The Need for Quantum Mechanics in Molecular Spectroscopy

Interaction of Light with Matter

What have we learned from classical physics so far?

(1) There must be an interaction between the charges in a molecule and the light.

• A charge or a set of charges that interact with the E-field of the light wave:

\[
\text{Force} \quad \sum q_i |e| E
\]

\[
\text{Energy of interaction} \quad - \sum q_i |e| (r_i \cdot E) = - \mu \cdot E
\]

where \( \mu \) is the electric dipole moment of the system.  \([\cdot \equiv \text{dot product}]\)

(2) Exchange of energy between the molecule and the light wave (absorption and emission of light) can only occur when the frequency of the light wave is equal to the resonance frequency of the interacting charge or charges:

\[
\omega = \omega_o (\text{radians/sec})
\]

where or \( \omega = 2\pi \nu \) and \( \nu \) is the frequency of the light wave in Hz; \( \omega_o = 2\pi \nu_o \) is the resonance frequency of the interacting charge(s).

In principle, there could be many resonances, corresponding to electrons with different force or “spring” constants (k) in the classical picture.

Note that

\[
\omega = \omega_o (\text{radians/sec})
\]

\( \nu \lambda = c \), where \( c \) is the speed of light.

Speed of light in vacuum = \( 2.99792 \times 10^8 \) m/s

or 3 \times 10^{10} \text{ cm/s}

Speed of light in a medium of refractive index \( n \)

\( = c/n \)
Since light is an electromagnetic wave, there is also a time-dependent magnetic field associated with the light wave: \( H(t) = H_0 \cos \omega t \) at each point in space where there is an E field associated with the light \( (E(t) = E_0 \sin \omega t) \). The magnetic and electric components \( H(t) \) and \( E(t) \) are orthogonal and out of phase. In light of this, it follows then that there can be spectroscopy arising from interaction between a magnetic dipole in a molecule with the \( H \) field of light.

\[ \text{Torque: } \mu_m \times H(t) \quad [\times \equiv \text{cross product}] \]

\[ \text{Energy of interaction: } - \mu_m H(t) \]

Example of this kind of spectroscopy: NMR and EPR.

Next question: What are the resonances in the absorption or emission of light by a molecule?

These resonances are the transitions of a molecule among its electronic, vibrational, and rotational energy levels.

Since these energy levels are quantized in a molecule, we must appeal to quantum mechanics to obtain these resonances.

Energy of an isolated molecule:

Consider an isolated molecule in a vacuum or a very dilute gas (infinite dilution). This could be a small molecule, or a fully hydrated bio-macromolecule, such as a protein or nucleic acid. The energy of the molecule (\( \varepsilon \)) can be approximated by

\[ \varepsilon_{\text{molecule}} = \varepsilon_{\text{nuclear}} + \varepsilon_{\text{electronic}} + \varepsilon_{\text{vibrational}} + \varepsilon_{\text{rotational}} + \varepsilon_{\text{translational}} + \varepsilon_{\text{nuclear spin}} \]

where

\[ \Delta \varepsilon_{\text{nuclear}} \gg \Delta \varepsilon_{\text{electronic}} \gg \Delta \varepsilon_{\text{vibrational}} \gg \Delta \varepsilon_{\text{rotational}} \gg \Delta \varepsilon_{\text{translational}} > > \Delta \varepsilon_{\text{nuclear spin}} \]
Typically, the rotational and translational energy levels for a large molecule are so closely spaced ($\Delta\varepsilon_{\text{rotational}}$ and $\Delta\varepsilon_{\text{translational}}$ between adjacent levels are very small) and so densely packed that we may assume that these energy states form a continuum.

In contrast, the excited nuclear energy states and electronic states are so widely separated that excited states associated with these degrees of freedom are normally not accessible under ambient conditions. In other words, only the ground states are occupied.

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**Various forms of Spectroscopy**

**Where does it occur?**

<table>
<thead>
<tr>
<th>Frequency</th>
<th>X-ray</th>
<th>UV/Vis</th>
<th>Infrared</th>
<th>Far Infrared</th>
<th>Microwave</th>
<th>Radio</th>
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</thead>
<tbody>
<tr>
<td>Transition</td>
<td>Electronic</td>
<td>Vibration</td>
<td>Rotation</td>
<td>Nuclear</td>
<td>/Electron spin</td>
<td>spin</td>
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</table>

<table>
<thead>
<tr>
<th>Spectrometer</th>
<th>X-ray</th>
<th>UV/VIS/Raman</th>
<th>Infrared</th>
<th>Microwave/EPR</th>
<th>NMR</th>
<th>Fluorescence</th>
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</table>
The energy levels of a molecule are obtained by solving the Schrödinger Equation in quantum mechanics.

We express the energy of electrons and atoms in a molecule in the form of the Hamiltonian ($\hat{H}$) as follows:

$$\hat{H}_{\text{isolated molecule}} (p_1, r_1; p_2, r_2; .. p_i, r_i; ..)$$

$$= \Sigma_i \frac{p_i^2}{2m_i} + V(r_1; r_2;.. r_i;...)$$

where $p_i$, $r_i$ and $m_i$ refer to the momentum, coordinates, and the mass of the $i$th particle (electrons and nuclei), respectively.

Typically for a molecule

$$V(r_1; r_2;.. r_i;...)$$

$$= \Sigma_N \Sigma_k (-z_N e^2/r_{NK}) \quad \text{(coulomb attraction between nuclei and electrons)}$$

$$+ \Sigma_{k'\neq k} (e^2/r_{kk'}) \quad \text{(electrostatic repulsion between electrons)}$$

$$+ \Sigma_{N'\neq N} z_N z_{N'} e^2/R_{NN'} \quad \text{(nuclear-nuclear repulsion)}$$

An example: The Hydrogen Molecule

Where $\Sigma_k$ denotes sum over all electrons; and $\Sigma_N$ denotes sum over all nuclei in the molecule.
We obtain the energy levels by solving the following operator equation:
\[ \hat{H} \Phi_n (r_1, r_2, \ldots r_i, \ldots) = E_n \Phi_n (r_1, r_2, \ldots r_i, \ldots) \]
where \( \hat{H} \) is the hamiltonian operator for the molecule, \( E_n \) is the energy for one of the energy states (denoted by the quantum \( n \)) and \( \Phi_n \) is the wavefunction for that particular energy state.

\[ \Phi_n^*(r_1, r_2, \ldots r_i, \ldots) \Phi_n (r_1, r_2, \ldots r_i, \ldots) \]
gives the probability of finding the particles at positions \((r_1, r_2, \ldots r_i, \ldots)\).

A note on the complex conjugate

A complex number: \( a + i b \) \( (i = \sqrt{-1}) \)

Complex conjugate: \( a - i b \)

\[ e^{i\theta} = \cos \theta + i \sin \theta \]
\[ e^{-i\theta} = \cos \theta - i \sin \theta \]

Note that \((a + i b)(a - i b) = e^{i\theta} e^{-i\theta} = a^2 + b^2 = 1.\)

Since each of the \( p_i^2/2m_i \) operators in the Hamiltonian operator \( \hat{H} \) is

\[ - \left( \frac{\hbar^2}{2m_i} \right) \nabla_i^2 \]

where \( \nabla_i^2 = \partial^2/\partial x_i^2 + \partial^2/\partial y_i^2 + \partial^2/\partial z_i^2 \),

the operator equation

\[ \hat{H} \Phi_n (r_1, r_2, \ldots r_i, \ldots) = E_n \Phi_n (r_1, r_2, \ldots r_i, \ldots) \]
corresponds to the differential equation

\[ - \sum_i \left( \frac{\hbar^2}{2m_i} \right) \Phi_n (r_1, r_2, \ldots r_i, \ldots) + V(r_1; r_2; \ldots r_i; ...) \Phi_n (r_1, r_2, \ldots r_i, \ldots) = E_n \Phi_n (r_1, r_2, \ldots r_i, \ldots) \]

Wavefunctions

Since \( \Phi_n^*(r_1, r_2, \ldots r_i, \ldots) \Phi_n (r_1, r_2, \ldots r_i, \ldots) \) gives the probability of finding the particles at positions \((r_1, r_2, \ldots r_i, \ldots)\),

\[ \int v \Phi_n^*(r_1, r_2, \ldots r_i, \ldots) \Phi_n (r_1, r_2, \ldots r_i, \ldots) \, dr_1dr_2\ldots \]

\[ = \int v \Phi_n^*(r)\Phi_n (r) \, d\tau \quad = \quad 1 \]

Total probability of finding the system in the space is unity.

[Wavefunctions that satisfy this condition are said to be normalized.]
Also, one can show that
\[ \int \Phi_n^*(r) \Phi_m(r) \, d\tau = 0 \]
if \( n \) and \( m \) belong to quantum states of different energies, that is, \( \Phi_n \) and \( \Phi_m \) are wavefunctions for quantum states with different energies.

[Wavefunctions belonging to different quantum states of different energies are orthogonal.]

### Stationary states

The \( \Phi_n, \Phi_m \) are solutions of the time-independent Schröedinger equation
\[
- \sum_i \left( \frac{\hbar^2}{2m_i} \right) \nabla_i^2 \Phi_n (r_1, r_2, \ldots r_i, \ldots) + V(r_1, r_2; \ldots r_i; \ldots) \Phi_n (r_1, r_2, \ldots r_i, \ldots) = E_n \Phi_n (r_1, r_2, \ldots r_i, \ldots)
\]
because \( V(r_1, r_2; \ldots r_i; \ldots) \) is time-independent. These solutions are called the stationary states of the problem. For stationary states, the probabilities are independent to time.

If I had solved the time-dependent Schröedinger equation (see later), the time-dependent wavefunctions would have been
\[
\Psi_n(r, t) = \Phi_n (r_1, r_2, \ldots r_i, \ldots) \exp\left(-i\frac{E_n}{\hbar}t\right)
\]
\[
\Psi_m(r, t) = \Phi_m (r_1, r_2, \ldots r_i, \ldots) \exp\left(-i\frac{E_m}{\hbar}t\right)
\]
and so on, but
\[
\Psi_n^*(r, t) \Psi_n(r, t) = \Phi_n^*(r) \Phi_n(r) \exp\left(i\frac{E_n}{\hbar}t\right) \exp\left(-i\frac{E_n}{\hbar}t\right)
\]
\[
= \Phi_n^*(r) \Phi_n(r) \quad \text{(independent of time)}
\]

### Simple examples of quantum mechanics

- A particle in an one-dimensional box
- One-dimensional harmonic oscillator
The Hamiltonian

The Hamiltonian ($\hat{H}$) is the sum of the kinetic energies and potential energies associated with an atomic and molecular system:

$$\hat{H}_{\text{isolated molecule}} (p_1, r_1; p_2, r_2; ..., p_i, r_i; ...)$$

$$= \sum_i \frac{p_i^2}{2m_i} + V(r_1; r_2; ...; r_i; ...)$$

where $p_i$, $r_i$ and $m_i$ refer to the momentum, coordinates, and the mass of the $i$th particle (electrons and nuclei), respectively.

A particle in an one-dimensional box

$$\hat{H}_{\text{particle}} (\vec{p}, \vec{r})$$

$r = x$ in one dimension

$$= \frac{p_x^2}{2m} + V(x)$$

$V(x)$:
- $V(x) = 0$ within the box ($0 \leq x \leq L$)
- $V(x) = \infty$ outside the box ($x \leq 0; \ x \geq L$)

Potential energy

Schroedinger equation (time-independent)

We obtain the energy levels by solving the following operator equation:

$$\hat{H} \Phi_n (x) = E_n \Phi_n (x),$$

or

$$[\frac{p_x^2}{2m} + V(x)] \Phi_n (x) = E_n \Phi_n (x).$$

Within the box: $V(x) = 0$

Therefore, $$(p_x^2/2m) \Phi_n (x) = E_n \Phi_n (x).$$

Outside the box: $V(x) = \infty$

$$[\frac{p_x^2}{2m} + \infty] \Phi_n (x) = E_n \Phi_n (x).$$
Now, in quantum mechanics, the operator $p_x$ performs the operation 
\[
\frac{\hbar}{2\pi}(1/i) \frac{\partial}{\partial x} = \frac{\hbar}{i} \frac{\partial}{\partial x}
\]
on the function to the right; the operator $p_y$ performs the operation 
\[
\frac{\hbar}{i} \frac{\partial}{\partial y}
\]
on the function to the right; and the operator $p_z$ performs the operation 
\[
\frac{\hbar}{i} \frac{\partial}{\partial z}
\]
on the function to the right.

So
\[
p_x^2 = -\hbar^2 \frac{\partial^2}{\partial x^2}; \quad p_y^2 = -\hbar^2 \frac{\partial^2}{\partial y^2}; \quad p_z^2 = -\hbar^2 \frac{\partial^2}{\partial z^2};
\]
and $p^2 = p_x^2 + p_y^2 + p_z^2 = -\hbar^2 \nabla^2$

So the Schroedinger equation for a particle in a 1-D box
\[
[p_x^2/2m + V(x)] \Phi_n(x) = E_n \Phi_n(x)
\]
becomes:

Within the box:
\[
(-\hbar^2/2m) \frac{d^2 \Phi_n(x)}{dx^2} = E_n \Phi_n(x).
\]

Outside the box:
\[
((-\hbar^2/2m) \frac{d^2 \Phi_n(x)}{dx^2} + (\infty)) \Phi_n(x) = E_n \Phi_n(x).
\]

\[\text{Solutions are simple.}\]

Outside the box: \((x \leq 0; \ x \geq L)\)
\[
\Phi_n(x) = 0 \text{ only solution.}
\]

Inside the box:
\[
\Phi_n(x) = \sin kx \text{ or } \cos kx
\]
or \[A \sin kx + B \cos kx\]
Show \[(d/dx) \sin kx = k \cos kx\]
\[(d^2/dx^2) \sin kx = -k^2 \sin kx\]

So, \((-\hbar^2/2m) (d^2/dx^2) \sin kx\)
\[
= (\hbar^2 k^2/2m) \sin kx = E_k \sin kx
\]

Immediate result: \(E_k = (\hbar^2 k^2/2m)\)

Now boundary conditions restrict the values of $k$!

What are the boundary conditions?

(1) \(\Phi_n(0) = \Phi_n(0) = 0\)
(2) \(\Phi_n(L) = \Phi_n(L) = 0\)
Quantization of the energy levels

Boundary condition (1) limits the solutions of the Schrödinger equation to \( \sin kx \) only. Only \( \sin kx \) has a node at \( x = 0 \).

Application of boundary condition (2) limits \( k \) to the values of
\[
k = n\pi/L, \text{ where } n = 1, 2, 3, 4, \ldots
\]

So, \( E_k = (\hbar^2 k^2/2m) = E_n = (\hbar^2 n^2\pi^2/2mL^2) \)

Wavefunctions

\[ \Phi_n(x) = (2/L)^{1/2} \sin kx \] (normalized)

Show:
\[
\int_0^L \Phi_n^* (x) \Phi_n (x) \, dx = (2/L) \int_0^L \sin^2 kx \, dx
\]
\[
= (2/L) \left( \frac{1}{2} \right) (L) = 1.
\]

Energy spacing between adjacent energy levels

\[
E_{n+1} - E_n = (\hbar^2 \pi^2/2mL^2) [(n+1)^2 - n^2]
\]
\[
= (\hbar^2 \pi^2/2mL^2)(2n +1)
\]
A particle in a harmonic potential

\[ \hat{H}_{\text{particle}}(\vec{p}, \vec{r}) = \frac{p_x^2}{2m} + \frac{1}{2} k x^2 \]

and Schrödinger equation:

\[ (-\hbar^2 /2m) \frac{d^2 \Phi_n(x)}{dx^2} + \left( \frac{1}{2} k x^2 \right) \Phi_n(x) = E_n \Phi_n(x) \]

where

\[ k \] is the force or spring constant of the harmonic oscillator.

Energy levels

\[ E_n = \hbar v_o (n + \frac{1}{2}), \quad n = 0, 1, 2, 3, \ldots \]

\[ v_o = \left( \frac{1}{2\pi} \right) \left( \frac{k}{m} \right)^{1/2} \]

Energy spacing between adjacent energy levels

\[ E_{n+1} - E_n = \hbar v_o \]

for \( n = 0, 1, 2, \ldots \)
Reading assignment

James P. Allen, Chapters 9 and 10.

Suggested reading

Eisenberg and Crothers (EC), Chapter 10, pp. 401-439.