Week 8

PHY 402 Atomic and Molecular Physics
Instructor: Sebastian Wüster, IISER Bhopal, 2018

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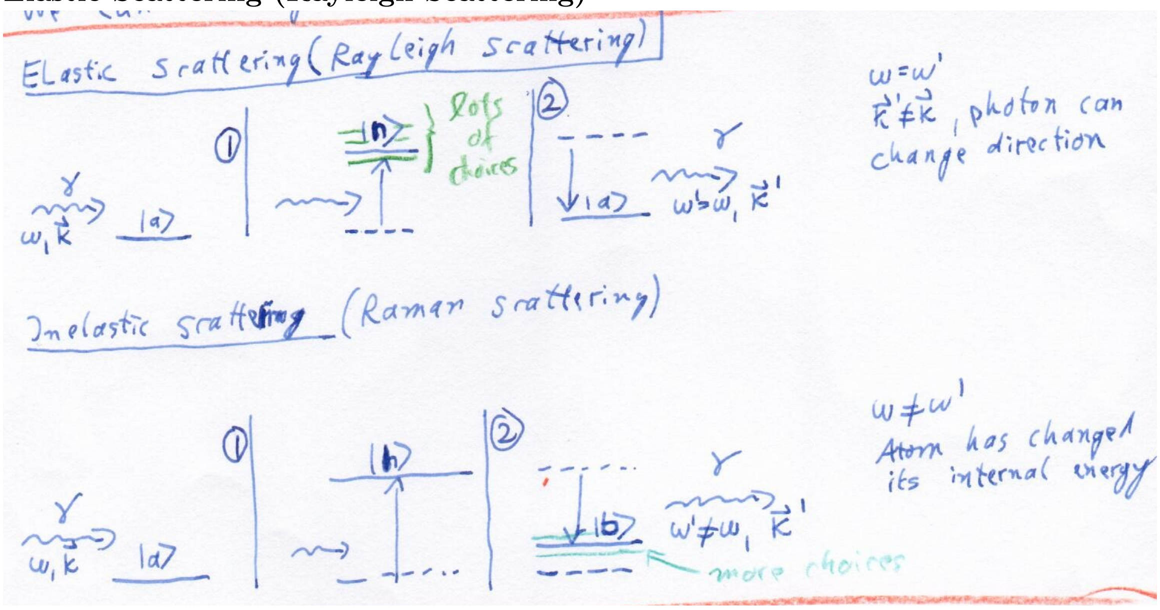
3.6 Scattering of radiation by atoms

- So far we looked at processes where an atom makes a transition (b to a) and a photon is created, or the reverse using first order perturbation theory.
- Combining these in 2nd order perturbation theory yields the physics of light scattering.

We can distinguish two different possibilities:

Elastic Scattering (Rayleigh Scattering)



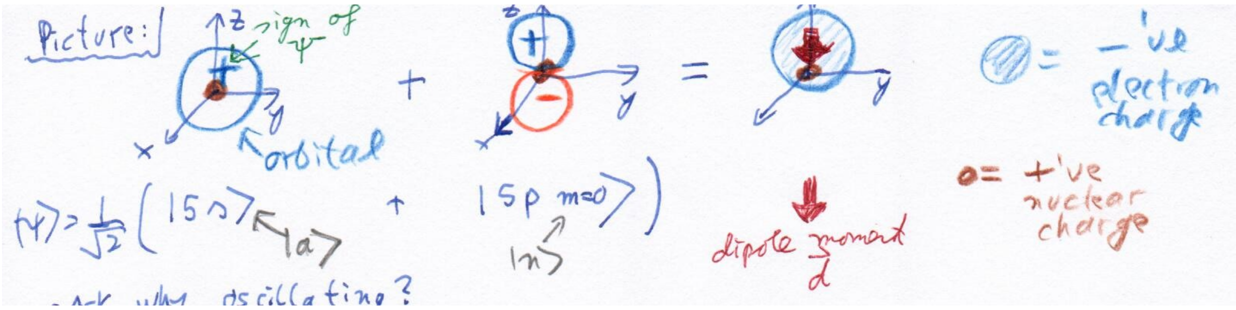
- Both processes can occur in a <u>resonant</u> or <u>non-resonant</u> version, depending on wether $\omega = \omega_{na}$ for two states a, n. They happen <u>regardless</u> of whether this is the case.

3.6.1 Rayleigh Scattering

The initial step (1), is a quantum mechanical amplitude for the atom to make the $|\,a\,\rangle \rightarrow |\,n\,\rangle$ transition. Afterwards/ during the process he 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. *Self-test: Why is the dipole oscillating?.*



top: Sketch of oscillating charge distribution in atomic superposition states

- In turn, the oscillating dipole excited by the initial absorption of the incoming photon now emits radiation $\rightarrow$ step 2, re-emission = scattering of the photon.
- This intuitive picture motivates a

Classical Treatment:

Electron as driven oscillator

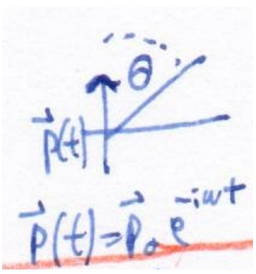
$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = -\frac{e}{m}E(t), \tag{3.73}$$

where $E(t) = E_0 \exp -i\omega t$ is the oscillating electric field of the incoming light, acting on the electron.

To retain connection with our quantum state picture above, we set $\omega_0 = \omega_{na}$ and $\gamma = \Gamma$ (decay rate, see Eq. (3.64)). The steady solution without initial transients is:

$$x(t) = \frac{-e/m}{\omega_0^2 - i\gamma\omega - \omega^2} E_0 e^{-i\omega t} \tag{3.74}$$

The resulting oscillating dipole moment of the electron is $p(t) = -e\,x(t)$. From electrodynamics, we know the power radiated by an oscillating dipole into a certain spherical angle $d\Omega$ is



left:

$$\frac{dP}{d\Omega} = \frac{c}{8\pi}k^4|\mathbf{p}_0|^2\sin^2\theta, \tag{3.75}$$

when the dipole moment is $\mathbf{p}(t) = \mathbf{p}_0 \exp[-i\omega t]$, $\omega = ck$ and θ is the angle to the dipole axis, see sketch.

Combining Eq. (3.74) and Eq. (3.75) we reach the

Rayleigh Scattering formula

$$\frac{dP}{d\Omega} \sim \left(\frac{e}{m}\right)^2 \frac{\omega^4}{(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2} \sin^2\theta \tag{3.76}$$

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

  Blue 450nm   Red 650nm $\Longrightarrow$ Blue scattered 4.3 times more effectively
- Dipole direction $\mathbf{p}_0$ wil be given by incoming polarisation vector $\boldsymbol{\epsilon} \implies \theta$ is with respect to polarization of incoming light.

Sketch of quantum treatment:

Second order time-dependent perturbation theory version of Eq. (1.57) (see QM textbook) is:

$$c_b^{(2)}(t) = -\frac{1}{\hbar^2}\sum_n \int_0^t dt' \int_0^{t'} dt'' e^{i\omega_{bn}t'} e^{\omega_{na}t''} \underbrace{H'_{bn}(t')H'_{na}(t'')}_{\text{see } Eq.\ (3.11)} \tag{3.77}$$

Note, time-ordering $0 < t^{''} < t^{'} < t$

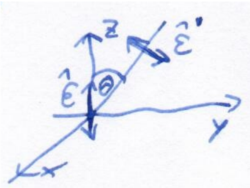
We can follow similar steps (but using QED) as for absorption cross-section (3.19) to find

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

$$\frac{d\sigma}{d\Omega} = r_0 \omega \omega'^3 \left(\frac{m^2}{\hbar^2 e^4}\right) \left| \sum_n \frac{(\boldsymbol{\epsilon}' \cdot \mathbf{D_{bn}})(\boldsymbol{\epsilon} \cdot \mathbf{D_{na}})}{\omega_{na} - \omega} + \frac{(\boldsymbol{\epsilon} \cdot \mathbf{D_{bn}})(\boldsymbol{\epsilon}' \cdot \mathbf{D_{na}})}{\omega_{na} + \omega'} \right|^2 . \tag{3.78}$$

- This describes both, Raman and Rayleigh scattering.
- Angular dependence of scattering is hidden in $\boldsymbol{\epsilon} \cdot \mathbf{D}_{na}$.
- $\boldsymbol{\epsilon}$ is the polarisation of the incoming photon, $\boldsymbol{\epsilon}'$ of the outgoing one.

To check this with our earlier classical result on Rayleigh scattering, we assume that the only contributing intermediate state $|\, n\,\rangle$ is some p-state as in the picture above. We can set $\hat{\epsilon} \parallel \hat{k}$ along the z-axis as usual. Then one finds $\hat{D}_{na} \parallel \hat{k}$ for the reasons graphically shown in the picture. Let also $\omega = \omega^{'}$ and assume $\omega_{na} >> \omega$ as before.



left: We finally know $\boldsymbol{\epsilon}' \cdot \mathbf{D}_{na} \sim \sin(\theta)$ from the diagram involving incoming and outgoing polarisation vectors.

With all these assumptions the cross-section (3.78) scales like

$$\frac{d\sigma}{d\Omega} \sim \left(\frac{\omega}{\omega_{na}}\right)^4 \sin^2\theta \tag{3.79}$$

which reproduces the main features of the classical result.

We will take a closer look on Raman scattering later, in the context of molecules.

3.7 Interaction of many-electron atoms with radiation

All our discussion so far in chapter 3 generalizes from hydrogenic atoms to N-electron atoms if we replace the earlier matrix elements, e.g. M^D_{bd} instead by

Dipole Matrix element for many electrons

$$M^D_{ba} = \frac{m\omega_{ba}}{\hbar e}\boldsymbol{\epsilon} \cdot \sum_{k=1}^{N} \langle\, \phi_b\,|(-e\mathbf{r}_k)|\,\phi_a\,\rangle \tag{3.80}$$

where $\mathbf{r}_k$ is the coordinate of electron number k.

- To compare with Eq. (3.27).
- Since electrons are indistinguishable, we can instead also write

$$M^D_{ba} = \frac{Nm\omega_{ba}}{\hbar e}\boldsymbol{\epsilon} \cdot \langle\, \phi_b\,|(-e\mathbf{r}_1)|\,\phi_a\,\rangle \tag{3.81}$$

It turns out that also the selection rules generalize quite straightforwardly:

Selection rules for many electron atoms:

$$\Delta J = 0, \pm 1 \quad (\text{No } \; J = 0 \to J^{'} = 0), \quad \Delta M_J = 0, \pm 1 \tag{3.82}$$

where J now pertains to the total angular momentum of <u>all electrons</u>.