Theoretical Spectroscopy Lectures

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Matteo Guzzo, Lucia Reining

European Theoretical Spectroscopy Facility (ETSF)

Palaiseau, 6 February 2012

Theory Lectures

- Introduction to Spectroscopy ..... Francesco
- Microscopic-Macroscopic Connection ..... Valérie
- Time-Dependent DFT ..... Francesco
- Green's functions' theory ..... Lucia
- GW Approximation ..... Lucia
- Bethe-Salpeter Equation ..... Francesco

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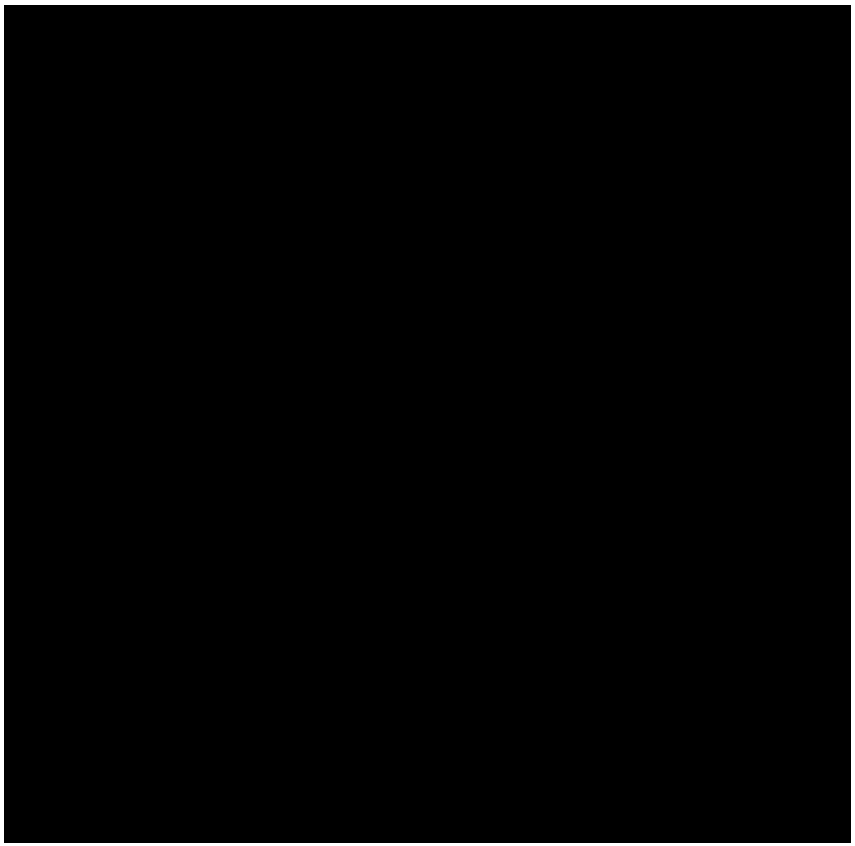
Practical Hands-On

- DFT Practice ..... ABINIT ..... Valérie, Francesco
- TDDFT Practice ..... DP ..... Valérie, Francesco
- GW Practice ..... ABINIT ..... Matteo
- BSE Practice ..... EXC ..... Francesco

Just an Introduction

Outline

Spectroscopy: Why?



Spectroscopy: Why?

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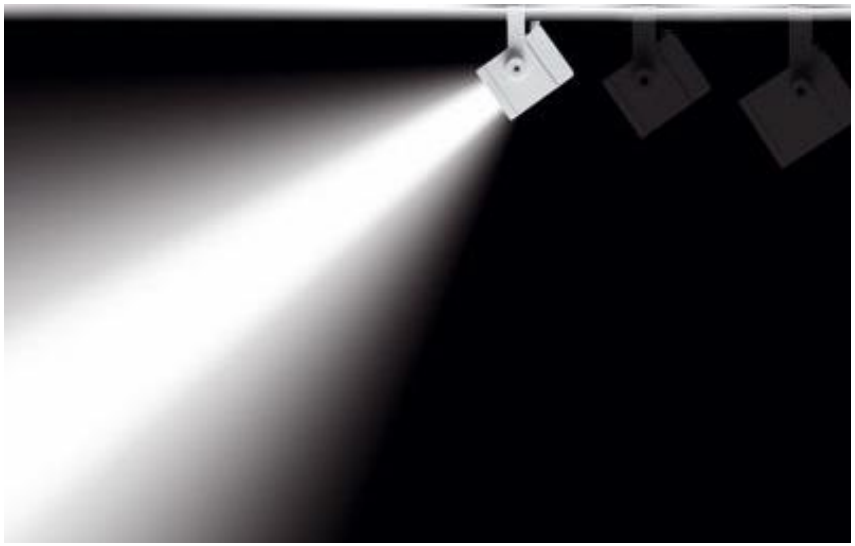

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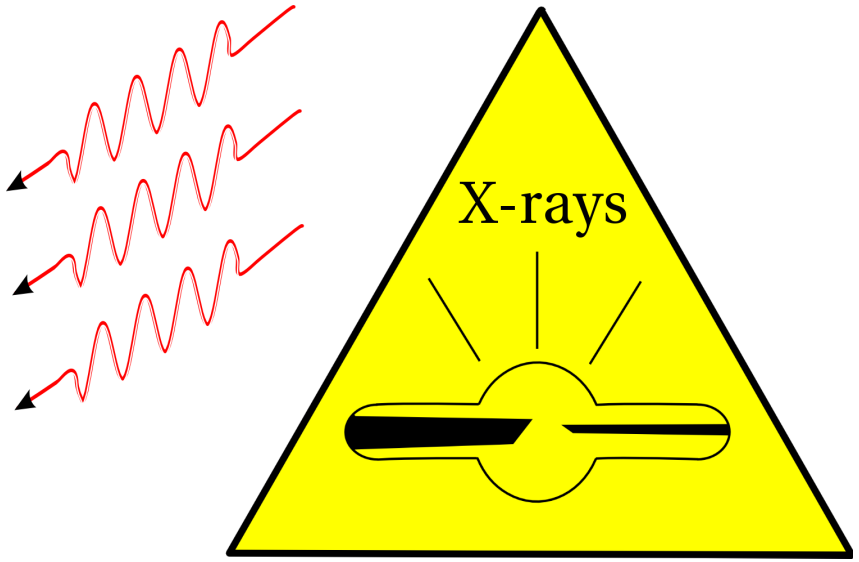
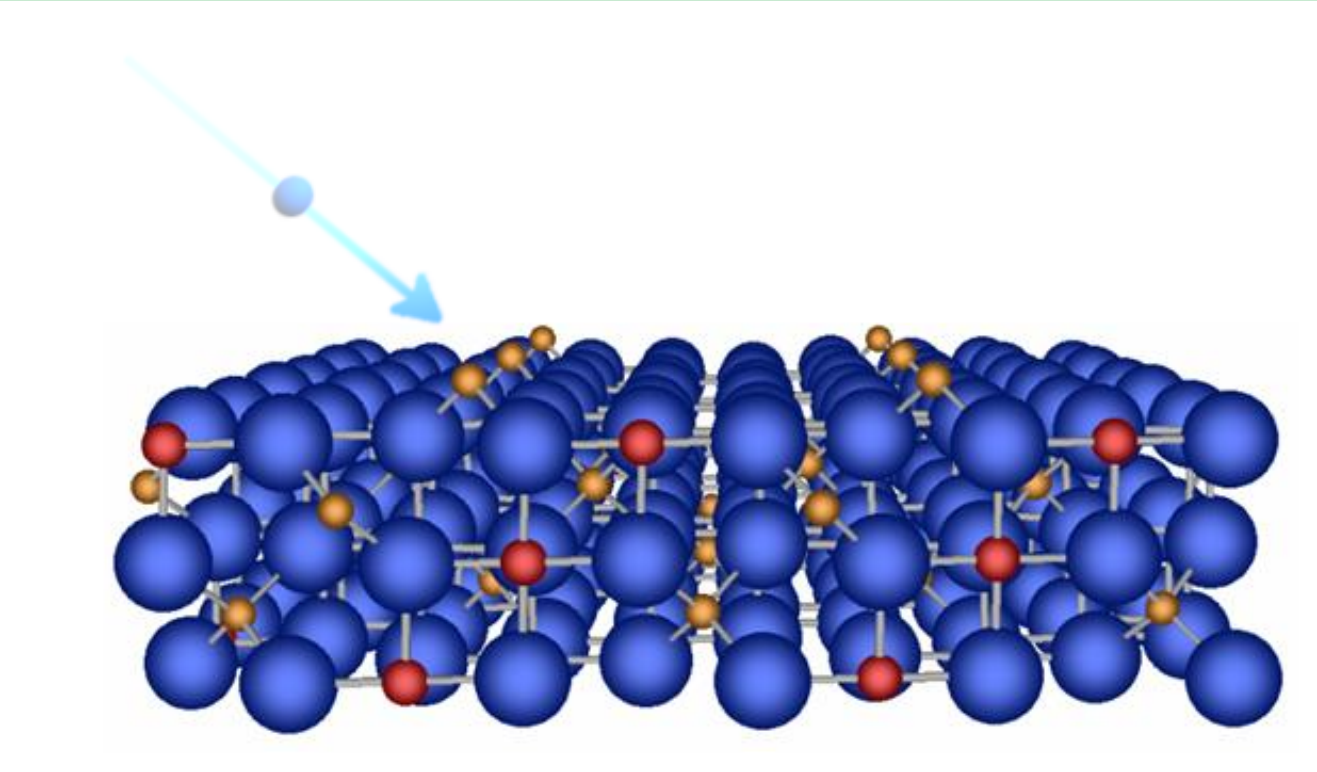
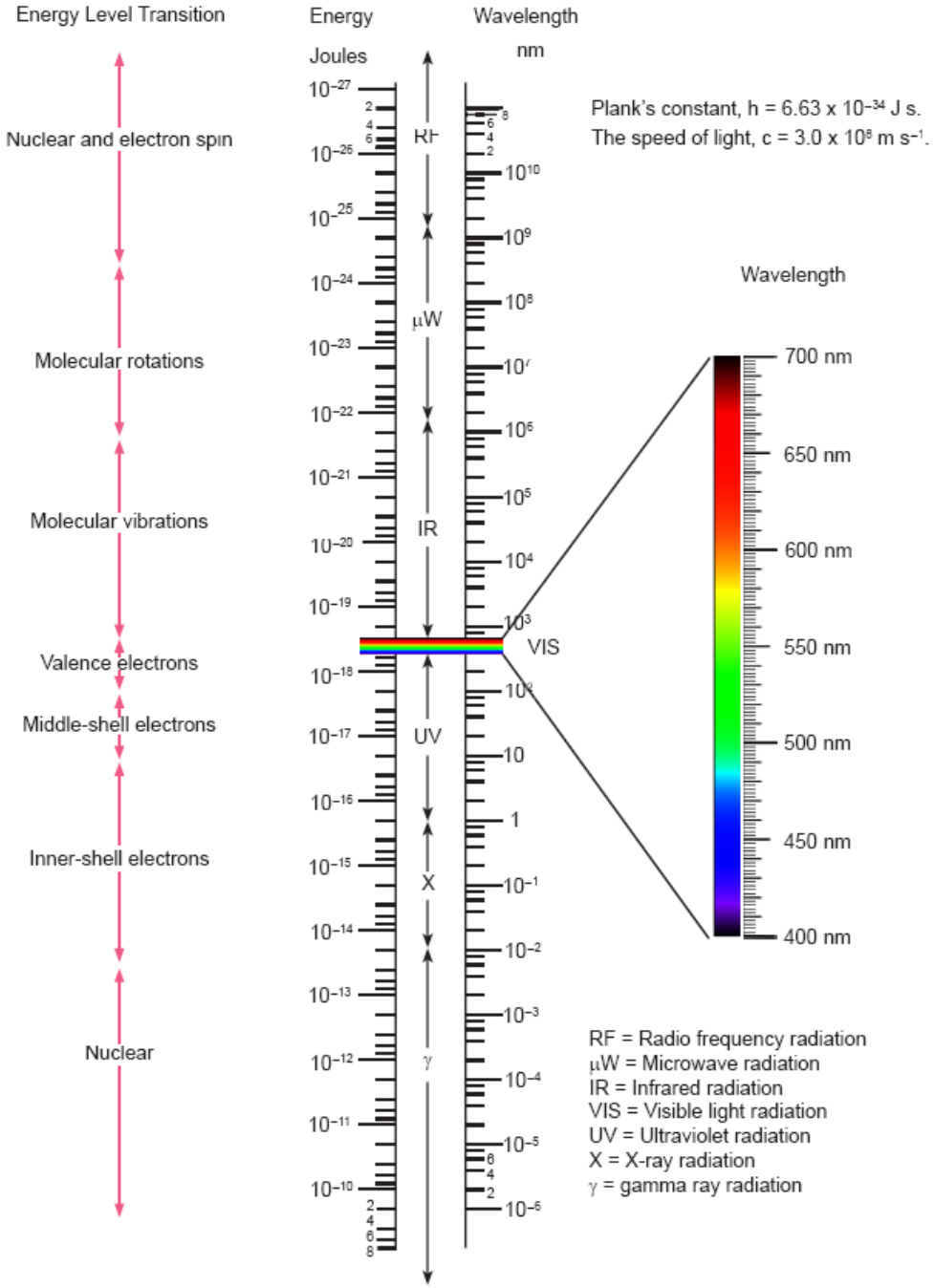


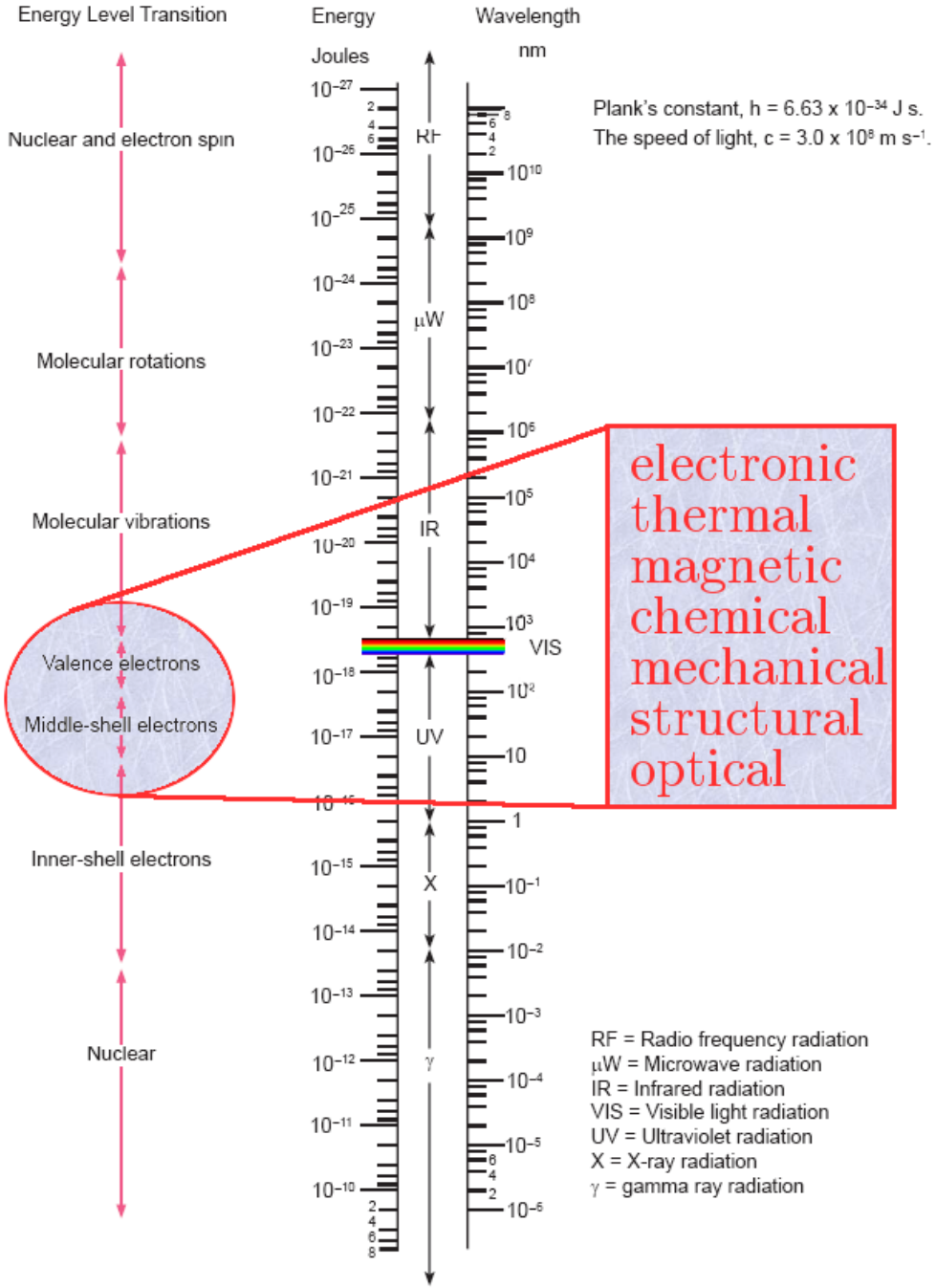
Spectroscopy: Why?

Spectroscopies

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




Energy Level Transition
Nuclear and electron spin
Molecular rotations
Molecular vibrations
Valence electrons
Middle-shell electrons
Inner-shell electrons
Nuclear
Energy
Joules
Wavelength
nm
RF
μW
IR
VIS
UV
X
γ
Plank's constant, h = 6.63 x 10⁻³⁴ J s.
The speed of light, c = 3.0 x 10⁸ m s⁻¹.
Wavelength
700 nm
650 nm
600 nm
550 nm
500 nm
450 nm
400 nm
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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electronic
thermal
magnetic
chemical
mechanical
structural
optical
RF = Radio frequency radiation
μW = Microwave radiation
IR = Infrared radiation
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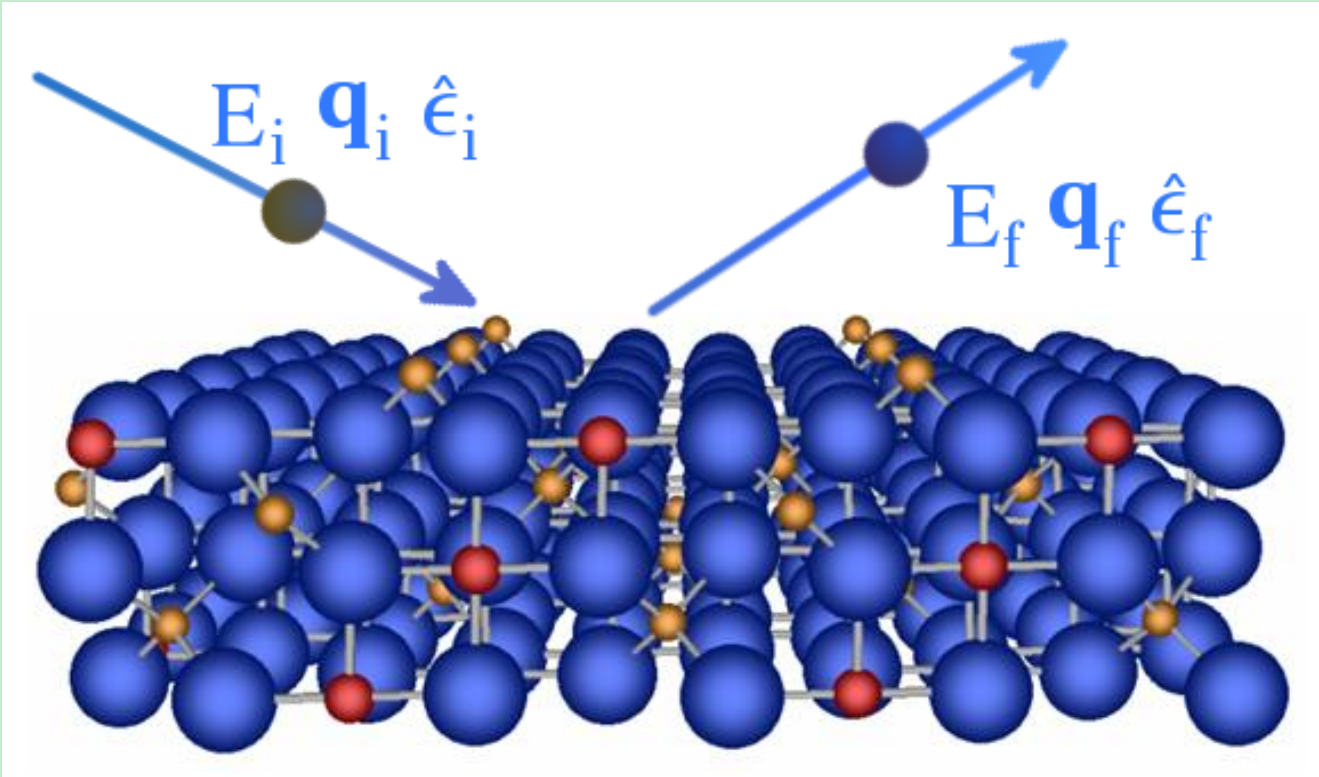
Spectroscopy

Scattering

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



Spectroscopy

Elastic Scattering

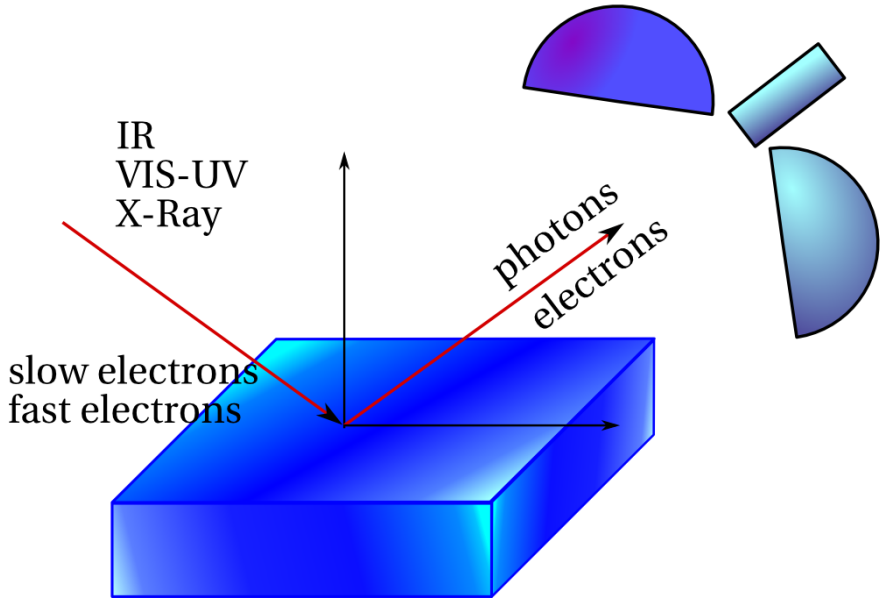
- the differential cross section is defined by the probability to observe a scattered particle into a solid angle unit if the target is irradiated by a flux of one particle by surface unit

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

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

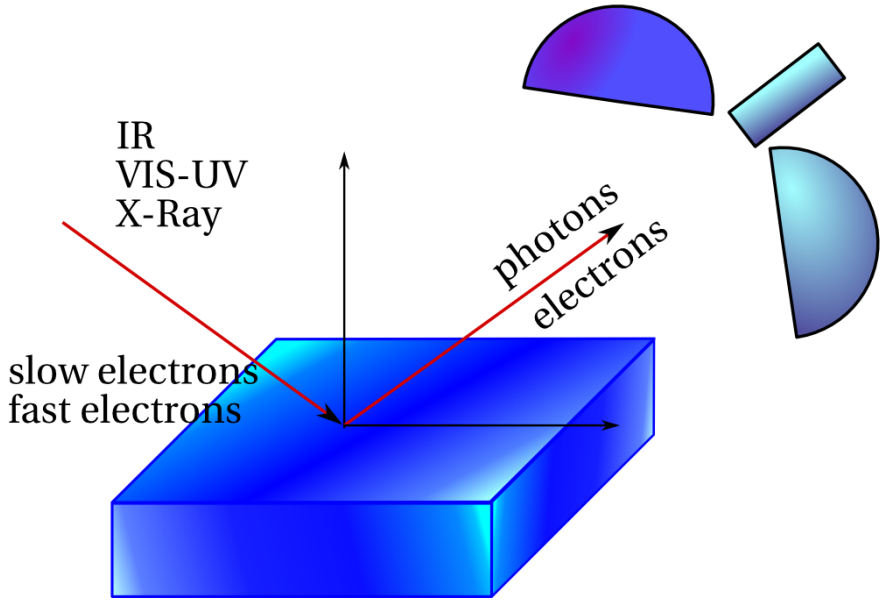
Spectroscopy



Electronic Excitations

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

Spectroscopy



Electronic Excitations

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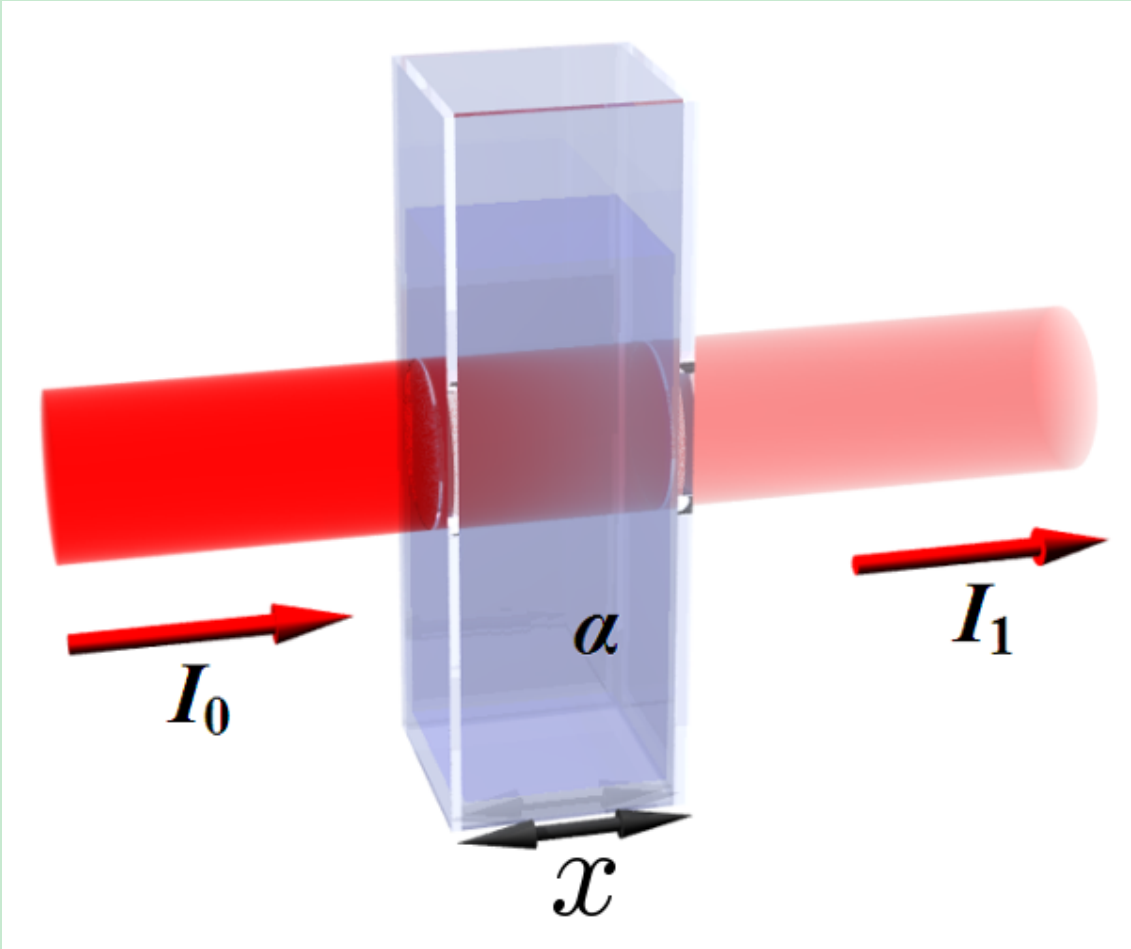
Outline

Absorption

Beer Law

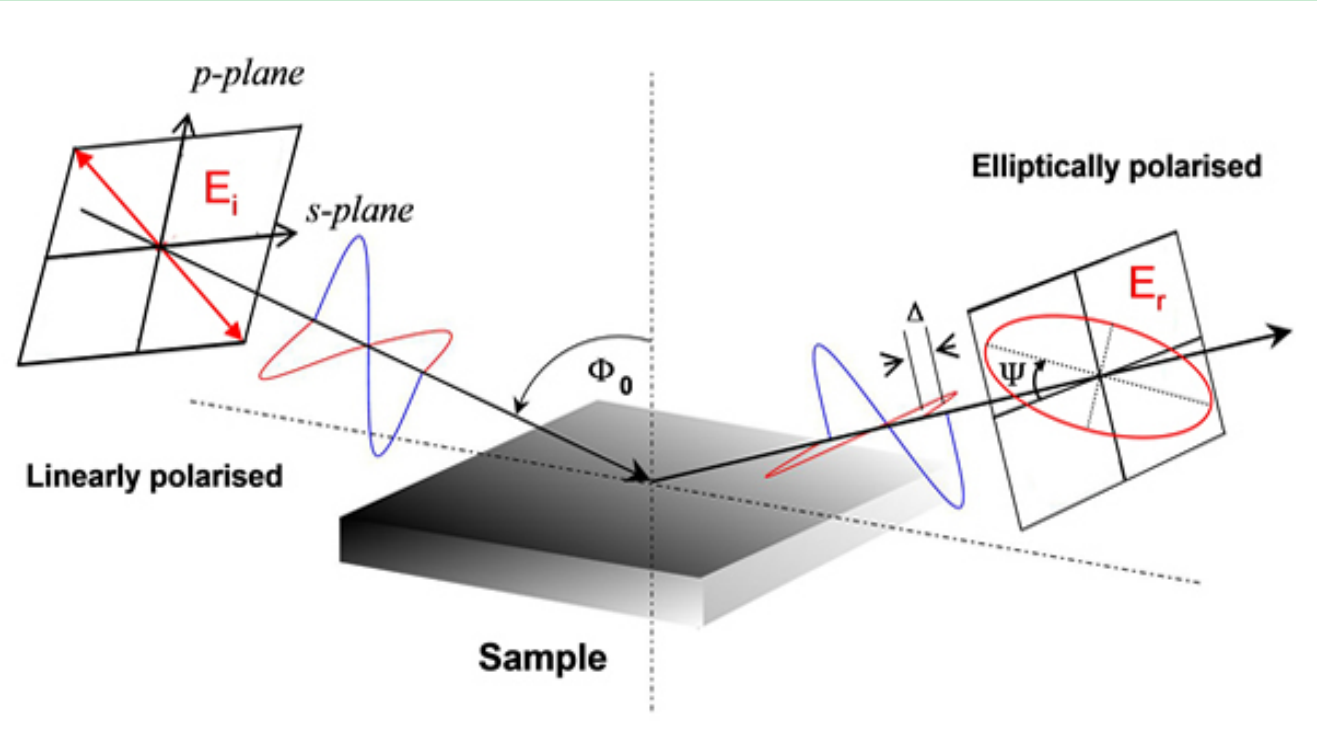
$$I(x) = I_0 e^{-\alpha x}$$

$$\alpha \Longleftrightarrow \varepsilon$$



Absorption

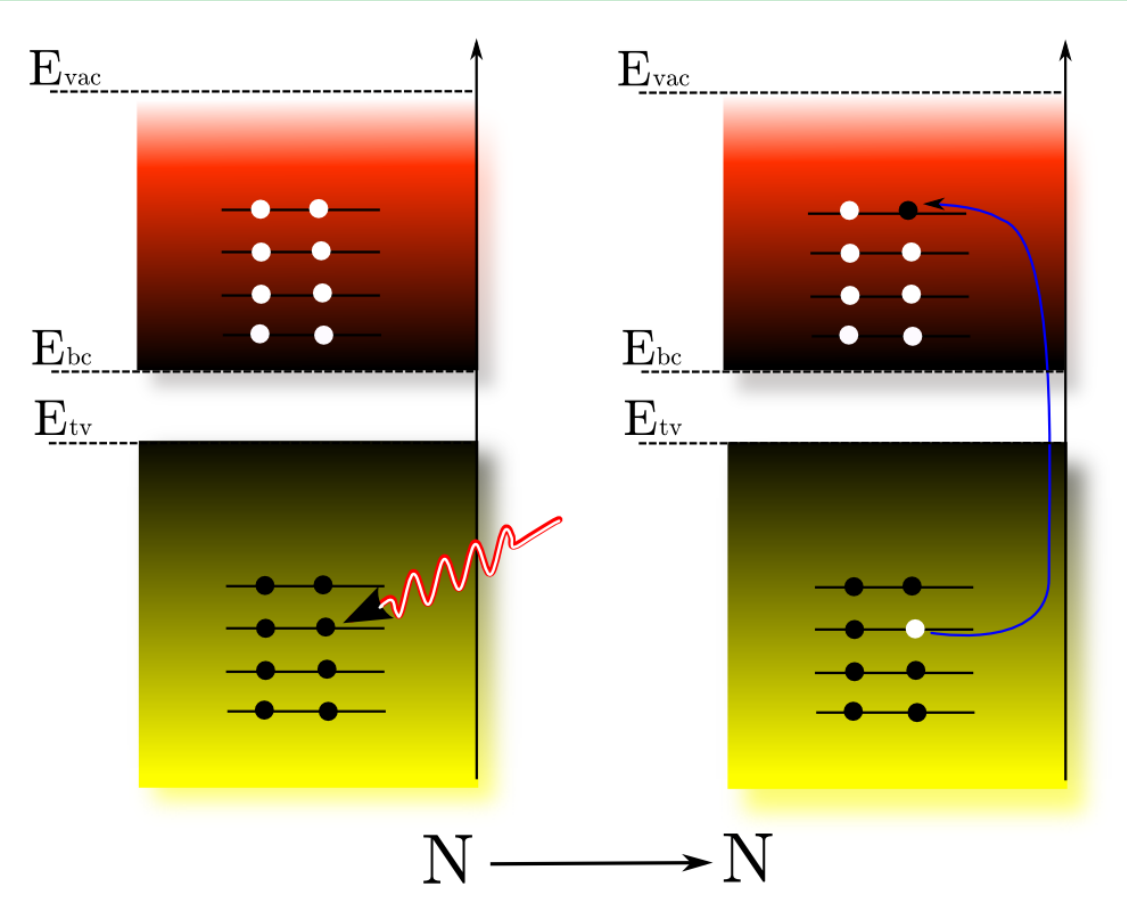
Ellipsometry Experiments



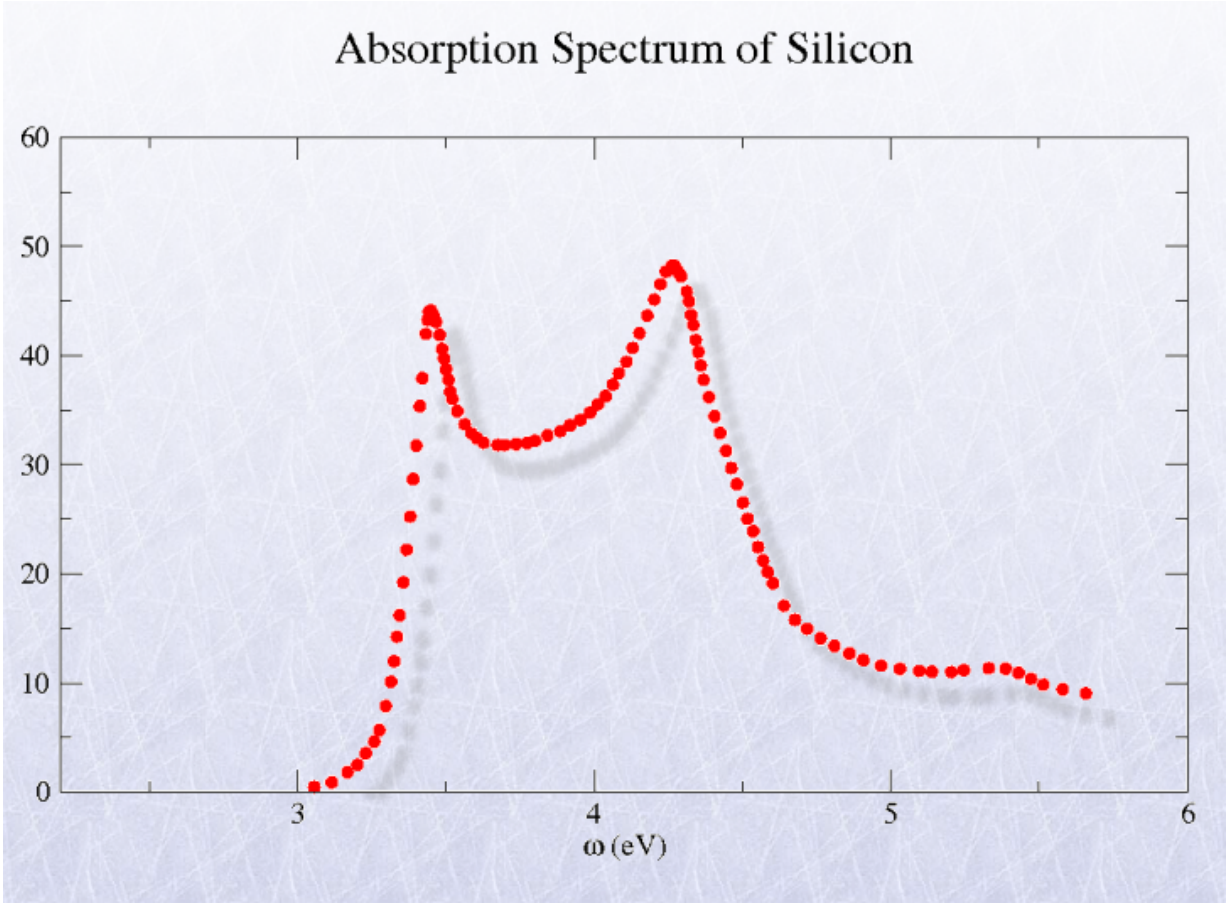
$$\varepsilon = sin^2\Phi + sin^2\Phi tan^2\Phi \left(\frac{1 - \frac{E_r}{E_i}}{1 + \frac{E_r}{E_i}} \right)$$

Absorption

Creation of an electron-hole pair

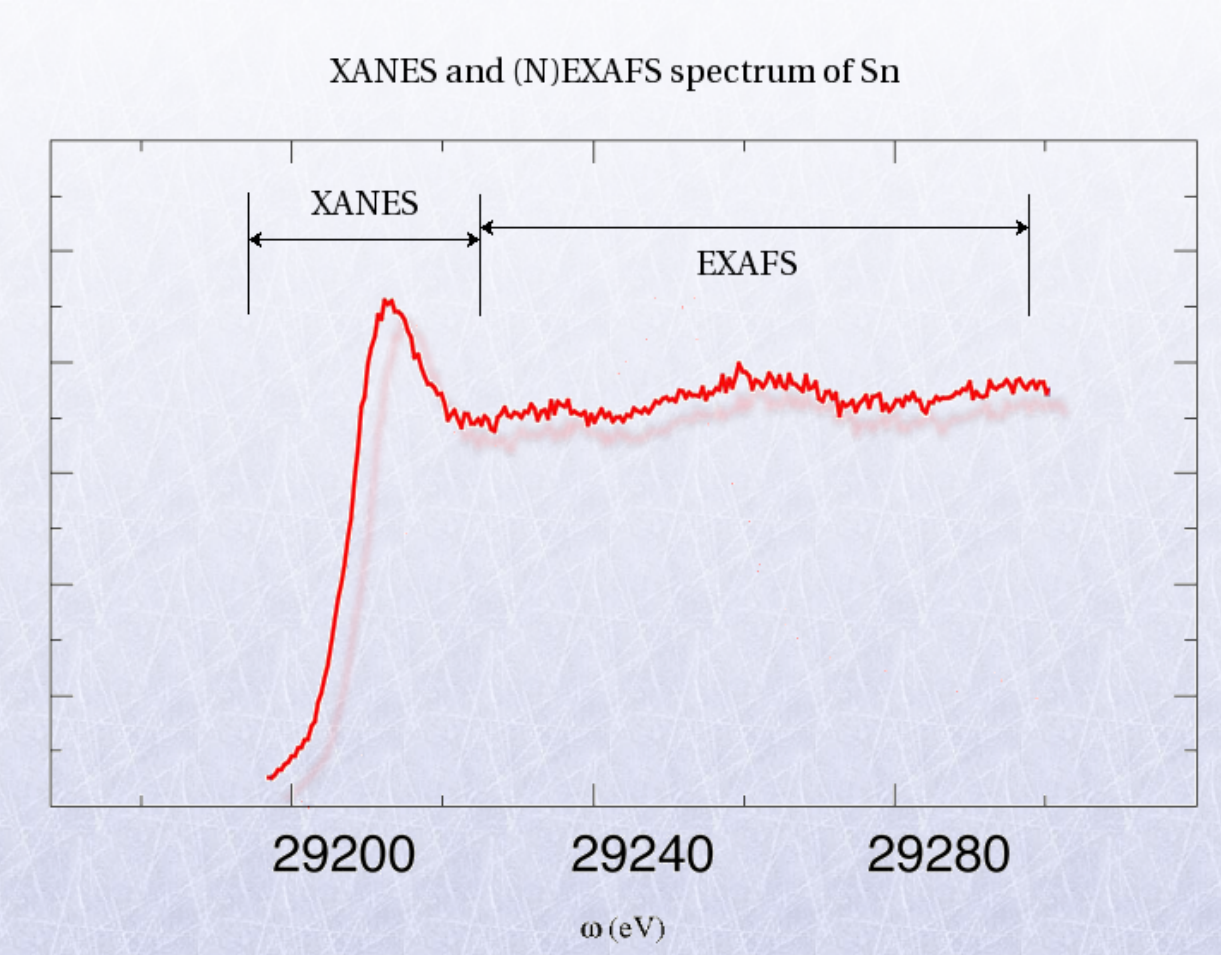


Absorption



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

Absorption

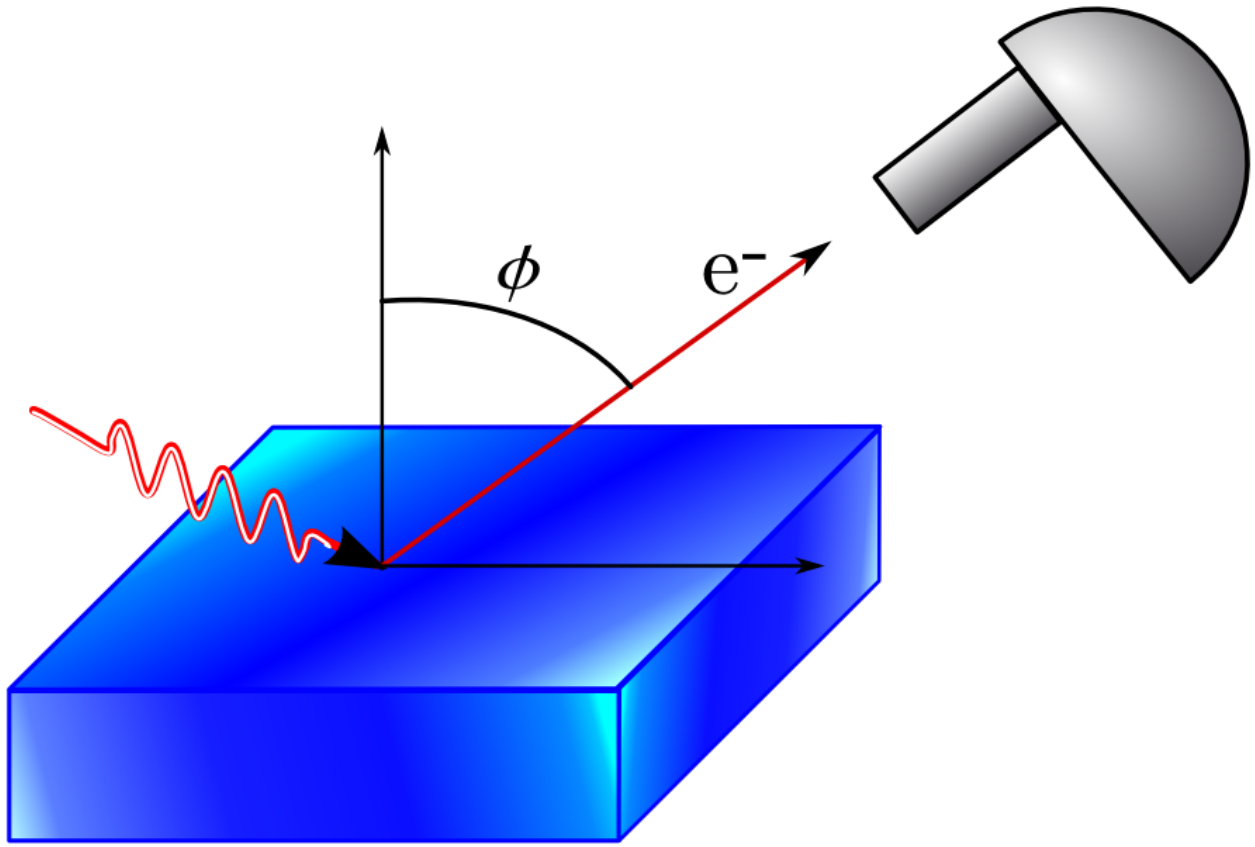


Izumi *et al.*, Anal.Chem. **77**, 6969 (2005)

Outline

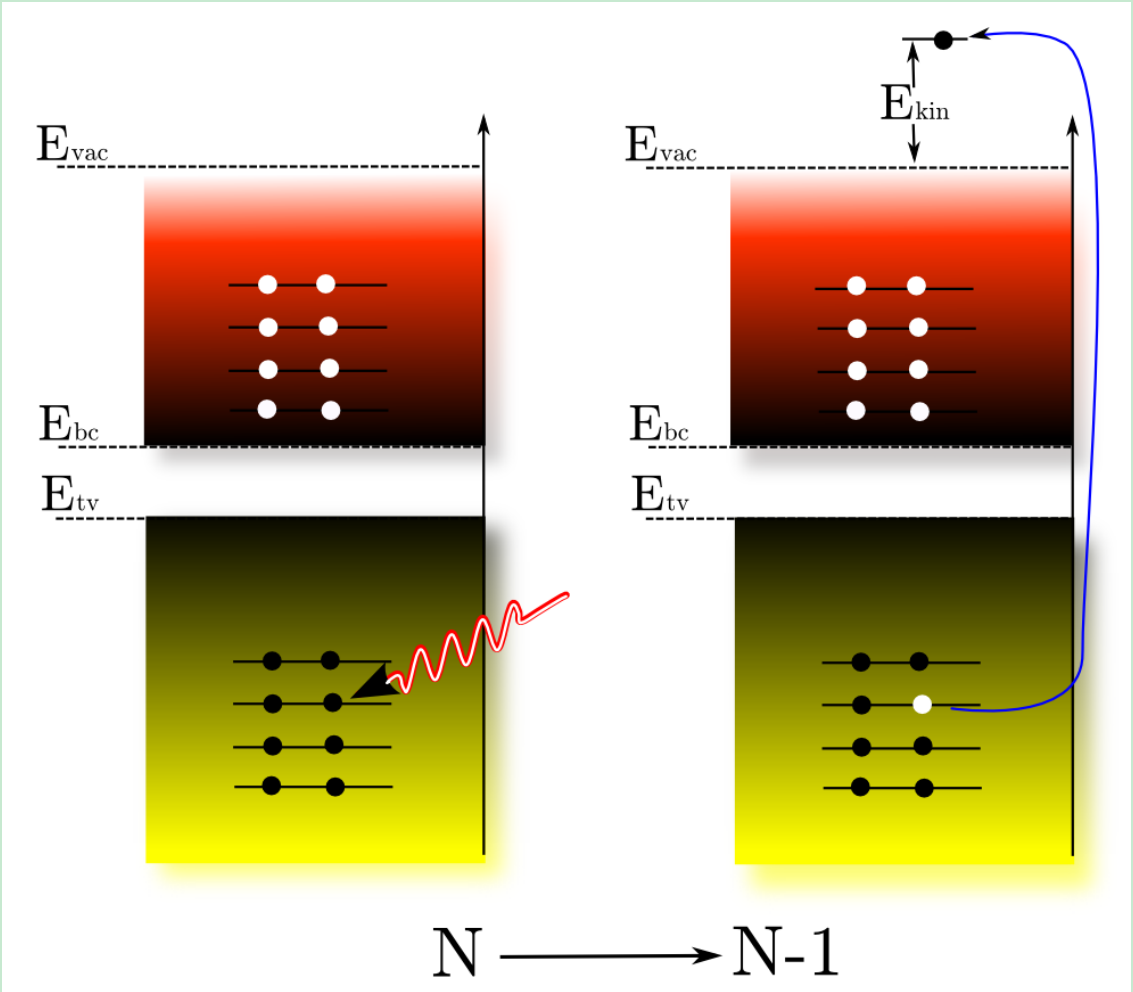
Spectroscopy: Photo-emission Spectroscopy

UPS,XPS,ARPES

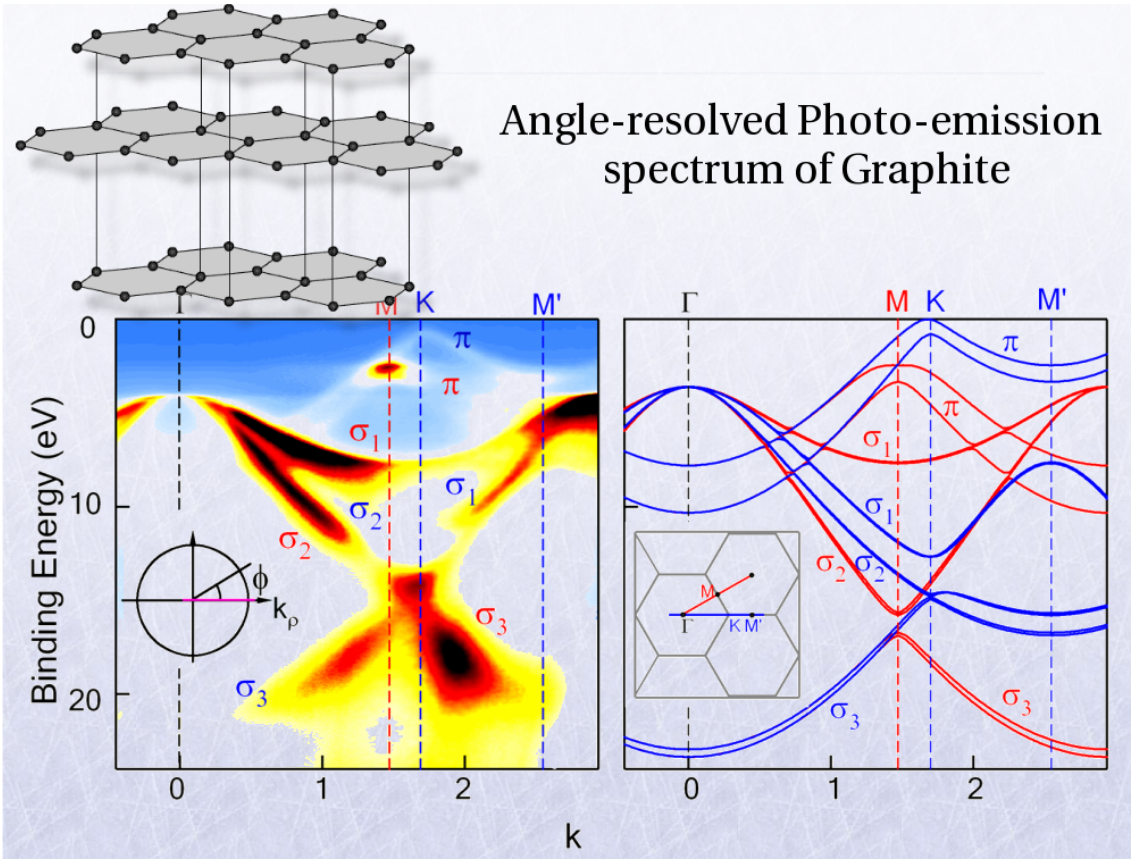


Spectroscopy: Photo-emission Spectroscopy

Electron out. Investigation of occupied bands. ARPES



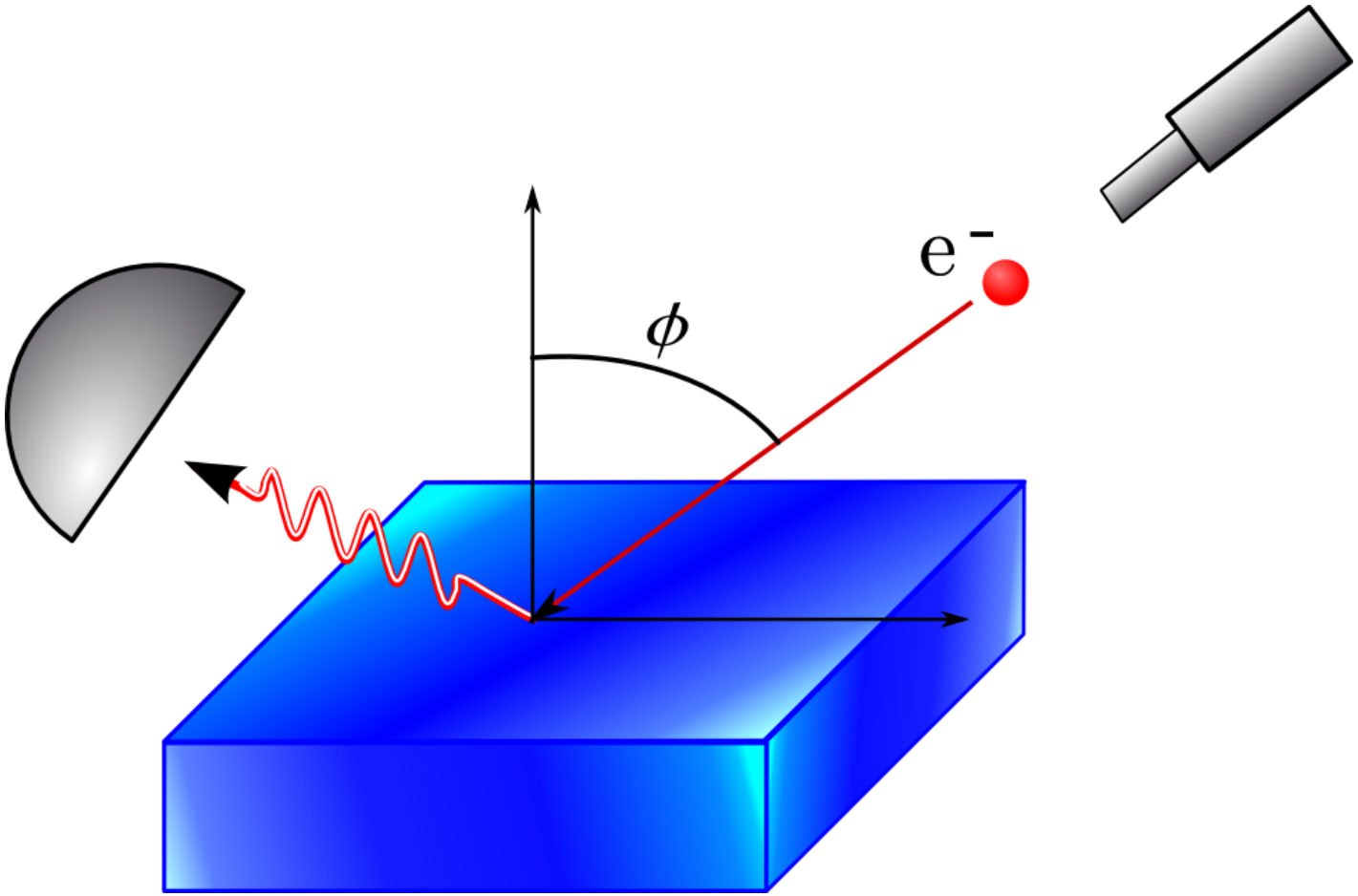
Spectroscopy: Photo-emission Spectroscopy



Zhou *et al.*, PRB **71**, 161403 (2005)

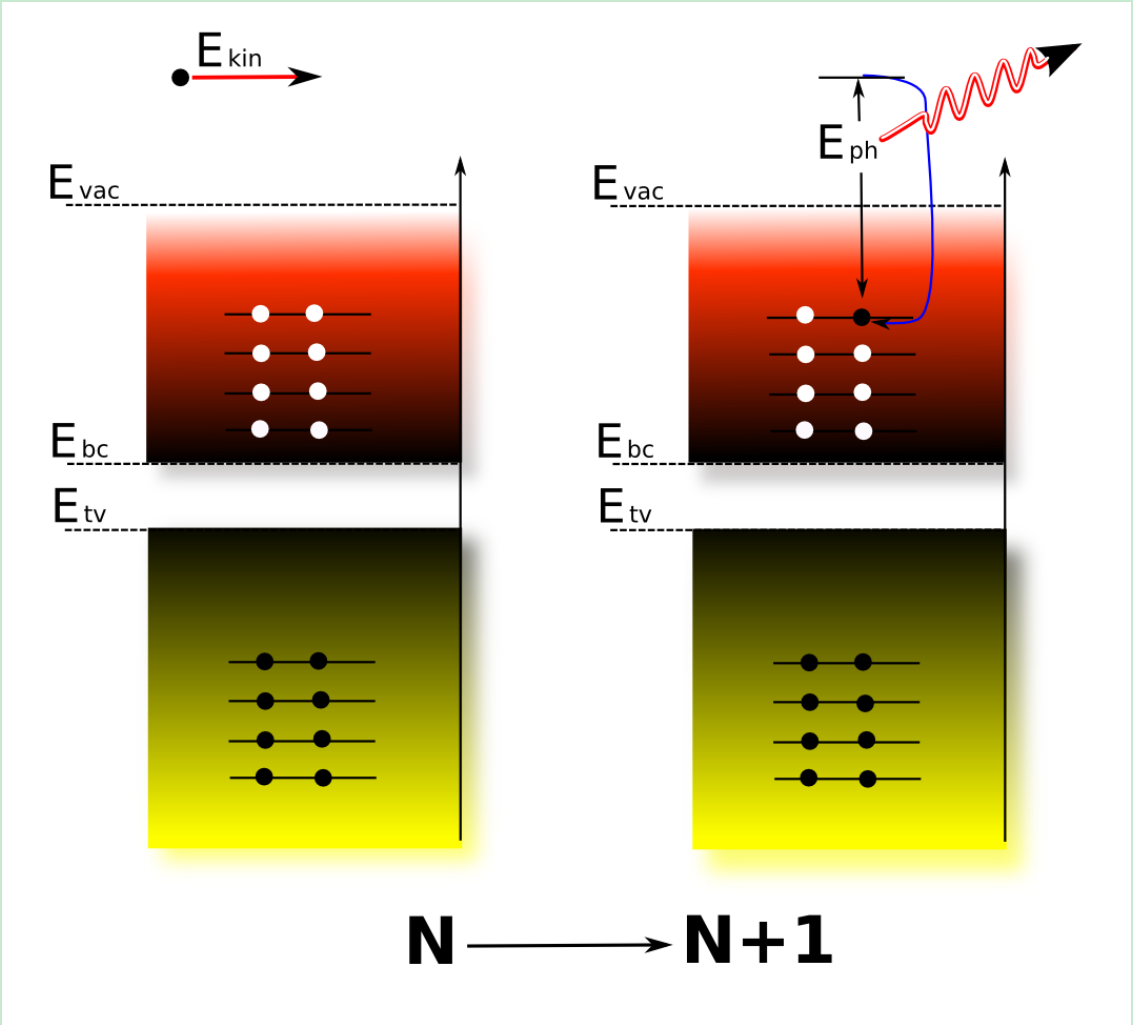
Spectroscopy: Inverse Photo-emission Spectroscopy

ARIPES



Spectroscopy: Inverse Photo-emission Spectroscopy

Electron in. Investigation of empty bands. ARIPES



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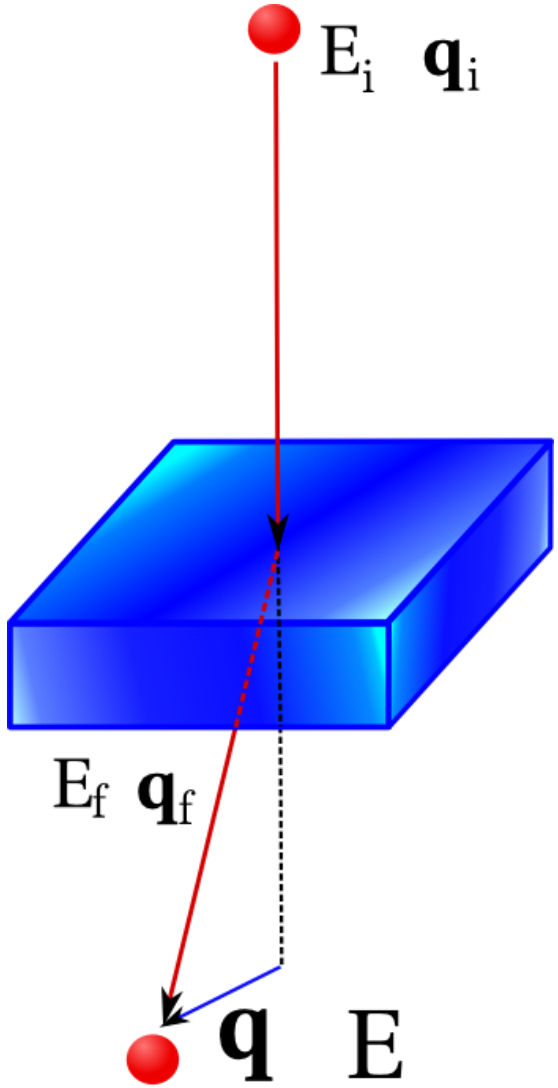
Spectroscopy: Electron Scattering

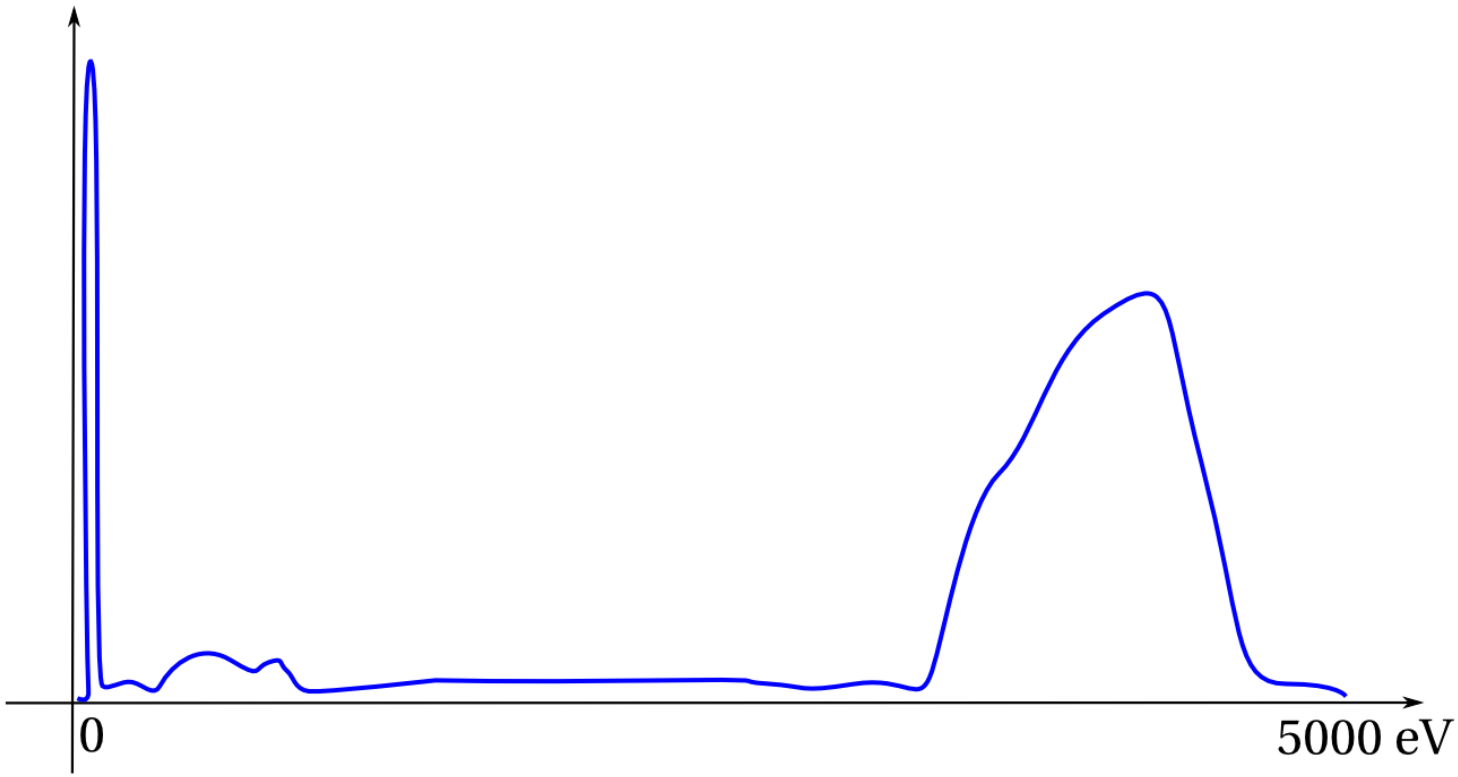


Spectroscopy: Electron Scattering

Energy Loss Function

$$\frac{d^2\sigma}{d\Omega dE} \propto \mathrm{Im}\left\{\varepsilon^{-1}\right\}$$

Spectroscopy: Electron Scattering



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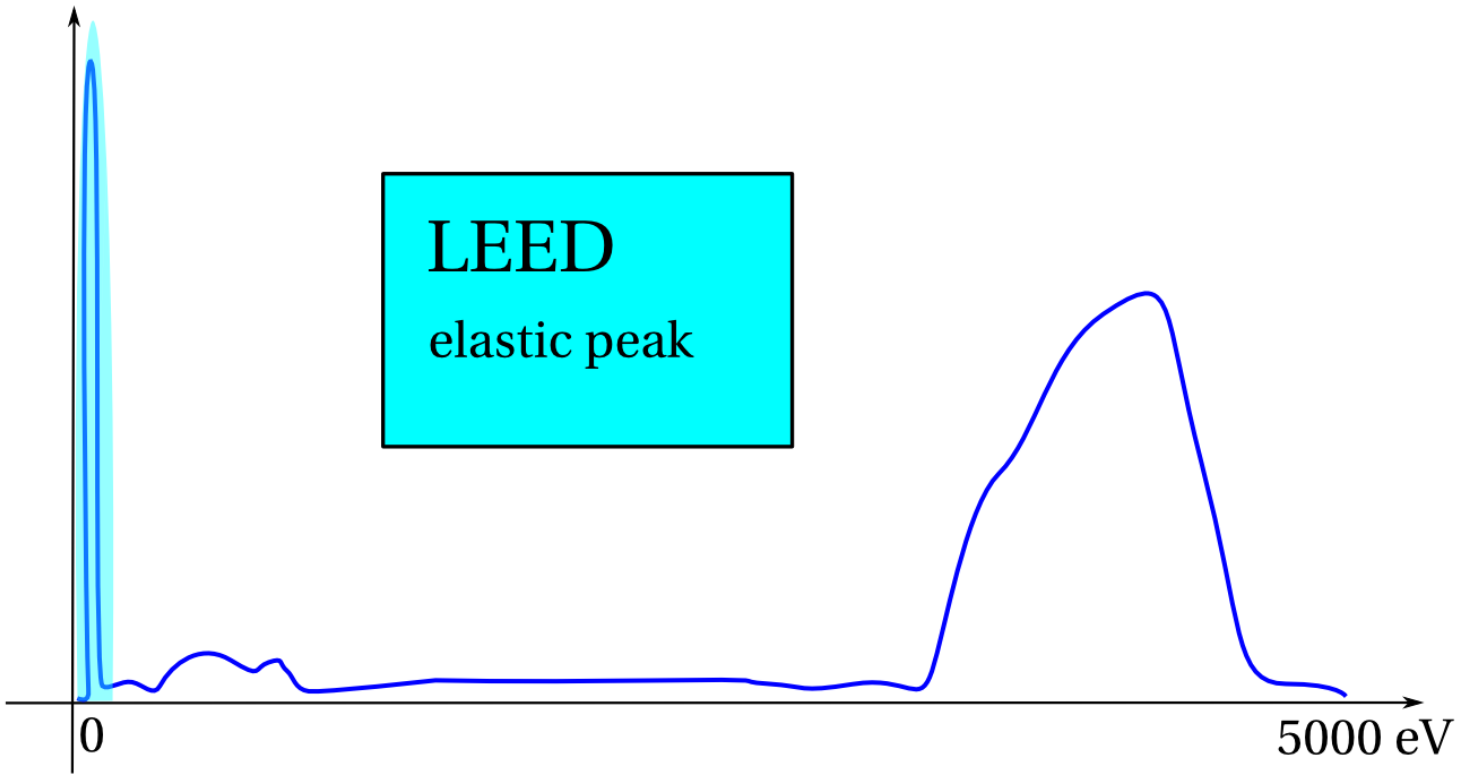

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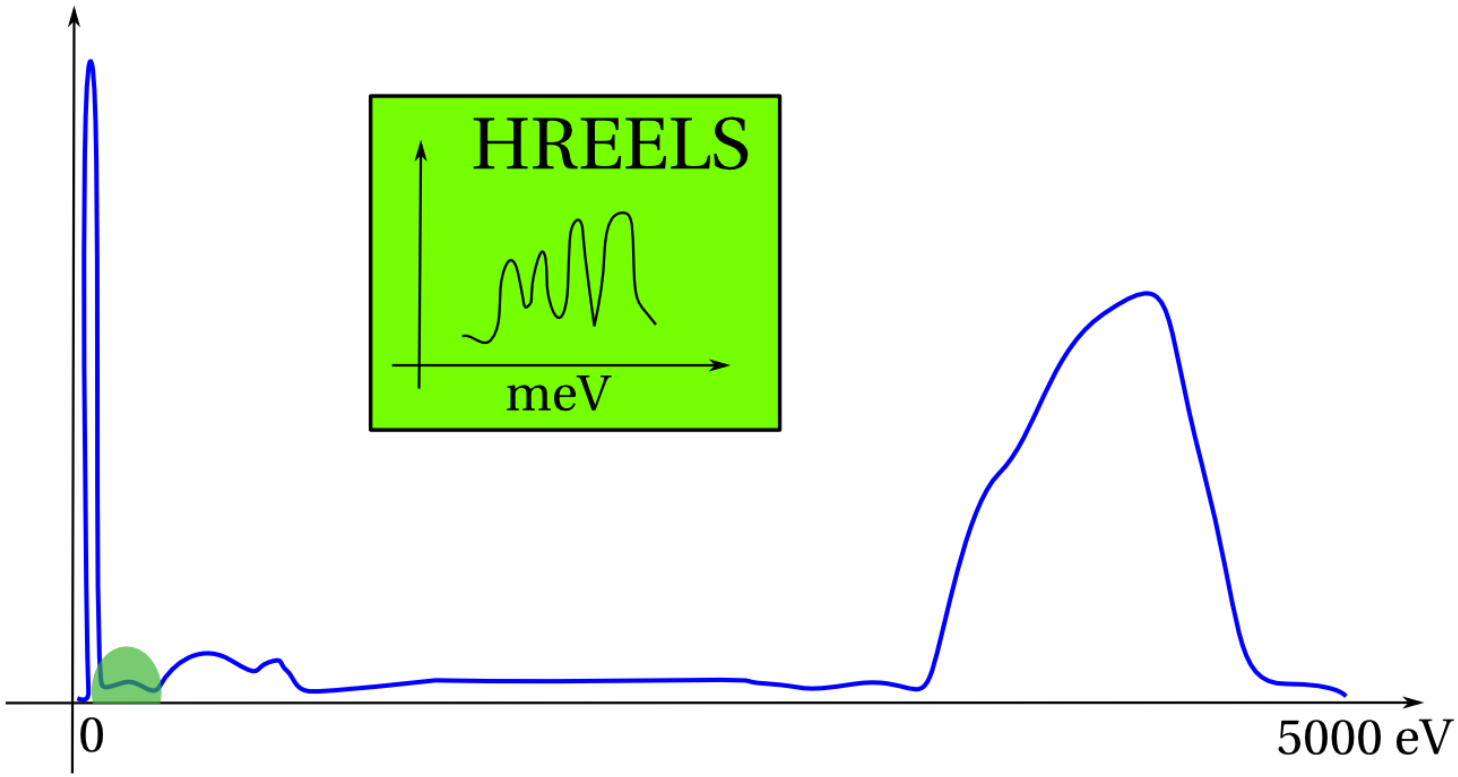

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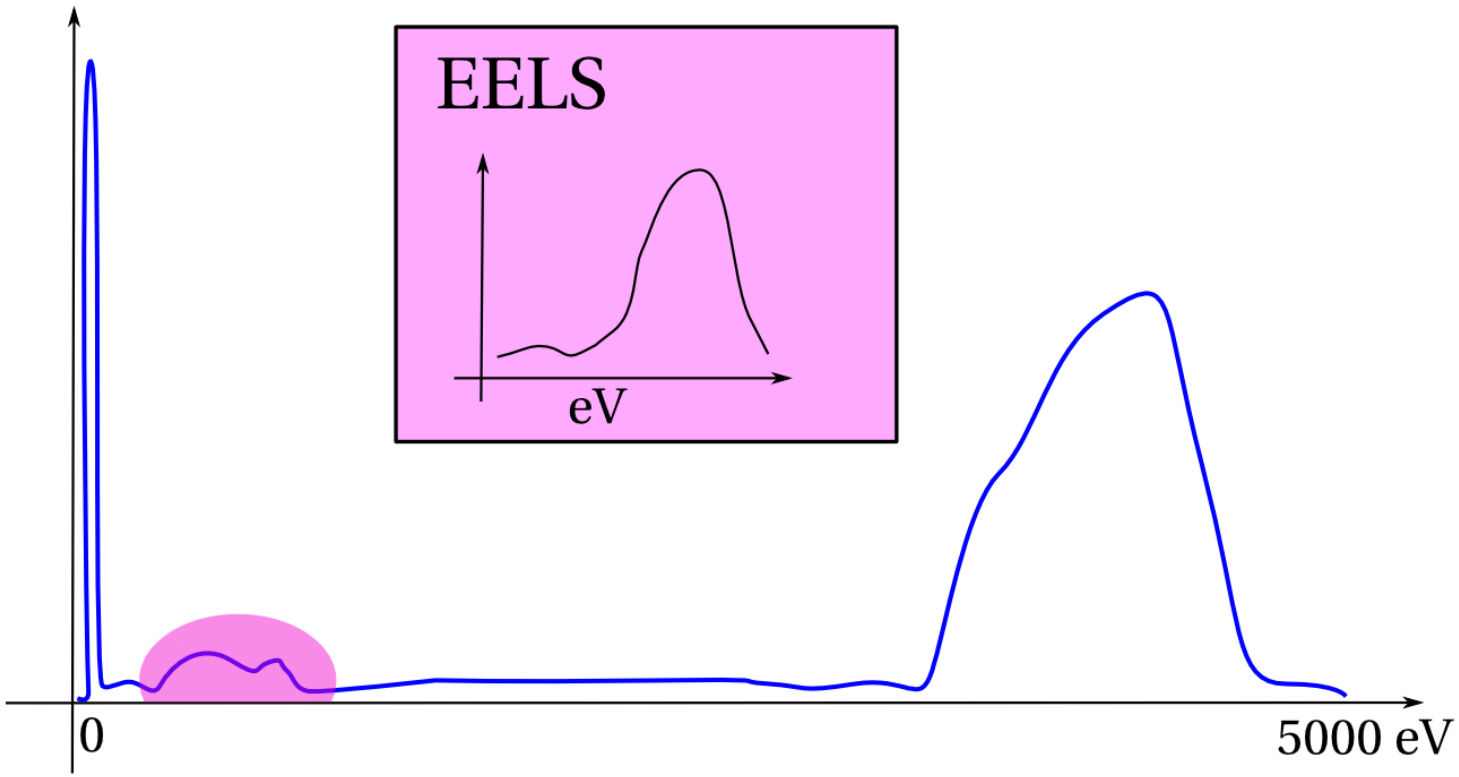

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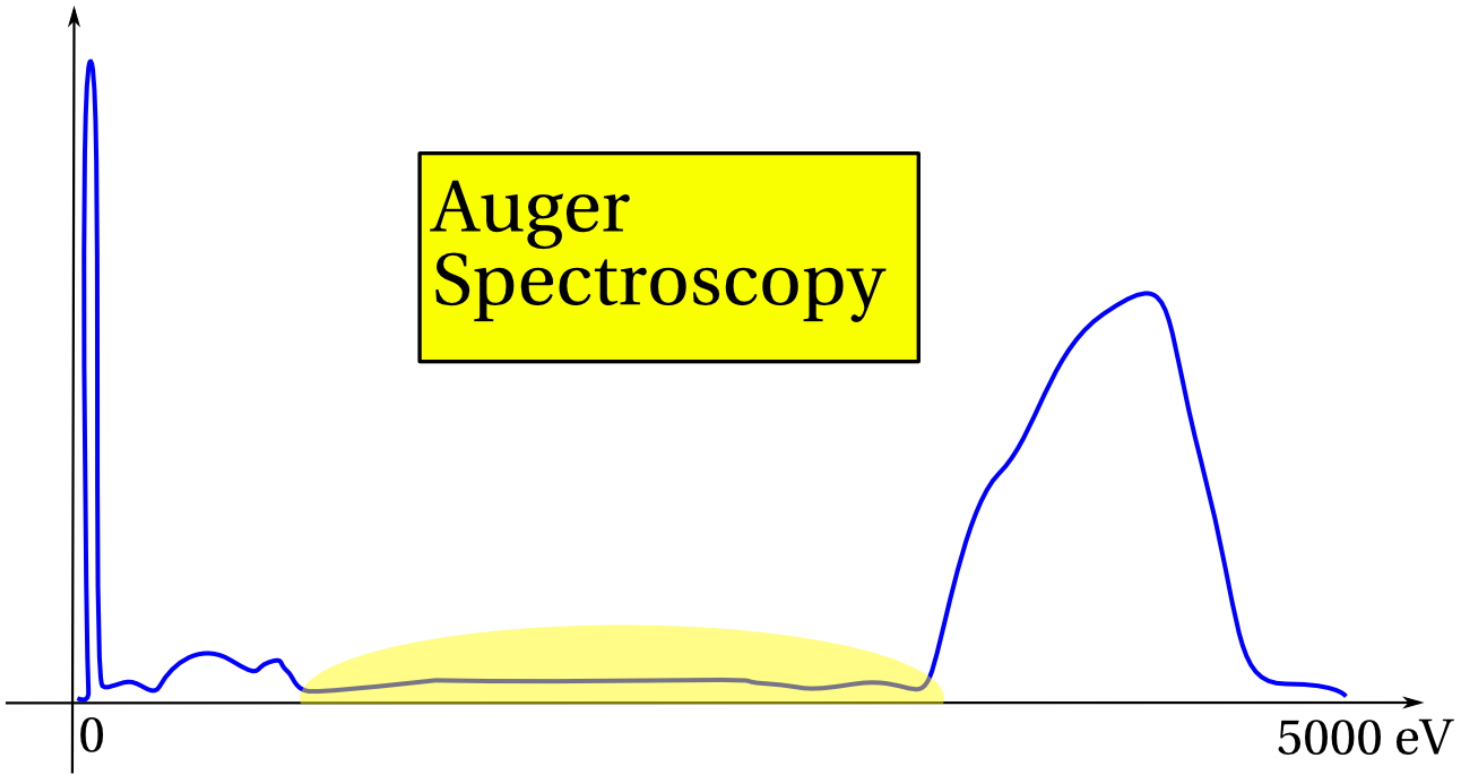

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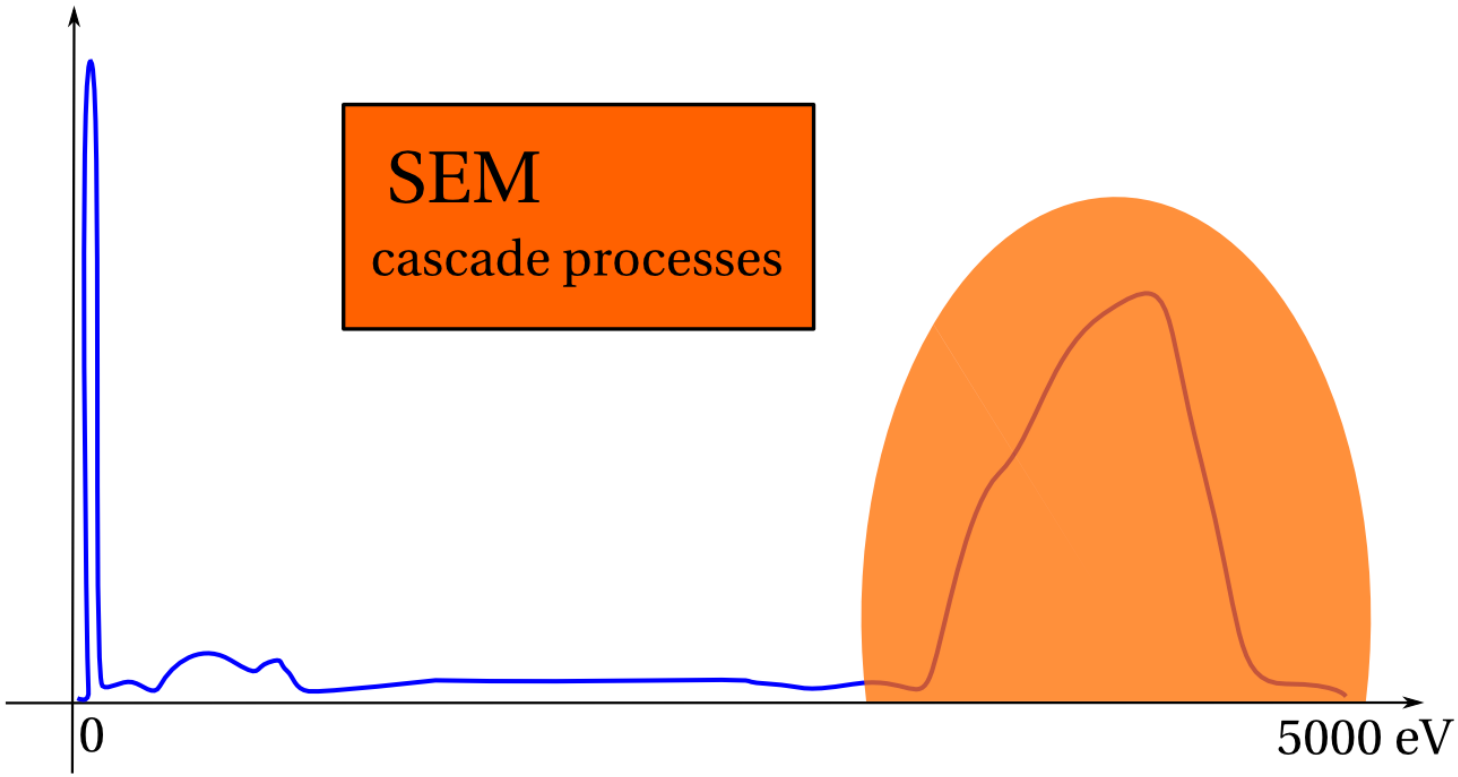

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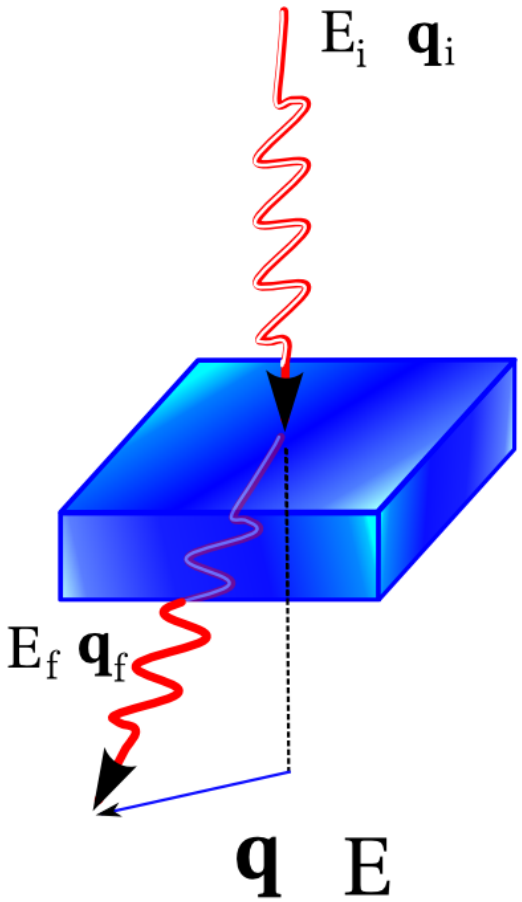
Spectroscopy: X-ray Scattering



Spectroscopy: X-ray Scattering

Energy Loss Function

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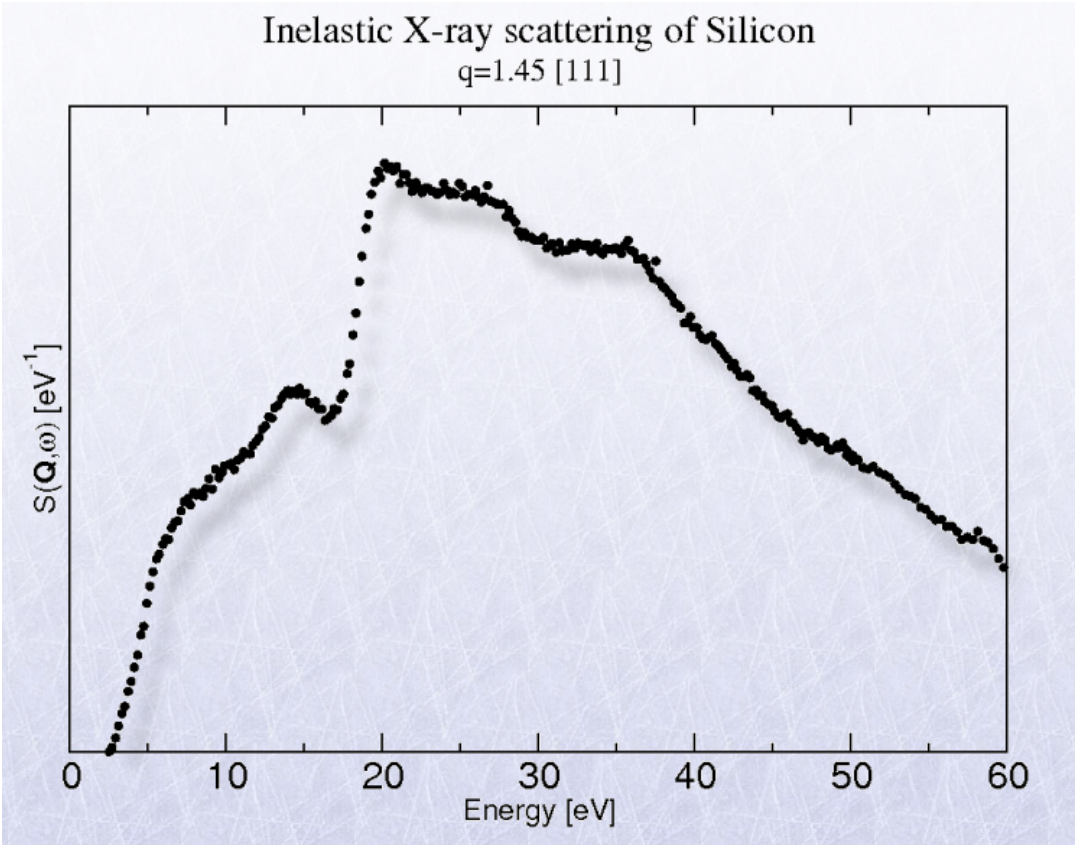

Weissker *et al.*, PRL **97**, 237602 (2006)

Spectroscopy: Energy Loss Spectroscopies

EELS vs IXS

- IXS is more sensitive to bulk
- IXS is better for big $\mathbf{q}$
- IXS simpler to analize (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 $\mathbf{q}$
- both expensive (100k-1M €)!

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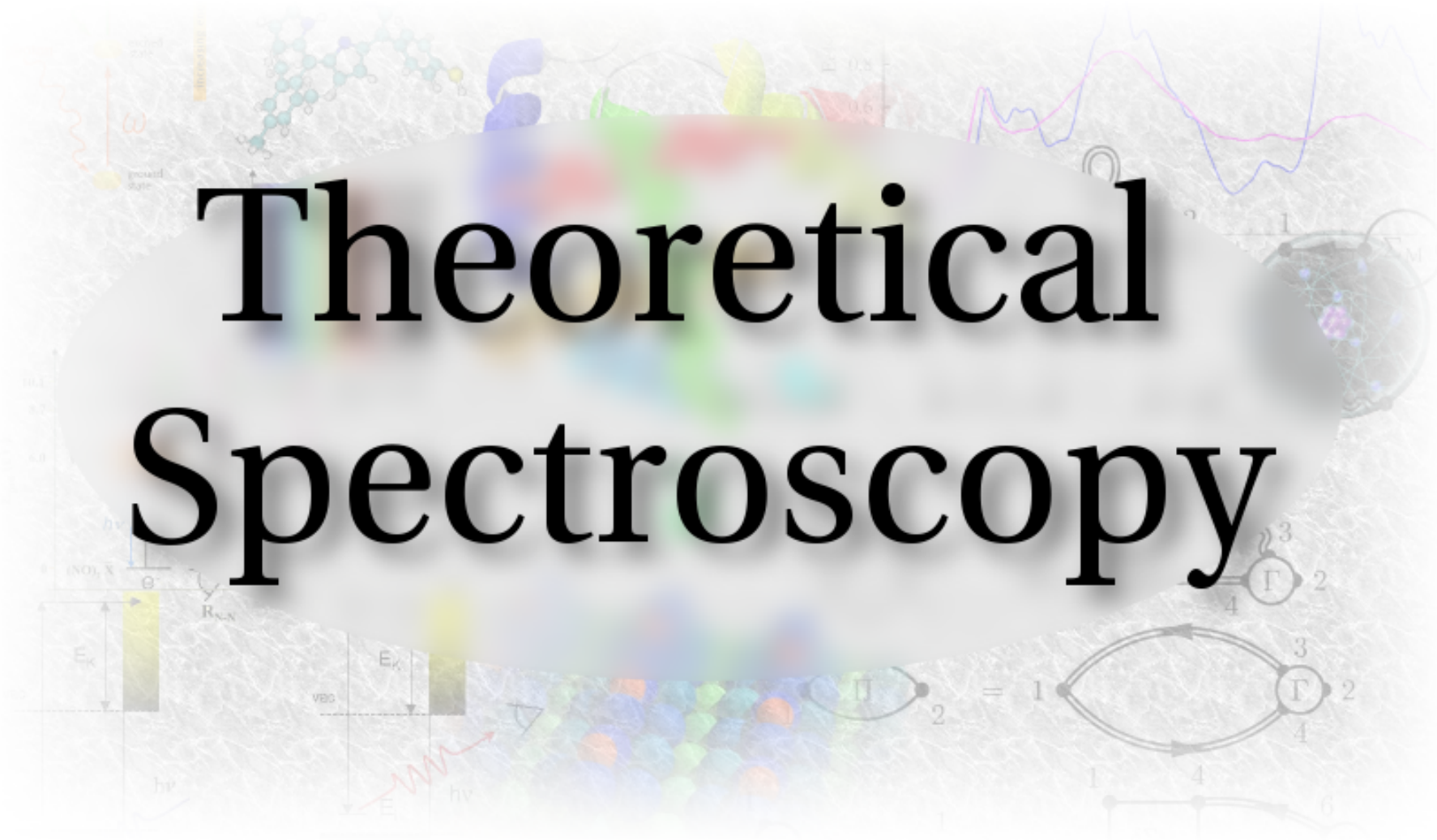

Theoretical Spectroscopy