Optical transitions in low-dimensional structures

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1 Optical transitions and Fermi's golden rule

To include the effect of light in a quantum mechanical description, the electromagnetic field is generally described by the appropriate vector potential $\mathbf{A}$. Let us choose

$$\mathbf{A} = \mathbf{e}\frac{2E_0}{\omega}\sin\left(\mathbf{Q}\cdot\mathbf{R} - \omega t\right) \tag{1}$$

with the corresponding electric field

$$\mathbf{E} = -\frac{\partial\mathbf{A}}{\partial t} = \mathbf{e}2E_0\cos(\mathbf{Q}\cdot\mathbf{R} - \omega t) \tag{2}$$

This is the electric field in an electromagnetic wave propagating in $\mathbf{Q}$-direction and with a polarization $\mathbf{e}$. The corresponding photon flux (i. e. the number of photons per time and area) is

$$\Phi_0 = \frac{2\epsilon_0 c n E_0^2}{\hbar\omega} \tag{3}$$

The Schrödinger equation including the vector potential is

$$\left[\frac{(\hat{\mathbf{p}} + e\mathbf{A})^2}{2m_0} + V_{\text{crystal}}\right]\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{4}$$

Expanding the squared parenthesis

$$(\hat{\mathbf{p}} + e\mathbf{A})^2 = \hat{\mathbf{p}}^2 + e\hat{\mathbf{p}}\cdot\mathbf{A} + e\mathbf{A}\cdot\hat{\mathbf{p}} + e^2\mathbf{A}^2 \tag{5}$$

The last term is of second order and, assuming a weak field, is usually neglected. Moreover, the second term can be modified by noting that the momentum operator is essentially the divergence which is zero for a transverse wave:

$$e\hat{\mathbf{p}}\cdot\mathbf{A}\Psi = -i\hbar e\nabla\cdot(\mathbf{A}\Psi) = -i\hbar e(\mathbf{A}\cdot\nabla\Psi + \Psi\underbrace{\nabla\cdot\mathbf{A}}_{=0}) = e\mathbf{A}\cdot\hat{\mathbf{p}}\Psi \tag{6}$$

The Schrödinger equation Eq 4 can now be written

$$\left[\hat{H}_0 + \hat{V}_{\text{EM}}\right]\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{7}$$

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with

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m_0} + V_{\text{crystal}} \tag{8}$$

$$\hat{V}_{\text{EM}} = \frac{e\mathbf{A} \cdot \hat{\mathbf{p}}}{m_0} = \frac{2eE_0}{m_0\omega} \sin(\mathbf{Q} \cdot \mathbf{R} - \omega t)\mathbf{e} \cdot \hat{\mathbf{p}} \tag{9}$$

where $\hat{V}_{\text{EM}}$ can be treated as a perturbation. The wavelength of the light is much longer than the extension of the wavefunctions (or, for de-localised states, the unit cell) and the electric field is therefore assumed to be spatially constant on the quantum mechanical lengthscale. This means that we can put $\mathbf{Q} = 0$, the so called electric dipole approximation. Using this and rewriting the sin-function with exponentials, the perturbing term becomes

$$\hat{V}_{\text{EM}} = \frac{eE_0}{im_0\omega}\mathbf{e} \cdot \hat{\mathbf{p}} \left(e^{-i\omega t} - e^{i\omega t} \right) \tag{10}$$

Fermi's golden rule is an approximation describing the probability for a transition between two (unperturbed) states when exposed to a perturbation. If the perturbation is of the form given above, i. e. with a harmonic time dependence, it can be shown that the first term in Eq 10 gives rise to absorption and the second term gives rise to stimulated emission. We will first limit the discussion to absorption and thus only include the first term in Eq 10. Using Fermi's golden rule, the transition rate W_{ji} from a state $|i\rangle$ to a state $|j\rangle$ due to absorption of a photon is given by:

$$W_{ji} = \frac{2\pi}{\hbar} \left(\frac{eE_0}{m_0\omega} \right)^2 \left| \langle j|\mathbf{e} \cdot \hat{\mathbf{p}}|i\rangle \right|^2 \delta(E_j - E_i - \hbar\omega) \tag{11}$$

The operator $\mathbf{e} \cdot \hat{\mathbf{p}}$ in the matrix element should be understood as

$$\mathbf{e} \cdot \hat{\mathbf{p}} = (e_x p_x + e_y p_y + e_z p_z) = -i\hbar \left(e_x \frac{\partial}{\partial x} + e_y \frac{\partial}{\partial y} + e_z \frac{\partial}{\partial z} \right) \tag{12}$$

For example if the light is polarized along the x-direction ($e_x = 1, e_y = e_z = 0$) the matrix element will be $\langle j|p_x|i\rangle$.

The absorption α due to the excitation of an electron from state i to state j is now given as the number of transitions (i. e. the number of photons disappearing) normalized to the incoming number of photons

$$\alpha = \frac{W_{ji}}{\Phi_0\Omega} = \frac{\pi e^2}{m_0^2\omega\epsilon_0 cn\Omega} \left| \langle j|\mathbf{e} \cdot \hat{\mathbf{p}}|i\rangle \right|^2 \delta(E_j - E_i - \hbar\omega) \tag{13}$$

Ω is a normalization volume and, as we will see later, it will in general cancel out when evaluating the matrix element. Instead of using the absorption coefficient α Davies uses the real part σ_1 of a complex conductivity $\tilde{\sigma} = \sigma_1 + i\sigma_2$. These two quantities are related by $\sigma_1 = \alpha\epsilon_0 cn$. Another quantity describing light-matter interaction is the

complex refractive index $\tilde{n}_r = n_r + i\kappa_r$. It can be defined by the dispersion relation between wave number q and frequency ω

$$q = \frac{\tilde{n}_r \omega}{c} = \frac{n_r \omega}{c} + i\frac{\kappa_r \omega}{c} \tag{14}$$

A wave with this wave number can be written as

$$e^{iqx} = e^{i\frac{n_r \omega}{c}x}e^{-\frac{\kappa_r \omega}{c}x} \tag{15}$$

which (due to the second exponential function) is an exponentially damped wave. The damping is determined by κ_r and can e. g. be due to absorption. In an excercise it its shown that $\alpha = 2\omega\kappa_r/c$.

2 The matrix element within the effective mass approximation

Within the effective mass approximation, the wave function can be written as a product of an envelope function and a Bloch funcion

$$\Psi(\mathbf{R}) = \Omega^{\frac{1}{2}}\chi(\mathbf{R})u_{n0}(\mathbf{R}) \tag{16}$$

The normalization volume Ω is introduced to properly normalize Ψ (provided that χ and u_{n0} are normalized). Using this wave function, the matrix element in Eq 13 can be written

$$\langle j|\mathbf{e}\cdot\hat{\mathbf{p}}|i\rangle = \Omega \int \chi_j^*(\mathbf{R})u_{j0}^*(\mathbf{R})(\mathbf{e}\cdot\hat{\mathbf{p}})\chi_i(\mathbf{R})u_{i0}(\mathbf{R})d^3R \tag{17}$$

Since the momentum operator is a first derivative, we can use the product rule to get

$$\langle j|\mathbf{e}\cdot\hat{\mathbf{p}}|i\rangle = \Omega \int \left[\chi_j^*(\mathbf{R})\chi_i(\mathbf{R})\right]\left[u_{j0}^*(\mathbf{R})(\mathbf{e}\cdot\hat{\mathbf{p}})u_{i0}(\mathbf{R})\right]d^3R$$

$$+\Omega \int \left[u_{j0}^*(\mathbf{R})u_{i0}\right]\left[\chi_j^*(\mathbf{R}))(\mathbf{R})(\mathbf{e}\cdot\hat{\mathbf{p}}\chi_i(\mathbf{R})\right]d^3R \tag{18}$$

The envelope functions vary slowly on the scale of a unit cell (or lattice constant). By splitting the integrals in Eq 18 into sums of integrals, each one with an integration volume of one unit cell, then the envelope functions are approximately constant. The

first term in Eq 18 can thus be written

$$\Omega \sum_{\substack{\# \text{ of} \\ \text{cells}}} \chi_j^*(\mathbf{R})\chi_i(\mathbf{R}) \int_{\substack{\text{one} \\ \text{cell}}} u_{j0}^*(\mathbf{R})(\mathbf{e}\cdot\hat{\mathbf{p}})u_{i0}(\mathbf{R})d^3R$$

$$=\Omega \sum_{\substack{\# \text{ of} \\ \text{cells}}} \chi_j^*(\mathbf{R})\chi_i(\mathbf{R})\frac{\Omega_{cell}}{\Omega} \int_{\Omega} u_{j0}^*(\mathbf{R})(\mathbf{e}\cdot\hat{\mathbf{p}})u_{i0}(\mathbf{R})d^3R$$

$$=\int_{\Omega} \chi_j^*(\mathbf{R})\chi_i(\mathbf{R}) \int_{\Omega} u_{j0}^*(\mathbf{R})(\mathbf{e}\cdot\hat{\mathbf{p}})u_{i0}(\mathbf{R})d^3R$$

$$=\langle \chi_j | \chi_i \rangle \langle u_{j0} | \mathbf{e}\cdot\hat{\mathbf{p}} | u_{i0} \rangle \tag{19}$$

Here we used that the Bloch functions are lattice periodic and thus give the same contribution in every unit cell. Ω_{cell} is the volume of a unit cell and cancels out when converting the summation over cells with an integral. The second term in Eq 18 can be rewritten in a similar way. The total matrix element will therefore be

$$\langle j|\mathbf{e}\cdot\hat{\mathbf{p}}|i\rangle = \underbrace{\langle \chi_j|\chi_i\rangle\langle u_{j0}|\mathbf{e}\cdot\hat{\mathbf{p}}|u_{i0}\rangle}_{\text{interband transition}} + \underbrace{\langle \chi_j|\mathbf{e}\cdot\hat{\mathbf{p}}|\chi_i\rangle\langle u_{j0}|u_{i0}\rangle}_{\text{intraband transition}} \tag{20}$$

As indicated in 20, the first term describes transitions between two different bands. This can be understood by considering that for transitions from e. g. valence to conduction band, u_{j0} and u_{i0} are orthogonal (remember: Eigenstates of the same Hamiltonian) and thus the second term in Eq 20 vanishes, leaving

$$\langle j|\mathbf{e}\cdot\hat{\mathbf{p}}|i\rangle = \langle \chi_j|\chi_i\rangle \underbrace{\langle u_{j0}|\mathbf{e}\cdot\hat{\mathbf{p}}|u_{i0}\rangle}_{\equiv \mathbf{e}\cdot\mathbf{p}_{ji}} \tag{21}$$

The matrix element of the Bloch functions, $\mathbf{p}_{ji}$, can be seen as a material constant. The case of transitions between two states within the same band, i. e. intraband transitions, is governed by the second term of 20 and will be discussed later. First, however, let us investigate interband transitions in a quantum well.

3   Application to a quantum well: Interband transitions

The envelope function for a quantum well consists of a planewave parallel to the well and a bound state perpendicular to the well

$$\chi_{n\mathbf{k}}(\mathbf{R}) = A^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}}\phi_n(z) \tag{22}$$

The matrix element will now be

$$\langle j|\mathbf{e}\cdot\hat{\mathbf{p}}|i\rangle = \mathbf{e}\cdot\mathbf{p}_{cn,vm}\langle \mathbf{k}'|\mathbf{k}\rangle\langle cn|vm\rangle$$
$$= \underbrace{\mathbf{e}\cdot\mathbf{p}_{cn,vm}}_{A}\underbrace{\delta(\mathbf{k}'-\mathbf{k})}_{B}\underbrace{\langle cn|vm\rangle}_{C} \tag{23}$$

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The factor A gives the polarization dependence, which for som experimental conditions is different for light and heavy holes. The factor B confirms what we have already guessed, namely that only vertical transitions are allowed, i. e. that the in-plane momentum is conserved. The factor C gives rise to some selection rules.

3.1 Selection rules

The transition probability is zero for some combinations of initial and final states. This gives rise to selection rules: only certain transitions are allowed. The selection rules in band-to-band transitions are determined by the overlap between the envelope functions, $\langle cn|vm \rangle$. Investigating this overlap, we can list the following selection rules:

- The electron and hole state have to be of the same parity, provided that the potential is symmetric.

- If the well for electrons and holes are identical (i. e. $\Delta E_c = \Delta E_v$ and same m^*) then only transitions with the same quantum number for the electron and hole states are allowed ($\langle cn|vm \rangle = \delta_{n,m}$, "The $\Delta n = 0$ rule").

- Also when the electron and hole wells are not strictly identical, $\Delta n = 0$ usually gives the strongest transitions.

3.2 Absorption spectrum

Let us now return to the absorption expression Eq 13, which, using the matrix element Eq 23 for inter band transitions in a quantum well, will be

$$\alpha_{nm\mathbf{k}'\mathbf{k}} = \frac{\pi e^2}{m_0^2 \omega \epsilon_0 cn\Omega} \left| \mathbf{e} \cdot \mathbf{p}_{cn,vm} \right|^2 \left| \langle cn|vm \rangle \right|^2 \delta(\mathbf{k}' - \mathbf{k})\delta(E_{cn}(\mathbf{k}') - E_{vm}(\mathbf{k}) - \hbar\omega) \quad (24)$$

Note that this is the absorption of light due to transitions from an initial state $|m\mathbf{k}\rangle$ to a final state $|n\mathbf{k}'\rangle$, as indicated by the subscripts on α. The "normal" absorption at a given photon energy $\hbar\omega$, as can be measured experimentally, is obtained by summing over all initial and final states

$$\alpha = \frac{\pi e^2}{m_0^2 \omega \epsilon_0 cn\Omega} \sum_{n,m} \left| \mathbf{e} \cdot \mathbf{p}_{cn,vm} \right|^2 \left| \langle cn|vm \rangle \right|^2 2 \sum_{\mathbf{k}',\mathbf{k}} \delta(\mathbf{k}' - \mathbf{k})\delta[E_{cn}(\mathbf{k}') - E_{vm}(\mathbf{k}) - \hbar\omega]$$

$$= \frac{\pi e^2}{m_0^2 \omega \epsilon_0 cnL} \sum_{n,m} \left| \mathbf{e} \cdot \mathbf{p}_{cn,vm} \right|^2 \left| \langle cn|vm \rangle \right|^2 \underbrace{\frac{2}{A} \sum_{\mathbf{k}} \delta[E_{cn}(\mathbf{k}) - E_{vm}(\mathbf{k}) - \hbar\omega]}_{joint\ density\ of\ states} \quad (25)$$

Here the normalization volume Ω was split into an area A and a length L. The factor 2 is due to spin. Assuming parabolic bands, the (optical) joint density of states n_{opt}

becomes

$$n_{opt}(\hbar\omega) = \frac{2}{A} \sum_{\mathbf{k}} \delta[E_{cn}(\mathbf{k}) - E_{vm}(\mathbf{k}) - \hbar\omega]$$

$$= \frac{2}{A} \sum_{k_x,k_y} \delta[E_c + \varepsilon_{cn} + \frac{\hbar^2(k_x^2 + k_y^2)}{2m_{cn}^*} - E_v + \varepsilon_{vm} + \frac{\hbar^2(k_x^2 + k_y^2)}{2m_{vm}^*} - \hbar\omega]$$

$$= \frac{2}{A} \sum_{k_x,k_y} \delta[E_g + \varepsilon_{cn} + \varepsilon_{vm} + \frac{\hbar^2(k_x^2 + k_y^2)}{2m_{nm}^*} - \hbar\omega] \qquad (26)$$

where ε_{cn} and ε_{vm} are the confinement in z-direction for electrons and holes and m_{nm}^* is the reduced effective mass defined by $1/m_{nm}^* = 1/m_{cn}^* + 1/m_{vm}^*$.

4 Application to a quantum well: Intersubband transitions

Assuming that there is a charge carrier (electron or hole) in the quantum well, an incoming photon can promote the charge carrier to an excited state. In this case, both initial and final states are in the conduction band. This is an example of an *interband* transition, also called *intersubband* transition. Repeating Eq 20 with the two states originating from the same Bloch function, i. e. $u_{j0} = u_{i0}$:

$$\langle j|\mathbf{e} \cdot \hat{\mathbf{p}}|i \rangle = \langle \chi_j|\chi_i \rangle \underbrace{\langle u_{i0}|\mathbf{e} \cdot \hat{\mathbf{p}}|u_{i0} \rangle}_{=0} + \langle \chi_j|\mathbf{e} \cdot \hat{\mathbf{p}}|\chi_i \rangle \underbrace{\langle u_{i0}|u_{i0} \rangle}_{=1} \qquad (27)$$

The second term will no longer vanish but instead the first term will be zero. This is because u_{i0} is the wavefunction of a bulk electron at $k = 0$ and the matrix element with $\hat{\mathbf{p}}$ is therefore the expectation value of the momentum of an electron at the concuction band minimum. As with all band minima (and maxima) the momentum should be zero. The transition probability in the case of an intraband transition is thus determined by the momentum matrix element of the envelope functions. As in the case of interband transitions, the envelope function for a quantum well can be written as a product of a planewave parallel to the well and a bound state perpendicular to the well (Eq 22).

$$\chi_{n\mathbf{k}}(\mathbf{R}) = A^{-1/2} e^{i\mathbf{k}\cdot\mathbf{r}} \phi_n(z) \qquad (28)$$

Assume now that the polarization vector is in x-direction. Then

$$\mathbf{e} \cdot \hat{\mathbf{p}} = p_x = -i\hbar \frac{\partial}{\partial x} \qquad (29)$$

$$\mathbf{e} \cdot \hat{\mathbf{p}}\chi_{n\mathbf{k}} = \hbar k_x \chi_{n\mathbf{k}} \qquad (30)$$

$$\langle m\mathbf{k}'|\mathbf{e} \cdot \hat{\mathbf{p}}|n\mathbf{k} \rangle = \underbrace{\langle m\mathbf{k}'|n\mathbf{k} \rangle}_{\text{orhtogonal}} = 0 \qquad (31)$$

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The result is the same for polarization in y-direction. However, assuming z-polarization yields

$$\mathbf{e} \cdot \hat{\mathbf{p}} = p_z \tag{32}$$

$$\langle m\mathbf{k}'|\mathbf{e} \cdot \hat{\mathbf{p}}|n\mathbf{k}\rangle = \underbrace{\langle \mathbf{k}'|\mathbf{k}\rangle}_{\delta(\mathbf{k}'-\mathbf{k})} \langle m|\hat{p_z}|n\rangle \tag{33}$$