

4.1 $\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$ since ψ_{100} does not depend on θ and ϕ .

$$-\frac{\hbar^2}{2m_e} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi_{100}}{\partial r} \right) + 0 + 0 \right] - \frac{e^2}{4\pi\epsilon_0 r} \psi_{100} = E \psi_{100} \quad (5)$$

$$\text{left} = -\frac{\hbar^2}{2m_e} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} \left(-\frac{1}{a_0}\right) \right) \right] - \frac{e^2}{4\pi\epsilon_0 r} \psi_{100}$$

$$= +\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{\partial}{\partial r} \left(r^2 e^{-r/a_0} \right) - \frac{e^2}{4\pi\epsilon_0 r} \psi_{100} \quad (1)$$

$$= \frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left[2r e^{-r/a_0} + r^2 e^{-r/a_0} \left(-\frac{1}{a_0}\right) \right] - \frac{e^2}{4\pi\epsilon_0 r} \psi_{100} \quad (2)$$

$$= \frac{\hbar^2}{2m_e} \frac{1}{r} \frac{1}{\sqrt{\pi}} \frac{1}{a_0} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} - \frac{\hbar^2}{2m_e} \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^2 \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} - \frac{e^2}{4\pi\epsilon_0 r} \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$= \left(\frac{\hbar^2}{m_e} \frac{1}{r} \frac{1}{a_0} - \frac{\hbar^2}{2m_e} \left(\frac{1}{a_0}\right)^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi_{100} \quad \text{remember } a_0 = \frac{\epsilon_0 \hbar^2}{\pi m_e e^2}$$

$$= \left(\frac{\hbar^2}{4\pi^2 m_e r} \cdot \frac{\pi m_e e^2}{\epsilon_0 \hbar^2} - \frac{\hbar^2}{8\pi^2 m_e} \frac{\pi^2 m_e^2 e^4}{\epsilon_0^2 \hbar^4} - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi_{100} \quad (1)$$

$$= \left(\frac{e^2}{4\pi\epsilon_0 r} - \frac{m_e e^4}{8\epsilon_0^2 \hbar^2} - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi_{100} = -\frac{m_e e^4}{8\epsilon_0^2 \hbar^2} \psi_{100}$$

$$E_{100} = -\frac{m_e e^4}{8\epsilon_0^2 \hbar^2} = -\frac{e^2}{8\pi\epsilon_0 a_0} \quad (1)$$

9.2 a) $E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} = -\frac{e^2}{32\pi\epsilon_0 a_0} \Rightarrow n=2 \quad (1)$ Degeneracy = $n^2 = 4$ (1)

$\psi_{200}, \psi_{211}, \psi_{210}, \psi_{21-1}$ (1)

b) $E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} = -\frac{e^2}{72\pi\epsilon_0 a_0} \Rightarrow n=3 \quad (1)$ Degeneracy = $n^2 = 9$ (1)

$\psi_{300}, \psi_{311}, \psi_{310}, \psi_{31-1}, \psi_{322}, \psi_{321}, \psi_{320}, \psi_{32-1}, \psi_{32-2}$ (1)

c) $E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} = -\frac{e^2}{128\pi\epsilon_0 a_0} \Rightarrow n=4 \quad (1)$ Degeneracy = $n^2 = 16$ (1)

$\psi_{400}, \psi_{411}, \psi_{410}, \psi_{41-1}, \psi_{422}, \psi_{421}, \psi_{420}, \psi_{42-1}, \psi_{42-2}$

$\psi_{433}, \psi_{432}, \psi_{431}, \psi_{430}, \psi_{43-1}, \psi_{43-2}, \psi_{43-3}$ (1)

9.7 (b) Hydrogen atom in the ground state: wavefunction = $\psi_{1,0,0}$

$$\text{Probability} = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^r \psi_{1,0,0}^* \psi_{1,0,0} r^2 dr \quad (1)$$

$$= \frac{1}{\pi a_0^3} \cdot 2\pi \cdot 2 \int_0^r r^2 e^{-\frac{2r}{a_0}} dr$$

$$= \frac{4}{a_0^3} \int_0^r r^2 e^{-\frac{2r}{a_0}} dr$$

$$= \frac{4}{a_0^3} \int_0^r r^2 \left(-\frac{a_0}{2}\right) d\left(e^{-\frac{2r}{a_0}}\right)$$

$$= -\frac{2}{a_0^3} \left[r^2 e^{-\frac{2r}{a_0}} \Big|_0^r - \int_0^r e^{-\frac{2r}{a_0}} 2r dr \right]$$

~~$$\frac{4}{a_0^3} \left[r^2 e^{-\frac{2r}{a_0}} \Big|_0^r - \int_0^r e^{-\frac{2r}{a_0}} 2r dr \right]$$~~

~~$$\frac{4}{a_0^3} \left[r^2 e^{-\frac{2r}{a_0}} \Big|_0^r - \int_0^r e^{-\frac{2r}{a_0}} 2r dr \right]$$~~

$$= -\frac{2}{a_0^3} \left[r^2 e^{-\frac{2r}{a_0}} - 2\left(-\frac{a_0}{2}\right) \left(r e^{-\frac{2r}{a_0}} \Big|_0^r - \int_0^r e^{-\frac{2r}{a_0}} dr \right) \right] \quad (1)$$

$$= -\frac{2}{a_0^3} \left[r^2 e^{-\frac{2r}{a_0}} + a_0 \left(r e^{-\frac{2r}{a_0}} + \frac{a_0}{2} e^{-\frac{2r}{a_0}} \Big|_0^r \right) \right]$$

$$= -\frac{2}{a_0^3} \left[r^2 e^{-\frac{2r}{a_0}} + a_0 r e^{-\frac{2r}{a_0}} + \left(\frac{a_0^2}{2}\right) \left(e^{-\frac{2r}{a_0}} - 1 \right) \right] \quad (1)$$

$$= -\frac{2r^2}{a_0^3} e^{-\frac{2r}{a_0}} - \frac{2r}{a_0} e^{-\frac{2r}{a_0}} - e^{-\frac{2r}{a_0}} + 1$$

$$= 1 - e^{-\frac{2r}{a_0}} - \frac{2r}{a_0} \left(1 + \frac{r}{a_0} \right) e^{-\frac{2r}{a_0}} \quad \text{as requested!}$$

9.7 (c) when $r = 0.10 a_0$, probability = $1 - e^{-0.2} - 0.2(1+0.1)e^{-0.2}$ (1)

$$= 1.2 \times 10^{-3}$$

$r = 1.0 a_0$, probability = $1 - e^{-2} - 2(1+1)e^{-2}$ (1)

$$= 0.32$$

$r = 4.0 a_0$, probability = $1 - e^{-8} - 8(1+4)e^{-8}$ (1)

$$= 0.986$$

9.13. $\Psi_{210}(r, \theta, \varphi) = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{\frac{3}{2}} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \cos\theta$

$\langle r \rangle = \frac{\int \Psi_{210}^* r \Psi_{210} d\tau}{\int \Psi_{210}^* \Psi_{210} d\tau}$ in spherical coordinate systems.

$$\begin{aligned} \langle r \rangle &= \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta \int_0^\infty \Psi_{210}^* r \Psi_{210} r^2 dr \\ &= 2\pi \int_0^\pi \sin\theta \cos^2\theta d\theta \cdot \frac{1}{32\pi} \left(\frac{1}{a_0}\right)^3 \frac{1}{a_0} \int_0^\infty r^5 e^{-\frac{r}{a_0}} dr \\ &= \frac{1}{16} \frac{1}{a_0^5} \cdot \frac{2}{3} \int_0^\infty r^5 e^{-\frac{r}{a_0}} dr \\ &= \frac{1}{24 a_0^5} \int_0^\infty r^5 e^{-\frac{r}{a_0}} dr \quad \text{remember } \int_0^\infty r^n e^{-ar} = \frac{n!}{a^{n+1}} \\ &= \frac{1}{24 a_0^5} \frac{5!}{\left(\frac{1}{a_0}\right)^6} = \frac{5 \cdot 4 \cdot 3 \cdot 2 \cdot 1 \cdot a_0^6}{24 a_0^5} = 5 a_0 \end{aligned}$$

- 10.2 a) $\Psi_{(1,2)} = [1s(1)2s(2) + 2s(1)1s(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)] = -\Psi_{(1,2)}$ Antisymmetric (2)
- b) $\Psi_{(2,1)} = [1s(2)2s(1) + 2s(2)1s(1)] \alpha(2)\alpha(1) = \Psi_{(1,2)}$ Symmetric (3)
- c) $\Psi_{(2,1)} = [1s(2)2s(1) + 2s(2)1s(1)] [\alpha(2)\beta(1) + \beta(2)\alpha(1)] = \Psi_{(1,2)}$ Symmetric (3)
- d) $\Psi_{(2,1)} = [1s(2)2s(1) - 2s(2)1s(1)] [\alpha(2)\beta(1) + \beta(2)\alpha(1)] = -\Psi_{(1,2)}$ Antisymmetric (3)
- e) $\Psi_{(2,1)} = [1s(2)2s(1) + 2s(2)1s(1)] [\alpha(2)\beta(1) - \beta(2)\alpha(1) + \alpha(2)\alpha(1)] \neq \Psi_{(1,2)}$ or $-\Psi_{(1,2)}$ Neither (2)

10.5 $\hat{S}_{total} = (\hat{S}_1 + \hat{S}_2)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2(\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z})$

(3) $\hat{S}_{total}^2 \alpha(1)\beta(2) = \hat{S}_1^2 \alpha(1)\beta(2) + \hat{S}_2^2 \alpha(1)\beta(2) + 2(\hat{S}_{1x}\hat{S}_{2x} \alpha(1)\beta(2) + \hat{S}_{1y}\hat{S}_{2y} \alpha(1)\beta(2) + \hat{S}_{1z}\hat{S}_{2z} \alpha(1)\beta(2))$

$$\begin{aligned} &= \frac{3\hbar^2}{4} \alpha(1)\beta(2) + \frac{3\hbar^2}{4} \alpha(1)\beta(2) + 2\left[\frac{\hbar}{2} \beta(1) \frac{\hbar}{2} \alpha(2) + \frac{i\hbar}{2} \beta(1) \left(-\frac{i\hbar}{2}\right) \alpha(2) + \frac{\hbar}{2} \alpha(1) \left(-\frac{\hbar}{2}\right) \beta(2) \right] \\ &= \frac{3\hbar^2}{4} \alpha(1)\beta(2) + \frac{3\hbar^2}{4} \alpha(1)\beta(2) + \frac{\hbar^2}{2} \beta(1)\alpha(2) + \frac{\hbar^2}{2} \beta(1)\alpha(2) - \frac{\hbar^2}{2} \alpha(1)\beta(2) \\ &= \frac{3\hbar^2}{2} \alpha(1)\beta(2) - \frac{\hbar^2}{2} \alpha(1)\beta(2) + \hbar^2 \beta(1)\alpha(2) \\ &= \hbar^2 \alpha(1)\beta(2) + \hbar^2 \beta(1)\alpha(2) \quad (2) \end{aligned}$$

(3) $\hat{S}_{total}^2 \beta(1)\alpha(2) = \hat{S}_1^2 \beta(1)\alpha(2) + \hat{S}_2^2 \beta(1)\alpha(2) + 2(\hat{S}_{1x}\hat{S}_{2x} \beta(1)\alpha(2) + \hat{S}_{1y}\hat{S}_{2y} \beta(1)\alpha(2) + \hat{S}_{1z}\hat{S}_{2z} \beta(1)\alpha(2))$

$$\begin{aligned} &= \frac{3\hbar^2}{4} \beta(1)\alpha(2) + \frac{3\hbar^2}{4} \beta(1)\alpha(2) + 2\left[\frac{\hbar}{2} \alpha(1) \frac{\hbar}{2} \beta(2) + \left(-\frac{i\hbar}{2}\right) \alpha(1) \left(i\frac{\hbar}{2}\right) \beta(2) - \frac{\hbar^2}{4} \beta(1)\alpha(2) \right] \\ &= \frac{3\hbar^2}{2} \beta(1)\alpha(2) + \frac{\hbar^2}{2} \alpha(1)\beta(2) + \frac{\hbar^2}{2} \alpha(1)\beta(2) - \frac{\hbar^2}{2} \beta(1)\alpha(2) \\ &= \hbar^2 \beta(1)\alpha(2) + \hbar^2 \alpha(1)\beta(2) \quad (2) \end{aligned}$$

OR S_{pts} each w.f.
 Setup S_{total} with 3 pts
 Process with 3 w.f. pts

$$\begin{aligned} \text{Total force} \int_{\text{total}}^{\lambda^2} \frac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}} &= \frac{\hbar^2 \alpha(1)\beta(2) + \hbar^2 \beta(1)\alpha(2) + \hbar^2 \beta(1)\alpha(2) + \hbar^2 \alpha(1)\beta(2)}{\sqrt{2}} \\ &= 2\hbar^2 \cdot \frac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}} \\ \text{eigenvalue} &= 2\hbar^2. \end{aligned}$$

$$\begin{aligned} \int_{\text{total}}^{\lambda^2} \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}} &= \frac{\hbar^2 \alpha(1)\beta(2) + \hbar^2 \beta(1)\alpha(2) - \hbar^2 \beta(1)\alpha(2) - \hbar^2 \alpha(1)\beta(2)}{\sqrt{2}} \\ &= 0 \quad \therefore \text{eigenvalue} = 0. \end{aligned}$$

(a) $\hat{H}\phi = -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi(r)}{\partial r} \right) - \frac{e^2}{4\pi\epsilon_0 r} \phi(r) \quad \phi(r) = e^{-\alpha r}$

$$\begin{aligned} &= -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 e^{-\alpha r} (-\alpha) \right] - \frac{e^2}{4\pi\epsilon_0 r} \phi(r) \\ &= \frac{\hbar^2}{2m_e} \frac{1}{r^2} \alpha \cdot \left[2r e^{-\alpha r} + r^2 e^{-\alpha r} (-\alpha) \right] - \frac{e^2}{4\pi\epsilon_0 r} \phi(r) \quad (2) \\ &= \frac{\alpha \hbar^2}{2m_e r^2} [2r - \alpha r^2] e^{-\alpha r} - \frac{e^2}{4\pi\epsilon_0 r} e^{-\alpha r} \end{aligned}$$

(b) $\int \phi^* \hat{H} \phi d\tau = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty e^{-\alpha r} \left[\frac{\alpha \hbar^2}{2m_e r^2} [2r - \alpha r^2] - \frac{e^2}{4\pi\epsilon_0 r} \right] e^{-\alpha r} r^2 dr \quad (1)$

$$\begin{aligned} &= 4\pi \cdot \left[\int_0^\infty \frac{\alpha \hbar^2}{2m_e} 2r e^{-2\alpha r} dr - \int_0^\infty \frac{\alpha^2 \hbar^2}{2m_e} r^2 e^{-2\alpha r} dr - \int_0^\infty \frac{e^2}{4\pi\epsilon_0} r e^{-2\alpha r} dr \right] \\ &= 4\pi \cdot \left[\frac{\alpha \hbar^2}{m_e} \int_0^\infty r e^{-2\alpha r} dr - \frac{\alpha^2 \hbar^2}{2m_e} \int_0^\infty r^2 e^{-2\alpha r} dr - \frac{e^2}{4\pi\epsilon_0} \int_0^\infty r e^{-2\alpha r} dr \right] \\ &= 4\pi \cdot \left[\frac{\alpha \hbar^2}{m_e} \frac{1!}{4\alpha^2} - \frac{\alpha^2 \hbar^2}{2m_e} \cdot \frac{2!}{8\alpha^3} - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1!}{4\alpha^2} \right] \quad (1) \\ &= 4\pi \cdot \left[\frac{\alpha \hbar^2}{4m_e \alpha} - \frac{\hbar^2}{8m_e \alpha} - \frac{e^2}{4\pi\epsilon_0 \cdot 4\alpha^2} \right] \\ &= \frac{\pi \hbar^2}{2m_e \alpha} - \frac{e^2}{4\pi\epsilon_0 \alpha^2} \quad \text{as requested} \end{aligned}$$

(c) $\int \phi^* \phi d\tau = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty \phi^* \phi r^2 dr \quad (1)$

$$\begin{aligned} &= 4\pi \int_0^\infty r^2 e^{-2\alpha r} dr \\ &= 4\pi \cdot \frac{2!}{8\alpha^3} = \frac{\pi}{\alpha^3} \quad \text{as requested.} \end{aligned}$$

(1)

$$(d) E(\alpha) = \frac{\pi^2 \alpha^2}{2me} - \frac{e^2 \alpha}{4\pi \epsilon_0}$$

$$\frac{d}{d\alpha} E(\alpha) = \frac{2\pi^2 \alpha}{2me} - \frac{e^2}{4\pi \epsilon_0} \stackrel{\text{optimal}}{=} 0 \quad \alpha = \frac{me e^2}{4\pi \epsilon_0 \hbar^2}$$

$$(e) E(\alpha_{\text{optimal}}) = \frac{\hbar^2}{2me} \cdot \frac{me^2 e^4}{16\pi^2 \epsilon_0^2 \hbar^4} - \frac{e^2}{4\pi \epsilon_0} \frac{me e^2}{4\pi \epsilon_0 \hbar^2}$$

$$= \frac{me e^4}{32\pi^2 \epsilon_0^2 \hbar^2} - \frac{me e^4}{16\pi^2 \epsilon_0 \hbar^2} = - \frac{me e^4}{32\pi^2 \epsilon_0^2 \hbar^2}$$

$$= E_{\text{true}}$$

Trial w.f. has the same form as the true wave function.

10.12 (a) $^4S : L=0, 2S+1=4 \Rightarrow S=3/2$ 2.5 levels

(b) $^4G : L=4, 2S+1=4, S=3/2$

(c) $^3P : L=1, 2S+1=3, S=1$

(d) $^2D : L=2, 2S+1=2, S=1/2$

10.21 (a) $s^1 d^5$: $s \uparrow_0 = m_s$

$d \uparrow \uparrow \uparrow \uparrow \uparrow$ (1)

$2 \ 1 \ 0 \ -1 \ -2 = m_l$

Spatial m_l
0 1 2 3 4 5

$M_{L_{\text{max}}} = |0+2+1+0+(-1)+(-2)| = 0 \rightarrow S$ (1)

$M_{S_{\text{max}}} = |1/2 + 1/2 + 1/2 + 1/2 + 1/2 + 1/2| = 3$

$2S+1 = 7 \Rightarrow \boxed{^7S}$

(b) f^3 : $\uparrow \uparrow \uparrow \text{---} \text{---} \text{---} \text{---}$
 $m_l = 3 \ 2 \ 1 \ 0 \ -1 \ -2 \ -3$

$M_{L_{\text{max}}} = |3+2+1| = 6 \rightarrow I$

$M_{S_{\text{max}}} = |1/2 + 1/2 + 1/2| = 3/2 \rightarrow \boxed{^4I}$
 $2S+1 = 4$

etc
:
:

(c) g^2 : $\uparrow \uparrow \text{---} \text{---} \text{---} \text{---} \text{---} \text{---}$
 $m_l = 4 \ 3 \ 2 \ 1 \ 0 \ -1 \ -2 \ -3 \ -4$

$M_{L_{\text{max}}} = |4+3| = 7 \rightarrow J$

$M_{S_{\text{max}}} = |1/2 + 1/2| = 1 \rightarrow \boxed{^3J}$
 $2S+1 = 3$