Importance of Electronic Correlations for the Structural Stability and Lattice Dynamics of Solids

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Importance of Electronic Correlations for the Structural Stability and Lattice Dynamics of Solids

Outline:

- *ab initio* approach to correlated electron materials: LDA+DMFT
- Application to correlation-driven structural transformations in Fe:
  - $\alpha$-$\gamma$ ($bcc$-$fcc$) phase transition
  - Lattice dynamics and phonon dispersions
Correlations

\[ \langle AB \rangle \neq \langle A \rangle \langle B \rangle \]

e.g., densities in the interaction:

\[ \langle n(\mathbf{r})n(\mathbf{r}') \rangle \neq \langle n(\mathbf{r}) \rangle \langle n(\mathbf{r}') \rangle = n^2 \]

Correlations:
Effects beyond factorization approximations or static mean-field theories (e.g., Hartree-Fock)
Electronic Correlations in Solids
Correlated electron materials have unusual properties

- huge resistivity changes
- gigantic volume anomalies
- colossal magnetoresistance
- high-$T_c$ superconductivity
- metallic behavior at interfaces of insulators

With potential for technological applications:
- sensors, switches, Mottronics
- spintronics
- thermoelectrics
- high-$T_c$ superconductors
- functional materials: oxide heterostructures...

How to study correlated systems theoretically?
How to combine?

<table>
<thead>
<tr>
<th>DFT/LDA</th>
<th>Model Hamiltonians</th>
</tr>
</thead>
<tbody>
<tr>
<td>+   material specific: “ab initio”</td>
<td>−  input parameters unknown</td>
</tr>
<tr>
<td>+   fast code packages</td>
<td>−  computationally expensive</td>
</tr>
<tr>
<td>−   fails for strong correlations</td>
<td>+  systematic many-body approach</td>
</tr>
</tbody>
</table>

Held (2004)

How to combine?

- time-averaged electron density
- lattice potential
Investigation of correlated electron systems with Dynamical Mean-Field Theory (DMFT)

Metzner, DV (1989)
Georges, Kotliar (1992)

Kotliar, DV (2004)
Computational scheme for correlated electron materials:

**Material specific electronic structure**  
(Density functional theory: LDA, GGA, ...) or GW

+ 

**Local electronic correlations**  
(Many-body theory: DMFT)

\[ X = \text{LDA, GGA; GW, ...} \]

\[ \rightarrow X + \text{DMFT} \]

Metzner, DV (1989)  
Georges, Kotliar (1992)
Computational scheme for correlated electron materials:

**Material specific electronic structure**

(Density functional theory: LDA, GGA, …) or GW

+ 

**Local electronic correlations**

(Many-body theory: DMFT)

- LDA+DMFT

Metzner, DV (1989)
Georges, Kotliar (1992)

Anisimov et al. (1997)
Lichtenstein, Katsnelson (1998)
Held et al. (2003)
Kotliar et al. (2006)
LDA+DMFT (simplest version)

1) Calculate LDA band structure: \( \varepsilon_{lml'm'(k)} \) \( \xrightarrow{\text{basis}} \) \( \hat{H}_{LDA} \)

2) Supplement LDA by local Coulomb interaction (only for correlated bands)

\[
\hat{H} = \sum_{k l m l' m' \sigma} \varepsilon_{lml'm'(k)} \hat{c}_{klm\sigma}^\dagger \hat{c}_{kl'm'\sigma} - \sum_{i=i_d, m\sigma} \sum_{l=l_d} \Delta \varepsilon_d \hat{n}_{ilm\sigma} \\
\hat{H}_{LDA} + \sum_{i=i_d, m\sigma, m'\sigma'} \sum' \frac{U_{mm'}}{2} \hat{n}_{ilm\sigma} \hat{n}_{ilm'\sigma'} - \sum_{i=i_d, m\sigma, m'\sigma'} \sum' J_{mm'} \hat{c}_{ilm\sigma}^\dagger \hat{c}_{ilm'\sigma'} \hat{c}_{ilm'\sigma} \hat{c}_{ilm\sigma}^\dagger
\]

local Coulomb interaction  
\[\text{Hund’s rule coupling}\]
3) Solve within DMFT
→ effective multi-orbital Anderson impurity model with self-consistency condition

(i) Effective single impurity problem

\[ G = -\frac{1}{\mathcal{Z}} \int \mathcal{D}[\psi \psi^*] \psi \psi^* e^{\psi^* [G^{-1} + \Sigma]} \psi - U \psi^* \psi \psi^* \psi + J \psi^* \psi \psi^* \psi \]

(ii) \( k \)-integrated Dyson equ.

\[ G^\sigma_{mm'}(\omega) = \frac{1}{V_B} \int d^3 k \left[ (\omega - \Sigma^\sigma(\omega)) \delta_{m,m'} - \left( H_{\text{LDA}}(k) \right)_{m,m'} \right]^{-1} \]

Employ an impurity solver, e.g., QMC
Goal: Dynamical mean-field approach with predictive power for strongly correlated materials
Application of LDA+DMFT

- Most abundant element by mass on Earth
- Ferromagnetism: Longest known quantum many-body phenomenon
- Still most widely used metal in modern day industry ("iron age")
Narrow d,f-orbitals/bands → electronic correlations important
DMFT: Ferromagnetism in the one-band Hubbard model

Generalized fcc lattice ($Z \to \infty$)

Ferromagnetic order of itinerant local moments

LDA+DMFT

Ulmke (1998)

Lichtenstein, Katsnelson, Kotliar (2001)
Application of LDA+DMFT

Until recently: Investigation of electronic correlation effects for given lattice structure

→ Influence of electrons on lattice structure ignored

- How do electrons + ions influence each other?
- Which lattice structure is stabilized?
Application of LDA+DMFT to correlation-driven structural transformations

(i) \(\alpha-\gamma\) transition in paramagnetic Fe

Collaborators: Ivan Leonov (Augsburg)  
Vladimir Anisimov (Ekaterinburg)  
Alexander Poteryaev (Ekaterinburg)

Leonov, Poteryaev, Anisimov, DV; PRL 106, 106405 (2011)
• Abundance of allotropes: α, γ, δ, ε, ... phases
• α-phase: high Curie temperature ($T_C \sim 1043$ K)
Cohesion favors close packed structure (fcc, hcp) for P, T→0

- bcc at higher T (lattice vibrations)
- Polymorphic metals usually melt from bcc phase due to soft T₁-phonon

In general:

- bcc structure at P, T→0: exceptional

Zener (1952)
DFT(GGA): finds paramagnetic bcc structure to be unstable

Goal: Understand bcc-fcc structural phase transition in paramagnetic Fe
**bcc-fcc structural transition in paramagnetic Fe**

Total energies calculated along *bcc-fcc* Bain transformation path:

- continuous transformation path from *bcc-phase* to *fcc-phase*
- volume per atom fixed at exp. value of α-Fe

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**bcc (c/a=1)**

- $Z = 8$
- $c/a = 1$

**fcc (c/a = $\sqrt{2}$)**

- $Z = 12$
- $c/a = \sqrt{2}$
Goal: Determine structural stability of paramagnetic \textit{bcc} phase

Construct Wannier functions for partially filled Fe \textit{sd} orbitals

\textbf{GGA:}
Only paramagnetic \textit{fcc} structure is stable

First-principles multi-band Hamiltonian

\[ \hat{H} = \hat{H}_{\text{GGA}} + \frac{1}{2} \sum_{imm',\sigma\sigma'} U_{mm'}^{\sigma\sigma'} \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} - \hat{H}_{\text{DC}} \]

Coulomb interaction between Fe 3d electrons: \( U=1.8 \text{ eV}, J=0.9 \text{ eV} \)
**bcc-fcc structural transition in paramagnetic Fe**

**Goal:** Determine structural stability of paramagnetic *bcc* phase

Construct Wannier functions for partially filled Fe *sd* orbitals

**GGA:**
Only paramagnetic *fcc* structure is stable

**GGA+DMFT:**
- *bcc-fcc* structural transition at $T_{struct} \approx 1.2 \, T_C > T_C$
- LDA+DMFT and GGA+DMFT: qualitatively similar results

What determines the temperature and *c/a* dependence of the total energy?
**bcc-fcc structural transition in paramagnetic Fe**

Contributions to the GGA+DMFT total energy:

\[ E_{tot} = E_{kin} + E_{int} \]

**Kinetic energy**

\[ E_{kin} = E_{GGA} + \langle \hat{H}_{GGA} \rangle - \sum_{m,k} \varepsilon_{m,k}^{GGA} \]

**Interaction energy**

\[ E_{int} = \langle \hat{H}_U \rangle - E_{DC} \]

- **Total energy in GGA**
- **Thermal average of GGA Wannier Hamiltonian**
- **Fe sd valence-state eigenvalues**
- **Average Coulomb repulsion between electrons in Fe sd Wannier orbitals**

*vs.*
**bcc-fcc structural transition in paramagnetic Fe**

Contributions to the GGA+DMFT total energy:

\[ E_{\text{tot}} = E_{\text{kin}} + E_{\text{int}} \]

Kinetic energy

\[ E_{\text{kin}} = E_{GGA} + \langle \hat{H}_{GGA} \rangle - \sum_{m,k} \varepsilon_{m,k}^{GGA} \]

thermal contribution

Interaction energy

\[ E_{\text{int}} = \langle \hat{H}_U \rangle - E_{DC} \]

- kinetic energy favors fcc structure
- correlation energy indifferent

\( \Rightarrow \) as in GGA \( \rightarrow \) fcc structure stable
**bcc-fcc structural transition in paramagnetic Fe**

Contributions to the GGA+DMFT total energy:

\[ E_{tot} = E_{kin} + E_{int} \]

**Kinetic energy**

\[ E_{kin} = E_{GGA} + \langle \hat{H}_{GGA} \rangle - \sum_{m,k} \varepsilon_{m,k}^{GGA} \]

vs.

**Interaction energy**

\[ E_{int} = \langle \hat{H}_U \rangle - E_{DC} \]

- kinetic energy favors *fcc* structure
- correlation energy increases

\[ \rightarrow fcc \text{ structure still stable} \]
**bcc-fcc structural transition in paramagnetic Fe**

Contributions to the GGA+DMFT total energy:

\[ E_{tot} = E_{kin} + E_{int} \]

**Kinetic energy**

\[ E_{kin} = E_{GGA} + \langle \hat{H}_{GGA} \rangle - \sum_{m,k} \varepsilon_{m,k}^{GGA} \]

**Interaction energy**

\[ E_{int} = \langle \hat{H}_{U} \rangle - E_{DC} \]

• kinetic energy favors *fcc* structure
• correlation energy increases

→ *bcc* structure becomes stable
**bcc-fcc structural transition in paramagnetic Fe**

Contributions to the GGA+DMFT total energy:

\[ E_{tot} = E_{kin} + E_{int} \]

**Kinetic energy**

\[ E_{kin} = E_{GGA} + \langle \hat{H}_{GGA} \rangle - \sum_{m,k} \varepsilon_{m,k}^{GGA} \]

**Interaction energy**

\[ E_{int} = \langle \hat{H}_{U} \rangle - E_{DC} \]

- kinetic energy favors *fcc* structure
- correlation energy increases

\[ \rightarrow \text{bcc structure remains stable} \]
Electronic correlations responsible for $T_{\text{struct}} > T_C$
**bcc-fcc structural transition in paramagnetic Fe**

Interaction energy

\[
\hat{n}_{i\uparrow} \hat{n}_{i\downarrow} = \frac{1}{4} \left[ \left( \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow} \right)^2 - \left( \hat{n}_{i\uparrow} - \hat{n}_{i\downarrow} \right)^2 \right]
\]
**bcc-fcc structural transition in paramagnetic Fe**

### Interaction energy

Equal Fe $t_{2g}$ and $e_g$ occupations:

$$
\hat{H}_U = \frac{1}{2} \overline{U} \hat{N}^2 - \frac{1}{4} I \hat{m}_z
$$

- $\overline{U}$: magnetic correlation energy
- $I$: interaction energy
- $\hat{N}$: total number of particles
- $\hat{m}_z$: local magnetic moment

**Total # particles:**

$$
\hat{N} = \sum_{i,m,\sigma} \hat{n}_{im\sigma}
$$

### Local magnetic moment:

$$
\hat{m}_z = \sum_{i,m} \left( \hat{n}_{im\uparrow} - \hat{n}_{im\downarrow} \right)
$$

### Conclusion:

**Magnetic correlation energy stabilizes bcc phase at $T \to 0$**

- high $T$: independent of $c/a$
- low $T$: max. in $bcc$ phase; min. in $fcc$ phase

### Graphical data

- $\overline{U} \approx 0.75 \text{ eV}$,
- $I = \frac{1}{5}(U + 4J) \approx 1.08 \text{ eV}$
**bcc-fcc structural transition in paramagnetic Fe**

**Equilibrium volume V**

**GGA+DMFT**

<table>
<thead>
<tr>
<th>Pressure, GPa</th>
<th>Equilibrium volume (au³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>162</td>
</tr>
<tr>
<td>1</td>
<td>161</td>
</tr>
<tr>
<td>1.2</td>
<td>160</td>
</tr>
<tr>
<td>1.4</td>
<td>159</td>
</tr>
<tr>
<td>1.6</td>
<td>158</td>
</tr>
<tr>
<td>1.8</td>
<td>157</td>
</tr>
</tbody>
</table>

- **bcc Fe**
- **fcc Fe**

$\Delta V \sim -2\%$

Agrees well with exp. data:

$V_{exp} \sim 165 / 158$ au³

**Non-magnetic GGA:**

- $V \sim 141/138$ au³ in *bcc/fcc* phase
  - too small $\rightarrow$ density too high

**GGA+DMFT:**

- $V \sim 161.5/158.5$ au³ in *bcc/fcc* phase
  - increased by electronic repulsion
**bcc-fcc structural transition in paramagnetic Fe**

**Equilibrium volume** and **bulk modulus**

### GGA+DMFT

**bcc Fe**

**fcc Fe**

### Non-magnetic GGA:
- Bulk modulus ~ 2.66/ 2.82 Mbar in bcc/fcc phase too large

### GGA+DMFT:
- Bulk modulus ~ 1.48/ 1.61 Mbar reduced by electronic repulsion

Agrees well with exp. data: \(B_{exp} \sim 1.62 - 1.76\) Mbar

**Conclusion:**

Structural transformation caused by electronic correlations
Application of LDA+DMFT to correlation-driven structural transformations

(ii) Lattice dynamics and phonon spectra of Fe

Leonov, Poteryaev, Anisimov, DV; PRB 85, 020401(R) (2012)
Lattice dynamics of paramagnetic \textit{bcc} iron

Non-magnetic GGA phonon dispersion

1. Brillouin zone

Leonov, Poteryaev, Anisimov, DV (2012)

Exp.: Neuhaus, Petry, Krimmel (1997)
Lattice dynamics of paramagnetic \textit{bcc} iron

- phonon frequencies calculated with frozen-phonon method
  Stokes, Hatch, Campbell (2007)
- harmonic approximation

\begin{itemize}
  \item Calculated:
    \begin{itemize}
      \item equilibrium lattice constant \( a \sim 2.883 \text{ Å} \quad (a_{\text{exp}} \sim 2.897 \text{ Å}) \)
      \item Debye temperature \( \Theta \sim 458 \text{ K} \)
    \end{itemize}
\end{itemize}

Exp.: Neuhaus, Petry, Krimmel (1997)

Leonov, Poteryaev, Anisimov, DV (2012)
Phonon frequencies computed for different temperatures

GGA+DMFT phonon dispersion

Closer look 1: Phonon dispersion of \textit{bcc} iron near $T_C$

- Phonons depend only weakly on the magnetic state
- Anomalous behavior of the transverse $T_1$ acoustic mode near the $N$-point
  \[ \rightarrow \text{phonon softening at the } \textit{bcc-fcc} \text{ phase transition?} \]
Closer look 2: Phonon dispersion of \textit{bcc} iron at higher $T$

Phonon frequencies computed for different temperatures

\textbf{GGA+DMFT phonon dispersion}

- Above \textit{bcc-fcc} phase transition ($\sim 1.2 \, T_C$):
  - Instability of \textit{bcc} phase due to soft $T_1$-mode near $N$-point

- Even higher temperatures: Additional instabilities due to anomaly near $P$-point

\[ N \, [110] \text{ displacement at } 1.4 \, T_C: \]

\[ \text{Anharmonic effects stronger} \]
Lattice dynamics of paramagnetic \textit{fcc} iron

Non-magnetic GGA phonon dispersion

1. Brillouin zone

Leonov, Poteryaev, Anisimov, DV (2012)

Exp.: Zarestky, Stassis (1987)

Elastic constants much too large
Lattice dynamics of paramagnetic \textit{fcc} iron

GGA+DMFT phonon dispersion at 1.4 $T_C$

Calculated:
- equilibrium lattice constant $a \sim 3.605 \, \text{Å}$ \hspace{1cm} ($a_{\text{exp}} \sim 3.662 \, \text{Å}$)
- Debye temperature $\Theta \sim 349 \, \text{K}$

Leonov, Poteryaev, Anisimov, DV (2012)
T_1 mode becomes strongly anharmonic $\rightarrow$ high lattice entropy
$\rightarrow$ lowers free energy $F = E - TS$:

Quasi-harmonic equation of state of soft phonon branch       Drummond, Ackland (2002)
$\rightarrow$ phonon free energy $\Delta F \equiv F_{bcc} - F_{fcc} +$ electronic energy $\Delta E = E_{bcc} - E_{fcc}$

1.4 \( T_C \): - 0.007 + 0.03 eV/atom \( \rightarrow \) \( fcc \) (\( \gamma \)) phase stable
1.8 \( T_C \): - 0.055 + 0.04 eV/atom \( \rightarrow \) \( bcc \) (\( \delta \)) phase stable

$\rightarrow$ \( bcc \) (\( \delta \)) phase of iron stabilized by electronic correlations + lattice entropy
Summary

Correlations between electrons in Fe (KCuF$_3$, V$_2$O$_3$, …)

(i) determine electronic properties (magnetism, spectra, …)

and

(ii) strongly influence

- phonon dispersion
- lattice structure

\[ \rightarrow \text{structural phase diagram} \]

Outlook: Linear-response theory/calculation of forces

\[ \rightarrow \text{Calculate equilibrium lattice structure even} \]
\[ \begin{itemize}
  \item for complex correlated materials
  \item in the vicinity of a Mott metal-insulator transition
\end{itemize} \]

Leonov, Anisimov, DV; arXiv:1311.4493