A short introduction to the theoretical basis of X-ray absorption and related spectroscopies

Peter Krüger

Chiba University

October 2018

Outline I

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2. Basic electronic structure theory
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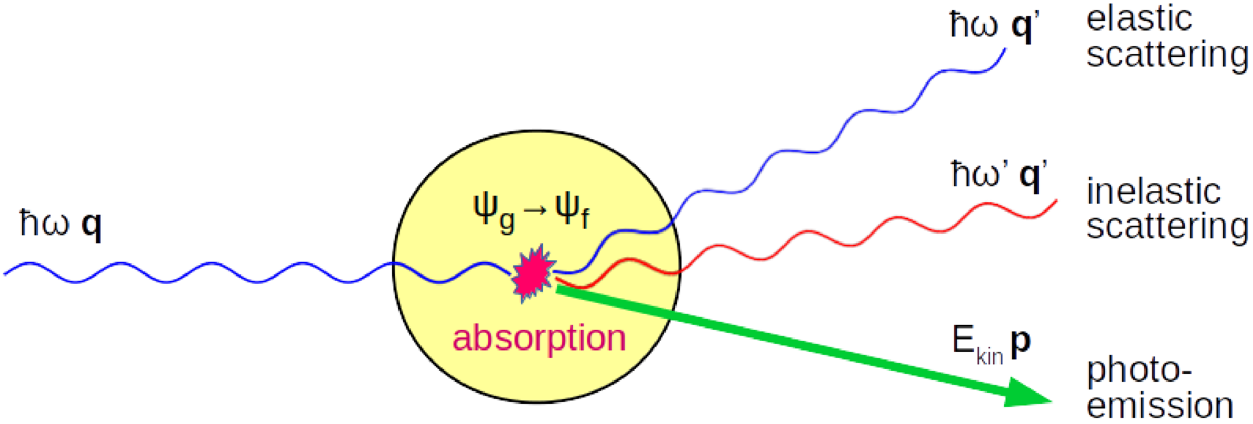
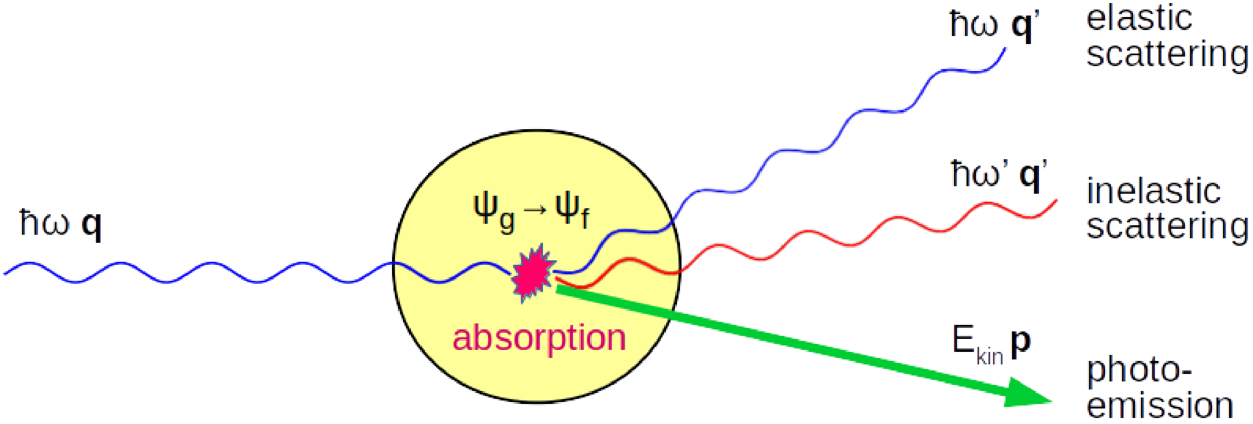
    - Density Functional Theory
3. X-ray absorption in independent particle approximation
    - Dipole selection rules
    - X-ray absorption and density of states
    - Linear dichroism and magnetic circular dichroism
4. Linear response and time-dependent DFT
5. Green's functions and quasi-particles
    - Self-energy(1) — GW approximation
    - Particle-hole interaction — Bethe-Salpeter Equation
6. Photoelectron spectroscopy
    - Core-level photoemission and photoelectron diffraction
    - Valence photoemission — spin- and angle-resolved
    - Self-energy(2) — Dynamical mean field theory

Light-Matter interaction

- photons (Energy $\hbar\omega$, wave vector $\mathbf{q}$) get absorbed or scattered in matter by electrons, in quantum states ψ_n
  – scattering off nuclei (→ phonons) is weak and not considered here
- $(\omega\mathbf{q}, \psi_g) \to (-, \psi_f)$ light absorption
- $(\omega\mathbf{q}, \psi_g) \to (\omega\mathbf{q}', \psi_g)$ elastic (Bragg) scattering: momentum transfer to lattice → structural probe (XRD)
- $(\omega\mathbf{q}, \psi_g) \to (\omega'\mathbf{q}', \psi_f)$ inelastic scattering: momentum and energy transfer to electrons → probes electronic excitations



Light-Matter interaction



- Absorption: $(\omega \mathbf{q}, \psi_n) \rightarrow (-, \psi_m)$ light absorption
- if $E_f > E_{\mathrm{vac}}$ then possible **photoelectron emission**
  Measure energy, angle, spin distribution
  → most direct information about electronic states

Light-Matter interaction

- $H = H_e + H_p + H_{\text{int}}$
- Here: classical treatment of light
  (quantized photon field: see J.J.Sakurai, Adv. Quantum Mechanics)
- electron momentum $\mathbf{p} \longrightarrow \mathbf{p} - e\mathbf{A}/c$

$$H_{\text{int}} = -\frac{e}{2mc}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}) + \frac{e^2}{2mc^2}A^2$$

- $\mathbf{A}$ vector potential. $\mathbf{E} = -\frac{1}{c}\partial\mathbf{A}/\partial t, \quad \mathbf{B} = \nabla \times \mathbf{A}$
- Electromagnetic wave $\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_0 \exp(i\mathbf{q}\cdot\mathbf{r} - i\omega t)$
- Coulomb gauge $\nabla \cdot \mathbf{A} = 0 \to \mathbf{p}\cdot\mathbf{A} - \mathbf{A}\cdot\mathbf{p} = -i\hbar\nabla\cdot\mathbf{A} = 0$
- Gauge freedom ? $\longrightarrow$ Christian Brouder's lecture
- $\mathbf{A}\cdot\mathbf{p} \to$ absorption/stimulated emission
- A^2 non-resonant scattering

Perturbation theory

- light-electron interaction is a weak coupling $\alpha = e^2/\hbar c = 1/137 \Rightarrow$ Perturbation theory in H_{int}.
- except for laser, light intensity/number of photons is small $\Rightarrow$ lowest order terms often sufficient
- transition rate for oscilating perturbation $H_{\text{int}}(t) = V \exp(-i\omega t)$

$$w_{fg} \equiv \frac{d}{dt} P_{f \leftarrow g} = \frac{2\pi}{\hbar} |\langle f|T|g\rangle|^2 \delta(E_f - E_g - \hbar\omega)$$

$$\langle f|T|g\rangle = \langle f|V|g\rangle + \sum_m \frac{\langle f|V^+|m\rangle\langle m|V|g\rangle}{\hbar\omega + E_g - E_m + i\Gamma_m/2} + \dots$$

1st order: Fermi's golden rule. 2nd order: Kramers-Heisenberg.

Transition amplitudes

- $V_o = \frac{e}{mc}\mathbf{A}\cdot\mathbf{p}$ 1-photon-electron interaction
- 1st order → photon absorption (+emission) $\langle f|T|g\rangle \sim \langle f|\mathbf{A}\cdot\mathbf{p}|g\rangle$
- 2nd order →

$$\langle f|T|g\rangle = \sum_m \frac{\langle f|V_o^+|m\rangle\langle m|V_o|g\rangle}{\hbar\omega + E_g - E_m + i\Gamma_m/2}$$

→ resonant scattering (inelastic: resonant Raman scattering)

- $V = V_o + V_{AI}$ autoionization operator: electron-electron scattering with continuum states ⟨ c,k$|1/r|$ p,q ⟩

$$\langle f|T|g\rangle = \sum_m \frac{\langle f|V_{AI}|m\rangle\langle m|V_o|g\rangle}{\hbar\omega + E_g - E_m + i\Gamma_m/2}$$

→ resonant Auger electron emission

Electronic structure theory

One-electron system, e.g. hydrogen atom. $H\psi = \epsilon\psi$.

$$\text{Bound states} \qquad \psi_{nlm}(\mathbf{r})\chi_s(\sigma) \qquad \epsilon_{nlms} = -\frac{13.6\ \text{eV}}{n^2}$$

$$\text{Scattering states} \qquad \psi_{\epsilon lm}(\mathbf{r})\chi_s(\sigma) \qquad \epsilon > 0 \quad (\text{any})$$

The wave functions $\psi(\mathbf{r})$ and all excitation energies are known exactly.

Atoms ($\neq$H), **molecules, solides**: $N_e > 1$ electrons $\Rightarrow$ trouble

$$H = \sum_i \left(-\frac{\hbar^2}{2m}\nabla_i^2 + V_{\text{nucl}}(\mathbf{r}_i) \right) + \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$H\Psi = E\Psi \ , \qquad \Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \ldots \mathbf{r}_N\sigma_N)$$

This electronic many-body problem cannot be solved exactly.
Strong approximations are needed.

Electronic structure theory

Most popular approaches for electron spectroscopy:

1. Hartree-Fock approximation
2. “Post-HF”, configuration interaction
3. Density functional theory
4. Time-dependent DFT
5. Quasi-particle Green’s function methods
    - GW approximation (semiconductors)
    - Dynamical mean field theory (strongly correlated systems)
6. Bethe-Salpeter equation

Pauli principle, Slater determinants

Simplest many-electron wave function: product of one-electron states (spin-orbitals). Why?

If $H(x_1, x_2) = H_a(x_1) + H_b(x_2)$ then $\Psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2)$

But electrons are indistinguishable → Pauli-principle
Ψ antisymmetric under exchange $\Psi(x_1, x_2) = -\Psi(x_2, x_1)$
Antisymmetrized product →

$$\Psi(x_1, x_2) = [\psi_a(x_1)\psi_b(x_2) - \psi_a(x_2)\psi_b(x_1)]/\sqrt{2}$$

N electrons → Slater-determinant

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \dots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \dots & \phi_2(x_N) \\ \dots & \dots & \dots & \dots \\ \phi_N(x_1) & \phi_N(x_2) & \dots & \phi_N(x_N) \end{vmatrix}$$

Hartree-Fock approximation

Assume ground state is Slater Determinant. HFA gives “best” orbitals.

$$H = \sum_i \left[\frac{1}{2} \nabla_i^2 + V_{\text{ext}}(\mathbf{r}_i) \right] + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

“Rayleigh-Ritz” variational principle

$$E[\Psi] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} , \qquad \frac{\delta E[\Psi]}{\delta \Psi} = 0$$

Assuming Ψ=Slater Deteterminant results in Hartree-Fock equations

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + \hat{V}_X \right] \phi_n(\mathbf{r}) = \epsilon_n \phi(\mathbf{r})$$

The ground state wave function is the Slater-determinant made of the $n = N_e/2$ orbitals of lowest energy. $\Psi^{HF} = |\phi_1 \dots \phi_n|$.

Hartree-Fock equations

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + \hat{V}_X\right]\phi_n(\mathbf{r}) = \epsilon_n(\mathbf{r})$$

In HF approximation, the dynamical electron-electron interaction is replaced by a static mean ("effective") field potential $V_H + V_X$.

$$V_H(\mathbf{r}) = \sum_m^{\text{occ}} \int d\mathbf{r}' \frac{|\phi_m(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

V_H "Hartree potential"= classical electrostatic potential of electronic charge density. Repulsive

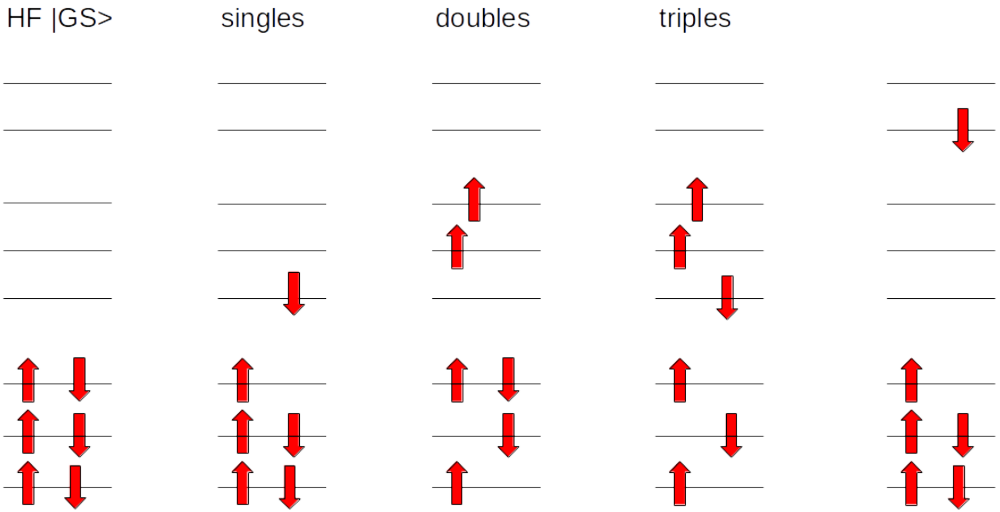
$$\hat{V}_X\ \phi_n(\mathbf{r}) = -\sum_m^{\text{same spin}} \int d\mathbf{r}' \frac{\phi_m^*(\mathbf{r}')\phi_m(\mathbf{r})\phi_n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

V_X "Exchange potential". No classical analogue. Due to antisymmetry of Ψ. Non-local. Attractive.

Configuration Interaction

- The HF (or "SCF=self-consistent field") method, is the standard in quantum chemistry / molecular orbital theory. It has been extremely successful for molecules.
- Difference between exact theory and HFA is called "correlation".
- The most straightforward method to include correlation effects is Configuration Interaction (C.I.)
- C.I. wave functions are linear combinations of Slater Determinants, including HF ground state and particle-hole excitations.
  How?

Configuration Interaction

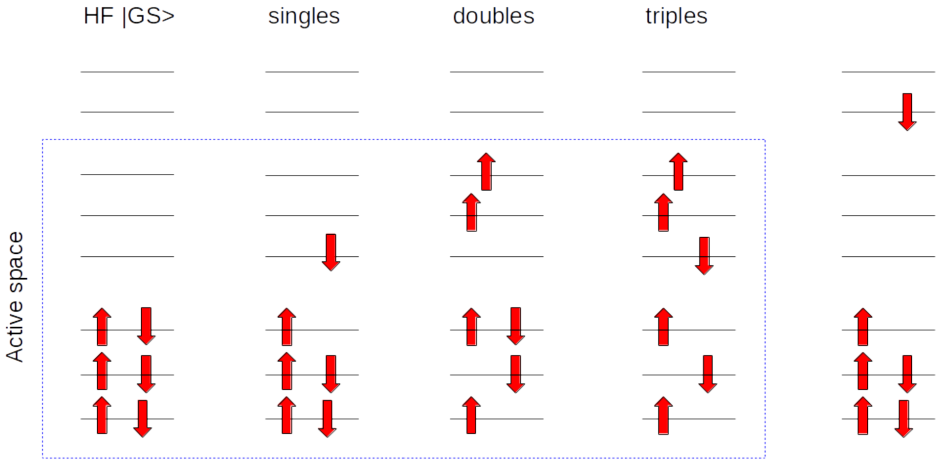


- compute HF orbitals $1, 2, \ldots n, n+1 \ldots \qquad (n = N_e/2)$
- build S.D. basis: not only the HF-GS $|1\;2 \ldots n|$, but also particle-hole excitations $|1 \ldots \underline{h_1} \ldots \underline{h_2} \ldots n\; p_1\; p_2|$
- diagonalize hamiltonian in the space of these SD
- → "correlated" wave functions = linear combination of S.D.

Configuration Interaction

- is very precise
- computational cost scales exponentially with number of electrons. $\Rightarrow$ full C.I. only possible for about 10 electrons (CH_4).
- restricted CI: e.g. only single + double particle-hole excitations
- "CAS-SCF" complete active space self-consistent field
  - select the "active space" = small set of molecular orbitals (around HOMO-LUMO) that you think are relevant for correlation
  - do CI calculation with all particle-hole excitations in active space
  - case of transition metal complexes:
    active space = MO's with dominant metal-*d* character.
  - implemented for *L*-edge XAS by Ogazawara, Ikeno et al.
    → "ab initio ligand field multiplet" method

Complete active space self-consistent field CAS-SCF



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Density Functional Theory (DFT)

Hartree-Fock is difficult for solids and performs poorly for metals

1964: DFT becomes a new paradigm for electronic structure theory

Idea: use electron density $n(\mathbf{r})$ as basic object of the theory rather than the many-electron wave functions $\Psi_n(\mathbf{r}_1, \ldots \mathbf{r}_N)$.

Hohenberg-Kohn theorems on interacting, inhomogenous electron gas:

1. Ground state electron density $n_0(\mathbf{r})$ uniquely determines external potential $V_{\text{ext}}(\mathbf{r})$ (and thus H and thus in principle Ψ_n)
2. The total energy is a unique functional of the density. The exact ground state density n_0 minimizes this functional.

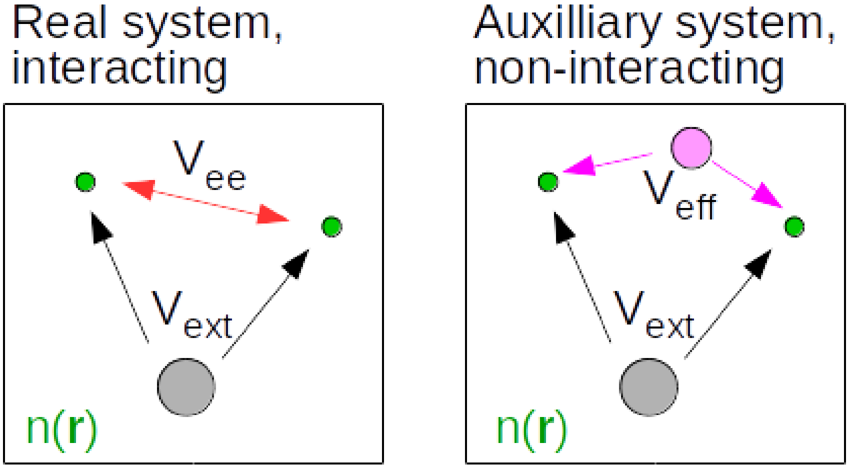
We all knew: $H \longrightarrow \Psi_n \longrightarrow n_0(\mathbf{r}) = \int dr_2 \ldots dr_N |\Psi_0(r, r_2 \ldots r_N)|^2$

HK showed: $H \longleftarrow V_{\text{ext}} \longleftarrow n_0(\mathbf{r})$.
and $E = F[n(\mathbf{r})]$, $\delta F = 0$ for $n = n_0$

Kohn-Sham Density Functional Theory

With the HK theorems, one may think that we don't need wave functions any more. Everything could be calculated directly from the denstiy $n(\mathbf{r})$. But the only practical DFT is Kohn-Sham theory, where single-particle orbitals are used, much like in HF theory.

K.S. introduced an auxiliary non-interacting system with the **same density** as the real interacting system, but a different external potential, called effective or Kohn-Sham potential V_{KS}.



Kohn-Sham Density Functional Theory

- The auxiliary system is non-interacting, so it can be solved exactly. The wave functions are Slater determinants made of orbitals ϕ_i corresponding to $V_{KS}(\mathbf{r})$.
- V_{KS} is not known exactly, must be approximated
- Make approximation to universal functional $E[n]$,
  i.e. to its unknown part, called "exchange-correlation" energy
  $E_{XC} = E_{\text{tot}} - E_{\text{ext}} - E_H - E^0_{\text{kin}}$
  Functionals: Local Density Approx, GGA, hybrid=HF+GGA
- $V_{KS} = V_{\text{ext}} + V_H + V_{XC}, \qquad V_{XC}(\mathbf{r}) = \delta E_{XC}[n]/\delta n(\mathbf{r})$

$$\begin{tikzcd}
V_{\text{ext}}(\mathbf{r}) \arrow[d, Rightarrow] & n_0(\mathbf{r}) \arrow[l, Rightarrow, "\text{HK}"'] \arrow[r, Leftrightarrow, "\text{KS}"] & n_0(\mathbf{r}) \arrow[r, Rightarrow, "\text{HK}"] & V_{\text{KS}}(\mathbf{r}) \arrow[d, Rightarrow] \\
\Psi_n(\{\mathbf{r}\}) \arrow[r, Rightarrow] & \Psi_0(\{\mathbf{r}\}) \arrow[u, Rightarrow] & \phi_{i=1,N_e}(\mathbf{r}) \arrow[u, Rightarrow] & \phi_i(\mathbf{r}) \arrow[l, Rightarrow]
\end{tikzcd}$$

real system auxiliary system

Spectra from HF or DFT

Task: compute $\langle \Psi_n | T | \Psi_m \rangle$. (Mostly $m = 0$)

- Independent particle approximation.

Compute molecular orbitals ϕ_i (using HF or DFT).
Assume that all Ψ_n are Slater-determinants made of $|\{\phi_i\}|$.

$$\langle \Psi_n | T | \Psi_m \rangle = \langle \phi_j | T | \phi_i \rangle \qquad \Delta E = \epsilon_j - \epsilon_i$$

- Delta SCF

In reality, HF and DFT are ground state theories, i.e. orbitals only good for GS. In the excited state, there is a hole. One can do "constraint" HF calculations for particle-hole excitations. This gives different orbitals $\tilde{\phi}_i$ and much better excitation energy.

$$\langle \Psi_n | T | \Psi_m \rangle = \langle SD\{\tilde{\phi}_j\} | T | SD\{\phi_i\} \rangle \qquad \Delta E = E[SD\{\tilde{\phi}_j\}] - E[SD\{\phi_i\}]$$

Takes account of orbital relaxation around hole.

- often neglect "spectator" orbitals →

$$\langle \Psi_n | T | \Psi_m \rangle \approx \langle \tilde{\phi}_j | T | \phi_i \rangle \qquad \Delta E \approx \tilde{\epsilon}_j - \epsilon_i$$

Spectra from HF or DFT – in practice

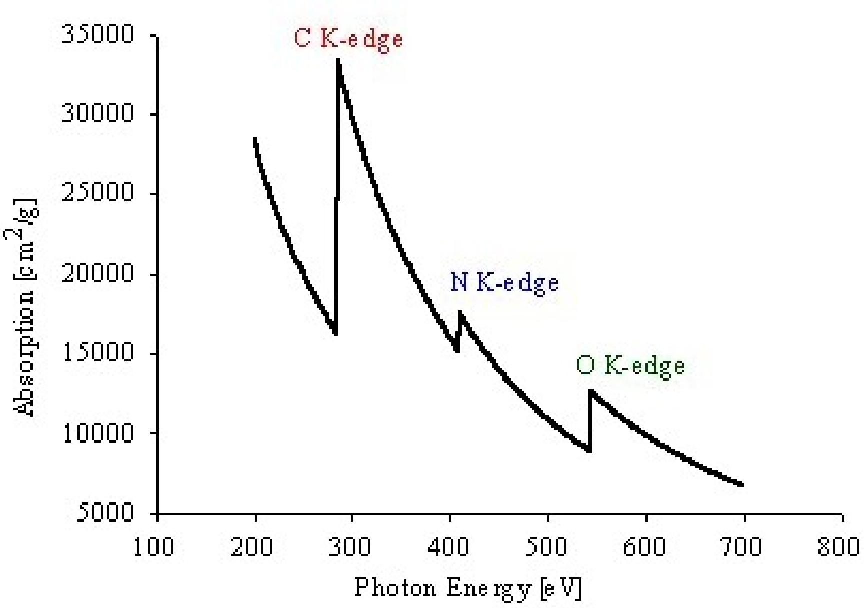
Take electronic structure code. Compute molecular or band orbitals. Compute absorption spectra

$$\sigma(\omega) = 4\pi^2 \alpha \hbar\omega \sum_f |\langle f|\boldsymbol{\epsilon} \cdot \mathbf{r}|c\rangle|^2 \delta(\hbar\omega + \epsilon_c - \epsilon_f)$$

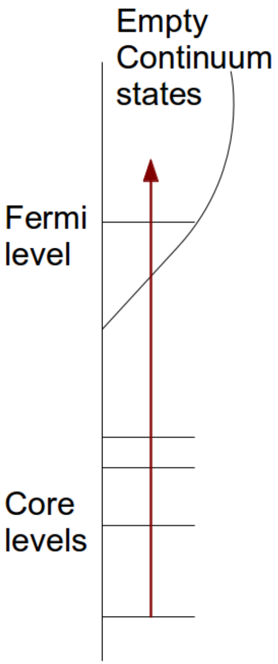
If possible include core-hole effect, i.e. calculate the final state energies ϵ_f and orbitals ϕ_f in the presence of a core-hole. Since the core-hole is localized on one site, the symmetry is generally lowered. In crystals: use supercell with one core-hole site.

DFT codes can be used, if the basis is sufficiently complete for states above E_F (“virtual molecular orbitals”).

X-ray absorption in independent particle approximation



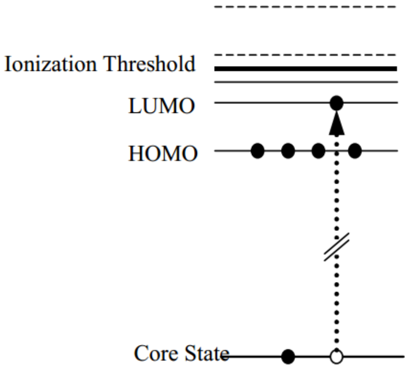
From I. Koprinarov, A. P. Hitchcock



1st row elements: 1s = K-edge, transition metals: 2p = L23-edges, etc

XANES X-ray absorption near-edge structure

Chemical analysis. Example: C K-edge of polymers



Ionization Threshold

LUMO

HOMO

Core State

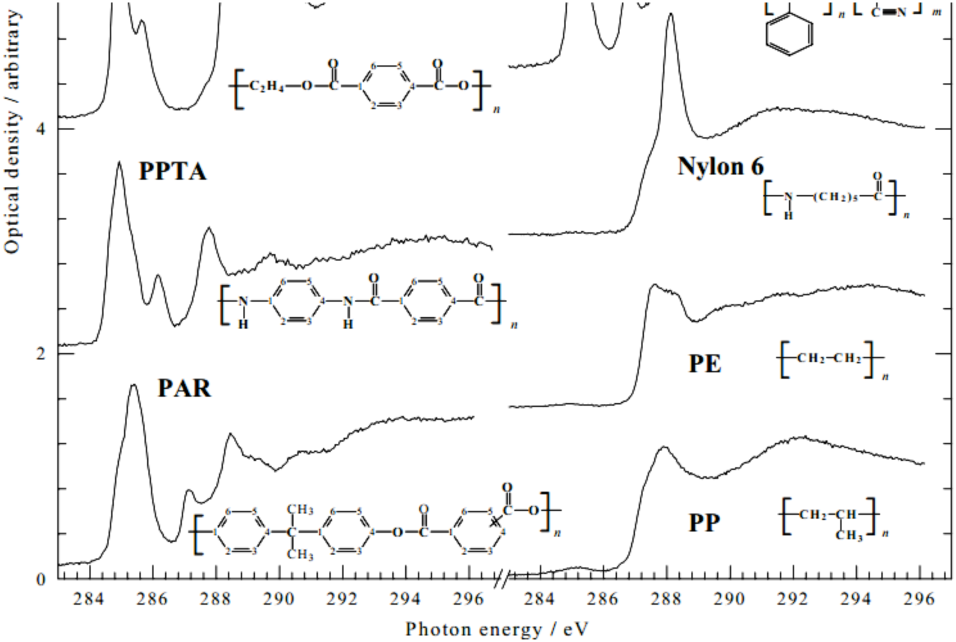


Fig. 3 C 1s NEXAFS spectra of some common polymers. Abbreviation as follows: PC, polycarbonate; PET, poly(ethylene terephthalate); PPTA, poly(p-phenylene terephthalamide); PAR, polyacrylate; PS, polystyrene; SAN, styrene-acrylonitrile; Nylon-6, poly(ε-caprolactam); PP, polypropylene; PE, polyethylene. (Figure adopted from [Ade 97])

From I. Koprinarov, A. P. Hitchcock

XAS formula

X-ray beam = plane wave with polarization $\boldsymbol{\epsilon}$.
$\mathbf{A}_0(\mathbf{r}) = \boldsymbol{\epsilon} A_0 \exp(i\mathbf{q}\cdot\mathbf{r})$.

$\hbar\omega < 1$ keV $\Leftrightarrow \lambda > 12$ Å, much larger than core orbital.

$\Rightarrow$ for matrix elements, $\exp(i\mathbf{q}\cdot\mathbf{r}) \approx 1$ "dipole approximation"

Instead of $\mathbf{p}$, we can use $\mathbf{r}$. $[\mathbf{r}, H] = \frac{i\hbar}{m}\mathbf{p}$ and $|\phi\rangle$'s are eigenstates of H.

Dropping all constants, the XAS intensity

$$I(\omega) = \sum_f |\langle \Phi_f | \boldsymbol{\epsilon} \cdot \sum_i \mathbf{r}_i | \Phi_g \rangle|^2 \, \delta(E_f - E_g - \omega)$$

From many-electron to single-electron formula

$$I(\omega) = \sum_f |\langle \Phi_f | \boldsymbol{\epsilon} \cdot \sum_i \mathbf{r}_i | \Phi_g \rangle|^2 \; \delta(E_f - E_g - \omega)$$

If $\quad |\Phi_g\rangle = |\Phi^c_0\rangle |\phi_c\rangle \qquad |\Phi_f\rangle = |\tilde{\Phi}^c_j\rangle |\phi_k\rangle \qquad \langle \phi_k | \phi_c \rangle = 0$

$S_j \equiv \langle \tilde{\Phi}^c_j | \Phi^c_0 \rangle \qquad E_g = E^c_0 + \epsilon_c \qquad E_f = \tilde{E}^c_j + \epsilon_k \qquad \Delta_j \equiv \tilde{E}^c_j - E^c_0$

$$I(\omega) = \sum_j |S_j|^2 \sum_k |\langle \phi_k | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_c \rangle|^2 \; \delta(\epsilon_k - \epsilon_c - \omega + \Delta_j)$$

$$= \sum_k |\langle \phi_k | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_c \rangle|^2 \; \delta(\epsilon_k - \epsilon_c - \omega) \; * \; \sum_j |S_j|^2 \delta(\omega - \Delta_j)$$

Convolution of one-electron XAS formula with $N-1$ electron excitation spectrum ($\sim$ core-level XPS).

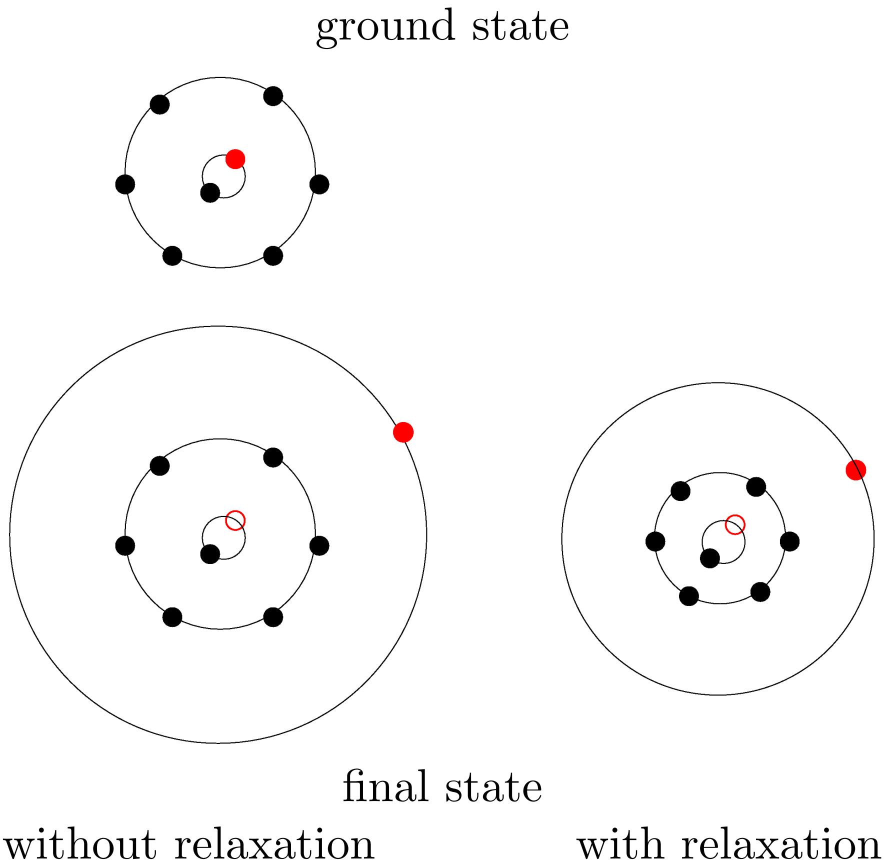
Single-electron approximation

Only $j = 0$ ("fully relaxed channel") →

$$I(\omega) = |S_0|^2 \sum_k |\langle\phi_k|\boldsymbol{\epsilon}\cdot\mathbf{r}|\phi_c\rangle|^2\, \delta(\epsilon_k - \tilde{\epsilon}_c - \omega)\ , \qquad \tilde{\epsilon}_c = \epsilon_c - \Delta_0$$

- XAS can be calculated approximately from single electron states ϕ_c and ϕ_k.
- Intensity reduced $|S_0| < 1$. Rest $1 - |S_0|$ in many-body excited states ($\sim$ photoemission shake-up satellites etc) which adds to background.
- Core-level energy shifted by $N-1$ electron relaxation energy to core-hole, Δ_0. (In practice $\epsilon_k - \tilde{\epsilon}_c = E_f - E_g$, from ΔSCF calc.)

Core hole — orbital relaxation — screening



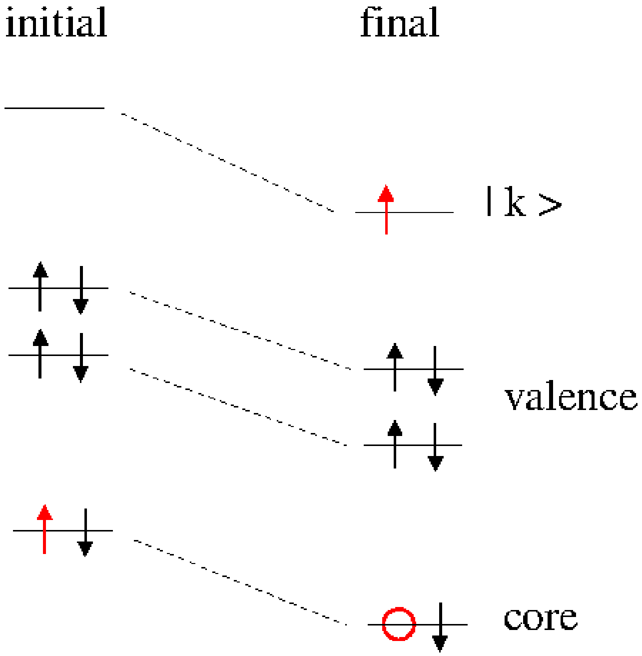
ground state

final state

without relaxation

with relaxation

What is the best potential for final state $|k\rangle$?



Final state rule

photoelectron wave function $|k\rangle$ computed in presence of core-hole, and all electronic states fully relaxed

Slater transition state

compute $|c\rangle$ and $|k\rangle$ with half a core-hole

transition: ground (0 holes) to final (1 hole)

in solids: impurity problem, supercell calculation

Dipole selection rules

Matrix element $\langle \phi_k | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_c \rangle$. Expand ϕ_k in atomic-like orbitals at sites $\mathbf{R}_i$.

$$\phi_k = \sum_{ilm} B^k_{ilm} \phi_{ilm} \ , \quad \phi_{ilm}(\mathbf{r}) = R^k_{il}(r_i) Y_{lm}(\Omega_i) \ , \quad \mathbf{r}_i \equiv \mathbf{r} - \mathbf{R}_i \equiv (r_i, \Omega_i)$$

Y_{lm} are spherical harmonics = complete, orthonormal set of angular functions ($\sim$ s,p,d,f…orbitals). The core-orbital is localized at site i_c, so only orbitals at i_c contribute to the matrix element.

Consider core-s state and linearly polarized light along z, $\mathbf{e} = \mathbf{z}$.

$\mathbf{e} \cdot \mathbf{r} = z = r Y_{10} \sqrt{4\pi/3}$ spherical harmonic

$$\langle \phi_{lm} | z | \phi_s \rangle = \int d\Omega \, dr \, r^2 \ R_l Y^*_{lm} \ z \ R_s Y_{00} = \frac{1}{\sqrt{3}} \int dr \ r^3 R_l R_s \int d\Omega Y^*_{lm} Y_{10}$$

Y_{lm} orthonormal set $\Rightarrow$ only $(lm) = (10)$ gives non-zero integral.

$\Rightarrow$ selection rule $\quad \langle \phi_{lm} | z | \phi_s \rangle = 0$, except for $(lm) = p_z$.

Light polarization $q = 0$ linear z, $q = \pm 1$ circular left/right.
Wigner-Eckart theorem

$$\langle n'l'm's' | r_q | nlms \rangle = \delta_{s's} \, (-1)^{l'-m'} \begin{pmatrix} l' & 1 & l \\ -m' & q & m \end{pmatrix} \langle n'l' || r || nl \rangle$$

Wigner 3-j symbols $(\dots)$ (=angular integrals) non-zero only for:

$$\boxed{l' = l \pm 1 \qquad\qquad m' = m + q \qquad\qquad s' = s}$$

dipole selection rules

circular pol., spherical harmonics

q	s	p_0	p_1	p_{-1}
0	p_0	s,d_0	d_1	d_{-1}
1	p_1	d_1	d_2	s, d_0
-1	p_{-1}	d_{-1}	s, d_0	d_{-2}

linear pol., cubic harmonics

q'	s	p_x	p_y	p_z
x	p_x	s, d_e	d_{xy}	d_{xz}
y	p_y	d_{xy}	s, d_e	d_{yz}
z	p_z	d_{xz}	d_{yz}	s, d_e

$d_e = \{ d_{x^2-y^2}, d_{3z^2-r^2} \}$

Density of states (DOS)

Eigenstates ψ_k, eigenvalues ϵ_k.

$$\rho(\epsilon) = \sum_k \delta(\epsilon - \epsilon_k) \quad \text{total DOS}$$

$$\rho(\epsilon, \mathbf{r}) = \sum_k |\psi_k(\mathbf{r})|^2 \delta(\epsilon - \epsilon_k) \quad \text{local (point) DOS}$$

$$\rho_{ilm}(\epsilon) = \sum_k |\langle \phi_{ilm} | \psi_k \rangle|^2 \delta(\epsilon - \epsilon_k) \quad \text{partial (ilm) DOS}$$

ϕ_{ilm} = normalized basis function centered on site i, symmetry lm

X-ray absorption and density of states

$$I_q(\omega) = \sum_k |\langle \psi_k | r_q | \phi_c \rangle|^2 \, \delta(\epsilon_k - \epsilon_c - \omega)$$

Develop $|k\rangle$ in local basis $|ilm\rangle$

$$\langle k | r_q | i_c l_c m_c \rangle = \sum_{ilm} \langle k | ilm \rangle \langle ilm | r_q | i_c l_c m_c \rangle$$

$$= \sum_{\pm} \langle k | i_c, l_c \pm 1, m + q \rangle \langle i_c, l_c \pm 1, m + q | r_q | i_c l_c m_c \rangle$$

Localization of $|c\rangle$ and selection rules → only one or two terms survive, e.g. $c = s$, $q = z \Rightarrow \langle || \rangle = 0$ except for $i = 0$, $(lm) = p_0$

$$I_q(\omega) = \sum_{\pm} \sum_k |\langle k | i_c l_{\pm} m \rangle \langle i_c l_{\pm} m | r_q | c \rangle|^2 \, \delta(\epsilon_k - \epsilon_c - \omega)$$

$$I_q(\omega) \approx \sum_{\pm} |\langle i_c l_\pm m | r_q | c \rangle|^2 \sum_k |\langle k | i_c l_\pm m \rangle|^2 \, \delta(\epsilon_k - \epsilon_c - \omega)$$

$$I_q(\omega) \;\sim\; A_+ \rho_{i_c l_+ m}(\omega + \epsilon_c) + A_- \rho_{i_c l_- m}(\omega + \epsilon_c)$$

K-edge, $s \to p$, $A_- = 0$. $L23$ edges often $A_+ \gg A_-$
So, in single electron approximation, the

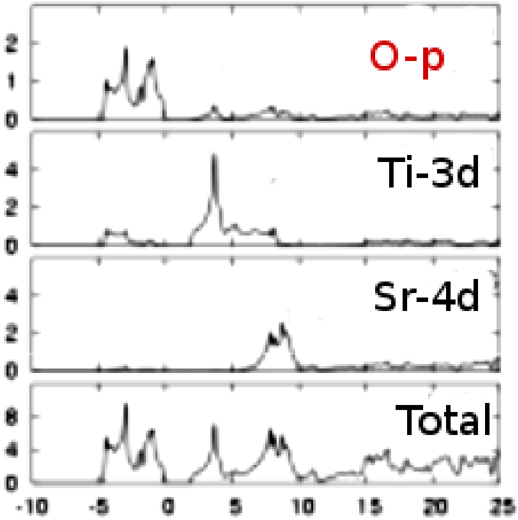
XAS is approximately proportional to a partial DOS at absorber site

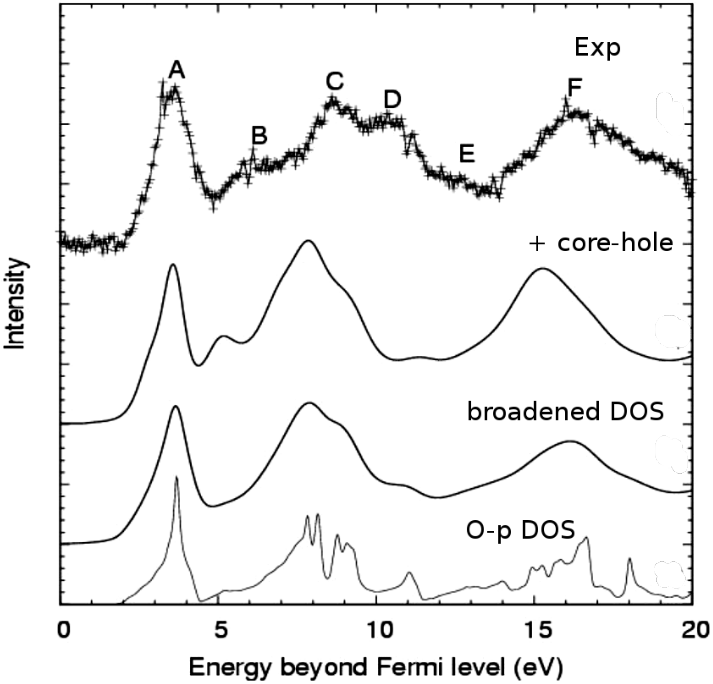
Example: K-edge, x-polarization. XAS $\sim p_x$-DOS

→ **element-resolved / local electronic structure** (unoccupied states)

Example: SrTiO3, O-K edge

Partial density of states from DFT (Wien2k) code





XAS spectrum essentially broadened O-p projected DOS. Some improvement with final state rule.

[G. Ratdke, G. Botton, Microscopy and Microanalysis 2010]

Multiple scattering

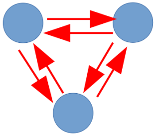
Continuum wave expanded in energy-dependent spherical waves $|ilm\rangle$ located at sites i.

$$|\mathbf{k}\rangle = \sum_{ilm} B^{\mathbf{k}}_{ilm} |ilm\rangle$$

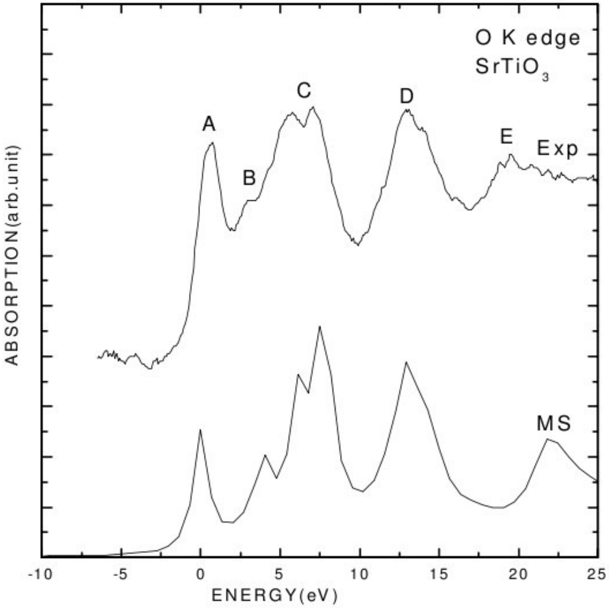
$$B^{\mathbf{k}}_{ilm} = \sum_{jl'm'} \tau_{ilm,jl'm'} A^{\mathbf{k}}_{jl'm'}$$

$A^{\mathbf{k}}_{jl'm'}$ = plane-wave coefficients
τ_{ij} = scattering path operator

$$\tau_{ij} = \delta_{ij} t_i + t_i G_{ij} t_j + t_i \sum_k G_{ik} t_k G_{kj} t_j + \dots$$



t_i atomic scattering matrix (phase shifts)
G_{ij} free electron propagator



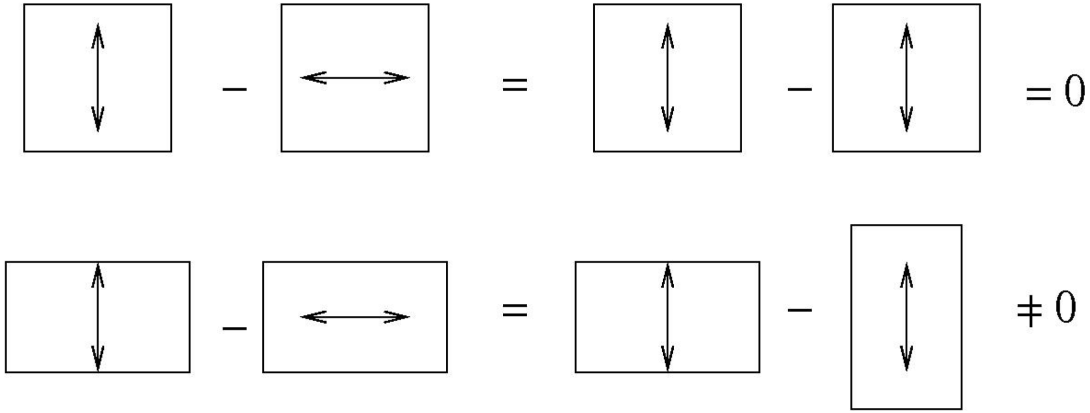
Z. Wu et al J. Synchrotron Rad. (2001)

Dichroism

= polarisation dependence of light absorption

Linear Dichroism (LD) is the difference in absorption of light linearly polarized parallel and perpendicular to an orientation axis (e.g. molecular axis, crystal axis, magnetisation direction)

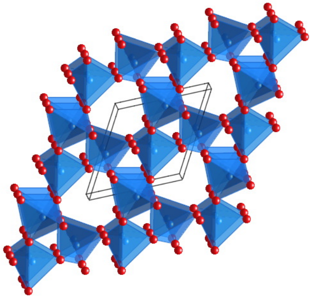
$$\mathrm{LD} = I(||) - I(\perp) = I_z - I_x$$



LD is sensitive to anisotropy of electronic density (and/or atomic structure) around the absorber site

Linear dichroism

reflects anisotropy of charge distribution in low symmetry crystal.



α-quartz single crystal

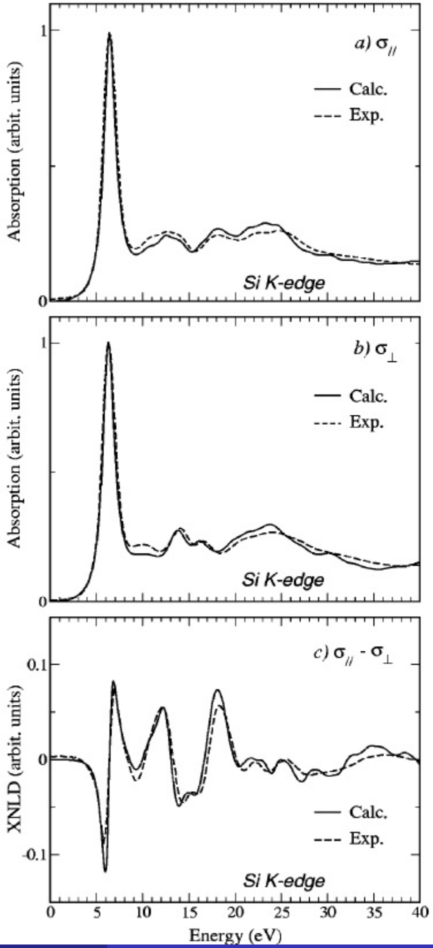
hexagonal, c≠a ⇒ LD≠ 0

$I(||) - I(\perp) \sim \rho_{pz} - \rho_{px}$

Si K-edge XAS

[Taillefumier et al. PRB 2002]

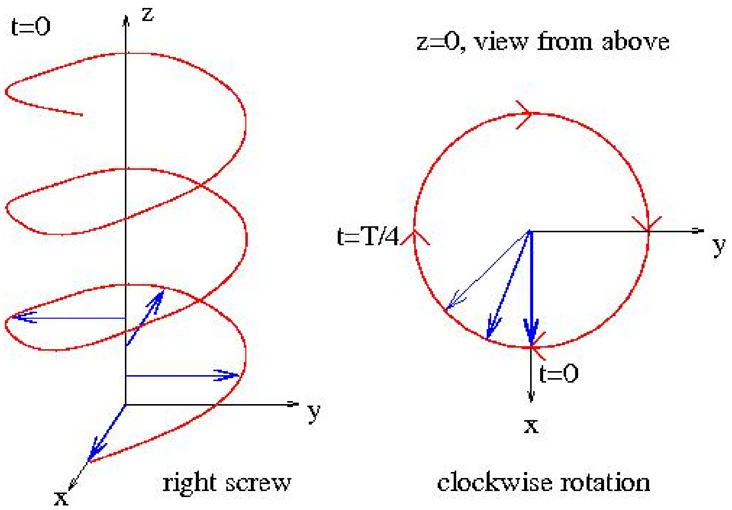
PHYSICAL REVIEW B **66**, 195107 (2002)

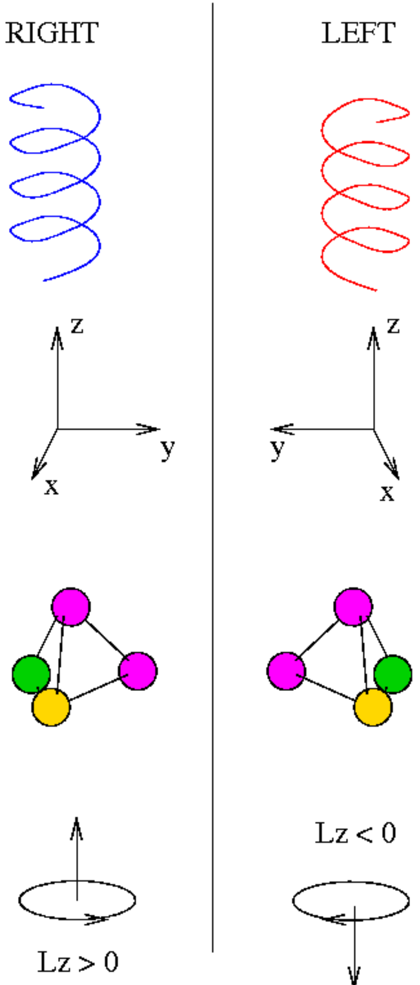


Circular dichroism

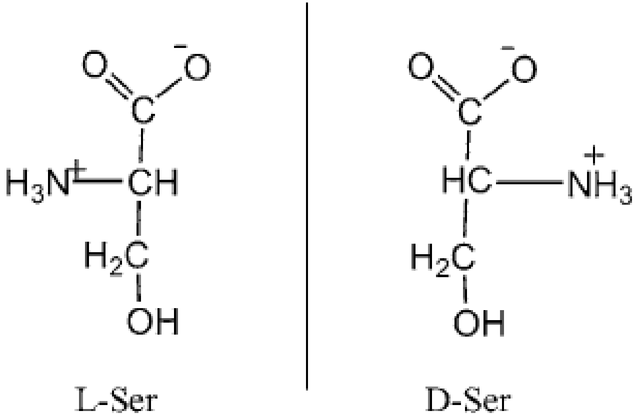
is the difference in absorption of left- and right-handed circularly polarized light.

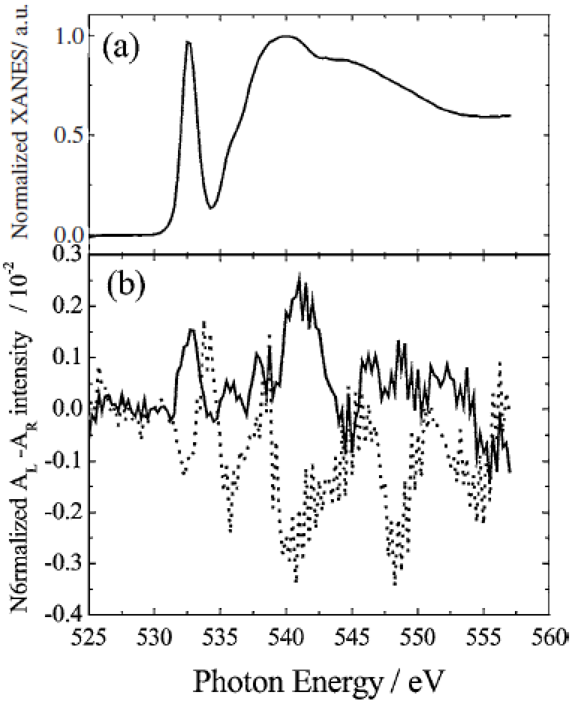
Right circularly polarized light





X-ray circular dichroism of chiral molecules

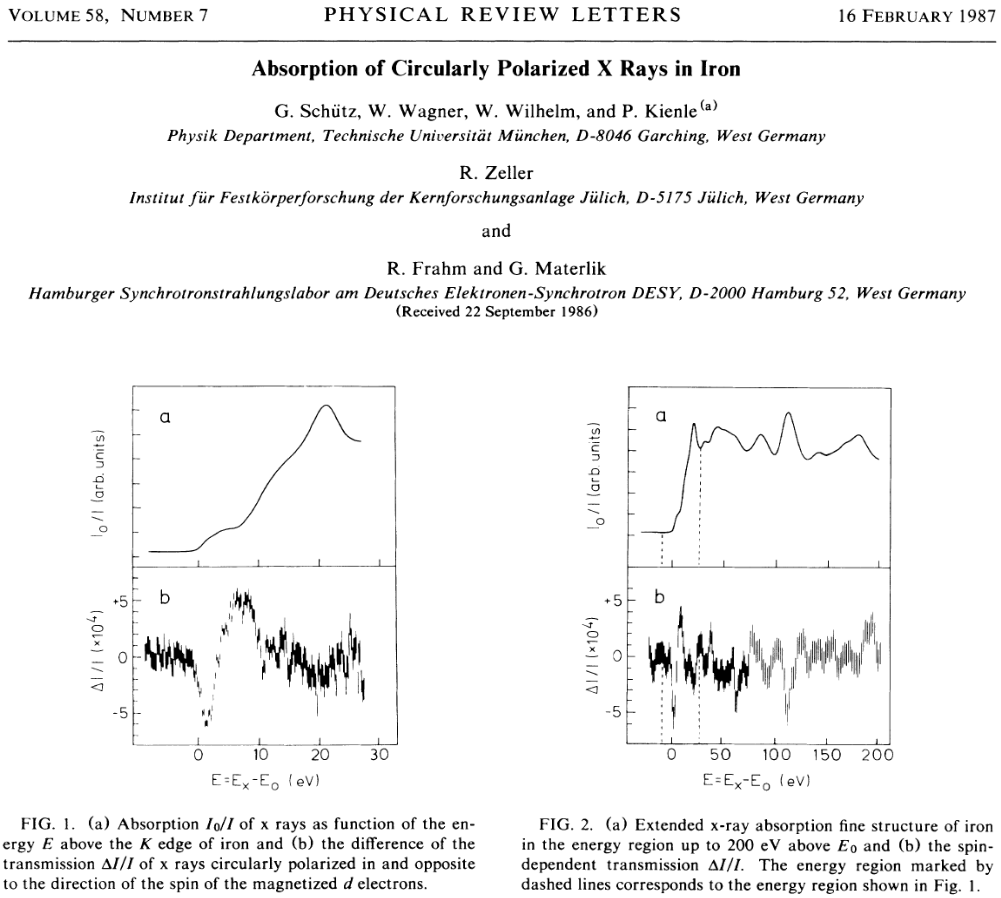




Serine. [Physica Scripta T115, 873]

~ optical activity. But effect much weaker for x-rays than vis-UV light.

X-ray Magnetic Circular Dichroism



VOLUME 58, NUMBER 7 PHYSICAL REVIEW LETTERS 16 FEBRUARY 1987

Absorption of Circularly Polarized X Rays in Iron

G. Schütz, W. Wagner, W. Wilhelm, and P. Kienle[a]
Physik Department, Technische Universität München, D-8046 Garching, West Germany

R. Zeller
Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5175 Jülich, West Germany

and

R. Frahm and G. Materlik
Hamburger Synchrotronstrahlungslabor am Deutsches Elektronen-Synchrotron DESY, D-2000 Hamburg 52, West Germany
(Received 22 September 1986)

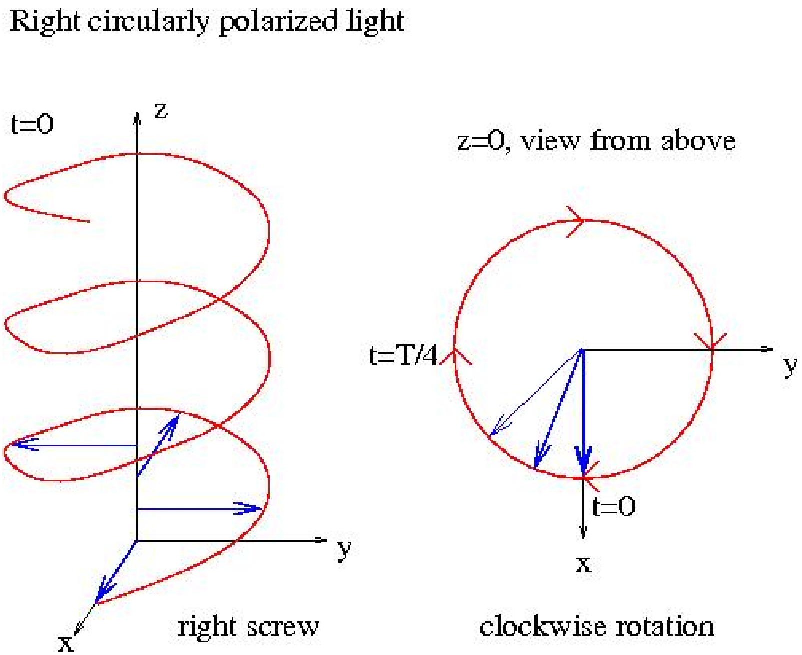
FIG. 1. (a) Absorption I_0/I of x rays as function of the energy E above the K edge of iron and (b) the difference of the transmission $\Delta I/I$ of x rays circularly polarized in and opposite to the direction of the spin of the magnetized d electrons.

FIG. 2. (a) Extended x-ray absorption fine structure of iron in the energy region up to 200 eV above E_0 and (b) the spin-dependent transmission $\Delta I/I$. The energy region marked by dashed lines corresponds to the energy region shown in Fig. 1.

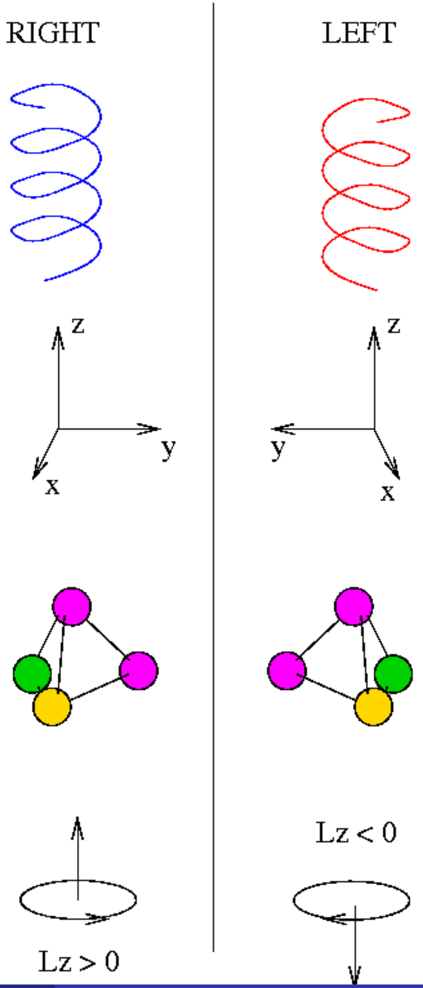
Fe K-edge.

Origin of magnetic circular dichroism

circular light is chiral (= parity-odd) but also **time-reversal odd** $\longrightarrow$ dichroism for time-reversal broken states



Right circularly polarized light



Circular light has angular momentum (helicity)

absorption → angular momentum transferred to orbital moment of electron

if states orbitally polarized → transition probabilites different for left/right

→ circular dichroism detects orbital polarization of electronic states

Ex. K-edge. $1s \rightarrow p$.

XMCD $\sim$ DOS(p_+) - DOS(p_-)

orbital magnetic polarization $L_z(\epsilon)$ of p-projected conduction band

However, orbital polarization of conduction-p band usually small, because spin-orbit coupling $\ll$ hybridization

Time-Dependent Density Functional Theory

Generalization of DFT to time-dependent phenomena, i.e. $V_{\text{ext}}(\mathbf{r}, \mathbf{t})$.

History

1980 Zangwill, Soven linear response theory with LDA kernel (= time-dependent, adiabatic LDA)

1984 Runge-Gross theorems → equivalent of Hohenberg-Kohn for time-dependent $V_{\text{ext}}(\mathbf{r}, t)$ = functional of $n(\mathbf{r}, t)$ (and given initial state).

1995 Casida's equations Implementation of TD-DFT in quantum chemistry codes → standard tool for optical spectra

1998 Schwitalla, Ebert 1st application to XAS: L-edge of 3d metals

2003 Stener, Fronzoni et al. implement TD-DFT for XAS in ADF code

2003 Ankudinov et al. TD-DFT in FEFF (Feff9 doc. 2013': "still under development")

2012 Bunau, Joly implement TD-DFT in FDMNES code

Linear response theory

[A. Zangwill and P. Soven, Phys. Rev. A 21 (1980) 1561]

Perturbation $H'(t) = \int \varphi_{\text{ext}}(\mathbf{r}, t) n(\mathbf{r}, t) d\mathbf{r}$.
Induced density change $\delta n(\mathbf{r}, t) = n(\mathbf{r}, t) - n^0(\mathbf{r})$

Linear Response $$\delta n(\mathbf{r}, t) = \int d\mathbf{r}' dt' \chi(\mathbf{r}, \mathbf{r}'; t - t') \varphi_{\text{ext}}(\mathbf{r}', t')$$

$$\chi(\mathbf{r}, \mathbf{r}'; t - t') = -i\theta(t - t') \langle 0 | [\hat{n}(\mathbf{r}, t), \hat{n}(\mathbf{r}', t')] | 0 \rangle \ , \quad \hat{n}(t) = e^{iHt} \hat{n} e^{-iHt}$$

χ = reponse function = retarded density-density Green's function

Harmonic perturbation: $\varphi_{\text{ext}}(t) = \varphi_{\text{ext}}(\omega) \exp(i\omega t)$
$\Rightarrow \quad \delta n(\mathbf{r}, \omega) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}'; \omega) \varphi_{\text{ext}}(\mathbf{r}', \omega)$.

$$\chi(\mathbf{r}, \mathbf{r}'; \omega) = \sum_m \frac{\langle 0 | \hat{n}(\mathbf{r}) | m \rangle \langle m | \hat{n}(\mathbf{r}') | 0 \rangle}{\hbar\omega - (E_m - E_0) + i\eta} - \sum_m \frac{\langle 0 | \hat{n}(\mathbf{r}') | m \rangle \langle m | \hat{n}(\mathbf{r}) | 0 \rangle}{\hbar\omega + (E_m - E_0) + i\eta}$$

Independent particle response function χ_0

$$\chi(\mathbf{r},\mathbf{r}';\omega) = \sum_m \frac{\langle 0|\hat{n}(\mathbf{r})|m\rangle\langle m|\hat{n}(\mathbf{r}')|0\rangle}{\hbar\omega - (E_m - E_0) + i\eta} - \sum_m \frac{\langle 0|\hat{n}(\mathbf{r}')|m\rangle\langle m|\hat{n}(\mathbf{r})|0\rangle}{\hbar\omega + (E_m - E_0) + i\eta}$$

Non-interacting electrons. $|0\rangle, |m\rangle$ = Slater determinants.

$\Rightarrow \quad |m\rangle = c_p^{+} c_h |0\rangle$ **single particle-hole excitations**

$$\chi_0(\mathbf{r},\mathbf{r}',\omega) = \sum_{hp} \frac{\phi_h^*(\mathbf{r})\phi_p(\mathbf{r})\phi_p^*(\mathbf{r}')\phi_h(\mathbf{r}')}{\hbar\omega - (\epsilon_p - \epsilon_h) + i\eta} - [p \leftrightarrow h]$$

Response function in independent particle approximation

Absorption coefficient

$\varphi_{\text{ext}}(\mathbf{r},t) = eE_0\boldsymbol{\epsilon}\cdot\mathbf{r}e^{i\omega t}$ (Approx. $e^{-i\mathbf{q}\cdot\mathbf{r}} \approx 1$.) $\varphi_{\text{ext}}(\mathbf{r},\omega) = eE_0\boldsymbol{\epsilon}\cdot\mathbf{r}$.
Dipole moment

$$\boldsymbol{\mu}(\omega) = -e\int \mathbf{r}\delta n(\mathbf{r},\omega)d\mathbf{r} = -e^2E_0\int \mathbf{r}\chi(\mathbf{r},\mathbf{r}';\omega)\boldsymbol{\epsilon}\cdot\mathbf{r}'d\mathbf{r}d\mathbf{r}'$$

Absorption $\sim \langle\mathbf{j}\cdot\mathbf{E}\rangle = \int \frac{d}{dt}\boldsymbol{\mu}\cdot\mathbf{E} = E_0^2\sum_{ab}\epsilon_a\sigma_{ab}\epsilon_b$

Absorption coefficient

$$\sigma(\omega) = -4\pi\alpha\hbar\omega\int d\mathbf{r}d\mathbf{r}'\boldsymbol{\epsilon}\cdot\mathbf{r}\,\mathrm{Im}\chi(\mathbf{r},\mathbf{r}';\omega)\boldsymbol{\epsilon}\cdot\mathbf{r}'$$

With χ_0 we get

$$\sigma_0(\omega) = 4\pi^2\alpha\hbar\omega\sum_{hp}|\langle\phi_p|\boldsymbol{\epsilon}\cdot\mathbf{r}|\phi_h\rangle|^2\delta(\hbar\omega+\epsilon_h-\epsilon_p)$$

Fermi's golden rule in 1-particle case

Linear response in TD-DFT

$$\delta n(\mathbf{r},\omega) = \int d\mathbf{r}' dt \chi(\mathbf{r},\mathbf{r}';\omega)\varphi_{\text{ext}}(\mathbf{r}',\omega)$$

If the electrons didn't interact: $\chi = \chi_0$.

But they do interact. In TD-DFT the interaction is handled as in DFT, by introducing an auxiliary, non-interacting system with the same electron density $n(\mathbf{r},t)$. The non-interacting electrons feel an **effective** field which replaces the electron-electron interaction.

Linear response TD-DFT

Real system

$n(\mathbf{r}) \longleftrightarrow V_{\text{nucl}}(\mathbf{r}) \qquad n(\mathbf{r},t) \longleftrightarrow V_{\text{nucl}}(\mathbf{r}) + \varphi_{\text{ext}}(\mathbf{r},t)$

$\delta n(\mathbf{r},t) \longleftrightarrow \varphi_{\text{ext}}(\mathbf{r},t)$

Auxiliary system

$n(\mathbf{r}) \longleftrightarrow V_{\text{KS}}[n(\mathbf{r})] \qquad n(\mathbf{r},t) \longleftrightarrow V_{\text{KS}}[n(\mathbf{r},t)] + \varphi_{\text{ext}}(\mathbf{r},t)$

$\delta n(\mathbf{r},t) \longleftrightarrow \varphi_{\text{ext}}(\mathbf{r},t) + \delta V_{\text{KS}}[n(\mathbf{r},t)] \quad = \varphi_{\text{ext}} + \varphi_{\text{ind}}$

$\varphi_{\text{ind}}(\mathbf{r},t)$ is **induced field** due to charge density change $\delta n(\mathbf{r},t)$.

There a is feedback effect: $\varphi_{\text{ext}} \to \delta n \to \varphi_{\text{ind}} \to \delta^2 n \to \delta\varphi_{\text{ind}} \ldots$

Linear response TD-DFT

In the auxillary system, the electrons are independent, so they respond with χ_0, but not to the external, but to the “local” field $\varphi_{\text{ext}} + \varphi_{\text{ind}}$

$$\delta n = \chi\, \varphi_{\text{ext}} = \chi_0\, (\varphi_{\text{ext}} + \varphi_{\text{ind}})$$

$$\varphi_{\text{ind}}(\mathbf{r}t, \mathbf{r}'t') = \int d\mathbf{r}' dt' K(\mathbf{r}t, \mathbf{r}'t') \delta n(\mathbf{r}'t')$$

which defines the interaction **Kernel** K.

$$\varphi_{\text{ind}} = \delta V_{KS} = \delta V_H + \delta V_{XC}$$

$$\delta V_H(\mathbf{r}t) = \int d\mathbf{r}' \frac{\delta n(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|}\,, \quad \delta V_{XC}(\mathbf{r}t) = \int d\mathbf{r}' dt' \frac{\delta V_{XC}}{\delta n(\mathbf{r}'t')} \delta n(\mathbf{r}t)$$

Linear response TD-DFT

From χ_0 and K, we can calculate the full χ by iteration or inversion

$$\chi\, \varphi_{\text{ext}} = \delta n = \chi_0(\varphi_{\text{ext}} + \varphi_{\text{ind}}) = \chi_0(\varphi_{\text{ext}} + K\delta n) = \chi_0(1 + K\chi)\varphi_{\text{ext}}$$

$$\chi = \chi_0 + \chi_0 K \chi \qquad \Leftrightarrow \qquad \chi = (\chi_0^{-1} - K)^{-1}$$

In a basis set, this leads to matrix inversion/linear system [Casida]
Alternatively, one can solve interatively for $\varphi_{\text{loc}} = \varphi_{\text{ext}} + K\delta n$ [ZS]

Zangwill, Soven: Adiabatic and local density approximation

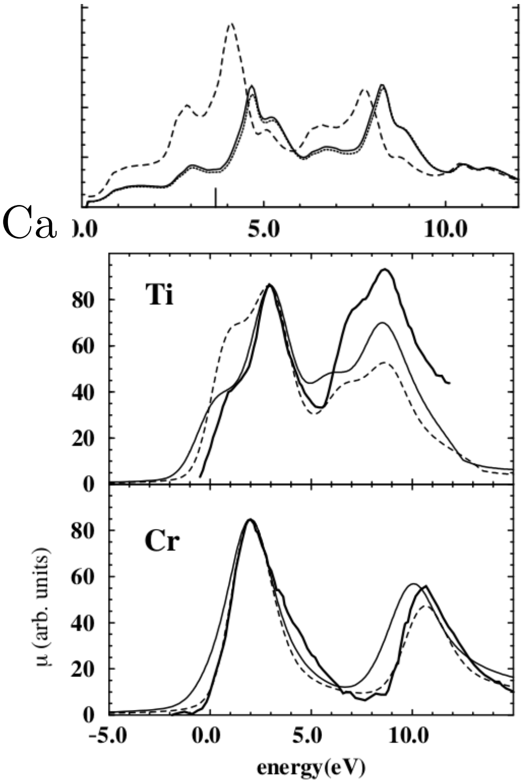
$$\frac{\delta V_{XC}}{\delta n(\mathbf{r}t)} = \left.\frac{dV_{XC}}{dn}\right|_{n(\mathbf{r})} \delta(t - t')$$

In adiabatic approximation, $\varphi_{\text{ind}}(t)$ changes instantaneously with $\delta n(t)$.
There are no delay or memory effects.
$\Rightarrow K(\mathbf{r}, \mathbf{r}'; \omega)$ is static, i.e. frequency independent.

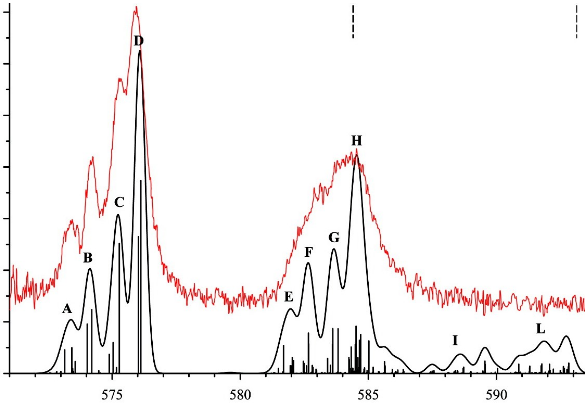
Time-dependent DFT

- In adiabatic TD-DFT, the kernel can be calculated directly from standard DFT
- if $K_{XC} = 0$ we get the random-phase approximation (RPA)
- the space of excitations is one particle-hole excitations (as in χ_0) but there is mixture and spectral weight transfer
- collective oscillation of electron gas (plasmons) OK
- double and higher particle hole-excitations (complex multiplets) cannot be reproduced with static kernels
- going beyond the adiabatic approximation is difficult

X-ray absorption spectra with TD-DFT



Schwitalla, Ebert, PRL 80, 4586, 1998



VO3Cl.

Fronzoni,Stener.. JPCA 113, 2914, 2009

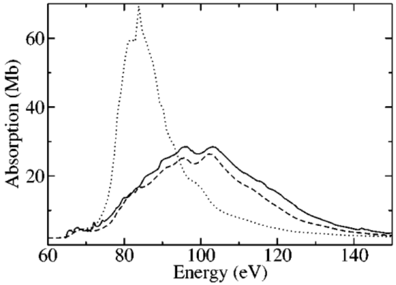


FIG. 2. $N_{4,5}$-edge XAS vs x-ray energy for solid Xe from experiment (solid),[25] and as calculated using the adiabatic TDLDA kernel $f_{xc}(0)$ (dashes) and with the independent particle approximation (dots).

Ankudinov..Rehr, PRB 67, 115120, 2003

Green's functions and quasi-particles

- Green's functions are the favorite tool of many-body theorists
- GF describe propagation of particles interacting with many others
- Free particles' properties: bare mass, free dispersion $p^2/2m \dots$
- Under interaction, the particles properties become renormalized.
  $\rightarrow$ different dispersion $\epsilon(k)$, effective mass, finite lifetime, ...
  the particles become "dressed", or "quasi-particles".
- More generally, quasi-particles are the elementary excitations of the interacting many-body system, including "dressed" single-electron states (e.g. polarons) and collective excitations (e.g. phonons, plasmons, etc)
- There's a Green's functions for each of them ...

Green's functions in scattering theory

Free particles $H_0 = -\frac{\hbar^2}{2m}\nabla^2$. $\quad (E - H_0)\phi = 0.$
Add potential $H = H_0 + V$. $\quad (E - H_0)\psi = V\psi$

$$\psi = \phi + [E - H_0]^{-1}V\psi = \phi + \mathcal{G}_0 V\psi = \phi + \mathcal{G}_0 T\phi$$

$\mathcal{G}_0 = (E - H_0)^{-1}$ free Green's Fct. $\quad E \to E \pm i\eta \Rightarrow$ retarded/advanced.
T = scattering matrix. $T\phi = V\psi$.

$T = V + V\mathcal{G}_0 V + \dots$ $\quad$ Born series.

Full Green's function $\quad \mathcal{G} = (E - H)^{-1}$

$\mathcal{G} = (E - H_0 - V)^{-1} = (\mathcal{G}_0^{-1} - V)^{-1} = \mathcal{G}_0 + \mathcal{G}_0 V \mathcal{G}_0 + \dots$

Plane wave basis $H_0|\mathbf{k}\rangle = \epsilon_k|\mathbf{k}\rangle$, $\epsilon_k = \hbar^2 k^2/2m$.

$$\mathcal{G}_0(\mathbf{k}, \mathbf{k}'; E) \equiv \langle\mathbf{k}|(E - H_0)^{-1}|\mathbf{k}'\rangle = \frac{\delta_{\mathbf{k}\mathbf{k}'}}{E - \epsilon_k}$$

Green's functions in many-body theory

Retarded 1-part.GF: $G(\mathbf{r},\mathbf{r}',t-t') = -i\theta(t-t')\langle 0|[\Psi(\mathbf{r}t),\Psi^+(\mathbf{r}'t')]|0\rangle$

= Probability amplitude for a particle at $\mathbf{r}t$ if one was added at $\mathbf{r}'t'$
→ 1-part. addition/removal spectrum = inverse/direct photoemission

Non-interacting: $H_0 = \sum_\mathbf{k} \epsilon_\mathbf{k} c^+_\mathbf{k} c_\mathbf{k} \Rightarrow G_0(\mathbf{k},\omega) = (\omega-\epsilon_\mathbf{k})^{-1} = \mathcal{G}_0$

Interacting: $G = G_0 + G_0 \Sigma G \quad \Leftrightarrow \quad G^{-1} = G_0^{-1} - \Sigma$

Dyson equation. Σ = self-energy

Free space or crystal $G^{-1}(\mathbf{k},\omega) = \omega - \epsilon_\mathbf{k} - \Sigma_\mathbf{k}(\omega)$

$\mathrm{Re}\Sigma$ → shift of eigenvalue (band). $\mathrm{Im}\Sigma$ → finite lifetime $\tau = \hbar/\mathrm{Im}\Sigma$.

Describes **quasiparticles** (Fermi-liquid theory)

GW approximation

In 1965 Lars Hedin reformulated many-body problem in terms of a closed set of equations between
G = Green's function $\leftrightarrow$ Σ = self-energy $\leftrightarrow$ P = polarization $\leftrightarrow$ W = screened interaction $\leftrightarrow$ Γ = vertex function

Neglect $\Gamma \longrightarrow$ "GW approximation"
= very successful for weakly correlated systems, e.g. semi-conductors

Coulomb interaction

$$v(r,r') = \frac{e^2}{4\pi\epsilon_0}\frac{1}{|r-r'|} \qquad \text{bare}$$

$$W(r,r') = \frac{e^2}{4\pi\epsilon_0\boldsymbol{\epsilon_r}}\frac{1}{|r-r'|} \qquad \text{statically screened}$$

$$W(r,r';\omega) = \frac{e^2}{4\pi\epsilon_0}\int dr''\frac{\epsilon^{-1}(r,r'';\omega)}{|r''-r'|} \qquad \text{dynamically screened}$$

F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. 61 , 237 (1998)

GW approximation

In practice usually
non-self-consistent version: G_0W_0

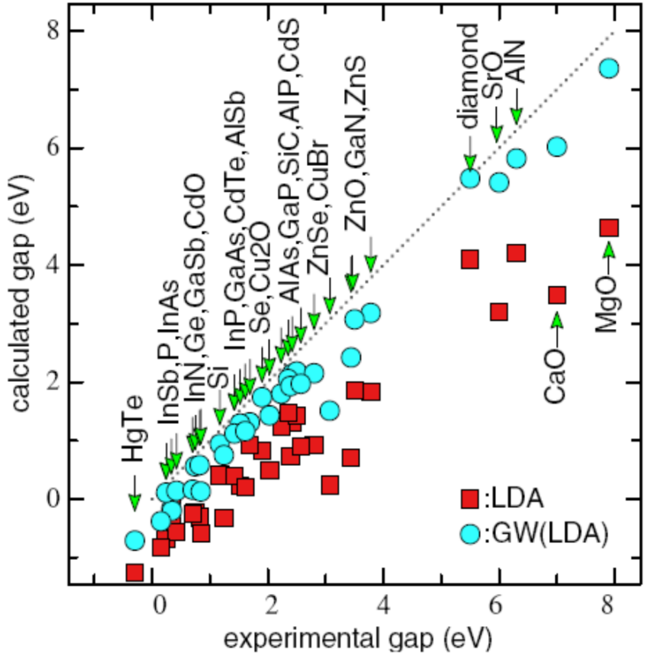
DFT → G_0, χ_0

$$\epsilon^{-1}(r,r';\omega) =$$
$$\delta(r-r') + \int dr'' v(r,r'')\chi_0(r'',r';\omega)$$
(RPA)

$$W_0(r,r';\omega) =$$
$$\int dr''\epsilon^{-1}(r,r'';\omega)v(r'',r')$$

$$\Sigma = i\int G_0W_0$$

$$G = (G_0^{-1}-\Sigma)^{-1}$$



after van Schilfgaarde *et al* PRL **96** 226402 (2008)

Bethe-Salpeter Equation (BSE) approach

- historically: explicit solution of interacting two-particle problem
- absorption spectra: interaction between excited electron and hole
- compute electron and hole Green's functions $G_e(1,1')$ and $G_h(1,1')$ using, e.g. GW approximation.
- electron-hole GF

$$G_{eh}(1,2;1',2') =$$

$$G_e(1,1')G_h(2,2') + \int G_e(1,3)G_h(2,4)K(3,4;5,6)G_{eh}(5,6;1',2')$$

- Kernel K = bare exchange and screened Coulomb interaction W
- describes well excitonic effects
- very accurate for 1-electron – 1-hole interaction, but lacks multi-electron excitations (e.g. multiplets)

X-ray absorption spectra with BSE

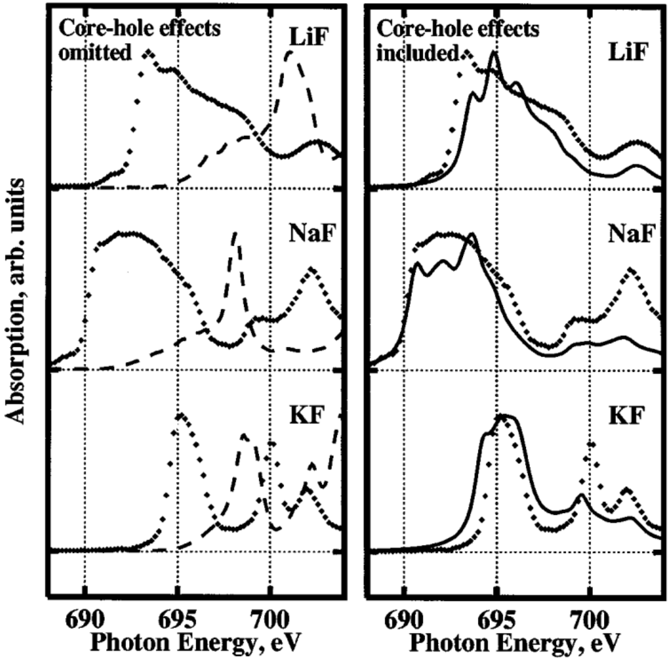
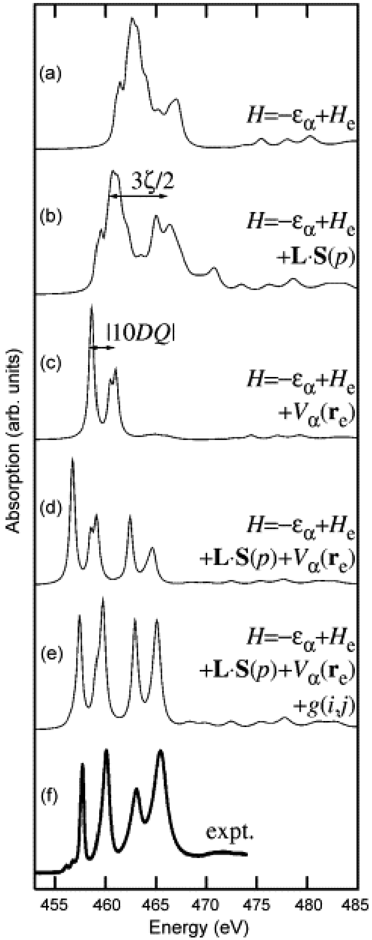


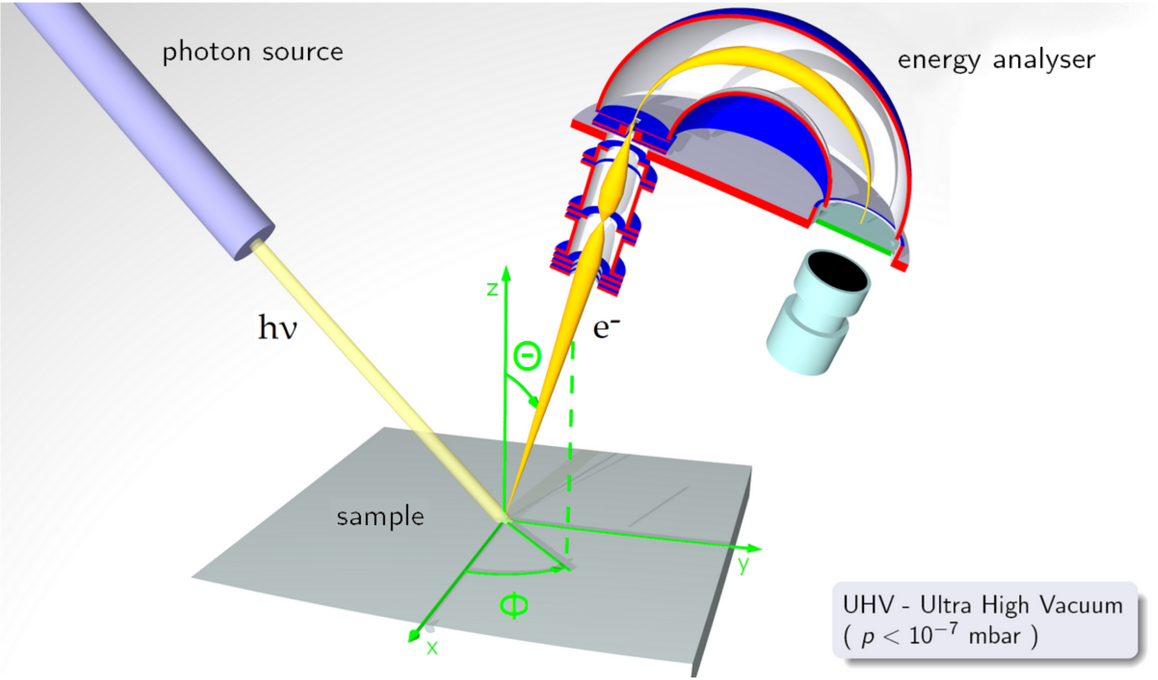
FIG. 2. XAS spectra near F K edge in LiF, NaF, and KF. Solid lines, with core-hole effects; dashed lines, without core-hole effects; points are experimental results [10].

E. L. Shirley, PRL 80, 794 (1998)

idem JESRP 144, 1187 (2005) → SrTiO3



Photoelectron spectroscopy



[wikipedia]

Energy, angular and spin destribution of photoexcited electrons

XPS: X-ray Photoelectron Spectroscopy

Elemental Analysis

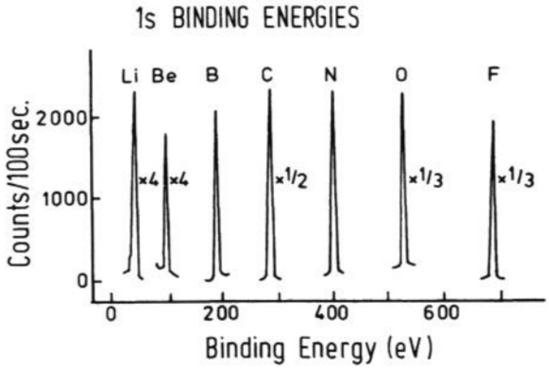


Fig. 2.2. XPS spectra of the 1s core levels of Li, Be, B, C, N, O, F

[S. Hüfner, Photoelectron Spectroscopy]

Chemical Shift

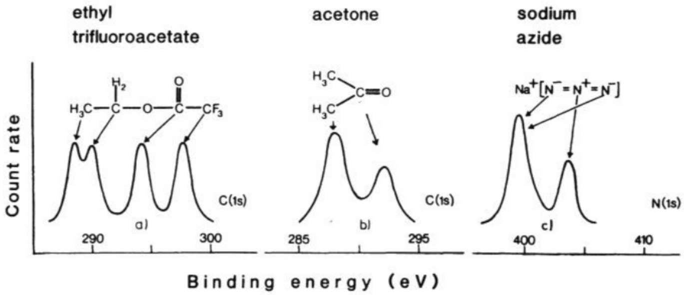
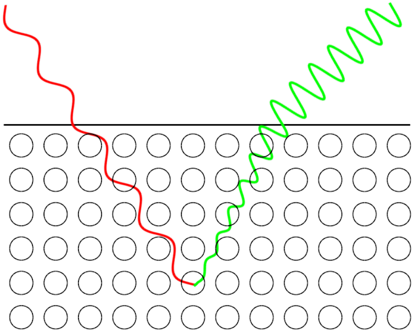


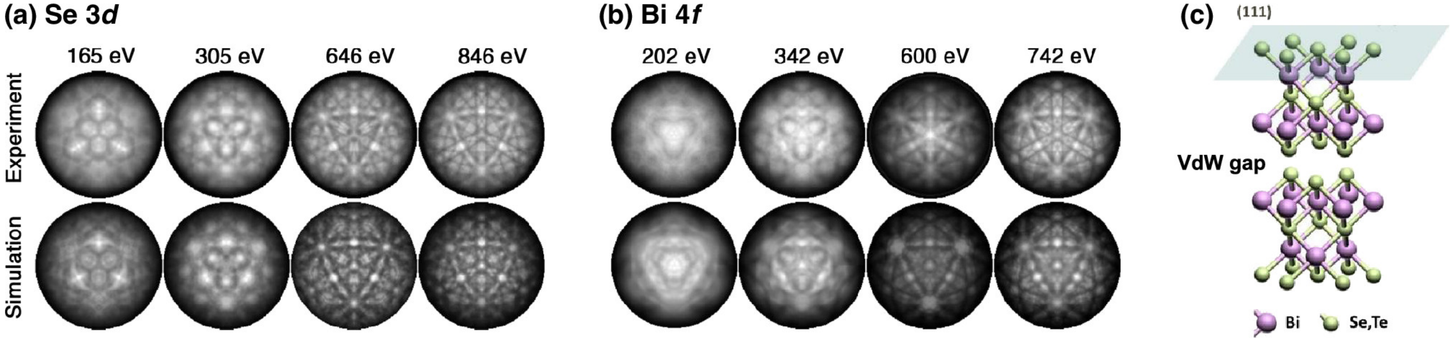
Fig. 2.5. Chemical shifts for the C 1s levels in ethyl trifluoroacetate (**a**), and acetone (**b**), and the N 1s levels in sodium azide (**c**). Chemical shifts can be crudely related to electronegativity differences: The known [2.8] electronegativity differences (Δx) are $\mathrm{C-H}: \ \Delta x = 0.4$, $\mathrm{C-O}: \ \Delta x = 1.0$: $\mathrm{C-F}: \ \Delta x = 1.5$, which rationalize the chemical shifts in ethyl trifluoroacetate [2.3]

- peak position: Electron Spectroscopy for Chemical Analysis ESCA
- lineshape: electron correlation effects due to core-hole screening asymmetry, plasmons peak, charge-transfer satellites, multiplets

XPD: X-ray Photoelectron Diffraction

- angular distribution of XPS signal
- needs single crystal surface but no long-range order of impurities
- → local structure probe with chemical sensitivity → impurities/adsorbates
- theory: real-space multiple scattering in finite cluster, e.g. EDAC code





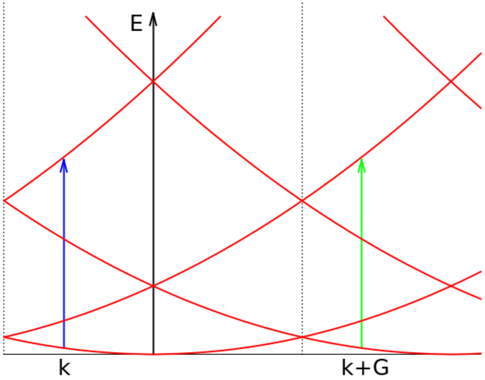
[M

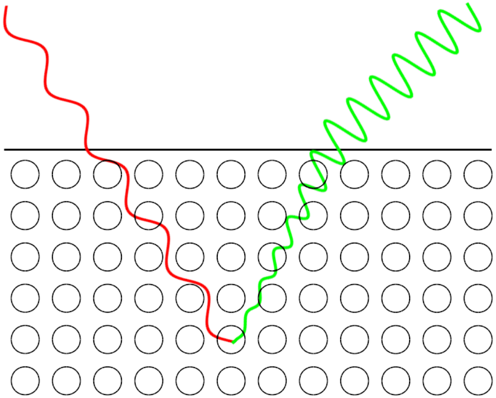
V. Kuznetsov et al., J. Phys. Soc. Jpn 87, 061005 (2018)]

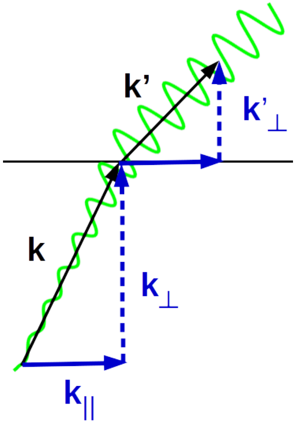
ARPES: Angle-Resolved Photoelectron Spectroscopy

3-step model

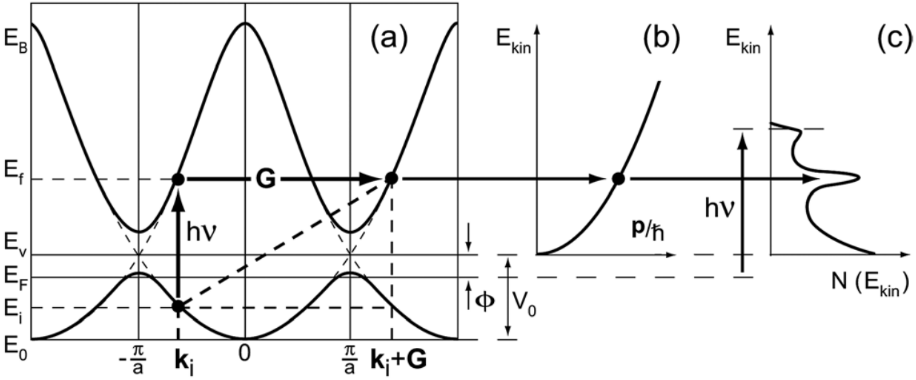
1. photon absorption in bulk
   → vertical band transition
   $(\mathbf{k}, \epsilon_i) \rightarrow (\mathbf{k}, \epsilon_f), \quad \epsilon_f = \epsilon_i + \hbar\omega$
2. propagation to surface with damping
   $\psi(\mathbf{r}) = \phi_{n\mathbf{k}}(\mathbf{r}) e^{z/\lambda}$
3. transmission through surface
   matching with free wave $\quad e^{i\mathbf{k}'\cdot\mathbf{r}}$
   $\mathbf{k}'_{||} = \mathbf{k}_{||}, \quad k'^2_{\perp} = k^2_{\perp} + 2mV_0/\hbar^2$

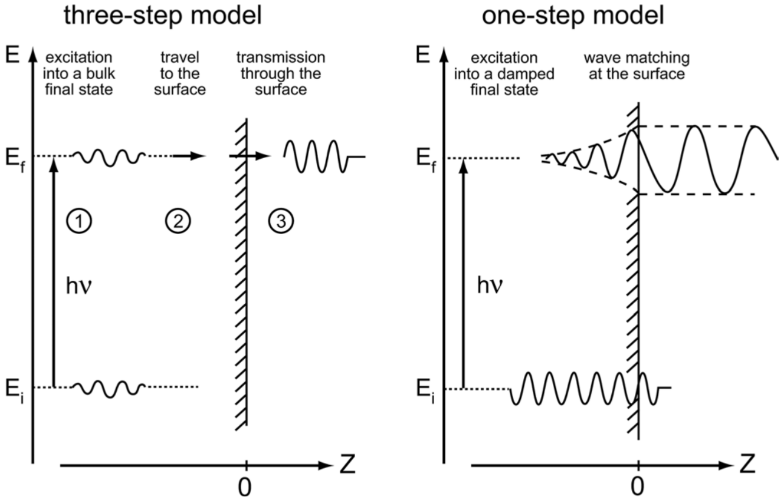






ARPES: Angle-Resolved Photoelectron Spectroscopy

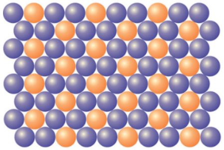


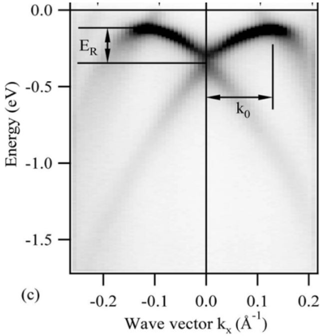


A. Damascelli, 2004.
Phys. Scr. T109, 61.

Spin-resolved ARPES – Rashba effect

$BiAg_2/Ag(111)$





C. R. Ast et al., PRL 98, 186807 (2007)

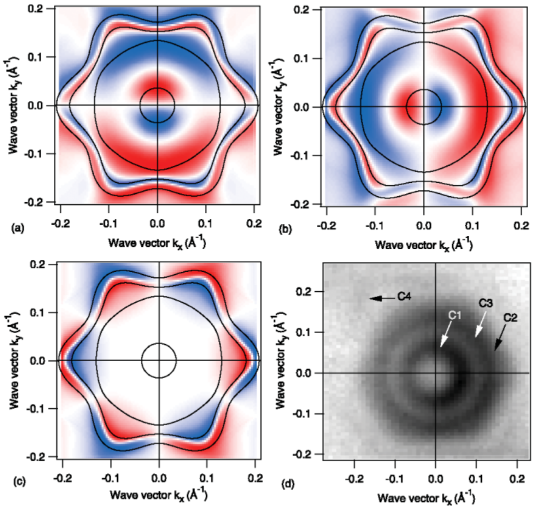
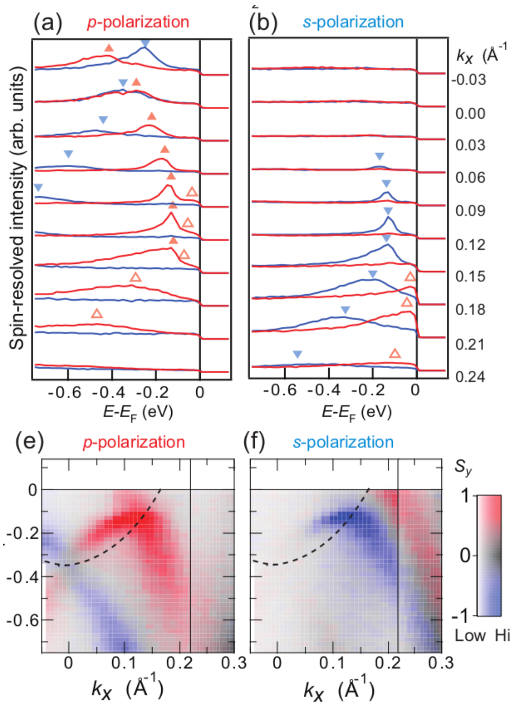


FIG. 3 (color). (a)–(c) Constant energy contour of the spin polarization $\boldsymbol{P}$ in x, y, and z direction, respectively, at an energy of -0.55 eV. The projection in x, y, and z direction is shown in (a)–(c), respectively. The intensity scale is linear with red and blue coloring corresponding to positive and negative values,

Calculated S_x,S_y,S_z at -0.55 eV



R. Noguchi et al. PRB 2017

System is **non-magnetic**. Strong spin-orbit coupling and breaking of inversion symmetry cause large spin-polarization of bands.

Self-energy(2) — Dynamical mean field theory

Strongly correlated systems: $3d$-metal oxides, $5f$ elements …
Competition between kinetic energy and local Coulomb repulsion
→ band magnetism, metal-insulator transition, high-T_c super-conductivity (?)

Hubbard model

$$H = \sum_{k\sigma} \epsilon_k n_{k\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} = \sum_{ij\sigma} t_{ij} c^+_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

$$G_{k\sigma}(\omega) = [\omega - \epsilon_k - \Sigma_{k\sigma}(\omega)]^{-1}$$

Static mean-field theory (e.g. exchange, HFA)

$$\Sigma_{k\sigma}(\omega) = U \langle n_{k-\sigma} \rangle \qquad \neq \mathrm{fct}(\omega)$$

Dynamical mean-field theory

$$\Sigma_{k\sigma}(\omega) \to \Sigma_\sigma(\omega) \qquad \neq \mathrm{fct}(k)$$

Self-energy(2) — Dynamical mean field theory

In DMFT, Hubbard model ($U \neq 0$ on all sites) is mapped on Anderson impurity model ($U \neq 0$ only at one site) → $\Sigma(\omega)$ local, k-independent.
Self-consistency: Anderson impurity GF coincide with local Hubbard (lattice) Green's function

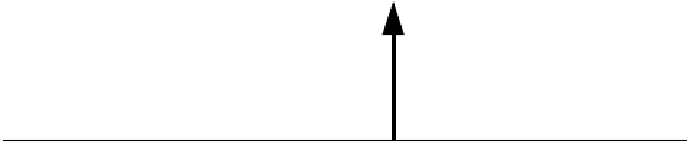
$$G_{imp}(\omega) = G_{00}(\omega) = \sum_k [\omega + \epsilon_k - \Sigma_k(\omega)]^{-1}$$

Approximation of DMFT: $\Sigma_k(\omega) = \Sigma_{imp}(\omega)$
This gives self-consistent equation for $\Sigma_{imp}(\omega)$
The difficult part is the solution of the Anderson impurity model.
Various numerical "solvers" exist, with different advantages and disadvantages.
DMFT has been combined with DFT.
DFMT becomes exact in infinite dimensions [W. Metzner PhD 1999].

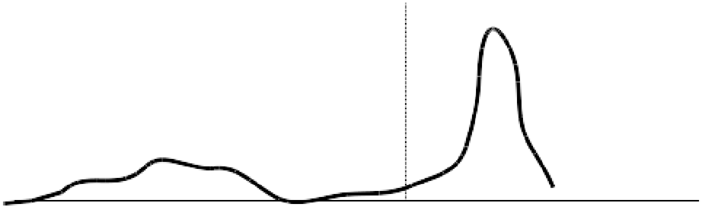
Spectral function

$$A_k(\omega) = -\frac{1}{\pi}\mathrm{Im}G_k(\omega)$$

non-interacting system
$A_k^0(\omega) = \delta(E - \epsilon_k)$

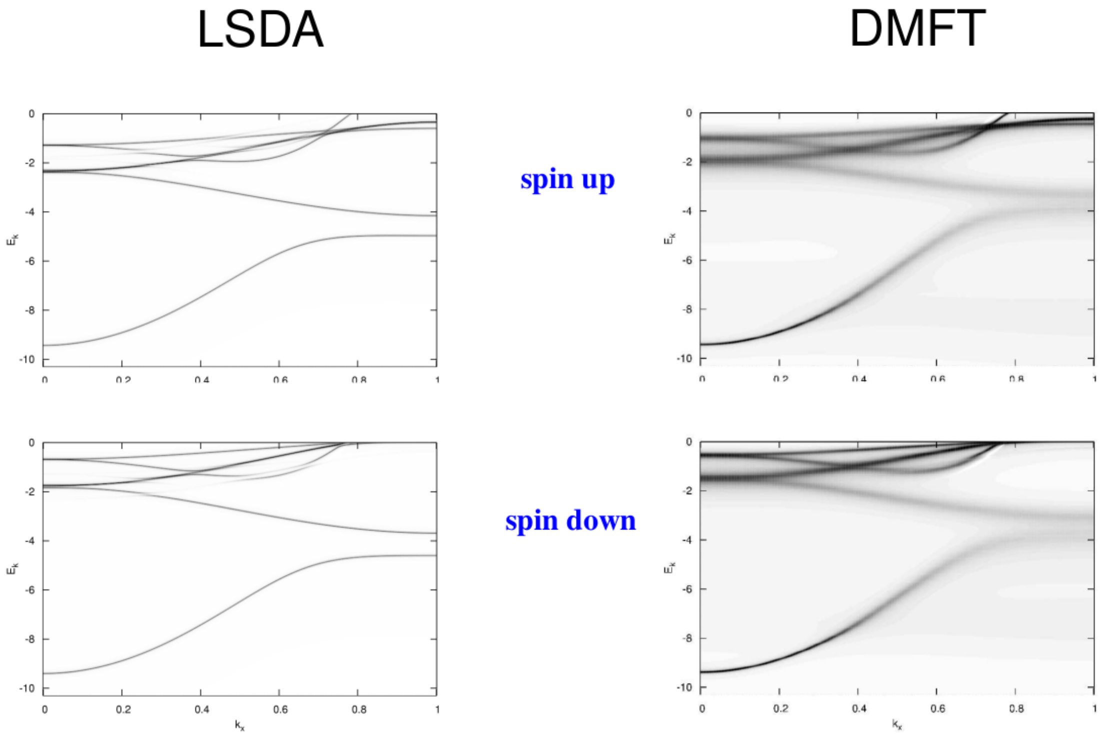


interacting system $A_k(\omega)$



Bloch spectral functions

Spin-resolved results for Ni for $\vec{k} \parallel [001]$



LSDA

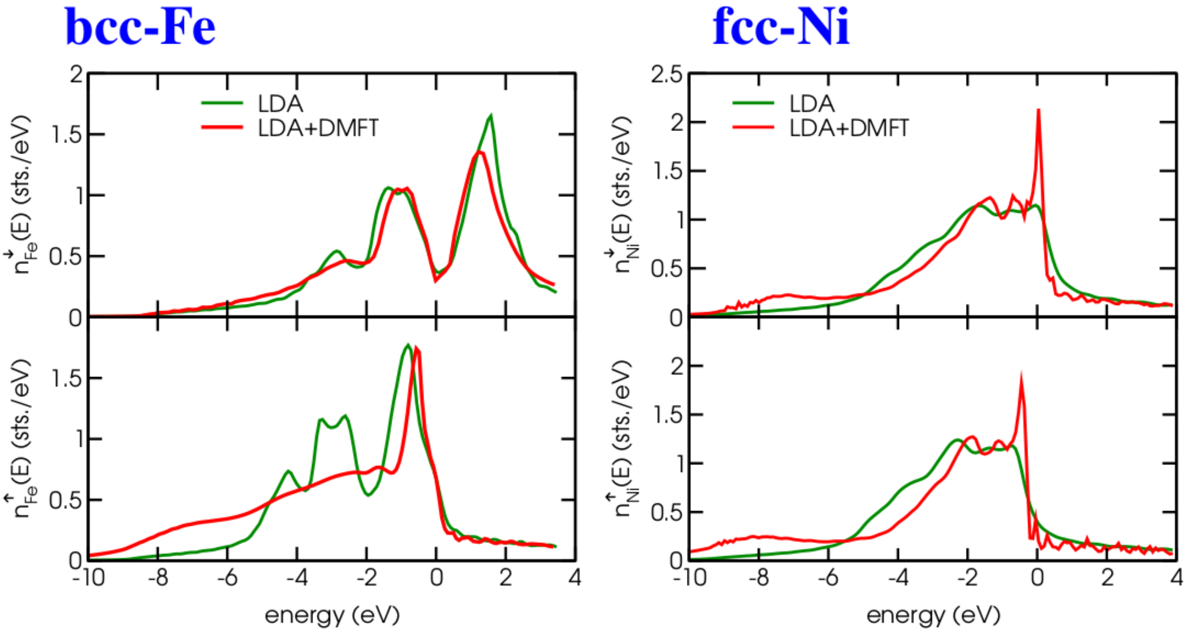
DMFT

spin up

spin down

Courtesy of LMU H. Ebert's group

Spin resolved DOS of bcc-Fe and fcc-Ni



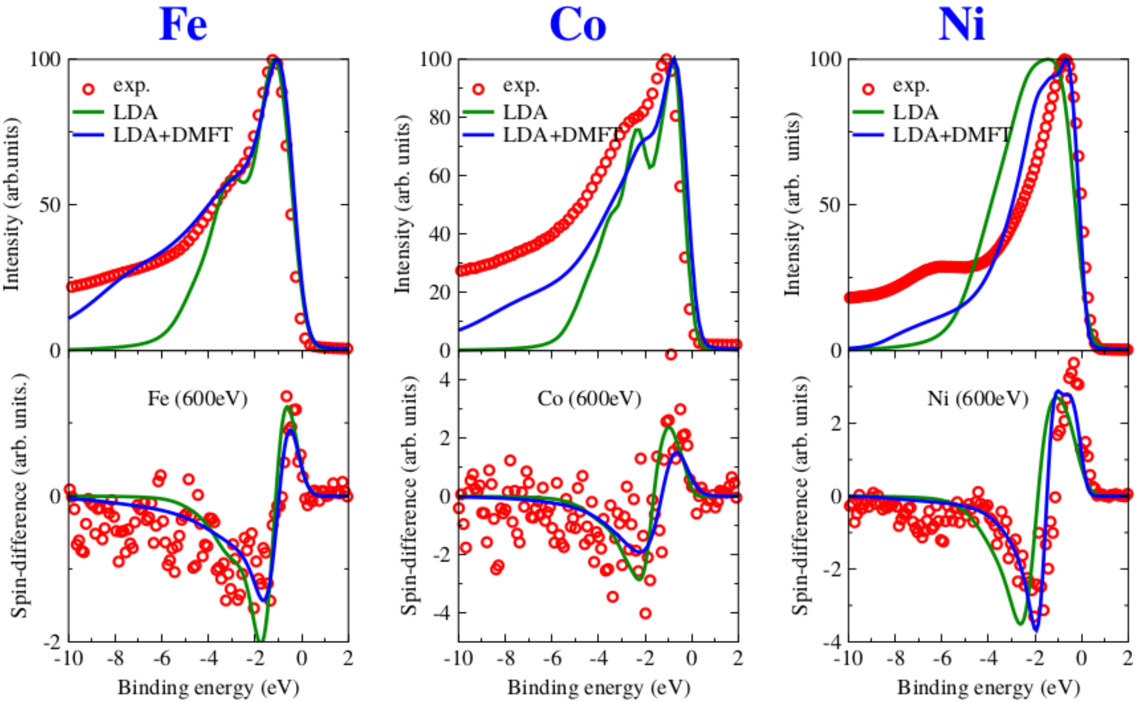
- Fe: $U = 2.0$ eV, $J = 0.9$ eV, $T = 400$ K
- Ni: $U = 3.0$ eV, $J = 0.9$ eV, $T = 400$ K

Courtesy of LMU H. Ebert's group

Fano effect in VB-XPS of ferromagnets

Photocurrent and spin-difference $E_{phot} = 600$ eV

Experiments - N. Brookes *et al.*, ESRF



Courtesy of LMU H. Ebert's group

That's all

Thanks for your attention.