Mathematical Treatment of Crystal Field Theory

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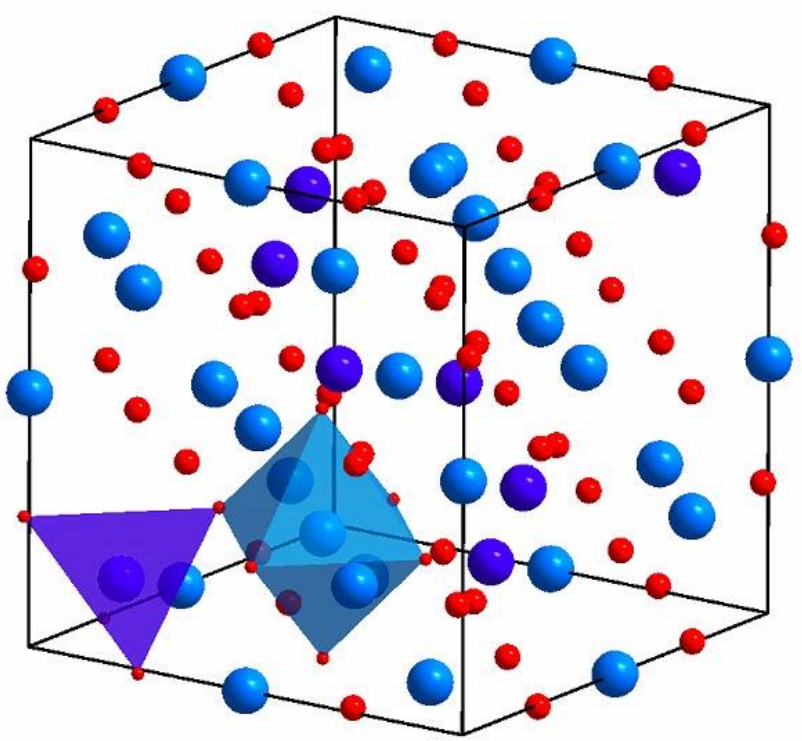
Crystal Field Theory

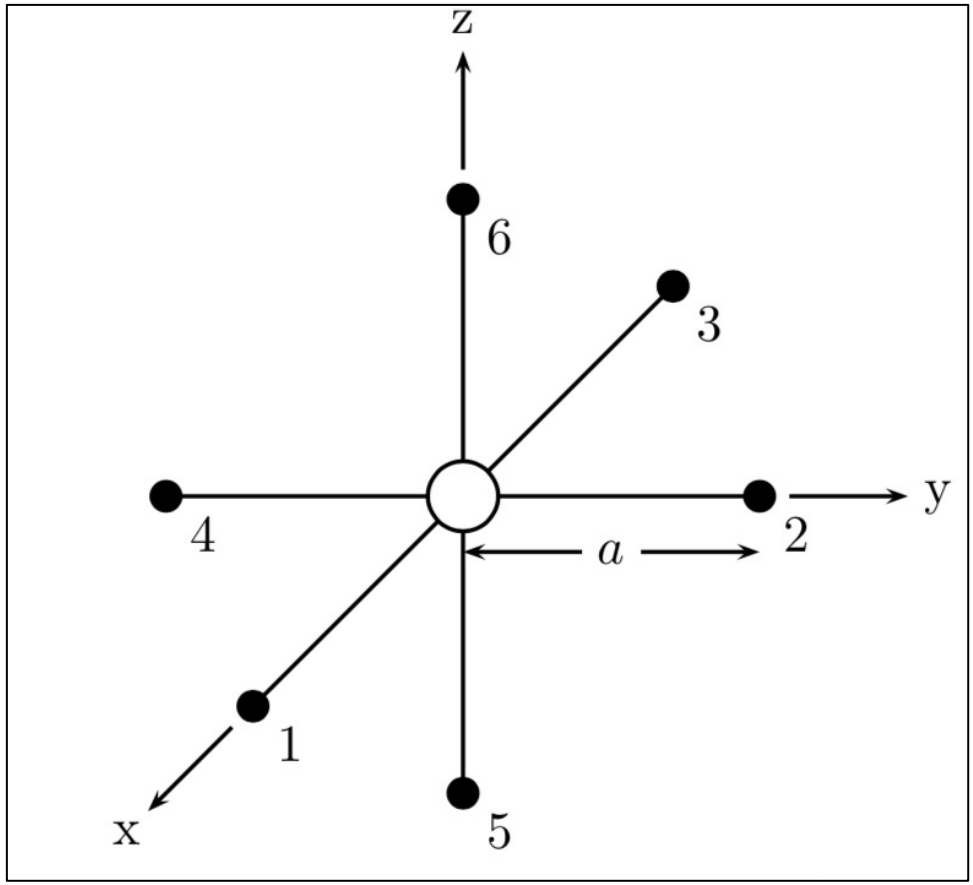
- Periodic unit cell subjects atoms to a certain local environment
  - e.g. O_h, T_d symmetries around Ni/Co atoms in $NiCo_2O_4$
- Electrons on metal ions subject to Coulomb force by negatively-charged anions (Oxygens), so their spatial distribution affects energy of the electron
- Assume highly localized electron wavefunctions



CF Hamiltonian

- $\hat{V}_{CF}(\vec{r}) = \sum_i \frac{Ze^2}{4\pi\varepsilon|\vec{r}-\vec{R}_i|}$ is the energy of charge

  –e, crystal charges –Ze at positions $\vec{r}, \vec{R}_i$
  - For system of $i > 1$, sum over positions of all atoms next to metal ion
- CF energy for wavefunction ψ:
  - $\langle\psi_1|\hat{V}_{CF}|\psi_2\rangle = \int \psi_1^* \hat{V}_{CF}\psi_2 r^2 \sin(\theta)\, dr\, d\theta\, d\phi$
- Recast CF Hamiltonian into integrable parts with electron wavefunction



Legendre Polynomials

- Expansion:

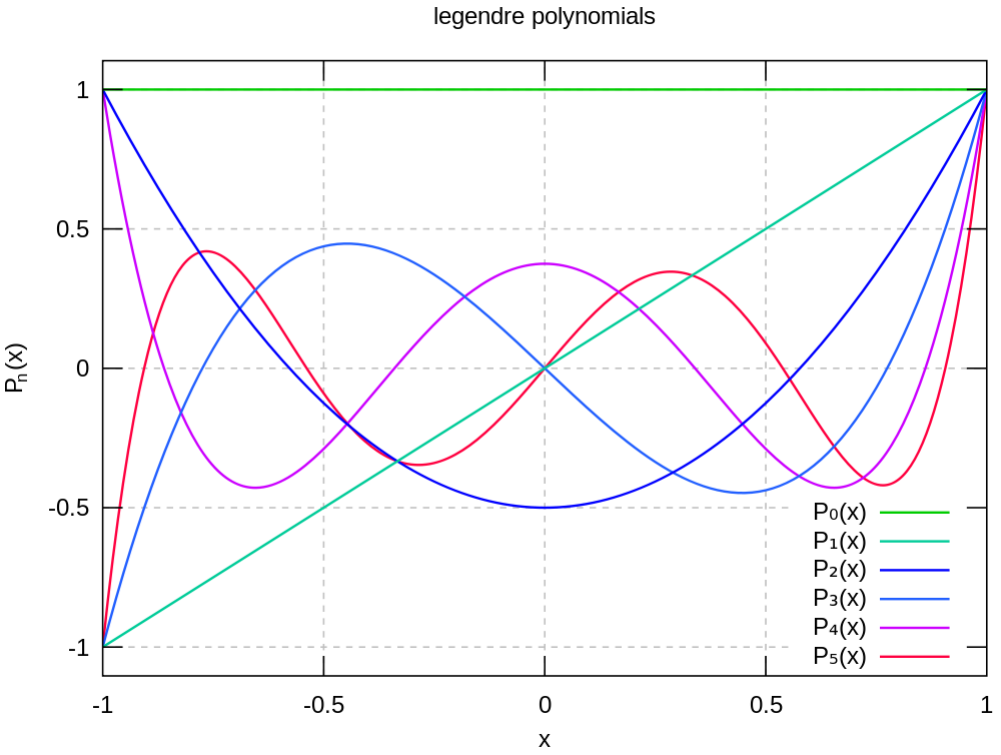
$$\sum_{i=1}^{N} \frac{1}{\left|\vec{r} - \vec{R}_i\right|} = \sum_{i=1}^{N} \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} P_k(\cos(\omega_i))$$

  - $P_k(x)$: Legendre polynomials (plotted on right)

- Further expansion:

$$P_k(\cos(\omega_i))_k = \frac{4\pi}{2k+1} \sum_{m=-k} Y_{km}^*(\theta_i, \phi_i) Y_{km}(\theta, \phi)$$

- In terms of spherical harmonics, which we know how to integrate!



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(Rewritten) Hamiltonian

- $V_{CF}(\vec{r}) = \frac{Ze^2}{4\pi\varepsilon R}\sum_{k=0}^{\infty}\sum_{m=-k}^{k}\left(\frac{r}{R}\right)^k\sqrt{\frac{4\pi}{2k+1}}\gamma_{km}\ Y_{km}(\theta,\phi)$
  - $\gamma_{km} \equiv \sqrt{\frac{4\pi}{2k+1}}\sum_{i=1}^{N}\left(\frac{R}{R_i}\right)^{k+1} Y_{km}^*(\theta_i,\phi_i)$
- $V_{CF}^{m_1,m_2} = \iiint R_{n,l}^*\, Y_{l,m_1}^* V_{CF}(\vec{r}) R_{n,l} Y_{l,m_2} r^2 \sin(\theta)\, dr\, d\theta\, d\phi$

$$= \sum_{k=0}^{\infty}\sqrt{\frac{4\pi}{2k+1}}\gamma_{k,m_1-m_2}\, U_{n,l,k} C^k(l,m_1,l,m_2)$$

- $U_{n,l,k}$: $\frac{Z_o e^2}{4\pi\epsilon R^{k+1}}\int_0^{\infty} R_{n,l}^2(r) r^{k+2} dr$: energy scale
- $C^k(l,m_1,l,m_2)$: $\sqrt{\frac{4\pi}{2k+1}}\int Y_{l,m_1}^*(\theta,\phi) Y_{k,m_1-m_2}(\theta,\phi) Y_{l,m_2}(\theta,\phi)\sin(\theta)\, d\theta d\phi$
  - Gaunt coefficients, related to Clebsch-Gordan coefficients

Gaunt Coefficients

- Relevant non-zero values tabulated
- k from 0 to $l_1 + l_2$, so e.g. d-electrons run k=0-4

l	l'	m	m'	$k=0$	$k=2$	$k=4$
$l+l'=even$						
s	s	0	0	$+1$		
s	d	0	±2		$+1/\sqrt{5}$	
		0	±1		$-1/\sqrt{5}$	
		0	0		$+1/\sqrt{5}$	
p	p	±1	±1	$+1$	$-1/5$	
		±1	0		$+\sqrt{3}/5$	
		0	0	$+1$	$+2/5$	
		±1	∓1		$-\sqrt{6}/5$	
d	d	±2	±2	$+1$	$-2/7$	$+1/21$
		±2	±1		$+\sqrt{6}/7$	$-\sqrt{5}/21$
		±2	0		$-2/7$	$+\sqrt{15}/21$
		±1	±1	$+1$	$+1/7$	$-4/21$
		±1	0		$+1/7$	$+\sqrt{30}/21$
		0	0	$+1$	$+2/7$	$+6/21$
		±2	∓2			$+\sqrt{70}/21$
		±2	∓1			$-\sqrt{35}/21$
		±1	∓1		$-\sqrt{6}/7$	$-2\sqrt{10}/21$

Octahedral Symmetry

- Atom positions:
  $(R, 0,0), (-R, 0,0), (0, R, 0), (0, -R, 0), (0,0, R), (0,0, -R)$
  - Odd k give $\gamma_{mk} = 0$
  - e.g. $\gamma_{1,0} = \sqrt{\frac{4\pi}{2(1)+1}} \sum_{i=1}^{6} \left(\frac{R}{R_i}\right)^1 Y^*_{k=1,m=0} = \sqrt{\frac{4\pi}{3}} \left(\frac{R}{R}\right)^2 \left\{\sqrt{\frac{3}{4\pi}} \left[\frac{R}{R} + \frac{-R}{R}\right]\right\} = 0$

$$\gamma_{1,\pm 1} = \sqrt{\frac{4\pi}{3}} \left(\frac{R}{R}\right)^2 \left\{\sqrt{\frac{3}{8\pi}} \left[\frac{R - iR - R + iR}{R}\right]\right\} = 0$$

$$Y_1^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}} \cdot e^{-i\varphi} \cdot \sin\theta = \frac{1}{2}\sqrt{\frac{3}{2\pi}} \cdot \frac{(x - iy)}{r}$$

$$Y_1^{0}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{\pi}} \cdot \cos\theta = \frac{1}{2}\sqrt{\frac{3}{\pi}} \cdot \frac{z}{r}$$

$$Y_1^{1}(\theta,\varphi) = -\frac{1}{2}\sqrt{\frac{3}{2\pi}} \cdot e^{i\varphi} \cdot \sin\theta = -\frac{1}{2}\sqrt{\frac{3}{2\pi}} \cdot \frac{(x + iy)}{r}$$

Matrix Elements

- $\gamma_{k=2,m} = 0$ for this symmetry additionally (by calculation)
- $H_{CF} = U_{3,2,4}\begin{bmatrix} \gamma_{4,0}C^4_{-2,-2} & 0 & 0 & 0 & \gamma_{4,4}C^4_{-2,2} \\ 0 & \gamma_{4,0}C^4_{-1,-1} & 0 & 0 & 0 \\ 0 & 0 & \gamma_{4,0}C^4_{0,0} & 0 & 0 \\ 0 & 0 & 0 & \gamma_{4,0}C^4_{1,1} & 0 \\ \gamma_{4,4}C^4_{2,-2} & 0 & 0 & 0 & \gamma_{4,0}C^4_{2,2} \end{bmatrix}$

$= \frac{U_{3,2,4}}{6}\begin{bmatrix} 1 & 0 & 0 & 0 & 5 \\ 0 & -4 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 \\ 0 & 0 & 0 & -4 & 0 \\ 5 & 0 & 0 & 0 & 1 \end{bmatrix}$. Diagonalize to get eigenvalues, split e_g and t_{2g}

Perturbations to CF Geometry

$$
\begin{aligned}
Y_2^{-2}(\theta,\varphi) &= \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot e^{-2i\varphi}\cdot\sin^2\theta &&= \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x-iy)^2}{r^2}\\
Y_2^{-1}(\theta,\varphi) &= \frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot e^{-i\varphi}\cdot\sin\theta\cdot\cos\theta &&= \frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x-iy)z}{r^2}\\
Y_2^{0}(\theta,\varphi) &= \frac{1}{4}\sqrt{\frac{5}{\pi}}\cdot(3\cos^2\theta-1) &&= \frac{1}{4}\sqrt{\frac{5}{\pi}}\cdot\frac{(2z^2-x^2-y^2)}{r^2}\\
Y_2^{1}(\theta,\varphi) &= -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot e^{i\varphi}\cdot\sin\theta\cdot\cos\theta &&= -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x+iy)z}{r^2}\\
Y_2^{2}(\theta,\varphi) &= \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot e^{2i\varphi}\cdot\sin^2\theta &&= \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x+iy)^2}{r^2}
\end{aligned}
$$

- Atom positions adjust:

$(R+a,0,0),(-R-a,0,0),(0,R+a,0),(0,-R-a,0),(0,0,R+c),(0,0,-R-c)$

$\gamma_{2,m} \neq 0$ under this perturbation

$$\gamma_{2,0} = \sqrt{\frac{4\pi}{5}}\sqrt{\frac{5}{16\pi}}\left\{4\left(\frac{R}{R+a}\right)^3\frac{-(R+a)^2}{(R+a)^2}+2\left(\frac{R}{R+c}\right)^3\frac{2(R+c)^2}{(R+c)^2}\right\}$$

$$= 2\left\{\left(\frac{R}{R+a}\right)^3-\left(\frac{R}{R+c}\right)^3\right\} = 2\left\{\left(1+\frac{a}{R}\right)^{-3}-\left(1+\frac{c}{R}\right)^{-3}\right\} \approx \frac{6(a-c)}{R}$$

Perturbations to CF Geometry

- Only terms involving $\gamma_{2,0}$ added to Hamiltonian:

- $V'_{CF} = \frac{6U_{3,2,2}}{7}\frac{(a-c)}{R}\begin{bmatrix} -2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & -2 \end{bmatrix}$