

Week 7

PHY 402 Atomic and Molecular Physics

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3.3 Rabi-Oscillations

- Consider again the Hamiltonian (3.7) $\hat{H}(t) = \hat{H}_0 + \hat{H}'(t)$, neglecting the \mathbf{A}^2 term. For this section we choose a simpler vector potential

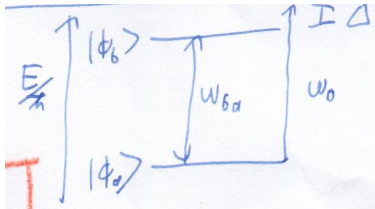
$$\mathbf{A}(\mathbf{r}, t) = A_0 \boldsymbol{\epsilon} \cos(\mathbf{k} \cdot \mathbf{r} - \omega_0 t) \quad (3.40)$$

In terms of the more complicated expression (3.5), this could be monochromatic/narrow band laser which thus has $\delta_\omega \equiv 0$ and $A_0(\omega)$ sharply peaked around $\omega = \omega_0$.

From (3.1), we have

$$\mathbf{E}(\mathbf{r}, t) = \underbrace{\omega_0 A_0 \boldsymbol{\epsilon}}_{\mathbf{E}_0} \sin(\mathbf{k} \cdot \mathbf{r} - \omega_0 t) \quad (3.41)$$

for the Electric field.



left: Two level atom with laser coupling

For simplicity consider only two atomic states $|\phi_a\rangle, |\phi_b\rangle$ with $\omega_{ba} \approx \omega_0$, and introduce the

Detuning $\Delta = \omega_0 - \omega_{ba}$, the difference between laser and atomic transition frequency.

We want to determine the full time evolution of the atom, which we can write as

$$|\psi(t)\rangle = c_a(t) e^{-\frac{i}{\hbar} E_a t} |\phi_a\rangle + c_b(t) e^{-\frac{i}{\hbar} E_b t} |\phi_b\rangle, \quad (3.42)$$

thanks to our restriction to just two atomic states. For writing the TDSE (1.45) we nextly require

all possible matrix elements of \hat{H} with states $|\phi_{a/b}\rangle$. These are:

$$\langle\phi_a|\hat{H}_0|\phi_a\rangle = E_a, \quad \langle\phi_b|\hat{H}_0|\phi_b\rangle = E_b, \quad (3.43)$$

$$\langle\phi_b|\hat{H}'(t)|\phi_a\rangle \stackrel{\text{Eq. (3.7)}}{=} -i\hbar\frac{A_0e}{m}\langle\phi_b|\boldsymbol{\epsilon}\cos(\mathbf{k}\cdot\mathbf{r}-\omega_0t)\cdot\nabla|\phi_a\rangle \quad (3.44)$$

$$= -i\hbar\frac{A_0e}{2m}\langle\phi_b|\boldsymbol{\epsilon}\left(\underbrace{e^{i\mathbf{k}\cdot\mathbf{r}}}_{\approx 1}e^{-i\omega_0t} + \underbrace{e^{-i\mathbf{k}\cdot\mathbf{r}}}_{\approx 1}e^{i\omega_0t}\right)\cdot\nabla|\phi_a\rangle \quad (\text{dipole approximation})$$

$$= -i\hbar\frac{A_0e}{2m}(e^{-i\omega_0t} + e^{i\omega_0t})\boldsymbol{\epsilon}\cdot\langle\phi_b|\nabla|\phi_a\rangle$$

$$\stackrel{\text{Eq. (3.27)}}{=} -i\frac{A_0\omega_{ba}}{2}(e^{-i\omega_0t} + e^{i\omega_0t})\boldsymbol{\epsilon}\cdot\langle\phi_b|(-e\hat{\mathbf{r}})|\phi_a\rangle$$

$$\approx -\frac{i}{2}(e^{-i\omega_0t} + e^{i\omega_0t})\mathbf{E}_0\cdot\underbrace{\langle\phi_b|(-e\hat{\mathbf{r}})|\phi_a\rangle}_{\text{atomic transition dipole}}. \quad (3.45)$$

Now rewrite TDSE (1.45) as matrix equation

$$i\hbar\begin{pmatrix}\dot{c}_a(t) \\ \dot{c}_b(t)\end{pmatrix} = \begin{pmatrix}o & \tilde{H}_{ab} \\ \tilde{H}_{ab}^* & 0\end{pmatrix}\begin{pmatrix}c_a(t) \\ c_b(t)\end{pmatrix} \quad (3.46)$$

where,

$$\tilde{H}_{ab} = \frac{i}{2}(e^{-i\omega_0t} + e^{i\omega_0t})\mathbf{E}_0\cdot\langle\phi_b|(-e\hat{\mathbf{r}})|\phi_a\rangle e^{\frac{i}{\hbar}(E_a-E_b)t}, \quad (3.47)$$

which we further re-write with two steps:

- We see complex exponentials such as $e^{-i(\omega_0 + \omega_{ba})t}$ and also $e^{i(\omega_0 - \omega_{ba})t}$. We neglect the fast oscillating exponential, assuming the complex number averages to zero. This is called the rotating wave approximation.
- We define the

Rabi-frequency as

$$\hbar\Omega = \langle\phi_b|\mathbf{d}\cdot\mathbf{E}_0|\phi_a\rangle \quad (3.48)$$

where, $\mathbf{d} = -e\hat{\mathbf{r}}$. This describes the strength with which atoms undergo a transition from $|\phi_a\rangle$ to $|\phi_b\rangle$ and is not to be confused with the laser frequency ω_0 or transition frequency ω_{ab} .

We can then re-write our matrix equation:

$$i\hbar\begin{pmatrix}\dot{c}_a(t) \\ \dot{c}_b(t)\end{pmatrix} = \begin{pmatrix}o & i\frac{\hbar\Omega}{2}e^{-i\Delta t} \\ -i\frac{\hbar\Omega}{2}e^{i\Delta t} & 0\end{pmatrix}\begin{pmatrix}c_a(t) \\ c_b(t)\end{pmatrix}, \quad (3.49)$$

and finally redefine $\tilde{c}_b(t) = ie^{-i\Delta t}c_b(t)$ and $\tilde{c}_a(t) = c_a(t)$, to reach

Effective SE and Hamiltonian for two-level atom in dipole and rotating-wave approximation

$$i \begin{pmatrix} \dot{\tilde{c}}_a(t) \\ \dot{\tilde{c}}_b(t) \end{pmatrix} = \underbrace{\begin{pmatrix} 0 & \frac{\Omega}{2} \\ \frac{\Omega}{2} & -\Delta \end{pmatrix}}_{\hat{H}_{\text{eff}}} \begin{pmatrix} \tilde{c}_a(t) \\ \tilde{c}_b(t) \end{pmatrix}. \quad (3.50)$$

Can solve with standard methods [exercise], using eigensystem of \hat{H}_{eff} . For the initial condition $\tilde{c}_a(0) = 1$, $\tilde{c}_b(0) = 0$, i.e. an atom in state a , we find

$$\begin{aligned} \tilde{c}_a(t) &= e^{i\frac{\Delta t}{2}} \left\{ \cos\left(\frac{t\Omega_{\text{eff}}}{2}\right) - i\frac{\Delta}{\Omega_{\text{eff}}} \sin\left(\frac{t\Omega_{\text{eff}}}{2}\right) \right\}, \\ \tilde{c}_b(t) &= -i\frac{\Omega}{\Omega_{\text{eff}}} e^{i\frac{\Delta t}{2}} \sin\left(\frac{t\Omega_{\text{eff}}}{2}\right). \end{aligned} \quad (3.51)$$

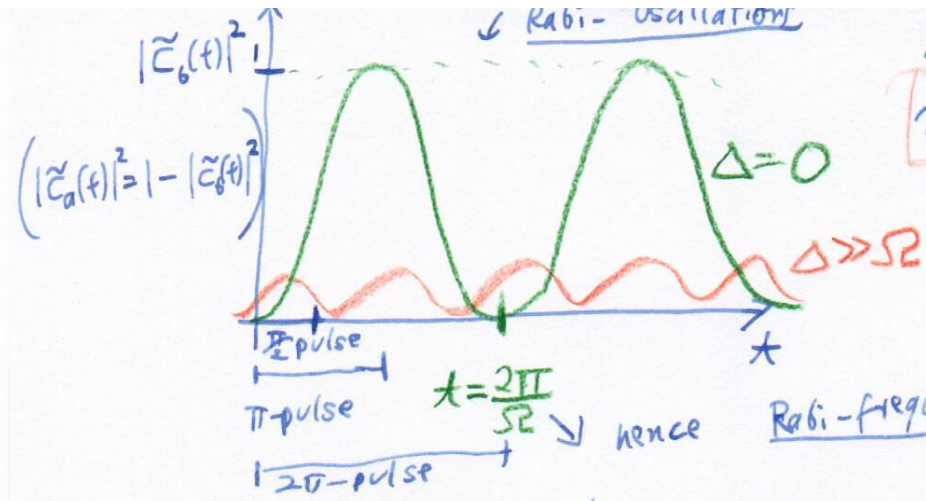
with $\Omega_{\text{eff}} = \sqrt{\Omega^2 + \Delta^2}$.

These are the ubiquitous

Rabi-oscillations:

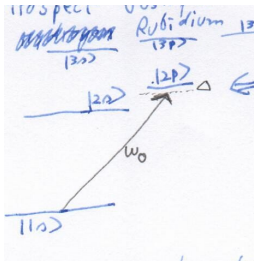
$$n_b(t) = |\tilde{c}_b(t)|^2 = \frac{\Omega^2}{\Omega_{\text{eff}}^2} \sin^2\left(\frac{\Omega_{\text{eff}}}{2}t\right) \quad (3.52)$$

where, $\Omega_{\text{eff}} = \sqrt{\Delta^2 + \Omega^2}$.



On resonance, $\Delta = 0$, the atom undergoes oscillations between states $|\phi_a\rangle$ and $|\phi_b\rangle$ with the Rabi frequency.

- For large detuning $\Delta \gg \Omega$, the probability to reach the state $|\phi_b\rangle$ remains small: $n_b(t)|_{\text{max}} = \Omega^2/\Omega_{\text{eff}}^2 \approx (\Omega/\Delta)^2 \ll 1$. This often in retrospect justifies our initial approximation to consider only two atomic states, see diagram below.



left: Rubidium level diagram with laser light at frequency ω_0 that is near-resonant with $|1s\rangle \rightarrow |2p\rangle$. This means however that it is far-off resonant with any other transition (e.g. $|2s\rangle \rightarrow |2p\rangle$). According to the arguments above other states than $|2p\rangle$ will thus not become populated.

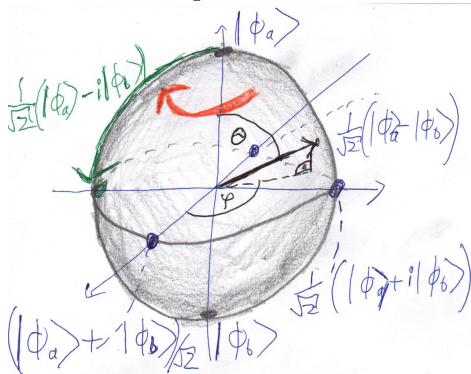
- The system of two laser coupled electronic states in an atom realizes a coherent two-level system as long as we ignore spontaneous decay. To discuss manipulations of this system, we use

Nomenclature for Rabi pulses: Suppose we apply the laser coupling only for a duration T . The indicated effects are for resonant pulses with $\Delta = 0$.

$$\begin{aligned}
 \pi/2 \text{ pulse} &\Leftrightarrow T = \frac{\pi}{2} \frac{1}{\Omega} & |\Psi(t=0)\rangle &= |\phi_a\rangle \rightarrow \frac{1}{\sqrt{2}}(|\phi_a\rangle - i|\tilde{\phi}\rangle), \\
 \pi \text{ pulse} &\Leftrightarrow T = \pi \frac{1}{\Omega} & |\phi_a\rangle &\rightarrow -i|\tilde{\phi}\rangle, \\
 2\pi \text{ pulse} &\Leftrightarrow T = 2\pi \frac{1}{\Omega} & |\phi_a\rangle &\rightarrow -|\phi_a\rangle. \tag{3.53}
 \end{aligned}$$

Bloch-sphere representation: The most general two-state superposition has the form $|\Psi\rangle = \cos[\theta/2]|\phi_a\rangle + e^{i\varphi}\sin[\theta/2]|\phi_b\rangle$ where $0 \leq \theta \leq \pi$ and $0 \leq \varphi \leq 2\pi$ are simply some parametrisation of the superposition^(*). However we can now also view θ and φ as the usual angles in spherical polar coordinates. This allows us to visualize any such superposition as a point on the surface of the Bloch sphere shown below.

From Eq. (3.51) we can also understand the simplest types of time evolution: For a resonant pulse starting in $|\phi_a\rangle$ with $\Delta = 0$ we identify $\theta = t\Omega$ (green arrow). For uncoupled states $\Omega = 0$ with different energies $\Delta E \neq 0$, we see $\varphi = \Delta E t/2$ (red arrow). More generally evolution due to any unitary operator \hat{U} in the space $|\phi_{a/b}\rangle$ corresponds to a specific rotation on the Bloch sphere.



left: Visualisation of states and dynamics on Bloch sphere.

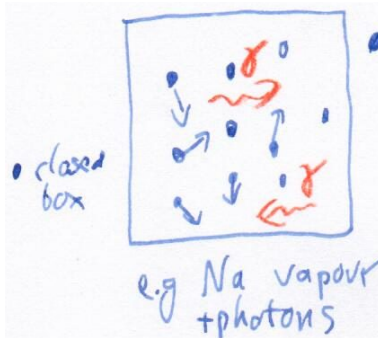
Bloch-sphere representation contd.:

The visualisation can be extended to include spontaneous decay (optical Bloch equations).

(*) Originally $|\Psi\rangle = c_1|\phi_a\rangle + c_2|\phi_b\rangle$ with $c_1, c_2 \in \mathbb{C}$ contained 4 real numbers. Due to the constraint $1 = |c_1|^2 + |c_2|^2$ we reduce one of those, one more can be removed since the overall phase of the state is irrelevant.

3.4 Spectral Lines

3.4.1 Thermal gas of atoms



left: Consider a box with atomic vapor and photons in equilibrium at temperature T

- Again let's consider two atomic levels $|\phi_{a/b}\rangle$ only, with $E_b > E_a$. In thermal equilibrium atoms are found in both states with some probability, let the number of atoms in a be N_a . Photons can thus take part in a statistical mix of stimulated emission, absorption and spontaneous emission.
- The number of atoms making the transition $a \rightarrow b$ per unit time is³

$$\dot{N}_{ba} = B_{ba}N_a\rho(\omega_{ba}), \quad (3.54)$$

where B_{ba} is the Einstein coefficient for absorption and $\rho(\omega_{ba})$ is the energy density in the radiation field (of the photons) at frequency ω_{ba} .

- For the reverse transition

$$\dot{N}_{ab} = A_{ab}N_b + B_{ab}N_b\rho(\omega_{ba}), \quad (3.55)$$

where A_{ab} is the Einstein coefficient for spontaneous emission and B_{ab} the Einstein coefficient for stimulated emission.

- In thermal equilibrium we must have $\dot{N}_{ab} = \dot{N}_{ba}$ and also

$$\frac{N_a}{N_b} = \exp[-(E_a - E_b)/(k_B T)] = \exp[\hbar\omega_{ba}/(k_B T)]. \quad (3.56)$$

³It is logical that \dot{N}_{ba} must be $\sim N_a$. We know from Eq. (3.19) that it must be $\sim \rho(\omega_{ba})$. Finally we just give the remaining proportionality constant the name B_{ba} .

We can use these relations to get an expression for the radiation density

$$\rho(\omega_{ba}) = \frac{A_{ab}}{B_{ba} \exp[\hbar\omega_{ba}/(k_B T)] - B_{ab}} \quad (3.57)$$

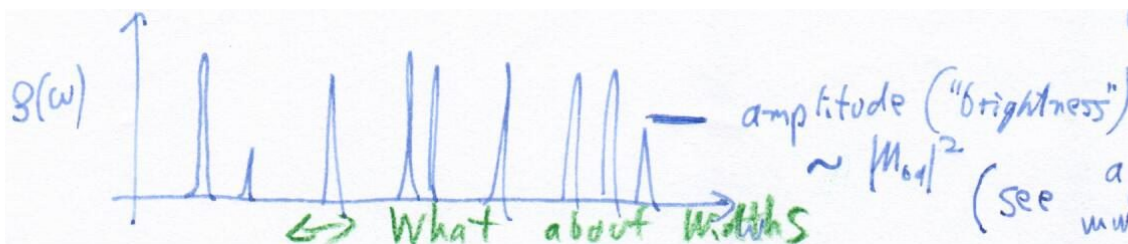
By requiring that (3.57) is identical with Planck's law from thermodynamics, we can deduce that

$$B_{ba} = B_{ab}, \quad (3.58)$$

$$A_{ab} = \left(\frac{\hbar\omega_{ba}^3}{\pi c^3} \right) B_{ab}. \quad (3.59)$$

This argument, due to Einstein, gives some link between stimulated and spontaneous emission without even solving the atomic physics problem. The result is consistent with the detailed calculations in section 3.1.2. There, from Eq. (3.19) we can write $B_{ba} = W_{ba}/[I(\omega_{ba})/c] \sim |M_{ba}|^2$, where the factor in square brackets is the energy density.

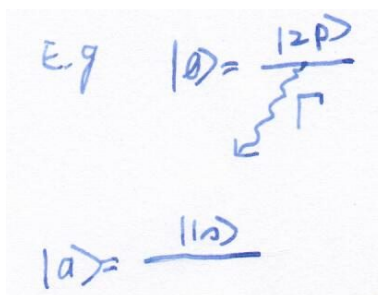
From Eq. (3.57) we also infer that there are photons in the box at equilibrium, at all frequencies belonging to any transition between two states a, b . This would look like:



top: From the picture of a gas in the box in thermal equilibrium above, we would also expect that in the radiation spectrum, all transitions frequencies for allowed transitions between atomic levels are present. Their amplitude (“brightness”) will be determined by $|M_{ba}|^2$. For a tabulation of experimental data on allowed transition frequencies and their strength (matrix elements), see www.nist.gov/pml/atomic-spectra-database .

- The remaining question regarding a spectrum such as above is, what sets the width and shape of the spectral lines?

3.4.2 Line shapes



left: As discussed in section 3.1.2 atomic excited states decay via spontaneous emission

A calculation of the corresponding decay rate, based on Eq. (3.22) and (3.39) gives for example a spontaneous decay rate $\Gamma_{2p \rightarrow 1s} = \left(\frac{2}{3}\right)^8 \frac{m\alpha^5 Z^4 c^2}{h} = 6.2710^8 Z^4 s^{-1}$. Does the emission really only go into the mode with the resonance frequency $\omega = \omega_{ab}$?

A rigorous QED approach: would be to calculate the amplitude for the process $|b, \text{no photons}\rangle \rightarrow |a, \text{one photon with frequency } \omega, \text{polarisation } \epsilon \text{ and momentum } \mathbf{p}\rangle$, then integrate over all possible ϵ, \mathbf{p} to reach the rate as a function of ω .

We follow a simpler, semi-classical approach. Assume a single atom in an excited state $|\phi_b\rangle$ starts emitting light at time t , while returning to the ground-state $|\phi_a\rangle$ with a rate Γ . Ignoring the vector character of the light, the emitted field strength for $t \geq 0$ will look like:

$$E(t) = E_0 \left(e^{[-\Gamma t/2]} e^{i\omega_{ba}t} + \text{c.c.} \right), \quad (3.60)$$

while $E(t) = 0$ for $t < 0$. We took into account that the field intensity must be proportional to the probability of the atom actually remaining in $|\phi_b\rangle$, which drops as $e^{[-\Gamma t]}$.

Now we do the Fourier transform of Eq. (3.60) to find the frequency spectrum via

$$E(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(\omega) e^{i\omega t} d\omega, \quad (3.61)$$

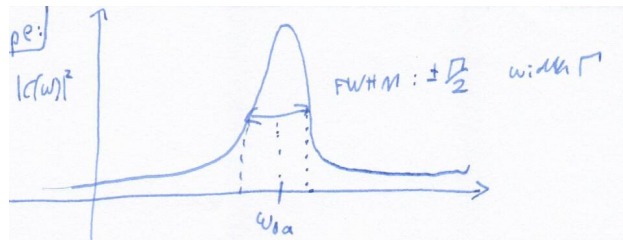
$$c(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} E(t) e^{-i\omega t} dt, \quad (3.62)$$

and reach

$$c(\omega) = -\frac{E_0}{\sqrt{2\pi}} \left(\frac{1}{i(\omega_{ba} - \omega) - \Gamma/2} + \frac{1}{i(-\omega_{ba} - \omega) - \Gamma/2} \right). \quad (3.63)$$

The second term is typically much smaller and can hence be neglected. The overall frequency spectrum of spontaneously emitted light thus follows the

Natural line profile, also called Lorentzian frequency spectrum:

$$|c(\omega)|^2 = \frac{E_0^2}{2\pi} \frac{1}{(\omega_{ba} - \omega)^2 + (\Gamma/2)^2}. \quad (3.64)$$


top: Sketch of natural line profile Eq. (3.64). We also define the

Life-time of the upper state:

$$\tau = 1/\Gamma. \quad (3.65)$$

- Note, for quite highly excited states a large number of spontaneous decay channels k are often possible, each with rate Γ_k . In that case define the total decay rate as $\Gamma = \sum_k \Gamma_k$, then use Eq. (3.65).
- An intuitive picture for the origin of the frequency width is that the energy of a decaying state is uncertain by ΔE according to the energy time uncertainty relation $\Delta E \tau \sim \hbar$.

Measured line-profiles are frequently much broader and differently shaped than Eq. (3.64) due to the following effects:

- **Pressure broadening:** Also atomic collisions can cause a transition $b \rightarrow a$. If the collision rate exceeds the spontaneous decay rate, this can significantly shorten the life-time to $\rightarrow \tau_{\text{coll}}$. In this case the spectral line remains of Lorentzian shape, but with a width $\Gamma \sim 1/\tau_{\text{coll}}$. This effect becomes stronger with increasing gas pressure.
- **Doppler broadening:** Atoms of mass M move relative to the lab frame with some random velocity \mathbf{v} . The associated Doppler shift $\omega' = \omega - \mathbf{v} \cdot \mathbf{k}$ is then also randomly distributed. The distribution of velocities follows the Maxwell-Boltzmann form $\sim \exp[-M\mathbf{v}^2/(2k_B T)]$, which is a Gaussian in $|\mathbf{v}|$. The Doppler effect can thus broaden spectral lines from a gas and turn their shape into a Gaussian for high temperatures.

In the general case we have a mixture of Lorentzian and Gaussian shapes, called a Voigt profile.

3.4.3 Oscillator strength and sum rules

A useful concept to do with a spectral line due to a transition from a to k is their

Oscillator strength

$$f_{ka} = \frac{2m\omega_{ka}}{3\hbar} |\langle \phi_b | \hat{r} | \phi_a \rangle|^2 \quad (3.66)$$

- These fulfill

Thomas-Reiche-Kuhn Sum rule

$$\sum_k f_{ka} = 1, \quad (3.67)$$

where the sum extends over all other states than a , including the continuum (see next section).

- The rule is useful to assess the importance of a certain transition. Knowing the matrix element for one transition we can infer f_{ka} . If this is close to one, we know from Eq. (3.67) that there are not going to be a lot of other important (strong) transitions.
- For proof see BJ book.

3.5 The photo-electric effect, photo ionization

Our treatment of atoms and atom light interaction so far only dealt with atomic bound states $|\phi_a\rangle$, $E_b < 0$. We can also find solutions of the Hydrogen TISE (1.30) with $E_b > 0$. These are called

Atomic continuum states, and fulfill

$$\left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 - \frac{Ze^2}{4\pi\epsilon_0 |\mathbf{r}|} \right) \Psi_b(\mathbf{k}_f, \mathbf{r}) = \underbrace{\frac{\hbar^2 \mathbf{k}_f^2}{2m}}_{=E_f > 0} \Psi_b(\mathbf{k}_f, \mathbf{r}). \quad (3.68)$$

- Continuum states $\Psi_b(\mathbf{k}_f, \mathbf{r})$ represent an electron that is not bound to the nucleus, so far away from the nucleus the solution behaves like a plane-wave $\sim \exp[i\mathbf{k}_f \cdot \mathbf{r}]$. Close to the nucleus, the plane-wave is modified since it feels the nuclear Coulomb potential.
- Ionisation by absorption of a photon can now be viewed as a transition between a bound and a continuum state.
- For $E_f \gg |E_a|$ we can even approximate $\Psi_b(\mathbf{k}_f, \mathbf{r}) \sim \exp[i\mathbf{k}_f \cdot \mathbf{r}]$ near the nucleus, and use our earlier result

$$\sigma = \frac{4\pi^2 \alpha \hbar^2}{m} \int d^3 \mathbf{k}_f \frac{1}{\omega_{ka}} |M_{ka}(\mathbf{k}_f, \omega_{fa})|^2 \delta(\omega - \omega_{ka}). \quad (3.69)$$

- This is just Eq. (3.21) and Eq. (3.19) for the absorption cross section with slight re-arrangements of constants, adding $\delta(\omega - \omega_{ka})$, which was implicitly assumed in Eq. (3.19) and integrating over all ejected electron momenta \mathbf{k}_f to get a total cross section.
- Note the matrix element

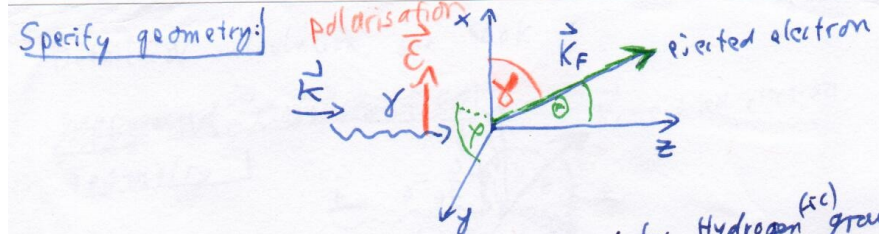
$$M_{ka} = \frac{1}{(2\pi)^{3/2}} \int d^3 \mathbf{r} \underbrace{\exp[-i\mathbf{k}_f \mathbf{r}]}_{\text{from } \Psi_b} \underbrace{\exp[i\mathbf{k} \mathbf{r}]}_{\text{from light}} \boldsymbol{\epsilon} \cdot \nabla \Psi_a(\mathbf{r}) \quad (3.70)$$

depends on \mathbf{k}_f , including its direction.

- We can re-write (3.69) using integration by parts to reach

$$M_{ka} = \frac{1}{(2\pi)^{3/2}} (-i\boldsymbol{\epsilon} \cdot (\mathbf{k} - \mathbf{k}_f)) \int d^3\mathbf{r} \exp[-i(\mathbf{k} - \mathbf{k}_f)\mathbf{r}] \Psi_a(\mathbf{r}). \quad (3.71)$$

We now recognize that it is proportional to the 3D Fourier-Transform $\tilde{\Psi}_a(\mathbf{k} - \mathbf{k}_f)$ of $\Psi_a(\mathbf{r})$.



top: Specific geometry for calculation of differential photo-ionization cross-section. The x -axis is chosen along the light polarisation.

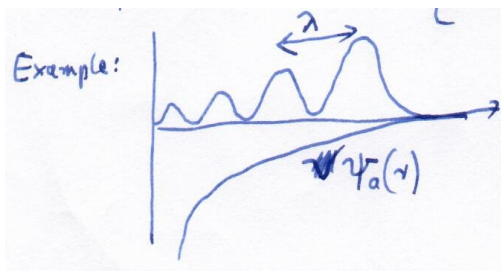
- Detailed calculation see BJ, using the geometry in the figure, one finds:

Differential cross-section for photo-ionization:

$$\frac{d\sigma}{d\Omega} = 32\alpha \frac{\hbar k_f^3}{m \omega} \frac{Z^5 a_0^3 \cos^2[\gamma]}{(Z^2 + \kappa^2 a_0^2)^4}, \quad (3.72)$$

where $\Omega = \{\theta, \varphi\}$ now corresponds to the ejection direction of the electron, $\kappa = |\boldsymbol{\kappa}|$, $\boldsymbol{\kappa} = \mathbf{k} - \mathbf{k}_f$

- κ depends on θ .
- We see that electron ejection is most likely for $\gamma = 0, \pi$, where γ is the angle between the ejection direction and the incoming light linear polarisation axis. Hence the electron is ejected preferentially along the direction of E-field polarisation.



left: From Eq. (3.71) we can see that laser wavelength has to match size /oscillation scales of the wavefunction ^a. The fourier-transform of the example wavefunction shown on the left $\tilde{\Psi}_a(k)$, will have its main contributions at $k = 2\pi/\lambda$.

^aFor this argument assume $|\mathbf{k} - \mathbf{k}_f| \approx \mathcal{O}(|\mathbf{k}|)$, other cases are suppressed since $\gamma \approx 0, \pi/2$

- For this reason, X-rays are most likely to photo-ionize tightly bound electrons from the inner shells of heavy atom (their wavefunction has smallest “ λ ”, matching X-ray wavelengths).