CHEM 3541

Physical Chemistry

Week 12

Properties of spherical harmonics

$$\Lambda^2 Y_{lm} = -l(l+1)Y_{lm}$$

- Energy: $\hat{H} = -\frac{\hbar^2}{2m} \cdot \frac{\Lambda^2}{r^2}$, $\hat{H}Y_{lm} = \frac{\hbar^2}{2I} \cdot l(l+1)Y_{lm}$, $E_l = \frac{l(l+1)\hbar^2}{2I}$
- Square of angular momentum ($\hat{L}^2$):
  - Classical: $E = L^2/2I$; quantum: $\hat{L}^2 = -\hbar^2\Lambda^2$
  - $\hat{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}$, $\langle \hat{L}^2 \rangle_l = l(l+1)\hbar^2$

Angular momentum ($\hat{\vec{L}}$)

- Classical: $\vec{L} = \vec{r} \times \vec{p}$; quantum: $\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}}$
  - $\hat{\vec{r}} = x\vec{e}_x + y\vec{e}_y + z\vec{e}_z$, $\hat{\vec{p}} = \hat{p}_x\vec{e}_x + \hat{p}_y\vec{e}_y + \hat{p}_z\vec{e}_z$
  - $\hat{p}_\mu = \frac{\hbar}{i}\frac{\partial}{\partial\mu}, \mu = x, y, z$
  - ‘×’ means cross product
    - $\vec{a} \times (k\vec{b}) = k(\vec{a} \times \vec{b})$, $\vec{a} \times \vec{a} = \vec{0}$, $\vec{a} \times \vec{b} = -\vec{b} \times \vec{a}$, $\vec{a} \times (\vec{b} + \vec{c}) = \vec{a} \times \vec{b} + \vec{a} \times \vec{c}$
  - $\vec{e}_x \times \vec{e}_y = \vec{e}_z$, $\vec{e}_y \times \vec{e}_z = \vec{e}_x$, $\vec{e}_z \times \vec{e}_x = \vec{e}_y$

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$$\hat{\vec{L}} = \left(x\vec{e}_x + y\vec{e}_y + z\vec{e}_z\right)\times\frac{\hbar}{i}\left(\frac{\partial}{\partial x}\vec{e}_x + \frac{\partial}{\partial y}\vec{e}_y + \frac{\partial}{\partial z}\vec{e}_z\right)$$

$$= \frac{\hbar}{i}\left[\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\vec{e}_z + \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\vec{e}_x + \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\vec{e}_y\right]$$

$$\hat{L}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{L}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Commutation relations

$$\left[\hat{L}_x, \hat{L}_y\right] = -\hbar^2\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) - \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right]$$

$$= -\hbar^2\left(y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial z\partial x} - yx\frac{\partial^2}{\partial z^2} - z^2\frac{\partial^2}{\partial y\partial x} + zx\frac{\partial^2}{\partial y\partial z}\right)$$

$$+\hbar^2\left(zy\frac{\partial^2}{\partial x\partial z} - z^2\frac{\partial^2}{\partial x\partial y} - xy\frac{\partial^2}{\partial z^2} + x\frac{\partial}{\partial y} + xz\frac{\partial^2}{\partial z\partial y}\right)$$

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

$$= i\hbar\hat{L}_z$$

- $\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z, \left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x, \left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y$

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- $\left[\hat{L}^2, \hat{L}_z\right] = \left[\hat{L}_x^2, \hat{L}_z\right] + \left[\hat{L}_y^2, \hat{L}_z\right] + \left[\hat{L}_z^2, \hat{L}_z\right]$
  - $\left[\hat{L}_z^2, \hat{L}_z\right] = \hat{L}_z^3 - \hat{L}_z^3 = 0$
  - $\left[\hat{L}_x^2, \hat{L}_z\right] = \hat{L}_x^2\hat{L}_z - \hat{L}_x\hat{L}_z\hat{L}_x + \hat{L}_x\hat{L}_z\hat{L}_x - \hat{L}_z\hat{L}_x^2$
    $= \hat{L}_x\left[\hat{L}_x, \hat{L}_z\right] + \left[\hat{L}_x, \hat{L}_z\right]\hat{L}_x$
    $= -i\hbar\left(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x\right)$
  - $\left[\hat{L}_y^2, \hat{L}_z\right] = i\hbar\left(\hat{L}_y\hat{L}_x + \hat{L}_x\hat{L}_y\right)$
- $\left[\hat{L}^2, \hat{L}_z\right] = 0$

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- $\left[\hat{H}, \hat{L}_z\right] = \left[\frac{\hat{L}^2}{2I}, \hat{L}_z\right] = 0$
- These commutation relations confirm that Y_{lm} are the eigenfunctions for $\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$, i.e.

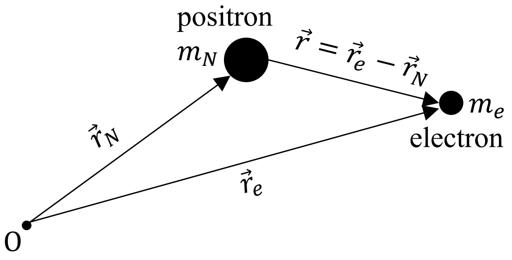
$$\hat{H}Y_{lm} = \frac{l(l+1)\hbar^2}{2I}Y_{lm}$$

$$\hat{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}$$

$$\hat{L}_z Y_{lm} = m\hbar Y_{lm}$$

Schrödinger equation for hydrogen atom

- Some notations
  - Mass: nucleus m_N, electron m_e, total $m_{\text{CM}} = m_N + m_e$, reduced $\mu = \frac{m_e m_N}{m_e + m_N}$
  - Position vector: nucleus $\vec{r}_N$, electron $\vec{r}_e$, centre of mass (CM) $\vec{R} = \frac{m_e \vec{r}_e + m_N \vec{r}_N}{m_e + m_N}$, electron relative to nucleus $\vec{r} = \vec{r}_e - \vec{r}_N$
  - If $\vec{R} = R_x \vec{e}_x + R_y \vec{e}_y + R_z \vec{e}_z$, $\nabla^2_{\vec{R}} = \frac{\partial^2}{\partial R_x^2} + \frac{\partial^2}{\partial R_y^2} + \frac{\partial^2}{\partial R_z^2}$ (similar for $\nabla^2_{\vec{r}}$)
  - Classical momentum: nucleus $\vec{p}_N = m_N \dot{\vec{r}}_N$, electron $\vec{p}_e = m_e \dot{\vec{r}}_e$, CM $\vec{p}_{\text{CM}} = m_{\text{CM}} \dot{\vec{R}}$, electron relative to nucleus $\vec{p}_\mu = \mu \dot{\vec{r}}$
  - Vector without arrow means modulus $r = |\vec{r}|$, etc



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- Classical energy: $E = \frac{p_e^2}{2m_e} + \frac{p_N^2}{2m_N} - \frac{e^2}{r} = \frac{p_{\mathrm{CM}}^2}{2m_{\mathrm{CM}}} + \frac{p_\mu^2}{2\mu} - \frac{e^2}{r}$, CM motion and relative motion are separated
- Quantum Hamiltonian: $\hat{H} = -\frac{\hbar^2}{2m_{\mathrm{CM}}}\nabla_{\vec{R}}^2 - \frac{\hbar^2}{2\mu}\nabla_{\vec{r}}^2 - \frac{e^2}{r}$
- S.E. $\left(-\frac{\hbar^2}{2m_{\mathrm{CM}}}\nabla_{\vec{R}}^2 - \frac{\hbar^2}{2\mu}\nabla_{\vec{r}}^2 - \frac{e^2}{r}\right)\Phi(\vec{r},\vec{R}) = E\Phi(\vec{r},\vec{R})$

Separation of $\vec{r}$ and $\vec{R}$

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

$$-\frac{\hbar^2}{2m_{\mathrm{CM}}}\left(\nabla_{\vec{R}}^2\chi\right)\psi - \frac{\hbar^2}{2\mu}\chi\nabla_{\vec{r}}^2\psi - \frac{e^2}{r}\chi\psi = E\chi\psi$$

divide both sides by $\chi\psi$:

$$-\frac{\hbar^2}{2m_{\mathrm{CM}}}\frac{\nabla_{\vec{R}}^2\chi}{\chi} - \frac{\hbar^2}{2\mu}\frac{\nabla_{\vec{r}}^2\psi}{\psi} - \frac{e^2}{r} = E$$

Thus

$$-\frac{\hbar^2}{2m_{\mathrm{CM}}}\frac{\nabla_{\vec{R}}^2\chi}{\chi} = E_{\mathrm{CM}} \text{ and } -\frac{\hbar^2}{2\mu}\frac{\nabla_{\vec{r}}^2\psi}{\psi} - \frac{e^2}{r} = E_e \text{ where } E_{\mathrm{CM}} + E_e = E$$

Equation of χ

$$-\frac{\hbar^2}{2m_{\mathrm{CM}}}\nabla_{\vec{R}}^2\chi = E_{\mathrm{CM}}\chi$$

- This is just a free particle moving in 3D space
- Plane wave solution
  - $\chi(\vec{R}) = Ae^{i\vec{k}_{\mathrm{CM}}\cdot\vec{R}}$
  - Wave vector: $\vec{k}_{\mathrm{CM}}$ with modulus $\frac{\sqrt{2m_{\mathrm{CM}}E_{\mathrm{CM}}}}{\hbar}$ and along the direction of $\vec{v}_p$

Equation of ψ

$$-\frac{\hbar^2}{2\mu}\nabla_{\vec{r}}^2\psi - \frac{e^2}{r}\psi = E_e\psi$$

- $\nabla_{\vec{r}}^2$ can be expressed in spherical coordinate system located at nucleus

$$\nabla_{\vec{r}}^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{\Lambda^2}{r^2}$$

- From now on, we will omit the subscript of E_e for simplicity
- Let $\psi(\vec{r}) = R(r)Y(\theta,\phi)$

$$-\frac{\hbar^2}{2\mu}r^2\left(\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r}\right)Y - e^2 rRY - Er^2RY - \frac{\hbar^2}{2\mu}R\Lambda^2 Y = 0$$

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divide both sides by RY:

$$-\frac{\hbar^2 r^2}{2\mu R}\left(\frac{\partial^2 R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}\right)-e^2 r-Er^2-\frac{\hbar^2}{2\mu Y}\Lambda^2 Y=0$$

Thus

$$-\frac{\hbar^2}{2\mu Y}\Lambda^2 Y=A$$

$$-\frac{\hbar^2 r^2}{2\mu R}\left(\frac{\partial^2 R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}\right)-e^2 r-Er^2=-A$$

Equation of Y

- Rearrange $-\frac{\hbar^2}{2\mu Y}\Lambda^2 Y = A$ as $\Lambda^2 Y = -\frac{2\mu A}{\hbar^2}Y$
- $Y = Y_{lm_l}(\theta, \phi)$, $-\frac{2\mu A}{\hbar^2} = -l(l+1)$
- $A = \frac{l(l+1)\hbar^2}{2\mu}$

Equation of R

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

i.e.

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