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ADDITIONAL NOTES on MAGNETIC MOMENT FORMATION

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These are preliminary lecture notes, intended only for distribution to participants.

Magnetic Moment Formation

(from an itinerant point of view)

Goals:

- not details, but flavor
- appreciation of underlying (often unstated) assumptions; physical picture

Topics:

- Atomic physics
- Simple band theory
- Model of magnetism (generalized Stoner)
- Density functional theory – first-principles calculations
- Applications

Basic atomic physics:

Hydrogenic atom:

$$H = -\tfrac{1}{2}\nabla^2 - \frac{Z}{r}$$

Quantum numbers:

$[H, L^2] = 0$, $[H, L_z] = 0 \Rightarrow \psi \sim Y_{lm}(\hat{r})$

shell structure : n, l

$[H, S^2] = 0$, $[H, s_z] = 0$

spinors $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$

single-particle case.

shell structure remains if $V(r)$

N electron atom:

$$H = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla^2 - \frac{Z}{r_i} \right) + \frac{1}{2}{\sum_{i,j}}' \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$\equiv \sum_{i=1}^{N} \underbrace{\Omega_i}_{\text{1-particle}} + \frac{1}{2}{\sum_{i,j}}' \underbrace{\Omega_{ij}}_{\text{2-particle}} \quad \text{operators}$$

$$= \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla^2 - \frac{Z}{r_i} + \underbrace{\frac{1}{2}{\sum_{j}}' \frac{1}{|\vec{r}_i - \vec{r}_j|}}_{\text{Coulomb potential from all other electrons}} \right)$$

$$H_{\text{mean-field}} = \sum_{i=1}^{N} \left\{ -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \langle V_i \rangle \right\}$$

How to solve these problems?

How to write wave functions to obey antisymmetric requirement for fermions?

Slater determinants:

$$\psi(\vec{r}_1,\sigma_1,\vec{r}_2,\sigma_2,\ldots,\vec{r}_N,\sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(1) & u_2(2) & \cdots & u_1(N) \\ u_2(1) & u_2(2) & \cdots & u_2(N) \\ \vdots & \vdots & & \\ u_N(1) & u_N(2) & \cdots & u_N(N) \end{vmatrix}$$

(single-particle orbitals)

$$= \frac{1}{\sqrt{N!}} \sum_{\underbrace{j=1}_{\text{by column}}}^{N} u_c(j) A_{ij} = \frac{1}{\sqrt{N!}} \sum_{\underbrace{i=1}_{\text{by row}}}^{N} u_c(j) A_{ij}$$

(A_{ij}: cofactors)

$$A_{ij} = (-1)^{i+j} M_{ij} \quad (\text{minor})$$

From properties of determinants, clearly

antisymmetric

Other properties:

$$\det(AB) = (\det A)(\det B)$$

$$\det A^T = \det A$$

Most general form?

$$\vec{r}_i - \vec{r}_j \rightarrow -(\vec{r}_i - \vec{r}_j)$$

2-particle effects

$$f(\vec{r}_1 - \vec{r}_2, \vec{r}_1 - \vec{r}_3, \vec{r}_1 - \vec{r}_4, \ldots, \vec{r}_2 - \vec{r}_3, \vec{r}_2 - \vec{r}_4, \ldots)$$

Hard to write down analytic form.

Extra freedom (correlations) than Slater determinants

These types of correlations include (sometimes) via Jastrow factor

$$\phi^* \psi = \frac{1}{N!} \begin{vmatrix} \sum_i v_i^*(1) u_i(1) & \cdots & \sum_{i=1} v_i^*(1) u_i(N) \\ \vdots & & \\ \sum_i v_i^*(N) u_i(1) & \cdots & \sum_{i=1} v_i^*(N) u_i(N) \end{vmatrix}$$

Expand & integrate (overlap $(\langle \rangle = \int d1\, d2 \cdots dN \cdots)$

$$\langle \phi | \psi \rangle = \frac{1}{N!} \begin{vmatrix} \langle v_1 | u_1 \rangle & \cdots & \langle v_N | u_1 \rangle \\ \vdots & & \\ \langle v_1 | u_N \rangle & \cdots & \langle v_n | u_N \rangle \end{vmatrix}$$

If $\phi = \psi$ and $\langle u_i | u_j \rangle = \delta_{ij}$

$$\langle \psi | \psi \rangle = 1 = \begin{vmatrix} 1 & 0 & \cdots \\ 0 & 1 & \\ \vdots & & \ddots \end{vmatrix}$$

Single-particle orbitals important

Determinantal wave functions behave pretty much like single-particle orbits, at least for normalization and overlap.

Single-particle operator: $\hat{\Omega} = \sum_{\nu=1}^{N} \Omega_\nu$

$$\langle \psi | \hat{\Omega} | \psi \rangle = \sum_{\nu=1}^{N} \langle \psi | \Omega_\nu | \psi \rangle$$

$$= \sum_{i,j=1}^{N} \sum_{\nu=1}^{N} \frac{1}{N!} \int d1 \cdots dN \; u_j^*(\nu) \Omega_\nu u_i(\nu) (-1)^{i+j} M_{j\nu}^* M_{i\nu}$$

$$= \frac{1}{N!} \sum_{i,j=1}^{N} \underbrace{\sum_{\nu=1}^{N} \langle u_j(\nu) | \Omega_\nu | u_i(\nu) \rangle}_{N \langle u_j | \Omega_\nu | u_i \rangle} (-1)^{i+j} \int d1 \cdots d(\nu-1) \, d(\nu+1) \cdots dN \, M_{j\nu}^* M_{i\nu}$$

$M_{j\nu}$, $M_{i\nu}$ are $(N-1)$ wavefunctions, with same basis, hence

$$\langle \psi | \hat{\Omega} | \psi \rangle = \sum_{i,j=1}^{N} \frac{1}{N!} N \langle u_j | \Omega_\nu | u_i \rangle \, (N-1)! \, \delta_{ij} \, (-1)^{i+j}$$

$$= \sum_{i=1}^{N} \langle u_i | \Omega_\nu | u_i \rangle$$

Agrees with naive single-particle case.

If ϕ, ψ arbitrary matrices

$$\langle \phi | \hat{\Omega} | \psi \rangle = \sum_{i,j} \langle v_j | \Omega_\nu | u_i \rangle (-1)^{i+j} \underbrace{S_{ji}}_{\text{overlap of } (N-1) \text{ matrices}}$$

2 particle operators (e.g. Coulomb interaction)

$$\hat{\Omega} = \frac{1}{2}\sum_{\mu,\nu}{}' \Omega_{\mu\nu}$$

$$\langle\psi|\Omega|\psi\rangle = \frac{1}{2}\sum_{ij}{}' \Big\{ \langle u_i(1)u_j(2)|\Omega_{12}|u_i(1)u_j(2)\rangle - \underbrace{\langle u_j(1)u_i(2)|\Omega_{12}|u_i(1)u_j(2)\rangle}_{\text{exchange}} \Big\}$$

$1 = \{\vec{r}_1, \sigma_1\}$, $2 = \{\vec{r}_2, \sigma_2\}$

If Ω_{12} not spin-dependent, then

$$-\langle u_j(1)u_i(2)|\Omega_{12}|u_i(1)u_j(2)\rangle = -\delta_{\sigma_1\sigma_2}\langle u_j(1)u_i(2)|\Omega_{12}|u_i(1)u_j(2)$$

For $\Omega_{12} = \dfrac{1}{|\vec{r}_1 - \vec{r}_2|}$,

Exchange is attractive between like spins.

Consequence of anti-symmetrization requirement.

Use determinantal wavefunctions as basis:

$$\Psi = \sum_{\alpha} c_\alpha \psi_\alpha$$

Then, assuming $\langle \psi_\alpha | \psi_\beta \rangle = \delta_{\alpha\beta}$, and (N-1) also orthonormal

then properties of multi-det. wave functions is additive: e.g.

density operator: $\rho(\vec{r}) = \langle \Psi | \sum_{i=1}^{N} \delta(\vec{r} - \hat{r}_i) | \Psi \rangle$

$$= \sum_{\alpha} |c_\alpha|^2 \sum_{i=1}^{N} u_i^{\alpha *}(\vec{r}) u_i^{\alpha}(\vec{r})$$

Full many-body wave function can be built up as sum of single-particle states.

How to obtain single particle states?

quantum Monte Carlo

mean-field theories

- Hartree, Hartree-Fock, DFT

Atoms:

For a given configuration (making use of shell structure) $d^n s$ or d^n, determine set of orthonormal single-particle orbitals $\{\ell, m_\ell, s, s_z\}$

Generate all possible N-particle determinants.

Diagonalize

$$\langle \psi_\alpha | H | \psi_\beta \rangle$$

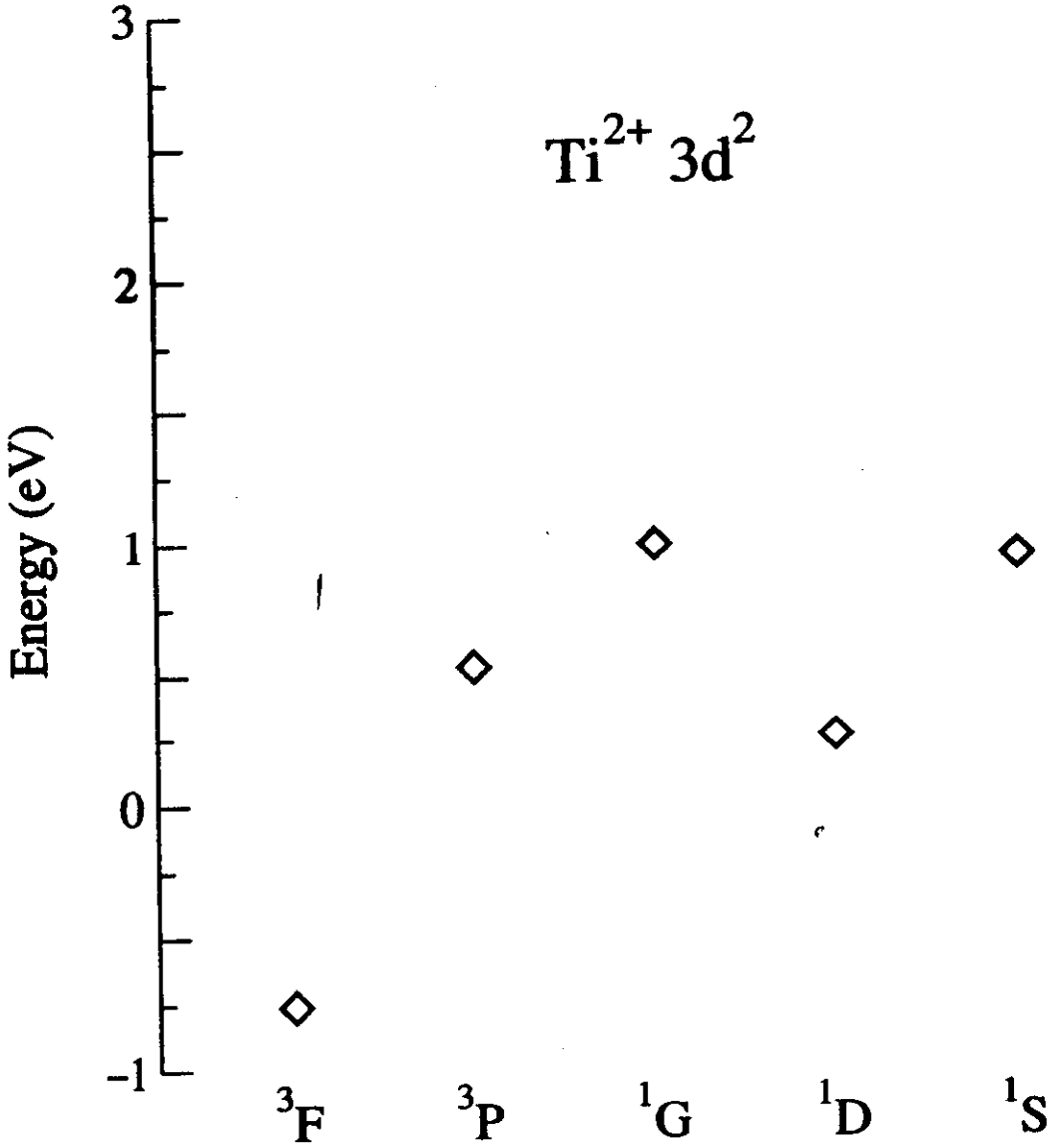
get $\Psi_{i\alpha} = \sum c_{i\alpha} \psi_\alpha$, E_i

$\Rightarrow$ Multiplet structure

$$L, S, \underbrace{M_L}_{(2L+1)}, \underbrace{M_S}_{(2S+1)}, \text{degeneracy } (2L+1)(2S+1)$$

can include other configurations
$\Rightarrow$ configuration interaction

Number of determinants: $\binom{N_{states}}{n_{electrons}} = \frac{N!}{n!(N-n)!}$



Hund's Rules:

1. ground state has max. S (exchange)
2. for maximal S, max. L lies lower

For $S < S_{max}$, L can be in any order.

$\binom{10}{2} = \frac{10!}{2!\,8!} = 45$ ^3F ^3P ^1G ^1D ^1S

$3 \cdot 7 + 3 \cdot 3 + 1 \cdot 9 + 1 \cdot 5 + 1 \cdot 1 = 45$

Both single- and multi-determinant wavefunctions:

Ti^{2+} $d^2(d^8)$:

$$^3F\big|_{m_L=3,m_S=1} = \phi(2^+, 1^+)$$

$$^3F\big|_{21} = \phi(2^+, 0^+)$$

$$^1G\big|_{40} = \phi(2^+, 2^-)$$

$$^1S\big|_{00} = \frac{1}{\sqrt{5}}\Big\{ \phi(2^+,2^-) - \phi(2^-,2^+) + \phi(1^-,1^+) - \phi(1^+,1^-) + \phi(0^+,0^-)\Big\}$$

Theory does good job of reproducing experiment

Configuration interactions can be important - including different correlations.

Direct vs. Exchange

For given multiplet, <u>sum</u> of direct & exchange

same for all levels, but not each separately

$$\frac{1}{|\vec{r}_1-\vec{r}_2|} = \sum_\lambda \frac{4\pi}{2\lambda+1} \frac{r_<^\lambda}{r_>^{\lambda+1}} Y_\lambda^*(\hat{r}_1)\, Y_\lambda(\hat{r}_2)$$

$$F^k(dd) \sim \int dr\, r^2\, dr'^2\, \frac{r_<^k}{r_>^{k+1}}\, u^2(r)\, u^2(r')$$

direct: $\sim F^2 (2m_i|20|2m_i)^* (2m_j|20|2m_j) + F^4 (2m_i|40|2m_i)^* (2m_j|40|2m_j)$

exchange: $\sim \delta_{\sigma_i\sigma_j} \{ F^2 |(2m_j|2\, m_{\text{sp}}-m_i|2m_c)|^2 + F^4 |(2m_j|4\, m_j-m_c|2m_c)|^2$

Compare ${}^3F_{(31)}$, ${}^3F_{(21)}$

direct: ${}^3F_{(31)} - {}^3F_{(21)} = F^2 (22|20|22)^* [(21|20|21) - (20|20|20)] + F^4 (22|40|22)^* [(21|40|21) - (20|40|20)] \neq 0$

Atoms: Summary

Ground state maximum of S (and L)

Multiplet structure in localized system

Shell structure

Wavefunctions are described in terms of single-particle orbitals

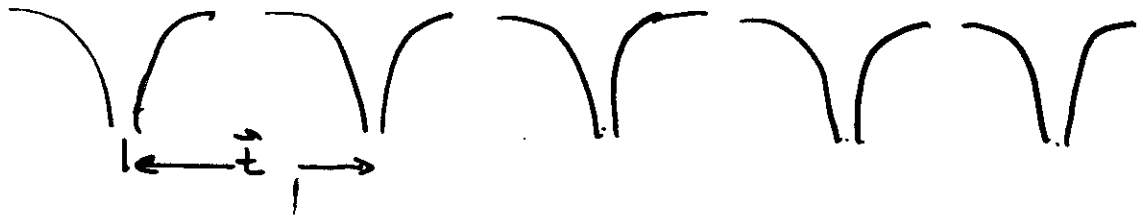
Exchange is attractive interaction among electrons of same spin

$\Rightarrow$ Magnetism

Configuration interaction schemes suffer from the expotential growth in number of determinant with the number of electrons considered.

Simple Band Theory

Periodic potential $V(\vec{r}+\vec{t}) = V(\vec{r})$



T be translation operation $[H, T] = 0$ since periodic

Pick ψ to be eigenfunction of both H (energy) and T (momentum)

Translational symmetry: character is $e^{i\vec{k}\cdot\vec{t}}$

$T\psi_{\vec{k}}(\vec{r}) = \psi_{\vec{k}}(\vec{r}+\vec{t}) = e^{i\vec{k}\cdot\vec{t}}\psi_{\vec{k}}(\vec{r})$ ← requirement

Bloch form:

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \underbrace{u_{\vec{k}}(\vec{r})}_{\text{periodic}}$$

Start from atomic orbitals:

$$\phi_{\vec{k}}(\vec{r}) = \sum_{\vec{t}} e^{i\vec{k}\cdot\vec{t}}\, \phi(\vec{r}-\vec{t})$$

Check:

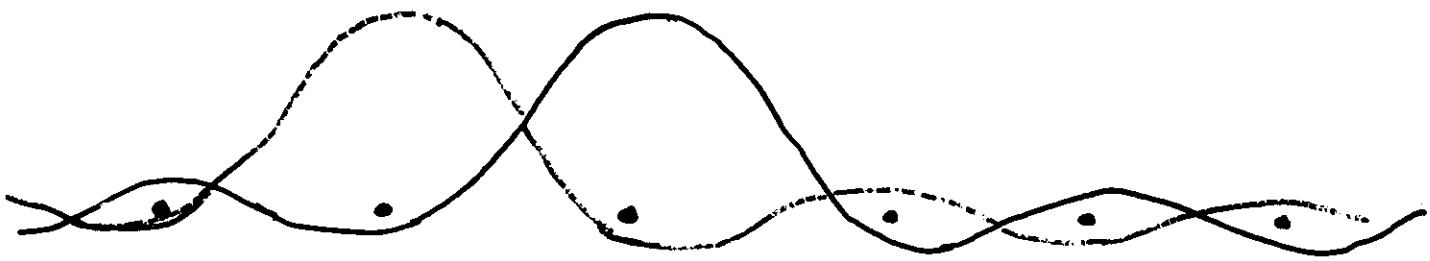
$$\begin{aligned}
\phi_{\vec{k}}(\vec{r}+\vec{t}_0) &= \sum_{\vec{t}} e^{i\vec{k}\cdot\vec{t}}\phi(\vec{r}+\vec{t}_0-\vec{t}) \\
&= \sum_{\vec{t}} e^{ik\cdot(\vec{t}-\vec{t}_0+\vec{t}_0)}\phi(\vec{r}-(\vec{t}-\vec{t}_0)) \\
&= e^{i\vec{k}\cdot\vec{t}_0} \sum_{\vec{t}} e^{i\vec{k}\cdot\hat{t}}\,\phi(\vec{r}-\hat{t}) \\
&= e^{i\vec{k}\cdot\vec{t}_0}\,\psi_{\vec{k}}(\vec{r})
\end{aligned}$$

Fourier transform of Bloch form of the eigenfunctions gives atomic-like orbitals $a(\vec{r}-\vec{R})$ - **Wannier functions**

Since $e^{i\theta}\psi_{\vec{k}}(\vec{r})$ is still a solution, choice of phase free; different possibilities

Wannier functions orthonormal - useful in discussing localized interactions.

Wannier function:

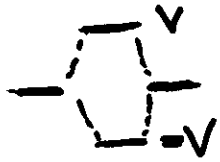


Mainly localized on a site, but must have weights on other sites also.

orthonormal $\int d\vec{r}\, w_i(\vec{r}) w_j(\vec{r}) = \delta_{ij}$

Why "band" theory? Overlap of orbitals

2 atoms; ϕ $\quad \langle \phi_i | \phi_j \rangle = \delta_{ij}$

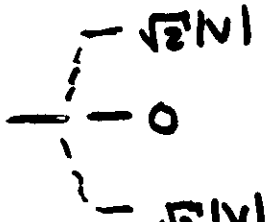


$\langle \phi_i | H | \phi_i \rangle = \epsilon_0$

$\langle \phi_1 | H | \phi_2 \rangle = V = \langle \phi_2 | H | \phi_1 \rangle$

$\epsilon = \epsilon_0 \pm |V|$

3 atoms: $\begin{vmatrix} \epsilon_0 - \epsilon & V & 0 \\ V & \epsilon_0 - \epsilon & V \\ 0 & V & \epsilon_0 - \epsilon \end{vmatrix} = 0$



$\Rightarrow (\epsilon_0 - \epsilon)\left[(\epsilon_0 - \epsilon)^2 - V^2 - V^2\right] = 0$

$\Rightarrow \epsilon = \epsilon_0, \ \epsilon_0 \pm \sqrt{2}V$

Chain:

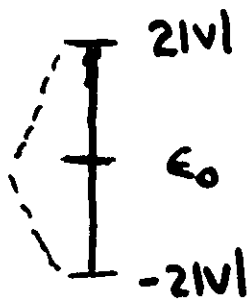
$$\epsilon(\vec{k}) = \langle \varphi_{\vec{k}} | H | \varphi_{\vec{k}} \rangle = \frac{1}{N} \sum_{ij} e^{i(\vec{R}_j - \vec{R}_i)} \langle \varphi(\vec{r} - R_i) | H | \varphi(\vec{r} - r_j) \rangle$$

$$= \sum_j e^{i\vec{k}\cdot\vec{R}_j} \langle \phi(\vec{r} - \vec{R}_j) | H | \varphi(\vec{r}) \rangle$$

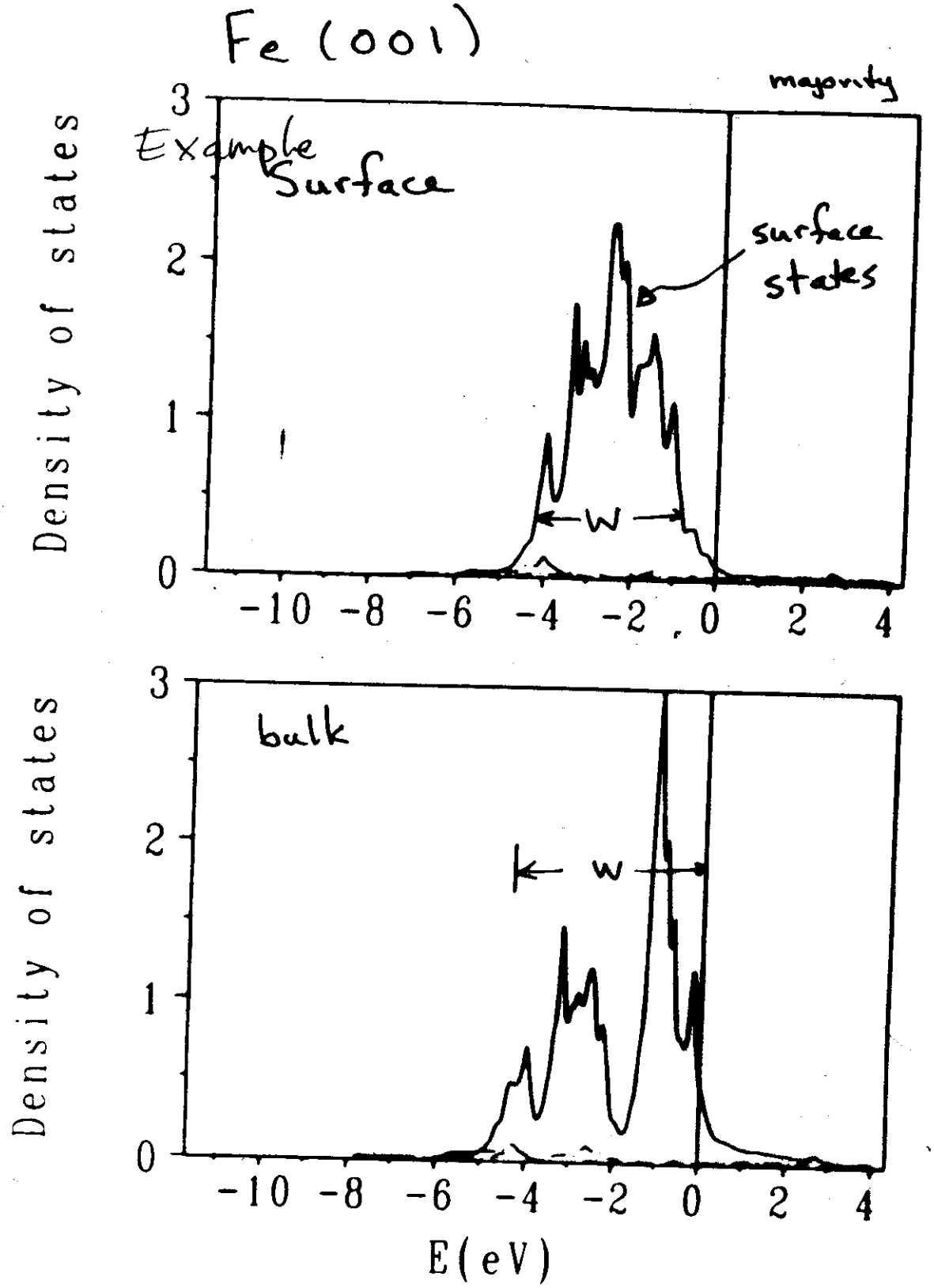
$$= \underbrace{\langle \varphi | H | \varphi \rangle}_{\epsilon_0} + e^{i\vec{k}\cdot\vec{a}} \langle \varphi(\vec{r} - a) | H | \varphi(r) \rangle_{\leftarrow V} + e^{-i\vec{k}\cdot\vec{a}} \langle \varphi(\vec{r} + \vec{a}) | H | \varphi(r) \rangle$$

$$= \epsilon_0 + V e^{i\vec{k}\cdot\vec{a}} + e^{-i\vec{k}\cdot\vec{a}}$$

$$= \epsilon + 2V \cos \vec{k}\cdot\vec{a}$$



form band of energies; depends on interactions


Fe (001)
majority
Example
Surface
surface
states
W
bulk
W
Density of states
Density of states
E(eV)

Many-body wave function made up of orbitals from periodic potential

Large single determinant wavefunction (hidden)

e.g.,

$$\rho(\vec{r}) = \sum_{\vec{k},i} \underbrace{f(\epsilon_{\vec{k}i})}_{\text{Fermi occupation}} |\psi_{\vec{k}i}(\vec{r})|^2$$

($N \to \infty$ case)

Effective (mean-field) potential

Treats Coulomb interactions among electrons

Relationship between N & N-1 determinantal wavefunctions, some multi-configurational correlations included; depends on construction of effective potential..

Band calculation does not get multiplet structure:

single determinant hence can only get one level.

exactly same situation in atomic limit:

need other determinants at the same time to get multiplet structure

For some/many properties, the result of band theory is the starting point, not the end.

Density Functional Theory

Hohenberg - Kohn Theorem:

Ground state energy of a many-electron system, is a unique functional of the charge (spin) density and is a minimum for true ground state density

→ Existence theorem ←

Limit to ground state (of given symmetry); not excited states

No information about functional itself.

Kohn-Sham:

Write energy functional in terms of non-interacting / single-particle orbitals:

$$E[n] = T_s[n] + U[n] + E_{xc}[n]$$

Classical Hartree (Coulomb) energy

$$U[n] = \frac{1}{2}\int d\vec{r}\,d\vec{r}\,' \frac{n(\vec{r})\,n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + \int d\vec{r}\, V_{ext}(\vec{r})\, n(\vec{r}) + \tilde{U}_0$$

$$V_{ext}(\vec{r}) = \sum_{\nu} \frac{-Z_\nu}{|\vec{r}-\vec{R}_\nu|} \; ; \; \tilde{U}_0 = \frac{1}{2}{\sum_{\nu\nu'}}' \frac{Z_\nu Z_{\nu'}}{|\vec{R}_\nu - \vec{R}_{\nu'}|}$$

"Kinetic" Energy given in terms of orbitals $\psi_{i\sigma}(\vec{r})$

$$T_s[n] = \sum_{i\sigma} \int d\vec{r}\, \psi^*_{i\sigma}(\vec{r}) \left(-\tfrac{1}{2}\nabla^2\right) \psi_{i\sigma}(\vec{r})$$

so that

$$n_\sigma(\vec{r}) = \sum_{i\sigma} \psi^*_{i\sigma}(\vec{r})\,\psi_{i\sigma}(\vec{r})$$

$$m(\vec{r}) = n_\uparrow(\vec{r}) - n_\downarrow(\vec{r}) \qquad \text{spin density}$$

$$n(\vec{r}) = n_\uparrow(\vec{r}) + n_\downarrow(\vec{r}) \qquad \text{total charge}$$

Exchange - correlation $E_{xc}[n]$

Everything left over : all many-body effects

Form still unknown:

Variational principle : $\psi_i^* \to \psi_i^* + \delta\psi_i^*$

$$\delta n = \delta\psi_i^* \psi_i$$

$$\delta E[\psi_i^* + \delta\psi_i^*] = \int d\vec{r}\, \delta\psi_i^* \left(-\tfrac{1}{2}\nabla^2\right)\psi_i$$

$$+ \int d\vec{r}\, V_{ext}(\vec{r})\, \delta\psi_i^* \psi_i$$

$$+ \frac{1}{2}\int d\vec{r}\, d\vec{r}\,' \frac{1}{|\vec{r}-\vec{r}\,'|}\left\{\delta\psi_i^*(\vec{r}\,')\,\psi_i(\vec{r}\,')\,n(\vec{r}) + \delta\psi_i^*(\vec{r})\,\psi_i(\vec{r})\,n(\vec{r}\,')\right\}$$

$$+ \int d\vec{r}\, \frac{\delta E_{xc}}{\delta n(\vec{r})}\, \delta\psi_i^* \psi_i \quad \leftarrow \quad \epsilon_i \int d\vec{r}\, \delta\psi_i^* \psi_i$$

ϵ_i ↑ Lagrange multipler for normalization condition

$$\frac{\delta E}{\delta \psi_i^*} = 0$$

Set of single-particle equations:

$$\left\{-\frac{1}{2}\nabla^2 + V_{ext}(\vec{r}) + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + \mu_{xc}(\vec{r})\right\}\psi_i = \epsilon\psi_i$$

$\mu_{xc} = \frac{\delta E_{xc}}{\delta n(\vec{r})}$ "exchange-correlation" potential

$$n(\vec{r}) = \sum |\psi_i(\vec{r})|^2$$

Need to solve self-consistently for ψ_i, $n(\vec{r})$

Converted many-body problem into equivalent set of single particle equations.

ψ_i's not quasi-particle states.

If ψ_i used in (single)-determinantal wavefunction of band theory, correct density

Approximations for E_{xc}

Local density: (LDA)

$$E_{xc}^{LDA} \approx \int d\vec{r}\, n(\vec{r})\, \epsilon_{xc}[n]$$

$\epsilon_{xc}[n]$ from electron gas data

$$\epsilon_x \sim \left(n_\uparrow^{4/3} + n_\downarrow^{4/3}\right)$$

$$\mu_x \sim n^{1/3}$$

Exact in the limit of constant density
" " infinite density (dominated by Coulomb)

Works surprisingly well - electrostatics correct
sum rules

Generalized Gradient Approximation (GGA)

$$E_{xc}^{GGA} \approx \int d\vec{r}\, n(\vec{r})\, \epsilon_{xc}[n, |\nabla n|]$$

improvements; more sum rules satisfied

shape of density taken into account better.

Deficiencies :

- Spin and lattice decoupled; problem in any theory without spin-orbit coupling.

- Hund's second rule (orbital angular momentum) not handled correctly

  multiplet levels not degenerate (→)

- Any exchange-correlation functional depending only on charge & spin densities must fail

  – levels exist with same charge/spin densities belonging to different multiplets (many)

d^2: ^3F, $m_L=3$, $M_S=0$ $\quad \frac{1}{\sqrt{2}}\left[(2^+, 1^-)+(2^-, 1^+)\right]$

^1G, $m_L=3$, $M_S=0$ $\quad \frac{1}{\sqrt{2}}\left[(2^+, 1^-)-(2^-, 1^+)\right]$

Current density can distinguish

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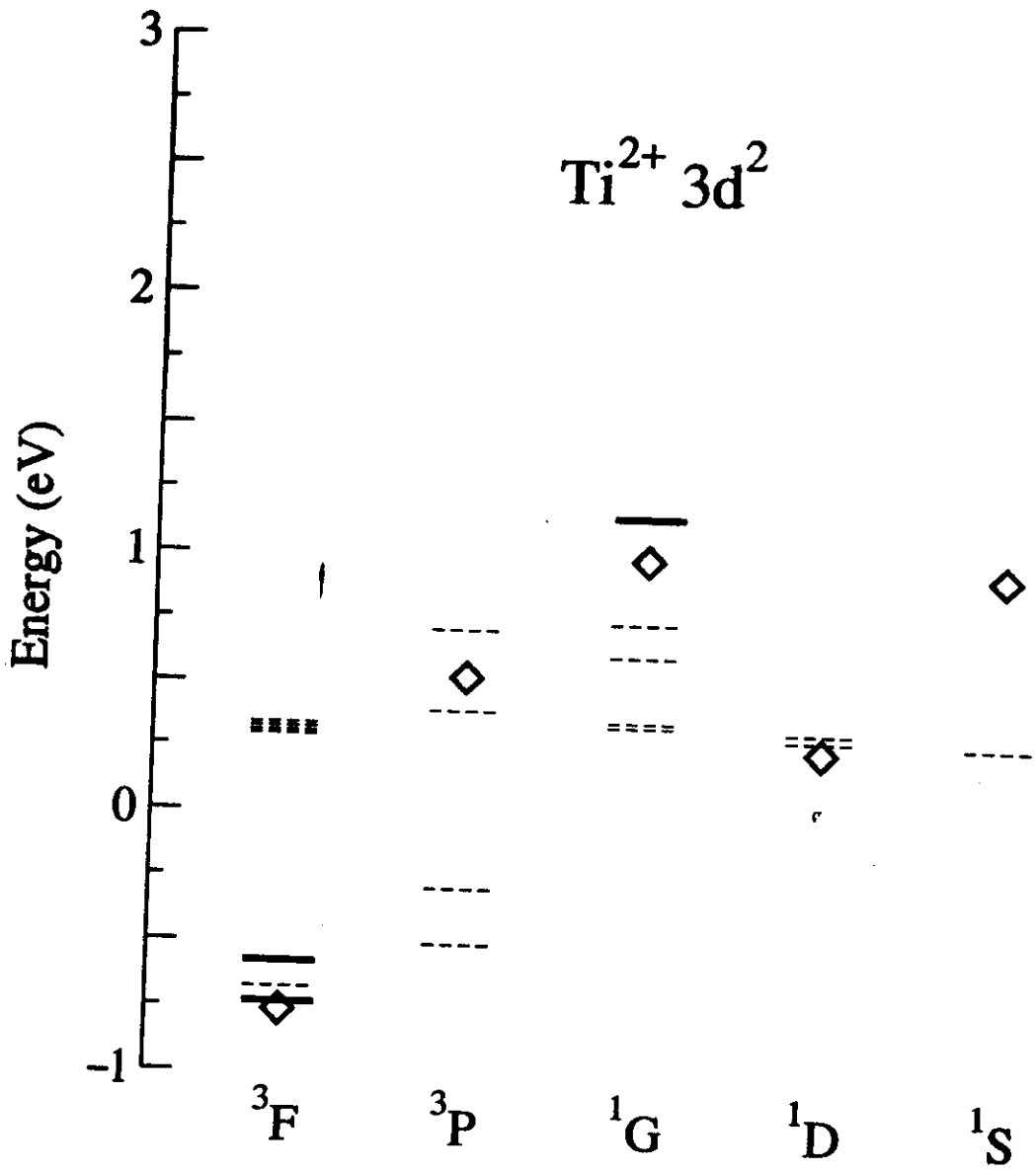


Energies split ~ according to S_z

Broken generacies, even for singe-det. wave fun.

Solution of DFT equations:

Non-trivial; self-consistent solution

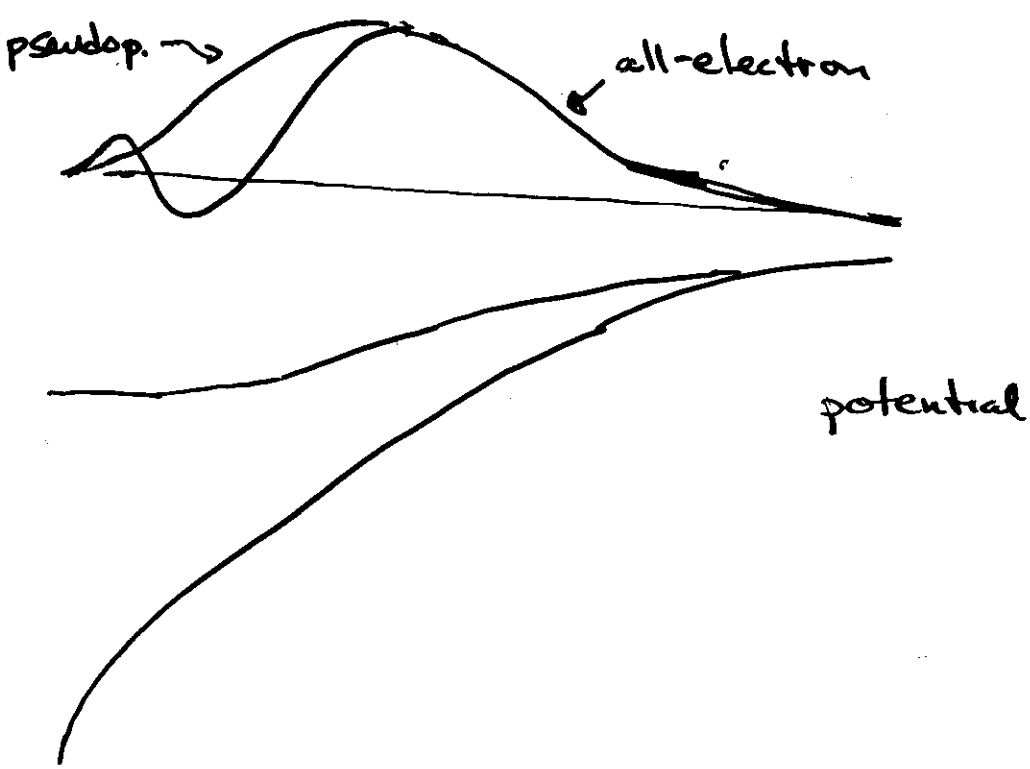
Many different approaches, each with advantages / disadvantages.

Linear Combination of Atomic Orbitals

- atomic functions (Bloch sum) $\sum e^{i\vec{k}\cdot\vec{R}}\varphi(\vec{r}-\vec{R})$
- not limited to tight-binding
- physically appealing basis
- slowly convergent basis, not systematic
- does not satisfy cusp condition $\left(\left.\frac{\partial n}{\partial r}\right|_{r=0} = -2Zn(0)\right)$
- matrix elements difficult to calculate accurately

Pseudopotentials:

- Since interested in valence electron properties, replace effect of core electrons by effective potential; wave functions smooth!

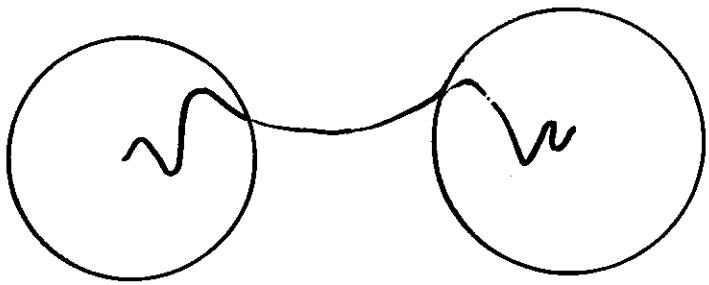


Pseudopotentials (con't)

- Smooth pseudo wave functions smooth can be expanded in plane waves ; simple
- can fit for particular purpose (optical spectra) or obtain "first-principles"
- at best, approximation to all-electron calculations
- results can depend on choice of pseudopotential

Augmented methods:

- Around atom, electronic structure dominated by atomic effects (nucleus)
- In interstitial, density smooth.
- In sphere around atoms, use solutions to atomic problem for the actual potential; in interstitial, use smooth(er) function

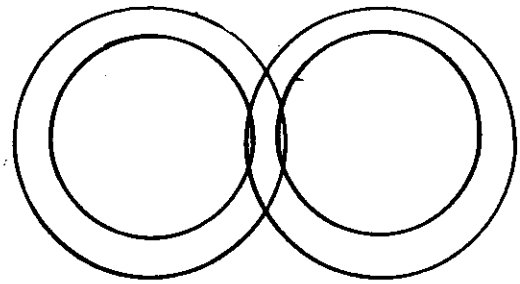


- cusp condition satisfied by construction
- can treat all-electrons
- more complicated: matching, various representations, full-potential harder.

Linearized Muffin-tin orbitals (LMTO)

- tails $\frac{1}{r^{\ell+1}} = \left(\lim_{kr\to 0} n_\ell(kr)\right.$ spherical Neuman function)
- often Atomic sphere approximation used

not always accurate!



full-potential can be done, most FLMTO still approximate

- fast
- best for close-packed systems
- basis not flexible enough in all cases.

- linearized methods:

$$\sum_L 4\pi i^\ell \left[\alpha_L^i u_\ell(r,\epsilon_0) + \beta_L^c \dot{u}_\ell(r,\epsilon_0)\right] Y_{\ell m}(\hat{r})$$

$$\dot{u}_\ell = \frac{\partial}{\partial \epsilon} u_\ell(\epsilon) \quad ; \quad \int_S d\vec{r}\; u_\ell(\epsilon)\dot{u}_\ell(\epsilon) = 0$$

(Full-potential) Linearized Augmented Plane Wave (FLAPW)

- tails plane waves
- full-potential
  - linearized basis
  - accurate [generally considered most accurate]
    - systematic basis set
    - complicated (more than pseudopotentials or LMTO)
    - reasonably expensive

KKR :

- scattering approach
- spherical waves for whole cell
- full-potential more difficult.
- easier to combine with averaging procedures such as Coherent Potential Approximation.
- natural way to generate Green's function, treatment of defects

Result from DFT calculations

- Charge and spin densities
  - compare to neutron / x-ray
- total energies:

  Structure: lattice constants, internal parameters

  phase stability: competition among structures

  phonons: forces

  spin-waves

  "easy" directions (magnetocrystalline anisotropy)
- single particle properties
  - photoemission, other spectroscopies
  - understanding single-particle properties

Simple model of magnetism:

Non-magnetic band Hamilton:

$$H_0 = \sum_{k,\sigma} \epsilon_k \, a^{+}_{k\sigma} a_{k\sigma}$$

Band Annihilation operator $a_{k\sigma}$: momentum k, spin σ

Wannier function - localized on site i, with spin σ

$$a_{k\sigma} = \frac{1}{\sqrt{N}} \sum_{i} e^{-i\vec{k}\cdot\vec{R}_i} c_{i\sigma}$$

Assume interactions between Wannier functions screened. Interaction term (direct & change)

$$\langle |H| \rangle = \langle \phi_i(1)\phi_j(2) | \tfrac{1}{r_{12}} | \phi_i(1)\phi_j(2) \rangle - \langle \phi_j(1)\phi_i(2) | \tfrac{1}{r_{12}} | \phi_i(1)\phi_j(2) \rangle$$

(c^{+}_{σ} $c^{+}_{\bar{\sigma}}$ $\Downarrow$)

$$H_I = U \sum_{i\sigma} \left[\langle c^{+}_{i\bar{\sigma}} c_{i\bar{\sigma}} \rangle \, c^{+}_{i\sigma} c_{i\sigma} - \langle c^{+}_{i\sigma} c_{i\bar{\sigma}} \rangle \, c^{+}_{i\bar{\sigma}} c_{i\sigma} \right]$$

U: interaction strength

$\langle c^{+}_{i\bar{\sigma}} c_{i\bar{\sigma}} \rangle$: mean field

Total Energy:

$$E_T = \sum_{k\sigma} \epsilon_k \langle a^+_{k\sigma} a_{k\sigma} \rangle + \tfrac{1}{2} U \sum_{i\sigma} \left[\langle c^+_{i\bar{\sigma}} c_{i\bar{\sigma}} \rangle \langle c^+_{i\sigma} c_{i\sigma} \rangle - \langle c^+_{i\sigma} c_{i\bar{\sigma}} \rangle \langle c^+_{i\bar{\sigma}} c_{i\sigma} \rangle \right]$$

Restrict to $Q = G/2$ for magnetic case:

$$c^+_{i\sigma'} c_{i\sigma} = \frac{1}{N} \sum_{kk'} e^{i(k-k')R_i} a^+_{k'\sigma'} a_{k\sigma}$$

$$= \frac{1}{N} \sum_{kq} e^{-iq \cdot R_i} a^+_{k+q\sigma'} a_{k\sigma}$$

$$H_I = \frac{U}{N^2} \sum_{\substack{kk' \\ qq'}} \sum_{i\sigma} \left\{ e^{-iq'R_i} \langle a^+_{k'+q'\bar{\sigma}} a_{k'\bar{\sigma}} \rangle e^{iqR_i} a^+_{k\sigma} a_{k+q\sigma} - e^{-iq'R_i} \langle a^+_{k'+q\sigma} a_{k'\bar{\sigma}} \rangle e^{i\vec{q} \cdot R_i} a^+_{k\bar{\sigma}} a_{k+q\sigma} \right\}$$

Lattice δ-function

$$\sum_i e^{-i(q'-q)R_i} = N \delta(q - q' - G)$$

G ↑ lattice vector

Consider a given $\vec{k}$: $a_{k\sigma}$, $a_{k+Q\sigma}$, $Q = \frac{G}{2}$

$$H_I = U \sum_{k\sigma} \Big\{ \underbrace{\langle \textstyle\sum_{k'} a^+_{k\bar{\sigma}} a_{k\bar{\sigma}} \rangle}_{n^*_{\bar{\sigma}}} \left(a^+_{k\sigma} a_{k\sigma} + a^+_{k+Q\sigma} a_{k+Q,\sigma} \right)$$

$$+ \langle \textstyle\sum_{k'} a^+_{k'+Q\bar{\sigma}} a_{k'\bar{\sigma}} \rangle \left(a^+_{k+Q\sigma} a_{k\sigma} + a^+_{k+Q\sigma} a_{k+Q\sigma} \right)$$

$$- \langle \textstyle\sum_{k'} a^+_{k'\sigma} a_{k\bar{\sigma}} \rangle \left(a^+_{k\bar{\sigma}} a_{k\sigma} + a^+_{k+Q,\bar{\sigma}} a_{k+Q\sigma} \right)$$

$$- \langle \textstyle\sum_{k} a^+_{k+Q\sigma} a_{k\bar{\sigma}} \rangle \left(a^+_{k\bar{\sigma}} a_{k+Q\sigma} + a^+_{k+Q\bar{\sigma}} a_{k\sigma} \right) \Big\}$$

c_0 , c_Q

To solve, want an operator transform

$$\gamma_k = B_1 a_{k\uparrow} + B_2 a_{k\downarrow} + B_3 a_{k+Q\uparrow} + B_4 a_{k+Q\downarrow}$$

that puts the Hamiltonian $H = H_0 + H_I$ into diagonal form.

$$[\gamma^+_k, H] = E_k \gamma^+_k$$

equivalent to diagonalizing matrix

$$U\begin{pmatrix} \frac{\epsilon_k}{U}+n_\downarrow^0 & c_0 & n_Q^\downarrow & c_Q \\ c_0 & \frac{\epsilon_k}{U}+n_\uparrow^0 & c_Q & n_Q^\uparrow \\ n_Q^\downarrow & c_Q & \frac{\epsilon_k}{U}+n_\downarrow^0 & c_0 \\ c_Q & n_Q^\uparrow & c_0 & \frac{\epsilon_k}{U}+n_\uparrow^0 \end{pmatrix}$$

Since elements depend on eigenvectors, self consistency conditions:

$$n_\downarrow^0 = \frac{1}{N}\sum_k f_k\left(B_2^2+B_4^2\right)$$

$$n_\uparrow^0 = \frac{1}{N}\sum_k f_k\left(B_1^2+B_3^2\right)$$

$$c_0 = -\frac{1}{N}\sum_k f_k\left(B_1B_2+B_3B_4\right)$$

$$n_\downarrow^Q = \frac{2}{N}\sum_k f_k B_2B_4$$

$$n_\uparrow^Q = \frac{2}{N}\sum_k f_k B_1B_3$$

$$c_Q = -\frac{1}{N}\sum_k f_k\left(B_1B_4+B_2B_3\right)$$

Density:

$$n(q) = \frac{1}{N} \sum_{i,\sigma} e^{iq \cdot R_i} \langle c_{i\sigma}^{+} c_{i\sigma} \rangle$$

$$n(0) = n = n_{\uparrow}^{0} + n_{\downarrow}^{0}$$

$$n(Q) = n_{\uparrow}^{Q} + n_{\downarrow}^{Q}$$

Spin-density

$$\vec{M}(q) = \frac{1}{N} \sum_{i} e^{iq \cdot R_i} \mu_B \sum_{\sigma\sigma'} \underbrace{\langle i\sigma | \vec{\sigma} | i\sigma' \rangle}_{\text{spinor part}} \langle c_{i\sigma}^{+} c_{i\sigma'} \rangle$$

$$\vec{M}(0) = \mu_B \left[-2C_0 \hat{x} + (n_{\uparrow}^{0} - n_{\downarrow}^{0}) \hat{z} \right]$$

$$\vec{M}(Q) = \mu_B \left[-2C_Q \hat{x} + (n_{\uparrow}^{Q} - n_{\downarrow}^{Q}) \hat{z} \right]$$

Possible spin ordering: non-zero $n_{\sigma}^{0}, n_{\sigma}^{Q}, C_0, C_Q$

paramagnetic : $n_{\uparrow}^{0} = n_{\downarrow}^{0}$

ferromagnetic : $n_{\uparrow}^{0}, n_{\downarrow}^{0}$

AFM : $n_{\uparrow}^{0} = n_{\downarrow}^{0}, C_Q$

or $n_{\uparrow}^{0} = n_{\downarrow}^{0}, n_{\uparrow}^{Q} = n_{\downarrow}^{Q}$

Paramagnetic :

$$\gamma_{k\sigma} = a_{k\sigma}$$

$$E_{k\sigma} = \epsilon_k + n^0_{\uparrow} U = \epsilon_k + \tfrac{1}{2} U n$$

$$E_T = \sum_{k\sigma} F_k E_{k\sigma} - \tfrac{1}{2} \tfrac{1}{2} U n^2$$

Ferromagnetism :

$$\gamma_{k\sigma} = a_{k\sigma}$$

$$E_{k\sigma} = \epsilon_k + U n^0_{\sigma}$$

matrix :

$$\begin{pmatrix} \epsilon_k + U n^0_{\downarrow} & 0 \\ 0 & \epsilon_k + U n^0_{\uparrow} \end{pmatrix} \qquad q = 0$$

Antiferromagnetism for later)

Simple Stoner model of Ferromagnetism

$$\mathcal{H} = \sum_{k\sigma} \epsilon_k a^\dagger_{k\sigma} a_{k\sigma} \qquad \text{"band" term}$$

$$+ I \sum_{kk'} (a^\dagger_{k+} a_{k+})(a^\dagger_{k'-} a_{k'-}) \qquad \text{Exchange}$$

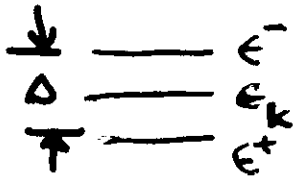
Mean-field approximation

$$\mathcal{H}_{MF} = \sum_{k\sigma} \left[\epsilon_k + I \underbrace{\left\langle \sum_{k'} a^\dagger_{k'\bar{\sigma}} a_{k'\bar{\sigma}} \right\rangle}_{n_{\bar{\sigma}}} \right] a^\dagger_{k\sigma} a_{k\sigma}$$

Eigenvalues:

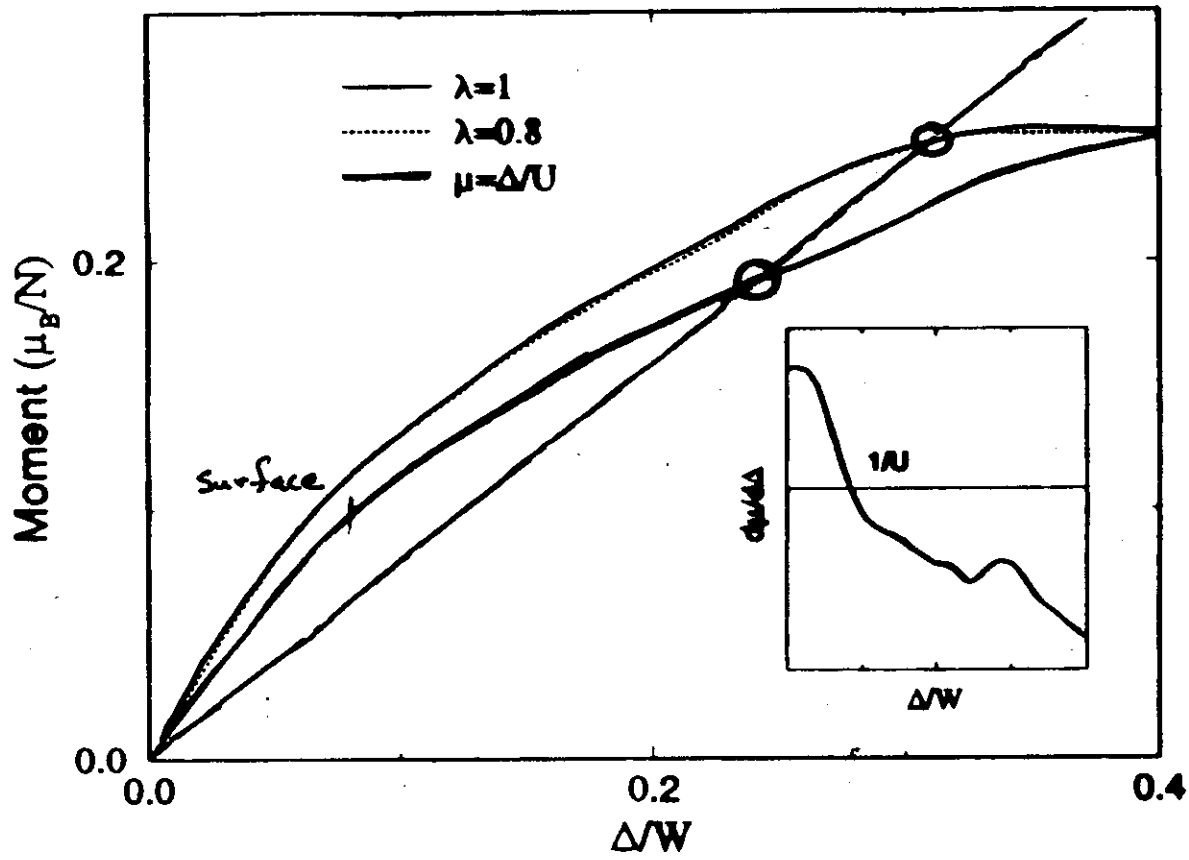
$$\epsilon^\pm_k = \epsilon_k + I n_\mp = \epsilon_k + \tfrac{1}{2} I (N \mp \mu)$$

$$\Rightarrow \quad \epsilon^\pm_k = \epsilon_k \mp \tfrac{1}{2}\Delta$$



Exchange splitting: $\Delta = I\mu$

$\Rightarrow$ self-consistency condition between $\mu(\Delta)$ and $\mu = \frac{\Delta}{I}$



Density of states determines $\mu(\Delta)$:

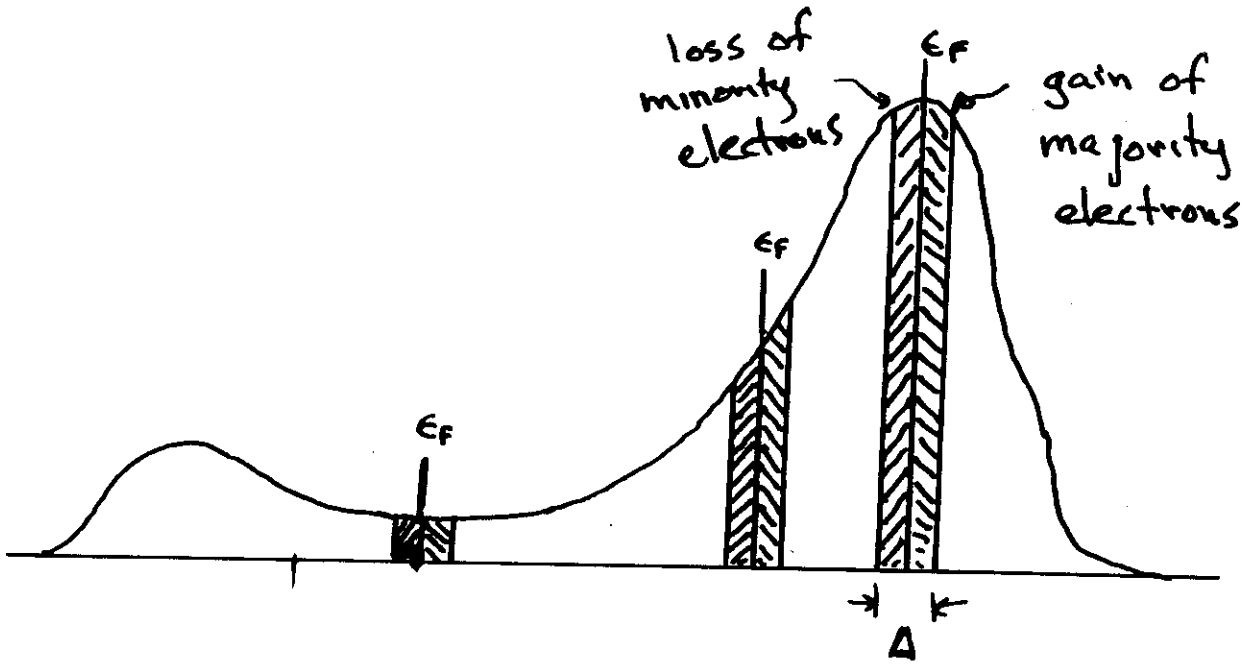
$$\mu(\Delta) \underset{\Delta \to 0}{=} \tfrac{1}{2} n(\epsilon_F)\, \Delta$$

Condition for magnetic solution:

$$\tfrac{1}{2} n(\epsilon_F)\, \Delta > \frac{\Delta}{I} \quad \Rightarrow \quad \tfrac{1}{2} I\, n(\epsilon_F) > 1$$

(Susceptibility: linear response

$$\chi/\chi_0 = \frac{1}{1 - \tfrac{1}{2} I\, n(\epsilon_F)} \quad)$$



$\mu(\Delta)$ will depend on position of ϵ_F

" " " density of states

Density functional theory:

Stoner parameter (exchange-correlation integral)

$$I = \int d\vec{r}\, \gamma^2(\vec{r})\, K(\vec{r})$$

(normalized) / density at E_F:

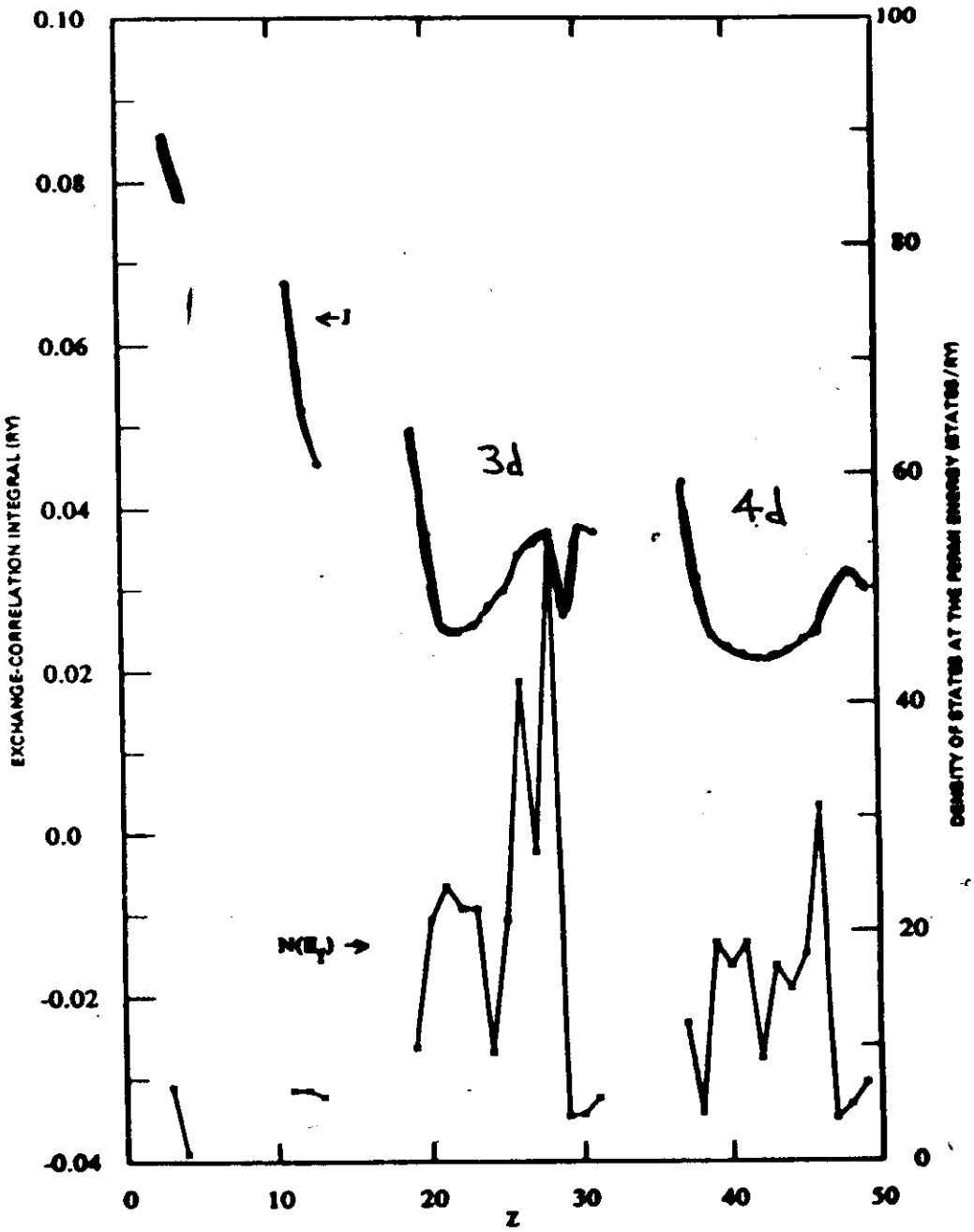
$$\gamma(\vec{r}) = \frac{1}{n(\epsilon_F)} \sum_i |\psi_i(\vec{r})|^2\, \delta(\epsilon_i - \epsilon_F)$$

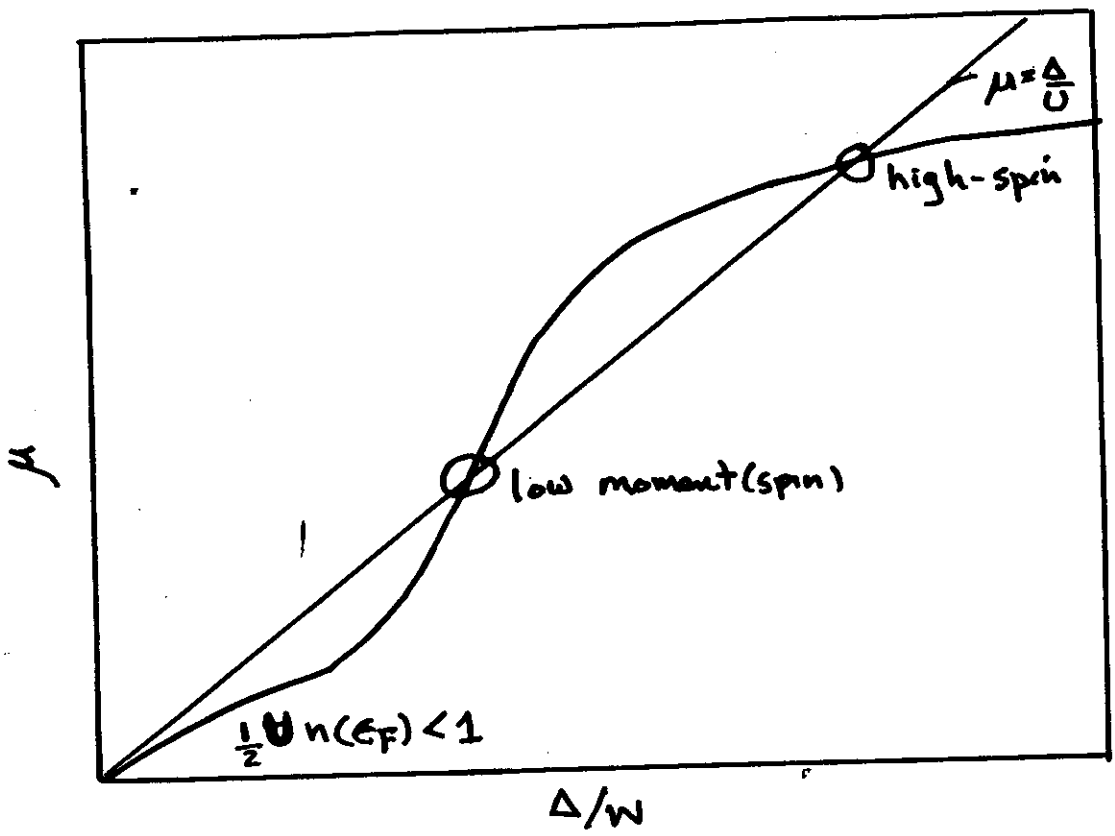
Kernel:

$$K(\vec{r}) = -\frac{1}{2} \left.\frac{\partial^2 E_{xc}}{\partial m^2}\right|_{m(\vec{r})=0}$$

I increases to right of row (Z larger):
more compact orbitals (d only)

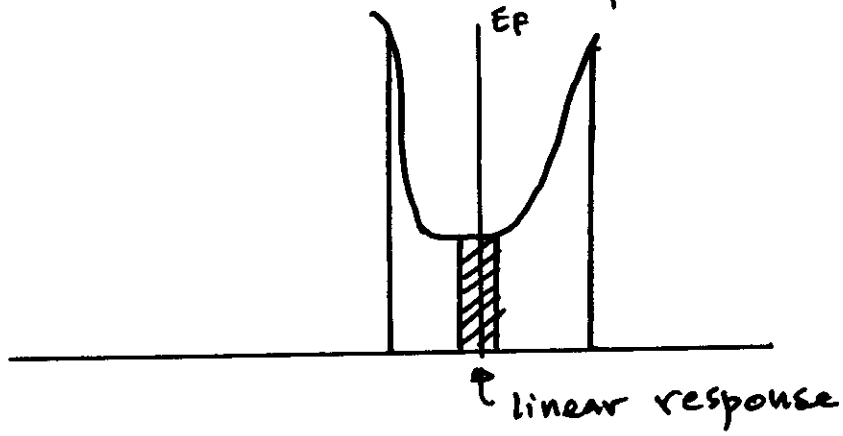
Stoner parameter





Linear response not always correct;

possible to have multiple solutions.



Aside:

Green's functions / resolvent (matrix)

$$(E-H)\,G(E) = 1 \Rightarrow G(E) = (E-H)^{-1}$$

poles at eigenvalues of H

spectral representation:

$$G(E,\vec{r},\vec{r}') = \sum_c \frac{\psi_c^*(\vec{r}')\,\psi_c(\vec{r})}{\epsilon-\epsilon_c+i\delta}$$

Let $(E-H_0)\,G_0 = 1$

$$(E-H)\,G = [E-(H_0+V)]\,G = 1$$

$$G_0\left[\underbrace{(E-H_0)}_{G_0^{-1}} - V\right] G = G_0$$

$$[1 - G_0 V]\,G = G_0 \Rightarrow \boxed{G = G_0 + G_0 V G}$$ Dyson's Eq.

$$\Rightarrow \quad G = [1 - G_0 V]^{-1} G_0$$

If properties of ideal system are known (G_0), then can obtain the perturbed system.

Green's functions (cont'd)

$$G(\epsilon) = h(\epsilon) - i\pi n(\epsilon)$$

($n(\epsilon)$: density of states)

$$h(\epsilon) = \mathcal{P} \int_{-\infty}^{+\infty} d\omega \, \frac{n(\omega)}{\epsilon - \omega}$$

Direct connection to spectral properties.

$$G(\epsilon) = \frac{G_0(\epsilon)}{1 - G_0 V} = \frac{h_0 - i\pi n_0}{1 - (h_0 - i\pi n_0)}$$

$$= \frac{(h_0 - i\pi n_0)(1 - h_0 - i\pi n_0)}{(1 - h_0 V)^2 + (\pi n_0 V)^2}$$

$$= \frac{\left[h_0(1 - h_0) - \pi^2 n_0^2\right] - i\pi n_0(\epsilon)}{(1 - h_0 V)^2 + (\pi n_0 V)^2}$$

Density of states of perturbed system:

$$n(\epsilon) = \frac{n_0(\epsilon)}{(1 - h_0 V)^2 + (\pi n_0 V)^2}$$

Model for correlations, magnetism, impurities

(Clogston-Wolff model, Cini-Swatsky)

Site representation:

$$G(E) = \sum_k |k\rangle \frac{1}{\epsilon - \epsilon_k + i\delta} \langle k|$$

site orbitals $|i\rangle$

$$G(E) = \sum_{ij} \sum_k |i\rangle\langle i|k\rangle \frac{1}{\epsilon - \epsilon_k + i\delta} \langle k|j\rangle\langle j|$$

$$= \sum_{ij} |i\rangle \left(\sum_k \langle i|k\rangle \frac{\langle k|j\rangle}{\epsilon - \epsilon_k + i\delta} \right) \langle j|$$

$$= \sum_{ij} G_{ij}(E)$$

Identity:

$$G^2(E) = -\frac{\partial G(E)}{\partial E}$$

$$G(E) = (E-H)^{-1}$$

$$\frac{\partial G(E)}{\partial E} = -\frac{1}{(E-H)^{-2}} = -\frac{1}{(E-H)}\frac{1}{(E-H)} = -G^2(E)$$

Formally:

$$\frac{\partial G(E)}{\partial E} = \lim_{\delta E \to 0} \frac{G(E+\delta E) - G(E)}{\delta E}$$

$$= \lim_{\delta E \to 0} \frac{1}{\delta E}\left[(E+\delta E - H)^{-1} - (E-H)^{-1} \right]$$

$$= \lim_{\delta E \to 0} \frac{1}{\delta E}\left[(E-\underbrace{(H-\delta E)}_{V})^{-1} - (E-H)^{-1} \right]$$

$$(E-(H-\delta E))^{-1} = (E-H)^{-1} + (E-H)^{-1}(-\delta E)(E-(H-\delta E))^{-1}$$

$$= (E-H)^{-1} + (E-H)^{-1}(-\delta E)(E-H)^{-1} + \mathcal{O}(\delta E^2)$$

$$\frac{\partial G(E)}{\partial E} = \lim_{\delta E \to 0} \frac{1}{\delta E}\left[(E-H)^{-1} + (E-H)^{-1}(-\delta E)(E-H)^{-1} + \mathcal{O}(\delta E^2) - (E-H)^{-1} \right]$$

$$= \lim_{\delta E \to 0} \frac{1}{\delta E}(-\delta E)(E-H)^{-1}(E-H)^{-1} + \frac{1}{\delta E}\mathcal{O}(\delta E^2) = -G^2(E)$$

Linear response:

$$G_1 = G_0 + G_0 V G_0$$

Let potential actual locally on each site

$$V_\pm = \mp \sum_k \Delta_k$$

In site representation

$$G^{(\pm)}_{ij} = G^0_{ij} \mp \sum_k G^0_{ik} \Delta_k G^0_{kj}$$

On site density is given by

$$n_i^{(\pm)} = -\frac{1}{\pi} \mathrm{Im}\, G^{\pm}_{ii}(E) = -\frac{1}{\pi} \mathrm{Im} \left[G^0_{ii} \mp \sum_k G^0_{ik} \Delta_k G^0_{ki} \right]$$

moment:

$$m_i = \int^{E_F} dE \left[n_i^+(E) - n_i^-(E) \right] = \mathrm{Im} \frac{1}{\pi} \sum_k \Delta_k \int^{E_F} dE\, G^0_{ik} G^0_{ki}$$

$$\equiv \sum_k \chi_{ik} \Delta_k$$

$$\chi_{ik} = \mathrm{Im} \frac{1}{\pi} \int_{-\infty}^{E_F} dE'\, G^0_{ik}(E)\, G^0_{ki}(E)$$

Non-local susceptibility

Local susceptibility χ_{oo}

$$\chi_{oo}(E_F) = \mathrm{Im}\frac{1}{\pi}\int_{-\infty}^{E_F} dE \left(G^0_{oo}(E)\right)^2$$

$$= \frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{E_F} dE \left[h(E) - i\pi n(E)\right]^2$$

$$= -\frac{1}{\pi}\pi 2\int_{-\infty}^{E_F} dE\; h(E)\, n(E)$$

$$= -2\int_{-\infty}^{E_F} dE\; n(E) \oint_{-\infty}^{+\infty} dz\; \frac{n(z)}{E-z}$$

Contributions from states in all of band, occupied and unoccupied. Atomic exchange

Sum rule:

$$\sum_i \chi_{oi} = \frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{E_F} dE \sum_i \left[G^0_{oi}(E)\right]^2$$

$$= -\frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{E_F} dE \sum_i \frac{\partial}{\partial E} G^0_{oi}$$

$$= -\frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{E_F} dE\, \frac{\partial}{\partial E} G_0(E) = -\frac{1}{\pi}\,\mathrm{Im}\, G^0(E_F)$$

$$= n(\epsilon_F)$$

Susceptibility:

$$\vec{m}_i = \sum_j \chi_{ij} \vec{m}_j$$

For different orderings, $\chi(\vec{q})$; enhancement is

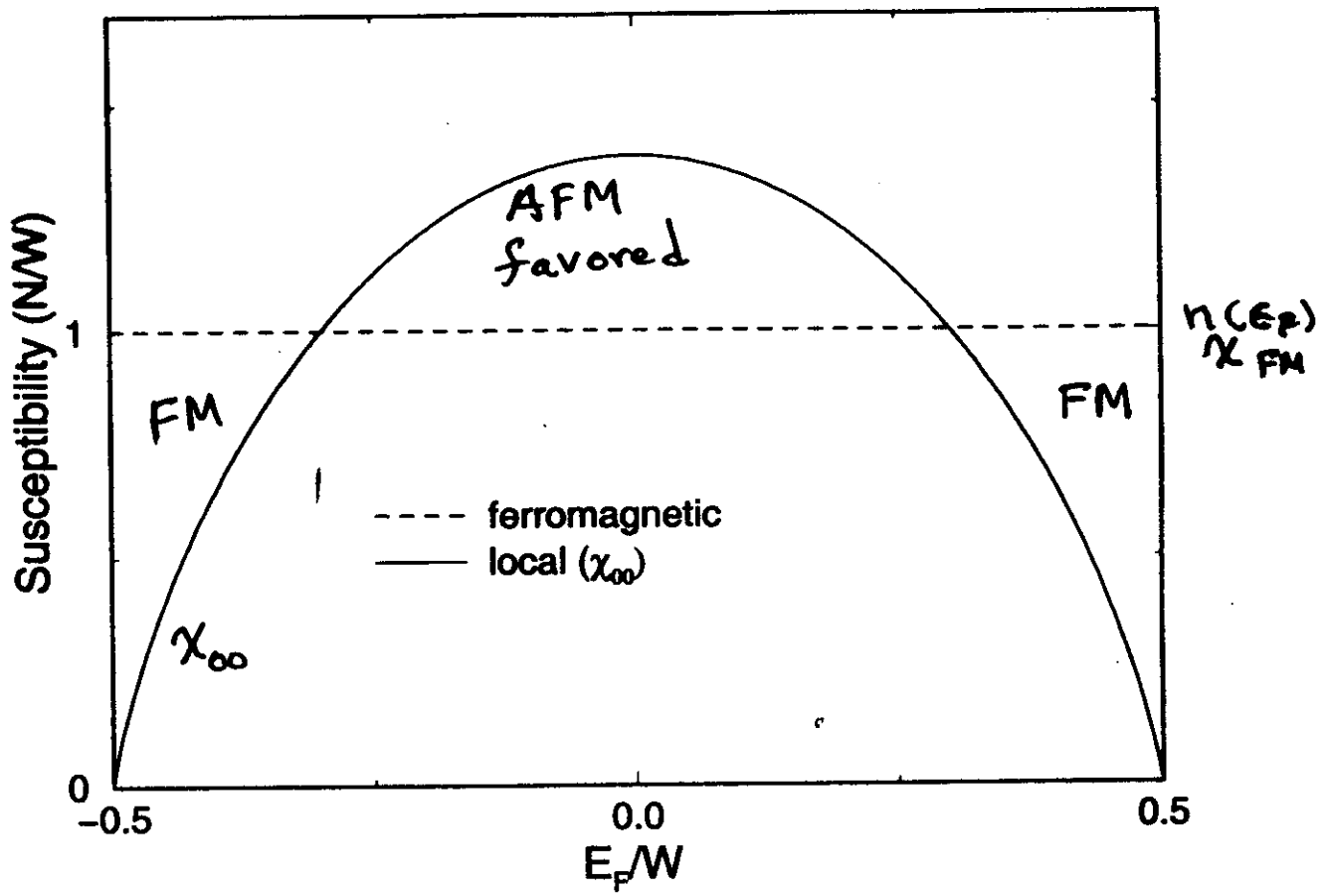
$$\frac{\chi(\vec{q})}{\chi_0(q)} = \frac{1}{1 - \frac{1}{2} I \chi_0(\vec{q})}$$

Valid for FM or AFM. Stoner criterion is

$$\frac{1}{2} I \chi_0(q) > 1$$

for instability

Non-local χ_{ij} is long-ranged, depending on the states.



$$\chi_{AFM} \approx \chi_{oo} - \sum_{i \neq o} \chi_{oi} = 2\chi_{oo} - \underbrace{\chi_{FM}}_{n(\epsilon_F)}$$

$$\Rightarrow \chi_{AFM} - \chi_{FM} = 2(\chi_{oo} - n(\epsilon_F))$$

---

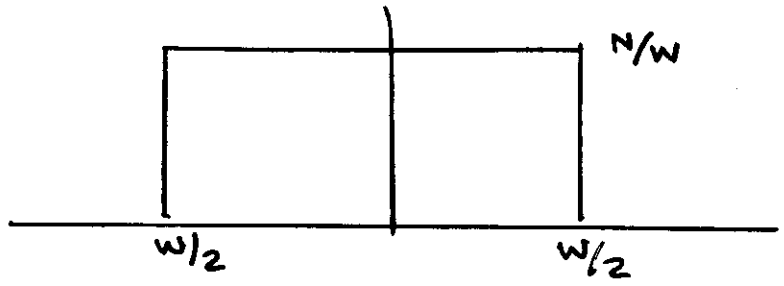
rectangular density of states:

$$n(\epsilon_F) = N/W$$

$$\chi_{oo} = \frac{N}{W}\left[2\ln 2 - (1+x)\ln(1+x) - (1-x)\ln(1-x)\right]$$

$$x = \frac{2\epsilon_F}{W}$$

Rectangular DOS (model for d-bands)



$$n(\epsilon) = \frac{N}{W}$$

$$h(\epsilon) = \int_{-\infty}^{+\infty} dz \, \frac{n(z)}{E-z} = \int_{-W/2}^{W/2} dz \, \frac{N}{W} \, \frac{1}{\epsilon - z}$$

$|\epsilon| \leq W/2$

$$= \lim_{\delta \to 0} \frac{N}{W} \int_{-W/2}^{\epsilon-\delta} \frac{dz}{E-z} + \frac{N}{W} \int_{\epsilon+\delta}^{W/2} \frac{dz}{E-z}$$

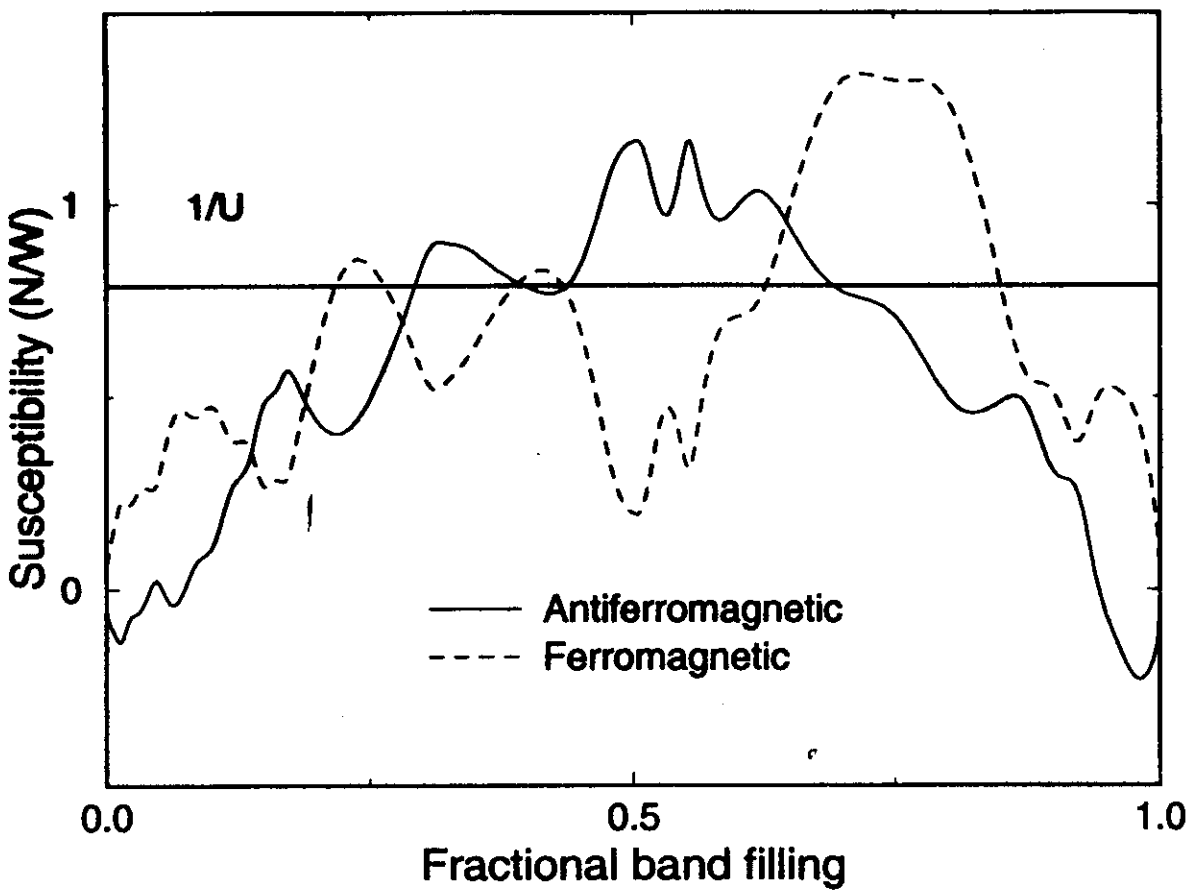
$$= \frac{N}{W} \lim_{\delta \to 0} \left[-\ln \frac{\delta}{\epsilon + W/2} - \ln \frac{W/2 - \epsilon}{\delta} \right]$$

$$= \frac{N}{W} \ln \frac{\frac{W}{2} + \epsilon}{\frac{W}{2} - \epsilon}$$

$$\chi_{00}(E_F) = -2 \frac{1}{N} \int_{-W/2}^{\epsilon_F} d\epsilon \, \frac{N}{W} \frac{N}{W} \ln \frac{\frac{W}{2} + \epsilon}{W/2 - \epsilon}$$

$$\Rightarrow \chi_{00}(\epsilon_F) = \frac{N}{W} \left[-(1+x)\ln(1+x) - (1-x)\ln(1-x) + 2\ln 2 \right]$$

$$x = \frac{2\epsilon_F}{W}$$



Model DOS : χ_{00} & χ_{FM}

same trends : AFM favored in middle of row

existence of magnetic phase depend on value of U ; U greater at end

max. in χ_{00} ($> \chi_{FM}$) origin in Hund's rule (spin alignment $\Rightarrow \chi = \frac{\partial M}{\partial H}$ largest.)

General Magnetic Coupling

$$\mathcal{H}_{MF} = \sum_{k\sigma} \epsilon_k a^{+}_{k\sigma} a_{k\sigma}$$

$$+ I \sum_{i\sigma} \langle c^{+}_{i\bar{\sigma}} c_{i\bar{\sigma}} \rangle c^{+}_{i\sigma} c_{i\sigma}$$

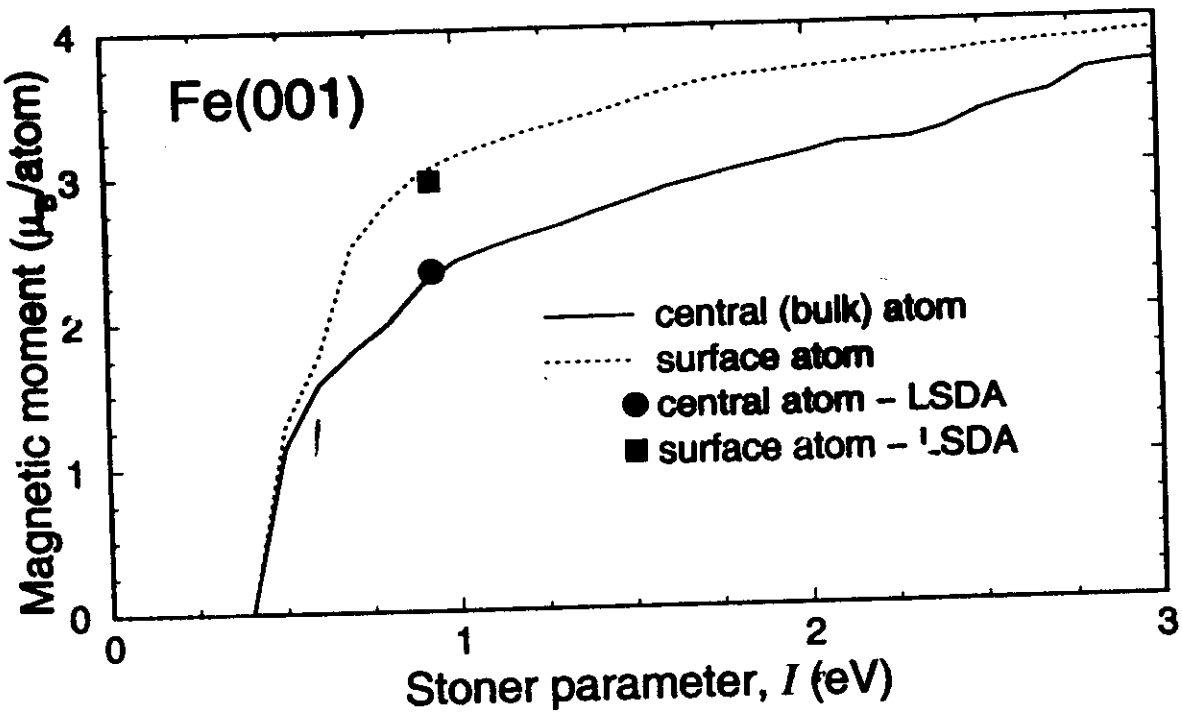
Same self-consistency conditions

$$\Delta_i = I \mu_i(\Delta_i)$$

All magnetic couplings treated equivalently

Simple to include in tight-binding approach

or even in first-principles calculations

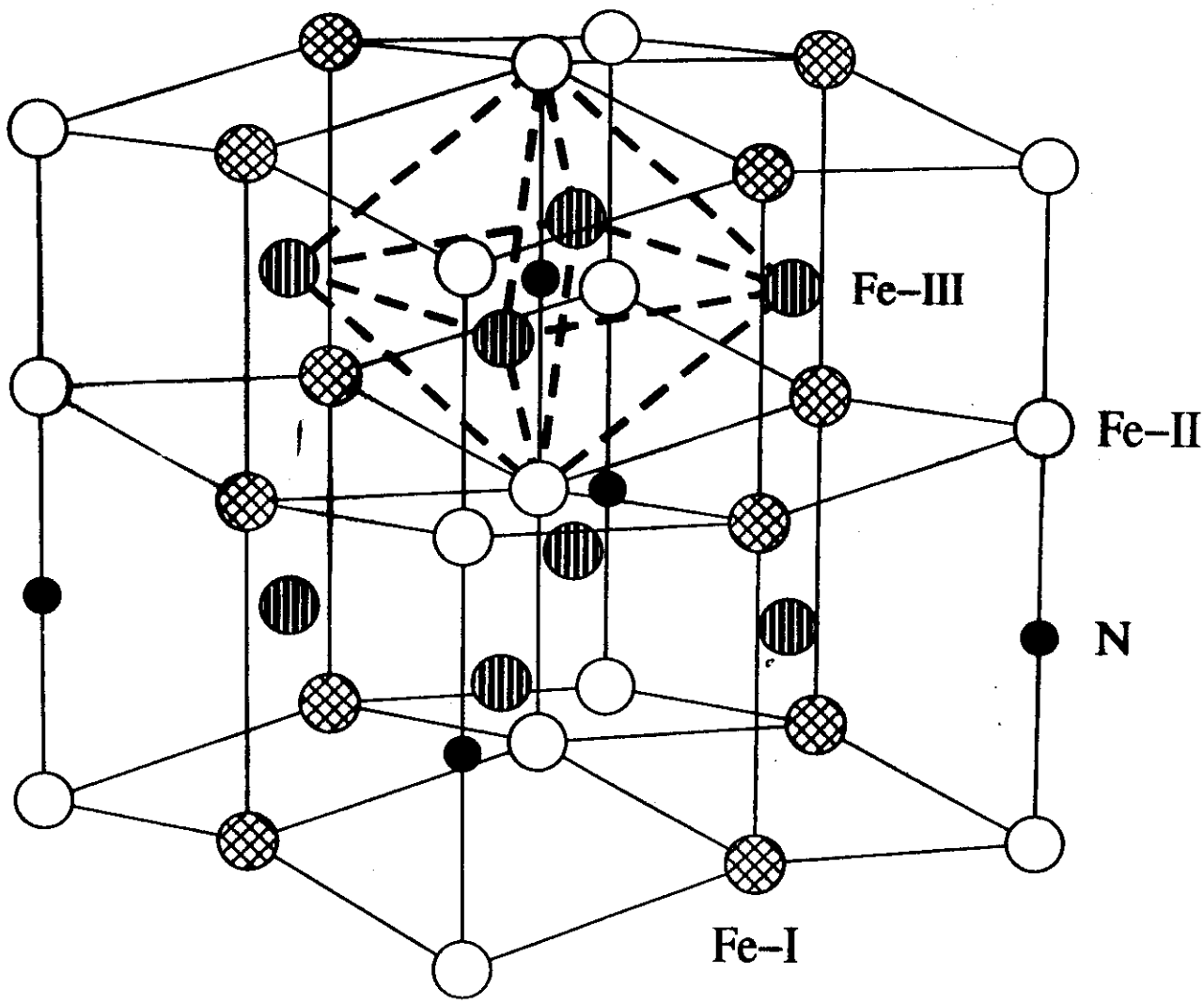


Starting from paramagnetic LDA bands,

including rehybridization effects.

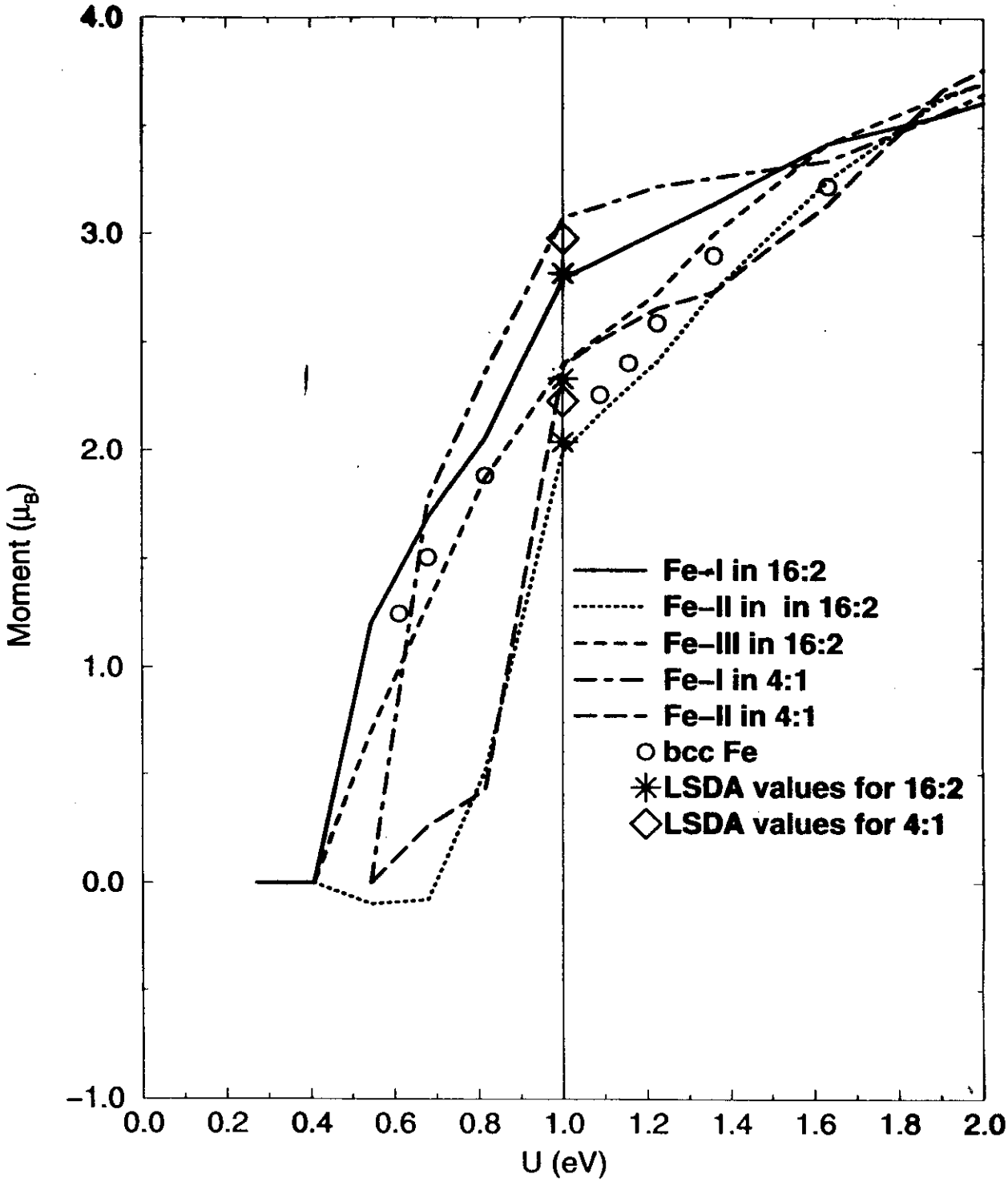
LSDA & generalized model agree well

moments depend on strength of I



Fe_8N : possibly large (~3.5μ_B/Fe) moments

(Mössbauer spectroscopy – hyperfine fields)



Large Fe μ. possible, but only for large I

(~ 1.8 times larger than for other Fe systems)

First-principles calculations

Only Fe, Co, Ni predicted ferromagnetic.

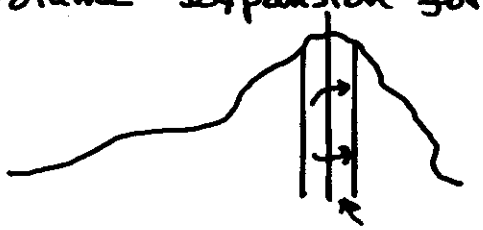
Cr, Mn " antiferromagnetic.

Moments in good agreement with experiment:

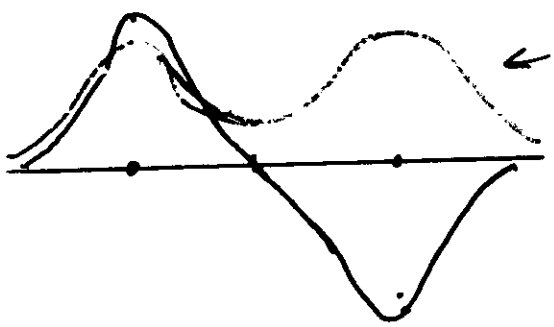
$\mu_s(Fe) \approx 2.2\ \mu_B$

$\mu_s(Ni) \approx 0.56\ \mu_B$

Volume expansion for magnetic system



more antibonding, higher kinetic energy

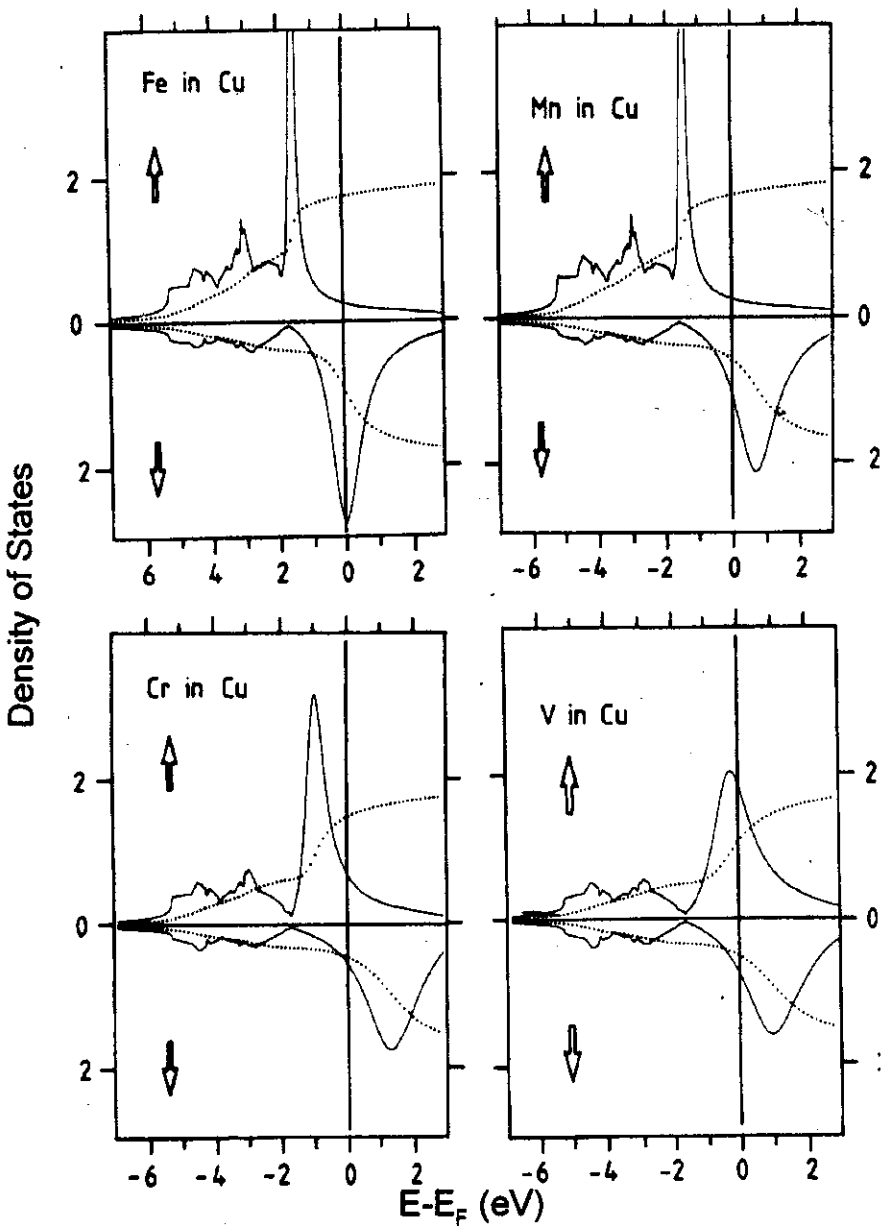


← bonding

expansion relieves kinetic energy

Fe few % effect

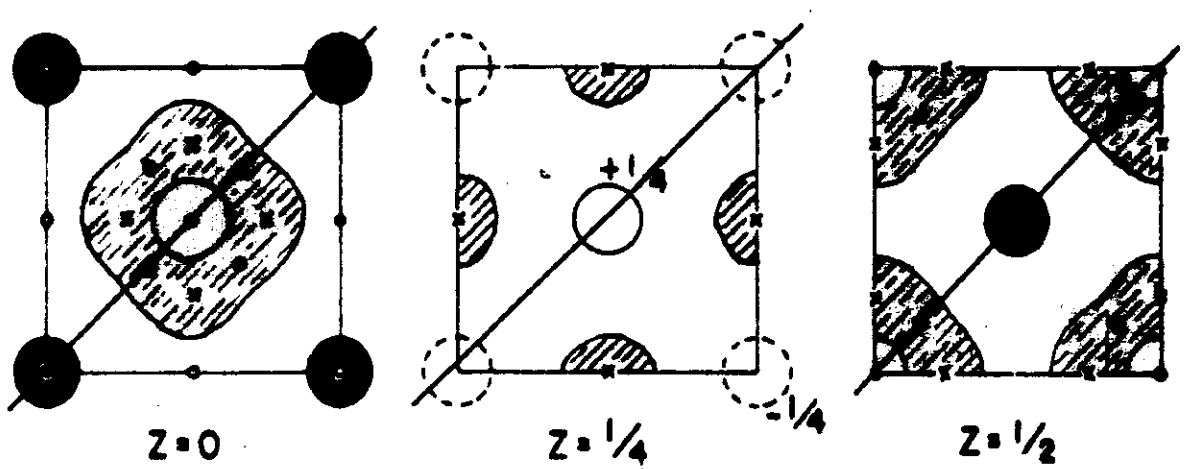
Ni <1% "



Local moment formation:

- single impurities in Cu
- virtual bound states

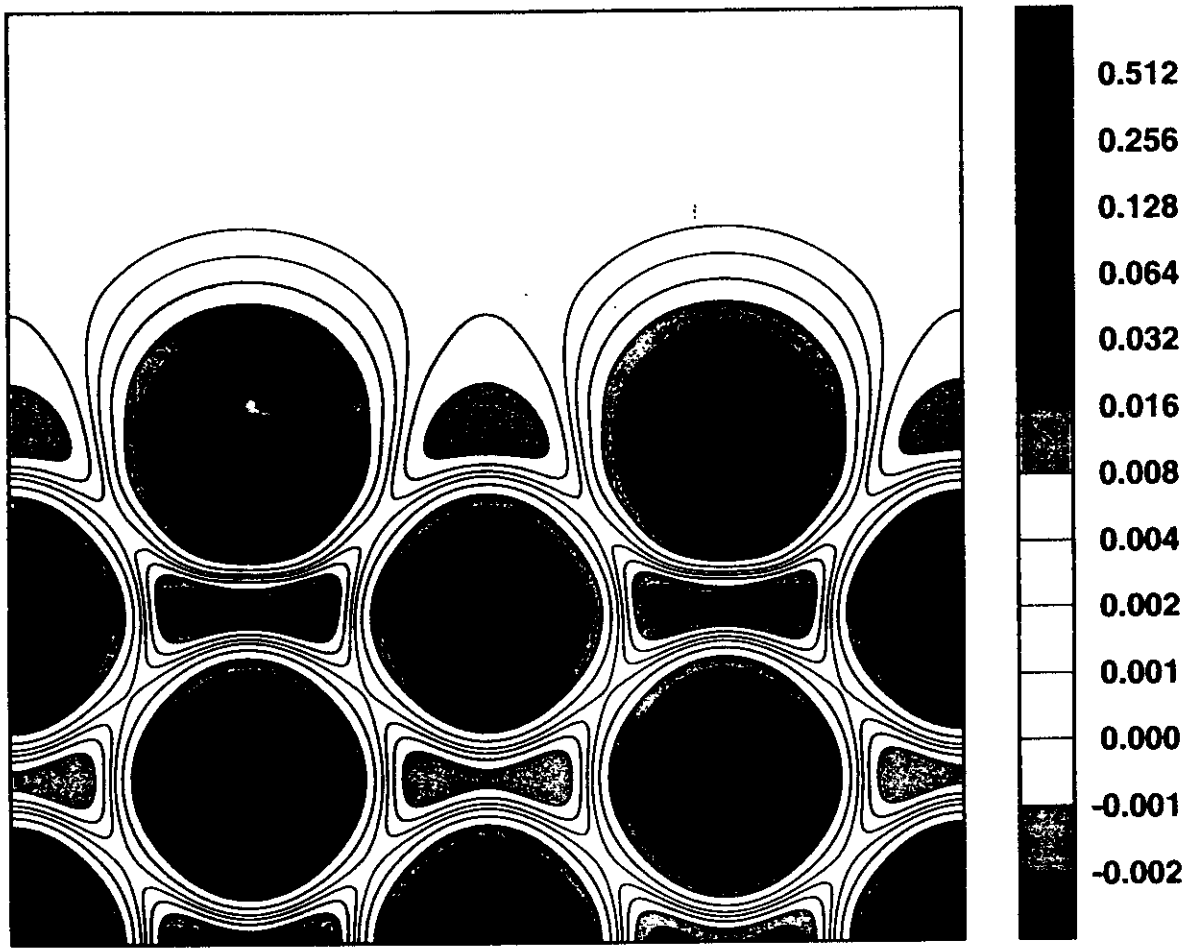
Fe magnetization density from neutron scattering



Negative spin density in interstitial regions

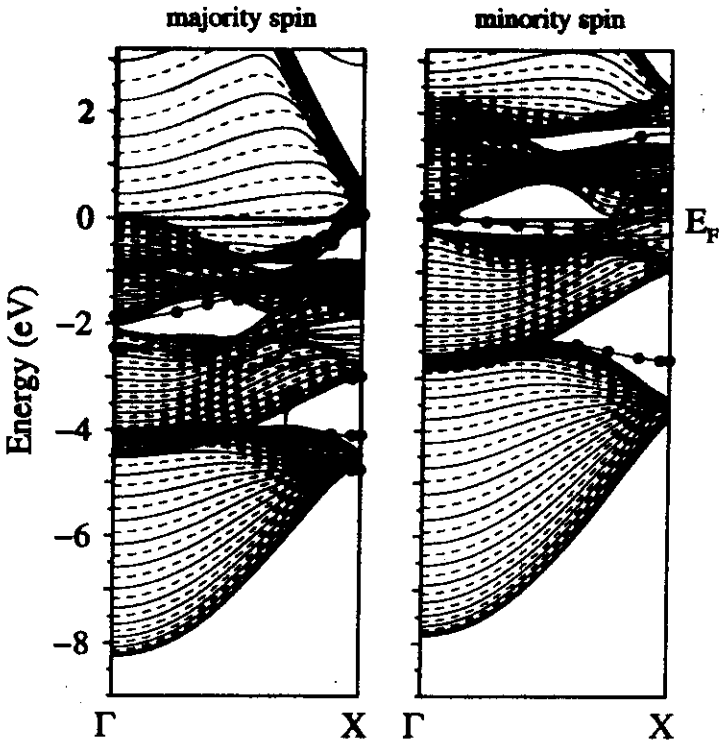
Schull and Mook, PRL 16, 184 (1966)

Fe(001) Spin Density



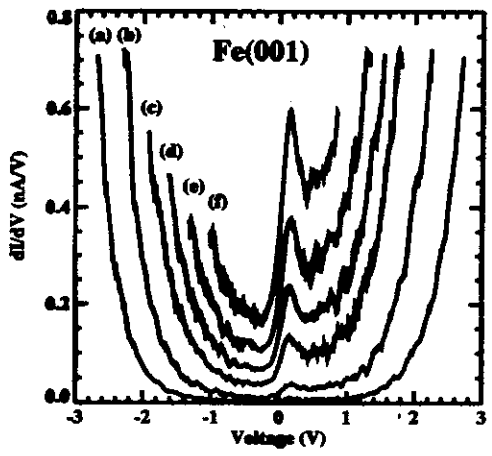
Fe(001)

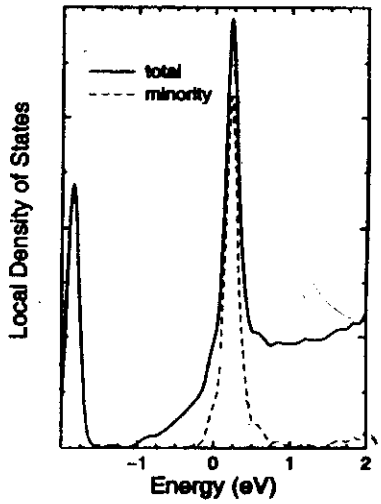
Bulk and Surface States:



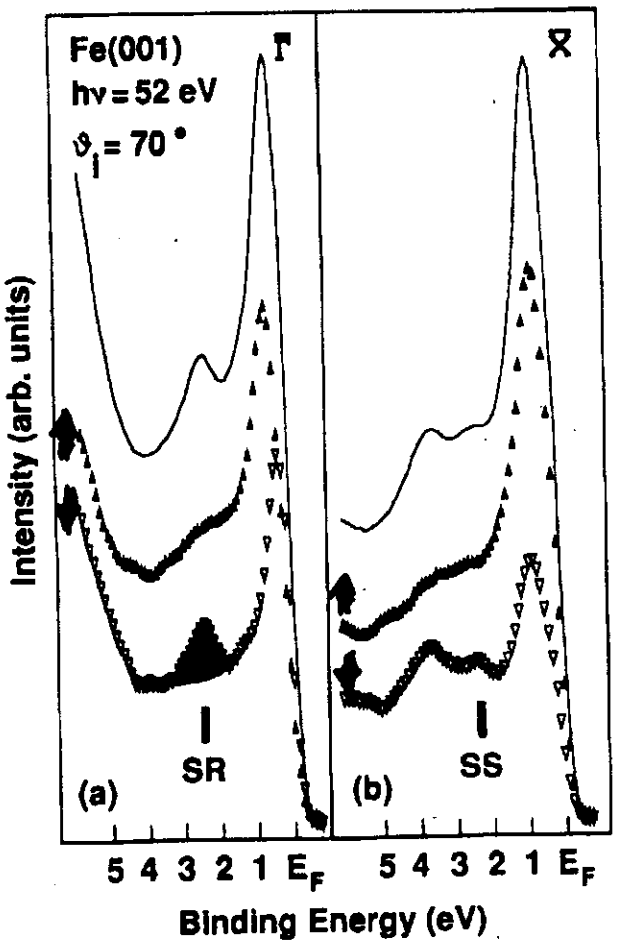
- Well studied: ARPES, STS
- Good agreement between theory and experiment
- Magnetic surface states

Scanning Tunneling Spectroscopy:

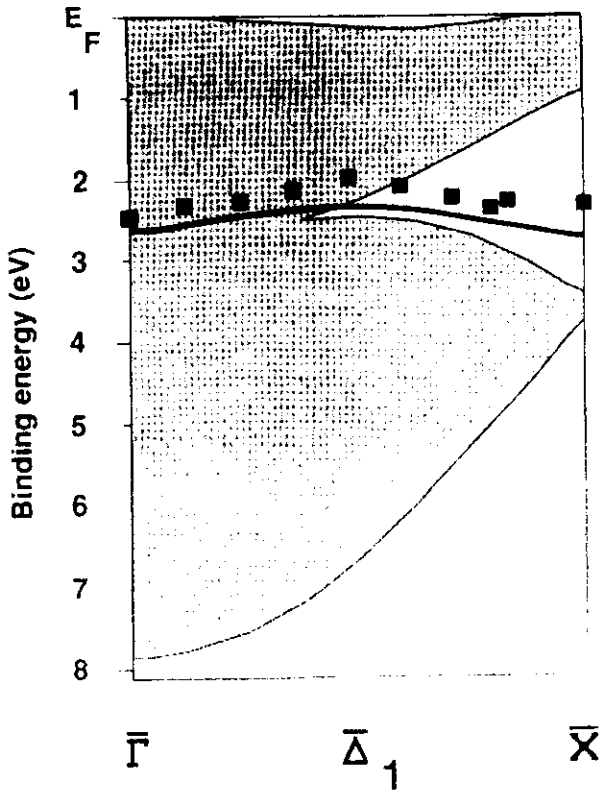




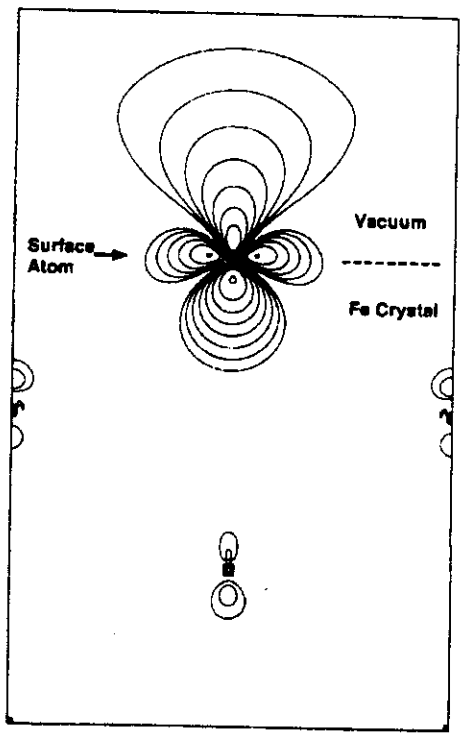
PRL 75, 2960 (95)



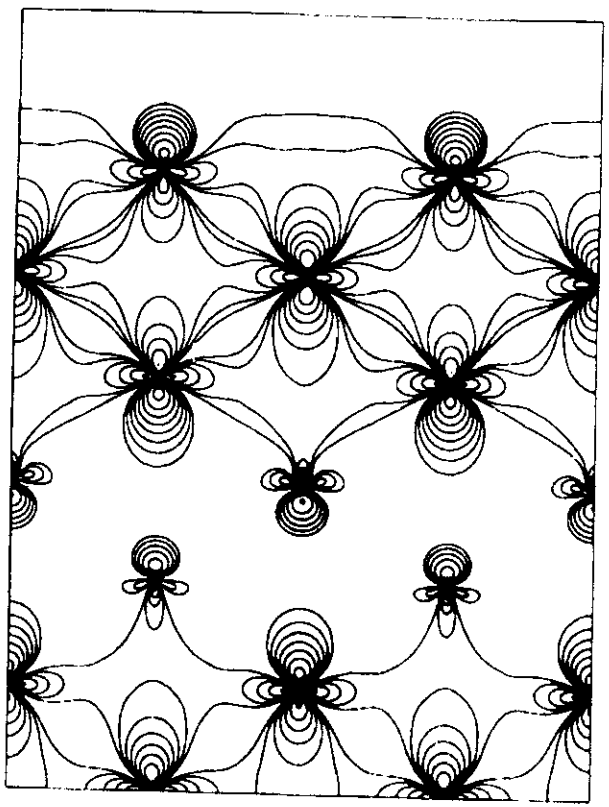
Spin-polarized photoemission



Minority states: theory and experiment



minority surface state



minority surface resonance

Orbital Moments: $\langle L_z \rangle$

Atomic picture - large moments; for transition metals, $\ell = 2$; major contribution to moment is orbital

Experimentally, small orbital moments in solids.

WHY?

"Quenching" due to crystal field

$$V(\vec{r}) = V_0(r) + \sum_L V_L(r) Y_L(\hat{r})$$

For atoms, only V_0 and $[L_z, V_0] = 0$

$\Rightarrow$ eigenfunctions of L_z also

Solid: $[L_z, V] = \sum_{\ell m} m V_{\ell m}(r) Y_{\ell m} \neq 0$

Not eigenfunctions of $L_z \Rightarrow \langle L_z \rangle = 0$.

Quenching, Part II.

Let $\psi_{\vec{k}}(\vec{r})$ and $\psi_{-k}(\vec{r})$ be eigenfunctions of H

$$H\psi_k(\vec{r}) = \epsilon_k \psi_k(\vec{r}) \; ; \; H\psi_{-k}(\vec{r}) = \epsilon_{-k}\psi_{-k}(\vec{r})$$

$$\left(H\psi_k\right)^* = \left(\epsilon_k \psi_k\right)^* \Rightarrow H\psi_k^* = \epsilon_k \psi_k^*$$

Bloch form:

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_k(\vec{r})$$

$$\psi_{\vec{k}}^*(\vec{r}) = e^{-i\vec{k}\cdot\vec{r}} u_k^*(\vec{r})$$

$$\psi_{\vec{k}}^*(\vec{r}+\vec{t}) = e^{-i\vec{k}\cdot(\vec{r}+\vec{t})} u_k^*(\vec{r}) = \underline{e^{-i\vec{k}\cdot\vec{t}}} \psi_{\vec{k}}^*(\vec{r})$$

transforms as function with $-\vec{k}$, hence

$$\psi_{-k}(\vec{r}) = e^{i\theta} \psi_k^*(\vec{r})$$

Time reversal symmetry

Let $\psi_k(\hat{r}) = \sum_L a_L Y_{\ell m}(\hat{r})$

$$\psi_{-k}(\hat{r}) = e^{i\theta} \sum_L a_L^* Y_{\ell m}^*(\hat{r})$$

$$= e^{i\theta} \sum_L a_L^* (-1)^m Y_{\ell -m}(\hat{r})$$

$$\langle \psi_k | L_z | \psi_k \rangle = \sum_{LL'} a_{L'}^* a_L \langle Y_{\ell' m'} | L_z | Y_{\ell m} \rangle$$

$$m \, \delta_{L'L}$$

$$= \sum_L |a_L|^2 m$$

$$\langle \psi_{-k} | L_z | \psi_{-k} \rangle = \sum_{LL'} a_{L'} a_L^* (-1)^{m'+m} \langle Y_{\ell -m'} | L_z | Y_{\ell -m} \rangle$$

$$= m \, \delta_{L'L}$$

$$= -\sum_L |a_L|^2 m$$

$$\Rightarrow \langle \psi_{-k} | L_z | \psi_{-k} \rangle = -\langle \psi_k | L_z | \psi_k \rangle$$

Since $\epsilon_{-k} = \epsilon_k$, both states enter with equal weight $\Rightarrow \langle L_z \rangle = 0$

To get orbital moment, need to break symmetry.

Spin-orbit interaction

$\xi \vec{L} \cdot \vec{S}$ of relativistic origin.

Couples spin and orbital. Energy will depend on angle between $\vec{L}$ & $\vec{S}$

Magnetic field will then break time-reversal symmetry, and hence $\langle L_z \rangle \neq 0$, although small.

Choice of $\vec{S}$ will change coupling of states $\Rightarrow$ magnetocrystalline anisotropy (easy axis)

Time reversal symmetry

$$T = \sigma K \qquad \sigma_y \begin{pmatrix} \downarrow \\ \uparrow \end{pmatrix} \sim \begin{pmatrix} \uparrow \\ \downarrow \end{pmatrix}$$

→ flips spin and angular momentum

$$T\,\vec{L}\cdot\vec{S}\,T = (-\vec{L})\cdot(-\vec{S}) = \vec{L}\cdot\vec{S}$$

Time reversal ⇒ $\epsilon_{k\sigma} = \epsilon_{-k-\sigma}$

Without magnetic field, nothing new.

With field

$$\epsilon_{k\sigma} \to \epsilon_{k\sigma} + \sigma B$$

$$\epsilon_{-k-\sigma} \to \epsilon_{k\sigma} - \sigma B$$

Then no longer cancellation between states of $\pm\vec{k}$ ⇒ $\langle L_z \rangle \neq 0$

Magnetocrystalline anisotropy:

Include spin-orbit in Hamilton, choosing different directions for the spin.

$\Rightarrow$ Energy differences between directions

Cubic systems: $\Delta E \sim \xi^4$

Surfaces ($\ell=1$ potential) $\Delta E \sim \xi^2$

possibly much larger at surface than bulk; also different

$$a_i^\dagger a_i |n_i\rangle = n_i |n_i\rangle$$

$$a_i a_i^\dagger |n_i\rangle = (1-n_i)|n_i\rangle$$

$$\Rightarrow a_i^\dagger a_i + a_i a_i^\dagger = 1$$

2. Eigenvector:

$$\gamma_k = B_1 a_{k+} + B_2 a_{k-} + B_3 a_{k+q+} + B_4 a_{k+q-}$$

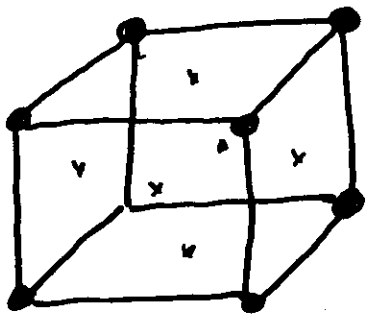
$\gamma_k^\dagger |0\rangle$ is the eigenvector

Assume we operator $\hat{A}$. Then

$\langle 0 | \gamma_k A \gamma_k^\dagger |0\rangle \Rightarrow$

$$B_1^2 (a_{k+} \hat{A} a_{k+}^\dagger) + B_2^2 (a_{k-} \hat{A} a_{k-}^\dagger)$$
$$+ B_3^2 (a_{k+q+} \hat{A} a_{k+q+}^\dagger) + B_4^2 (a_{k+q-} \hat{A} a_{k+q-}^\dagger)$$
$$+ B_1 B_2 (a_{k+} \hat{A} a_{k-}^\dagger + a_{k-} \hat{A} a_{k+}^\dagger)$$
$$+ B_1 B_3 (a_{k+} \hat{A} a_{k+q+}^\dagger + a_{k+q+} \hat{A} a_{k+}^\dagger)$$
$$+ B_1 B_4 (a_{k+} \hat{A} a_{k+q-}^\dagger + a_{k+q-} \hat{A} a_{k+}^\dagger)$$
$$+ B_2 B_3 (a_{k-} \hat{A} a_{k+q+}^\dagger + a_{k+q+} \hat{A} a_{k-}^\dagger)$$
$$+ B_2 B_4 (a_{k-} \hat{A} a_{k+q-}^\dagger + a_{k+q-} \hat{A} a_{k-}^\dagger)$$
$$+ B_3 B_4 (a_{k+q+} \hat{A} a_{k+q-}^\dagger + a_{k+q-} \hat{A} a_{k+q+}^\dagger)$$

Cu_3Au structure (fcc)



Au: 12 Cu neighbors

Cu: 4 Au, 8 Cu

Assuming χ_{oi}° non-zero only for nearest neighbors.

For each site:

$$\sum_{c} \chi_{oc}(E_F) = n_o(E_F)$$

$$= \chi_{oo}(E_F) + \sum_{nn} \chi_{oi}^{\circ}(\epsilon_F)$$

From $n_c(\epsilon_F) \leftrightarrow \chi_{oo}^{c}(E_F)$,

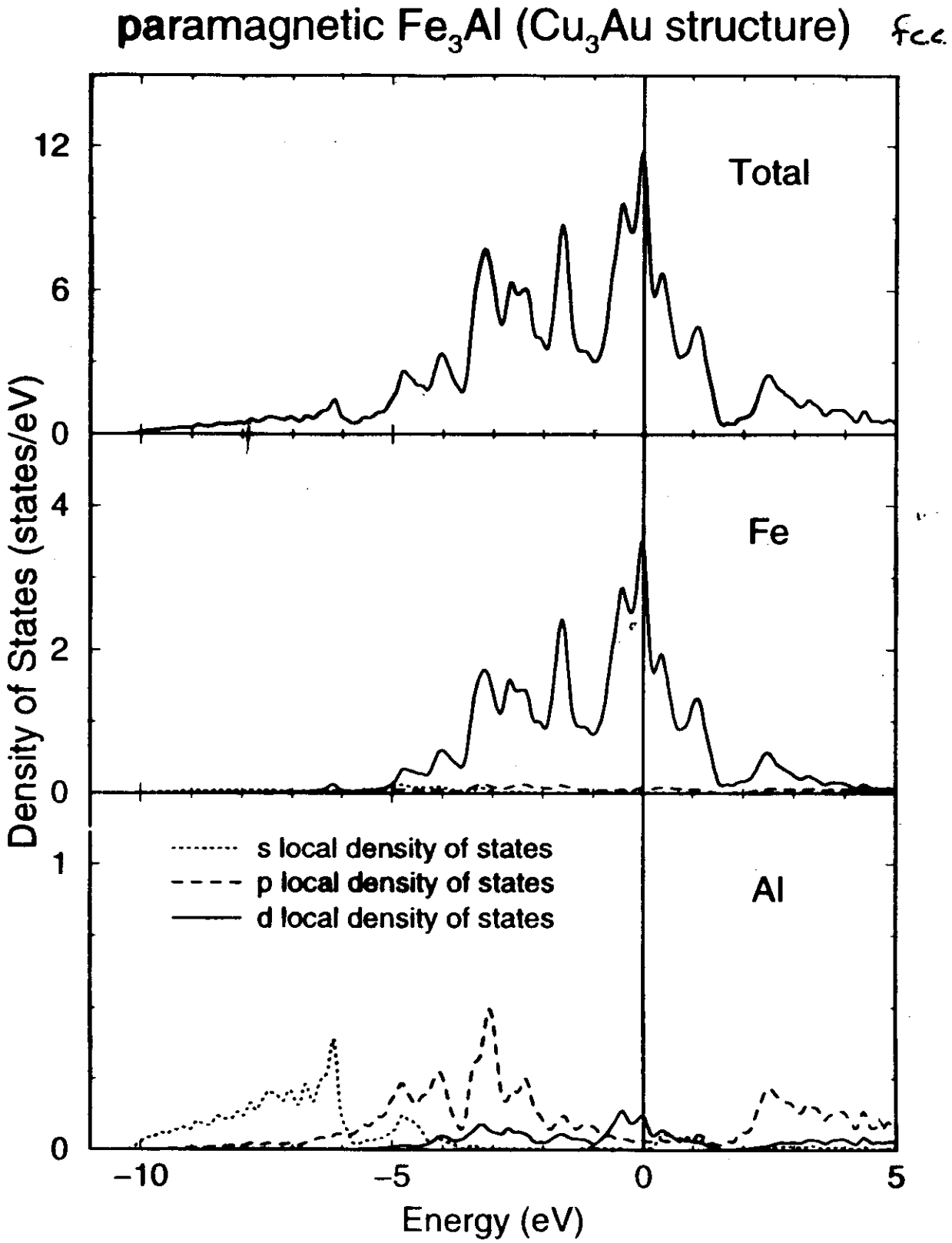
Au site: $\chi_{oo}^{Au} + 12\,\chi_{Au\text{-}Cu} = n_{Au}(\epsilon_F)$

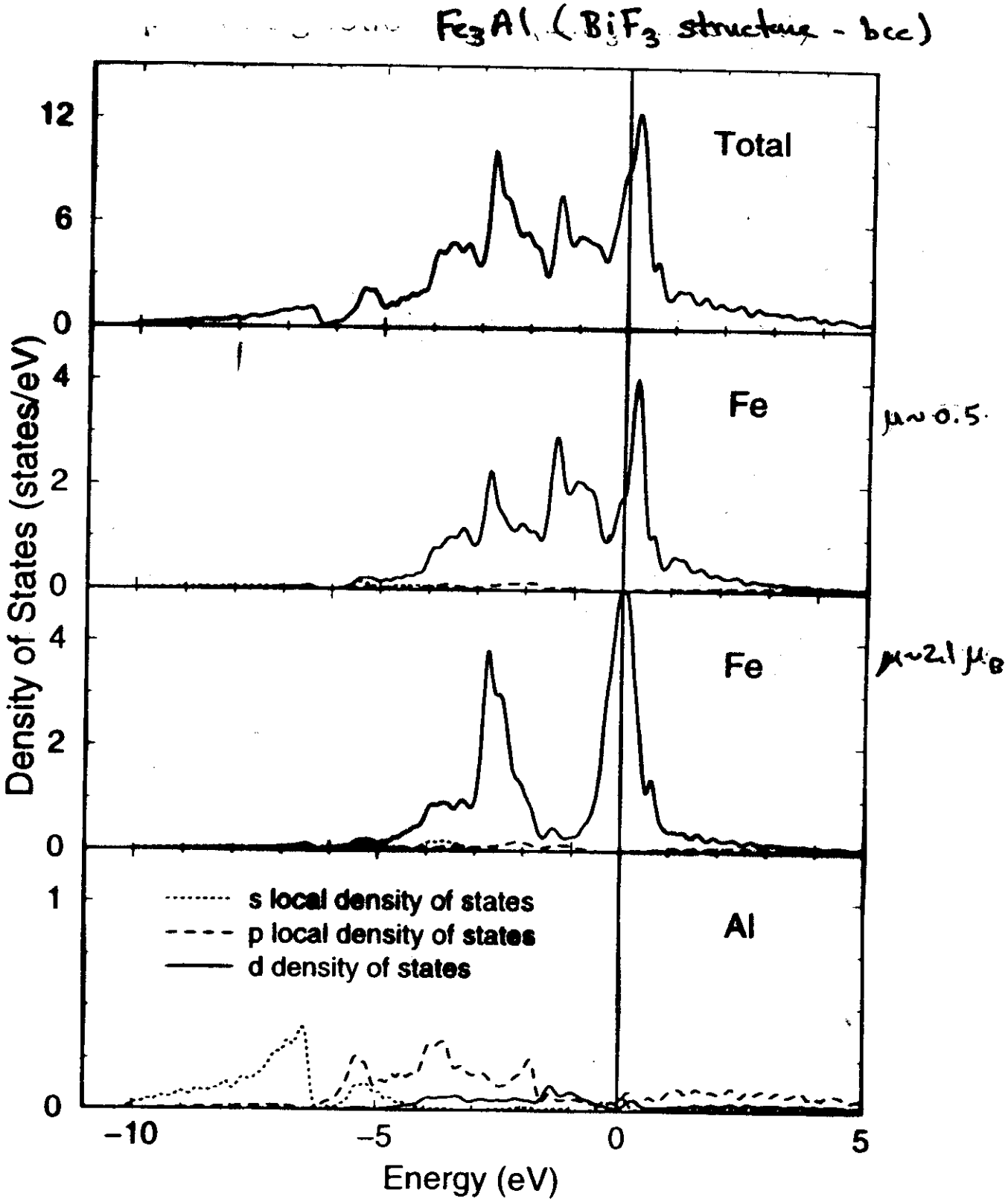
$$\Rightarrow \chi_{Au\text{-}Cu} = \frac{1}{12}\left[n_{Au}(\epsilon_F) - \chi_{oo}^{Au} \right]$$

Cu site: $\chi_{oo}^{Cu} + 4\,\chi_{Au\text{-}Cu} + 8\,\chi_{Cu\text{-}Cu} = n_{Cu}(\epsilon_F)$

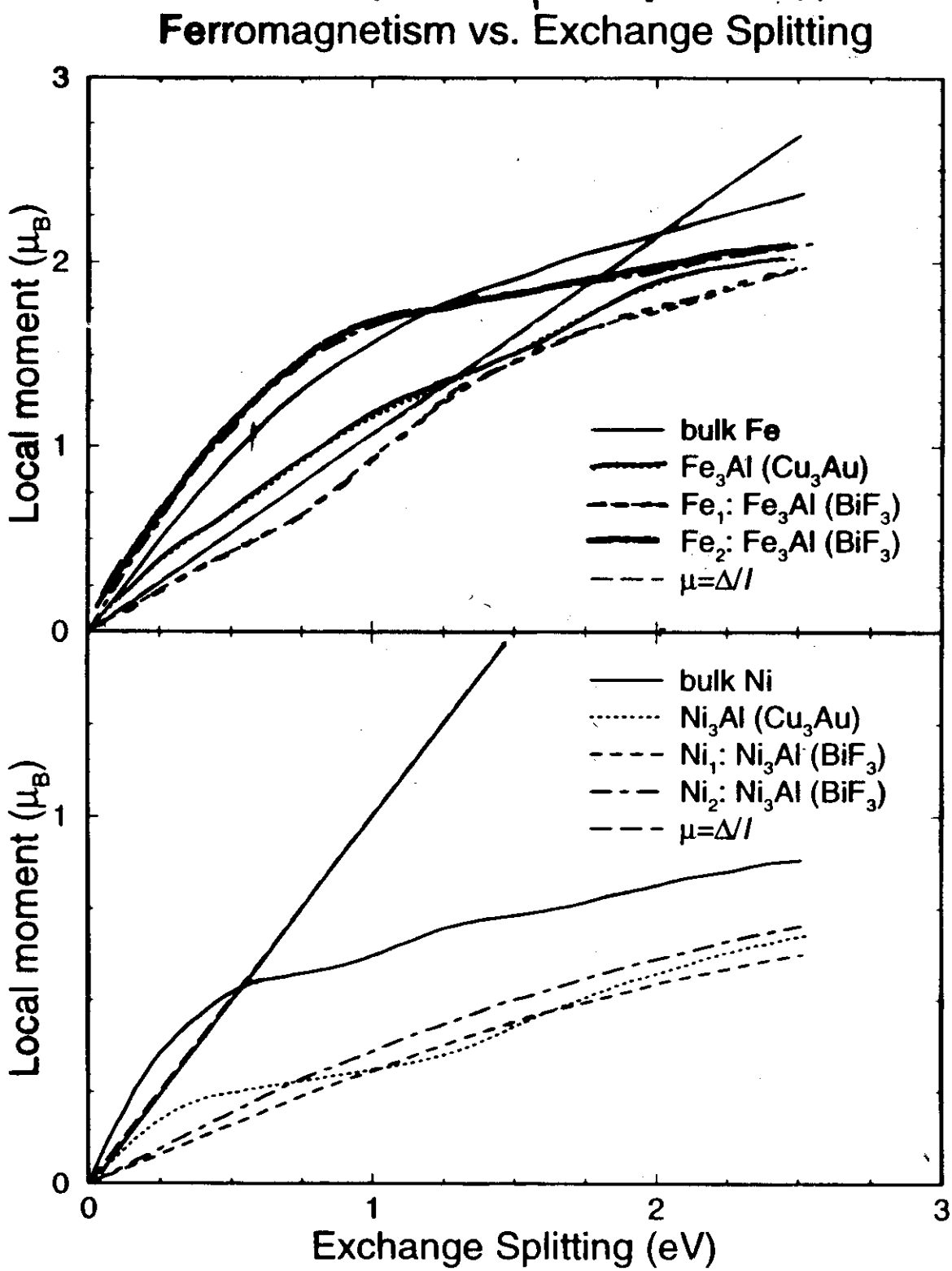
$$\chi_{Cu\text{-}Cu} = \frac{1}{8}\left[n_{Cu}(\epsilon_F) - \chi_{oo}^{Cu} - 4\,\chi_{Au\text{-}Cu} \right]$$

$$= \frac{1}{8}\left[n_{Cu}(\epsilon_F) - \chi_{oo}^{Cu} - \frac{1}{3}\left\{ n_{Au}(\epsilon_F) - \chi_{oo}^{Au} \right\} \right]$$


paramagnetic Fe_3Al (Cu_3Au structure) fcc
Total
Fe
Al
s local density of states
p local density of states
d local density of states
Density of States (states/eV)
Energy (eV)
12
6
0
4
2
0
1
0
−10
−5
0
5


Fe_3Al (BiF_3 structure - bcc)
Total
Fe
Fe
Al
$\mu \sim 0.5$
$\mu \sim 2.1\ \mu_B$
s local density of states
p local density of states
d density of states
Density of States (states/eV)
Energy (eV)
12
6
0
4
2
0
4
2
0
1
0
−10
−5
0
5

Linear response, local approximation.



Spherical potential: B field

	-.000002	-.000001	.000000	.000001	.000002
eigenvector	1:				
	1	1.0000	.0000		
	2	.0000	.0000		
	3	.0000	.0000		
	4	.0000	.0000		
	5	.0000	.0000		
===> <L_z> =	-2.000000				
eigenvector	2:				
	1	.0000	.0000		
	2	1.0000	.0000		
	3	.0000	.0000		
	4	.0000	.0000		
	5	.0000	.0000		
===> <L_z> =	-1.000000				
eigenvector	3:				
	1	.0000	.0000		
	2	.0000	.0000		
	3	1.0000	.0000		
	4	.0000	.0000		
	5	.0000	.0000		
===> <L_z> =	.000000				
eigenvector	4:				
	1	.0000	.0000		
	2	.0000	.0000		
	3	.0000	.0000		
	4	1.0000	.0000		
	5	.0000	.0000		
===> <L_z> =	1.000000				
eigenvector	5:				
	1	.0000	.0000		
	2	.0000	.0000		
	3	.0000	.0000		
	4	.0000	.0000		
	5	1.0000	.0000		
===> <L_z> =	2.000000				

	-.000002	-.000001	.000000	.000001	.000002
eigenvector	1:				
	xy	.7071	.0000		
	xz	.0000	.0000		
	yz	.0000	.0000		
	3z^2-r^2	.0000	.0000		
	x^2-y^2	-.7071	.0000		
===> <L_z> =	-2.000000				
eigenvector	2:				
	xy	.0000	.0000		
	xz	.7071	.0000		
	yz	-.7071	.0000		
	3z^2-r^2	.0000	.0000		
	x^2-y^2	.0000	.0000		
===> <L_z> =	-1.000000				
eigenvector	3:				
	xy	.0000	.0000		
	xz	.0000	.0000		
	yz	.0000	.0000		
	3z^2-r^2	-1.0000	.0000		
	x^2-y^2	.0000	.0000		
===> <L_z> =	.000000				
eigenvector	4:				
	xy	.0000	.0000		
	xz	.7071	.0000		
	yz	.7071	.0000		
	3z^2-r^2	.0000	.0000		
	x^2-y^2	.0000	.0000		
===> <L_z> =	1.000000				
eigenvector	5:				
	xy	.7071	.0000		
	xz	.0000	.0000		
	yz	.0000	.0000		
	3z^2-r^2	.0000	.0000		
	x^2-y^2	.7071	.0000		
===> <L_z> =	2.000000				

Cubic potential

-.003708 -.003708 -.003708 .005561 .005561

eigenvector 1:

xy	.0000	.0000
xz	1.0000	.0000
yz	.0000	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	.0000	.0000

===> <L_z> = .000000

eigenvector 2:

xy	.0000	.0000
xz	.0000	.0000
yz	1.0000	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	.0000	.0000

===> <L_z> = .000000

eigenvector 3:

xy	1.0000	.0000
xz	.0000	.0000
yz	.0000	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	.0000	.0000

===> <L_z> = .000000

eigenvector 4:

xy	.0000	.0000
xz	.0000	.0000
yz	.0000	.0000
3z^2-r^2	-1.0000	.0000
x^2-y^2	.0000	.0000

===> <L_z> = .000000

eigenvector 5:

xy	.0000	.0000
xz	.0000	.0000
yz	.0000	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	1.0000	.0000

===> <L_z> = .000000

Cubic potential with B

-.003709 -.003708 -.003707 .005561 .005561

eigenvector 1:

xy	.0000	.0000
xz	.7071	.0000
yz	-.7071	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	.0000	.0000

===> <L_z> = -1.000000

eigenvector 2:

xy	1.0000	.0000
xz	.0000	.0000
yz	.0000	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	-.0002	.0000

===> <L_z> = -.000863

eigenvector 3:

xy	.0000	.0000
xz	.7071	.0000
yz	.7071	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	.0000	.0000

===> <L_z> = 1.000000

eigenvector 4:

xy	.0000	.0000
xz	.0000	.0000
yz	.0000	.0000
3z^2-r^2	-1.0000	.0000
x^2-y^2	.0000	.0000

===> <L_z> = .000000

eigenvector 5:

xy	.0002	.0000
xz	.0000	.0000
yz	.0000	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	1.0000	.0000

===> <L_z> = .000863

Tetragonal:

-.005510 -.002806 -.002806 .003759 .007364

eigenvector 1:

xy	1.0000	.0000
xz	.0000	.0000
yz	.0000	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	.0000	.0000

===> <L_z> = .000000

eigenvector 2:

xy	.0000	.0000
xz	1.0000	.0000
yz	.0000	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	.0000	.0000

===> <L_z> = .000000

eigenvector 3:

xy	.0000	.0000
xz	.0000	.0000
yz	1.0000	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	.0000	.0000

===> <L_z> = .000000

eigenvector 4:

xy	.0000	.0000
xz	.0000	.0000
yz	.0000	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	1.0000	.0000

===> <L_z> = .000000

eigenvector 5:

xy	.0000	.0000
xz	.0000	.0000
yz	.0000	.0000
3z^2-r^2	-1.0000	.0000
x^2-y^2	.0000	.0000

===> <L_z> = .000000

Tetragonal with B

-.005510 -.002807 -.002805 .003759 .007364

eigenvector 1:

xy	1.0000	.0000
xz	.0000	.0000
yz	.0000	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	-.0002	.0000

===> <L_z> = -.000863

eigenvector 2:

xy	.0000	.0000
xz	.7071	.0000
yz	-.7071	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	.0000	.0000

===> <L_z> = -1.000000

eigenvector 3:

xy	.0000	.0000
xz	.7071	.0000
yz	.7071	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	.0000	.0000

===> <L_z> = 1.000000

eigenvector 4:

xy	.0002	.0000
xz	.0000	.0000
yz	.0000	.0000
3z^2-r^2	.0000	.0000
x^2-y^2	1.0000	.0000

===> <L_z> = .000863

eigenvector 5:

xy	.0000	.0000
xz	.0000	.0000
yz	.0000	.0000
3z^2-r^2	-1.0000	.0000
x^2-y^2	.0000	.0000

===> <L_z> = .000000

Arbitary potential (spherical harmonic basis)

	-.048852	-.006914	.001732	.020124	.033910
eigenvector	1:				
	1	-.1852	-.5060		
	2	-.4275	.1163		
	3	-.1342	-.0938		
	4	.0378	.4414		
	5	-.5388	.0000		
===> <L_z> =	.000000				
eigenvector	2:				
	1	-.2924	-.2317		
	2	-.5600	.1954		
	3	-.0027	.0078		
	4	-.3239	-.5059		
	5	.3730	.0000		
===> <L_z> =	.000000				
eigenvector	3:				
	1	-.0773	-.2663		
	2	.1612	.1389		
	3	.5220	-.6951		
	4	.1784	.1161		
	5	.2773	.0000		
===> <L_z> =	.000000				
eigenvector	4:				
	1	.1623	-.4031		
	2	.4589	.3167		
	3	.0144	.0213		
	4	-.1224	-.5439		
	5	-.4345	.0000		
===> <L_z> =	.000000				
eigenvector	5:				
	1	-.1834	.5208		
	2	-.2467	-.1609		
	3	.3800	-.2691		
	4	-.0698	-.2862		
	5	-.5521	.0000		
===> <L_z> =	.000000				

Arbitary basis

	-.048852	-.006914	.001732	.020124	.033910
eigenvector	1:				
	1	-.1852	-.5060		
	2	-.4275	.1163		
	3	-.1342	-.0938		
	4	.0378	.4414		
	5	-.5388	.0000		
===> <L_z> =	.000000				
eigenvector	2:				
	1	-.2924	-.2317		
	2	-.5600	.1954		
	3	-.0027	.0078		
	4	-.3239	-.5059		
	5	.3730	.0000		
===> <L_z> =	.000000				
eigenvector	3:				
	1	-.0773	-.2663		
	2	.1612	.1389		
	3	.5220	-.6951		
	4	.1784	.1161		
	5	.2773	.0000		
===> <L_z> =	.000000				
eigenvector	4:				
	1	.1623	-.4031		
	2	.4589	.3167		
	3	.0144	.0213		
	4	-.1224	-.5439		
	5	-.4345	.0000		
===> <L_z> =	.000000				
eigenvector	5:				
	1	-.1834	.5208		
	2	-.2467	-.1609		
	3	.3800	-.2691		
	4	-.0698	-.2862		
	5	-.5521	.0000		
===> <L_z> =	.000000				