Photoionization: We wish to understand the following process: a high-energy photon strips an electron from an atom. We work in the rest frame of the atom and make some simplifying assumptions: the electron is initially in a $1s$ state, with wavefunction

$$
\psi_a(\hat{r}) = \left( \frac{2}{\pi a_0^3} \right)^{1/2} e^{-2r/a_0},
$$

and the final energy

$$
E_b = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad |E_a| = \frac{\frac{3}{2} e^2}{(4\pi \epsilon_0)^2 a_0}.
$$

but still nonrelativistic. We expect the final state to be a plane wave of energy $E_b = E_a + \hbar \omega$.

We use "Dirac normalization", $\psi_b(\hat{q}, \hat{r}) = \frac{1}{(2\pi)^{3/2}} e^{i \hat{q} \cdot \hat{r}}$.

The numerical factor is chosen so that

$$
\int \psi_b(\hat{q}, \hat{r})^* \psi_b(\hat{q}', \hat{r}) d\hat{r} = \delta(\hat{q} - \hat{q}').
$$

Note (1) that now $\psi_b$ does not have the normal units of a wavefunction, $\frac{1}{\text{volume}}$, and (2) that Dirac normalization tells us how to count states:

$$
\int d\hat{q}_1 d\hat{q}_2 \int \psi_b(\hat{q}_1, \hat{r})^* \psi_b(\hat{q}_2, \hat{r}) d\hat{r} = \int d\hat{q}_1 d\hat{q}_2 <\psi_b | \psi_b> = \int d\hat{q}_1 \delta(\hat{q}_1 - \hat{q}_2) = \int d\hat{q}_1.
$$
and the number of states in a "volume of \( \hat{z} \) space" is just the integral of \( d\hat{z} \). (This state counting will actually be the trickier part of the calculation.)

The perturbation Hamiltonian is

\[
\hat{H} = (\hat{z} \cdot \hat{D}) E_0(w) \sin(\omega t - \delta w).
\]

The Golden Rule for one process tells us

\[
W_{ba} = \frac{2\pi}{\hbar} |\langle \hat{H}\rangle|_b^2 \rho(E_b)
\]

where \( \rho(E_b) \) is the density of final states.

Here, we have to sum this over the different possible directions of the final electron state (\( \hat{b} \)). The angle \( \theta \) between \( \hat{D}_b \) and \( \hat{z} \) also depends on \( \delta k_b \).

Total:

\[
W_{ba} = \frac{2\pi}{\hbar} \frac{E_0^2(w)}{4} \int dL \cos^2 \theta |\langle \hat{H}\rangle|_b^2 \rho(E_b)
\]

The final density of states should satisfy

\[
\rho_b(E_b) dE_b d\Omega = dE_b = k_b^2 dk_b d\Omega
\]

what we arrived before was \# of states.

\[
\Rightarrow \rho_b(E_b) = k_b^2 \frac{dk_b}{dE_b} = \frac{k_b^2 m}{\hbar^2 k_b} = \frac{mk_b}{\hbar^2}.
\]
Writing \[ \frac{e_0 E_0^2(w)}{2} = \frac{I(w)}{c} = E_0^2(w) = \frac{\gamma I(w)}{c e_0}, \]

let \( k_f = k_p \).

\[ W_{ba} = \frac{\pi m k_p}{\hbar^2 c e_0} \int \cos^2 \theta \left| P_{ba} \right|^2 d\Omega = \text{total rate}. \]

Check units:

- \( k_f \): (energy/area/time)
- \( E_0 \): (energy/length)
- \( I(w) \): (energy/area)
- \( \hbar^2/m \): (energy/length)
- \( \gamma m c \): (time)

\[ = \frac{1}{\text{time } \gamma}. \]

We want to think about this as an (inelastic) scattering process for photons. \( W_{ba} \) is the number of events per time.

\[ W_{ba} = N = F \sigma, \quad F = \frac{I(w)}{\hbar c} \]

\( \sigma \): cross-section

\[ \sigma = \frac{\hbar c W_{ba}}{I(w)} = \frac{\pi m k_p}{\hbar^2 c e_0} \int \cos^2 \theta \left| P_{ba} \right|^2 d\Omega. \]

For the 1s state, the integrals that give \( P_{ba} \) are not too hard to do in closed form (cf. Bransden),

\[ \left| P_{ba} \right|^2 = \frac{8 e^2 h^2}{m^2 c^2 \pi^2} \left( \frac{Z}{\alpha_0} \right)^5 \frac{k_f^2}{\left[ (Z/\alpha_0)^2 + k_f^2 \right]^{5/2}}. \]

Assuming the final state is a perfect plane wave, as done here, it
Using \( a = \frac{e^2}{(4\pi \varepsilon_0) \frac{1}{c}} \) and assuming \( k_F^2 \gg (\frac{\pi}{a_0})^2 \), required by our high-energy assumption, we have

\[
\sigma(\omega) = 32\pi \left( \frac{\hbar}{\text{mv}} \right) \left( \frac{\omega}{k_F a_0} \right)^5 \int \cos^2 \theta \, d\Omega.
\]

We see that there is a very rapid increase with \( \omega \).

The differential cross-section is

\[
\frac{d\sigma}{d\Omega} = 32\pi \left( \frac{\hbar}{\text{mv}} \right) \left( \frac{\omega}{k_F a_0} \right)^5 \cos^2 \theta.
\]

Here \( \theta \) is the angle between \( \vec{B} \) and \( \vec{\omega} \).

\( \vec{B} \) is found to be in the direction of \( \vec{k}_F \)

(which makes sense since there is no other direction to use!),

choose the following coordinate system:

Let \( \vec{k}_F \) be described by polar angles

\[
(\Theta, \Phi) \quad k_F^2 = k_F \cos \Theta, \text{ etc.}
\]

Then \( \cos^2 \Theta = (\vec{k}_F \cdot \hat{\zeta})^2 = k_{Fx}^2 = \cos^2 \Phi \sin^2 \Theta \),

so unlike most of our previous examples, there is

a dependence on the azimuthal angle (for a polarized beam).
We see from the $\sin^2 \Theta$ dependence that the dominant outgoing electrons are at right angles to the incident photon beam. For unpolarized radiation, we average over $\hat{\Sigma}$. Note that $\hat{\Sigma}$ must be perpendicular to $\hat{\epsilon}$, the photon direction, so this is an average over the unit circle, or the unit sphere. Equivalently, we can average over $\hat{\epsilon}$ in the previous formula, so for unpolarized radiation

\[
\frac{d\sigma}{d\Omega} = 16 \pi \kappa \left( \frac{k}{m \omega} \right) (\frac{\epsilon}{k \epsilon_{\infty}})^5 \sin^2 \Theta.
\]

In our high-energy limit, $\frac{\hbar^2 k^2}{2m} \approx \frac{\hbar^2}{2m}$,

\[
\sigma(\epsilon) \approx \frac{16 \pi \sqrt{2}}{3} \kappa \left( \frac{\epsilon}{\epsilon_{\infty}} \right)^5 \left( \frac{\epsilon}{m \omega} \right)^{7/2},
\]

and the total cross-section decreases rapidly with increasing $\epsilon$. 

Imagine two states of an atom that are connected by the dipole operator, i.e., $\hat{V}_{ba} \neq 0$. Assume $E_b > E_a$ and consider the effects of light at frequency $\omega_{ba}$.

If we had a population of atoms all in the low-energy state, the light would drive some absorption transitions. The energy for there must come from the wave, so the light wave is weakened.

If the atoms were all initially in the high-energy state, there would instead be stimulated emission transition. There increase the strength of the light wave.

(Note: an intermediate case is the thermal equilibrium we calculated before. All three kinds of transitions take place, and the wave/cavity mode is, on average, neither strengthened or weakened.)

Why would it be useful to prepare a "population inversion" with more atoms in the high-energy state? The key is that stimulated emission is a "positive feedback" process:
since the rate is proportional to $I(w)$, and each
transition increases $I(w)$, we have

$$\frac{dI(w)}{dt} = \alpha I(w) \Rightarrow \text{exponential growth of the intensity.}$$

One way to understand why lasers are useful: they
do not create energy, of course, but input energy
over a long period of time can be output very rapidly
and concentrated to a very small spatial region.

Orders of magnitude for a modern tabletop laser:
1 J pulse in 1 fs ($10^{-15}$s) — quick enough to
observe chemical processes in real time.

How do we make the population inversion?

I. Conceptually simple and old-fashioned way:
find a way to physically separate an initial thermal
distribution. Pick out, using Stern–Gerlach for example,
only the excited atoms.

Actually this was first done (Townes et al.) using states
of the molecule NH$_3$. Resulting photons are microwave...
Modern way: "Pump" excited states of atoms, often in a solid.

Ruby: $\text{Cr}^{3+}$ in $\text{Al}_2\text{O}_3$

$\lambda = 5500 \, \text{Å}$ input (green)
$\lambda = 6940 \, \text{Å}$ output (red)

Idea: Green light causes $1 \rightarrow 3$ transition.

Most of the 3 atoms go through a "fast nonradiative decay" (result of solid-state physics) to level 2, allowing the $1 \rightarrow 3$ transition to continue. Once enough atoms are prepared in 2, a single photon will start the exponential growth of the light wave. Traditional lasers use a reflector cavity so that the light wave goes through the optical many times.

$\uparrow$ reflector $\uparrow$ partially transparent.
ATOMS IN STATIC ELECTRIC FIELDS: STARK EFFECT

Example of time-independent perturbation theory and dipole selection rules

To Stark, consider a H atom in an applied electric field \( E_\parallel \). Ignore fine structure (OK unless \( E \)-field splittings turn out to be smaller than fine structure splittings). The perturbation Hamiltonian is

\[
H' = -e\vec{D} = eE_\parallel z = -ED_\parallel
\]

Where \( \vec{D} = -e\vec{r} \), the dipole operator.

What does this do to the ground state (\( 1s \))? First-order: \( \langle 1s | z | 1s \rangle = 0 \). Why?

Well, our parity selection rule tells us that \( D_\parallel \) is only nonzero between states of different parity.

Second-order: "quadratic Stark effect"

\[
E_{100}^{(2)} = e^2E^2 \sum_{n \neq 1} \sum_{l,m} |K_{nlm} |21Y_{100} > |21Y_{100} > |^2
\]

Actually computing this requires a sum over bound states + an integral over the continuum. But, since quadratic
What about the $n=2$ levels? Now it is a bit more interesting. We start with 4 degenerate states: $2s$, $2p$

$m=0$ \quad m=1, m=0, m=-1.$

The dipole selection rule for the $z$ direction was $\Delta m = 0$, $\Delta l = \pm 1$.

Since $\Delta m = 0$, the $\psi_{210}$ and $\psi_{21-1}$ states are not connected to any other state, while $\psi_{210}$ and $\psi_{200}$ will be connected:

$$\langle \psi_{210} | z | \psi_{200} \rangle \neq 0.$$ 

The matrix of $H'$ between the subspace of $\{\psi_{210}, \psi_{200}\}$ then has the form

$$\begin{pmatrix} 0 & H'_{12} \\ H'_{21} & 0 \end{pmatrix}, \quad H'_{12} = \langle \psi_{210} | eEz | \psi_{200} \rangle \quad H'_{21} = \langle \psi_{210} | H' \psi_{200} \rangle.$$

The eigenvalue of this matrix are $E_+ = \pm |H'_{12}|$.

Using hydrogenic wavefunctions, an integration gives

$$H'_{12} = \frac{-3eE_0}{2}.$$
So the energy shifts are \( \pm \frac{Se E_0}{2} \).

There are linear in \( E \) and hence much larger than the quadratic shift of 1s. Note that \( e E_0 \) is the potential difference across the atom in the electric field.

The eigenfunctions are

\[
\chi_1 = \frac{1}{\sqrt{2}} \left( \psi_{200} - \psi_{210} \right)
\]

\[
\chi_2 = \frac{1}{\sqrt{2}} \left( \psi_{200} + \psi_{210} \right)
\]