CHEM 3541

Physical Chemistry

Week 13

Wavefunction for hydrogen atom (rev.)

$$\Phi(\vec{r}, \vec{R}) = \chi(\vec{R})\psi(\vec{r})$$

- Since $m_N \gg m_e, m_{\mathrm{CM}} \approx m_e$.
- Roughly, $\chi(\vec{R})$ and $\psi(\vec{r})$ are nuclear and electron wavefunction resp.

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{e^2}{r}\right] R = ER$$

- $l(l+1)\hbar^2/2\mu r^2$: effective potential due to angular momentum

$$\langle \hat{L}^2 \rangle = l(l+1)\hbar^2$$

Solution for $R(r)$

$$R_{nl}(r) = N_{nl}\rho^l L_{n-l-1}^{2l+1}(\rho)e^{-\rho/2}$$

- $\rho = 2r/na,\ a = \hbar^2/\mu e^2 \approx 0.529$ Å
  - $a_0 = \hbar^2/m_e e^2$ is the unit length in atomic unit
- L_b^a: associated Laguerre polynomial
- $N_{nl} = \left\{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}\right\}^{1/2}$
- $n = 1,2,3, \dots;\ l = 0,1,2, \dots, n-1$
- Energy $E_n = -\frac{1}{n^2}\frac{e^2}{2a}$ (or in SI $-\frac{1}{n^2}\frac{e^2}{8\pi\varepsilon_0 a}$)

Electronic solution

- Wavefunction: $\psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\theta, \phi)$
- $n = 1,2,3, \ldots; l = 0,1,2, \ldots, n-1; m = 0, \pm 1, \pm 2, \ldots, \pm l$
- Energy: $E_n = -\frac{1}{n^2}\frac{e^2}{2a}$ only depends on principal quantum number n
  - Ground state: $n = 1, l = 0, m = 0$, non-degenerate
  - First excited state: $n = 2, \begin{cases} l = 0, m = 0 \\ l = 1, \begin{cases} m = 0 \\ m = \pm 1 \end{cases} \end{cases}$, degeneracy=4

First few electronic wavefunctions

$$\psi_{1s} = \psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-\frac{r}{a}}$$

$$\psi_{2s} = \psi_{200} = \frac{1}{\sqrt{8\pi a^3}} \left(1 - \frac{r}{2a}\right) e^{-\frac{r}{2a}}$$

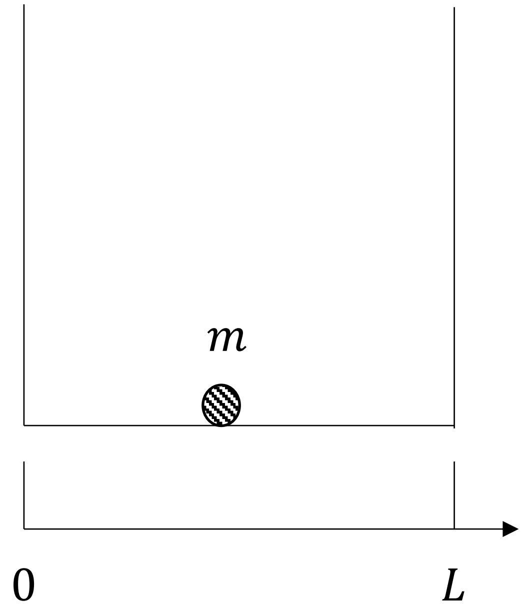
$$\psi_{2p_z} = \psi_{210} = \frac{1}{4\sqrt{2\pi a^5}} r e^{-\frac{r}{2a}} \cos\theta$$

$$\psi_{2p_x} = \frac{\psi_{211} + \psi_{21-1}}{\sqrt{2}} = \frac{1}{4\sqrt{2\pi a^5}} r e^{-\frac{r}{2a}} \sin\theta \cos\phi$$

$$\psi_{2p_y} = \frac{\psi_{211} - \psi_{21-1}}{i\sqrt{2}} = \frac{1}{4\sqrt{2\pi a^5}} r e^{-\frac{r}{2a}} \sin\theta \sin\phi$$

Summary

1. Particle in a box (1D)



$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi \quad \psi = Ne^{\pm ikx} \quad k = \frac{\sqrt{2mE}}{\hbar}$$

Boundary condition: $\psi(x = 0) = \psi(x = L) = 0$

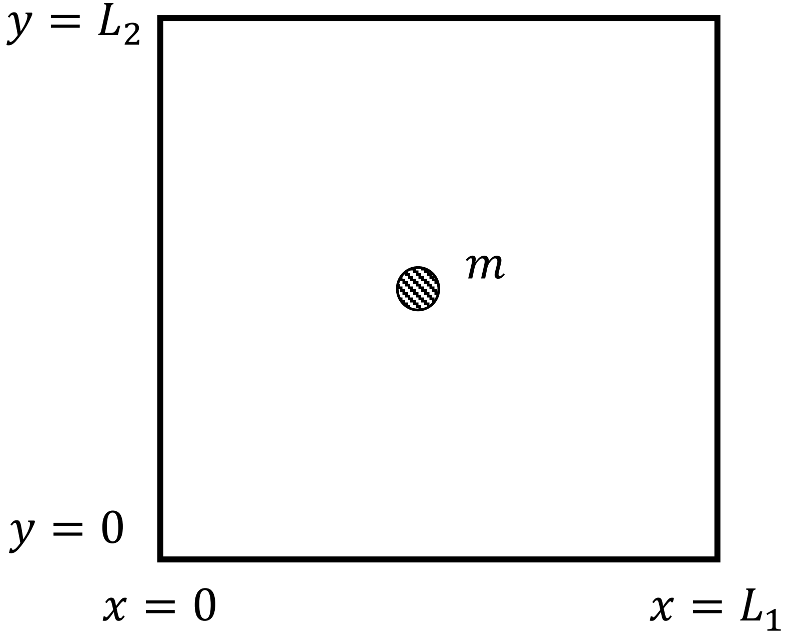
Applying B.C.: $\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$

$$E_n = \frac{n^2h^2}{8mL^2}$$

$$n = 1,2,3, \ldots$$

Continued

2. Particle in a box (2D)



$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2}\right) = E\psi$$

Separation of variables:

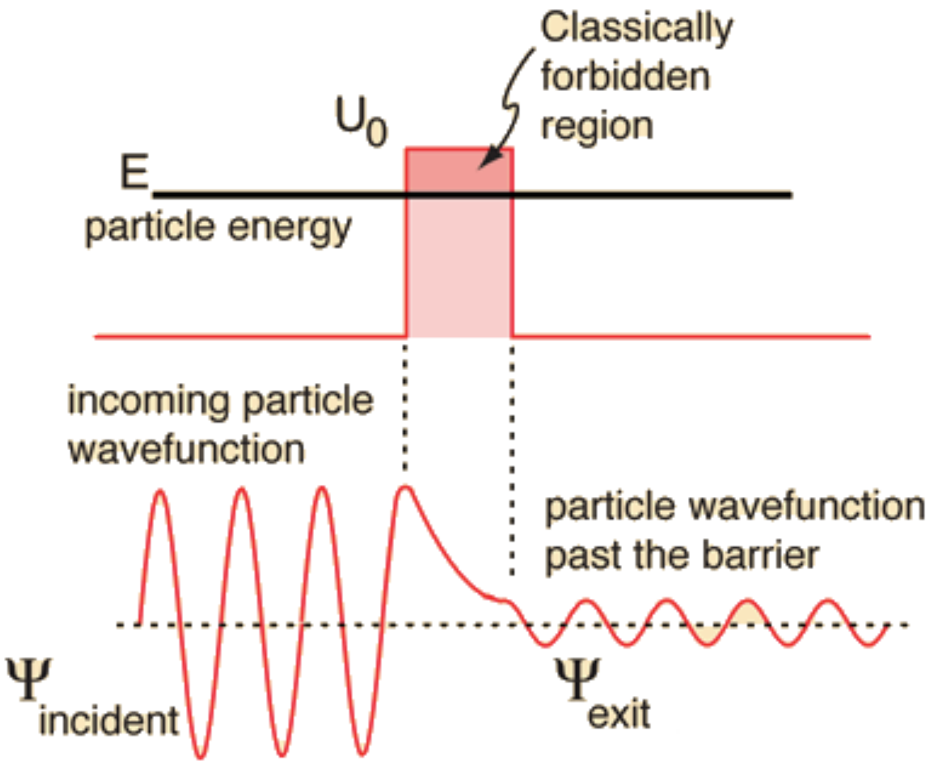
$$\psi = X(x)Y(y)$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} = E_xX$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} = E_xY$$

Continued

3. Transmission



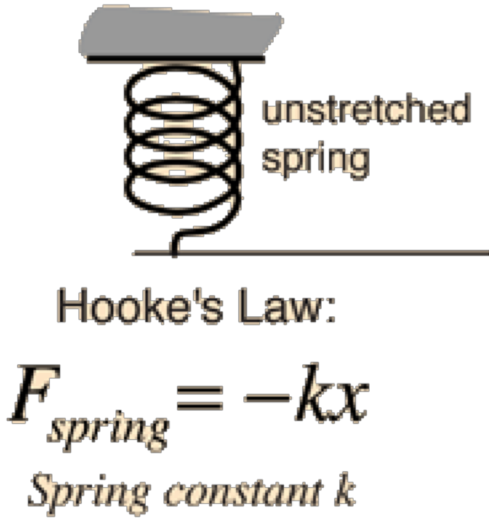
Transmission coefficient $T = \left|\frac{A'}{A}\right|$

Key points to solve the problem:

- Wavefunction is continuous
- Derivative of wavefunction is continuous

Continued

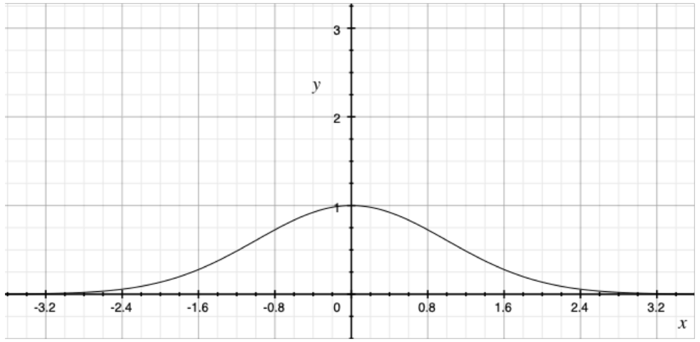
4. Vibration (1D quantum harmonic oscillator)



Force: $F = -k_f x$

Potential: $V(x) = -\int_0^x F \mathrm{d}x' = \frac{1}{2} k_f x$

$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2} k_f x^2$



Ground state wavefunction: $\psi_0 = N e^{-\frac{x^2}{2\alpha^2}}$, $\alpha = \left(\frac{\hbar^2}{m k_f}\right)^{\frac{1}{4}}$

Energy: $E_\nu = \hbar\omega\left(\nu + \frac{1}{2}\right), \nu = 0,1,2, \ldots, \omega = \sqrt{\frac{k_f}{m}}$

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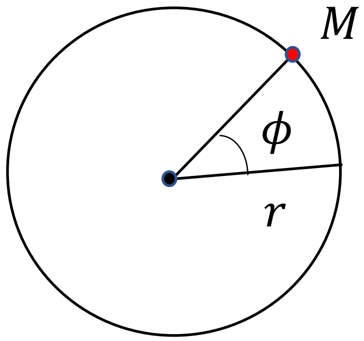
5. Rotation (2D)



$$\hat{H} = -\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{\mathrm{d}l^2} = -\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{r^2\mathrm{d}\phi^2} = -\frac{\hbar}{2I}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2}, I = Mr^2$$

S.E. $-\frac{\hbar^2}{2I}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2}\psi = E\psi$

Boundary condition: $\psi(\phi = 0) = \psi(\phi = 2\pi)$

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}, E_m = \frac{m^2\hbar^2}{2I}, m = 0, \pm 1, \pm 2, \ldots$$

Continued

6. Rotation (3D)

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\Lambda^2}{r^2}, \Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)$$

- S.E. $-\frac{\hbar^2}{2I}\Lambda^2 Y = EY$
- $\Lambda^2 Y_{lm} = -l(l+1)Y_{lm}, l = 0,1,2,\ldots, m = 0, \pm 1, \pm 2, \ldots, \pm l$
- $E_l = \frac{l(l+1)\hbar^2}{2I}$ (classically, $E = \frac{L^2}{2I}$), $\left\langle \hat{L}^2 \right\rangle_l = l(l+1)\hbar^2$
- Expression of $\hat{L}_i$: $\hat{L}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \hat{L}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right), \hat{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$
- Commutator: $\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z, \left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x, \left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y$

Continued

7. Hydrogen atom

- Reduced mass $\mu = \frac{m_e m_N}{m_e + m_N}$
- Relative displacement $\vec{r} = \vec{r}_e - \vec{r}_N$
- S.E. for electron $-\frac{\hbar^2}{2\mu}\nabla_{\vec{r}}^2\psi - \frac{e^2}{r}\psi = E\psi$, $\nabla_{\vec{r}}^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{\Lambda^2}{r^2}$
- Electronic wavefunction $\psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\theta, \phi)$
- Energy $E_n = -\frac{1}{n^2}\frac{e^2}{2a}$, $a \approx a_0 = 0.529\text{Å}$, a_0 is Bohr radius
- $n = 1,2,3, \ldots; l = 0,1, \ldots, n-1; m = 0, \pm 1, \ldots, \pm l$