Interaction of light with matter: Quantum mechanical treatment

What happens if $\mathcal{H}$ is not time-dependent?

Then the wavefunction $\psi(r_1, r_2, \ldots; t)$ could be written as a product of two functions, one that depends on the spatial coordinates of the system and a second function that depends on time.

$$\psi(r_1, r_2, \ldots; t) = \Phi(r_1, r_2, \ldots) \, T(t)$$

Substituting into time-dependent Schroedinger equation

$$\mathcal{H} \psi = (i \hbar) \frac{\partial \psi}{\partial t}$$

where $\hbar = h / 2\pi$ and

$\mathcal{H}$ is the Hamiltonian for the problem that we are trying to solve, and it could be time-dependent.
Divide by $\Phi(r_1, r_2, \ldots) T(t)$:

$$T(t) \left[ \mathcal{H} \Phi(r_1, r_2, \ldots) \right] / \left[ \Phi(r_1, r_2, \ldots) T(t) \right] = (i \hbar) \Phi(r_1, r_2, \ldots) \left[ \frac{\partial T(t)}{\partial t} \right] / \left[ \Phi(r_1, r_2, \ldots) T(t) \right]$$

or

$$\left[ \mathcal{H} \Phi(r_1, r_2, \ldots) \right] / \left[ \Phi(r_1, r_2, \ldots) \right] = (i \hbar) \left[ \frac{\partial T(t)}{\partial t} \right] / [T(t)]$$

Left-hand side is a function of the spatial coordinates of the system only; and the right-hand side is a function of time only. The equality applies for all $r_1, r_2, \ldots$ and all times. So the two sides must be equal to some constant. I pick a real number and call it $\lambda$. So we have

$$\left[ \mathcal{H} \Phi(r_1, r_2, \ldots) \right] / \left[ \Phi(r_1, r_2, \ldots) \right] = (i \hbar) \left[ \frac{\partial T(t)}{\partial t} \right] / [T(t)] = \lambda$$

We end up with 2 differential equations!

(1) $$\left[ \mathcal{H} \Phi (r_1, r_2, \ldots) \right] = \lambda \left[ \Phi (r_1, r_2, \ldots) \right]$$

which is just the time-independent Schroedinger equation if we set $\lambda = E_n$ and $\Phi = \Phi_n$.

(2) $$\left( i \hbar \right) \left[ \frac{\partial T(t)}{\partial t} \right] = \lambda \left[ T(t) \right]$$

Solution:

$$T(t) = \exp - i (\lambda / \hbar) t = \exp - i (E_n / \hbar) t = \exp - i \omega_n t$$

if we set $\lambda = E_n$ and $E_n = \hbar \omega_n$

So, time-dependent wavefunctions for stationary states

$$\Psi_n(r_1, r_2, \ldots, t) = \Phi_n(r_1, r_2, \ldots) \exp - i (E_n / \hbar) t = \Phi_n(r_1, r_2, \ldots) \exp - i \omega_n t$$

standing waves!
Need to solve the time-dependent Schröedinger equation for problem because the potential energy is now time-dependent!

\[ \mathcal{H} \psi = (i \hbar) \left( \frac{\partial \psi}{\partial t} \right) \]

where \( \hbar = h / 2\pi \)

\[ \mathcal{H} = \mathcal{H}^0_{\text{isolated molecule}} + V(t) \]

where \( V(t) \) describes the interaction of electrons with the light wave.

Assume one electron.

If interaction is electrical, then

\[ V(t) = - \mu_{\text{el}} \cdot \mathbf{E}^*(v,t) \]

If interaction is magnetic, then

\[ V(t) = - \mu_{\text{mag}} \cdot \mathbf{B}^*(v,t) \]
Focus on electrical interaction, where $\mu_{el} = -|e| \vec{r}$

Treat for simplicity a two-level system:

\[
\begin{align*}
  b & \quad W_b, \quad \Psi_b(\vec{r},t) \\
  a & \quad W_a, \quad \Psi_a(\vec{r},t)
\end{align*}
\]

\[
\Psi_b(\vec{r},t) = \Phi_b(\vec{r}) e^{-i\omega_b t} \\
\Psi_a(\vec{r},t) = \Phi_a(\vec{r}) e^{-i\omega_a t}
\]

Stationary states: Solutions to time-dependent Schrödinger equation for $V(t) = 0$

\[
W_b = \hbar \omega_b, \quad W_a = \hbar \omega_a, \text{ where } \hbar = \frac{h}{2\pi}
\]

In the presence of $V(t)$,

\[\Psi(\vec{r},t)\] must be a linear combination of these states, but the coefficients $C_a$ and $C_b$ must be time-dependent.

That is,

\[
\Psi(\vec{r},t) = C_a(t) \Psi_a(\vec{r},t) + C_b(t) \Psi_b(\vec{r},t)
\]

Substituting this solution into the time-dependent Schrödinger equation, we obtain

\[
i\hbar \left( \frac{dC_a}{dt} \right) = V_{aa} C_a(t) + V_{ab} C_b(t) e^{-i(\omega_b - \omega_a)t}
\]

\[
i\hbar \left( \frac{dC_b}{dt} \right) = V_{ba} C_a(t) + V_{bb} C_b(t) e^{-i(\omega_a - \omega_b)t}
\]

where

\[
V_{aa} = (\int \Phi_a^*(\vec{r}) V(t) \Phi_a(\vec{r}) \, d\vec{r})
\]

\[
V_{ab} = (\int \Phi_a^*(\vec{r}) V(t) \Phi_b(\vec{r}) \, d\vec{r})
\]

\[
V_{bb} = (\int \Phi_b^*(\vec{r}) V(t) \Phi_b(\vec{r}) \, d\vec{r})
\]

A set of coupled first-order differential equations!
If we take \( V(t) = -\tilde{\mu} \cdot \vec{E}_0^* e^{i\omega t} \)
where \( \tilde{\mu} = -|\epsilon| \vec{r} \)
then, \( V_{aa} = 0 \), and \( V_{bb} = 0 \), and

\[
\begin{align*}
- i \hbar \left( \frac{dC_a}{dt} \right) &= C_b(t) \mu_{ab} \cdot \vec{E}_0^* e^{-i(\omega_{ba}-\omega)t} \\
- i \hbar \left( \frac{dC_b}{dt} \right) &= C_a(t) \mu_{ba} \cdot \vec{E}_0^* e^{-i(\omega_{ab}-\omega)t}
\end{align*}
\]

where \( W_b - W_a = \hbar \omega_{ba} \), \( W_a - W_b = \hbar \omega_{ab} \)

Solving simultaneously, with boundary condition \( |C_b(0)|^2 = C_b(0) \ast C_b(0) = 0 \) at \( t = 0 \); i.e., electron is in quantum state \( a \) at \( t = 0 \),

and for small \( E_{0}^* \),

\[
|C_b(t)|^2 = \frac{\sin^2[\omega_{ba} - \omega]t/2}{2 [(\omega_{ba} - \omega)t/2]^2}
\]

where

\[
\begin{align*}
\mu_{ba} &= \int \Phi_b(r)^* \tilde{\mu} \Phi_a(r) \, dr \\
\mu_{ab} &= \int \Phi_a(r)^* \tilde{\mu} \Phi_b(r) \, dr
\end{align*}
\]

Now, the rate at which molecules in state \( a \) are transformed to state \( b \) by the presence of light is given by

\[
\frac{dP_b}{dt} = \frac{d}{dt} \left[ \int |C_b(t)|^2 \, dv \right] \\
= \frac{1}{2\hbar^2} |\mu_{ba} \cdot \vec{E}_0^*|^2
\]
Customary to write

\[
dP_b/dt = B_{ab} I(\nu)
\]

where \( B_{ab} \) is the transition rate per unit energy density of radiation, and \( I(\nu) \) is the energy density incident on the sample at frequency \( \nu \).

From E&M, \( I(\nu) = |E_o^*|^2 / 4\pi \).

So, \( B_{ab} = (2\pi/\hbar^2) |\mu_{ba}|^2 \cos^2 \theta \)
where \( \theta \) is the angle between \( \vec{\mu} \) and \( \vec{E_o}^* \).

Above result for \textbf{oriented} molecules illuminated by polarized light.
In solution, molecules reorient with respect to \( \vec{E_o}^* \), so must average \( \cos^2 \theta \).
Since \( \cos^2 \theta = \frac{1}{3} \),

\[
B_{a\rightarrow b} \text{(solution)} = (2\pi/3 \hbar^2) |\mu_{ba}|^2
\]

The rate at which energy is removed from light will depend on the number of \( a \rightarrow b \) absorption transitions stimulated by light, on the number of \( b \rightarrow a \) emission transitions (also stimulated by light), and on the energy of the photon \( (W_b - W_a = \hbar \omega_{ba} = \hbar \nu_{ba}) \).

\[- \frac{d I(\nu)}{dt} = \hbar \nu (N_a B_{ab} - N_b B_{ba}) I(\nu)\]
where \( N_a \) and \( N_b \) are the number of molecules per cm\(^3\) in state \( a \) and \( b \), respectively; and \( I(\nu) \) is the energy density of light incident on the sample at frequency \( \nu \).
Beer-Lambert’s Law

For optical transitions, $N_b$ is negligible.

$$- \frac{d l(\nu)}{dt} = h \nu N_a B_{ab} l(\nu) = h \nu (10^{-3}) c N_A B_{ab} l(\nu)$$

$c$ is the concentration of absorbers (all in state $a$) in moles /1000 cm$^3$.

Now, $- \frac{d l(\nu)}{dl} = - \left( \frac{d l(\nu)}{dt} \right) \left( \frac{dt}{dl} \right)$

$$= - \left( \frac{1}{c_{light}} \right) \left( \frac{d l(\nu)}{dt} \right)$$

$$= \left( \frac{h \nu}{c_{light}} \right)(10^{-3}) c N_A B_{ab} l(\nu)$$

Reading assignment

James P. Allen, Chapter 9, pp. 175-195.

Suggested reading

Eisenberg and Crothers (EC), Chapter 12, pp. 535-546.