Practical Implementation and Applications of DFT Methods

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Theory Winter School,
Tallahassee, Florida

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Blueberry Muffins

The blueberries change the taste, but the muffin is still basically a muffin.
The taste does not depend much on the distribution of berries.
The Electron Gas

**bcc Fe:** \( n_{av} = 2.2 \times 10^{24} \text{ e/cm}^3 \) (total); \( n_{av} = 6.8 \times 10^{23} \text{ e/cm}^3 \) (valence)

*Nothing Interesting Happens in the Uniform Electron Gas at Densities of Solids*

The Electron Gas Now With Nuclei

He: liquid at 0 K
W: melts at 3695 K
First Principles Modeling

• Connect properties with atomic level structure.
• Sort out physical models.
• Ask “what if” questions.
• Microscopic mechanisms and understanding.
• Screen ideas for new/modified materials.
• Analyze failures.

Image courtesy of E. Wimmer
“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations that are much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.”


\[ H\psi = E\psi \]: Many Body Problem, with correlated many-body wavefunctions \( \Rightarrow \) Too hard.
“If one had a great calculating machine, one might apply it to the problem of solving the Schrodinger equation for each metal and obtain thereby the interesting physical quantities, such as cohesive energy, the lattice constant, and similar parameters. Presumably, the results would agree with experimentally determined quantities and nothing vastly new would be gained from the calculation. It would be preferable, instead, to have a vivid picture of the behavior of the wave functions, a simple description of the essence of the factors which determine cohesion, and an understanding of the origins ...”

WARNING

If you do not ask questions, I will.

(corollary) If you do not contradict me, I will.
“Hell, there are no rules here - we’re trying to accomplish something.”

Thomas Edison
TODAY’S PLAN

• General Remarks about DFT and Applications.
• Magnetism and Superconductivity (Iron-Based Superconductors).
• Very Short Introduction to the LAPW Method and the ELK code for the Hand’s-On.
Property Prediction and Surprises
High-\(T_c\) Electronic Structures are 2D

YBa\(_2\)Cu\(_3\)O\(_{6+x}\)

\[\text{Cu(1), O(4)}\]
\[\text{Ba, O(1)}\]
\[\text{Cu(2), O(2), O(3)}\]
\[\text{Y}\]
\[\text{Cu(2), O(2), O(3)}\]
\[\text{Ba, O(1)}\]
\[\text{Cu(1), O(4)}\]

Pickett, Cohen, Krakauer, Singh

M. Opel
**La$_3$Ni$_2$B$_2$N$_3$ (12K SC)**

**NEWS: 1994**  
(Nagarajan, PRL; Cava, Nature)

A new family of superconductors with $T_c$ up to 23K

*Is 23K the tip of the iceberg?*
ANSWER: 1994  (Pickett and Singh, PRL)  NO!

Fermi Surface of $\text{YNi}_2\text{B}_2\text{C} (T_c=16\text{K})$

- Electronic structures are very three dimensional
- Due to strong B-C bonds
- Large electron phonon coupling is responsible for superconductivity (conventional mechanism).

- NOT THE BASIS OF A NEW FAMILY OF HIGH TEMPERATURE SUPERCONDUCTORS
**Density Functional Theory**

**Standard approach:** properties are governed by a wavefunction:

\[ \Psi(r_1, r_2, \ldots, r_N) ; \quad H\Psi = E\Psi \]

Given the Hamiltonian, we focus on solving for the wavefunction and extract observables as expectation values of operators with this wavefunction – for \( N \) electrons this is a \( 3N \) dimensional problem.

**Density Functional Theory:** Hohenberg-Kohn theorem tells us

- Energy and other observables of the ground state are given as functionals of the density \( \rho(r) \) which exists in 3 dimensions only.
- The ground state density is unique and is the density that minimizes this functional.

\[ E = E[\rho] ; \quad \rho = \min_{E[\rho]} \{ \rho \} \]

The functional \( E \) is proven to exist, but is not given by the theorem.
Kohn-Sham Approach

Any density \( N \) electron density can be written as the density corresponding to an \( N \) electron Slater determinant (never mind that the true wavefunction cannot).

\[
\rho(\mathbf{r}) = \sum \varphi_i(\mathbf{r})^* \varphi_i(\mathbf{r}) \ ; \ i=1,2, \ldots , N
\]

Where the \( \varphi_i(\mathbf{r}) \) are the Kohn-Sham orbitals

\( \to \) variational principle for \( \rho \) yields a variational principle for the \( \varphi_i(\mathbf{r}) \).

Kohn and Sham then separated terms that should be large in the functional leaving a (hopefully) small remainder as the unknown functional.

\[
E[\rho] = T_s[\rho] + E_{ext}[\rho] + U_{Hartree}[\rho] + E_{xc}[\rho]
\]

where, like \( E \), \( E_{xc} \) is unknown. \( E_{xc} \) is defined by this equation.
Kohn-Sham Equations

Use the variational principle to write single particle equations for the Kohn-Sham orbitals.

\[
\{ T_s + V_{\text{ext}} + V_{\text{Hartree}} + V_{\text{xc}} \} \phi_i = \varepsilon_i \phi_i
\]

\[
\rho(\mathbf{r}) = \sum \phi_i(\mathbf{r})^* \phi_i(\mathbf{r}) ; i=1,2, \ldots , N
\]

Here, \( V_{\text{Hartree}} \) and \( V_{\text{xc}} \) are functionals of the density (functional derivatives of the energy terms with respect to density), so generally these equations must be solved self-consistently.

This is straightforwardly generalizable to magnetic systems via spin-density functional theory where instead of a single function one has spin-densities, \( \rho_{\uparrow}(\mathbf{r}) \) and \( \rho_{\downarrow}(\mathbf{r}) \) for the collinear case and a four component spinor for non-collinear.
The Local Density Approximation

Generally one may write

\[ E[\rho] = \int \rho(r) \varepsilon_{xc}[\rho](r) \, d^3r \]

The local (spin) density approximation consists of taking \( \varepsilon_{xc}[\rho] \) at each point \( r \) as the value for the uniform electron gas at the density for this \( r \).

This exceedingly simple approximation works remarkably well, especially considering that the electron gasses of solids are nothing close to the uniform electron gas.
One of many early works of this type.
Modern Density Functionals

\[ E[\rho] = \int \rho(r) \varepsilon_{xc}[\rho](r) \, d^3r \]

(1) Local (spin) density approximation: \( \varepsilon_{xc}[\rho](r) = \varepsilon_{local}(\rho(r)) \)

- Widely used, especially for metals.

(2) Generalized gradient approximations (GGA, Langreth, Perdew):
  \( \varepsilon_{xc}[\rho](r) = \varepsilon_{gga}(\rho(r),|\nabla \rho(r)|) \)

- Much improved binding energies compared to LDA (chemical accuracy).
- Not gradient expansions, but sophisticated functionals based on exact scaling relations for the inhomogeneous electron gas (electron gas in solids is very non-uniform – can’t use gradient expansions).
- New versions, e.g. PBE-SOL, Wu-Cohen, give almost uniform improvement over LDA in structural properties.
(3) Hybrid functionals (Becke and others):

• Mixture of GGA and Hartree-Fock exchange on the Kohn-Sham orbitals.

• Common in chemistry and semiconductor physics (band gaps are better than standard LDA or GGA’s).

(4) Van der Waal’s Functionals (Langreth, Lundqvist):

• Non-local functionals that incorporate dispersion interactions.

• Surface science, molecular systems, water, DNA, carbon materials, etc.
Salt

NaCl:
Structures generally show cations in locally symmetric anion cages, but the overall lattice structures of halides are often very non-isotropic (Pauling Rules).

**CaI₂** – light yield is >100,000 ph/MeV with Eu²⁺ activators (Hofstadter, 1964, Cherepy, 2008), but this has not proven useful because of **difficulties with crystal growth** – very anisotropic, micaceous, rhombohedral material that invariably cracks.
Optical Properties of CaI$_2$

Low energy limit: $n_{zz}/n_{xx} = 0.991$

Not the expected result
Not All Halides Are Near Isotropic

1.6 eV: 
\[ n_{zz}/n_{xx} = 0.956 \]

Measurements (G.E. Jellison, Jr., et al.):  \( n_{AV}(1.6 \text{ eV}) = 3.1 \)
First principles:  \( n_{AV}(1.6 \text{ eV}) = 3.11 \quad \text{in excellent agreement} \)
But we found that many are: BaIBr

Orthorhombic:
L.Y. > 80,000 ph/MeV with Eu$^{2+}$
Energy resolution better than 5% (Bourret-Courchesne, et al., 2010).
Transparent Ceramics

Key:
High density ceramic.
Low light scattering due to use of cubic (isotropic) materials.

*Crystal growth is not part of the process.*

Casio transparent ceramic camera lens (2004).

*Opportunity for lower-cost manufactured scintillators with uniform characteristics.*
First principles theory, not fit to experiment → results that can point in unanticipated directions.
Dynamics

Giant anharmonic phonon scattering in PbTe

O. Delaire\(^1\)*, J. Ma\(^1\), K. Marty\(^1\), A. F. May\(^2\), M. A. McGuire\(^2\), M-H. Du\(^2\), D. J. Singh\(^2\), A. Podlesnyak\(^1\), G. Ehlers\(^1\), M. D. Lumsden\(^1\) and B. C. Sales\(^2\)
Magnetism

S. Blugel, Julich, Germany: Non-collinear magnetism on a thin film.
Fermi Surfaces

Based on Kohn-Sham eigenvalues, which are not fundamentally related to excitation energies in exact DFT – but this is known to be predictive and useful based on experience.
Band Structures

D.H Lu (2009)
Band Structure Related Quantities

- Optical properties.
- Excitation energies.
- Electronic transport.
- Electron-Phonon interactions.
- etc.

None of these are fundamental in DFT, but they are often quite accurate, and the inaccuracies are well established from much experience.

This is very useful because DFT is tractable, microscopic and predictive.
Hartree-Fock vs. Approximate DFT

• Hartree-Fock is a controlled approximation. Approximate DFT is not.
  ➢ We can systematically improve Hartree-Fock, but with DFT we always have to “guess” about what is / is not already included. LDA+x need not be better than LDA (but it may very well be). *Be Judicious.*

• Hartree-Fock gives poor results for materials. Modern approximate DFT is typically excellent for structures, energies etc.

• There are no metals, no stable Fermi surfaces and no Fermi liquids in Hartree-Fock. There are in DFT, perhaps too many.

*Never equate DFT calculations with Hartree-Fock.*
bcc Iron

- Ferromagnetic metal: $m_{\text{spin}}=2.13\mu_B$, $m_{\text{orb}}=0.09\mu_B$.
- LAPW calculations with GGA (PBE) and spin-orbit.
- LDA+U with SIC double counting.

<table>
<thead>
<tr>
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<th>PBE</th>
<th>Expt.</th>
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<tr>
<td>$m_{\text{spin}}$</td>
<td>2.21</td>
<td>2.13</td>
</tr>
<tr>
<td>$m_{\text{orb}}$</td>
<td>0.05</td>
<td>0.09</td>
</tr>
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bcc Iron (Ferromagnetic) Density of States

As $U$ is increased go from metallic partially polarized $3d$ metal to a fully polarized metal with 5 electrons in the $t_{2g}$ manifold $\Rightarrow$ expected ground state will become orbital ordered antiferromagnetic insulator.

$U-J=3$ eV
References: DFT and Methods


Magnetism and Superconductivity
Pd is not a superconductor because of nearness to ferromagnetism.

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Pd is not a superconductor because of nearness to ferromagnetism.
Singlet $(s,d)$

Hg, Pb, Cuprates

Singlet Channel:
Charge fluctuations (phonons) are attractive.
Ferromagnetic fluctuations are pair breaking
Spin fluctuations in general are repulsive.

Since electron phonon is always attractive the $s$-wave channel is most favored by it.
Inferred Phase Diagram

*Competition of superconductivity and magnetism.*

- **Ferromagnet**
- **Paramagnetic metal**
- **S.C.**

\[ T \]

\[ N(E_F)I \]
Metals Near Quantum Critical Points

Classical criticality: Thermal density fluctuations grow indefinitely close to the Critical Point (CP).

Quantum criticality: Quantum density fluctuations grow indefinitely close to the Quantum Critical Point (QCP).

Interesting things happen near critical points: In this region fluctuations are important and DFT does badly.
Something Different?

Interesting things may happen near critical points: In this region fluctuations are important and DFT does badly.

UGe$_2$, after Huxley et al, 2001 and Saxena et al, 2000

CePd$_2$Si$_2$, after Mathur et al, 1998
“Strontium Ruthenate”

\[ \text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1} \]

\( \text{Ru}^{4+} \) (4 d-electrons)

- \( n = \infty \):
  - Ferromagnet

- \( n = 1 \):
  - Triplet superconductor

- \( n = 2 \):
  - Metamagnetic quantum critical point
Magnetic Order in $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$

Experiment:
- $\text{SrRuO}_3$ is FM $T_C \approx 165\text{K}$.
- $T_C$ falls smoothly with $x$, reaching 0 near $x=1$.
- CaRuO$_3$ was reported AFM, but now thought PM.

LSDA: Octahedral Tilt Broadens DOS.

**Fixed Spin Moment**

- $m_{SCF} = 1.59 \mu_B$
\[ \Delta E = \frac{1}{2} \int_{0}^{m} \left[ m' \, dm' / N(m') \right] - I_{TOT} m^2/4 \]

\[ \Delta E = - I_{TOT} m^2/4 = - \sum_{\alpha} I_{\alpha} m_{\alpha}^2 / 4 \]

For SrRuO$_3$

- \( I_{TOT} = 0.41 \text{eV} \)
- \( I_{Ru} = 0.35 \text{eV} \)

\[ \Rightarrow \text{Significant on-site O contribution} \]
- Favors Ferromagnetism.
- Over Antiferromagnetism.

Also band KE.

Nagler and Chakoumakos, ORNL
Quantum Critical Points and the LDA

Density Functional Theory: LDA & GGA are widely used for first principles calculations but have problems:

• Mott-Hubbard: Well known poor treatment of on-site Coulomb correlations.
• Based on uniform electron gas. Give mean field treatment of magnetism: Fluctuations missing (generally small, but important near quantum critical points)

Resistivity exponent in \( \text{Sr}_3\text{Ru}_2\text{O}_7 \)


LDA overestimate of ferromagnetic tendency is a signature of quantum critical fluctuations – neglected fluctuations suppress magnetism
Electronic Structure of $\text{Sr}_2\text{RuO}_4$

- Highly 2D electronic structure.
- FS agrees in detail with dHvA.
- Mass renormalizations $\sim 4$

What are the pairing interactions on the FS? Unconventional symmetry $\Rightarrow$ not electron-phonon.

$\Rightarrow$ Spin-fluctuations?
Ingredients:

1. On-Site Stoner (O) - Ru-O hybridization

\[ \text{Sr}_2\text{YRuO}_6 \rightarrow \text{AFM} \]

\[ \text{SrRuO}_3 \rightarrow \text{FM} \]

\[ \text{Sr}_2\text{RuO}_4 \rightarrow \text{FM fluct.} \]

- Shared O in RuO\(_2\) planes will favor FM fluctuations.

Can model by smooth background using calculations of

- \(I_{\text{Ru}}\) and \(I_O\).
- Projections of \(N(E_F)\).
- Taking full O contribution at \(\mathbf{k}=(0,0)\) and no O contribution at \(\mathbf{k}=(1/2,1/2)\).
2. Nesting:

\[ \chi(q) = \frac{\chi_0(q)}{1 - I(q)\chi_0(q)} \]

Previous slide had \( I(q) \) from Stoner but no \( q \) dependence in \( \chi_0 \).

Fermi Surfaces: Simple and 2-dimensional \( \Rightarrow \) strong nesting.
• Non-s depends on $q$ dependence in $V(q)$.
• Generally higher $\ell$ needs more structure in $V(q)$.
• The details of the Fermi surface and $V(q)$ are crucial.

**Singlet:**

$$V(q) = -\frac{I^2(q)\chi_0(q)}{1 - I^2(q)\chi_0(q)}$$

**Triplet:**

$$V(q) = \frac{I^2(q)\chi_0(q)}{1 - I^2(q)\chi_0(q)}$$

Note signs.
SUPERCONDUCTIVITY (Con’t)

What we did:

- Calculate matrix elements $V_{k,k'}$ for a set of $k,k'$ on the FS.
- Set-up gap equation -- diagonalize $V$.
- Use $\chi_0(q) = N(0) + \alpha \chi_{\text{nesting}}(q)$. -- i.e. FM Stoner + adjustable strength nesting -- $\alpha = 0$ means no nesting; $\alpha = 0.98$ is AFM.

Result:

- Triplet wins over a wide range ($\alpha < 0.85$)

Note lack of pairing on $\alpha$ sheet.
A Brief Introduction to Cuprates

- Prominent Mott Insulating Phases (not described in band structure)
- Structural complexity (perovskite)
- Doping is essential
- Copper is essential (e.g. Zn alloying destroys superconductivity)
Discovery of Superconductivity in Fe-As Compounds

Kamihara et al., JACS, 2006
LaFePO, $T_c \sim 4K$

Kamihara, Watanabe and Hosono, JACS, Feb. 2008
LaFeAsO$_{1-x}$F$_x$, $T_c=26K$
A Big Family of High $T_c$ Superconductors

Common Features:
- High $T_c$.
- Near magnetism.
- Fe square lattice.
- Near divalent Fe.
- Tetrahedral coordination.

Sefat et al., MRS Bull. 36, 216 2011
A Word About Structure

• Large size of $\text{As}^{3-},\text{Se}^{2-}$ relative to $\text{Fe}^{2+}$ leads to tetrahedral structures with anion contact (edge shared tetrahedra). Tendency to high symmetry, small unit cells without structural distortion.

• Cuprates, etc. are based on corner shared units, with resulting tendency to complex structure distortions. The interplay with properties greatly complicates the physics.

Experimental Proof of a Structural Origin for the Shadow Fermi Surface of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8+\delta$

A. Mans,¹ I. Santoso,¹ Y. Huang,¹ W. K. Sin,¹ S. Tavaddol,¹ V. Arpiainen,² M. Lindroos,² H. Berger,³ V. N. Strocov,⁴ M. Shi,⁴ L. Patthey,⁴ and M. S. Golden¹

¹Van der Waals-Zeeman Institute, University of Amsterdam, NL-1018XE Amsterdam, The Netherlands
²Department of Physics, Tampere University of Technology, PO Box 692, FIN-33101 Tampere, Finland
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(Received 3 August 2005; published 16 March 2006)

In summary, by proving the microscopic structural origins of the shadow bands in the Bi2212 and Bi2201 families of cuprate superconductors, we have finally been able to close this chapter in the rich and complex tale of the high $T_c$ superconductors.
FeSe - The “Simplest” Fe-Superconductor

- Simple tetragonal structure, four atoms per unit cell (Hagg and Kindstrom, Z. Phys. Chem. (1933)).
- Actual material is $\text{Fe}_{1+x}\text{Se}$, with extra Fe in holes of Se lattice.
- LiFeAs is similar, but extra sites are filled with Li.

$d_{\text{Fe-Fe}} = 2.66 \text{ Å}$
Not List:

- Doping is not essential.
- Not in proximity to Mott phases.
- Magnetic order & superconductivity not incompatible (compete).
- Orthorhombicity occurs without magnetic order, but not always, and highest $T_c$ is tetragonal (but large orthorhombic regions).
- Maximum $T_c$ in different families is not so different (factor of $\sim 2$).
Metallic Antiferromagnetic State

SrFe$_2$As$_2$ (Sebastian et al.)

Shubnikov – de Hass measured by tunnel diode method.

SDW state has quantum oscillations reflecting a Fermi surface and is therefore a metal.
Phonons and Electron-Phonon Interaction

- First principles calculations allow direct calculation of pairing interaction, and almost first principles calculation of $T_c$.
- Calculations show weak coupling, no superconductivity ($\lambda_{ep} \sim 0.2$).

- Fe/As phonons are below 300 cm$^{-1}$.
- Corresponding Ni compounds, LaNiPO, LaNiAsO, BaNi$_2$As$_2$ ... are electron-phonon superconductors!
- Fe compounds are not electron-phonon superconductors.

Neutron Scattering – Magnetism & Structure

LaFeAsO:
Ordered $m(\text{Fe}) = 0.36 \mu_B$
(other compounds so far are between 0.3 and 1 $\mu_B$)

C. de la Cruz et al., Nature 453, 899 (2008)
In-plane SDW structure

1 D Chains of parallel spin Fe atoms.
Hund’s Coupling

• Hund’s coupling in 3d ions is strong (Stoner $I \sim 0.8$ eV)

• Spin-fluctuations are then expected to couple to electronic states in the $d$-band going up to high energy (i.e. the $d$-band width) – may be observable in spectroscopy. Drude weight seems reduced in optics.


Fig. 3. The temperature dependent reflectivity of chromium normalized to $T=400$ K.
$1/T_1 T$ shows strong spin fluctuations (constant for ordinary F.L.)

Ning, et al., JPSJ 78, 013711 (2009).
LDA Electronic Structure of FeSe

- A rather ionic material – Fe$^{2+}$ and Se$^{2-}$ with some hybridization, as in an oxide $\Rightarrow$ metallic sheets of Fe$^{2+}$ modified by interaction of anions.
- Pauling electronegativities: Fe = 1.83; Se = 2.55; As = 2.18.
Formation of Band Structure

- Bands from -2 eV to +2 eV are derived from Fe$^{2+}$ $d$-states.
- Fe$^{2+}$ has 6 $d$-electrons.

**Tetrahedral Crystal Field Scheme:**

```
3d 10e  e_g 4e  t_2g 6e
```

Does not correspond to the calculated electronic structure.

Key is the short Fe-Fe bond length $\rightarrow$

*direct* Fe-Fe interactions.
Arsenide Electronic Structure: LaFeAsO

- LaFeAsO: Rather ionic electronic structure: $O^{2-}$, $As^{3-}$, $La^{3+}$
- Bands near $E_F$ are derived from Fe with little As admixture

Metallic sheets of Fe$^{2+}$

$E_F$ is at the bottom edge of a pseudogap

High $N(E_F)$ near magnetism

Metallic Character

Photoemission: LaFePO (D.H. Lu et al.)

Very prominent Fermi edge (not like cuprates).

Fe d bands are narrower (by ~2) compared to LDA.
LaFePO (M.M. Qazilbash et al.)

Drude has lower weight than in band calculation.

Re-distribution of spectral weigh in d-bands.

No Hubbard bands.
Coulomb Correlations

- LDA and correlated approaches give different predictions.
- So far Hubbard bands are not seen; strong Fe d character is seen at Fermi edge.
- There is however a renormalization of ~2 in band width c.f. LDA.

X-ray spectra, Kurmaev, et al.
Density Functional Study of $\text{LaFeAsO}_{1-x}\text{F}_x$: A Low Carrier Density Superconductor Near Itinerant Magnetism

D.J. Singh and M.-H. Du

*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6114, USA*

(Received 4 March 2008; published 12 June 2008)

Fermi Surface of $\text{LaFeAsO}$

(not spin polarized)

Low carrier density:

$n_e=n_h=0.13 / \text{Fe}$

Band anisotropy: $<v_x^2>/ <v_z^2> \sim 15$ ➔

a modest value that is favorable for applications.
Lindhard Function (Metal Physics)

• LaFeAs(O,F) neglecting matrix elements:

\[ \text{Im } \chi_0/\omega \]

\[ \text{Re } \chi_0 \]

Scattering, Transport

Magnetism, Superconductivity

Note the pronounced peak at the zone corner.

Spin Fluctuations and Superconductivity

One way to proceed (weak coupling):
• Calculate matrix elements $V_{k,k'}$ for a set of $k,k'$ on the FS.
• Set-up gap equation -- diagonalize $V$.

**Berk-Schrieffer-Fay-Appel weak coupling theory, 1966-1980:**

Singlet:

$$ V(q) = - \frac{l^2(q) \chi_0(q)}{1 - l^2(q) \chi_0^2(q)} $$

In a singlet channel there is a minus sign for spin fluctuations (repulsive), which then favors opposite order parameters on the electron and hole sheets $\Rightarrow s +/-$ state.

Note prior work, Aronov & Sonin (1972); Kuroki and Arita (2001)

Does not have an obvious strongly $q$-dependent interaction for nodes in a FS.

Unconventional superconductivity in $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ from inelastic neutron scattering

A. D. Christianson$^1$, E. A. Goremychkin$^{2,3}$, R. Osborn$^2$, S. Rosenkranz$^2$, M. D. Lumsden$^1$, C. D. Malliakas$^{2,4}$, I. S. Todorov$^2$, H. Claus$^2$, D. Y. Chung$^2$, M. G. Kanatzidis$^{2,4}$, R. I. Bewley$^3$ & T. Guidi$^3$

$T=7\text{K}$

$T=50\text{K}$

Magnetic Resonance

Sign changing gap with $q$ corresponding to $(\pi,\pi)$
Small Fermi Surfaces in General

- Does superconductivity arise in general if one has small Fermi surfaces with nesting driven spin fluctuations? – Answer seems to be no.

- $p$-wave state (triplet): spin-fluctuation pairing interaction has $+$ sign $\rightarrow$ Pair breaking for the state shown.

- $s$-wave state (singlet): spin-fluctuation pairing interaction has $-$ sign $\rightarrow$ Pair breaking for the state shown.

e.g. small pockets on Na$_x$CoO$_2$ (Johannes et al., 2004).

In such cases, look for chemistry with strong electron phonon and low Stoner parameter, to obtain Kohn anomaly and e-p superconductivity or maybe strange states, e.g. odd frequency.
Normal Metallic State

- Low carrier density semi-metal (dis-connected small Fermi surfaces).
- Less anisotropic than cuprates, even YBa$_2$Cu$_3$O$_7$.
- High $N(E_F)$.
  - Near itinerant magnetism in general.
  - Expect short coherence length relative to $T_c$.
  - Expect high superfluid density.
- Electron-Phonon interaction is weak ($\lambda \sim 0.2$, $T_c=0$)
Nesting, Doping and the Lindhard Function

Disorder affects both magnetism and superconductivity
Neutron Scattering – Structure Details

LaFeAsO (Tetragonal $\rightarrow$ Orth/Mono):

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<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
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<td>La</td>
<td>2e</td>
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<td>0.1426(3)</td>
<td>0.54(6)</td>
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<tr>
<td>Fe</td>
<td>2f</td>
<td>$\frac{3}{4}$</td>
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<td>0.5006(12)</td>
<td>0.16(4)</td>
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<tr>
<td>As</td>
<td>2e</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>0.6499(4)</td>
<td>0.23(7)</td>
</tr>
<tr>
<td>O</td>
<td>2f</td>
<td>$\frac{3}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>$-0.0057(17)$</td>
<td>0.69(7)</td>
</tr>
</tbody>
</table>

$z_{As}(4K) = 1.308 \text{ Å}$

$z_{As}(175K) = 1.317 \text{ Å}$

LaFeAsO$_{0.92}$F$_{0.08}$ (Tetragonal):

$z_{As}(10K) = 1.323 \text{ Å}$

$z_{As}(175K) = 1.331 \text{ Å}$

Non-magnetic LDA calc. (LaFeAsO – Tetragonal)

$z_{As}(\text{LDA}) = 1.159 \text{ Å}$

A huge difference!

C. de la Cruz et al., Nature 453, 899 (2008)
Structure and Magnetism

• As height is too low by $>0.1$ Å in non-magnetic LSDA calculations.

• SDW is too robust in DFT.

• Using GGA and including magnetism one can obtain much better As height. In that case magnetism is extremely robust ($m \sim 2\mu_B$) contrary to experiment.

• Discrepancy in As height persists in the paramagnetic (superconducting) doped phases.
Metals Where the LSDA Overestimates Ferromagnetism

Class 1: Ferromagnets where the LDA overestimates the magnetization.

<table>
<thead>
<tr>
<th>Material</th>
<th>m (LDA, (\mu_B/f.u))</th>
<th>m (expt., (\mu_B/f.u))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrZn(_2)</td>
<td>0.72</td>
<td>0.17</td>
</tr>
<tr>
<td>Ni(_3)Al</td>
<td>0.71</td>
<td>0.23</td>
</tr>
<tr>
<td>Sc(_3)In</td>
<td>1.05</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Class 2: Paramagnets where the LDA predicts ferromagnetism

<table>
<thead>
<tr>
<th>Material</th>
<th>m (LDA, (\mu_B/f.u))</th>
<th>m (expt., (\mu_B/f.u))</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeAl</td>
<td>0.80</td>
<td>0.0</td>
</tr>
<tr>
<td>Ni(_3)Ga</td>
<td>0.79</td>
<td>0.0</td>
</tr>
<tr>
<td>Sr(_3)Ru(_2)O(_7)</td>
<td>1.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Na(_{0.7})CoO(_2)</td>
<td>0.30</td>
<td>0.0</td>
</tr>
</tbody>
</table>

c.f. “Normal” Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>m (DFT, (\mu_B/f.u))</th>
<th>m (expt., (\mu_B/f.u))</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc Fe</td>
<td>2.17</td>
<td>2.12</td>
</tr>
<tr>
<td>SrRuO(_3)</td>
<td>1.59</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Renormalization and The Fluctuation Dissipation Theorem

Relates fluctuation amplitude to dissipation term, i.e. spin fluctuation spectrum:

$$\xi^2 = \frac{4\hbar}{\Omega} \int d^3 q \int \frac{d\omega}{2\pi} \frac{1}{2} \text{Im} \chi(q, \omega)$$

Landau functional approach (after Moriya, Shimizu, others) is based on the magnetic moment dependence of the total energy without fluctuations:

$$\Delta E(M) = aM^2 + bM^4 + cM^6 \quad a^{-1}/2 = \chi, \text{ susceptibility}$$

Spin fluctuations renormalize this dependence, i.e. $a \Rightarrow \alpha$, etc. via integration of the Landau functional with Gaussian of rms width $\xi$.

1. Large renormalization $\Rightarrow$ large fluctuation amplitude.
2. Large amplitude requires large integral $\Rightarrow \text{Im} \chi$ large over wide range of $q$ and $\omega$. 
Example: ZrZn$_2$ (Weak Itinerant Ferromagnet)

Bare LDA moment of $\sim 0.7 \mu_B$ to $\sim 0.2 \mu_B$ by fluctuations $\xi \sim 0.4 \mu_B$

Evidence of strong interplay of magnetic ordering and Fermi surface.

Evidence of spin fluctuations.
Strong Spin Fluctuations in Normal State

- Transport data.
- Susceptibility - $\chi(T)$.
- Spectroscopy.
- Scattering.
- Overly magnetic in LDA.
- Precursor structural transition.

Bondino et al. (2008); c.f. NbFe$_2$
Superconductivity in Metal Doped Materials

- Superconductivity requires destruction of SDW by doping.
- Remarkably, doping with Co or Ni works (c.f. cuprates).

Calculations show that alloy behaves very much in a rigid band sense.

Fe-Co-Ni behave very similarly apart from electron count.

Mn and Cr show strong spin dependent hybridization (different).

Is iron essential?

ThCr$_2$Si$_2$ Structure

Examples: BaZn$_2$P$_2$, BaFe$_2$As$_2$, BiN$_2$Th$_2$, CaAl$_2$Ga$_2$, SrCd$_2$Ga$_2$ ...
ThCr$_2$Si$_2$ Structure $DT_2As_2$

<table>
<thead>
<tr>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
</table>

Strong spin dependent $T$-As hybridization, G-type AF with high $T_N$.
BaCr$_2$As$_2$ is itinerant metal. BaMn$_2$As$_2$ is a semiconductor.

Metallic $M^{2+}$ sheets. As is anionic. $M$ can be alloyed.
Fe: SDW and superconductivity.
Co: Near FM
Ni: electron-phonon superconductor.

BaCu$_2$As$_2$ has Cu $d^{10}$ with As-As and Cu-As sp bonding.

Chemistry of chalcogenides may be expected to differ.
Properties of the Over-Doped Side: TlFe\textsubscript{2}Se\textsubscript{2}

Haggstrom, 1986

First Principles Results (GGA):

- Electronic structure is very similar to FeSC, but with higher electron count (0.5 e/Fe).
- Strong instability against nearest neighbor AFM (78 meV/Fe) and weaker instability against FM (44 meV/Fe). No instability for SDW type chain order $\rightarrow$ itinerant n.n. AFM

Antiferromagnetic with $T_N \sim 450$ K. Unknown order.

Non spin polarized Fermi surface
Competing Magnetic States

Competition between different magnetic states provides phase space for fluctuations and works against ordering.

SDW - c(2x2)  N.N (1x1)  (2x1)

LaFeAsO  TlFe$_2$Se$_2$  Fe$_{1+x}$Te
Possible Electron Doped Phase Diagram

$T$

Metal with strong spin fluctuations – competing magnetic orders.

Itinerant AFM Metal (n.n. ordering)

No competition from SDW

<table>
<thead>
<tr>
<th>Doping</th>
<th>Loss of nesting</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Suppressed SDW

Superconductor
Conclusions

• Iron superconductors behave very differently from cuprates – perhaps a rather different mechanism or perhaps we need to look deeper for the connections.

• Strong renormalization of magnetic properties due to strong spin fluctuations – almost certainly necessary for understanding of the normal state and the superconductivity.

• Extended s-wave (+/-) state.

• Interesting interplay between magnetism and structure.

• *Competition between different magnetic states helps set up superconductivity as opposed to order magnetism in Fe-based superconductors and Ruthenates.*
Questions

• Can we identify materials with “strong” spin fluctuations and quantify “strong”? 
• Can we identify competing magnetic states, even those with relatively weak q-dependence? 
• Could we connect inelastic scattering with magnetic renormalization (fluctuation-dissipation)? 
• Can we connect with transport experiments? 
• Can we identify trends in magnetic behavior that would allow us to predict new superconductors, or ways to vary composition to improve superconductivity? 
• …
Hands On Science
Binding energy of Fe: 2541.025 Ry
bcc-fcc energy difference in Fe: 0.013 Ry (austenite-ferrite in steels)

Binding of PZT (Piezoelectrics): 46730.476 Ry
Ferroelectric instability in PZT: 0.006 Ry

Binding of Mn-ferrite (oxide mag.): 15987.192 Ry
Magnetic coupling of Mn-ferrite: 0.070 Ry

*Small differences between very large energies are the keys to materials properties*

⇒ We rely on careful choice of numerical methods and error cancellation in the differences.
The Linearized Augmented Planewave (LAPW) Method

\[ E_T[\rho] = T_s[\rho] + E_{ei}[\rho] + E_H[\rho] + E_{xc}[\rho] + E_{ii} \]

\[ \{T_s + V_{ks}[\rho, r]\} \varphi_I(r) = \varepsilon_i \varphi_i(r) \]

Need tools that are reliable and predictive.
DFT ALGORITHMS

• Find $\varphi_I$ and $\rho$ to solve:

$$\{ T_s + V_{KS}[\rho, r] \} \varphi_I(r) = \varepsilon_I \varphi_I(r)$$

• Expand $\varphi_I$ in a basis $\{ \phi_j \}$.

• Many methods, PW, FE, LAPW, LMTO, LCAO ...

• For fixed $V_{KS}$ get a linear algebra problem.
  (eigenvalue).

$$<\phi|H|\phi> x_i = \varepsilon_i <\phi|\phi> x_i$$

• Iterate to find self-consistent $\rho$.

Standard Solution:

• Expand $\varphi_I$ in a basis $\{ \phi_j \}$.

• For fixed $V_{KS}$ get a linear algebra problem.
  (eigenvalue).

Some Numbers:

• $# \varphi_I \sim 10$ / atom.

• $# \phi_j \sim 10$’s - 1000’s / atom.

• # atoms (State of the Art): 100 – 1000’s.
Motivation for Augmentation

Schrödinger Equation:

$$(T+V-\varepsilon)\varphi = 0$$

For valence states: $\varepsilon$ is small $\Rightarrow$

$T\varphi$ is also small except where $V$ is strong, i.e. near the nucleus.
Augmented Planewave (APW) Method


Divide Space Into 2 Regions:
- Atom Centered Spheres
- Interstitial

“Basis” Consists of Planewaves in the Interstitial and Radial Functions in the Spheres.

$$
\varphi(r) = \begin{cases} 
\Omega^{-1/2} \sum_G c_G e^{i(G+k) \cdot r} & r \in \text{Interstitial (I)} \\
\sum_{lm} A_{lm} u_l(r) Y_{lm}(r) & r \in \text{Sphere (S)}
\end{cases}
$$

- $u_l(r)$ are the radial solutions of Schrödinger’s equation at the energy of interest (i.e. the band energy).
Augmented Planewave (APW) Method

\[ \varphi(r) = \begin{cases} 
\Omega^{-1/2} \sum_G c_G e^{i(G+k) \cdot r} & r \in \text{Interstitial (I)} \\
\sum_{lm} A_{lm} u_l(r) Y_{lm}(r) & r \in \text{Sphere (S)}
\end{cases} \]

Key points:

1. The \( A_{lm} \) are not variational parameters. They are determined by a matching condition. That is the value of the basis functions, \( \phi_{k+G} \) is fixed to be continuous at the sphere boundary.

2. The full crystal potential can be used because one may show that the \( u_l \) are orthogonal to “core” states.

\[
\left[ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right] r u_l(r) = 0
\]

So:

\[
(E_2 - E_1) r u_1 u_2 = u_2 \left( \frac{d^2 r u_1}{dr^2} \right) - u_1 \left( \frac{d^2 r u_2}{dr^2} \right)
\]

Integrate by parts to get overlap of \( u_1 \) and \( u_2 \). They are orthogonal if one of them is 0 on the sphere boundary.
Problems with the APW Method

1) Must solve secular equation for each energy band: prohibitive for many bands. No clear way to make full-potential.

2) Asymptote problem: cannot match at energies where \( u(r) \) is zero on the sphere boundary. This will in general happen at some energy – particular problem for \( d \) and \( f \) band materials.
The Linearized Augmented Planewave (LAPW) Method


Key Ideas:

• The problem with the APW method is the energy dependence of the secular equation which is a result of the energy dependence of the augmenting function.

• Solution: Add variational freedom: particularly \( \hat{u}(r) = \partial u(r)/\partial E \).

\[
\varphi(r) = \begin{cases} 
\Omega^{-1/2} \sum_G c_G e^{i(G+k) \cdot r} & \text{r} \in I \\
\sum_{lm} (A_{lm} u_l(r) + B_{lm} \hat{u}_l(r)) Y_{lm}(r) & \text{r} \in S 
\end{cases}
\]

• Where \( A_{lm} \text{ and } B_{lm} \) are determined by matching the value and derivative of the basis functions at the sphere boundary.
THE LAPW METHOD

Results of adding $\hat{u}_i$ to the basis:

1. Basis is flexible enough to use a single diagonalization (energy errors are now $O(\delta^4)$).

2. Must have additional matching conditions to connect both $u$ and $\hat{u}$ to the planewaves. This means that for a given level of convergence, more planewaves are needed.

3. The transferability also extends to variations in the potential: this enables full-potential methods.

The full potential, all electron, nature combined with the flexible basis (fully flexible in the interstitial) made the (F)LAPW method the state of the art for calculating electronic structures, especially for transition elements and their compounds – Many groups developed codes 1980 – present.
References


The Elk FP-LAPW Code

An all-electron full-potential linearised augmented-plane wave (FP-LAPW) code with many advanced features. Written originally at Karl-Franzens-Universität Graz as a milestone of the EXCITING EU Research and Training Network, the code is designed to be as simple as possible so that new developments in the field of density functional theory (DFT) can be added quickly and reliably. The code is freely available under the GNU General Public License.

Latest version: 1.3.31

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http://elk.sourceforge.net/
Superconducting-like behaviour of the layered Chalcogenides CuS and CuSe below 40 K

B. Raveau*, Tapati Sarkar

Laboratoire CRISMAT, UMR 6509 CNRS ENSICAEN, 6 bd Maréchal Juin, 14050 CAEN, France

Abstract

The investigation of strongly sintered “quasi molten” CuS and CuSe chalcogenides shows that they exhibit a sharp diamagnetic transition and a resistivity drop around 40 K. The reminiscence of such high temperature superconductivity features, never observed to date for these phases, is strongly supported by two chemical characteristics: bidimensionality of the structure and mixed valency of copper. The absence of zero resistance suggests that the internal chemical pressure in the samples has a key role in the existence of superconductivity: the S–S or Se–Se interlayer distances are very sensitive to the pressure, so that the critical distance for the percolation can be reached in the core of the samples, but not at the vicinity of the surface, where relaxation may appear.

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Fig. 3. Temperature dependence of resistivity of (a) CuS (sample 1) and (b) CuSe (sample 2) in the presence and absence of external magnetic field. The insets show the variation of the % MR as a function of temperature for the two samples.
Fig. 2. Temperature dependence of a.c. magnetic susceptibility of (a) CuS (sample 1) and (b) CuSe (sample 2) measured in the presence of two different d.c. magnetic fields.
Structure of CuS
Experimental and theoretical investigation of the crystal structure of CuS

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† Physics Department, Keele University, Keele, Staffs ST5 5BG, UK
‡ Neutron Division, Rutherford–Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK

Received 24 August 1992, in final form 14 October 1992

Abstract. The crystal structure of CuS has been confirmed experimentally using the powder diffraction method on the high-resolution powder diffractometer at the Rutherford–Appleton Laboratory. The observed crystal structure is $P6_3/mmc$. Standard density functional calculations on CuS on a variety of crystal structures are also reported. The calculations also predict $P6_3/mmc$ as the stable crystal structure. On the basis of the agreement between theory and experiment we are able to discuss the details of the bonding in this material.
Klockmannite, CuSe: structure, properties and phase stability from \textit{ab initio} modeling

The details of the electronic and crystal structure, the nature of the interatomic bonding and the phase stability of three modifications of klockmannite, CuSe, are analysed using first principles modeling. The hexagonal modification of CuSe is predicted to be less stable than the orthorhombic phase under pressure. The stabilizing force for the orthorhombic phase is identified as the Cu—Cu bond formation between the Cu atoms in the flat hexagonal CuSe layer and in the buckled Cu$_2$Se$_2$ layer. Furthermore, klockmannite is shown to be unstable under compression with respect to the decomposition into umangite, Cu$_3$Se$_2$, and krutaite, CuSe$_2$ II.