

# Rate

- Therefore  $w = \frac{4e^2\omega_k^3}{3\hbar c^3} |\langle n'\ell'm_{\ell'} | \mathbf{x} | n\ell m_{\ell} \rangle|^2$

- Note  $|\langle f | \mathbf{x} | i \rangle|^2 = |\langle f | x | i \rangle|^2 + |\langle f | y | i \rangle|^2 + |\langle f | z | i \rangle|^2$ 

$$= \left| \langle f | -\frac{1}{\sqrt{2}}(x + iy) | i \rangle \right|^2 + \left| \langle f | \frac{1}{\sqrt{2}}(x - iy) | i \rangle \right|^2 + |\langle f | z | i \rangle|^2$$

$$= \frac{4\pi}{3} \left\{ |\langle f | rY_{11} | i \rangle|^2 + |\langle f | rY_{1-1} | i \rangle|^2 + |\langle f | rY_{10} | i \rangle|^2 \right\}$$

$$\Rightarrow \frac{4\pi}{3} \sum_{\mu} |\langle n'\ell'm'_{\ell'} | rY_{1\mu} | n\ell m_{\ell} \rangle|^2$$

- Need

$$\begin{aligned} \langle n'\ell'm'_{\ell'} | rY_{1\mu} | n\ell m_{\ell} \rangle &= \frac{(\ell m_{\ell} 1 \mu | \ell' m'_{\ell'})}{\sqrt{2\ell+1}} \langle n'\ell' || rY_1 || n\ell \rangle \\ &= \int dr r^2 \left\{ \int d\Omega Y_{\ell'm'_{\ell'}}^*(\Omega) Y_{1\mu}(\Omega) Y_{\ell m_{\ell}}(\Omega) \right\} R_{n'\ell'}(r) r R_{n\ell}(r) \\ &= \int dr r^3 R_{n'\ell'}(r) R_{n\ell}(r) \times \sqrt{\frac{3}{4\pi}} \sqrt{\frac{2\ell+1}{2\ell'+1}} (\ell 0 1 0 | \ell' 0) (\ell m_{\ell} 1 \mu | \ell' m'_{\ell'}) \end{aligned}$$

- So that

$$\begin{aligned} \langle n'\ell' || rY_1 || n\ell \rangle &= \int dr r^3 R_{n'\ell'}(r) R_{n\ell}(r) \times \sqrt{\frac{3}{4\pi}} \frac{2\ell+1}{\sqrt{2\ell'+1}} (\ell 0 1 0 | \ell' 0) \\ &\equiv I_{n'\ell'n\ell} \sqrt{\frac{3}{4\pi}} \frac{2\ell+1}{\sqrt{2\ell'+1}} (\ell 0 1 0 | \ell' 0) \end{aligned}$$

## Experimental conditions

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

$$\begin{aligned}
 \sum_{m'_\ell} |\langle \dots | \mathbf{x} | \dots \rangle|^2 &= \sum_{m'_\ell} \frac{4\pi}{3} \sum_{\mu} |\langle n' \ell' m'_\ell | r Y_{1\mu} | n \ell m_\ell \rangle|^2 \\
 &= \frac{4\pi}{3} \sum_{m'_\ell \mu} \frac{(\ell m_\ell 1 \mu | \ell' m'_\ell)^2}{2\ell + 1} I_{n' \ell' n \ell}^2 \frac{3}{4\pi} \frac{(2\ell + 1)^2}{2\ell' + 1} (\ell 0 1 0 | \ell' 0)^2 \\
 &= \sum_{m'_\ell \mu} \frac{2\ell' + 1}{2\ell + 1} \frac{(\ell' - m'_\ell 1 \mu | \ell - m_\ell)^2}{2\ell + 1} I_{n' \ell' n \ell}^2 \frac{(2\ell + 1)^2}{2\ell' + 1} (\ell 0 1 0 | \ell' 0)^2 \\
 &= I_{n' \ell' n \ell}^2 (\ell 0 1 0 | \ell' 0)^2
 \end{aligned}$$

- So 
$$\sum_{m'_\ell} w_{n\ell \rightarrow n'\ell'} = \frac{e^2}{\hbar c} \frac{4\omega_k^3}{3c^2} I_{n' \ell' n \ell}^2 (\ell 0 1 0 | \ell' 0)^2$$

$$\begin{aligned}
 (\ell 0 1 0 | \ell' 0)^2 &\Rightarrow \frac{\ell + 1}{2\ell + 1} && \text{for } \ell' = \ell + 1 \\
 &\Rightarrow \frac{\ell}{2\ell + 1} && \text{for } \ell' = \ell - 1
 \end{aligned}$$

- 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  $2p \Rightarrow \frac{1}{\sqrt{24a_0^3}} \frac{r}{a_0} e^{-r/2a_0}$

$$1s \Rightarrow \frac{2}{a_0^3} e^{-r/a_0}$$

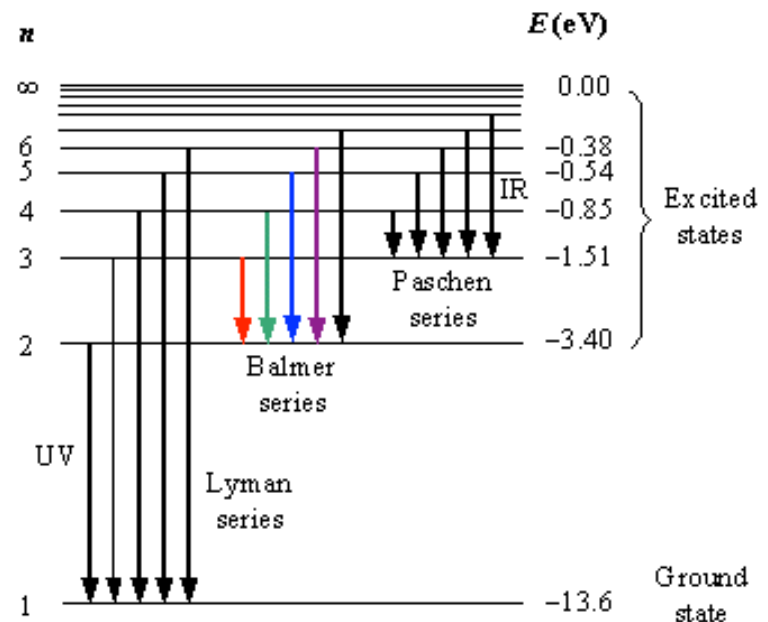
- Lifetime

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

- 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  $\mathbf{k}\alpha \Rightarrow n_{\mathbf{k}\alpha}$

- Atom absorbs 1 photon

- initial state  $|n_{\mathbf{k}\alpha}\rangle |A\rangle$

- final state  $|n_{\mathbf{k}\alpha} - 1\rangle |B\rangle$

- $\hat{H}_{int}$  contribution with  $a_{\mathbf{k}\alpha}$  so  $a_{\mathbf{k}\alpha} |n_{\mathbf{k}\alpha}\rangle = \sqrt{n_{\mathbf{k}\alpha}} |n_{\mathbf{k}\alpha} - 1\rangle$

- "Before" TDPT -->

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

- Can obtain equivalent classical result by taking classical vector potential

$$\mathbf{A}^{abs}(\mathbf{x}, t) = \mathbf{A}_0^{abs} e^{i(\mathbf{k}\cdot\mathbf{x} - \omega_k t)}$$

$$\mathbf{A}_0^{abs} = c \left( \frac{2\pi\hbar n_{\mathbf{k}\alpha}}{\omega_k V} \right)^{1/2} \mathbf{e}_{\mathbf{k}\alpha}$$

- for  $n_{\mathbf{k}\alpha}$  large; then do minimal substitution

# Absorption rate in dipole approximation

- TDPT

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

## Absorption cross section

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

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

# 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  $|A\rangle = |\Phi_0\rangle$

- Final state: excited state  $|B\rangle = a_{n>\ell'm'_\ell m'_s}^\dagger a_{n<\ell m_\ell m_s} |\Phi_0\rangle$

- 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

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

- **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

$$\begin{aligned} \sigma_{abs}(\omega) &= \frac{4\pi^2 e^2}{\hbar c} (\varepsilon_{n>\ell'} - \varepsilon_{n<\ell}) |\langle n>\ell'm'_\ell m'_s | x | n<\ell m_\ell m_s \rangle|^2 \delta(\varepsilon_{n>\ell'} - \varepsilon_{n<\ell} - \hbar\omega) \delta_{m'_s m_s} \\ &= 4\pi^2 \alpha \omega_{n>n<} |\langle n>\ell'm'_\ell m'_s | x | n<\ell m_\ell m_s \rangle|^2 \delta(\omega_{n>n<} - \omega) \delta_{m'_s m_s} \end{aligned}$$

# Thomas-Reiche-Kuhn sum rule

- Simple model of absorption cross section: delta spike at every allowed combination of  $n_{>\ell'} \rightarrow n_{<\ell}$

- Dipole matrix element: see before

- Consider integral over all possible absorption contributions

$$\int d\omega \sigma_{abs}(\omega) = 4\pi^2\alpha \sum_{n_{>n_{<}}} \omega_{n_{>n_{<}}} |\langle n_{>\ell'} m'_{\ell'} m'_s | x | n_{<\ell} m_{\ell} m_s \rangle|^2$$

- More general expression

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

## Evaluate double commutator

- Only kinetic contribution of Hamiltonian survives

$$\begin{aligned} [X_Z, [H, X_Z]] &= \frac{1}{2m} \left[ \sum_i x_i, \left[ \sum_j p_{x_j}^2, \sum_k x_k \right] \right] \\ &= \frac{1}{2m} \sum_{ijk} [x_i, [p_{x_j}^2, x_k]] \\ &= \frac{1}{2m} \sum_{ijk} [x_i, (-2i\hbar)p_{x_j} \delta_{jk}] \\ &= -\frac{i\hbar}{m} \sum_{ij} [x_i, p_{x_j}] = -\frac{i\hbar}{m} \sum_{ij} i\hbar \delta_{ij} \\ &= \frac{Z\hbar^2}{m} \end{aligned}$$

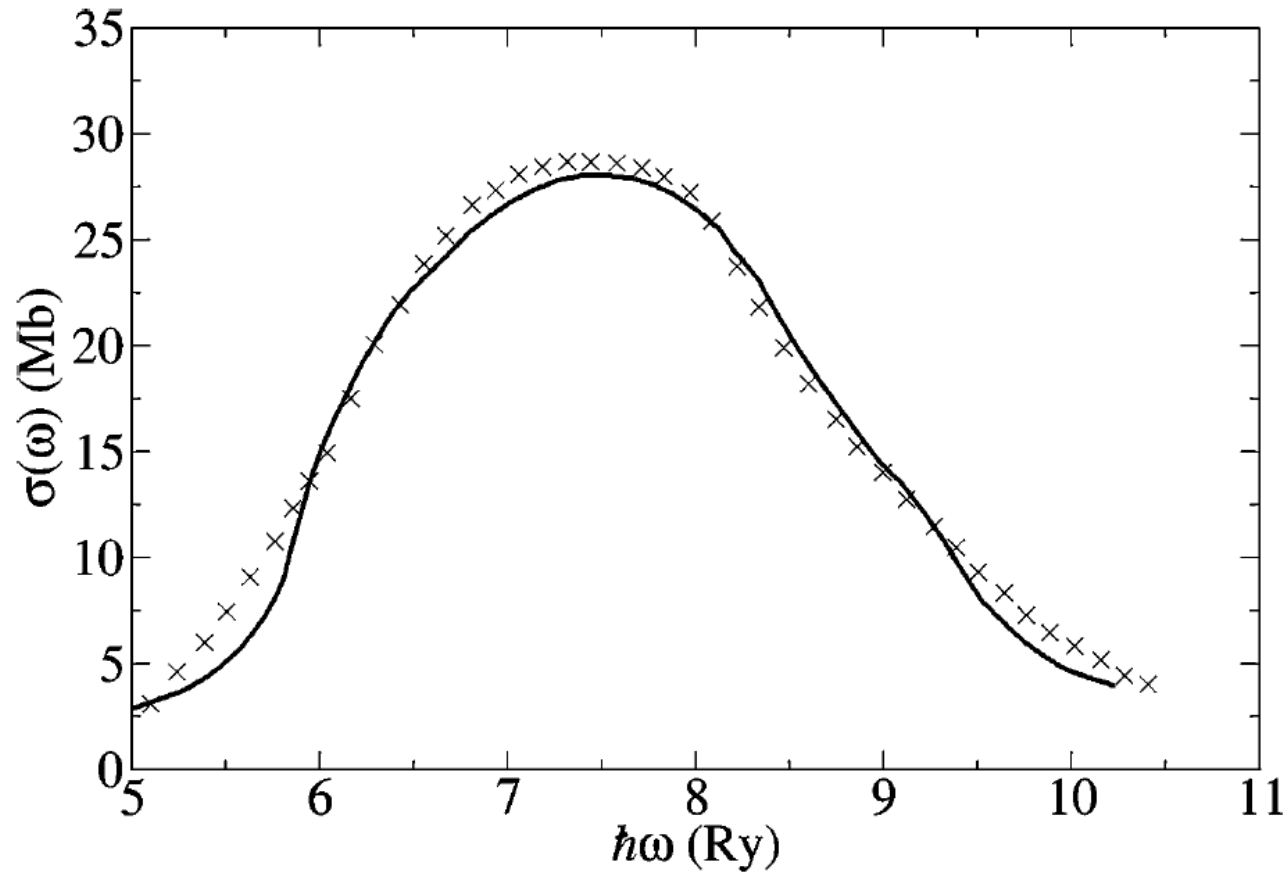
- and therefore 
$$\begin{aligned} \int d\omega \sigma_{abs}(\omega) &= \frac{4\pi^2 \alpha}{\hbar} \langle A | \frac{1}{2} [X_Z, [H, X_Z]] | A \rangle \\ &= \frac{4\pi^2 e^2}{\hbar c \hbar} \frac{Z\hbar^2}{2m} = Z 2\pi^2 c \left( \frac{e^2}{mc^2} \right) \end{aligned}$$

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



# Absorption cross sections in nature

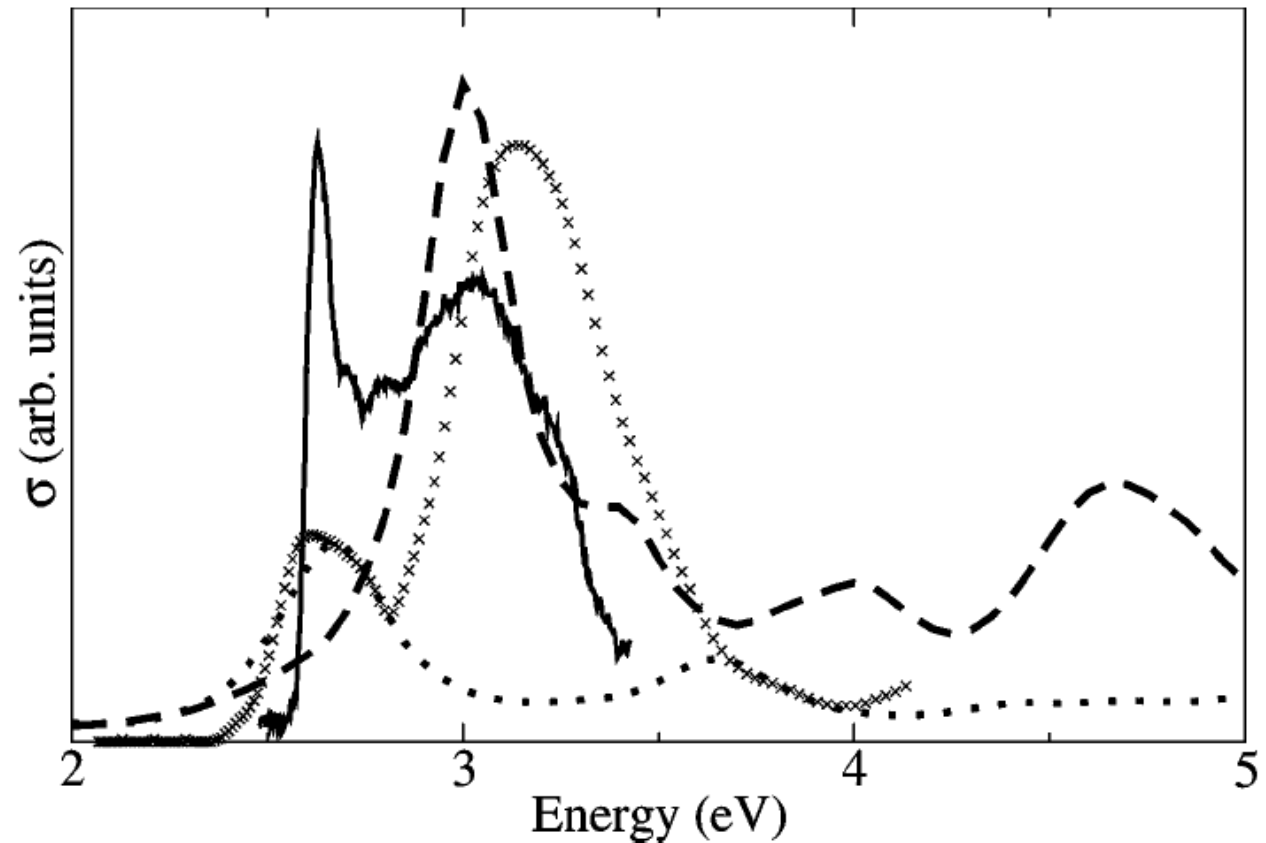
- Atoms



**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

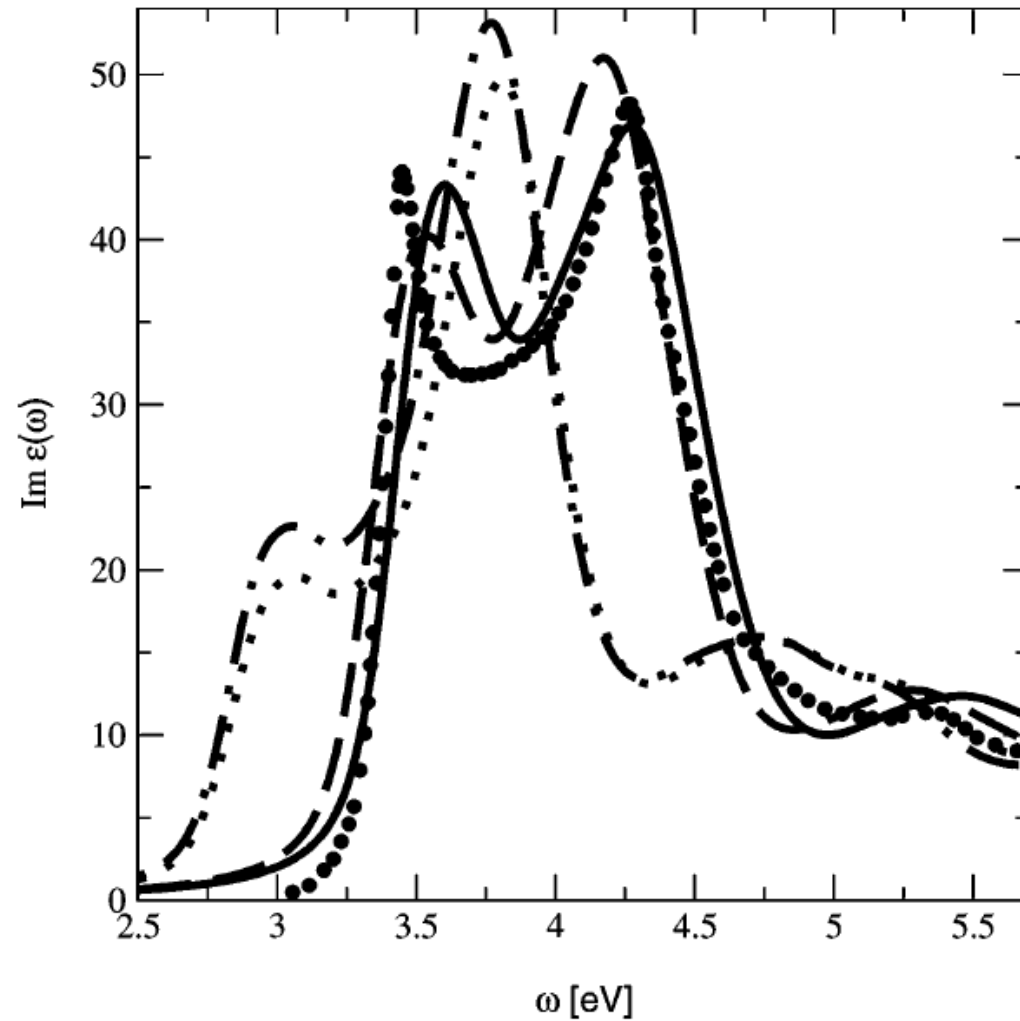
- Big molecules



**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 chromophore, 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

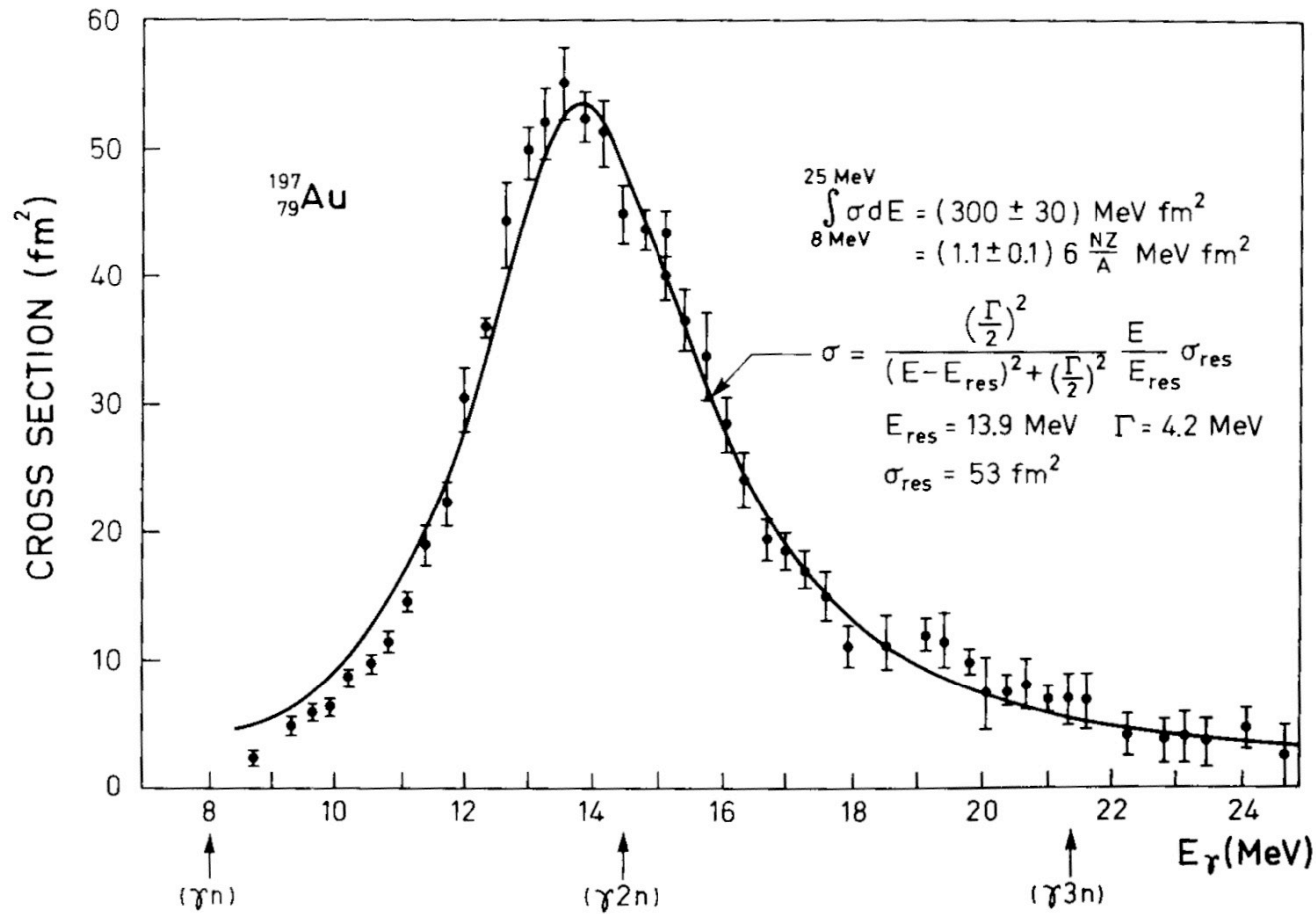
- Silicon



**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-Salpeter equation (*dashed curve*). Figure reproduced from Onida et al. (18).

# for nuclei

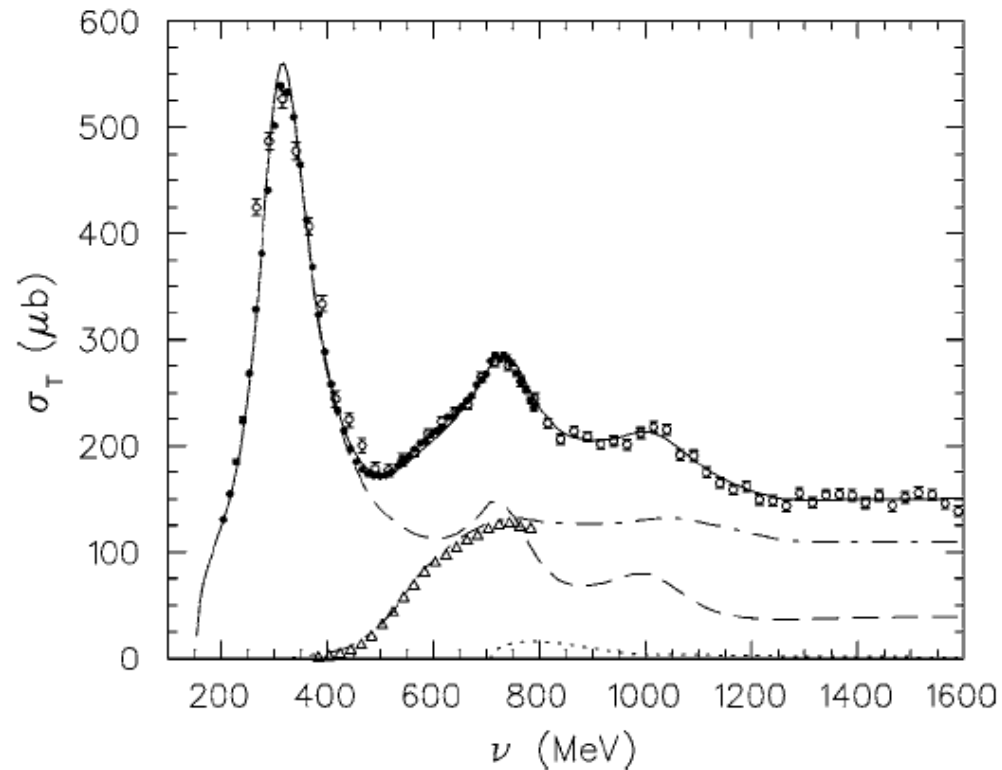
- $^{197}\text{Au}$  nucleus



**Figure 6-18** Total photoabsorption cross section for  $^{197}\text{Au}$ . 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  $|A\rangle = |\Phi_0\rangle$
- Final state  $|B\rangle = a_{\mathbf{k}_f m_s}^\dagger a_{n < \ell m_\ell m_s} |\Phi_0\rangle$
- Evaluate density of states for plane wave

# Density of states

- Wave function  $\langle \mathbf{x} | \mathbf{k}_f \rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_f \cdot \mathbf{x}}$

- As usual  $k_{x_f} = \frac{2\pi}{L} n_x$  etc.

- Energy  $E_f = \frac{\hbar^2 k_f^2}{2m}$

- So  $(\# \text{ of states } \leq E_f + dE_f) - (\# \text{ of states } \leq E_f) = \rho_{d\Omega} dE_f$ 

$$= \frac{V}{(2\pi)^3} \int_0^{k_f + dk_f} dk k^2 d\Omega - \frac{V}{(2\pi)^3} \int_0^{k_f} dk k^2 d\Omega$$

$$= \frac{V}{(2\pi)^3} d\Omega \int_{E_f}^{E_f + dE_f} dE \frac{mk_f}{\hbar^2} = \frac{V}{(2\pi)^3} \frac{mk_f}{\hbar^2} d\Omega dE_f$$

- Cross section

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

## Explicit example

- K-shell knockout  $a_{n<} = a_{1s}$

$$\langle B | a_{\beta}^{\dagger} a_{\gamma} | A \rangle = \langle \Phi_0 | a_{1s}^{\dagger} a_{\mathbf{k}_f m_s} a_{\beta}^{\dagger} a_{\gamma} | \Phi_0 \rangle \simeq \delta_{\mathbf{k}_f m_s \beta} \delta_{1s \gamma}$$

- Then

$$\frac{d\sigma}{d\Omega} = \frac{4\pi^2 e^2}{m^2 \omega c} \left| \mathbf{e}_{\mathbf{k}\alpha} \cdot \langle \mathbf{k}_f | e^{i\mathbf{k} \cdot \mathbf{x}} \mathbf{p} | 1s \rangle \right|^2 \frac{V}{(2\pi)^3} \frac{m k_f}{\hbar^2}$$

- Consider

$$\begin{aligned} \langle \mathbf{k}_f | e^{i\mathbf{k} \cdot \mathbf{x}} \mathbf{p} | 1s \rangle &= \int d^3 x' \langle \mathbf{k}_f | e^{i\mathbf{k} \cdot \mathbf{x}} | \mathbf{x}' \rangle \langle \mathbf{x}' | \mathbf{p} | 1s \rangle \\ &= \int d^3 x' \langle \mathbf{k}_f | e^{i\mathbf{k} \cdot \mathbf{x}'} | \mathbf{x}' \rangle (-i\hbar) \nabla' \left[ e^{-Zr'/a_0} \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \right] \\ &= \frac{1}{\sqrt{V}} \int d^3 x' e^{i(\mathbf{k}-\mathbf{k}_f) \cdot \mathbf{x}'} (-i\hbar) \nabla' \left[ e^{-Zr'/a_0} \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \right] \\ &= \hbar \mathbf{k}_f \frac{1}{\sqrt{V}} \int d^3 x' e^{i\mathbf{q} \cdot \mathbf{x}'} \left[ e^{-Zr'/a_0} \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \right] \\ &= \hbar \mathbf{k}_f \frac{1}{\sqrt{V}} 8\pi \left( \frac{Z^3}{\pi a_0^3} \right)^{1/2} \frac{Z/a_0}{[(Z/a_0)^2 + q^2]^2} \end{aligned}$$

- Finally

$$\frac{d\sigma}{d\Omega} = \frac{32e^2 k_f}{m\omega c} (\mathbf{e}_{\mathbf{k}\alpha} \cdot \mathbf{k}_f)^2 \frac{Z^5}{a_0^5} \frac{1}{[(Z/a_0)^2 + q^2]^4}$$



# General issues related to emission

- Emission

- Initial state: assume only one type of photons  $\mathbf{k}\alpha \Rightarrow n_{\mathbf{k}\alpha}$

- Atom emits 1 photon

- initial state  $|n_{\mathbf{k}\alpha}\rangle |A\rangle$

- final state  $|n_{\mathbf{k}\alpha} + 1\rangle |B\rangle$

- $\hat{H}_{int}$  contribution with  $a_{\mathbf{k}\alpha}^\dagger$  so  $a_{\mathbf{k}\alpha}^\dagger |n_{\mathbf{k}\alpha}\rangle = \sqrt{n_{\mathbf{k}\alpha} + 1} |n_{\mathbf{k}\alpha} + 1\rangle$

- Induced emission

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

- Can obtain equivalent classical result by taking classical vector potential

$$\mathbf{A}_0^{emis} = c \left( \frac{2\pi\hbar(n_{\mathbf{k}\alpha} + 1)}{\omega_k V} \right)^{1/2} \mathbf{e}_{\mathbf{k}\alpha}$$

- for  $n_{\mathbf{k}\alpha}$  large; then do minimal substitution

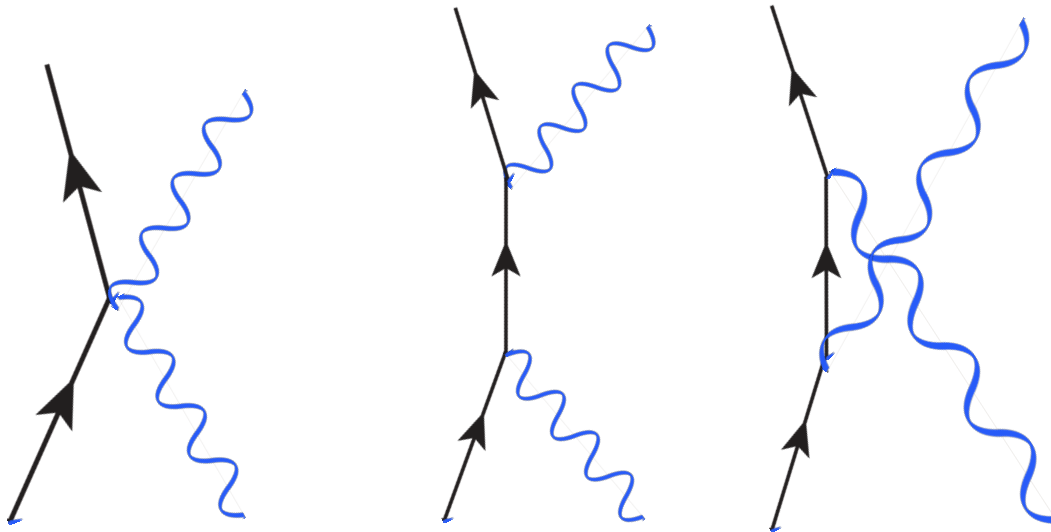
- QM: induced and spontaneous emission on the same footing

## Other applications

- Remember  $H_{int} = \sum_i^Z \left[ \frac{e}{2mc} (\mathbf{p}_i \cdot \mathbf{A}(\mathbf{x}_i, t) + \mathbf{A}(\mathbf{x}_i, t) \cdot \mathbf{p}_i) + \frac{e^2}{2mc^2} \mathbf{A}(\mathbf{x}_i, t) \cdot \mathbf{A}(\mathbf{x}_i, t) \right]$
- 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  $N(B) w_{abs}^{B \rightarrow A} = N(A) w_{emis}^{A \rightarrow B}$

- and also 
$$\frac{N(A)}{N(B)} = \frac{e^{-E_A/k_B T}}{e^{-E_B/k_B T}} = e^{-\hbar\omega_k/k_B T} \quad \hbar\omega_k = E_A - E_B$$

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

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

# Thermal occupation of modes

- Ratio of rates

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

- and therefore  $\frac{N(B)}{N(A)} = \frac{w_{emis}^{A \rightarrow B}}{w_{abs}^{B \rightarrow A}} = e^{\hbar\omega_{\mathbf{k}}/k_B T} = \frac{n_{\mathbf{k}\alpha} + 1}{n_{\mathbf{k}\alpha}}$

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

- 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  $(\# \text{ of states } \leq (\omega + d\omega) - (\# \text{ of states } \leq \omega) = \rho_\omega d\omega$   
 $\Rightarrow \frac{V}{(2\pi)^3} \frac{\omega^2}{c^3} d\omega d\Omega$
- Now all angles  $d\Omega \Rightarrow 4\pi$  and polarizations  $\rightarrow 2$
- Multiply with energy  $\times$  population per volume

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

## Planck --> 1900 where it all began

- Switch to frequency distribution

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

- Planck's famous radiation law!

The end! Thanks for a great semester!