Crystal Field Effects - Outline

- What is the “crystal field”?
- Quenching of orbital momentum in 3d metals
- Strength of the crystal field
- Crystal field in 4f elements
- Point-charge model (PCM)
- Stevens operators
- Crystal field Hamiltonian
- Magnetization, susceptibility, specific heat, magnetic entropy
What is CF?

- For an atom in crystal, surrounding atoms reduce the symmetry – influence of the *crystal field*

\[ \phi_{cf}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \]

where \[ \Phi(\mathbf{r}) = \frac{q}{4\pi \varepsilon} \frac{1}{R} = \frac{q}{4\pi \varepsilon} \frac{1}{\sqrt{r^2 + r'^2 - 2r'r \cos \gamma}}. \]

can be expanded as (Laplace expansion)

\[ \Phi(\mathbf{r}) = \frac{q}{4\pi \varepsilon} \sum_{l=0}^{\infty} \frac{r^l}{r'^{l+1}} \left( \frac{4\pi}{2l + 1} \right) \sum_{m=-l}^{l} Y_{lm}(\theta, \phi) Y_{lm}^*(\theta', \phi') \]

- In situation nearby the atom (\( r < r' \)) we obtain

\[ \phi_{cf}(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} r^l \gamma_{lm} Y_{lm}^*(\theta, \phi) \]

where

\[ \gamma_{lm} = \frac{4\pi}{2l + 1} \int \frac{\rho(\mathbf{r}') Y_{lm}^*(\theta', \phi')}{4\pi \epsilon_0 r'^{l+1}} d\mathbf{r}' \]
Reminder: rare-earth paramagnets

Good agreement theory-experiment, except for Sm & Eu

Sm & Eu have low-lying excited states, which we neglected

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<table>
<thead>
<tr>
<th>ELEMENT (TRIPLY IONIZED)</th>
<th>BASIC ELECTRON CONFIGURATION</th>
<th>GROUND-STATE TERM</th>
<th>CALCULATED $^b$ p</th>
<th>MEASURED$^c$ p</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>$4f^0$</td>
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<tr>
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<tr>
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<td>Lu</td>
<td>$4f^{14}$</td>
<td>$^1S$</td>
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<td>diemagnetic</td>
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</table>

* Note the discrepancy in Sm and Eu having its origin in low-lying $J$-multiplets assumed absent in the theory.

$^b$ Equation (31.50).

$^c$ Equation (31.49).

Reminder: 3d transition metals

For 3d transition metals Curie's law works if we assume L=0

Quenching of orbital momentum due to crystal field splitting

Modification of the third Hund's rule

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| ELEMENT (AND IONIZATION) | BASIC ELECTRON CONFIGURATION | GROUND-STATE TERM \((J = S)\) | CALCULATED \(p\) \((J = |L \pm S|)\) | MEASURED \(p\) |
|--------------------------|-----------------------------|-------------------------|-------------------------|-----------------|
| Ti\(^{3+}\) | 3\(d\)\(^1\) | \(2D_{3/2}\) | 1.73 | 1.55 | — |
| V\(^{4+}\) | 3\(d\)\(^1\) | \(2D_{3/2}\) | 1.73 | 1.55 | 1.8 |
| V\(^{3+}\) | 3\(d\)\(^2\) | \(3F_{2}\) | 2.83 | 1.63 | 2.8 |
| V\(^{2+}\) | 3\(d\)\(^3\) | \(4F_{3/2}\) | 3.87 | 0.77 | 3.8 |
| Cr\(^{3+}\) | 3\(d\)\(^3\) | \(4F_{3/2}\) | 3.87 | 0.77 | 4.0 |
| Mn\(^{4+}\) | 3\(d\)\(^3\) | \(5D_{0}\) | 4.90 | 0 | 4.8 |
| Cr\(^{2+}\) | 3\(d\)\(^4\) | \(5D_{0}\) | 4.90 | 0 | 5.0 |
| Mn\(^{3+}\) | 3\(d\)\(^5\) | \(6S_{5/2}\) | 5.92 | 5.9 | 5.9 |
| Mn\(^{2+}\) | 3\(d\)\(^5\) | \(6S_{5/2}\) | 5.92 | 5.9 | 5.9 |
| Fe\(^{3+}\) | 3\(d\)\(^6\) | \(5D_{4}\) | 4.90 | 6.70 | 5.4 |
| Fe\(^{2+}\) | 3\(d\)\(^6\) | \(5D_{4}\) | 4.90 | 6.70 | 5.4 |
| Co\(^{2+}\) | 3\(d\)\(^7\) | \(5D_{5/2}\) | 3.87 | 6.54 | 4.8 |
| Ni\(^{2+}\) | 3\(d\)\(^8\) | \(3F_{4}\) | 2.83 | 5.59 | 3.2 |
| Cu\(^{2+}\) | 3\(d\)\(^9\) | \(2D_{5/2}\) | 1.73 | 3.55 | 1.9 |

* Because of quenching, much better theoretical values are obtained by taking \(J\) equal to \(S\), the total spin, than by taking the value \(J = |L \pm S|\) appropriate to the free ion.

\(^{b}\) Equation (31.50). In the case \(J = S\), one takes \(L = 0\).

\(^{c}\) Equation (31.49).

Estimate of strength of CF

- That adds a new term into a Hamiltonian of an atom:
  \[ \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{so}} + \mathcal{H}_{\text{cf}} + \mathcal{H}_Z \]

- Typical magnitudes of terms (in Kelvin; 1eV ~ 10000K):

<table>
<thead>
<tr>
<th></th>
<th>( \mathcal{H}_0 )</th>
<th>( \mathcal{H}_{\text{so}} )</th>
<th>( \mathcal{H}_{\text{cf}} )</th>
<th>( \mathcal{H}_Z ) in 1 T</th>
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</thead>
<tbody>
<tr>
<td>3d</td>
<td>1 - 5 10^4</td>
<td>10^2 -10^3</td>
<td>1 - 10^4</td>
<td>1</td>
</tr>
<tr>
<td>4f</td>
<td>1 - 6 10^5</td>
<td>1 - 5 10^3</td>
<td>( \approx3 \ 10^2 )</td>
<td>1</td>
</tr>
</tbody>
</table>

- Implications:
  - For 3d the crystal field Hamiltonian is stronger than SO coupling and we can expect violations of the 3rd Hund's rule
  - For 4f the CF can be considered as a perturbation to the lowest multiplet derived by following all 3 Hund's rules
Crystal field vs Hund's rules

- Free Mn(3+) atom – 3d⁴ configuration → Hund's rules state
  \( S = 4 \times 1/2 = 2 \), \( L = 2 + 1 + 0 - 1 = 2 \), \( J = L - S = 0 \)
  – consequence of the Coulomb repulsion and spin-orbital interaction

- Mn atom in solid – surrounded by other atoms → strong electrostatic interaction causing crystal field splitting (chemists say: ligand field splitting)

- Crystal field splitting – a “geometry” effect due to breaking of spherical symmetry inside crystal

- For 3d elements \( SO \ll CF \) → \( J \) is no longer a good quantum number, \( SO \) is rather a weak perturbation compared to \( CF \)

- In cubic CF the five 3d orbitals split into triple degenerate \( t_{2g} \) and double degenerate \( e_g \)

- Distance of these levels decide the spin state – high (weak CF), low (strong CF)

Right: example for Cr in crystal field →
Quenching of orbital momentum

- Crystal field: real (non-imaginary) potential $\rightarrow$ the ground state wavefunction can be chosen as a real function

- Case 1: degenerate ground state $\psi \rightarrow$ also $\psi^*$ has the same energy, then we can construct states $\psi_{1,2} = \psi \pm \psi^*$, which are real

- Case 2: Assume non-degenerate ground state $\psi$
  - Again, its complex conjugate $\psi^*$ is an eigenstate of the real potential
  - Here $\psi$ and $\psi^*$ must be linearly dependent
  - If both are normalized, $\psi^* = \exp(i\phi)\psi$ for a suitable $\phi$
  - We can pick $\psi' = \exp(i\phi/2)\psi$, then $\psi'^* = \exp(-i\phi/2)\psi^* = \exp(i\phi/2)\psi = \psi'$, which is a real eigenfunction

- For real valued ground-state wave function $\psi$, the expectation value of a purely imaginary operator of an observable quantity must be real, thus zero $\rightarrow$ this is the case of angular momentum operator $L = -i \, \vec{r} \times \vec{\nabla}$
Strength of CF effects

- Depending on overlap between wavefunctions of neighboring atoms, the crystal field interaction can be:
  - Strong for delocalized electrons, e.g., 3d, 4d, 5d
  - Weak(er) for localized (shielded) electrons, e.g., 4f, 5f
- Spin-orbit interaction strength grows with atomic number
- We can have two limiting situations
  - For 3d: CF $\gg$ SO, i.e., SO is a weak perturbation to CF levels
  - For 4f: SO $\gg$ CF, i.e., CF is a weak perturbation to the lowest J multiplet
- The relation between strengths goes approximately as
  - $\frac{\text{CF}}{\text{SO}}$: 3d $\rightarrow$ 4d $\rightarrow$ 5d $\rightarrow$ 5f $\rightarrow$ 4f
- The rest of lecture: crystal field theory for 4f systems (rare-earths)
$Pr^3+$  \hspace{1cm} J = 4
Fig. 1: Inelastic neutron spectra of NdCu$_2$ in the paramagnetic state at $T = 10$ K obtained with different incident neutron energies $E_0$. The deduced crystal field transitions are given by the level scheme in the inset. Nine crystal field parameters have been obtained with the superposition model from these data (full curve).
Figure 10. The crystal field splitting of the $^4I_{11/2}(A)$ level of Er$^{3+}$ in Y$_2$O$_3$ as seen in absorption and fluorescence.
Fig. 7.13. MF calculation of the magnetization of Pr at 4.2 K as a function of a magnetic field applied in the $a$- and $c$-directions. The circles are the experimental measurements of McEwen et al. (1973), while the squares are deduced from the neutron-diffraction results of Lebech and Rainford (1971).
CF theory for rare-earths

- Point charge model
- Stevens operator equivalents
- Crystal field Hamiltonian in external magnetic field
- Examples for cubic, tetragonal and hexagonal symmetries
- CF eigenvalue problem
- Magnetization, susceptibility, Schottky specific heat, entropy
Point charge model

- The charge density cloud is replaced by a point-like charge at atoms positions
- Let's consider octahedral environment (six-fold cubic coordination)
- We have 6 point charges at 
  \[ \pm (a, 0, 0), \pm (0, a, 0), \pm (0, 0, a) \]
- They cause a potential \( V(x,y,z) \) at point \( P(x,y,z) \) given by
  \[
  V = V_x + V_y + V_z \quad \text{where} \quad V_x = \frac{q}{\sqrt{r^2 + a^2 + 2ax}} + \frac{q}{\sqrt{r^2 + a^2 - 2ax}}
  \]
- Expanding up to 6\textsuperscript{th} degree in \( x,y,z \), assuming \( a>r \)
  \[
  V(x, y, z) = \frac{6q}{a} + \frac{35q}{4a^5} \left[ (x^4 + y^4 + z^4) - r^4 \right] \\
  - \frac{21q}{2a^7} \left[ (x^6 + y^6 + z^6) + \frac{15}{4} (x^2y^4 + x^2z^4 + y^2x^4 + y^2z^4 + z^2x^4 + z^2y^4) - \frac{15}{14} r^6 \right]
  \]
Point charge model

- Repeating the same for tetrahedral environment (four-fold cubic coordination) we obtain very similar result:

\[
V(x, y, z) = \frac{4q}{d} - \frac{35q}{9d^5} \left[(x^4 + y^4 + z^4) - r^4\right] \\
- \frac{112q}{9d^7} \left[(x^6 + y^6 + z^6) + \frac{15}{4}(x^2y^4 + x^2z^4 + y^2x^4 + y^2z^4 + z^2x^4 + z^2y^4) - \frac{15}{14}r^6\right]
\]

- In summary, for cubic symmetry of the environment, the x,y,z dependence is the same, only prefactors differ

\[
W = C_4 \left[(x^4 + y^4 + z^4) - r^4\right] \\
+ D_6 \left[(x^6 + y^6 + z^6) + \frac{15}{4}(x^2y^4 + x^2z^4 + y^2x^4 + y^2z^4 + z^2x^4 + z^2y^4) - \frac{15}{14}r^6\right]
\]

with prefactors are given by table

<table>
<thead>
<tr>
<th>Coordination</th>
<th>$C_4$</th>
<th>$D_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Four-fold</td>
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<td>$\frac{-112q}{9d^7}$</td>
</tr>
<tr>
<td>Six-fold</td>
<td>$\frac{35q}{4d^5}$</td>
<td>$\frac{-21q}{2d^7}$</td>
</tr>
<tr>
<td>Eight-fold</td>
<td>$\frac{-70q}{9d^5}$</td>
<td>$\frac{-224q}{9d^7}$</td>
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</table>