Brief Tutorial on QM and StatMech

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CHEM674

Quantum mechanics

Postulates of quantum mechanics

Eigen Functions and Eigen Equations: Shroedinger Equation

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

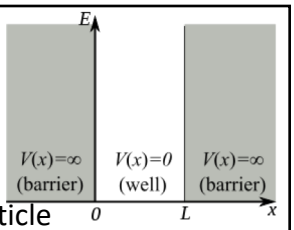
Hamiltonian Operator (Energy operator)

Energy eigenvalue

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

Kinetic Energy + *Potential Energy* = *Total Energy*

Quantum mechanics



Postulates of quantum mechanics

Eigen Functions and Eigen Equations: Shroedinger Equation

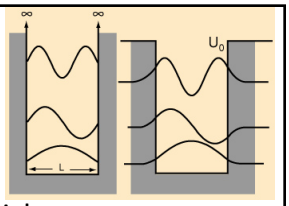
Need to include all types of motion: translation (starting model particle in a box); vibration (start with harmonic oscillator and include non-harmonicity terms); rotation (start with rigid rotor, combine with radial distribution function to get hydrogen atom description), and include different electronic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

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

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

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

Quantum mechanics



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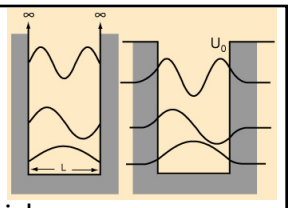

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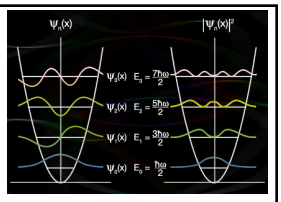
Vibration: $\frac{d^2\Psi}{dy^2} - y^2\Psi + \varepsilon\Psi = 0$

$y = \frac{x}{\alpha}$ $\alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}$ $\varepsilon = \frac{2}{\hbar\omega_0}E$

Quantum mechanics



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H are Hermit polynomials

υ	$H_\upsilon(y)$	Symmetry
0	1	Even
1	2y	Odd
2	$4y^2 - 2$	Even
3	$8y^3 - 12y$	Odd

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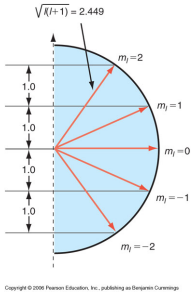


Rotation:

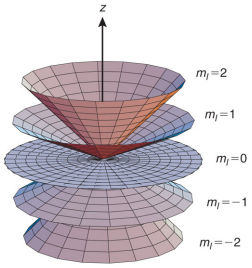
$$\Psi_{km}(\theta,\phi) = \Theta_{km}(\theta)\Phi_m(\phi)$$

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

$$Y_{\ell m}(\theta,\phi) = A_{\ell m}P_\ell^{|m|}(\cos\theta)\Phi_m(\phi)$$

where

$$k = \ell(\ell+1) \quad \text{and} \quad \ell = 0, 1, 2, \ldots$$



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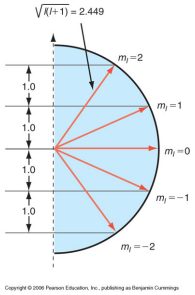
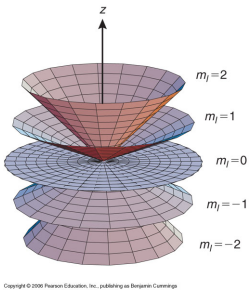


Rotation:

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

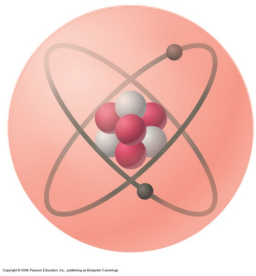
$$\frac{1}{2mr_0^2}\hat{L}^2Y_{\ell m}(\theta,\phi) = \frac{1}{2mr_0^2}\ell(\ell+1)\hbar^2Y_{\ell m}(\theta,\phi)$$

$$E_{\ell m} = \frac{\hbar^2}{2mr_0^2}\ell(\ell+1)$$



Hydrogen Atom

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



Coulomb potential

$$U = -\frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}|} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

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

$$-\frac{h^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\phi)}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi(r,\theta,\phi)}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi(r,\theta,\phi)}{\partial\varphi^2}\right]-\frac{e^2}{4\pi\varepsilon_0 r}\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

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:

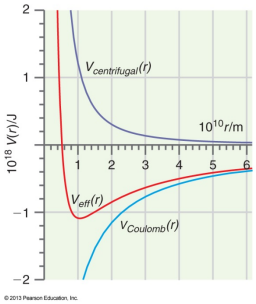
$$-\frac{h^2}{2m_e}\Theta(\theta)\Phi(\phi)\frac{d}{dr}\left[r^2\frac{dR(r)}{dr}\right]+\frac{1}{2m_e r^2}R(r)\hat{l}^2\Theta(\theta)\Phi(\phi)-\Theta(\theta)\Phi(\phi)\left[\frac{e^2}{4\pi\varepsilon_0 r}\right]R(r)=ER(r)\Theta(\theta)\Phi(\phi)$$

Know that $\hat{l}^2\Theta(\theta)\Phi(\phi)=\hbar^2 l(l+1)\Theta(\theta)\Phi(\phi)$

can remove angular dependence from the Schrödinger equation:

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

Effective potential, centrifugal + Coulomb



Hydrogen Atom: Eigenvalues and Eigenfunctions of Total Energy

Eigenfunctions:

$$\psi_{n,l,m_l}(r,\theta,\phi) = \underbrace{R_{nl}(r)}_{\text{radial}}\underbrace{\left(\Theta(\theta)\Phi(\phi)\right)_{n,l,m_l}}_{\text{Spherical harmonics}} = R_{nl}(r)Y_l^{m_l}(\theta,\phi)$$

Quantum numbers:

$$n = 1,\ 2\ ,3\ ,4\ ,\ldots$$
$$l = 0,\ 1,\ 2,\ 3,\ \ldots,\ n-1$$
$$m_l = 0,\ \pm 1,\ \pm 2,\ \pm 3,\ \ldots,\ \pm l$$

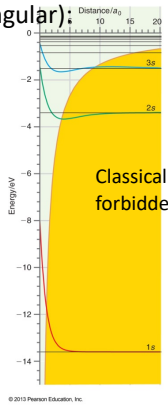
Hydrogen Atom: Eigenvalues and Eigenfunctions of Total Energy

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

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2},\quad n = 1,2,3,4,\ldots$$

Bohr radius:

$$a_0 = -\frac{\varepsilon_0^2 h^2}{\pi m_e e^2},\quad a_0 = 0.529\times 10^{-10} m$$

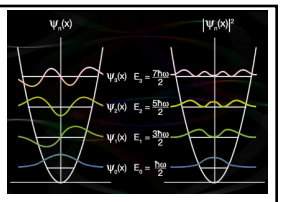


Classically forbidden region

Energy taking Bohr radius into account:

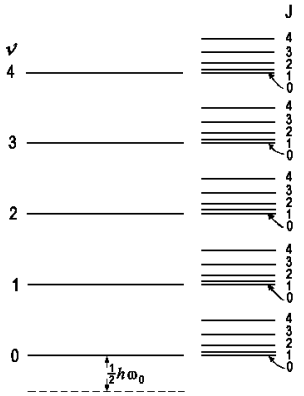
$$E_n = -\frac{e^4}{8\pi\varepsilon_0 a_0 n^2} = -\frac{2.179\times 10^{-18} J}{n^2} = -\frac{13.60 eV}{n^2},\quad n = 1,2,3,4,\ldots$$

Vibrations and Rotations: Diatomic Molecules



vibrational levels
$E_v = (v + ½)\, h\omega_0$

rovibrational levels
$E_r = B \cdot J\,(J + 1)$



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$E_v = (v + ½)\, h\omega_0$

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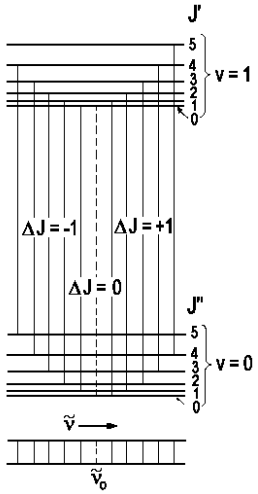
$E_r = B \cdot J\,(J + 1)$

Selectrion rules:
1) The molecule must have a permanent dipole moment;
2) $\Delta n = \pm 1; \pm 2, \pm 3\ldots$
3) $\Delta J = \pm 1$



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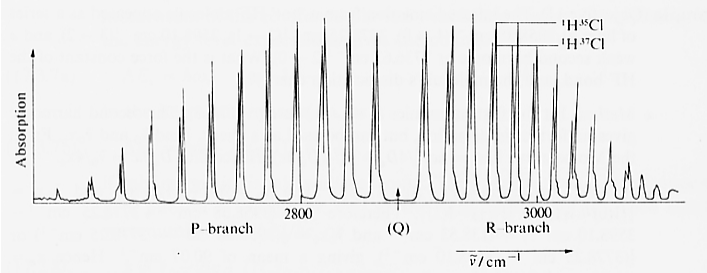
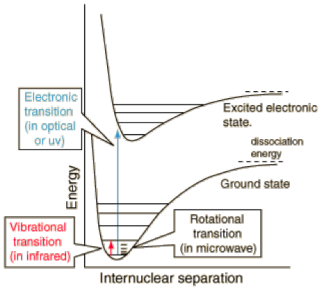
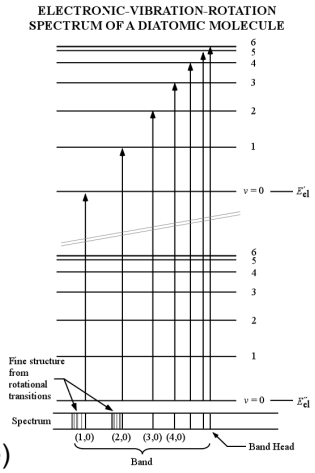


http://www.pci.tu-bs.de/aggericke/PC4e/Kap_III/Rot-Vib-Spektren.htm

Electronic Spectroscopy for Diatomic Molecules



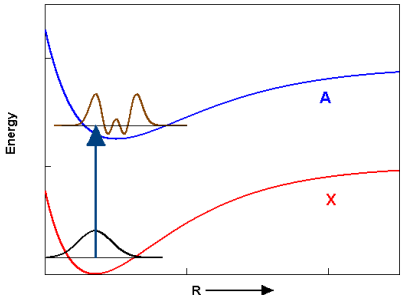


Selection rules for electronic spectroscopy:
1) $\Delta\Lambda = 0, \pm 1$;
2) $\Delta S = 0$ (no singlet-triplet transitions allowed)
3) g ↔ u (the inversion symmetry must change)
4) $\Sigma^+ \leftrightarrow \Sigma^-$ Is not allowed

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

$$\Delta E = \Delta E_{elect} + \Delta E_{vib} + \Delta E_{rot}$$



Statistical Thermodynamics

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