Inclusion of the electromagnetic field in Quantum Mechanics similar to Classical Mechanics but with interesting consequences

- Maxwell's equations
- Scalar and vector potentials
- Lorentz force
- Transform to Lagrangian
- Then Hamiltonian
- Minimal coupling to charged particles

#### Maxwell's equations

#### Gaussian units

 $\nabla \cdot \boldsymbol{E}(\boldsymbol{x},t) = 4\pi\rho(\boldsymbol{x},t)$  $\nabla \cdot \boldsymbol{B}(\boldsymbol{x},t) = 0$  $\nabla \times \boldsymbol{E}(\boldsymbol{x},t) = -\frac{1}{c}\frac{\partial}{\partial t}\boldsymbol{B}(\boldsymbol{x},t)$  $\nabla \times \boldsymbol{B}(\boldsymbol{x},t) = \frac{1}{c}\frac{\partial}{\partial t}\boldsymbol{E}(\boldsymbol{x},t) + \frac{4\pi}{c}\boldsymbol{j}(\boldsymbol{x},t)$ 

# Scalar and Vector potential

Quantum applications require replacing electric and magnetic fields!

$$B = \nabla \times A \quad \text{implies} \quad \nabla \cdot B = 0$$
  
From Faraday  $\nabla \times \left( E + \frac{1}{c} \frac{\partial}{\partial t} A \right) = 0$   
so  $E + \frac{1}{c} \frac{\partial}{\partial t} A = -\nabla \Phi$   
or  $E = -\nabla \Phi - \frac{1}{c} \frac{\partial A}{\partial t}$ 

in terms of vector and scalar potentials. Homogeneous equations are automatically solved.

# Gauge freedom

Remaining equations using  $\nabla \times (\nabla \times A) = \nabla (\nabla \cdot A) - \nabla^2 A$ 

$$\nabla^2 \Phi + \frac{1}{c} \frac{\partial}{\partial t} (\nabla \cdot A) = -4\pi \rho \bigstar$$
$$\nabla^2 A - \frac{1}{c^2} \frac{\partial^2 A}{\partial t^2} - \nabla \left( \nabla \cdot A + \frac{1}{c} \frac{\partial \Phi}{\partial t} \right) = -\frac{4\pi}{c} j \bigstar$$

To decouple one could choose (gauge freedom)  $\nabla \cdot A + \frac{1}{c} \frac{\partial \Phi}{\partial t} = 0$ 

more later... first

# Coupling to charged particles

Lorentz 
$$\boldsymbol{F} = q \left\{ \boldsymbol{E} + \frac{1}{c} \boldsymbol{v} \times \boldsymbol{B} \right\}$$

**Rewrite** 
$$\boldsymbol{F} = q \left\{ -\boldsymbol{\nabla}\Phi - \frac{1}{c} \frac{\partial \boldsymbol{A}}{\partial t} + \frac{1}{c} \boldsymbol{v} \times (\boldsymbol{\nabla} \times \boldsymbol{A}) \right\} \bigstar$$

Note 
$$\mathbf{v} \times (\mathbf{\nabla} \times \mathbf{A}) = \mathbf{\nabla} (\mathbf{v} \cdot \mathbf{A}) - (\mathbf{v} \cdot \mathbf{\nabla}) \mathbf{A}$$
  
and  $\frac{\partial \mathbf{A}}{\partial t} + (\mathbf{v} \cdot \mathbf{\nabla}) \mathbf{A} = \frac{d\mathbf{A}}{dt}$   
So that  $\mathbf{F} = -\mathbf{\nabla}U + \frac{d}{dt}\frac{\partial U}{\partial \mathbf{v}}$  with  $U = q\Phi - \frac{q}{c}\mathbf{v} \cdot \mathbf{A}$ 

Check

Yields Lorentz from 
$$L = T - U = rac{1}{2}moldsymbol{v}^2 - q\Phi + rac{q}{c}oldsymbol{v}\cdotoldsymbol{A}$$

- Equations of motion  $\frac{d}{dt}\frac{\partial L}{\partial v} \frac{\partial L}{\partial x} = 0$
- Generalized momentum  $\boldsymbol{p} = \frac{\partial L}{\partial \boldsymbol{v}} = m\boldsymbol{v} + \frac{q}{c}\boldsymbol{A}$

Solve for **v** and substitute in Hamiltonian --> Hamiltonian for a charged particle

$$H = \mathbf{p} \cdot \mathbf{v} - L = \frac{\left(\mathbf{p} - \frac{q}{c}\mathbf{A}\right)^2}{2m} + q\Phi \quad \bigstar$$

Include external electromagnetic field in QM

- Static electric field: nothing new (position --> operator)
- Include static magnetic field with momentum and position operators  $\left( \boldsymbol{p} - rac{q}{c} \boldsymbol{A}(\boldsymbol{x}) 
  ight)^2$

$$H = \frac{(\mathbf{p} - \frac{1}{c}\mathbf{A}(\mathbf{x}))}{2m}$$

Note velocity operator

$$\boldsymbol{v} = \frac{1}{m} \left( \boldsymbol{p} - \frac{q}{c} \boldsymbol{A} \right)$$

- Note Hamiltonian not "free" particle one
- $[p_i, A_j] = \frac{\hbar}{i} \frac{\partial A_j}{\partial x_i}$ Use
- to show that [v\_i, v\_j] = i \frac{q\hbar}{m^2 c} \epsilon\_{ijk} B\_k
  Gauge independent! So think in terms of H = \frac{1}{2}m|v|^2

#### Include external electromagnetic field

- Include uniform magnetic field
- For example by  $\boldsymbol{B}(\boldsymbol{x}) = B\hat{\boldsymbol{z}}$
- Only nonvanishing commutator  $[v_x, v_y] = i \frac{q\hbar B}{m^2 c}$
- Write Hamiltonian as

$$H = \frac{1}{2}m\left(v_{x}^{2} + v_{y}^{2} + v_{z}^{2}\right)$$

- but now  $v_z = \frac{p_z}{m}$  so this corresponds to free particle motion parallel to magnetic field (true classically too)
- Only consider

$$H = \frac{1}{2}m\left(v_x^2 + v_y^2\right)$$

- Operators don't commute but commutator is a complex number!
- So...

#### Harmonic oscillator again...

Motion perpendicular to magnetic field --> harmonic oscillator

• Introduce  $a = \sqrt{\frac{m}{2\hbar\omega_c}} (v_x + iv_y)$  $a^{\dagger} = \sqrt{\frac{m}{2\hbar\omega_c}} (v_x - iv_y)$ • with cyclotron frequency  $\omega_c = \frac{qB}{mc}$ 

- Straightforward to check  $\left[a,a^{\dagger}
  ight]=1$
- So Hamiltonian becomes

$$H = \hbar\omega_c \left( a^{\dagger}a + \frac{1}{2} \right)$$

and consequently spectrum is (called Landau levels)

$$E_n = \hbar \omega_c \left( n + \frac{1}{2} \right) \qquad n = 0, 1, \dots$$

#### Aharanov-Bohm effect (bound states)

• Consider hollow cylindrical shell



- Magnetic field inside inner cylinder either on or off
- Charged particle confined between inner and outer radius as well as top and bottom

#### Discussion

- Without field:
  - Wave function vanishes at the radii of the cylinders as well as top and bottom --> discrete energies
- With field (think of solenoid)
  - No magnetic field where the particle moves; inside in z-direction and constant
  - Spectrum changes because the vector potential is needed in the Hamiltonian
  - Use Stokes theorem  $\int_{S} (\nabla \times A) \cdot \hat{n} \, da = \oint_{C} A \cdot d\ell$
  - Only z-component of magnetic field so left-hand side becomes

$$\int_{S} (\boldsymbol{\nabla} \times \boldsymbol{A}) \cdot \hat{\boldsymbol{n}} \, da = \int_{S} B\theta(r_1 - \rho) da = B\pi r_1^2$$

- for any circular loop outside inner cylinder (and centered)
- Vector potential in the direction of  $\,\hat{oldsymbol{\phi}}\,$  and line integral -->  $2\pi r$
- Resulting in  $m{A}=rac{Br_1^2}{2r}\hat{m{\phi}}$  modifying the Hamiltonian and the spectrum!!

#### Example

- No field
- Example of radial wave function
- Problem solved in cylindrical coordinates



Figure 2: Radial eigenfunction for n = 4 and f = 0



#### Quantize electromagnetic field

- •Classical free field equations
- •Quantize
- Photons
- Coupling to charged particles
- •One-body operator acting on charged particles and photons

#### Maxwell's equations

#### Gaussian units

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# Scalar and Vector potential

Quantum applications require replacing electric and magnetic fields!

$$E = -\nabla \Phi - \frac{1}{c} \frac{\partial A}{\partial t}$$
$$B = \nabla \times A$$

in terms of vector and scalar potentials. Homogeneous equations are automatically solved.

# Gauge freedom

Remaining equations

$$\nabla^2 \Phi + \frac{1}{c} \frac{\partial}{\partial t} (\nabla \cdot A) = -4\pi\rho$$
$$\nabla^2 A - \frac{1}{c^2} \frac{\partial^2 A}{\partial t^2} - \nabla \left( \nabla \cdot A + \frac{1}{c} \frac{\partial \Phi}{\partial t} \right) = -\frac{4\pi}{c} \mathbf{j}$$

To decouple employ gauge freedom. Observe: adding gradient of scalar function to vector potential yields same magnetic field To keep electric field the same: change scalar potential accordingly!

#### Gauge transformation

• Explicitly  $A \Rightarrow A' = A + \nabla \Lambda$ 

$$\Phi \quad \Rightarrow \quad \Phi' = \Phi - \frac{1}{c} \frac{\partial H}{\partial t}$$

- With  $E = -\nabla \Phi \frac{1}{c} \frac{\partial A}{\partial t}$  --> same E&M fields  $B = \nabla \times A$
- Can always find potentials that satisfy  $\nabla \cdot A + \frac{1}{c} \frac{\partial \Phi}{\partial t} = 0$
- If not: choose  $\Lambda$  such that

$$0 = \boldsymbol{\nabla} \cdot \boldsymbol{A}' + \frac{1}{c} \frac{\partial \Phi'}{\partial t} = \boldsymbol{\nabla} \cdot \boldsymbol{A} + \frac{1}{c} \frac{\partial \Phi}{\partial t} + \boldsymbol{\nabla}^2 \Lambda - \frac{1}{c^2} \frac{\partial^2 \Lambda}{\partial^2 t}$$

Employ this gauge freedom  

$$\nabla^{2}\Phi + \frac{1}{c}\frac{\partial}{\partial t}(\nabla \cdot A) = -4\pi\rho$$

$$\nabla^{2}A - \frac{1}{c^{2}}\frac{\partial^{2}A}{\partial t^{2}} - \nabla\left(\nabla \cdot A + \frac{1}{c}\frac{\partial\Phi}{\partial t}\right) = -\frac{4\pi}{c}j$$
Can choose  $\nabla \cdot A + \frac{1}{c}\frac{\partial\Phi}{\partial t} = 0$  (Lorentz gauge)

Leads to wave equations

$$\nabla^2 \Phi - \frac{1}{c^2} \frac{\partial^2 \Phi}{\partial t^2} = -4\pi\rho$$
$$\nabla^2 A - \frac{1}{c^2} \frac{\partial^2 A}{\partial t^2} = -4\pi j$$

# Radiation gauge $\nabla^2 \Phi + \frac{1}{c} \frac{\partial}{\partial t} (\nabla \cdot A) = -4\pi\rho$ $\boldsymbol{\nabla}^{2}\boldsymbol{A} - \frac{1}{c^{2}}\frac{\partial^{2}\boldsymbol{A}}{\partial t^{2}} - \boldsymbol{\nabla}\left(\boldsymbol{\nabla}\cdot\boldsymbol{A} + \frac{1}{c}\frac{\partial\Phi}{\partial t}\right) = -\frac{4\pi}{c}\boldsymbol{j}$ Alternative: radiation gauge (Coulomb, or transverse gauge)--> useful for quantizing free field $\nabla \cdot A = 0$ yields $\nabla^2 \Phi = -4\pi\rho$ $\boldsymbol{\nabla}^{2}\boldsymbol{A} - \frac{1}{c^{2}}\frac{\partial^{2}\boldsymbol{A}}{\partial t^{2}} = \frac{1}{c}\boldsymbol{\nabla}\frac{\partial\Phi}{\partial t} - \frac{4\pi}{c}\boldsymbol{j}$

#### Instantaneous Coulomb

- Yields instantaneous Coulomb potential  $\Phi(x,t) = \int_V d^3x' \frac{\rho(x',t)}{|x-x'|}$ Vector potential --> inhomogeneous wave equation rhs can be calculated from instantaneous Coulomb potential
- Now no sources  $\Rightarrow$  free field  $\mathbf{E} = -\frac{1}{c} \frac{\partial A}{\partial t}$   $\mathbf{B} = \nabla \times A$ and  $\nabla^2 A - \frac{1}{c^2} \frac{\partial^2 A}{\partial t^2} = 0 \Rightarrow$  solve in large box with volume  $V = L^3$

# Free field solutions

Use periodic BC so expand in plane waves to avoid standing ones Allowed values  $k_x = n_x \frac{2\pi}{L}$   $n_x = 0, \pm 1, \pm 2, ...$ also for y and z Normalization  $\frac{1}{V} \int_{V} d\boldsymbol{x} \ e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}} = \delta_{\boldsymbol{k}\boldsymbol{k}'}$ 

So solution can be written as Gauge choice  $\Rightarrow \mathbf{k} \cdot \mathbf{A}_{\mathbf{k}} = 0$ 

$$\boldsymbol{A}(\boldsymbol{x},t) = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} \boldsymbol{A}_{\boldsymbol{k}}(t) \ e^{i\boldsymbol{k}\cdot\boldsymbol{x}}$$

So for future reference:  $A_k = \sum e_{k\alpha} A_{k\alpha}$  (polarizations)  $\alpha = 1.2$ 

From wave equation  $\frac{\partial^2 A_k(t)}{\partial t^2} + c^2 k^2 A_k(t) = 0$  for each mode

# Harmonic solutions

Fourier coefficients oscillate harmonically  $\Rightarrow \omega_k = ck$ 

So time dependence:  $A_k(t) = e^{-i\omega_k t} A_k$ 

Given initial distribution of  $A_k(t=0)$  --> problem solved!

E&M fields real so make vector potential explicitly real

$$\begin{aligned} \mathbf{A}(\mathbf{x},t) &= \frac{1}{2\sqrt{V}} \left( \sum_{\mathbf{k}} \mathbf{A}_{\mathbf{k}}(t) e^{i\mathbf{k}\cdot\mathbf{x}} + \sum_{\mathbf{k}} \mathbf{A}_{\mathbf{k}}^{*}(t) e^{-i\mathbf{k}\cdot\mathbf{x}} \right) \\ &= \frac{1}{2\sqrt{V}} \sum_{\mathbf{k}} \left[ \mathbf{A}_{\mathbf{k}}(t) + \mathbf{A}_{-\mathbf{k}}^{*}(t) \right] e^{i\mathbf{k}\cdot\mathbf{x}} \end{aligned}$$

# Fields

Use 
$$A(\boldsymbol{x},t) = \frac{1}{2\sqrt{V}} \sum_{\boldsymbol{k}} \left[ \boldsymbol{A}_{\boldsymbol{k}}(t) + \boldsymbol{A}_{-\boldsymbol{k}}^{*}(t) \right] e^{i\boldsymbol{k}\cdot\boldsymbol{x}}$$

Then electric field

$$\begin{split} \boldsymbol{E}(\boldsymbol{x},t) &= -\frac{1}{c} \frac{\partial \boldsymbol{A}}{\partial t} \\ &= -\frac{1}{2c\sqrt{V}} \sum_{\boldsymbol{k}} \left( -i\omega_{\boldsymbol{k}} \ \boldsymbol{A}_{\boldsymbol{k}}(t) + i\omega_{\boldsymbol{k}} \ \boldsymbol{A}_{-\boldsymbol{k}}^{*}(t) \right) e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \\ &= \frac{i}{2c\sqrt{V}} \sum_{\boldsymbol{k}} \omega_{\boldsymbol{k}} \left[ \boldsymbol{A}_{\boldsymbol{k}}(t) - \boldsymbol{A}_{-\boldsymbol{k}}^{*}(t) \right] e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \end{split}$$

and magnetic field

$$\begin{aligned} \boldsymbol{B}(\boldsymbol{x},t) &= \boldsymbol{\nabla} \times \boldsymbol{A} \\ &= \frac{i}{2\sqrt{V}} \sum_{\boldsymbol{k}} \boldsymbol{k} \times \left[ \boldsymbol{A}_{\boldsymbol{k}}(t) + \boldsymbol{A}_{-\boldsymbol{k}}^{*}(t) \right] e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \end{aligned}$$

# Energy in field

General

$$H_{em} = rac{1}{8\pi} \int_{V} d\boldsymbol{x} \ (\boldsymbol{E} \cdot \boldsymbol{E} + \boldsymbol{B} \cdot \boldsymbol{B})$$

Use 
$$\boldsymbol{E}(\boldsymbol{x},t) = \frac{i}{2c\sqrt{V}} \sum_{\boldsymbol{k}} \omega_{\boldsymbol{k}} \left[ \boldsymbol{A}_{\boldsymbol{k}}(t) - \boldsymbol{A}_{-\boldsymbol{k}}^{*}(t) \right] e^{i\boldsymbol{k}\cdot\boldsymbol{x}}$$

Note fields are real so

$$\begin{split} \int_{V} d\boldsymbol{x} \ \boldsymbol{E} \cdot \boldsymbol{E} &= \int_{V} d\boldsymbol{x} \ \boldsymbol{E} \cdot \boldsymbol{E}^{*} \\ &= \int_{V} d\boldsymbol{x} \sum_{\boldsymbol{k}} \sum_{\boldsymbol{k}'} \frac{1}{4c^{2}V} \omega_{\boldsymbol{k}} \left( \boldsymbol{A}_{\boldsymbol{k}}(t) - \boldsymbol{A}_{-\boldsymbol{k}}^{*}(t) \right) e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \\ &\times \cdot \omega_{\boldsymbol{k}'} \left( \boldsymbol{A}_{\boldsymbol{k}'}^{*}(t) - \boldsymbol{A}_{-\boldsymbol{k}'}(t) \right) e^{-i\boldsymbol{k}'\cdot\boldsymbol{x}} \\ \end{split}$$

$$\begin{aligned} \text{Orthogonality} &= \frac{1}{4c^{2}} \sum_{\boldsymbol{k}} \omega_{\boldsymbol{k}}^{2} \left| \boldsymbol{A}_{\boldsymbol{k}}(t) - \boldsymbol{A}_{-\boldsymbol{k}}^{*}(t) \right|^{2} \\ &= \frac{1}{4} \sum_{\boldsymbol{k}} k^{2} \left| \boldsymbol{A}_{\boldsymbol{k}}(t) - \boldsymbol{A}_{-\boldsymbol{k}}^{*}(t) \right|^{2} \end{split}$$

E&M

# Energy in field continued

Similarly  

$$\int_{V} d\mathbf{x} \ \mathbf{B} \cdot \mathbf{B} = \int_{V} d\mathbf{x} \ \mathbf{B} \cdot \mathbf{B}^{*}$$

$$= \frac{1}{4} \sum_{\mathbf{k}} k^{2} \left| \mathbf{A}_{\mathbf{k}}(t) + \mathbf{A}_{-\mathbf{k}}^{*}(t) \right|^{2}$$
So with  

$$\int_{V} d\mathbf{x} \ \mathbf{E} \cdot \mathbf{E} = \frac{1}{4} \sum_{\mathbf{k}} k^{2} \left| \mathbf{A}_{\mathbf{k}}(t) - \mathbf{A}_{-\mathbf{k}}^{*}(t) \right|^{2}$$
Energy becomes  

$$H_{em} = \frac{1}{8\pi} \int_{V} d\mathbf{x} \ (\mathbf{E} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{B})$$

$$= \frac{1}{8\pi} \frac{1}{4} \sum_{\mathbf{k}} 2k^{2} \left( \left| \mathbf{A}_{\mathbf{k}}(t) \right|^{2} + \left| \mathbf{A}_{-\mathbf{k}}(t) \right|^{2} \right)$$

$$= \frac{1}{8\pi} \sum_{\mathbf{k}} k^{2} \left| \mathbf{A}_{\mathbf{k}}(t) \right|^{2} = \frac{1}{8\pi} \sum_{\mathbf{k}} k^{2} \left| \mathbf{A}_{\mathbf{k}}(t) \right|^{2}$$

Note: no time dependence!

# Expand Fourier coefficients along polarization vectors

Use 
$$A_{k} = \sum_{\alpha=1,2} e_{k\alpha} A_{k\alpha}$$
  
-->  $H_{em} = \frac{1}{8\pi} \sum_{k\alpha} k^{2} |A_{k\alpha}|^{2}$ 

# Preparation for QUANTIZATION

In order to quantize, introduce real canonical variables

$$Q_{k}(t) = \frac{i}{2c\sqrt{4\pi}} \left[ A_{k}(t) - A_{k}^{*}(t) \right]$$
$$P_{k}(t) = \frac{k}{2\sqrt{4\pi}} \left[ A_{k}(t) + A_{k}^{*}(t) \right]$$
Invert --> 
$$A_{k}(t) = -ic\sqrt{4\pi} \left[ Q_{k}(t) + \frac{i}{\omega_{k}} P_{k}(t) \right]$$

**So** 
$$|\mathbf{A}_{k}(t)|^{2} = c^{2} 4\pi \left[ \mathbf{Q}_{k}^{2}(t) + \frac{\mathbf{P}_{k}^{2}(t)}{\omega_{k}^{2}} \right] = c^{2} 4\pi \left[ \mathbf{Q}_{k}^{2} + \frac{\mathbf{P}_{k}^{2}}{\omega_{k}^{2}} \right]$$

And thus .....(what else)

# Oscillators of course

$$H_{em} = \frac{1}{8\pi} \sum_{\mathbf{k}} k^2 |\mathbf{A}_{\mathbf{k}}(t)|^2$$
$$= \frac{1}{8\pi} \sum_{\mathbf{k}} k^2 c^2 4\pi \left( \mathbf{Q}_{\mathbf{k}}^2 + \frac{\mathbf{P}_{\mathbf{k}}^2}{\omega_k^2} \right)$$
$$= \frac{1}{2} \sum_{\mathbf{k}} \left( \mathbf{P}_{\mathbf{k}}^2 + \omega_k^2 \mathbf{Q}_{\mathbf{k}}^2 \right)$$

Expand in polarizations  $P_k = \sum_{\alpha=1,2} e_{k\alpha} P_{k\alpha}$   $Q_k = \sum_{\alpha=1,2} e_{k\alpha} Q_{k\alpha}$ 

then

$$H_{em} = \frac{1}{2} \sum_{\boldsymbol{k}\alpha} \left( P_{\boldsymbol{k}\alpha}^2 + \omega_k^2 Q_{\boldsymbol{k}\alpha}^2 \right)$$

E&M

# True canonical variables

 $Q_{k}, P_{k}$  are canonical variables

Check 
$$\boldsymbol{A}_{\boldsymbol{k}}(t) = e^{-i\omega_k t} \boldsymbol{A}_{\boldsymbol{k}}$$

So 
$$\dot{A}_{k}(t) = -i\omega_{k}A_{k}(t)$$

and from 
$$\boldsymbol{Q}_{\boldsymbol{k}}(t) = \frac{i}{2c\sqrt{4\pi}} \left[ \boldsymbol{A}_{\boldsymbol{k}}(t) - \boldsymbol{A}_{\boldsymbol{k}}^{*}(t) \right]$$
  
it follows  $\dot{\boldsymbol{Q}}_{\boldsymbol{k}}(t) = \frac{i}{2c\sqrt{4\pi}} \left[ -i\omega_{\boldsymbol{k}}\boldsymbol{A}_{\boldsymbol{k}}(t) - (i\omega_{\boldsymbol{k}})\boldsymbol{A}_{\boldsymbol{k}}^{*}(t) \right] = \boldsymbol{P}_{\boldsymbol{k}}(t)$ 

But also: 
$$\dot{\boldsymbol{Q}}_{\boldsymbol{k}} = \boldsymbol{P}_{\boldsymbol{k}} = \frac{\partial H_{em}}{\partial \boldsymbol{P}_{\boldsymbol{k}}}$$

Similarly for generalized momentum

$$\dot{P}_{k} = -rac{\partial H_{em}}{\partial Q_{k}}$$

#### And now....

- Back to Hamiltonian
- Looks like a sum of oscillators --> treat as such!
- From canonical classical variables in classical mechanics
- Quantize by introducing commutation relations between operators!!! (Dirac)

$$[P_{\boldsymbol{k}\alpha}, P_{\boldsymbol{k}'\alpha'}] = 0$$
  
$$[Q_{\boldsymbol{k}\alpha}, Q_{\boldsymbol{k}'\alpha'}] = 0$$
  
$$[Q_{\boldsymbol{k}\alpha}, P_{\boldsymbol{k}'\alpha'}] = i\hbar\delta_{\boldsymbol{k},\boldsymbol{k}'}\delta_{\alpha,\alpha'}$$

# Photons

Introduce the usual operators

$$a_{\boldsymbol{k}\alpha} = \frac{1}{\sqrt{2\hbar\omega_{\boldsymbol{k}}}} \left( P_{\boldsymbol{k}\alpha} - i\omega_{\boldsymbol{k}}Q_{\boldsymbol{k}\alpha} \right)$$
$$a_{\boldsymbol{k}\alpha}^{\dagger} = \frac{1}{\sqrt{2\hbar\omega_{\boldsymbol{k}}}} \left( P_{\boldsymbol{k}\alpha} + i\omega_{\boldsymbol{k}}Q_{\boldsymbol{k}\alpha} \right)$$

with commutators

 $[a_{\mathbf{k}\alpha}, a_{\mathbf{k}'\alpha'}] = 0$ 

$$\left[a_{\boldsymbol{k}\alpha}^{\dagger}, a_{\boldsymbol{k}'\alpha'}^{\dagger}\right] = 0$$

$$\left[a_{\boldsymbol{k}\alpha}, a_{\boldsymbol{k}'\alpha'}^{\dagger}\right] = \delta_{\boldsymbol{k},\boldsymbol{k}'}\delta_{\alpha,\alpha'}$$

E&M

# Each mode HO

Number operator for each mode  $\hat{N}_{k\alpha} = a^{\dagger}_{k\alpha}a_{k\alpha}$ Then  $\begin{bmatrix} a_{k\alpha}, \hat{N}_{k'\alpha'} \end{bmatrix} = a_{k\alpha}a^{\dagger}_{k'\alpha'}a_{k'\alpha'} - a^{\dagger}_{k'\alpha'}a_{k'\alpha'}a_{k\alpha}$   $= a_{k\alpha}a^{\dagger}_{k'\alpha'}a_{k'\alpha'} - a^{\dagger}_{k'\alpha'}a_{k\alpha}a_{k'\alpha'}$   $= \begin{bmatrix} a_{k\alpha}a^{\dagger}_{k'\alpha'} - a^{\dagger}_{k'\alpha'}a_{k\alpha} \end{bmatrix} a_{k'\alpha'}$  $= \delta_{kk'}\delta_{\alpha\alpha'}a_{k\alpha}$ 

and

$$\left[a_{\boldsymbol{k}\alpha}^{\dagger}, \hat{N}_{\boldsymbol{k}'\alpha'}\right] = -\delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\alpha\alpha'}a_{\boldsymbol{k}\alpha}^{\dagger}$$

So enough to work with one mode  $\hat{N} = a^{\dagger}a$ Eigenkets of this Hermitian operator  $\hat{N} |n\rangle = n |n\rangle$ Consider  $\hat{N}a^{\dagger} |n\rangle = \left[a^{\dagger}\hat{N} + a^{\dagger}\right] |n\rangle = (n+1)a^{\dagger} |n\rangle$ also eigenket with eigenvalue n+1

#### More

- Similarly  $\hat{N}a |n\rangle = \left[a\hat{N}-a\right] |n\rangle = (n-1)a |n\rangle$
- So  $a^{\dagger} \left| n \right\rangle = c_{+} \left| n + 1 \right\rangle$  $a \left| n \right\rangle = c_{-} \left| n - 1 \right\rangle$
- Normalization from

$$n = \langle n | \hat{N} | n \rangle = \langle n | a^{\dagger} a | n \rangle \ge 0$$

- Phase choice  $a |n\rangle = \sqrt{n} |n-1\rangle$
- Also  $a^{\dagger} \left| n \right
  angle = \sqrt{n+1} \left| n+1 
  ight
  angle$
- Integers otherwise negative norm appears

$$a |n\rangle = \sqrt{n} |n-1\rangle$$
  
 $a |n-1\rangle = \sqrt{n-1} |n-2\rangle$ 

. . .

$$egin{array}{rcl} a \left| 2 
ight
angle &=& \sqrt{2} \left| 1 
ight
angle \ a \left| 1 
ight
angle &=& \sqrt{1} \left| 0 
ight
angle \ a \left| 0 
ight
angle &=& 0 \end{array}$$

#### Photon states

- Operator that adds a photon with momentum  $\hbar {m k}$  and polarization  $\alpha$   $a^{\dagger}_{{m k}\alpha}$ 

$$a_{\boldsymbol{k}\alpha}^{\dagger} \left| 0 \right\rangle = \left| 0, 0, ..., 0, 1_{\boldsymbol{k}\alpha}, 0.... \right\rangle = \left| 1_{\boldsymbol{k}\alpha} \right\rangle$$

- No quantum: vacuum state  $\ket{0}$
- Normalized two-photon state (same mode)

$$\frac{1}{\sqrt{2}}a_{\boldsymbol{k}\alpha}^{\dagger}a_{\boldsymbol{k}\alpha}^{\dagger}\left|0\right\rangle=\left|0,0,...,0,2_{\boldsymbol{k}\alpha},0....\right\rangle=\left|2_{\boldsymbol{k}\alpha}\right\rangle$$

Different modes

 $a_{\boldsymbol{k}\alpha}^{\dagger}a_{\boldsymbol{k}'\alpha'}^{\dagger}\left|0\right\rangle=\left|0,0,...,0,1_{\boldsymbol{k}\alpha},0...,0,1_{\boldsymbol{k}'\alpha'},0....\right\rangle=\left|1_{\boldsymbol{k}\alpha}1_{\boldsymbol{k}'\alpha'}\right\rangle=a_{\boldsymbol{k}'\alpha'}^{\dagger}a_{\boldsymbol{k}\alpha}^{\dagger}\left|0\right\rangle$ 

#### Development

- General state  $|n_{\boldsymbol{k}_{1}\alpha_{1}}n_{\boldsymbol{k}_{2}\alpha_{2}}n_{\boldsymbol{k}_{3}\alpha_{3}}...\rangle = \prod_{\boldsymbol{k}_{i}\alpha_{i}} \frac{\left(a_{\boldsymbol{k}_{i}\alpha_{i}}^{\dagger}\right)^{n_{\boldsymbol{k}_{i}\alpha_{i}}}}{\sqrt{n_{\boldsymbol{k}_{i}\alpha_{i}}!}} |0\rangle$
- So that

$$a_{\boldsymbol{k}_{i}\alpha_{i}}^{\dagger}\left|n_{\boldsymbol{k}_{1}\alpha_{1}}...n_{\boldsymbol{k}_{i}\alpha_{i}}...\right\rangle=\sqrt{n_{\boldsymbol{k}_{i}\alpha_{i}}+1}\left|n_{\boldsymbol{k}_{1}\alpha_{1}}...(n_{\boldsymbol{k}_{i}\alpha_{i}}+1)...\right\rangle$$

 Photons: quantum excitations of the radiation field since classical vector potential has been replaced by quantum operator acting on photon states!

$$A_{k\alpha} \Rightarrow -ic\sqrt{4\pi} \left[ Q_{k\alpha} + \frac{i}{\omega_k} P_{k\alpha} \right] = \frac{c\sqrt{4\pi}}{\omega_k} \left[ -i\omega_k Q_{k\alpha} + P_{k\alpha} \right] \frac{1}{\sqrt{2\hbar\omega_k}} \times \sqrt{2\hbar\omega_k}$$
$$= c\sqrt{\frac{8\pi\hbar}{\omega_k}} a_{k\alpha}$$
also  $A_{k\alpha}^* \Rightarrow c\sqrt{\frac{8\pi\hbar}{\omega_k}} a_{k\alpha}^\dagger$ 

E&M

#### Vector potential operator

$$\boldsymbol{A}(\boldsymbol{x},t) = \sum_{\boldsymbol{k}\alpha} \left( \frac{2\pi\hbar c^2}{\omega_k V} \right)^{1/2} \left\{ a_{\boldsymbol{k}\alpha} \boldsymbol{e}_{\boldsymbol{k}\alpha} e^{i(\boldsymbol{k}\cdot\boldsymbol{x}-\omega_k t)} + a_{\boldsymbol{k}\alpha}^{\dagger} \boldsymbol{e}_{\boldsymbol{k}\alpha} e^{-i(\boldsymbol{k}\cdot\boldsymbol{x}-\omega_k t)} \right\}$$

Acts on photon states: adds or removes one!

Acts on charged particle at x and t (first quantization)

First rewrite Hamiltonian of free field for further interpretation No work...
# Hamiltonian free field

- Number operator for each mode $\hat{N}_{k\alpha} = a_{k\alpha}^{\dagger} a_{k\alpha}$ Hamiltonian operator $\hat{H}_{em} = \sum_{k\alpha} \hbar \omega_k \left( \hat{N}_{k\alpha} + \frac{1}{2} \right) \Rightarrow \sum_{k\alpha} \hbar \omega_k \hat{N}_{k\alpha}$
- Momentum operator from Poynting vector (exercise)

$$\hat{\boldsymbol{P}}_{em} = \frac{1}{8\pi c} \int_{V} d^{3}x \left(\boldsymbol{E} \times \boldsymbol{B} - \boldsymbol{B} \times \boldsymbol{E}\right)$$
$$= \sum_{\boldsymbol{k}\alpha} \hbar \boldsymbol{k} \left(\hat{N}_{\boldsymbol{k}\alpha} + \frac{1}{2}\right) = \sum_{\boldsymbol{k}\alpha} \hbar \boldsymbol{k} \hat{N}_{\boldsymbol{k}\alpha}$$

Single photon state

$$\begin{split} \hat{H}_{em} a_{\boldsymbol{k}\alpha}^{\dagger} \left| 0 \right\rangle &= \hbar \omega_{k} \, a_{\boldsymbol{k}\alpha}^{\dagger} \left| 0 \right\rangle \\ \hat{\boldsymbol{P}}_{em} a_{\boldsymbol{k}\alpha}^{\dagger} \left| 0 \right\rangle &= \hbar \boldsymbol{k} \, a_{\boldsymbol{k}\alpha}^{\dagger} \left| 0 \right\rangle \end{split}$$

So massless!

$$m^{2}c^{4} = E^{2} - p^{2}c^{2} = \hbar^{2}\omega_{k}^{2} - \hbar^{2}k^{2}c^{2} = \hbar^{2}k^{2}c^{2} - \hbar^{2}k^{2}c^{2} = 0$$

### More on photon states

- Characterized also by polarization vector  $e_{oldsymbol{k}lpha}$
- Transforms as vector --> interpret as 1 unit of intrinsic angular momentum or spin of the photon
- Consider circular polarization vectors  $e_{k}^{(\pm)} = \mp \frac{1}{\sqrt{2}} \left( e_{k,1} \pm i e_{k,2} \right)$
- Rotate by angle  $\,\delta\phi\,$  about propagation axis

$$\begin{array}{ll} \boldsymbol{e}_{\boldsymbol{k},1}' &= \cos \delta \phi \; \boldsymbol{e}_{\boldsymbol{k},1} + \sin \delta \phi \; \boldsymbol{e}_{\boldsymbol{k},2} &\Rightarrow \boldsymbol{e}_{\boldsymbol{k},1} + \delta \phi \; \boldsymbol{e}_{\boldsymbol{k},2} \\ \boldsymbol{e}_{\boldsymbol{k},2}' &= -\sin \delta \phi \; \boldsymbol{e}_{\boldsymbol{k},1} + \cos \delta \phi \; \boldsymbol{e}_{\boldsymbol{k},2} &\Rightarrow -\delta \phi \; \boldsymbol{e}_{\boldsymbol{k},1} + \boldsymbol{e}_{\boldsymbol{k},2} \end{array}$$

• New circular polarization vectors  $e_{k}^{\pm'} = \mp \frac{1}{\sqrt{2}} (e_{k,1'} \pm i e_{k,2'})$   $= e_{k}^{(\pm)} \mp \frac{1}{\sqrt{2}} \delta \phi (e_{k,2} \pm (-) i e_{k,1})$   $= e_{k}^{(\pm)} \mp i \delta \phi e_{k}^{(\pm)}$  $= (1 \mp i \delta \phi) e_{k}^{(\pm)}$ E&M

# Angular momentum

• Compare  ${\boldsymbol{e_k^{\pm}}}' = (1 \mp i \delta \phi) \, {\boldsymbol{e_k^{(\pm)}}}$ 

# • With $e^{-\frac{i}{\hbar}J_z\phi}|1m\rangle = e^{-im\phi}|1m\rangle$ $\Rightarrow (1-im\delta\phi)|1m\rangle$

• Interpret  $m = 1 \Rightarrow e_k^{(+)}$  $m = -1 \Rightarrow e_k^{(-)}$ 

- Quantization axis along k so photons can have helicity 1 or -1 but not 0 --> no longitudinal photons
- No contradiction (no rest frame where photon is at rest)
- Photons with good helicity

$$a_{\mathbf{k}\pm}^{\dagger} = \mp \frac{1}{\sqrt{2}} \left( a_{\mathbf{k},1}^{\dagger} \pm i a_{\mathbf{k},2}^{\dagger} \right)$$

### Interaction of electrons with photons

- Complete Hamiltonian includes interaction of charges and their coupling to the electromagnetic field
- Use radiation gauge
- Vector potential in minimal substitution
- Hamiltonian for Z electrons in an atom plus radiation field

$$H = \sum_{i=1}^{Z} \frac{\left(\boldsymbol{p}_{i} + \frac{e}{c}\boldsymbol{A}(\boldsymbol{x}_{i}, t)\right)^{2}}{2m} - \sum_{i=1}^{Z} \frac{Ze^{2}}{|\boldsymbol{x}_{i}|} + \sum_{i < j}^{Z} \frac{e^{2}}{|\boldsymbol{x}_{i} - \boldsymbol{x}_{j}|} + \hat{H}_{em}$$
$$= H_{electrons} + H_{int} + \hat{H}_{em}$$

$$\hat{H}_{em} = \sum_{\boldsymbol{k}\alpha} \hbar \omega_k a^{\dagger}_{\boldsymbol{k}\alpha} a_{\boldsymbol{k}\alpha}$$

### Electron and interaction Hamiltonian

Electrons

$$H_{electrons} = \sum_{i=1}^{Z} \frac{p_i^2}{2m} - \sum_{i=1}^{Z} \frac{Ze^2}{|x_i|} + \sum_{i$$

Coupling

$$H_{int} = \sum_{i}^{Z} \left[ \frac{e}{2mc} \left( \boldsymbol{p}_{i} \cdot \boldsymbol{A}(\boldsymbol{x}_{i}, t) + \boldsymbol{A}(\boldsymbol{x}_{i}, t) \cdot \boldsymbol{p}_{i} \right) + \frac{e^{2}}{2mc^{2}} \boldsymbol{A}(\boldsymbol{x}_{i}, t) \cdot \boldsymbol{A}(\boldsymbol{x}_{i}, t) \right]$$

with

$$\mathbf{A}(\mathbf{x}_{i},t) = \sum_{\mathbf{k}\alpha} \left(\frac{2\pi\hbar c^{2}}{\omega_{k}V}\right)^{1/2} \left\{ a_{\mathbf{k}\alpha} \mathbf{e}_{\mathbf{k}\alpha} e^{i(\mathbf{k}\cdot\mathbf{x}_{i}-\omega_{k}t)} + a_{\mathbf{k}\alpha}^{\dagger} \mathbf{e}_{\mathbf{k}\alpha} e^{-i(\mathbf{k}\cdot\mathbf{x}_{i}-\omega_{k}t)} \right\}$$

No spin yet. Add by hand  $H_{int}^{spin} = \frac{e}{mc} \sum_{i=1}^{Z} s_i \cdot [\nabla \times A(x,t)]_{x=x_i}$ as before from  $E = -\mu \cdot B$  Towards transitions between atomic levels

- Solve electron Hamiltonian (approximately)
- Hartree-Fock method for example
- Ground state: occupy lowest HF orbits
- Treat atoms in IPM with e.g. in second quantization

$$\hat{H}_{electrons} = \sum_{n\ell m_{\ell} m_{s}} \varepsilon_{n\ell} \ a^{\dagger}_{n\ell m_{\ell} m_{s}} a_{n\ell m_{\ell} m_{s}}$$

- Free electromagnetic field solved
- Transitions between  $|atom\rangle\,|photons\rangle\,$  states --> coupling
- Usually emission or absorption of one photon
- Use second quantization for electrons as well

### Second quantized

Using transversality  $\boldsymbol{p}_i \cdot \boldsymbol{A}(\boldsymbol{x}_i,t) = \boldsymbol{A}(\boldsymbol{x}_i,t) \cdot \boldsymbol{p}_i$ 

Remember

$$\begin{split} \mathbf{A}(\mathbf{x}_{i},t) &= \sum_{\mathbf{k}\alpha} \left(\frac{2\pi\hbar c^{2}}{\omega_{k}V}\right)^{1/2} \left\{ a_{\mathbf{k}\alpha} e_{\mathbf{k}\alpha} e^{i(\mathbf{k}\cdot\mathbf{x}_{i}-\omega_{k}t)} + a_{\mathbf{k}\alpha}^{\dagger} e_{\mathbf{k}\alpha} e^{-i(\mathbf{k}\cdot\mathbf{x}_{i}-\omega_{k}t)} \right\} \\ \text{then} \\ \hat{H}_{int} &= \frac{e}{m} \sum_{\beta\gamma} \sum_{\mathbf{k}\alpha} \left(\frac{2\pi\hbar}{\omega_{k}V}\right)^{1/2} e_{\mathbf{k}\alpha} \cdot \left\{ \langle \beta | e^{i(\mathbf{k}\cdot\mathbf{x}-\omega_{k}t)} \mathbf{p} | \gamma \rangle \right. a_{\beta}^{\dagger} a_{\gamma} a_{\mathbf{k}\alpha} \\ &+ \langle \beta | e^{-i(\mathbf{k}\cdot\mathbf{x}-\omega_{k}t)} \mathbf{p} | \gamma \rangle \right. a_{\beta}^{\dagger} a_{\gamma} a_{\mathbf{k}\alpha}^{\dagger} \\ \hat{H}_{int}^{spin} &= \frac{e}{m} \sum_{\beta\gamma} \sum_{\mathbf{k}\alpha} \left(\frac{2\pi\hbar}{\omega_{k}V}\right)^{1/2} (i\mathbf{k}\times\mathbf{e}_{\mathbf{k}\alpha}) \\ &\cdot \left\{ \langle \beta | e^{i(\mathbf{k}\cdot\mathbf{x}-\omega_{k}t)} \mathbf{s} | \gamma \rangle \right. a_{\beta}^{\dagger} a_{\gamma} a_{\mathbf{k}\alpha} + \langle \beta | e^{-i(\mathbf{k}\cdot\mathbf{x}-\omega_{k}t)} \mathbf{s} | \gamma \rangle \right. a_{\beta}^{\dagger} a_{\gamma} a_{\mathbf{k}\alpha}^{\dagger} \end{split}$$

neglect term with vector potential squared

### Next step

 Use standard time-dependent perturbation theory for transitions of the type

### $|A\rangle |n_{\boldsymbol{k}\alpha}\rangle \equiv |A; n_{\boldsymbol{k}\alpha}\rangle \Rightarrow |B; n_{\boldsymbol{k}\alpha} \pm 1\rangle$

- Do only lowest order (otherwise squared term must be included)
- Validity
  - present results for "slow" particles
  - not good for interaction with modes  $\ \hbar\omega\geq mc^2$  (--> pair creation)
  - can be eliminated by cut-off: sum only  $|m k| \leq k_c$  with  $\hbar c k_c = \hbar \omega_c \ll mc^2$
  - should still be large with respect to transition frequency of particles so

$$\hbar\omega_0 \ll \hbar\omega_c \ll mc^2$$

- Hydrogen:

$$\begin{array}{rcl} & \hbar\omega_0 & \sim & \alpha^2 m c^2 \simeq 1 \mathrm{H} \\ & \hbar\omega_c & \sim & \alpha m c^2 \\ & m c^2 & \sim & 0.5 \mathrm{\ MeV} \end{array}$$

$$\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137} \quad {\rm Eam}$$

Apply time-dependent perturbation theory

- Results from TDPT
- Constant potential
  - Transition rate from Fermi's Golden Rule

$$w_{i \to [f]} = \frac{2\pi}{\hbar} \rho(E_f) \left| \langle f | V | i \rangle \right|^2$$

- No change when Fock space formulation is used
- Except: "potential" now includes  $e^{-i\omega t}$  or  $e^{i\omega t}$
- So instead of  $~~E_f=E_i~~ \dashrightarrow ~~E_f=E_i+\hbar\omega$  for removing a photon (absorption)

-> 
$$E_f=E_i-\hbar\omega$$
 for adding a photon

(emission)

- Corresponding Golden Rule becomes

$$w_{i \to [f]} = \frac{2\pi}{\hbar} \left| \langle f | \hat{H}'_{int} | i \rangle \right|^2 \rho_f$$

- With  $\hat{H}_{int}'$  no longer including time dependence

### Emission of a photon

• We want to describe transitions of the kind

$$|A; n_{\boldsymbol{k}\alpha} = 0\rangle \Rightarrow |B; n_{\boldsymbol{k}\alpha} = 1\rangle$$

So we need a transition rate of the kind

$$w_{d\Omega} = \frac{2\pi}{\hbar} \left| \langle B; n_{\boldsymbol{k}\alpha} = 1 | \hat{H}'_{int} | A; n_{\boldsymbol{k}\alpha} = 0 \rangle \right|^2 \rho_{\hbar\omega, d\Omega}$$

• Density of states --> # of allowed states in interval  $\hbar\omega + d(\hbar\omega), \hbar\omega$ for photon emitted into solid angle  $d\Omega$ 

• First evaluate  $(\# \text{ of states} \le \hbar \omega) = \sum_{|\mathbf{k}| \le \omega/c}$  (note  $dn_x = \frac{L}{2\pi} dk_x$ )  $\Rightarrow \int dn_x \int dn_y \int dn_z$  with  $|\mathbf{k}| \le \omega/c$  $= \frac{V}{(2\pi)^3} \int d^3k = \frac{V}{(2\pi)^3} \int dk \ k^2 \ d\Omega$ 

### Density of states

#### Required density of states is then obtained from

$$\begin{array}{rcl} (\# \mbox{ of states } \leq \hbar(\omega + d\omega)) - (\# \mbox{ of states } \leq \hbar\omega) &=& \rho_{\hbar\omega,d\Omega} \ d\hbar\omega \\ &=& \frac{V}{(2\pi)^3} \int_0^{(\omega + d\omega)/c} dk \ k^2 \ d\Omega - \frac{V}{(2\pi)^3} \int_0^{\omega/c} dk \ k^2 \ d\Omega \\ &=& \frac{V}{(2\pi)^3} d\Omega \int_{\omega}^{\omega + d\omega} \frac{d\omega'}{c} \left(\frac{\omega'}{c}\right)^2 = \frac{V}{(2\pi)^3} d\Omega \frac{1}{3} \left(\frac{\omega'}{c}\right)^3 \Big|_{\omega}^{\omega + d\omega} \\ &\Rightarrow& \frac{V}{(2\pi)^3} \frac{\omega^2}{\hbar c^3} d\hbar\omega \ d\Omega \\ \hline & \text{Therefore} \quad \rho_{\hbar\omega,d\Omega} = \frac{V}{(2\pi)^3} \frac{\omega^2}{\hbar c^3} d\Omega \\ \hline & \text{Initial state} \quad |A\rangle \ |0\rangle = |i\rangle \\ \hline & \text{with} \quad \left(\hat{H}_{electrons} + \hat{H}_{em}\right) |i\rangle = E_A \ |i\rangle \\ \hline & \text{Final state} \quad |B\rangle \ |1_{k\lambda}\rangle = |f\rangle \\ \hline & \text{with} \quad \left(\hat{H}_{electrons} + \hat{H}_{em}\right) |f\rangle = (E_B + \hbar\omega_k) \ |f\rangle \\ \hline & \text{such that} \quad E_A = E_B + \hbar\omega_k \end{array}$$

## Corresponding rate

- Insert density of states  $w_{d\Omega} = \frac{2\pi}{\hbar} \frac{V}{(2\pi)^3} \frac{\omega_k^2}{\hbar c^3} d\Omega \left| \langle f | \hat{H}'_{int} | i \rangle \right|^2$
- Keep in mind

$$\hat{H}_{int}' = \frac{e}{m} \sum_{\beta\gamma} \sum_{\mathbf{k}'\alpha} \left( \frac{2\pi\hbar}{\omega_{\mathbf{k}'}'V} \right)^{1/2} \boldsymbol{e}_{\mathbf{k}'\alpha} \cdot \left\{ \left\langle \beta \right| e^{i\mathbf{k}'\cdot\boldsymbol{x}} \boldsymbol{p} \left| \gamma \right\rangle \ a_{\beta}^{\dagger} a_{\gamma} a_{\mathbf{k}'\alpha} + \left\langle \beta \right| e^{-i\mathbf{k}'\cdot\boldsymbol{x}} \boldsymbol{p} \left| \gamma \right\rangle \ a_{\beta}^{\dagger} a_{\gamma} a_{\mathbf{k}'\alpha}^{\dagger} \right\}$$

- Only second term contributes
- Single-particle matrix elements require evaluation
- Also matrix element connecting initial and final atomic state plus photon involving  $a^{\dagger}_{\beta}a_{\gamma}a^{\dagger}_{{m k}'lpha}$

### Rate continued

• So right now

$$w_{d\Omega} = \frac{2\pi}{\hbar} \frac{V}{(2\pi)^3} \frac{\omega_k^2}{\hbar c^3} \frac{e^2}{m^2} \left(\frac{2\pi\hbar}{V}\right) \left| \sum_{\beta\gamma} \sum_{\mathbf{k}'\alpha} \frac{1}{\sqrt{\omega_k'}} \mathbf{e}_{\mathbf{k}'\alpha} \cdot \left\{ \left<\beta\right| e^{-i\mathbf{k}'\cdot\mathbf{x}} \mathbf{p} \left|\gamma\right> \left< B\mathbf{1}_{\mathbf{k}\lambda}\right| \mathbf{a}_{\beta}^{\dagger} \mathbf{a}_{\gamma} \mathbf{a}_{\mathbf{k}'\alpha}^{\dagger} \left|A\right> \right\} \right|^2$$

- Typical transition: optical ~ eV -->  $\hbar\omega_k$  (green --> 2 eV)
- Atomic dimension: ~  $10^{-10}$  m
- So from  $\hbar\omega_k \Rightarrow kr = \frac{\hbar\omega_k}{\hbar c}r \simeq \frac{\text{eV }10^{-10} \text{ m}}{1.24 \times 10^{-6} \text{ eV m}} \sim 10^{-4}$
- therefore  $e^{-i\mathbf{k}'\cdot\mathbf{x}} \Rightarrow 1 i\mathbf{k}'\cdot\mathbf{x} \Rightarrow 1$
- Electric dipole (E1) approximation
- Photon matrix element  $\langle 1_{\boldsymbol{k}\lambda} | a^{\dagger}_{\boldsymbol{k}'\alpha} | 0 \rangle = \delta_{\boldsymbol{k}\boldsymbol{k}'} \delta_{\lambda\alpha}$
- Consider alkali atom in IPM

### Atom

• Alkali atom: one particle outside closed shell

$$|A\rangle = |n\ell m_{\ell}m_s; \Phi_0\rangle = a^{\dagger}_{n\ell m_{\ell}m_s} |\Phi_0\rangle$$

Transition to final state

$$|B\rangle = |n'\ell'm'_{\ell}m'_{s};\Phi_{0}\rangle = a^{\dagger}_{n'\ell'm'_{\ell}m'_{s}} |\Phi_{0}\rangle$$

• Evaluate

$$\begin{array}{lcl} \langle B | \, a_{\beta}^{\dagger} a_{\gamma} \, | A \rangle &= \langle \Phi_{0} | \, a_{n'\ell'm_{\ell}'m_{s}'} a_{\beta}^{\dagger} a_{\gamma} a_{n\ell m_{\ell} m_{s}}^{\dagger} \, | \Phi_{0} \rangle \\ &= \langle \Phi_{0} | \left( \delta_{n'\beta} - a_{\beta}^{\dagger} a_{n'\ell'm_{\ell}'m_{s}'} \right) \left( \delta_{n\gamma} - a_{n\ell m_{\ell} m_{s}}^{\dagger} a_{\gamma} \right) | \Phi_{0} \rangle \\ &= \delta_{n'\beta} \delta_{n\gamma} \end{array}$$

- not unexpected...
- So we also need

$$\boldsymbol{e}_{\boldsymbol{k}\lambda}\cdot \langle n'\ell'm'_{\ell}m'_{s}|\, \boldsymbol{p}\,|n\ell m_{\ell}m_{s}
angle$$

## Dipole matrix element

Use central field from

 $\hat{H}_{electrons} = \sum \varepsilon_{n\ell} a^{\dagger}_{n\ell m_{\ell}m_{s}} a_{n\ell m_{\ell}m_{s}} \Rightarrow$  $H_0 \left| n\ell m_\ell m_s \right\rangle = \varepsilon_{n\ell} \left| n\ell m_\ell m_s \right\rangle$  $n\ell m_\ell m_s$ 

- to evaluate  $e_{k\lambda} \cdot \langle n'\ell' m'_{\ell} m'_{s} | p | n\ell m_{\ell} m_{s} \rangle$
- First note that  $[m{p}^2,m{x}]=-2i\hbarm{p}$

So  

$$\begin{bmatrix} \frac{p^2}{2m}, \boldsymbol{x} \end{bmatrix} = -i\hbar \frac{p}{m}$$

$$\begin{bmatrix} \frac{p^2}{2m} + V_{nucleus} + V_{central}, \boldsymbol{x} \end{bmatrix} = -i\hbar \frac{p}{m}$$

$$[H_0, \boldsymbol{x}] = -i\hbar \frac{p}{m}$$

• Replace  $\boldsymbol{p} = i \frac{m}{\hbar} \left[ H_0, \boldsymbol{x} \right]$ 

### Matrix element

Then (hence dipole approximation) & note change in parity •  $\boldsymbol{e}_{\boldsymbol{k}\lambda} \cdot \langle n'\ell'm'_{\ell}m'_{s} | \boldsymbol{p} | n\ell m_{\ell}m_{s} \rangle = \boldsymbol{e}_{\boldsymbol{k}\lambda} \cdot \langle n'\ell'm'_{\ell}m'_{s} | i\frac{m}{\hbar} [H_{0}, \boldsymbol{x}] | n\ell m_{\ell}m_{s} \rangle$  $= i\frac{m}{\hbar} \boldsymbol{e}_{\boldsymbol{k}\lambda} \cdot \langle n'\ell'm_{\ell}' | \boldsymbol{x} | n\ell m_{\ell} \rangle \, \delta_{m_s m_s'} \left( \varepsilon_{n'\ell'} - \varepsilon_{n\ell} \right)$  $= -im\omega_k \boldsymbol{e}_{\boldsymbol{k}\lambda} \cdot \langle n'\ell'm_\ell' | \boldsymbol{x} | n\ell m_\ell \rangle \, \delta_{m_s m_s'}$  $w_{d\Omega} = \frac{e^2}{2\pi} \frac{\omega_k^3}{\hbar c^3} d\Omega \left| \boldsymbol{e}_{\boldsymbol{k}\lambda} \cdot \langle n'\ell' m_{\ell'} \right| \boldsymbol{x} \left| n\ell m_{\ell} \rangle \right|^2$ Insert all ingredients  $= \frac{e^2}{2\pi} \frac{\omega_k^3}{\hbar c^3} d\Omega \, \cos^2 \Theta_\lambda \left| \langle n' \ell' m_{\ell'} | \, \boldsymbol{x} \, | n \ell m_\ell \rangle \right|^2$ Sum over polarization & integrate over all directions  $\cos \Theta_1 = \sin \theta \cos \phi$  $\cos\Theta_2 = \sin\theta\sin\phi$  $e_{k,2}$   $\sum_{\lambda} \Rightarrow \sin^2 \theta$  $\int d\Omega \sin^2 \theta = 2\pi \int d(\cos \theta) \sin^2 \theta = \frac{8\pi}{3}$  $e_{oldsymbol{k},1}$ E&M

### Rate

• Therefore  $w = \frac{4e^2\omega_k^3}{2\hbar c^3} \left| \langle n'\ell' m_{\ell'} | \boldsymbol{x} | n\ell m_{\ell} \rangle \right|^2$  $\left|\left\langle f \left| \boldsymbol{x} \left| i \right\rangle \right|^{2} \right| = \left|\left\langle f \left| x \left| i \right\rangle \right|^{2} + \left|\left\langle f \left| y \left| i \right\rangle \right|^{2} + \left|\left\langle f \left| z \left| i \right\rangle \right|^{2} \right|^{2} \right|^{2} \right|^{2}$ • Note  $= \left| \langle f | -\frac{1}{\sqrt{2}} (x + iy) | i \rangle \right|^{2} + \left| \langle f | \frac{1}{\sqrt{2}} (x - iy) | i \rangle \right|^{2} + \left| \langle f | z | i \rangle \right|^{2}$  $= \frac{4\pi}{3} \left\{ \left| \langle f | rY_{11} | i \rangle \right|^2 + \left| \langle f | rY_{1-1} | i \rangle \right|^2 + \left| \langle f | rY_{10} | i \rangle \right|^2 \right\}$  $\Rightarrow \quad \frac{4\pi}{3} \sum_{\mu} \left| \langle n'\ell' m_{\ell}' | \, r Y_{1\mu} \, | n\ell m_{\ell} \rangle \right|^2$ Need  $\langle n'\ell'm'_{\ell} | rY_{1\mu} | n\ell m_{\ell} \rangle = \frac{(\ell m_{\ell} 1 \mu | \ell' m'_{\ell})}{\sqrt{2\ell+1}} \langle n'\ell' | | rY_{1} | | n\ell \rangle$  $= \int dr \ r^2 \left\{ \int d\Omega \ Y^*_{\ell' m'_{\ell}}(\Omega) Y_{1\mu}(\Omega) Y_{\ell m_{\ell}}(\Omega) \right\} R_{n'\ell'}(r) r R_{n\ell}(r)$  $= \int dr \ r^3 R_{n'\ell'}(r) R_{n\ell}(r) \times \sqrt{\frac{3}{4\pi}} \sqrt{\frac{2\ell+1}{2\ell'+1}} \left(\ell \ 0 \ 1 \ 0 \ | \ \ell' \ 0 \ \right) \left(\ell \ m_\ell \ 1 \ \mu \ | \ \ell' \ m_\ell' \ \right)}$ So that  $\langle n'\ell' || rY_1 || n\ell \rangle = \int dr \ r^3 R_{n'\ell'}(r) R_{n\ell}(r) \times \sqrt{\frac{3}{4\pi} \frac{2\ell+1}{\sqrt{2\ell' \pm 1}}} \left(\ell \ 0 \ 1 \ 0 \ | \ \ell' \ 0 \ \right)$  $\equiv I_{n'\ell'n\ell} \sqrt{\frac{3}{4\pi} \frac{2\ell+1}{\sqrt{2\ell'+1}}} \left(\ell \ 0 \ 1 \ 0 \ | \ \ell' \ 0 \ \right)$ 

E&M

### Experimental conditions

• Sum also over all projections  $m'_\ell$  of final state

$$\begin{split} \sum_{m'_{\ell}} |\langle ..| \, \boldsymbol{x} \, |..\rangle|^2 &= \sum_{m'_{\ell}} \frac{4\pi}{3} \sum_{\mu} |\langle n'\ell' m'_{\ell}| \, rY_{1\mu} \, |n\ell m_{\ell}\rangle|^2 \\ &= \frac{4\pi}{3} \sum_{m'_{\ell}\mu} \frac{(\ell m_{\ell} \ 1 \ \mu \ | \ \ell' \ m'_{\ell} \ )^2}{2\ell + 1} I_{n'\ell'n\ell}^2 \frac{3}{4\pi} \frac{(2\ell + 1)^2}{2\ell' + 1} \left(\ell \ 0 \ 1 \ 0 \ | \ \ell' \ 0 \ )^2 \\ &= \sum_{m'_{\ell}\mu} \frac{2\ell' + 1}{2\ell + 1} \frac{(\ell' - m'_{\ell} \ 1 \ \mu \ | \ \ell \ - m_{\ell} \ )^2}{2\ell + 1} I_{n'\ell'n\ell}^2 \frac{(2\ell + 1)^2}{2\ell' + 1} \left(\ell \ 0 \ 1 \ 0 \ | \ \ell' \ 0 \ )^2 \\ &= I_{n'\ell'n\ell}^2 \left(\ell \ 0 \ 1 \ 0 \ | \ \ell' \ 0 \ )^2 \end{split}$$

$$\begin{aligned} \mathsf{So} \qquad \sum_{m'_{\ell}} w_{n\ell \to n'\ell'} &= \frac{e^2}{\hbar c} \frac{4\omega_k^3}{3c^2} I_{n'\ell'n\ell}^2 \left(\ell \ 0 \ 1 \ 0 \ | \ \ell' \ 0 \ )^2 \\ &= (\ell \ 0 \ 1 \ 0 \ | \ \ell' \ 0 \ )^2 \end{split}$$

$$(\ell \ 0 \ 1 \ 0 \ | \ \ell' \ 0 \ )^{2} \Rightarrow \frac{1}{2\ell + 1} \qquad \text{for } \ell' = \ell + 1$$

$$\Rightarrow \frac{\ell}{2\ell + 1} \qquad \text{for } \ell' = \ell - 1$$

• Lifetime:  $\frac{1}{\tau_A} = \sum_f w_{A \Rightarrow B_f} = \lambda_A$  exponential decay:  $e^{-\lambda_A t} = e^{-t/\tau_A}$ 

## Explicit example

- Hydrogen atom  $2p \Rightarrow 1s$  transition
- Radial wave functions  $2p \Rightarrow \frac{1}{\sqrt{24a_0^3}} \frac{r}{a_0} e^{-r/2a_0}$  $1s \Rightarrow \frac{2}{a_0^3} e^{-r/a_0}$

Lifetime  

$$au(2p \to 1s) = 3 \frac{\hbar c}{e^2} \frac{3c^2}{4\omega_k^3} I^{-2} = 1.6 \times 10^{-9} s$$

using

$$I^{2} = a_{0}^{2} \left[ \frac{4!}{\sqrt{6}} \left( \frac{2}{3} \right)^{5} \right]^{2}$$

• in agreement with experiment ...



Energy levels of the hydrogen atom with some of the transitions between them that give rise to the spectral lines indicated.

# General issues related to absorption (emission)

- Absorption
  - Initial state: assume only one type of photons  $~~m klpha \Rightarrow n_{m klpha}$
  - Atom absorbs 1 photon
    - initial state  $\ket{n_{m{k}lpha}}\ket{A}$
    - $\cdot$  final state  $\ket{n_{m klpha}-1}\ket{B}$
  - $\hat{H}_{int}$  contribution with  $a_{k\alpha}$  so  $a_{k\alpha} |n_{k\alpha}\rangle = \sqrt{n_{k\alpha}} |n_{k\alpha} 1\rangle$
  - "Before" TDPT -->

$$\langle B | \hat{H}_{int} | A \rangle = \frac{e}{mc} \left( \frac{2\pi\hbar n_{\boldsymbol{k}\alpha}}{\omega_{\boldsymbol{k}} V} \right)^{1/2} c \sum_{\beta\gamma} \boldsymbol{e}_{\boldsymbol{k}\alpha} \cdot \langle \beta | e^{i(\boldsymbol{k}\cdot\boldsymbol{x}-\omega_{\boldsymbol{k}}t)} \boldsymbol{p} | \gamma \rangle \ \langle B | \boldsymbol{a}_{\beta}^{\dagger}\boldsymbol{a}_{\gamma} | A \rangle$$

- Can obtain equivalent classical result by taking classical vector potential  $A^{abs}(\boldsymbol{x},t) = A^{abs}_{0}e^{i(\boldsymbol{k}\cdot\boldsymbol{x}-\omega_{k}t)}$   $A^{abs}_{0} = c\left(\frac{2\pi\hbar n_{\boldsymbol{k}\alpha}}{\omega_{k}V}\right)^{1/2}\boldsymbol{e}_{\boldsymbol{k}\alpha}$
- for  $n_{{\bm k}\alpha}$  large; then do minimal substitution

# Absorption rate in dipole approximation

$$w_{i\Rightarrow[f]} = \frac{2\pi}{\hbar} \frac{e^2}{m^2} \frac{2\pi\hbar n_{\boldsymbol{k}\alpha}}{\omega_k V} \left| \sum_{\beta\gamma} \boldsymbol{e}_{\boldsymbol{k}\alpha} \cdot \langle \beta | \boldsymbol{p} | \gamma \rangle \langle B | \boldsymbol{a}_{\beta}^{\dagger} \boldsymbol{a}_{\gamma} | A \rangle \right|^2 \delta(E_B - E_A - \hbar\omega_k)$$

### Absorption cross section

•

 Defined --> Energy per unit time absorbed by atom A --> B energy flux of radiation field

$$\sigma_{abs}(\omega) = \frac{\hbar\omega w_{A\Rightarrow B}}{n_{k\alpha}\hbar\omega c/V}$$
$$= \frac{4\pi^2 e^2}{m^2\omega c} \left| \sum_{\beta\gamma} e_{k\alpha} \cdot \langle \beta | \mathbf{p} | \gamma \rangle \langle B | \mathbf{a}_{\beta}^{\dagger} \mathbf{a}_{\gamma} | A \rangle \right|^2 \delta(E_B - E_A - \hbar\omega)$$

### Example

- Take photon momentum along z-axis and polarized light --> x-axis
- As before use  $p_x = \frac{m}{i\hbar} [x, H_0]$
- Initial state: ground state of closed shell atom  $|A
  angle=|\Phi_0
  angle$
- Final state: excited state  $|B\rangle = a^{\dagger}_{n_{>}\ell'm'_{\ell}m'_{s}}a_{n_{<}\ell m_{\ell}m_{s}} |\Phi_{0}\rangle$
- Simple particle-hole state
- Evaluate  $\langle B | a_{\beta}^{\dagger} a_{\gamma} | A \rangle = \langle \Phi_0 | a_{n_{<}}^{\dagger} a_{n_{>}} a_{\beta}^{\dagger} a_{\gamma} | \Phi_0 \rangle = \delta_{n_{>}\beta} \delta_{n_{<}\gamma}$
- So absorption cross section

 $\sigma_{abs}(\omega) = \frac{4\pi^2 e^2}{\hbar\omega\hbar c} \left| \langle n_> \ell' m'_\ell m'_s \right| \left[ x, H_0 \right] \left| n_< \ell m_\ell m_s \rangle \right|^2 \delta(E_B - E_A - \hbar\omega)$ 

- **IPM**  $\hat{H}_0 |B\rangle = E_B |B\rangle = \hat{H}_0 a_{n_>\ell' m'_\ell m'_s}^{\dagger} a_{n_<\ell m_\ell m_s} |\Phi_0\rangle = (\varepsilon_{n_>\ell'} \varepsilon_{n_<\ell} + E_{\Phi_0}) |B\rangle$
- $\hat{H}_0 |A\rangle = E_A |A\rangle = \hat{H}_0 |\Phi_0\rangle = E_{\Phi_0} |A\rangle$  and  $H_0 |n_> \ell' m'_\ell m'_s\rangle = \varepsilon_{n_> \ell'} |n_> \ell' m'_\ell m'_s\rangle$  $H_0 |n_< \ell m_\ell m_s\rangle = \varepsilon_{n_< \ell} |n_< \ell m_\ell m_s\rangle$

• thus  $\sigma_{abs}(\omega) = \frac{4\pi^2 e^2}{\hbar c} \left(\varepsilon_{n>\ell'} - \varepsilon_{n<\ell}\right) \left|\langle n_> \ell' m'_\ell m'_s | x | n_< \ell m_\ell m_s \rangle\right|^2 \delta(\varepsilon_{n>\ell'} - \varepsilon_{n<\ell} - \hbar \omega) \delta_{m'_s m_s}$   $= 4\pi^2 \alpha \omega_{n>n<} \left|\langle n_> \ell' m'_\ell m'_s | x | n_< \ell m_\ell m_s \rangle\right|^2 \delta(\omega_{n>n<} - \omega) \delta_{m'_s m_s} \quad \text{E&M}$ 

### Thomas-Reiche-Kuhn sum rule

- Simple model of absorption cross section: delta spike at every allowed combination of  $n_>\ell' \to n_<\ell$
- Dipole matrix element: see before
- Consider integral over all possible absorption contributions  $\int d\omega \ \sigma_{abs}(\omega) = 4\pi^2 \alpha \sum_{n>n<} \omega_{n>n<} \left| \langle n_> \ell' m'_{\ell} m'_s | x | n_< \ell m_{\ell} m_s \rangle \right|^2$
- More general expression  $n_{>n_{<}}$

$$\int d\omega \ \sigma_{abs}(\omega) = \frac{4\pi^2 \alpha}{\hbar} \sum_B (E_B - E_A) \left| \langle B | \sum_{i=1}^Z x_i | A \rangle \right|^2$$
$$= \frac{4\pi^2 \alpha}{\hbar} \sum_B (E_B - E_A) \langle A | X_Z | B \rangle \langle B | X_Z | A \rangle$$
$$= \frac{4\pi^2 \alpha}{\hbar} \left\{ \langle A | X_Z H X_Z | A \rangle - \frac{1}{2} \langle A | H X_Z X_Z | A \rangle - \frac{1}{2} \langle A | X_Z X_Z H | A \rangle \right\}$$
$$= \frac{4\pi^2 \alpha}{\hbar} \langle A | \frac{1}{2} [X_Z, [H, X_Z]] | A \rangle$$

### Evaluate double commutator

Only kinetic contribution of Hamiltonian survives

$$[X_{Z}, [H, X_{Z}]] = \frac{1}{2m} \left[ \sum_{i} x_{i}, \left[ \sum_{j} p_{x_{j}}^{2}, \sum_{k} x_{k} \right] \right]$$

$$= \frac{1}{2m} \sum_{ijk} \left[ x_{i}, \left[ p_{x_{j}}^{2}, x_{k} \right] \right]$$

$$= \frac{1}{2m} \sum_{ijk} \left[ x_{i}, (-2i\hbar) p_{x_{j}} \delta_{jk} \right]$$

$$= -\frac{i\hbar}{m} \sum_{ij} \left[ x_{i}, p_{x_{j}} \right] = -\frac{i\hbar}{m} \sum_{ij} i\hbar \delta_{ij}$$

$$= \frac{Z\hbar^{2}}{m}$$
and therefore
$$\int d\omega \ \sigma_{abs}(\omega) = \frac{4\pi^{2}\alpha}{\hbar} \left\langle A |_{\frac{1}{2}} \left[ X_{Z}, \left[ H, X_{Z} \right] \right] |A\rangle$$

$$= \frac{4\pi^{2}e^{2}}{\hbar c\hbar} \frac{Z\hbar^{2}}{2m} = Z2\pi^{2}c \left( \frac{e^{2}}{mc^{2}} \right)$$

Planck's constant has disappeared --> classical result (Jackson)

### Absorption cross sections in nature



**Figure 1** Total photoabsorption cross section of xenon versus photon energy in the vicinity of the 4d threshold. The solid line is the TDDFT calculations of Zangwill & Soven (23) and the crosses are the experimental results of Haensel et al. (80).

### More

• Big molecules



**Figure 2** The photoabsorption cross section of the chromophore of the green fluorescent protein calculated by Marques et al. (64) compared with the experimental measurements. The dashed line corresponds to the neutral chromphore, the dotted line to the anionic, whereas the crosses and solid curves are the experimental results of Nielsen et al. (86) and Creemers et al. (87), respectively.

### and more





Figure 3 Optical absorption spectrum of silicon. In the figure are represented the following spectra: experiment (93) (*thick dots*), RPA (*dotted curve*), TDDFT using the ALDA (*dot-dashed curve*), TDDFT using the RORO kernel (72) (*solid curve*), and the results obtained from the solution of Bethe-Saltpeter equation (*dashed curve*). Figure reproduced from Onida et al. (18).

### for nuclei

• <sup>197</sup>Au nucleus



Figure 6-18 Total photoabsorption cross section for <sup>197</sup>Au. The experimental data are from S. C. Fultz, R. L. Bramblett, J. T. Caldwell, and N. A. Kerr, *Phys. Rev.* 127, 1273 (1962). The solid curve is of Breit-Wigner shape with the indicated parameters.

## and finally

Proton



Figure 3 The total absorption cross section  $\sigma_T$  for the proton. The various lines represent the MAID results (34) for the total cross section (*solid line*), one-pion channels (*dashed line*), more-pion channels (*dash-dotted line*), and  $\eta$  channel (*dotted line*). The data for the total cross section are from MAMI (35) (*filled circles*) and Daresbury (36) (*open circles*). The triangles represent the data for the  $2\pi$  channels (37).

### Photoelectric effect (--> beginning 1905)

- Absorb high-energy photon (energy still much less than electron rest mass)
- Must overcome binding of electron
- Close to threshold Coulomb cannot be neglected for outgoing electron
- At higher energy approximate final electron by plane wave
- Use absorption cross section but replace delta function by appropriate density of final states
- But don't make dipole approximation!
- Initial state  $|A
  angle = |\Phi_0
  angle$
- Final state  $|B
  angle = a^{\dagger}_{{m k}_f m_s} a_{n_< \ell m_\ell m_s} |\Phi_0
  angle$
- Evaluate density of states for plane wave

### Density of states

- Wave function  $\langle \boldsymbol{x} | \boldsymbol{k}_f \rangle = \frac{1}{\sqrt{V}} e^{i \boldsymbol{k}_f \cdot \boldsymbol{x}}$  As usual  $k_{x_f} = \frac{2\pi}{L} n_x$  etc.
- **Energy**  $E_f = \frac{\hbar^2 k_f^2}{2m}$
- **So** (# of states  $\leq E_f + dE_f$ ) (# of states  $\leq E_f$ )  $= \rho_{d\Omega} dE_f$  $= \frac{V}{(2\pi)^3} \int_0^{k_f + ak_f} dk \ k^2 \ d\Omega - \frac{V}{(2\pi)^3} \int_0^{k_f} dk \ k^2 \ d\Omega$  $= \frac{V}{(2\pi)^3} d\Omega \int_{\Sigma}^{E_f + dE_f} dE \frac{mk_f}{\hbar^2} = \frac{V}{(2\pi)^3} \frac{mk_f}{\hbar^2} d\Omega dE_f$
- **Cross section**

$$\frac{d\sigma_{abs}(\omega)}{d\Omega} = \frac{4\pi^2 e^2}{m^2 \omega c} \left| \sum_{\beta\gamma} \boldsymbol{e}_{\boldsymbol{k}\alpha} \cdot \langle \beta | e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \boldsymbol{p} | \gamma \rangle \left| \langle B | \boldsymbol{a}_{\beta}^{\dagger} \boldsymbol{a}_{\gamma} | A \rangle \right|^2 \frac{V}{(2\pi)^3} \frac{mk_f}{\hbar^2}$$

## Explicit example

K-shell knockout  $a_{n<} = a_{1s}$  $\langle B | a_{\beta}^{\dagger} a_{\gamma} | A \rangle = \langle \Phi_0 | a_{1s}^{\dagger} a_{k_f m_s} a_{\beta}^{\dagger} a_{\gamma} | \Phi_0 \rangle \simeq \delta_{k_f m_s \beta} \delta_{1s\gamma}$ Then  $\frac{d\sigma}{d\Omega} = \frac{4\pi^2 e^2}{m^2 \omega c} \left| \boldsymbol{e}_{\boldsymbol{k}\alpha} \cdot \langle \boldsymbol{k}_f | e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \boldsymbol{p} | 1s \rangle \right|^2 \frac{V}{(2\pi)^3} \frac{mk_f}{\hbar^2}$ **Consider**  $\langle \mathbf{k}_f | e^{i\mathbf{k}\cdot\mathbf{x}}\mathbf{p} | 1s \rangle = \int d^3x' \langle \mathbf{k}_f | e^{i\mathbf{k}\cdot\mathbf{x}} | \mathbf{x}' \rangle \langle \mathbf{x}' | \mathbf{p} | 1s \rangle$  $= \int d^3x' \langle \boldsymbol{k}_f | e^{i\boldsymbol{k}\cdot\boldsymbol{x}'} | \boldsymbol{x}' \rangle (-i\hbar) \boldsymbol{\nabla}' \left| e^{-Zr'/a_0} \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \right|$  $= \frac{1}{\sqrt{W}} \int d^3x' \ e^{i(\boldsymbol{k}-\boldsymbol{k}_f)\cdot\boldsymbol{x}'} (-i\hbar) \boldsymbol{\nabla}' \left[ e^{-Zr'/a_0} \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \right]$  $= \hbar \boldsymbol{k}_f \frac{1}{\sqrt{V}} \int d^3 x' \ e^{i \boldsymbol{q} \cdot \boldsymbol{x}'} \left[ e^{-Zr'/a_0} \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \right]$  $= \hbar k_f \frac{1}{\sqrt{V}} 8\pi \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} \frac{Z/a_0}{[(Z/a_0)^2 + a^2]^2}$  $\frac{d\sigma}{d\Omega} = \frac{32e^2k_f}{m\omega c} \left( \boldsymbol{e}_{\boldsymbol{k}\alpha} \cdot \boldsymbol{k}_f \right)^2 \frac{Z^5}{a_0^5} \frac{1}{\left[ (Z/a_0)^2 + q^2 \right]^4}$ Finally

E&M

### General issues related to emission

- Emission
  - Initial state: assume only one type of photons  $~~m klpha \Rightarrow n_{m klpha}$
  - Atom emits 1 photon
    - initial state  $\left| n_{m{k}lpha} 
      ight
      angle \left| A 
      ight
      angle$
    - $\cdot$  final state  $\ket{n_{m klpha}+1}\ket{B}$
  - $\hat{H}_{int}$  contribution with  $a^{\dagger}_{k\alpha}$  so  $a^{\dagger}_{k\alpha} |n_{k\alpha}\rangle = \sqrt{n_{k\alpha} + 1} |n_{k\alpha} + 1\rangle$
  - Induced emission

$$\langle B | \hat{H}_{int}' | A \rangle = \frac{e}{m} \left( \frac{2\pi\hbar(n_{\boldsymbol{k}\alpha}+1)}{\omega_{\boldsymbol{k}}V} \right)^{1/2} \sum_{\beta\gamma} \boldsymbol{e}_{\boldsymbol{k}\alpha} \cdot \langle \beta | e^{-i\boldsymbol{k}\cdot\boldsymbol{x}} \boldsymbol{p} | \gamma \rangle \ \langle B | \boldsymbol{a}_{\beta}^{\dagger}\boldsymbol{a}_{\gamma} | A \rangle$$

- Can obtain equivalent classical result by taking classical vector potential

$$\boldsymbol{A}_{0}^{emis} = c \left(\frac{2\pi\hbar(n_{\boldsymbol{k}\alpha}+1)}{\omega_{k}V}\right)^{1/2} \boldsymbol{e}_{\boldsymbol{k}\alpha}$$

- for  $n_{{\bm k}\alpha}$  large; then do minimal substitution
- QM: induced and spontaneous emission on the same footing

### Other applications

- Remember  $H_{int} = \sum_{i}^{Z} \left[ \frac{e}{2mc} \left( \boldsymbol{p}_i \cdot \boldsymbol{A}(\boldsymbol{x}_i, t) + \boldsymbol{A}(\boldsymbol{x}_i, t) \cdot \boldsymbol{p}_i \right) + \frac{e^2}{2mc^2} \boldsymbol{A}(\boldsymbol{x}_i, t) \cdot \boldsymbol{A}(\boldsymbol{x}_i, t) \right]$
- Photon scattering can also be handled with this Hamiltonian

$$\langle B; n_{\mathbf{k}'\alpha'} = 1 | H'_{int} | A; n_{\mathbf{k}\alpha} = 1 \rangle$$

- Squared vector potential term contributes directly
- Linear terms in vector potential should be considered simultaneously in second order



### Towards Planck's radiation law --> 1900

- Consider atoms and radiation field that exchange energy by a reversible process  $A \Leftrightarrow \gamma + B$  such that thermal equilibrium is established
- N(A) population of higher level
- N(B) population of lower level
- Equilibrium  $N(B) w_{abs}^{B \to A} = N(A) w_{emis}^{A \to B}$
- and also  $\frac{N(A)}{N(B)} = \frac{e^{-E_A/k_BT}}{e^{-E_B/k_BT}} = e^{-\hbar\omega_k/k_BT} \qquad \hbar\omega_k = E_A E_B$
- emission  $\langle B | \hat{H}'_{int} | A \rangle = \frac{e}{m} \left( \frac{2\pi\hbar(n_{\boldsymbol{k}\alpha} + 1)}{\omega_{\boldsymbol{k}}V} \right)^{1/2} \sum_{\beta\gamma} \boldsymbol{e}_{\boldsymbol{k}\alpha} \cdot \langle \beta | e^{-i\boldsymbol{k}\cdot\boldsymbol{x}} \boldsymbol{p} | \gamma \rangle \ \langle B | \boldsymbol{a}^{\dagger}_{\beta} \boldsymbol{a}_{\gamma} | A \rangle$
- $\begin{array}{l} \mathbf{A} \mid \hat{H}_{int}' \mid B \rangle = \frac{e}{m} \left( \frac{2\pi\hbar n_{\boldsymbol{k}\alpha}}{\omega_{\boldsymbol{k}}V} \right)^{1/2} \sum_{\beta'\gamma'} \boldsymbol{e}_{\boldsymbol{k}\alpha} \cdot \langle \beta' \mid e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \mid \boldsymbol{p} \mid \gamma' \rangle \quad \langle A \mid \boldsymbol{a}_{\beta'}^{\dagger} \boldsymbol{a}_{\gamma'} \mid B \rangle \end{array}$

## Thermal occupation of modes

### • Ratio of rates

$$\frac{w_{emis}^{A \to B}}{w_{abs}^{B \to A}} = \frac{\left(n_{\boldsymbol{k}\alpha} + 1\right) \left|\sum_{\beta\gamma} \boldsymbol{e}_{\boldsymbol{k}\alpha} \cdot \langle\beta| \, e^{-i\boldsymbol{k}\cdot\boldsymbol{x}} \, \boldsymbol{p} \,|\gamma\rangle \, \left\langle B| \, \boldsymbol{a}_{\beta}^{\dagger}\boldsymbol{a}_{\gamma} \,|A\rangle\right|^{2}}{n_{\boldsymbol{k}\alpha} \, \left|\sum_{\beta'\gamma'} \boldsymbol{e}_{\boldsymbol{k}\alpha} \cdot \langle\beta'| \, e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \, \boldsymbol{p} \,|\gamma'\rangle \, \left\langle B| \, \boldsymbol{a}_{\beta'}^{\dagger}\boldsymbol{a}_{\gamma'} \,|A\rangle\right|^{2}} = \frac{n_{\boldsymbol{k}\alpha} + 1}{n_{\boldsymbol{k}\alpha}}$$

- and therefore  $\frac{N(B)}{N(A)} = \frac{w_{emis}^{A \to B}}{w_{abs}^{B \to A}} = e^{\hbar \omega_k / k_B T} = \frac{n_{k\alpha} + 1}{n_{k\alpha}}$
- So thermal occupation

$$n_{\mathbf{k}\alpha}(T) = \frac{1}{e^{\hbar\omega_k/k_B T} - 1}$$

- Familiar?
- Onward to Planck!
## **Derivation of Planck**

- Consider radiation in a black box / cavity
- Made of atoms that emit and absorb all types of radiation
- Use previous results to determine energy density of radiation field in angular frequency interval  $\omega + d\omega, \omega$
- Familiar calculation: count contribution of all states in interval
- **Before**  $(\# \text{ of states} \le (\omega + d\omega)) (\# \text{ of states} \le \omega) = \rho_{\omega} d\omega$  $\Rightarrow \frac{V}{(2\pi)^3} \frac{\omega^2}{c^3} d\omega d\Omega$
- Now all angles  $d\Omega \Rightarrow 4\pi$  and polarizations --> 2
- Multiply with energy X population per volume

$$U(\omega) = \frac{1}{e^{\hbar\omega/k_B T} - 1} \frac{\hbar\omega}{V} 4\pi \ 2\frac{V}{(2\pi)^3} \frac{\omega^2}{c^3} = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

## Planck --> 1900 where it all began

• Switch to frequency distribution

$$U(\nu) = U(\omega)\frac{d\omega}{d\nu} = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/k_B T} - 1} 2\pi$$
$$= \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\hbar\nu/k_B T} - 1}$$

Planck's famous radiation law!