Brief Tutorial on QM and StatMech

Andrew V. Teplyakov
CHEM674

Quantum mechanics

Postulates of quantum mechanics
Eigen Functions and Eigen Equations: Shroedinger Equation

$$\hat{H}\Psi = E\Psi$$

Hamiltonian Operator (Energy operator)
Energy eigenvalue

$$\frac{-\hbar^2}{2m}\nabla^2\Psi(r) + V(r)\Psi(r) = E\Psi(r)$$

Kinetic Energy + Potential Energy = Total Energy
Quantum mechanics

Postulates of quantum mechanics

Eigen Functions and Eigen Equations: Shroedinger Equation

Need to include all types of motion: translation (starting model particle in a box); vibration (start with harmonic oscillator and include non-harmonicity terms); rotation (start with rigid rotor, combine with radial distribution function to get hydrogen atom description), and include different electronic states

Translation:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \left( \frac{n \pi x}{a} \right)$$

$$E_n = \frac{n^2 \hbar^2}{8ma^2} \text{ (here } \hbar = \frac{\hbar}{2\pi} \text{)}$$

Vibration:

$$\Psi_v(x) = A_v H_v \left( \frac{x}{\alpha} \right) \exp \left( -\frac{x^2}{2\alpha^2} \right) \quad v = 0, 1, 2, 3, \ldots$$

$$E_v = \left( v + \frac{1}{2} \right) \hbar \omega_0 = \left( v + \frac{1}{2} \right) \hbar \nu_0$$
Quantum mechanics

Postulates of quantum mechanics

Eigen Functions and Eigen Equations: Shroedinger Equation

Need to include all types of motion: translation (starting model particle in a box); vibration (start with harmonic oscillator and include non-harmonicity terms); rotation (start with rigid rotor, combine with radial distribution function to get hydrogen atom description), and include different electronic states

Translation:
\[ \psi_n(x) = \frac{2}{\sqrt{a}} \sin \left( \frac{n \pi x}{a} \right) \]
\[ E_n = \frac{n^2 \hbar^2}{8ma^2} \quad \text{(here } \hbar = \frac{\hbar}{2\pi} \text{)} \]

Vibration:
\[ \frac{d^2 \Psi}{dy^2} - \left(y^2 - \alpha \right) \Psi + \epsilon \Psi = 0 \]
\[ y = \frac{x}{\alpha} \quad \alpha = \left( \frac{\hbar^2}{mk} \right)^{1/4} \quad \epsilon = \frac{2}{\hbar \omega_0} E \]

Quantum mechanics

Postulates of quantum mechanics

Eigen Functions and Eigen Equations: Shroedinger Equation

Need to include all types of motion: translation (starting model particle in a box); vibration (start with harmonic oscillator and include non-harmonicity terms); rotation (start with rigid rotor, combine with radial distribution function to get hydrogen atom description), and include different electronic states

Translation:
\[ \psi_n(x) = \frac{2}{\sqrt{a}} \sin \left( \frac{n \pi x}{a} \right) \]
\[ E_n = \frac{n^2 \hbar^2}{8ma^2} \quad \text{(here } \hbar = \frac{\hbar}{2\pi} \text{)} \]

Vibration:
\[ \Psi_n(x) = A_n H_\nu \left( \frac{x}{\alpha} \right) \exp \left( -\frac{x^2}{2\alpha^2} \right) \]
\[ \nu = 0, 1, 2, 3, \ldots \]

<table>
<thead>
<tr>
<th>( \nu )</th>
<th>( H_\nu )</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>Even</td>
</tr>
<tr>
<td>1</td>
<td>2\nu</td>
<td>Odd</td>
</tr>
<tr>
<td>2</td>
<td>4\nu^2 - 2</td>
<td>Even</td>
</tr>
<tr>
<td>3</td>
<td>8\nu^2 - 12\nu</td>
<td>Odd</td>
</tr>
</tbody>
</table>

\( H \) are Hermit polynomials
Quantum mechanics

Postulates of quantum mechanics

Eigen Functions and Eigen Equations: Shroedinger Equation

Need to include all types of motion: translation (starting model particle in a box); vibration (start with harmonic oscillator and include non-harmonicity terms); rotation (start with rigid rotor, combine with radial distribution function to get hydrogen atom description), and include different electronic states

$$\Psi_{km}(\theta, \phi) = \Theta_{km}(\theta)\Phi_{m}(\phi)$$

$$\Phi_{m}(\phi) = \frac{1}{\sqrt{2\pi}} \exp(im\phi)$$

Rotation:

$$Y_{lm}(\theta, \phi) = A_{lm} P_{l}^{m}(\cos\theta)\Phi_{m}(\phi)$$

where

$$k = \ell(\ell+1)$$ and $$\ell = 0, 1, 2, \ldots$$

Quantum mechanics

Postulates of quantum mechanics

Eigen Functions and Eigen Equations: Shroedinger Equation

Need to include all types of motion: translation (starting model particle in a box); vibration (start with harmonic oscillator and include non-harmonicity terms); rotation (start with rigid rotor, combine with radial distribution function to get hydrogen atom description), and include different electronic states

$$\hat{H}Y_{lm}(\theta, \phi) = E_{lm}Y_{lm}(\theta, \phi)$$

Rotation:

$$\frac{1}{2mr_{0}^{2}} \hat{L}^{2}Y_{lm}(\theta, \phi) = \frac{1}{2mr_{0}^{2}} \ell(\ell+1)\hbar^{2}Y_{lm}(\theta, \phi)$$

$$E_{lm} = \frac{\hbar^{2}}{2mr_{0}^{2}} \ell(\ell+1)$$
Hydrogen Atom

*Hydrogen atom in quantum mechanics*- electron moving about a proton located at the origin of the coordinate system

**Coulomb potential**

\[ U = -\frac{e^2}{4\pi\varepsilon_0 r} \]

Centrosymmetric potential, use spherical polar coordinates to formulate the Schrödinger equation:

\[
\frac{-\hbar^2}{2m_e} \left[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) + \frac{1}{r^2 \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\psi}{d\theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{d^2\psi}{d\phi^2} \right] + \frac{e^2}{4\pi\varepsilon_0 r} \psi = E \psi
\]

Hydrogen Atom: Solving the Schrödinger Equation

**Separation of variables**- since \( U(r) \) does not depend on the angles:

\[ \psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \]

Solution of the Schrödinger equation greatly simplified:

\[
-\frac{\hbar^2}{2m_e} i^l \Theta(\theta) \Phi(\phi) \frac{d}{dr} \left[ r^2 \frac{dR(r)}{dr} \right] + \frac{1}{2m_e r^2} R(r) i^l i^l \Theta(\theta) \Phi(\phi) - \Theta(\theta) \Phi(\phi) \left[ \frac{e^2}{4\pi\varepsilon_0 r} R(r) = E \psi(r, \theta, \phi) \right]
\]

Know that \( i^l \Theta(\theta) \Phi(\phi) = \hbar^2 (l+1) \Theta(\theta) \Phi(\phi) \)

can remove angular dependence from the Schrödinger equation:

\[
-\frac{\hbar^2}{2m_e} \frac{d}{dr} \left[ r^2 \frac{dR(r)}{dr} \right] + \frac{\hbar^2 (l+1)}{2m_e r^2} \frac{e^2}{4\pi\varepsilon_0 r} R(r) = ER(r)
\]

Effective potential, centrifugal + Coulomb
Hydrogen Atom: Eigenvalues and Eigenfunctions of Total Energy

Eigenfunctions:

\[ \psi_{n,l,m_l} (r, \theta, \phi) = R_{nl}(r) \Theta_l(\theta) \Phi_{ml}(\phi) \]

Quantum numbers:

\[ n = 1, 2, 3, 4, ... \]
\[ l = 0, 1, 2, 3, ..., n-1 \]
\[ m_l = 0, \pm 1, \pm 2, \pm 3, ..., \pm l \]

Hydrogen Atom: Eigenvalues and Eigenfunctions of Total Energy

Energy - appears only in the radial equation (not angular):

\[ E_n = -\frac{m_e e^4}{8 \varepsilon_0^2 \hbar^2 n^2}, \quad n = 1, 2, 3, 4, ... \]

Bohr radius:

\[ a_0 = -\frac{e^2 \hbar^2}{4 \pi m_e \varepsilon_0}, \quad a_0 = 0.529 \times 10^{-10} m \]

Energy taking Bohr radius into account:

\[ E_n = -\frac{e^4}{8 \pi e_0^2 a_0 n^2} = -\frac{2.179 \times 10^{-18} J}{n^2} = -\frac{13.60 eV}{n^2}, \quad n = 1, 2, 3, 4, ... \]
Vibrations and Rotations: Diatomic Molecules

vibrational levels
\[ E_v = (v + \frac{1}{2}) \hbar \omega_0 \]
ovibrational levels
\[ E_r = B \cdot J (J + 1) \]

Selection rules:
1) The molecule must have a permanent dipole moment;
2) \( \Delta n = \pm 1; \pm 2, \pm 3 \ldots \)
3) \( \Delta J = \pm 1 \)
Vibrations and Rotations: Diatomic Molecules

http://www.pcl.tu-bs.de/aggericke/PC4e/Kap_III/Rot-Vib-Spektren.htm

Electronic Spectroscopy for Diatomic Molecules

Selection rules for electronic spectroscopy:
1) $\Delta \Lambda = 0, \pm 1$;
2) $\Delta S = 0$ (no singlet-triplet transitions allowed)
3) $g \leftrightarrow u$ (the inversion symmetry must change)
4) $\Sigma^+ \leftrightarrow \Sigma^-$ is not allowed
Electronic Spectroscopy for Diatomic Molecules

- Energy change in a transition is a sum of changes
  - Electronic
  - Vibrational
  - Rotational
- Franck-Condon principle
  - During an electronic transition, the nuclear centers remain fixed.
  - Estimate intensities by overlap of wave functions

\[ \Delta E = \Delta E_{\text{elect}} + \Delta E_{\text{vib}} + \Delta E_{\text{rot}} \]

Statistical Thermodynamics

https://www.slideshare.net/VirajDande/lecture-7-8-statistical-thermodynamics-introduction