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

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

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

Electron and interaction Hamiltonian

Electrons

$$H_{electrons} = \sum_{i=1}^{Z} \frac{\boldsymbol{p}_i^2}{2m} - \sum_{i=1}^{Z} \frac{Ze^2}{|\boldsymbol{x}_i|} + \sum_{i<j}^{Z} \frac{e^2}{|\boldsymbol{x}_i - \boldsymbol{x}_j|}$$

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

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

No spin yet. Add by hand $\quad H_{int}^{spin} = \frac{e}{mc} \sum_{i=1}^{Z} \boldsymbol{s}_i \cdot [\boldsymbol{\nabla} \times \boldsymbol{A}(\boldsymbol{x}, t)]_{\boldsymbol{x}=\boldsymbol{x}_i}$

as before from $E = -\boldsymbol{\mu} \cdot \boldsymbol{B}$

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

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

then

$$\hat{H}_{int} = \frac{e}{m} \sum_{\beta\gamma} \sum_{\boldsymbol{k}\alpha} \left(\frac{2\pi\hbar}{\omega_k V} \right)^{1/2} \boldsymbol{e}_{\boldsymbol{k}\alpha} \cdot \left\{ \langle\beta| e^{i(\boldsymbol{k}\cdot\boldsymbol{x} - \omega_k t)} \, \boldsymbol{p} \, |\gamma\rangle \; a^\dagger_\beta a_\gamma a_{\boldsymbol{k}\alpha} \right.$$

$$\left. + \langle\beta| e^{-i(\boldsymbol{k}\cdot\boldsymbol{x} - \omega_k t)} \, \boldsymbol{p} \, |\gamma\rangle \; a^\dagger_\beta a_\gamma a^\dagger_{\boldsymbol{k}\alpha} \right\}$$

and

$$\hat{H}^{spin}_{int} = \frac{e}{m} \sum_{\beta\gamma} \sum_{\boldsymbol{k}\alpha} \left(\frac{2\pi\hbar}{\omega_k V} \right)^{1/2} (i\boldsymbol{k} \times \boldsymbol{e}_{\boldsymbol{k}\alpha})$$

$$\cdot \quad \left\{ \langle\beta| e^{i(\boldsymbol{k}\cdot\boldsymbol{x} - \omega_k t)} \, \boldsymbol{s} \, |\gamma\rangle \; a^\dagger_\beta a_\gamma a_{\boldsymbol{k}\alpha} + \langle\beta| e^{-i(\boldsymbol{k}\cdot\boldsymbol{x} - \omega_k t)} \, \boldsymbol{s} \, |\gamma\rangle \; a^\dagger_\beta a_\gamma a^\dagger_{\boldsymbol{k}\alpha} \right\}$$

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 $|\boldsymbol{k}| \leq k_c$ 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:

$$\begin{aligned} \hbar\omega_0 &\sim \alpha^2 mc^2 \simeq 1\mathrm{H} \\ \hbar\omega_c &\sim \alpha\, mc^2 \\ mc^2 &\sim 0.5\ \mathrm{MeV} \end{aligned}$$

  -

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

E&M

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 $E_f = E_i$ --> $E_f = E_i + \hbar\omega$ 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 (note $dn_x = \frac{L}{2\pi} dk_x$)

$$(\#\text{ of states} \leq \hbar\omega) = \sum_{|\boldsymbol{k}| \leq \omega/c}$$

$$\Rightarrow \int dn_x \int dn_y \int dn_z \qquad \text{with } |\boldsymbol{k}| \leq \omega/c$$

$$= \frac{V}{(2\pi)^3} \int d^3k = \frac{V}{(2\pi)^3} \int dk \; k^2 \; d\Omega$$

Density of states

- Required density of states is then obtained from

$$
\begin{aligned}
(\#\text{ of states} \le \hbar(\omega+d\omega) - (\#\text{ of states} \le \hbar\omega) &= \rho_{\hbar\omega,d\Omega}\, d\hbar\omega \\
&= \frac{V}{(2\pi)^3}\int_0^{(\omega+d\omega)/c} dk\; k^2\; d\Omega - \frac{V}{(2\pi)^3}\int_0^{\omega/c} dk\; k^2\; d\Omega \\
&= \frac{V}{(2\pi)^3} d\Omega \int_\omega^{\omega+d\omega} \frac{d\omega'}{c}\left(\frac{\omega'}{c}\right)^2 = \frac{V}{(2\pi)^3} d\Omega \frac{1}{3}\left(\frac{\omega'}{c}\right)^3\Bigg|_\omega^{\omega+d\omega} \\
\Rightarrow \quad & \frac{V}{(2\pi)^3}\frac{\omega^2}{\hbar c^3} d\hbar\omega\; d\Omega
\end{aligned}
$$

- Therefore $\rho_{\hbar\omega,d\Omega} = \dfrac{V}{(2\pi)^3}\dfrac{\omega^2}{\hbar c^3} d\Omega$
- Initial state $|A\rangle\,|0\rangle = |i\rangle$
- with $\left(\hat{H}_{electrons} + \hat{H}_{em}\right)|i\rangle = E_A\,|i\rangle$
- Final state $|B\rangle\,|1_{\boldsymbol{k}\lambda}\rangle = |f\rangle$
- with $\left(\hat{H}_{electrons} + \hat{H}_{em}\right)|f\rangle = (E_B + \hbar\omega_k)\,|f\rangle$
- such that $E_A = E_B + \hbar\omega_k$

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

$$\hat{H}'_{int} = \frac{e}{m}\sum_{\beta\gamma}\sum_{\boldsymbol{k}'\alpha}\left(\frac{2\pi\hbar}{\omega'_k V}\right)^{1/2} \boldsymbol{e}_{\boldsymbol{k}'\alpha}\cdot\Big\{\langle\beta|\,e^{i\boldsymbol{k}'\cdot\boldsymbol{x}}\;\boldsymbol{p}\,|\gamma\rangle\;\; a^\dagger_\beta a_\gamma a_{\boldsymbol{k}'\alpha}$$

$$+\,\langle\beta|\,e^{-i\boldsymbol{k}'\cdot\boldsymbol{x}}\;\boldsymbol{p}\,|\gamma\rangle\;\; a^\dagger_\beta a_\gamma a^\dagger_{\boldsymbol{k}'\alpha}\Big\}$$

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

Rate continued

- So right now

$$w_{d\Omega} = \frac{2\pi}{\hbar}\frac{V}{(2\pi)^3}\frac{\omega_k^2}{\hbar c^3}\frac{e^2}{m^2}\left(\frac{2\pi\hbar}{V}\right)\left|\sum_{\beta\gamma}\sum_{\boldsymbol{k}'\alpha}\frac{1}{\sqrt{\omega_k'}}\boldsymbol{e}_{\boldsymbol{k}'\alpha}\cdot\left\{\langle\beta|\, e^{-i\boldsymbol{k}'\cdot\boldsymbol{x}}\,\boldsymbol{p}\,|\gamma\rangle\;\langle B1_{\boldsymbol{k}\lambda}|\, a_\beta^\dagger a_\gamma a_{\boldsymbol{k}'\alpha}^\dagger\,|A\rangle\right\}\right|^2$$

- Typical transition: optical ~ eV --> $\hbar\omega_k$ (green --> 2 eV)
- Atomic dimension: ~ 10^{-10} m
- So from $\hbar\omega_k \Rightarrow kr = \dfrac{\hbar\omega_k}{\hbar c}r \simeq \dfrac{\text{eV } 10^{-10}\text{ m}}{1.24\times10^{-6}\text{ eV m}} \sim 10^{-4}$
- therefore $e^{-i\boldsymbol{k}'\cdot\boldsymbol{x}} \Rightarrow 1 - i\boldsymbol{k}'\cdot\boldsymbol{x} \Rightarrow 1$
- Electric dipole (E1) approximation
- Photon matrix element $\langle 1_{\boldsymbol{k}\lambda}|\, a_{\boldsymbol{k}'\alpha}^\dagger\,|0\rangle = \delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\lambda\alpha}$
- 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

$$\begin{aligned}
\langle B| a^\dagger_\beta a_\gamma |A\rangle &= \langle \Phi_0| a_{n'\ell' m'_\ell m'_s} a^\dagger_\beta a_\gamma a^\dagger_{n\ell m_\ell m_s} |\Phi_0\rangle \\
&= \langle \Phi_0| \left(\delta_{n'\beta} - a^\dagger_\beta a_{n'\ell' m'_\ell m'_s}\right)\left(\delta_{n\gamma} - a^\dagger_{n\ell m_\ell m_s} a_\gamma\right) |\Phi_0\rangle \\
&= \delta_{n'\beta}\delta_{n\gamma}
\end{aligned}$$

- not unexpected...
- So we also need $\boldsymbol{e}_{\boldsymbol{k}\lambda} \cdot \langle n'\ell' m'_\ell m'_s| \boldsymbol{p} |n\ell m_\ell m_s\rangle$

Dipole matrix element

- Use central field from

$$\hat{H}_{electrons} = \sum_{n\ell m_\ell m_s} \varepsilon_{n\ell}\, a^\dagger_{n\ell m_\ell m_s} a_{n\ell m_\ell m_s} \Rightarrow \qquad H_0 \left|n\ell m_\ell m_s\right\rangle = \varepsilon_{n\ell} \left|n\ell m_\ell m_s\right\rangle$$

- to evaluate $\boldsymbol{e}_{\boldsymbol{k}\lambda} \cdot \langle n'\ell' m'_\ell m'_s | \, \boldsymbol{p} \, | n\ell m_\ell m_s \rangle$
- First note that $\left[\boldsymbol{p}^2, \boldsymbol{x}\right] = -2i\hbar\boldsymbol{p}$
- So

$$\left[\frac{\boldsymbol{p}^2}{2m}, \boldsymbol{x}\right] = -i\hbar\frac{\boldsymbol{p}}{m}$$

$$\left[\frac{\boldsymbol{p}^2}{2m} + V_{nucleus} + V_{central}, \boldsymbol{x}\right] = -i\hbar\frac{\boldsymbol{p}}{m}$$

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

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

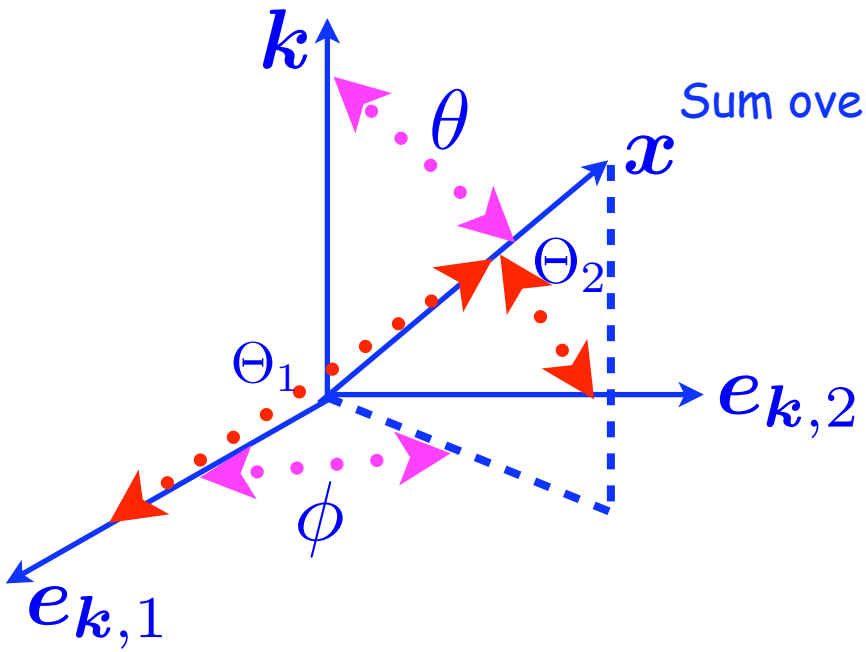
Matrix element

- Then (hence dipole approximation) & note change in parity

$$\begin{aligned}
\boldsymbol{e}_{\boldsymbol{k}\lambda}\cdot\langle n'\ell'm'_\ell m'_s|\,\boldsymbol{p}\,|n\ell m_\ell m_s\rangle &= \boldsymbol{e}_{\boldsymbol{k}\lambda}\cdot\langle n'\ell'm'_\ell m'_s|\,i\frac{m}{\hbar}\,[H_0,\boldsymbol{x}]\,|n\ell m_\ell m_s\rangle \\
&= i\frac{m}{\hbar}\boldsymbol{e}_{\boldsymbol{k}\lambda}\cdot\langle n'\ell'm'_\ell|\,\boldsymbol{x}\,|n\ell m_\ell\rangle\,\delta_{m_s m'_s}\,(\varepsilon_{n'\ell'}-\varepsilon_{n\ell}) \\
&= -im\omega_k\boldsymbol{e}_{\boldsymbol{k}\lambda}\cdot\langle n'\ell'm'_\ell|\,\boldsymbol{x}\,|n\ell m_\ell\rangle\,\delta_{m_s m'_s}
\end{aligned}$$

- Insert all ingredients

$$\begin{aligned}
w_{d\Omega} &= \frac{e^2}{2\pi}\frac{\omega_k^3}{\hbar c^3}d\Omega\,|\boldsymbol{e}_{\boldsymbol{k}\lambda}\cdot\langle n'\ell'm_{\ell'}|\,\boldsymbol{x}\,|n\ell m_\ell\rangle|^2 \\
&= \frac{e^2}{2\pi}\frac{\omega_k^3}{\hbar c^3}d\Omega\,\cos^2\Theta_\lambda\,|\langle n'\ell'm_{\ell'}|\,\boldsymbol{x}\,|n\ell m_\ell\rangle|^2
\end{aligned}$$



Sum over polarization & integrate over all directions

$$\begin{aligned}
\cos\Theta_1 &= \sin\theta\cos\phi \\
\cos\Theta_2 &= \sin\theta\sin\phi
\end{aligned}$$

$$\sum_\lambda \Rightarrow \sin^2\theta$$

$$\int d\Omega\sin^2\theta = 2\pi\int d(\cos\theta)\sin^2\theta = \frac{8\pi}{3}$$

Rate

- Therefore $w = \dfrac{4e^2\omega_k^3}{3\hbar c^3}\left|\langle n'\ell' m_{\ell'}|\,\boldsymbol{x}\,|n\ell m_\ell\rangle\right|^2$
- Note

$$\begin{aligned}
|\langle f|\,\boldsymbol{x}\,|i\rangle|^2 &= |\langle f|\,x\,|i\rangle|^2 + |\langle f|\,y\,|i\rangle|^2 + |\langle f|\,z\,|i\rangle|^2 \\
&= \left|\langle f|-\frac{1}{\sqrt{2}}(x+iy)\,|i\rangle\right|^2 + \left|\langle f|\,\frac{1}{\sqrt{2}}(x-iy)\,|i\rangle\right|^2 + |\langle f|\,z\,|i\rangle|^2 \\
&= \frac{4\pi}{3}\left\{|\langle f|\,rY_{11}\,|i\rangle|^2 + |\langle f|\,rY_{1-1}\,|i\rangle|^2 + |\langle f|\,rY_{10}\,|i\rangle|^2\right\} \\
&\Rightarrow \frac{4\pi}{3}\sum_\mu |\langle n'\ell' m'_\ell|\,rY_{1\mu}\,|n\ell m_\ell\rangle|^2
\end{aligned}$$

- Need

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

- So that

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

Experimental conditions

- Sum also over all projections m'_ℓ of final state

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

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

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

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

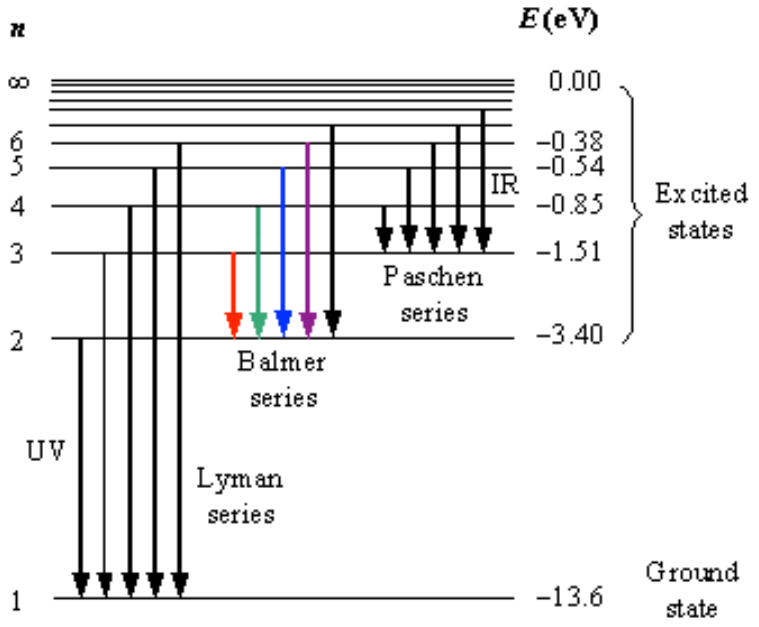
Explicit example

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

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

  $$\tau(2p \to 1s) = 3 \frac{\hbar c}{e^2} \frac{3c^2}{4\omega_k^3} I^{-2} = 1.6 \times 10^{-9} \mathrm{s}$$
- 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 $\boldsymbol{k}\alpha \Rightarrow n_{\boldsymbol{k}\alpha}$
  - Atom absorbs 1 photon
    - initial state $|n_{\boldsymbol{k}\alpha}\rangle\,|A\rangle$
    - final state $|n_{\boldsymbol{k}\alpha}-1\rangle\,|B\rangle$
  - $\hat{H}_{int}$ contribution with $a_{\boldsymbol{k}\alpha}$ so $a_{\boldsymbol{k}\alpha}\,|n_{\boldsymbol{k}\alpha}\rangle = \sqrt{n_{\boldsymbol{k}\alpha}}\,|n_{\boldsymbol{k}\alpha}-1\rangle$
  - "Before" TDPT -->

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

  - Can obtain equivalent classical result by taking classical vector potential

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

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

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

Absorption rate in dipole approximation

- TDPT

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

Absorption cross section

- Defined --> Energy per unit time absorbed by atom A --> B

energy flux of radiation field

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

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 $|B\rangle = a^\dagger_{n_>\ell' m'_\ell m'_s} a_{n_<\ell m_\ell m_s} |\Phi_0\rangle$
- Simple particle-hole state
- Evaluate $\langle B| a^\dagger_\beta a_\gamma |A\rangle = \langle \Phi_0| a^\dagger_{n_<} a_{n_>} a^\dagger_\beta a_\gamma |\Phi_0\rangle = \delta_{n_>\beta}\delta_{n_<\gamma}$
- 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 $\hat{H}_0 |B\rangle = E_B |B\rangle = \hat{H}_0 a^\dagger_{n_>\ell' m'_\ell m'_s} a_{n_<\ell m_\ell m_s} |\Phi_0\rangle = (\varepsilon_{n_>\ell'} - \varepsilon_{n_<\ell} + E_{\Phi_0}) |B\rangle$
- $\hat{H}_0 |A\rangle = E_A |A\rangle = \hat{H}_0 |\Phi_0\rangle = E_{\Phi_0} |A\rangle$ 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 $n_> \ell' \to n_< \ell$
- 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

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

Evaluate double commutator

- Only kinetic contribution of Hamiltonian survives

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

- and therefore

$$
\begin{aligned}
\int d\omega\ \sigma_{abs}(\omega) &= \frac{4\pi^2\alpha}{\hbar}\left\langle A\right|\tfrac{1}{2}\left[X_Z,[H,X_Z]\right]\left|A\right\rangle \\
&= \frac{4\pi^2e^2}{\hbar c\hbar}\frac{Z\hbar^2}{2m} = Z2\pi^2c\left(\frac{e^2}{mc^2}\right)
\end{aligned}
$$

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

Absorption cross sections in nature

- Atoms

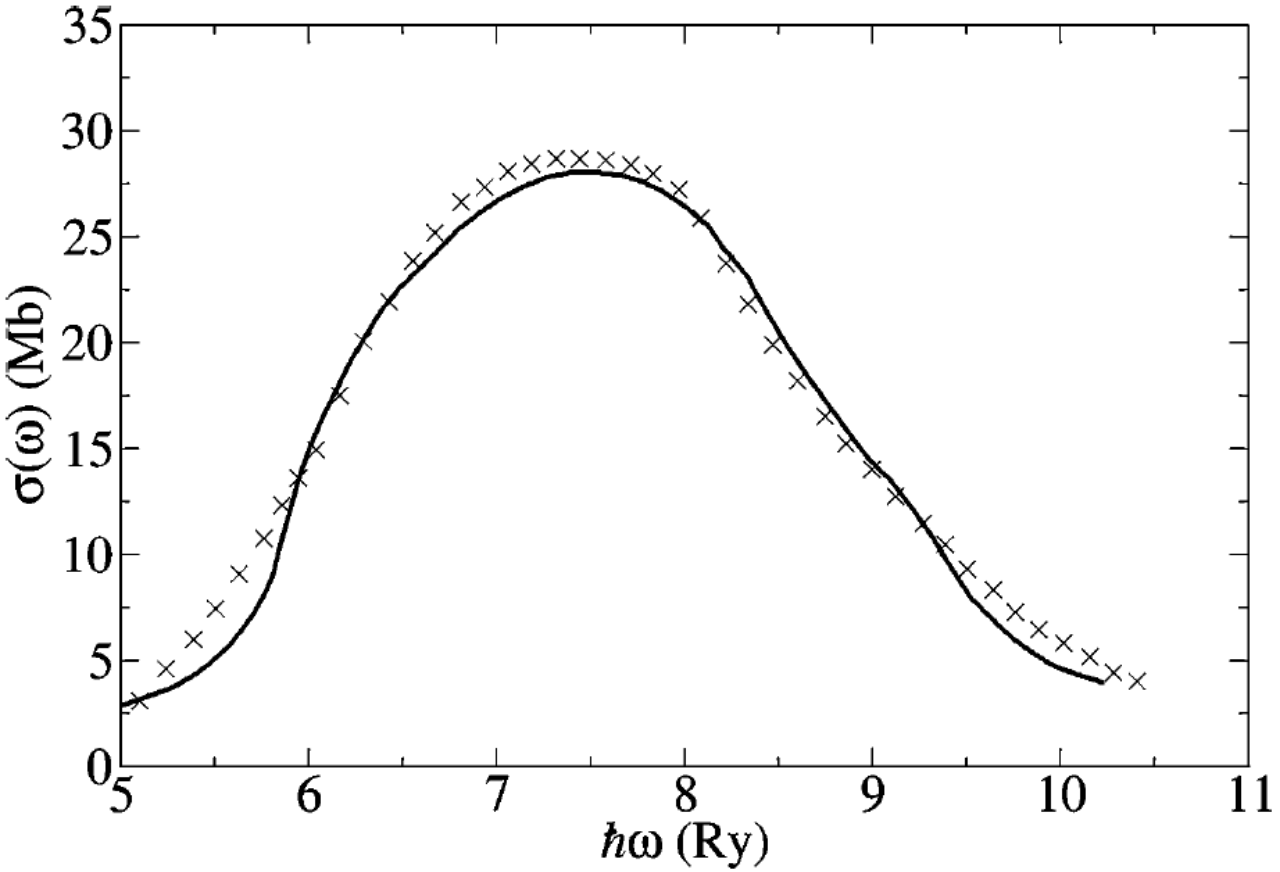


Figure 1 Total photoabsorption cross section of xenon versus photon energy in the vicinity of the 4d threshold. The solid line is the TDDFT calculations of Zangwill & Soven (23) and the crosses are the experimental results of Haensel et al. (80).

More

- Big molecules

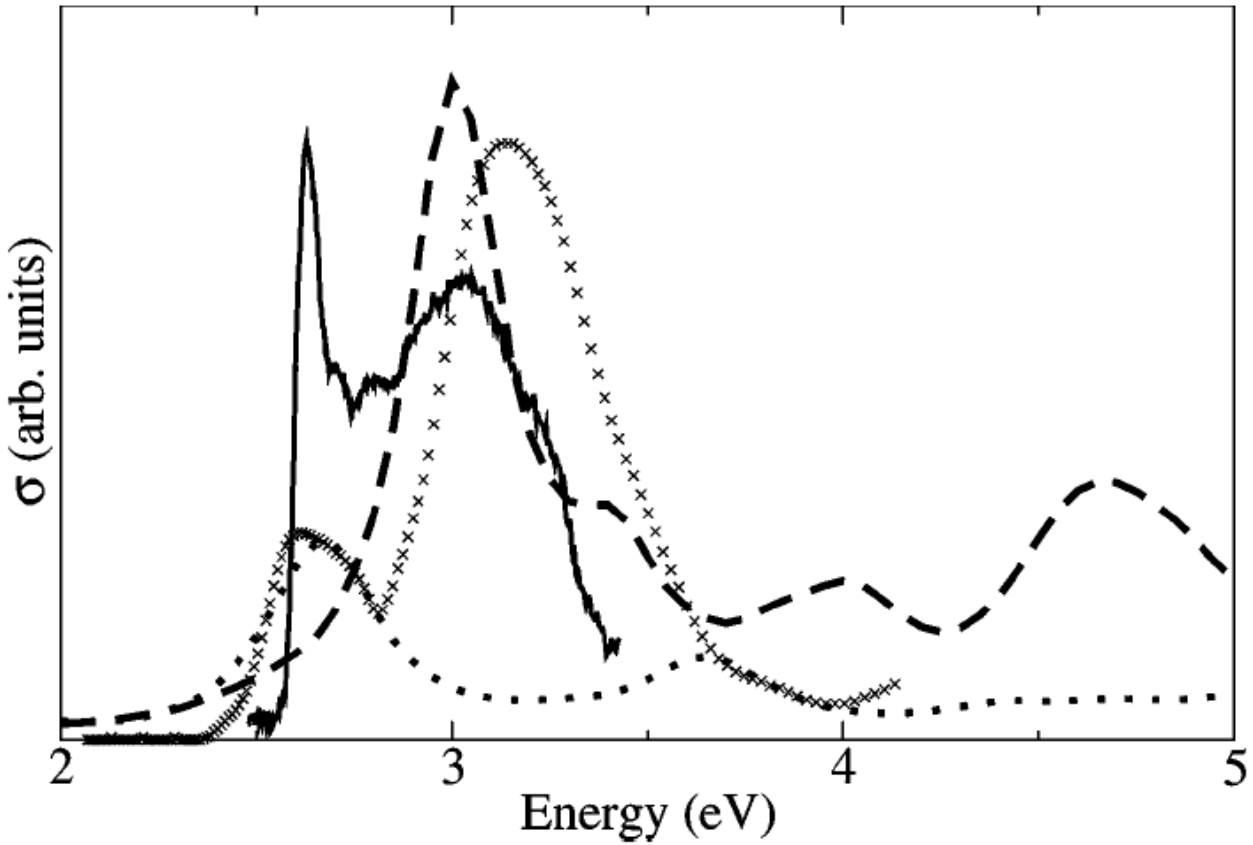


Figure 2 The photoabsorption cross section of the chromophore of the green fluorescent protein calculated by Marques et al. (64) compared with the experimental measurements. The dashed line corresponds to the neutral chromphore, the dotted line to the anionic, whereas the crosses and solid curves are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

and more

- Silicon

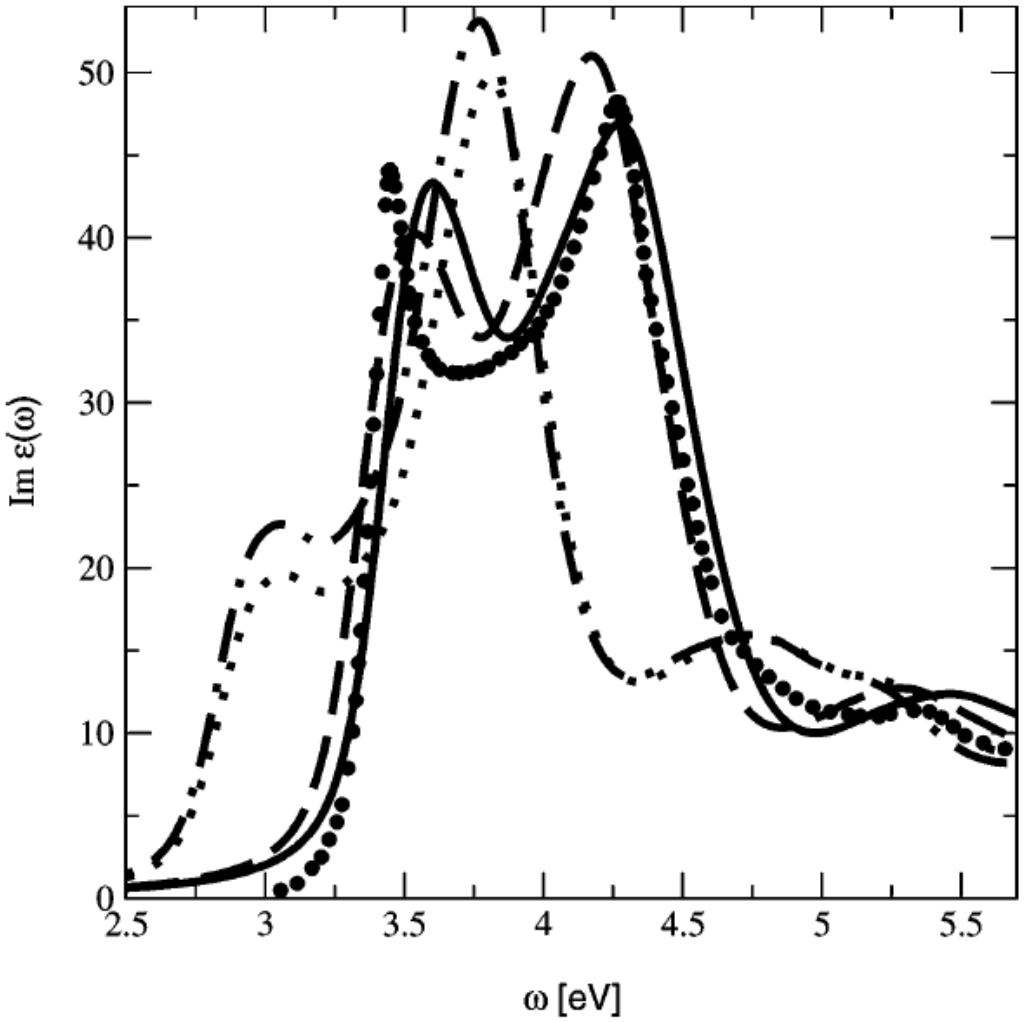


Figure 3 Optical absorption spectrum of silicon. In the figure are represented the following spectra: experiment (93) (*thick dots*), RPA (*dotted curve*), TDDFT using the ALDA (*dot-dashed curve*), TDDFT using the RORO kernel (72) (*solid curve*), and the results obtained from the solution of Bethe-Saltpeter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

E&M

for nuclei

- ^{197}Au nucleus

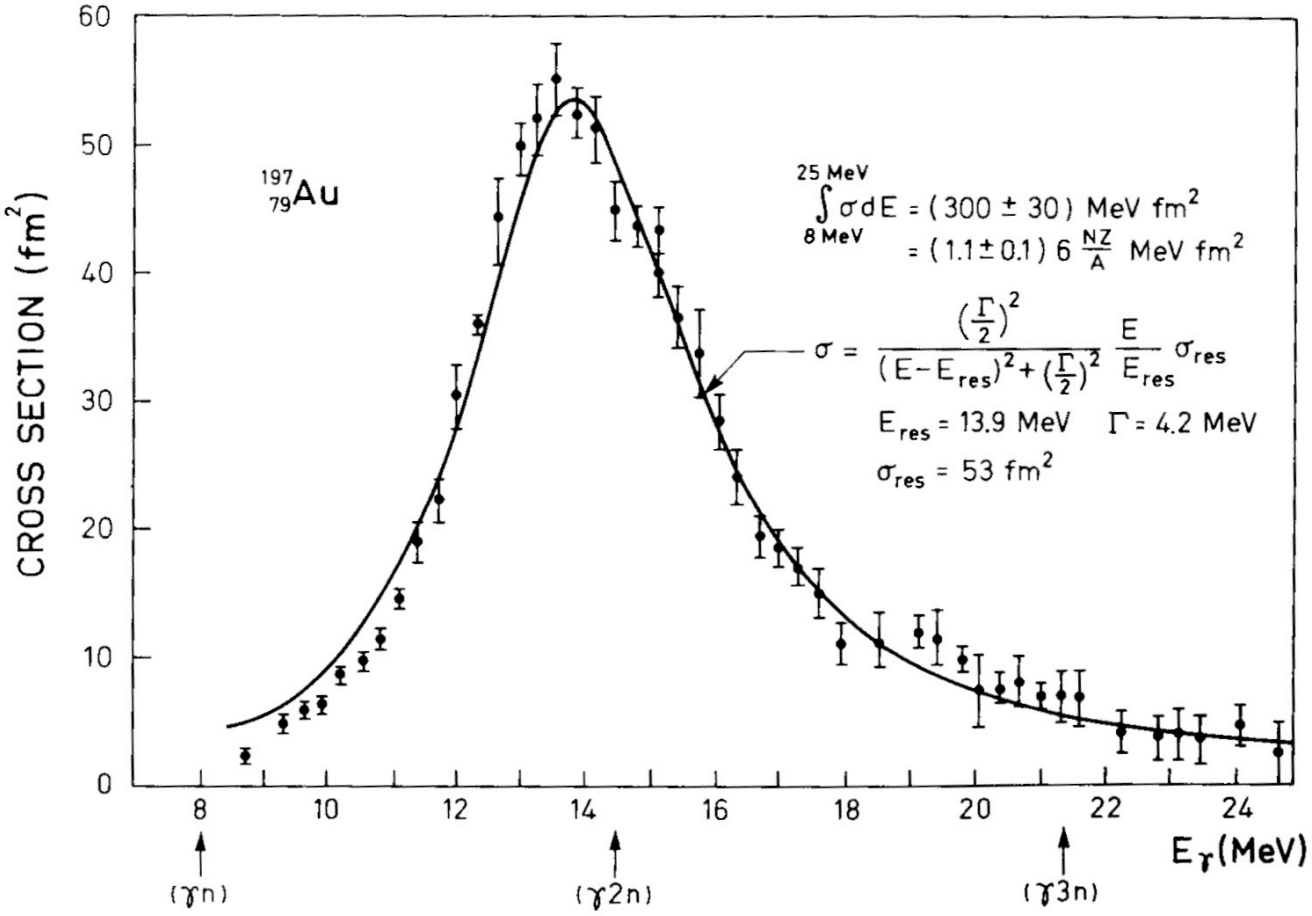


Figure 6-18 Total photoabsorption cross section for ^{197}Au. The experimental data are from S. C. Fultz, R. L. Bramblett, J. T. Caldwell, and N. A. Kerr, *Phys. Rev.* **127**, 1273 (1962). The solid curve is of Breit-Wigner shape with the indicated parameters.

and finally

- Proton

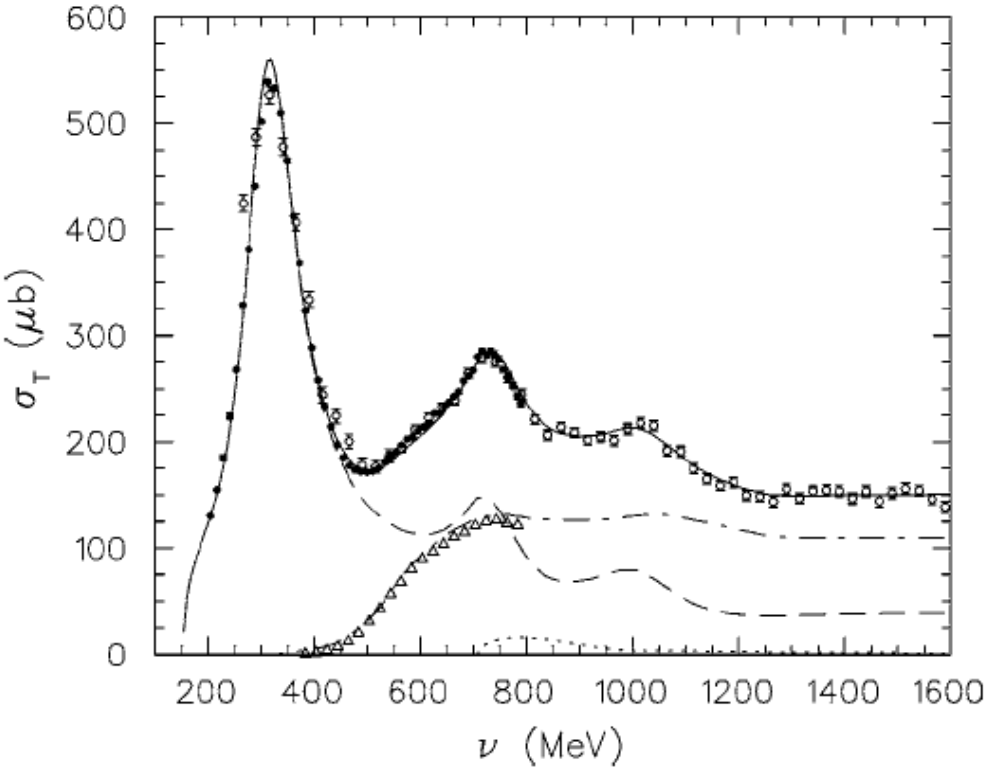


Figure 3 The total absorption cross section σ_T for the proton. The various lines represent the MAID results (34) for the total cross section (*solid line*), one-pion channels (*dashed line*), more-pion channels (*dash-dotted line*), and η channel (*dotted line*). The data for the total cross section are from MAMI (35) (*filled circles*) and Daresbury (36) (*open circles*). The triangles represent the data for the 2π 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 $|B\rangle = a^\dagger_{\boldsymbol{k}_f m_s} a_{n_< \ell m_\ell m_s} |\Phi_0\rangle$
- 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

$$\begin{aligned}(\#\text{ of states} \le E_f + dE_f) - (\#\text{ of states} \le E_f) &= \rho_{d\Omega}\, dE_f \\ &= \frac{V}{(2\pi)^3}\int_0^{k_f+dk_f} dk\; k^2\; d\Omega - \frac{V}{(2\pi)^3}\int_0^{k_f} dk\; k^2\; d\Omega \\ &= \frac{V}{(2\pi)^3} d\Omega \int_{E_f}^{E_f+dE_f} dE\; \frac{mk_f}{\hbar^2} = \frac{V}{(2\pi)^3}\frac{mk_f}{\hbar^2} d\Omega\; dE_f\end{aligned}$$

- Cross section

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

Explicit example

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

$$\langle B|\, a^\dagger_\beta a_\gamma\, |A\rangle = \langle \Phi_0|\, a^\dagger_{1s} a_{\boldsymbol{k}_f m_s} a^\dagger_\beta a_\gamma\, |\Phi_0\rangle \simeq \delta_{\boldsymbol{k}_f m_s \beta}\delta_{1s\gamma}$$

- 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

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

- Finally $\qquad \dfrac{d\sigma}{d\Omega} = \dfrac{32e^2k_f}{m\omega c}\left(\boldsymbol{e}_{\boldsymbol{k}\alpha}\cdot\boldsymbol{k}_f\right)^2\dfrac{Z^5}{a_0^5}\dfrac{1}{\left[(Z/a_0)^2+q^2\right]^4}$

General issues related to emission

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

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

  - Can obtain equivalent classical result by taking classical vector potential

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

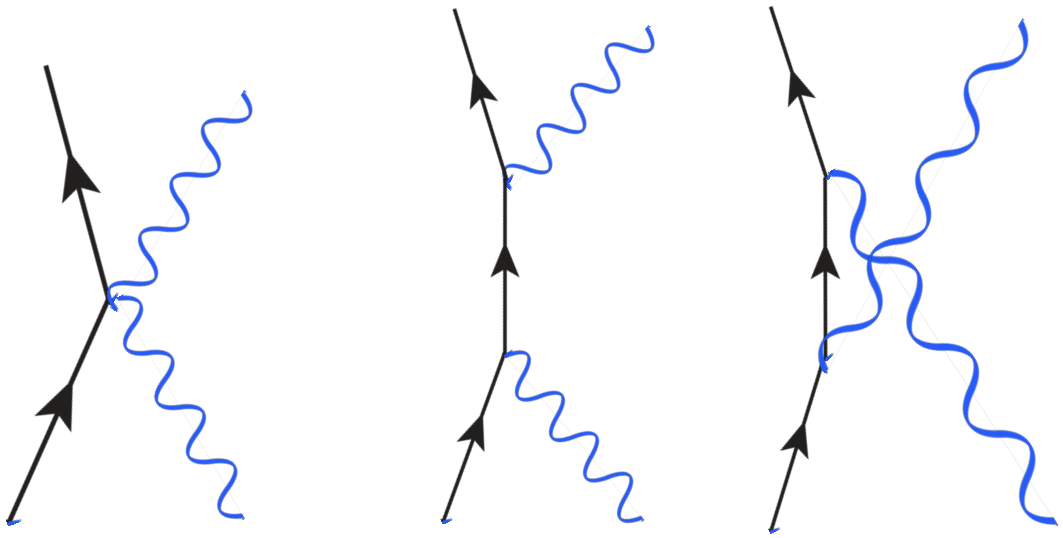
  - for $n_{\boldsymbol{k}\alpha}$ large; then do minimal substitution
  - QM: induced and spontaneous emission on the same footing

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

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

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

Thermal occupation of modes

- Ratio of rates

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

- and therefore $$\frac{N(B)}{N(A)} = \frac{w^{A\to B}_{emis}}{w^{B\to A}_{abs}} = e^{\hbar\omega_k/k_BT} = \frac{n_{\boldsymbol{k}\alpha}+1}{n_{\boldsymbol{k}\alpha}}$$

- So thermal occupation $$n_{\boldsymbol{k}\alpha}(T) = \frac{1}{e^{\hbar\omega_k/k_BT}-1}$$
- 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 $(\#\text{ of states} \leq (\omega + d\omega) - (\#\text{ of states} \leq \omega) \quad = \quad \rho_\omega \; d\omega$

$$\Rightarrow \quad \frac{V}{(2\pi)^3}\frac{\omega^2}{c^3} d\omega \; d\Omega$$

- 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

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

$$= \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/k_B T}-1}$$

- Planck's famous radiation law!

The end! Thanks for an enjoyable year!