# Radiation-Matter Interaction

The aim:

1) To give a description of the process of interaction in terms of the electronic structure of the system (atoms, molecules, solids, liquid or amorphous samples) .

2) To use the interaction with radiation as a probe of the microscopic structure of matter at the atomic level.

The Method: Modern (QUANTUM) Physics.

1) Classical Physics of matter and e.m. field
   + Quantum conditions (the old quantum theory; 1900-1925)
2) Quantum theory of the electromagnetic field. Quantum mechanics of (wave mechanics) of charged particles or systems of many particles. (1927 and following years)
3) Quantum field theory. Quantum electrodynamics. (1940 and foll.)
4) Quantum theory of condensed matter. (since 1940 to today)

The tools:

Perturbation Theory of the interaction between radiation and electron sistems (fermions) provides a powerful instrument of calculation and a visualization scheme (Feynman diagrams) of elementary processes.

# Summary.

Ingredients:

- The e.m. classical field.
- The e.m. field is quantized; photons.
- Systems of moving charges and their interaction with the field.
- The set of quntum states of the e.m. field and of matter.
- The elementary processes. (The subject of our investigtion but also the toos of our detection systems.)
- Transition amplitudes, matrix elements, cross sections.
- Dipole approximation and beyond.

Processes at first and second order:

- Absorption (and emission). One-photon processes.
  Optical absorption. X-ray absorption. Magnetic systems.
- Photoexcitation and photoemission. Photon in >> electron out.
  In atoms, molecules, solids. Core vs. valence. Band mapping (in solids).
- Diffusion: elastic and indelastic. Resonant diffusion.
  Fluorescence.Thomson scattering, magnetic scattering.

# Maxwell equations

The classical theory of electromagnetic field.
In c.g..s-Gauss units (non-razionalized) the equations of e.m. are

$$\nabla \cdot \mathbf{E} = 4\pi\rho \qquad \nabla \times \mathbf{B} = \frac{4\pi \mathbf{J}}{c} + \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t}$$

$$\nabla \cdot \mathbf{B} = 0 \qquad \nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}$$

$\rho$ charge density, $\mathbf{J}$ current density.
Starting from SI (more familiar) system, we can put

$4\pi\epsilon_0 = 1$ $\mu_0 = 1/\varepsilon_0 c^2$ **B** → **B**/c

The electric field and the magnetic induction field have here the same units. Thus the force on the charge q that moves with velocity **v** is given by

$$\mathbf{F} = q\mathbf{E} + q\frac{\mathbf{v}}{c} \times \mathbf{B}$$

Remember: $\varepsilon_0\mu_0 = 1/c^2$

One-minute note – In electromagnetism we must use 3D notation for differential operators. For non common users we must summarize in few lines what *grad*, *div* and *rot* are.

~~In this chapter from the first section we have used some symbols, whose definitions follow.~~ The gradient operator $\nabla$ in three dimensions is

$$\nabla \equiv \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) \tag{48}$$

We summarize in the following lines its actions on a a function $f(\mathbf{r})$ or on a vector $\mathbf{a}(\mathbf{r})$.

$$\nabla f = \left(\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, \frac{\partial f}{\partial z}\right) \tag{49}$$

is a vector also labeled grad $f$;

$$\nabla \cdot \mathbf{a} = \frac{\partial a_x}{\partial x} + \frac{\partial a_y}{\partial y} + \frac{\partial a_z}{\partial z} \tag{50}$$

is a scalar (a function) also named div $\mathbf{a}$; while

$$\nabla \times \mathbf{a} = \left(\frac{\partial a_z}{\partial y} - \frac{\partial a_y}{\partial z}, \frac{\partial a_x}{\partial z} - \frac{\partial a_z}{\partial x}, \frac{\partial a_y}{\partial x} - \frac{\partial a_x}{\partial y}\right) \tag{51}$$

is a vector, named rot $\mathbf{a}$.

# Scalar and vector potentials.

The fields can be obtained by the potentials (scalar & vector)

$$\mathbf{E}(\mathbf{r},t) = -\boldsymbol{\nabla}\varphi(\mathbf{r},t) - \frac{1}{c}\frac{\partial \mathbf{A}(\mathbf{r},t)}{\partial t}$$

$$\mathbf{B}(\mathbf{r},t) = \boldsymbol{\nabla} \times \mathbf{A}(\mathbf{r},t)$$

They are left unchanged under Gauge transformations on the potentials

$$\varphi(\mathbf{r},t) \rightarrow \varphi(\mathbf{r},t) + \frac{\partial f(\mathbf{r},t)}{c\,\partial t} \qquad \mathbf{A}(\mathbf{r},t) \rightarrow \mathbf{A}(\mathbf{r},t) - \boldsymbol{\nabla} f(\mathbf{r},t)$$

From Maxwell equations we obtain by substitution the equations of motion for the potentials

$$\boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\mathbf{A}) - \boldsymbol{\nabla}^2\mathbf{A} + \frac{1}{c^2}\frac{\partial}{\partial t}\boldsymbol{\nabla}\varphi + \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial^2 t} = \frac{4\pi}{c}\mathbf{J}$$

$$-\boldsymbol{\nabla}^2\varphi - \boldsymbol{\nabla}\cdot\left(\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}\right) = 4\pi\rho$$

# Coulomb gauge

A vector field can be written as a sum of a conservative or non-rotational field (transverse) and a solenoidal field with zero divergence (longitudinal).

$$\mathbf{J}(\mathbf{r},t) = \mathbf{J}_T(\mathbf{r},t) + \mathbf{J}_L(\mathbf{r},t)$$

$$\boldsymbol{\nabla}\cdot\mathbf{J}_T = 0 \qquad \boldsymbol{\nabla}\times\mathbf{J}_L = \mathbf{0}$$

For the **J** field, the current density field, only the longitudinal part appears in the continuity equation

$$\boldsymbol{\nabla}\cdot\mathbf{J}_L = -\frac{\partial\rho}{\partial t}$$

For the vector potential field, we can choose the gauge in order to have

$$\boldsymbol{\nabla}\cdot\mathbf{A} = 0$$

It is the gauge called Coulomb gauge, where the equations of the potentials are decoupled

$$-\boldsymbol{\nabla}^2\varphi = 4\pi\rho \qquad -\boldsymbol{\nabla}^2\mathbf{A} + \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial^2 t} = \frac{4\pi}{c}\mathbf{J}_T$$

# Coulomb gauge II.

The equations for the potentials are inhomogeneous PDEs. Each of them has a general solution that is the sum of a particular solution plus the general solution of the corresponding homogeneous PDE (without sources). The particular solution can be chosen to have:

$$\varphi(\mathbf{r},t) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}',t)}{|\,\mathbf{r}-\mathbf{r}'\,|}$$

- The scalar potential becomes the ELECTROSTATIC potential determined by the charge distribution at the same *fixed* time in all space (instantaneous Coulomb potential).

$$\mathbf{A}(\mathbf{r},t) = \int d\mathbf{r}' \frac{\mathbf{J}_T(\mathbf{r}',t')}{|\,\mathbf{r}-\mathbf{r}'\,|} \qquad t' = t - \frac{|\,\mathbf{r}-\mathbf{r}'\,|}{c}$$

- The vector potential is due to the distribution of the transverse density of current, accounting for the delay due to the finite speed of light.
- In absence of charge and current we have:

$$\varphi = 0 \qquad \boldsymbol{\nabla}^2\mathbf{A} - \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial^2 t} = 0$$

# The classical free e.m. field

The solution for the free field can be expanded in plane waves

$$\mathbf{A}(\mathbf{r},t) = \sum_{\mathbf{k},s} \left( \mathcal{A}(\mathbf{k},s)\hat{\boldsymbol{\epsilon}}_{s\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}-i\omega_{\mathbf{k}}t} + \mathcal{A}^*(\mathbf{k},s)\hat{\epsilon}^*_{s\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}+i\omega_{\mathbf{k}}t} \right)$$

(Note: The fist part is called the *'positive' frequency* term, the second the negative frequency tem, so $A=A^{(+)}+A^{(-)}$.)

The volume of normalization is $\mathcal{V} = L_x L_y L_z$

Periodic boundary conditions in a box → 3D grid of allowed wavevectors

$$\mathbf{k} = 2\pi\left(\frac{n_x}{L_x}, \frac{n_y}{L_y}, \frac{n_z}{L_z}\right)$$

Polarizations and the wavevectors are orthogonal

$$\hat{\boldsymbol{\epsilon}}_{1\mathbf{k}} \cdot \mathbf{k} = \mathbf{0} \qquad \hat{\boldsymbol{\epsilon}}_{2\mathbf{k}} \cdot \mathbf{k} = \mathbf{0}$$

The angular frequency of each mode is $\omega_{\mathbf{k}} = c \mid \mathbf{k} \mid$

The total energy of the free field is the Hamiltonian

**E** and **B** are obtained from **A**.

$$\mathcal{H}_f = \frac{1}{8\pi} \int (\mathbf{E}^2 + \mathbf{B}^2) d\mathbf{r}$$

# The quantized free e.m. field

We rewrite the coefficient of the expansion as

$$\mathbf{A}(\mathbf{r},t)=\sum_{\mathbf{k},s}\left(\frac{4\pi\hbar c^2}{2\mathcal{V}\omega_{\mathbf{k}}}\right)^{\frac{1}{2}}\left(a_{\mathbf{k}s}(t)\hat{\boldsymbol{\epsilon}}_{s\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}+a^{\dagger}_{\mathbf{k}s}(t)\hat{\epsilon}^{*}_{s\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{r}}\right)$$

With new adimensional *dynamical variables* (complex numbers) $a_{\mathbf{k}s}(t)$ $a^{\dagger}_{\mathbf{k}s}(t)$
The time dependence is given by the new eq.s of motions

$$\frac{\partial^2}{\partial t^2}a_{\mathbf{k}s}(t)=-\omega^2_{\mathbf{k}}a_{\mathbf{k}s}(t)\quad\rightarrow\quad a_{\mathbf{k}s}(t)=a_{\mathbf{k}s}e^{-i\omega_{\mathbf{k}}t}\qquad a^{\dagger}_{\mathbf{k}s}(t)=a^{\dagger}_{\mathbf{k}s}e^{i\omega_{\mathbf{k}}t}$$

The Hamiltonian of the field becomes

$$\mathcal{H}_f=\sum_{\mathbf{k},s}\frac{1}{2}\hbar\omega_{\mathbf{k}}(a^{\dagger}_{\mathbf{k}s}a_{\mathbf{k}s}+a_{\mathbf{k}s}a^{\dagger}_{\mathbf{k}s})$$

that is the sum of an infinite set of harmonic oscillators of different frequencies (one for each mode). We pass from the classical to the quantum description, by transforming the complex dynamical variables into operators, imposing the commutation relations

$$[a_{\mathbf{k}s},a^{\dagger}_{\mathbf{k}'s'}]=\delta_{\mathbf{k}\mathbf{k}'}\delta_{ss'}$$

# Radiation field quantization. II

- The Hamiltonian $\mathcal{H}_f = \sum_{\mathbf{k},s} \hbar\omega_{\mathbf{k}} \left( a^{\dagger}_{\mathbf{k}s} a_{\mathbf{k}s} + \frac{1}{2} \right)$
- Hermitian number operators $\check{n}_{\mathbf{k}s} = a^{\dagger}_{\mathbf{k}s} a_{\mathbf{k}s}$
- **Eigenstates & eigenvalues of number operators** $\check{n}_{\mathbf{k}s} \mid n_{\mathbf{k}s} > = n_{\mathbf{k}s} \mid n_{\mathbf{k}s} >$
- Properties following from the commutation relations

$$\check{n}_{\mathbf{k}s}(a_{\mathbf{k}s} \mid n_{\mathbf{k}s} >) = (n_{\mathbf{k}s} - 1)(a_{\mathbf{k}s} \mid n_{\mathbf{k}s} >)$$

$$\check{n}_{\mathbf{k}s}(a^{\dagger}_{\mathbf{k}s} \mid n_{\mathbf{k}s} >) = (n_{\mathbf{k}s} + 1)(a^{\dagger}_{\mathbf{k}s} \mid n_{\mathbf{k}s} >)$$

$n_{\mathbf{k}s}$ =0,1,2,…

$$< n_{\mathbf{k}s} \mid n_{\mathbf{k}s} > = 1$$

- $a$ and $a^{\dagger}$ are respectively the operators of absorption (lowering) and creation (increasing). They change by a unit the number of photons in the states with defined photon number.

$$a_{\mathbf{k}s} \mid n_{\mathbf{k}s} > = \sqrt{n_{\mathbf{k}s}} \mid n_{\mathbf{k}s} - 1 >$$

$$a^{\dagger}_{\mathbf{k}s} \mid n_{\mathbf{k}s} > = \sqrt{n_{\mathbf{k}s} + 1} \mid n_{\mathbf{k}s} + 1 >$$

$$\mid n_{\mathbf{k}s} > = \frac{\left(a^{\dagger}_{\mathbf{k}s}\right)^{n_{\mathbf{k}s}}}{\sqrt{n_{\mathbf{k}s}!}} \mid 0_{\mathbf{k}s} >$$

# e.m. fields and photons

A quantum state defined by the number of photons in each mode is

$$| \{n_{\mathbf{k}s}\} > = | \dots n_{\mathbf{k}s} \dots > = \prod_{\mathbf{k}_i} \prod_{s_i} | n_{\mathbf{k}_i s_i} >$$

A basis state is defined by a succession of positive or zero integer numbers that indicate the number of photon in each mode.
These states have a well defined number of photons and a well defined energy. They are eigenstates of *N* e of $H_f$ (…they commute!)

$$N_{\{n_{\mathbf{k}s}\}} = \sum_{k_i \ s_i} n_{\mathbf{k}_i s_i} \qquad E_{\{n_{\mathbf{k}s}\}} = \sum_{\mathbf{k}_i s_i} \hbar\omega_{\mathbf{k}_i} (n_{\mathbf{k}_i s_i} + \frac{1}{2})$$

The form a basis to representany state Physical state of free e.m. field: a linear combination of these states with complex coefficients
is a possible state of the systems. The state of a system –remember - in quantum physics is not an observable.
The fields are, on the contrary, quantum operators, with a part containing absorption operators, where only positive frequencies appear and another containing creation operators where only negative frequencies are present in the phase factors. They are observable with expectation values given by the average value (expectation value) on the quantum state.

$$\mathbf{A}(\mathbf{r},t) = \sum_{\mathbf{k},s}\left(\frac{4\pi\hbar c^2}{2\mathcal{V}\omega_{\mathbf{k}}}\right)^{\frac{1}{2}}\left(a_{\mathbf{k}s}\hat{\boldsymbol{\epsilon}}_{s\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}-i\omega_{\mathbf{k}}t} + a^{\dagger}_{\mathbf{k}s}\hat{\epsilon}^{*}_{s\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{r}+i\omega_{\mathbf{k}}t}\right)$$

$$= \mathbf{A}^{(+)}(\mathbf{r},t) + \mathbf{A}^{(-)}(\mathbf{r},t)$$

The first term is a combination of operators that in each mode destroy a photon, the second is made of operators that create a photon. Both are acting on the vector space of quantum states at defined photon number. We can derive the operator of the same form that represent the electric And the magnetic field.

$$\mathbf{E}(\mathbf{r},t) = \sum_{\mathbf{k},s} i\left(\frac{4\pi\hbar\omega_{\mathbf{k}}}{2\mathcal{V}}\right)^{\frac{1}{2}}\left(a_{\mathbf{k}s}\hat{\boldsymbol{\epsilon}}_{s\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}-i\omega_{\mathbf{k}}t} - a^{\dagger}_{\mathbf{k}s}\hat{\epsilon}^{*}_{s\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{r}+i\omega_{\mathbf{k}}t}\right)$$

$$\mathbf{B}(\mathbf{r},t) = \sum_{\mathbf{k},s} i\left(\frac{4\pi\hbar\omega_{\mathbf{k}}}{2\mathcal{V}}\right)^{\frac{1}{2}}\left(a_{\mathbf{k}s}(\hat{\mathbf{k}}\times\hat{\boldsymbol{\epsilon}}_{s\mathbf{k}})e^{i\mathbf{k}\cdot\mathbf{r}-i\omega_{\mathbf{k}}t} - a^{\dagger}_{\mathbf{k}s}(\hat{\mathbf{k}}\times\hat{\epsilon}^{*}_{s\mathbf{k}})e^{-i\mathbf{k}\cdot\mathbf{r}+i\omega_{\mathbf{k}}t}\right)$$

Where $\hat{\mathbf{k}} = \mathbf{k}/k$ is the unit vector of the direction of the wave propagation.

# Attention!

The states at defined number of photons have surprising properties; the value of the electric field at a given point and at a given time over an eigenstate of the photon numbers *is always ZERO*!

On the contrary, the square modulus of the electric field is completely well defined. The same for magnetic field.

$$\langle n_{\vec{k}s} | \vec{E} | n_{\vec{k}s} \rangle = 0$$

$$\langle n_{\vec{k}s} | \vec{E}^2 | n_{\vec{k}s} \rangle = 4\pi \hbar \omega_{\vec{k}} \left( n_{\vec{k}s} + \frac{1}{2} \right)$$

$|n_{\vec{k}s}\rangle$ state with n photons in **k**,s

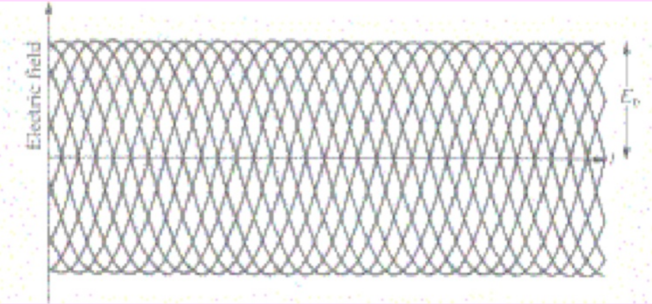
To build a state |c> that looks like

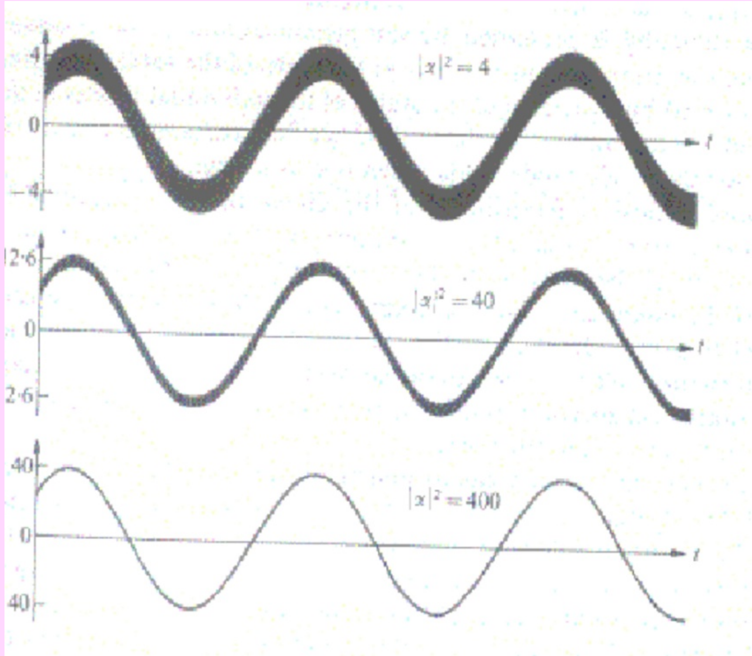
$$\langle c | \vec{E} | c \rangle \propto \sin(\vec{k} \cdot \vec{r} - \omega t + \varphi)$$

We mustcombine many states with different n

$$|c\rangle = e^{-\frac{1}{2}|\alpha|^2} \sum_n \frac{\alpha^n}{(n!)^{1/2}} |n\rangle$$

$$\langle c | \hat{n} | c \rangle = |\alpha|^2$$





## Interaction of the e.m. field with a system of charged particles. I.

An electron, an atom, a molecule, a solid are systems of *N* charged particles. The dynamical variables are the coordinates and their conjugate momenta that obey the commutation rules

$$[r_{i\alpha,}, p_{j\beta}] = i\hbar\delta_{ij}\delta_{\alpha\beta}$$

In the Coulomb gauge the electric field contains, in the presence of charges, a part which is unrotational, or conservative, contributing to the total energy with the term

$$\frac{1}{8\pi}\int \mathbf{E}_L^2 d\mathbf{r} = \frac{1}{8\pi}\int (\boldsymbol{\nabla}\varphi)^2\, d\mathbf{r} = \frac{1}{8\pi}\int \left(-\varphi\boldsymbol{\nabla}^2\varphi\right) d\mathbf{r} = \frac{1}{2}\int \frac{\rho(\mathbf{r},t)\rho(\mathbf{r}',t)}{\mid \mathbf{r}-\mathbf{r}' \mid} d\mathbf{r}d\mathbf{r}'$$

That, for a system of point charges, becomes, is just the Coulombic potential energy.

$$\frac{1}{2}\sum_{i\neq j}\frac{q_i q_j}{\mid \mathbf{r}_i - \mathbf{r}_j \mid}$$

One has to add the kinetic energy of the point charges $\sum_i \frac{\mathbf{p}_i^2}{2m_i}$

If the charge are moving in a radiation field we have to make the substitution

$$\mathbf{p}_i \rightarrow \mathbf{p}_i - \frac{q_i}{c}\mathbf{A}(\mathbf{r}_i)$$

# Interaction of the e.m. field with the charges. II

The Hamiltonian of the system of charges interacting with the external field becomes

$$\mathcal{H}_s = \sum_i \frac{\mathbf{1}}{2m_i}\left(\mathbf{p}_i - \frac{q}{c}\mathbf{A}(\mathbf{r}_i)\right)^2 + \frac{1}{2}\sum_{i\neq j}\frac{q_i q_j}{\mid \mathbf{r}_i - \mathbf{r}_j \mid}$$

The total Hamiltonian (charge system + free firld +interaction) is

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_f = \mathcal{H}_s^0 + \mathcal{H}_f + \mathcal{H}_I = \mathcal{H}_0 + \mathcal{H}_I$$

Where we separate the unperturbed Hamiltonian

$$\mathcal{H}_0 = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2}\sum_{i\neq j}\frac{q_i q_j}{\mid \mathbf{r}_i - \mathbf{r}_j \mid} + \sum_{\mathbf{k},s}\hbar\omega_{\mathbf{k}}\left(a_{\mathbf{k}s}^{\dagger}a_{\mathbf{k}s} + \frac{1}{2}\right)$$

from the hamiltonian of the interaction that, in the Coulomb gauge, is written

$$\mathcal{H}_I = \sum_i\left(-\frac{q_i}{m_i c}\mathbf{A}(\mathbf{r}_i)\cdot\mathbf{p}_i + \frac{q_i^2}{2m_i c^2}\mathbf{A}^2(\mathbf{r}_i)\right)$$

# Interaction of the e.m. field with the charges. III

By including relativistic corrections (among them the spin of the electron) there are other terms in $H_0$ and in $H_I$. See Appendix.

The state of the system of *N* charges with its appropriate quantum numbers $\alpha$ and corresponding energy eigenvalue $E_\alpha$ can be projected onto the coordinate space, giving the (more familiar) wavefunction

$$\psi_\alpha(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = < \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N \mid \psi_\alpha >$$

For our purposes the system of charges is made by the electrons. The positions of the nuclei can be treated as *classical variables*. The state and the wave function of the electrons change sign if we exchange the coordinates of two electrons. They are *Fermions.*

The unperturbed eigenstates of $H_0$ are

$$\mid \Psi > = \mid \psi_\alpha > \otimes \mid \{n_{\mathbf{k}s}\} >$$

and the interaction can create transitions from an unperturbed state to another. I. e. nonzero transition matrix elements can exist between two states.

# Power expansion of the interaction.

If the interaction is switched on at $t_i$ and is turned off at $t_f$, we can describe the evolution of the system in term of an amplitude of transition among the states of the unperturbed system.

$$< \Psi_b \mid U(t_f, t_i) \mid \Psi_a >$$

In the Heisemberg representation for the non interacting system (interaction representation) the states of the *free* system do not evolve in time.

$$\mid \Psi_a^I > = e^{i\mathcal{H}_0 t/\hbar} \mid \Psi_a >$$

The transition amplitude can be written as

$$S_{ba} = < \Psi_b^I \mid \tilde{U}(t_f, t_i) \mid \Psi_a^I >$$

$$\tilde{U}(t_f, t_i) = e^{i\mathcal{H}_0 t_f/\hbar} U(t_f, t_i) e^{-i\mathcal{H}_0 t_i/\hbar}$$

The evolution operator can be expanded in powers of the interaction.

$$\tilde{U}(t_f, t_i) = 1 + \sum_{n=1}^{\infty} \tilde{U}^{(n)}(t_f, t_i)$$

$$\tilde{U}^{(n)}(t_f, t_i) =$$

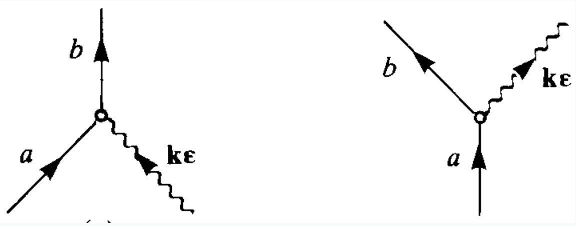
$$= \left(\frac{i}{i\hbar}\right)^n \int_{t_f \geq \tau_n \geq \tau_{n-1}} d\tau_n \ldots \int_{\tau_3 \geq \tau_2 \geq \tau_1} d\tau_2 \int_{\tau_2 \geq \tau \geq t_i} d\tau_1 \widetilde{\mathcal{H}}_I(\tau_n) \ldots \widetilde{\mathcal{H}}_I(\tau_2) \widetilde{\mathcal{H}}_I(\tau_1) \qquad (30)$$

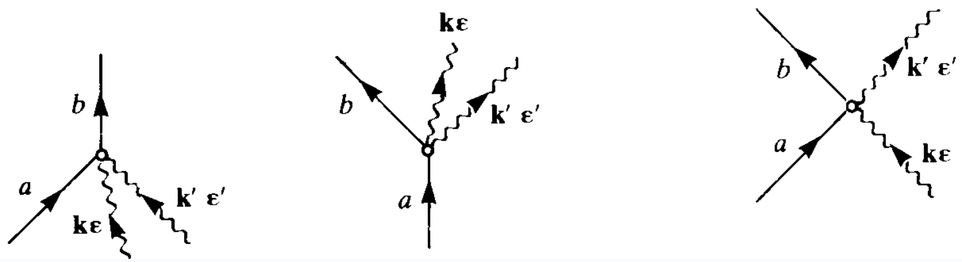
The perturbative expansion is a series of Feynman diagrams.

# Elementary processes.

*First order contributions* in

$$\mathcal{H}_I = \sum_i \left( -\frac{q_i}{m_i c}\mathbf{A}(\mathbf{r}_i)\cdot\mathbf{p}_i + \frac{q_i^2}{2m_i c^2}\mathbf{A}^2(\mathbf{r}_i) \right)$$

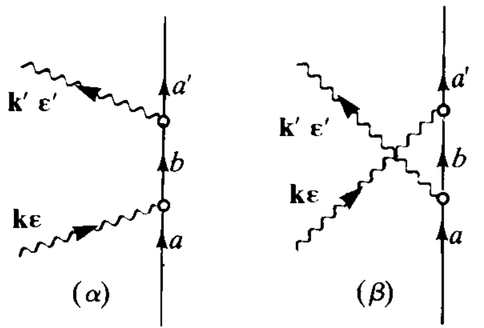




- Absorption of one photon
- Emission of one photon
- Absorption of two photons
- Emission of two photons
- Diffusion

Note: Conservation of energy, total momentum,…

Contributions at *second order*

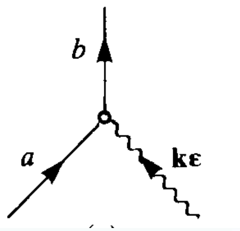


- Absorption of a photon followed by emission
- Emission of a photon followed by absorption

Note: Sum (interference) among intermediate states.

# Absorption and Emission.

The first diagram of the first order represents the absorption of a photon. We get for a system of electrons in an atom or a molecules



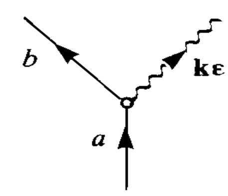
$$S_{ab}^{(1)} = \frac{1}{i\hbar}\frac{e}{m}\left(\frac{4\pi\hbar}{2\mathcal{V}\omega_{\mathbf{k}}}\right)^{\frac{1}{2}} < n_{\mathbf{k}s}-1 \mid a_{\mathbf{k}s} \mid n_{\mathbf{k}s} >< \Psi_B \mid \sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i}\, \hat{\boldsymbol{\epsilon}}_{s\mathbf{k}}\cdot\mathbf{p}_i \mid \Psi_A >$$

$$\times \int_{t_f \geq \tau \geq \tau_i} d\tau \exp(+\frac{i}{h}(E_B - E_A - \hbar\omega_{\mathbf{k}})) =$$

$$= -2\pi i\frac{e}{m}\left(\frac{4\pi\hbar}{2\mathcal{V}\omega_{\mathbf{k}}}\right)^{\frac{1}{2}} (n_{\mathbf{k}s})^{\frac{1}{2}}\; \hat{\boldsymbol{\epsilon}}_{s\mathbf{k}}\cdot \; < \Psi_B \mid \sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i}\, \mathbf{p}_i \mid \Psi_A > \delta(E_B - E_A - \hbar\omega_{\mathbf{k}})$$

where $-e$ and $m$ are the charge and the mass of the electron. The time integral extended from the beginning to the end of the interaction (from minus infinite to plus infinite) gives the conservation of energy.

The second diagrams represents the emission



$$S_{ab}^{(1b)} = -2\pi i\frac{e}{m}\left(\frac{4\pi\hbar}{2\mathcal{V}\omega_{\mathbf{k}}}\right)^{\frac{1}{2}} (n_{\mathbf{k}s}+1)^{\frac{1}{2}}$$

$$\hat{\boldsymbol{\epsilon}}^{*}_{s\mathbf{k}}\cdot \; < \Psi_B \mid \sum_i e^{-i\mathbf{k}\cdot\mathbf{r}_i}\, \mathbf{p}_i \mid \Psi_A > \delta(E_B - E_A + \hbar\omega_{\mathbf{k}})$$

that takes place only starting from an excited states ($E_a > E_b$).

# The matrix element.

The matrix element of the linear part of the interaction

$$< \Psi_B \mid \sum_i e^{-i\mathbf{k}\cdot\mathbf{r}_i}\ \mathbf{p}_i \mid \Psi_A >$$

appears also in higher order terms; we notice that we can expand

$$e^{i\mathbf{k}\cdot\mathbf{r}_i} = 1 + i\mathbf{k}\cdot\mathbf{r}_i + \ldots$$

Generally the wavelength $\lambda=2\pi/k$ is great respect to the atomic dimensions and we can consider only the first term (dipole approx.).

$$< \Psi_B \mid \ \mathbf{p}_i \mid \Psi_A >$$

To go beyond the dipole approximation or when the dipole matrix element is zero, we can include also the second term originating the magnetic dipole and the electrical quadrupole.

$$\epsilon_{s\mathbf{k}}\cdot < \Psi_B \mid \sum_i (-i\mathbf{k}\cdot\mathbf{r}_i)\,\mathbf{p}_i \mid \Psi_A >= -i\frac{1}{2}\sum_{\alpha,\beta}\epsilon_{s\mathbf{k}\alpha}k_\beta < \Psi_B \mid \sum_i r_{i\beta}p_{i\alpha} \mid \Psi_A >=$$

$$= -\frac{i}{2}\sum_{\alpha,\beta}\epsilon_{s\mathbf{k}\alpha}k_\beta < \Psi_B \mid \sum_i (r_{i\beta}p_{i\alpha} - r_{i\alpha}p_{i\beta}) \mid \Psi_A > -\frac{i}{2}\sum_{\alpha,\beta}\epsilon_{s\mathbf{k}\alpha}k_\beta < \Psi_B \mid \sum_i (r_{i\beta}p_{i\alpha} + r_{i\alpha}p_{i\beta}) \mid \Psi_A >$$

Magnetic dipole term Electrical quadrupole

# Other forms of dipole matrix element

From the commutator

$$[\mathbf{r}_i, H_S^0] = \frac{i\hbar}{m}\mathbf{p}_i$$

We obtain from the form *dipole velocity* (matrix element of **p**)

$$< \Psi_B \mid \mathbf{p}_i \mid \Psi_A >= \frac{m}{i\hbar} < \Psi_B \mid \mathbf{r}_i H_S^0 - H_S^0 \mathbf{r}_i \mid \Psi_A >=$$

$$im\frac{E_B - E_A}{\hbar} < \Psi_B \mid \mathbf{r}_i \mid \Psi_A >= im\omega_{\mathbf{k}} < \Psi_B \mid \mathbf{r}_i \mid \Psi_A >$$

the form *dipole length.*

There is also a form called *dipole acceleration*.

# Absorption. I

In the dipole approximation the total cross section is obtained by the square modulus of the transition amplitude divided by the flux of incident photons (*c/V*), then summing on final states

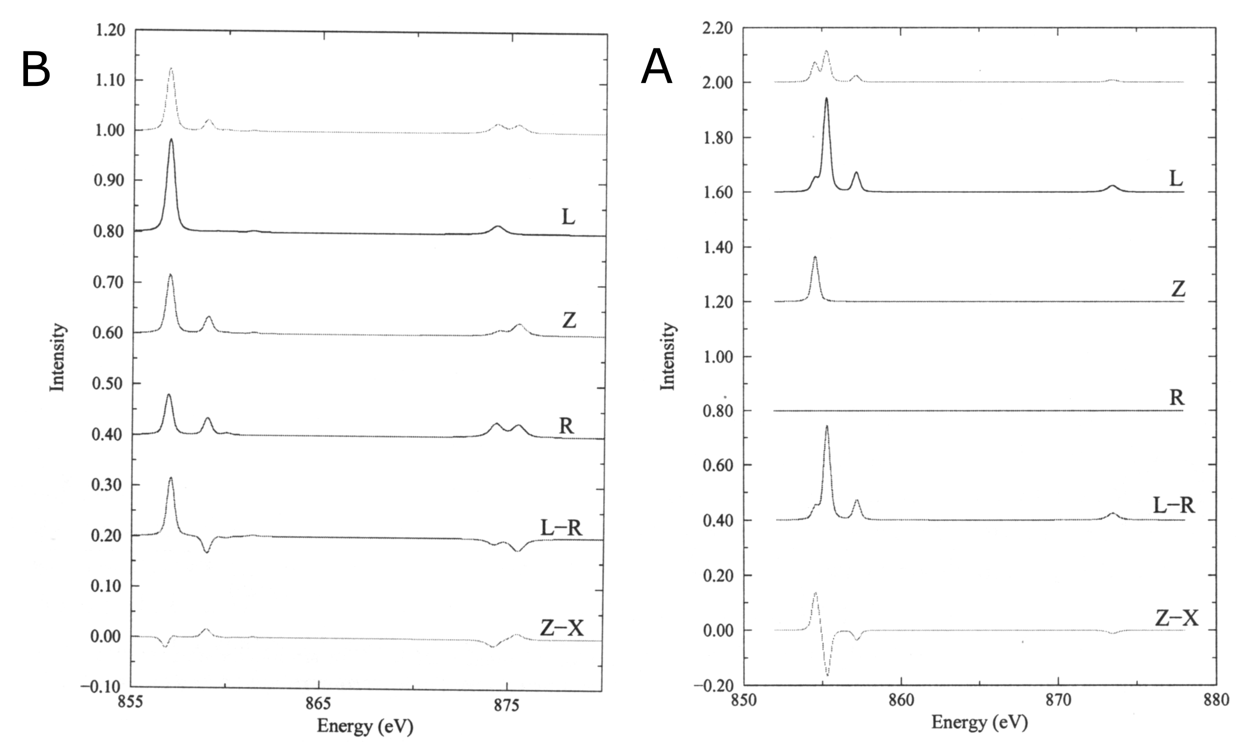
$$\sigma(\omega) = 4\pi^2\hbar\omega \sum_B | \boldsymbol{\epsilon}_s \cdot < \Psi_B | \sum_i \mathbf{r}_i | \Psi_A >|^2 \, \delta(E_B - E_A - \hbar\omega)$$

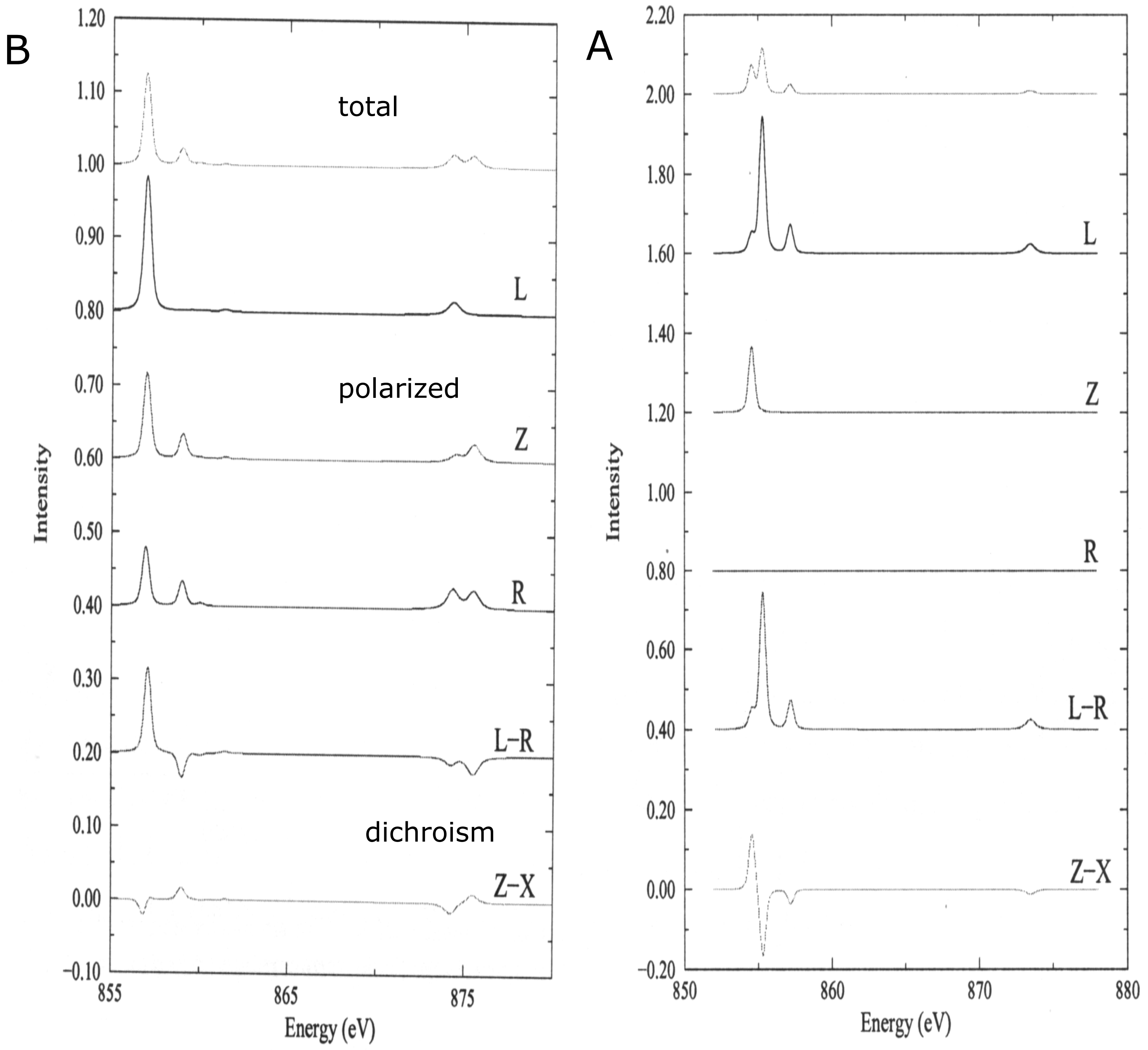
$|\Psi_A>$ e $|\Psi_B>$ are many-electron states corrisponding to different configurations. Esemple: absorption of x-rays from $Ni^{2+}$ at the threshold *2p*

$3d^8 \rightarrow 2p^5 3d^9$ Eccitation from ground state $^3F$ $J=4$ $M_J=-4$ to some states of the multiplet of the 60 levels of the final configuration.

A: atomic symmetry

B: with crystal field.





$Ni^{2+}$

$3d^8 \rightarrow 2p^5 3d^9$

*2p core level absorption*

# $L_{2,3}$ Ni absorption edges

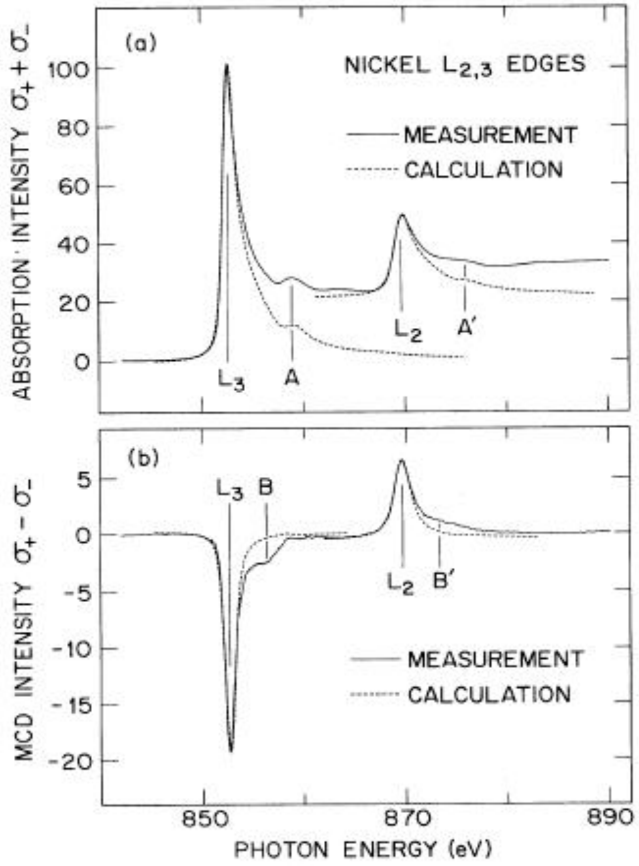


FIG. 1. Comparison between experimental soft-x-ray spectra (full curves) and an optimal tight-binding simulation (dashed curves) of the $L_3$ and $L_2$ white lines in Ni: (a) the total absorption $(\sigma_+ + \sigma_-)$; (b) the magnetic-circular-dichroism $(\sigma_+ - \sigma_-)$. The raw experimental MCD spectrum shown here has been magnified by a factor of 1.85 to account for incomplete photon polarization and sample magnetization.

Chen, Smith, Sette, PRB 43,6785(91)

The ratios between the peaks in the total signal and in the dichroism is analysed as a function of the values of ξ (spin-obit) and $\Delta_{ex}$ (exchange splitting).

The form, the branching ratios and sometimes the same sign of the peaks in the dichroic signal depend on the ingredients of the calculations. (single-electron, many-electron, in the atomic limit, in the bulk crystal).

# $L_{2,3}$ absorption edges

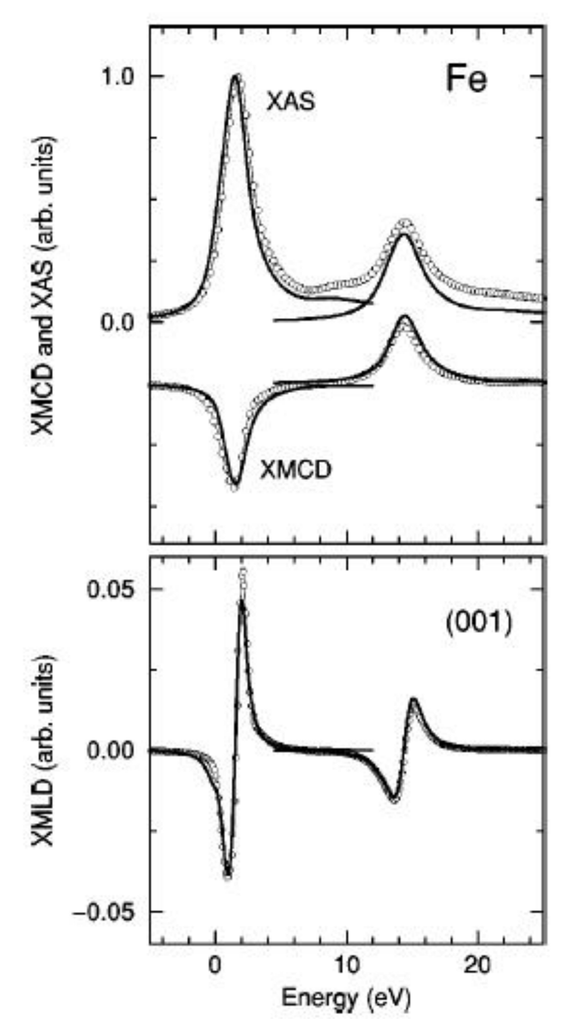


FIG. 2. The XAS, XMCD, and XMLD spectra of (001) bcc Fe as obtained from the model calculation (solid curves) and the full calculation (symbols). The XAS spectrum at the $L_3$ edge has been normalized to 1.

Kunes, Oppeneer, PRB 67,024431(2003)

Example of a calculation of absorption circular dichroism a linear dichroism obtained from the ferromagnetic band structure and from a model based on partial density of electron states.

Note the typical shape of the lineshape of linear dichroism.

# Absorption II.

We can treat the absorption problem in aone-electron scheme, neglecting Many-electron effects or, better,

- separating the electron involved in the excitation process and its initial and final states, from the other N-1 electrons.
- embedding the interaction with other electrons into an effective potential.

Not always this separation is possible.

The absorption cross section

$$\sigma\,(\omega) = 4\pi^2\hbar\omega \sum_B \mid \boldsymbol{\epsilon}_s \cdot < \Psi_B \mid \sum_i \mathbf{r}_i \mid \Psi_A >\mid^2 \delta(E_B - E_A - \hbar\omega)$$

becomes:

$$\sigma\,(\omega) = 4\pi^2\alpha\hbar\omega \sum_k \mid \boldsymbol{\epsilon}_s \cdot < \psi_k(\mathbf{r}) \mid \; \mathbf{r} \mid \varphi_c(\mathbf{r}) >\mid^2 \delta(E_k - E_c - \hbar\omega)$$

$\varphi_c(\mathbf{r})$ s the wavefunction of the initial core state, $\psi_k(r)$ is one of the final unoccupied states above $E_f$

# Absorption III

- Absorpion is a tool for basic analysis of the electronic structure of atom, molecules and solids over different energy scales.
- We are mainly interested in the region of X-rays near the threshold of the core levels of an atom in a compound or in a solid and above.
- The transitions from core electron levels to empty states produce in the absorption spectrum:
  - Threshold structures
  - Structures around few eV above the threshold (NEXAFS)
  - Structures well above the theshold (EXAFS)

- Problems: one-electron ⇔many-electron pictures.
- Information obtainable: good local probe
  - of electronic properties
  - of magnetic properties (p→d, d →f)
  - of the local atomic structure.

# Photoemission from core and valence states.

If the system that absorbed the photon is left in state of the *continuum*, the latter can be decomposed into a state with N-1 electrons, with a *hole,* in the core or in the valence, plus an electron that is photoemitted.

The energy of the final state is

$$E_f^{N-1} + \frac{\hbar^2 k^2}{2m}$$

The kinetic energy of the electron is

$$\frac{\hbar^2 k^2}{2m} = \hbar\omega - (E_f^{N-1} - E_i^N)$$

and $E_f^{N-1}$ is a level **of a set** of excited states containing a hole.

$$(E_f^{N-1} - E_i^N) = -\,\epsilon_i - \triangle E_{rel} - \triangle E_{corr}$$

This expression gives an interpretation of the energy difference as a sum of three terms: an orbital energy (referred to the vacuum level) of the photoemitted electron and corrections that are due to the relaxation effects of the other N-1 electrons and correlation energy.

In metals for valence states near the Fermi energy these corrections are negligible. But it is not always so. We use to write

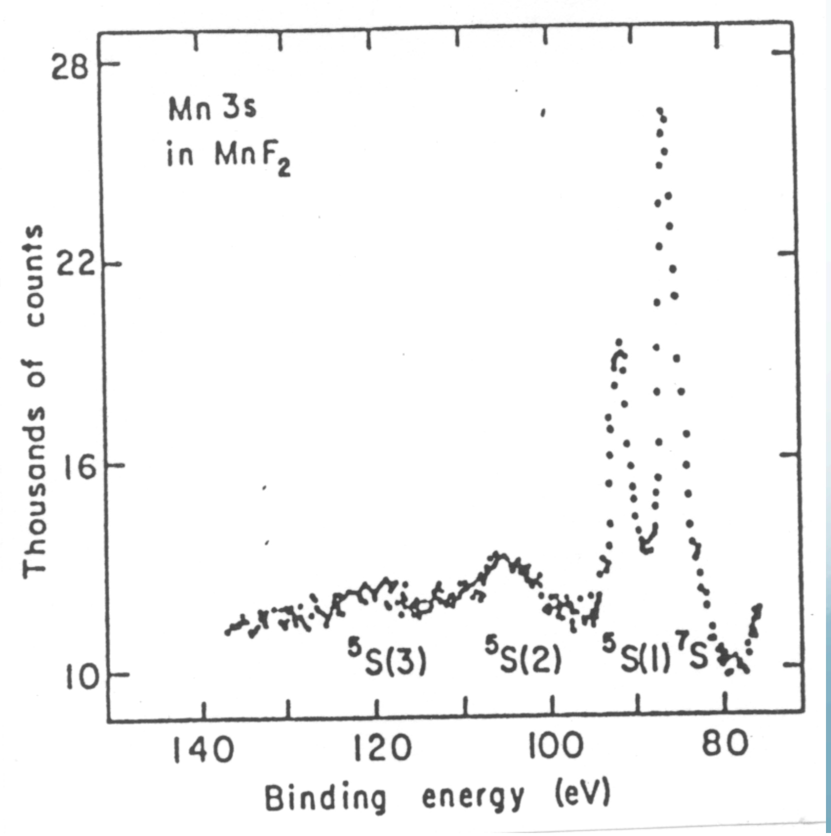
$(E_f^{N-1} - E_i^N) =$ $E_b$+W. (W correlation energy).

# Core level photoemission.

At fixed photon energy we examine the structures as a function of $E_b$ (EDC, energy distribution curve). Only in some cases they are made of a single peak at a well defined orbital energy. Correlation introduces spectral features at higher $E_b$ (lower kin. en.)

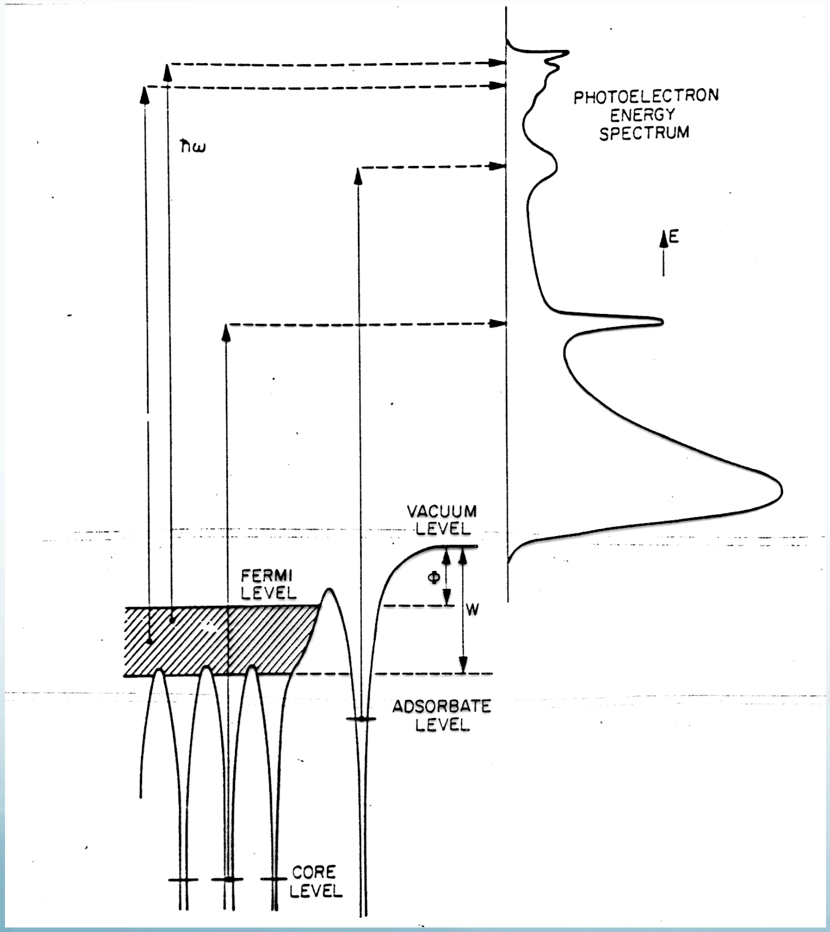
- Multiplet effect
- Configuration interaction.
- Adiabatic relaxation.
- Matrix element effecs.
- Chemical shift.
- Change of relaxation and and correlation at surfaces respect to bulk.

An extreme case: *3s in Mn*→



# Photoemission in one-electron scheme.

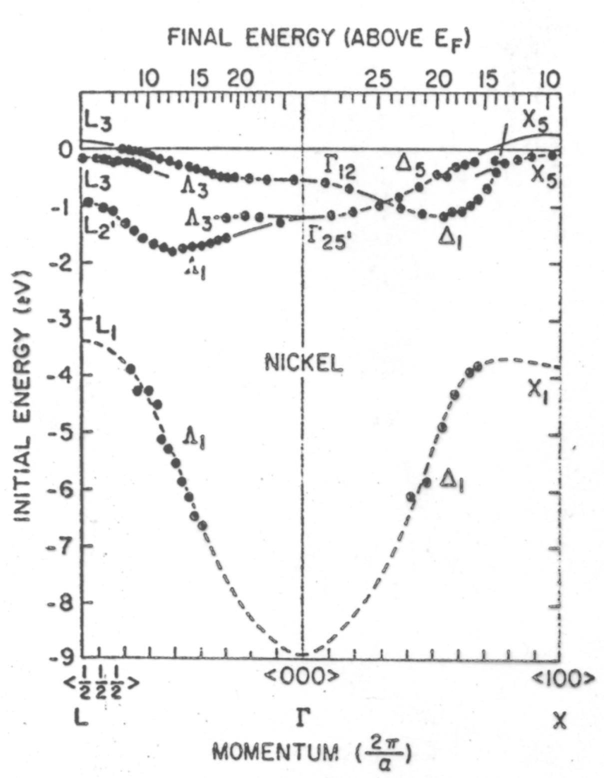
In solids, for extended electron states (uncorrelated), it is usual to work in one-electron approximation.



Note: valence spectrum and core core plus secondary electrons.

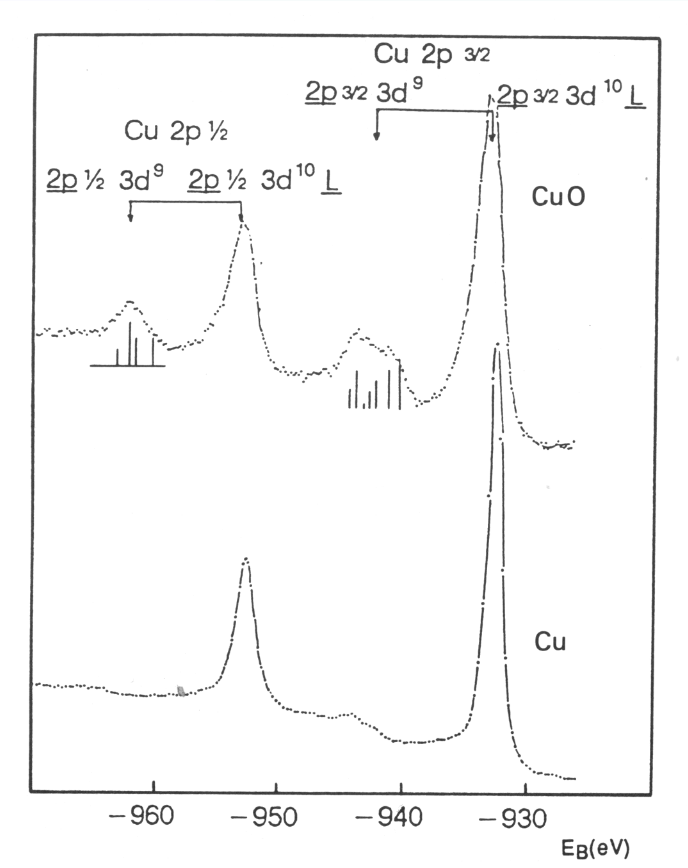
<<<

- Band mapping of Ni obtained by photoemission with high resolution in energy and angle. >>>

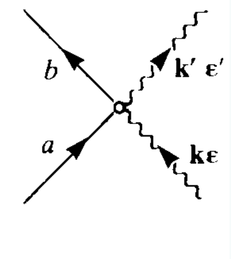


# Photoemission.

- In non correlated systems
  - Bulk Band mapping
  - Surface states
  - Symmetry of the electronic states through light polarization
  - Photoelectron diffraction
- In atomic and localized systems
  - Multiplet effects
  - Configuration interaction
  - Cooper maxima and minima of the matrix element modulus
- Transition between different conditions are importan:
  - Sudden and adiabatic limit
  - Quasiparticles and incoherent background
  - Phase transition and changes of density of states.



# Thomson scattering.



Evaluating the diffusion amplitude depending on **A**$^2$ we have

$$\frac{1}{i\hbar}\sum_i < \mathbf{k}'\epsilon'; \Psi_B \mid \mathbf{A}^2(\mathbf{r}_i, 0) \mid \mathbf{k}\epsilon; \Psi_A > \int_{t_i}^{t_f} dt e^{i(E_B+\hbar\omega_{\mathbf{k}'}-E_A-\hbar\omega_{\mathbf{k}})t}$$

$$\mathbf{A}^2(r_i, 0) = \sum_{\mathbf{k}_1 s_1}\sum_{\mathbf{k}_2 s_2} \frac{4\pi\hbar c^2}{2\mathcal{V}\omega_{\mathbf{k}_1}\omega_{\mathbf{k}_2}} (\epsilon_{\mathbf{k}_1 s_1}\cdot\epsilon_{\mathbf{k}_1 s_1}) \left(a_{\mathbf{k}_1 s_1} + a^\dagger_{\mathbf{k}_1 s_1}\right)\left(a_{\mathbf{k}_2 s_2} + a^\dagger_{\mathbf{k}_2 s_2}\right)$$

If A=B the scattering is elastinc and we get:

$$(\epsilon' \cdot \epsilon)\,\frac{e^2}{mc^2}\sum_i < \Psi_A \mid e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}_i} \mid \Psi_A >= (\epsilon' \cdot \epsilon)\, r_0 n(\mathbf{k}'-\mathbf{k})$$

Summing on the two polarizations, we calculate the cross section

$$\sigma\,(\omega)\, d\Omega =\mid n(\mathbf{k}'-\mathbf{k}) \mid^2 r_0^2(1+\cos^2\theta)d\Omega.$$

which depends on the Fourier transform of the charge density of the electrons. Passing from an atom to a crystal we have the x-ray diffraction.

# Other contributions to scattering.

Other contributions to elastic scattering come from interaction terms between field and spin, see Appendix, and at second order in A•p.

We have the *Bragg-Thomson amplitude,* considered before

$$f_{BT} = r_0 \sum_i < \Psi_0 \mid e^{-i\mathbf{q}\cdot\mathbf{r}_i} \mid \Psi_0 > (\varepsilon'^{*}\cdot\varepsilon),$$

*the orbital magnetic scattering* amplitude

$$f_{M_L} = -ir_0 \frac{\hbar\omega_{\mathbf{k}}}{mc^2} < \Psi_0 \mid \sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i} \frac{\mathbf{q}\times\mathbf{p}_i}{i\hbar k^2} \mid \Psi_0 > \cdot(\varepsilon'^{*}\times\varepsilon).$$

and, including spin, the *spin magnetic scattering* amplitude

$$f_{M_S} = -ir_0 \frac{\hbar\omega_{\mathbf{k}}}{mc^2} < \Psi_0 \mid \sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i} \mathbf{s}_i \mid \Psi_0 > \cdot\mathbf{b}$$

where

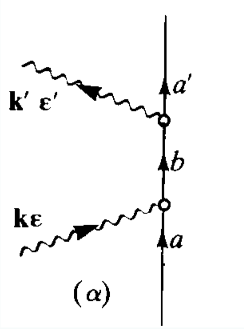
$$\mathbf{b} = (\varepsilon'^{*}\times\varepsilon) + (\mathbf{k}'\times\varepsilon'^{*})(\mathbf{k}'\cdot\varepsilon) - (\mathbf{k}\times\varepsilon)(\mathbf{k}\cdot\varepsilon'^{*}) - (\mathbf{k}'\times\varepsilon'^{*})\times(\mathbf{k}\times\varepsilon)$$

and

$$\mathbf{q} = \mathbf{k} - \mathbf{k}'.$$

- incomplete shells of electrons
- periodicity of charge can be different respect to magnetic periodicity
- out of resonance

# Resonant scattering of x-rays.



In resonant conditions when the photon absorbed has an energy similar to the binding energy of the core electrons, the main term is given by the diagram + higher order terms in the perturbation expansion. The dominating interaction term is the A•p term.

- Elastic and anelastic diffusion.
- Core and valence de-excitation processes.
- Specially useful for transition metals and rare earth wher the intermidiate states involve unfilled shells.
- Interference effects among intermediate states.
- Important is the high resolution in energy and angle of scattered photons, available in the best synchrotron radiation facilities.

$$\frac{d^2\sigma^{\epsilon\epsilon'}}{d\Omega' d(\hbar\omega')} = \sum_{|f\rangle} \left| \sum_{qq'} (-1)^{q'} \epsilon_q (\epsilon'_{-q'} \sum_{|n\rangle} \frac{\left\langle i \left| r C_q^{(1)}(\widehat{r}) \right| n \right\rangle \left\langle n \left| r C_{q'}^{(1)}(\widehat{r}) \right| f \right\rangle}{E_i - E_n + \hbar\omega + i\Gamma_n/2} \right|^2$$

$$\delta\left(E_i - E_f + \hbar(\omega - \omega')\right)$$

$$\epsilon \cdot \mathbf{r} = \sum_q (-1)^q \epsilon_{-q} C_q^{(1)}(\widehat{r})$$

# X-ray resonant scattering.

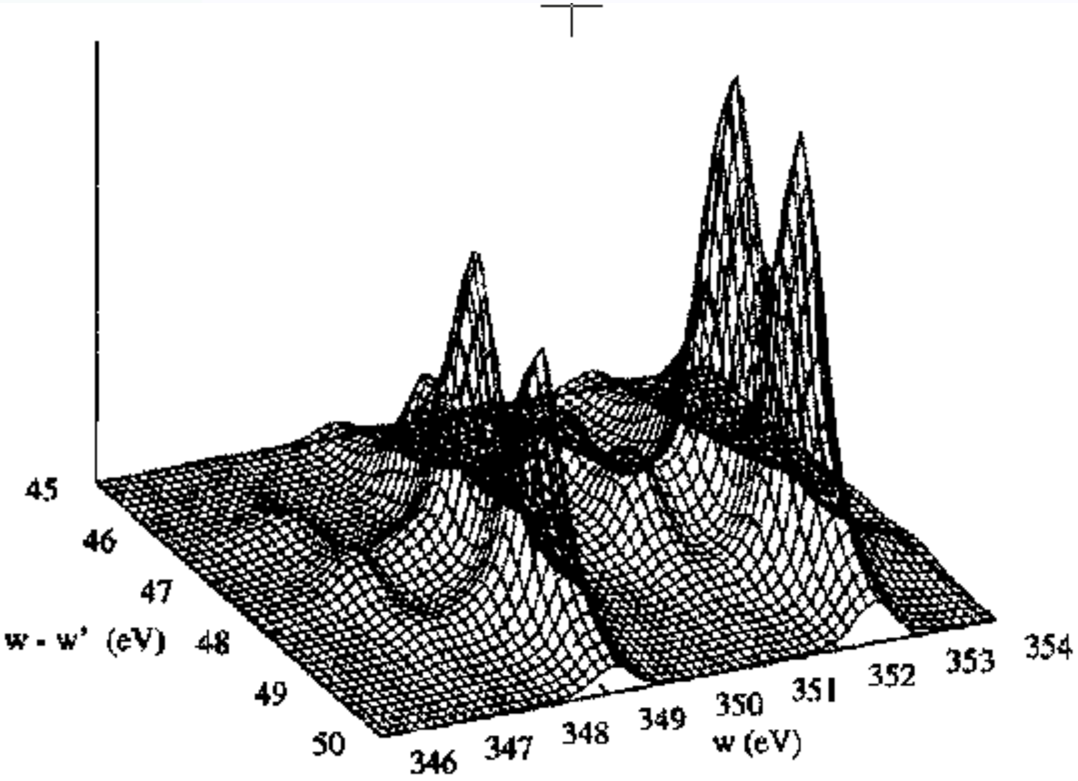


Fig. 8. – Resonant inelastic scattering of $Ca^{2+}$ corresponding to the transitions $3d^0 \rightarrow 2p^5 3d^1 \rightarrow 3s^1 3d^1$.

END

# Appendix.

Relativistic corrections to the hamiltonian $\mathcal{H}_0$ of the electron system:

$$\frac{1}{2m^2c^2}(-e)\sum_i \mathbf{S}_i\cdot(\nabla\varphi(\mathbf{r}_i)\times\mathbf{p}_i)-\frac{1}{8m^3c^6}\sum_i \mathbf{p}_i^4-\frac{e\hbar^2}{8m^2c^2}\sum_i \Delta\varphi(\mathbf{r}_i)$$

spin-orbit kin. Energy correct. Darwin term

Other two terms in the interaction hamiltonian $\mathcal{H}_I$ (3rd and 4th)

$$\frac{e}{mc}\sum \mathbf{S}_i\cdot(\nabla\times\mathbf{A}(\mathbf{r}_i,t))-\frac{e^2}{2m^2c^4}\sum \mathbf{S}_i\cdot((\frac{\partial}{\partial t}\mathbf{A}(\mathbf{r}_i,t))\times\mathbf{A}(\mathbf{r}_i,t))$$

describing the interaction between the spin of the electrons and the field after 1st and 2nd

$$\mathcal{H}_I=\sum_i\left(-\frac{q_i}{m_ic}\mathbf{A}(\mathbf{r}_i)\cdot\mathbf{p}_i+\frac{q_i^2}{2m_ic^2}\mathbf{A}^2(\mathbf{r}_i)\right)$$

where $q_i=-e$ $m_i=m$

In eq. (60) $\mathbf{S}_i$ is the *intrinsic angular momentum* vector operator for each electron, in $\hbar$ units

$$\mathbf{S}_i = \frac{1}{2}\sigma_i \tag{61}$$

where $\sigma$ is a vector operator represented by the three Pauli matrices

$$\sigma = (\sigma_1, \sigma_2, \sigma_3) = \left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right]. \tag{62}$$