POSTECH 이성익 교수의
양자 세계에 관한 강연
- 8장 -

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Chapter 8

The Schrödinger Equation in Three Dimensions

And the Hydrogen Atom

$$p^2(r,\theta,\phi) = p_x{}^2 + p_y{}^2 + p_z{}^2$$

$$\vec{L}^2 + \left(\vec{r}\cdot\vec{p}\right)^2 = r^2 p^2 + i\hbar\left(\vec{r}\cdot\vec{p}\right)$$

Proof) $\vec{L}^2 = \left(\vec{r}\times\vec{p}\right)_x{}^2 + \left(\vec{r}\times\vec{p}\right)_y{}^2 + \left(\vec{r}\times\vec{p}\right)_z{}^2$

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

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

$$\left. -\left(y\frac{\partial}{\partial z}z\frac{\partial}{\partial y} + z\frac{\partial}{\partial y}y\frac{\partial}{\partial z} + z\frac{\partial}{\partial x}x\frac{\partial}{\partial z} + x\frac{\partial}{\partial z}z\frac{\partial}{\partial x} + x\frac{\partial}{\partial y}y\frac{\partial}{\partial x} + y\frac{\partial}{\partial x}x\frac{\partial}{\partial y}\right)\right)$$

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

$$\left. -2\left(x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + z\frac{\partial}{\partial z}\right) - 2\left(xy\frac{\partial}{\partial x}\frac{\partial}{\partial y} + yz\frac{\partial}{\partial y}\frac{\partial}{\partial z} + xz\frac{\partial}{\partial x}\frac{\partial}{\partial z}\right)\right)$$

$$\left(\vec{r}\cdot\vec{p}\right)^2 = -\hbar^2\left(x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + z\frac{\partial}{\partial z}\right)\cdot\left(x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + z\frac{\partial}{\partial z}\right)$$

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

$$\left. +2\left(xy\frac{\partial}{\partial x}\frac{\partial}{\partial y} + yz\frac{\partial}{\partial y}\frac{\partial}{\partial z} + zx\frac{\partial}{\partial z}\frac{\partial}{\partial x}\right)\right)$$

$$\therefore \vec{L}^2 + \left(\vec{r}\cdot\vec{p}\right)^2$$

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

$$= r^2p^2 + i\hbar\left(\vec{r}\cdot\vec{p}\right)$$

$$\therefore p^2 = \frac{1}{r^2}\left(\vec{L}^2 + \left(\vec{r}\cdot\vec{p}\right)^2 - i\hbar\left(\vec{r}\cdot\vec{p}\right)\right)$$

Laplace equation and Hydrogen atom problem

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\cdot\psi_I(r,\theta,\phi) = E\cdot\psi_I(r,\theta,\phi)$$

$$\psi_I(r,\theta,\phi) = R_I(r)\cdot\Theta_I(\theta)\cdot\Phi_I(\phi)$$

Hydrogen Atom의 Schrödinger Equation을 만족시키는 solution은 위와 같이 세 개 항의 곱으로 표현된다.

$\nabla^2\psi_{II}(r,\theta,\phi) = 0$ -> Laplace equation

$$\psi_{II}(r,\theta,\phi) = R_{II}(r)\cdot\Theta_{II}(\theta)\cdot\Phi_{II}(\phi) = R_{II}(r)\cdot Y_{l,m}(\theta,\phi)$$

$$\Theta_I(\theta)\cdot\Phi_I(\phi) = \Theta_{II}(\theta)\cdot\Phi_{II}(\phi) = Y_{l,m}(\theta,\phi)$$

Laplace equation과 Hydrogen atom문제의 angular part는 같다.
따라서 Laplace equation의 solution을 이용하면 Hydrogen atom의 radial part(R(r))만 구함으로서 Hydrogen atom의 total solution을 구할 수 있다.

Separation of Variable

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\cdot U_E(x,y,z)+V(x,y,z)\cdot U_E(x,y,z)=E\cdot U_E(x,y,z)$$

만약 potential이 다음과 같이 표현되면

$$V(x,y,z)=V_1(x)+V_2(y)+V_3(z)$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\cdot U_E(x,y,z)+\left[V_1(x)+V_2(y)+V_3(z)\right]\cdot U_E(x,y,z)$$

$$=E\cdot U_E(x,y,z)$$

Let $U_E(x,y,z)=U_{E_1}(x)\cdot U_{E_2}(y)\cdot U_{E_3}(z)$,

$$\therefore -\frac{\hbar^2}{2m}\frac{d^2U_{E_1}(x)}{dx^2}\frac{1}{U_{E_1}(x)}+V_1(x)$$

$$-\frac{\hbar^2}{2m}\frac{d^2U_{E_2}(y)}{dy^2}\frac{1}{U_{E_2}(y)}+V_2(y)$$

$$-\frac{\hbar^2}{2m}\frac{d^2U_{E_3}(z)}{dz^2}\frac{1}{U_{E_3}(z)}+V_3(z)=E=E_1+E_2+E_3$$

$$\therefore -\frac{\hbar^2}{2m}\frac{d^2U_{E_1}(x)}{dx^2}+V_1(x)\cdot U_{E_1}(x)=E_1\cdot U_{E_1}(x)$$

$$-\frac{\hbar^2}{2m}\frac{d^2U_{E_2}(y)}{dy^2}+V_2(y)\cdot U_{E_2}(y)=E_2\cdot U_{E_2}(y)$$

$$-\frac{\hbar^2}{2m}\frac{d^2U_{E_3}(z)}{dz^2}+V_3(z)\cdot U_{E_3}(z)=E_3\cdot U_{E_3}(z)$$

Hydrogen Atom

$$-\frac{\hbar^2}{2u}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)\cdot\psi(r)+\frac{\vec{L}^2}{2ur^2}\psi(r)+V(r)\cdot\psi(r)=E\cdot\psi(r)$$

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

Let $\psi(r)=R(r)\cdot Y_{l,m}(\theta,\phi)$

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}+\frac{2u}{\hbar^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}-\frac{\hbar^2 l(l+1)}{2ur^2}\right)\right]\cdot R(r)=0$$

$$\rho=\sqrt{\frac{8u|E|}{\hbar^2}}r \qquad \lambda=\frac{Ze^2}{4\pi\varepsilon_0\hbar}\sqrt{\frac{u}{2|E|}}$$

$$\therefore \frac{d^2R(\rho)}{d\rho^2}+\frac{2}{\rho}\frac{dR(\rho)}{d\rho}-\frac{l(l+1)}{\rho^2}R(\rho)+\left(\frac{\lambda}{\rho}-\frac{1}{4}\right)R(\rho)=0$$

$\rho\to\infty$ 에서 $\frac{1}{\rho}\to 0$ 이므로.

$$\therefore \frac{d^2R(\rho)}{d\rho^2}-\frac{1}{4}R(\rho)=0$$

$$\therefore R(\rho)\sim e^{-\frac{\rho}{2}}$$

$$\therefore R(\rho)=e^{-\frac{\rho}{2}}\cdot G(\rho)$$

$\rho\to 0$ 에서,

$$\frac{d^2G(\rho)}{d\rho^2}+\frac{2}{\rho}\frac{dG(\rho)}{d\rho}-\frac{l(l+1)}{\rho^2}G(\rho)=0$$

$$\therefore G(\rho) \sim \rho^{l}$$
$$\therefore G(\rho) = \rho^{l} \cdot H(\rho)$$

$$\therefore \frac{d^2 H(\rho)}{d\rho^2} + \left(\frac{2l+2}{\rho} - 1\right) \cdot \frac{dH(\rho)}{d\rho} + \frac{\lambda - l - 1}{\rho} H(\rho) = 0$$

Let $H(\rho) = \sum_{k=0}^{\infty} a_k \rho^k$.

$$\sum_{k=2}^{\infty} a_k k(k-1)\rho^{k-2} + \left(\frac{2l+2}{\rho} - 1\right) \sum_{k=1}^{\infty} a_k k \rho^{k-1} + \left(\frac{\lambda - l - 1}{\rho}\right) \sum_{k=0}^{\infty} a_k \rho^k$$
$$= \sum_{k=2}^{\infty} a_k k(k-1)\rho^{k-2} + \sum_{k=1}^{\infty} (2l+2) a_k k \rho^{k-2} - \sum_{k=1}^{\infty} a_k k \rho^{k-1} + \sum_{k=0}^{\infty} (\lambda - l - 1) a_k \rho^{k-1}$$
$$= \sum_{k=1}^{\infty} a_{k+1} k(k+1)\rho^{k-1} + \sum_{k=0}^{\infty} (2l+2) a_{k+1} (k+1) \rho^{k-1} - \sum_{k=1}^{\infty} a_k k \rho^{k-1} + \sum_{k=0}^{\infty} (\lambda - l - 1) a_k \rho^{k-1}$$

$$\therefore a_{k+1} k(k+1) + (2l+2) a_{k+1}(k+1) - a_k k + (\lambda - l - 1) a_k = 0$$
$$\therefore a_{k+1}(k+1)(k+2l+2) - a_k (k + l + 1 - \lambda) = 0$$
$$\therefore a_{k+1}(k+1)(k+2l+2) = a_k (k + l + 1 - \lambda)$$
$$\therefore \frac{a_{k+1}}{a_k} = \frac{(k + l + 1 - \lambda)}{(k+1)(k+2l+2)}$$

k가 커지면,

$$\frac{a_{k+1}}{a_k} \simeq \frac{1}{k}$$

$$H(\rho) \simeq e^{\rho}$$

$$R(\rho) \simeq e^{-\frac{\rho}{2}} \cdot \rho^{l} \cdot e^{\rho} = e^{\frac{\rho}{2}} \cdot \rho^{l}$$

이렇게 되면 R(r)이 diverge 하므로,

$\lambda \equiv n_r + l + 1$ 와 같이 정의해 준다.

$$\therefore n = n_r + l + 1$$

n: principle quantum number
l: angular momentum quantum number
m: magnetic quantum number

1. $E = -\frac{1}{2}uc^2 \frac{(Z\alpha)^2}{n^2}$
2. $n \geq l + 1$
3. n is integer

위에서 문제를 풀 때는 상대론적인 영향을 고려하지 않았다. 상대론적인 영향을 고려한 방정식을 풀어내면 총 4개의 solution이 나온다.

$$\left.\begin{matrix} spin\uparrow \\ spin\downarrow \end{matrix}\right\} \quad E > 0$$

$$\left.\begin{matrix} spin\uparrow \\ spin\downarrow \end{matrix}\right\} \quad E < 0 \quad \Rightarrow \text{반입자}$$

$$n = n_r + l + 1$$

$2l+1$의 degeneracy (spin을 고려하면 $2(2l+1)$)

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2 g^2}{2ur^2}$$

만약 potential을 위와 같이 잡아주면 n_r 과 l에 의한 degeneracy 를 없애줄 수 있다. 이 때의 energy는,

$$\therefore E = -\frac{1}{2}uc^2 \frac{(Z\alpha)^2}{\left(n_r + \frac{1}{2} + \sqrt{\left(l + \frac{1}{2}\right)^2 + g^2}\right)^2}$$