# Remaining Topics

* General perturbation $\to$ Adiabatic / Sudden

* Light - Matter Interaction

## General perturbation

We can always try to calculate the

$$P_{n\to m}(t) = \left|\frac{\lambda}{\hbar}\right|^2 \left| \int_0^t e^{i\omega_{mn}t'} \langle m|V_I(t')|n\rangle \, dt' \right|^2$$

Alternatively, we can take the state to be

$$|\psi_n\rangle \to |\psi(t)\rangle = \sum \tilde{c}_m(t) \, |\psi_m\rangle \quad \text{with}$$

$\forall m \quad H_0 |\psi_m\rangle = E_m |\psi_m\rangle$

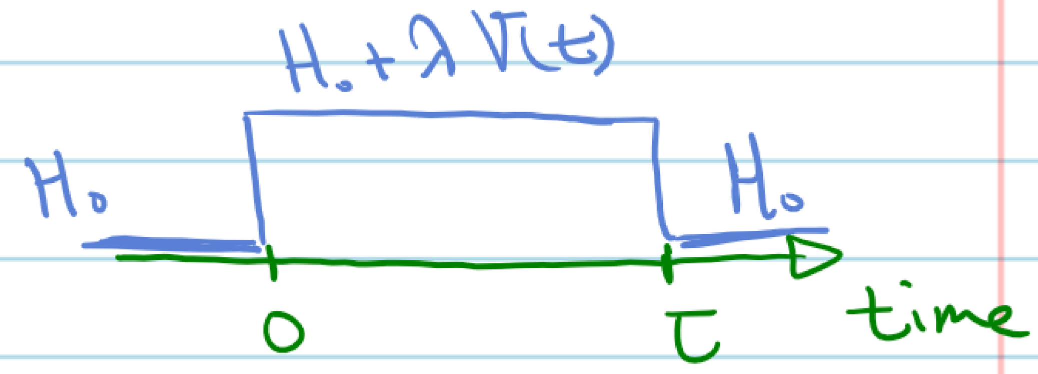
and find the dynamical eq. for $c(t)$. $\to$ Assignment.

Here we consider two distinct senarios:

- $V(t)$ changes slowly with time. Adiabatic
- " " fast. Sudden

# Time-dependent Perturbation

$$H = H_0 + \lambda V(t)$$




We are interested in the transition probabilities.

$$Pr_{n \to m} = |\langle m | U(\tau) | n \rangle|^2$$

We introduced the interaction picture for which

$$|\psi(t)\rangle_I = e^{+\frac{iH_0 t}{\hbar}} |\psi(t)\rangle$$

$$\frac{d|\psi(t)\rangle_I}{dt} = -\frac{i}{\hbar}\lambda V_I(t)\, |\psi(t)\rangle_I \quad ; \quad V_I(t) = e^{+iH_0t/\hbar}\, V(t)\, e^{-iH_0t/\hbar}$$

For the transition probabilities, we also transformed the time-evolution into the interaction picture which gave

$$\tilde{\mathcal{U}}_I(t) = e^{iH_0t/\hbar}\, \mathcal{U}(t)\, e^{-iH_0t/\hbar}$$

and used perturbation to calculate it $\longrightarrow$ Dyson Series

$$\tilde{U}_I^{(0)}(t) = \mathbb{1}, \qquad \tilde{\mathcal{U}}_I^{(1)}(t) = -\frac{i}{\hbar}\int_0^t V_I(t')\, dt'$$

$$\tilde{\mathcal{U}}_I^{(k+1)}(t) = -\frac{i}{\hbar}\int_0^t V_I(t')\, \tilde{\mathcal{U}}_I^{(k)}(t')\, dt'$$

We investigated two examples:

$V(t) = V_0$ : Const. perturbation

$V(t) = v e^{i\omega t} + v^{*} e^{-i\omega t}$ Harmonic perturbation.

$\rightarrow$ This gave the Fermi's Golden rules for the transition rates.

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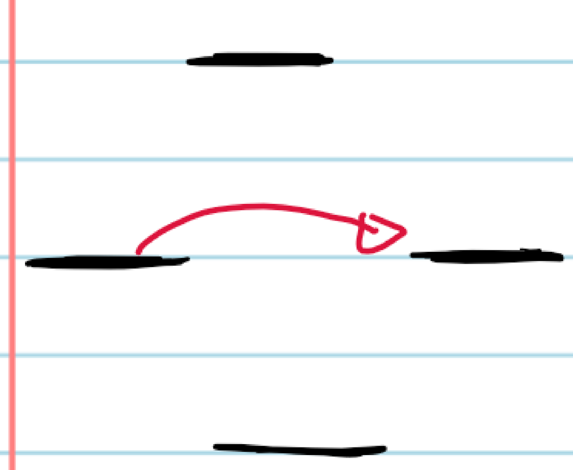
Const.

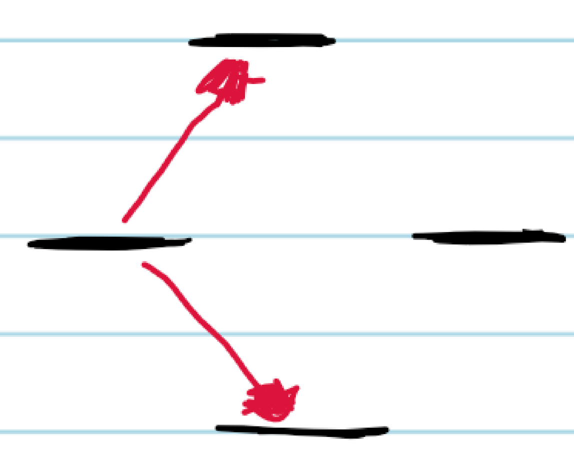
$\Gamma \propto \delta(E_i - E_f)$



Only transitions to states with close energies are allowed.

Harmonic.

$\Gamma \propto \delta(E_f - E_i - \hbar\omega) + \delta(E_f - E_i + \hbar\omega)$



Only transitions to states with

$E_f = E_i + \hbar\omega$ (absorption)

$E_f = E_i - \hbar\omega$ (Stimulated emission)

are allowed.

We now get to one of the important applications of this: the light_matter interaction.

# Light – Matter interaction:

## Hamiltonian

We have seen that in the presence of E&M field

$$\begin{cases} P \to P - \frac{q}{c}\vec{A} \\ V \to V + q\phi \end{cases}$$

A is the vector potential

$\phi$ is the scalar "

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

Time dep.

We use the Coulomb gauge: $\phi = 0$, $\nabla . \vec{A} = 0$.

$$\left(P + \frac{e}{c}A\right)^2 = P^2 + \frac{e}{c}\left(\vec{A}.\vec{P} + \vec{P}.A\right) + \left(\frac{e}{c}\right)^2 A^2$$

Assignment: Show that $A.P = P.A$ if $\nabla . A = 0$.

Assignment: Calculate $\frac{e}{c}$. Can we ignore the last term ?

$$H = \frac{\hat{P}^2}{2m} + V(r) + \boxed{\frac{e}{mc}\vec{P}.\vec{A}}$$ Perturbation

We now consider the $\vec{A}(r,t)$ for an E&M wave and calculate this, both for in the classical regime and Quantum regime.

# E&M Field: classical

The wave eq. would be (Coulomb Gauge)

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

$\hookrightarrow A = A_0 \vec{\varepsilon}\left[e^{i(\vec{k}.\vec{r} - wt)} + e^{-i(\vec{k}.\vec{r} - wt)}\right]$ $\quad \vec{k} = k\vec{n}$, $k = \frac{\omega}{c}$

For a large enough field, we can treat the $\vec{A}$ classically.

Assignment: Calculate $A_0$. Use the fact that the energy density is (on average) $\frac{\hbar\omega}{V}$ where $V$ is the Volume.

Perturbation $\leftarrow V = \frac{eA_0}{mc}\vec{p}.\vec{\varepsilon}\left[e^{ik.r}\underbrace{e^{-i\omega t}}_{T1} + e^{-ik.r}\underbrace{e^{i\omega t}}_{T2}\right]$

This is a harmonic oscillator with $\mathcal{V} = \frac{eA_0}{mc}\vec{p}.\vec{\varepsilon}\, e^{i\vec{k}.\vec{r}}$.

T1: $\mathcal{V} e^{-i\omega t} \longrightarrow$ Absorption

T2: $\mathcal{V}^{\dagger} e^{i\omega t} \longrightarrow$ Stimulated emission

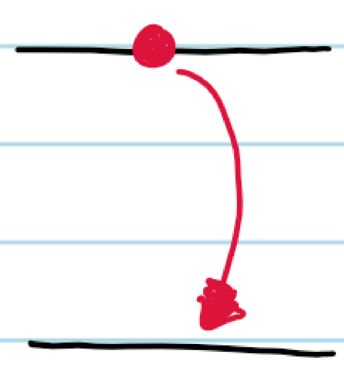
## Transition Rates:

$$\Gamma^{Abs}_{n\to m} = \left|\frac{eA_0}{mc}\right|^2 \left|\langle m|\vec{P}.\vec{\varepsilon}\, e^{i\vec{k}.\vec{r}}|n\rangle\right|^2 \delta(E_f-E_i-\hbar\omega)$$

$$\Gamma^{emi}_{n\to m} = \left|\frac{eA_0}{mc}\right|^2 \left|\langle m|\vec{P}.\vec{\varepsilon}\, e^{-i\vec{k}.\vec{r}}|n\rangle\right|^2 \delta(E_f-E_i+\hbar\omega)$$

* **Remark:** For $\vec{A}=0$, then

$\Gamma^{abs} = \Gamma^{emi} = 0$, this does not account for the spontaneous emission



We'll see how the Quantum treatment of the field resolves this.

# Quantization of the E&M field:

$$\vec{A}(r,t) = \sum_{k,\lambda} \left[ A_{\lambda,k}\, \vec{\varepsilon}_\lambda\, e^{i(k\cdot r - \omega t)} + A^*_{\lambda,k}\, \vec{\varepsilon}^{\,*}_\lambda\, e^{-i(\vec{k}\cdot\vec{r} - \omega t)} \right]$$

$\lambda \to$ Polarization

Energy

$$\mathcal{U} \to H = \frac{1}{8\pi} \int \left( \varepsilon_0 |E|^2 + \frac{1}{\mu_0} |B|^2 \right) dV$$

$E$ & $B$ in terms of $A$ $\left( E \propto \frac{\partial A}{\partial t},\ B = \nabla \times A \right) \ldots$

$$H = \frac{V}{8\pi c^2} \sum_{k,\lambda} (\hbar k)^2\, A_{k,\lambda} A^*_{k,\lambda}$$

## Define:

$$Q_{\lambda,k} = \frac{1}{\sqrt{4\pi c^2}} \left( A^*_{\lambda,k} + A_{\lambda,k} \right)$$

$$P_{\lambda,k} = \frac{i\omega_k}{\sqrt{4\pi c^2}} \left( A^*_{\lambda,k} - A_{\lambda,k} \right)$$

Check that these make conjugate variables.

$$\left[ \hat{Q}_{\lambda,k}, \hat{P}_{\lambda',k'} \right] = i\hbar\, \delta_{k',k}\, \delta_{\lambda,\lambda'}$$

With these, $H = \sum_{k,\lambda} h_{k,\lambda}$

$$h_{k,\lambda} = \frac{P^2_{\lambda,k}}{2m} + \frac{\omega_k^2}{2} Q^2_{\lambda,k}$$

This is similar to the Harmonic Oscillator. So our next step would be constructing the ladder operators.

$$\hat{a}_{\lambda,k} = \sqrt{\frac{\omega_k}{2\hbar}}\,\hat{Q}_{\lambda,k} + \frac{i}{\sqrt{2\hbar\omega}}\,\hat{P}_{\lambda k}$$

Assignment: Check that $a_{\lambda,k}$, $a^{\dagger}_{\lambda,k}$ satisfy the commutation relations of the ladder operators.

We get:

$$\Rightarrow h_{\lambda,k} = \hbar\omega_k\left(\hat{N}_{\lambda,k} + 1/2\right), \quad \hat{N}_{\lambda,k} = a^{\dagger}_{\lambda,k} a_{\lambda,k}.$$

State of the field $\quad \underbrace{|n_{\lambda_1,k_1}\rangle}_{\#\text{excitations in mode } \lambda_1 \,\&\, k_1} \otimes \underbrace{|n_{\lambda_2,k_2}\rangle}_{\text{excitations in } \lambda_2 \,\&\, k_2} \otimes \cdots$ ...

$$A_{\lambda,k} = \sqrt{\frac{2\pi\hbar c^2}{\omega_k}}\,a_{\lambda,k}, \quad A^{\dagger}_{\lambda,k} = \sqrt{\frac{2\pi\hbar c^2}{\omega_k}}\,a^{\dagger}_{\lambda,k}$$

$$\vec{A}(r,t) = \sum_{k,\lambda}\sqrt{\frac{2\pi\hbar c^2}{\omega_k V}}\left[a_{\lambda,k}\,e^{i(\vec{k}.\vec{r}-\omega t)}\,\varepsilon_\lambda + a^{\dagger}_{\lambda,k}\,e^{-i(\vec{k}.\vec{r}-\omega t)}\,\varepsilon^*_\lambda\right]$$

Perturbation:

$$V(t) = \sum_{k,\lambda}\left(v_{k,\lambda}\,e^{i\omega t} + v^{\dagger}_{k,\lambda}\,e^{-i\omega t}\right)$$

$$v_{k,\lambda} = \frac{e}{mc}\sqrt{\frac{2\pi\hbar c^2}{\omega_k V}}\,a_{\lambda,k}\,e^{+i\vec{k}.\vec{r}}\,\vec{\varepsilon}_\lambda\cdot\vec{P}$$

# Light - Matter Interaction : Quantum

**Reminder** : Quantization of the E&M Field :

$$H = \sum_{k,\lambda} \hbar\omega_k \left( a^\dagger_{k,\lambda} a_{k,\lambda} + 1/2 \right) \rightarrow |n_{k\lambda}\rangle$$

$\downarrow$
\# excitations in mode $(\vec{k},\lambda)$.
(\# photons).

$$\hat{A}_{\vec{k},\lambda} = \sqrt{\frac{2\pi\hbar c^2}{\omega_k}}\ \hat{a}_{\vec{k},\lambda}$$

$$\rightarrow \vec{A}(r,t) = \sum_{\vec{k},\lambda} \sqrt{\frac{2\pi\hbar c^2}{\omega_k}} \left[ e^{i(\vec{k}.r - \omega t)} a_{\vec{k},\lambda} \vec{\varepsilon}_\lambda + h.c. \right]$$

## Perturbation :

$$V(t) = \frac{e}{mc} \vec{P}.\vec{A}(r,t) =$$

$$\frac{e}{mc} \sum_{\vec{k},\lambda} \sqrt{\frac{2\pi\hbar c^2}{\omega_k}} \left[ e^{i(\vec{k}.\vec{r} - \omega_k t)} a_{k,\lambda} \vec{P}.\vec{\varepsilon}_\lambda + e^{-i(\vec{k}.r - \omega_k t)} a^\dagger_{\vec{k},\lambda} \vec{P}.\vec{\varepsilon}^*_\lambda \right]$$

$$= \sum_{\vec{k}} \left( \hat{\nu}_{\vec{k}}\, e^{-i\omega_k t} + \hat{\nu}^\dagger_{\vec{k}}\, e^{i\omega_k t} \right)$$

$$\hat{\nu}_{\vec{k}} = \frac{e}{mc} \sum_\lambda \sqrt{\frac{2\pi\hbar c^2}{\omega_k}}\ e^{i\vec{k}.\vec{r}}\ a_{\vec{k},\lambda} \vec{P}.\vec{\varepsilon}_\lambda$$

$$\hat{\nu}^\dagger_{\vec{k}} = \frac{e}{mc} \sum_\lambda \sqrt{\frac{2\pi\hbar c^2}{\omega_k}}\ e^{-i\vec{k}.\vec{r}}\ a^\dagger_{\vec{k},\lambda} \vec{P}.\vec{\varepsilon}^*_\lambda$$

# Transition Rates

$$|\Phi_i\rangle, |\Phi_f\rangle \in \mathcal{H}_{Atom} \otimes \mathcal{H}_{Field}$$

$$|\Phi_i\rangle = |\psi_i\rangle_{Atom} \otimes |n_i\rangle_{Field}$$

$$|\Phi_f\rangle = |\psi_f\rangle_{Atom} \otimes |n_f\rangle_{Field}$$

$$\Gamma^{Abs}_{i\to f} \propto \left|\langle \Phi_f | \hat{\mathcal{O}}_k | \Phi_i\rangle\right|^2, \quad \Gamma^{Em}_{i\to f} \propto \left|\langle \Phi_f | \hat{\mathcal{O}}^\dagger_k | \Phi_i\rangle\right|^2$$

$$\langle \Phi_f | \hat{\mathcal{O}}_k | \Phi_i\rangle \propto \langle \psi_f | \vec{P}\cdot\varepsilon_\lambda e^{i\vec{k}\cdot\vec{r}} |\psi_i\rangle \langle n_f | a | n_i\rangle$$

$$= \quad '' \quad \left(\sqrt{n_i}\, \delta_{n_f, n_i - 1}\right)$$

$$\left(\Gamma^{Abs}_{i\to f}\right)_{k,\lambda} \propto n_i \left|\langle \psi_f | e^{i\vec{k}\cdot\vec{r}}\, \vec{P}\cdot\vec{\varepsilon}_\lambda | \psi_i\rangle\right|^2 \delta(E_f - E_i - \hbar\omega_k)$$

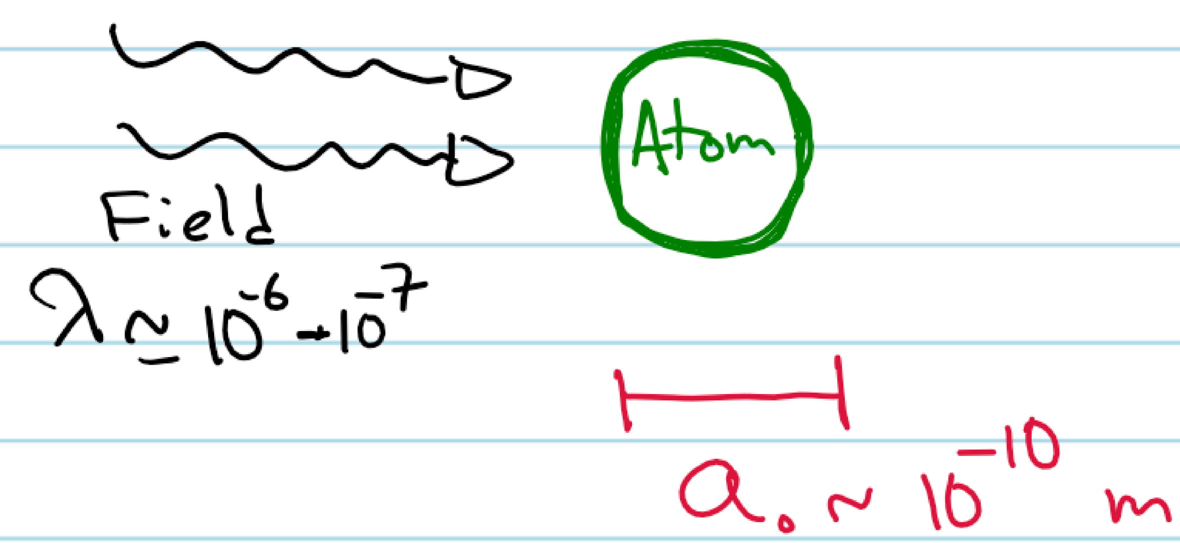
$$\left(\Gamma^{Em}_{i\to f}\right)_{k\lambda} \propto (n_i+1) \left|\langle \psi_f | e^{-i\vec{k}\cdot\vec{r}}\, \vec{P}\cdot\vec{\varepsilon}^{\,*}_\lambda | \psi_i\rangle\right|^2 \delta\left(E_f - E_i + \hbar\omega_k\right)$$

## * Spontaneous Emission

When the field is off, i.e. $\boxed{n_i = 0}$, classically there would be no emission or absorption. But from the result above, we see that, even when $n_i = 0$, there could be emission.

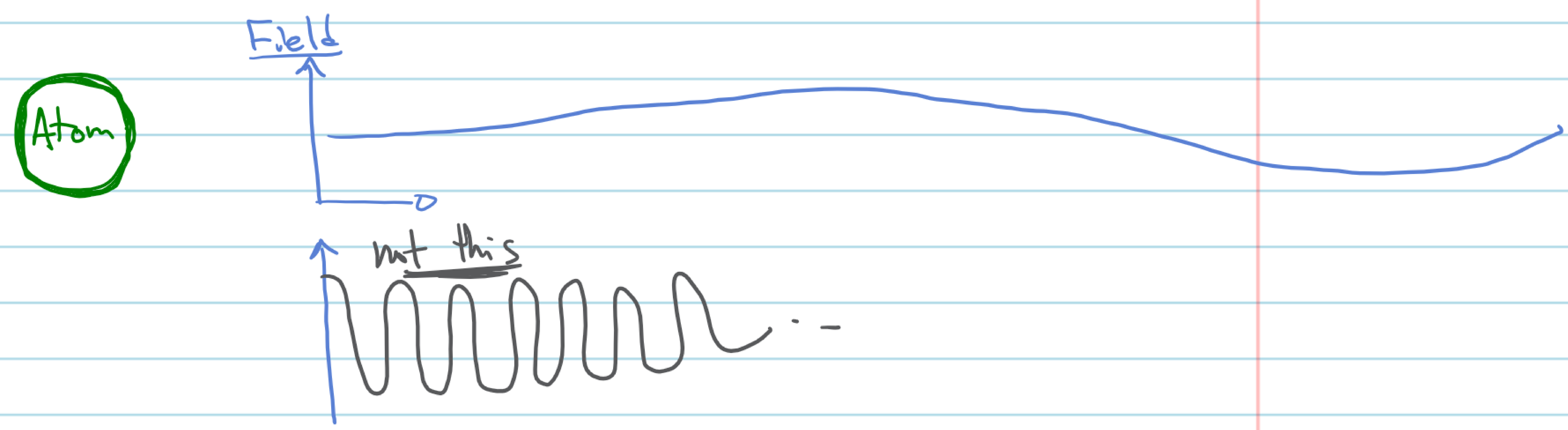
$$\langle \psi_f | e^{i\vec{k}\cdot\vec{r}} \vec{P}\cdot\varepsilon_\lambda | \psi_i \rangle \quad ?$$

## Dipole Approx.




$$\vec{k}\cdot\vec{r} \simeq \frac{2\pi}{\lambda} a_0 = 2\pi \, 10^{-3}$$

This means that $e^{ik.r}$ is not changing significantly over the atom and the field is almost constant.




So, we can take $e^{ik.r}$ to be the same all over the atom

$$|\langle \psi_f | e^{ik.r} \vec{P}\cdot\vec{\varepsilon}_\lambda | \psi_i \rangle| \simeq |\langle \psi_f | \vec{P}\cdot\vec{\varepsilon}_\lambda | \psi_i \rangle|$$

$$\langle \psi_f | \vec{P}\cdot\vec{\varepsilon} | \psi_i \rangle = \left(\langle \psi_f | \vec{P} | \psi_i \rangle\right)\cdot\vec{\varepsilon}_\lambda$$

$$\vec{P} = \frac{1}{2i\hbar}\left[\vec{r}, \vec{P}^2\right] \Rightarrow \vec{P} = \frac{m}{i\hbar}\left[\vec{r}, \underbrace{\frac{\vec{P}^2}{2m} + V(r)}_{H}\right]$$

$$\langle \psi_f | \vec{P} | \psi_i \rangle = \frac{m}{i\hbar} \langle \psi_f | (\vec{r}H - H\vec{r}) | \psi_i \rangle =$$

$$\frac{m}{i\hbar}\left(E_i - E_f\right) \langle \psi_f | \vec{r} | \psi_i \rangle = \frac{m\,\omega_{if}}{i} \langle \psi_f | \vec{r} | \psi_i \rangle$$

$$\Rightarrow \left(\Gamma^{Ab}_{i\to f}\right)_{\vec{k},\lambda} \tilde{\propto}\ n_i \left[ m^2\omega_{if}^2 \left| \langle \psi_f | \underbrace{(e\vec{r})\,\varepsilon_\lambda}_{\vec{d}\,\cdot\,\vec{\varepsilon}_\lambda} | \psi_i \rangle \right|^2 \right] \delta\left(E_f - E_i - \hbar\omega_k\right)$$

Electric dipole moment.

$$\Rightarrow \Gamma^{Em}_{i\to f} \tilde{\propto} \left(n_i + 1\right)\left[ m^2\omega_{if}^2 \left| \langle \psi_f | \vec{d}\cdot\vec{\varepsilon}^{\,*}_\lambda | \psi_i \rangle \right|^2 \right] \delta\left(E_f - E_i + \hbar\omega_k\right)$$

# Dipole Selection Rules

We can calculate $\langle \psi_f | \vec{r} | \psi_i \rangle$ for diff. $\psi_f, \psi_i$.

But here are some of the key points:

$$r \to (r \sin\theta \cos\varphi,\ r \sin\theta \sin\varphi,\ r \cos\theta)$$

Switch to spherical coordinates

and use $Y_{\ell m}$ as a basis.

$$\sin\theta \cos\varphi = -\sqrt{\frac{2\pi}{3}} \left( Y_{11} - Y_{1,-1} \right)$$

$$\sin\theta \sin\varphi = i\sqrt{\frac{2\pi}{3}} \left( Y_{11} + Y_{1,-1} \right)$$

$$\cos\theta = \sqrt{\frac{4\pi}{3}}\, Y_{10}$$

$$\Rightarrow \langle \psi_f | \vec{\varepsilon} \cdot \vec{r} | \psi_i \rangle = \sqrt{\frac{4\pi}{3}} \int_0^\infty R_{n_f \ell_f}(r)\, R_{n_i \ell_i}\, r^3\, dr \ \times$$

$$\int Y^*_{\ell_f, m_f}(\theta,\varphi) \left[ \frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}} Y_{1,1} + \frac{\varepsilon_x - i\varepsilon_y}{\sqrt{2}} Y_{1,-1} + \varepsilon_z Y_{10} \right] Y_{\ell_i, m_i}\, d\Omega$$

Three terms

$$\int Y^*_{\ell_f, m_f} \left( Y_{11}\, Y_{\ell_i m_i} \right) d\Omega \to m_f = m_i + 1$$

$$\int Y^*_{\ell_f m_f} \left( Y_{1,-1}\, Y_{\ell_i m_i} \right) d\Omega \to m_f = m_i - 1$$

$$\int Y^*_{\ell_f m_f} \left( Y_{1,0}\, Y_{\ell_i m_i} \right) d\Omega \to m_f = m_i$$

Also $\ell_i - \ell_f \in \{1, 0, -1\}$

$$\int Y^*_{\ell_f m_f} \left( Y_{1,m} \; Y_{\ell_i m_i} \right) d\Omega \propto \langle \ell_f m_f | \left( |1 m\rangle \otimes |\ell_i m_i\rangle \right)$$

From addition of angular momentum

* $m_f = m_i + m$

* $\ell_f : 1 \otimes \ell_i = (\ell_i + 1) \oplus \ell_i \oplus (\ell_i - 1)$ $\quad (\ell_i = 0 \to \ell_f = 1)$

* Also, since $Y_{1m}$ is odd parity, $\ell_f \neq \ell_i$, otherwise

$$\int Y^*_{\ell_f m_f} \left( Y_{1m} \; Y_{\ell_i m_i} \right) d\Omega = 0$$

( $\ell_f$ should have a diff. parity from $\ell_i$ )

* Spin does not change $\Delta S = 0$.

Examples:

$1S \to 2S$ Forbidden $\Delta \ell \neq 0$

$1S \to 2P$ ✓ $\Delta \ell = 1$