Ab-initio Wannier Functions, Coulomb Matrix Elements, Hartree (-Fock) and LSDA Calculations for the 3d Transition Metals Fe, Co, Ni and Cu

15. 10. 2002

Ilan Schnell
Institut für Theoretische Physik
Universität Bremen

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Motivation

Two approaches for electronic ground state properties:

Ab-initio DFT/LDA		Model Hamiltonian
☺	Real materials	☹
☹	Strongly correlated	☺

- Model Hubbard Hamiltonian:

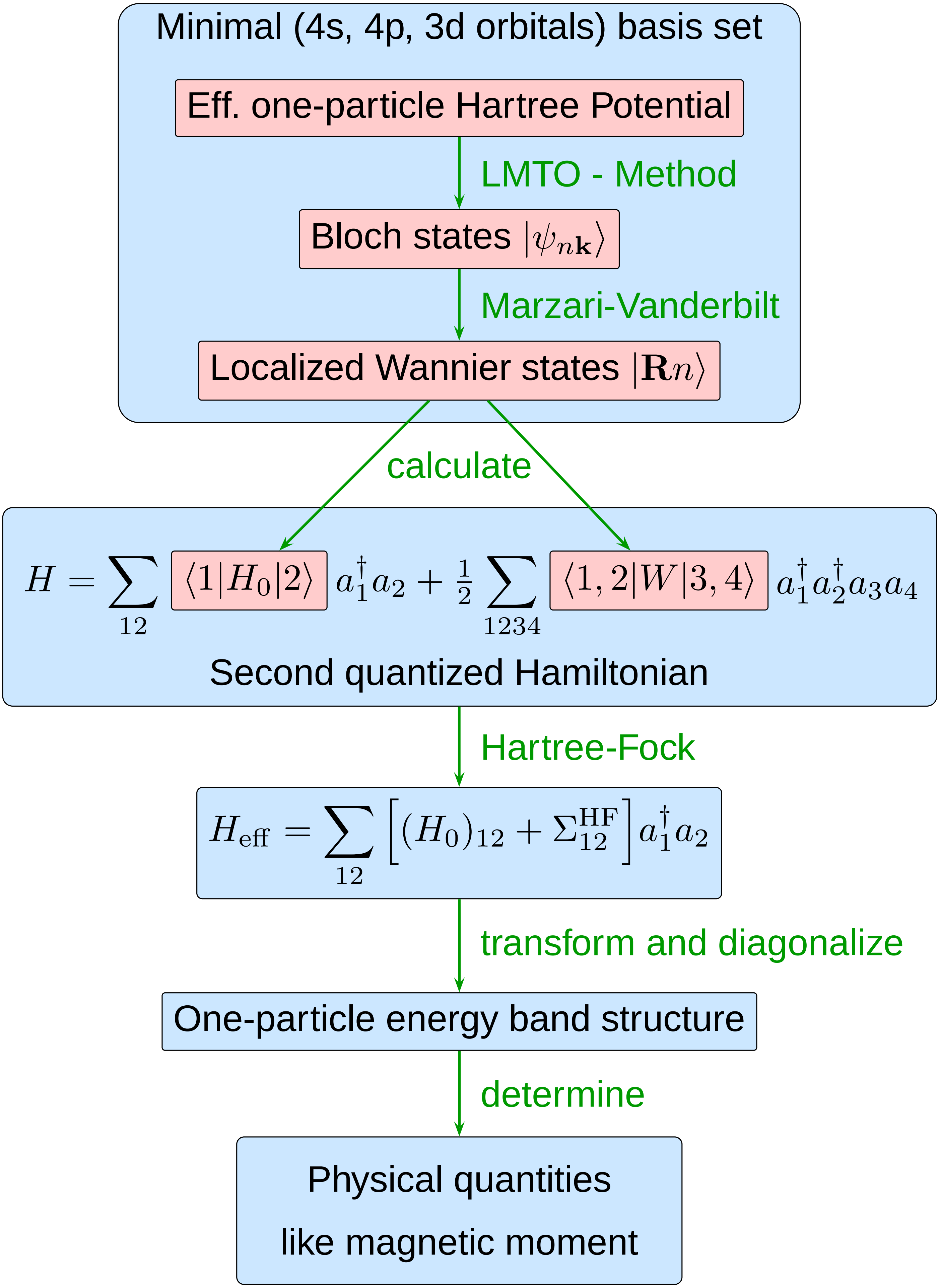
  $$H = t \sum_{ij\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

  t and the Hubbard-U are empirical parameters.

- Ab-initio calculations are mostly based on LDA, and systematic improvement is difficult.

- The goal of this work is a combination of the two approaches.
  - Determine t and U from first principles.
  - Solve the second quantized Hamiltonian in Hartree-Fock approximation.

Overall Procedure



Minimal (4s, 4p, 3d orbitals) basis set

Eff. one-particle Hartree Potential

LMTO - Method

Bloch states $|\psi_{n\mathbf{k}}\rangle$

Marzari-Vanderbilt

Localized Wannier states $|\mathbf{R}n\rangle$

calculate

$$H = \sum_{12} \boxed{\langle 1|H_0|2\rangle}\, a_1^\dagger a_2 + \frac{1}{2} \sum_{1234} \boxed{\langle 1,2|W|3,4\rangle}\, a_1^\dagger a_2^\dagger a_3 a_4$$

Second quantized Hamiltonian

Hartree-Fock

$$H_{\text{eff}} = \sum_{12} \left[(H_0)_{12} + \Sigma_{12}^{\text{HF}} \right] a_1^\dagger a_2$$

transform and diagonalize

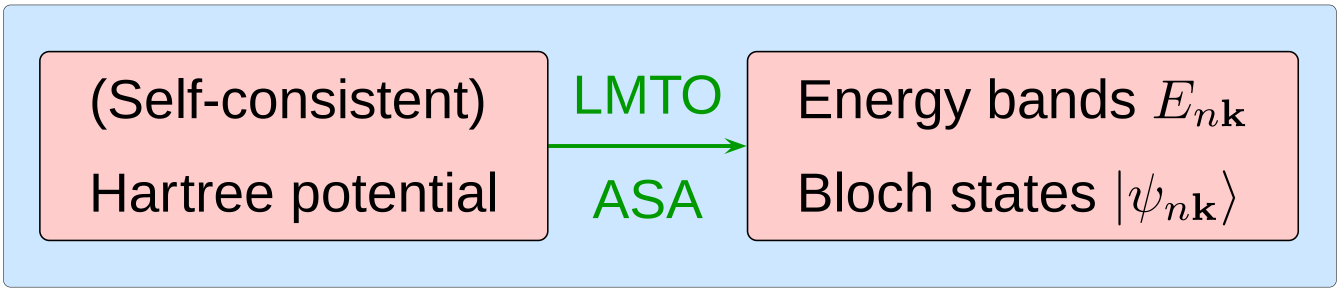
One-particle energy band structure

determine

Physical quantities

like magnetic moment

LMTO-ASA

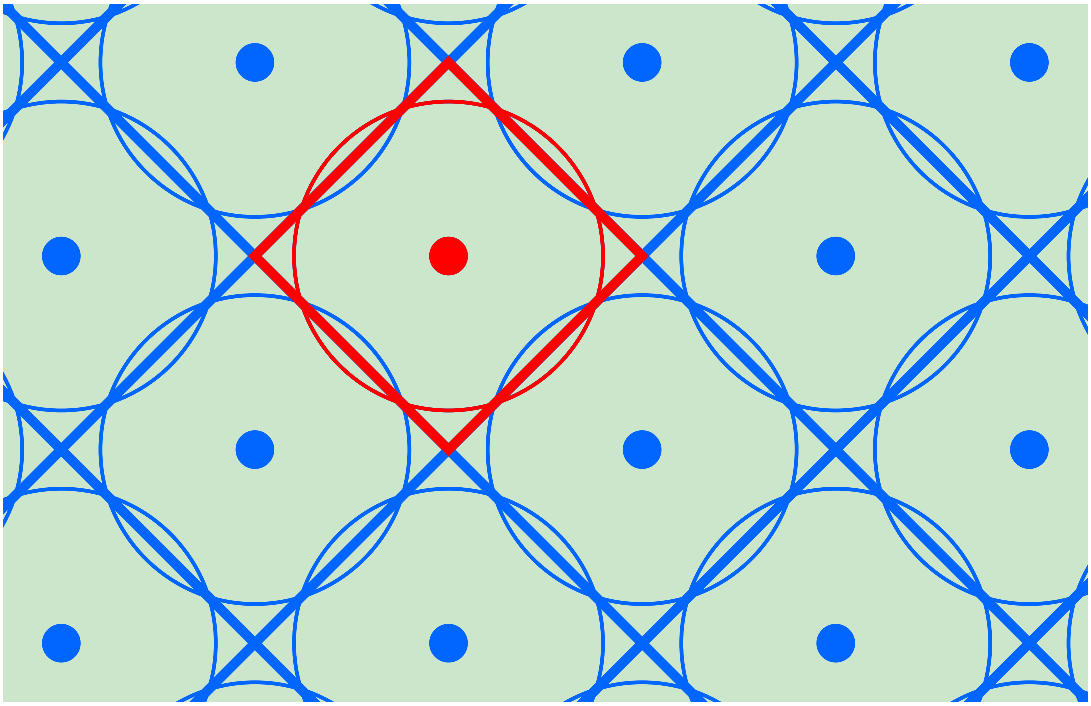


(Self-consistent)
Hartree potential

$\xrightarrow[\text{ASA}]{\text{LMTO}}$

Energy bands $E_{n\mathbf{k}}$
Bloch states $|\psi_{n\mathbf{k}}\rangle$

- Atomic Sphere Approximation (ASA):



- A result of the LMTO-ASA equations are the Bloch functions inside each atomic sphere:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\ell,m} \left(\phi_{\nu\ell}(r) A_{\ell m}^{n\mathbf{k}} + \dot{\phi}_{\nu\ell}(r) B_{\ell m}^{n\mathbf{k}} \right) Y_\ell^m(\hat{\mathbf{r}})$$

$\phi_{\nu\ell}(r)$: Solution of the radial Schrödinger equation at fixed energy $E_{\nu\ell}$.

$\dot{\phi}_{\nu\ell}(r)$: its energy derivative.

Wannier Functions

Bloch: $|\psi_{n\mathbf{k}}\rangle$ (delocalized) $\xrightarrow{\text{construct}}$ Wannier: $|w_{\mathbf{R}n}\rangle$ (localized)

- Wannier functions are defined by Bloch functions as:

$$w_{\mathbf{R}n}(\mathbf{r}) \equiv \frac{V}{(2\pi)^3} \int_{\mathrm{BZ}} d^3\mathbf{k}\, e^{-i\mathbf{k}\mathbf{R}}\, \psi_{n\mathbf{k}}(\mathbf{r})$$

- From Bloch's theorem:

$$w_{\mathbf{R}n}(\mathbf{r}) = w_{\mathbf{0}n}(\mathbf{r} - \mathbf{R})$$

- Wannier functions are not unique.
  Their non-uniqueness corresponds to the
  gauge transformation (for each **k**-point):

$$|\psi_{n\mathbf{k}}\rangle \quad \rightarrow \quad \exp(i\phi_n^{\mathbf{k}})\, |\psi_{n\mathbf{k}}\rangle \ , \qquad\qquad \phi_n^{\mathbf{k}} \text{ real}$$

- Generalized Bloch functions

$$|\psi_{n\mathbf{k}}\rangle \quad \rightarrow \quad \sum_m U_{mn}^{\mathbf{k}}\, |\psi_{m\mathbf{k}}\rangle \ , \qquad U^{\mathbf{k}} \text{ unitary,}$$

  allowing more gauge freedom.

- (Generalized) Wannier functions span the same one-particle Hilbert space as the Bloch functions.

Wannier Functions (cont.)

- The Wannier functions for which the spread functional

  $$\Omega = \sum_n \left[\langle w_n | r^2 | w_n \rangle - \langle w_n | r | w_n \rangle^2 \right]$$

  assumes a (global) minimum are called
  "maximally localized" Wannier functions.

- Marzari and Vanderbilt [Phys. Rev. **B56**, 12847 (1997)] proposed an elegant procedure to (numerically) construct maximally localized Wannier functions.

- This procedure can be employed to the ASA without any problems.

- Final result can be written in LMTO fashion as:

  $$w_{\mathbf{0}n}(\mathbf{R};\mathbf{r}) = \sum_{\ell,m} \left(\phi_{\nu l}(r) A_{\ell m}^{\mathbf{R}n} + \dot{\phi}_{\nu l}(r) B_{\ell m}^{\mathbf{R}n} \right) Y_\ell^m(\hat{\mathbf{r}})$$

  I.e., $w_{\mathbf{0}n}$ is expanded in spheres around $\mathbf{R}$.

- The WF's we obtain are well localized with more than 87% of their density in the center atomic sphere.

- Unlike atomic orbitals, WF's are not pure with respect to their ℓ-character.

Hopping Matrix Elements

Hopping matrix elements are

- defined in terms of (generalized) Wannier functions as

  $$H_{\mathbf{R}nm} \equiv \langle w_{\mathbf{R}n} | H | w_{\mathbf{0}m} \rangle \quad ,$$

  where H is a one-particle Hamiltonian.

- related to the band structure by:

  $$H^{\mathbf{k}}_{nm} \equiv \langle \psi_{n\mathbf{k}} | H | \psi_{m\mathbf{k}} \rangle = \sum_{\mathbf{R}} e^{-i\mathbf{k}\mathbf{R}} \, H_{\mathbf{R}nm}$$

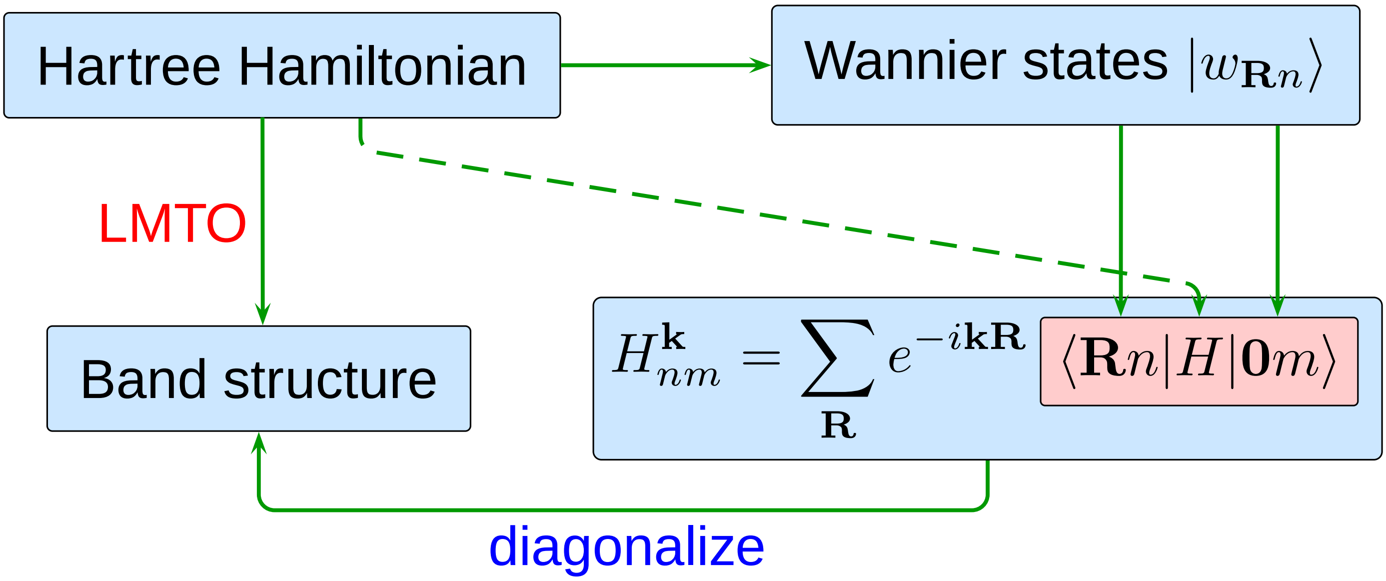
  The eigenvalues of $H^{\mathbf{k}}$ are the energy bands $E_{n\mathbf{k}}$.

- decaying with increasing $\mathbf{R}$,
  allowing the truncation of $\mathbf{R}$-sums.

- evaluated in our sphere expansion: $(w_n \equiv w_{\mathbf{0}n})$

  $$H_{\mathbf{R}nm} = \sum_i \int d^3\mathbf{r} \; w_n^*(\mathbf{R}_i - \mathbf{R}; \mathbf{r}) H w_m(\mathbf{R}_i; \mathbf{r})$$

Hopping Matrix Elements (check)



Hartree Hamiltonian

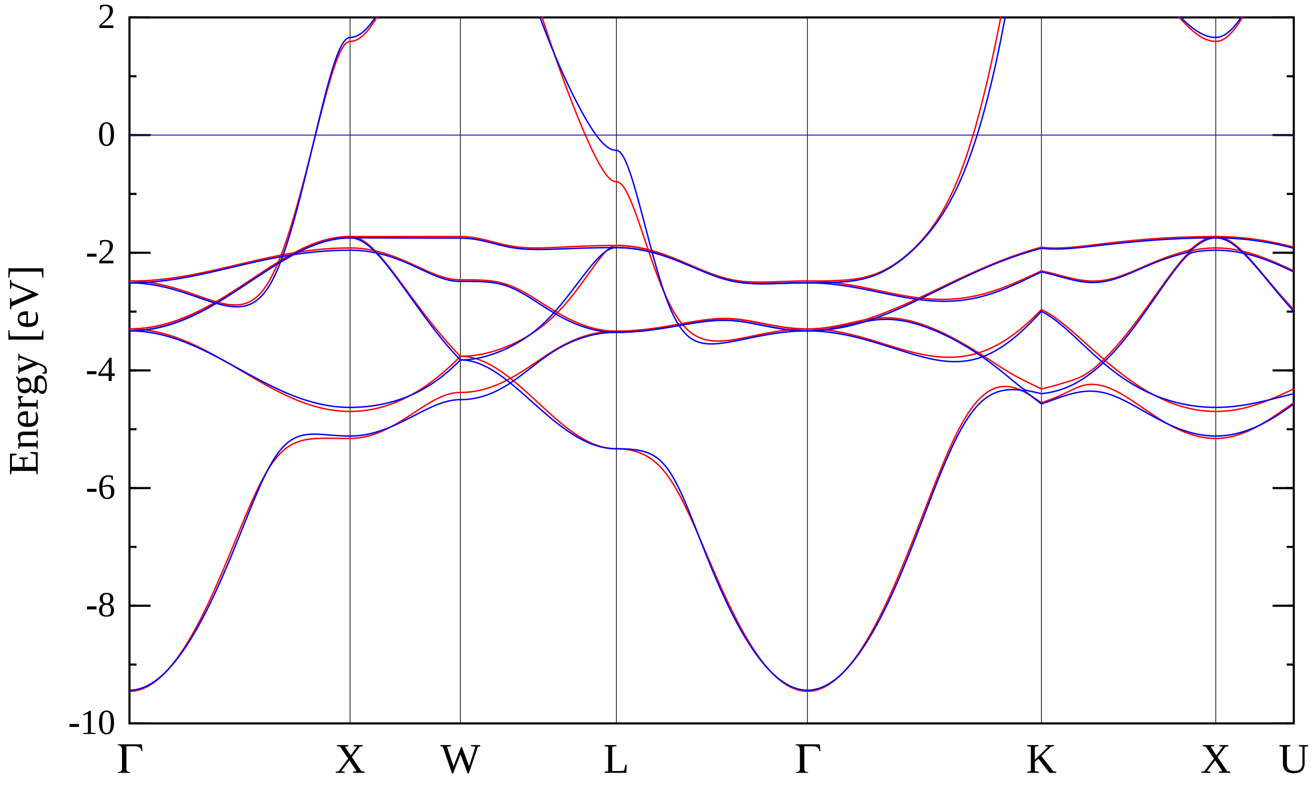
Wannier states $|w_{\mathbf{R}n}\rangle$

LMTO

Band structure

$$H^{\mathbf{k}}_{nm} = \sum_{\mathbf{R}} e^{-i\mathbf{k}\mathbf{R}} \langle \mathbf{R}n|H|\mathbf{0}m\rangle$$

diagonalize



Energy bands of copper relative to Fermi energy.
$\mathbf{R}$-sum up to 5th nearest neighbors.

Coulomb Matrix Elements

The Coulomb matrix elements are given by:

$$W_{12,34} = \int d^3\mathbf{r}\, d^3\mathbf{r}'\, w_1^*(\mathbf{r})\, w_2^*(\mathbf{r}')\, \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\, w_3(\mathbf{r}')\, w_4(\mathbf{r})$$

For evaluation, we propose two independent methods:

1. The spherical expansion method makes use of:

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \sum_{\ell=0}^{\infty} \frac{4\pi}{2\ell+1} \frac{r_<^\ell}{r_>^{\ell+1}} \sum_{m=-\ell}^{\ell} Y_\ell^{m^*}(\hat{\mathbf{r}}')\, Y_\ell^m(\hat{\mathbf{r}}) \quad ,$$

2. The FFT method uses the Fourier transform:

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{1}{2\pi^2} \int d^3\mathbf{q} \frac{e^{i\,\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}}{q^2}$$

The Coulomb integrals arising from both methods are in excellent agreement, providing reliable Coulomb matrix elements.

Hartree-Fock Approximation

Second quantized Hamiltonian:

$$H = \sum_{12} (H_0)_{12}\, a_1^\dagger a_2 + \tfrac{1}{2} \sum_{1234} W_{12,34}\, a_1^\dagger a_2^\dagger a_3 a_4$$

In the HF approximation, $a_1^\dagger a_2^\dagger a_3 a_4$ is replaced by

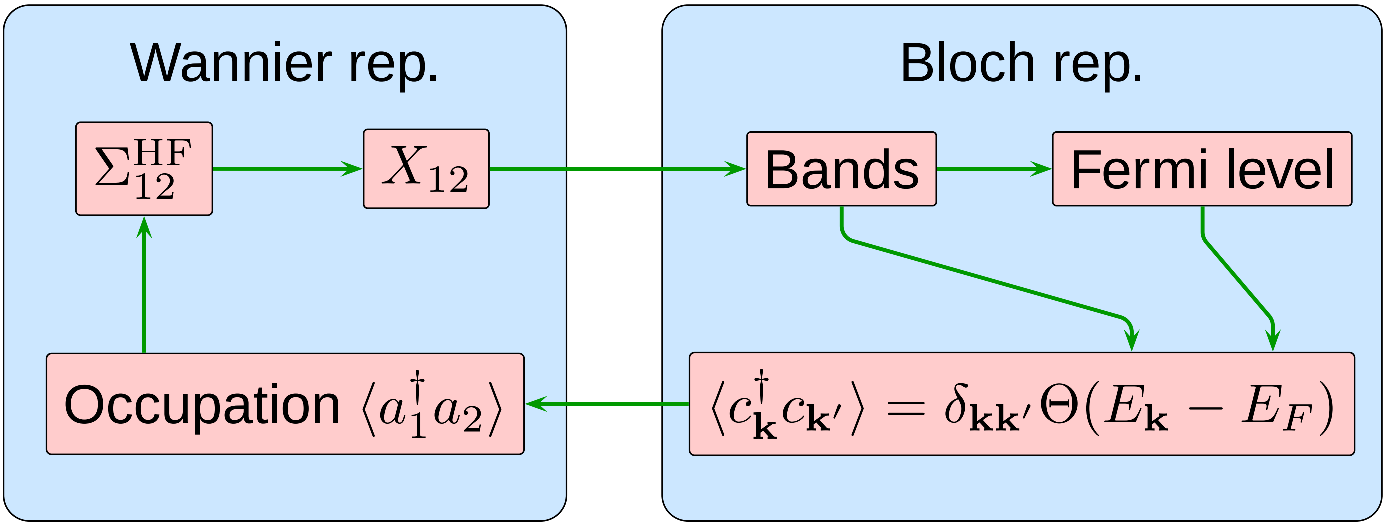
$$\langle a_2^\dagger a_3\rangle a_1^\dagger a_4 + \langle a_1^\dagger a_4\rangle a_2^\dagger a_3 - \langle a_1^\dagger a_3\rangle a_2^\dagger a_4 - \langle a_2^\dagger a_4\rangle a_1^\dagger a_3$$

which yields an effective non-interacting Hamiltonian:

$$H_{\text{eff}} = \sum_{12} X_{12}\, a_1^\dagger a_2 \qquad \text{where}$$

$$X_{12} = (H_0)_{12} + \underbrace{\sum_{34} [W_{13,42} - W_{31,42}] \langle a_3^\dagger a_4\rangle}_{\text{HF Self-energy } \Sigma_{12}^{\text{HF}}}$$

We solve this self-consistency problem by iteration:



Wannier rep.

Σ_{12}^{HF}

X_{12}

Occupation $\langle a_1^\dagger a_2\rangle$

Bloch rep.

Bands

Fermi level

$\langle c_{\mathbf{k}}^\dagger c_{\mathbf{k}'}\rangle = \delta_{\mathbf{k}\mathbf{k}'}\Theta(E_{\mathbf{k}} - E_F)$

Why 3d Transition Metals ?

We have applied the Hartree-Fock method to the 3d transition metals Fe, Co, Ni and Cu because

- the magnetic moment can be studied and be compared to experimental data.
- their localized 3d states make them interesting with respect to model Hamiltonians.
- there is controversy about the size of the Hubbard-U.
- the LSDA can be applied.
- these materials condense to simple crystal structures (FCC and BCC).

Wannier Functions

Recall that our Wannier functions

- serve as a minimal basis.
- stem from the Hartree Hamiltonian and are therefore independent of spin.
- include 4s, 4p and 3d-orbitals. Thus, we have nine WF's.

For example for iron, we obtain (in terms of densities):

n^{th} WF	0	1	2	3	4	5	6	7	8
zero MT	.98	.98	.96	.98	.98	.88	.87	.88	.88
s-portion	.00	.00	.01	.00	.00	.22	.24	.23	.22
p-portion	.10	.07	.18	.06	.07	.55	.55	.53	.54
d-portion	.90	.93	.81	.94	.93	.23	.21	.24	.24
			$3d$-states						

We note that the states 0 thru 4

- have very large d-character.
- are most localized.

The Coulomb interaction is often restricted to these orbitals.

Coulomb Matrix Elements

An averaged direct (on-site) Coulomb interaction U and an averaged exchange interaction J can be defined as:

$$U \equiv \frac{1}{25} \sum_{mn}^{3d} W_{mnnm} \quad , \quad J \equiv \frac{1}{20} \sum_{m \neq n}^{3d} W_{mnmn}$$

Usually, U and J are empirical parameters.

[eV]	Fe		Co		Ni		Cu	
Ref.	U	J	U	J	U	J	U	J
A	1.2	0.73	2.4	0.50	3.7	0.27		
B	1.63	1.09			2.45	1.70	4.08	
C	2.3	0.9	3	0.9	4	0.9	4	0.9
here	21.1	0.81	22.6	0.87	22.6	0.88	24.5	0.94

A: M.M. Steiner, R.C. Albers and L.J. Sham, Phys. Rev. B **45**, 13272 (1992)

B: V. Drchal, V. Janis and J. Kudrnovsky, Phys. Rev. B **60**, 15664 (1999)

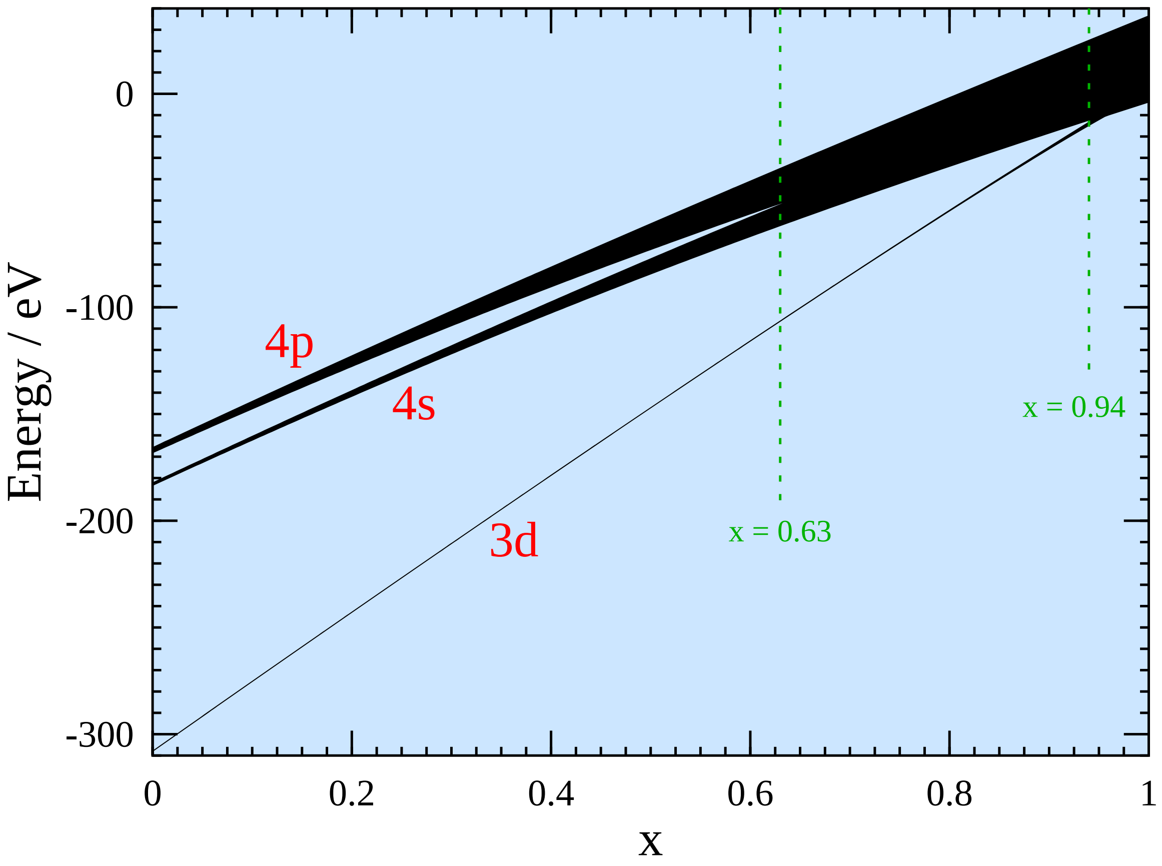
C: A.I. Lichtenstein and M.I. Katsnelson, Phys. Rev. B **57**, 6884 (1998)

Reasons indicating small U's in model Hamiltonian studies:

- Screening is often assumed to be included in the unperturbed band structure.
- Coulomb interaction is restricted to d-orbitals.
- One can always argue that the underlying Wannier states are assumed less localized.
  However, this is in contrast with the model assumptions.

Band Structure

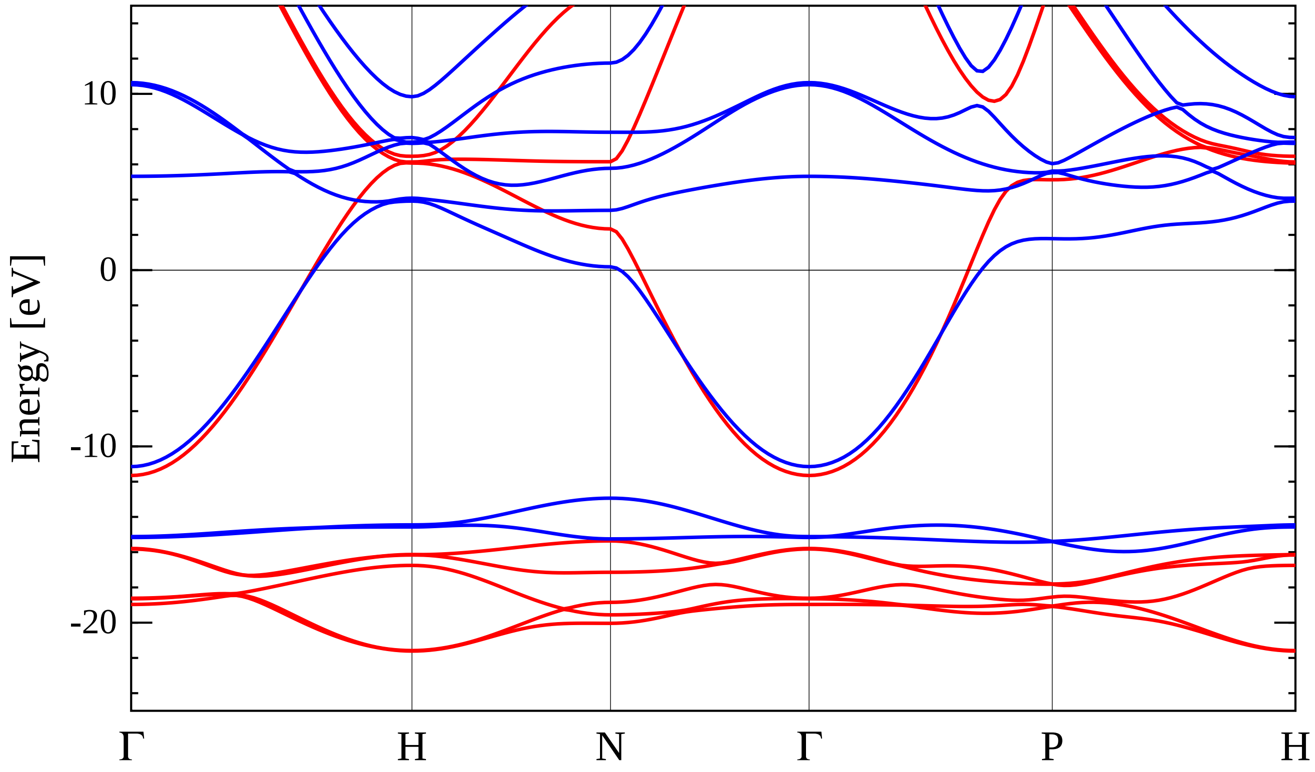
Position of bands as a function of x for copper:



$$H(x) = \underbrace{\frac{\mathbf{p}^2}{2m} + v_{\mathrm{c}}}_{H_0} + x\, v_{\mathrm{H}}$$

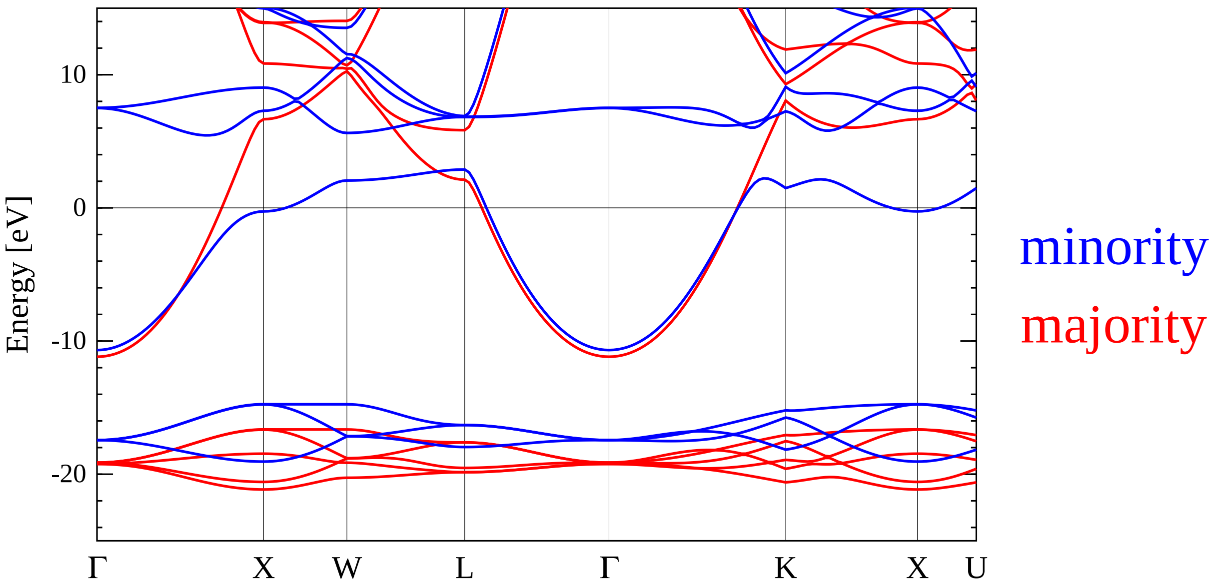
- v_{c} is the frozen-core potential.
- v_{H} is the Hartree potential found upon solving the Hartree equations self-consistently.
- $H(0)$ contains no interactions among the valence bands.
- $H(1)$ contains the Hartree interactions among the valence bands, i.e. the “Hartree Hamiltonian”.

HF Bands for Iron

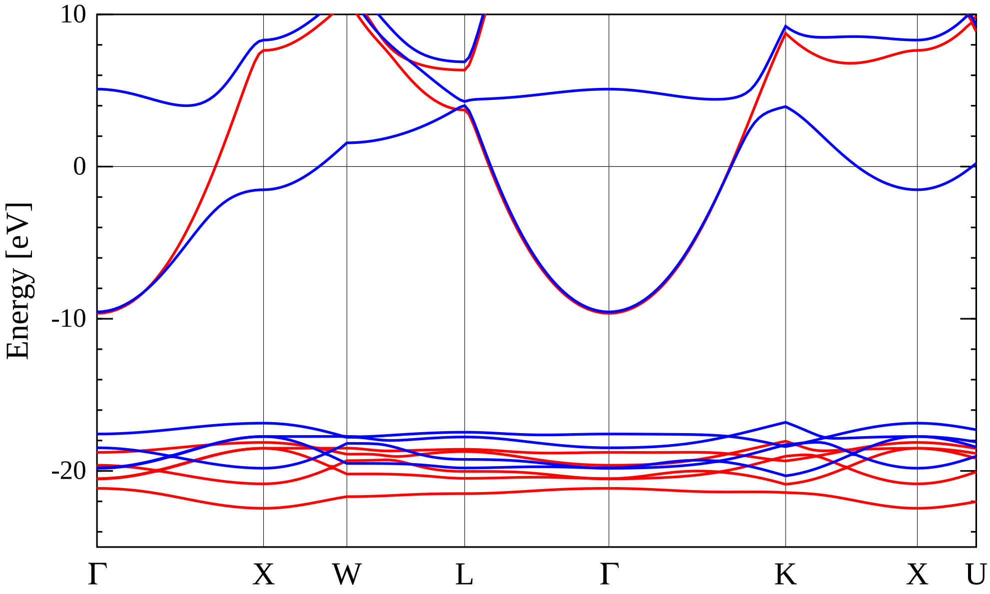


- Spin-polarized Hartree-Fock band structure relative to Fermi level E_F.
- Minority spin is plotted blue.
- Majority spin is plotted red.
- There are 3 unoccupied d-bands above E_F, resulting in a spin magnetic moment of about 3 μ_B/atom.

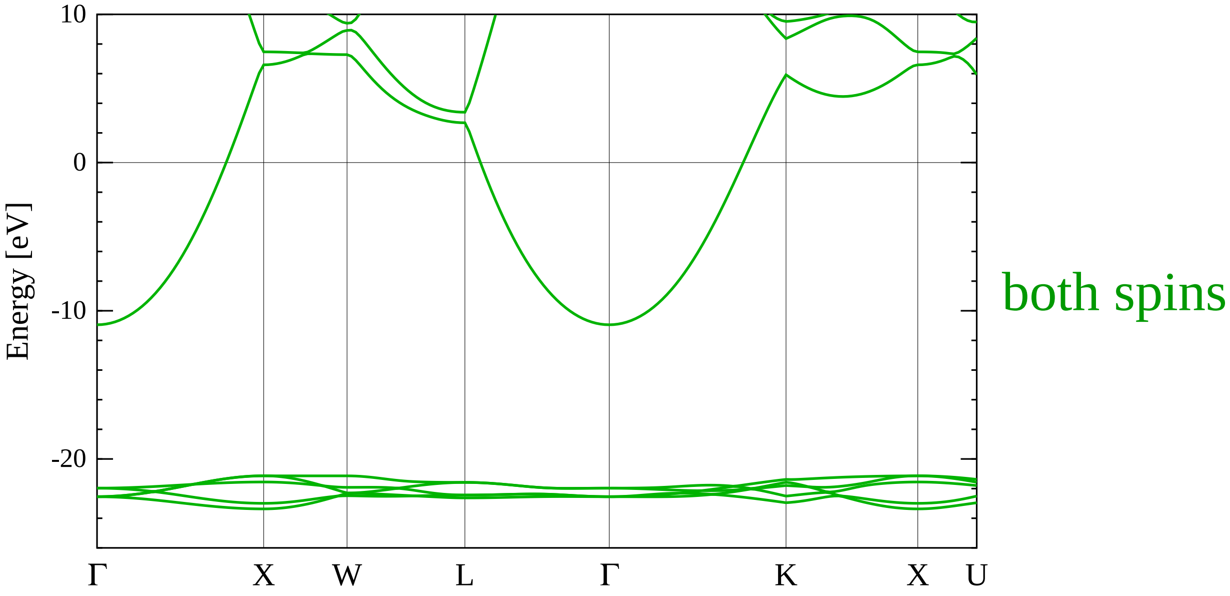
Co


10
0
-10
-20
Energy [eV]
Γ
X
W
L
Γ
K
X
U
minority
majority

Ni

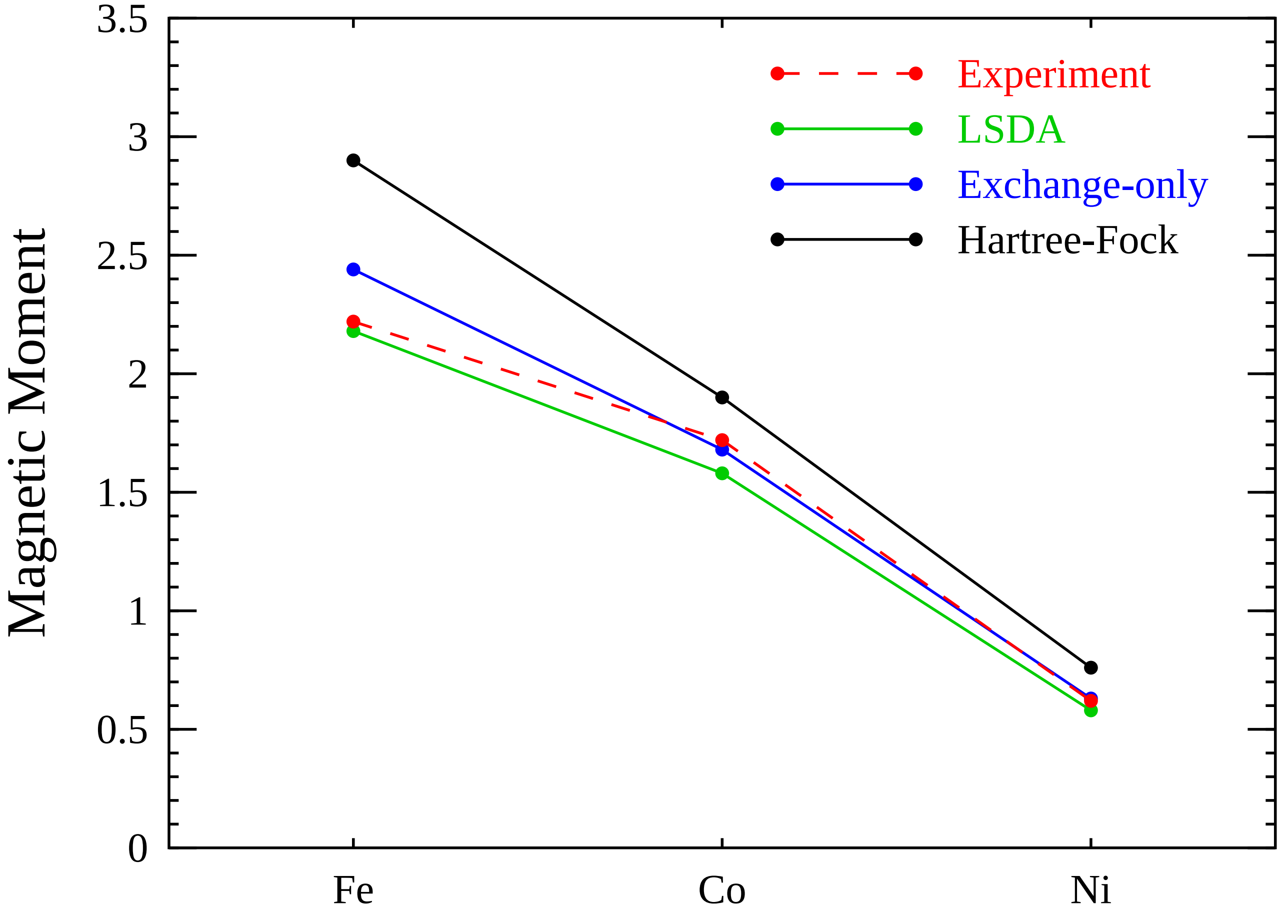

10
0
-10
-20
Energy [eV]
Γ
X
W
L
Γ
K
X
U

Cu


10
0
-10
-20
Energy [eV]
Γ
X
W
L
Γ
K
X
U
both spins

Magnetic Moment

Magnetic moments for $3d$ ferromagnets in units of μ_B/atom:



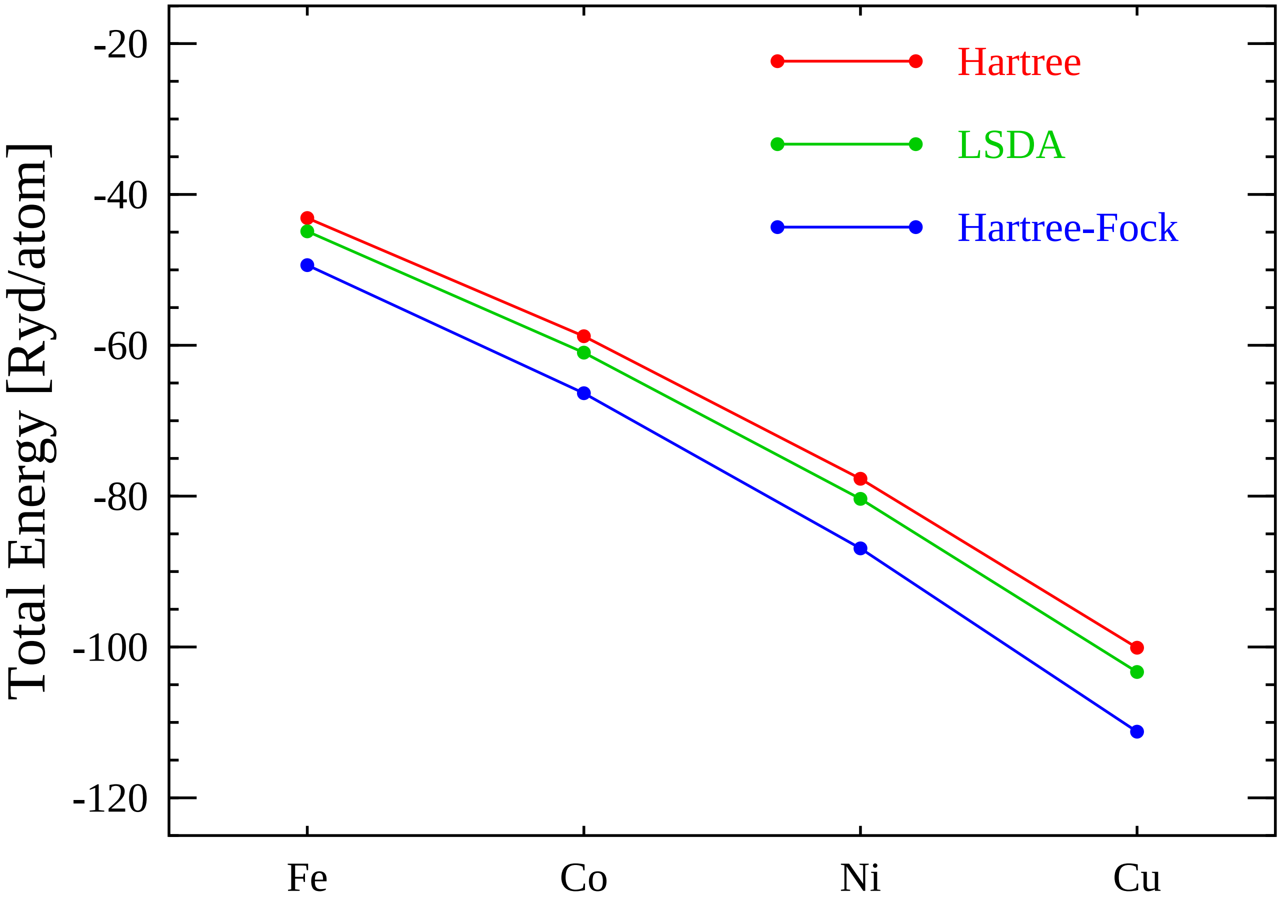
LSDA: Local spin density approximation for exchange and correlation.

Exchange-only: Local approximation for exchange term, i.e. for the non-local Hartree-Fock potential.

Hartree-Fock: Exchange exact, correlations omitted. Overestimates exchange effects (such as magnetism).

Total Energy

Total (valence) energies from different approximations:



- Hartree-Fock total energy comes closest to the true ground state energy.
- Hartree and LSDA total energies are higher.
- LSDA includes exchange and correlations, lowering the total energy (compared to Hartree).

Conclusion

- Maximally localized Wannier functions have at least 87% of their charge density within the center sphere.
- Hopping matrix elements are obtained from non-interacting valence electrons.
- The problem of double counting interactions does not occur.
- Hubbard-U's are on the magnitude of 21 to 25 eV for 3d states.
- Multi-band Hamiltonian with first-principles matrix elements studied within Hartree-Fock.
- Hartree-Fock magnetic moments found about 20 to 30 % larger than experimental results.

Thank you

for your

attention !