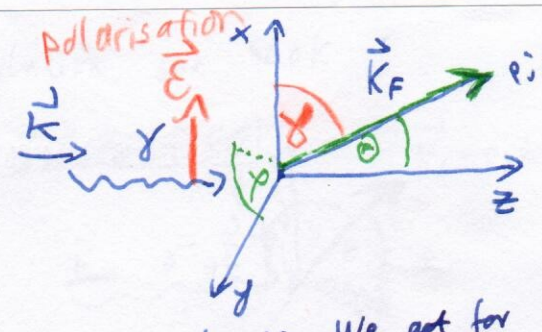
8

Can rewrite (3.35) using integration by parts:

$$M_{ba} = (2\pi)^{-\frac{3}{2}} \left(-i\,\vec{\varepsilon}\cdot(\vec{k}-\vec{k}_f)\right) \int \exp\left(i(\vec{k}-\vec{k}_f)\cdot\vec{r}\right) \psi_a(\vec{r})\, d^3\vec{r} \qquad (3.36)$$

This is proportional to the Fourier-transform $\tilde{\psi}_a(\vec{k}-\vec{k}_f)$ of $\psi_a(\vec{r})$.

Specify geometry:



We get for Hydrogen (-like) groundstate $|a\rangle = |1s\rangle$

- Details of calculation, see book.

$\Omega = (\theta, \varphi)$ direction of electron

Differential cross-section for photo-ionization:

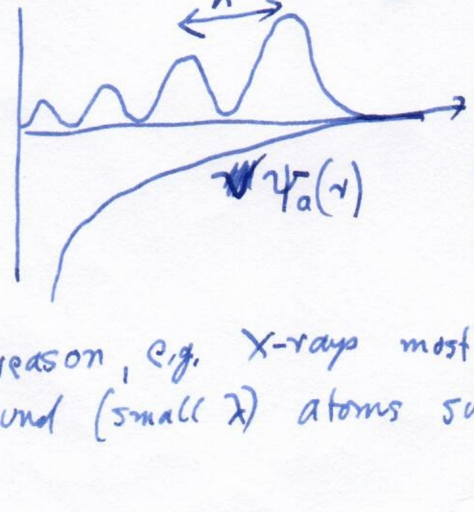
$$\frac{d\sigma}{d\Omega} = 32\,\alpha \left(\frac{\hbar}{m}\right)\left(\frac{k_f^3}{\omega}\right) \frac{Z^5 a_0^3 \cos^2\gamma}{\left[Z^2 + K^2 a_0^2\right]^4} \qquad (3.37)$$

$K = |\vec{K}|$, $\vec{K} = \vec{k} - \vec{k}_f$ (assumes $E_f \gg |E_a|$)

- K depends on θ
- ejection most likely for $\gamma = 0, \pi$, along $\vec{E}$-field polarisation
- From (3.36) we see that laser-wavelength has to match size/oscillation scales of wave function: let $|\vec{k}-\vec{k}_f| \approx \mathcal{O}(|\vec{k}|)$

* [We can ignore $|\vec{k}-\vec{k}_f| \gg \ll \mathcal{O}(|\vec{k}|)$ because then $\gamma \approx 0$ or $\gamma \approx \frac{\pi}{2}$ $\Rightarrow \sigma \approx 0$]

Example:



$\tilde{\psi}_a(k)$ will have main contributions at $k = \frac{2\pi}{\lambda}$

- For this reason, e.g. X-rays most likely photo-ionize tightly bound (small λ) atoms such as from inner K-shells

8

3.4. Scattering of radiation by atoms

- So far we looked at processes where atom makes a transition $b \to a$ and a photon is created or the reverse, using first order PT.

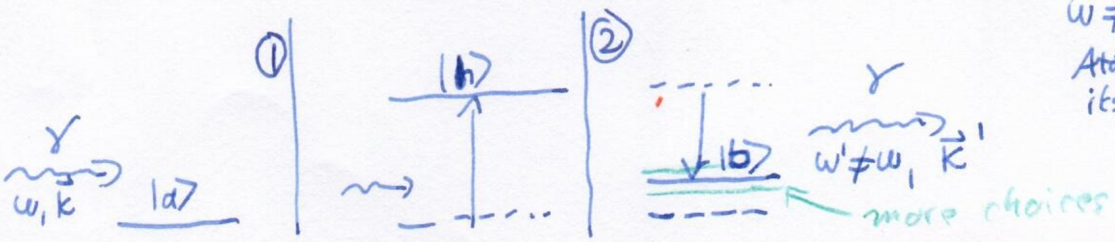
- Combining these in 2nd order PT yields light scattering.

We can distinguish two different possibilities

Elastic scattering (Rayleigh scattering)

$\omega = \omega'$
$\vec{k}' \neq \vec{k}$, photon can change direction

Inelastic scattering (Raman scattering)



$\omega \neq \omega'$
~~Atom~~ has changed its internal energy

- both processes can occur in a resonant or non-resonant version, depending on ~~wether~~ whether $\omega \approx \omega_{na}$ for two states a, n. They happen regardless of whether this is the case.

3.4.1 Rayleigh Scattering

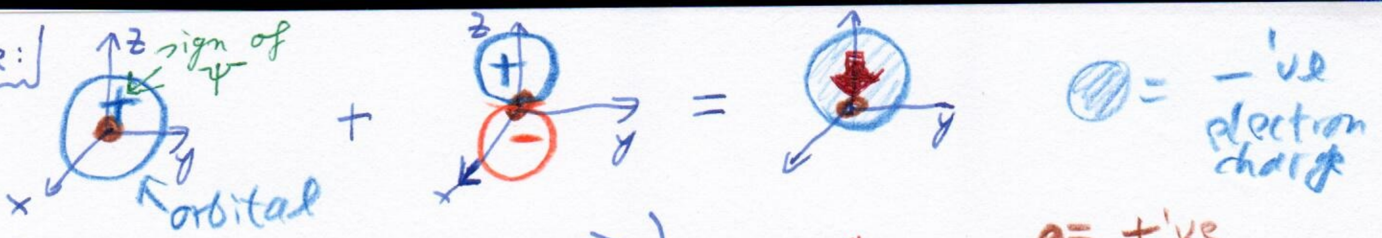
The initial step ①, is a quantum mechanical amplitude for the atom to make the $|a\rangle \to |n\rangle$ transition.

Afterwards/ during the process the atom will generically be in a superposition state

$$|\psi\rangle = c_a|a\rangle + c_n|n\rangle$$

Such a superposition state in general corresponds to an oscillating dipole

Picture:



$$|\psi\rangle = \frac{1}{\sqrt{2}}\Big(\underbrace{|1s\rangle}_{|a\rangle} + \underbrace{|1p\ m=0\rangle}_{|n\rangle} \Big)$$

dipole moment $\underline{d}$

- Ask why oscillating?

Oscillating dipole emits radiation ⇒ step 2.

The intuitive picture above motivates

Classical treatment

Electron as driven oscillator (3.38)

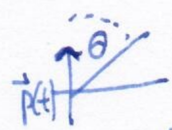
$$\ddot{\underline{x}} + \gamma \dot{\underline{x}} + \omega_0^2 \underline{x} = -\frac{e}{m} \underbrace{\underline{E}(t)}_{\underline{E}_0 e^{-i\omega t}}$$

To retain connection with our quantum state picture above, we set $\omega_0 = \omega_{na}$ and $\gamma = \Gamma$ (decay rate, see (3.29))

Steady solution (3.39)

$$x(t) = \frac{-e/m}{\omega_0^2 - i\gamma\omega - \omega^2} E_0 e^{-i\omega t}$$

Electrodynamics, power radiated by dipole $\omega = c \cdot k$



$\vec{p}(t) = \vec{p}_0 e^{-i\omega t}$

$$\frac{dP}{d\Omega} = \frac{c}{8\pi} k^4 |\vec{p}_0|^2 \sin^2\theta$$

Rayleigh scattering formula (3.40)

$$\boxed{\frac{dP}{d\Omega} \sim \left(\frac{e}{m}\right)^2 \frac{\omega^4}{(\omega^2-\omega_0^2)^2 + \gamma^2\omega^2} \sin^2\theta}$$

- For $\omega_0 \gg \omega$ this is $\sim \left(\frac{\omega}{\omega_0}\right)^4$
- This explains ~~both~~ blue sky and red sunset via Rayleigh scattering off photons from atoms/molecules in the atmosphere; optical wavelengths $\lambda \sim 400-800\,nm$ here $\omega_0 \gg \omega$ is true for N_2, O_2

blue 450 nm red 650 nm ⇒ blue scattered 4.3 times more effectively

- Dipole direction $\vec{p}_0$ will be given by incoming polarisation vector $\vec{\varepsilon}$ ⇒ θ is wrt. polarization of incoming light.

Quantum treatment

Second order time-dependent P.T. (c.f. Eq. (1.32))

$$c_b^{(2)}(t) = -\frac{1}{\hbar^2}\sum_n \int_0^t dt' \int_0^{t'} dt'' \, e^{i\omega_{bn}t'} e^{i\omega_{na}t''} H'_{bn}(t') H'_{na}(t'') \qquad (3.41)$$

$\uparrow$ see Eq. (3.9)

Note, time-ordering $0 < t' < t'' < t$

We can follow similar steps (but using QED) as for absorption cross-section (3.15 b) to find

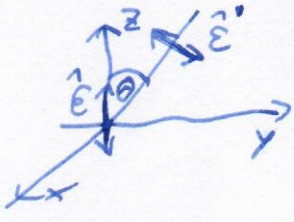
Differential cross-section for photon scattering into (θ, φ)

$$\frac{d\sigma}{d\Omega}(\theta, \phi) = r_0 \, \omega\omega'^3 \left(\frac{m^2}{\hbar^2 e^4}\right) \left| \sum_n \frac{(\hat{\varepsilon}' \cdot \hat{D}_{bn})(\hat{\varepsilon} \cdot \hat{D}_{na})}{\omega_{na} - \omega} + \frac{(\hat{\varepsilon} \cdot \hat{D}_{bn})(\hat{\varepsilon}' \cdot D_{na})}{\omega_{na} + \omega'} \right|^2 \quad (3.42)$$

- describes Raman and Rayleigh
- Angles are hidden in $\hat{\varepsilon} \cdot \hat{D}_{na}$ etc.
- $\hat{\varepsilon}$ polarisation of incoming photon, $\hat{\varepsilon}'$ outgoing

To apply to Rayleigh scattering, assume $|a\rangle \to |0\rangle$ state, we select a single $|n\rangle$ in a p-state, as in the picture on page 58. Also $\hat{\varepsilon} \parallel \hat{z}$ again, $\hat{D}_{na} \parallel \hat{z}$ for same reason as in picture. Also $\omega = \omega'$ and we assume $\omega_{na} \gg \omega$ as before.

We finally know $\hat{\varepsilon}' \cdot \hat{D}_{an} \sim \sin\theta$:



With all these assumptions the cross-section scales like

$$\frac{d\sigma}{d\Omega} \sim \left(\frac{\omega}{\omega_{na}}\right)^4 \sin^2\theta \qquad (3.43)$$

which reproduces main features of the classical result.

We will look more on Raman scattering later, in the context of molecules.

3.5. Interactions of many-electron atoms with radiation

All our discussion so far in chapter 3 generalizes from hydrogenic to many electron atoms if we replace the earlier matrix elements, e.g M^{D}_{ba} to

dipole matrix element for many electrons

$$M^{D}_{ba} = \frac{m\,\omega_{ba}}{\hbar e}\,\vec{\varepsilon}\cdot\sum_{k=1}^{N}\langle\phi_b|-e\,\vec{r}_k|\phi_a\rangle \qquad (3.46)$$

- compare with Eq. (3.18)
- since electrons are indistinguishable, we can also write

$$M^{D}_{ba} = +\frac{N\,m\,\omega_{ba}}{\hbar e}\,\vec{\varepsilon}\cdot\langle\phi_b|-e\vec{r}_1|\phi_a\rangle$$

It turns out that also selection rules generalize:

Selection rules for many electron atom:

$$\Delta J = 0, \pm 1 \qquad (\text{No } J=0 \Rightarrow J'=0)$$

$$\Delta M_J = 0, \pm 1$$

where J now pertains to the total angular momentum of all electrons.