldsymbol{u}_2(q_1) &= -\tfrac{1}{\sqrt{2}} q_1 (0,1,0) & \boldsymbol{u}_2(q_2) &= -\tfrac{1}{\sqrt{6}} q_2 (0,1,0) \\
\boldsymbol{u}_3(q_1) &= (0,0,0) & \boldsymbol{u}_3(q_2) &= \tfrac{2}{\sqrt{6}} q_2 (0,0,1) \\
\boldsymbol{u}_4(q_1) &= -\tfrac{1}{\sqrt{2}} q_1 (1,0,0) & \boldsymbol{u}_4(q_2) &= \tfrac{1}{\sqrt{6}} q_2 (1,0,0) \\
\boldsymbol{u}_5(q_1) &= \tfrac{1}{\sqrt{2}} q_1 (0,1,0) & \boldsymbol{u}_5(q_2) &= \tfrac{1}{\sqrt{6}} q_2 (0,1,0) \\
\boldsymbol{u}_6(q_1) &= (0,0,0) & \boldsymbol{u}_6(q_2) &= -\tfrac{2}{\sqrt{6}} q_2 (0,0,1)
\end{aligned}
$$

e ⊗ E Jahn-Teller

E phonons

$$\hat{U}_n^{\mathrm{PH}} = \frac{1}{2} C (q_1^2 + q_2^2).$$

e electrons

$$\begin{aligned}
\hat{\tau}_z |3z^2 - r^2\rangle &= -|3z^2 - r^2\rangle, & \hat{\tau}_z |x^2 - y^2\rangle &= |x^2 - y^2\rangle, \\
\hat{\tau}_x |3z^2 - r^2\rangle &= |x^2 - y^2\rangle, & \hat{\tau}_x |x^2 - y^2\rangle &= |3z^2 - r^2\rangle.
\end{aligned}$$

$$\hat{\tau}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \hat{\tau}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

$$|\theta\rangle_E = -\sin\frac{\theta}{2}|x^2 - y^2\rangle + \cos\frac{\theta}{2}|3z^2 - r^2\rangle.$$

$$|\theta\rangle_G = -\sin\frac{\theta - \pi}{2}|x^2 - y^2\rangle + \cos\frac{\theta - \pi}{2}|3z^2 - r^2\rangle.$$

e ⊗ E Jahn-Teller

TB crystal-field elements

$$\Delta\varepsilon^{\alpha}_{lm,l'm'} = \int d\boldsymbol{r}\, \overline{\psi}_{lm}(\boldsymbol{r}-\boldsymbol{R}_\alpha)[v_R(\boldsymbol{r}) - v(\boldsymbol{r}-\boldsymbol{R}_\alpha)]\psi_{l'm'}(\boldsymbol{r}-\boldsymbol{R}_\alpha),$$

variations due to Q_1 and Q_2

$$\Delta\varepsilon_{lm,l'm'}(\boldsymbol{0},\boldsymbol{R}_\alpha+\boldsymbol{u}) - \Delta\varepsilon_{lm,l'm'}(\boldsymbol{0},\boldsymbol{R}_\alpha) \sim \nabla\Delta\varepsilon_{lm,l'm'}(\boldsymbol{0},\boldsymbol{R}_\alpha)\cdot\boldsymbol{u}$$

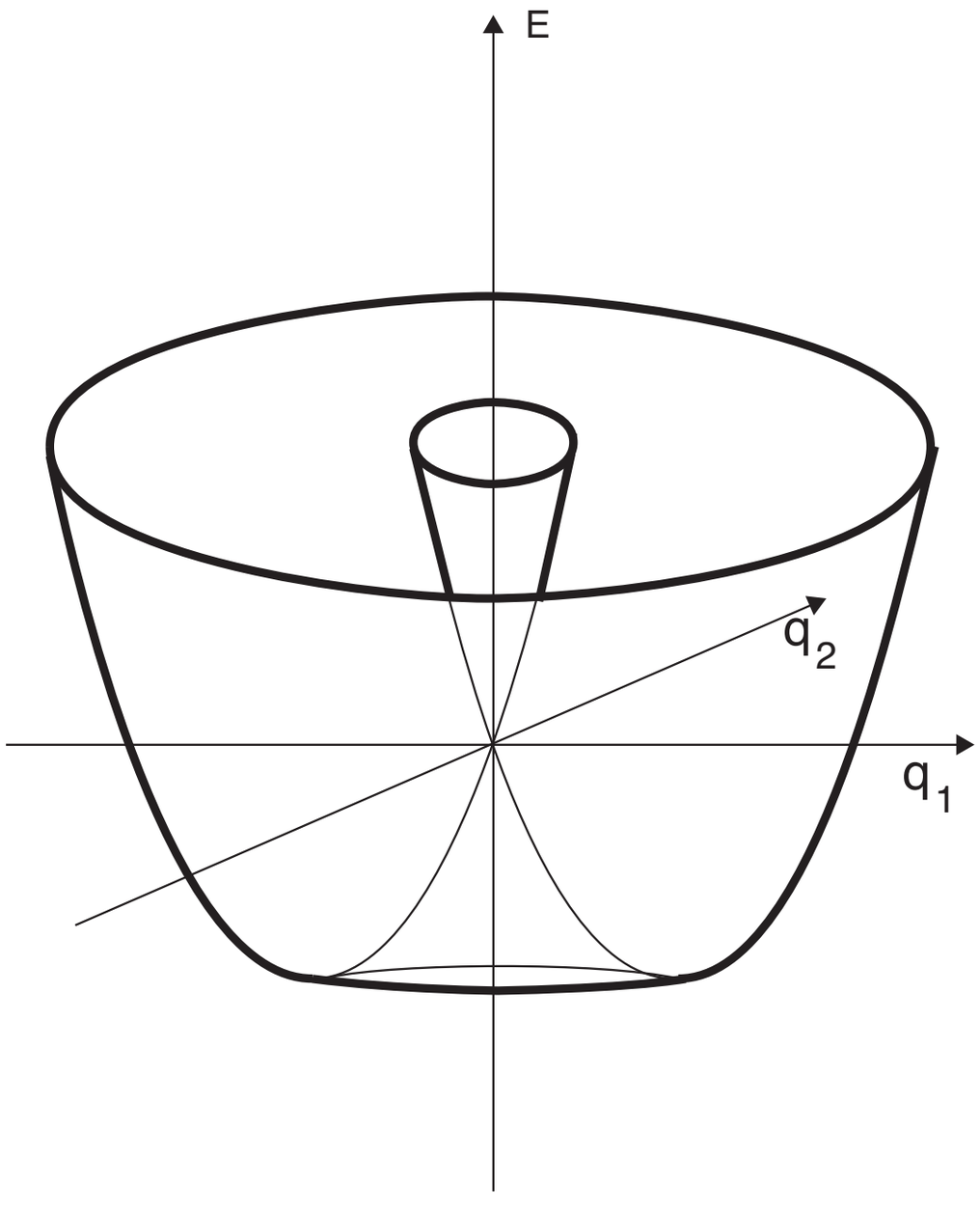
$$\begin{aligned}
\Delta\varepsilon_{3z^2-r^2,3z^2-r^2} &\sim \left[n^2 - \frac{1}{2}(l^2+m^2)\right]^2 \tilde{V}_{dd\sigma},\\
\Delta\varepsilon_{3z^2-r^2,x^2-y^2} &\sim \frac{\sqrt{3}}{2}(l^2-m^2)\left[n^2 - \frac{1}{2}(l^2+m^2)\right]\tilde{V}_{dd\sigma},\\
\Delta\varepsilon_{x^2-y^2,x^2-y^2} &\sim \frac{3}{4}(l^2-m^2)^2\tilde{V}_{dd\sigma}.
\end{aligned}$$

sum all terms....

$$\hat{U}^{\mathrm{JT}}(q_1,q_2) = -\lambda\begin{pmatrix} q_2 & q_1 \\ q_1 & -q_2 \end{pmatrix} = -\lambda\left(q_1\hat{\tau}_x + q_2\hat{\tau}_z\right), \quad \lambda \propto |\tilde{V}'_{dd\sigma}|$$

e ⊗ E Jahn-Teller

$$U(q_1, q_2) = \hat{U}^{\mathrm{JT}} + \hat{U}_n^{\mathrm{PH}} = -\lambda \begin{pmatrix} q_2 & q_1 \\ q_1 & -q_2 \end{pmatrix} + \frac{1}{2} C (q_1^2 + q_2^2).$$



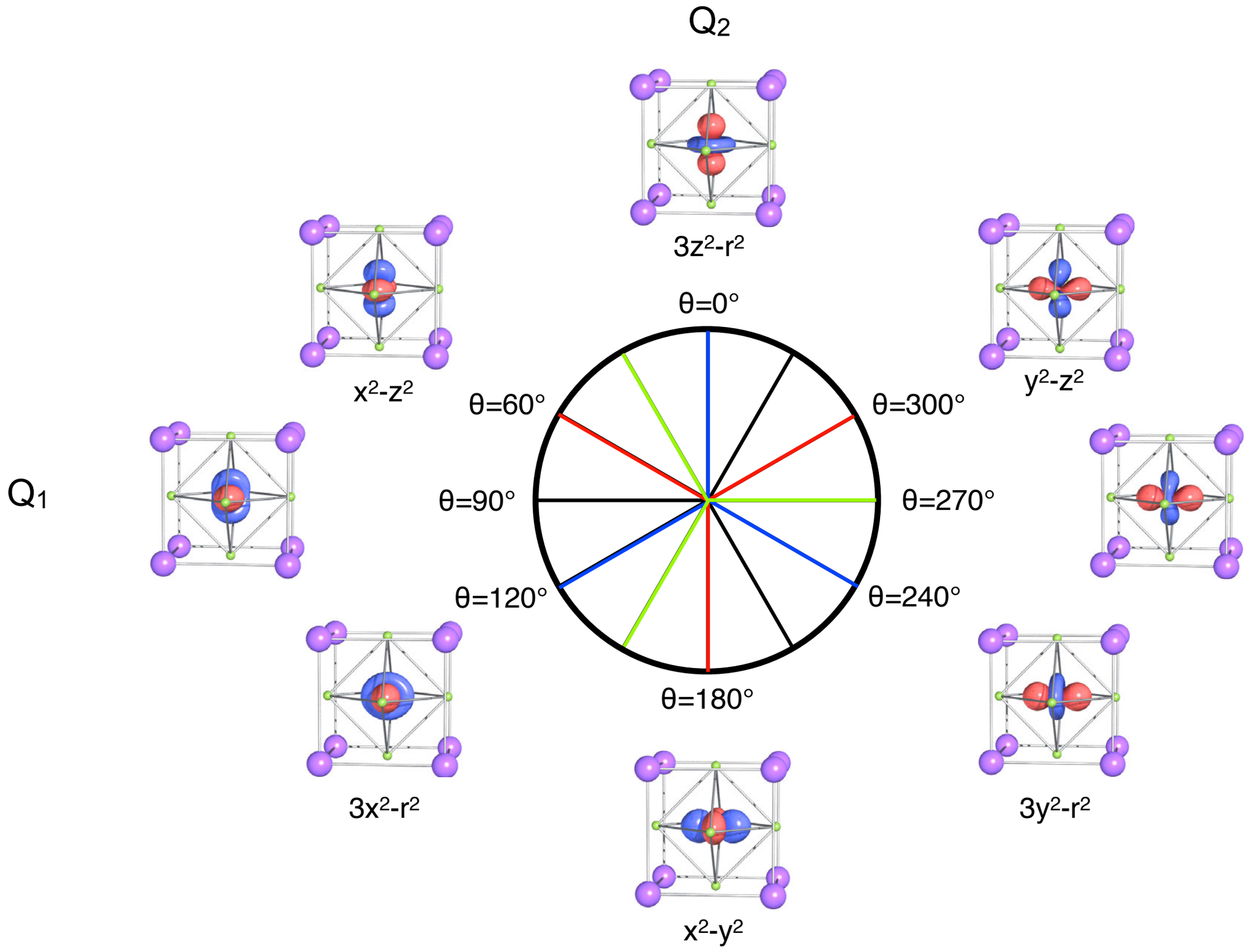
$$U^{\mathrm{JT}} = -\lambda q \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}$$

$$E = \lambda q \pm \tfrac{1}{2} q^2$$

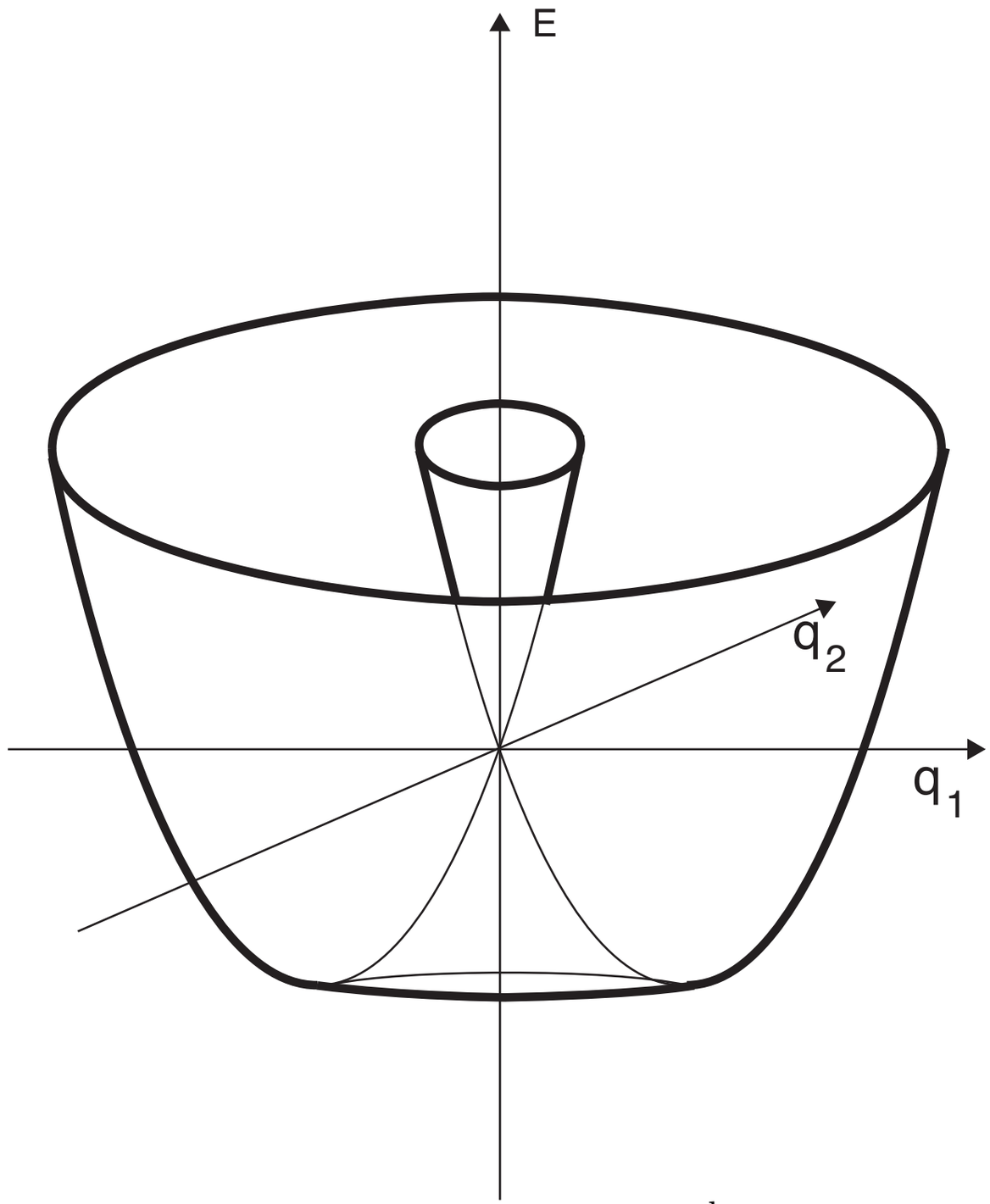
JT energy

$$E_{\mathrm{JT}} = -\lambda^2 / 2C$$

empty orbitals

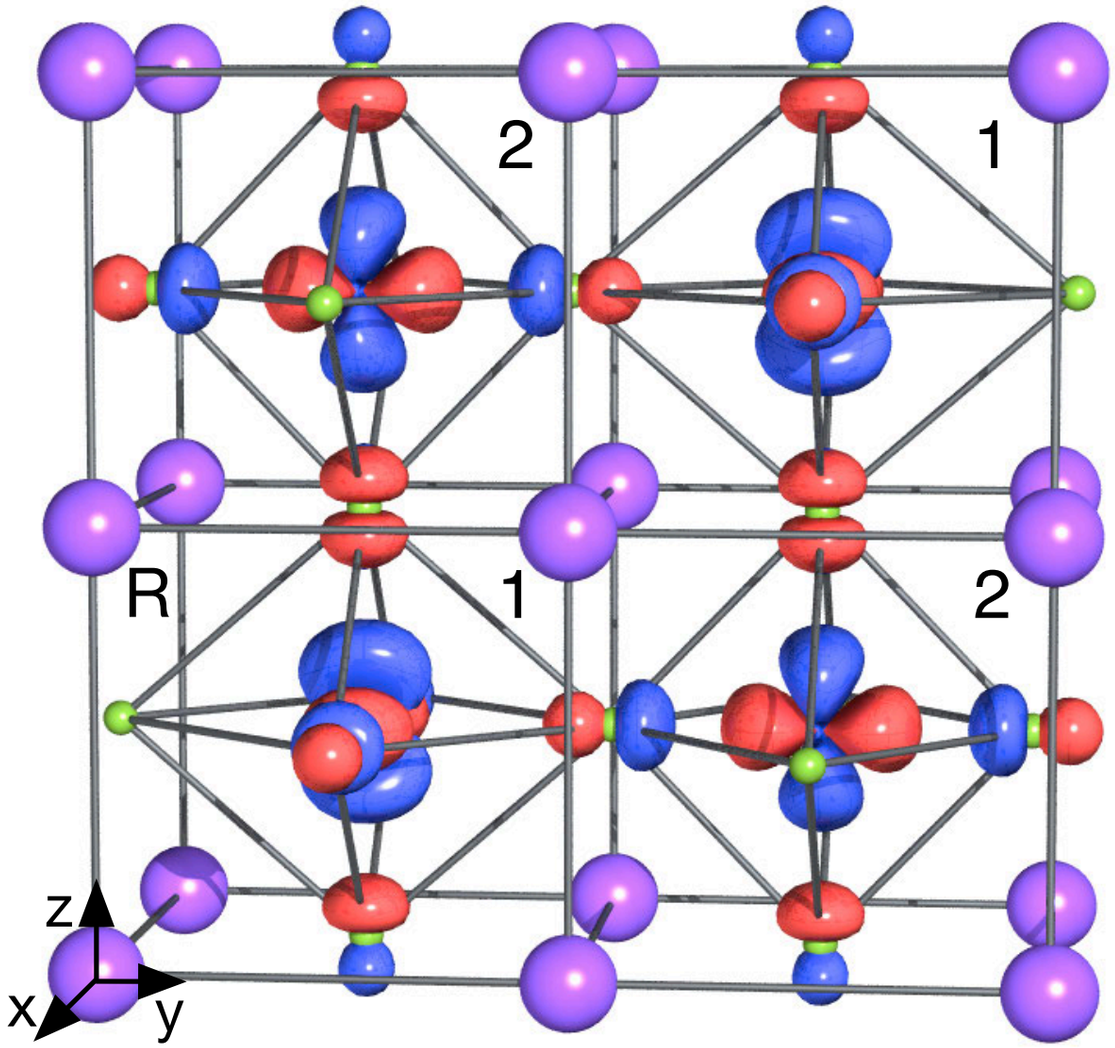


e ⊗ E Jahn-Teller



$$U^{\mathrm{anh}}(q_1, q_2) = -\beta(Q_2^3 - 3Q_2Q_1^2) \propto \cos 3\theta$$

$KCuF_3$



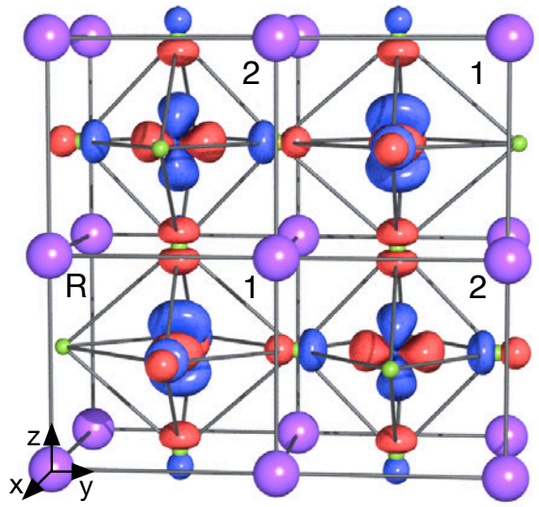
K
Cu
F

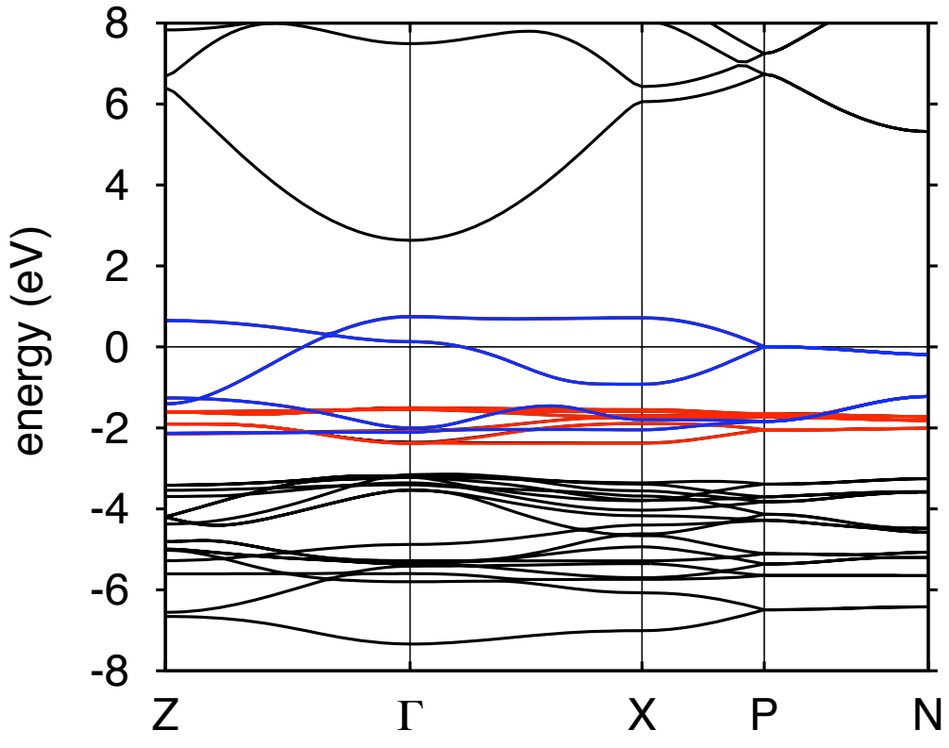
1 ↔ 2

(x,y,z) ↔ (y,x,-z)

conclusions

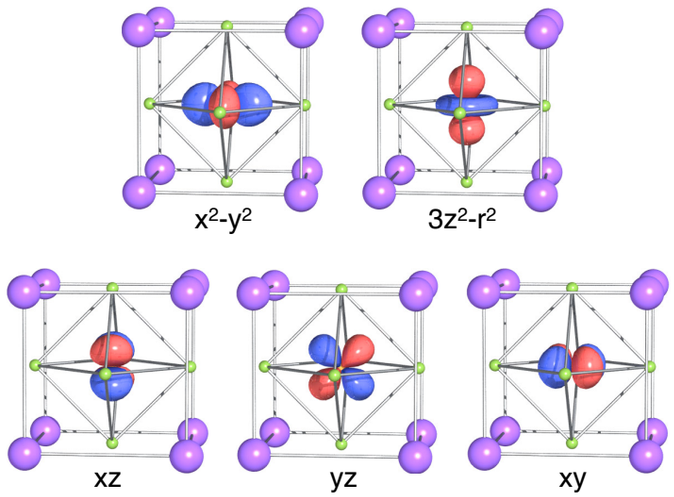
$KCuF_3$

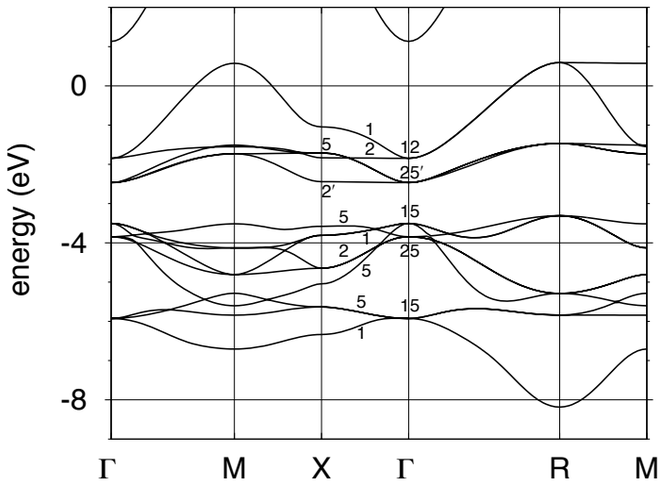




conclusions

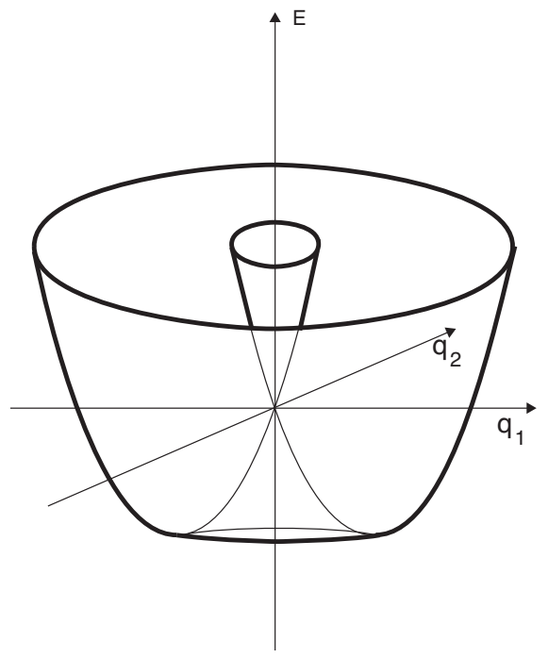
crystal-field





tight-binding model
e_g and t_{2g} band

Jahn-Teller



symmetries are important!

In DMFT: e.g. symmetry of local self-energy