Lecture 16 — 11/1

$\Rightarrow$ selection rules:

$\langle \alpha | \hat{A} | \beta \rangle \neq 0$ "allowed"

(transition from $|\beta\rangle$ to $|\alpha\rangle$ using interaction $\hat{A}$)

$= 0$ "forbidden"

'coupling'/interaction operator, e.g. $e\hat{\vec{r}}$.

parity selection rules:

$\hat{\pi}|\alpha\rangle = p_\alpha |\alpha\rangle$, $\hat{\pi}|\beta\rangle = p_\beta |\beta\rangle$ $\quad p_\alpha, p_\beta = \pm 1$

$$\langle \beta | \hat{\vec{r}} | \alpha \rangle = \underbrace{\langle \beta | \hat{\pi}^\dagger}_{\langle \beta | p_\beta} \underbrace{\hat{\pi} \, \hat{\vec{r}} \, \hat{\pi}^\dagger}_{-\hat{\vec{r}}} \underbrace{\hat{\pi} | \alpha \rangle}_{p_\alpha |\alpha\rangle} = - p_\alpha p_\beta \langle \beta | \hat{\vec{r}} | \alpha \rangle$$

$\Rightarrow$ "allowed" only for $p_\alpha = - p_\beta$

(same for any odd coupling operator)

even coupling operator: "allowed" for $p_\alpha = p_\beta$

$\boxed{[H_0, \hat{\pi}] = 0}$ $\quad H_0 \propto \vec{p}^{\,2}, \frac{1}{r^{2n}}, \frac{1}{|\vec{r}|}$ (even)

$\Rightarrow$ eigenfunctions of (undisturbed) atomic Hamiltonian all odd or even! (as a basis)

Same if magnetic field is present: $\vec{B}$ even, $\vec{J}$ even

(ii) Static DC field

Perturbation theory:

- non-degenerate energy levels: $\vec{E} = E\hat{z}$

$\Delta E_n^{(1)} = eE \langle n | \hat{z} | n \rangle = 0$ $\quad (H|n\rangle = E_n|n\rangle)$

$$\Delta E_n^{(2)} = (eE)^2 \sum_{m\neq n} \frac{|\langle m|\hat{z}|n\rangle|^2}{E_n - E_m} \qquad (\neq 0 \text{ in general})$$

$$\underset{\text{LW}}{\propto E^2} \Rightarrow \text{"quadratic Stark effect"}$$

$$|\tilde{n}'\rangle = |n\rangle + eE \sum_{m\neq n} \frac{|\langle m|\hat{z}|n\rangle|^2}{E_n - E_m} |m\rangle$$

$\Rightarrow |n'\rangle$ <u>not</u> eigenfct of $\hat{\pi}$!

N electrons: $\hat{z} \to \sum_{i=1}^{N} \hat{z}_i$ (same)

- polarizability α_d:

$$\vec{d} = -e\langle n'|\hat{z}|n'\rangle =$$

$$= 2e^2 \sum_{m\neq n} \frac{|\langle m|\hat{z}|n\rangle|^2}{E_n - E_m} E + \mathcal{O}(E^2)$$

$$\equiv \alpha_d \vec{E}$$

$\Rightarrow$ quadratic Stark effect:

$$\boxed{\Delta E_n^{(2)} = -\frac{\alpha_d}{2} E^2}$$

- <u>Degenerate</u> energy levels

$\Delta E_n^{(1)} \neq 0$ in general:

Example: $n = 2$:

$$H \propto \begin{array}{c} \begin{pmatrix} E_1 & 0 & 0 & eE\langle z\rangle_{14} & 0 \\ 0 & E_2 & 0 & 0 & 0 \\ 0 & 0 & E_2 & 0 & 0 \\ eE\langle z\rangle_{41} & 0 & 0 & E_2 & eE\langle z\rangle_{45} \\ 0 & 0 & 0 & eE\langle z\rangle_{54} & E_2 \end{pmatrix} \end{array} \begin{array}{ll} |100\rangle & 1 \\ |211\rangle & 2 \\ |21{-1}\rangle & 3 \\ |210\rangle & 4 \\ |200\rangle & 5 \end{array}$$

all "0" b/o $\Delta m \neq 0$, or $\Delta \ell = 0$ diagonalize...

Ex: $\frac{1}{\sqrt{2}}(|210\rangle \pm |200\rangle)$ - eigenstate with $E_2 \pm eE\langle z\rangle$

$w/ \langle z\rangle = |\langle 210|\hat{z}|200\rangle|$

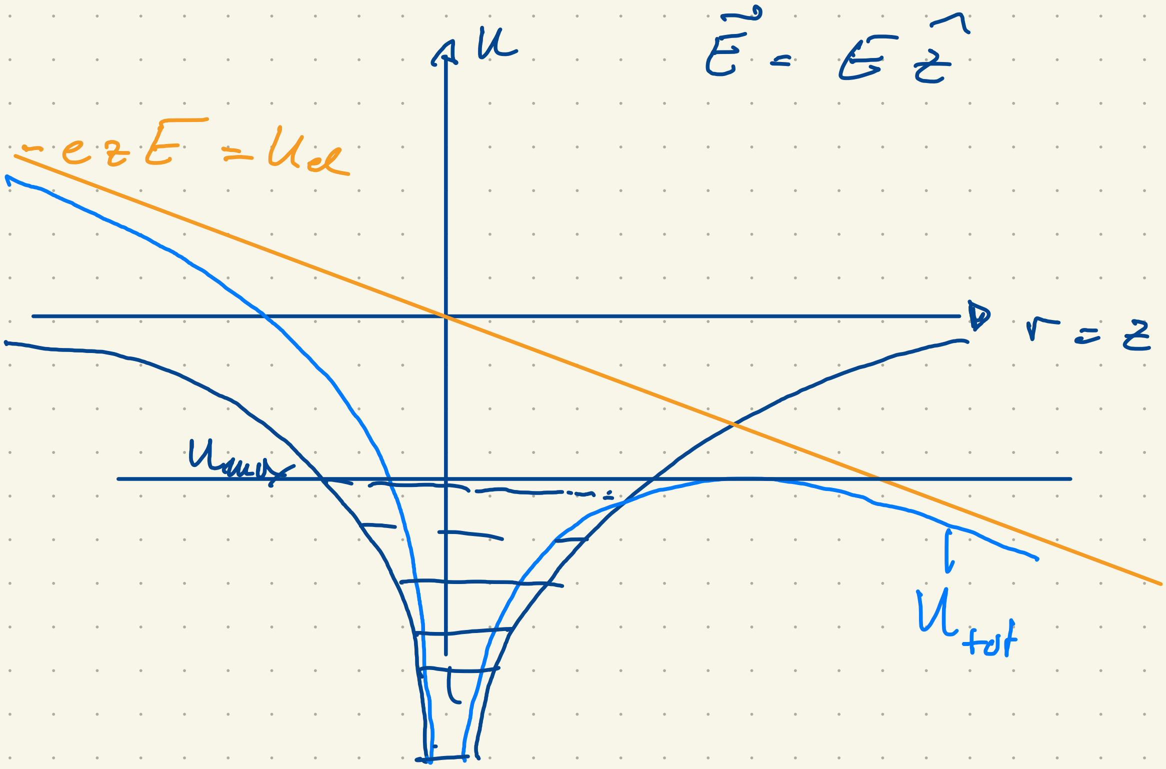
linear in E !

$\Rightarrow$ linear Stark effect

(see effect H. Friedrich)

Carefull: calculation changes if $\vec{E} \not\parallel$ quantiz. axis

(iii) Strong fields: Field ionization



$$U_{tot} = U_{atom} + U_{el} = -\frac{Z\tilde{e}^2}{|z|} - eEz$$

$$\Rightarrow U_{max} \text{ for } z = \sqrt{\frac{Ze}{4\pi\epsilon_0 E}}$$

for $\langle H\rangle = U_{max}$

Here: H atomic Hamiltonian

$$E_{ion} = \frac{\langle H\rangle^2}{4\tilde{e}^2 Z} \approx \frac{3.2\cdot 10^8}{Zn^{*4}}\frac{V}{cm}$$

field needed for ionization

$(n^* = n - \delta_{nl})$

This estimate is correct to ~20%

neglected: - effect of $\vec{E}$ on H

- tunneling ... strong

(iv) Oscillating electric field

assume case where $H' = -d\,E\,\hat{z}\cos\nu t$, but where $\hbar\nu$ is potentially very far away from any transition resonance ($\Rightarrow$ no transition necessarily)

Assume multiple (≥ 2) states: $|\psi\rangle = \sum_n a_n e^{-i\omega_n t}|n\rangle$

$$\dot{a}_k = \frac{1}{i\hbar}\sum_n \langle k|H'|n\rangle a_n e^{i\omega_{kn}t}$$

$\Rightarrow$ solve for $\vec{d} = \langle\psi|e\vec{r}|\psi\rangle$

(similar calc. as for classical dipole in chapter 1)

$\Rightarrow d(\nu,t) = \alpha(\nu)\,E\cos\nu t$ with

$$\boxed{\alpha(\nu) = \frac{2e^2}{\hbar}\sum_k \frac{\omega_{kg}\,|\langle k|\hat{r}|g\rangle|^2}{\omega_{kg}^2 - \nu^2}}$$

AC polarizability

6) Atoms in electromagnetic fields

a) Spontaneous & stimulated emission

1917 Einstein: 2 questions

1) How do internal states get into thermal equilibrium?
   $\Rightarrow$ concept of spontaneous emission
2) How do motional states of atoms get into thermal equilibrium?
   $\Rightarrow$ concept of photon recoil

1) $\Rightarrow$

$N = N_e + N_g$ two-level atoms
(total # of electrons)

$E_e - E_g = \hbar\omega$

Planck radiation law: $\bar{n}_{ph} = \frac{1}{e^{\frac{\hbar\omega}{kT}}-1}$
(average # of photons of freq. ω)

$(*)$ $\quad \rho_E(\omega)\,d\omega = \frac{\hbar\omega^3}{\pi^2c^3}\frac{1}{e^{\frac{\hbar\omega}{kT}}-1}\,d\omega$ field density of states

$(**)$ $\quad \frac{N_e}{N_g} = \frac{g_e}{g_g}e^{-\frac{\hbar\omega}{kT}}$ Boltzmann

degeneracies

$$\boxed{0 \stackrel{!}{=} \dot{N}_e = -\dot{N}_g = -\rho_E(\omega)B_{eg}N_e + \rho_E(\omega)B_{ge}N_g - A_{eg}N_e}$$

equil.

$\Rightarrow$ ↯ w/ $(*)$, $(**)$

B_{eg}, B_{ge} should not depend on T!

solve...

A_{eg} ($A_{e\to g}$) "spontaneous emission"

$$\Rightarrow \boxed{\begin{aligned} g_e B_{eg} &= g_g B_{ge} \\ \frac{\hbar\omega^3}{\pi^2 c^3} B_{eg} &= A_{eg} \\ &\Updownarrow \\ \rho_E(\omega) B_{eg} &= \bar{n}_{ph} A_{eg} \end{aligned}}$$

$\rightarrow$ emission: $B_{eg}\,\rho_E(\omega) + A_{eg} = (\bar{n}_{ph}+1) A_{eg}$

absorption $B_{ge}\,\rho_E(\omega) = \frac{g_e}{g_g}\bar{n}_{ph} A_{eg}$

$$\frac{\text{absorption}}{\text{emission}} = \frac{\bar{n}_{ph}}{\bar{n}_{ph}+1} \quad (\text{for } g_e = g_g)$$

"Einstein A- and B-coefficients".

b) Quantum theory of absorption & emission

- single - mode quantized field

$$\hat{\vec{E}} = -ig\left(\hat{a}\,\hat{\vec{e}}\,e^{i(\vec{k}\cdot\vec{r}-\omega t)} - h.c.\right)$$

annihilation op.

polarization dir. of $\vec{E}$

$$H_{\substack{\text{field} \\ \text{single freq}}} \stackrel{!}{=} \hbar\omega\left(a^+a + \tfrac{1}{2}\right)$$

$$\Rightarrow \langle H_{\text{field, vac.}}\rangle = \tfrac{1}{2}\hbar\omega = \epsilon_0 \vec{E}^2 V$$

volume

(average energy density in vacuum in a volume V)

$$\Rightarrow \boxed{g = \sqrt{\frac{\hbar\omega}{2\epsilon_0 V}}}$$

- interaction w/ atoms:

$$\begin{aligned} U &= -\vec{d}\cdot\vec{E} \\ &= -ieg\,\hat{\vec{r}}\,a\,\hat{\vec{e}}\,e^{-i\omega t} + h.c. \end{aligned}$$

- interaction w/ atom:

$$\boxed{U = -\vec{d}\cdot\vec{E}} \qquad \boxed{= -ie\,g\,\hat{\vec{r}}\,a\,\hat{\vec{e}}\,e^{-i\omega t} + h.c}$$

g: "vacuum Rabi frequency"

where "dipole approximation" is assumed

$$e^{i\vec{k}\cdot\vec{r}} \approx 1 \quad \left(\text{Because } \vec{r} \ll \frac{1}{k}\right)$$

here: ($|n\rangle$ eigenstate H_{field})

$a|n\rangle = \sqrt{n}\,|n-1\rangle$, $a^+|n\rangle = \sqrt{n+1}\,|n+1\rangle$

final total state $|f\rangle = |b, n'\rangle$

initial state $|i\rangle = |a, n\rangle$

$|a\rangle, |b\rangle$ atomic levels

$$\langle f|U|i\rangle = \qquad (\hat{e}\,||\,\hat{z})$$

$$= -ie\,\langle\tilde{b}|\hat{z}|\tilde{a}\rangle\, g\,\langle n'|a e^{-i\omega t} - a^+ e^{i\omega t}|n\rangle\, e^{i\omega_{ba}t}$$

$$= -ie\,\langle\tilde{b}|\hat{z}|\tilde{a}\rangle\, g\left(\sqrt{n}\,\delta_{n',n-1}\,e^{-i(\omega-\omega_{ba})t} - \sqrt{n+1}\,\delta_{n',n+1}\,e^{-i(\omega+\omega_{ba})t}\right)$$

where the atomic states $|\tilde{a}\rangle, |\tilde{b}\rangle$ are depicted now in the rotating frame.

example: absorption: $\omega_{ba} = \omega$ $\left(\Rightarrow |b\rangle = |e\rangle, \; |a\rangle = |g\rangle\right)$

$$\Rightarrow n' = n-1$$

emission: $\omega_{ba} = \omega$, $|b\rangle = |g\rangle$ ...

$$n' = n+1$$

$$P = |\langle f|U|i\rangle|^2$$

$$\Rightarrow \frac{P_{abs}}{P_{em}} = \frac{n}{n+1}$$

☺

c) Oscillator strength

Define dimensionless quantity f

defining how strong field & atoms couple:

$$\boxed{f_{kj} = \frac{2m_e}{\hbar} \omega_{kj} \left| \langle k | z | j \rangle \right|^2}$$ (for z-polarization)

"oscillator strength"

$$d_g = \sum_k f_{kg} \frac{e^2}{m(\omega_{kg}^2 - \nu^2)} E \cos \nu t$$

dipole moment of atom in oscillating field

⇒ behavior of an atom in oscillating field mimics classical oscillating dipole with same but with having effective charge

$$\boxed{q_k^2 = f_{kg} e^2}$$

$$\sum_k f_{kg} = Z$$ (# of e^- in state $|g\rangle$)

($3Z$ for all 3 polarizations together)