CH 8

SE in 3D

\[ H = \frac{p^2}{2m} + V(r) \]

\[ \frac{P^2}{2\mu} = -\frac{k^2}{2\mu} \Delta \]

\[ \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \]

Central potential:

\[ V(r) = V(r) \]

Example:

\[ \Delta (x^2 y^2 z) = 2xy^2z + 2x^2yz \]

\[ \Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{L^2}{\hbar^2 r^2} \]

\[ L^2 = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \]

Angular momentum operator transforms only spherical angles.

\[ A = (x, y, z) \]

Cartesian coordinates

\[ A = (r, \theta, \phi) \]

spherical coordinates

Example:

\[ \Delta (x^2 y^2 z) = 2xy^2z + 2x^2yz \]
\[ -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \Psi(r) + \frac{L^2}{2\mu r^2} \Psi(r) + V(r) \Psi(r) = E \Psi(r) \]

\[ \Psi(r) = R_n(r) Y_{\ell m}(\theta, \phi) \]

Spherical harmonic

\[ L^2 Y_{\ell m}(\theta, \phi) = \hbar^2 \ell (\ell + 1) Y_{\ell m}(\theta, \phi) \]

\[ -\frac{\hbar^2}{2\mu} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{\ell(\ell + 1)}{r^2} \right) R_n(\ell)(r) + V(r) R_n(\ell)(r) = E_{n\ell} R_n(\ell)(r) \]

energy spectrum

For hydrogen atom:

\[ E_{n\ell} = -13.6 \text{ eV} \frac{Z^2}{n^2} \]

energy is independent of quantum number \( \ell \).
Quantum numbers

\[ n = n_r + l + 1 \]

principal quantum number \[ n \geq 0 \]

azimuthal (magnetic) quantum number \[ e \geq 0 \] \[ e \leq n - 1 \]

Degeneracy: for each \( l \) there are \( 2l+1 \) azimuthal (magnetic) quantum numbers \( m \).

They correspond to different atomic orbitals:

- \( Y_{10}(\theta, \phi) \leftarrow s\text{-orbital} \)
- \( Y_{1,-1}(\theta, \phi), Y_{10}(\theta, \phi), Y_{11}(\theta, \phi) \leftarrow 3 \text{ } p\text{-orbitals} \)
- \( Y_{2,m}(\theta, \phi) \leftarrow 5 \text{ } d\text{-orbitals} \)

For each given \( n \), the overall degeneracy of \( l \) and \( m \) quantum numbers is

\[
\sum_{l=0}^{n-1} (2l+1) = \frac{n^2}{2} \text{ number of elements in a period of the periodic table.}
\]
Hydrogen spectrum:

\[ E \]

\[ n = 3 \quad l = 2 \quad \text{d-orb.} \]
\[ n = 2 \quad l = 1 \quad \text{p-orb.} \]
\[ n = 1 \quad l = 0 \quad \text{s-orb.} \]

\[ n_r = 0 \quad n_r = 1 \quad n_r = 2 \]
Matrix representation of operators

Harmonic oscillator:

\[ A^+ |n \rangle = \sqrt{n+1} |n+1 \rangle, \quad \langle n | A^+ \rangle = \delta_{n,n+1} \]

\[ \langle n | A^+ \rangle = \sqrt{n+1} \delta_{n,n+1} \]

\[ \langle n | A \rangle = \sqrt{n} \delta_{n,n-1} \]

One may construct matrix representations for operator \( A \):

\[
A = \begin{pmatrix}
0 & \sqrt{1} & 0 & 0 & \cdots \\
0 & 0 & \sqrt{2} & 0 & \cdots \\
0 & 0 & 0 & \sqrt{3} & \cdots \\
& & & & \\
& & & & 
\end{pmatrix}
\]

Product of operators

\[ \langle i | F G | j \rangle = \sum_n \langle i | F | n \rangle \langle n | G | j \rangle = \sum_n \text{completeness} \]

\[ \sum_n F_{i,n} G_{n,j} \]

\[ \text{product of two matrices} \]

Commutation relations follow as commutation relations of matrix product.