Theoretical Spectroscopy Methods in Condensed Matter Physics

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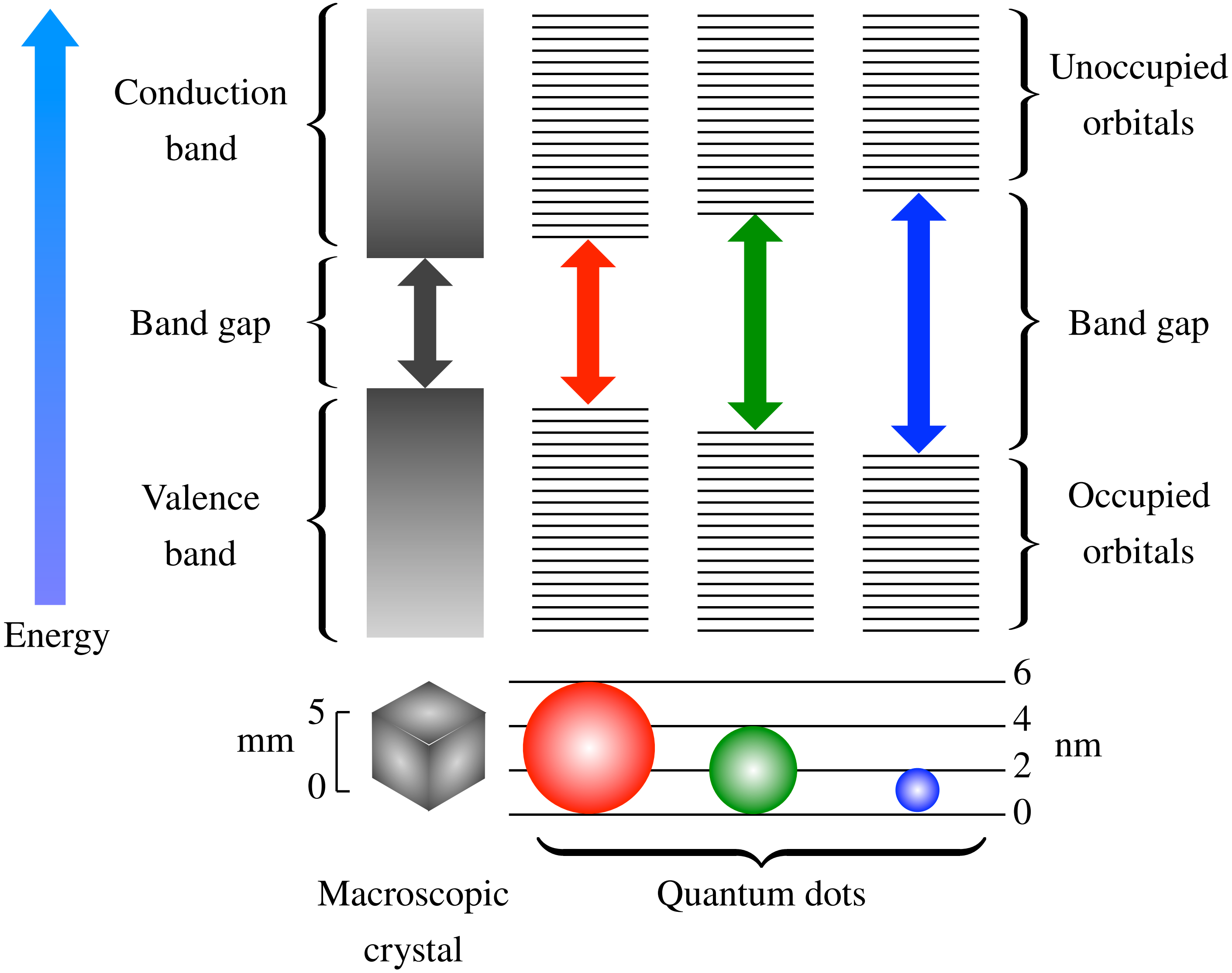
Why is electronic structure important?



Energy

Conduction band

Band gap

Valence band

Unoccupied orbitals

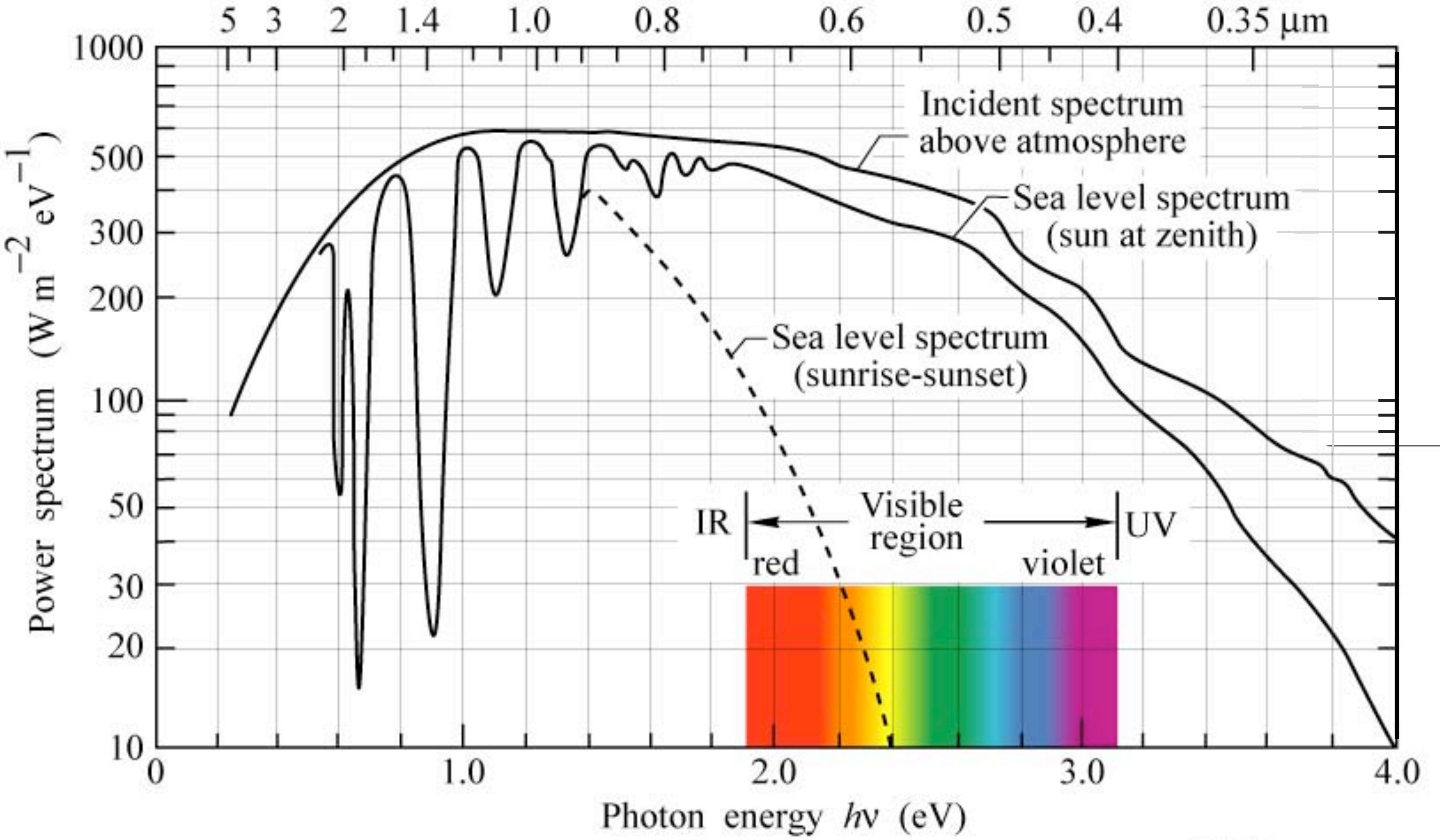
Band gap

Occupied orbitals

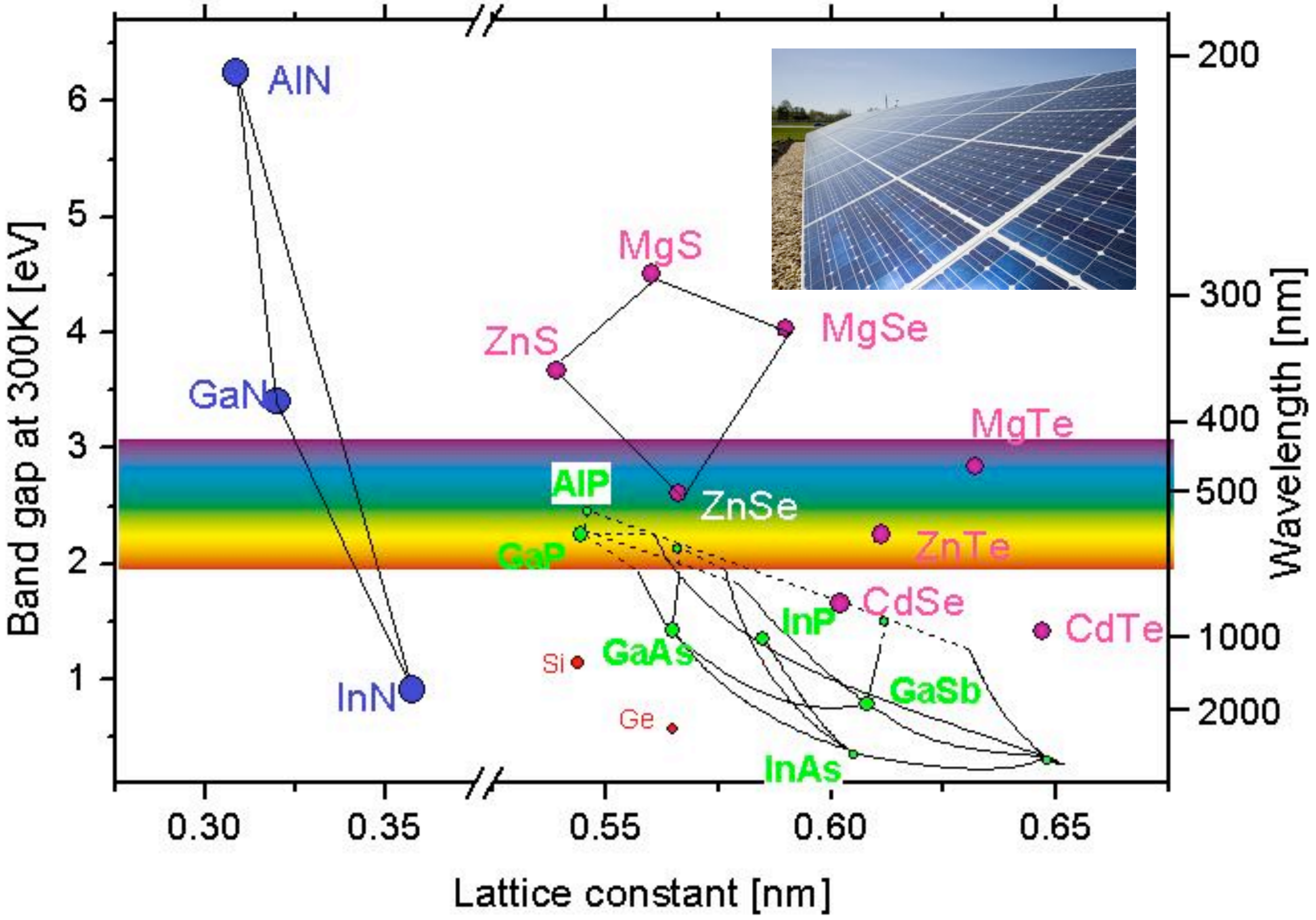
Macroscopic crystal

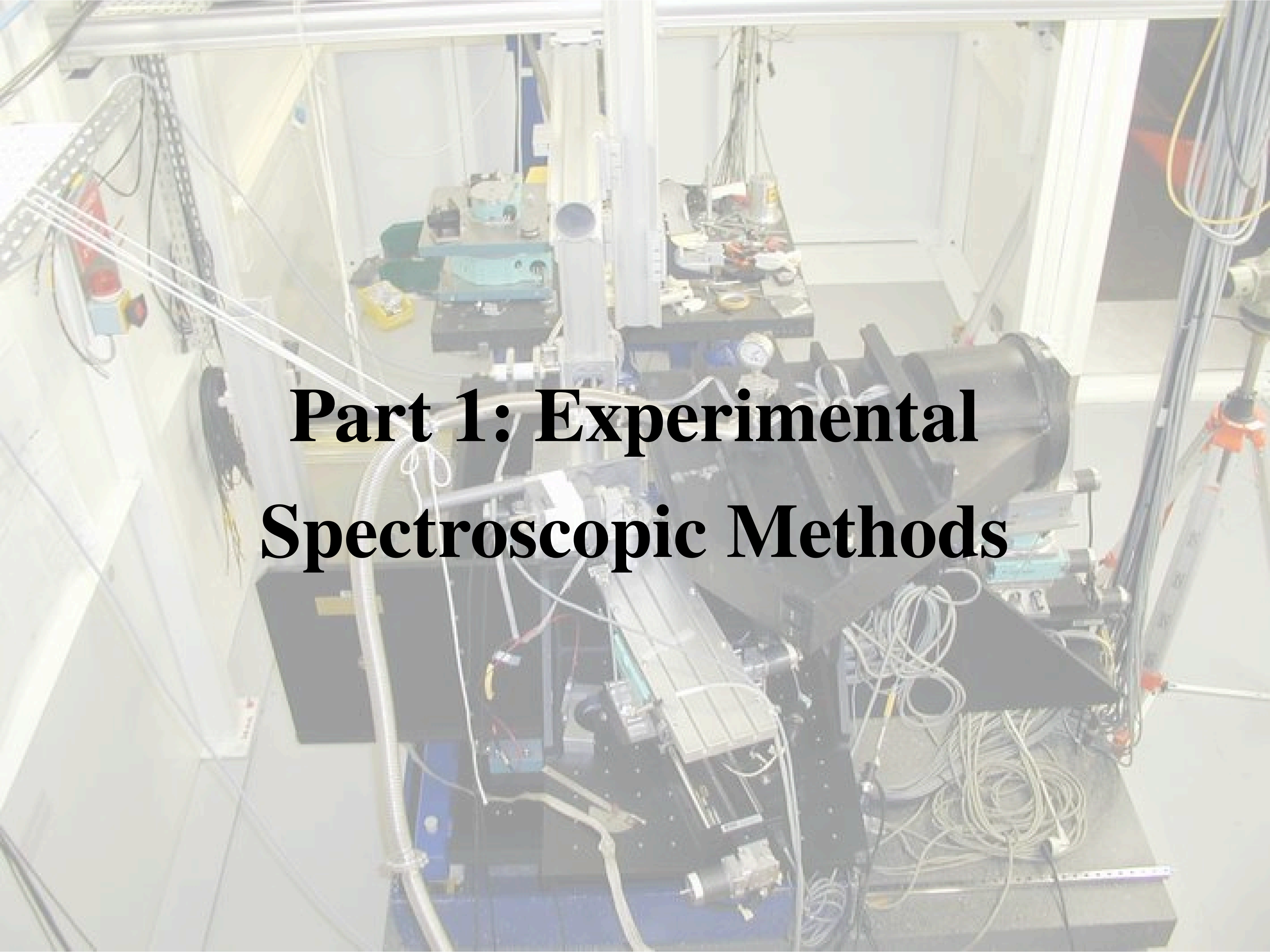
Quantum dots

Why is electronic structure important?



Why is electronic structure important?



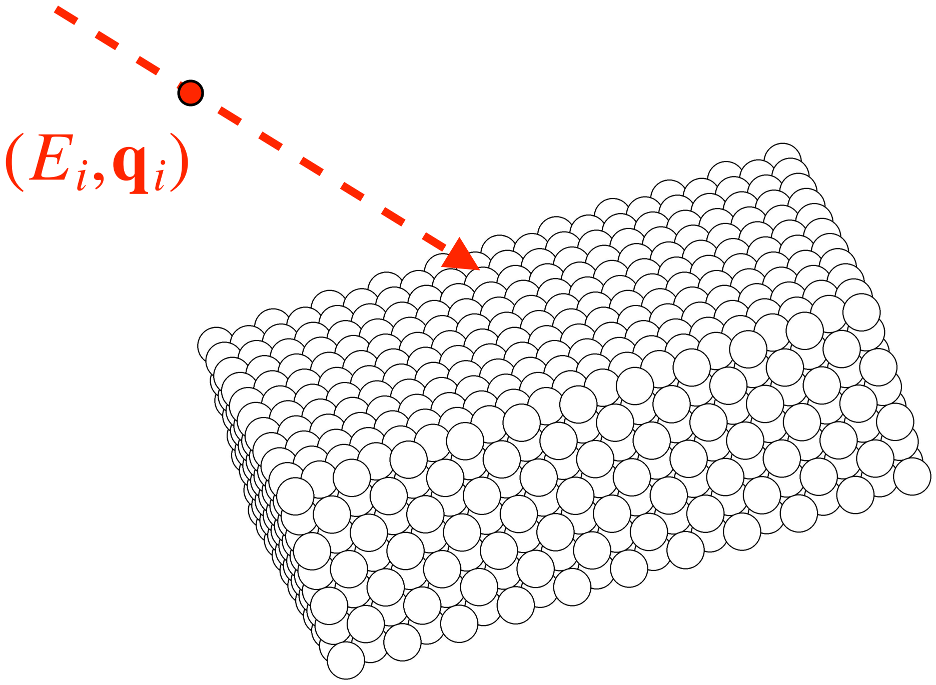


Part 1: Experimental Spectroscopic Methods

Introduction

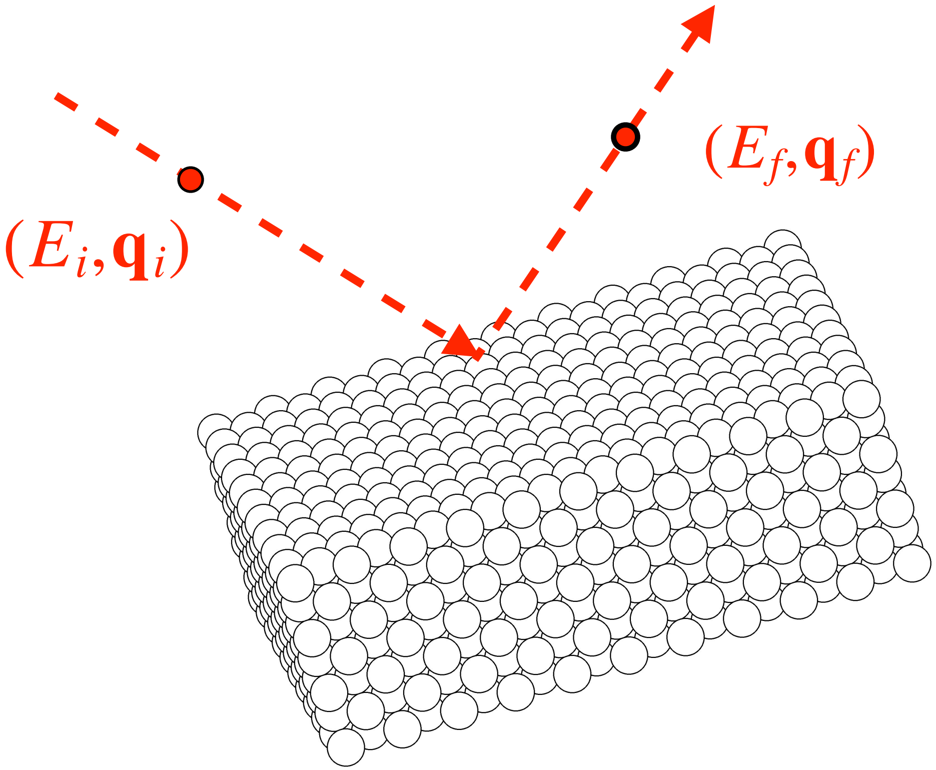
How is the electronic structure measured?

- The **spectroscopies** are the experimental methods to study of the **properties of matter** (atoms, molecules, and solids) by investigating its **interactions with particles** (photons, electrons, neutrons, ions, ...).



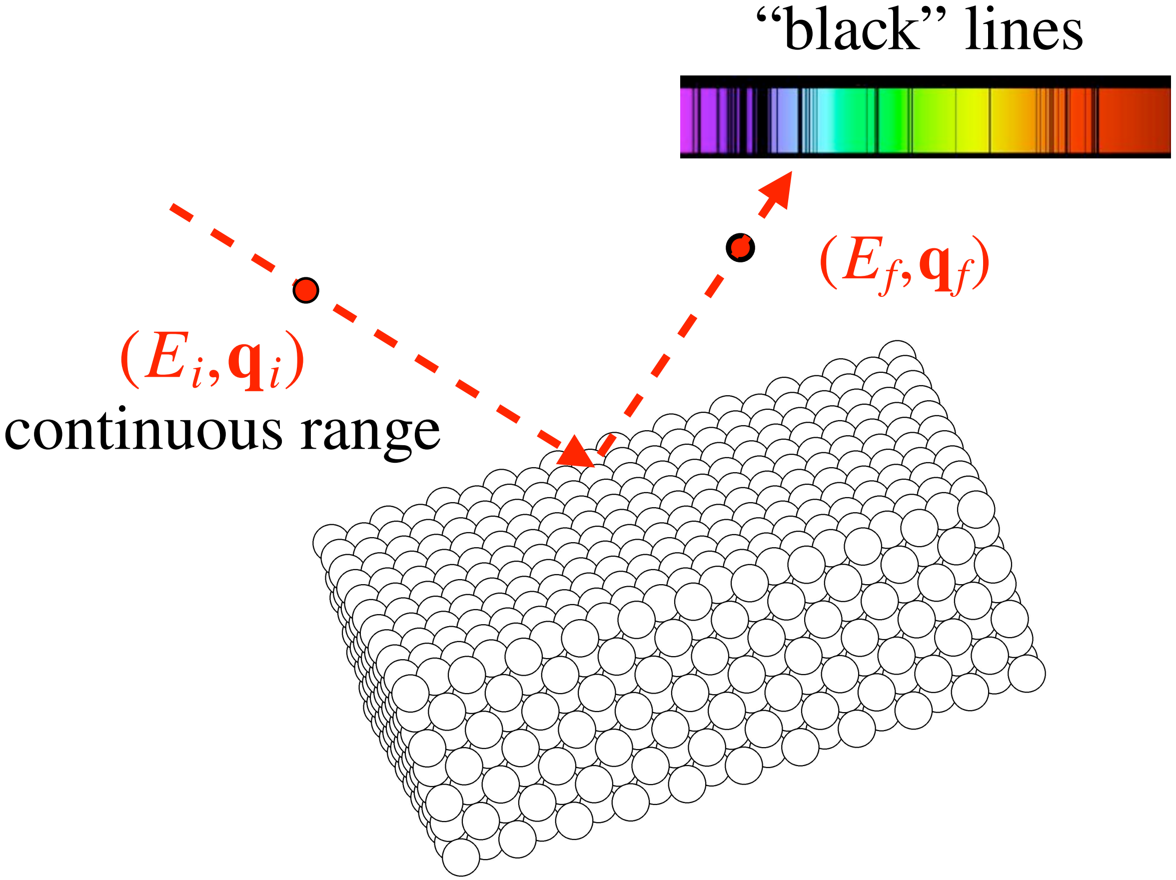
How is the electronic structure measured?

- The **spectroscopies** are the experimental methods to study of the **properties of matter** (atoms, molecules, and solids) by investigating its **interactions with particles** (photons, electrons, neutrons, ions, ...).
- This can result in **scattering** either **elastic** ($E_i = E_f$ and $\mathbf{q}_i \neq \mathbf{q}_f$) or **inelastic** ($E_i \neq E_f$ and $\mathbf{q}_i \neq \mathbf{q}_f$).



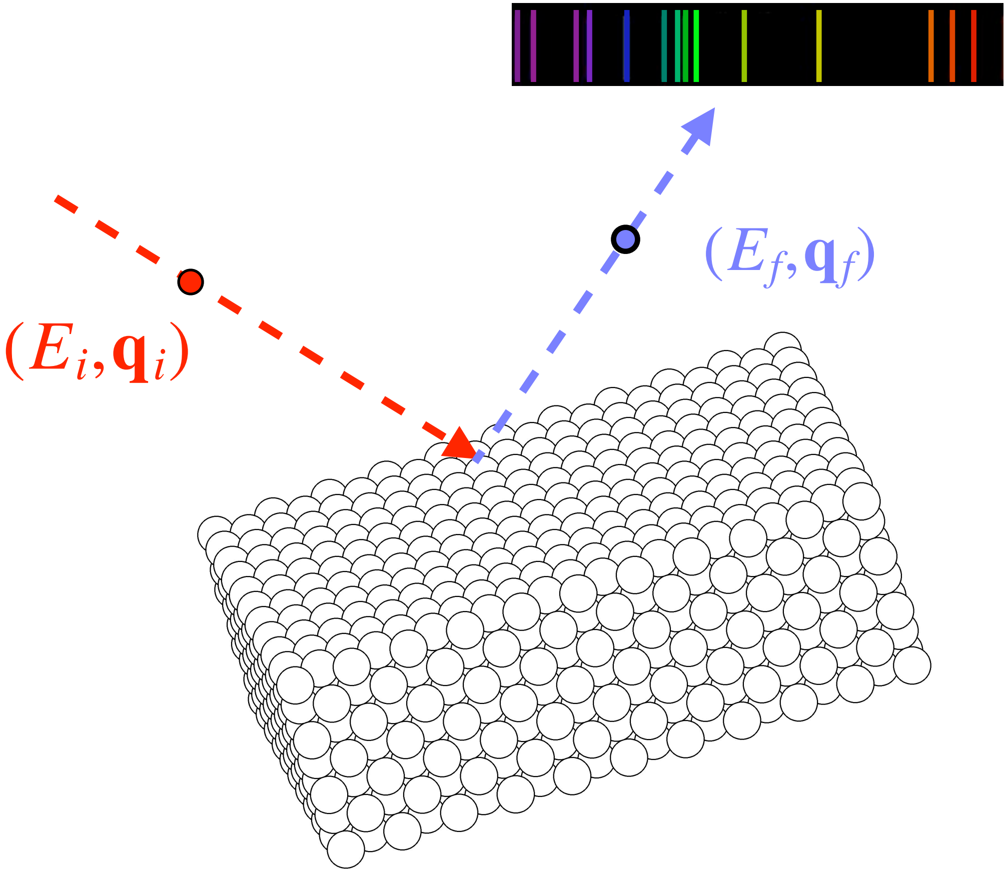
How is the electronic structure measured?

- The **spectroscopies** are the experimental methods to study of the **properties of matter** (atoms, molecules, and solids) by investigating its **interactions with particles** (photons, electrons, neutrons, ions, ...).
- This can result in **absorption** (ionization, electron excitations, plasmons).

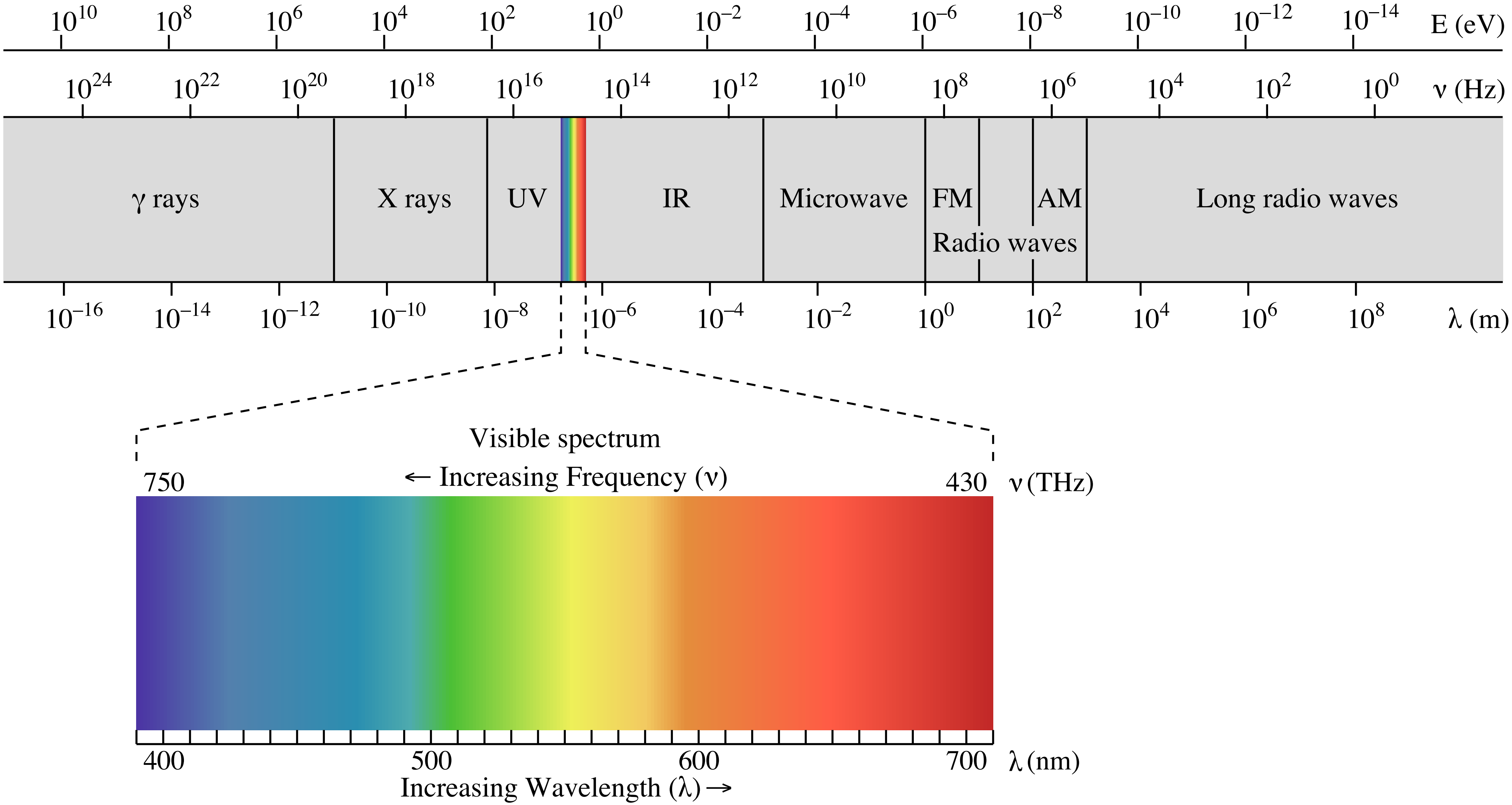


How is the electronic structure measured?

- The **spectroscopies** are the experimental methods to study of the **properties of matter** (atoms, molecules, and solids) by investigating its **interactions with particles** (photons, electrons, neutrons, ions, ...).
- This can result in **emission**.

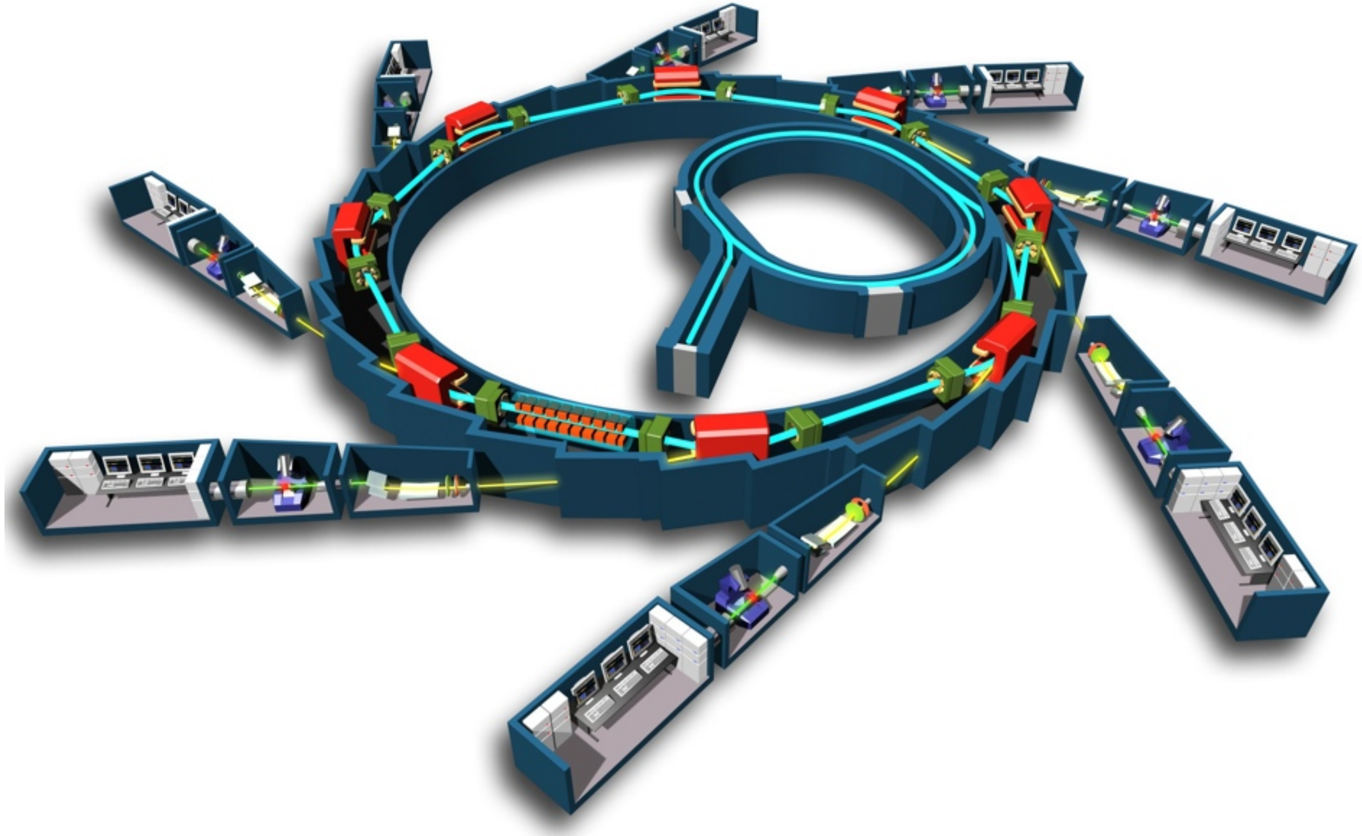


What is the energy range to cover?



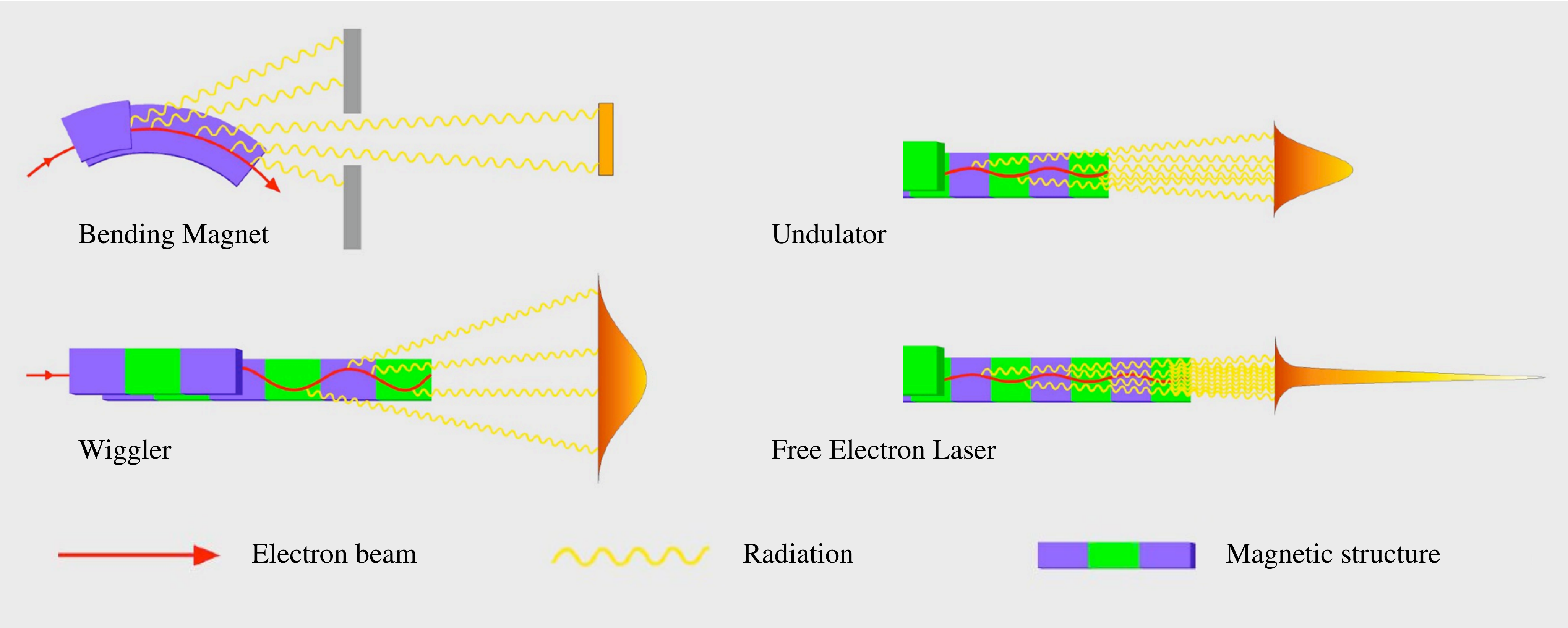
What are the possible particle sources?

- Photons:
  - UV, visible, or IR lamps
  - X-ray tubes
  - Synchrotrons (wide range of ν : sub eV up to MeV)



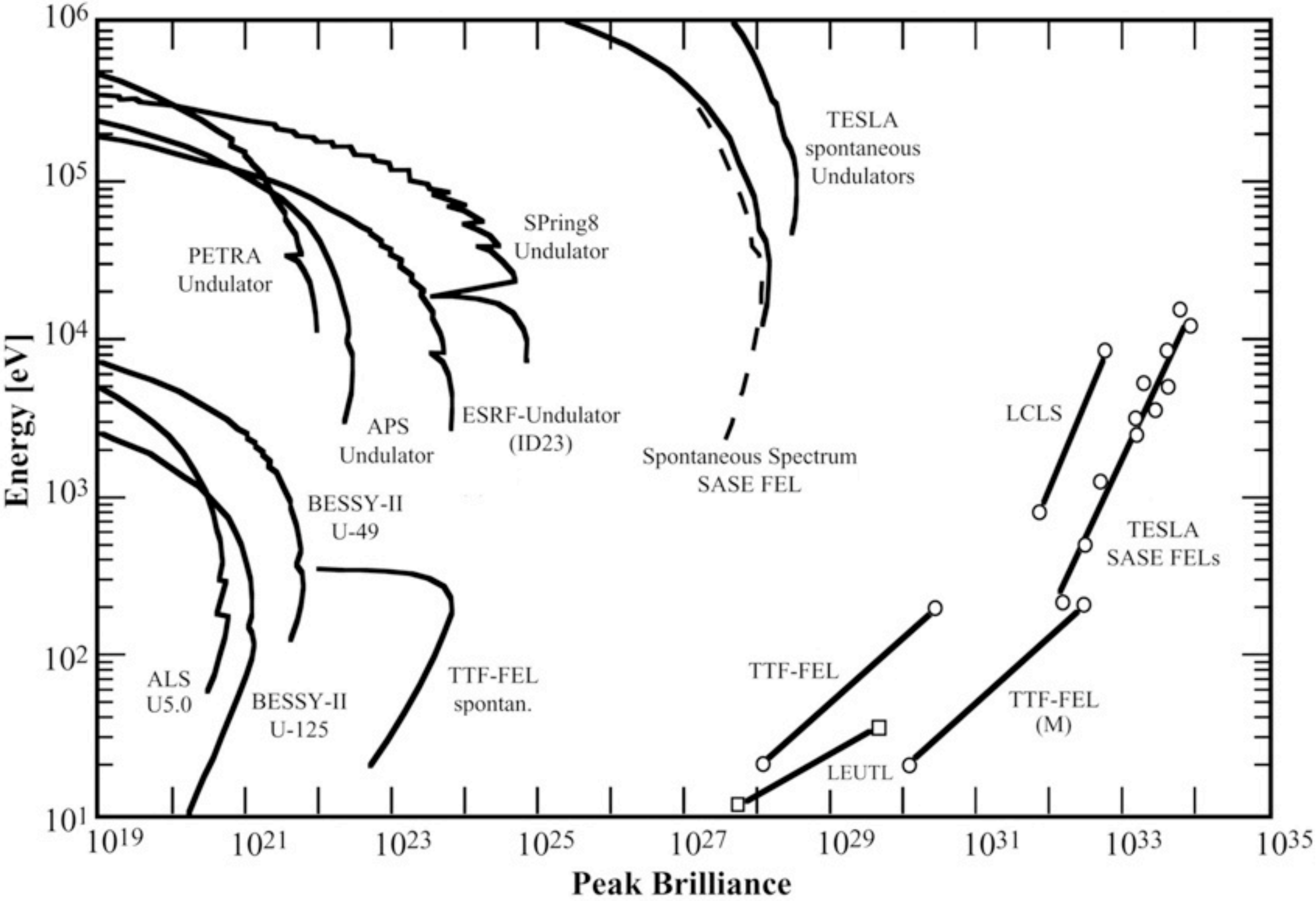
What are the possible particle sources?

- Photons (continued):
  - Free Electron Lasers



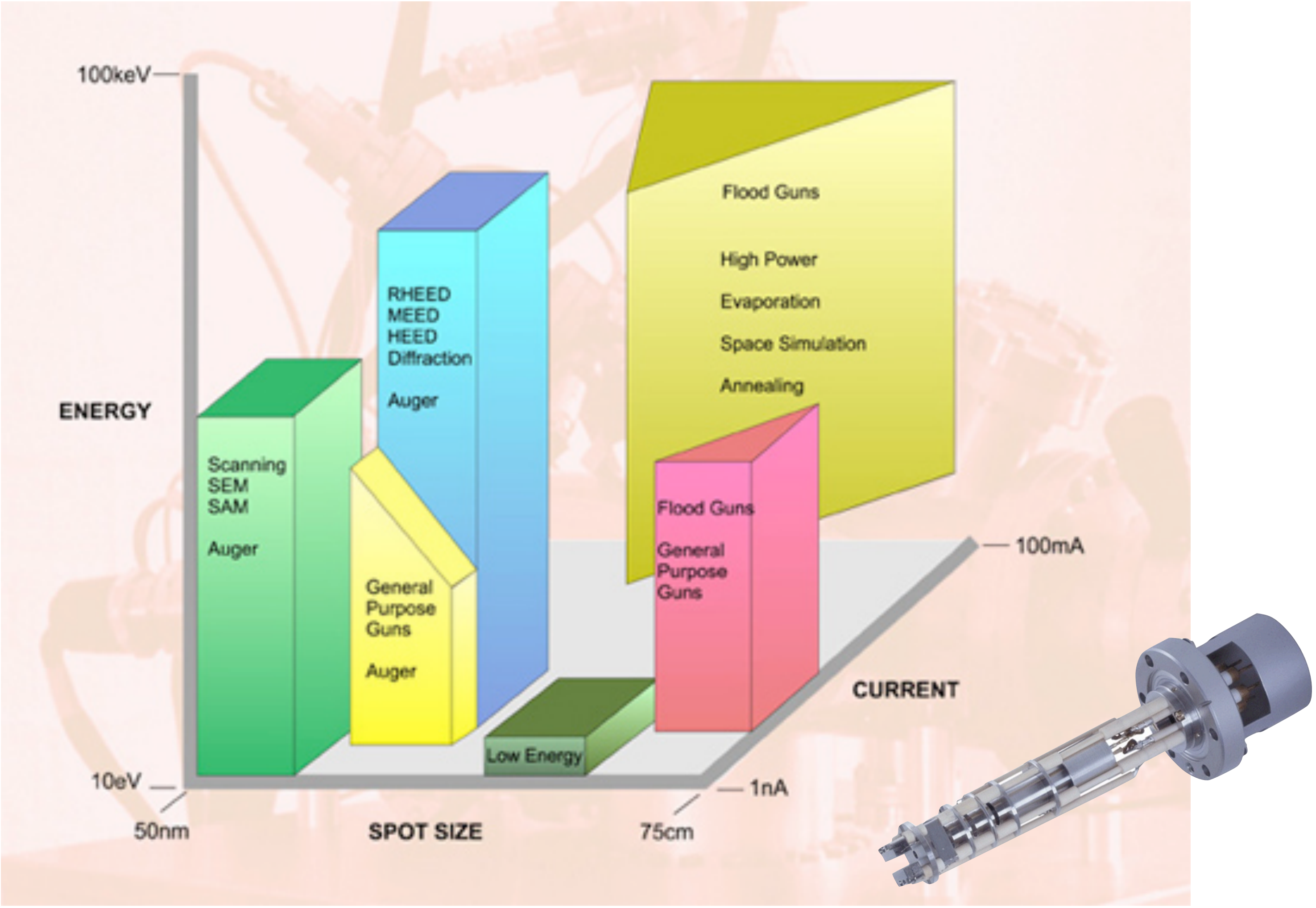
What are the possible particle sources?

- Photons (continued):



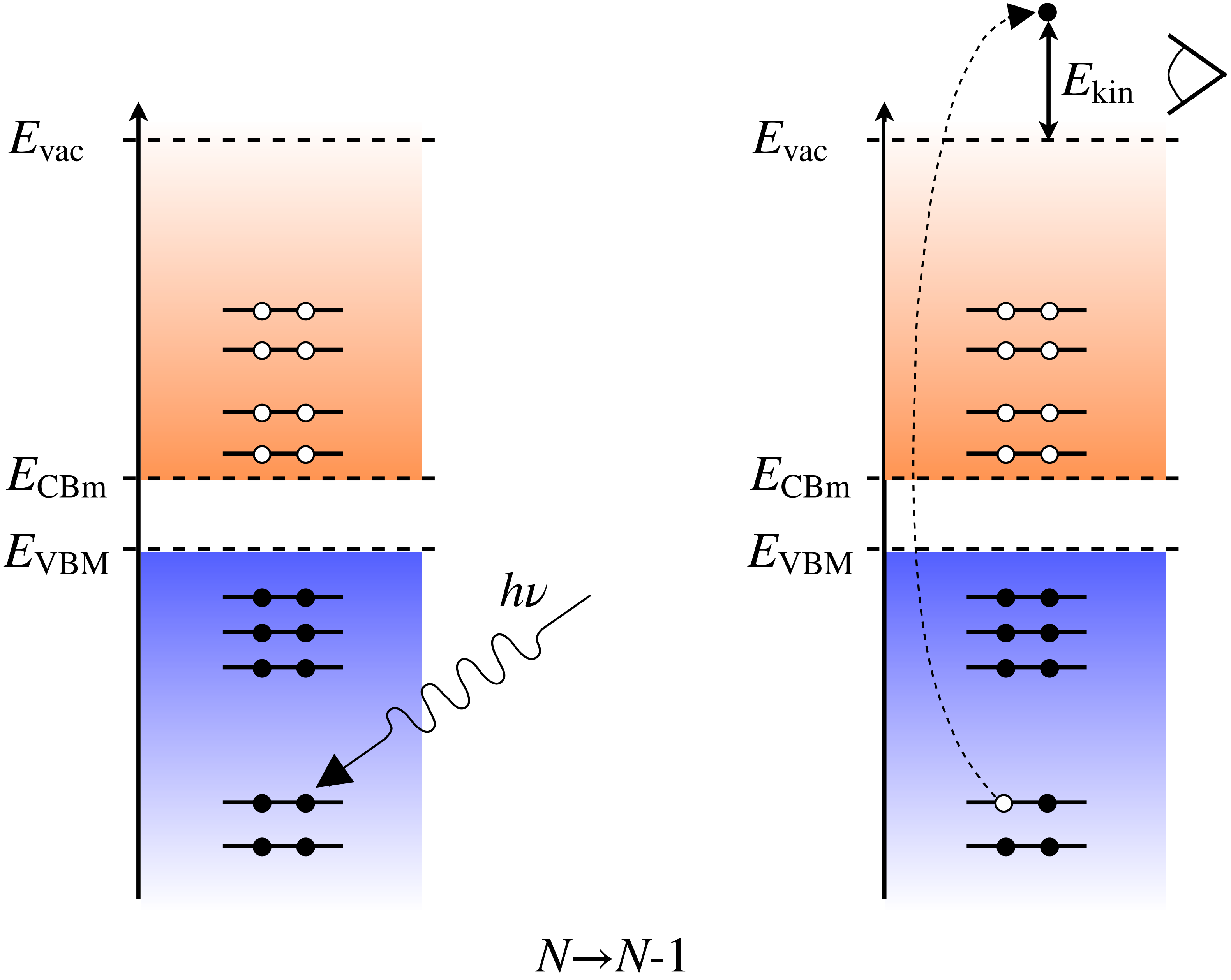
What are the possible particle sources?

- Electrons:
  - Guns (thermionic, high-field, photo emission)

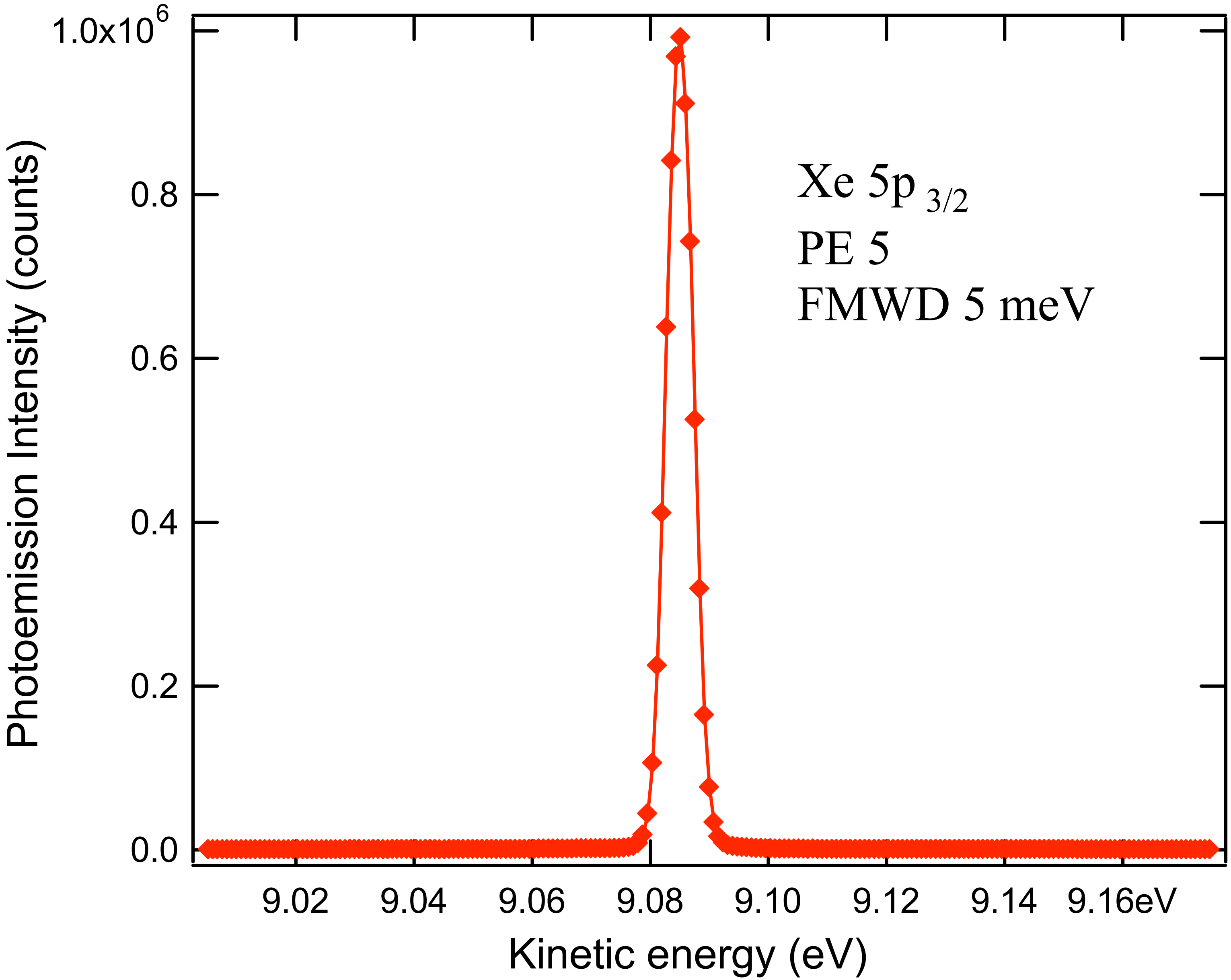


PhotoEmission Spectroscopy (PES)

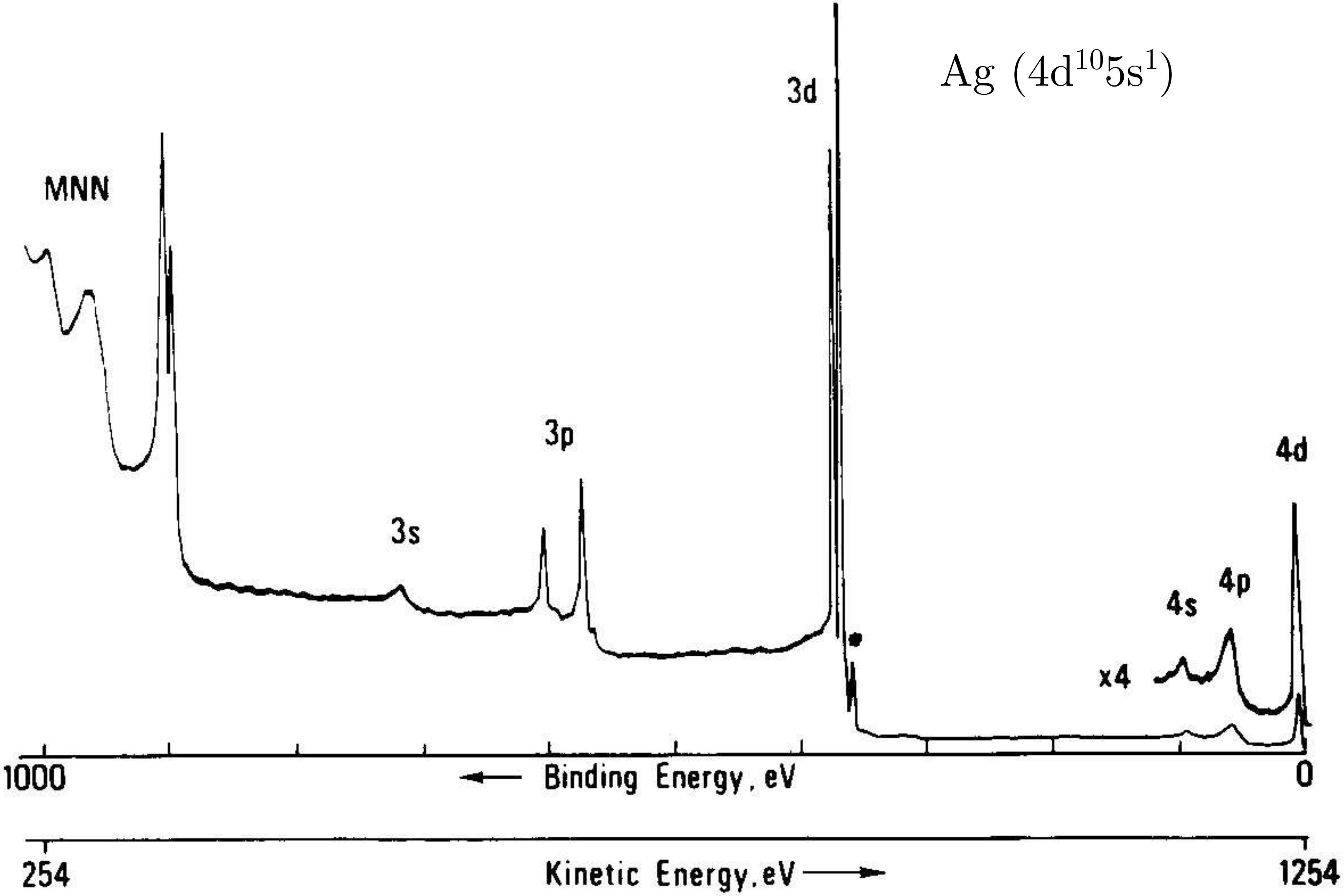
Process


E_{vac}
E_{CBm}
E_{VBM}
$h\nu$
E_{vac}
E_{kin}
E_{CBm}
E_{VBM}
$N \rightarrow N\text{-}1$

Spectra


1.0x10^6
0.8
0.6
0.4
0.2
0.0
Photoemission Intensity (counts)
9.02
9.04
9.06
9.08
9.10
9.12
9.14
9.16eV
Kinetic energy (eV)
Xe 5p 3/2
PE 5
FMWD 5 meV

Spectra

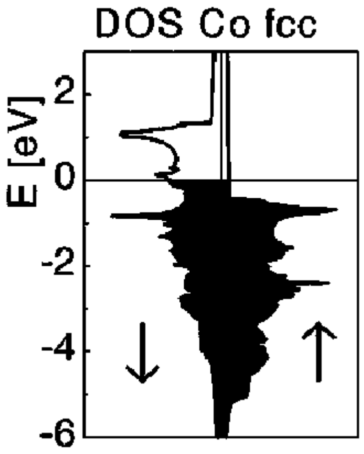


Binding Energy (BE)= hν - E_{kin}

Spectra

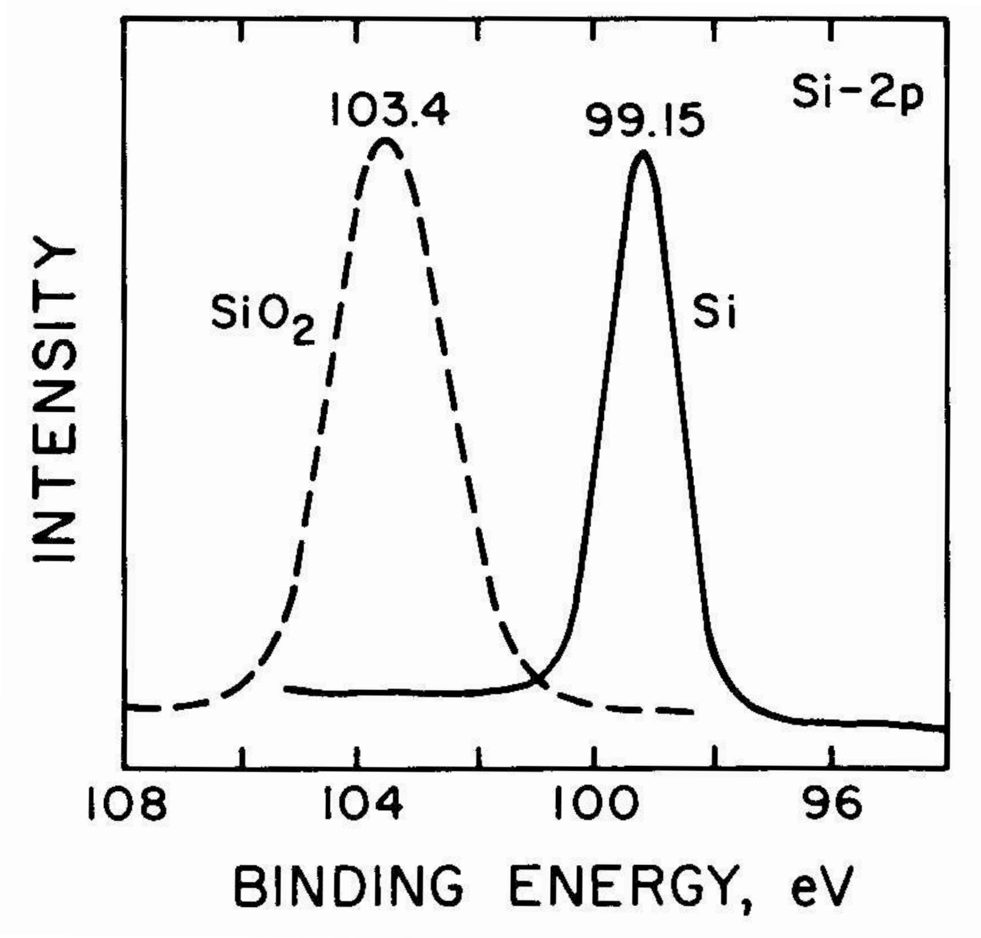
- Exciting radiation:
  - UV ($h\nu$ <50 eV) for valence electrons (**UPS**)
  - X-rays ($h\nu$=0.1-100keV) for core electrons (**XPS**)
  - Synchroton radiation ($h\nu$=5-5000 eV)

- Exploiting dichroism (dependance of the process on the polarization), the spin of the electrons can be differentiated.



Spectra

- BE is a function of the chemical environment of atoms (**ESCA**=Electron Spectroscopy for Chemical Analysis)



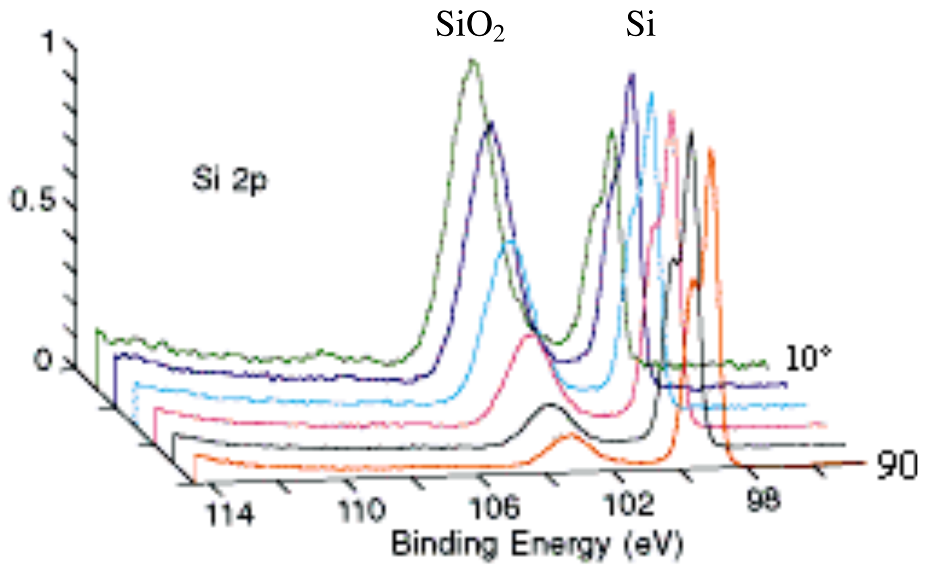
Spectra

- Detection as a function of the angle of emission

  ARPES (AR=angle resolved): **ARUPS**, **ARXPS**

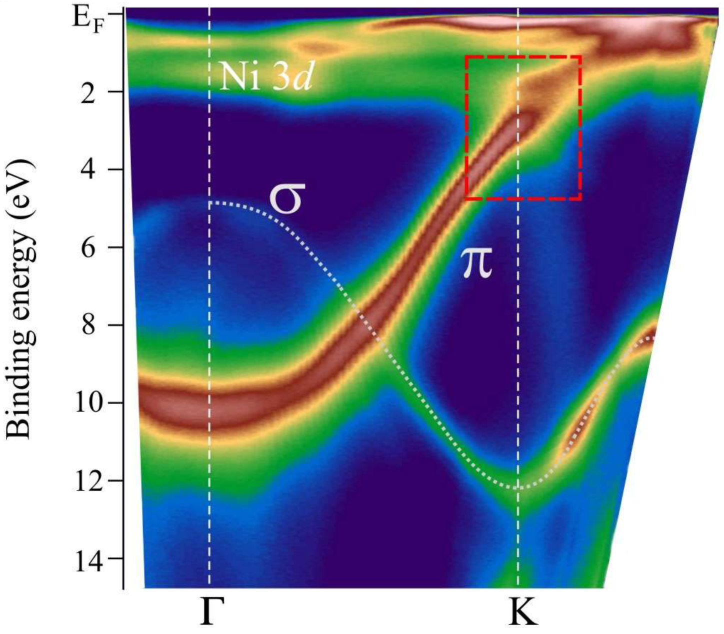
→ **depth profiling**

→ **band mapping**



Silicon wafer with a native oxide layer

[www.phi.com]

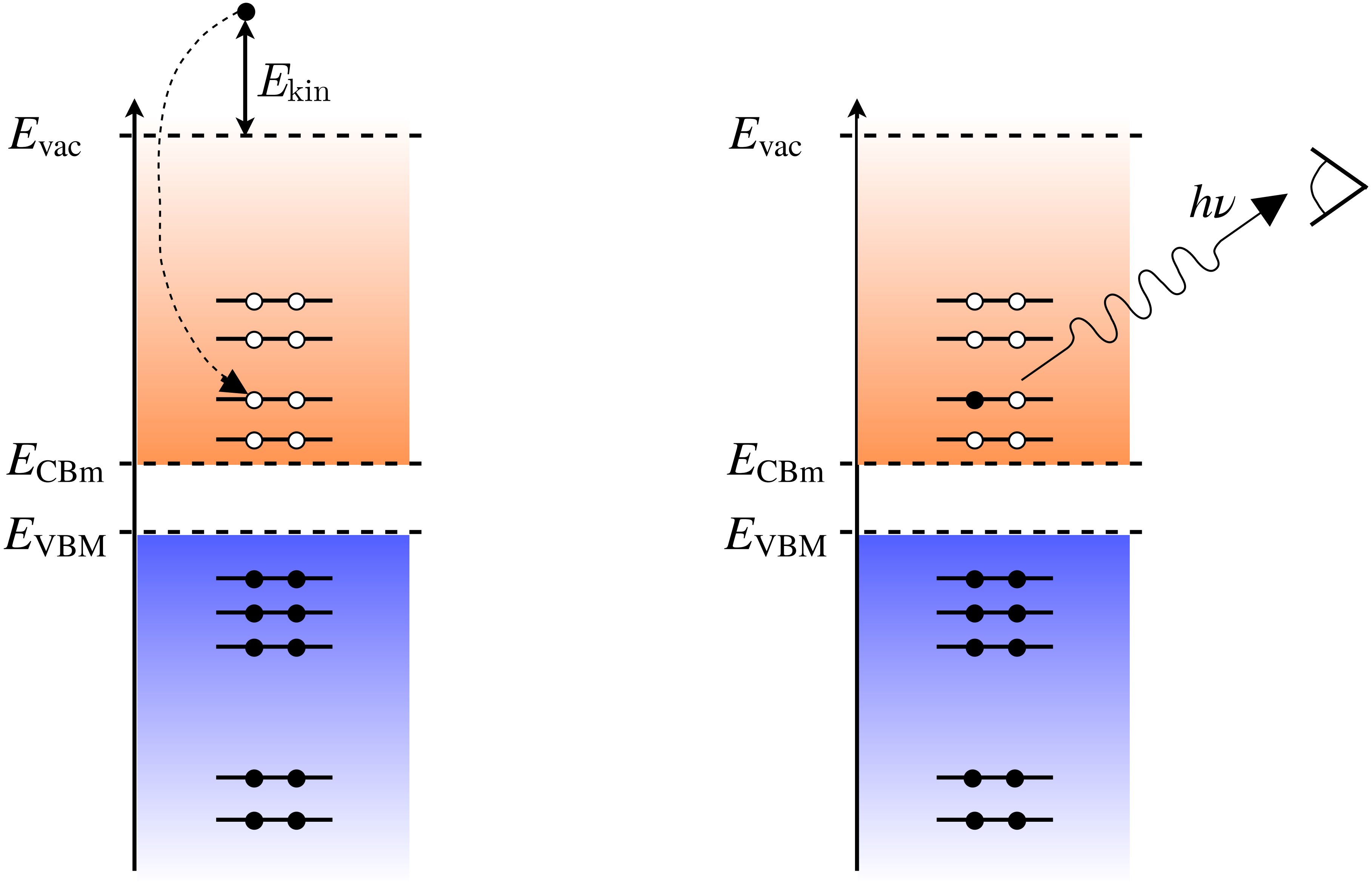


Graphene on Ni(111)

[New J. Phys. **11**, 070350 (2009).]

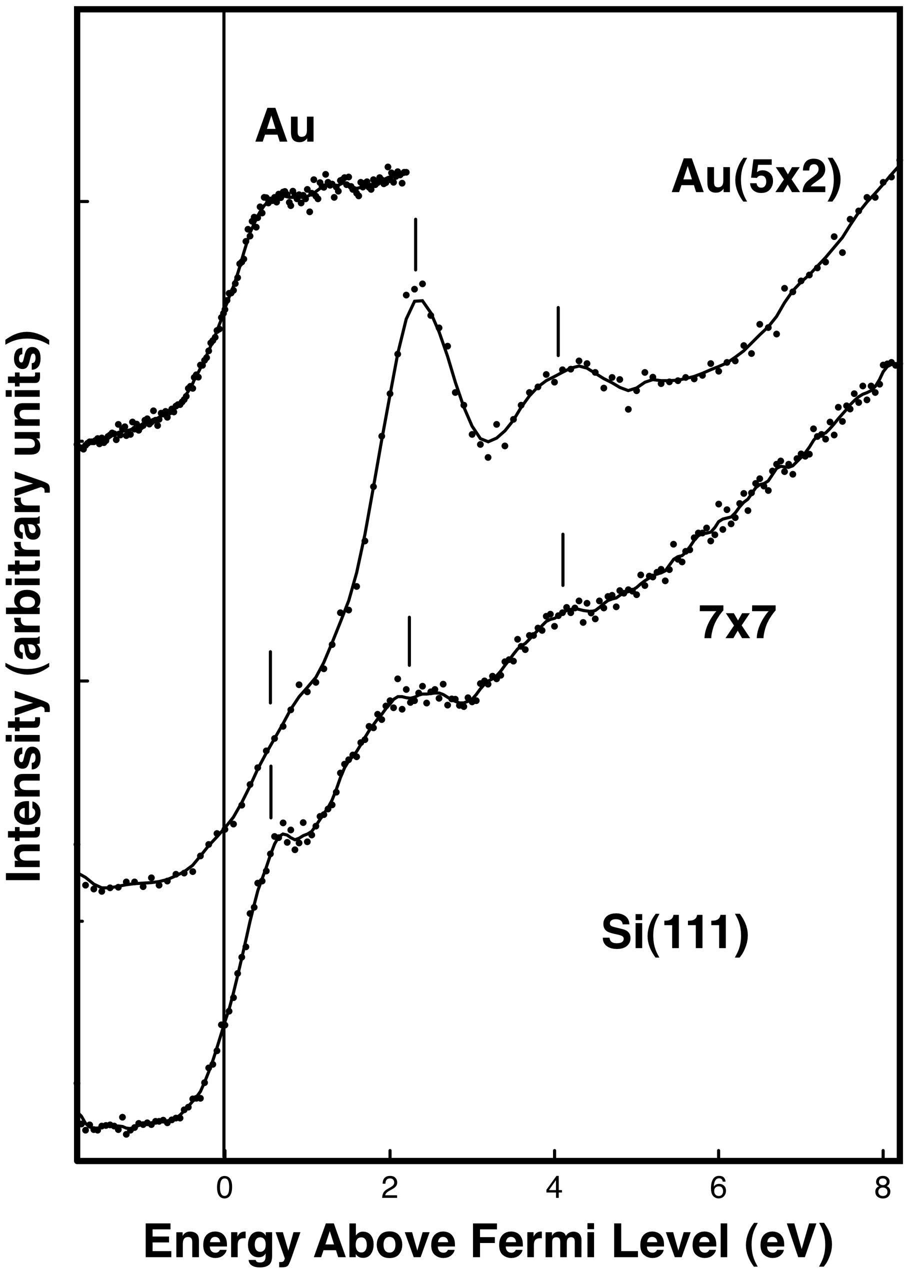
Inverse PhotoEmission Spectroscopy (IPES) or Bremsstrahlung Isochromat Spectroscopy (BIS)

Process



$N \rightarrow N+1$

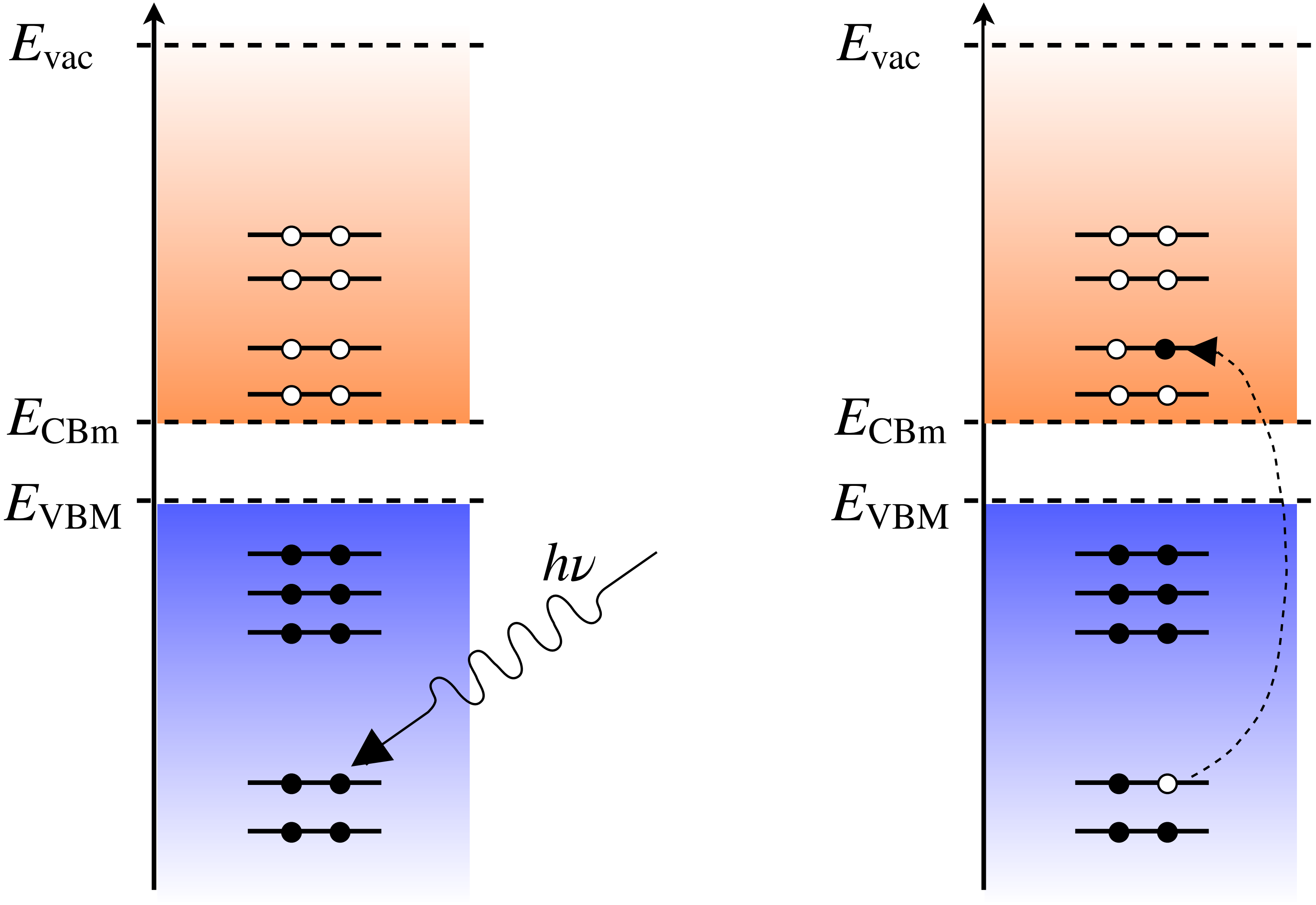
Spectra



$BE = E_{\mathrm{kin}} - h\nu$

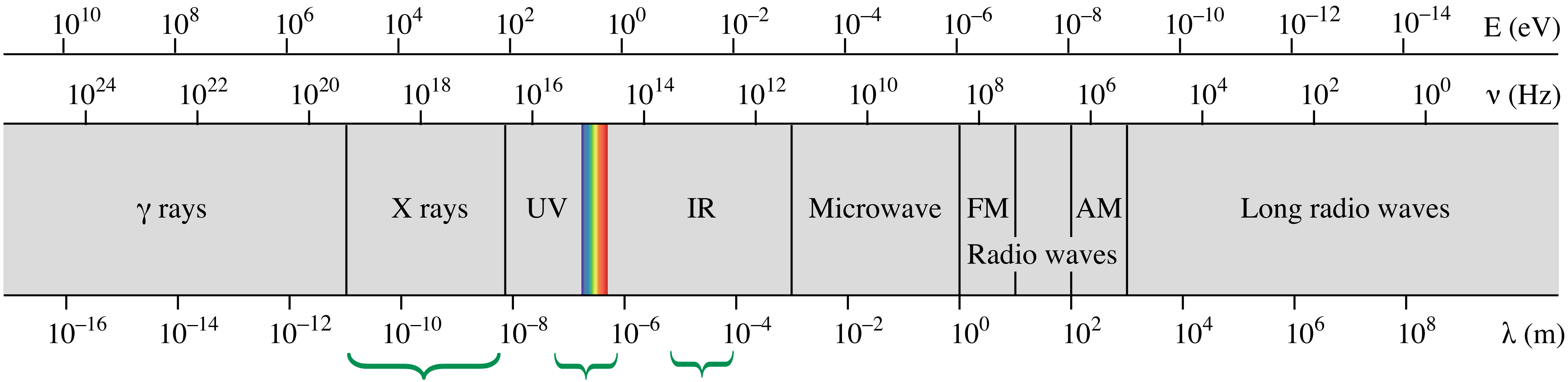
Absorption Spectroscopy

Process



$N \rightarrow N$

Exciting radiations



IR (absorption) spectroscopy:

molecular vibrations, phonons

Optical (absorption) spectroscopy:

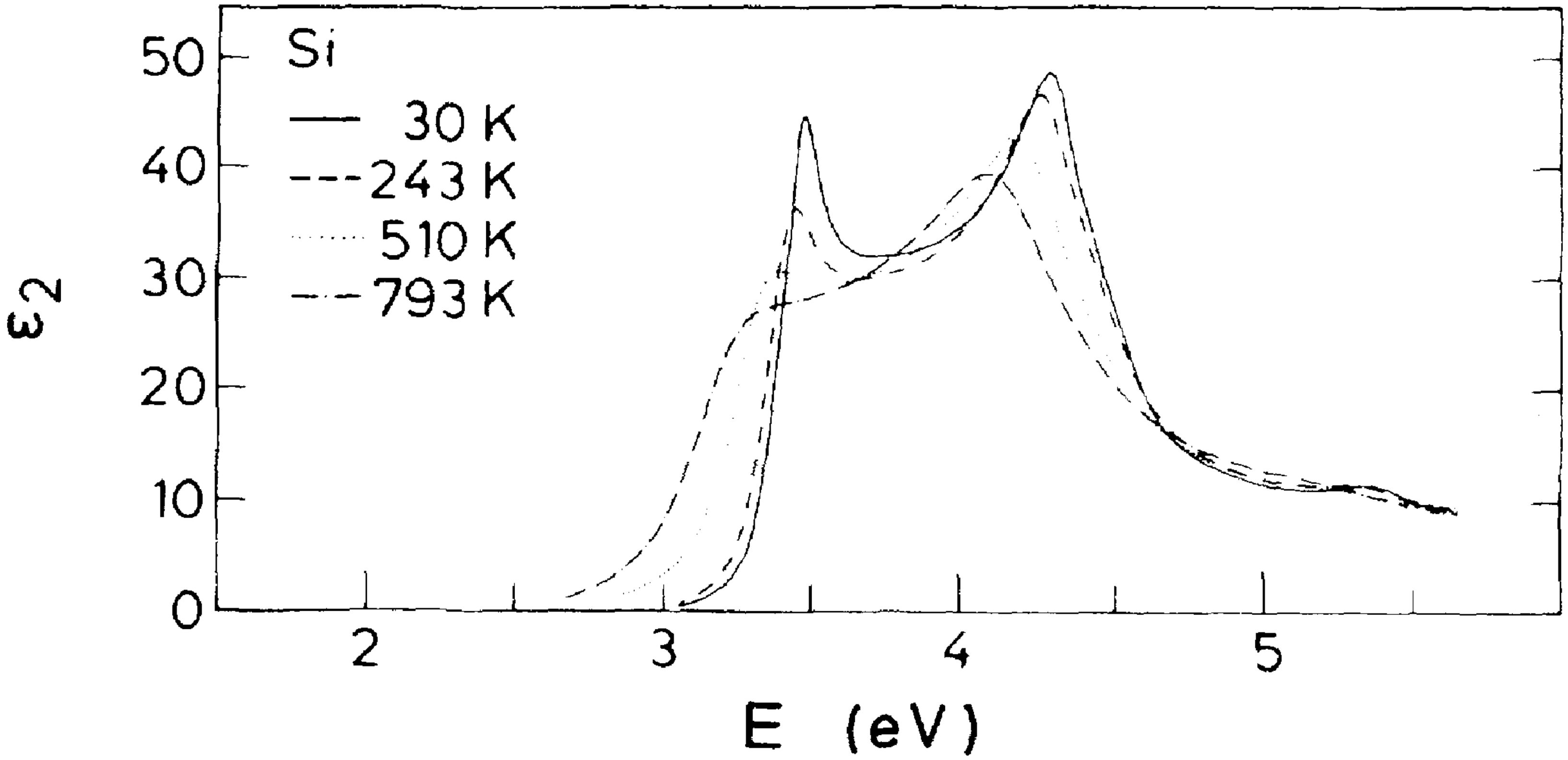
interband and intraband transitions, plasmons

X-Ray absorption spectroscopy:

interband and intraband transitions, plasmons

Spectra

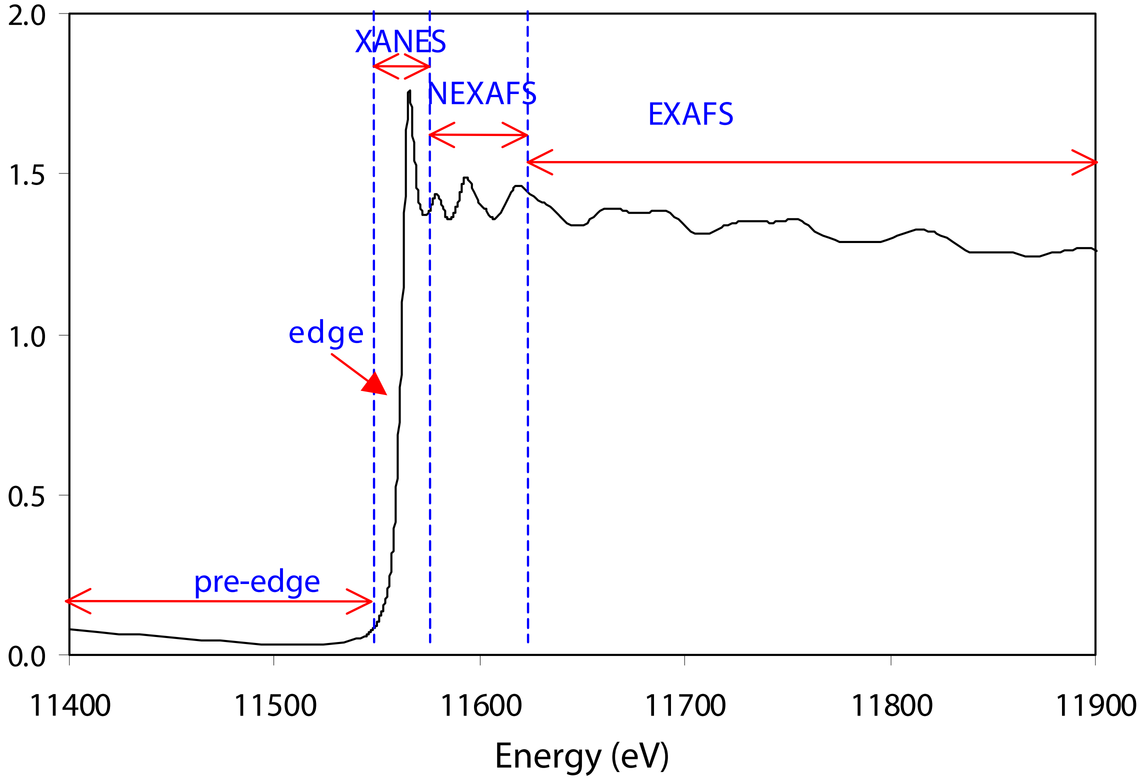
- Exciting radiation:
  - Visible light ($h\nu$=2-3 eV) for valence electrons (Optical absorption)



[Lautenschlager *et al.*, Phys. Rev. B **36**, 4830 (1987)]

Spectra

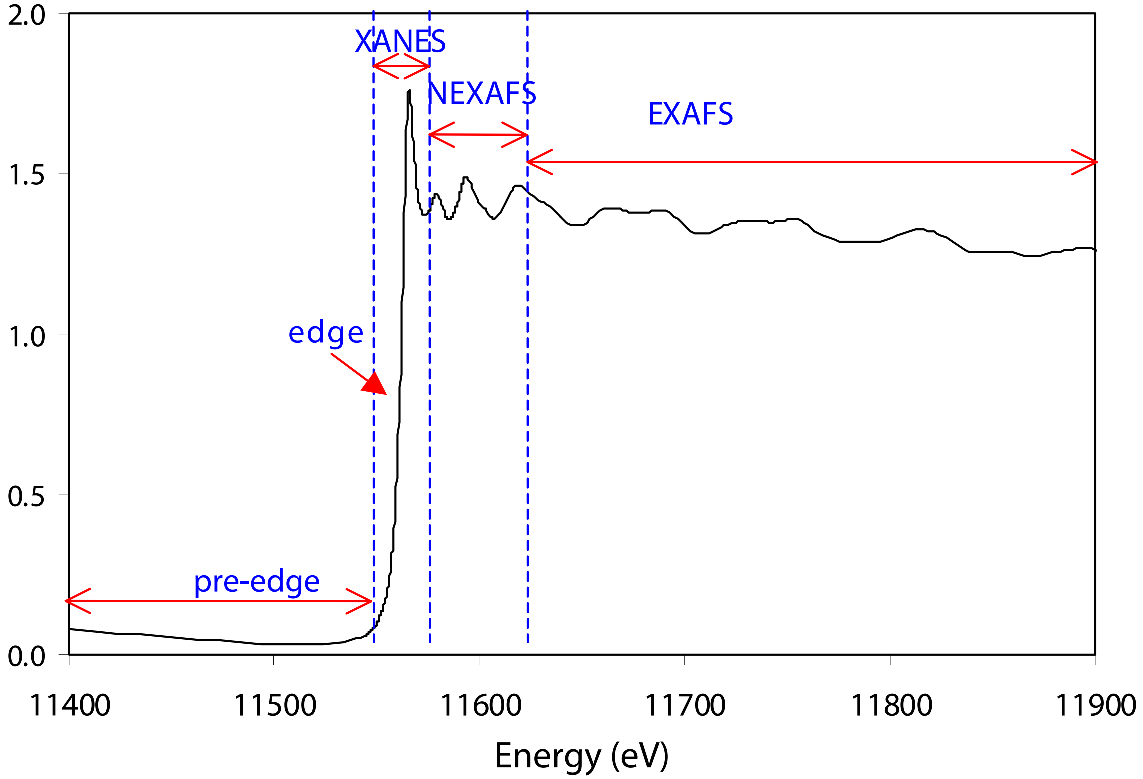
- Exciting radiation:
  - X-rays ($h\nu$=0.12-120 keV) for core electrons (XAS)



The **edge** is energy necessary to excite a core electron to a continuum state

Spectra

- Exciting radiation:
  - X-rays ($h\nu$=200-2000 eV) for core electrons (XAS)

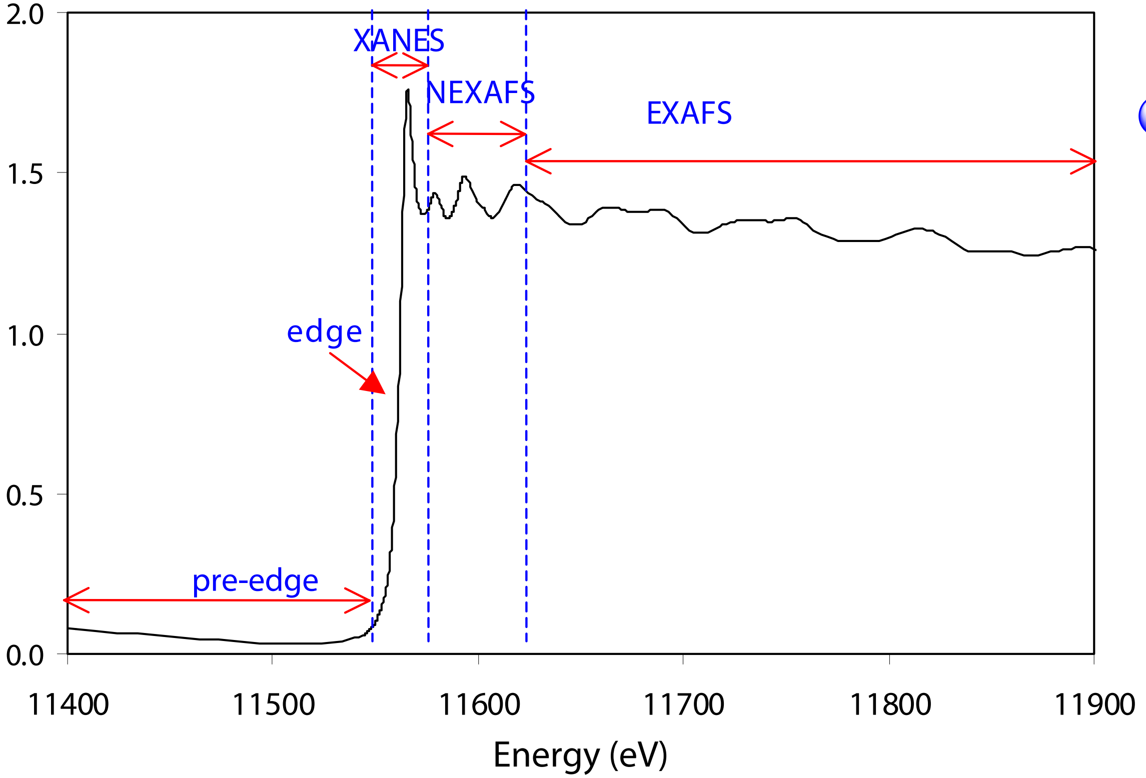


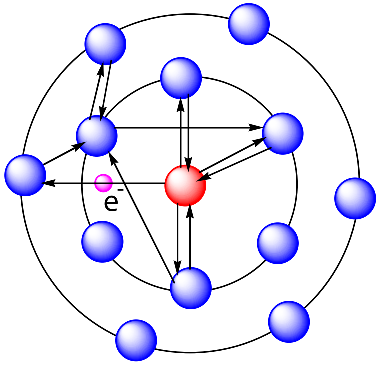
XANES=X-ray Absorption Near-Edge Spectroscopy

($E = E_{\text{edge}} \pm 10$ eV)

Spectra

- Exciting radiation:
  - X-rays ($h\nu$=200-2000 eV) for core electrons (XAS)





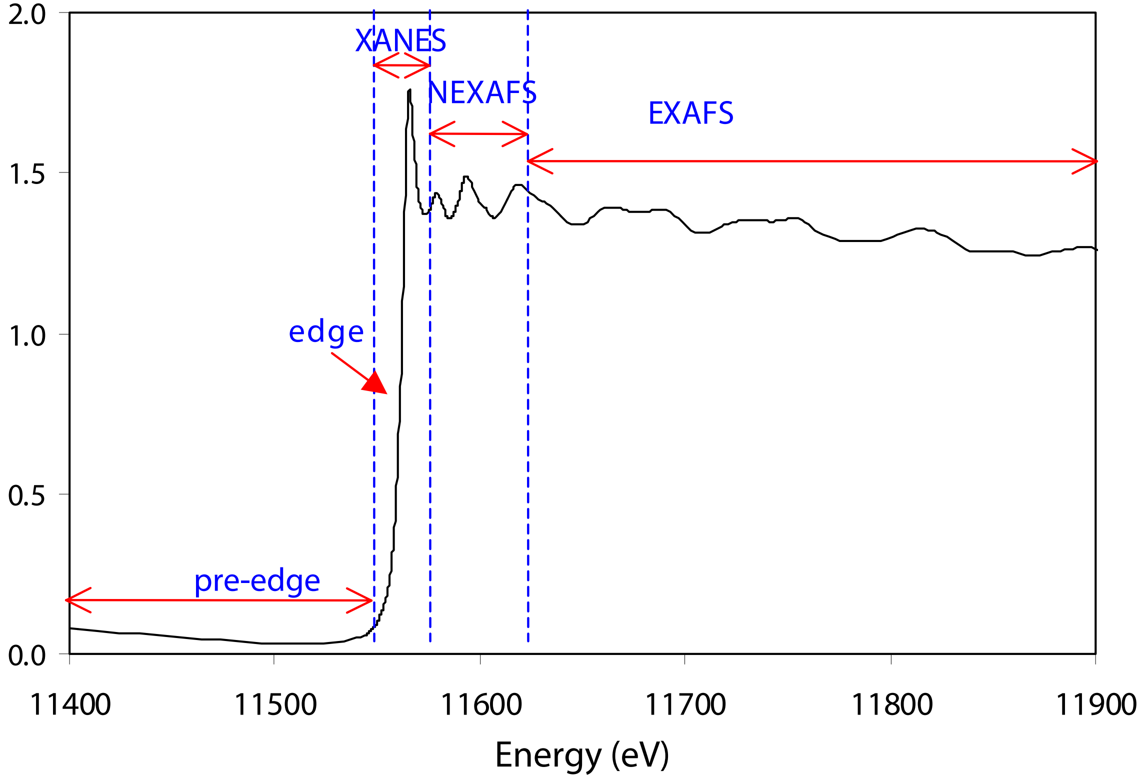
Multiple scattering

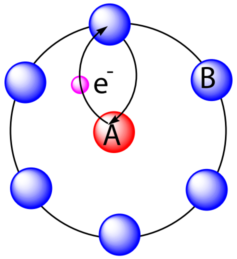
NEXAFS=Near-Edge X-ray Absorption Fine Structure

($E = E_{\text{edge}}$ + 10-50 eV)

Spectra

- Exciting radiation:
  - X-rays ($h\nu$=200-2000 eV) for core electrons (XAS)





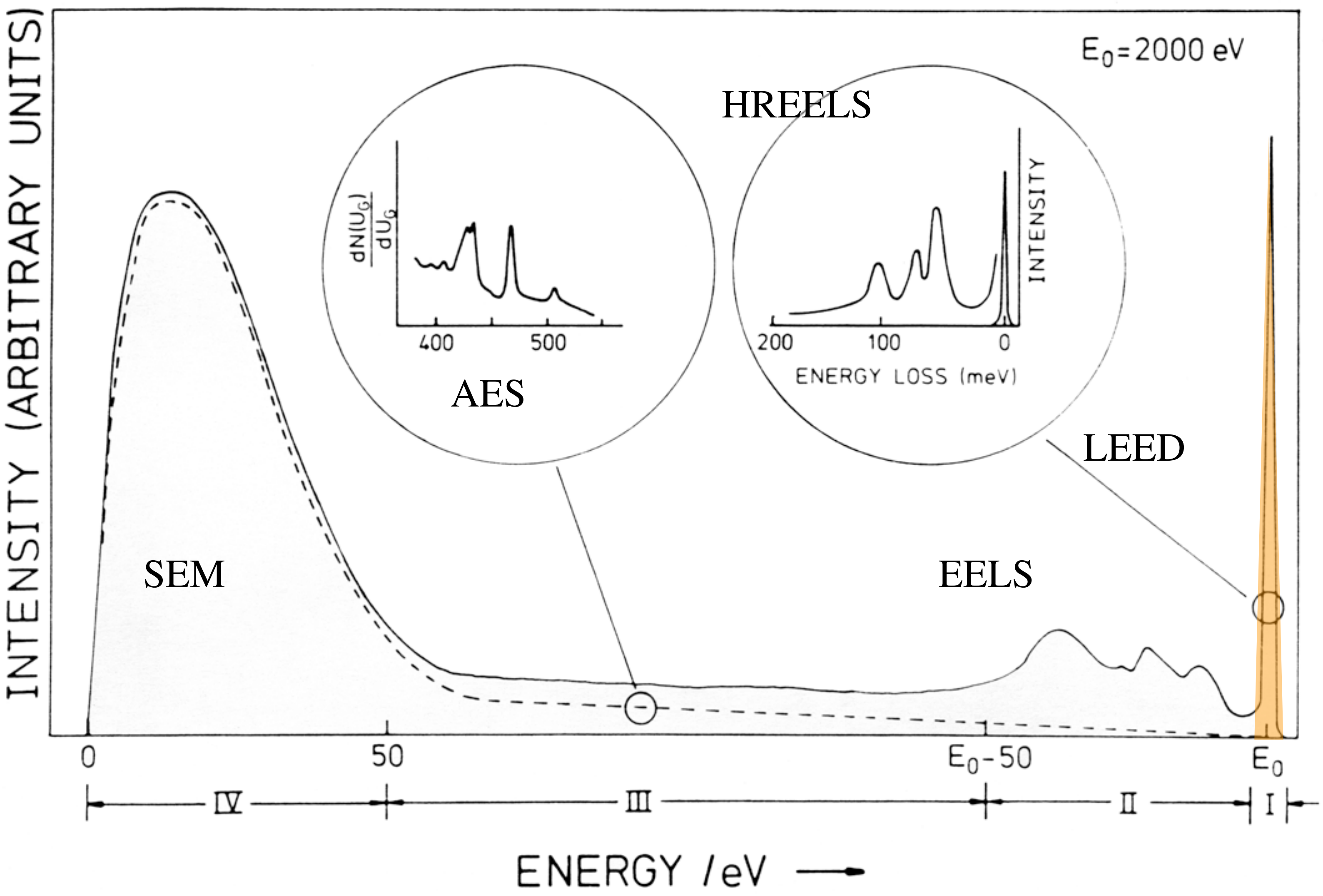
Single scattering

EXAFS=Extended X-ray Absorption Fine Structure

$$(E = E_{\text{edge}} + 50\text{-}1000 \text{ eV})$$

Electron Energy Loss Spectroscopy (EELS)

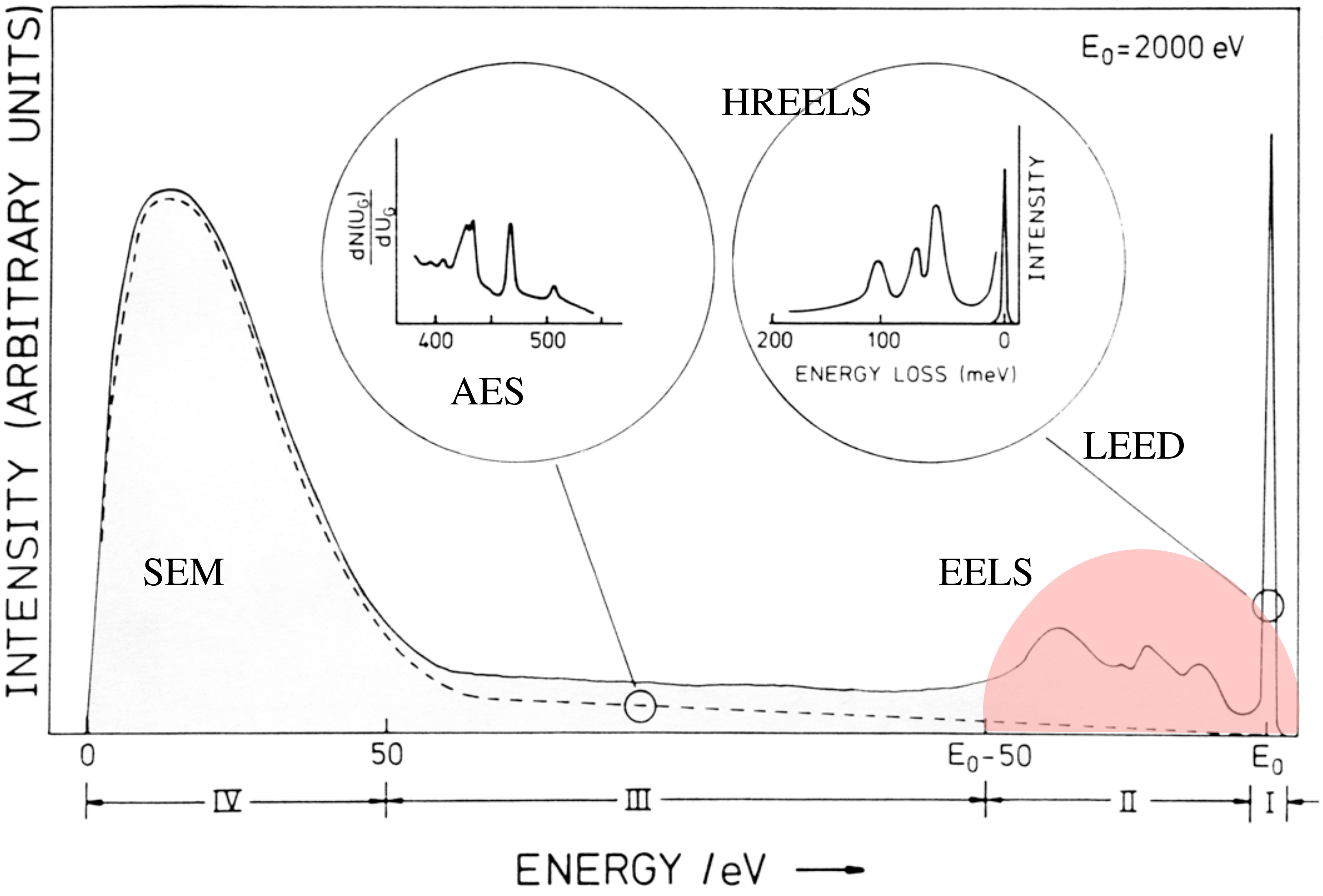
Electron scattering



LEED=Low Energy Electron Diffraction

(elastic scattering E=E_0)

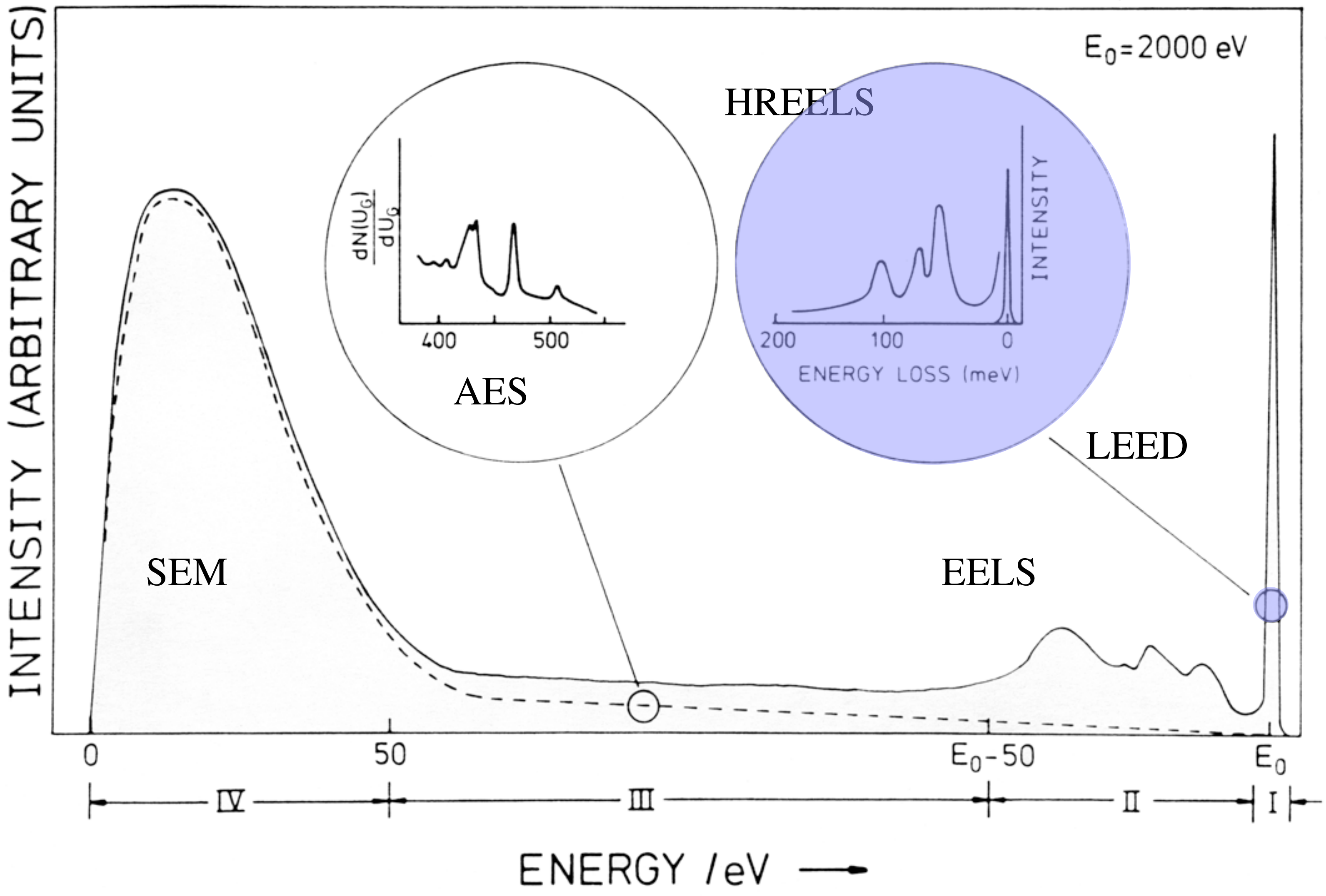
Electron scattering



EELS=Electron Energy Loss Spectroscopy

(inelastic scattering due to plasmons E_0 - 50 eV $\leq E \leq E_0$)

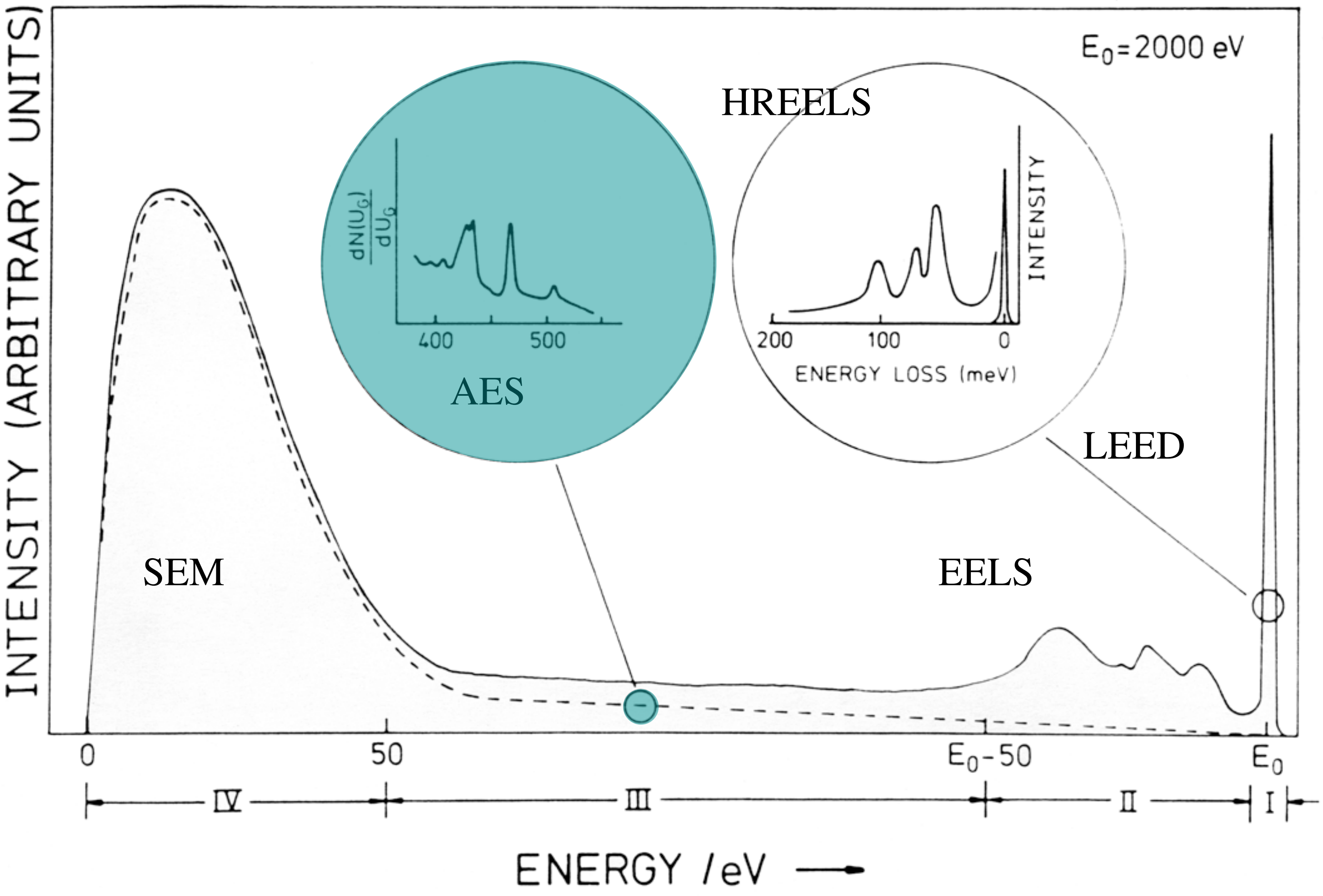
Electron scattering



HREELS=High Resolution Electron Energy Loss Spectroscopy

(inelastic scattering due to phonons E_0 - 0.1 eV $\leq E \leq E_0$)

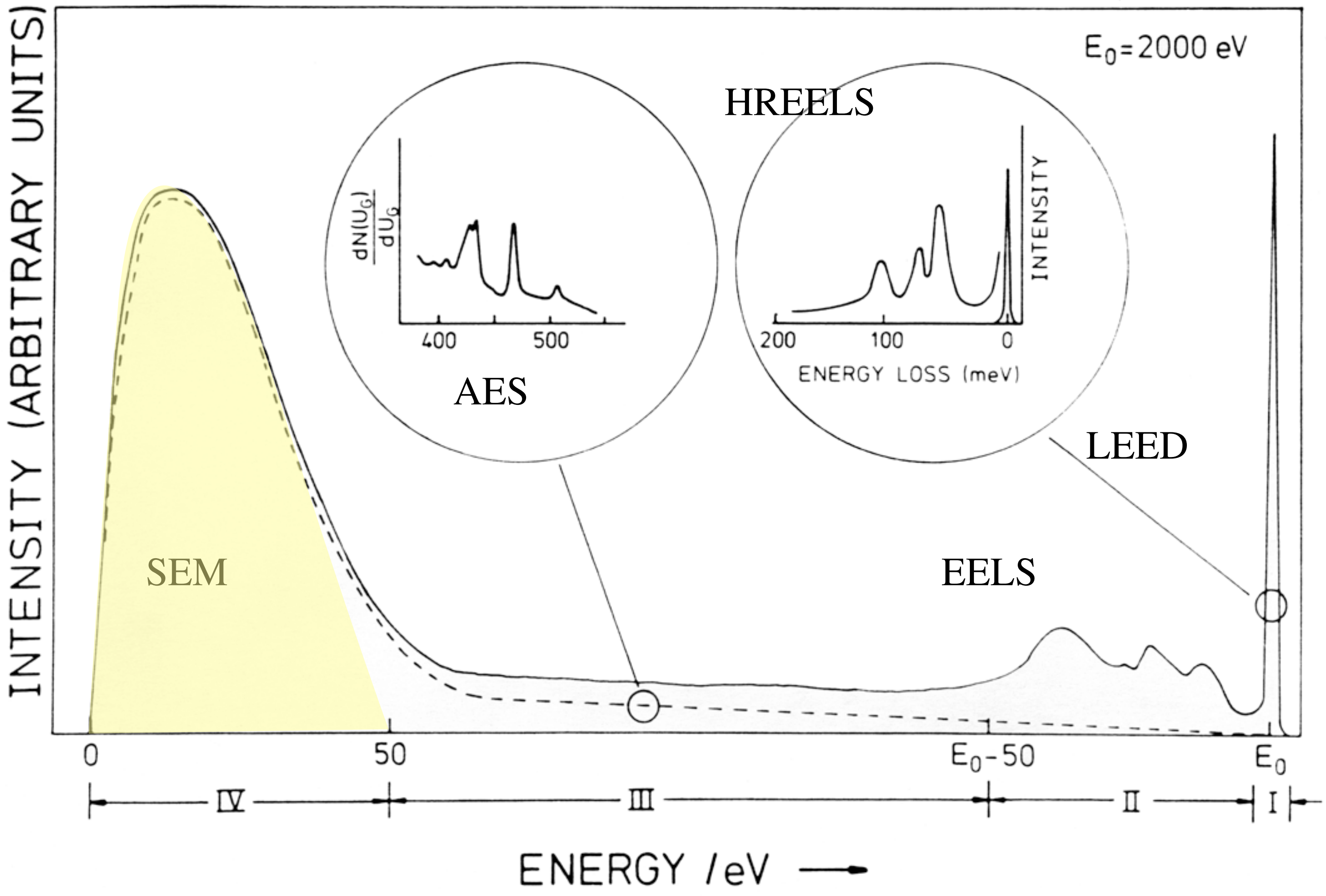
Electron scattering



AES=Auger Electron Spectroscopy

(50 eV $\leq E \leq E_0$ - 50 eV)

Electron scattering



SEM=Scanning Electron Microscopy
(true secondary electrons originating
from cascade processes $0 \leq E \leq 50$ eV)

Spectra

- 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

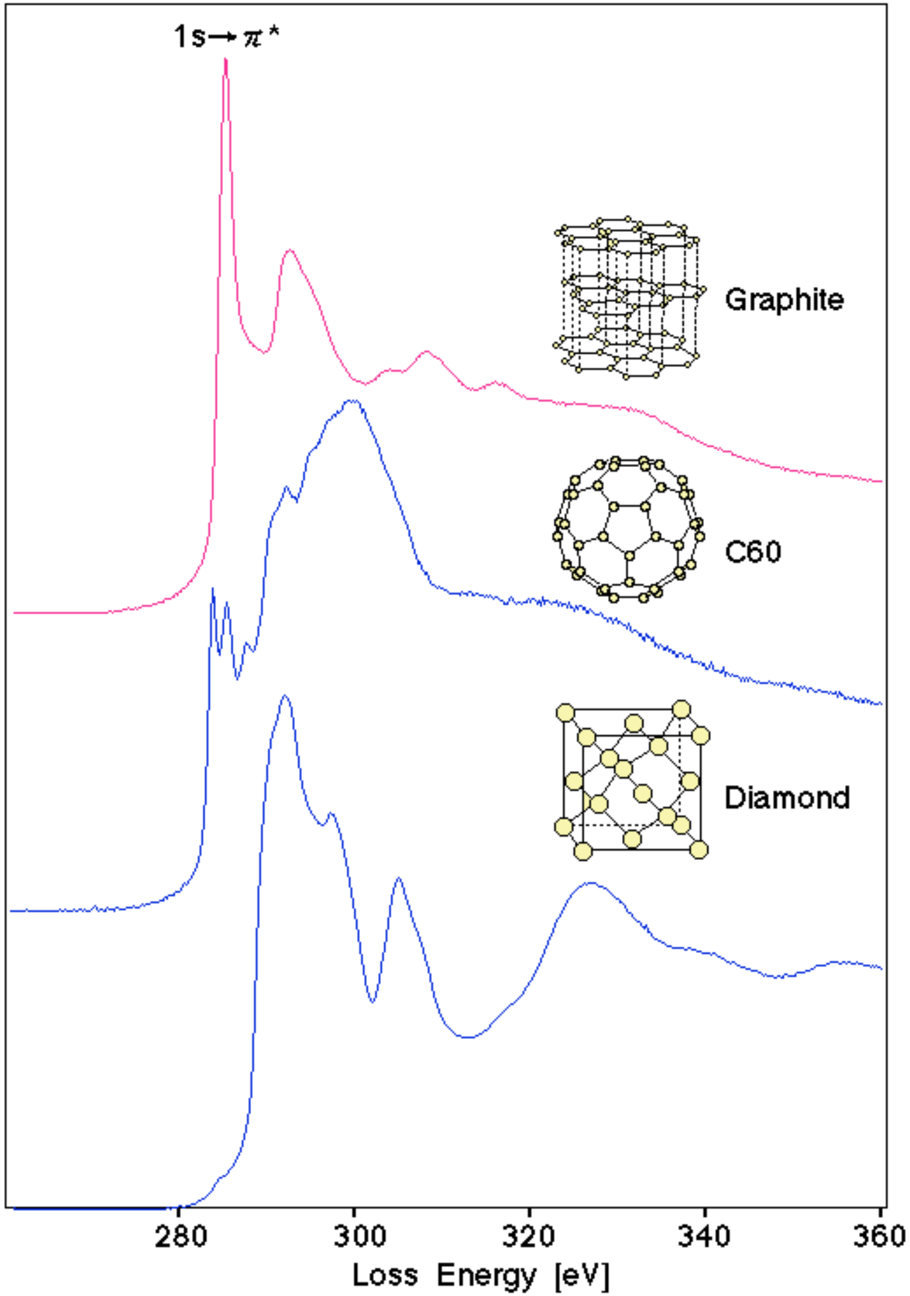
$$\frac{d\sigma}{d\Omega} = \frac{\text{Scattered flux / Unit of solid angle}}{\text{Incident flux / Unit of surface}}$$

- The **double differential cross section** $\frac{d^2\sigma}{d\Omega\,dE}$ is the differential cross section within a unit energy range.

- In EELS experiments, the double differential cross section is proportional to the loss function:

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

Spectra



Inelastic X-ray Scattering (IXS) Spectroscopy

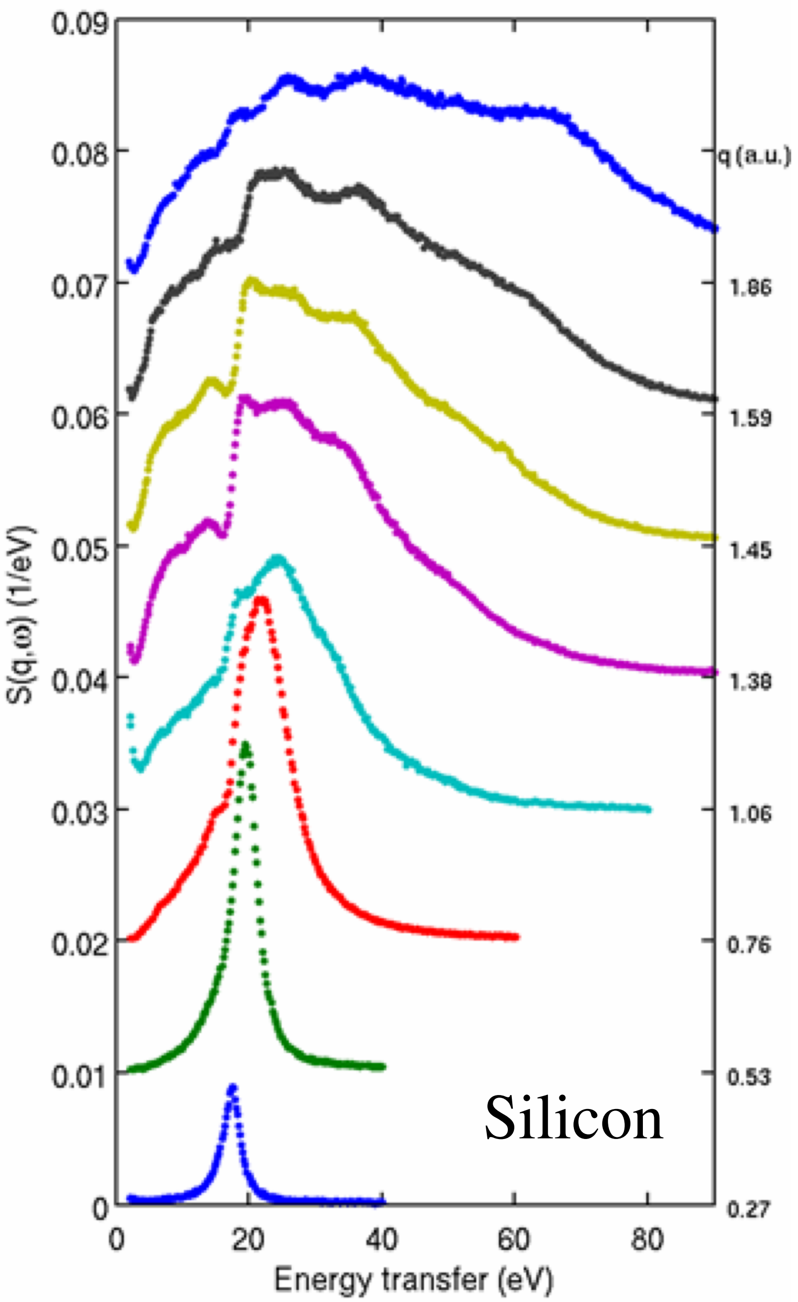
Spectra

- In IXS experiments, the double differential cross section is proportional to the loss function

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

- IXS vs. EELS:
  - IXS can probe large momentum transfer: $\epsilon = \epsilon(\mathbf{q})$ for $\mathbf{q} \neq 0$
  - IXS is more sensitive to bulk
  - EELS has better energy and spatial resolution

Spectra



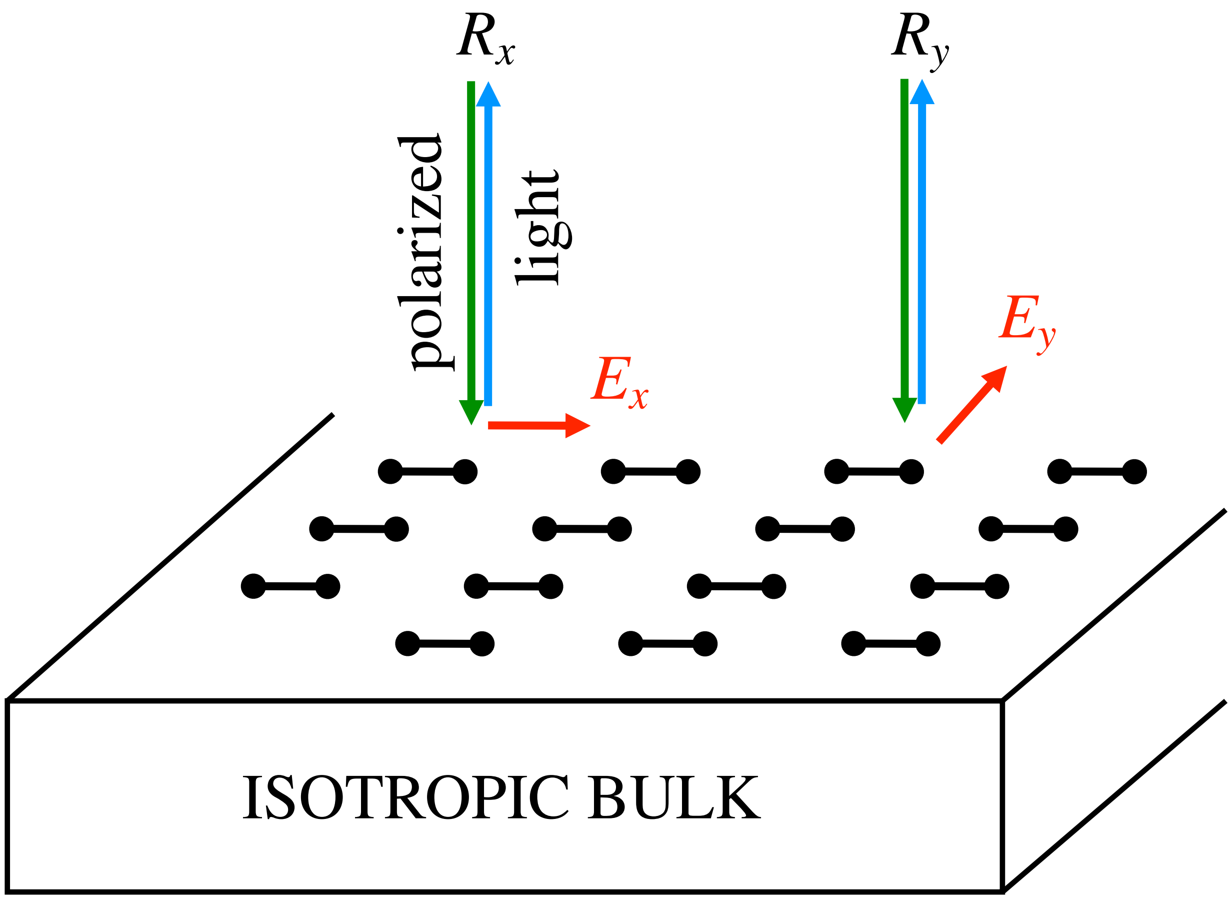
$$\frac{d^2\sigma}{d\Omega\, d\omega} \propto S(\mathbf{q},\omega)$$

$$\propto -\Im\left\{\epsilon^{-1}(\mathbf{q},\omega)\right\}$$

Reflectance Anisotropy Spectroscopy (RAS) or Reflectance Difference Spectroscopy (RDS)

Process

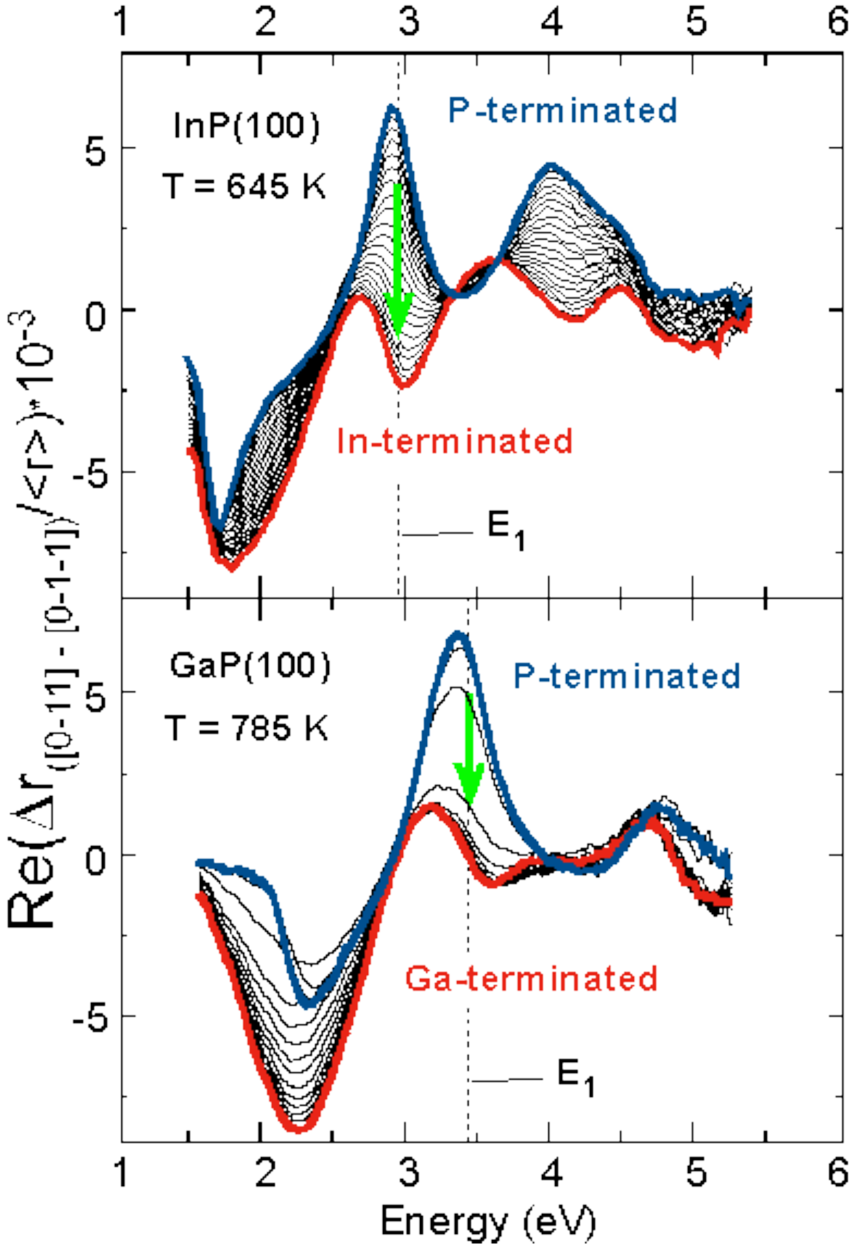
- measure the spectral dependence of $\dfrac{\Delta R}{R} = \dfrac{R_x - R_y}{R_x + R_y}$

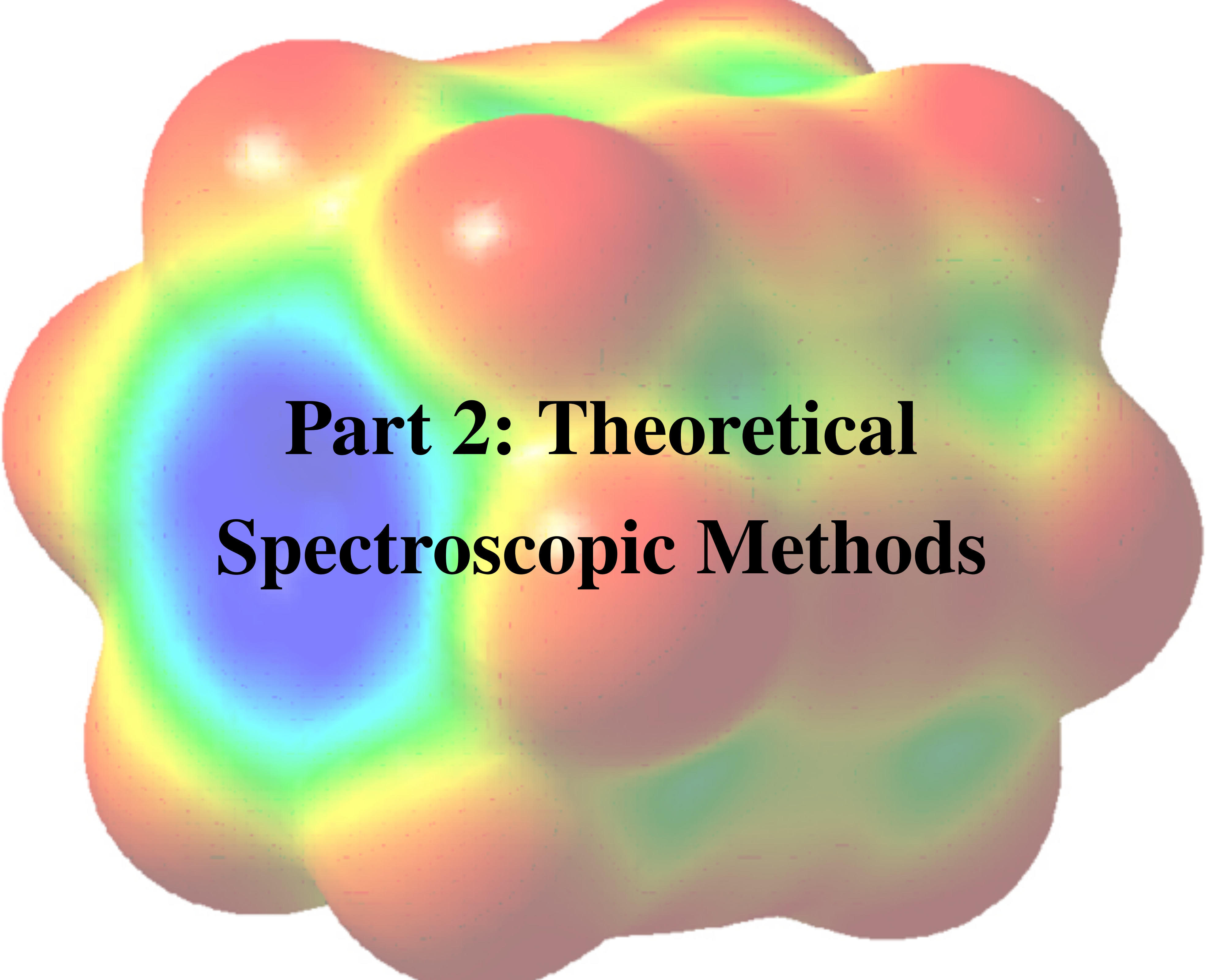


$R_{x,y}$ are the reflectivities

$$R = \left|\frac{\tilde{n} - 1}{\tilde{n} + 1}\right|^2 = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}$$

Spectra


InP(100)
T = 645 K
P-terminated
In-terminated
E_1
GaP(100)
T = 785 K
P-terminated
Ga-terminated
E_1
$\mathrm{Re}(\Delta r_{([0\text{-}11]-[0\text{-}1\text{-}1])}/\langle r\rangle)\cdot 10^{-3}$
Energy (eV)
1
2
3
4
5
6
5
0
-5



Part 2: Theoretical Spectroscopic Methods

Introduction

Born-Oppenheimer approximation

- Let us consider a crystalline solid with N electrons et N_N nuclei, the system will be completely quantum-mechanically described by its **wavefunction** Ψ:

  $$\Psi = \Psi\left(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_{N_N}\right)$$

  where $\mathbf{r}_i$ ($i = 1, ..., N_e$) and $\mathbf{R}_\alpha$ ($\alpha = 1, ..., N_N$) are the coordinates of the electrons and of the nuclei, respectively.

- As the nuclei are much heavier (hence slower) than the electrons ($M_\alpha >> 1$), their respective dynamics can be decoupled. Hence, the wavefunction of the system can be broken into its electronic and nuclear components:

  $$\Psi = \psi\left(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\right) \times \psi^N\left(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_{N_N}\right)$$

Electronic *N*-body problem

- In practice, it is thus assumed that the nuclei positions can be considered as fixed when studying the electrons dynamics.

- In the end, we have to consider a system of N interacting electrons in an external potential $V_{\text{ext}}(\mathbf{r})$, such as the one generated by the nuclei.

- It is completely described by its **wavefunction**:

$$\psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$$

which is obtained by solving the **Schrödinger equation**:

$$\hat{H}\psi = \sum_n \left(-\frac{\nabla_n^2}{2} + V_{\text{ext}}(\mathbf{r}_n) + \sum_{m>n} \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \right) \psi = E\psi$$

$$\hat{T}_e = \sum_n -\frac{\nabla_n^2}{2} \qquad \hat{V}_{ee} = \sum_n \sum_{m>n} \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|}$$

Variational Quantum Monte Carlo

- Basically, it is impossible to solve this Schrödinger equation for more than two electrons analytically.
- A first class of numerical methods relies on the variational principle for the ground-state energy of the electronic system:

$$E = \frac{\langle\psi|\,\hat{H}\,|\psi\rangle}{\langle\psi\,|\,\psi\rangle}$$

- Namely, for any arbitrary function ϕ, called trial-wavefunction, its expectation value E_ϕ , which is defined as:

$$E_\phi = \frac{\langle\phi|\,\hat{H}\,|\phi\rangle}{\langle\phi\,|\,\phi\rangle}$$

is such that $E_\phi \geq E$ and it reaches its minimum when:

$$\frac{\delta E_\phi}{\delta\phi} = 0$$

Variational Quantum Monte Carlo

- This variational principle can be exploited to approach the ground-state energy as much as possible.

- A trial-wavefunction $\phi(a)$ depending on one or more parameters is chosen. The different many-dimensional integrals are evaluated numerically (Monte Carlo methods) so as to obtain:

$$E(a) = \frac{\langle \phi(a) | \hat{H} | \phi(a) \rangle}{\langle \phi(a) \mid \phi(a) \rangle}$$

- The minimum is then located by varying the parameter(s):

$$\frac{\partial E(a)}{\partial a} = 0$$

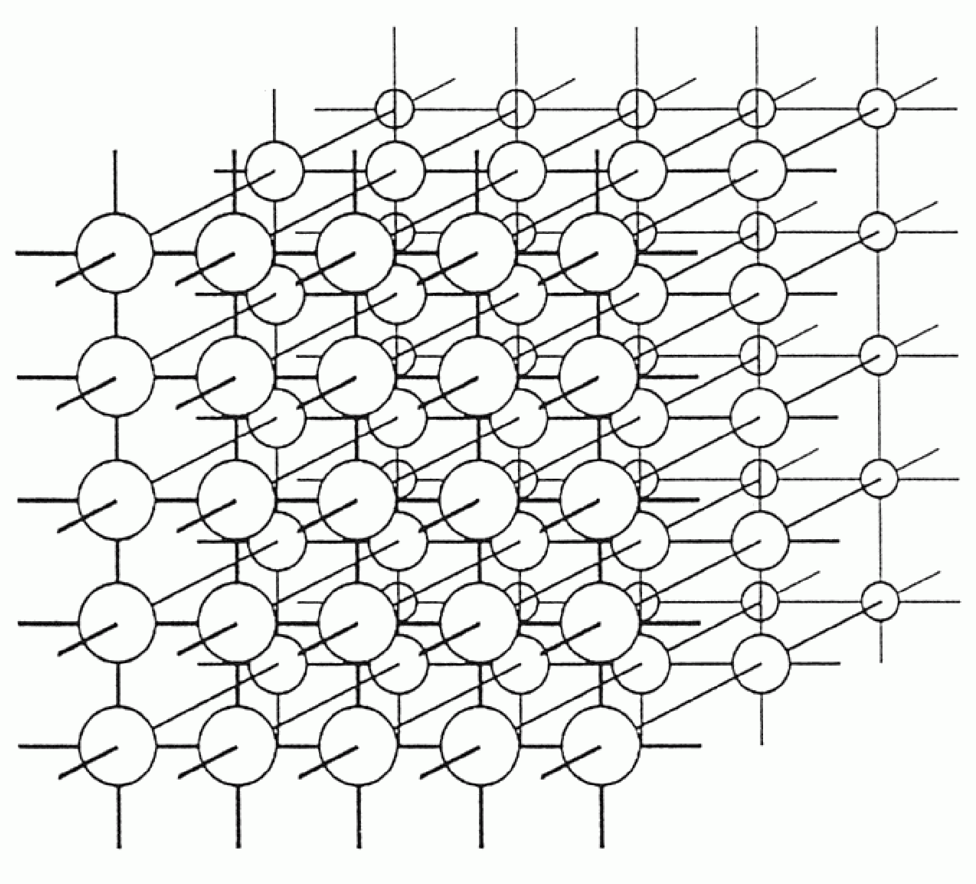
- The choice of the trial-wavefunction is obviously very critical.

Variational Quantum Monte Carlo

- Moreover, the *N*-electrons wavefunction soon becomes an object very difficult to handle in a computer.

- For instance, the wavefunction of the oxygen atom (with 8 electrons) defined on a 10×10×10 real space-grid is an object which consists of 10^{24} real numbers.

  Note: in classical mechanics, the very same system is fully described by 48 real numbers (the positions and the velocities of the 8 electrons).



One-particle approximations

Independent electron approximation

- In fact, electron-electron interactions are the real problem.

$$\hat{H}\psi = \sum_n \left(-\frac{\nabla_n^2}{2} + V_{\text{ext}}(\mathbf{r}_n) + \sum_{m>n} \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \right) \psi = E\psi$$

- Assuming that these are negligible with respect to the external potential (the electron-ion interactions), the problem simplifies to:

$$\hat{H}\psi = \sum_n \left(-\frac{\nabla_n^2}{2} + V_{\text{ext}}(\mathbf{r}_n) \right) \psi = E\psi$$

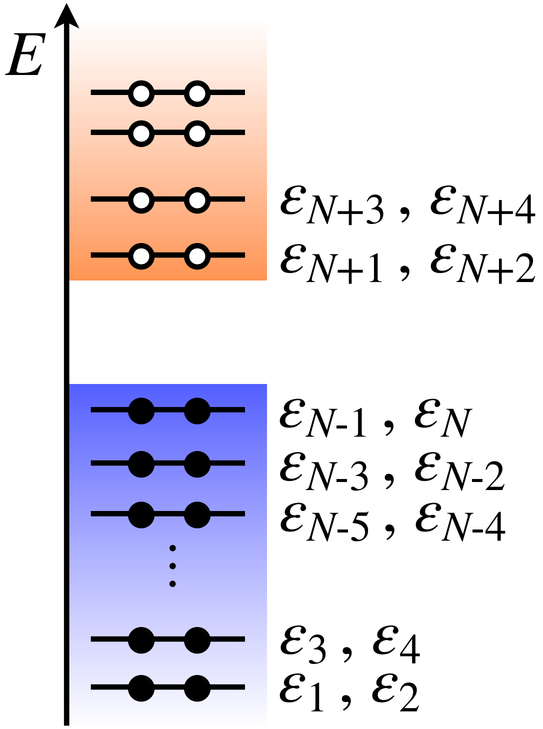
Separating the variables

- The form of the Hamiltonian calls for a separation of variables. The *N*-electrons wavefunction can be replaced by the product of *N* 1-electron wavefunctions:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)$$

which are the solutions of a 1-electron Schrödinger equation:

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



- The total energy is simply given by:

$$E = \sum_n \varepsilon_n$$

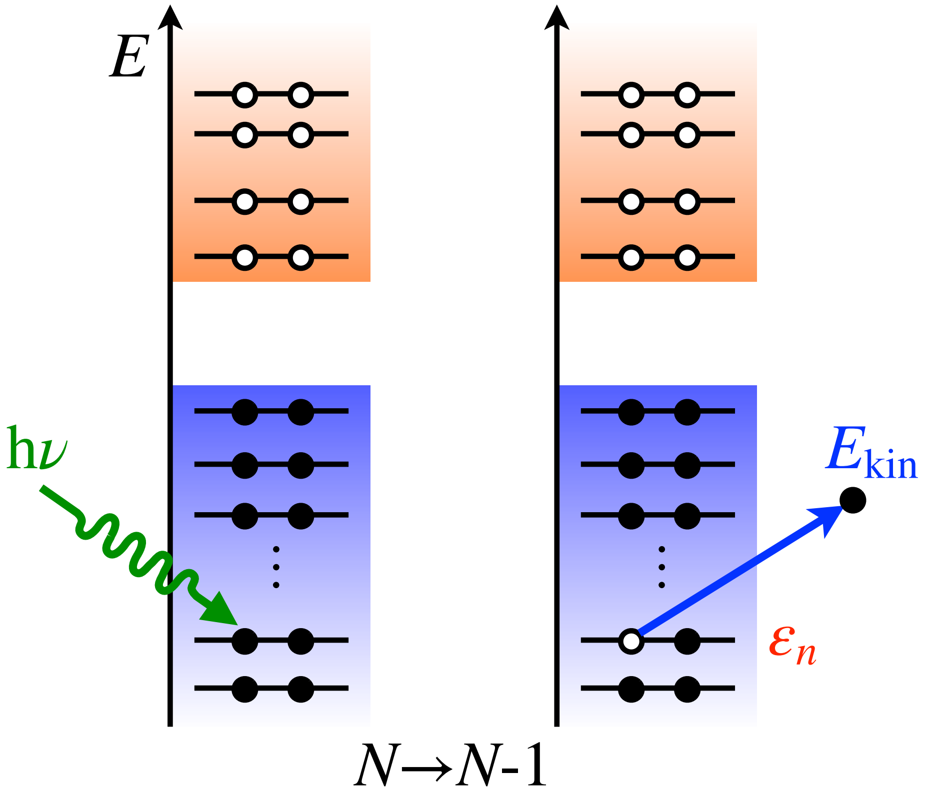
$$E_{N,0} = \varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_{N\text{-}1} + \varepsilon_N$$

Connection to photoemission

- By solving the 1-electron Schrödinger equation:

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

we obtain the band structure ε_n which can be determined experimentally by photoemission or inverse photoemission (valence or conduction bands).



Energy conservation:

before $\rightarrow h\nu + E_{N,0}$

after $\rightarrow E_{\text{kin}} + E_{N\text{-}1,n}$

The binding energy is:

$$E_{\text{kin}} - h\nu = E_{N,0} - E_{N\text{-}1,n} = \varepsilon_n$$

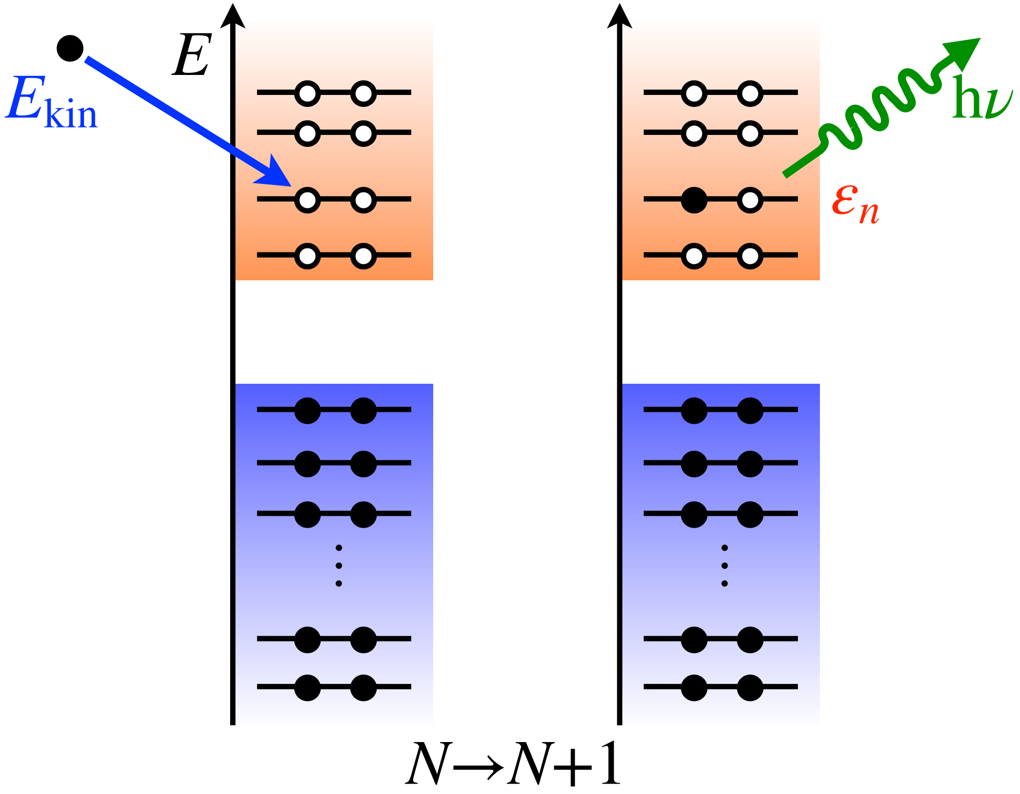
$$E_{N\text{-}1,n} = \varepsilon_1 + \ldots + \cancel{\varepsilon_n} + \ldots + \varepsilon_N$$

Connection to inverse photoemission

- By solving the 1-electron Schrödinger equation:

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

we obtain the band structure ε_n which can be determined experimentally by photoemission or inverse photoemission (valence or conduction bands).



Energy conservation:

before → $E_{\text{kin}} + E_{N,0}$

after → $h\nu + E_{N+1,n}$

The binding energy is:

$$E_{\text{kin}} - h\nu = E_{N+1,n} - E_{N,0} = \varepsilon_n$$

$$E_{N+1,n} = \varepsilon_1 + \ldots + \varepsilon_N + \varepsilon_n$$

Wavefunction methods

Hartree approximation

- The **Hartree approximation** assumes that the N-electrons wavefunction can be replaced by the product of N 1-electron wavefunctions even when the electron-electron interactions are not neglected.

- Hence, we need to find the 1-electron wavefunctions ϕ_i that minimize the total energy:

$$E = \left\langle \psi | \hat{H} | \psi \right\rangle$$

under the normalization constraint:

$$\langle \phi_n | \phi_n \rangle = 1$$

- Introducing Lagrange multipliers, we simply need to minimize a functional of the 1-electron wavefunctions:

$$\min_{\{\phi_n\}} F\left[\{\phi_n\}\right] = \left\langle \psi | \hat{H} | \psi \right\rangle - \sum_n \varepsilon_n^{\mathrm{H}} \langle \phi_n | \phi_n \rangle$$

Hartree approximation

- It can be shown that the 1-electron wavefunctions are the solutions of the following 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \sum_{m\neq n} \hat{J}_m\right] \phi_n(\mathbf{r}) = \varepsilon_n^{\mathrm{H}} \phi_n(\mathbf{r})$$

where $\hat{J}_m$ is the **Coulomb operator** defined by:

$$\hat{J}_m \phi_n(\mathbf{r}) = \left\{ \int \phi_m^*(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_m(\mathbf{r}') d\mathbf{r}' \right\} \phi_n(\mathbf{r})$$

Hartree approximation

- The electronic eigenenergies can be written as:

$$\varepsilon_n^{\mathrm{H}} = \langle \phi_n | -\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) \, | \phi_n \rangle + \sum_{m \neq n} J_{nm}$$

where $J_{nm} = \int \phi_n^*(\mathbf{r})\phi_m^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_n(\mathbf{r})\phi_m(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$

- So that the total electronic energy writes:

$$\begin{aligned} E = \langle \psi | \hat{H} \, | \psi \rangle &= \sum_n \langle \phi_n | -\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) \, | \phi_n \rangle + \frac{1}{2}\sum_n \sum_{m \neq m} J_{nm} \\ &= \sum_n \varepsilon_n^{\mathrm{H}} - \frac{1}{2}\sum_n \sum_{m \neq n} J_{nm} \end{aligned}$$

Hartree approximation

- The 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \sum_{m\neq n} \hat{J}_m\right] \phi_n(\mathbf{r}) = \varepsilon_n^{\text{H}} \phi_n(\mathbf{r})$$

where $\hat{J}_m \phi_n(\mathbf{r}) = \left\{ \int \phi_m^*(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_m(\mathbf{r}') d\mathbf{r}' \right\} \phi_n(\mathbf{r})$

is almost identical (apart from the self-interaction) to:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r})\right] \phi_n(\mathbf{r}) = \varepsilon_n^{\text{H}} \phi_n(\mathbf{r})$$

with $V_{\text{H}}(\mathbf{r})$, the **Hartree potentiel**, defined by:

$$V_{\text{H}}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$

where $n(\mathbf{r}) = \sum_n |\phi_n(\mathbf{r})|^2$ is the electronic density.

Hartree approximation

- In this case, the total electronic energy is written as:

$$E = \sum_n \varepsilon_n^{\mathrm{H}} - E_{\mathrm{H}}$$

where E_{H} is the **Hartree energy**, defined by:

$$E_{\mathrm{H}} = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

Hartree approximation

- However, there is a new difficulty:
  - to obtain the Hartree potential $V_H(\mathbf{r})$, the electronic density $n(\mathbf{r})$ and hence all the wavefunctions $\phi_i(\mathbf{r})$ are needed
  - to obtain the wavefunctions $\phi_i(\mathbf{r})$, the Hartree potential $V_H(\mathbf{r})$ is required
- In practice, one starts from a trial electronic density and then iterates the equations until **self-consistency** is reached:

$$\begin{tikzcd}
n_0(\mathbf{r}) \arrow[r] & V_H(\mathbf{r}) \arrow[r] & \hat{H}(\mathbf{r}) \arrow[d, "\hat{H}(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})"] \\
 & n(\mathbf{r}) \arrow[u, "V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'"] & \phi_i(\mathbf{r}) \arrow[l, "n(\mathbf{r}) = \sum_{i=1}^{N_e} |\phi_i(\mathbf{r})|^2"']
\end{tikzcd}$$

Hartree-Fock approximation

- In order to take Pauli exclusion principle into account, the product of N 1-electron wavefunctions should be replaced by

  a **Slater determinant**:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{!N}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_2) \\ \vdots & \vdots & & \vdots \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

  That is the **Hartree-Fock** approximation.

- Again, we simply need to minimize a functional of the 1-electron wavefunctions with Lagrange multipliers:

$$\min_{\{\phi_n\}} F\left[\{\phi_n\}\right] = \left\langle \psi | \hat{H} | \psi \right\rangle - \sum_n \varepsilon_n^{\mathrm{HF}} \left\langle \phi_n | \phi_n \right\rangle$$

Hartree-Fock approximation

- It can be shown that the 1-electron wavefunctions are the solutions of the following 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \sum_{m\neq n}(\hat{J}_m - \hat{K}_m)\right]\phi_n(\mathbf{r}) = \varepsilon_n^{\text{HF}}\phi_m(\mathbf{r})$$

where $\hat{J}_m$ is the **Coulomb operator** defined by:

$$\hat{J}_m\phi_n(\mathbf{r}) = \left\{\int \phi_m^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_m(\mathbf{r}')d\mathbf{r}'\right\}\phi_n(\mathbf{r})$$

and $\hat{K}_m$ is the **exchange operator** defined by:

$$\hat{K}_m\phi_n(\mathbf{r}) = \left\{\int \phi_m^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_n(\mathbf{r}')d\mathbf{r}'\right\}\phi_m(\mathbf{r})$$

Hartree-Fock approximation

- The electronic eigenenergies can be written as:

$$\varepsilon_n^{\mathrm{HF}} = \langle\phi_n| -\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r})\,|\phi_n\rangle + \sum_{m\neq n}(J_{nm} - K_{nm})$$

where

$$J_{nm} = \int \phi_n^*(\mathbf{r})\phi_m^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_n(\mathbf{r})\phi_m(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

and

$$K_{nm} = \int \phi_n^*(\mathbf{r})\phi_m^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_m(\mathbf{r})\phi_n(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

- So that the total electronic energy is:

$$E = \langle\psi|\,\hat{H}\,|\psi\rangle = \sum_n \varepsilon_n^{\mathrm{HF}} - \frac{1}{2}\sum_n\sum_{m\neq n}(J_{nm} - K_{nm})$$

Hartree-Fock approximation

- The 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \sum_{m\neq n}(\hat{J}_m - \hat{K}_m)\right]\phi_n(\mathbf{r}) = \varepsilon_n^{\text{HF}}\phi_n(\mathbf{r})$$

is identical (here, the self-interaction cancel in *J* and *K*) to:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + \hat{V}_{\text{x}}\right]\phi_n(\mathbf{r}) = \varepsilon_n^{\text{HF}}\phi_n(\mathbf{r})$$

with $\hat{V}_{\text{x}}$, the **exchange potential** operator, defined by:

$$\hat{V}_{\text{x}}\phi_n(\mathbf{r}) = \sum_m \left\{\int \phi_m^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_n(\mathbf{r}')d\mathbf{r}'\right\}\phi_m(\mathbf{r})$$

It is a non-local operator.

Hartree-Fock approximation

- A link with photoemission experiments can be established if we assume that the wavefunction of the N-1 electrons system can be written as:

$$|N-1,n\rangle = \psi_{N-1,n}(\mathbf{r}_1,\dots,\mathbf{r}_{n-1},\mathbf{r}_{n+1},\dots,\mathbf{r}_{N-1})$$

$$= \frac{1}{\sqrt{!(N-1)}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \cdots & \phi_{n-1}(\mathbf{r}_1) & \phi_{n+1}(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1) \\ \vdots & & \vdots & \vdots & & \vdots \\ \phi_1(\mathbf{r}_{n-1}) & \cdots & \phi_{n-1}(\mathbf{r}_{n-1}) & \phi_{n+1}(\mathbf{r}_{n-1}) & \cdots & \phi_N(\mathbf{r}_{n+1}) \\ \phi_1(\mathbf{r}_{n+1}) & \cdots & \phi_{n-1}(\mathbf{r}_{n+1}) & \phi_{n+1}(\mathbf{r}_{n+1}) & \cdots & \phi_N(\mathbf{r}_{n+1}) \\ \vdots & & \vdots & \vdots & & \vdots \\ \phi_1(\mathbf{r}_N) & \cdots & \phi_{n-1}(\mathbf{r}_N) & \phi_{n+1}(\mathbf{r}_N) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

  (meaning that we neglect the relaxation of the 1-electron wavefunctions on electron removal).

- Indeed, we can write:

$$E_{N,0} - E_{N-1,n} = \langle N,0|\hat{H}|N,0\rangle - \langle N-1,n|\hat{H}|N-1,n\rangle = \varepsilon_n^{\mathrm{HF}}$$

Hartree-Fock approximation

- A link with inverse photoemission experiments can be established if we assume that the wavefunction of the N+1 electrons system can be written as:

$$
\begin{aligned}
|N+1,n\rangle &= \psi_{N+1,n}(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{r}_{N+1}) \\
&= \frac{1}{\sqrt{!(N-1)}}\begin{vmatrix}
\phi_1(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1) & \phi_n(\mathbf{r}_1) \\
\vdots & & \vdots & \vdots \\
\phi_1(\mathbf{r}_N) & \cdots & \phi_N(\mathbf{r}_N) & \phi_n(\mathbf{r}_N) \\
\phi_1(\mathbf{r}_{N+1}) & \cdots & \phi_N(\mathbf{r}_{N+1}) & \phi_n(\mathbf{r}_{N+1})
\end{vmatrix}
\end{aligned}
$$

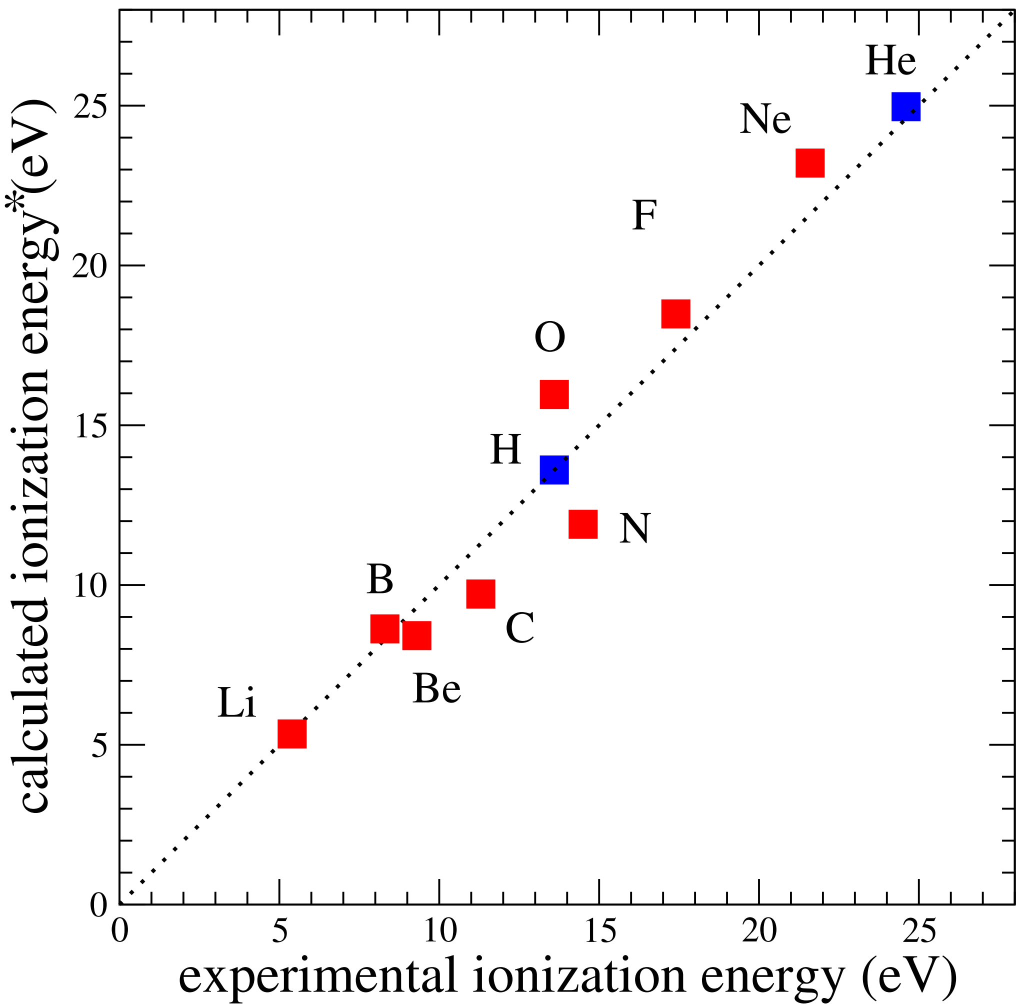
  (meaning that we neglect the relaxation of the 1-electron wavefunctions on electron addition).

- Indeed, we can write:

$$E_{N+1,n} - E_{N,0} = \langle N+1,n|\hat{H}|N+1,n\rangle - \langle N,0|\hat{H}|N,0\rangle = \varepsilon_n^{\mathrm{HF}}$$

Hartree-Fock approximation

- Results for the ionization energy

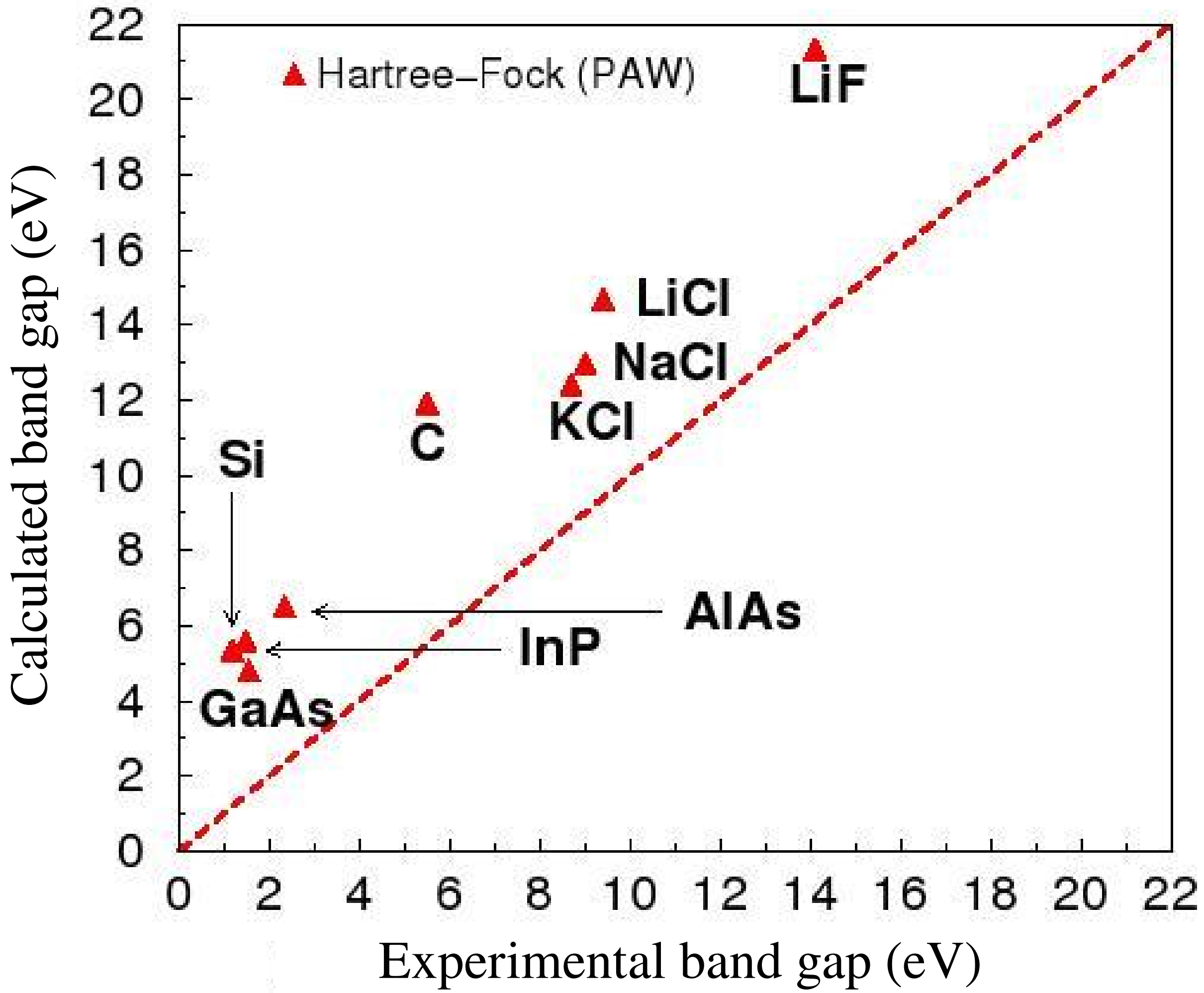


(*) HOMO energy computed with Gaussian03

[courtesy of Fabien Bruneval (CEA-DEN, Gif-sur-Yvette, France)]

Hartree-Fock approximation

- Band gap of semiconductors and insulators



[courtesy of Brice Arnaud (Université de Rennes, France)]

Post-Hartree-Fock methods

- **Configuration Interaction** (CI): the *N*-electrons wavefunction is approximated by a linear combination of Slater determinants (including 1-electron wavefunctions associated to excited states).

- **Coupled Cluster** (CC): the *N*-electrons wavefunction is obtained by applying an exponential of the excitation operator on the Slater determinant (hence producing a linear combination of excited Slater determinants).

- **Møller-Plasset** (MP): the *N*-electrons wavefunction is obtained by means of perturbation theory in terms of the correlation potential (i.e. the difference between the exact Hamiltonian and the one of Hartree-Fock approximation). The correlation potential does not contribute in first-order to the exact electronic energy. The higher-order terms are written on basis of doubly-excited Slater determinants (singly-excited do not contribute).

Density Functional Theory

Hohenberg-Kohn theorem

- Let us consider all possible Schrödinger equation for N_e electrons which only differ by the external potential $V_{\text{ext}}(\mathbf{r})$:

$$\hat{H}\psi = \sum_{n}\left(-\frac{\nabla_n^2}{2} + V_{\text{ext}}(\mathbf{r}_n) + \sum_{m>n}\frac{1}{|\mathbf{r}_n - \mathbf{r}_m|}\right)\psi = E\psi$$

  Hohenberg and **Kohn** have demonstrated that the electronic density of the ground-state $n(\mathbf{r})$ defined by:

$$n(\mathbf{r}) = N_e \int [\psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_{N_e})]^* \psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_{N_e}) d\mathbf{r}_2 \ldots d\mathbf{r}_{N_e}$$

  determines uniquely the external potential $V_{\text{ext}}(\mathbf{r})$, modulo a global constant.

- The external potential is thus a functional of the density.

Hohenberg-Kohn theorem

- It is also the case for all the quantities which can be formally obtained once the potential is fixed modulo a global constant (for instance, the wavefunctions of the ground-state), hence the name of the theory (acronym: DFT).

- Moreover, if the arbitrary constant for the external potential is fixed through a simple condition (for instance, the potential goes to zero when the distance goes to infinity), the total electronic energy is also a functional of the density:

$$E = \left\langle \psi \middle| \hat{H} \middle| \psi \right\rangle = E[n]$$

  Indeed, the Hamiltonian is uniquely defined by specifying the external potential, and its expectation value gives the total electronic energy.

Hohenberg-Kohn theorem

- Starting from the variational principle, it is possible to gain insight about this energy functional:

$$E = \min_{\phi}\left\{\langle\phi|\,\hat{H}\,|\phi\rangle\right\} = \min_{n}\left\{\min_{\phi\to n}\left\{\langle\phi|\,\hat{H}\,|\phi\rangle\right\}\right\}$$

$$= \min_{n}\left\{\min_{\phi\to n}\left\{\langle\phi|\,\hat{T}_e + \hat{V}_{ee} + \sum_{i=1}^{N_e} V_{\text{ext}}(\mathbf{r}_i)\,|\phi\rangle\right\}\right\}$$

$$= \min_{n}\left\{\min_{\phi\to n}\left\{\langle\phi|\,\hat{T}_e + \hat{V}_{ee}\,|\phi\rangle\right\} + \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r}\right\}$$

$$= \min_{n}\left\{F[n] + \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r}\right\}$$

where $F[n] = \min_{\phi\to n}\left\{\langle\phi|\,\hat{T}_e + \hat{V}_{ee}\,|\phi\rangle\right\}$ is a universal functional of the density, but it is **not known explicitly**.

Kohn-Sham equation

- In fact, $F[n]$ represents an important part of the total electronic energy. It is thus critical to make a reasonable approximation for it in order to obtain a good value for $E[n]$

- **Kohn** and **Sham** tried to establish a connection with a system of non-interacting electrons with the same electronic density:

$$F[n] = \min_{\phi \to n} \left\{ \langle \phi | \hat{T}_e + \hat{V}_{ee} | \phi \rangle \right\} \qquad \longrightarrow \qquad T_0[n] = \min_{\phi \to n} \left\{ \langle \phi | \hat{T}_e | \phi \rangle \right\}$$

The kinetic energy is a known functional $T_0[n]$ of the density. Moreover, the functional for the associated Hartree energy is also known explicitly:

$$E_{\mathrm{H}}[n] = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

Kohn-Sham equation

- If this two pieces are substracted from $F[n]$, the rest represents a much smaller part of the total electronic energy. This difference is called **exchange-correlation energy functional**:

  $$E_{\mathrm{xc}}[n] = F[n] - T_0[n] - E_{\mathrm{H}}[n]$$

  Indeed, it should contain an exchange term (see Hartree-Fock) and a correlation term. But, it also contains the difference between the kinetic energies of the systems of interacting and non-interacting electrons.

- Moreover, it is much easier to obtain a reasonable approximation for it (see below). Let us suppose that this functional is known.

Kohn-Sham equation

- The problem has now turned into minimizing the functional :

$$E[n] = T_0[n] + \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + E_{\text{xc}}[n]$$

under constraint of a fixed number of electrons: $\int n(\mathbf{r})d\mathbf{r} = N_e$

- Introducing Lagrange multipliers, one has to solve:

$$\frac{\delta\left(E[n] - \lambda\left[\int n(\mathbf{r})d\mathbf{r} - N_e\right]\right)}{\delta n} = 0$$

$$\frac{\delta T_0[n]}{\delta n} + V_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta E_{\text{xc}}[n]}{\delta n} = \lambda$$

Kohn-Sham equation

- This equation is strictly equivalent to that of a system of non-interacting electrons with the same electronic density in an external potential, called **Kohn-Sham potential**:

$$V_{\mathrm{KS}}(\mathbf{r}) = V_{\mathrm{ext}}(\mathbf{r}) + \underbrace{\int \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'}_{V_{\mathrm{H}}(\mathbf{r})} + \underbrace{\frac{\delta E_{\mathrm{xc}}[n]}{\delta n}}_{V_{\mathrm{xc}}(\mathbf{r})}$$

  where $V_{xc}(\mathbf{r})$ is the **exchange-correlation potential**.

- It is thus also equivalent to solve the 1-electron Schrödinger equation self-consistently:

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\mathbf{r})\right]\phi_n^{\mathrm{KS}}(\mathbf{r}) = \varepsilon_n^{\mathrm{KS}}\phi_n^{\mathrm{KS}}(\mathbf{r})$$

  with the electronic density $n(\mathbf{r}) = \sum_{i=1}^{N} \left|\phi_i^{\mathrm{KS}}(\mathbf{r})\right|^2$

Kohn-Sham equation

- By construction, when self-consistency is reached, the electronic density and hence the total energy will be the exact ones (assuming the exchange-correlation functional to be exact).
- However, the Kohn-Sham wavefunctions and eigenenergies correspond to a fictitious set of independent electrons, so they do not correspond to any exact quantity.
- The solution of the Kohn-Sham self-consistent system of equations is equivalent to the minimization of

$$E[\{\phi_i\}] = \sum_i \left\langle \phi_i \middle| -\frac{1}{2}\nabla^2 \middle| \phi_i \right\rangle +$$

$$\int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n]$$

under constraints of orthonormalization $\langle \phi_i \mid \phi_j \rangle = \delta_{ij}$ for the occupied orbitals.

Local Density Approximation

- Let us come back to the problem of finding a reasonable approximation for the exchange-correlation energy functional.

- It is possible to show that this functional of the density can be written as the integral over the whole space of the density multiplied by the local exchange-correlation energy per electron:

$$E_{xc}[n] = \int n(\mathbf{r})\,\varepsilon_{xc}(\mathbf{r}, n)d\mathbf{r}$$

- The Local Density Approximation (acronym: LDA), due to Kohn and Sham, consists in assuming that the local exchange-correlation energy per electron only depends on the local density and that it is equal to that of an homogeneous electron gas with the same density (in a neutralizing background – the “jellium”):

$$\varepsilon_{xc}^{LDA}(\mathbf{r}, n) = \varepsilon_{xc}^{\mathrm{hom}}(n(\mathbf{r}))$$

Local Density Approximation

- The exchange part can be calculated analytically:

$$\varepsilon_x^{\text{hom}}(n(\mathbf{r})) = -\frac{3}{4\pi}\left[3\pi^2 n(\mathbf{r})\right]^{1/3}$$

- The correlation part is obtained from accurate numerical simulations beyond DFT (e.g. Quantum Monte Carlo)

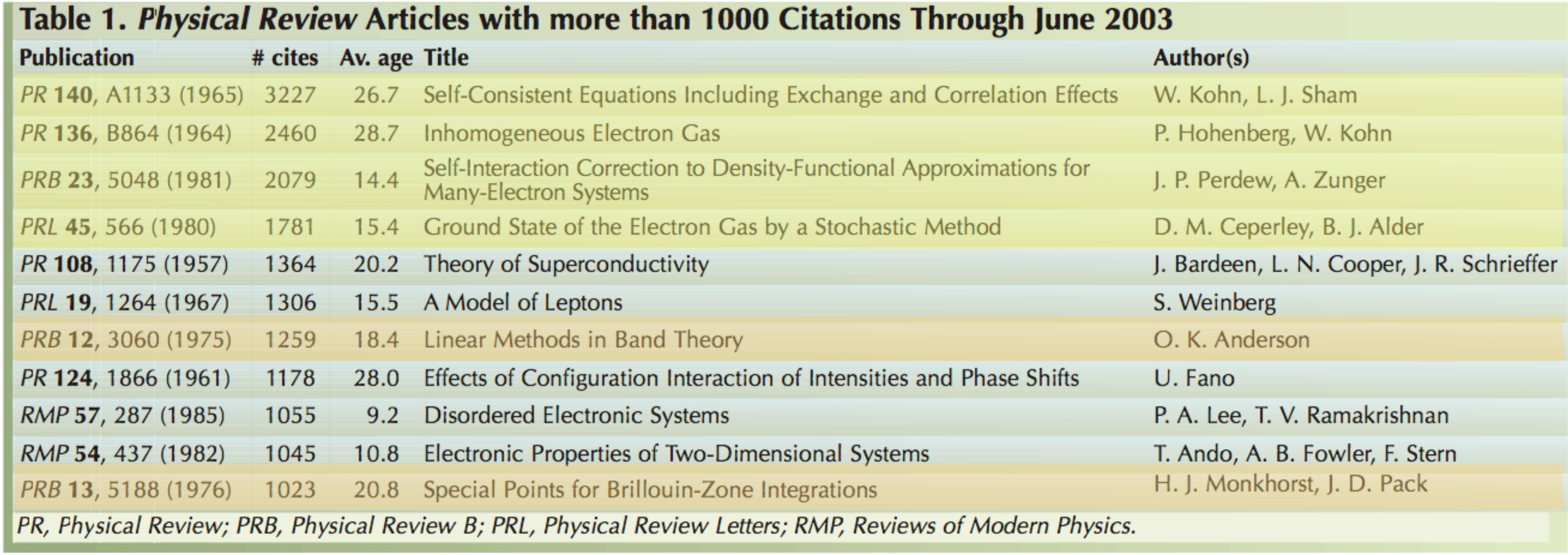


Table 1. *Physical Review* Articles with more than 1000 Citations Through June 2003

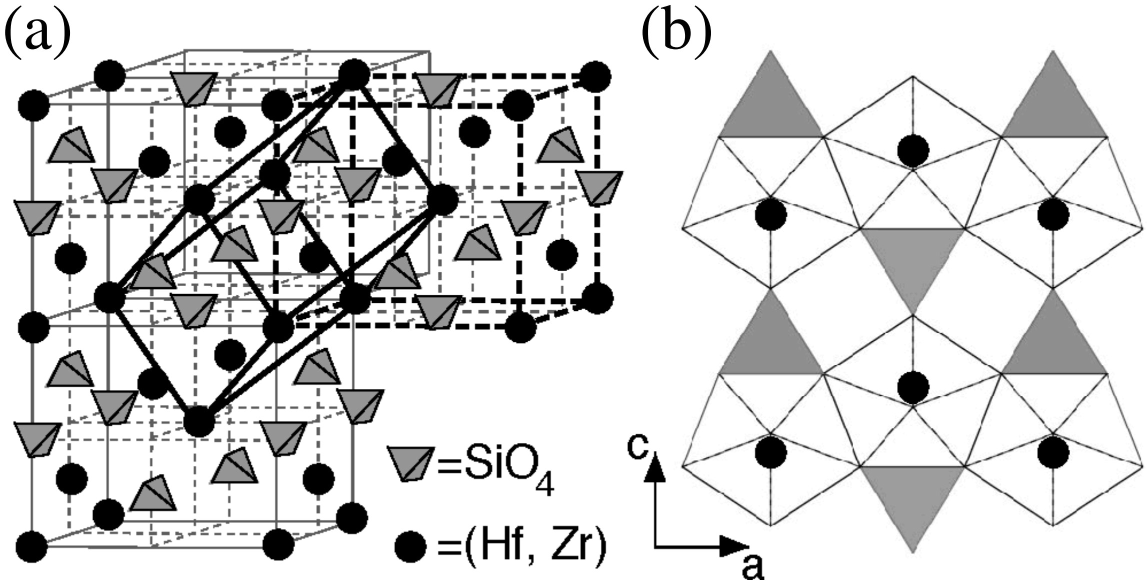
Publication	# cites	Av. age	Title	Author(s)
PR **140**, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR **136**, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB **23**, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
PRL **45**, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
PR **108**, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
PRL **19**, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
PRB **12**, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Anderson
PR **124**, 1866 (1961)	1178	28.0	Effects of Configuration Interaction of Intensities and Phase Shifts	U. Fano
RMP **57**, 287 (1985)	1055	9.2	Disordered Electronic Systems	P. A. Lee, T. V. Ramakrishnan
RMP **54**, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
PRB **13**, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack

PR, Physical Review; PRB, Physical Review B; PRL, Physical Review Letters; RMP, Reviews of Modern Physics.

Local Density Approximation

- Globally, LDA works very well (hence, it is widely used).

  Example: hafnon ($HfSiO_4$) / zircon ($ZrSiO_4$)



  - body-centered tetragonal
  - primitive cell with 2 formula units of $MSiO_4$
  - alternating SiO_4 tetrahedra and MO_8 units, sharing edges to form chains parallel to [0 0 1]
  - in the MO_8 units, four O atoms are closer to the Zr atoms than the four other ones
  - O atoms are 3-fold coordinated

Local Density Approximation

- Globally, LDA works very well (hence, it is widely used).

  Example: hafnon ($HfSiO_4$) / zircon ($ZrSiO_4$)

	$HfSiO_4$		$ZrSiO_4$	
	Th.	Expt.	Th.	Expt.
a	6.61	6.57	6.54	6.61
c	5.97	5.96	5.92	6.00
u	0.0672	0.0655	0.0645	0.0646
v	0.1964	0.1948	0.1945	0.1967
Volume	130.42	128.63	126.60	131.08
d(Si-O)	1.62	1.61	1.61	1.62
d(M-O)	2.14	2.10	2.10	2.13
	2.27	2.24	2.24	2.27
$\angle$(O-Si-O)	97°	97°	97°	97°
	116°	117°	116°	116°

Lattice parameters are within 1 or 2% from the experimental values.

Beyond LDA

- However, in some particular cases (for instance, the hydrogen bond), it clearly shows its limits.

- Considerable efforts are dedicated to improving this approximation. One of the tracks that are pursued is to include a dependence on the gradients of the local density:

$$E_{xc}^{\text{approx}}[n] = \int n(\mathbf{r})\, \varepsilon_{xc}^{\text{approx}}\Big(n(\mathbf{r}), |\nabla n(\mathbf{r})|\,, \nabla^2 n(\mathbf{r})\Big)\, d\mathbf{r}$$

  This is the **generalized gradients approximation** (acronym: GGA).

- In this case, there is no model (such as the homogeneous electron gas) for which an analytic expression can be obtained.

Beyond LDA

- There exists a wide variety of GGA functionals which have been constructed trying to account for various sum rules (acronyms: PBE, PW86, PW91, LYP, ...).

- Another kind of approximation consists in obtaining a local form for the exchange potential by deriving the exchange term that appears in the Hartree-Fock approximation. This approach is referred to as **exact exchange** (acronym: EXX).

- Another approximation consists in suppressing the self-interaction which is present in the Hartree term (acronym: SIC).

- Finally, there are **hybrid functionals** which are obtained by mixing (using an empirically adjusted parameter) a part of exact exchange and an approximated part (acronyms: B3LYP, HSE, ...).

DFT and the band gap problem

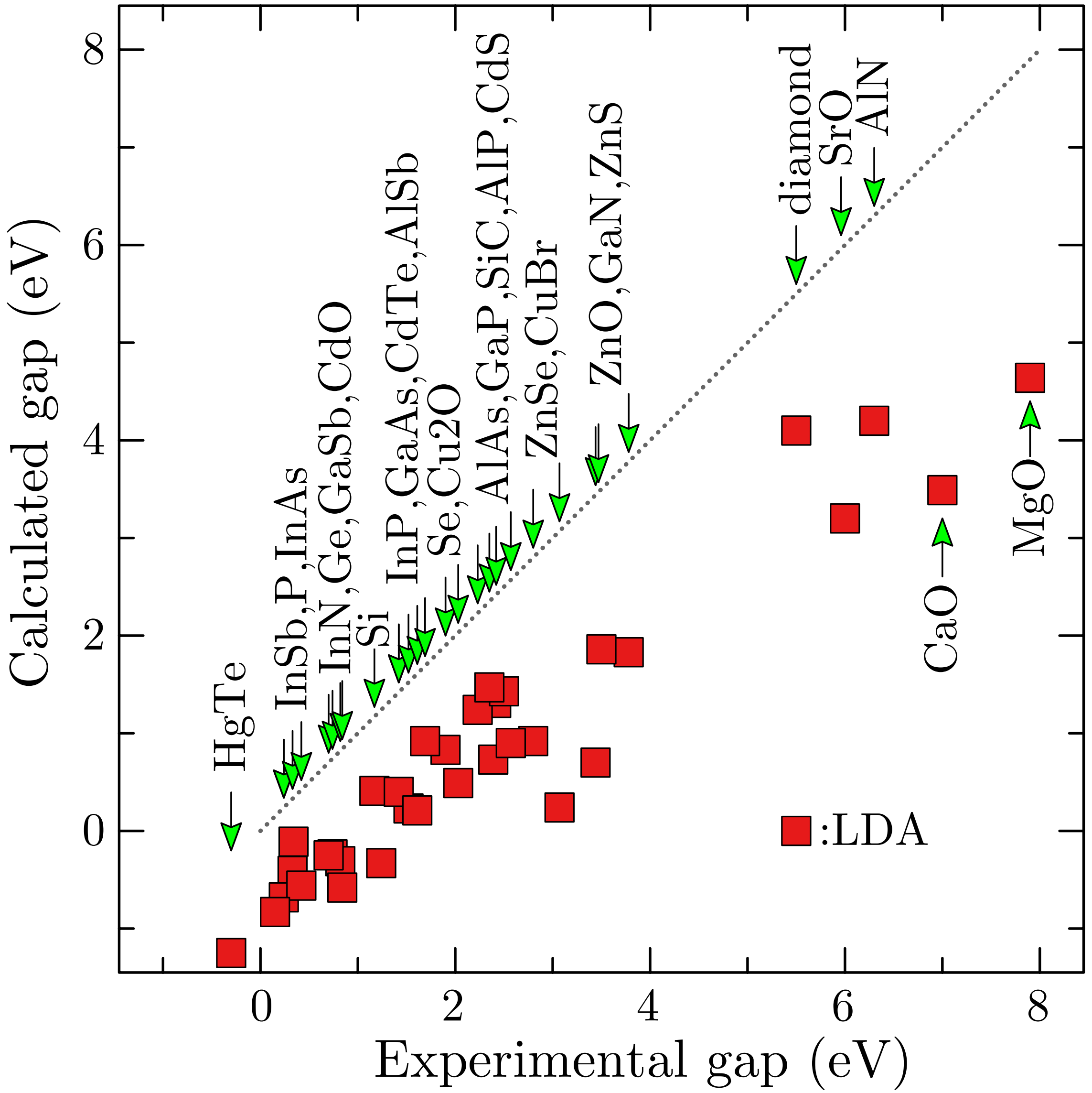
- The Density Functional Theory can (in principle) be used to compute exactly all the ground-state properties by solving the Kohn-Sham equation:

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right] \phi_{n\mathbf{k}}^{KS}(\mathbf{r}) = \epsilon_{n\mathbf{k}}^{KS} \phi_{n\mathbf{k}}^{KS}(\mathbf{r})$$

  As already indicated, there is no direct physical interpretation for the Kohn-Sham eigenenergies (these are simply Lagrange multipliers).

- However, the electronic bandstructures obtained within DFT (LDA or GGA) are in quite good agreement with the experimental data. The most notable exception is the **band gap** which is **systematically underestimated** by 30-50% (or even 100%). This problem is related to the existence of a discontinuity in the derivative of the exchange-correlation potential functional.

DFT and the band gap problem



[adapted from van Schilfgaarde et al., PRL 96, 226402 (2006)]

Green’s functions theory and quasiparticles

Definition of the 1-particle Green's function

- Green's function theory and the quasiparticle concept constitute an elegant alternative to DFT which allows to solve this problem.

- The 1-particle Green's function $G(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)$ is

$$\begin{aligned} G(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2) &= -i\langle N,0|T[\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_2,t_2)]|N,0\rangle \\ &= -i\langle N,0|\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_2,t_2)|N,0\rangle\theta(t_1-t_2) \\ &\quad +i\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2,t_2)\hat{\psi}(\mathbf{r}_1,t_1)|N,0\rangle\theta(t_2-t_1) \end{aligned}$$

where T is the **time-ordering operator**:

$$T[\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_2,t_2)] = \begin{cases} \hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_2,t_2) & \text{if } t_1 > t_2 \\ \hat{\psi}^\dagger(\mathbf{r}_2,t_2)\hat{\psi}(\mathbf{r}_1,t_1) & \text{if } t_2 > t_1 \end{cases}$$

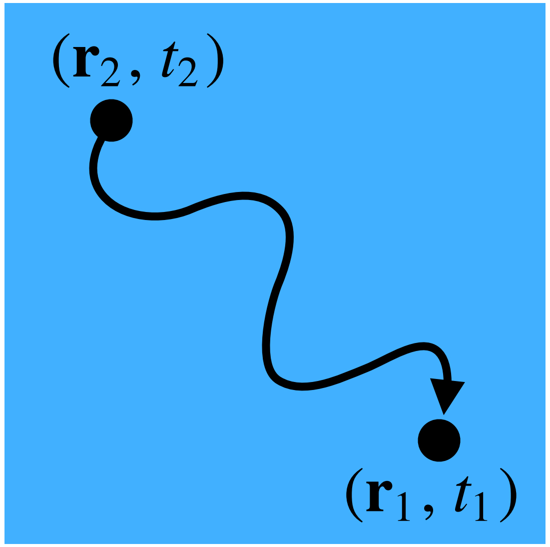
$\theta(t)$ is the Heaviside step function [$\theta(t) = 1$ for $t > 0$ and 0 for $t < 0$], $\hat{\psi}$ and $\hat{\psi}^\dagger$ are the field operators in the Heisenberg representation for annihilation and creation, respectively.

Interpretation of the 1-particle Green’s function

- It can be interpreted as the probability amplitude:
    - to detect an electron at point $\mathbf{r}_1$ and time t_1 when an electron has been added to the system at point $\mathbf{r}_2$ and time t_2 (if $t_1 > t_2$),
    - to detect a hole at point $\mathbf{r}_1$ and time t_1 when an electron has been added to the system at point $\mathbf{r}_2$ and time t_2 (if $t_2 > t_1$).

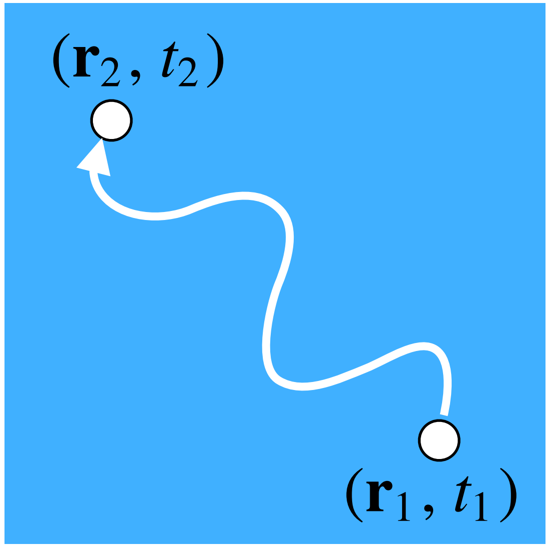
$$t_1 > t_2$$

$$\langle N,0|\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}^\dagger(\mathbf{r}_2,t_2)|N,0\rangle$$



$$t_2 > t_1$$

$$\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2,t_2)\hat{\psi}(\mathbf{r}_1,t_1)|N,0\rangle$$



Schrödinger representation

- Assuming that the Hamiltonian is not an explicit function of time, we now move to the Schrödinger representation:

$$\hat{\psi}(\mathbf{r}_1,t_1) = e^{i\hat{H}t}\,\hat{\psi}(\mathbf{r}_1)e^{-i\hat{H}t}$$

- Using the relation: $\hat{H}|N,0\rangle = E_{N,0}|N,0\rangle$ the 1-particle Green's function $G(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2)$ writes:

$$G(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2) = -\,ie^{iE_{N,0}(t_1-t_2)}\langle N,0|\hat{\psi}(\mathbf{r}_1)e^{-i\hat{H}t_1}e^{i\hat{H}t_2}\,\hat{\psi}^\dagger(\mathbf{r}_2)|N,0\rangle\,\theta(t_1-t_2)$$
$$+\,ie^{iE_{N,0}(t_2-t_1)}\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2)e^{-i\hat{H}t_2}e^{i\hat{H}t_1}\,\hat{\psi}(\mathbf{r}_1)|N,0\rangle\,\theta(t_2-t_1)$$

- It is now explicitly only a function of the time difference $\tau = t_1 - t_2$, we write:

$$\begin{aligned} G(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2) =& G(\mathbf{r}_1,\mathbf{r}_2;\tau) \\ =& -\,ie^{iE_{N,0}\tau}\langle N,0|\hat{\psi}(\mathbf{r}_1)e^{-i\hat{H}\tau}\,\hat{\psi}^\dagger(\mathbf{r}_2)|N,0\rangle\,\theta(\tau) \\ & +\,ie^{-iE_{N,0}\tau}\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2)e^{i\hat{H}\tau}\,\hat{\psi}(\mathbf{r}_1)|N,0\rangle\,\theta(-\tau) \end{aligned}$$

Lehman representation

- In order to remove the time operators inside the expectation values, we introduce the complete set of states with M particles: $|M,n\rangle$ where m is a general label to describe the possible excited states.

- Since the states form a complete set, we can write the closure relation:

$$\sum_{M,n} |M,n\rangle\,\langle M,n| = 1$$

  and also:

$$\hat{H}\,|M,n\rangle = E_{M,n}\,|M,n\rangle$$

- Introducing the closure relation between the pairs of exponentials in the expression of the 1-particle Green's function, we get:

$$\begin{aligned} G(\mathbf{r}_1,\mathbf{r}_2;\tau) = &-i\sum_{M,n} e^{i(E_{N,0}-E_{M,n})\tau}\langle N,0|\hat{\psi}(\mathbf{r}_1)|M,n\rangle\langle M,n|\hat{\psi}^\dagger(\mathbf{r}_2)|N,0\rangle\theta(\tau) \\ &+i\sum_{M,n} e^{-i(E_{N,0}-E_{M,n})\tau}\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2)|M,n\rangle\langle M,n|\hat{\psi}(\mathbf{r}_1)|N,0\rangle\theta(-\tau) \end{aligned}$$

Lehman representation

- Most often, it is more convenient to work with the Fourier transform of the 1-particle Green's function:

$$G(\mathbf{r}_1,\mathbf{r}_2;\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} G(\mathbf{r}_1,\mathbf{r}_2;\tau)e^{i\omega\tau}d\tau$$

- Thus, we have:

$$G(\mathbf{r}_1,\mathbf{r}_2;\omega) = \sum_{M,n} \frac{\langle N,0|\hat{\psi}(\mathbf{r}_1)|M,n\rangle\langle M,n|\hat{\psi}^\dagger(\mathbf{r}_2)|N,0\rangle}{\omega-(E_{M,n}-E_{N,0})+i\eta} + \sum_{M,n} \frac{\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2)|M,n\rangle\langle M,n|\hat{\psi}(\mathbf{r}_1)|N,0\rangle}{\omega+(E_{M,n}-E_{N,0})-i\eta}$$

where the infinitesimals $\pm i\eta$ reflect the time ordering.

Lehman representation

- The expectation values $\langle N,0|\hat{\psi}(\mathbf{r}_1)|M,n\rangle$ and $\langle M,n|\hat{\psi}^\dagger(\mathbf{r}_2)|N,0\rangle$ are different from zero only for $M=N+1$; while $\langle M,n|\hat{\psi}(\mathbf{r}_1)|N,0\rangle$ and $\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2)|M,n\rangle$ are different from zero only for $M=N-1$.

- Thus, the 1-particle Green's function can be written as:

$$G(\mathbf{r}_1,\mathbf{r}_2;\omega)=\sum_n \frac{\langle N,0|\hat{\psi}(\mathbf{r}_1)|N+1,n\rangle\langle N+1,n|\hat{\psi}^\dagger(\mathbf{r}_2)|N,0\rangle}{\omega-(E_{N+1,n}-E_{N,0})+i\eta}$$

$$+\sum_n \frac{\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2)|N-1,n\rangle\langle N-1,n|\hat{\psi}(\mathbf{r}_1)|N,0\rangle}{\omega+(E_{N-1,n}-E_{N,0})-i\eta}$$

Lehman representation

- Let us consider the energy terms appearing at the denominators, they can be rewritten as:

$$E_{N+1,n} - E_{N,0} = (E_{N+1,n} - E_{N+1,0}) + (E_{N+1,0} - E_{N,0})$$

$$E_{N,0} - E_{N-1,n} = (E_{N,0} - E_{N-1,0}) + (E_{N-1,0} - E_{N-1,n})$$

- The difference $E_{N+1,0} - E_{N,0}$ represents the minimum energy needed to add one electron to a system of N electrons.

  It is the **electron affinity** (EA) :

$$\mathrm{EA} = E_{N+1,0} - E_{N,0}$$

- The difference $E_{N,0} - E_{N-1,0}$ represents the minimum energy needed to remove one electron to a system of N electrons.

  It is the **ionization energy** (IE) :

$$\mathrm{IE} = E_{N,0} - E_{N-1,0}$$

Lehman representation

- It can be shown that IE $\leq$ EA, so that if we define:

$$\begin{aligned}\varepsilon_g &= \mathrm{EA} - \mathrm{IE} \\ &= \left(E_{N+1,0} - E_{N,0}\right) - \left(E_{N,0} - E_{N-1,0}\right)\end{aligned}$$

  the quantity ε_g is positive.

- In an atomic or molecular system, we have:
  IE (energy of HOMO) $<$ EA (energy of LUMO).

- In a solid, we define the **chemical potential** μ such that:

$$\mathrm{IE} \leq \mu \leq \mathrm{EA}$$

  In the thermodynamic limit (N, $V \to \infty$, with N/V=cst), we distinguish:
  - metallic systems in which $\varepsilon_g = 0$ (IE$\simeq\mu\simeq$EA)
  - insulating systems in which $\varepsilon_g > 0$ (IE$<\mu<$EA)

Lehman representation

- Coming back to the energy terms appearing at the denominators:

$$E_{N+1,n} - E_{N,0} = \overbrace{\left(E_{N+1,n} - E_{N+1,0}\right)}^{\geq 0} + \overbrace{\left(E_{N+1,0} - E_{N,0}\right)}^{\text{EA}}$$

$$E_{N,0} - E_{N-1,n} = \underbrace{\left(E_{N,0} - E_{N-1,0}\right)}_{\text{IE}} + \underbrace{\left(E_{N-1,0} - E_{N-1,n}\right)}_{\leq 0}$$

we define the **excitation energies** of the system:

$$\varepsilon_n = \begin{cases} E_{N,0} - E_{N-1,n} & \text{when } \varepsilon_n < \mu \\ E_{N+1,n} - E_{N,0} & \text{when } \varepsilon_n > \mu \end{cases}$$

Lehman representation

- If we define the **Lehman amplitudes** as:

$$\phi_n(\mathbf{r}) = \begin{cases} \langle N-1, n|\hat{\psi}(\mathbf{r})|N,0\rangle & \text{when } \varepsilon_n < \mu \\ \langle N,0|\hat{\psi}(\mathbf{r})|N+1,n\rangle & \text{when } \varepsilon_n > \mu \end{cases}$$

the numerators of the 1-particle Green's function can be rewritten like:

$$\langle N,0|\hat{\psi}^\dagger(\mathbf{r}_2)|N-1,n\rangle\langle N-1,n|\hat{\psi}(\mathbf{r}_1)|N,0\rangle = \phi_n^*(\mathbf{r}_2)\phi_n(\mathbf{r}_1)$$

$$\langle N,0|\hat{\psi}(\mathbf{r}_1)|N+1,n\rangle\langle N+1,n|\hat{\psi}^\dagger(\mathbf{r}_2)|N,0\rangle = \phi_n(\mathbf{r}_1)\phi_n^*(\mathbf{r}_2)$$

Lehman representation

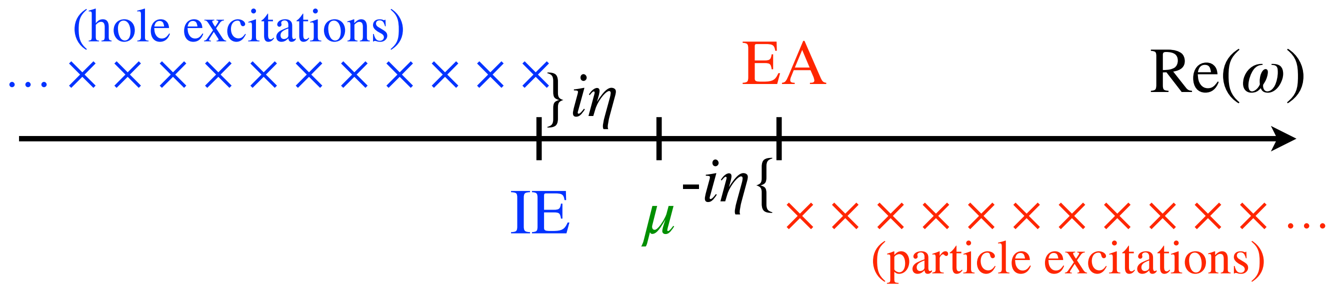
- The 1-particle Green's function can thus be written as :

$$G(\mathbf{r}_1,\mathbf{r}_2;\omega) = \sum_n \frac{\phi_n(\mathbf{r}_1)\phi_n^*(\mathbf{r}_2)}{\omega - \varepsilon_n + i\eta\,\mathrm{sgn}(\varepsilon_n-\mu)}$$

with

$$\varepsilon_n = \begin{cases} E_{N,0}-E_{N-1,n} \\ E_{N+1,n}-E_{N,0} \end{cases} \qquad \phi_n(\mathbf{r}) = \begin{cases} \langle N-1,n|\hat{\psi}(\mathbf{r})|N,0\rangle & \text{when } \varepsilon_n<\mu \\ \langle N,0|\hat{\psi}(\mathbf{r})|N+1,n\rangle & \text{when } \varepsilon_n>\mu \end{cases}$$

- Its poles are thus located as follows:

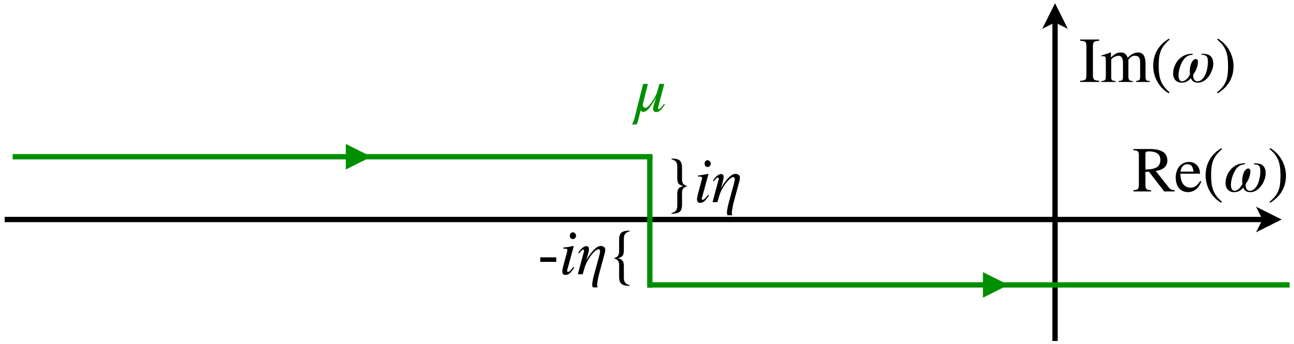


Spectral representation

- The 1-particle Green's function can also be cast into the so-called **spectral representation** like:

$$G(\mathbf{r}_1,\mathbf{r}_2;\omega) = \int_C \frac{A(\mathbf{r}_1,\mathbf{r}_2;\omega')}{\omega-\omega'}d\omega'$$

where the integral is to be taken on the contour C defined as follow:



- The is **spectral function** is simply given by:

$$A(\mathbf{r}_1,\mathbf{r}_2;\omega) = \sum_n \phi_n(\mathbf{r}_1)\phi_n^*(\mathbf{r}_2)\delta(\omega-\varepsilon_n)$$

$$\phi_n(\mathbf{r}) = \begin{cases} \langle N-1,n|\hat{\psi}(\mathbf{r})|N,0\rangle & \text{when } \varepsilon_n < \mu \\ \langle N,0|\hat{\psi}(\mathbf{r})|N+1,n\rangle & \text{when } \varepsilon_n > \mu \end{cases}$$

Spectral representation

- It can be shown that the spectral function satisfy the following sum-rule:

$$\int_{-\infty}^{+\infty} A(\mathbf{r}_1, \mathbf{r}_2; \omega) d\omega = \delta(\mathbf{r}_1 - \mathbf{r}_2)$$

- And, using the Sokhatsky-Weierstrass theorem which states that

$$\lim_{\eta \to 0^+} \int \frac{f(x)}{x \pm i\eta} = \mp i\pi \int f(x)\delta(x) dx + P \int \frac{f(x)}{x} dx$$

where *P* denotes the Cauchy principal value, we have that

$$A(\mathbf{r}_1, \mathbf{r}_2; \omega) = \frac{1}{\pi} \left| \mathrm{Im}[G(\mathbf{r}_1, \mathbf{r}_2; \omega)] \right|$$

Quasiparticles

- In an homogeneous and crystalline system, we have that:

  $$G(\mathbf{r}_1, \mathbf{r}_2; \omega) = G(\mathbf{r}_1 - \mathbf{r}_2; \omega)$$

  it is thus more convenient to perform a momentum transformation of the 1-particle Green's function:

  $$G(\mathbf{k}, \omega) = \int G(\mathbf{r}_1 - \mathbf{r}_2; \omega) e^{-i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)} d(\mathbf{r}_1 - \mathbf{r}_2)$$

- Using plane-wave states as a basis for the field operators:

  $$\hat{\psi}(\mathbf{r}) = \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \hat{c}_{\mathbf{k}} \qquad \hat{\psi}^\dagger(\mathbf{r}) = \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{c}^\dagger_{\mathbf{k}}$$

  the 1-particle Green's function rewritten as:

  $$G(\mathbf{k}, \omega) = \sum_n \frac{|\phi_{n\mathbf{k}}|^2}{\omega - \varepsilon_n + i\eta \operatorname{sgn}(\varepsilon_n - \mu)}$$

  $$\phi_{n\mathbf{k}} = \begin{cases} \langle N-1, n | \hat{c}_{\mathbf{k}} | N, 0 \rangle & \text{when } \varepsilon_n < \mu \\ \langle N, 0 | \hat{c}_{\mathbf{k}} | N+1, n \rangle & \text{when } \varepsilon_n > \mu \end{cases}$$

Quasiparticles

- The spectral representation thus becomes:

$$G(\mathbf{k},\omega) = \int_C \frac{A(\mathbf{k},\omega')}{\omega-\omega'}d\omega'$$

with

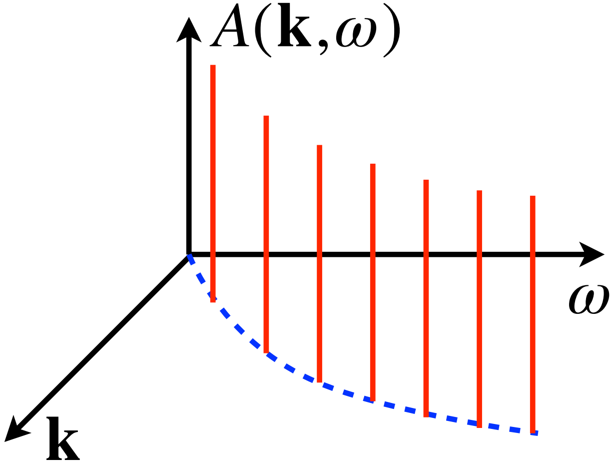
$$A(\mathbf{k},\omega) = \sum_n |\phi_{n\mathbf{k}}|^2 \, \delta(\omega-\varepsilon_n)$$

- For non-interacting electrons, we have:

$$\hat{c}^\dagger_{\mathbf{k}} |N,0\rangle = |N+1,n,\mathbf{k}\rangle$$
$$\hat{c}_{\mathbf{k}} |N,0\rangle = |N-1,n,-\mathbf{k}\rangle$$

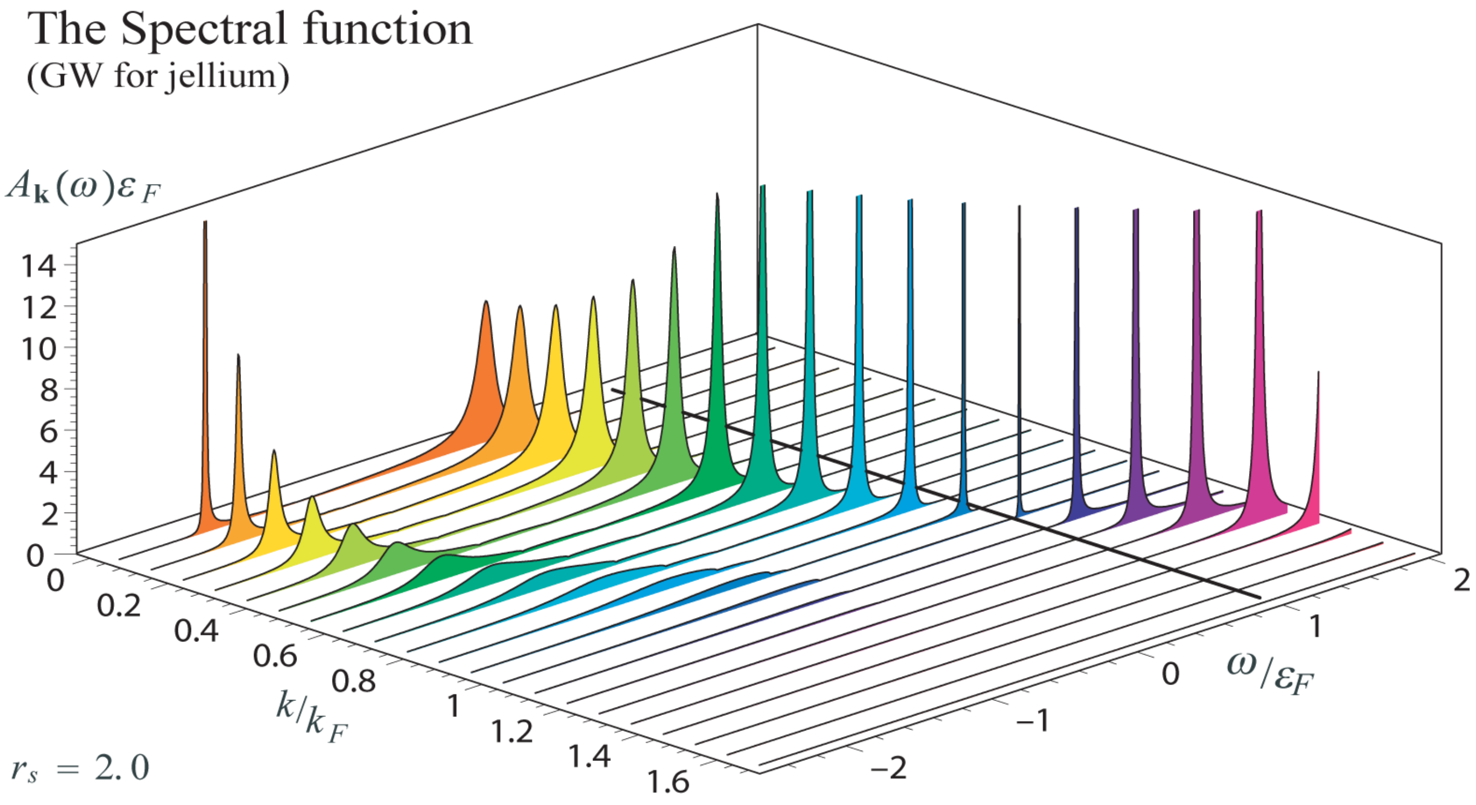
and the spectral function is simply:

$$A(\mathbf{k},\omega) = \sum_n \delta(\omega-\varepsilon_{n\mathbf{k}})$$



Quasiparticles

- For interacting electrons, if there is a strong overlap between $\langle N,0|\,\hat{c}_{\mathbf{k}}$ and $|N+1,n,\mathbf{k}\rangle$ (resp. $\hat{c}_{\mathbf{k}}\,|N,0\rangle$ and $\langle N-1,n,-\mathbf{k}|$), we will say that there exists a **quasi-electron** (resp. **quasi-hole**) of energy $\varepsilon_{n\mathbf{k}}$ ($\varepsilon_{n\text{-}\mathbf{k}}$).



[courtesy of Martin Stankovski (Université Catholique de Louvain, Belgium)]

Utility of Green's function

- As we have just seen, the 1-particle Green's function contains a lot of information about all the 1-particle excitations.

- It also also to compute the total ground-state energy.

  Indeed, using **Galitskii-Migdal formula**, it can be written:

$$E_{N,0} = \frac{1}{\pi} \int_{-\infty}^{\mu} \mathrm{Tr} \left[\left(\omega - \frac{1}{2}\nabla^2 + V_{\mathrm{ext}} \right) \mathrm{Im}\, G(\omega) \right] d\omega$$

- In fact, we can obtain the expectation value of 1-particle operator (be it local or non-local).

Many-Body Perturbation Theory

Equation of motion of the Green's function

- Starting from the equation of motion for the Heisenberg annihilation and creation field operators ($\hat{\psi}$ and $\hat{\psi}^\dagger$) a hierarchy of equations of motion for the Green's function can be derived.

- For the 1-particle Green's function, it gives

$$\left[i\frac{\partial}{\partial t_1} - \hat{H}_0(\mathbf{r}_1)\right] G(1,2) + i\int d3\, v(1^+,3) G_2(1,3;2,3^+) = \delta(1,2)$$

where $\hat{H}_0(\mathbf{r}_1) = -\frac{1}{2}\nabla^2 + V_{\text{ext}}$ and $v(1,2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\delta(t_1 - t_2)$

Note that we have adopted Hedin's simplified notation:

$1 \equiv (\mathbf{r}_1, t_1)$ and $1^+ \equiv (\mathbf{r}_1, t_1 + \eta)$ where η is a positive infinitesimal.

- The 1-particle Green's function depends on the 2-particles one:

$$G_2(1,2;3,4) = (i)^2 \langle N,0|T[\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}(\mathbf{r}_2,t_2)\hat{\psi}^\dagger(\mathbf{r}_3,t_3)\hat{\psi}^\dagger(\mathbf{r}_4,t_4)]|N,0\rangle$$

Equation of motion of the Green's function

- If we look at the structure of the equation of motion, we can distinguish:

$$\underbrace{\left[i\frac{\partial}{\partial t_1} - \hat{H}_0(\mathbf{r}_1)\right] G(1,2)}_{\text{non-interacting}} + \underbrace{i\int d3\; v(1^+,3)G_2(1,3;2,3^+)}_{\text{interaction terms}} = \delta(1,2)$$

- Since we are specifically interested in the interaction effects, we will assume that the non-interacting part of the equation part can always be solved exactly:

$$[i\frac{\partial}{\partial t_1} - \hat{H}_0(\mathbf{r}_1)]G_0(1,2) = \delta(1,2)$$

- This defines the **independent-particle Green function** G_0.

  Note that

  (i) the calculation of G_0 is non-trivial for a solid (except jellium);

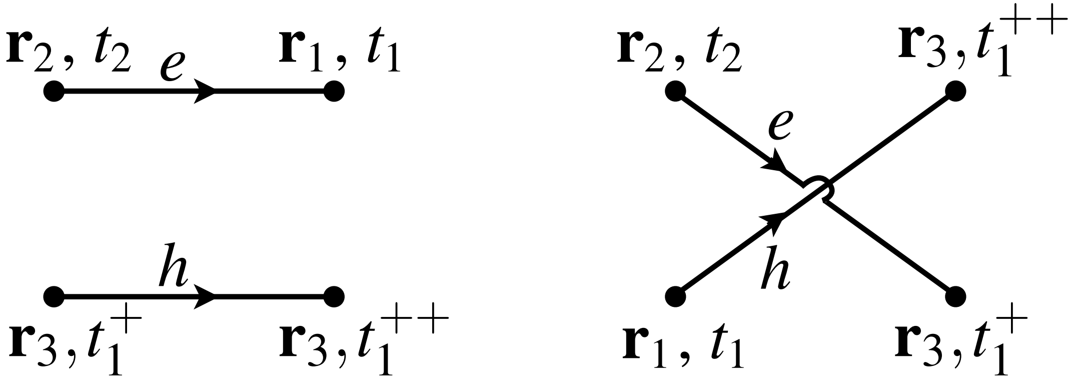
  (ii) some of the larger interaction effects, which produce an effective 1-particle potential, can be included in $\hat{H}_0$

Hartree and Hartree-Fock approximations

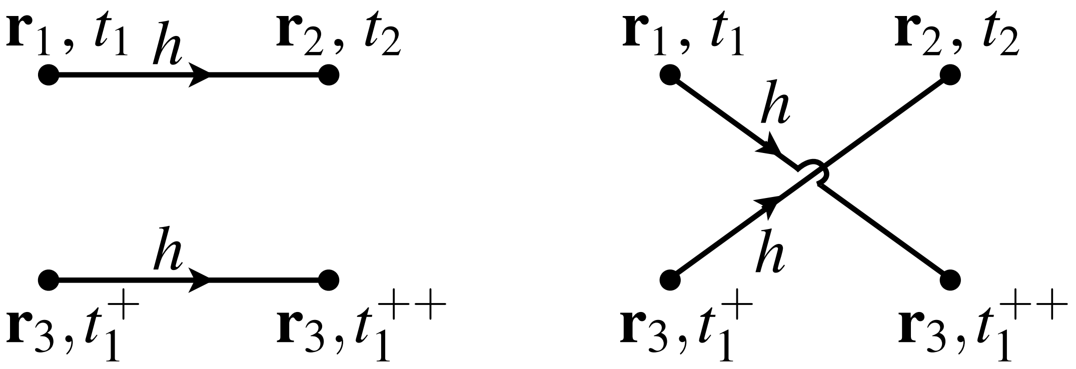
- We first consider the 2-particles Green's function:

$$G_2(1,3;2,3^+)\delta(t_1^+ - t_3) = (i)^2 \langle N,0|T[\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}(\mathbf{r}_3,t_1^+)\hat{\psi}^\dagger(\mathbf{r}_2,t_2)\hat{\psi}^\dagger(\mathbf{r}_3,t_1^{++})]|N,0\rangle$$

(a) $t_1 > t_2$



(b) $t_2 > t_1$



Hartree and Hartree-Fock approximations

- At this stage, we do not know how the 2 particles propagate, but the obvious first choice is to allow each particle to propagate independently according to the 1-particle Green's function.
- Thus, we write:

$$\begin{aligned} G_2(1,3;2,3^+)\delta(t_1^+ - t_3) = \\ \left[G(1,2)G(3,3^+) + G(1,3^+)G(3,2)\right]\delta(t_1^+ - t_3) \end{aligned}$$

The first term is the so-called **direct term** and the second one is the **exchange term**.

Hartree and Hartree-Fock approximations

- We first consider the direct term as an approximation to the 2-particles Green's function:

$$G_2(1,3;2,3^+)\delta(t_1^+ - t_3) = G(1,2)G(3,3^+)\delta(t_1^+ - t_3)$$

The equation of motion becomes:

$$\left\{\left[i\frac{\partial}{\partial t_1} - \hat{H}_0(\mathbf{r}_1)\right] + i\int d3\, v(1^+,3)G(3,3^+)\right\}G(1,2) = \delta(1,2)$$

- It is degenerated into a simple independent-particle like equation with an added potential, which nothing but the Hartree potential:

$$V_{\mathrm{H}}(1) = -i\int d3\, v(1^+,3)G(3,3^+) = \int \frac{n(\mathbf{r}_3,t_1)}{\mathbf{r}_1 - \mathbf{r}_3}d\mathbf{r}_3$$

$$\left[i\frac{\partial}{\partial t_1} - \hat{H}_0(\mathbf{r}_1) - V_{\mathrm{H}}(1)\right]G(1,2) = \delta(1,2)$$

Hartree and Hartree-Fock approximations

- The next step is to take both the direct and exchange terms as an approximation to the 2-particles Green's function:

$$G_2(1,3;2,3^+)\delta(t_1^+ - t_3) = \left[G(1,2)G(3,3^+) + G(1,3^+)G(3,2)\right]\delta(t_1^+ - t_3)$$

- The direct term obviously gives the Hartree potential again, so the equation of motion becomes:

$$\left[i\frac{\partial}{\partial t_1} - \hat{H}_0(\mathbf{r}_1) - V_{\mathrm{H}}(1)\right]G(1,2) + i\int d3\, v(1^+,3)G(1,3^+)G(3,2) = \delta(1,2)$$

- The interaction term is now a non-local operator. It can be shown that it is the Green's function variation of the exchange interaction appearing in the Hartree-Fock approximation.

The self-energy

- The obvious next step would be to carry on like this with the 3-particles Green's function, and so on... but this becomes rapidly far too difficult.
- The trick is to assume that we have solved the infinite series of equations of motions and to look for a solution in the form:

$$\left[i\frac{\partial}{\partial t_1} - \hat{H}_0(\mathbf{r}_1) - V(1)\right] G(1,2) - i\int d3\, \Sigma(1,3)G(3,2) = \delta(1,2)$$

  where $V(1) = \phi(1) + V_{\mathrm{H}}(1)$ with $\phi(1)$ being any external potential such as an experimental probe (that will be made equal to zero at the end).
- The operator Σ is called the **self-energy operator**. It includes all the interaction effects.

The self-energy

- To understand the physical meaning of the self-energy operator, we transform the equation of motion in the energy domain:

$$[\omega - \hat{H}_0(\mathbf{r}_1) - V(\mathbf{r}_1,\omega)]G(\mathbf{r}_1,\mathbf{r}_2,\omega) \\ - \int \Sigma(\mathbf{r}_1,\mathbf{r}_3;\omega)G(\mathbf{r}_3,\mathbf{r}_2;\omega)d\mathbf{r}_3 = \delta(\mathbf{r}_1 - \mathbf{r}_2)$$

  or adopting a matrix notation:

$$(\omega\mathbf{1} - \mathbf{H}_0 - \mathbf{V})\mathbf{G} - \Sigma\mathbf{G} = \mathbf{1} \qquad \Rightarrow \mathbf{G}^{-1} = \omega\mathbf{1} - \mathbf{H}_0 - \mathbf{V} - \Sigma$$

- By comparing with the non-interacting (i.e. without Σ) equation:

$$\mathbf{G}_0^{-1} = \omega\mathbf{1} - \mathbf{H}_0 - \mathbf{V}$$

  we can write:

$$\mathbf{G}^{-1} = \mathbf{G}_0^{-1} - \Sigma$$

  The poles of G are moved in energy by Σ compared to G_0.

Dyson's equation

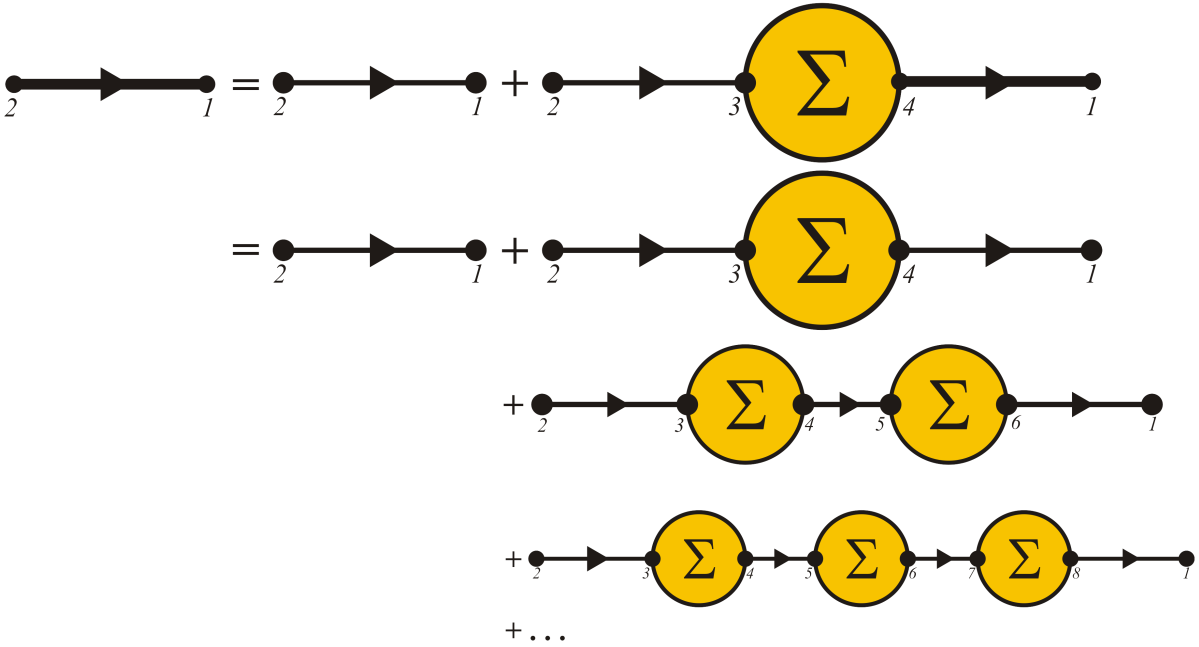
- The equation $\mathbf{G}^{-1} = \mathbf{G}_0^{-1} - \Sigma$ can also be written as:

$$\mathbf{G} = \mathbf{G}_0 + \mathbf{G}_0 \Sigma \mathbf{G}$$

  which is known as the **Dyson equation**.

- Coming back to the time domain, we get:

$$G(1,2) = G_0(1,2) + \int G_0(1,3)\Sigma(3,4)G(4,2)\mathrm{d}(3,4)$$



Hedin's equations

- We define the **inverse dielectric function** ϵ^{-1} as the change in δV due to a small variation $\delta\phi$ in the external potential:

$$\epsilon^{-1}(1,2) = \frac{\delta V(1)}{\delta\phi(2)}$$

- We can write:

$$V(1) = \phi(1) + \int v(1,3)n(3)d3 \qquad \phi(1) = V(1) - \int v(1,3)n(3)d3$$

$$\delta V(1) = \delta\phi(1) + \int v(1,3)\delta n(3)d3 \qquad \delta\phi(1) = \delta V(1) - \int v(1,3)\delta n(3)d3$$

$$\epsilon^{-1}(1,2) = \delta(1,2) + \int v(1,3)\underbrace{\frac{\delta n(3)}{\delta\phi(2)}}_{P^{red.}(3,2)}d3 \qquad \epsilon(1,2) = \delta(1,2) - \int v(1,3)\underbrace{\frac{\delta n(3)}{\delta V(2)}}_{P(3,2)}d3$$

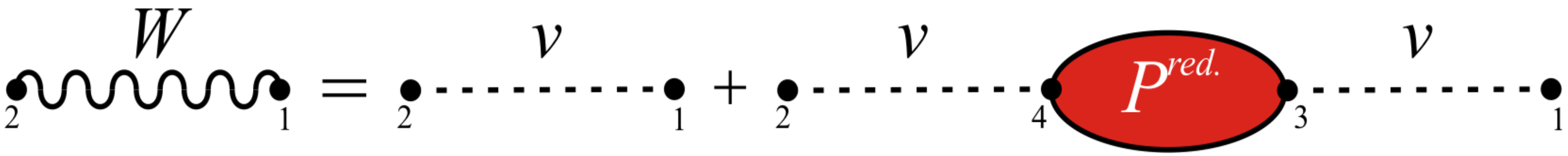
where we have defined the **reducible** and **irreducible polarizability**.

Hedin’s equations

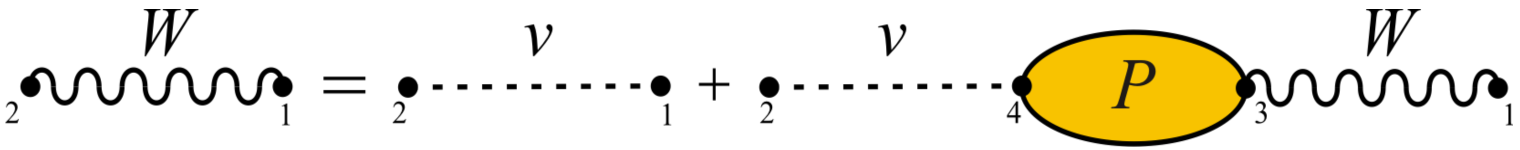
- We also define the **screened Coulomb potential** W :

$$W(1,2) = \int \epsilon^{-1}(1,3)v(3,2)d3$$

$$W(1,2) = v(1,2) + \int v(1,3)P^{red.}(3,4)v(4,2)d(3,4)$$



$$W(1,2) = v(1,2) + \int v(1,3)P(3,4)W(4,2)d(3,4)$$



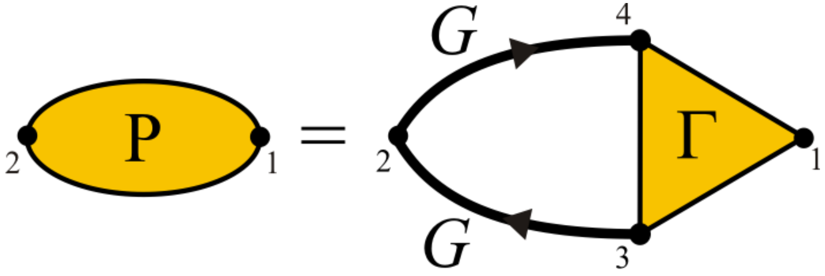
Hedin's equations

- The expression of the irreducible polarizability

$$P(1,2) = \frac{\delta n(1)}{\delta V(2)} = -i\frac{\delta G(1,1^+)}{\delta V(2)}$$

can be worked out to lead to:

$$P(1,2) = i\int G(2,3)\underbrace{\frac{\delta G^{-1}(3,4)}{\delta V(1)}}_{-\Gamma(3,4,1)}G(4,2^+)d(3,4)$$



where we have defined the **vertex function** Γ.

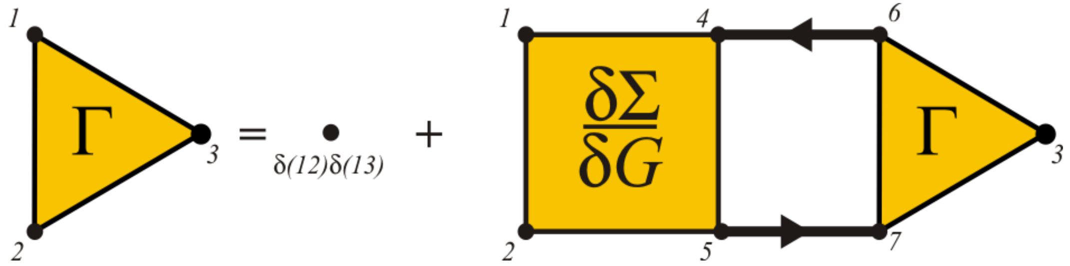
Hedin's equations

- The expression of the vertex function can also be rewritten using:

$$\Gamma(1,2,3) = -\frac{\delta G^{-1}(1,2)}{\delta V(3)} = -\frac{\delta G_0^{-1}(1,2)}{\delta V(3)} + \frac{\Sigma(1,2)}{\delta V(3)}$$

and, after some mathematics, we get:

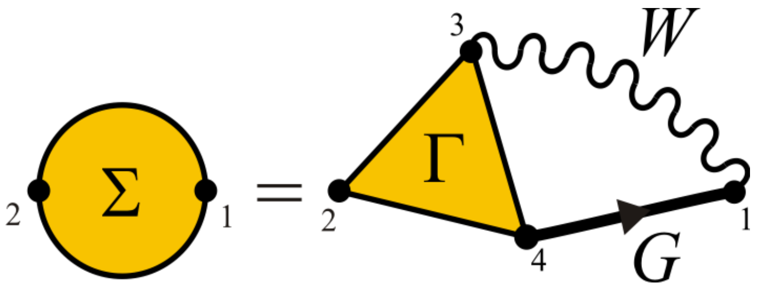
$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Gamma(6,7,3)d(4,5,6,7)$$



Hedin's equations

- Finally, after some more mathematics, an expression can be obtained for the self-energy:

$$\Sigma(1,2) = i\int G(1,4)W(1^+,3)\Gamma(4,2,3)d(3,4)$$



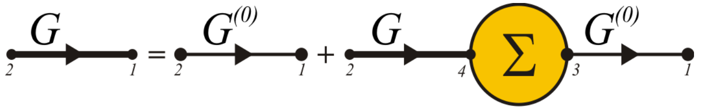
- Using W instead of V is a critical to achieve a converging series. It was the key finding of Hedin.

- Note that in the Hartree-Fock self-energy is simply given by:

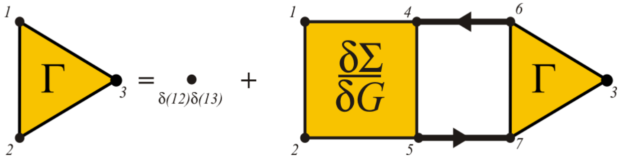
$$\Sigma(1,2) = iG(1,2)v(1,2^+)$$

Hedin's equations

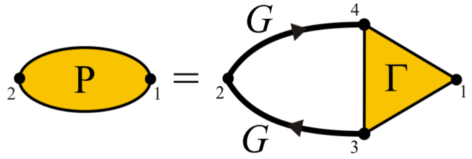
$$G(1,2) = G_0(1,2) + \int G_0(1,3)\Sigma(3,4)G(4,2)\mathrm{d}(3,4)$$



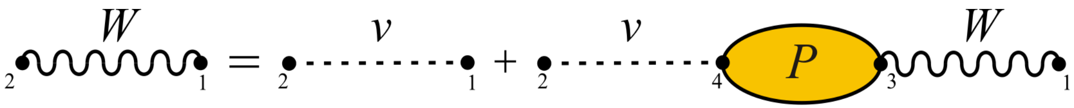
$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Gamma(6,7,3)d(4,5,6,7)$$



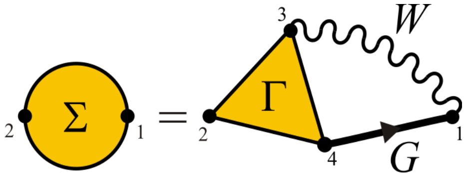
$$P(1,2) = -i \int G(2,3)\Gamma(3,4,1)G(4,2^+)d(3,4)$$



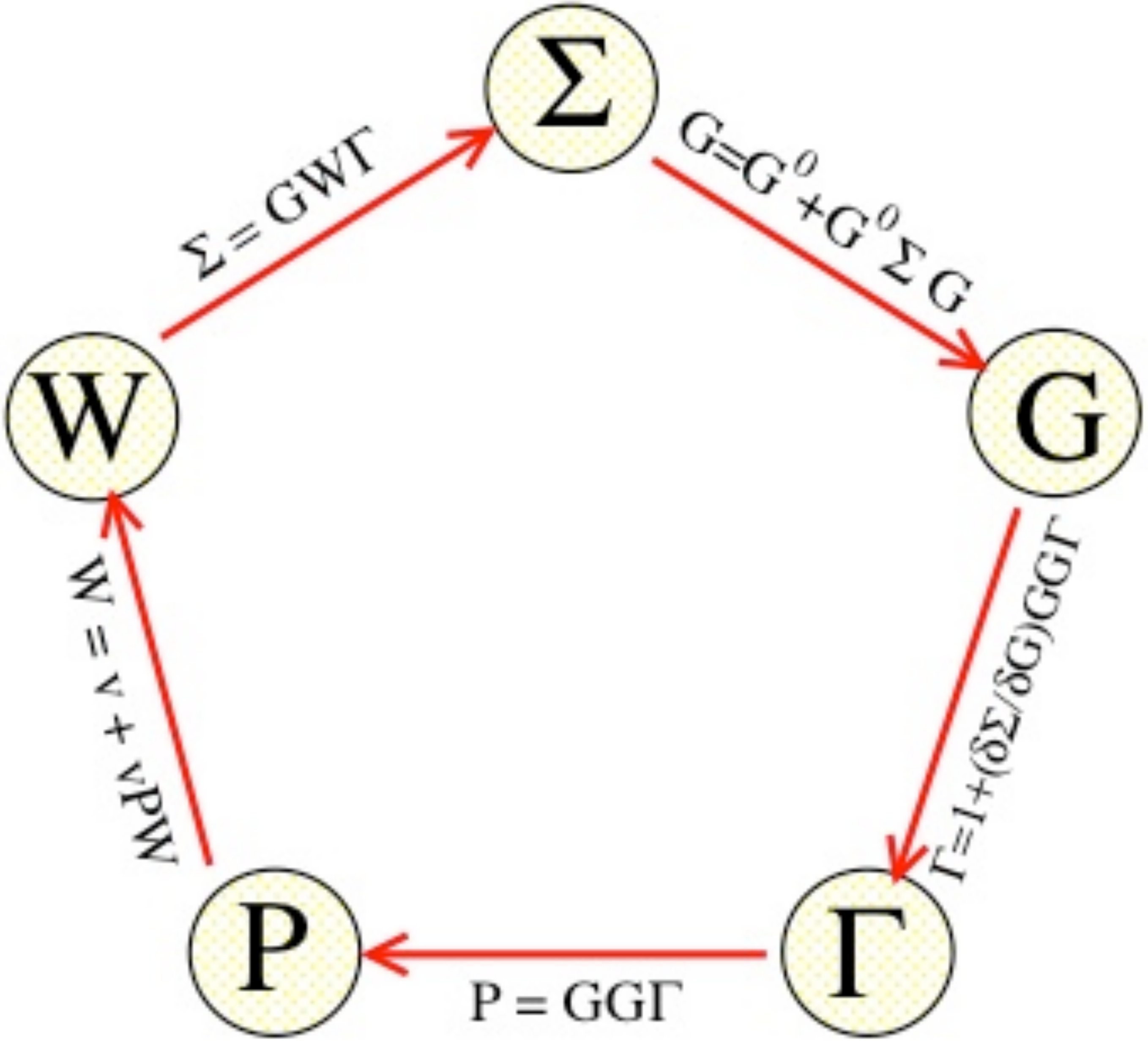
$$W(1,2) = v(1,2) + \int v(1,3)P(3,4)W(4,2)d(3,4)$$



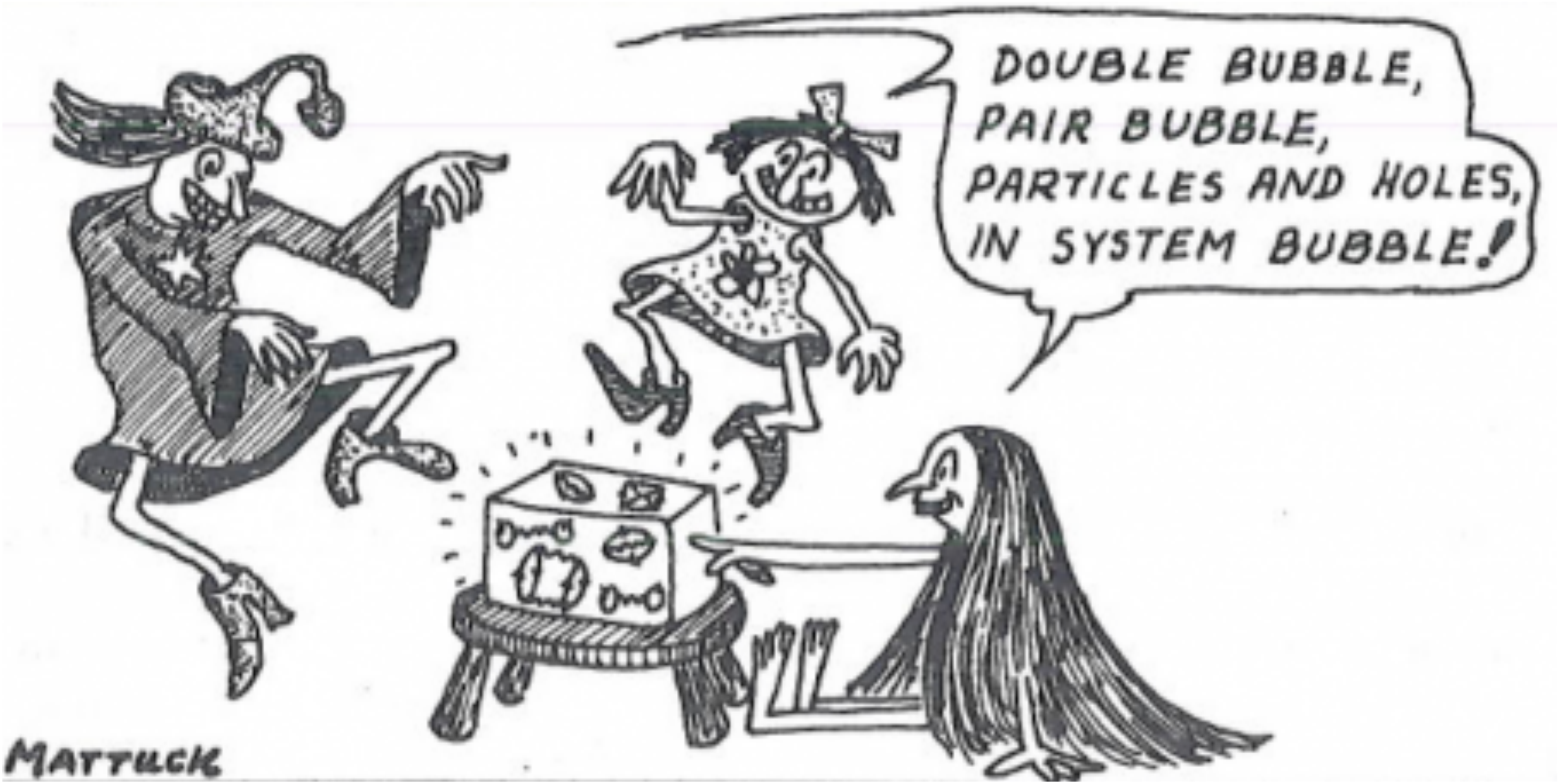
$$\Sigma(1,2) = i \int G(1,4)W(1^+,3)\Gamma(4,2,3)d(3,4)$$



Hedin’s equations



Many-Body Perturbation Theory



[From Richard Mattuck's "Guide to Feynman Diagrams in the Many-Body Problem"]

GW approximation

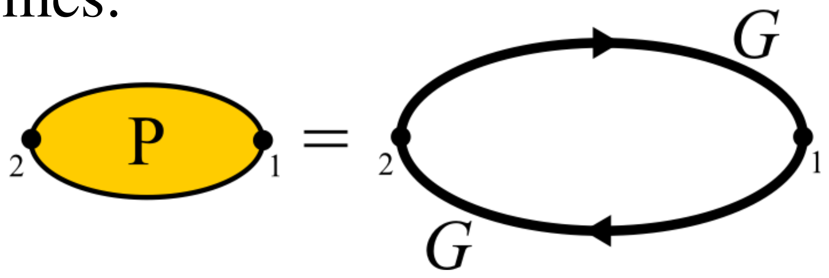
GW approximation

- In order to solve the Hedin's equations, one possible strategy could be to start from the top of the pentagon, with Σ=0.
- The 1-particle Green's function simply reduces to G_0.
- The vertex function is thus:

$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3)$$

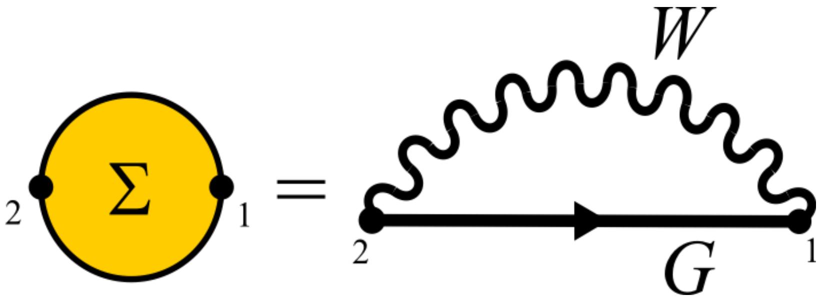
and the irreducible polarizability becomes:

$$P(1,2) = -iG(1,2)G(2,1)$$



- Finally, the self-energy writes:

$$\Sigma(1,2) = iG(1,2)W(1,2^+)$$



hence the name of the approximation.

GW vs. Hartree-Fock approximation

Screened Coulomb interaction

$$W(1,2) = \int \frac{\epsilon^{-1}(\mathbf{r}_3, \mathbf{r}_2, t_1 - t_2)}{|\mathbf{r}_1 - \mathbf{r}_3|} d\mathbf{r}_3$$

GW self-energy

$$\begin{aligned} \Sigma &= i\mathbf{G}\mathbf{W} \\ &= i\mathbf{G}\mathbf{v} + i\mathbf{G}(\mathbf{W} - \mathbf{v}) \\ &= \Sigma_x + \Sigma_c(\omega) \end{aligned}$$

non-local

non-hermitian dynamic

Coulomb interaction

$$v(1,2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\delta(t_1 - t_2)$$

Hartree-Fock self-energy

$$\Sigma = i\mathbf{G}\mathbf{v}$$

non-local

hermitian static

Practical *GW* approximation

- Usually, we start from independent-particle Green function G^0 provided by DFT solving the Kohn-Sham equation:

$$G_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_{n\mathbf{k}} \frac{\phi_{n\mathbf{k}}^{\mathrm{KS}}(\mathbf{r}_1) \left[\phi_{n\mathbf{k}}^{\mathrm{KS}}(\mathbf{r}_2)\right]^*}{\omega - \varepsilon_{n\mathbf{k}}^{\mathrm{KS}} + i\eta \,\mathrm{sgn}(\varepsilon_{n\mathbf{k}}^{\mathrm{KS}} - \mu)}$$

where μ is chemical potential and η a positive infinitesimal.

- The irreducible polarizability is given by the **independent-particle** or **Random Phase Approximation** (RPA) **polarizability**:

$$P_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = \frac{-i}{2\pi} \int G_0(\mathbf{r}_1, \mathbf{r}_2, \omega - \omega') G_0(\mathbf{r}_2, \mathbf{r}_1, \omega) e^{-i\eta\omega'} d\omega'$$

$$P_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_{n\mathbf{k}, m\mathbf{k}'} (f_{n\mathbf{k}} - f_{m\mathbf{k}'}) \frac{\phi_{n\mathbf{k}}^{\mathrm{KS}}(\mathbf{r}_1)[\phi_{m\mathbf{k}'}^{\mathrm{KS}}(\mathbf{r}_1)]^*[\phi_{n\mathbf{k}}^{\mathrm{KS}}(\mathbf{r}_2)]^*\phi_{m\mathbf{k}'}^{\mathrm{KS}}(\mathbf{r}_2)}{\omega - (\varepsilon_{n\mathbf{k}}^{\mathrm{KS}} - \varepsilon_{m\mathbf{k}'}^{\mathrm{KS}}) - i\eta \,\mathrm{sgn}(\varepsilon_{n\mathbf{k}}^{\mathrm{KS}} - \varepsilon_{m\mathbf{k}'}^{\mathrm{KS}})}$$

$$\varepsilon(\mathbf{r}_1, \mathbf{r}_2, \omega) = \delta(\mathbf{r}_1, \mathbf{r}_2) - \int \frac{P_0(\mathbf{r}_1, \mathbf{r}_3, \omega)}{|\mathbf{r}_3 - \mathbf{r}_2|} d\mathbf{r}_3$$

Practical *GW* approximation

- The screened Coulomb interaction is given by:

$$W_0(\mathbf{r}_1,\mathbf{r}_2,\omega) = \int \frac{\varepsilon^{-1}(\mathbf{r}_3,\mathbf{r}_2,\omega)}{|\mathbf{r}_1-\mathbf{r}_3|} d\mathbf{r}_3$$

- Finally, the self-energy is given by:

$$\Sigma(\mathbf{r}_1,\mathbf{r}_2,\omega) = \frac{i}{2\pi}\int G_0(\mathbf{r}_1,\mathbf{r}_2,\omega-\omega')W_0(\mathbf{r}_1,\mathbf{r}_2,\omega)e^{-i\eta\omega'}d\omega'$$

- In principle, this process should be iterated until full self-consistent resolution of Hedin's equations is reached.

- In practice, this is very cumbersome...

- Often, real calculations stop after one round.
  This is the **non-self-consistent *GW* approximation** or **G_0W_0 approximation**.

Quasiparticle equation

- Often, rather than computing the 1-particle Green's function, we try to solve the **quasiparticle equation**:

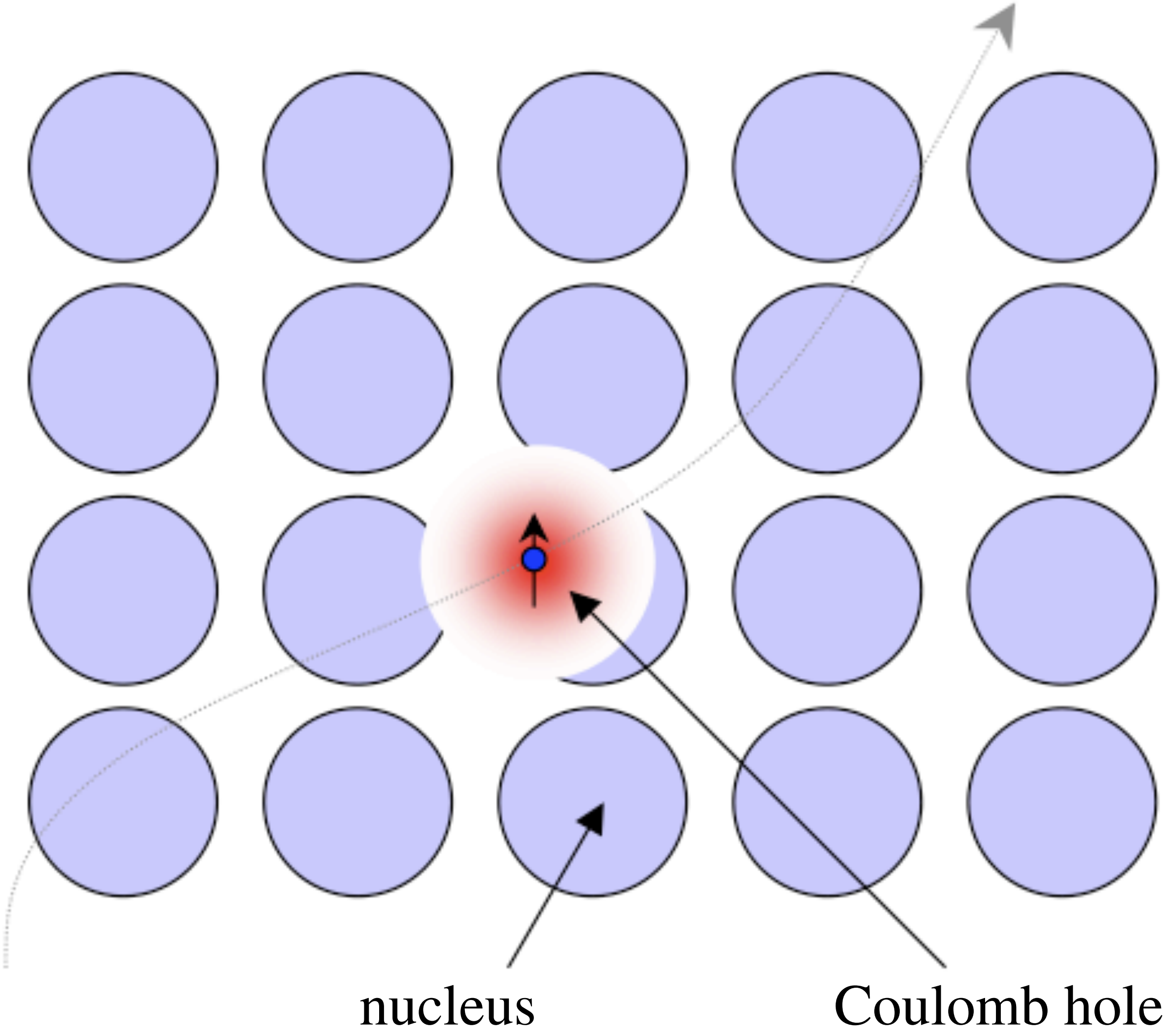
$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}_1} + V_{\text{ext}}(\mathbf{r}_1) + V_{\text{H}}(\mathbf{r}_1)\right]\phi_{n\mathbf{k}}(\mathbf{r}_1,\omega) + \int \Sigma(\mathbf{r}_1,\mathbf{r}_2,\omega)\,\phi_{n\mathbf{k}}(\mathbf{r}_2,\omega)d\mathbf{r}_2 = \varepsilon_{n\mathbf{k}}(\omega)\phi_{n\mathbf{k}}(\mathbf{r}_1,\omega)$$

  for $\omega{=}\varepsilon_{n\mathbf{k}}(\omega)$.

- In general, the eigenvalues $\varepsilon_{n\mathbf{k}}$ are complex. Their real part can be interpreted as a quasiparticle energy $\varepsilon^{\text{QP}}_{n\mathbf{k}}$ whereas their imaginary part is related to the lifetime of the quasiparticle: $\text{Im}\ \varepsilon_{n\mathbf{k}}(\omega) = 1/\tau^{\text{QP}}$

- An intuitive picture of the quasiparticle concept consists in considering that when a "bare" particle (an electron or a hole) enters in a system of interacting electrons, it perturbs the other particles in its neighborhood and hence it gets "dressed" with a charged (positive or negative) cloud and hence becomes a quasiparticle.

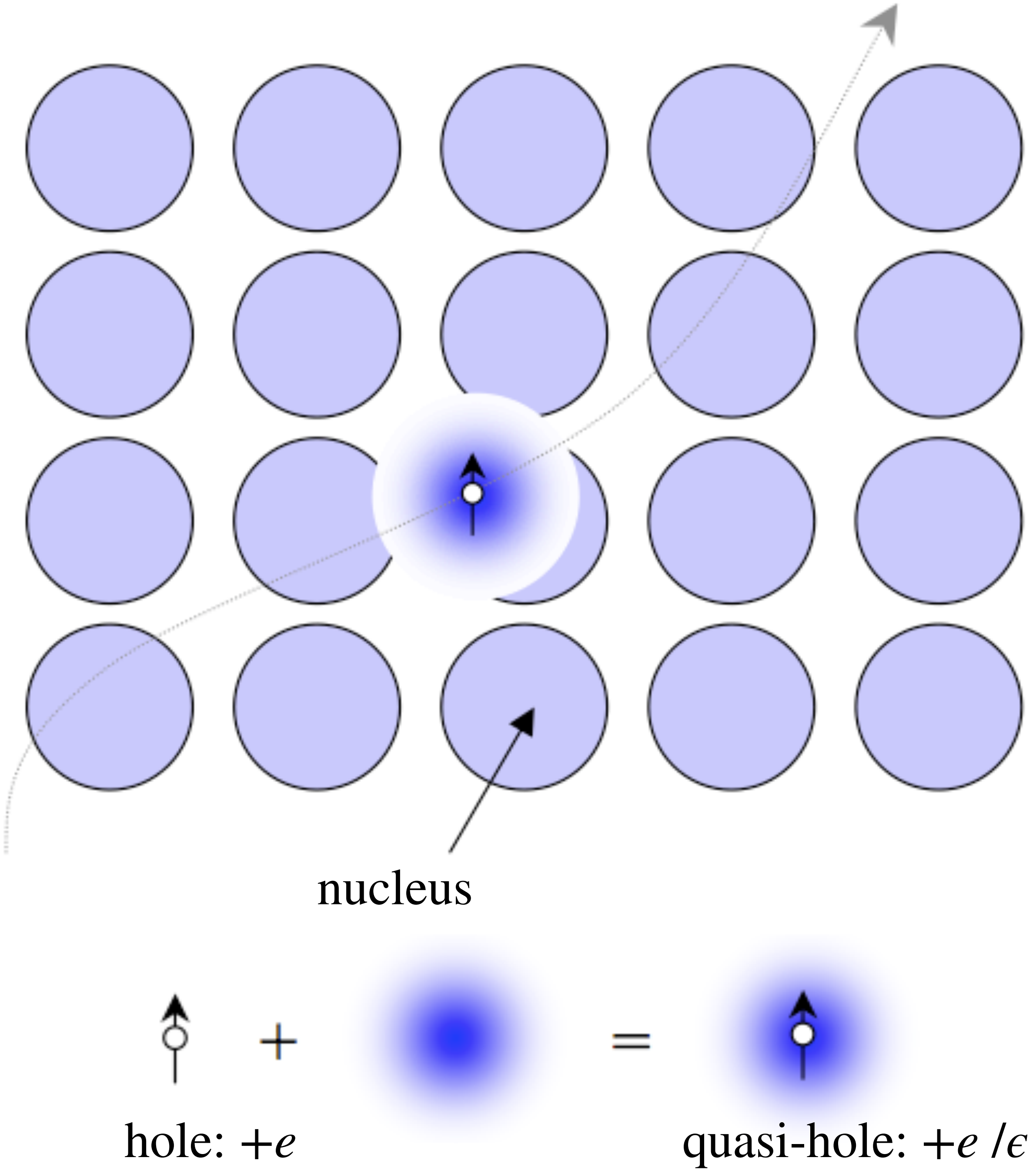
Quasi-electron



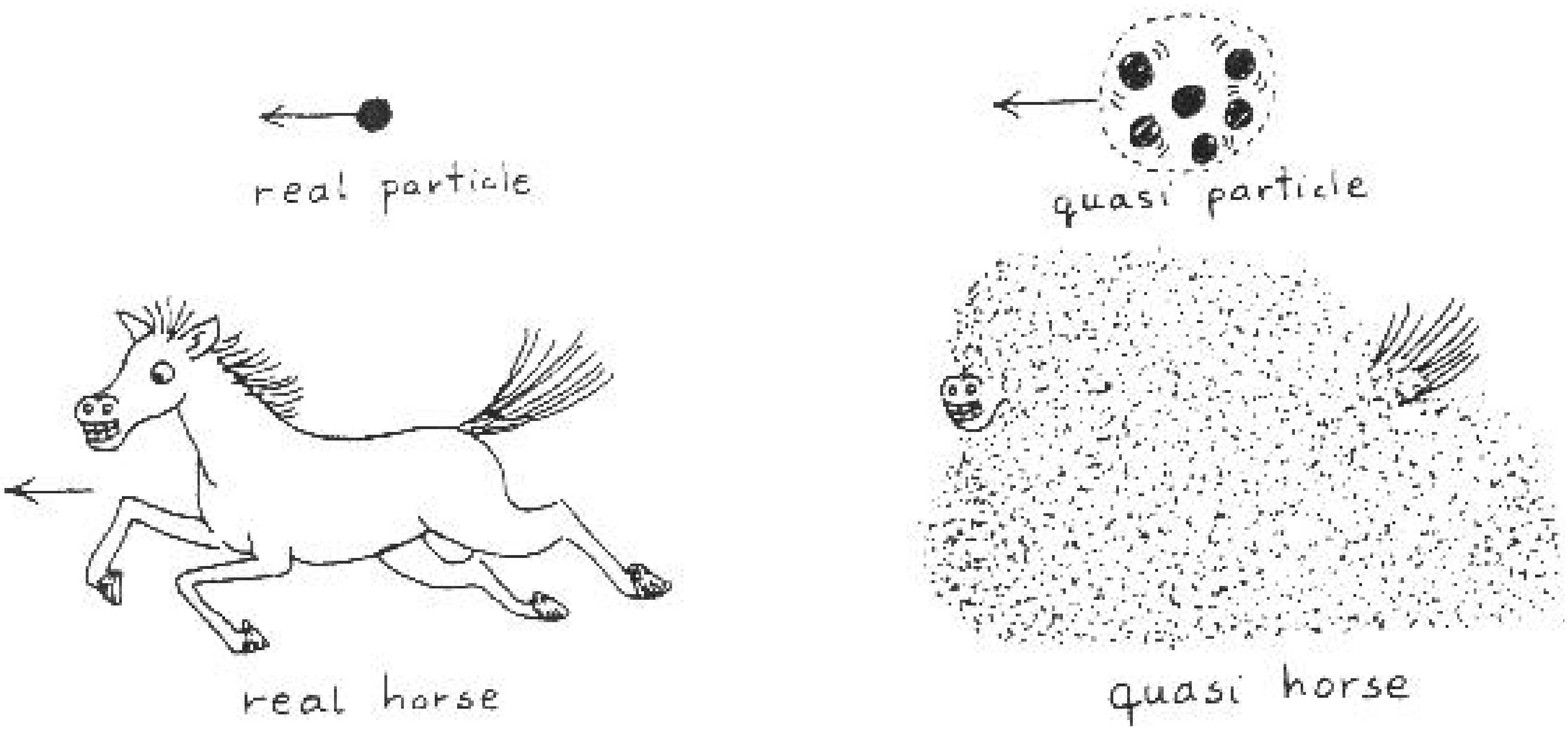
electron: $-e$

quasi-electron: $-e/\epsilon$

Quasi-hole

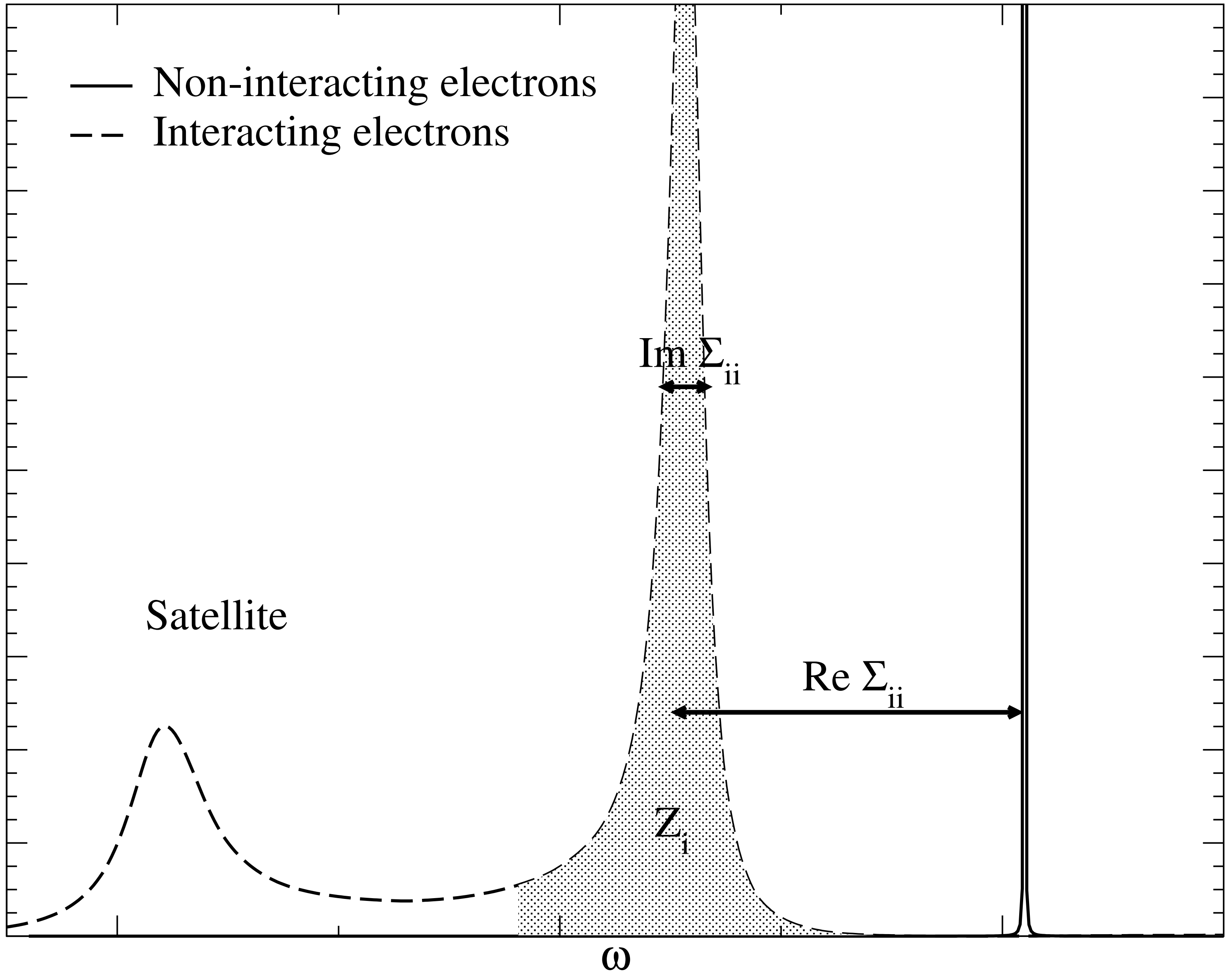


Quasi-horse



[From Richard Mattuck's "Guide to Feynman Diagrams in the Many-Body Problem"]

Spectral function



In practice...

- The similarity between the quasiparticle equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r})\right]\phi_{n\mathbf{k}}^{\text{QP}}(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}',\omega=\varepsilon_{n\mathbf{k}}^{\text{QP}})\,\phi_{n\mathbf{k}}^{\text{QP}}(\mathbf{r}')d\mathbf{r}' = \varepsilon_{n\mathbf{k}}^{\text{QP}}\phi_{n\mathbf{k}}^{\text{QP}}(\mathbf{r})$$

  and the DFT Kohn-Sham one:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r})\right]\phi_{n\mathbf{k}}^{\text{KS}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})\phi_{n\mathbf{k}}^{\text{KS}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}^{\text{KS}}\phi_{n\mathbf{k}}^{\text{KS}}(\mathbf{r})$$

  suggests to treat the difference between Σ and V_{xc} as a perturbation with respect to the Kohn-Sham calculations.

- In fact, the approximation $\phi_{n\mathbf{k}}^{\text{QP}}(\mathbf{r}) \simeq \phi_{n\mathbf{k}}^{\text{KS}}(\mathbf{r})$ is very reasonable for many materials so that we can write:

$$\epsilon_{n\mathbf{k}}^{\text{QP}} = \epsilon_{n\mathbf{k}}^{\text{KS}} + \left\langle \phi_{n\mathbf{k}}^{\text{KS}} \middle| \Sigma(\mathbf{r},\mathbf{r}',\omega=\epsilon_{n\mathbf{k}}^{\text{QP}}) - V_{\text{xc}}(\mathbf{r}) \middle| \phi_{n\mathbf{k}}^{\text{KS}} \right\rangle$$

In practice ...

- Since the self-energy Σ operator depends on the energy:

$$\epsilon_{n\mathbf{k}}^{\mathrm{QP}} = \epsilon_{n\mathbf{k}}^{\mathrm{KS}} + \left\langle \phi_{n\mathbf{k}}^{\mathrm{KS}} \left| \Sigma(\mathbf{r},\mathbf{r}',\omega = \epsilon_{n\mathbf{k}}^{\mathrm{QP}}) - V_{\mathrm{xc}}(\mathbf{r}) \right| \phi_{n\mathbf{k}}^{\mathrm{KS}} \right\rangle$$

this non-linear equation should in principle be solved self-consistently.

In practice, the self-energy operator Σ is linearized:

$$\left\langle \Sigma(\omega = \epsilon_{n\mathbf{k}}^{\mathrm{QP}}) \right\rangle = \left\langle \Sigma(\omega = \epsilon_{n\mathbf{k}}^{\mathrm{KS}}) \right\rangle + \left(\epsilon_{n\mathbf{k}}^{\mathrm{QP}} - \epsilon_{n\mathbf{k}}^{\mathrm{KS}} \right) \left\langle \left. \frac{\partial \Sigma(\omega)}{\partial \omega} \right|_{\omega = \epsilon_{n\mathbf{k}}^{\mathrm{KS}}} \right\rangle$$

- Hence, defining the renormalization constant $Z_{n\mathbf{k}}$ as:

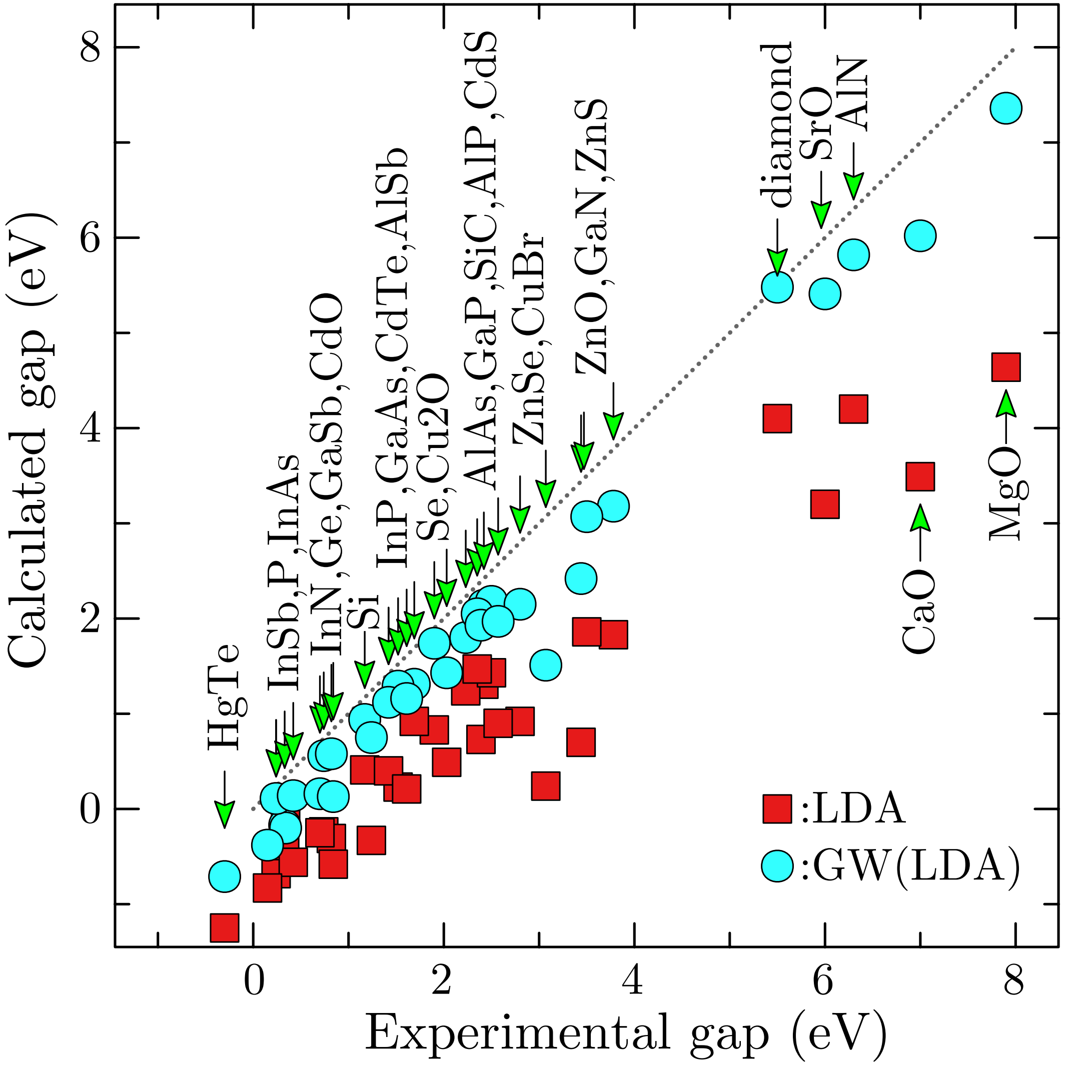
$$Z_{n\mathbf{k}} = \left(1 - \frac{\partial \left\langle \phi_{n\mathbf{k}}^{\mathrm{KS}} \left| \Sigma(\omega) \right| \phi_{n\mathbf{k}}^{\mathrm{KS}} \right\rangle}{\partial \omega} \right)^{-1}$$

the linearized equation to solve becomes:

$$\epsilon_{n\mathbf{k}}^{\mathrm{QP}} = \epsilon_{n\mathbf{k}}^{\mathrm{KS}} + Z_{n\mathbf{k}} \left\langle \phi_{n\mathbf{k}}^{\mathrm{KS}} \left| \Sigma(\mathbf{r},\mathbf{r}',\omega = \epsilon_{n\mathbf{k}}^{\mathrm{KS}}) - V_{\mathrm{xc}}(\mathbf{r}) \right| \phi_{n\mathbf{k}}^{\mathrm{KS}} \right\rangle$$

The band gap within *GW*

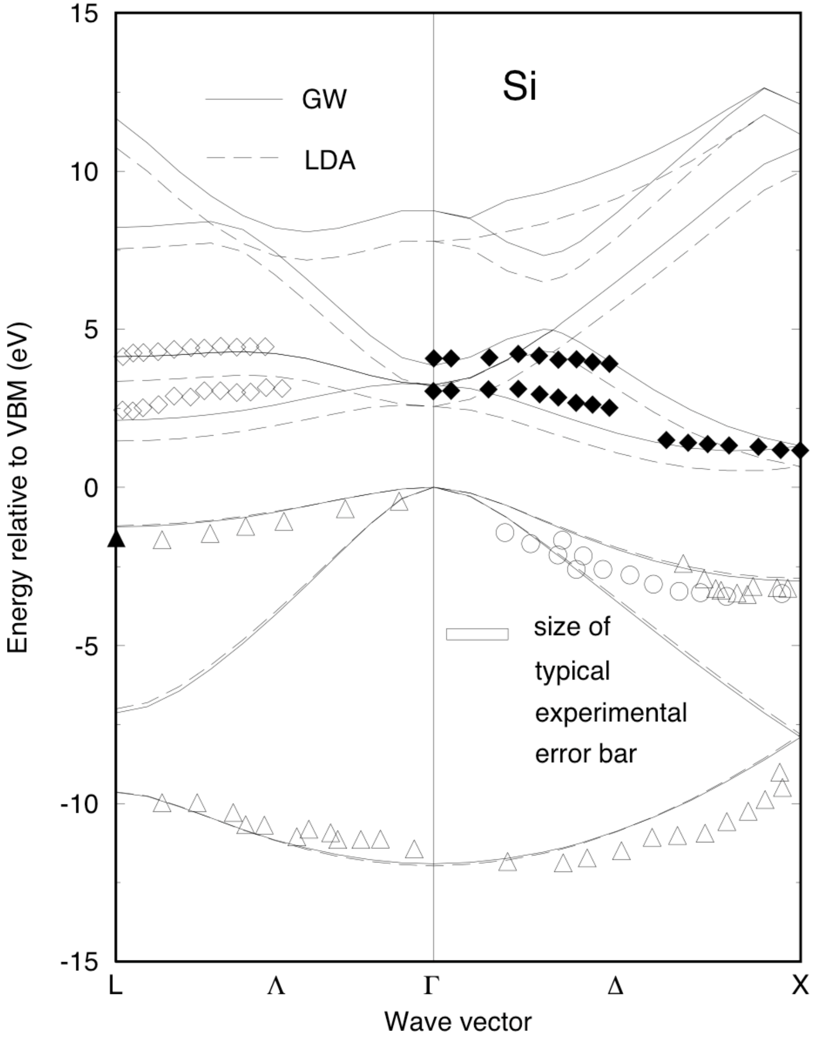
- The agreement with experiments is in much better!



[adapted from van Schilfgaarde *et al.*, PRL **96**, 226402 (2006)]

The band gap within *GW*

- The calculated band structures are in excellent agreement with those measured experimentally.



[from Aulbur *et al.*, Solid State Physics **54**, 1 (2000)]

Self-consitency in the *GW* approximation

- It may happen that the DFT wavefunctions are not adequate, these need to be updated as well in the self-consistent cycle by diagonalizing the self-energy operator. The problem is that the self-energy operator is not hermitian and energy dependent.
- A smart method has thus been devised, the **Quasiparticle Self-consistent GW (QSGW)**, which allows to overcome these problems

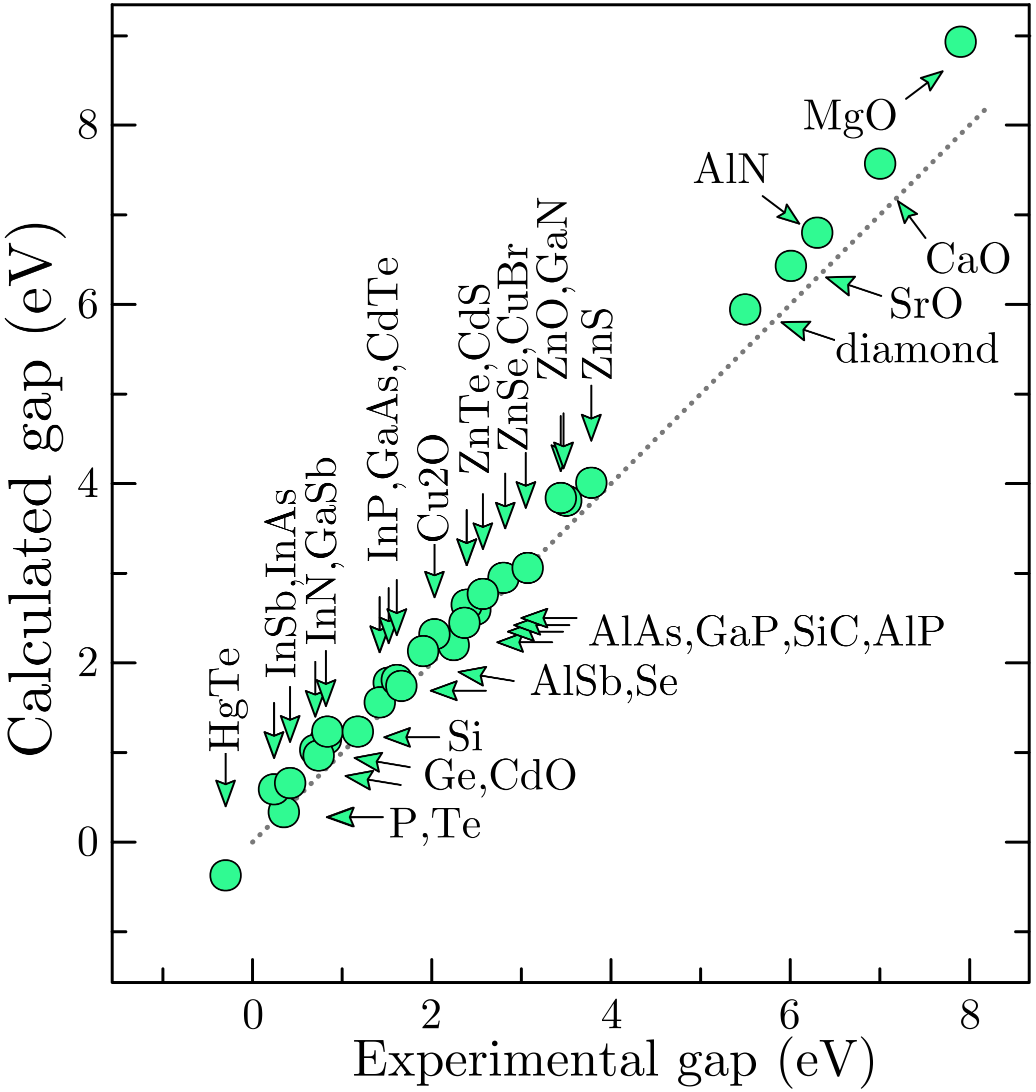
  [S. V. Faleev, M. van Schilfgaarde, and T. Kotani, Phys. Rev. Lett. **93**, 126406 (2004)]:

  $$\langle\phi_i|\Sigma|\phi_j\rangle = \frac{1}{2}\Re\left[\langle\phi_i|\Sigma(\varepsilon_i)|\phi_j\rangle + \langle\phi_i|\Sigma(\varepsilon_j)|\phi_j\rangle\right]$$

  where $\Re$ means that one only retains the hermitian part of the matrix. Along with self-consistency, the diagonal elements of the self-energy are better and better approximations to the true *GW* diagonal terms, as each of them is finally evaluated for the correct *GW* energy.

Self-consitency in the *GW* approximation

- The QS*GW* band gap is slightly bigger than the experimental one.



[adapted from van Schilfgaarde et al., PRL **96**, 226402 (2006)]

Self-consitency in the *GW* approximation

PRL **99,** 246403 (2007) PHYSICAL REVIEW LETTERS week ending 14 DECEMBER 2007

Accurate Quasiparticle Spectra from Self-Consistent *GW* Calculations with Vertex Corrections

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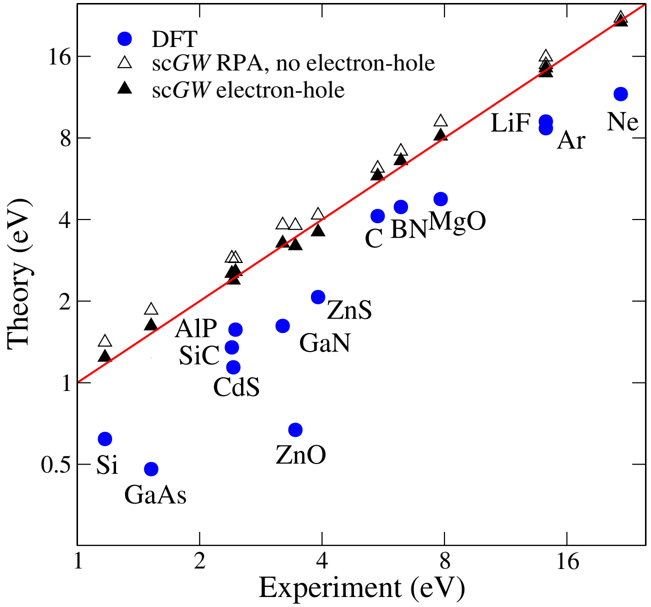
Self-consistent *GW* calculations, maintaining only the quasiparticle part of the Green's function *G*, are reported for a wide class of materials, including small gap semiconductors and large gap insulators. We show that the inclusion of the attractive electron-hole interaction via an effective nonlocal exchange correlation kernel is required to obtain accurate band gaps in the framework of self-consistent *GW* calculations. If these are accounted for via vertex corrections in *W*, the band gaps are found to be within a few percent of the experimental values.



The static screening properties calculated from gradient corrected functionals in the random phase approximation agree very well with the self-consistently determined screening properties in the sc*GW* method. This offers a convenient shortcut and legitimates the often applied GW_0 approximation.

Self-consitency in the *GW* approximation

Self-consistent *GW* calculations for semiconductors and insulators

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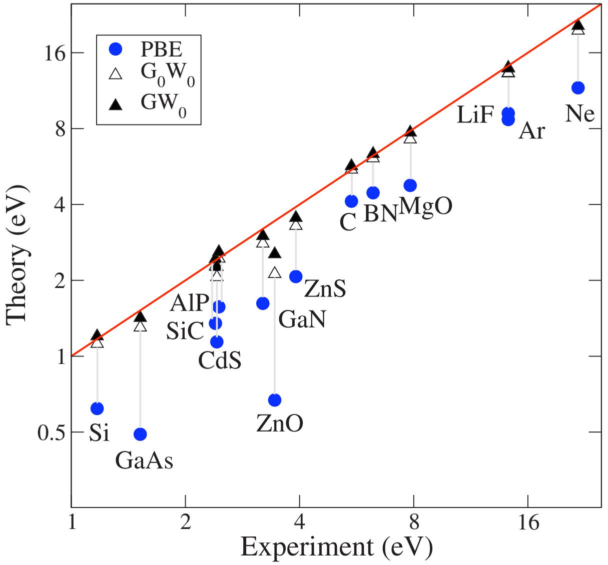
We present *GW* calculations for small and large gap systems comprising typical semiconductors (Si, SiC, GaAs, GaN, ZnO, ZnS, CdS, and AlP), small gap semiconductors (PbS, PbSe, and PbTe), insulators (C, BN, MgO, and LiF), and noble gas solids (Ar and Ne). It is shown that the G_0W_0 approximation always yields too small band gaps. To improve agreement with experiment, the eigenvalues in the Green's function G (GW_0) and in the Green's function and the dielectric matrix (GW) are updated until self-consistency is reached. The first approximation leads to excellent agreement with experiment, whereas an update of the eigenvalues in G and W gives too large band gaps for virtually all materials. From a pragmatic point of view, the GW_0 approximation thus seems to be an accurate and still reasonably fast method for predicting quasiparticle energies in simple *sp*-bonded systems. We furthermore observe that the band gaps in materials with shallow *d* states (GaAs, GaN, and ZnO) are systematically underestimated. We propose that an inaccurate description of the static dielectric properties of these materials is responsible for the underestimation of the band gaps in GW_0, which is itself a result of the incomplete cancellation of the Hartree self-energy within the *d* shell by local or gradient corrected density functionals.



Frequency dependence of *W*

- Within *GW*, the frequency dependence of the dynamically screened Coulomb potential *W* is most often approximated using various plasmon pole models (PPMs):

$$\mathrm{Re}\ \epsilon^{-1}(\omega) = A\delta(\omega - \tilde{\omega}) \qquad \mathrm{Im}\ \epsilon^{-1}(\omega) = 1 + \frac{\Omega^2}{\omega^2 - \tilde{\omega}^2}$$

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  - R.W. Godby and R.J. Needs, Phys. Rev. Lett. 62, 1169 (1989),
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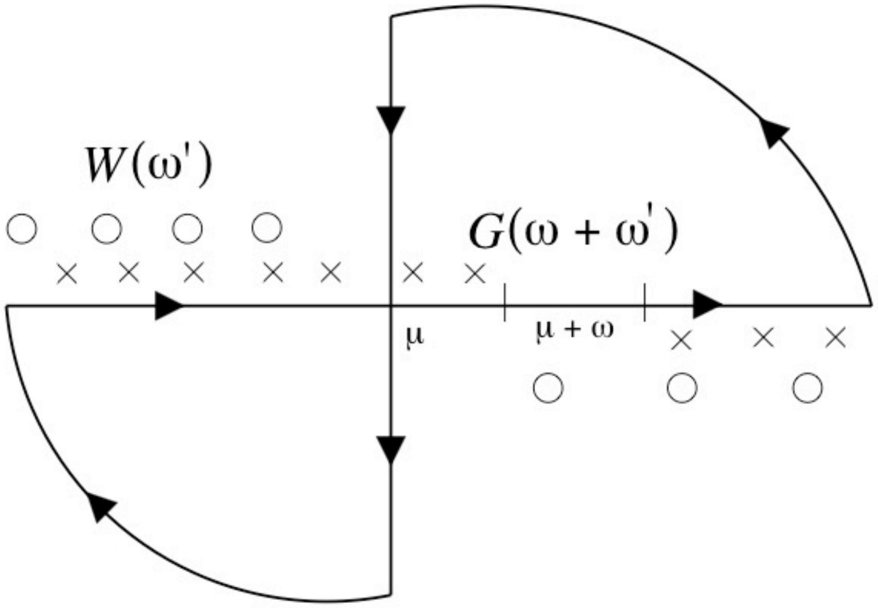
- The advantage is not only to reduce the computational load, but also to obtain an analytic expression for the self-energy.

Frequency dependence of *W*

- Alternatively, the explicit frequency dependence can be obtained using the deformed contour integration technique

  [S. Lebègue, B. Arnaud, M. Alouani and P.E. Bloechl, Phys. Rev. B **67**, 155208 (2003)].

- The integral along the real axis can be calculated from the integral over the contour depicted below: the integral along the imaginary axis requires less points (*Σ* is smoother) and the sum of the poles of *Σ* can be evaluated exactly.



× poles of G

○ poles of W

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