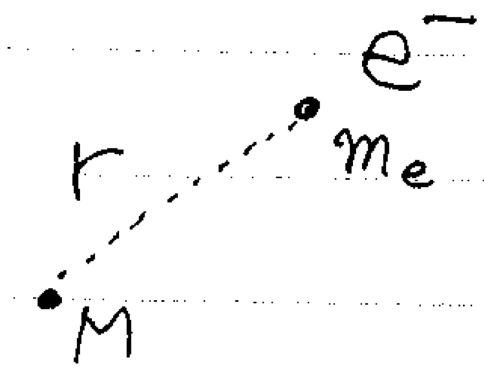
§ 水素原子に対する変分計算(1) (H.O. 型変分)

• (原子単位における)水素原子のハミルトニアン

$$\boxed{\hat{H} = -\frac{\hbar}{2\mu}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right) - \frac{Z^2}{r}} \cdots (1)$$

$Z = 1$



$\mu = \frac{M \cdot m_e}{M + m_e}$ 換算質量

$\left(\frac{1}{\mu} = \frac{1}{M} + \frac{1}{m_e}\right)$

半径方向の波動関数に対する(基底状態) (CGS単位系)

• 試行関数 $\boxed{\Psi(r) = e^{-\zeta r}}$ $\cdots (2)$ (ζ : 変分パラメタ)
ツェータ (zeta)

$$\rightarrow \frac{d\Psi(r)}{dr} = -\zeta \cdot e^{-\zeta r}, \quad \frac{d^2\Psi}{dr^2} = \zeta^2 e^{-\zeta r}$$

$$\rightarrow \hat{H}\Psi(r) = -\frac{\hbar}{2\mu}\left\{\zeta^2 e^{-\zeta r} - \frac{2\zeta}{r} e^{-\zeta r}\right\} - \frac{1}{r} e^{-\zeta r}$$

$$\rightarrow \underline{\Psi^*(r)\,\hat{H}\,\Psi(r) = -\frac{1}{2\mu}\left\{\zeta^2 e^{-2\zeta r} - \frac{2\zeta}{r} e^{-2\zeta r}\right\} - \frac{e^{-2\zeta r}}{r}} \cdots (3)$$

• 規格化積分

rについての微分

$$\int_0^\infty \Psi^*(r)\cdot\Psi(r)\, r^2 dr = \underline{\underline{\int_0^\infty e^{-2\zeta r} r^2 dr}} = \int_0^\infty \left(-\frac{e^{-2\zeta r}}{2\zeta}\right)' \cdot r^2 dr$$

$$= \underbrace{\left[-\frac{e^{-2\zeta r}}{2\zeta} r^2\right]_{r=0}^{r=\infty}}_{0} + \underbrace{\frac{1}{2\zeta}\int_0^\infty e^{-2\zeta r} \times 2r \cdot dr}$$

$$= \frac{1}{\zeta}\int_0^\infty e^{-2\zeta r} \cdot r\, dr =$$

$$= \frac{1}{\zeta}\left\{\underbrace{\left[-\frac{e^{-2\zeta r}}{2\zeta} \times r\right]_0^\infty}_{0} + \frac{1}{2\zeta}\int_0^\infty e^{-2\zeta r} dr\right\}$$

$$= \frac{1}{4\zeta^3}. \cdots (4)$$

• ハミルトニアンの積分

$$\int_0^\infty \Psi^*(r)\,\hat{H}\Psi(r)\, r^2 dr = \int_0^\infty \left\{-\frac{1}{2\mu}\left[\zeta^2 e^{-2\zeta r} - \frac{2\zeta}{r} e^{-2\zeta r}\right] - \frac{e^{-2\zeta r}}{r}\right\} r^2 dr$$

$$= \int_0^\infty \left\{-\frac{\zeta^2}{2\mu} e^{-2\zeta r} \cdot r^2 + \left(\frac{2\zeta}{2\mu} - 1\right)\frac{e^{-2\zeta r}}{r} \times r^2\right\} dr$$

$$= \int_0^\infty \left\{-\frac{\zeta^2}{2\mu} \underbrace{e^{-2\zeta r} \cdot r^2}_{\frac{1}{4\zeta^3}} + \left(\frac{2\zeta}{2\mu} - 1\right) \underline{e^{-2\zeta r} \cdot r}\right\} dr,$$

ここで

$$\int_0^\infty e^{-2\zeta r} r\,dr = \left[-\frac{e^{-2\zeta r}}{2\zeta} r\right]_0^\infty + \frac{1}{2\zeta}\int_0^\infty e^{-2\zeta r}dr$$

0

$$= \frac{1}{2\zeta}\left[-\frac{e^{-2\zeta r}}{2\zeta}\right]_0^\infty = \frac{1}{4\zeta^2}.$$

∴

$$\int_0^\infty \Phi^*(r)\hat{H}\Phi(r) r^2 dr = -\frac{\zeta^2}{2\mu}\times\frac{1}{4\zeta^3} + \left(\frac{2\zeta}{2\mu}-1\right)\times\frac{1}{4\zeta^2}$$

$$= \frac{1}{8\mu\zeta} - \frac{1}{4\zeta^2} \quad \cdots (5)$$

∴

$$\boxed{\xi(\zeta) \equiv \frac{\int_0^\infty \Phi^*(r)\hat{H}\Phi(r) r^2 dr}{\int_0^\infty \Phi^*(r)\Phi(r) r^2 dr}}$$

ξ : Xi

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$$= \frac{\left(\frac{1}{8\mu\zeta} - \frac{1}{4\zeta^2}\right)}{\left(\frac{1}{4\zeta^3}\right)} = \frac{\zeta^2}{2\mu} - \zeta. \quad \cdots (6)$$

∴ 変分

$$\boxed{0 = \frac{d\xi(\zeta)}{d\zeta}} \quad \cdots (7)$$

$$= \frac{2\zeta}{2\mu} - 1 \quad \therefore \boxed{\zeta = 1} \cdots (8)$$

$$\mu = \frac{M\cdot m_e}{M+m_e} = \frac{m_e}{1+\frac{m_e}{M}} = \frac{1}{1+\frac{1}{1860}} m_e \fallingdotseq 0.99946218\, m_e$$

$$\fallingdotseq m_e \,/\!/$$

$$\boxed{\xi(\zeta=1) = -0.500\,(\text{a.u.})} \Leftrightarrow \xi_{exact} = -0.500\,(\text{a.u.}) \quad \cdots (9)$$