1. **Tutorial on Fields & Potentials**

Potential due to one charged particle:

\[
\phi = \text{Electric Potential (Volts)} = \frac{\text{Joules}}{\text{Coul.}} = \frac{q}{\epsilon_0 \cdot R} \quad \text{(J)}
\]

- \(q\) = Charge in Coulombs \((C)\)
- \(R\) = Distance from particle in meters \((m)\)

\[
\frac{1}{\epsilon_0} = 9 \times 10^9 \quad \text{Jm} \over \text{C}^2
\]

**Electrostatic energy for 2 particles (Coulomb's law)**

\[
U = \text{Volts} \times \text{charge} = \frac{q_1 \cdot q_2}{\epsilon_0 \cdot R_{12}}
\]

Then when the 2nd particle has charge = \(e\)

\( q_2 = e = 1.6 \times 10^{-19} \text{ C} \)

\(U\) will be in \(eV\) electron Volts\n
\(1eV = 1.6 \times 10^{-19} \text{ J} \)

**Electric Field due to charged particle**

\[
E = \frac{Z}{\epsilon_0 \cdot R^2} = \frac{\text{Volts}}{\text{m}}
\]
Force on a charged particle = $\mathbf{E} \cdot \mathbf{q}$

Potential energy change when a particle with charge $q$ is moved distance $r$ in field $\mathbf{E}_0$.

$AV = \mathbf{E}_0 \cdot \mathbf{r} = \text{force} \times \text{distance}$.

This is also the energy of a dipole in a constant electric field:

$\mathbf{E} \cdot \mathbf{D} = \mathbf{E} \cdot \mathbf{m}$

where $\mathbf{m} = \mathbf{q} \mathbf{r}$.

Direction of the field vector is the direction that a positive charge is pushed.

For a single electron in an electric field, the perturbation is:

$W = \mathbf{E} \cdot \mathbf{r} + \text{constant}$

where $\mathbf{r} = \text{the position of the electron}$
Some reference points

Potential 1 Å away from a proton.

\[ \Phi = \frac{1.6 \times 10^{-19} \text{C}}{9.1 \times 10^{-10} \text{m}} \times \frac{(9 \times 10^9)(1.6 \times 10^{-19})}{1 \times 10^{-10}} = 1.44 \text{ volts} \]

Electric Field 1 Å from proton.

\[ \mathcal{E} = \frac{(9 \times 10^9)(1.6 \times 10^{-19})}{(1 \times 10^{-10})^2} = 14.4 \times 10^8 \frac{\text{Volts}}{\text{m}} = 14.4 \times 10^8 \text{ Volts/cm} \]

But at 10 Å from a proton:

\[ \Phi = 1.44 \text{ volts} \]

\[ \mathcal{E} = 14.4 \times 10^6 \text{ Volts/cm}. \]

The former case of \( \mathcal{E} \leq 10^9 \text{ Volts/cm} \) can obviously rip electrons away from atoms.
**Perturbation from light (dipole approximation)**

\[ W = \langle \vec{E}_0 \cos \omega t \rangle \cdot \vec{r} \text{ or } \mu \]

For plane polarized light, polarized \( \times \) electron

\[ |W_{\vec{r};i}| = e^2 |\vec{E}_0| |\vec{x}_{\vec{r};i}| = |E_0x| |\mu_{fi}|^2 \]

\( \vec{r} \) position of electron

where \( \mu_{fi} = \) electric transition dipole \( \text{moment} \)

\[ = e \langle f | \vec{x} | i \rangle \]

often abbreviated as "transition moment"

**Relating \( E_0^2 \) to intensity of light**

Energy density \( U_E = \frac{1}{2} |E_0|^2 \)

Intensity \( I = \frac{U_E c}{2} \) where \( c = \) speed of light.

Relate this to *Fermi Golden Rule*.

\[ \frac{P_{i\rightarrow f}}{\pi} = \frac{2\pi}{h^2} \left| W_{fi} \right|^2 \rho(\omega) \]

\( \rho(\omega) \) density of final states of molecule.
Here is where it gets tricky. Instead of doing the problem with one frequency of light and many final states of molecule, one may use the mathematically equivalent case of 1 final state of the molecule and many initial states (frequencies) of the light.

\[
\frac{P_{fi}}{t} = \frac{2\pi}{\hbar^2} \left| \frac{M_{fi}}{E_0} \right|^2 \omega \Rightarrow \frac{2\pi}{\hbar^2} M_{fi}^2 E_0^2 \omega
\]

\[
= \left( \frac{2\pi}{\hbar^2} \left| \frac{M_{fi}}{E_0} \right|^2 \frac{2}{E_0} \right) U_E(\omega)
\]

where \( U_E(\omega) = \text{Joules per unit } \omega \)

The quantity in parentheses is known as the Einstein B coefficient.

\[
\text{But since } \quad U_E(\omega) \text{ = Intensity } = I(\omega) \frac{J}{m^2 \text{s} (s^{-1})}
\]

Rate \( \left( i \rightarrow f \right) = \frac{4\pi}{\hbar^2} \left| \frac{M_{fi}}{E_0} \right|^2 \frac{I(\omega)}{c} \)
Consider a typical case

\[ x_{fi} \approx 0.1 \text{Å} = 10^{-11} \text{m} \]

so \[ |\mu_{fi}| = (6 \times 10^{-19} \text{m}^2)(10^{-11})^2 = 2.5 \times 10^{-28} \text{C m}^2 \]

laser pulse = \(10^{-3} \text{J}\) delivered in \(1 \text{ps}\)

and focused to area = \((10^{-6} \text{m})^2\)

Total \(I = \frac{10^{-3} \text{J}}{10^{-12} \text{m}^2 \cdot 10^{-12} \text{sec}} = 10^{21} \frac{\text{W}}{\text{m}^2}\)

But we need \(I(\omega)\). We showed before that temporal width will be \(\sim 33 \text{cm}^{-1}\) for \(1 \text{ps}\).

\[33 \text{cm}^{-1} \times 3 \times 10^{10} \text{cm/s} \Rightarrow \Delta \omega = 10^{12} \text{sec}^{-1}\]

or \(\Delta \omega = 6.28 \times 10^{12} \text{sec}^{-1}\)

\[
\begin{array}{c}
I(\omega) \\
\uparrow \\
\Delta \omega \\
\downarrow \omega \\
\end{array}
\]

\[
\text{area} = \int I(\omega) d\omega \approx \frac{I(\omega) \Delta \omega}{\text{max}} = I_{\text{max}} \\
\]

So

\[
\frac{I(\omega)}{I_{\text{max}}} = \frac{I_{\text{total}}}{\Delta \omega}
\]

\[
= 10^{21} \frac{\text{W/m}^2}{6 \times 10^{12} \text{s}^{-1}} = 1.6 \times 10^{8} \frac{\text{W}}{\text{m}^2 \text{s}^{-1}}
\]
This gives

\[ \text{rate (c\rightarrow f)} = \frac{(4\pi)(2.5 \times 10^{-60})(4\pi \times 9 \times 10^9)}{(105 \times 10^{-34})^2} \times 10^8 \]

\[ = 1.07 \times 10^{20} \text{ transitions/sec} . \]

Seems too large!

Check this number with the rate found from Beer's Law:

\[ dI = -2.3 \varepsilon CI dx \]

where \( \varepsilon = \frac{L}{\text{mol cm}^{-1}}, \ C = \text{mol/L} \ \ dx = \text{cm}, \ I = \text{intensity} \)

\[ I = \frac{J}{\text{cm}^2 \ \text{sec}}. \]

Integrating gives the familiar

\[ \frac{I}{I_0} = e^{-2.3 \varepsilon C l} \]

\[ A = \text{Absorbance} = -\log \frac{I}{I_0} . \]

Starting again with the first form:

\[ \frac{dI}{h^2} = -2.3 \varepsilon \left( \frac{N}{V} \right) (Adx) \left( \frac{10^3}{6 \times 10^3} \right) \cdot \left( \frac{I}{h^2} \right) \]

where \( A = \text{area of beam (cm}^2) \)

\[ N = \text{molecules cm}^{-3}, \ \frac{I}{h^2} = \text{photon flux cm}^{-2} \]

\[ \text{photons/sec} \]

\[ \text{= Total rate}. \]
\[
\text{Rate} \quad \frac{\text{molecule}}{\text{mol}} = \frac{2.3 \times 10^3}{6 \times 10^{22}} \cdot F
\]

\[
= 6 \left(\text{cm}^2\right) \frac{F}{\text{(photons cm}^2\text{s}^-1)}
\]

\[
\text{Cross section} = 0.383 \times 10^{-20} \text{ cm}^2
\]

For \( E = 10 \text{ MeV} \), \( \sigma = 4 \times 10^{-17} \text{ cm}^2 \)

Consider green light, \( \lambda = 500 \text{ nm} \), \( \bar{v} = 20,000 \text{ cm}^{-1} \)

\[
\frac{20,000 \text{ cm}^{-1}}{8000 \text{ cm}^{-1}/\text{eV}} = 2.5 \text{ eV}
\]

\[
2.5 \text{ eV} \times 1.6 \times 10^{-19} \text{ J/ev} = 4 \times 10^{-19} \text{ J/atom} = \text{ eV}
\]

\[
\text{Photo flux} = F = \frac{10^{-3} \text{ J}}{(10 \text{ cm})^2 \cdot 10^{-12} \text{ s}} = \frac{10^{17} \text{ J}}{4 \times 10^{-19} \text{ J/atom}} = 0.25 \times 10^{36} \text{ photons cm}^2 \text{s}^{-1}
\]

\[
\text{Rate} \quad \frac{\text{molecule}}{\text{mol}} = \frac{4 \times 10^{-19} \text{ cm}^2}{\text{molecule}} \cdot \frac{0.25 \times 10^{36} \text{ photons}}{\text{cm}^2 \text{s}}
\]

\[
= 1 \times 10^{19} \text{ transitions/second molecule}
\]

Agrees!!

End
Oscillating Perturbation

\[ W(t) = W_0 \cos(\omega t') \]

\[ b(t) = -\frac{i}{\hbar} \int_0^t \hat{W}_{fi}(t') e^{i\omega_{fi} t'} dt' \quad B-20 \]

\[ \cos(\omega t') = \frac{e^{i\omega t'} + e^{-i\omega t'}}{2} \]

\[ b''(t) = -\frac{iW_0}{\hbar} \int_0^t \left( \frac{e^{i(\omega_{fi} + \omega)t'} + e^{i(\omega_{fi} - \omega)t'}}{2} \right) dt' \]

The integral is non-zero (effectively) only when \( \omega_{fi} - \omega \neq 0 \) in 2nd term (\( \omega_{fi} \& \omega \) both +) or if \( \omega_{fi} + \omega \neq 0 \) in 1st term (if \( \omega_{fi} \& \omega \) are opposite signs)

In either case, the integral becomes

\[ b''(t) = -\frac{iW_0}{\hbar} \int e^{i\Delta\omega t'} dt' = -\frac{iW_0}{\hbar} \left( e^{i\Delta\omega t} - 1 \right) \quad \frac{t}{i\Delta\omega \hbar} \]

\[ |b(t)|^2 = \frac{W_0}{(\hbar \Delta\omega)^2} \left( 4 \sin^2 \left( \frac{\Delta\omega t}{2} \right) \right) \]

i.e. as with constant \( \omega_{fi} \) with \( \omega_{fi} \to \Delta\omega = \omega_{fi} - \omega \)

so, Now need \( \omega_{fi} = \omega \) instead of \( \omega_{fi} = 0 \)