Chapter 7: Problem S1

Start with the full wavefunction for the $3d_{\pm 2}$ states:

$$\Psi_{3,2,\pm 2} = \frac{1}{162\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin^2(\theta)e^{\pm 2i\phi}.$$

Now

$$\begin{aligned}\Psi_{3,2,2} + \Psi_{3,2,-2} &= \frac{1}{162\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin^2(\theta)\left(e^{2i\phi} + e^{-2i\phi}\right) \\ &= \frac{1}{81\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin^2(\theta)\cos(2\phi),\end{aligned}$$

and

$$\begin{aligned}\Psi_{3,2,2} - \Psi_{3,2,-2} &= \frac{1}{162\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin^2(\theta)\left(e^{2i\phi} - e^{-2i\phi}\right) \\ &= \frac{i}{81\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin^2(\theta)\sin(2\phi).\end{aligned}$$

Both wavefunctions (as well as the associated probability amplitudes) have $\sin^2\theta$ dependence which is maximized when $\theta = \pi/2$ at the x-y plane. The angle ϕ is measured from the x axis. The first wavefunction has $\cos(2\phi)$ which is at maximum when $\phi = 0, \pi/2, \pi, 3\pi/2, 2\pi$. It corresponds to the orbital labeled $x^2 - y^2$. The second wavefunction has $\sin(2\phi)$ which is at maximum when $\phi = \pi/4, 3\pi/4, 5\pi/4, 7\pi/4$. It corresponds to the orbital labeled xy.

Chapter 8: Problem S1

We have the permutation operator $\hat{P}_{12}$ which operates on a two-particle wavefunction according to

$$\hat{P}_{12}\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1).$$

A function $\psi(\vec{r}_1, \vec{r}_2)$ is an eigenfunction of $\hat{P}_{12}$ if

$$\hat{P}_{12}\psi(\vec{r}_1, \vec{r}_2) = C\psi(\vec{r}_1, \vec{r}_2)$$

for any constant (independent of $\vec{r}_1, \vec{r}_2$) C.

a)

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{100,+}(\vec{r}_1)\psi_{100,-}(\vec{r}_2) - \psi_{100,+}(\vec{r}_2)\psi_{100,-}(\vec{r}_1)$$

$$\begin{aligned}\hat{P}_{12}\psi(\vec{r}_1, \vec{r}_2) &= \psi_{100,+}(\vec{r}_2)\psi_{100,-}(\vec{r}_1) - \psi_{100,+}(\vec{r}_1)\psi_{100,-}(\vec{r}_2) \\ &= -\psi_{100,+}(\vec{r}_1)\psi_{100,-}(\vec{r}_2) + \psi_{100,+}(\vec{r}_2)\psi_{100,-}(\vec{r}_1) = -\psi(\vec{r}_1, \vec{r}_2)\end{aligned}$$

The wavefunction is antisymmetric (eigenvalue -1), so it works for fermions.

b)

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{100,+}(\vec{r}_1)\psi_{100,+}(\vec{r}_2)$$

$$\hat{P}_{12}\psi(\vec{r}_1,\vec{r}_2) = (\vec{r}_2)\psi_{100,+}(\vec{r}_1) = (\vec{r}_1)\psi_{100,+}(\vec{r}_2) = \psi(\vec{r}_1,\vec{r}_2)$$

The wavefunction is symmetric (eigenvalue 1), so it works for bosons.

c)

$$\psi(\vec{r}_1,\vec{r}_2) = \psi_{210,+}(\vec{r}_1)\psi_{21-1,-}(\vec{r}_2) - \psi_{21-1,-}(\vec{r}_1)\psi_{210,+}(\vec{r}_2)$$

$$\hat{P}_{12}\psi(\vec{r}_1,\vec{r}_2) = \psi_{210,+}(\vec{r}_2)\psi_{21-1,-}(\vec{r}_1) - \psi_{21-1,-}(\vec{r}_2)\psi_{210,+}(\vec{r}_1)$$
$$= -\psi_{21-1,-}(\vec{r}_2)\psi_{210,+}(\vec{r}_1) + \psi_{210,+}(\vec{r}_2)\psi_{21-1,-}(\vec{r}_1) = -\psi(\vec{r}_1,\vec{r}_2)$$

The wavefunction is antisymmetric, so it works for fermions.

d)

$$\psi(\vec{r}_1,\vec{r}_2) = \psi_{210,+}(\vec{r}_1)\psi_{21-1,-}(\vec{r}_2)$$

$$\hat{P}_{12}\psi(\vec{r}_1,\vec{r}_2) = \psi_{210,+}(\vec{r}_2)\psi_{21-1,-}(\vec{r}_1) \neq C\psi(\vec{r}_1,\vec{r}_2)$$

The wavefunction is not an eigenfunction of $\hat{P}_{12}$, so it is not a good choice for either fermions nor bosons.

Chapter 8: Problem S2

The two-electron wavefunction is

$$\psi(\vec{r}_1,\vec{s}_1;\vec{r}_2,\vec{s}_2) = \frac{1}{\sqrt{2}}\left[\varphi_{1s}(\vec{r}_1,\vec{s}_1=\uparrow)\varphi_{1s}(\vec{r}_2,\vec{s}_1=\downarrow) - \varphi_{1s}(\vec{r}_1,\vec{s}_1=\downarrow)\varphi_{1s}(\vec{r}_2,\vec{s}_2=\uparrow)\right]$$

We can assume that the individual wavefunctions are normalized, that is,

$$\int|\varphi_{1s}(\vec{r}_1,\vec{s}_1=\uparrow\downarrow)|^2 d\vec{r}_1 = 1 \qquad \int|\varphi_{1s}(\vec{r}_2,\vec{s}_1=\uparrow\downarrow)|^2 d\vec{r}_2 = 1$$

Then,

$$\int|\psi(\vec{r}_1,\vec{s}_1;\vec{r}_2,\vec{s}_2)|^2 d\vec{r}_1 d\vec{r}_2 =$$
$$\frac{1}{2}\int|\varphi_{1s}(\vec{r}_1,\vec{s}_1=\uparrow)|^2 d\vec{r}_1\int|\varphi_{1s}(\vec{r}_2,\vec{s}_1=\downarrow)|^2 d\vec{r}_2$$
$$+\frac{1}{2}\int|\varphi_{1s}(\vec{r}_1,\vec{s}_1=\downarrow)|^2 d\vec{r}_1\int|\varphi_{1s}(\vec{r}_2,\vec{s}_1=\downarrow)|^2 d\vec{r}_2$$
$$+\frac{1}{2}\int\varphi^*_{1s}(\vec{r}_1,\vec{s}_1=\uparrow)\varphi_{1s}(\vec{r}_1,\vec{s}_1=\downarrow)d\vec{r}_1\int\varphi^*_{1s}(\vec{r}_2,\vec{s}_1=\downarrow)\varphi_{1s}(\vec{r}_2,\vec{s}_1=\uparrow)d\vec{r}_2$$
$$+\frac{1}{2}\int\varphi_{1s}(\vec{r}_1,\vec{s}_1=\uparrow)\varphi^*_{1s}(\vec{r}_1,\vec{s}_1=\downarrow)d\vec{r}_1\int\varphi_{1s}(\vec{r}_2,\vec{s}_1=\downarrow)\varphi^*_{1s}(\vec{r}_2,\vec{s}_1=\uparrow)d\vec{r}_2$$
$$=\frac{1}{2}\times 1\times 1+\frac{1}{2}\times 1\times 1+\frac{1}{2}\times 0\times 0+\frac{1}{2}\times 0\times 0 = 1$$

The integrals in the first two terms are all equal to 1. The last two terms (the cross-terms) vanish because states with different spin are orthogonal.

Chapter 10: Problem S1

The vibrational states for the diatomic molecule are represented by the harmonic oscillator eigenstates

$$\psi_0(x) = a_0 e^{-\alpha x^2},$$

$$\psi_1(x) = a_1 x e^{-\alpha x^2},$$

$$\psi_2(x) = a_2 x^2 e^{-\alpha x^2} - a_3 e^{-\alpha x^2}.$$

for $v = 0, 1, 2$ respectively. Here, a_j and α are constants. The transition probability from state m to state n is proportional to

$$I \propto \left| \int_{-\infty}^{\infty} \psi_n(x)\ x\ \psi_m(x)\ dx \right|^2.$$

For the $0 \rightarrow 1$ transition the integral is

$$\int_{-\infty}^{\infty} \left(a_1 x e^{-\alpha x^2}\right) x \left(a_0 e^{-\alpha x^2}\right) dx = a_0 a_1 \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx.$$

Because the integrand is even, we can replace the integration by twice the integral from 0 to ∞ and then integrate.

$$a_0 a_1 \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx = 2a_0 a_1 \int_{0}^{\infty} x^2 e^{-2\alpha x^2} dx = \frac{a_0 a_1}{4\alpha^{3/2}} \sqrt{\frac{\pi}{2}}.$$

The integral is non-zero result, so the transition is allowed.

For the $0 \rightarrow 2$ transition the integral is

$$\int_{-\infty}^{\infty} \left(a_2 x^2 e^{-\alpha x^2} - a_3 e^{-\alpha x^2}\right) x \left(a_0 e^{-\alpha x^2}\right) dx =$$

$$a_0 a_2 \int_{-\infty}^{\infty} x^3 e^{-2\alpha x^2} dx - a_0 a_3 \int_{-\infty}^{\infty} x e^{-2\alpha x^2} dx = 0.$$

Both integrands are odd functions, so when integrated from $-\infty$ to ∞, both integrals are zero, so the transition is forbidden.