NB 2: The photophysics

Is hidden in $\sigma$

(So we haven’t done much yet)

**Einstein Coefficient**

$P_{i\rightarrow f} = n_f g_f B_{if} \rho(v_f)$

- # of transitions / second:
- # of molecules
- degeneracy
- Radiation density
  - # of photons/unit freq.

$B_{if} = \left( \frac{8\pi^3}{3\hbar^2 c} \right) \mathfrak{R}_{if} \psi_i^* \psi_f \mathrm{d}t$

Amplitude of transition moment

$\mathfrak{R}_{if} = \int_{-\infty}^{\infty} \psi_i^* \dot{M} \psi_f \mathrm{d}t$

$P_{i\rightarrow f} = n_f g_f B_{if} \rho(v_f)$

$P_{f\rightarrow i} = n_i g_i B_{fi} \rho(v_i)$

$B_{if} = B_{fi}$

$P_{i\rightarrow f} = n_f g_f B_{if} \rho(v_f)$

$P_{f\rightarrow i} = n_i g_i B_{fi} \rho(v_i)$

$\sum g_n n_n \leq 1$

- No population inversion!
- $A \rightarrow B \rightarrow g_n n_f \rightarrow g_f n_i$
- Large $\rho \rightarrow$ Saturation: $g_n n_f = g_f n_i$

Two-level atom

Three-level Laser

Four-level Laser
YAG laser

Oscillator strength

\[ f_r = 1 \text{ for an ideal electron} \]

\[ f_r = 4.32 \times 10^{-9} \left( \frac{e(\nu)d\nu}{\nu} \right) \]

\[ f_r = 1 \rightarrow e_{\text{max}}\Delta \nu \approx 2.5 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-2} \]

Molecule: \( \Delta = 5000 \text{ cm}^{-1} \rightarrow e_{\text{max}} = 10^5 \text{ L mol}^{-1} \text{ cm}^{-1} \)

Atom: \( \Delta = 0.5 \text{ cm}^{-1} \rightarrow e_{\text{max}} = 10^5 \text{ L mol}^{-1} \text{ cm}^{-1} \)

(When fully allowed)
Other interactions

Magnetic interaction of B with charge:
≈ \( \frac{1}{137} \) of electric interaction of E

(fine structure constant: \( e^2/hc = 1/137.036 \))

→ Magnetic dipole \( \approx 10^{-4} \) – \( 10^{-5} \) compared to electric dipole

Spatial variation:
Operators \( qx^2, qxy \), etc.

\( \lambda \approx 10^3 \) times the size of an atom

→ Electric quadrupole \( \approx 10^{-6} \) compared to electric dipole

Lifetimes

Einstein coefficients are rate constants

\[ \tau_0 = \frac{1}{4g} \]

\[ = \frac{3.3 \times 10^6}{E^2} \int \varepsilon(v) \, dv \]

\[ \approx \frac{1.4}{E^2} \]

\[ t_n = 4.32 \times 10^{-7} \varepsilon(v) \, dv \]

\( = 1 \) when fully allowed

UV at 30,000 cm\(^{-1} \) → \( \tau_0 \subseteq 1.6 \times 10^{-9} \) sec

Contributions to excited state lifetime

- Natural lifetime
- Pressure broadening
- Saturation broadening
- Doppler broadening

NB: \( f(v) \) in a gas is Gaussian

→ Doppler line shape is Gaussian

\[ \propto Ce^{-d(v-v_0)^2} \]
Line shapes (cont):
Homogeneous vs inhomogeneous

- Inhomogeneous line shape:
  - All molecules behave differently (distribution)
  - Gaussian line shape
  - Examples are:
    - Doppler broadening
    - Power broadening

Transition dipole moment:
\[ \mu_{\text{f}\rightarrow\text{i}} = \int_{-\infty}^{\infty} \psi^* \mathbf{M} \psi \, dt \]

Dipole moment operator:
\[ \hat{\mathbf{M}} = \hat{\mathbf{M}}_e + \hat{\mathbf{M}}_n \]
\[ \hat{\mathbf{M}}_e = \sum_p \mathbf{r}_p \hat{\mathbf{e}}_p \]
\[ \hat{\mathbf{M}}_n = \sum_i \mathbf{z}_i \hat{\mathbf{a}}_i \]

(contains coordinates of electrons and nuclei
And on time)
oscilates with:

\[ \frac{\mu}{E} \approx \frac{\hbar c}{\lambda} \]

\[ \nu = \frac{E_f - E_i}{\hbar} \approx \frac{\hbar c}{\lambda} \]

\[ \Delta E = \hbar \nu \]

\( \Rightarrow \Delta E = \hbar \nu \)

\( \mu \) oscillates with:

Bohr frequency

\( \nu = \frac{E_f - E_i}{\hbar} \)

\[ \rho \Rightarrow \Delta E = \hbar \nu \]

NB: Resonant frequency

Compare to IR:

\[ 2000 \text{ cm}^{-1} \rightarrow \nu = \frac{c}{\lambda} = \left(3 \times 10^7 \right) \text{ cm}^{-1} \]

\[ = 6 \times 10^{13} \text{ s}^{-1} \]

Electronic motion

Dipole moment operator \( \neq \mathbf{f}(t) \)

\[ \mu_{\nu} = \int_{-\infty}^{\infty} \psi_{\nu}^* \vec{M} \psi_{\nu} \cdot d \tau \psi_{\nu} \cdot e^\epsilon \]

\[ \approx \frac{6 \times 10^{-19}}{6 \times 10^{14}} = 10^{15} \text{ s}^{-1} \]

Nuclear motion is 2 orders of magnitude slower than electronic motion

\[ \psi_{\nu} = \psi_{\nu} \psi_{\nu} \]

Born-Oppenheimer approximation

\( \Rightarrow \Delta E = \hbar \nu \)

Max Born (1882-1970)

\( pq - qp = \hbar/2\pi \)

Ovia Newton-John

Max Delbrück

Walter Elsasser

Friedrich Hund

Maria Goeppert-Mayer

Lothar Wolfgang Nordheim

J. Robert Oppenheimer

Victor Weisskopf.

Enrico Fermi

Werner Heisenberg

Gerhard Herzberg

Friedrich Hund

Pascual Jordan

Wolfgang Pauli

Léon Rosenfeld

Edward Teller

Eugene Wigner

The Russell-Einstein Manifesto

Issued in London, 9 July 1955

Bertrand Russell and Albert Einstein

Max Born

Percy W. Bridgman

Albert Einstein

Leopold Infeld

Frederic Joliot-Curie

Herman J. Muller

Linus Pauling

Cecil F. Powell

Joseph Rotblat

Bertrand Russell

Niels Bohr

There lies before us, if we choose, continual progress in happiness, knowledge, and wisdom. Shall we, instead, choose death, because we cannot forget our quarrels? We appeal as human beings to human beings: Remember your humanity, and forget the rest. If you can do so, the way lies open to a new Paradise; if you cannot, there lies before you the risk of universal death.

Resolutions:

WE invite this Congress, and through it the scientists of the world and the general public, to subscribe to the following resolution:

"In view of the fact that in any future world war nuclear weapons will certainly be employed, and that such weapons threaten the continued existence of mankind, we urge the governments of the world to realize, and to acknowledge publicly, that their purpose cannot be furthered by a world war, and we urge them, consequently, to find peaceful means for the settlement of all matters of dispute between them."

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Max Born (physics 1954)
Percy W. Bridgman (physics 1946)
Albert Einstein (physics 1921)
Leopold Infeld
Frederic Joliot-Curie (physics 1935)
Herman J. Muller (physiology or medicine 1946)
Linus Pauling (chemistry 1954, peace 1962)
Cecil F. Powell (physics 1950)
Joseph Rotblat (peace 1995)
Bertrand Russell (literature 1950)

It's the psychology of war,' said Joseph Rotblat. 'Once we enter war, our moral values are thrown overboard. We are encouraged to kill people. Even people who in the past had been friends became, in our minds, our mortal enemies.'

Max Born (1882-1970)

\[
\mu_{\nu \gamma} = \int_{-\infty}^{\infty} \psi_{\nu}^* \hat{M} \psi_{\gamma} d\tau 
\]

Orthogonal (no overlap)

\[
= e^{i \frac{\hbar}{2} \int \psi_{\nu}^* \sum_{\nu} \psi_{\gamma} d\tau} \int_{-\infty}^{\infty} \psi_{\nu}^* \psi_{\gamma} d\tau
\]
tells if allowed or forbidden: must be symmetric \(
\rightarrow \) selection rules

Franck-condon factors

In an atom:
\[
\Delta l = 0 \quad 1s \\
\Delta l = 1 \quad 2s
\]

\[
\int (2p) \psi_{1s}^* d\tau = 0 \\
\int (2p) \psi_{1s}^* d\tau = 1
\]

forbidden allowed
One more parameter.

**Spin**

<table>
<thead>
<tr>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td>+½</td>
<td>-½</td>
</tr>
</tbody>
</table>

**Orthonormal:**

- \[ aαd = \int ββds = 1 \]
- \[ aβd = \int βαds = 0 \]

No spin flips!

**Pauli principle**

\[ ψ(\mathbf{r}_1, \mathbf{r}_2) = ψ(\mathbf{r}_1)ψ(\mathbf{r}_2) \pm ψ(\mathbf{r}_2)ψ(\mathbf{r}_1) \]

Minus sign for fermions.

So if \( ψ(\mathbf{r}_1) = ψ(\mathbf{r}_2) \) then \( ψ(\mathbf{r}_1, \mathbf{r}_2) = 0 \)!!

**NB:** \( ψ(\mathbf{r}_1, \mathbf{r}_2) = -ψ(\mathbf{r}_2, \mathbf{r}_1) \)

If we can separate space and spin (no spin-orbit coupling): 

\[
(\mathbf{μ}_i)_{α} = e\int_{-∞}^{∞} \sum_{p} \psi^*_p \sum_{r} \psi_{r,w} \, dr \, dt_i \int_{-∞}^{∞} \psi^*_w \psi_{r,w} \, dr \, dt_i
\]