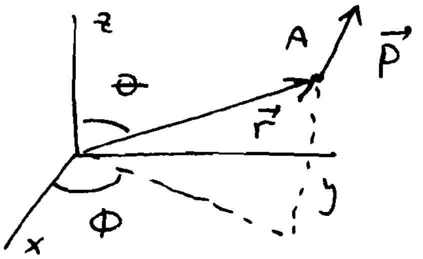
CH 8

SE in 3D

$$H = \frac{\vec{p}^{\,2}}{2\mu} + V(\vec{r})$$



$A = (x, y, z)$ ← Cartesian coordinates

$A = (r, \theta, \Phi)$ ← spherical coordinates

$$\frac{p^2}{2\mu} = -\frac{\hbar^2}{2\mu}\Delta$$

reduced mass, $\mu = \frac{m_1 m_2}{m_1 + m_2}$

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

Example:

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

Central potential: $V(\vec{r}) = V(r)$

example: $V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$

Coulomb attraction

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\vec{L}^2}{\hbar^2 r^2}$$

Angular momentum operator

$$\vec{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\Phi^2}\right)$$

angular momentum operator transforms only spherical angles

3D SE:

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)\psi(\vec{r})+\frac{\vec{L}^2}{2\mu r^2}\psi(\vec{r})+V(r)\psi(\vec{r})=$$
$$=E\,\psi(\vec{r})$$

$$\psi(\vec{r}) = R_{n\ell}(r)\,\underbrace{Y_{\ell m}(\theta,\phi)}_{\text{Spherical harmonic}}$$

two quantum numbers $\underline{\underline{n}}$ and $\underline{\underline{\ell}}$

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

$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{\ell(\ell+1)}{r^2}\right)R_{n\ell}(r)+$$
$$+V(r)\,R_{n\ell}(r) = \underline{E_{n\ell}}\,R_{n\ell}(r)$$

energy spectrum

For hydrogen atom:

$$E_{n\ell} = -13.6\,\text{eV}\,\frac{Z^2}{n^2}$$

energy is independent of quantum number ℓ

Quantum numbers

$$n = n_r + \ell + 1$$

principal quantum number → n

$n_r \geq 0$

$\ell \geq 0$

$\ell \leq n - 1$

Degeneracy: for each ℓ there are $\underline{\underline{2\ell+1}}$ azimuthal (magnetic) quantum numbers $\underline{\underline{m}}$.

They correspond to different atomic orbitals

$Y_{\ell 0}(\theta, \varphi) \leftarrow$ s-orbital

$Y_{1,-1}(\theta,\varphi)$, $Y_{10}(\theta,\varphi)$, $Y_{11}(\theta,\varphi) \leftarrow$ 3 p-orbitals

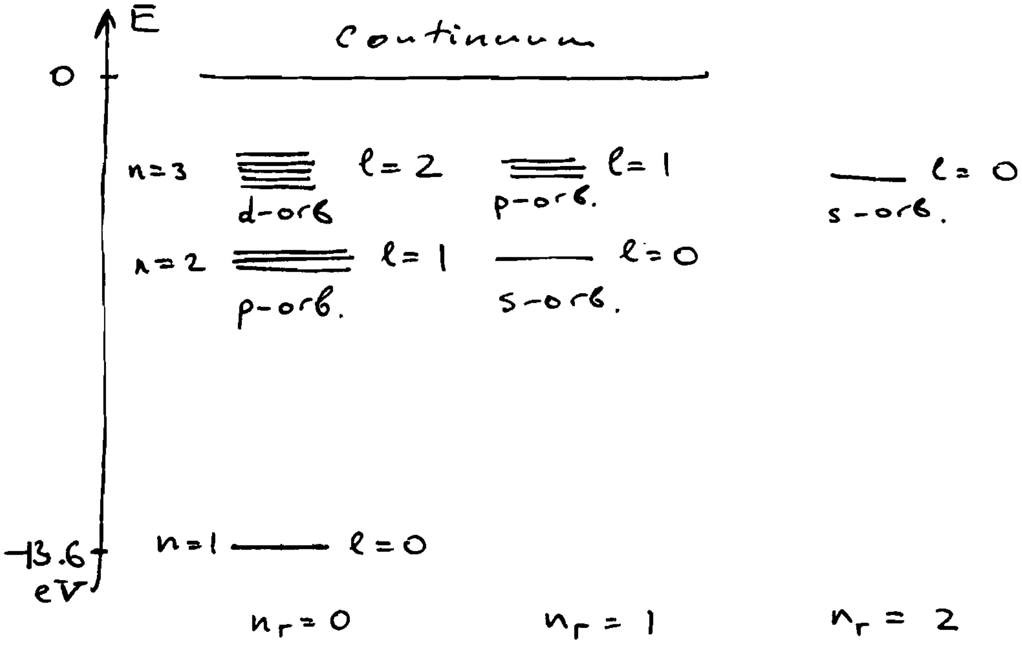
$Y_{2,m}(\theta,\varphi) \leftarrow$ 5 d-orbitals

For each given $\underline{\underline{n}}$, the overall degeneracy of $\underline{\underline{\ell}}$ and $\underline{\underline{m}}$ quantum numbers is

$$\sum_{\ell=0}^{n-1} (2\ell+1) = \underline{\underline{n^2}}$$

← number of elements in a period of the periodic table.

Hydrogen spectrum:



Matrix representation of operators

Harmonic oscillator :

$$A^{+}|n\rangle = \sqrt{n+1}\,|n+1\rangle, \qquad \langle n|m\rangle = \delta_{n,m}$$

$$\langle m|A^{+}|n\rangle = \sqrt{n+1}\,\delta_{m,n+1}$$

$$\langle m|A|n\rangle = \sqrt{n}\,\delta_{m,n-1}$$

One may construct matrix representations for operator A :

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

Product of operators

$$\langle i|FG|j\rangle = \sum_n \underbrace{\langle i|F|n\rangle\langle n|G|j\rangle}_{\text{completeness}} =$$

$$= \sum_n F_{in}\,G_{nj}$$

product of two matrices

Commutation relations follow as commutation relations of matrix product.