$\boxed{\text{P31.1}}$ For the hydrogen atom problem, the Hamiltonian is given by

$$H = \frac{-\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} \leftarrow \text{Coulomb potential} \quad \left(\begin{array}{l} m = \text{reduced mass of electron-proton system} \\ \approx m_e \text{ (mass of electron)} \end{array}\right)$$

[see Eq. (16.2) in text]
$$= \frac{-\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hbar^2 L^2}{2mr^2} - \frac{e^2}{r},$$

where $\vec{L}$ is the orbital angular momentum operator satisfying

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

and $Y_\ell^m(\theta,\phi)$ is a spherical harmonic. We use a <u>trial</u> ground state wave function (with a Gaussian orbital):

$$\langle \vec{r} \,|\, \overset{n}{1}\,\overset{\ell}{0}\,\overset{m}{0} \rangle = \psi_{100}(r,\theta,\phi) = N_{100}\, e^{-\alpha r^2}\, Y_0^0(\theta,\phi)$$

$$= \frac{N_{100}}{\sqrt{4\pi}} e^{-\alpha r^2}, \quad \left(\text{since } Y_0^0(\theta,\phi) = \frac{1}{\sqrt{4\pi}}\right)$$

normalization constant to be determined.

(see Eq. (21.53a) in text)

and a variation parameter α. Then the ground state energy $E_{100}(\alpha)$ is given by

integration over all solid angles

$$E_{100}(\alpha) = \langle 100 | H | 100 \rangle = \frac{|N_{100}|^2}{4\pi}\int_0^\infty dr\, r^2 \int d\Omega$$

$$\times\, e^{-\alpha r^2}\left[\frac{-\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \underbrace{\cancel{\frac{\hbar^2 \ell(\ell+1)}{2mr^2}}}_{=0 \text{ since } \ell=0} - \frac{e^2}{r}\right] e^{-\alpha r^2}$$

$$= |N_{100}|^2 \int_0^\infty dr\, r^2 e^{-\alpha r^2}\left\{\frac{-\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{e^2}{r}\right\} e^{-\alpha r^2}$$

$$r^2\frac{\partial}{\partial r}e^{-\alpha r^2} = r^2(-2\alpha r)e^{-\alpha r^2} = -2\alpha r^3 e^{-\alpha r^2}$$

$$\therefore \frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}e^{-\alpha r^2}\right) = -(2\alpha)\frac{\partial}{\partial r}\left(r^3 e^{-\alpha r^2}\right) = -2\alpha\left(3r^2 e^{-\alpha r^2} - 2\alpha r^4 e^{-\alpha r^2}\right)$$

$$= -2\alpha r^2(3 - 2\alpha r^2)e^{-\alpha r^2}$$

$\boxed{\text{P31.1}}$ cont'd

$$E_{100}(\alpha) = |N_{100}|^2 \int_0^\infty dr\, r^2 e^{-\alpha r^2} \left[\underbrace{-\frac{\hbar^2}{2mr^2}\left\{-2\alpha r^2(3-2\alpha r^2)e^{-\alpha r^2}\right\}}_{\frac{\hbar^2}{m}\alpha e^{-\alpha r^2}(3-2\alpha r^2)} - \frac{e^2}{r} \right] e^{-\alpha r^2}$$

$$= |N_{100}|^2 \left[\frac{\hbar^2}{m}\alpha \int_0^\infty dr\, r^2 e^{-2\alpha r^2}(3-2\alpha r^2) - e^2 \int_0^\infty dr\, r\, e^{-2\alpha r^2} \right]$$

$$= |N_{100}|^2 \left[\frac{\hbar^2}{m}\alpha \left\{ 3\int_0^\infty dr\, r^2 e^{-2\alpha r^2} - 2\alpha \int_0^\infty dr\, r^4 e^{-2\alpha r^2} \right\} - e^2 \int_0^\infty dr\, r\, e^{-2\alpha r^2} \right]$$

Use the given formulas for Gaussian integrals

$$\int_0^\infty dr\, e^{-\alpha r^2} = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

$$\int_0^\infty dr\, r^{2m} e^{-\alpha r^2} = \frac{1\cdot 3\cdot 5 \cdots (2m-1)}{2^{m+1}\alpha^m}\sqrt{\frac{\pi}{\alpha}}$$

$$\int_0^\infty dr\, r^{2m+1} e^{-\alpha r^2} = \frac{m!}{2\alpha^{m+1}}$$

to get

$$3\int_0^\infty dr\, r^2 e^{-2\alpha r^2} = 3\cdot\frac{1}{2^2(2\alpha)}\sqrt{\frac{\pi}{2\alpha}} = \frac{3}{8\alpha}\sqrt{\frac{\pi}{2\alpha}}$$

$$2\alpha\int_0^\infty dr\, r^4 e^{-2\alpha r^2} = \frac{(2\alpha)\cdot 1\cdot 3}{2^3(2\alpha)^2}\sqrt{\frac{\pi}{2\alpha}} = \frac{3}{8(2\alpha)}\sqrt{\frac{\pi}{2\alpha}}$$

$$e^2\int_0^\infty dr\, r\, e^{-2\alpha r^2} = e^2\cdot\frac{1}{2\cdot(2\alpha)} = \frac{e^2}{4\alpha}$$

$\boxed{\text{P31.1}}$ cont'd

$$\therefore\ E_{100}(\alpha) = |N_{100}|^2 \left[\frac{\hbar^2\alpha}{m} \left\{ 2\cdot \frac{3}{8(2\alpha)}\sqrt{\frac{\pi}{2\alpha}} - \frac{3}{8(2\alpha)}\sqrt{\frac{\pi}{2\alpha}} \right\} - \frac{e^2}{4\alpha} \right]$$

$$= |N_{100}|^2 \left[\frac{\hbar^2\alpha}{m} \cdot \frac{3}{8(2\alpha)} \sqrt{\frac{\pi}{2\alpha}} - \frac{e^2}{4\alpha} \right]$$

From the normalization requirement

$$\langle 100|100\rangle = 1$$

we have

$$\frac{|N_{100}|^2}{4\pi} \int d\Omega \int_0^\infty dr\, r^2 e^{-2\alpha r^2} = 1 \quad , \text{ that is}$$

$$|N_{100}|^2 \int_0^\infty dr\, r^2 e^{-2\alpha r^2} = \frac{|N_{100}|^2}{2^2(2\alpha)} \sqrt{\frac{\pi}{2\alpha}} = 1 \quad , \text{ that is}$$

$$|N_{100}|^2 = \frac{8\alpha\sqrt{2\alpha}}{\sqrt{\pi}} .$$

Thus

$$E_{100}(\alpha) = \frac{8\alpha\sqrt{2\alpha}}{\sqrt{\pi}} \left[\frac{\hbar^2\alpha}{m} \cdot \frac{3}{8(2\alpha)} \sqrt{\frac{\pi}{2\alpha}} - \frac{e^2}{4\alpha} \right] \quad , \text{ or}$$

$$\boxed{E_{100}(\alpha) = \frac{3\hbar^2}{2m}\cdot\alpha - 2e^2\sqrt{\frac{2\alpha}{\pi}}}$$

To minimize $E_{100}(\alpha)$ we set

$$\frac{d}{d\alpha} E_{100}(\alpha) = 0 \quad , \quad \text{get}$$

$$\frac{3\hbar^2}{2m} - \frac{2e^2}{2}\cdot\sqrt{\frac{2}{\pi}}\cdot\frac{1}{\sqrt{\alpha}} = 0$$

$$\Rightarrow \boxed{\alpha_0 = \frac{2}{\pi}\left(\frac{2me^2}{3\hbar^2}\right)^2} \longleftarrow \text{value of } \alpha \text{ leading to minimum value for } E_{100}(\alpha).$$

(Note: α_0 is indeed a minimum for $E_{100}(\alpha)$ since it is readily seen that $\frac{d^2}{d\alpha^2}E_{100}(\alpha) > 0$, from the above expression for the 1st. derivative.)

$\boxed{P31.1}$ cont'd

We thus have

$$E_{100}(\alpha_0) = \frac{3\hbar^2}{2m}\cdot\frac{2}{\pi}\left(\frac{2me^2}{3\hbar^2}\right)^2 - 2e^2\sqrt{\frac{2}{\pi}}\cdot\sqrt{\frac{2}{\pi}}\left(\frac{2me^2}{3\hbar^2}\right)$$

$$= \frac{4me^4}{3\pi\hbar^2} - \frac{8}{3\pi}\cdot\frac{me^4}{\hbar^2} = -\frac{4}{3\pi}\frac{me^4}{\hbar^2}$$

$\therefore$ Our variational calculation gives

$$\boxed{E_{100}^{\text{variational}} = -\frac{4}{3\pi}\frac{me^4}{\hbar^2}}$$

The exact value of E_{100} is given by [using $Z=1$ and $n=1$ in Eq. (30.61)]

$$E_{100}^{\text{exact}} = -\frac{me^4}{2\hbar^2}$$

$\therefore$ $E_{100}^{\text{variational}} > E_{100}^{\text{exact}}$ by only about 15 %

(not bad!)