Basics-1

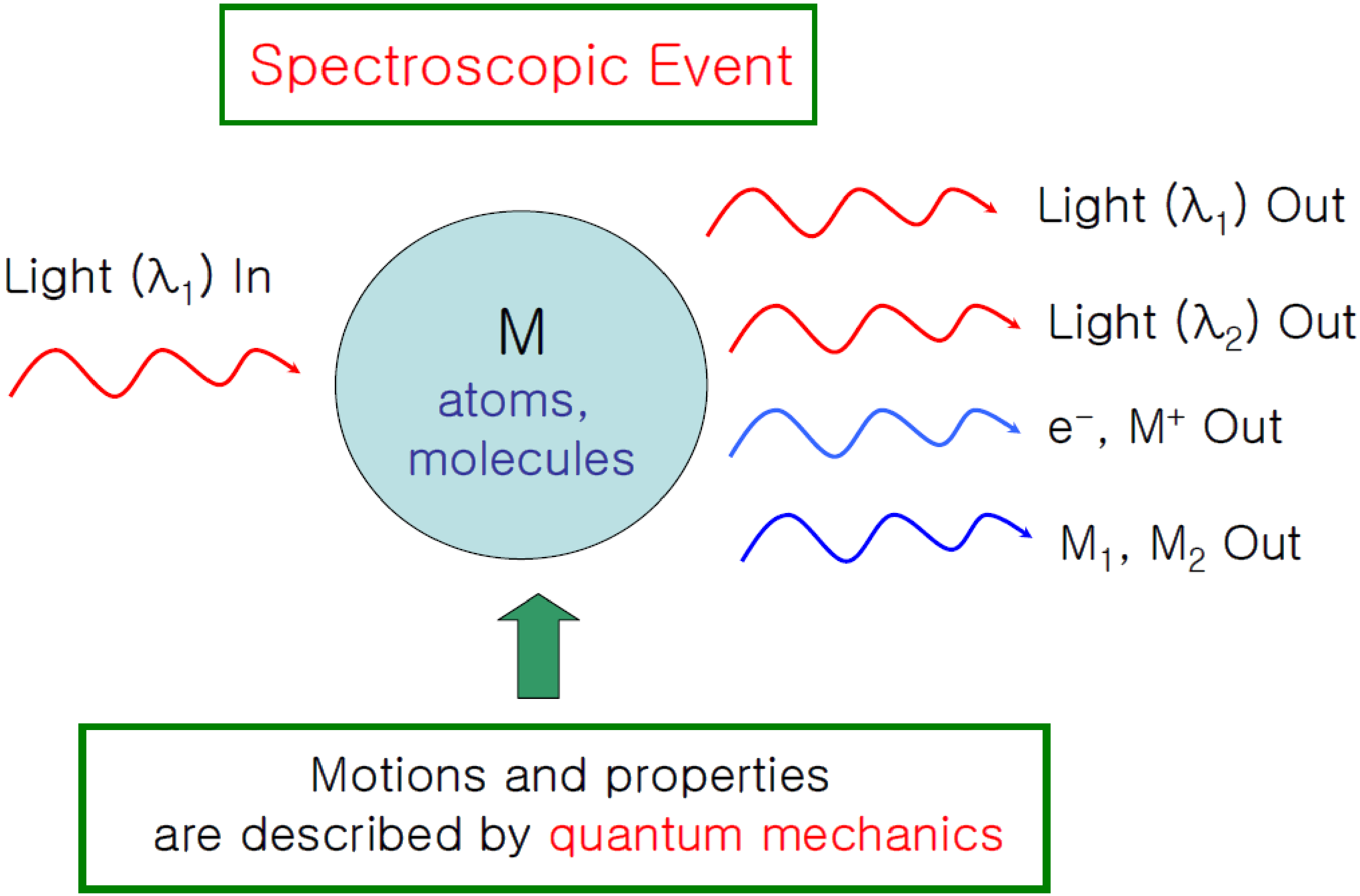
Spectroscopy
vs
Quantum Mechanics

Reference: "Basic Atomic and Molecular Spectroscopy"
by J.M. Hollas (Wiley, 2002)
"Introduction to Quantum Mechanics in Chemistry"
by M.A. Ratner & G.C. Schatz (Prentice-Hall, 2001)

What is Spectroscopy?

- Classically, Use light (or photons) as a probe to reveal the nature of molecules by inducing light-molecule interactions

- Recently, other probes (electrons, neutrons, spm, etc) are also used to understand the nature of molecules


Spectroscopic Event
Light (λ_1) In
M
atoms, molecules
Light (λ_1) Out
Light (λ_2) Out
e^-, M^+ Out
M_1, M_2 Out
Motions and properties are described by quantum mechanics

Quantum Mechanics

- Evolution of quantum theory

  * Planck, Bohr, De Broglie, Heisenberg, Schrödinger

  * postulates of quantum mechanics
  (Ψ, Ψ^2; E, $\hat{H}$; $H\Psi = i\hbar\partial\Psi/\partial t$; $A\Psi = a\Psi$; $\langle A \rangle$; spin)

- Schrödinger equation:

  * $H\Psi = E\Psi$ (time-independent)

  * $H\Psi = i\hbar\partial\Psi/\partial t$ (time-dependent)

  * $H = -\frac{\hbar^2}{2m}\nabla^2 + V$

Hydrogen-Like Atoms

$$\hat{H}\psi = -\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

solution

Wavefunction $\psi(r,\theta,\phi) = R_{nl}(r)\, Y_{lm_l}(\theta,\phi)$

$$= R_{nl}(r)\,\Theta_{lm_l}(\theta)\frac{1}{\sqrt{2\pi}}\exp(im_l\phi)$$

Energy $E = -\frac{e^2}{2a_0}\frac{1}{4\pi\varepsilon_0}\frac{Z^2}{n^2}$ a_0= 0.529 Å

* Quantum numbers: n, l, m_l, m_s
* Special functions: associated Laguerre polynomial in R_{nl},
associated Legendre polynomial in $\Theta_{lm}(\theta)$
spherical harmonics $Y_{lm}(\theta,\phi)$

Angular Momentum

- Orbital angular momentum

$$\hat{L} = [l(l+1)]^{1/2}\hbar,\ \hat{L}^2 = l(l+1)\hbar^2,\ \hat{L}_z = m_l\hbar$$

- Spin angular momentum
  - electron spin $\hat{S} = [s(s+1)]^{1/2}\hbar,\ \hat{S}^2 = s(s+1)\hbar^2,\ \hat{S}_z = m_s\hbar$
  - nuclear spin $\hat{I} = [I(I+1)]^{1/2}\hbar,\ \hat{I}^2 = I(I+1)\hbar^2,\ I_z = m_I\hbar$
- Rotational angular momentum
- Vibrational angular momentum

Born-Oppenheimer Approximation

Molecules are collections of electrons and nuclei:

$$H\psi(r,R) = E\psi(r,R)$$

$$H = T_e(\dot{r}) + T_n(\dot{R}) + V_{en}(r,R) + V_{ee}(r) + V_{nn}(R)$$

$$H_e = T_e(\dot{r}) + V_{en}(r,R) + V_{ee}(r)$$

… Nuclei move so slowly compared to electrons, so electrons adjust instantaneously to any nuclear motion.

$$\psi(r,R) = \psi_e(r;R)\psi_n(R)$$

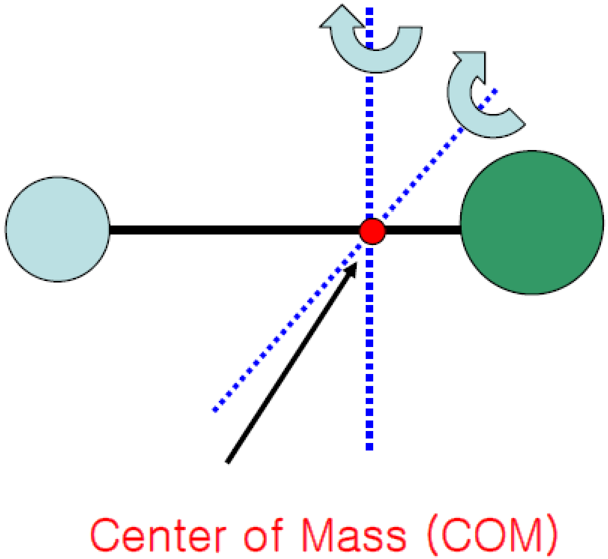
Solving S-eqn:

$$H_e\psi_e(r;R) = E_e(R)\psi_e(r;R),$$

$$H_n\psi_n(R) = (T_n + V_{nn}(R) + E_e(R))\psi_n(R) = E_n\psi_n(R)$$

$$\therefore\ E = E_e + E_n = E_e + E_v + E_r,\quad \psi = \psi_e\psi_v\psi_r$$

Rigid Rotor



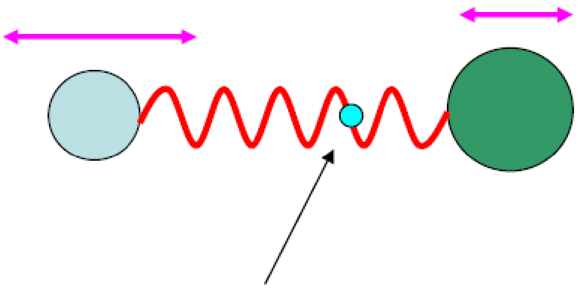
$$\hat{H} = \hat{T}_n = \frac{\hat{J}^2}{2I}, \quad I = \sum_{\alpha} m_{\alpha} R_{\alpha}^2$$

$$\hat{J}^2 = J(J+1)\hbar^2, \quad \hat{J}_z = M_J \hbar$$

$$\therefore \quad E_J = \frac{J(J+1)\hbar^2}{2I}, \quad J = 0, 1, 2, \ldots$$

$$\psi_{JM}(\theta, \phi) = Y_{JM}(\theta, \phi)$$

Harmonic Oscillator



$$\hat{H} = \hat{T}_n + V = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

$$\therefore \ E_v = h\nu(v + \frac{1}{2}), \ \ v = 0, 1, 2, ...$$

$$\psi_v = \left(\frac{1}{2^v v! \pi^{1/2}}\right)^{1/2} H_v(y) \exp\left(-\frac{y^2}{2}\right),$$

$$\leftarrow \ H_v(y) : \textit{Hermite Polynomial}$$

$$y = \left(\frac{4\pi^2 \nu \mu}{h}\right)^{1/2} (x - x_e)$$