Problem 4.34

(a)

$$S_-|1\ 0\rangle = (S_-^{(1)} + S_-^{(2)})\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) = \frac{1}{\sqrt{2}}\left[(S_- \uparrow)\downarrow + (S_- \downarrow)\uparrow + \uparrow(S_- \downarrow) + \downarrow(S_- \uparrow)\right].$$

But $S_- \uparrow = \hbar \downarrow$, $S_- \downarrow = 0$ (Eq. 4.143), so $S_-|10\rangle = \frac{1}{\sqrt{2}}\left[\hbar \downarrow\downarrow + 0 + 0 + \hbar \downarrow\downarrow\right] = \sqrt{2}\hbar \downarrow\downarrow = \sqrt{2}\hbar|1\ -1\rangle.$ ✓

(b)

$$S_\pm|0\ 0\rangle = (S_\pm^{(1)} + S_\pm^{(2)})\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) = \frac{1}{\sqrt{2}}\left[(S_\pm \uparrow)\downarrow - (S_\pm \downarrow)\uparrow + \uparrow(S_\pm \downarrow) - \downarrow(S_\pm \uparrow)\right].$$

$$S_+|0\ 0\rangle = \frac{1}{\sqrt{2}}(0 - \hbar\uparrow\uparrow + \hbar\uparrow\uparrow - 0) = 0;\quad S_-|0\ 0\rangle = \frac{1}{\sqrt{2}}(\hbar\downarrow\downarrow - 0 + 0 - \hbar\downarrow\downarrow) = 0.\ ✓$$

(c)

$$\begin{aligned}
S^2|1\ 1\rangle &= \left[(S^{(1)})^2 + (S^{(2)})^2 + 2\mathbf{S}^{(1)}\cdot\mathbf{S}^{(2)}\right]\uparrow\uparrow \\
&= (S^2\uparrow)\uparrow + \uparrow(S^2\uparrow) + 2\left[(S_x\uparrow)(S_x\uparrow) + (S_y\uparrow)(S_y\uparrow) + (S_z\uparrow)(S_z\uparrow)\right] \\
&= \frac{3}{4}\hbar^2\uparrow\uparrow + \frac{3}{4}\hbar^2\uparrow\uparrow + 2\left[\frac{\hbar}{2}\downarrow\frac{\hbar}{2}\downarrow + \frac{i\hbar}{2}\downarrow\frac{i\hbar}{2}\downarrow + \frac{\hbar}{2}\uparrow\frac{\hbar}{2}\uparrow\right] \\
&= \frac{3}{2}\hbar^2\uparrow\uparrow + 2\left(\frac{\hbar^2}{4}\uparrow\uparrow\right) = 2\hbar^2\uparrow\uparrow = 2\hbar^2|1\ 1\rangle = (1)(1+1)\hbar^2|1\ 1\rangle, \text{ as it } \textit{should} \text{ be.}
\end{aligned}$$

$$\begin{aligned}
S^2|1\ -1\rangle &= \left[(S^{(1)})^2 + (S^{(2)})^2 + 2\mathbf{S}^{(1)}\cdot\mathbf{S}^{(2)}\right]\downarrow\downarrow \\
&= \frac{3\hbar^2}{4}\downarrow\downarrow + \frac{3\hbar^2}{4}\downarrow\downarrow + 2\left[(S_x\downarrow)(S_x\downarrow) + (S_y\downarrow)(S_y\downarrow) + (S_z\downarrow)(S_z\downarrow)\right] \\
&= \frac{3}{2}\hbar^2\downarrow\downarrow + 2\left[\left(\frac{\hbar}{2}\uparrow\right)\left(\frac{\hbar}{2}\uparrow\right) + \left(-\frac{i\hbar}{2}\uparrow\right)\left(-\frac{i\hbar}{2}\uparrow\right) + \left(-\frac{\hbar}{2}\downarrow\right)\left(-\frac{\hbar}{2}\downarrow\right)\right] \\
&= \frac{3}{2}\hbar^2\downarrow\downarrow + 2\frac{\hbar^2}{4}\downarrow\downarrow = 2\hbar^2\downarrow\downarrow = 2\hbar^2|1\ -1\rangle.\ ✓
\end{aligned}$$

Problem 5.4

(a)

$$1 = \int |\psi_\pm|^2 d^3\mathrm{r}_1 d^3\mathrm{r}_2$$

$$= |A|^2 \int [\psi_a(\mathrm{r}_1)\psi_b(\mathrm{r}_2) \pm \psi_b(\mathrm{r}_1)\psi_a(\mathrm{r}_2)]^* [\psi_a(\mathrm{r}_1)\psi_b(\mathrm{r}_2) \pm \psi_b(\mathrm{r}_1)\psi_a(\mathrm{r}_2)]\, d^3\mathrm{r}_1 d^3\mathrm{r}_2$$

$$= |A|^2 \left[\int |\psi_a(\mathrm{r}_1)|^2 d^3\mathrm{r}_1 \int |\psi_b(\mathrm{r}_2)|^2 d^3\mathrm{r}_2 \pm \int \psi_a(\mathrm{r}_1)^* \psi_b(\mathrm{r}_1) d^3\mathrm{r}_1 \int \psi_b(\mathrm{r}_2)^* \psi_a(\mathrm{r}_2) d^3\mathrm{r}_2 \right.$$

$$\left. \pm \int \psi_b(\mathrm{r}_1)^* \psi_a(\mathrm{r}_1) d^3\mathrm{r}_1 \int \psi_a(\mathrm{r}_2)^* \psi_b(\mathrm{r}_2) d^3\mathrm{r}_2 + \int |\psi_b(\mathrm{r}_1)|^2 d^3\mathrm{r}_1 \int |\psi_a(\mathrm{r}_2)|^2 d^3\mathrm{r}_2 \right]$$

$$= |A|^2(1 \cdot 1 \pm 0 \cdot 0 \pm 0 \cdot 0 + 1 \cdot 1) = 2|A|^2 \Longrightarrow \boxed{A = 1/\sqrt{2}.}$$

(b)

$$1 = |A|^2 \int [2\psi_a(\mathrm{r}_1)\psi_a(\mathrm{r}_2)]^* [2\psi_a(\mathrm{r}_1)\psi_a(\mathrm{r}_2)]\, d^3\mathrm{r}_1 d^3\mathrm{r}_2$$

$$= 4|A|^2 \int |\psi_a(\mathrm{r}_1)|^2 d^3\mathrm{r}_1 \int |\psi_a(\mathrm{r}_2)|^2 d^3\mathrm{r}_2 = 4|A|^2. \qquad \boxed{A = 1/2.}$$

Problem 5.6

(a) Use Eq. 5.19 and Problem 2.4, with $\langle x \rangle_n = a/2$ and $\langle x^2 \rangle_n = a^2\left(\frac{1}{3} - \frac{1}{2(n\pi)^2}\right)$.

$$\langle (x_1 - x_2)^2 \rangle = a^2\left(\frac{1}{3} - \frac{1}{2(n\pi)^2}\right) + a^2\left(\frac{1}{3} - \frac{1}{2(m\pi)^2}\right) - 2 \cdot \frac{a}{2} \cdot \frac{a}{2} = \boxed{a^2\left[\frac{1}{6} - \frac{1}{2\pi^2}\left(\frac{1}{n^2} + \frac{1}{m^2}\right)\right].}$$

(b) $\langle x \rangle_{mn} = \frac{2}{a}\int_0^a x \sin\left(\frac{m\pi}{a}x\right)\sin\left(\frac{n\pi}{a}x\right)dx = \frac{1}{a}\int_0^a x\left[\cos\left(\frac{(m-n)\pi}{a}x\right) - \cos\left(\frac{(m+n)\pi}{a}x\right)\right]dx$

$$= \frac{1}{a}\left[\left(\frac{a}{(m-n)\pi}\right)^2 \cos\left(\frac{(m-n)\pi}{a}x\right) + \left(\frac{ax}{(m-n)\pi}\right)\sin\left(\frac{(m-n)\pi}{a}x\right)\right.$$

$$\left. - \left(\frac{a}{(m+n)\pi}\right)^2 \cos\left(\frac{(m+n)\pi}{a}x\right) - \left(\frac{ax}{(m+n)\pi}\right)\sin\left(\frac{(m+n)\pi}{a}x\right)\right]\Bigg|_0^a$$

$$= \frac{1}{a}\left[\left(\frac{a}{(m-n)\pi}\right)^2(\cos[(m-n)\pi] - 1) - \left(\frac{a}{(m+n)\pi}\right)^2(\cos[(m+n)\pi] - 1)\right].$$

But $\cos[(m \pm n)\pi] = (-1)^{m+n}$, so

$$\langle x \rangle_{mn} = \frac{a}{\pi^2}\left[(-1)^{m+n} - 1\right]\left(\frac{1}{(m-n)^2} - \frac{1}{(m+n)^2}\right) = \begin{cases} \frac{a(-8mn)}{\pi^2(m^2-n^2)^2}, & \text{if } m \text{ and } n \text{ have opposite parity,} \\ 0, & \text{if } m \text{ and } n \text{ have same parity.} \end{cases}$$

So Eq. 5.21 $\Rightarrow$ $\langle (x_1 - x_2)^2 \rangle = \boxed{a^2\left[\frac{1}{6} - \frac{1}{2\pi^2}\left(\frac{1}{n^2} + \frac{1}{m^2}\right)\right] - \frac{128a^2m^2n^2}{\pi^4(m^2-n^2)^4}.}$

(The last term is present only when m, n have opposite parity.)

Problem 5.12

(a) Hydrogen: $(1s)$; helium: $(1s)^2$; lithium: $(1s)^2(2s)$; beryllium: $(1s)^2(2s)^2$; boron: $(1s)^2(2s)^2(2p)$; carbon: $(1s)^2(2s)^2(2p)^2$; nitrogen: $(1s)^2(2s)^2(2p)^3$; oxygen: $(1s)^2(2s)^2(2p)^4$; fluorine: $(1s)^2(2s)^2(2p)^5$; neon: $(1s)^2(2s)^2(2p)^6$. These values agree with those in Table 5.1—no surprises so far.

(b) Hydrogen: ${}^2S_{1/2}$; helium: ${}^1S_0$; lithium: ${}^2S_{1/2}$; beryllium ${}^1S_0$. (These four are unambiguous, because the *orbital* angular momentum is zero in all cases.) For boron, the spin (1/2) and orbital (1) angular momenta could add to give 3/2 or 1/2, so the possibilities are $\boxed{{}^2P_{3/2} \text{ or } {}^2P_{1/2}.}$ For carbon, the two p electrons could combine for orbital angular momentum 2, 1, or 0, and the spins could add to 1 or 0: $\boxed{{}^1S_0, {}^3S_1, {}^1P_1, {}^3P_2, {}^3P_1, {}^3P_0, {}^1D_2, {}^3D_3, {}^3D_2, {}^3D_1.}$ For nitrogen, the 3 p electrons can add to orbital angular momentum 3, 2, 1, or 0, and the spins to 3/2 or 1/2:

$$\boxed{\begin{array}{l} {}^2S_{1/2}, {}^4S_{3/2}, {}^2P_{1/2}, {}^2P_{3/2}, {}^4P_{1/2}, {}^4P_{3/2}, {}^4P_{5/2}, {}^2D_{3/2}, {}^2D_{5/2}, \\ {}^4D_{1/2}, {}^4D_{3/2}, {}^4D_{5/2}, {}^4D_{7/2}, {}^2F_{5/2}, {}^2F_{3/2}, {}^4F_{3/2}, {}^4F_{5/2}, {}^4F_{7/2}, {}^4F_{9/2}. \end{array}}$$

↳ Should be 7/2 (Typo!!!)

(c) Here Eq. 5.21 $\Rightarrow \langle (x_1 - x_2)^2 \rangle = \boxed{a^2\left[\frac{1}{6} - \frac{1}{2\pi^2}\left(\frac{1}{n^2} + \frac{1}{m^2}\right)\right] + \frac{128a^2m^2n^2}{\pi^4(m^2-n^2)^4}.}$

(Again, the last term is present only when m, n have opposite parity.)