quantenmechanische Motivation Dipol Übergangsmatrixelemente

(18) $\hat{H}\psi = \cancel{\left(\frac{\hbar^2}{2m}\Delta + V\right)}\psi = E\psi$ stationäre Schrödinger Gl. / Eigenwert problem

(19) $\hat{H}\psi = -\frac{\hbar}{i}\frac{\partial \psi}{\partial t}$ zeitabhängige Schrödinger Gl.

Sei $H = H_0 + V'(x,t)$ mit $V'(x,t)$: Störpotential

$H_0 = \frac{\hbar^2}{2m}\Delta + V(x)$ ungestörter Hamiltonian ~~2 Niveaus Situation~~

sei $H\psi_\alpha = E_\alpha \psi_\alpha$ und $H\psi_\beta = E_\beta \psi_\beta$

$\psi_\alpha = u_\alpha(x,y,z)\, e^{-\frac{i}{\hbar}E_\alpha t}$ $\psi_\beta = u_\beta(x,y,z)\, e^{-\frac{i}{\hbar}E_\beta t}$

$\Psi = c_\alpha \psi_\alpha + c_\beta \psi_\beta$ ist auch Lsg von $H_0\psi = -\frac{\hbar}{i}\frac{\partial \psi}{\partial t}$ mit $c_{\alpha,\beta}$ zeitunabhängig, aber nicht mehr von $H\psi = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t}$

finde Lsg., bzw Näherungslösung (→ Übungen) $\overset{*}{\Rightarrow}$ mit Randbed. $c_\alpha = 1$, $c_\beta = 0$ @ $t=0$, ⇒ finde $c_\beta(t)$ ⇒ Dipolmatrix el.

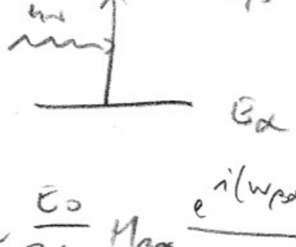
$$\frac{dc_\beta}{dt} \triangleq +\frac{i}{\hbar}\, e^{\frac{i}{\hbar}(E_\beta - E_\alpha)t}\, E_0 \cos(\omega t)\, M_{\beta\alpha} \qquad \omega_{\beta\alpha} = \frac{E_\beta - E_\alpha}{\hbar}$$

* unter Annahme:
- ebene EM Welle
- nur $\vec{E}$-Feld betrachten (nicht $\vec{B}$)
- $\vec{E}$ Feld homogen ($\lambda \gg a_0$)
- ~~Störung~~ Übergang von $\psi_\alpha \to \psi_\beta$ (stationärer Anfangszustand → stationärer Endzustand)

$$\frac{dc_\beta}{dt} = \frac{i}{2\hbar} E_0 M_{\beta\alpha}\left(e^{i(\omega_{\beta\alpha}+\omega)t} + e^{i(\omega_{\beta\alpha}-\omega)t}\right)$$

$$c_\beta(t) = \int_0^t \frac{dc_\beta}{dt}\,dt = \frac{E_0}{2\hbar} M_{\beta\alpha}\left\{\frac{e^{i(\omega_{\beta\alpha}+\omega)t}-1}{(\omega_{\beta\alpha}+\omega)} + \frac{e^{i(\omega_{\beta\alpha}-\omega)t}-1}{\omega_{\beta\alpha}-\omega}\right\}$$

Absorption



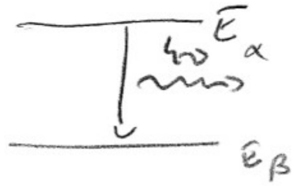
$$\omega_{\beta\alpha} = \frac{E_\beta - E_\alpha}{\hbar} > 0$$

$$\rightarrow |\omega_{\beta\alpha} + \omega| \gg |\omega_{\beta\alpha} - \omega| = \Delta\omega$$

$$c_\beta(t) \sim \frac{E_0}{2\hbar} M_{\beta\alpha} \frac{e^{i(\omega_{\beta\alpha}-\omega)t}-1}{\omega_{\beta\alpha}-\omega}$$, calculate $c^* c$, use $(e^{-ix}-1)(e^{ix}-1) = 2(1-\cos x) = 4\sin^2(\frac{x}{2})$

$$|c_\beta(t)|^2 \sim \frac{E_0^2}{\hbar^2} |M_{\beta\alpha}|^2 \frac{\sin^2\left(\frac{1}{2}\Delta\omega\, t\right)}{(\Delta\omega)^2}$$

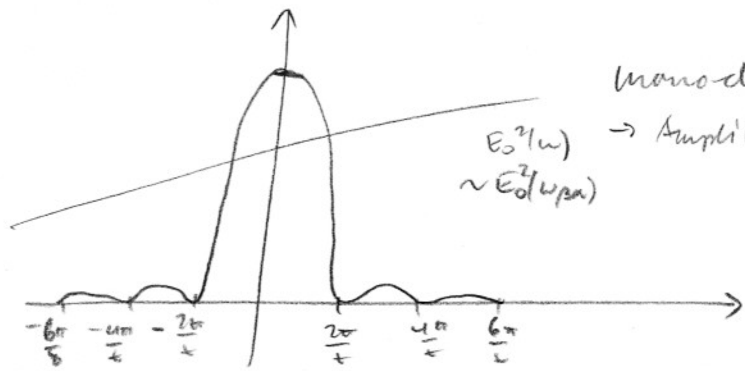
Emission



$$\omega_{\beta\alpha} = \frac{E_\beta - E_\alpha}{\hbar} < 0,$$
$$|\omega_{\beta\alpha} - \omega| \gg |\omega_{\beta\alpha} + \omega| = |\Delta\omega|$$

dito Absorption, i.a. same $|c_\beta(t)|^2$

→ $\boxed{\text{Absorption} = \text{Emissionswahrscheinlichkeit}}$



monochrom → Störung so lange eingeschaltet

→ Amplitude gegen Null → Zeit $t \to \infty$

→ δ-peak

→ $\omega_{\beta\alpha} = \omega$

$$\boxed{\hbar\omega = |E_\beta - E_\alpha|}$$

falls Licht kontinuierliches Spektrum: $E^2(\omega) \propto I(\omega)$

Integriere über ω, benutze $E_0^2(\omega) \sim E_0^2(\omega_{\beta\alpha})$, $d\omega = d\Delta\omega$

$$\int_{-\infty}^{\infty} d\Delta\omega \, \frac{E_0^2(\omega_{\beta\alpha})\,|M_{\beta\alpha}|^2}{\hbar^2} \, \frac{\sin^2(\frac{1}{2}\Delta\omega t)}{\Delta\omega^2}$$

$$= \frac{E_0^2(\omega_{\beta\alpha})\,|M_{\beta\alpha}|^2}{\hbar^2} \, \frac{t^2}{4} \int_{-\infty}^{\infty} \frac{\sin^2(\frac{1}{2}\Delta\omega t)}{\frac{1}{2}\Delta\omega t} \, d(\Delta\omega) \qquad \tfrac{1}{2}\Delta\omega t = \xi, \; d\Delta\omega = \tfrac{2}{t}\, d\xi$$

$$= \frac{E_0^2(\omega_{\beta\alpha})\,|M_{\beta\alpha}|^2}{\hbar^2} \, 2t \underbrace{\int_{-\infty}^{\infty} \frac{\sin^2\xi}{\xi^2}\, d\xi}_{\pi} = \frac{\pi E_0^2(\omega_{\beta\alpha})\,|M_{\beta\alpha}|^2}{2\hbar^2}\, t \quad \to \text{lin. in } t$$

Wahrscheinlichkeit, Atom in ψ_β zu finden wächst linear mit Zeit

→ Übergangswahrscheinlichkeit pro sec. $W_{\alpha\beta} = |c_\beta(t)|^2 / t$

$$\boxed{W_{\alpha\beta} = \frac{\pi E_0^2(\omega_{\beta\alpha})\,|M_{\beta\alpha}|^2}{2\hbar^2}}$$

Herleitung Einstein Koeffizienten

thermisches Strahlungsfeld: inkohärent → addiere Intensitäten / Übergangsraten für einzelne x, y, z Komponenten von $\vec{E}$.

polarisiert $\parallel x$, fortschreitend $\parallel z$, $E_x = B_y$, E-dichte:

$$\frac{1}{8\pi}\left(E_x^2 + B_y^2\right) = \frac{1}{4\pi} E_x^2$$

$$E_x = E_0 \cos(\omega t)$$
$$\overline{E_x^2} = \frac{1}{2} E_{0x}^2 \quad \text{Zeitmittel}$$

$$w_x(\omega)\, d\omega = \frac{1}{4\pi} \overline{E_x^2}(\omega)\, d\omega = \frac{1}{8\pi} E_{0x}^2\, d\omega$$

aber im isotropen Feld: $w_x = w_y = w_z = \frac{1}{3} w \rightarrow E_{0x}^2 = E_{0y}^2 = E_{0z}^2 = \frac{8\pi}{3} w(\omega)$

$$\rightarrow W_{\alpha\beta} = W_{\alpha\beta}^x + W_{\alpha\beta}^y + W_{\alpha\beta}^z = \overbrace{\frac{4\pi^2}{3\hbar^2} \underbrace{|M_{\beta\alpha}|^2}_{= |M_{\beta\alpha}^x|^2 + |M_{\beta\alpha}^y|^2 + |M_{\beta\alpha}^z|^2}}^{B_{\beta\alpha}} w(\omega_{\beta\alpha}) \xrightarrow[SI]{} \frac{\pi}{3\varepsilon_0\hbar^2} |M_{\beta\alpha}|^2\, w(\omega_{\beta\alpha})$$

$$\boxed{B_{\beta\alpha} = \frac{\pi}{3\varepsilon_0 \hbar^2} |M_{\beta\alpha}|^2}$$

benutze A_{ik} (17)

$$\frac{A_{ik}}{B_{ik}} = \frac{\cancel{4}}{\cancel{3}} \frac{\omega^3}{\cancel{4\pi\varepsilon_0} c^3 \hbar} \cdot \frac{\cancel{3\varepsilon_0}\hbar^2}{\cancel{4}\pi^2}$$

$$= \frac{\hbar\omega^3}{\pi^2 c^3} = w(\omega) \rightarrow \frac{8\pi h\nu^3}{c^3} \quad \text{wie vorher}$$

$$w(\omega)\, d\omega = \frac{\hbar\omega^3}{\pi^2 c^3}\, d\omega = \frac{8\pi h\nu^3}{c^3}\, d\nu = w(\nu)\, d\nu$$