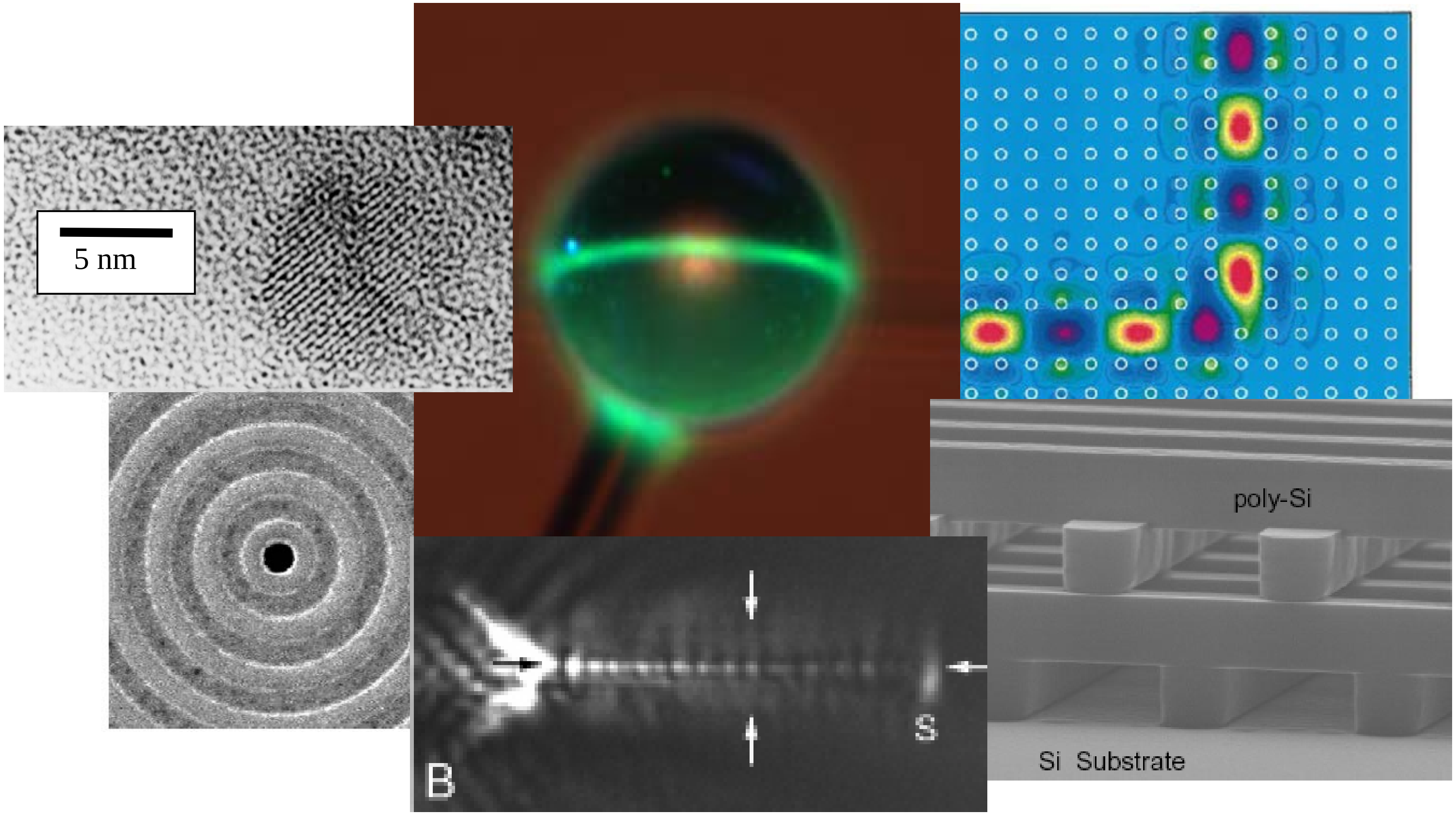
Lecture 3: Optical Properties of Bulk and Nano



Course Info

First H/W#1 is due Sept. 10

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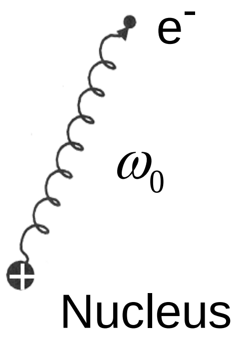
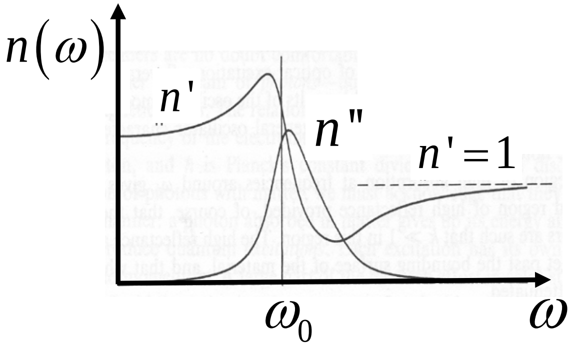
The Previous Lecture

Origin frequency dependence of χ in real materials

- Lorentz model (harmonic oscillator model)





Today optical properties of materials

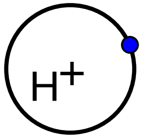
- Insulators (Lattice absorption, color centers…)
- Semiconductors (Energy bands, Urbach tail, excitons …)
- Metals (Response due to bound and free electrons, plasma oscillations..)

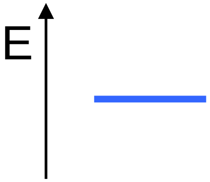
Optical properties of molecules, nanoparticles, and microparticles

Classification Matter: Insulators, Semiconductors, Metals

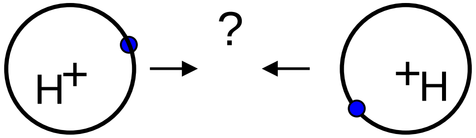
Bonds and bands

- One atom, e.g. H.   Schrödinger equation:

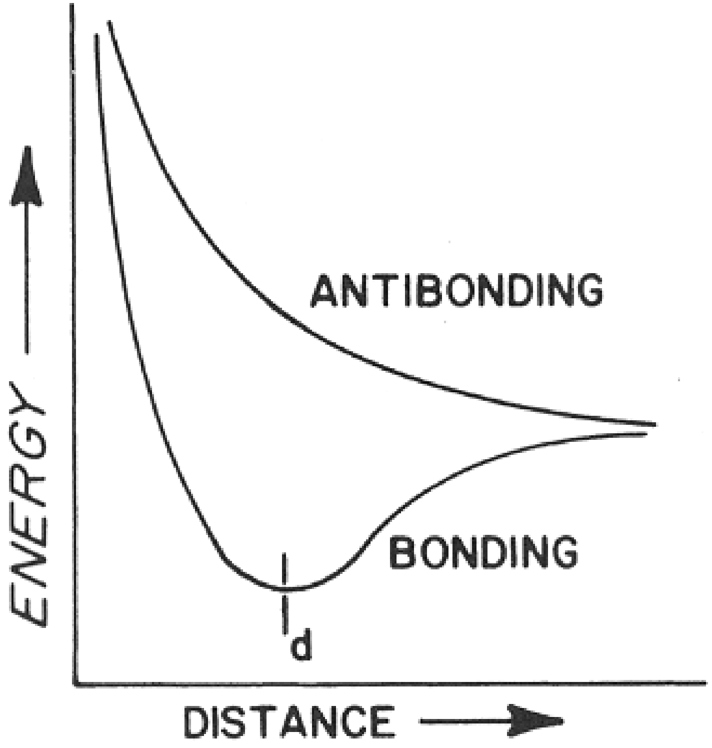




- Two atoms: bond formation

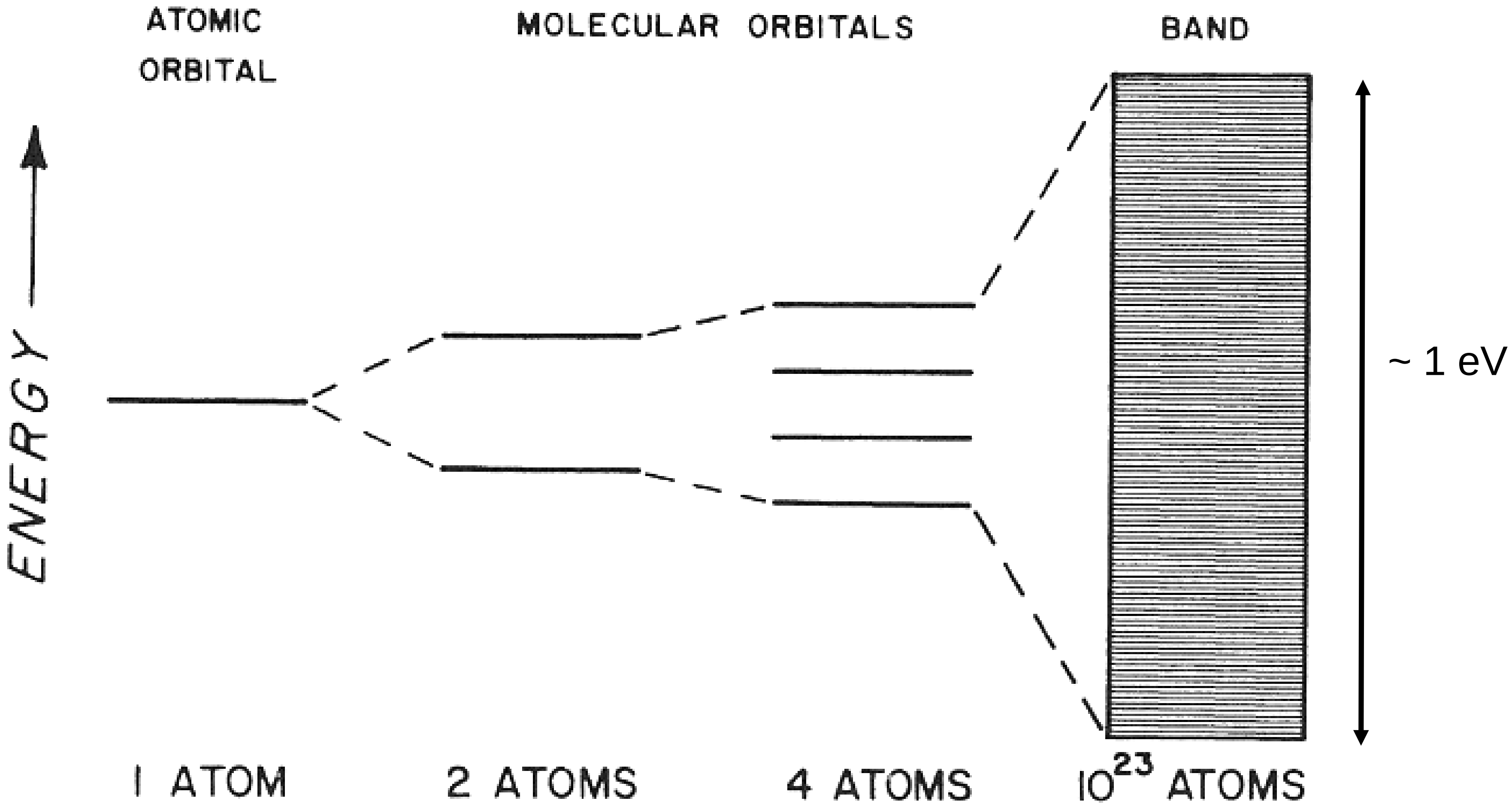


Every electron contributes one state →



- Equilibrium distance d (after reaction)

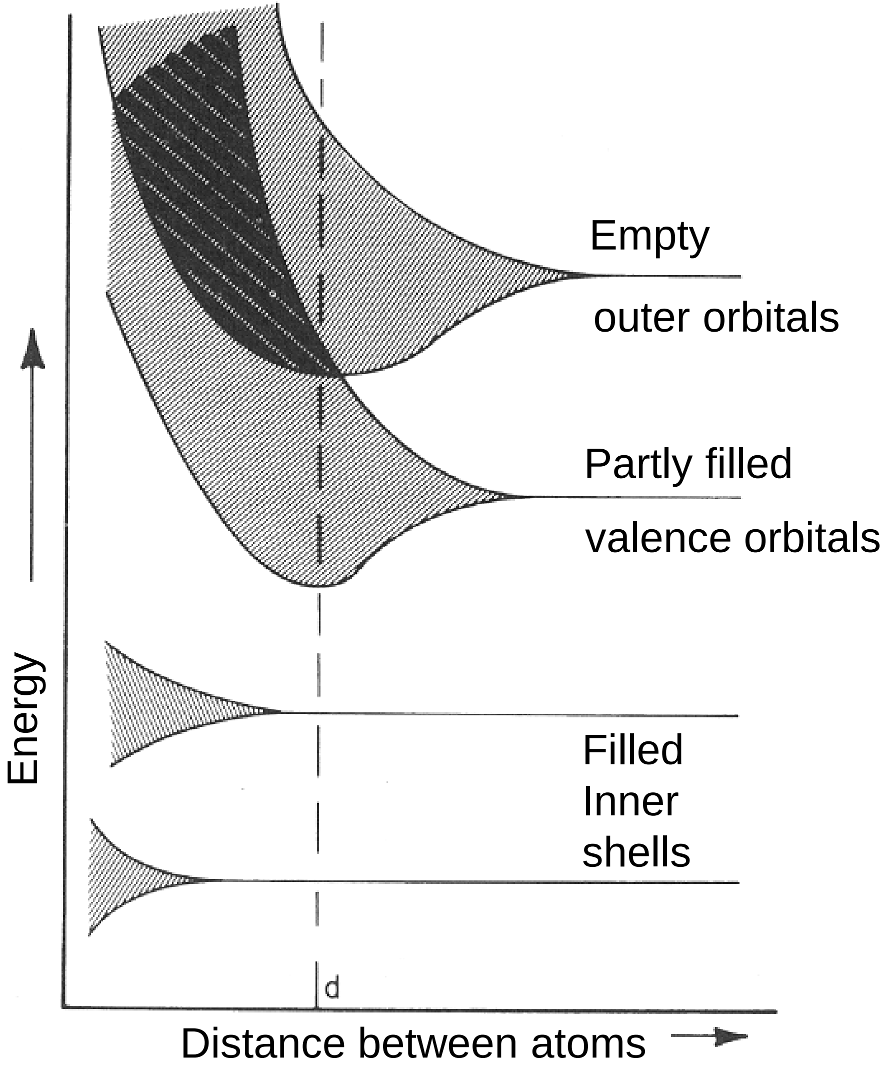
Classification Matter



- Pauli principle: Only 2 electrons in the same electronic state (one spin↑ & one spin↓)

Classification Matter

Atoms with many electrons



Outermost electrons interact

➡ Form bands

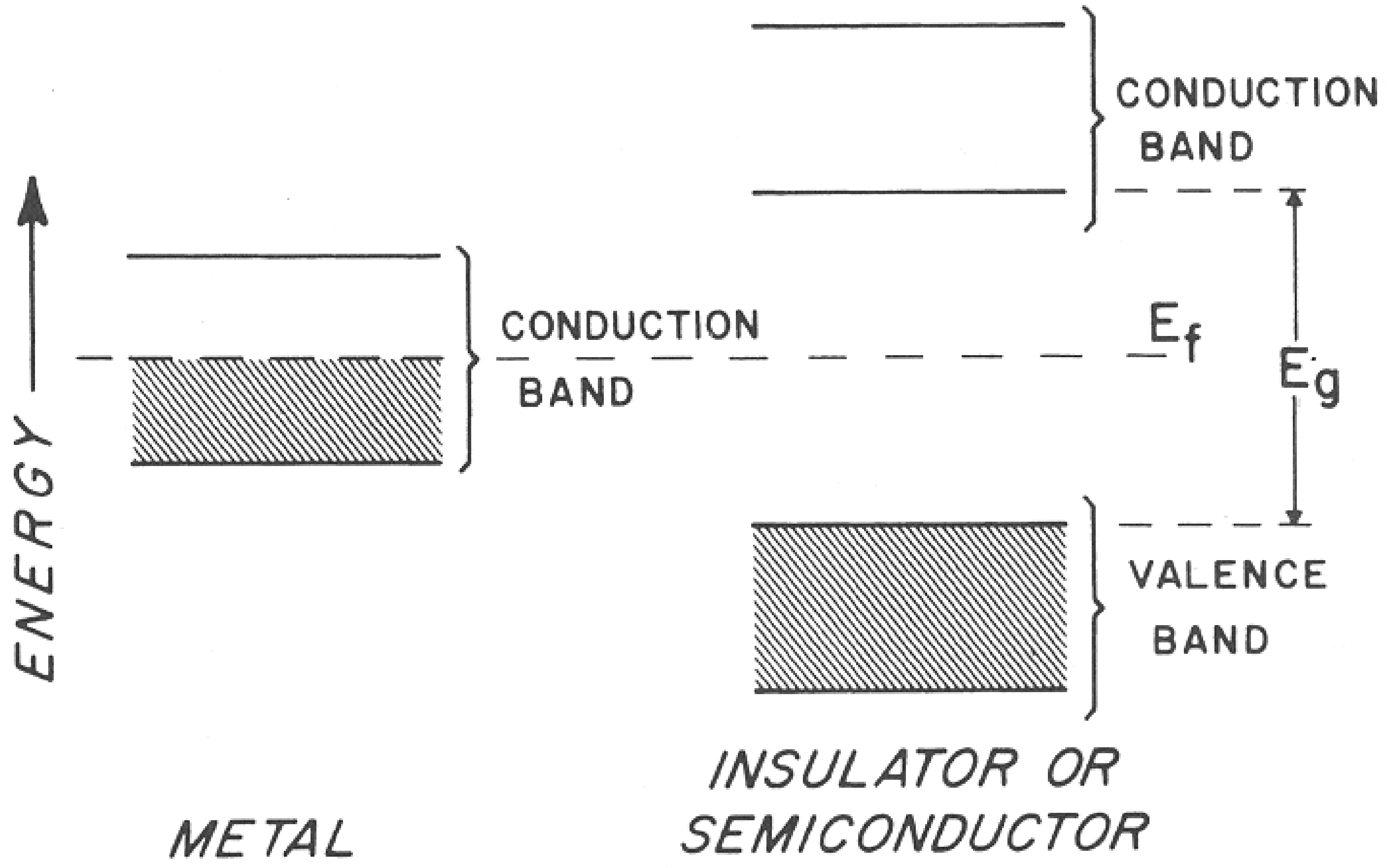
Electrons in inner shells do not interact

➡ Do not form bands

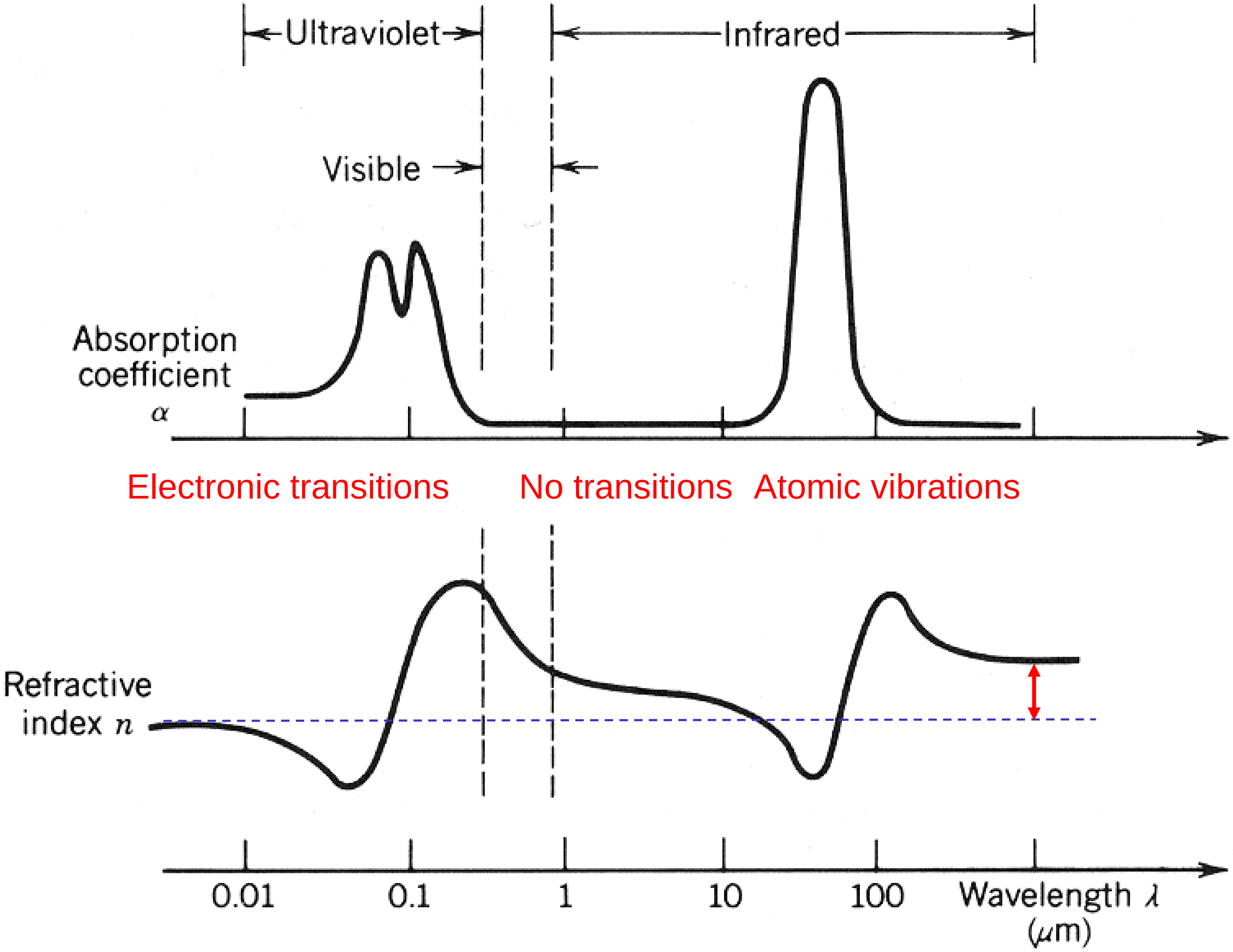
Classification Matter

Insulators, semiconductors, and metals

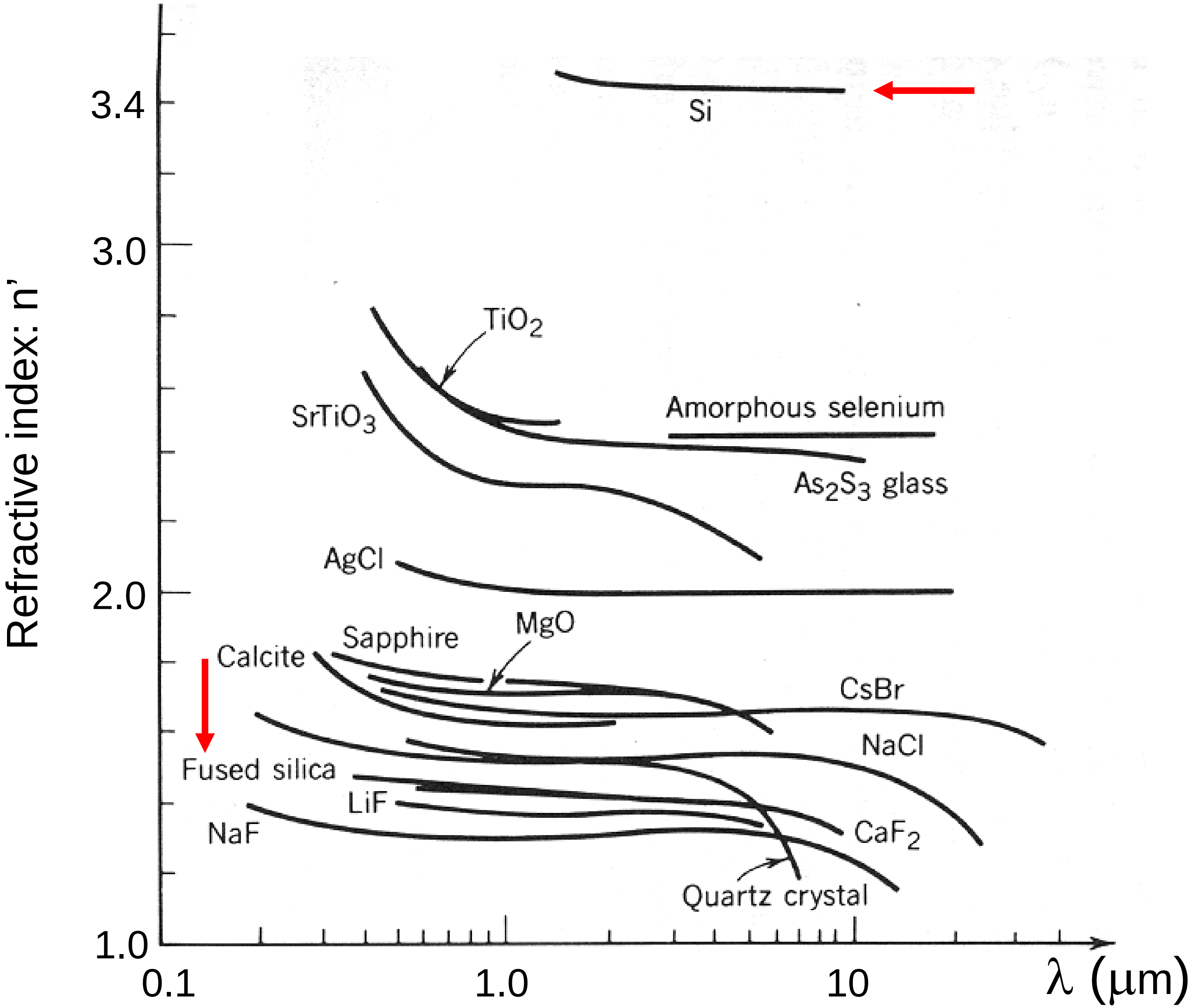
- Classification based on bandstructure



Dispersion and Absorption in Insulators



Refractive Index Various Materials

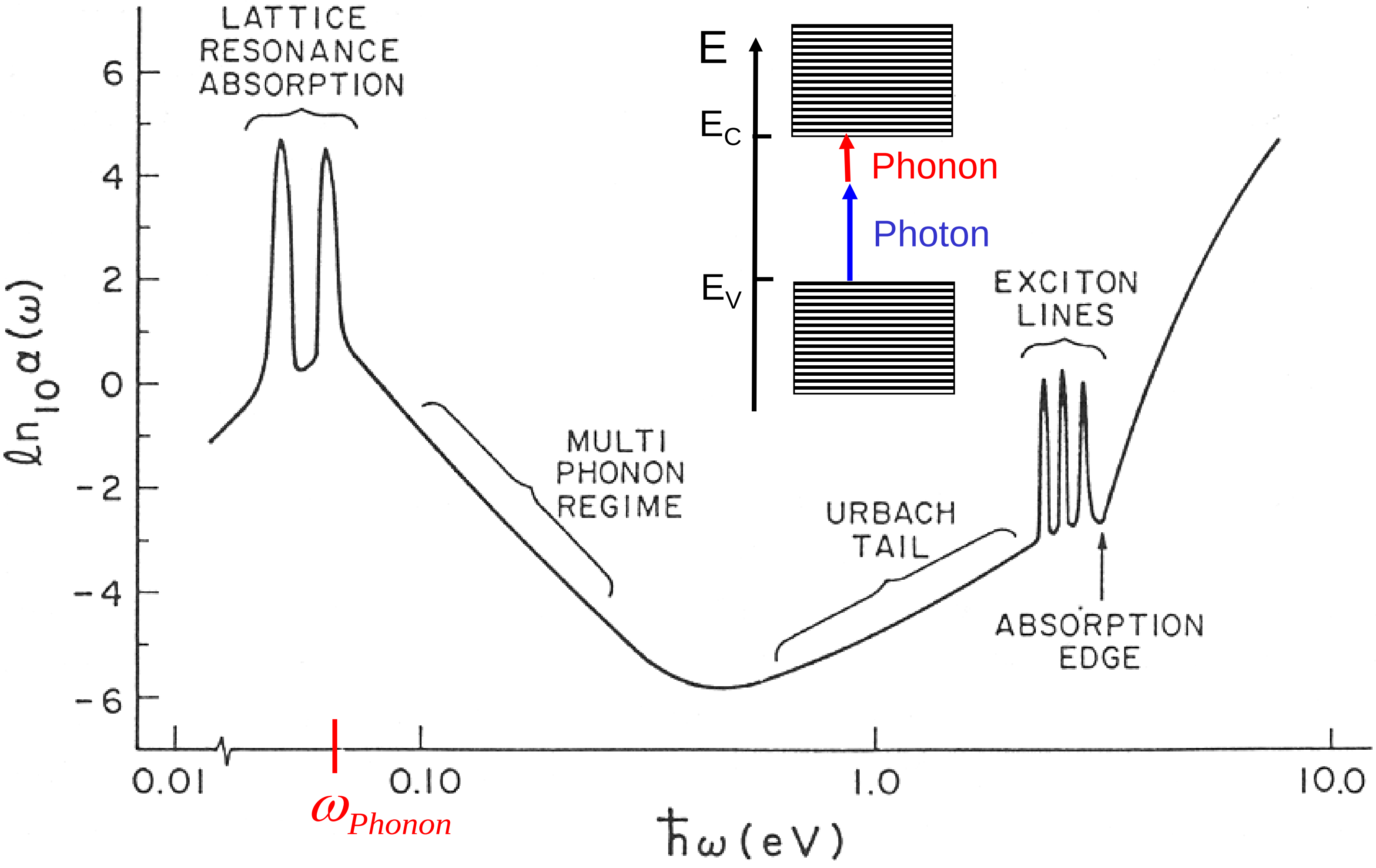


Color Centers

- Insulators with a large E_{GAP} should not show absorption…..or ?
- Ion beam irradiation or x-ray exposure result in beautiful colors!
- Due to formation of color (absorption) centers….(Homework assignment)

Absorption Processes in Semiconductors

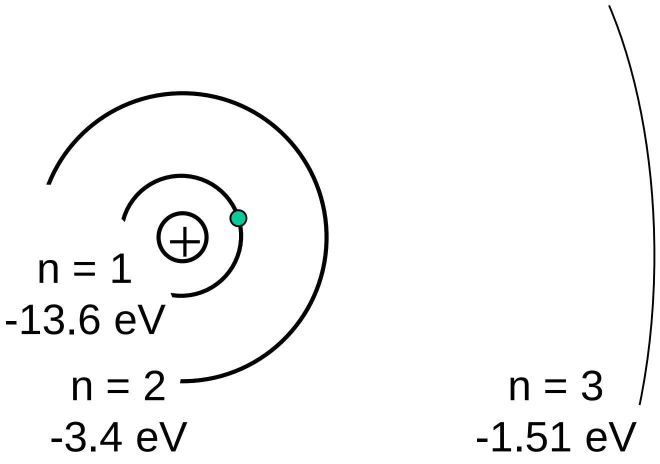
Absorption spectrum of a typical semiconductor



Excitons: Electron and Hole Bound by Coulomb

Analogy with H-atom

- Electron orbit around a hole is similar to the electron orbit around a H-core
- 1913 Niels Bohr: Electron restricted to well-defined orbits



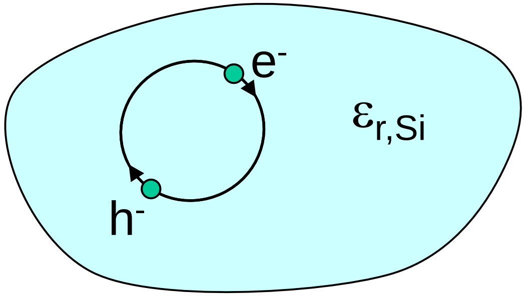
- Binding energy electron: $E_B = -\frac{m_e e^4}{2\left(4\pi\varepsilon_0 \hbar n\right)^2} = -\frac{13.6}{n^2} eV, n = 1, 2, 3, \ldots$

Where: m_e = Electron mass, ε_0 = permittivity of vacuum, $\hbar$ = Planck's constant
n = energy quantum number/orbit identifier

Binding Energy of an Electron to Hole

Electron orbit “around” a hole

- Electron orbit is expected to be qualitatively similar to a H-atom.
- Use reduced effective mass instead of m_e: ⇨ $1/m^* = 1/m_e + 1/m_h$
- Correct for the relative dielectric constant of Si, $\varepsilon_{r,Si}$ (screening).



⇨ Binding energy electron $E_B = \frac{m^*}{m_e}\frac{1}{\varepsilon^2 n^2}13.6eV, n = 1, 2, 3, \ldots$

- Typical value for semiconductors: $E_B = 10meV - 100meV$
- Note: Exciton Bohr radius ~ 5 nm (many lattice constants)

Optical Properties of Metals (determine ε)

Current induced by a time varying field

- Consider a time varying field:

$$\mathbf{E}(t)=\mathrm{Re}\left\{\mathbf{E}(\omega)\exp(-i\omega t)\right\}$$

- Equation of motion electron in a metal:

$$m\frac{d^2\mathbf{x}}{dt^2}=\frac{d\mathbf{v}}{dt}=-m\frac{\mathbf{v}}{\tau}-e\mathbf{E}$$

relaxation time ~ 10^{-14} s

- Look for a steady state solution:

$$\mathbf{v}(t)=\mathrm{Re}\left\{\mathbf{v}(\omega)\exp(-i\omega t)\right\}$$

- Substitution **v** into Eq. of motion:

$$-i\omega m\mathbf{v}(\omega)=-\frac{m\mathbf{v}(\omega)}{\tau}-e\mathbf{E}(\omega)$$

- This can be manipulated into:

$$\mathbf{v}(\omega)=\frac{-e}{m(1/\tau-i\omega)}\mathbf{E}(\omega)$$

- The current density is defined as:

$$\mathbf{J}(\omega)=-ne\mathbf{v}$$

Electron density

- It thus follows:

$$\mathbf{J}(\omega)=\frac{(ne^2/m)}{(1/\tau-i\omega)}\mathbf{E}(\omega)$$

Optical Properties of Metals

Determination conductivity

- From the last page: $\mathbf{J}(\omega)=\dfrac{\left(ne^2/m\right)}{\left(1/\tau-i\omega\right)}\mathbf{E}(\omega)$
- Definition conductivity: $\mathbf{J}(\omega)=\sigma(\omega)\mathbf{E}(\omega)$

$$\Rightarrow \boxed{\sigma(\omega)=\frac{\left(ne^2/m\right)}{\left(1/\tau-i\omega\right)}=\frac{\sigma_0}{\left(1-i\omega\tau\right)}}$$

where: $\sigma_0=\dfrac{ne^2\tau}{m}$

Both bound electrons and conduction electrons contribute to ε

- From the curl Eq.: $\nabla\times\boldsymbol{H}=\dfrac{\partial\boldsymbol{D}}{\partial\boldsymbol{t}}+\boldsymbol{J}=\dfrac{\partial\varepsilon_B\boldsymbol{E}(t)}{\partial\boldsymbol{t}}+\boldsymbol{J}$
- For a time varying field: $\mathbf{E}(t)=\mathrm{Re}\left\{\mathbf{E}(\omega)\exp(-i\omega t)\right\}$

$$\Rightarrow \nabla\times\boldsymbol{H}=\frac{\partial\varepsilon_B\boldsymbol{E}(t)}{\partial\boldsymbol{t}}+\boldsymbol{J}=-i\omega\varepsilon_B(\omega)\boldsymbol{E}(\omega)+\sigma(\omega)\boldsymbol{E}(\omega)=-i\omega\varepsilon_0\underbrace{\left(\varepsilon_B(\omega)-\frac{\sigma(\omega)}{i\varepsilon_0\omega}\right)}_{\varepsilon_{EFF}(\omega)}\boldsymbol{E}(\omega)$$

Currents induced by ac-fields modeled by ε_{EFF}

- For a time varying field: $\varepsilon_{EFF}=\varepsilon_B-\dfrac{\sigma}{i\varepsilon_0\omega}=\varepsilon_B+i\dfrac{\sigma}{\varepsilon_0\omega}$

Bound electrons

Conduction electrons

Optical Properties of Metals

Dielectric constant at $\omega \approx \omega_{visible}$

- Since $\omega_{vis}\tau >> 1$: $\sigma(\omega) = \dfrac{\sigma_0}{(1-i\omega\tau)} = \dfrac{\sigma_0(1+i\omega\tau)}{(1+\omega^2\tau^2)} \approx \dfrac{\sigma_0}{\omega^2\tau^2} + i\dfrac{\sigma_0}{\omega\tau}$

$$\left.\begin{array}{l} \text{• It follows that:} \; \varepsilon_{EFF} = \varepsilon_B + i\dfrac{\sigma}{\varepsilon_0\omega} = \varepsilon_B + i\dfrac{\sigma_0}{\varepsilon_0\omega^3\tau^2} - \dfrac{\sigma_0}{\varepsilon_0\omega^2\tau} \\ \text{• Define:} \; \omega_p^2 = \dfrac{\sigma_0}{\varepsilon_0\tau} = \dfrac{ne^2}{\varepsilon_0 m} \quad (\approx 10eV \;\; for\ metals) \end{array}\right\} \Rightarrow$$

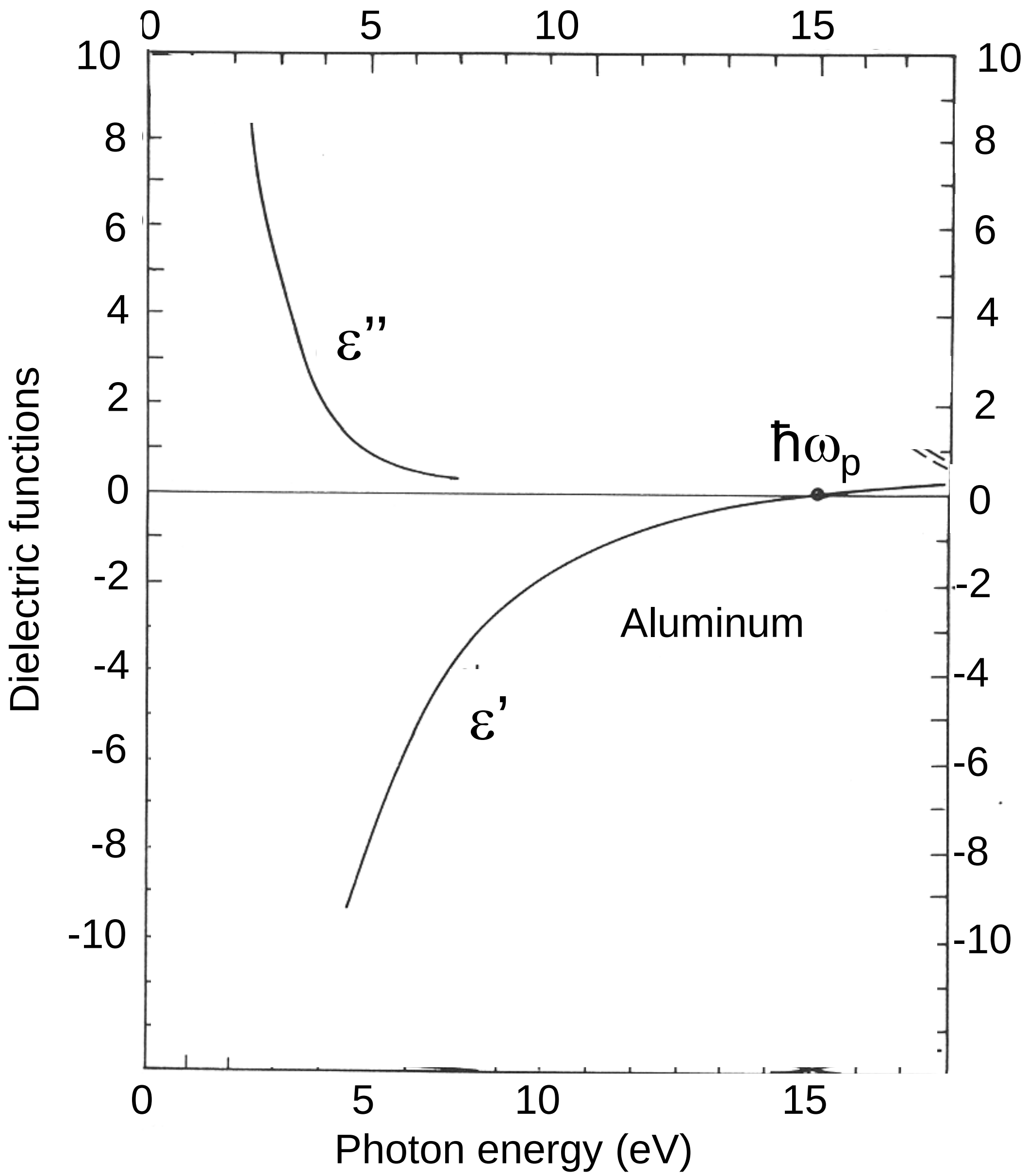
$$\boxed{\varepsilon_{EFF} = \varepsilon_B - \underline{\frac{\omega_p^2}{\omega^2} + i\frac{\omega_p^2}{\omega^3\tau}}}$$

Bound electrons

Free electrons

- What does this look like for a real metal?

Optical Properties of Aluminum (simple case)



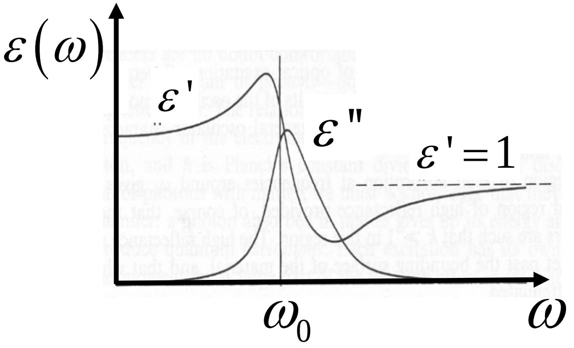
$$\varepsilon_{EFF} = \varepsilon_B - \frac{\omega_p^2}{\omega^2} + i\frac{\omega_p^2}{\omega^3\tau}$$

- Only conduction e's contribute to: ε_{EFF}

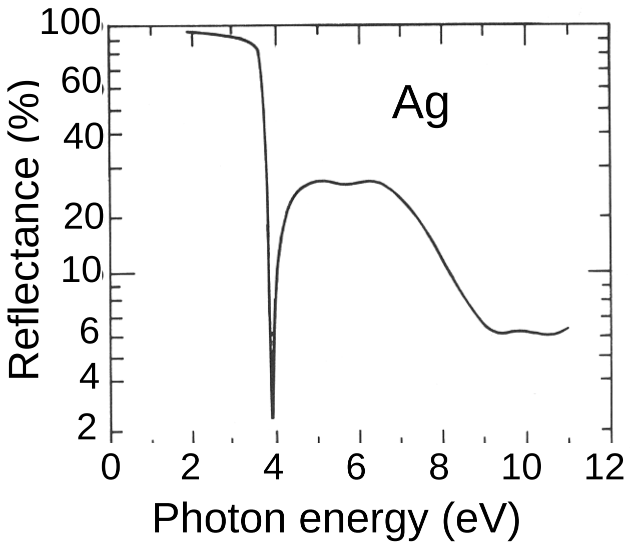
⇨ $\varepsilon_B \approx 1$

$$\varepsilon_{EFF,Al} \approx 1 - \frac{\omega_p^2}{\omega^2} + i\frac{\omega_p^2}{\omega^3\tau}$$

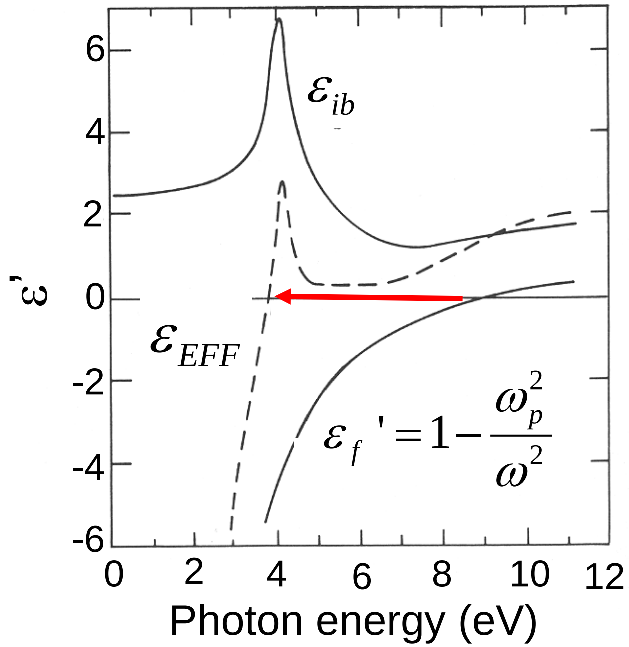
- Agrees with:



Ag: effects of Interband Transitions



- Ag show interesting feature in reflection
- Both conduction and bound e's contribute to ε_{EFF}



- Feature caused by interband transitions

Excitation bound electrons

interband

- For Ag: $\varepsilon_B = \varepsilon_{ib} \neq 0$

$$\varepsilon_{EFF} = \varepsilon_{ib} - \frac{\omega_p^2}{\omega^2} + i\frac{\omega_p^2}{\omega^3 \tau}$$