2022.6.29 Lecture 12

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

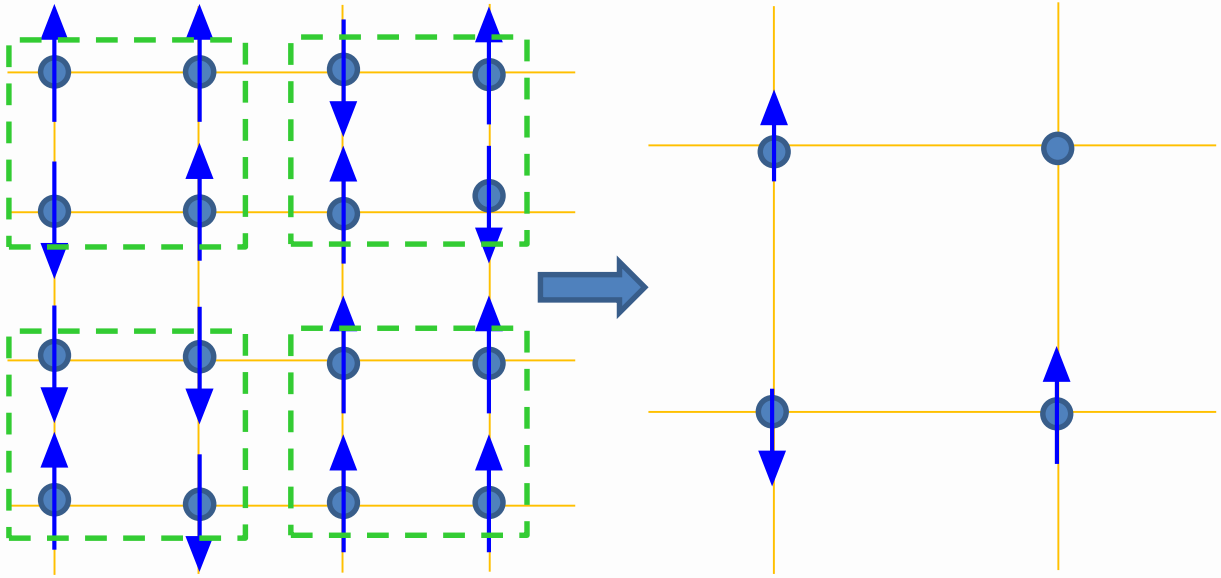
磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

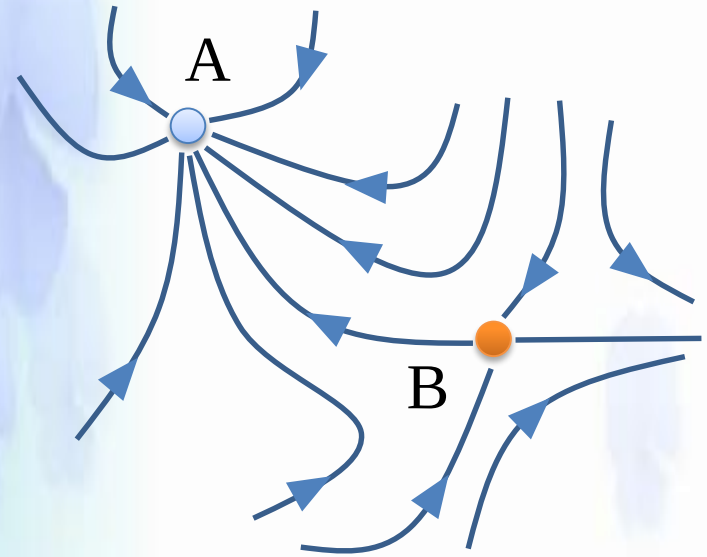
Shingo Katsumoto

Review

- Magnon condensates, Magnonics
- Scaling, Renormalization group



Coarse graining $s_q = \frac{1}{4}\sum_i s_{qi}$



$\mathcal{H}' = \mathcal{R}(x)\mathcal{H}$

System transition in a parameter space

Flow diagram

Stable fixed point: Extreme conditions

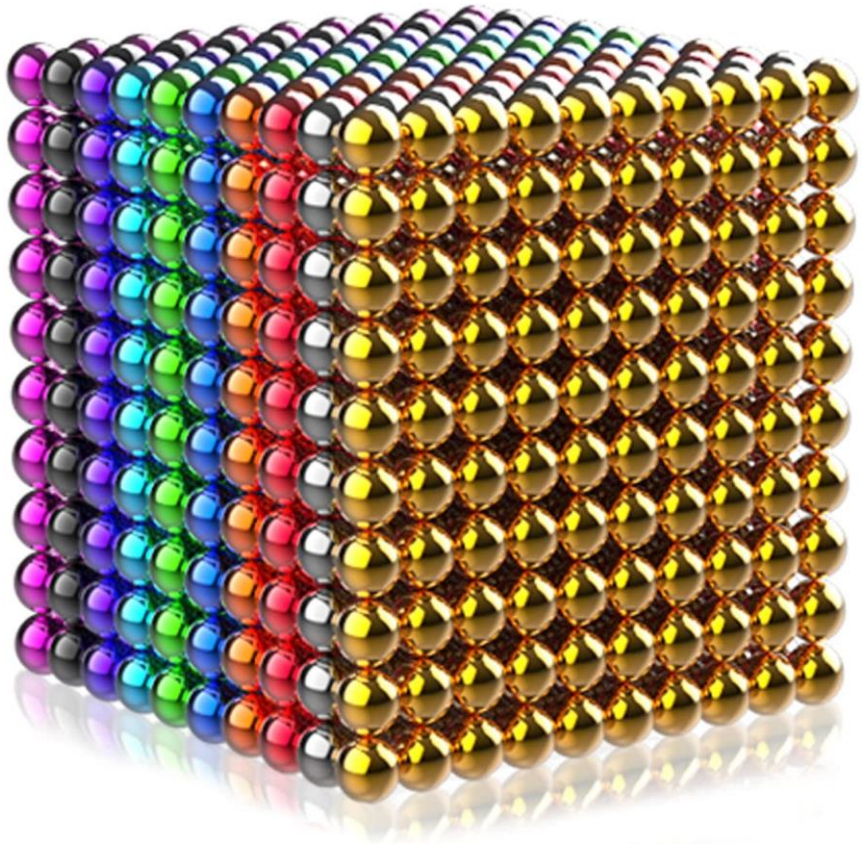
Unstable fixed point: critical point

Renormalization group transform with scaling factor x $\begin{cases} t' = g_1^{(x)}(t,h) \\ h' = g_2^{(x)}(t,h) \end{cases}$ Renormalization group equation

Chapter 6 Magnetism of Itinerant Electron Systems

- Ferromagnetism in Electron gas
  - Hartree-Fock approximation
  - Diffusion Monte-Carlo calculation
- Hubbard model: mean field theory
  - Hartree-Fock approximation: Stoner criterion
  - Magnetic susceptibility
- Magnetism in 3*d* transition metals
  - Slater-Pauling's curve
  - Density of states by APW method

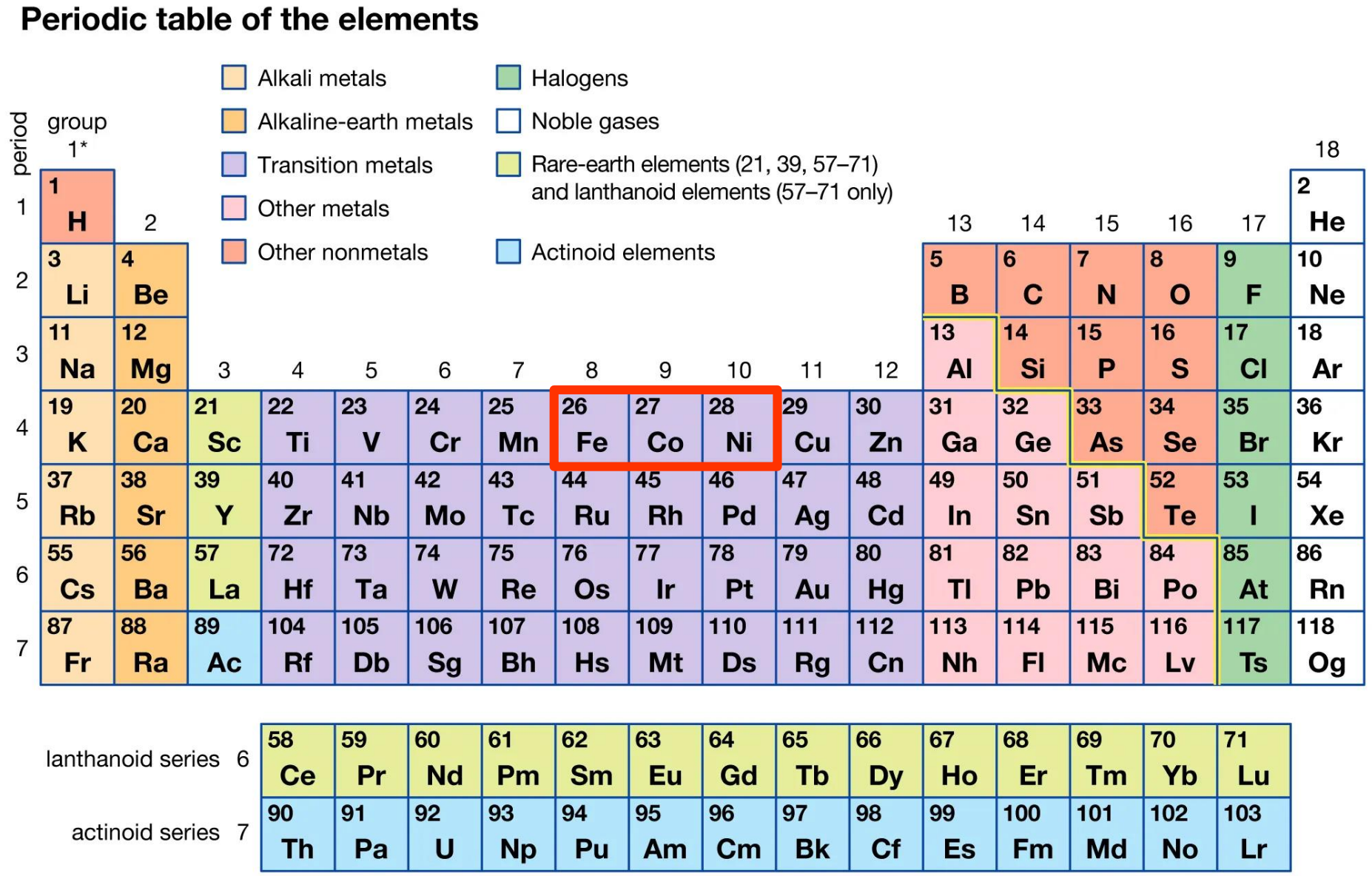
Chapter 6



Magnetism of Itinerant Electron Systems

Magnetic Puzzle

Periodic table of the elements



Hartree-Fock approximation for ferromagnetism in electron gas

Hartree-Fock approximation: A way to treat electron-electron interaction (correlation) in mean field theory.

Let us consider an *N*-particle system Single-particle wavefunctions $\varphi_{k_1}, \varphi_{k_2}, \cdots, \varphi_{k_N}$

Many-particle wavefunction fulfilling particle exchange statistics- Slater determinant:

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{k_1}(x_1) & \cdots & \varphi_{k_N}(x_1) \\ \vdots & \ddots & \vdots \\ \varphi_{k_1}(x_N) & \cdots & \varphi_{k_N}(x_N) \end{vmatrix}$$

x_i: all freedoms of a single particle

Assumption: Hamiltonian = single body + two-body:

$$\mathscr{H} = \sum_{j=1}^{N} h(x_j) + \sum_{\langle i,j \rangle} v(x_i, x_j)$$

Expectation value of the total energy: $\mathcal{W} = (\Phi, \mathscr{H}\Phi)$

Hartree-Fock approximation = minimize $\mathcal{W}$ in variational method on $\{\varphi_{k_j}\}$

Hartree-Fock approximation (2)

Constraint – Orthonormal basis: $\langle k_i|k_j\rangle = \delta_{ij}$

(1) Direct integral and (2) Exchange integral:

$$\mathcal{W} = \sum_{j=1}^{N} \langle k_j|h|k_j\rangle + \sum_{\langle i,j\rangle} [\underbrace{\langle k_i k_j|v|k_i k_j\rangle}_{(1)} - \underbrace{\langle k_i k_j|v|k_j k_i\rangle}_{(2)}]$$

We apply the method of Lagrange multipliers. Consider the quantity: $\mathcal{W} - \sum_{\langle i,j\rangle} \lambda_{ij} \langle k_i|k_j\rangle$

Extremals condition for the variation of $\{\varphi^*_{k_j}\}$ $h\varphi_{k_j} + \sum_{i=1}[\langle k_i|v|k_i\rangle \varphi_{k_j} - \langle k_i|v|k_j\rangle \varphi_{k_i}] = \sum_{i=1}^{N} \lambda_{ij}\varphi_{k_i}$

Density matrix (definition): $\rho(x,x') = \sum_{i=1}^{N} \varphi^*_{k_i}(x)\varphi_{k_i}(x')$

We further define $v_{\text{eff}}(x) = \int dx' v(x,x')\rho(x',x), \quad A(x)\varphi(x) = \int dx' v(x,x')\varphi(x')\rho(x',x)$

Then the extremal condition is $[h(x) + v_{\text{eff}}(x) - A(x)]\varphi_{k_j}(x) = \sum_{i=1}^{N} \lambda_{ij}\varphi_{k_i}(x)$

Hartree-Fock approximation (3)

$$\underbrace{[h(x) + v_{\text{eff}}(x) - A(x)]}_{\mathcal{O}}\varphi_{k_j}(x) = \sum_{i=1}^{N} \lambda_{ij}\varphi_{k_i}(x)$$

We take φ_{k_j} for an eigenfunction of operator $\mathcal{O}$ $\quad [h(x) + v_{\text{eff}}(x) - A(x)]\varphi_{k_j}(x) = \epsilon_{k_j}\varphi_{k_j}(x)$

Then taking *N* of eigenstates with the lowest eigen energies, and make the Slater determinant from them.

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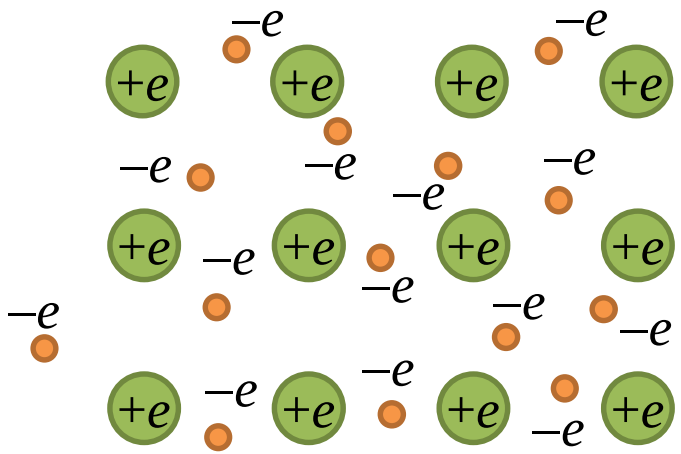
Hartree-Fock ground state

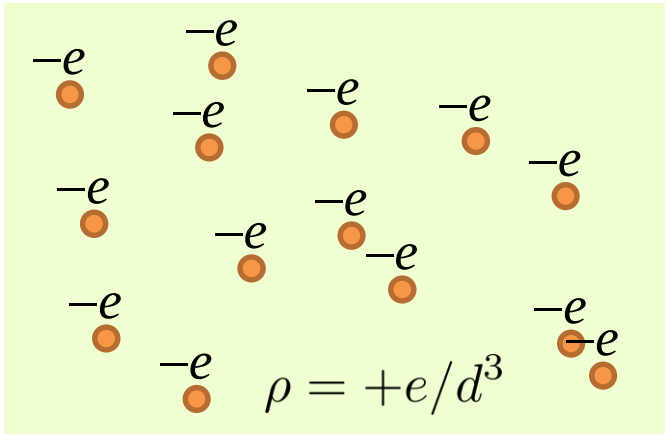
Operator $\mathcal{O}$ depends on $\{\varphi_{k_j}\}$ ⟹ Self-consistent equation

$$[h(x) + v_{\text{eff}}(x) - A(x)]\varphi_{k_j}(x) = \epsilon_{k_j}\varphi_{k_j}(x) \qquad \text{Hartree-Fock equation}$$

Magnetism in jellium model

Electrons in a lattice potential





Jellium model

Electrons in a uniform background

Jellium model ground state of non-interacting electrons

$$|\Psi\rangle = \prod_{E(\boldsymbol{k},\sigma)\le E_{\mathrm{F}}} c^{\dagger}_{\boldsymbol{k}\sigma}\,|0\rangle$$

Hamiltonian with interaction:

$$\mathscr{H} = \sum_{\boldsymbol{k},\sigma} \epsilon_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \frac{1}{2V} \sum_{\boldsymbol{k},\boldsymbol{k}',\sigma,\sigma',\boldsymbol{q}\neq 0} v_{\boldsymbol{q}} c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q},\sigma} c^{\dagger}_{\boldsymbol{k}'-\boldsymbol{q},\sigma'} c_{\boldsymbol{k}'\sigma} c_{\boldsymbol{k}\sigma}$$

$$\epsilon_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2m} \qquad v_{\boldsymbol{q}} = \frac{4\pi e^2}{q^2}$$

System parameter: Averaged particle distance measured by Bohr magneton:

$$r_s \equiv \frac{1}{a_{\mathrm{B}}} \left[\frac{3}{4\pi(k_{\mathrm{F}}^3/3\pi^2)}\right]^{1/3}$$

Magnetism in jellium model (2)

In the jellium model, plane waves are already the self-consistent equation. Then the plane wave states that minimize the energy is the solution of HF approximation.

Remember $$\mathcal{W} = \sum_{j=1}^{N} \langle k_j|h|k_j\rangle + \sum_{\langle i,j\rangle} [\langle k_i k_j|v|k_i k_j\rangle - \langle k_i k_j|v|k_j k_i\rangle]$$

Kinetic energy per an electron: $$\epsilon_{\mathrm{ke}} = \frac{1}{N}\sum_{\boldsymbol{k}s} \epsilon_{\boldsymbol{k}} n_{\boldsymbol{k}s} = \frac{2V}{N}\int \frac{d^3k}{(2\pi)^3}\frac{\hbar^2k^2}{2m} n_k = \frac{3}{10}\frac{\hbar^2 k_{\mathrm{F}}^2}{m} = \frac{2.21}{r_s^2}\mathrm{Ry}$$

No direct integral term (Hartree) due to the charge neutral condition in the case of jellium model.

Exchange energy per an electron: $$\epsilon_{\mathrm{ex}} = -\frac{1}{2NV}\sum_{\boldsymbol{k},\boldsymbol{q}\neq 0,s} v_{\boldsymbol{q}} \langle\psi|c_{\boldsymbol{k}+\boldsymbol{q},s} c_{\boldsymbol{k}+\boldsymbol{q},s} c^{\dagger}_{\boldsymbol{k}s} c_{\boldsymbol{k}s}|\psi\rangle = \frac{1}{2NV}\sum_{\boldsymbol{k}s} v_{\boldsymbol{q}} n_{\boldsymbol{k}+\boldsymbol{q}} n_{\boldsymbol{k}}$$

Integration gives $$\epsilon_{\mathrm{ex}} = -\frac{3e^2}{4}\frac{k_{\mathrm{F}}}{\pi} = -\frac{0.92}{r_s}\mathrm{Ry}$$

Hartree-Fock energy is given by $$\epsilon_{\mathrm{hf}} = \left(\frac{2.21}{r_s^2} - \frac{0.92}{r_s}\right)\mathrm{Ry}$$

Magnetism in jellium model (3)

Magnetic polarization: $p \equiv \dfrac{N_\uparrow}{N_\uparrow + N_\downarrow}$

$$E_{\rm ke}(p) = \frac{\hbar^2}{20\pi^2 m}(k_{\rm F\uparrow}^5 + k_{\rm F\downarrow}^5) = \frac{3(6\pi^2)^{2/3}\hbar^2}{10m}(n_\uparrow^{5/3} + n_\downarrow^{5/3}) = \frac{3(6\pi^2)^{2/3}\hbar^2}{10m}[p^{5/3} - (1-p)^{5/3}]n_0^{5/3},$$

$$E_{\rm ex}(p) = -\frac{3e^2}{4}\left(\frac{6}{\pi}\right)^{1/3}(n_\uparrow^{4/3} + n_\downarrow^{4/3}) = -\frac{3e^2}{4}\left(\frac{6}{\pi}\right)^{1/3}[p^{4/3} - (1-p)^{4/3}]n_0^{4/3}$$

$$\Delta E = [E_{\rm ke}(1) + E_{\rm ex}(1)] - [E_{\rm ke}(0.5) + E_{\rm ex}(0.5)]$$

$\Delta E < 0$ ⟹ Ferromagnetic state is the ground state

$r_s > 5.4531$

⇓

Overestimation of the stability of ferromagnetism

Table 1.1
FREE ELECTRON DENSITIES OF SELECTED METALLIC ELEMENTS[a]

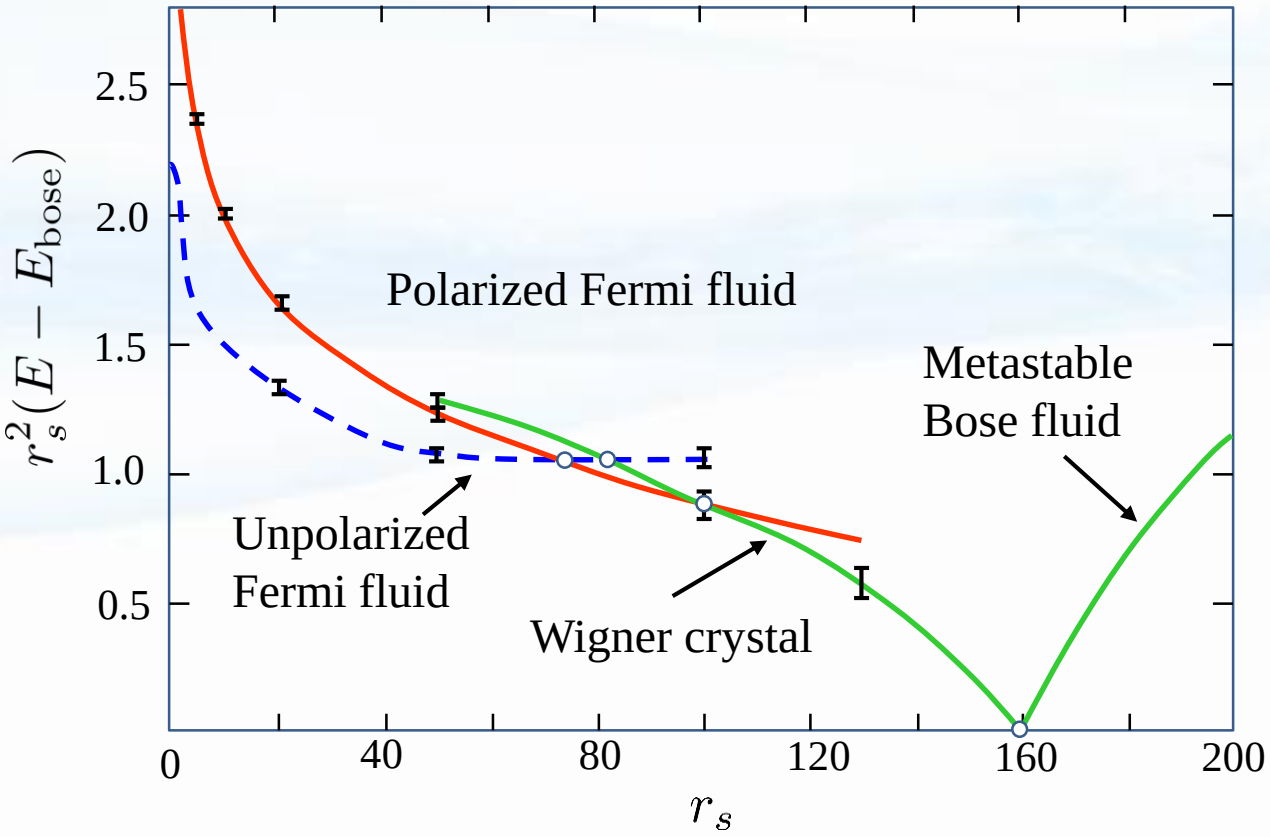
ELEMENT	Z	n (10^{22}/cm^3)	r_s(Å)	r_s/a_0
Li (78 K)	1	4.70	1.72	3.25
Na (5 K)	1	2.65	2.08	3.93
K (5 K)	1	1.40	2.57	4.86
Rb (5 K)	1	1.15	2.75	5.20
Cs (5 K)	1	0.91	2.98	5.62

Taken from Ashcroft-Mermin *Solid State Physics*

Correlation energy

In a realistic electron gas, the electrons keep away from each other lowering the Coulomb energy even between ones with the opposite spin directions.

Difference from the HF interaction energy: Correlation energy



Phase diagram by diffusion Monte-Carlo method

$70 < r_s < 90$

Huge deviation from 3*d* metals

Ceperly, Adler, PRL **45**, 566 (1980).

Hubbard model

24	25	26	27	28	29
Cr	Mn	Fe	Co	Ni	Cu
$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$

3*d* transition metals: 3*d*4*s* open shell

(1) 3*d*: Tendency to localize
(2) 4*s*: Delocalize, light mass → screen long range Coulomb interaction

Two-site Hubbard Hamiltonian

$$\mathscr{H} = t \sum_{\sigma=\uparrow\downarrow} (a^\dagger_{1\sigma} a_{2\sigma} + a^\dagger_{2\sigma} a_{1\sigma}) + U(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow})$$

General Hubbard Hamiltonian

$$\mathscr{H} = \sum_{i,j,s} t_{ij} c^\dagger_{is} c_{js} + U \sum_{i}^{N} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

(1) → Hopping On-site Coulomb ← (2)

Fermion commutation relation: $\{c^\dagger_{is}, c_{is'}\} = \delta_{ij}\delta_{ss'}$

In the present case, this Hamiltonian only acts on *d*-electrons explicitly.

Hubbard model (2)

Hubbard Hamiltonian $\mathscr{H} = \sum_{i,j,s} t_{ij} c_{is}^{\dagger} c_{js} + U \sum_{i}^{N} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$

Fourier expansion $c_{is} = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}} e^{i\boldsymbol{R}_i \cdot \boldsymbol{k}} a_{\boldsymbol{k}s}, \quad t_{ij} = \frac{1}{N} \sum_{\boldsymbol{k}} \epsilon_{\boldsymbol{k}} e^{i\boldsymbol{k} \cdot (\boldsymbol{R}_i - \boldsymbol{R}_j)}$

$$\sum_{\langle i,j \rangle, s} t_{ij} c_{is}^{\dagger} c_{js} = \sum_{i,j,s} \frac{2}{N^2} \sum_{\boldsymbol{k}_1, \boldsymbol{k}_2, \boldsymbol{k}_3} \epsilon_{\boldsymbol{k}_1} e^{i\boldsymbol{k}_1 \cdot (\boldsymbol{R}_i - \boldsymbol{R}_j)} e^{-i\boldsymbol{k}_2 \cdot \boldsymbol{R}_i} a_{\boldsymbol{k}_2 s}^{\dagger} e^{i\boldsymbol{k}_3 \cdot \boldsymbol{R}_j} a_{\boldsymbol{k}_3 s} = \sum_{\boldsymbol{k}, s} \epsilon_{\boldsymbol{k}} a_{\boldsymbol{k}s}^{\dagger} a_{\boldsymbol{k}s}$$

Tendency to localize but still itinerant

Itinerant electron system

$$\mathscr{H} = \sum_{\boldsymbol{k}, s} \epsilon_{\boldsymbol{k}} a_{\boldsymbol{k}s}^{\dagger} a_{\boldsymbol{k}s} + U \sum_{i}^{N} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

HF approximation in Hubbard model

Local magnetic moment, electron number (per site)

$$m = \langle n_\uparrow \rangle - \langle n_\downarrow \rangle , \quad n = \langle n_\uparrow \rangle + \langle n_\downarrow \rangle$$

$$U \sum_i \hat{n}_{i\uparrow}\hat{n}_{i\downarrow} = U \sum_i [\langle \hat{n}_\uparrow \rangle \hat{n}_{i\downarrow} + \langle \hat{n}_\downarrow \rangle \hat{n}_{i\uparrow} - \langle \hat{n}_\uparrow \rangle \langle \hat{n}_\downarrow \rangle + (\hat{n}_{i\uparrow} - \langle n_\uparrow \rangle)(\hat{n}_{i\downarrow} - \langle n_\downarrow \rangle)]$$

$$\simeq U \sum_i (\langle \hat{n}_\uparrow \rangle \hat{n}_{i\downarrow} + \langle \hat{n}_\downarrow \rangle \hat{n}_{i\uparrow}) - NU \langle n_\uparrow \rangle \langle n_\downarrow \rangle$$

Fluctuation term: dropped in HF approximation

$$\text{Take average} \rightarrow = \frac{NU}{4}(n^2 - m^2)$$

Moving in the averaged field of opposite spin

$$\mathscr{H}_{\mathrm{HF}} = \sum_{\boldsymbol{k},s} (\epsilon_{\boldsymbol{k}} + U \langle n_{-s} \rangle) n_{\boldsymbol{k}s} - NU \langle n_\uparrow \rangle \langle n_\downarrow \rangle$$

$$\uparrow, \downarrow \rightarrow s = \pm 1 \qquad \langle n_s \rangle = \frac{1}{2}(n + sm)$$

HF approximation in Hubbard model (2)

$\uparrow, \downarrow \to s = \pm 1 \qquad \langle n_s \rangle = \frac{1}{2}(n + sm) \qquad \sum_{\boldsymbol{k},s} \hat{n}_{\boldsymbol{k}s} \to N(\langle n_\uparrow \rangle + \langle n_\downarrow \rangle)$ averaging

$$\mathscr{H}_{\mathrm{HF}} = \sum_{\boldsymbol{k},s} (\epsilon_{\boldsymbol{k}} + U \langle n_{-s} \rangle) n_{\boldsymbol{k}s} - NU \langle n_\uparrow \rangle \langle n_\downarrow \rangle$$

$$\mathscr{H}_{\mathrm{HF}} = \sum_{\boldsymbol{k},s} \left(\epsilon_{\boldsymbol{k}} - \frac{sUm}{2} \right) \hat{n}_{\boldsymbol{k}s} + \frac{NU}{4}(n^2 + m^2)$$

$$\equiv \sum_{\boldsymbol{k},s} \tilde{\epsilon}_{\boldsymbol{k}s} \hat{n}_{\boldsymbol{k}s} + \frac{NU}{4}(n^2 + m^2)$$

Single electron energy shift: $\Delta\mu = (-s)Um/2$

Total energy:

$$E = \sum_{\tilde{\epsilon}_{\boldsymbol{k}s} \le \mu} \left(\epsilon_{\boldsymbol{k}} - \frac{sUm}{2} \right) + \frac{NU}{4}(n^2 + m^2)$$

$$= \sum_{\tilde{\epsilon}_{\boldsymbol{k}s} \le \mu} \epsilon_{\boldsymbol{k}} + \frac{NU}{4}(n^2 - m^2)$$

Energy shift by magnetization

Spin-dependence of $\Delta\mu$ ⇒ Difference in the numbers of ↑ electrons and ↓ electrons should be consistent with *m*

HF approximation in Hubbard model (3)

Self-consistent equation $m = 2\mathscr{D}(E_\mathrm{F})\Delta\mu = \mathscr{D}(E_\mathrm{F})Um$ $U\mathscr{D}(E_\mathrm{F}) = 1$ for non-zero *m*

Density of states

Increase in the kinetic energy by spontaneous magnetization $\mathscr{D}(E_\mathrm{F})(\Delta\mu)^2 = \dfrac{m^2}{4\mathscr{D}(E_\mathrm{F})}$

Decrease in interaction energy by spontaneous magnetization $-NUm^2/4$

$$\Delta E = \frac{N}{4}\left[\frac{m^2}{\mathscr{D}(E_\mathrm{F})} - Um^2\right]$$

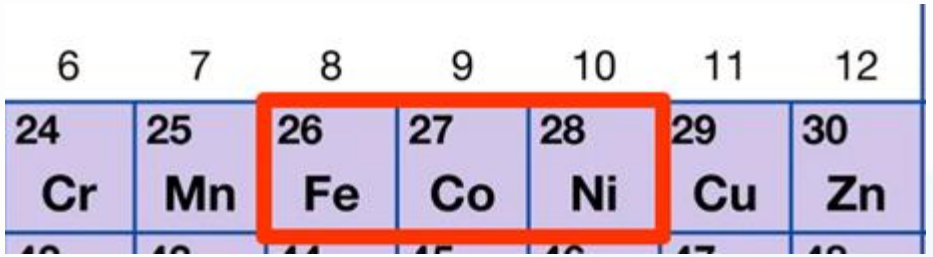
$\Delta E < 0$ $U\mathscr{D}(E_\mathrm{F}) \geq 1$ Stoner condition

For ferromagnetism to take place, the Coulomb energy should be larger than the band width.

(Still has a problem of overestimating the Coulomb effect in the case of anti-parallel spins.)

Magnetism in 3*d* transition metals

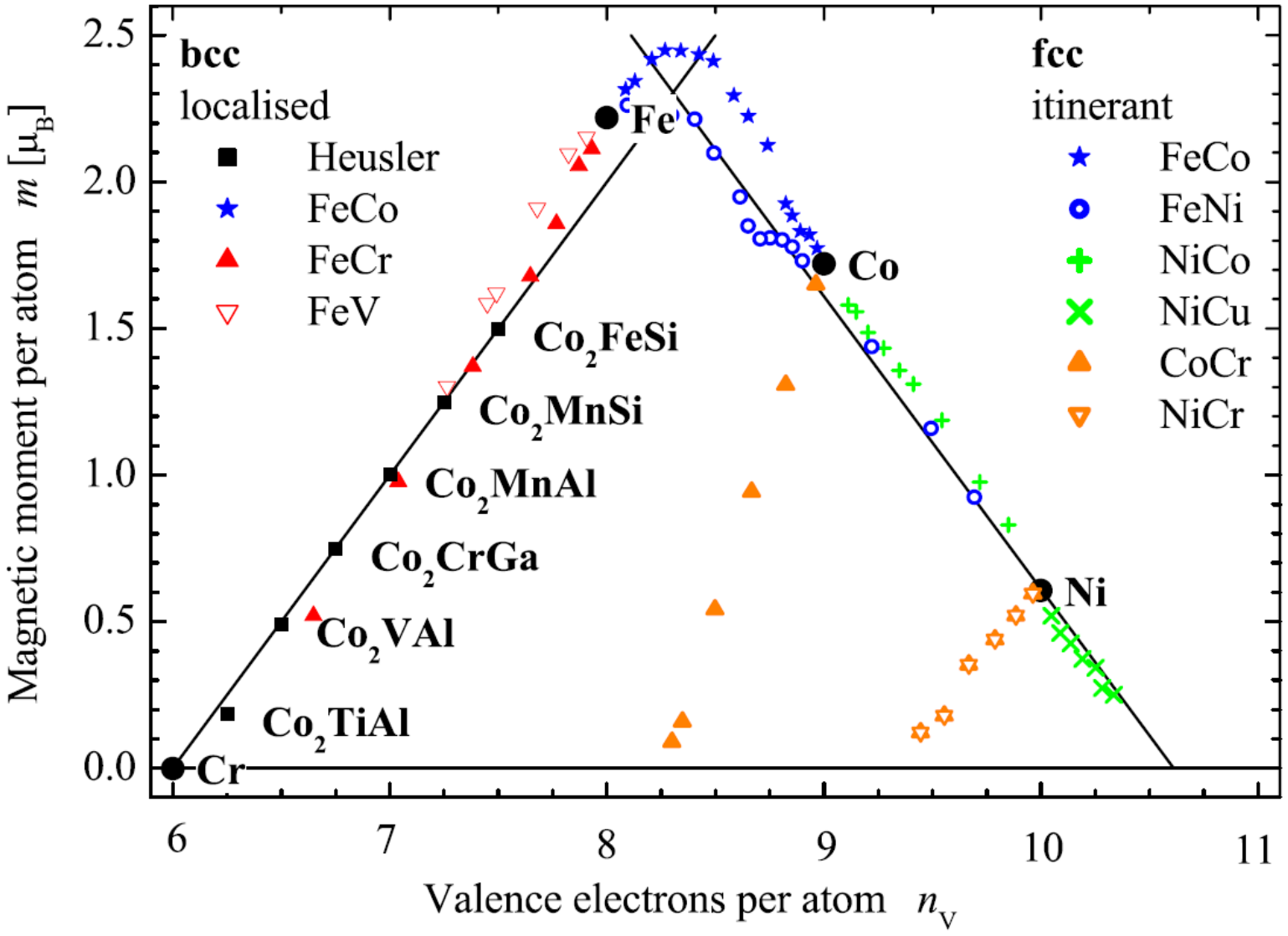
Elementary ferromagnetic metals



	structure /density ($\mathrm{kgm^{-3}}$)	lattice parameters (pm)	T_C (K)	M_S ($\mathrm{MAm^{-1}}$)	K_1 ($\mathrm{kJm^{-3}}$)	λ_S (10^{-6})	α	P (%)
Fe	bcc 7874	287	1044	1.71	48	−7	1.6	45
Co	hcp 8836	251 407 (fcc)	1388	1.45	530	−62	8.0	42
Ni	fcc 8902	352	628	0.49	−5	−34		44

From D. Coey in *Materials for Spin Electronics*, Springer 2008

Magnetism of 3*d* transition metals: Slater-Pauling's curve



Balke et al., Sci. Technol. Adv. Mater. **9**, 014102 (2008).

24	25	26	27	28	29
Cr	Mn	Fe	Co	Ni	Cu
$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$

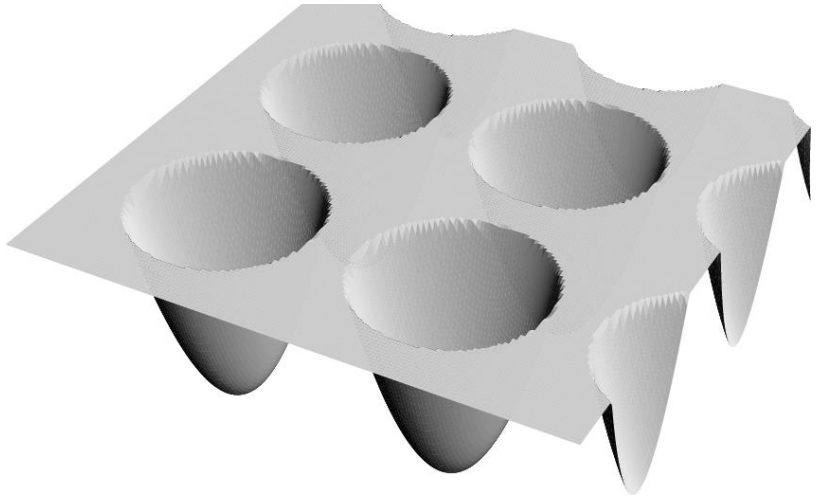
Slater-Pauling's curve

Experimental data are in line.

The gradient is ± 1 !

Abrupt change around Fe

APW method to calculate DOS



$$\mathscr{H}\phi(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\phi(\boldsymbol{r}) = E\phi(\boldsymbol{r})$$

Muffin-tin potential: $V(\boldsymbol{r}) = \begin{cases} V_{\mathrm{a}}(r)\ \ (\text{spherical}) & (r < r_{\mathrm{c}}) \\ V_{\mathrm{o}}\ (= V_{\mathrm{a}}(r_{\mathrm{c}})\text{: const.}) & (r \geq r_{\mathrm{c}}) \end{cases}$

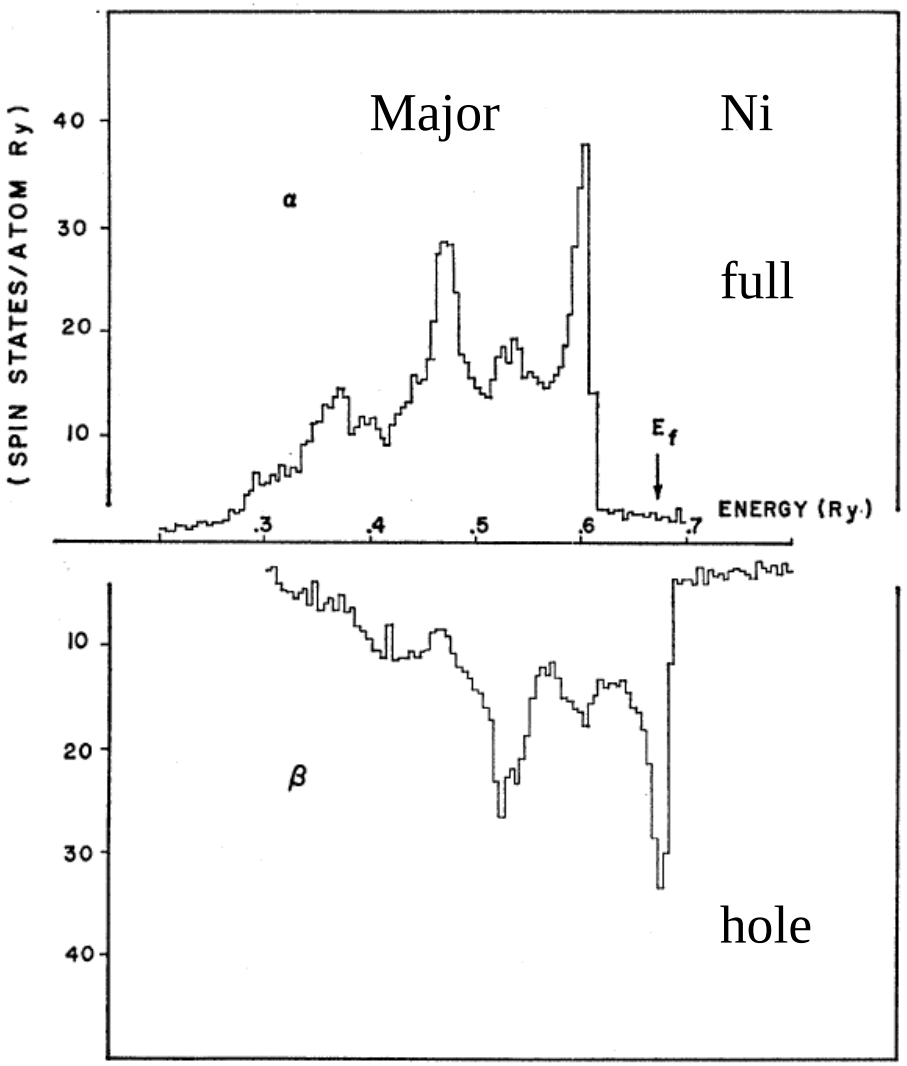
Hartree: $V_{\mathrm{d}}(\boldsymbol{r}) = \sum_i \langle\phi_i(\boldsymbol{r}')| \dfrac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|} |\phi_i(\boldsymbol{r}')\rangle$

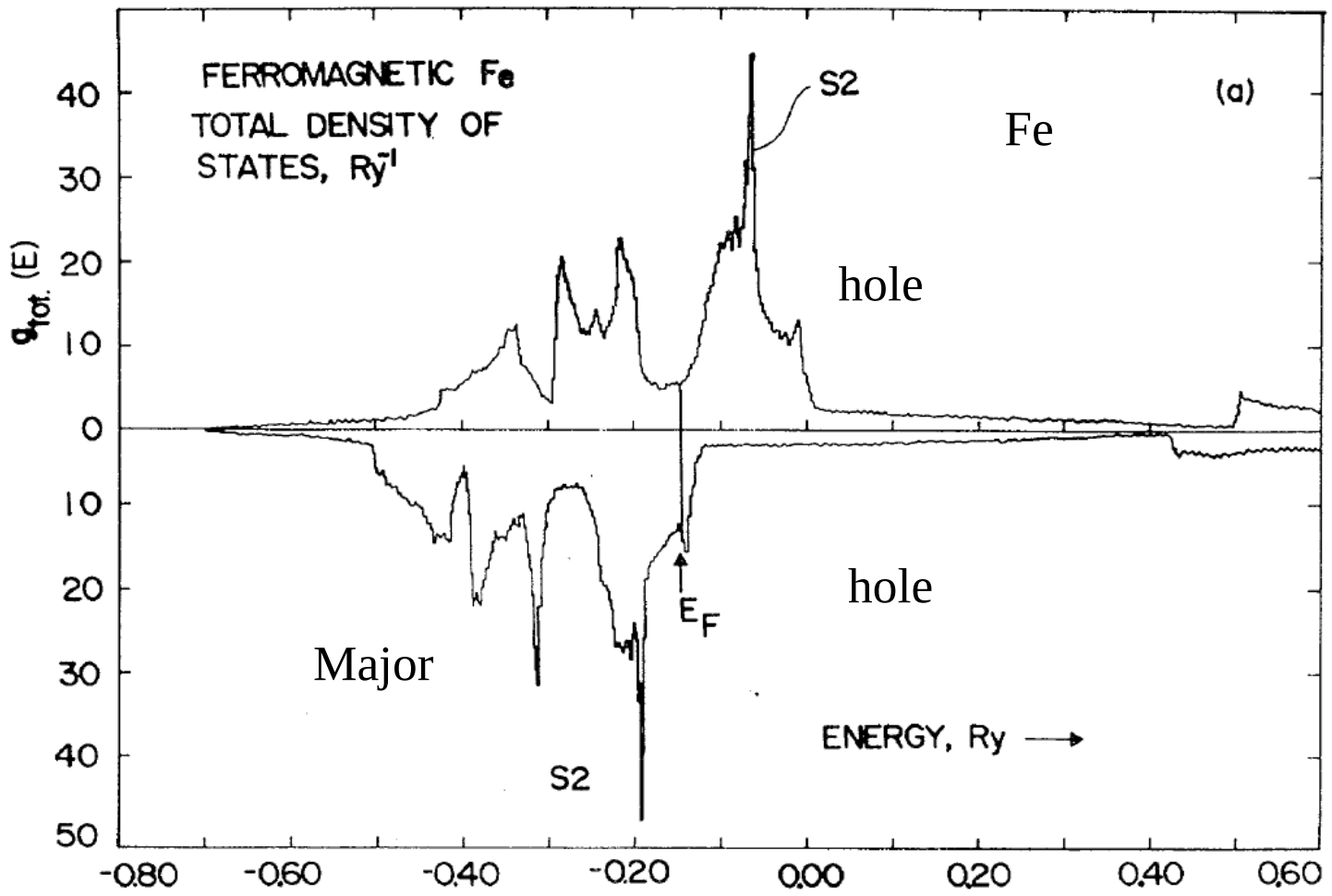
Exchange: $V_{\mathrm{ex}\uparrow} = -3e^2\left(\dfrac{3}{4\pi}\right)^{1/3} \rho_\uparrow(\boldsymbol{r})^{1/3}$

Variational wavefunction: $\Phi_{\mathrm{vr}}(\boldsymbol{r}) = \begin{cases} \sum_{l,m} A_{lm} R_l(r) Y_l^m(\theta,\varphi) & r < r_{\mathrm{c}}, \\ \sum_{n=0}^{N} B_n \exp[i(\boldsymbol{k}+\boldsymbol{K}_n)\cdot\boldsymbol{r}] & r > r_{\mathrm{c}} \end{cases}$

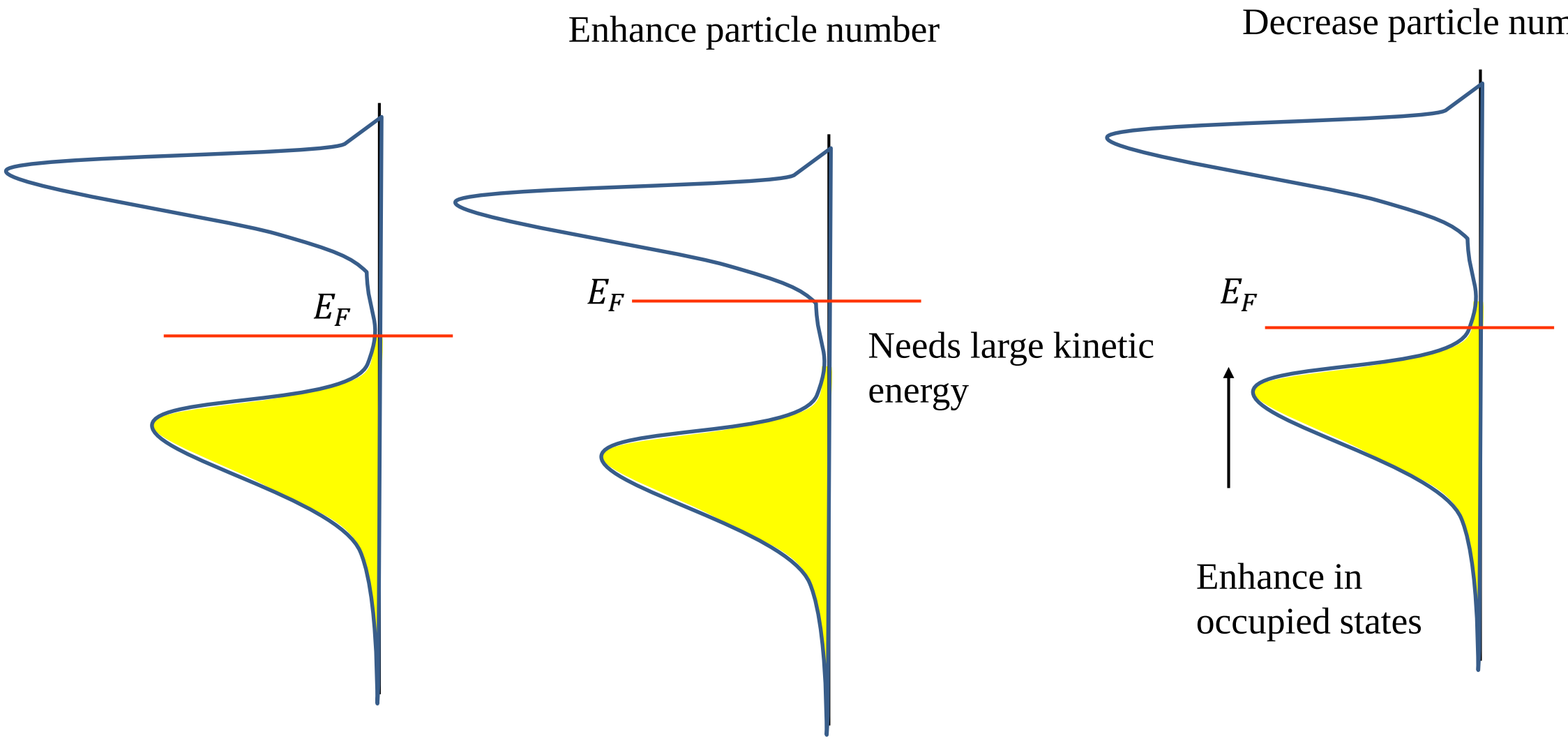
Iteration for convergence for each ***k***

Density of states in Ni and Fe





Fermi energy “locking” around a valley in density of states



Summary

Chapter 6 Magnetism of Itinerant Electron Systems

- Ferromagnetism in Electron gas
  - Hartree-Fock approximation
  - Diffusion Monte-Carlo calculation
- Hubbard model: mean field theory
- Magnetism in 3*d* transition metals
  - Slater-Pauling's curve
  - Density of states by APW method