

Light-matter interaction

(see for instance F. Bassani, G. Pastori Plallavicini, *Electronic states and optical transitions in solids*, Pergamon Press, Oxford, 1975, chapter 5)

Let us work in the semi-classical approximation, i.e. let us treat the matter with quantum mechanics and the electromagnetic field with the classical electrodynamics, without quantizing it. Let us consider propagating electromagnetic waves far from their source. In this case we can take a scalar potential $V=0$ and $\nabla \cdot \mathbf{A}=0$, where \mathbf{A} is the vector potential, because of the arbitrariness in the gauge.

From the standard classical mechanics we know that the kinetic energy of a system of N electrons

$$\sum_{i=1}^N \frac{\vec{p}_i^2}{2m}$$

has to be replaced, in the presence of an electromagnetic field, by the expression

$$\sum_{i=1}^N \frac{1}{2m} \left(\vec{p}_i + \frac{e\vec{A}(\vec{r}_i, t)}{c} \right)^2$$

where e is the absolute value of the electron charge. The terms in the brackets contain terms proportional to \vec{A} and terms proportional to A^2 . Let us consider weak electromagnetic fields, i.e. $\vec{A} \rightarrow 0$. This case corresponds to the normal situations, only for very powerful laser beams this approximation does not work. In the limit $\vec{A} \rightarrow 0$ the terms in A^2 can be neglected with respect to the terms in \vec{A} . Therefore the Hamiltonian of a system without the field

$$H_0 = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + U(r_1, \dots, r_N)$$

can be replaced in the presence of the field by the new Hamiltonian

$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + U(r_1, \dots, r_N) + \sum_{i=1}^N \frac{1}{2m} \left(\frac{e\vec{p}_i \cdot \vec{A}(\vec{r}_i, t) + e\vec{A}(\vec{r}_i, t) \cdot \vec{p}_i}{c} \right)$$

The third term is therefore the interaction Hamiltonian of the electrons in the radiation field. Since $\nabla \cdot \mathbf{A}=0$ the last term, the interaction Hamiltonian H_{eR} , can be written

$$H_{eR} = \frac{e}{mc} \sum_{i=1}^N \vec{A}(\vec{r}_i, t) \cdot \vec{p}_i$$

The effect of a radiation field on the crystal electronic states can be calculated by treating H_{eR} as a time dependent perturbation term on the states of the crystal. Let us take a simple plane electromagnetic wave described by

$$\vec{A}(\vec{r}, t) = \vec{A}_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)} + \text{c.c.}$$

It has the form of $O(\mathbf{r}) e^{\mp i\omega t}$. From elementary quantum mechanics we know that, to first order perturbation theory, the probability per unit time that a perturbation of the form $O(\mathbf{r}) e^{\mp i\omega t}$ induces a transition from the initial state $|i\rangle$ of energy E_i to the final state $|f\rangle$ of energy E_f is

$$P_{i \rightarrow f} = \frac{2\pi}{h} |\langle f | O(\vec{r}) | i \rangle|^2 \delta(E_f - E_i \mp h\omega) \quad *$$

* in this formula you should replace \hbar to h , I was not able to type \hbar .

The above relation has the interpretation that a perturbation $O(\mathbf{r}) e^{-i\omega t}$ induces transitions with the absorption of a quantum $\hbar\omega$, while a perturbation $O(\mathbf{r}) e^{i\omega t}$ gives rise to the emission of a quantum $\hbar\omega$. Since the perturbation must be real you have the sum of both absorption and emission terms, but the choice of the initial and final states select out the terms to be considered. If the initial state is the ground state, the emission term makes the expression for $P_{i \rightarrow f}$ to vanish. Thus only the absorption term needs to be considered in discussing the optical absorption spectrum of a crystal in the ground state. The emission term needs to be considered in discussing the radiative emission due to electrons initially in the excited states (luminescence, phosphorescence.....).

Let us calculate $\langle f | O(\vec{r}) | i \rangle$ in the case of crystal states. $u_{\vec{k}_i, v}(\vec{r}) e^{i\vec{k}_i \cdot \vec{r}}$ and

$u_{\vec{k}_f, c}(\vec{r}) e^{i\vec{k}_f \cdot \vec{r}}$ are the wave functions of the initial and final states of an electron that is excited from the valence band at \vec{k}_i to the conduction band at \vec{k}_f . We have

$$\begin{aligned} \langle f | O(\vec{r}) | i \rangle &= \int u_{\vec{k}_i, v}^*(\vec{r}) e^{-i\vec{k}_i \cdot \vec{r}} \left(\frac{e}{mc} \vec{A}(\vec{r}) \cdot \vec{p} \right) u_{\vec{k}_f, c}(\vec{r}) e^{i\vec{k}_f \cdot \vec{r}} d^3\vec{r} = \\ &= \vec{A}_0 \cdot \frac{e}{mc} \int u_{\vec{k}_i, v}^*(\vec{r}) e^{-i\vec{k}_i \cdot \vec{r}} (e^{i\vec{k} \cdot \vec{r}} \vec{p}) u_{\vec{k}_f, c}(\vec{r}) e^{i\vec{k}_f \cdot \vec{r}} d^3\vec{r} \end{aligned}$$

Let us write $\vec{r} = \vec{R}_n + \vec{\rho}$, where \vec{R}_n is the vector of the Bravais lattice closer to \vec{r} and $\vec{\rho}$ is a vector inside the unit cell. Let us change the integration variable in the integral above. This integral, because of the periodicity of the $u_{\mathbf{k}}$, will become a sum over all the Bravais vectors of an integral over the unit cell

$$\langle f | O(\vec{r}) | i \rangle = \sum_n \mathcal{R}_n e^{i(-\vec{k}_i + \vec{k} + \vec{k}_f) \cdot \vec{R}_n} \int u_{\vec{k}_i, v}^*(\vec{r}) e^{-i\vec{k}_i \cdot \vec{\rho}} (e^{i\vec{k} \cdot \vec{\rho}} \vec{p}) u_{\vec{k}_f, c}(\vec{r}) e^{i\vec{k}_f \cdot \vec{\rho}} d^3\vec{\rho}$$

The last integral is a number that does not depend on \vec{R}_n . Therefore the matrix element vanishes when $\vec{k} + \vec{k}_f - \vec{k}_i$ is different from a vector of the reciprocal lattice \mathbf{G} . The k of the electrons are of the order of π/a , i.e. of the order of 10^{10} m^{-1} , while the k of the visible photons are of the order of 10^7 m^{-1} . Therefore \vec{k} is negligible with respect to \vec{k}_f and \vec{k}_i . The matrix element is different from zero only when $\vec{k}_f - \vec{k}_i = \vec{G}$. This means that an electromagnetic wave can cause an excitation of one electron from one band to another band only if the initial state and the final state have the same k (conservation of the crystal momentum in the optical transitions, i.e. "vertical" transitions).

If the photon has a high energy – if it is an x-ray photon- its k is no more negligible and the wave vectors of the initial and final electronic states differ by this k .