Theory Lectures

- Introduction to Spectroscopy .................................. Francesco
- Density Functional Theory .......................................... Gian-Marco
- Time-Dependent DFT .................................................. Valerio
- Microscopic-Macroscopic Connection ................................. Valérie
- Many Body Perturbation Theory ...................................... Matteo
- GW Approximation ..................................................... Matteo
- Bethe-Salpeter Equation ............................................... Francesco
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Practical Hands-On

- DFT Practice .................. ABINIT ................ Matteo
- TDDFT Practice ................. DP ................ Matteo, Francesco
- GW Practice ................. ABINIT ................. Matteo x2, Valerio
- BSE Practice ................. EXC ................. Francesco, Matteo
Just an Introduction

1. Spectroscopy
2. Absorption
3. Photoemission
4. Electron Energy Loss Spectra
5. Inelastic X-ray Scattering
Outline

1. Spectroscopy
2. Absorption
3. Photoemission
4. Electron Energy Loss Spectra
5. Inelastic X-ray Scattering
Spectroscopy: Why?
Spectroscopy: Why?
Spectroscopy: Why?
Spectroscopy: Why?
Spectroscopy: Why?

Spectroscopies

- Methods to study the properties of **matter** (atoms, molecules, solids), investigating the interaction with **particles** (photons, electrons, ...).
Spectroscopy

Theoretical Spectroscopy Lectures

Energy Level Transition

- Nuclear and electron spin
- Molecular rotations
- Molecular vibrations
- Valence electrons
- Middle-shell electrons
- Inner-shell electrons
- Nuclear

Energy (Joules)

Wavelength (nm)

Plank's constant, $h = 6.63 \times 10^{-34}$ J s.
The speed of light, $c = 3.0 \times 10^8$ m s$^{-1}$.

- RF = Radio frequency radiation
- μW = Microwave radiation
- IR = Infrared radiation
- VIS = Visible light radiation
- UV = Ultraviolet radiation
- X = X-ray radiation
- γ = Gamma ray radiation
Spectroscopy Absorption Photoemission Electron Energy Loss Spectra Inelastic X-ray Scattering

Energy Level Transition

Nuclear and electron spin

Molecular rotations

Molecular vibrations

Valence electrons

Middle-shell electrons

Inner-shell electrons

Nuclear

Energy

Joules

10^{-7}

10^{-6}

10^{-5}

10^{-4}

10^{-3}

10^{-2}

10^{-1}

10^{0}

10^{1}

10^{2}

10^{3}

10^{4}

10^{5}

10^{6}

10^{7}

10^{8}

10^{9}

10^{10}

Wavelength

nm

Plank's constant, h = 6.63 x 10^{-34} J s.
The speed of light, c = 3.0 x 10^{8} m s^{-1}.

electronic thermal magnetic chemical mechanical structural optical

RF = Radio frequency radiation
μW = Microwave radiation
IR = Infrared radiation
VIS = Visible light radiation
UV = Ultraviolet radiation
X = X-ray radiation
γ = gamma ray radiation
Scattering

- Elastic Scattering: $E_i = E_f$
- Inelastic Scattering: $E_i \neq E_f$
Elastic Scattering

- The differential cross section is defined by the probability to observe a scattered particle into a solid angle unit if the target is irradiated by a flux of one particle by surface unit.

\[
\frac{d\sigma}{d\Omega} = \frac{\text{Scattered flux / Unit of solid angle}}{\text{Incident flux / Unit of surface}}
\]

Inelastic Scattering

- The double differential cross section \( \frac{d^2\sigma}{d\Omega dE} \) is defined as the differential cross section within a unit energy range.
Spectroscopy

Electronic Excitations

- Optical Absorption
- Electron Energy Loss
- Inelastic X-ray Scattering
- Photoemission
- Inverse Photoemission
Electronic Excitations

- Optical Absorption
- Electron Energy Loss
- Inelastic X-ray Scattering
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Outline

1. Spectroscopy
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Beer Law

\[ I(x) = I_0 e^{-\alpha x} \]

\[ \alpha \iff \varepsilon \]
Absorption

Ellipsometry Experiments

\[ \varepsilon = \sin^2 \Phi + \sin^2 \Phi \tan^2 \Phi \left( \frac{1 - \frac{E_r}{E_i}}{1 + \frac{E_r}{E_i}} \right) \]
Absorption

Creation of an electron-hole pair

\[ E_{\text{vac}} \]
\[ E_{\text{bc}} \]
\[ E_{\text{tv}} \]

N → N
Absorption

Lautenschlager et al., PRB 36, 4821 (1987)
Absorption

XANES and (N)EXAFS spectrum of Sn

\[ \omega \text{ (eV)} \]

29200 29240 29280

Outline

1. Spectroscopy
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5. Inelastic X-ray Scattering
Spectroscopy: Photo-emission Spectroscopy

UPS, XPS, ARPES
Spectroscopy: Photo-emission Spectroscopy

Electron out. Investigation of occupied bands. ARPES
Spectroscopy: Photo-emission Spectroscopy

Zhou et al., PRB 71, 161403 (2005)
Spectroscopy: Inverse Photo-emission Spectroscopy

ARIPES
Spectroscopy: Inverse Photo-emission Spectroscopy

Electron in. Investigation of empty bands. **ARIPES**

![Diagram](image.png)
Outline

1. Spectroscopy
2. Absorption
3. Photoemission
4. Electron Energy Loss Spectra
5. Inelastic X-ray Scattering
Spectroscopy: Electron Scattering

\[ E_i - q_i \]

\[ E_f - q_f \]

\[ q - E \]
Spectroscopy: Electron Scattering

Energy Loss Function

\[
\frac{d^2\sigma}{d\Omega dE} \propto \text{Im} \left\{ \varepsilon^{-1} \right\}
\]
Spectroscopy: Electron Scattering

Theoretical Spectroscopy Lectures

ETSF
Spectroscopy: Electron Scattering

LEED
elastic peak
Spectroscopy: Electron Scattering

Theoretical Spectroscopy Lectures

HREELS

meV

0

5000 eV
Spectroscopy: Electron Scattering

EELS

0

5000 eV
Spectroscopy: Electron Scattering

Auger Spectroscopy
Spectroscopy: Electron Scattering

SEM
cascade processes
Outline

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Spectroscopy: X-ray Scattering

\[ E_i \quad q_i \]

\[ E_f \quad q_f \]

\[ q \quad E \]
Spectroscopy: X-ray Scattering

Energy Loss Function

\[
\frac{d^2\sigma}{d\Omega dE} \propto \text{Im}\left\{\varepsilon^{-1}\right\}
\]

Weissker et al., PRL 97, 237602 (2006)
Spectroscopy: Energy Loss Spectroscopies

**EELS vs IXS**
- IXS is more sensitive to bulk
- IXS is better for big $q$
- IXS simpler to analyze (small background, multiple scattering negligible)
- EELS has a better energy resolution and spatial resolution
- Light elements are easier to see in EELS
- EELS is better for small $q$
- both expensive (100k-1M €)!
Spectroscopy: Energy Loss Spectroscopies

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Theoretical treatment of Schrödinger equation

$\Psi(r_1, r_2, ..., r_n)$
CI, CC, QMC

$G(r_1, r_2, E)$
MBPT
GW, BSE

$\rho(r)$
DFT
Theoretical treatment of Schrödinger equation

\[ \Psi(r_1, r_2, \ldots, r_n) \]
CI, CC, QMC

\[ G(r_1, r_2, E) \]
MBPT GW, BSE

\[ \gamma(r_1, r_2) \]
DMFT

\[ \rho(r) \]
DFT

simpler basic quantity
more complicate approximation
Theoretical treatment of Schrödinger equation

\[ \Psi (r_1, r_2, \ldots, r_n) \]

CI, CC, QMC

\[ G(r_1, r_2, E) \]

MBPT

GW, BSE

\[ \rho (r) \]

DFT

\[ \gamma (r_1, r_2) \]

DMFT

\[ j(r) \]

CDFT

Simpler basic quantity
More complicated approximation