Optical properties: microscopic theory

The single particle Hamiltonian of an electron in an external electromagnetic field is:

$$H = \frac{1}{2m}\left(\vec{p} + e\frac{\vec{A}\left(\vec{r}, t\right)}{c}\right)^2 - e\phi\left(\vec{r}, t\right) + V\left(\vec{r}\right)$$

where the electric and magnetic fields are given by:

$$\vec{E} = -\vec{\nabla}\phi - \frac{1}{c}\frac{\partial \vec{A}}{\partial t}$$
$$\vec{B} = \vec{\nabla} \times \vec{A}$$

Optical properties: microscopic theory

The hamiltonian derives from the fact that the Lagrangian for a charged particle is:

$$L = T - V = \frac{1}{2}mv^2 - q\phi + \frac{q}{c}\vec{A}\cdot\vec{v}$$

so the components of the canonic generalized moment are:

$$p_i = \frac{\partial L}{\partial \dot{q}_i} = mv_i + \frac{q}{c}A_i$$

The kinetic energy is therefore:

$$T = \frac{1}{2}mv^2 = \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2$$

from which:

$$H = \frac{1}{2m}\left(\vec{p} + e\frac{\vec{A}\left(\vec{r},t\right)}{c}\right)^2 - e\phi\left(\vec{r},t\right) + V\left(\vec{r}\right)$$

Optical properties: microscopic theory

When no external charges or currents are present, is is customary to define vector and scalar potentials in the so called “transverse gauge”:

$$\vec{\nabla} \cdot \vec{A} = 0$$

$$\phi = 0$$

which, inserted into Maxwell’s equations give that the vector potential satisfies the equation:

$$\nabla^2 \vec{A} - \frac{1}{c^2}\frac{\partial^2 \vec{A}}{\partial t^2} = 0$$

Optical properties: microscopic theory

By expanding the hamiltonian, we can write the Schrödinger equation:

$$\left[\frac{1}{2m}p^2 + \frac{e}{2mc}\left(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}\right) + \boxed{\frac{e}{2mc^2}A^2} + V\left(\vec{r}\right)\right]\psi = E\psi$$

≈0

The square term in the vector potential can be neglected

Moreover because of the transverse gauge we have that

$$\left[\vec{p}, \vec{A}\right] = 0$$

So:

$$\boxed{H = \frac{1}{2m}p^2 + \frac{e}{mc}\vec{A}\cdot\vec{p} + V\left(\vec{r}\right)}$$

Optical properties: microscopic theory

Which means that we can write the hamiltonian in the form

$$H = H_0 + H_1$$

in which H_1 is the perturbation due to the external electromagnetic field, given by:

$$H_1 = \frac{e}{mc}\vec{A}\cdot\vec{p} = -\frac{ie\hbar}{mc}\vec{A}\cdot\vec{\nabla}$$

Since the vector potential satisfies the wave equation, it can be expressed as a superposition of plane waves:

$$\vec{A} = \sum_{\omega}\vec{A}_{\omega}e^{-i(\vec{q}\cdot\vec{r}-\omega t)} + c.c.$$

Optical properties: microscopic theory

From the expression for the vector potential

$$\vec{A} = \sum_{\omega} \vec{A}_{\omega} e^{-i(\vec{q}\cdot\vec{r}-\omega t)} + c.c.$$

and reminding that in our gauge

$$\vec{E} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t}$$

we get immediately

$$\vec{E} = \sum_{\omega} \frac{i\omega}{c} \vec{A}_{\omega} e^{-i(\vec{q}\cdot\vec{r}-\omega t)} + c.c.$$

Optical properties: microscopic theory

The Fermi golden rule gives the transition probability per unit time from a the initial state *i* to the final state *f* as:

$$W_{f,i} = \frac{2\pi}{\hbar} \left| \langle f | H_1 | i \rangle \right|^2 \delta\left(E_f - E_i - \hbar\omega\right)$$

$$= 2\pi\hbar \left(\frac{e}{mc}\right)^2 \left| \vec{A}_\omega \cdot \langle f | e^{i\vec{q}\cdot\vec{r}} \vec{\nabla} | i \rangle \right|^2 \delta\left(E_f - E_i - \hbar\omega\right)$$

The oscillating term is in the first approximation

$$e^{i\vec{q}\cdot\vec{r}} = 1 + i\vec{q}\cdot\vec{r} + \ldots$$

The modulus of the wave vector, $|q|$ is given by $2\pi/\lambda$. For example at 100eV its value is $|q|_{(\hbar\omega=100\mathrm{eV})} \approx 0.05\text{Å}^{-1}$: the scalar product is negligible in the region where the wave functions are significantly ≠ 0

Optical properties: microscopic theory

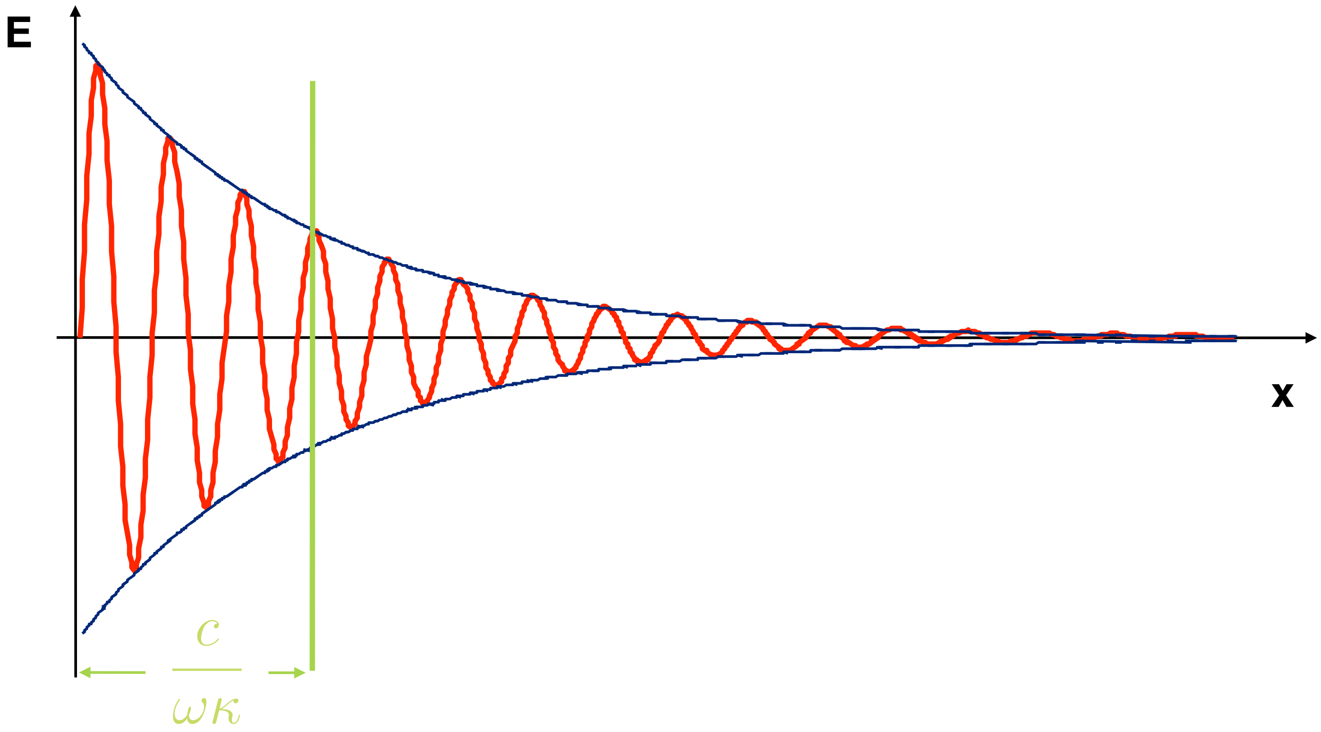
We can therefore write the transition probability in the **dipole approximation** as:

$$\begin{aligned} W_{f,i} &= 2\pi\hbar\left(\frac{e}{mc}\right)^2\left|\vec{A}_\omega\cdot\langle f|\,\vec{\nabla}\,|i\rangle\right|^2\delta\left(E_f-E_i-\hbar\omega\right)= \\ &= \frac{2\pi}{\hbar}\left(\frac{e}{mc}\right)^2\left|\vec{A}_\omega\cdot\langle f|\,\vec{p}\,|i\rangle\right|^2\delta\left(E_f-E_i-\hbar\omega\right) \end{aligned}$$

Macroscopic dielectric theory

A plane wave propagating along the x axis can be written in terms of the complex dielectric index:

$$\vec{E} = \vec{E}_0 e^{i(\vec{q}\cdot\vec{r}-\omega\, t)} + c.c. = \vec{E}_0 e^{-i\omega\left(t-\frac{\tilde{n}x}{c}\right)} + c.c. = \vec{E}_0 e^{-\frac{\omega\kappa x}{c}} e^{-i\omega\left(t-\frac{nx}{c}\right)} + c.c.$$



Optical properties: microscopic theory

The absorption coefficient η is defined by the equation:

$$\overline{W} = \overline{W}_0 e^{-\eta x}$$

We see immediately that:

$$\frac{\partial \overline{W}}{\partial t} = \frac{c}{n}\eta \overline{W}; \quad \eta = \frac{n}{c}\frac{1}{\overline{W}}\frac{\partial \overline{W}}{\partial t}$$

and, of course

$$\eta = \frac{2\omega\kappa}{c} = \frac{\omega\epsilon_2}{nc} = \frac{4\pi\sigma}{nc}$$

Optical properties: microscopic theory

The absorption coefficient is the energy absorbed per unit time and unit volume divided by the average energy flux:

$$\eta = \frac{\sum_{i,f} W_{i,f} \hbar\omega}{\frac{c}{n}\overline{W}}$$

i.e.:

$$\eta\left(\omega\right) = \frac{4\pi^2 e^2}{m^2 c}\frac{1}{n\omega}\sum_{if} \left|\hat{e}\cdot\langle f|\,\vec{p}\,|i\rangle\right|^2 \delta\left(E_f - E_i - \hbar\omega\right)$$

From which:

$$\epsilon_2\left(\omega\right) = \frac{4\pi^2 e^2}{m^2}\frac{1}{\omega^2}\sum_{if} \left|\hat{e}\cdot\langle f|\,\vec{p}\,|i\rangle\right|^2 \delta\left(E_f - E_i - \hbar\omega\right)$$

Optical properties: microscopic theory

Since $|f\rangle$ and $|i\rangle$ are eigenstates of the unperturbed hamiltonian and:

$$[\vec{p}, H_0] = -i\hbar\vec{\nabla}V(\vec{r})$$

$$[\vec{r}, H_0] = i\hbar\frac{\vec{p}}{m}$$

we can write

Optical properties: microscopic theory

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we can write

$$\begin{aligned}
\vec{M}_{f,i} &= \langle f|\,\vec{p}\,|i\rangle \\
&= -\frac{1}{E_f - E_i}\,\langle f|\,[\vec{p}, H_0]\,|i\rangle \\
&= \frac{i\hbar}{\omega_{f,i}}\,\langle f|\,\vec{\nabla}V\,(\vec{r})\,|i\rangle \\
&= im\omega_{f,i}\,\langle f|\,\vec{r}\,|i\rangle
\end{aligned}$$

Optical properties: microscopic theory

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dipole velocity

Optical properties: microscopic theory

Since $|f\rangle$ and $|i\rangle$ are eigenstates of the unperturbed hamiltonian and:

$$[\vec{p}, H_0] = -i\hbar\vec{\nabla}V(\vec{r})$$

$$[\vec{r}, H_0] = i\hbar\frac{\vec{p}}{m}$$

we can write

$$\begin{aligned}
\vec{M}_{f,i} &= \langle f|\,\vec{p}\,|i\rangle \longleftarrow \boxed{\text{dipole velocity}} \\
&= -\frac{1}{E_f - E_i}\langle f|\,[\vec{p}, H_0]\,|i\rangle \\
&= \frac{i\hbar}{\omega_{f,i}}\langle f|\,\vec{\nabla}V\left(\vec{r}\right)|i\rangle \longleftarrow \boxed{\text{dipole acceleration}} \\
&= im\omega_{f,i}\langle f|\,\vec{r}\,|i\rangle
\end{aligned}$$

Optical properties: microscopic theory

Since $|f\rangle$ and $|i\rangle$ are eigenstates of the unperturbed hamiltonian and:

$$[\vec{p}, H_0] = -i\hbar\vec{\nabla}V(\vec{r})$$

$$[\vec{r}, H_0] = i\hbar\frac{\vec{p}}{m}$$

we can write

$$\begin{aligned}\vec{M}_{f,i} &= \langle f|\,\vec{p}\,|i\rangle \\ &= -\frac{1}{E_f - E_i}\langle f|\,[\vec{p}, H_0]\,|i\rangle \\ &= \frac{i\hbar}{\omega_{f,i}}\langle f|\,\vec{\nabla}V\,(\vec{r})\,|i\rangle \\ &= im\omega_{f,i}\,\langle f|\,\vec{r}\,|i\rangle\end{aligned}$$

dipole velocity

dipole acceleration

dipole length

Optical properties: microscopic theory

The Dirac δ function in real cases becomes a Lorentzian line shape:

$$F_L = \frac{1}{\pi} \frac{\gamma/2}{(E_f - E_i)^2 + (\gamma/2)^2}$$

In which $\gamma \approx \hbar/\tau$ is the full width at half maximum (FWHM) and accounts for the decay of the excited state.

In the limit $\gamma \rightarrow 0$, the Lorentzian becomes a Dirac δ.

Optical properties: microscopic theory

Interband transitions

The matrix element for the optical transition for band states becomes:

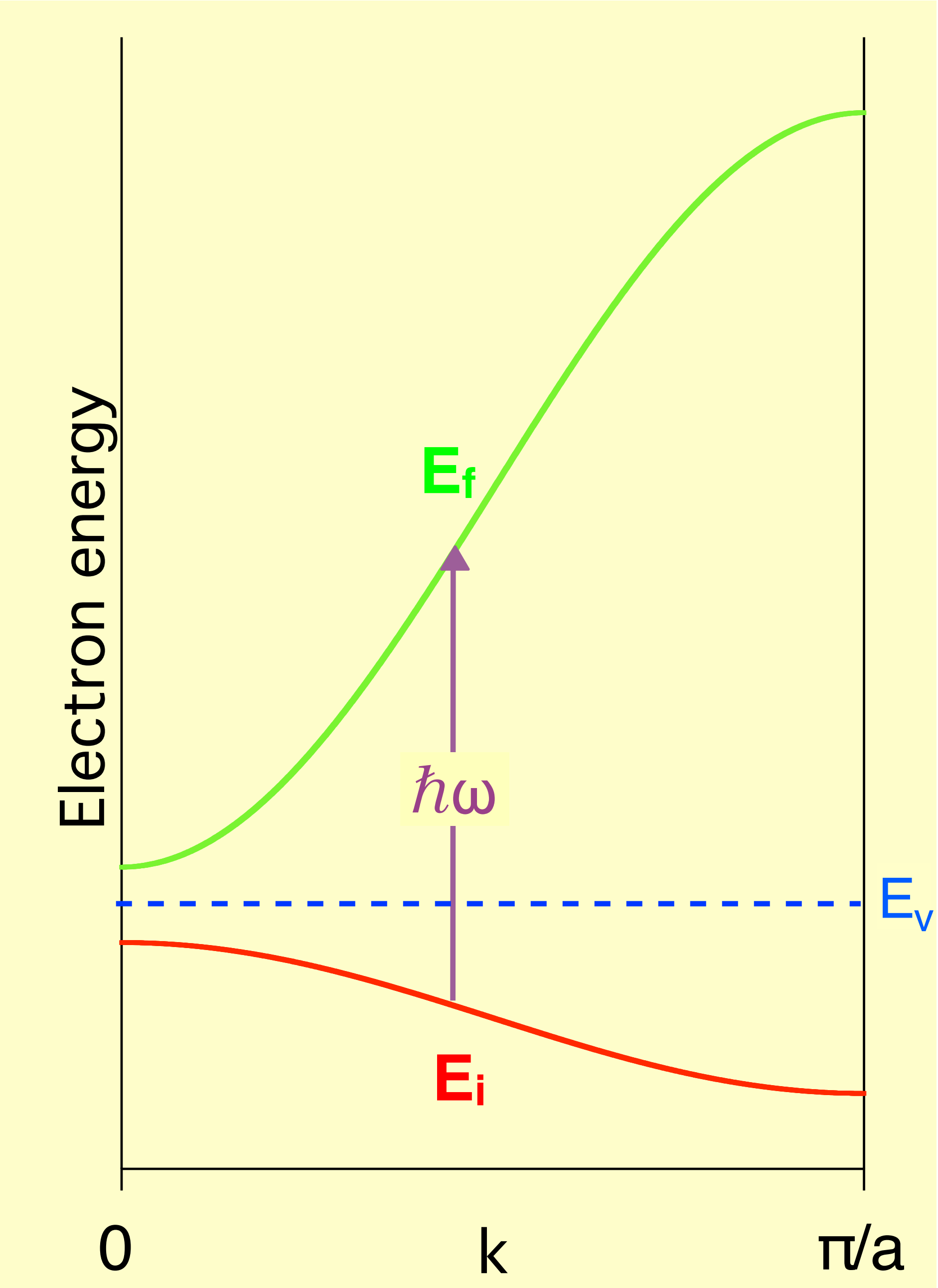
$$\langle \psi_{c,k_f} | e^{i\vec{q}\cdot\vec{r}} \hat{e}\cdot\vec{p} | \psi_{v,k_i} \rangle$$

since the wavefunctions are Bloch functions, the matrix element is 0 unless:

$$\vec{k}_f = \vec{k}_i + \vec{q} + \vec{h}$$

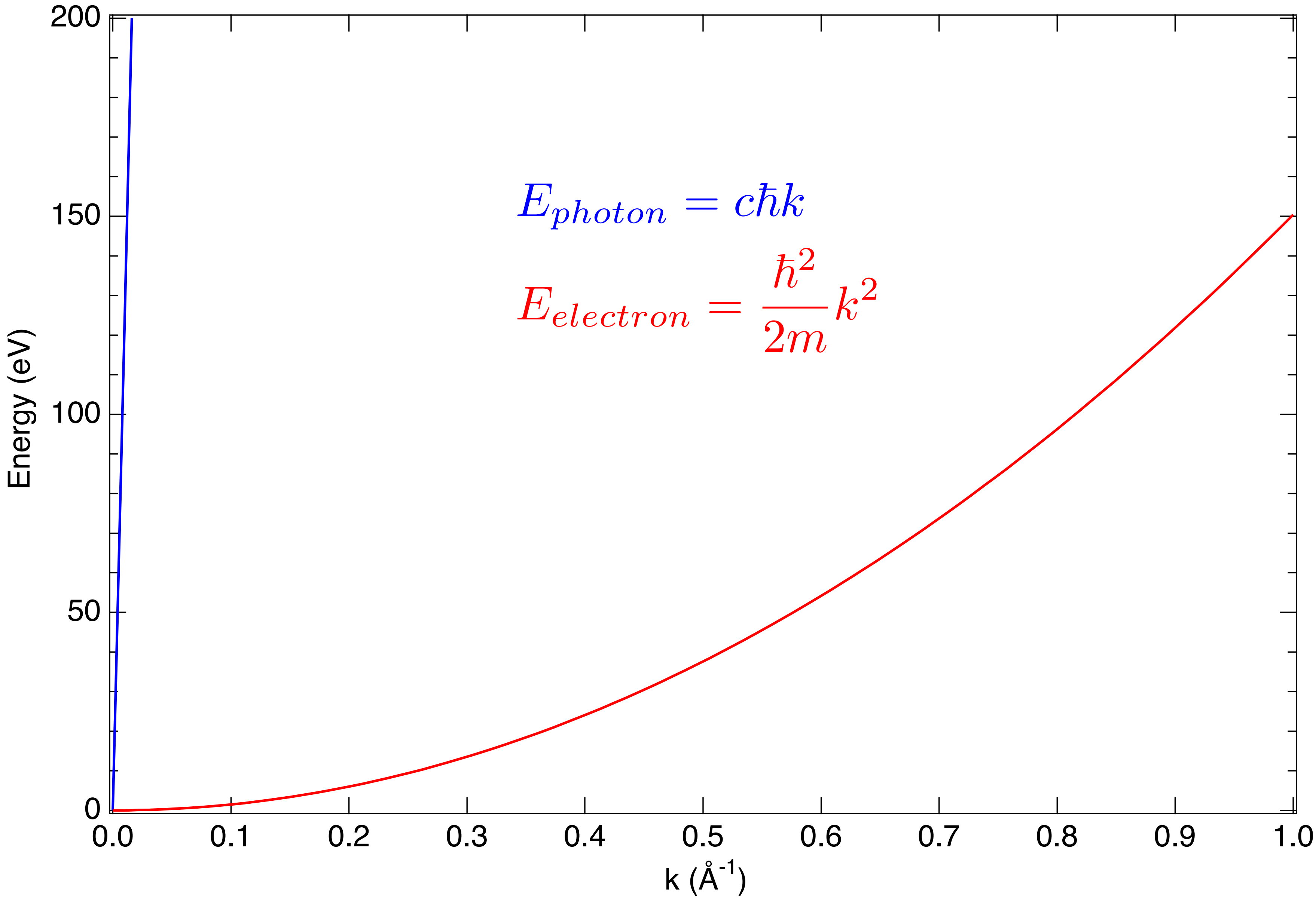
.

the initial and final state wavevectors differ by the photon wavevector and by a reciprocal lattice vector. Since the photon wavevector is 3 oders of magnitude smaller than the Brilluoin zone, it can be neglected: transitions are **vertical**



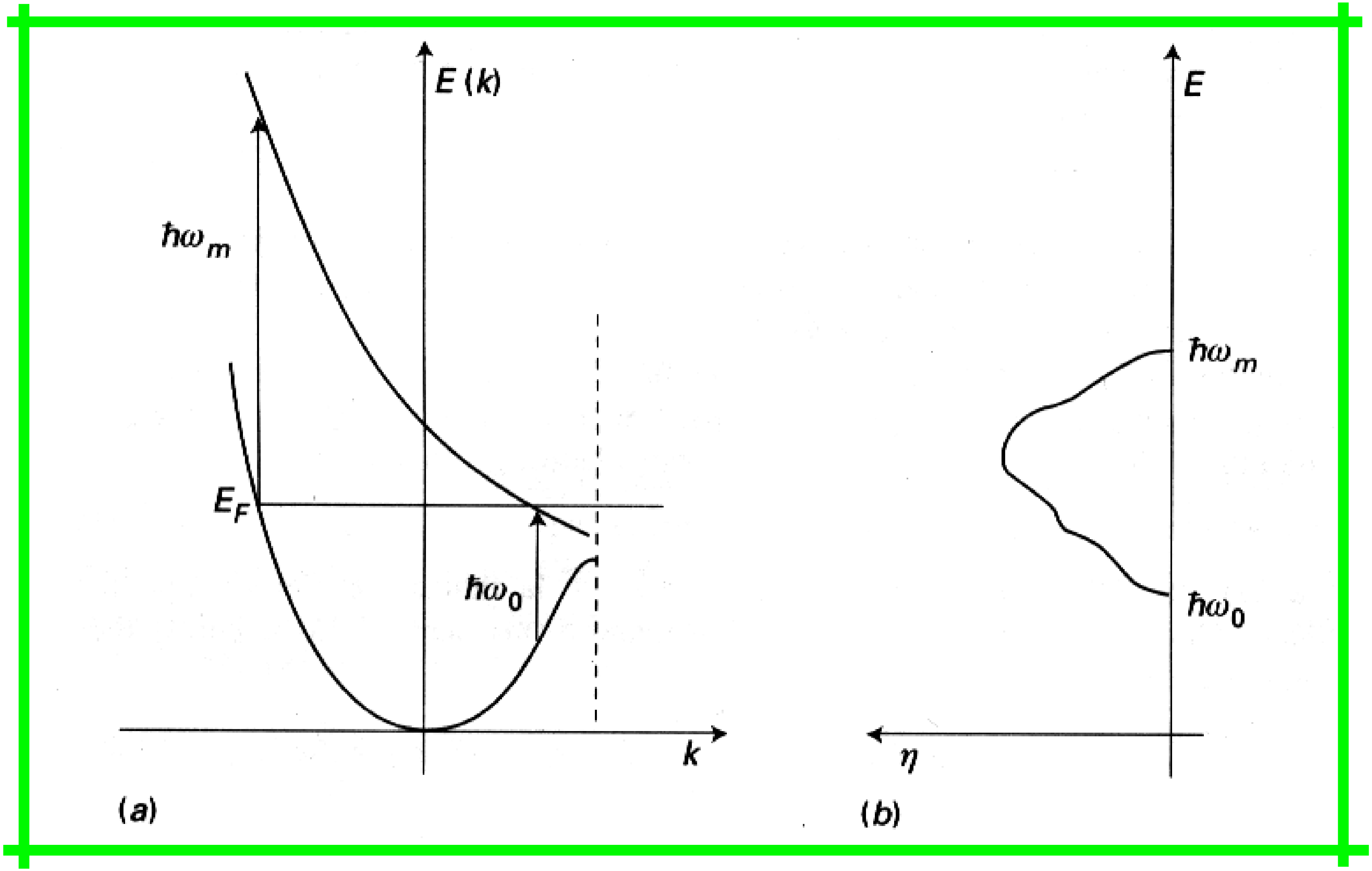
Optical properties: microscopic theory

Dispersion for Electrons and Photons



Optical properties: microscopic theory

Absorption band



Optical properties: microscopic theory

Interband transitions

For band states, the optical transition matrix element can be written as

$$\hat{e} \cdot \vec{M}_{c,v}(\vec{k}) = \hat{e} \cdot \int_{vol} \psi_c^*(\vec{k}, \vec{r})(-i\hbar\vec{\nabla})\psi_v(\vec{k}, \vec{r})d\vec{r}$$

$$\epsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2}\frac{1}{\omega^2}\sum_{v,c}\int_{B.Z.}\frac{2d\vec{k}}{(2\pi)^3}\left|\hat{e} \cdot \vec{M}_{c,v}\left(\vec{k}\right)\right|^2 \delta\left(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega\right)$$

$$JDOS_{c,v}(\hbar\omega) = \int_{B.Z.}\frac{2d\vec{k}}{(2\pi)^3}\delta\left(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega\right)$$

Optical properties: microscopic theory

Interband transitions

For band states, the optical transition matrix element can be written as

$$\hat{e}\cdot\vec{M}_{c,v}(\vec{k}) = \hat{e}\cdot\int_{vol}\psi_c^*(\vec{k},\vec{r})(-i\hbar\vec{\nabla})\psi_v(\vec{k},\vec{r})d\vec{r}$$

which describes the probability amplitude for transitions between pairs of band *v* and *c* (valence and conduction bands).

The dielectric function at $\hbar\omega$ is obtained by integrating over all possible transitions within the first Brillouin zone:

$$\epsilon_2(\omega) = \frac{4\pi^2e^2}{m^2}\frac{1}{\omega^2}\sum_{v,c}\int_{B.Z.}\frac{2d\vec{k}}{(2\pi)^3}\left|\hat{e}\cdot\vec{M}_{c,v}\left(\vec{k}\right)\right|^2\delta\left(E_c(\vec{k})-E_v(\vec{k})-\hbar\omega\right)$$

$$JDOS_{c,v}(\hbar\omega) = \int_{B.Z.}\frac{2d\vec{k}}{(2\pi)^3}\delta\left(E_c(\vec{k})-E_v(\vec{k})-\hbar\omega\right)$$

Optical properties: microscopic theory

Interband transitions

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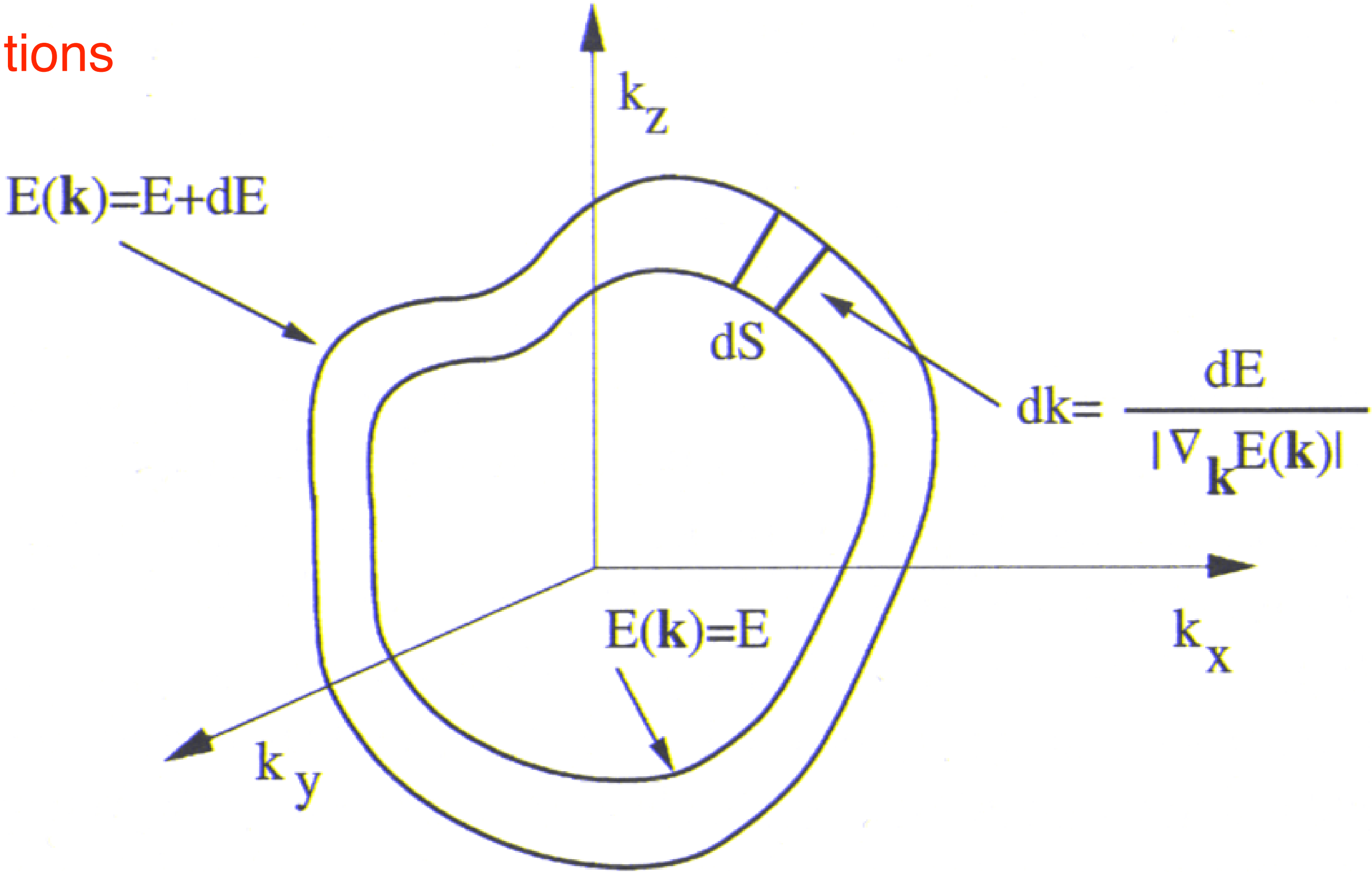
If we can assume the matrix element is constant, ε_2 is proportional to the *Joint Density Of States*:

$$JDOS_{c,v}(\hbar\omega) = \int_{B.Z.}\frac{2d\vec{k}}{(2\pi)^3}\delta\left(E_c(\vec{k})-E_v(\vec{k})-\hbar\omega\right)$$

Optical properties: microscopic theory

Interband transitions



The *JDOS* has a form similar to the *Density of States (DOS):*

$$DOS(E) = \int_{B.Z.} \frac{2d\vec{k}}{(2\pi)^3}\delta\left(E(\vec{k}) - E\right)$$

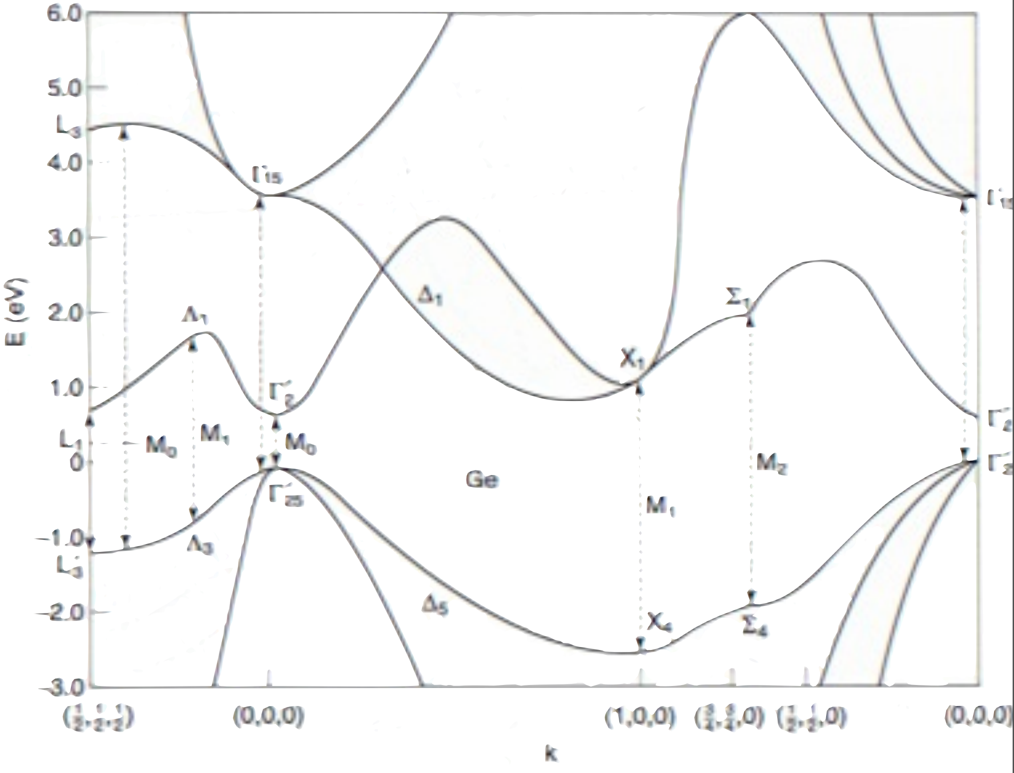
which can be written as:

$$DOS(E) = \int_{E(\vec{k})=E} \frac{2}{(2\pi)^3}\frac{dS}{\left|\vec{\nabla}_{\vec{k}}E(\vec{k})\right|}$$

Optical properties: microscopic theory

Interband transitions

$$JDOS\left(\hbar\omega\right) = \int_{\hbar\omega = E_c(\vec{k}) - E_v(\vec{k})} \frac{2}{(2\pi)^3} \frac{dS}{\left|\vec{\nabla}_{\vec{k}}\left[E_c(\vec{k}\ ) - E_v(\vec{k})\right]\right|}$$

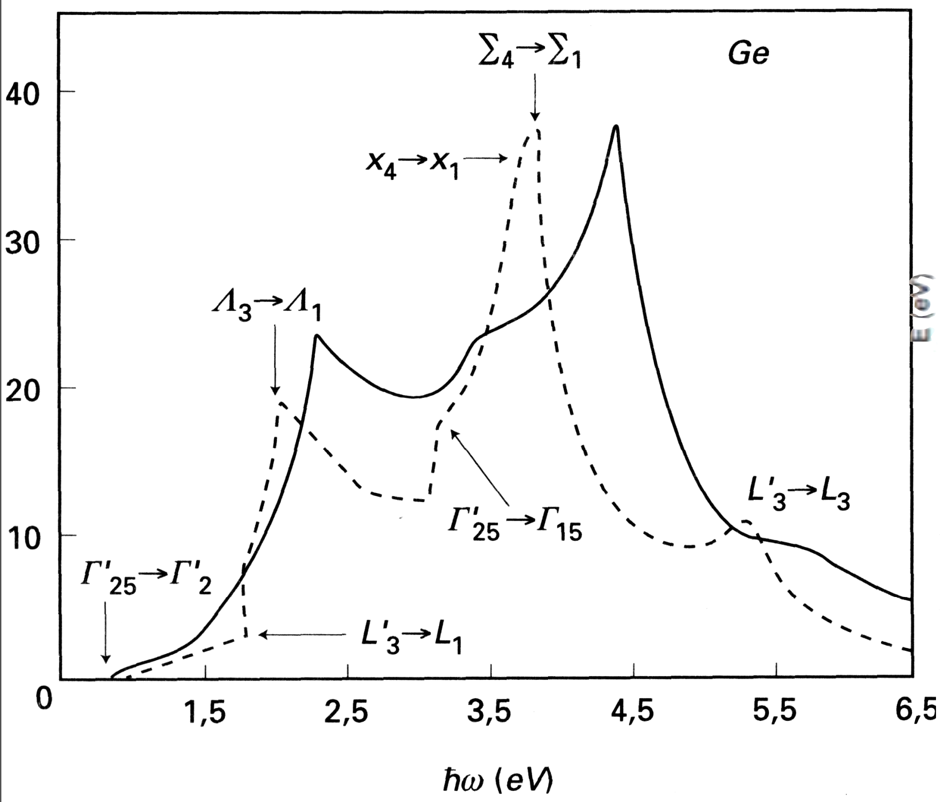


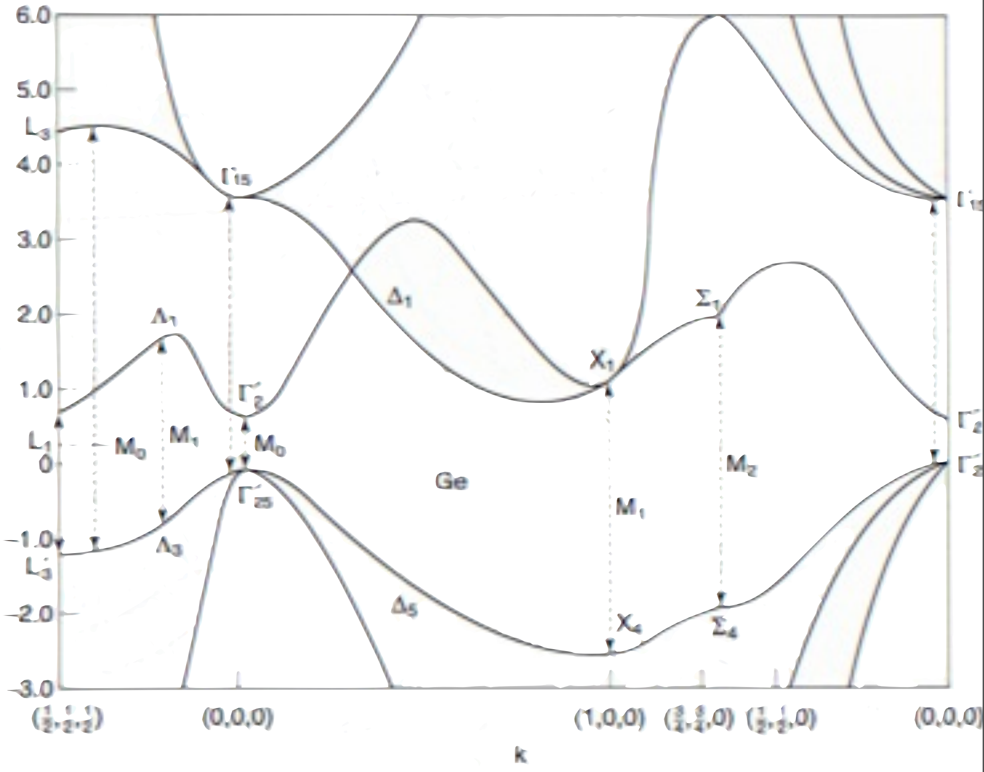
Ge band structure

Optical properties: microscopic theory

Interband transitions

$$JDOS\,(\hbar\omega) = \int_{\hbar\omega=E_c(\vec{k})-E_v(\vec{k})} \frac{2}{(2\pi)^3}\,\frac{dS}{\left|\vec{\nabla}_{\vec{k}}\left[E_c(\vec{k}\ ) - E_v(\vec{k})\right]\right|}$$



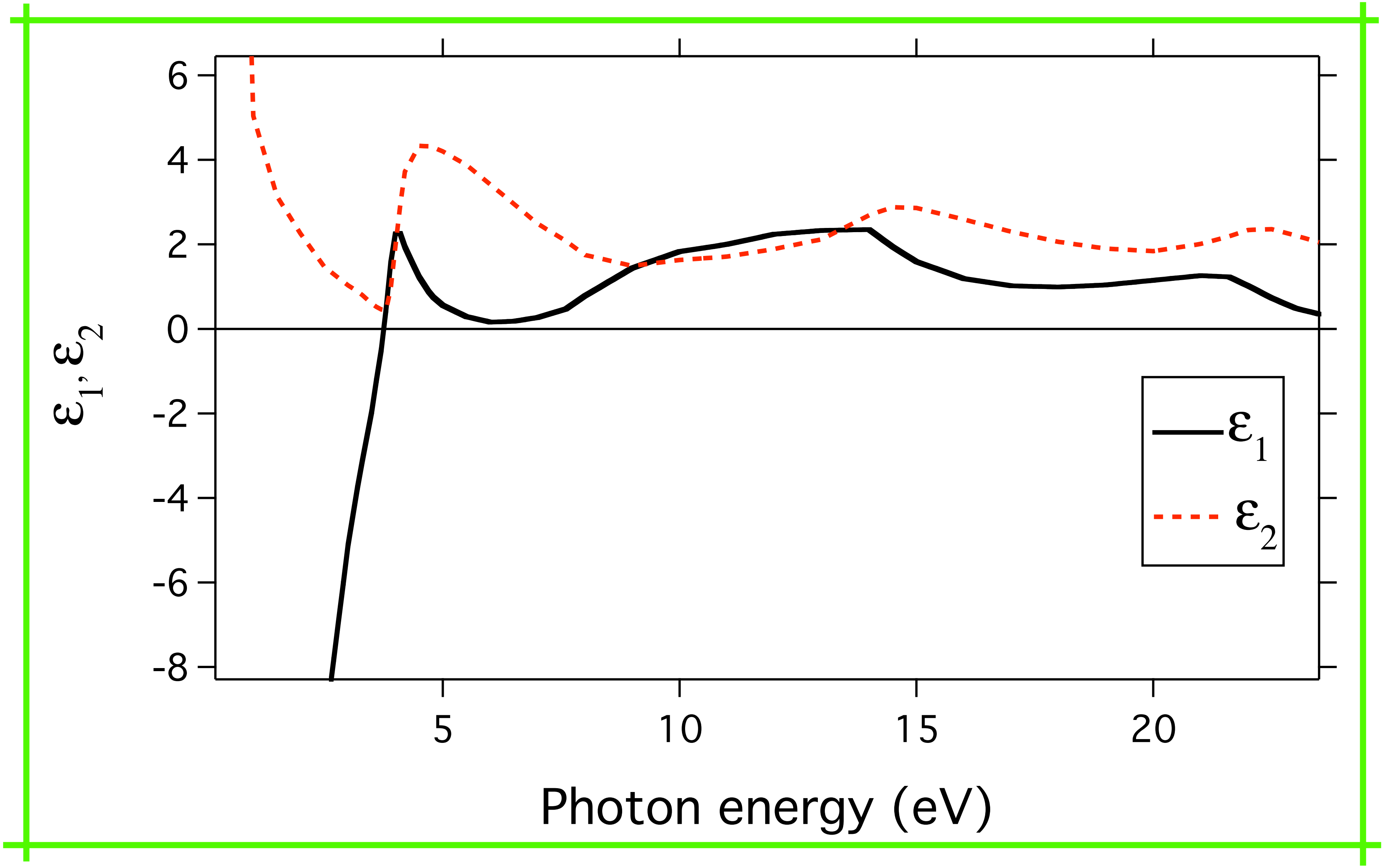


Imaginary part of Ge dielectric function
theory (---) and experiment (—)

Ge band structure

Optical properties: microscopic theory

Experimental dielectric function of Ag:



Optical properties: microscopic theory

Ag band structure

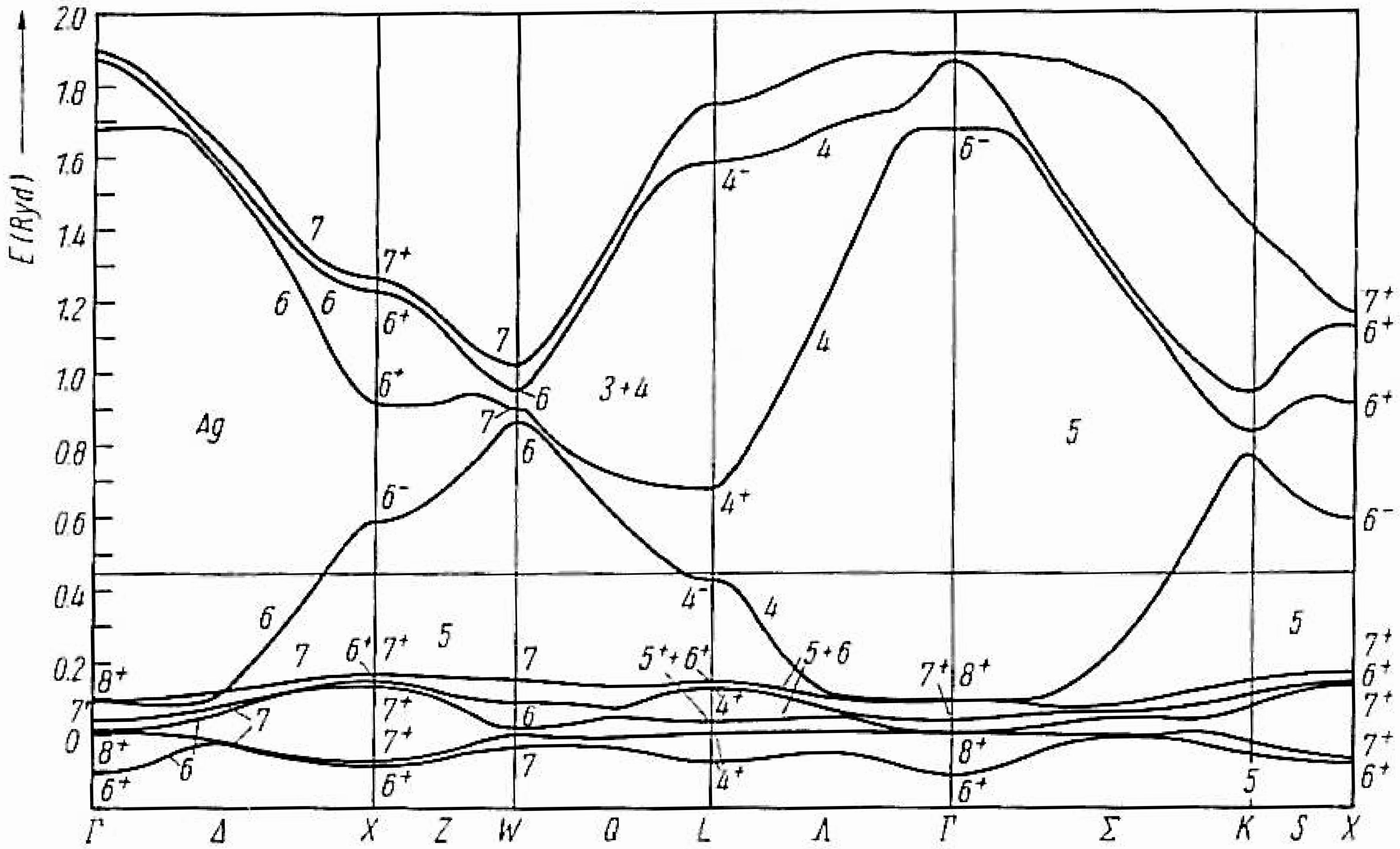
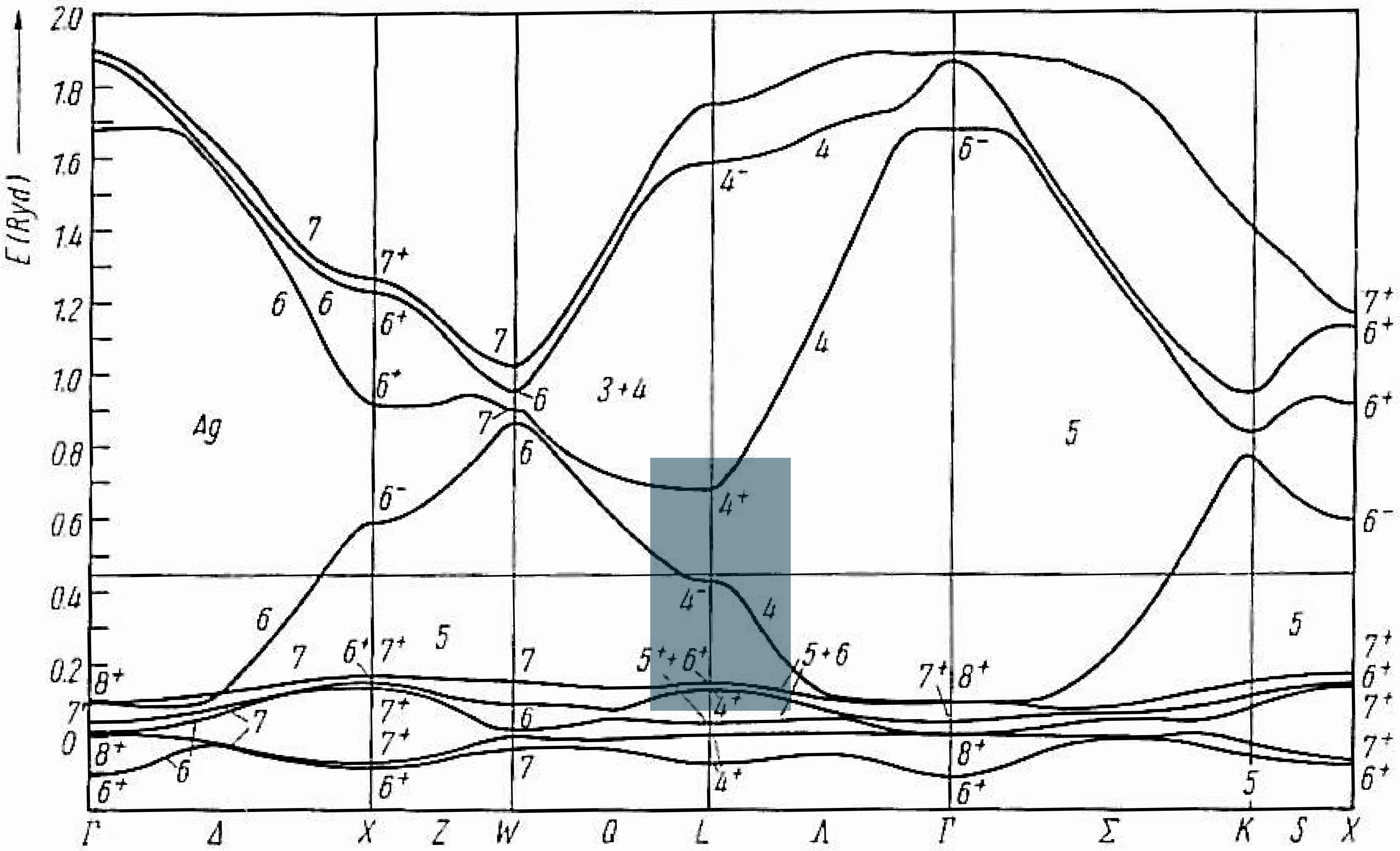


Fig. 1. RAPW band structure of silver along symmetry lines. (Note that the labels of the irreducible representations at L are not the 'conventional'). Energies are in Ryd above the muffin-tin zero (MTZ). The Fermi level lies 0.444 above MTZ

Optical properties: microscopic theory

Ag band structure



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Optical properties: microscopic theory

Ag band structure

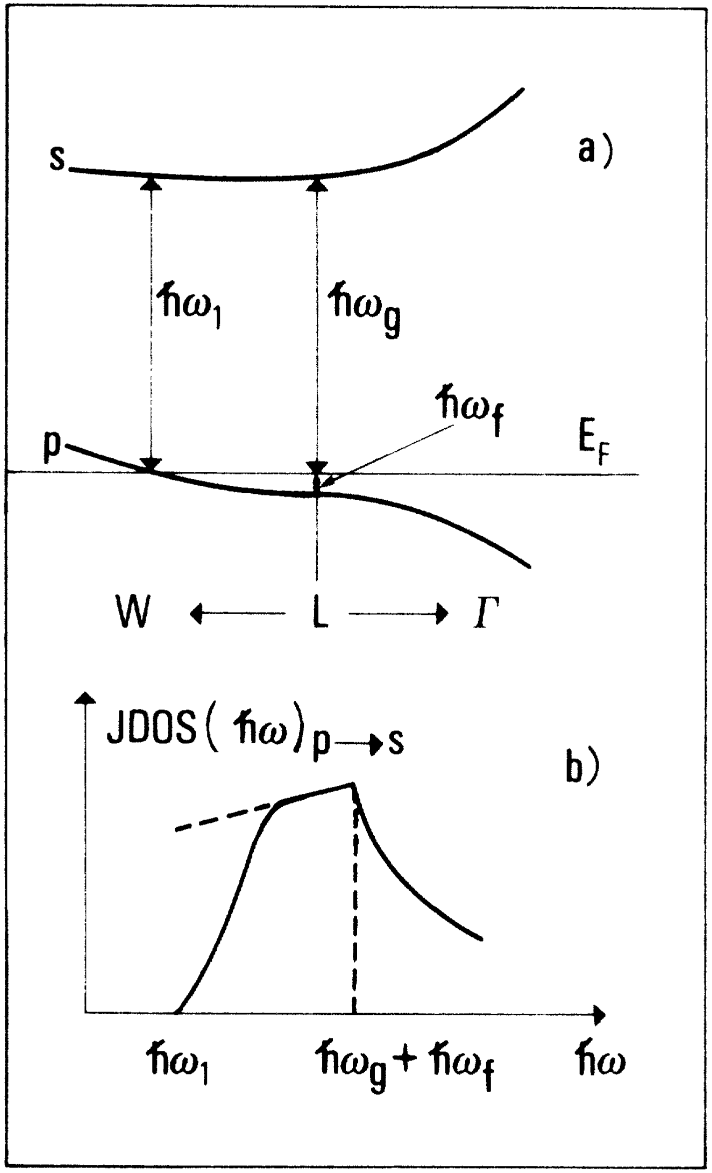


FIG. 3. (a) Bands responsible for inter-conduction-band transitions in Ag. (b) Schematic joint density of states for the $p \to s$ transitions in Ag (solid line).

Optical properties: microscopic theory

Ag band structure

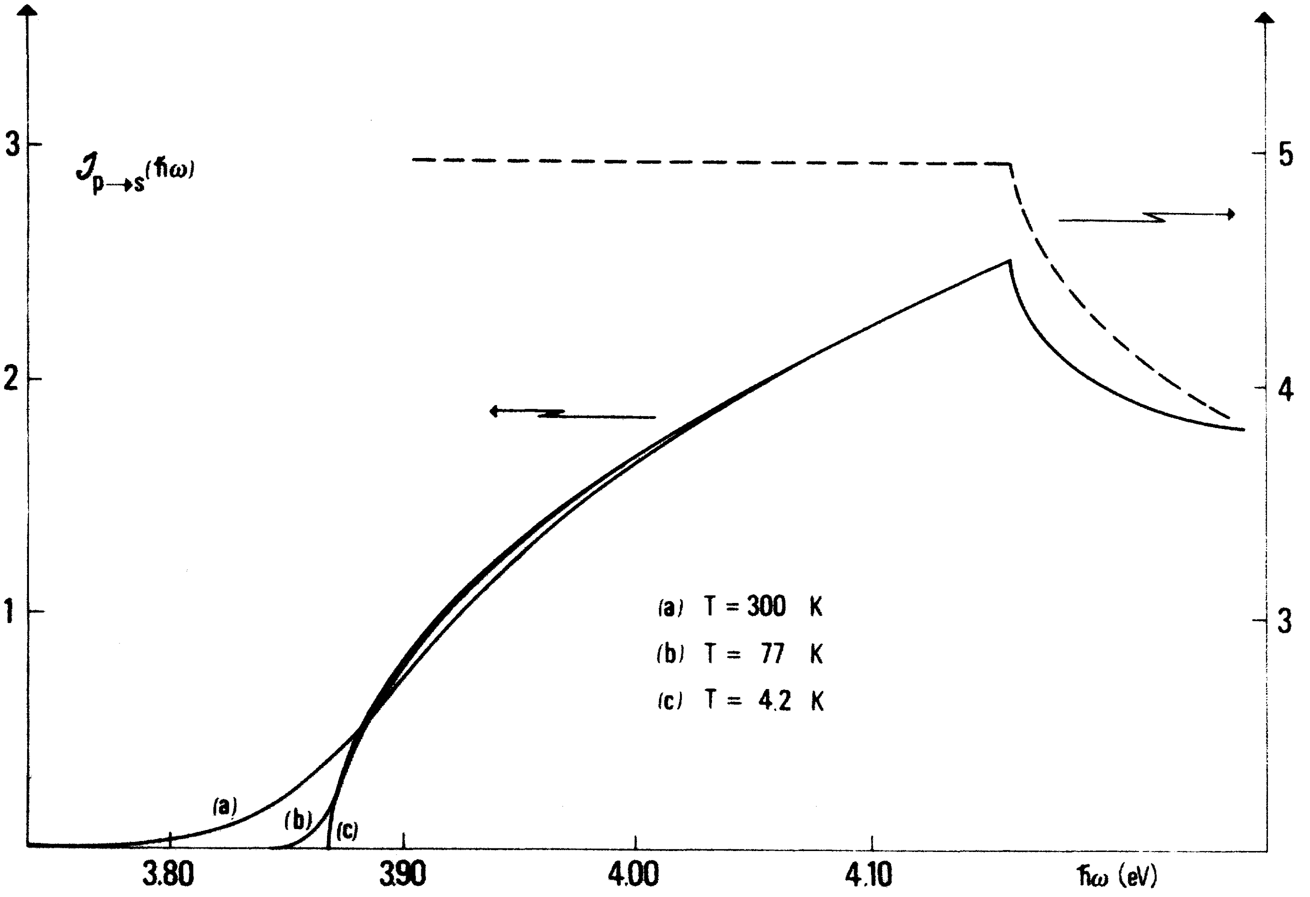
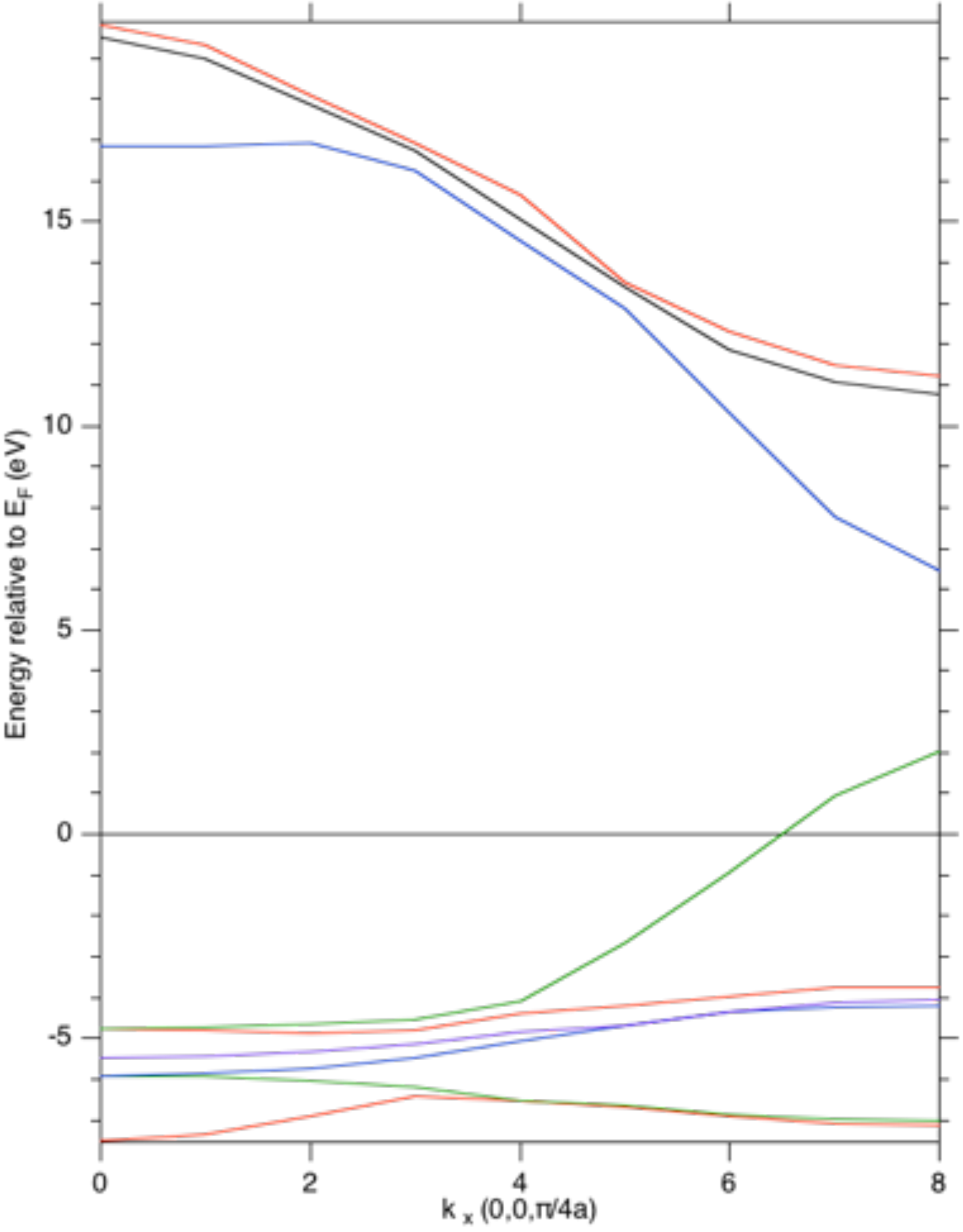


FIG. 7. Joint density of states (JDOS) of Ag due to the inter-conduction-band transitions near L calculated at different temperatures. The dashed line shows the JDOS that would be obtained were the p band completely filled.

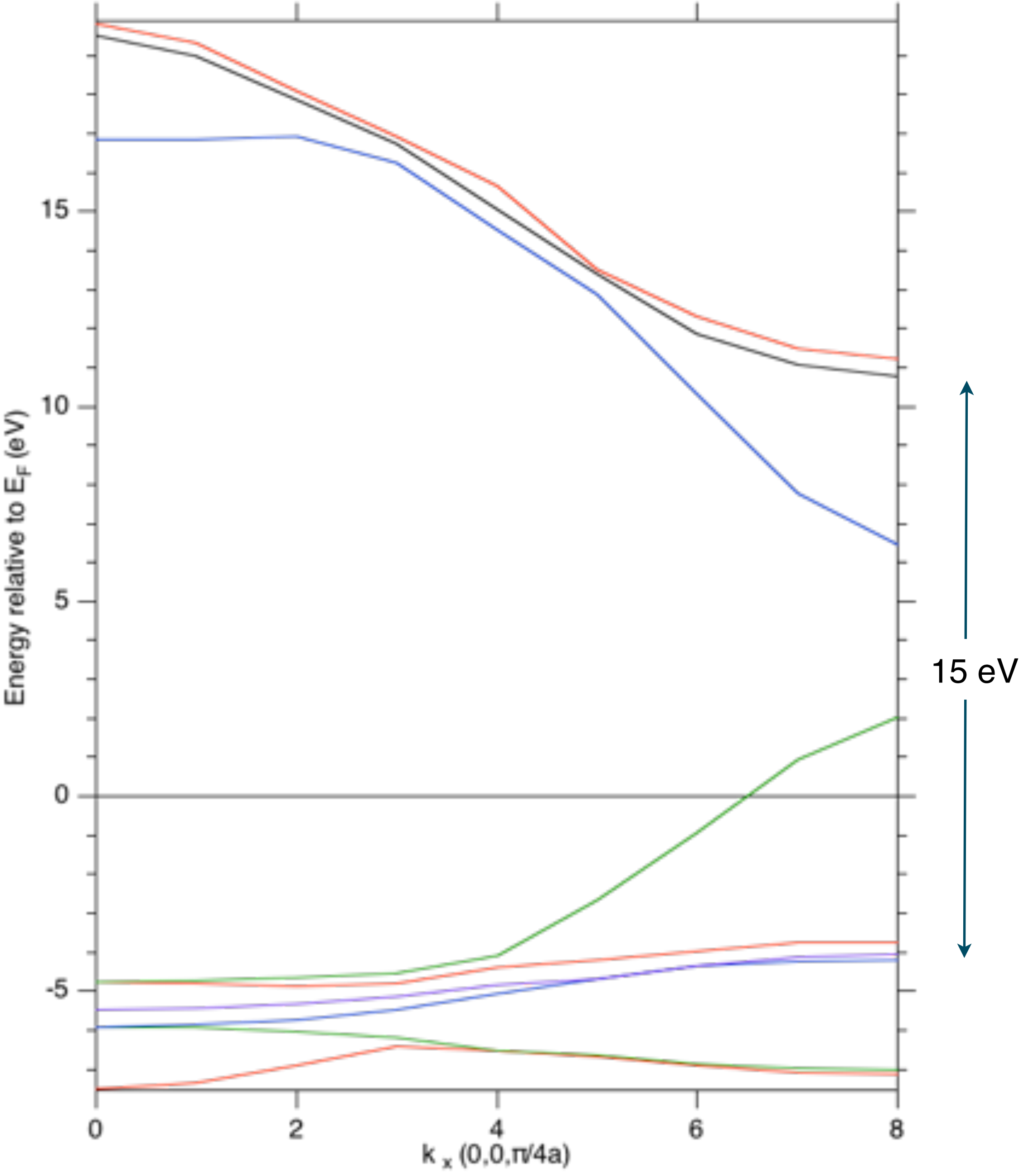
Optical properties: microscopic theory

Ag band structure



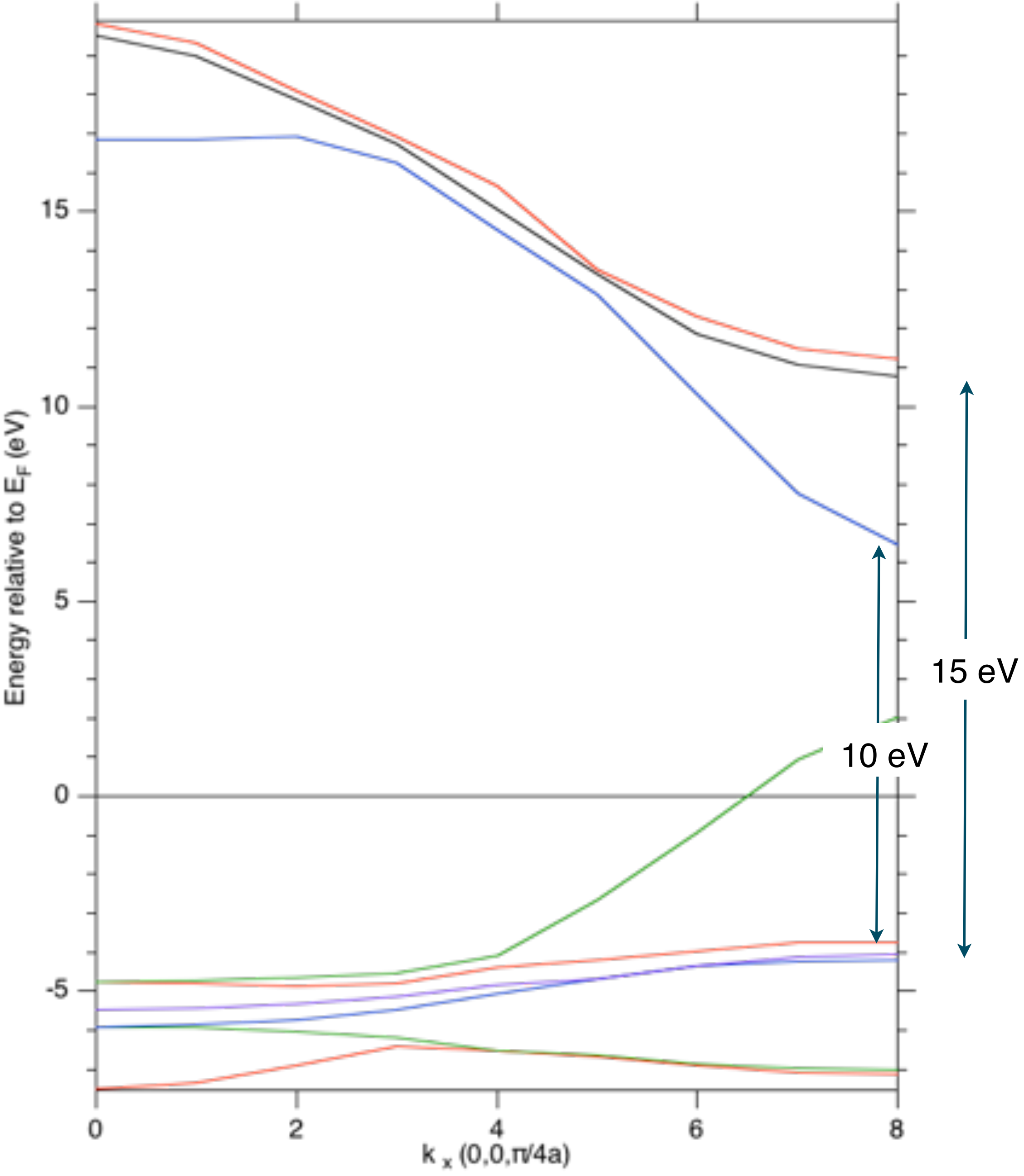
Optical properties: microscopic theory

Ag band structure



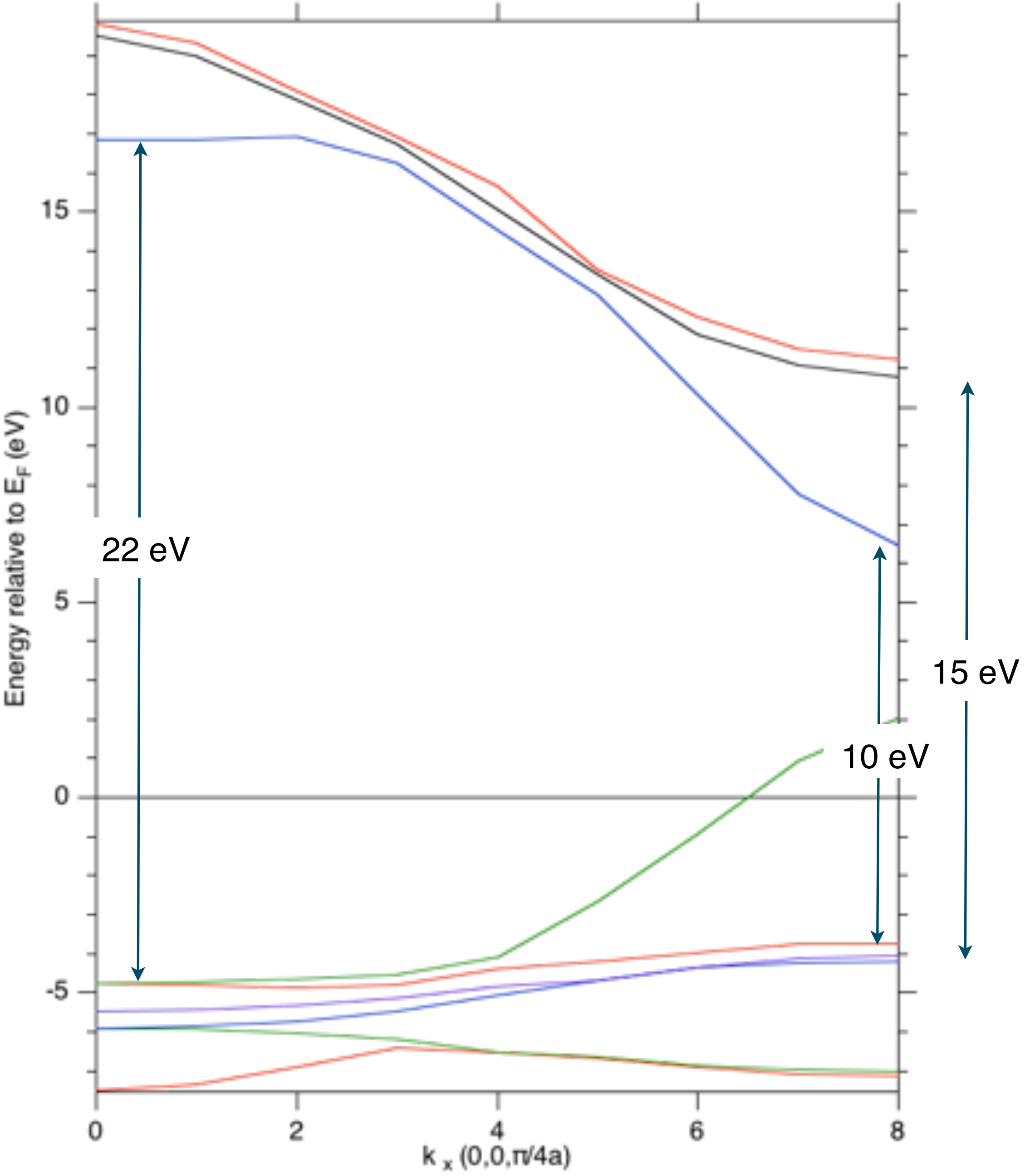
Optical properties: microscopic theory

Ag band structure



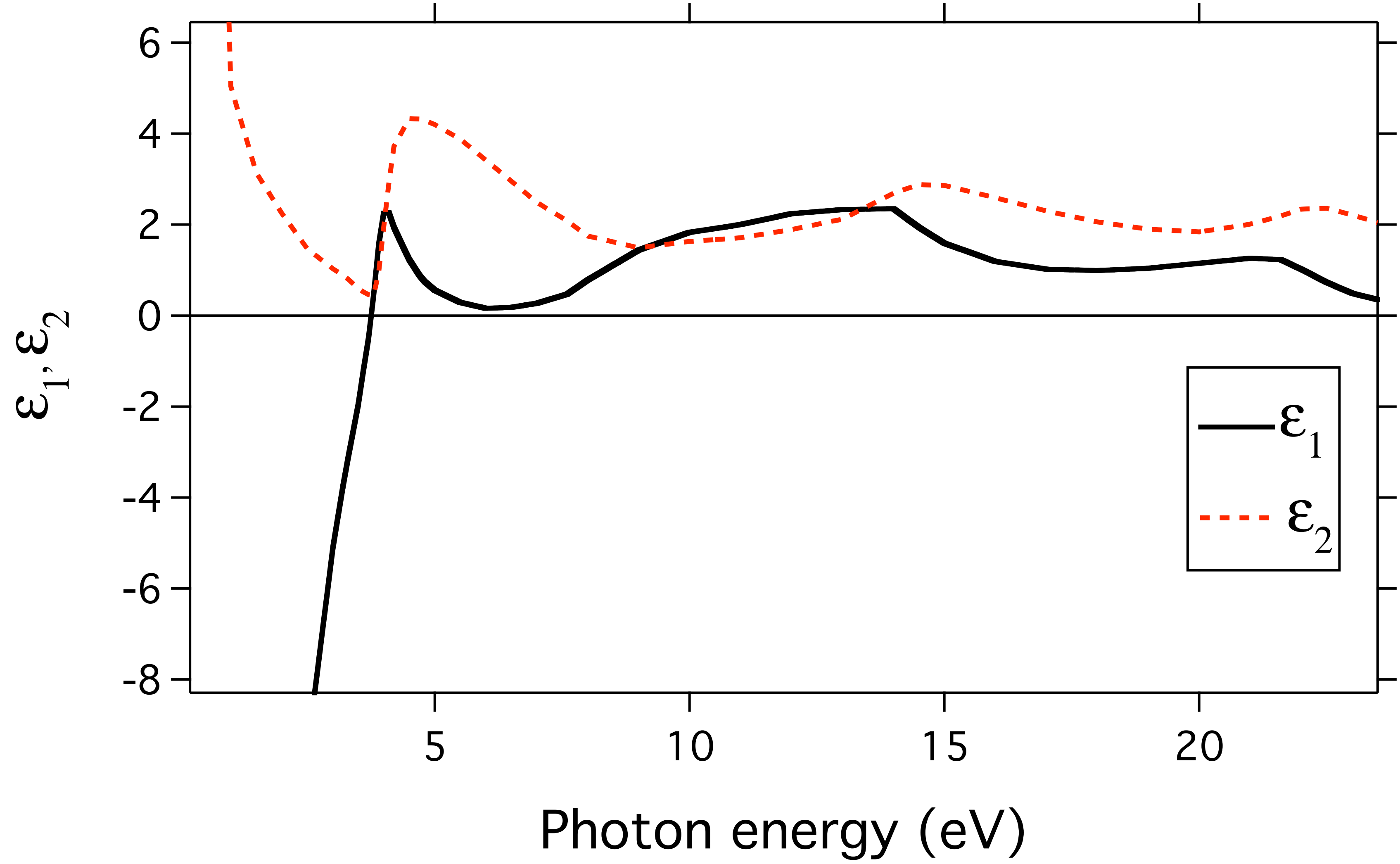
Optical properties: microscopic theory

Ag band structure

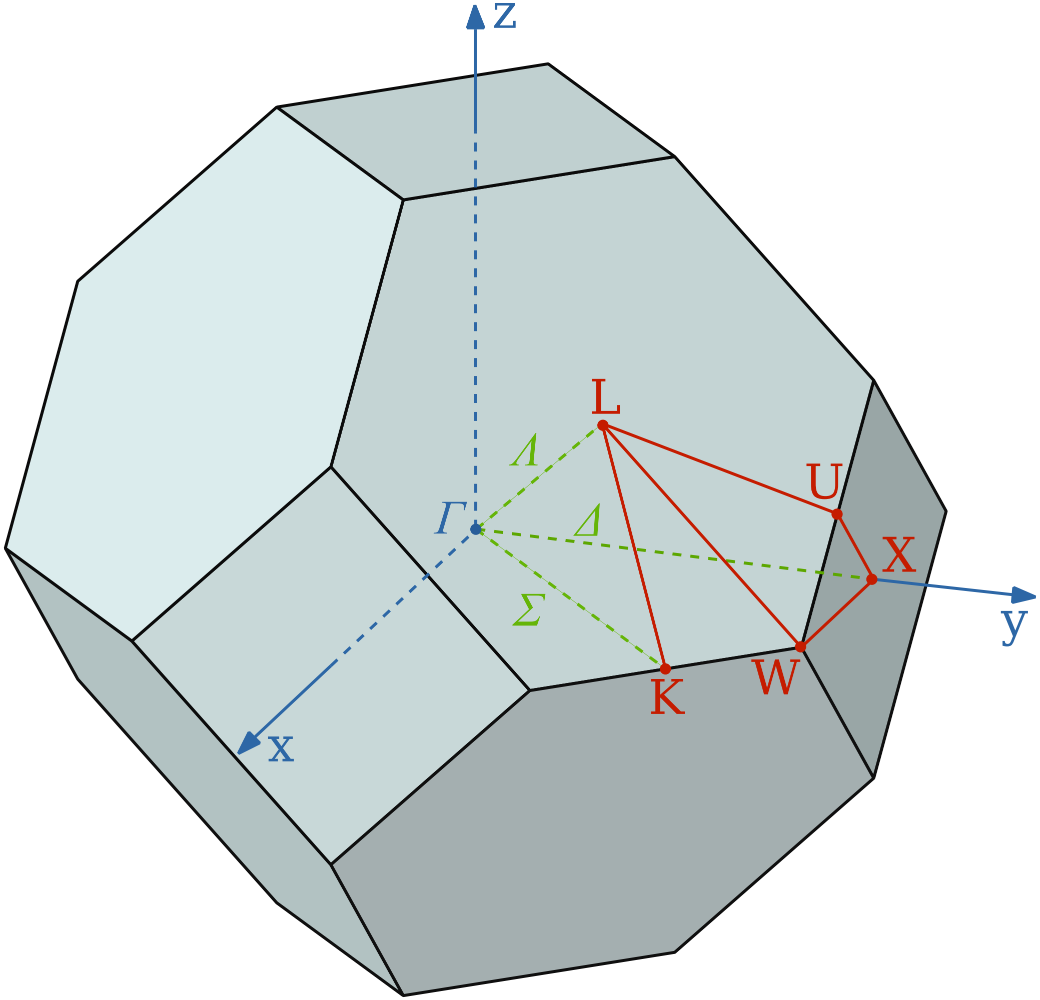


Optical properties: microscopic theory

Experimental dielectric function of Ag:

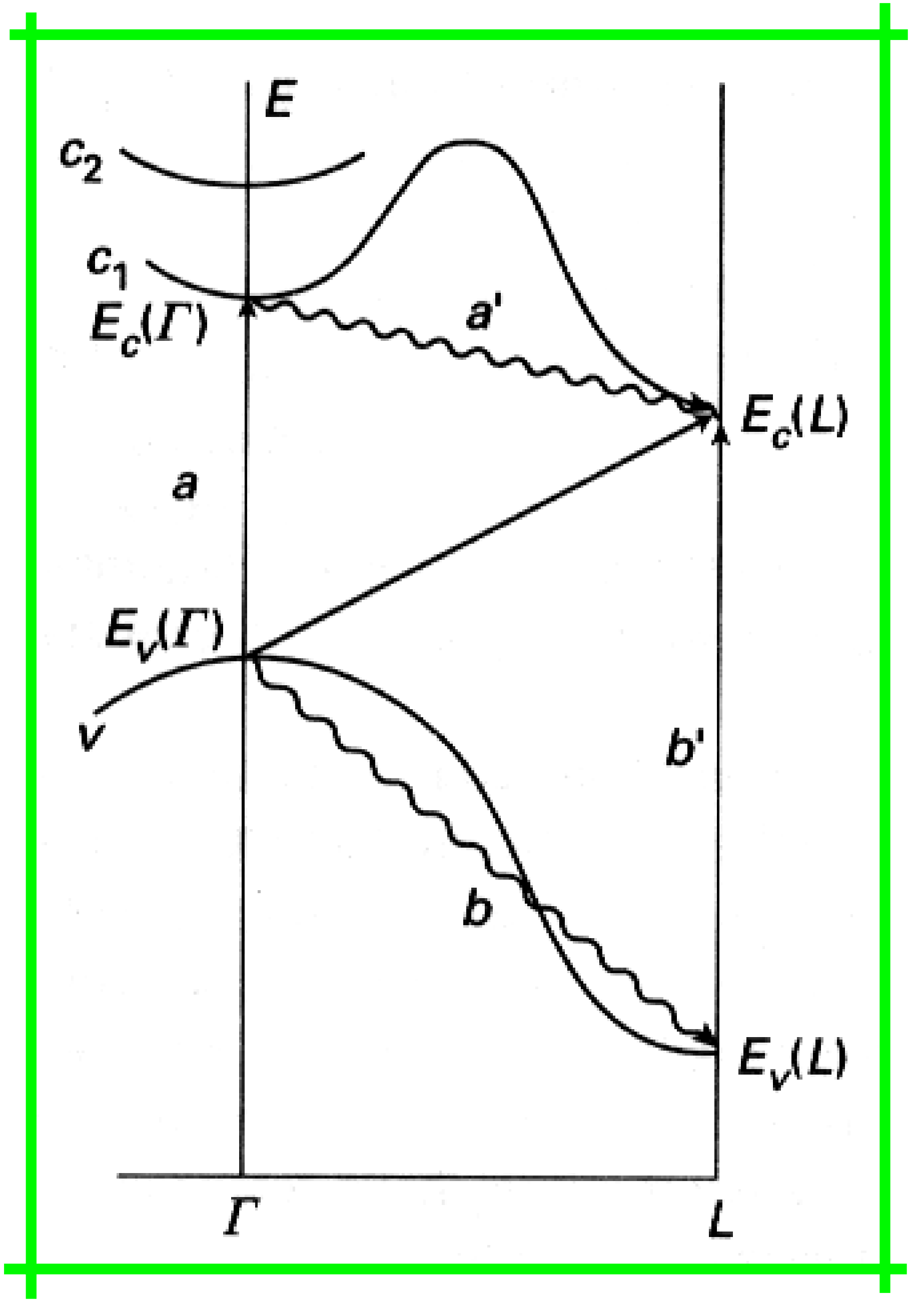


The fcc Brillouin zone



Optical properties: microscopic theory

Indirect phonon assisted transitions



Optical properties: microscopic theory

Two photon transitions

With intense radiation sources, one can have two photon processes:

$$\eta(\omega_1) = \frac{8\pi^3\hbar e^2 N_2}{cm^4 n_1 n_2^2 \omega_1\omega_2}\int_{B.Z.} \frac{2d\vec{k}}{(2\pi)^3}\left|D\right|^2 \delta\left[E_c(\vec{k}) - E_v(\vec{k}) - (\hbar\omega_1 + \hbar\omega_2)\right]$$

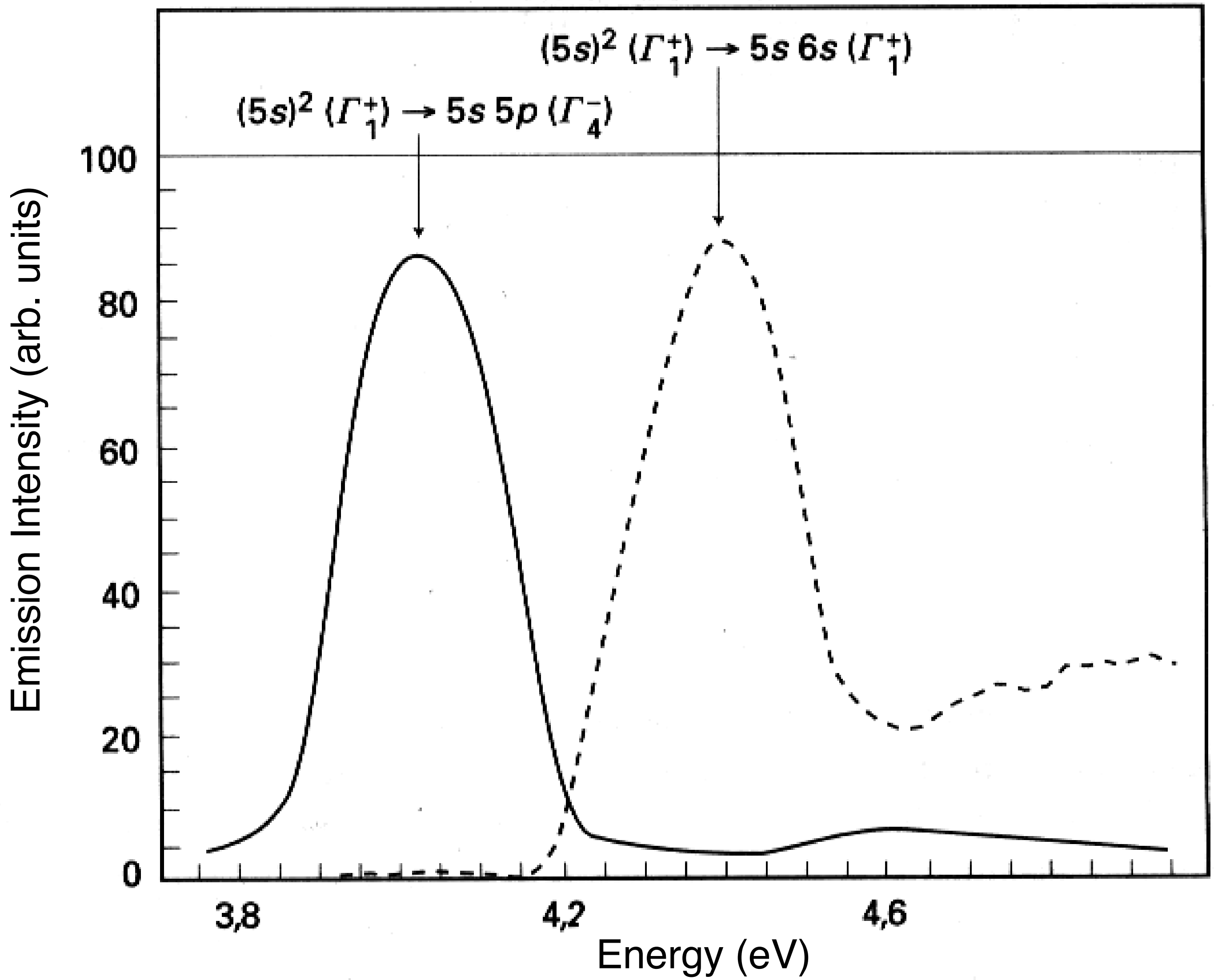
In which N_2 is the photon density at frequency ω_2 and D is the two photon transition matrix element:

$$D = \sum_{\gamma} (1 + P_{12}) \frac{\langle f|\,\hat{\epsilon}_1 \cdot \vec{p}\,|\gamma\rangle\,\langle\gamma|\,\hat{\epsilon}_2 \cdot \vec{p}\,|i\rangle}{E_\gamma(\vec{k}) - E_i(\vec{k}) - \hbar\omega_1}$$

where γ represent all the possible intermediate states.

Optical properties: microscopic theory

Two photon absorption (---) in the Ag- ion in RbBr compared with one photon absorption (—)

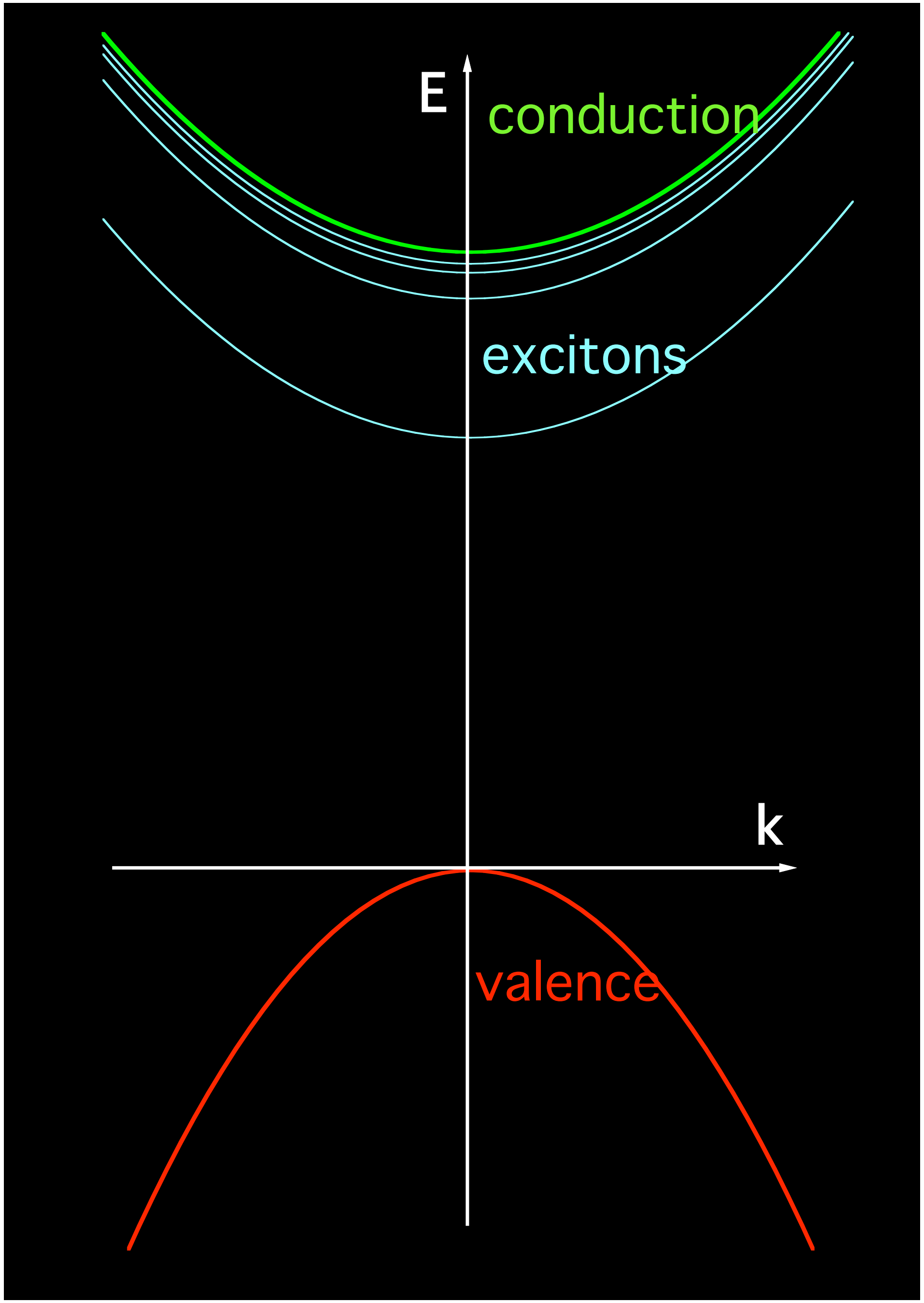


Optical properties: microscopic theory

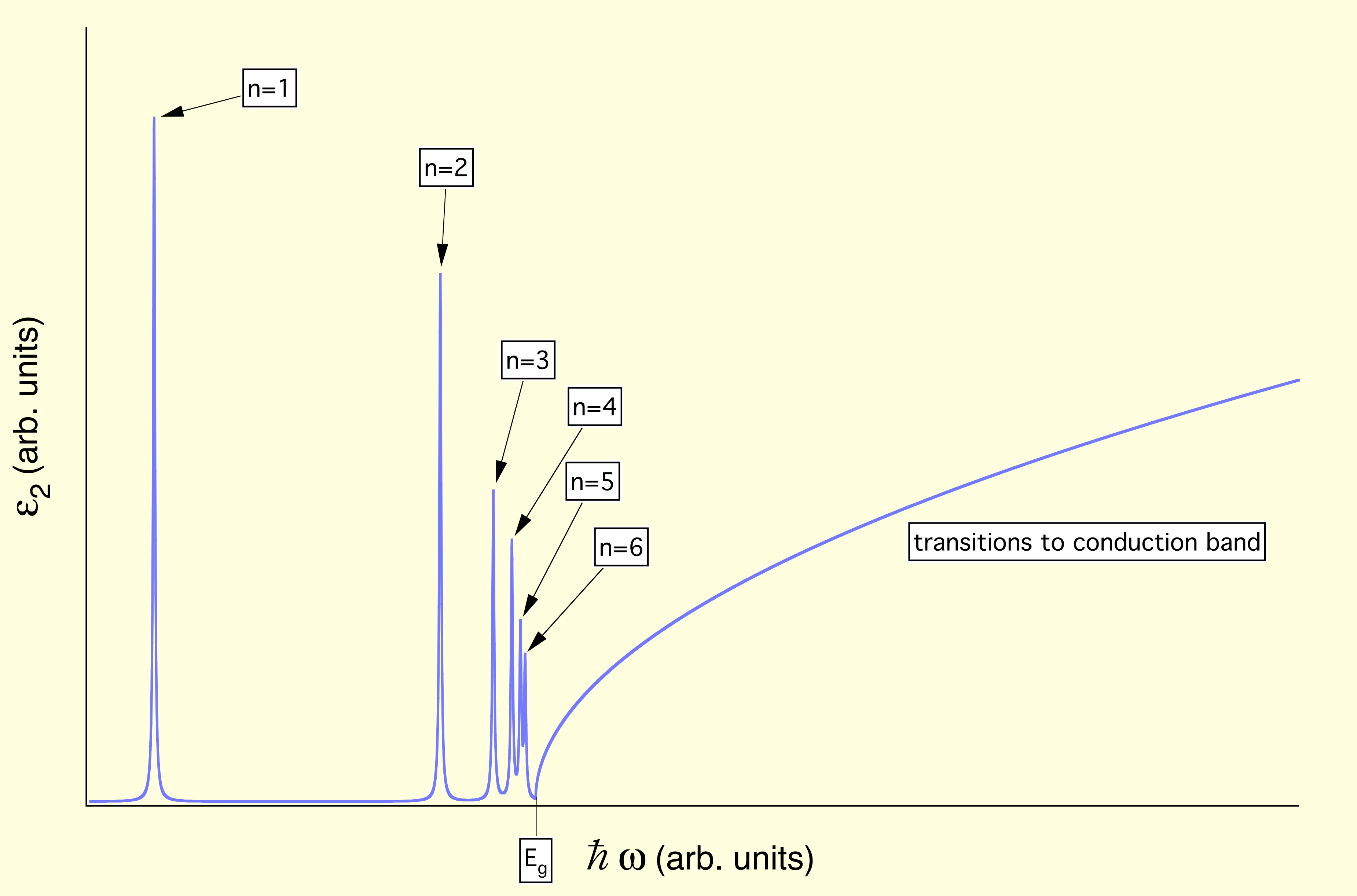
The formation of electron -hole pairs creates a sytem composed of two particle attracting each other. The relative energy levels fall in the forbidden gap and are observable in the absorption spectrum. They are hydrogen like states and are called excitons:

$$E_n = E_g - \frac{e^4}{2\hbar^2}\frac{\mu}{\epsilon^2}\frac{1}{n^2}$$

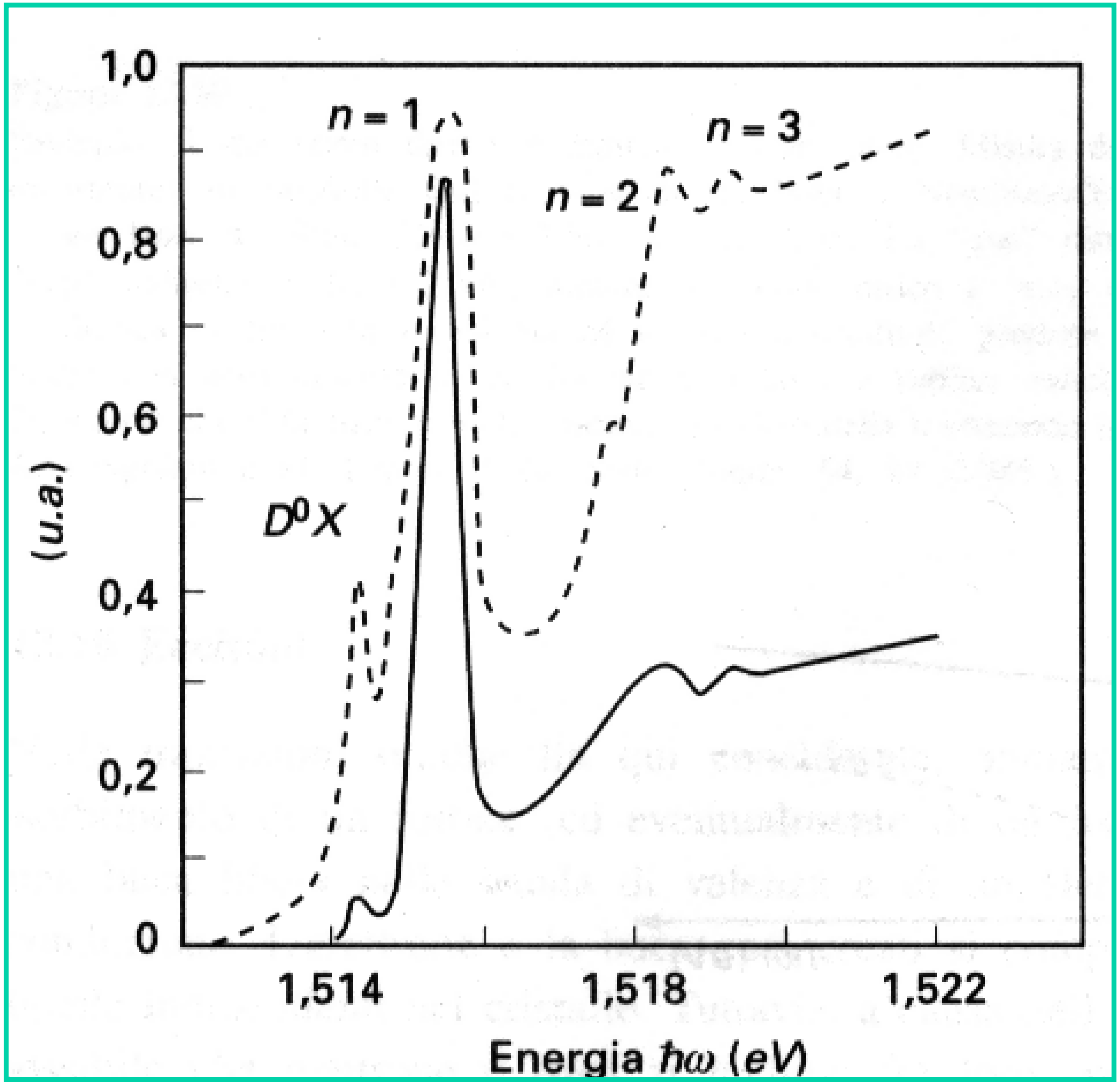
$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$



Optical properties: microscopic theory



Optical properties: microscopic theory



Eccitoni in GaAs