13.1 The exchange operator P_{12} is defined by its action on a general two-particle state:

$$P_{12}\left\{\varphi_{n_a}(\mathbf{r}_1)\varphi_{n_b}(\mathbf{r}_2)\left|s_1s_2m_1m_2\right\rangle\right\} = \varphi_{n_a}(\mathbf{r}_2)\varphi_{n_b}(\mathbf{r}_1)\left|s_2s_1m_2m_1\right\rangle$$

where we explicitly specify the space and spin parts of the state. The eigenvalue equation for the exchange operator is

$$P_{12}\left|\psi_\lambda\right\rangle = \lambda\left|\psi_\lambda\right\rangle$$

where λ is the eigenvalue and $\left|\psi_\lambda\right\rangle$ is the eigenstate. We can express the eigenstate as a general superposition of states:

$$\left|\psi_\lambda\right\rangle = \sum_{n_an_bm_1m_2}\varphi_{n_a}(\mathbf{r}_1)\varphi_{n_b}(\mathbf{r}_2)\left|s_1s_2m_1m_2\right\rangle$$

Act on the eigenstate with P_{12} twice:

$$\begin{aligned}
P_{12}P_{12}\left|\psi_\lambda\right\rangle &= P_{12}P_{12}\sum_{n_an_bm_1m_2}\varphi_{n_a}(\mathbf{r}_1)\varphi_{n_b}(\mathbf{r}_2)\left|s_1s_2m_1m_2\right\rangle \\
P_{12}\lambda\left|\psi_\lambda\right\rangle &= P_{12}\sum_{n_an_bm_1m_2}\varphi_{n_a}(\mathbf{r}_2)\varphi_{n_b}(\mathbf{r}_1)\left|s_2s_1m_2m_1\right\rangle \\
\lambda^2\left|\psi_\lambda\right\rangle &= \sum_{n_an_bm_1m_2}\varphi_{n_a}(\mathbf{r}_1)\varphi_{n_b}(\mathbf{r}_2)\left|s_1s_2m_1m_2\right\rangle \\
\lambda^2\left|\psi_\lambda\right\rangle &= \left|\psi_\lambda\right\rangle
\end{aligned}$$

Thus $\lambda^2 = 1$ and we find the eigenvalues of P_{12}:

$$\lambda = \pm 1$$

13.2 For two spin-0 bosons, the only possible state of the system is

$$\left|s_1s_2m_1m_2\right\rangle = \left|0000\right\rangle$$

written in the uncoupled basis. The total (coupled) spin $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ is zero, with the only possible state being $\left|SM\right\rangle = \left|00\right\rangle$. These two states must be the same state

$$\left|00\right\rangle = \left|0000\right\rangle$$

Hence the action of the exchange operator P_{12} is

$$P_{12}\left|00\right\rangle = P_{12}\left|0000\right\rangle = \left|0000\right\rangle = +\left|00\right\rangle$$

so the state $\left|SM\right\rangle = \left|00\right\rangle$ is symmetric with respect to exchange of the two particles.

13.3 For two spin-1 bosons, the states of the system written in the uncoupled basis are

$$\left|s_1s_2m_1m_2\right\rangle = \left|11m_1m_2\right\rangle$$

with 9 possible combinations of m_1 and m_2. The total (coupled) spin $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ is 0, 1, or 2, with the possible states being

$$|SM\rangle = \begin{cases} |00\rangle;\ 1\text{ state} \\ |1M\rangle;\ 3\text{ states} \\ |2M\rangle;\ 5\text{ states} \end{cases}$$

The spin states for this system that are symmetric or antisymmetric with respect to exchange of the two particles are the coupled basis states. To see this we need to write the coupled basis states in terms of the uncoupled basis states using the Clebsch-Gordan coefficients from Chapter 11. Using the coefficients in Table 11.5, we find the states

$$\begin{aligned}
|22\rangle &= |1111\rangle \\
|21\rangle &= \tfrac{1}{\sqrt{2}}|1110\rangle + \tfrac{1}{\sqrt{2}}|1101\rangle \\
|20\rangle &= \tfrac{1}{\sqrt{6}}|111,-1\rangle + \tfrac{\sqrt{2}}{\sqrt{3}}|1100\rangle + \tfrac{1}{\sqrt{6}}|11,-11\rangle \\
|2,-1\rangle &= \tfrac{1}{\sqrt{2}}|110,-1\rangle + \tfrac{1}{\sqrt{2}}|11,-10\rangle \\
|2,-2\rangle &= |11,-1,-1\rangle \\
|11\rangle &= \tfrac{1}{\sqrt{2}}|1110\rangle - \tfrac{1}{\sqrt{2}}|1101\rangle \\
|10\rangle &= \tfrac{1}{\sqrt{2}}|111,-1\rangle - \tfrac{1}{\sqrt{2}}|11,-11\rangle \\
|1,-1\rangle &= \tfrac{1}{\sqrt{2}}|110,-1\rangle - \tfrac{1}{\sqrt{2}}|11,-10\rangle \\
|00\rangle &= \tfrac{1}{\sqrt{3}}|111,-1\rangle - \tfrac{1}{\sqrt{3}}|1100\rangle + \tfrac{1}{\sqrt{3}}|11,-11\rangle
\end{aligned}$$

Considering the action of the exchange operator P_{12} on each of these 9 states, we see that

$$P_{12}|SM\rangle = \begin{cases} +|SM\rangle;\ S=0,\,2 \\ -|SM\rangle;\ S=1 \end{cases}$$

So the $S = 0,2$ states are **symmetric** with respect to exchange of the two particles and the $S = 1$ states are **antisymmetric** with respect to exchange of the two particles.

13.4 To determine the exchange symmetry of each state, act with the exchange operator P_{12}:

$$P_{12}\psi_a(x_1,x_2) = P_{12}\frac{1}{(x_1+x_2)} = \frac{1}{(x_2+x_1)} = \frac{1}{(x_1+x_2)} = +\psi_a(x_1,x_2)$$

So $\psi_a(x_1,x_2)$ is **symmetric** with respect to exchange of the two particles.

$$P_{12}\psi_b(x_1,x_2) = P_{12}\frac{a(x_1-x_2)}{(x_1-x_2)^2+b} = \frac{a(x_2-x_1)}{(x_2-x_1)^2+b} = \frac{-a(x_1-x_2)}{(x_1-x_2)^2+b} = -\psi_b(x_1,x_2)$$

So $\psi_b(x_1,x_2)$ is **antisymmetric** with respect to exchange of the two particles.

$$P_{12}\psi_c\left(x_1,x_2\right)=P_{12}\frac{a\left(x_1-3x_2\right)}{\left(x_1+x_2\right)^2+b}=\frac{a\left(x_2-3x_1\right)}{\left(x_2+x_1\right)^2+b}\neq\lambda\psi_c\left(x_1,x_2\right)$$

So $\psi_c\left(x_1,x_2\right)$ is neither symmetric nor antisymmetric with respect to exchange of the two particles. It is not an eigenstate of the exchange operator.
For the last state $\psi_d\left(x_1,x_2,x_3\right)$ we must consider the exchange of **any** pair of particles:

$$\begin{aligned}P_{12}\psi_d\left(x_1,x_2,x_3\right)&=P_{12}\frac{x_1x_2x_3}{x_1^2+x_2^2+x_3^2+b}=\frac{x_2x_1x_3}{x_2^2+x_1^2+x_3^2+b}=\frac{x_1x_2x_3}{x_1^2+x_2^2+x_3^2+b}\\&=+\psi_d\left(x_1,x_2,x_3\right)\end{aligned}$$

$$\begin{aligned}P_{13}\psi_d\left(x_1,x_2,x_3\right)&=P_{13}\frac{x_1x_2x_3}{x_1^2+x_2^2+x_3^2+b}=\frac{x_3x_2x_1}{x_3^2+x_2^2+x_1^2+b}=\frac{x_1x_2x_3}{x_1^2+x_2^2+x_3^2+b}\\&=+\psi_d\left(x_1,x_2,x_3\right)\end{aligned}$$

$$\begin{aligned}P_{23}\psi_d\left(x_1,x_2,x_3\right)&=P_{23}\frac{x_1x_2x_3}{x_1^2+x_2^2+x_3^2+b}=\frac{x_1x_3x_2}{x_1^2+x_3^2+x_2^2+b}=\frac{x_1x_2x_3}{x_1^2+x_2^2+x_3^2+b}\\&=+\psi_d\left(x_1,x_2,x_3\right)\end{aligned}$$

So $\psi_d\left(x_1,x_2,x_3\right)$ is **symmetric** with respect to exchange of any two particles.

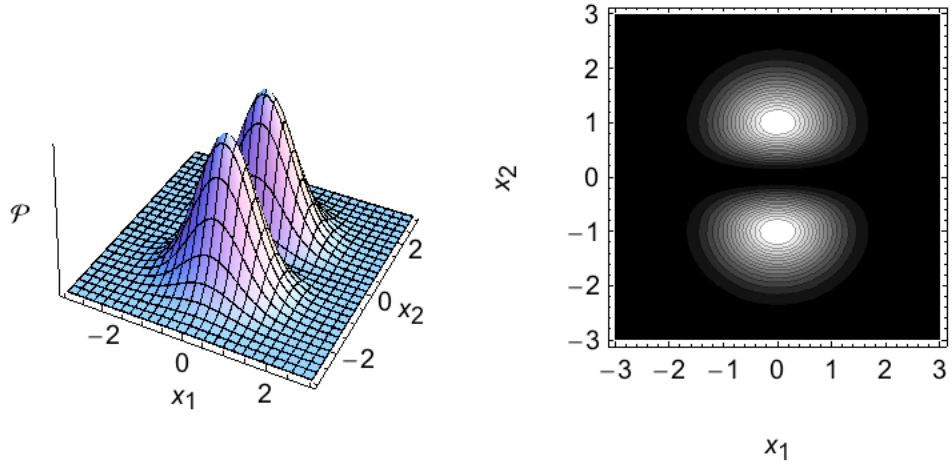
13.5 The 2-particle wave function is a product of two single-particle wave functions for distinguishable particles:

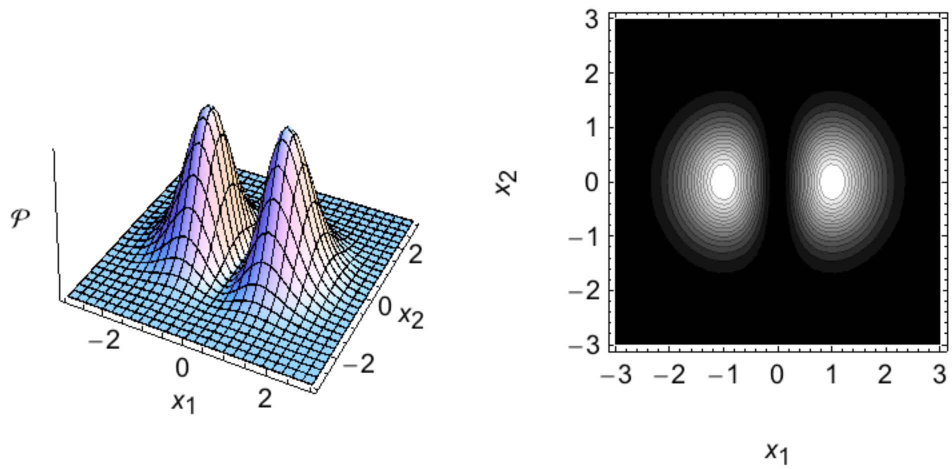
$$\psi_{n_a=0,n_b=1}(x_1,x_2)=\varphi_0(x_1)\varphi_1(x_2)\,.$$

For the single particle wave functions we use the dimensionless harmonic oscillator wave functions:

$$\begin{aligned}\varphi_0(x)&=\frac{1}{\pi^{1/4}}e^{-x^2/2}\\\varphi_1(x)&=\frac{\sqrt{2}}{\pi^{1/4}}xe^{-x^2/2}\end{aligned}.$$

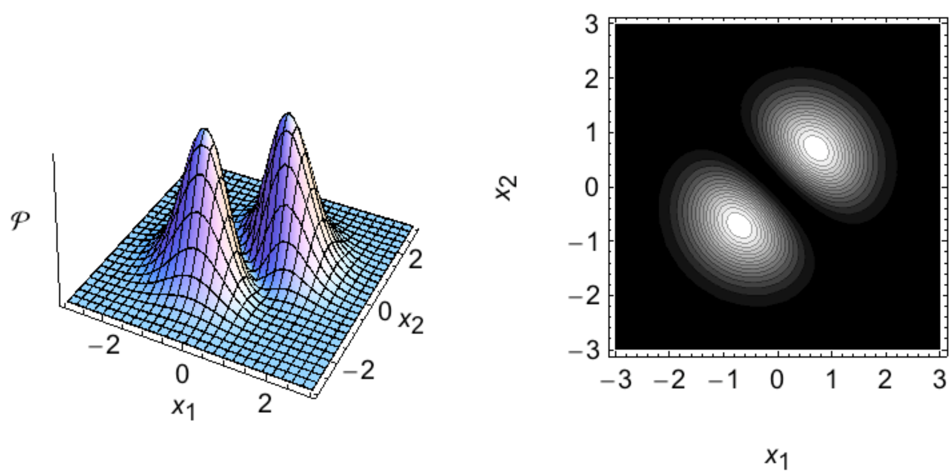
The following plots for the probability density result.
(a) Distinguishable particles: We could either have $n_a = 0$ and $n_b = 1$ or $n_a = 1$ and $n_b = 0$, which are different in this case:





(b) Spin-0 bosons. The spin part of the state is necessarily symmetric, so the space part must also be symmetric.

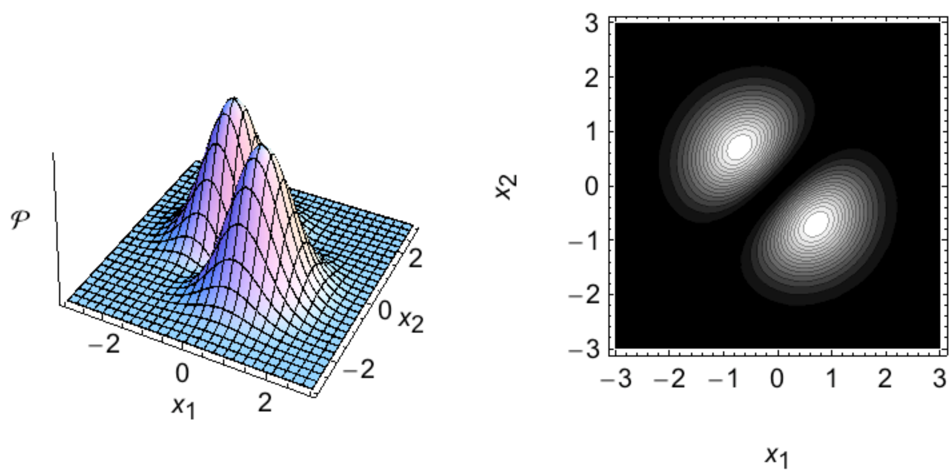
$$\psi^{S}_{n_a=0,n_b=1}(x_1,x_2)=\tfrac{1}{\sqrt{2}}\left[\varphi_0(x_1)\varphi_1(x_2)+\varphi_0(x_2)\varphi_1(x_1)\right]$$



Notice that the line $x_1 = x_2$ crosses regions of very high probability amplitude. In other words, if you asked the question, "What is the probability that particle #1 is in some interval around, say, $x_1 = L/3$, subject to particle #2 *also* being in that interval?", the answer would be "quite good", *regardless* of what position in the box you asked the question about. (Obviously not about $x_1 = 0$, but this is a node in one of the single-particle wave functions anyway, and the node doesn't appear because of the symmetrization requirement). Bosons in a box tend to seek each other out *even though they are "non-interacting" particles.*

(c) Spin ½ fermions in a spin triplet state. The spin triplet state is symmetric, so the space part must be antisymmetric:

$$\psi^{A}_{n_a=0,n_b=1}(x_1,x_2) = \tfrac{1}{\sqrt{2}}\left[\varphi_0(x_1)\varphi_1(x_2) - \varphi_0(x_2)\varphi_1(x_1)\right]$$



Notice that the line $x_1 = x_2$ falls in a region of very low probability amplitude. In other words, if you asked the question, "What is the probability that particle #1 is in some interval around, say, $x_1 = L/3$, subject to particle #2 *also* being in that interval?", the answer would be "very small", *regardless* of what position in the box you asked the question about. Fermions in a box tend to avoid each other *even though they are "non-interacting" particles.*

13.6. Let's use bra-ket notation until the very end to make life simpler.

$$|n\rangle \doteq \varphi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$$

The expectation value of the squared particle separation can be written as

$$\left\langle (x_1 - x_2)^2 \right\rangle = \left\langle x_1^2 - 2x_1x_2 + x_2^2 \right\rangle$$
$$\left\langle (x_1 - x_2)^2 \right\rangle = \left\langle x_1^2 \right\rangle + \left\langle x_2^2 \right\rangle - 2\left\langle x_1x_2 \right\rangle$$

For our three cases, the 2-particle wave function is a product of two single-particle wave functions either not symmetrized (distinguishable), symmetrized (Bosons), or antisymmetrized (Fermions) with respect to exchange of the two particles.

$$\begin{aligned} |\psi_D\rangle &= |nk\rangle \equiv |n\rangle_1 |k\rangle_2 \\ |\psi_B\rangle &= \tfrac{1}{\sqrt{2}}\left[|nk\rangle + |kn\rangle\right] \\ |\psi_F\rangle &= \tfrac{1}{\sqrt{2}}\left[|nk\rangle - |kn\rangle\right] \end{aligned}$$

Let's first look at distinguishable particles

$$\left\langle x_1^2 \right\rangle_D = \langle nk|x_1^2|nk\rangle = \langle n|x_1^2|n\rangle\langle k|k\rangle = \left\langle x^2 \right\rangle_n$$

where the dummy of integration does not matter so

$$\left\langle x^2 \right\rangle_n = \int_0^L \varphi_n^*(x)\; x^2 \varphi_n(x)dx \;= \int_0^L x^2 \left|\varphi_n(x)\right|^2 dx$$

is a single-particle expectation value. Likewise, we get

$$\begin{aligned} \left\langle x_2^2 \right\rangle_D &= \langle nk|x_2^2|nk\rangle = \langle n|n\rangle\langle k|x_2^2|k\rangle = \left\langle x^2 \right\rangle_k \\ \left\langle x_1 x_2 \right\rangle_D &= \langle nk|x_1 x_2|nk\rangle = \langle n|x_1|n\rangle\langle k|x_2|k\rangle = \langle x\rangle_n \langle x\rangle_k \\ \left\langle (x_1 - x_2)^2 \right\rangle_D &= \left\langle x^2 \right\rangle_n + \left\langle x^2 \right\rangle_k - 2\langle x\rangle_n \langle x\rangle_k \end{aligned}$$

Thus we only need to do two types of integrals $\left\langle x^2 \right\rangle_n$ and $\langle x\rangle_n$. Let's consider Fermions and Bosons before we do the integrals.

$$\begin{aligned} \left\langle x_1^2 \right\rangle_{B,F} &= \tfrac{1}{\sqrt{2}}\left[\langle nk| \pm \langle kn|\right] x_1^2 \tfrac{1}{\sqrt{2}}\left[|nk\rangle \pm |kn\rangle\right] \\ &= \tfrac{1}{2}\left[\langle n|x_1^2|n\rangle\langle k|k\rangle \pm \langle n|x_1^2|k\rangle\langle k|n\rangle \pm \langle k|x_1^2|n\rangle\langle n|k\rangle + \langle k|x_1^2|k\rangle\langle n|n\rangle\right] \\ &= \tfrac{1}{2}\left[\langle n|x_1^2|n\rangle \pm 0 \pm 0 + \langle k|x_1^2|k\rangle\right] = \tfrac{1}{2}\left[\left\langle x^2 \right\rangle_n + \left\langle x^2 \right\rangle_k\right] \end{aligned}$$

$$\begin{aligned} \left\langle x_1 x_2 \right\rangle_{B,F} &= \tfrac{1}{\sqrt{2}}\left[\langle nk| \pm \langle kn|\right] x_1 x_2 \tfrac{1}{\sqrt{2}}\left[|nk\rangle \pm |kn\rangle\right] \\ &= \tfrac{1}{2}\left[\langle n|x_1|n\rangle\langle k|x_2|k\rangle \pm \langle n|x_1|k\rangle\langle k|x_2|n\rangle \pm \langle k|x_1|n\rangle\langle n|x_2|k\rangle + \langle k|x_1|k\rangle\langle n|x_2|n\rangle\right] \\ &= \tfrac{1}{2}\left[\langle x\rangle_n \langle x\rangle_k \pm \langle x\rangle_{nk}\langle x\rangle_{kn} \pm \langle x\rangle_{kn}\langle x\rangle_{nk} + \langle x\rangle_k \langle x\rangle_n\right] = \langle x\rangle_n \langle x\rangle_k \pm \left|\langle x\rangle_{nk}\right|^2 \end{aligned}$$

where

$$\langle x\rangle_{nk} = \langle n|x|k\rangle = \int_0^L \varphi_n^*(x)\; x\; \varphi_k(x)dx\,.$$

Thus we get

$$\left\langle (x_1 - x_2)^2 \right\rangle_{B,F} = \left\langle x^2 \right\rangle_n + \left\langle x^2 \right\rangle_k - 2\langle x\rangle_n \langle x\rangle_k \mp 2\left|\langle x\rangle_{nk}\right|^2$$

So now we have to do an extra integral. Let's do those integrals:

$$\begin{aligned}
\langle x^2\rangle_n &= \int_0^L \varphi_n^*(x)\; x^2\varphi_n(x)dx \;= \int_0^L x^2\left|\varphi_n(x)\right|^2 dx \\
&= \frac{2}{L}\int_0^L x^2\sin^2\left(\frac{n\pi x}{L}\right)dx \;= \frac{2}{L}\left(\frac{L}{n\pi}\right)^3\int_0^{n\pi} y^2\sin^2(y)dy \\
&= \frac{2}{L}\left(\frac{L}{n\pi}\right)^3\left[\frac{y^3}{6}-\left(\frac{y^2}{4}-\frac{1}{8}\right)\sin 2y-\frac{y\cos 2y}{4}\right]_0^{n\pi} \\
&= \frac{2}{L}\left(\frac{L}{n\pi}\right)^3\left[\frac{(n\pi)^3}{6}-\left(\frac{(n\pi)^2}{4}-\frac{1}{8}\right)\sin(2n\pi)-\frac{(n\pi)\cos(2n\pi)}{4}\right] \\
&= \frac{2}{L}\left(\frac{L}{n\pi}\right)^3\left[\frac{(n\pi)^3}{6}-\frac{(n\pi)}{4}\right] = L^2\left(\frac{1}{3}-\frac{1}{2n^2\pi^2}\right)
\end{aligned}$$

$$\begin{aligned}
\langle x\rangle_n &= \int_0^L \varphi_n^*(x)\; x\; \varphi_n(x)dx \;= \int_0^L x\left|\varphi_n(x)\right|^2 dx \\
&= \frac{2}{L}\int_0^L x\sin^2\left(\frac{n\pi x}{L}\right)dx \;= \frac{2}{L}\left(\frac{L}{n\pi}\right)^2\int_0^{n\pi} y\sin^2(y)dy \\
&= \frac{2}{L}\left(\frac{L}{n\pi}\right)^2\left[\frac{y^2}{4}-\frac{y\sin 2y}{4}-\frac{\cos 2y}{8}\right]_0^{n\pi} \\
&= \frac{2}{L}\left(\frac{L}{n\pi}\right)^2\left[\frac{(n\pi)^2}{4}-\frac{n\pi\sin(2n\pi)}{4}-\frac{\cos(2n\pi)}{8}+\frac{1}{8}\right] = \frac{2}{L}\left(\frac{L}{n\pi}\right)^2\left[\frac{(n\pi)^2}{4}\right] = \frac{L}{2}
\end{aligned}$$

as expected. And

$$\begin{aligned}
\langle x\rangle_{nk} &= \langle n|x|k\rangle = \int_0^L \varphi_n^*(x)\; x\; \varphi_k(x)dx \;= \frac{2}{L}\int_0^L \sin\frac{n\pi x}{L}\,x\sin\frac{k\pi x}{L}dx \\
&= \frac{2}{L}\left(\frac{L}{\pi}\right)^2\int_0^{\pi} y\sin(ny)\sin(ky)dy \;= \frac{2}{L}\left(\frac{L}{\pi}\right)^2\int_0^{\pi} y\tfrac{1}{2}\left[\cos(n-k)y-\cos(n+k)y\right]dy \\
&= \frac{1}{L}\left(\frac{L}{\pi}\right)^2\left[\frac{\cos(n-k)y}{(n-k)^2}+\frac{y\sin(n-k)y}{(n-k)}-\frac{\cos(n+k)y}{(n+k)^2}-\frac{y\sin(n+k)y}{(n+k)}\right]_0^{\pi} \quad . \\
&= \frac{1}{L}\left(\frac{L}{\pi}\right)^2\left[\frac{\cos(n-k)\pi}{(n-k)^2}-\frac{\cos(n+k)\pi}{(n+k)^2}-\frac{1}{(n-k)^2}+\frac{1}{(n+k)^2}\right] \\
&= \frac{L}{\pi^2}\left[\frac{1}{(n+k)^2}-\frac{1}{(n-k)^2}\right]\left[1-(-1)^{n+k}\right] = \frac{-4Lnk}{\pi^2\left(n^2-k^2\right)^2}\left[1-(-1)^{n+k}\right]
\end{aligned}$$

This is zero when $(n + k)$ is even, meaning when n and k are both even or both odd, which relates to the odd or even symmetry of the wavefunctions. Putting this together gives

$$\left\langle \left(x_1-x_2\right)^2\right\rangle_D = \left\langle x^2\right\rangle_n + \left\langle x^2\right\rangle_k - 2\left\langle x\right\rangle_n \left\langle x\right\rangle_k = L^2\left(\frac{1}{3}-\frac{1}{2n^2\pi^2}\right) + L^2\left(\frac{1}{3}-\frac{1}{2k^2\pi^2}\right) - 2\frac{L}{2}\frac{L}{2}$$

$$= L^2\left(\frac{2}{3}-\frac{1}{2}-\frac{1}{2n^2\pi^2}-\frac{1}{2k^2\pi^2}\right) = L^2\left(\frac{1}{6}-\frac{1}{2\pi^2}\left(\frac{1}{n^2}+\frac{1}{k^2}\right)\right)$$

$$\left\langle \left(x_1-x_2\right)^2\right\rangle_{B,F} = \left\langle x^2\right\rangle_n + \left\langle x^2\right\rangle_k - 2\left\langle x\right\rangle_n \left\langle x\right\rangle_k \mp 2\left|\left\langle x\right\rangle_{nk}\right|^2$$

$$= L^2\left[\frac{1}{6}-\frac{1}{2\pi^2}\left(\frac{1}{n^2}+\frac{1}{k^2}\right)\right] \mp 2\left|\frac{-4Lnk}{\pi^2\left(n^2-k^2\right)^2}\left[1-\left(-1\right)^{n+k}\right]\right|^2$$

$$= L^2\left[\frac{1}{6}-\frac{1}{2\pi^2}\left(\frac{1}{n^2}+\frac{1}{k^2}\right)\right] \mp \frac{64L^2n^2k^2}{\pi^4\left(n^2-k^2\right)^4}\left[1-\left(-1\right)^{n+k}\right]$$

Summarizing:

$$\left\langle \left(x_1-x_2\right)^2\right\rangle_D = L^2\left(\frac{1}{6}-\frac{1}{2\pi^2}\left(\frac{1}{n^2}+\frac{1}{k^2}\right)\right)$$

$$\left\langle \left(x_1-x_2\right)^2\right\rangle_{B,F} = L^2\left[\frac{1}{6}-\frac{1}{2\pi^2}\left(\frac{1}{n^2}+\frac{1}{k^2}\right)\right] \mp \frac{64L^2n^2k^2}{\pi^4\left(n^2-k^2\right)^4}\left[1-\left(-1\right)^{n+k}\right]$$

For the lowest 2 states ($n = 1$, $k = 2$) the expected interparticle spacings are

$$\sqrt{\left\langle \left(x_1-x_2\right)^2\right\rangle_D} = 0.32L$$

$$\sqrt{\left\langle \left(x_1-x_2\right)^2\right\rangle_B} = 0.20L$$

$$\sqrt{\left\langle \left(x_1-x_2\right)^2\right\rangle_F} = 0.41L$$

showing the tendency for Bosons to attract and Fermions to repel.

13.7. We'll use bra-ket notation throughout this problem and then use the ladder operators to calculate any required matrix elements. The expectation value of the squared particle separation can be written as

$$\left\langle \left(x_1-x_2\right)^2\right\rangle = \left\langle x_1^2 - 2x_1x_2 + x_2^2\right\rangle$$

$$\left\langle \left(x_1-x_2\right)^2\right\rangle = \left\langle x_1^2\right\rangle + \left\langle x_2^2\right\rangle - 2\left\langle x_1x_2\right\rangle$$

For our three cases, the 2-particle wave function is a product of two single-particle wave functions either not symmetrized (distinguishable), symmetrized (Bosons), or antisymmetrized (Fermions) with respect to exchange of the two particles.

$$\left|\psi_D\right\rangle = \left|nk\right\rangle \equiv \left|n\right\rangle_1 \left|k\right\rangle_2$$
$$\left|\psi_B\right\rangle = \tfrac{1}{\sqrt{2}}\left[\left|nk\right\rangle + \left|kn\right\rangle\right]$$
$$\left|\psi_F\right\rangle = \tfrac{1}{\sqrt{2}}\left[\left|nk\right\rangle - \left|kn\right\rangle\right]$$

Let's first look at distinguishable particles

$$\left\langle x_1^2\right\rangle_D = \left\langle nk\right|x_1^2\left|nk\right\rangle = \left\langle n\right|x_1^2\left|n\right\rangle\left\langle k|k\right\rangle = \left\langle x^2\right\rangle_n$$

where $\left\langle x^2\right\rangle_n$ is a single-particle expectation value. Likewise, we get

$$\left\langle x_2^2\right\rangle_D = \left\langle nk\right|x_2^2\left|nk\right\rangle = \left\langle n|n\right\rangle\left\langle k\right|x_2^2\left|k\right\rangle = \left\langle x^2\right\rangle_k$$
$$\left\langle x_1x_2\right\rangle_D = \left\langle nk\right|x_1x_2\left|nk\right\rangle = \left\langle n\right|x_1\left|n\right\rangle\left\langle k\right|x_2\left|k\right\rangle = \left\langle x\right\rangle_n\left\langle x\right\rangle_k$$

giving

$$\left\langle\left(x_1-x_2\right)^2\right\rangle_D = \left\langle x^2\right\rangle_n + \left\langle x^2\right\rangle_k - 2\left\langle x\right\rangle_n\left\langle x\right\rangle_k$$

Thus we only need two types of matrix elements: $\left\langle x^2\right\rangle_n$ and $\left\langle x\right\rangle_n$. Let's consider Fermions and Bosons before we find the matrix elements.

$$\begin{aligned}\left\langle x_1^2\right\rangle_{B,F} &= \tfrac{1}{\sqrt{2}}\left[\left\langle nk\right| \pm \left\langle kn\right|\right]x_1^2\,\tfrac{1}{\sqrt{2}}\left[\left|nk\right\rangle \pm \left|kn\right\rangle\right]\\ &= \tfrac{1}{2}\left[\left\langle n\right|x_1^2\left|n\right\rangle\left\langle k|k\right\rangle \pm \left\langle n\right|x_1^2\left|k\right\rangle\left\langle k|n\right\rangle \pm \left\langle k\right|x_1^2\left|n\right\rangle\left\langle n|k\right\rangle + \left\langle k\right|x_1^2\left|k\right\rangle\left\langle n|n\right\rangle\right]\\ &= \tfrac{1}{2}\left[\left\langle n\right|x_1^2\left|n\right\rangle \pm 0 \pm 0 + \left\langle k\right|x_1^2\left|k\right\rangle\right] = \tfrac{1}{2}\left[\left\langle x^2\right\rangle_n + \left\langle x^2\right\rangle_k\right]\end{aligned}$$

$$\begin{aligned}\left\langle x_1x_2\right\rangle_{B,F} &= \tfrac{1}{\sqrt{2}}\left[\left\langle nk\right| \pm \left\langle kn\right|\right]x_1x_2\,\tfrac{1}{\sqrt{2}}\left[\left|nk\right\rangle \pm \left|kn\right\rangle\right]\\ &= \tfrac{1}{2}\left[\left\langle n\right|x_1\left|n\right\rangle\left\langle k\right|x_2\left|k\right\rangle \pm \left\langle n\right|x_1\left|k\right\rangle\left\langle k\right|x_2\left|n\right\rangle \pm \left\langle k\right|x_1\left|n\right\rangle\left\langle n\right|x_2\left|k\right\rangle + \left\langle k\right|x_1\left|k\right\rangle\left\langle n\right|x_2\left|n\right\rangle\right]\\ &= \tfrac{1}{2}\left[\left\langle x\right\rangle_n\left\langle x\right\rangle_k \pm \left\langle x\right\rangle_{nk}\left\langle x\right\rangle_{kn} \pm \left\langle x\right\rangle_{kn}\left\langle x\right\rangle_{nk} + \left\langle x\right\rangle_k\left\langle x\right\rangle_n\right] = \left\langle x\right\rangle_n\left\langle x\right\rangle_k \pm \left|\left\langle x\right\rangle_{nk}\right|^2\end{aligned}$$

where

$$\left\langle x\right\rangle_{nk} = \left\langle n\right|x\left|k\right\rangle.$$

Thus we get

$$\left\langle\left(x_1-x_2\right)^2\right\rangle_{B,F} = \left\langle x^2\right\rangle_n + \left\langle x^2\right\rangle_k - 2\left\langle x\right\rangle_n\left\langle x\right\rangle_k \mp 2\left|\left\langle x\right\rangle_{nk}\right|^2$$

So now we have to find an extra matrix element. Let's find them using the ladder operators:

$$\left\langle x^2\right\rangle_n = \langle n|x^2|n\rangle = \frac{\hbar}{2m\omega}\langle n|\left(a^\dagger + a\right)^2|n\rangle = \frac{\hbar}{2m\omega}\langle n|\left(a^\dagger\right)^2 + a^\dagger a + aa^\dagger + a^2|n\rangle$$
$$= \frac{\hbar}{2m\omega}\langle n|a^\dagger a + aa^\dagger|n\rangle = \frac{\hbar}{2m\omega}\langle n|\sqrt{n}\sqrt{n} + \sqrt{n+1}\sqrt{n+1}|n\rangle$$
$$= \frac{\hbar}{2m\omega}(2n+1) = \frac{\hbar}{m\omega}\left(n+\tfrac{1}{2}\right)$$

and

$$\langle x\rangle_n = \langle n|x|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\langle n|a^\dagger + a|n\rangle$$
$$= \sqrt{\frac{\hbar}{2m\omega}}\left[\langle n|a^\dagger|n\rangle + \langle n|a|n\rangle\right] = \sqrt{\frac{\hbar}{2m\omega}}\left[\langle n|\sqrt{n+1}|n+1\rangle + \langle n|\sqrt{n}|n-1\rangle\right]$$
$$= \sqrt{\frac{\hbar}{2m\omega}}\left[\sqrt{n+1}\langle n|n+1\rangle + \sqrt{n}\langle n|n-1\rangle\right] = 0 \quad \text{since} \quad \langle n|m\rangle = \delta_{nm}$$

as expected. And

$$\langle x\rangle_{nk} = \langle n|x|k\rangle = \sqrt{\frac{\hbar}{2m\omega}}\langle n|a^\dagger + a|k\rangle$$
$$= \sqrt{\frac{\hbar}{2m\omega}}\left(\langle n|a^\dagger|k\rangle + \langle n|a|k\rangle\right) = \sqrt{\frac{\hbar}{2m\omega}}\left(\langle n|\sqrt{k+1}|k+1\rangle + \langle n|\sqrt{k}|k-1\rangle\right).$$
$$= \sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{k+1}\langle n|k+1\rangle + \sqrt{k}\langle n|k-1\rangle\right) = \sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n}\delta_{n,k+1} + \sqrt{k}\delta_{n,k-1}\right)$$

Putting this together gives

$$\left\langle\left(x_1 - x_2\right)^2\right\rangle_D = \left\langle x^2\right\rangle_n + \left\langle x^2\right\rangle_k - 2\langle x\rangle_n\langle x\rangle_k = \frac{\hbar}{m\omega}\left(n+\tfrac{1}{2}\right) + \frac{\hbar}{m\omega}\left(k+\tfrac{1}{2}\right)$$
$$= \frac{\hbar}{m\omega}(n+k+1)$$
$$\left\langle\left(x_1 - x_2\right)^2\right\rangle_{B,F} = \left\langle x^2\right\rangle_n + \left\langle x^2\right\rangle_k - 2\langle x\rangle_n\langle x\rangle_k \mp 2\left|\langle x\rangle_{nk}\right|^2$$
$$= \frac{\hbar}{m\omega}(n+k+1) \mp \frac{\hbar}{m\omega}\left(n\delta_{n,k+1} + k\delta_{n,k-1}\right)$$

Summarizing:

$$\left\langle\left(x_1 - x_2\right)^2\right\rangle_D = \frac{\hbar}{m\omega}(n+k+1)$$
$$\left\langle\left(x_1 - x_2\right)^2\right\rangle_{B,F} = \frac{\hbar}{m\omega}(n+k+1) \mp \frac{\hbar}{m\omega}\left(n\delta_{n,k+1} + k\delta_{n,k-1}\right)$$

For the lowest 2 states ($n = 0$, $k = 1$) the expected interparticle spacings are

$$\sqrt{\left\langle \left(x_1 - x_2\right)^2 \right\rangle_D} = 2\frac{\hbar}{m\omega}$$
$$\sqrt{\left\langle \left(x_1 - x_2\right)^2 \right\rangle_B} = \frac{2\hbar}{m\omega} - \frac{\hbar}{m\omega} = 1\frac{\hbar}{m\omega}$$
$$\sqrt{\left\langle \left(x_1 - x_2\right)^2 \right\rangle_F} = \frac{2\hbar}{m\omega} + \frac{\hbar}{m\omega} = 3\frac{\hbar}{m\omega}$$

showing the tendency for Bosons to attract and Fermions to repel.

13.8 For the first excited state of the infinite square well system with one particle in the single-particle ground state and one particle in the first single-particle excited state, the probability densities for the distinguishable (*D*) particle case, the symmetric (*S*) identical particle case and the antisymmetric (*A*) case are

$$\mathcal{P}_D\left(x_1,x_2\right) = \left|\varphi_1\left(x_1\right)\varphi_2\left(x_2\right)\right|^2 = \frac{4}{L^2}\sin^2\left(\frac{\pi x_1}{L}\right)\sin^2\left(\frac{2\pi x_2}{L}\right)$$

$$\mathcal{P}_S\left(x_1,x_2\right) = \left|\frac{1}{\sqrt{2}}\left[\varphi_1\left(x_1\right)\varphi_2\left(x_2\right) + \varphi_1\left(x_2\right)\varphi_2\left(x_1\right)\right]\right|^2$$
$$= \frac{2}{L^2}\left[\sin\left(\frac{\pi x_1}{L}\right)\sin\left(\frac{2\pi x_2}{L}\right) + \sin\left(\frac{\pi x_2}{L}\right)\sin\left(\frac{2\pi x_1}{L}\right)\right]^2$$

$$\mathcal{P}_A\left(x_1,x_2\right) = \left|\frac{1}{\sqrt{2}}\left[\varphi_1\left(x_1\right)\varphi_2\left(x_2\right) - \varphi_1\left(x_2\right)\varphi_2\left(x_1\right)\right]\right|^2$$
$$= \frac{2}{L^2}\left[\sin\left(\frac{\pi x_1}{L}\right)\sin\left(\frac{2\pi x_2}{L}\right) - \sin\left(\frac{\pi x_2}{L}\right)\sin\left(\frac{2\pi x_1}{L}\right)\right]^2$$

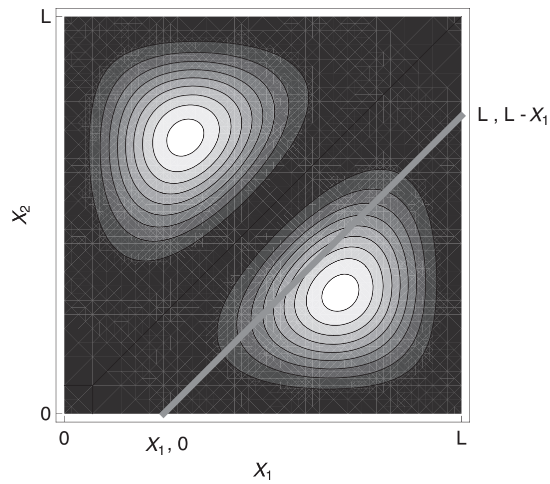
To find the particle separation probability density $\mathcal{P}\left(x_1 - x_2\right)$, make a change of variables from the individual coordinates x_1 and x_2 to the center-of-mass and relative coordinates, and make them dimensionless for notation simplification

$$\begin{aligned} X_{CM} &= \frac{x_1 + x_2}{2}\frac{\pi}{L} \equiv u \\ x_{rel} &= \left(x_1 - x_2\right)\frac{\pi}{L} \equiv v \end{aligned} \quad \Rightarrow \quad \begin{aligned} x_1 &= \frac{2u + v}{2}\frac{L}{\pi} \\ x_2 &= \frac{2u - v}{2}\frac{L}{\pi} \end{aligned}$$

and then integrate out the center-of-mass coordinate. The transformed probability densities are

$$\mathcal{P}_D(u,v) = \frac{4}{L^2}\sin^2\left[\tfrac{1}{2}(2u+v)\right]\sin^2(2u-v)$$
$$\mathcal{P}_S(u,v) = \frac{2}{L^2}\left[\sin\left[\tfrac{1}{2}(2u+v)\right]\sin(2u-v)+\sin\left[\tfrac{1}{2}(2u-v)\right]\sin(2u+v)\right]^2$$
$$\mathcal{P}_A(u,v) = \frac{2}{L^2}\left[\sin\left[\tfrac{1}{2}(2u+v)\right]\sin(2u-v)-\sin\left[\tfrac{1}{2}(2u-v)\right]\sin(2u+v)\right]^2$$

The integration is along a line for which $x_1 - x_2 = \text{constant}$. For example, from the point $x_1, 0$ to the point $L, L-x_1$, as shown below.



In terms of the transformed coordinates, this integral is from $u = v/2$ to $u = \pi - v/2$, which assumes that $x_1 > x_2$, and thus $v > 0$. For the distinguishable case, the integration gives

$$\begin{aligned}\mathcal{P}_D(v) &= \int_{v/2}^{\pi-v/2}\mathcal{P}_D(u,v)\,du = \frac{4}{L^2}\int_{v/2}^{\pi-v/2}\sin^2\left[\tfrac{1}{2}(2u+v)\right]\sin^2(2u-v)\,du \\ &= \frac{4}{L^2}\left[\frac{u}{4}+\tfrac{1}{16}\sin(2u-3v)-\tfrac{1}{16}\sin(4u-2v)+\tfrac{1}{48}\sin(6u-v)-\tfrac{1}{8}\sin(2u+v)\right]_{v/2}^{\pi-v/2} \\ &= \frac{4}{L^2}\left[\frac{\pi-v}{4}+\tfrac{1}{6}\sin 2v-\tfrac{1}{48}\sin 4v\right] = \frac{1}{L^2}\left(\pi - v + \tfrac{2}{3}\sin 2v - \tfrac{1}{12}\sin 4v\right)\end{aligned}$$

This is symmetric about $v = 0$, so the full result is

$$\mathcal{P}_D(v) = \frac{1}{L^2}\left(\pi - |v| + \tfrac{2}{3}\sin 2|v| - \tfrac{1}{12}\sin 4|v|\right)$$

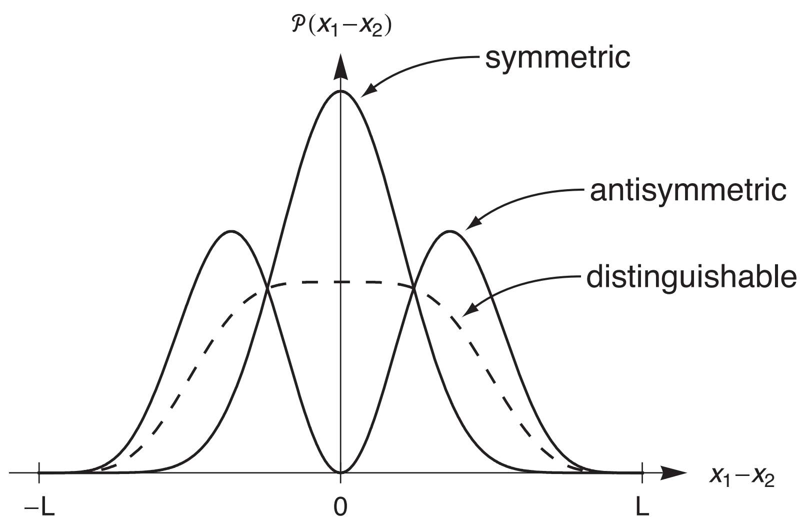
For the identical particle cases, we get

$$\begin{aligned}
\mathcal{P}_{S,A}(v) &= \int_{v/2}^{\pi-v/2} \mathcal{P}_{S,A}(u,v)\,du \\
&= \frac{2}{L^2}\int_{v/2}^{\pi-v/2}\left[\sin\left[\tfrac{1}{2}(2u+v)\right]\sin(2u-v) \pm \sin\left[\tfrac{1}{2}(2u-v)\right]\sin(2u+v)\right]^2 du \\
&= \frac{2}{L^2}\int_{v/2}^{\pi-v/2}\left\{\begin{array}{l}\sin^2\left[\tfrac{1}{2}(2u+v)\right]\sin^2(2u-v)+\sin^2\left[\tfrac{1}{2}(2u-v)\right]\sin^2(2u+v) \\ \pm\sin\left[\tfrac{1}{2}(2u+v)\right]\sin(2u-v)\sin\left[\tfrac{1}{2}(2u-v)\right]\sin(2u+v)\end{array}\right\}du \\
&= \frac{2}{L^2}\left[\begin{array}{l}\frac{u}{4}+\frac{1}{16}\sin(2u-3v)-\frac{1}{16}\sin(4u-2v)+\frac{1}{48}\sin(6u-v)-\frac{1}{8}\sin(2u+v) \\ \frac{u}{4}+\frac{1}{16}\sin(2u+3v)-\frac{1}{16}\sin(4u+2v)+\frac{1}{48}\sin(6u+v)-\frac{1}{8}\sin(2u-v) \\ \pm\left\{\frac{u}{8}(\cos v+\cos 3v)+\frac{1}{48}\sin 6u-\frac{1}{16}\sin 4u\cos v+\frac{1}{8}(1-2\cos 2v)\sin 2u\right\}\end{array}\right]_{v/2}^{\pi-v/2} \\
&= \frac{1}{3L^2}\left\{\begin{array}{l}(\pi-v)\left[12+6(\cos 2v\mp 2\cos v)\right] \\ \mp 9\sin v+9\sin 2v\mp\sin 3v\end{array}\right\}\left[\begin{array}{c}\cos^2(v/2) \\ \sin^2(v/2)\end{array}\right]
\end{aligned}$$

Again, this is symmetric about $v=0$, so the full result is

$$\mathcal{P}_{S,A}(v)=\frac{1}{3L^2}\left\{\begin{array}{l}(\pi-|v|)\left[12+6(\cos 2v\mp 2\cos v)\right] \\ \mp 9\sin|v|+9\sin 2|v|\mp\sin 3|v|\end{array}\right\}\left[\begin{array}{c}\cos^2(v/2) \\ \sin^2(v/2)\end{array}\right]$$

Plot:



13.9 If both particles are in the same state, then the probability density is

$$\mathcal{P}(x_1,x_2)=\left|\psi(x_1,x_2)\right|^2=\left|\varphi_{n_a}(x_1)\varphi_{n_a}(x_2)\right|^2=\left|\varphi_{n_a}(x_1)\right|^2\left|\varphi_{n_a}(x_2)\right|^2$$

for the distinguishable and boson cases, and is equal to zero for the fermion case. The one-particle probability density is

$$\mathcal{P}(x_1)=\int_{-\infty}^{\infty}\mathcal{P}(x_1,x_2)\,dx_2=\int_{-\infty}^{\infty}\left|\varphi_{n_a}(x_1)\right|^2\left|\varphi_{n_a}(x_2)\right|^2dx_2=\left|\varphi_{n_a}(x_1)\right|^2\int_{-\infty}^{\infty}\left|\varphi_{n_a}(x_2)\right|^2dx_2$$
$$=\left|\varphi_{n_a}(x_1)\right|^2$$

where the last step uses the normalization of the one-particle wave functions. The result is clearly the same for both cases (but not for the non-existent fermion case).
If the two particles are in different states, then the two-particle probability density is

$$\mathcal{P}_D(x_1,x_2)=\left|\varphi_{n_a}(x_1)\varphi_{n_b}(x_2)\right|^2\quad or\quad\left|\varphi_{n_a}(x_2)\varphi_{n_b}(x_1)\right|^2$$

$$\mathcal{P}_{S,A}(x_1,x_2)=\left|N\left[\varphi_{n_a}(x_1)\varphi_{n_b}(x_2)\pm\varphi_{n_a}(x_2)\varphi_{n_b}(x_1)\right]\right|^2$$
$$=\left|N\right|^2\begin{bmatrix}\left|\varphi_{n_a}(x_1)\right|^2\left|\varphi_{n_b}(x_2)\right|^2+\left|\varphi_{n_a}(x_2)\right|^2\left|\varphi_{n_b}(x_1)\right|^2\\ \pm\varphi_{n_a}(x_1)\varphi_{n_b}(x_2)\,\varphi^*_{n_a}(x_2)\varphi^*_{n_b}(x_1)\\ \pm\varphi^*_{n_a}(x_1)\varphi^*_{n_b}(x_2)\varphi_{n_a}(x_2)\varphi_{n_b}(x_1)\end{bmatrix}$$

for the distinguishable (*D*) particle case, the symmetric (*S*) identical particle case and the antisymmetric (*A*) case. For the distinguishable particle case, we average over the two possibilities, so the one-particle probability density is

$$\mathcal{P}_D(x_1)=\frac{1}{2}\left[\int_{-\infty}^{\infty}\left|\varphi_{n_a}(x_1)\right|^2\left|\varphi_{n_b}(x_2)\right|^2dx_2+\int_{-\infty}^{\infty}\left|\varphi_{n_a}(x_2)\right|^2\left|\varphi_{n_b}(x_1)\right|^2dx_2\right]$$
$$=\frac{1}{2}\left[\left|\varphi_{n_a}(x_1)\right|^2\int_{-\infty}^{\infty}\left|\varphi_{n_b}(x_2)\right|^2dx_2+\left|\varphi_{n_b}(x_1)\right|^2\int_{-\infty}^{\infty}\left|\varphi_{n_a}(x_2)\right|^2dx_2\right]$$
$$=\frac{1}{2}\left[\left|\varphi_{n_a}(x_1)\right|^2+\left|\varphi_{n_b}(x_1)\right|^2\right]$$

For the symmetric and antisymmetric cases, we get

$$\mathcal{P}_D(x_1) = \int_{-\infty}^{\infty} |N|^2 \begin{bmatrix} \left|\varphi_{n_a}(x_1)\right|^2 \left|\varphi_{n_b}(x_2)\right|^2 + \left|\varphi_{n_a}(x_2)\right|^2 \left|\varphi_{n_b}(x_1)\right|^2 \\ \pm\varphi_{n_a}(x_1)\varphi_{n_b}(x_2)\,\varphi_{n_a}^*(x_2)\varphi_{n_b}^*(x_1) \\ \pm\varphi_{n_a}^*(x_1)\varphi_{n_b}^*(x_2)\varphi_{n_a}(x_2)\varphi_{n_b}(x_1) \end{bmatrix} dx_2$$

$$= |N|^2 \begin{bmatrix} \int_{-\infty}^{\infty}\left|\varphi_{n_a}(x_1)\right|^2 \left|\varphi_{n_b}(x_2)\right|^2 dx_2 + \int_{-\infty}^{\infty}\left|\varphi_{n_a}(x_2)\right|^2 \left|\varphi_{n_b}(x_1)\right|^2 dx_2 \\ \pm\int_{-\infty}^{\infty}\varphi_{n_a}(x_1)\varphi_{n_b}(x_2)\,\varphi_{n_a}^*(x_2)\varphi_{n_b}^*(x_1)dx_2 \\ \pm\int_{-\infty}^{\infty}\varphi_{n_a}^*(x_1)\varphi_{n_b}^*(x_2)\varphi_{n_a}(x_2)\varphi_{n_b}(x_1)dx_2 \end{bmatrix}$$

$$= |N|^2 \begin{bmatrix} \left|\varphi_{n_a}(x_1)\right|^2 \int_{-\infty}^{\infty}\left|\varphi_{n_b}(x_2)\right|^2 dx_2 + \left|\varphi_{n_b}(x_1)\right|^2 \int_{-\infty}^{\infty}\left|\varphi_{n_a}(x_2)\right|^2 dx_2 \\ \pm\varphi_{n_a}(x_1)\varphi_{n_b}^*(x_1)\int_{-\infty}^{\infty}\varphi_{n_b}(x_2)\,\varphi_{n_a}^*(x_2)dx_2 \\ \pm\varphi_{n_a}^*(x_1)\varphi_{n_b}(x_1)\int_{-\infty}^{\infty}\varphi_{n_b}^*(x_2)\varphi_{n_a}(x_2)dx_2 \end{bmatrix}$$

$$= |N|^2 \left[\left|\varphi_{n_a}(x_1)\right|^2 + \left|\varphi_{n_b}(x_1)\right|^2\right]$$

where we used the orthogonality and the normalization of the single-particle wave functions. Clearly, $N = 1/\sqrt{2}$ to ensure normalization. Thus the results for the single-particle probability density are the same for all three cases.

13.10 The first-order perturbation energy in the first excited state is

$$\begin{aligned} E_{12}^{(1)} &= \left\langle \psi_{12}^S \middle| H' \middle| \psi_{12}^S \right\rangle \langle 00|00\rangle \\ &= \left\langle \psi_{12}^S \middle| V_{\text{int}}(x_1 - x_2) \middle| \psi_{12}^S \right\rangle \\ &= \tfrac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[\varphi_1^*(x_1)\varphi_2^*(x_2) + \varphi_1^*(x_2)\varphi_2^*(x_1)\right]V_{\text{int}}(x_1 - x_2) \\ &\qquad\qquad \left[\varphi_1(x_1)\varphi_2(x_2) + \varphi_1(x_2)\varphi_2(x_1)\right]dx_1 dx_2 \end{aligned}$$

Multiplying out the terms gives four integrals

$$\begin{aligned} E_{12}^{(1)} &= \tfrac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left|\varphi_1(x_1)\right|^2\left|\varphi_2(x_2)\right|^2 V_{\text{int}}(x_1 - x_2)\,dx_1\,dx_2 \\ &\quad + \tfrac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left|\varphi_1(x_2)\right|^2\left|\varphi_2(x_1)\right|^2 V_{\text{int}}(x_1 - x_2)\,dx_1\,dx_2 \\ &\quad + \tfrac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\varphi_1^*(x_1)\varphi_2^*(x_2)\varphi_1(x_2)\varphi_2(x_1)V_{\text{int}}(x_1 - x_2)\,dx_1\,dx_2 \\ &\quad + \tfrac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\varphi_1^*(x_2)\varphi_2^*(x_1)\varphi_1(x_1)\varphi_2(x_2)V_{\text{int}}(x_1 - x_2)\,dx_1\,dx_2 \end{aligned}$$

Now swap the integration dummy variables x_1 and x_2 in the 2nd and 4th integrals to get

$$\begin{aligned}E_{12}^{(1)} &= \tfrac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left|\varphi_1(x_1)\right|^2\left|\varphi_2(x_2)\right|^2 V_{\text{int}}(x_1-x_2)\,dx_1\,dx_2\\ &+\tfrac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left|\varphi_1(x_1)\right|^2\left|\varphi_2(x_2)\right|^2 V_{\text{int}}(x_2-x_1)\,dx_2\,dx_1\\ &+\tfrac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\varphi_1^*(x_1)\varphi_2^*(x_2)\varphi_1(x_2)\varphi_2(x_1)V_{\text{int}}(x_1-x_2)\,dx_1\,dx_2\\ &+\tfrac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\varphi_1^*(x_1)\varphi_2^*(x_2)\varphi_1(x_2)\varphi_2(x_1)V_{\text{int}}(x_2-x_1)\,dx_2\,dx_1\end{aligned}$$

The interaction potential energy depends on the particle separation $r=\left|x_1-x_2\right|$, so $V_{\text{int}}(x_2-x_1)=V_{\text{int}}(x_1-x_2)$. Thus the 1$^{\text{st}}$ and 2$^{\text{nd}}$ integrals are equal, as are the 3$^{\text{rd}}$ and 4$^{\text{th}}$, resulting in

$$\begin{aligned}E_{12}^{(1)} &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left|\varphi_1(x_1)\right|^2 V_{\text{int}}(x_1-x_2)\left|\varphi_2(x_2)\right|^2 dx_1\,dx_2\\ &+\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\varphi_1^*(x_1)\varphi_2^*(x_2)V_{\text{int}}(x_1-x_2)\varphi_1(x_2)\varphi_2(x_1)\,dx_1\,dx_2\end{aligned}$$

13.11 (a) In the unperturbed case, the two fermions are non-interacting, so the Hamiltonian is separable in the coordinates x_1 and x_2. This means that the two-particle spatial wave function is a product of the single-particle spatial wave functions and the energy is the sum of the two single-particle energies:

$$\begin{aligned}&E_{n_a,n_b}=\left(n_a+\tfrac{1}{2}\right)\hbar\omega+\left(n_b+\tfrac{1}{2}\right)\hbar\omega=\left(n_a+n_b+1\right)\hbar\omega\\ &\left|n_a n_b\right\rangle \doteq \varphi_{n_a}(x_1)\varphi_{n_b}(x_2)\end{aligned}$$

The total system state vector must be antisymmetric under particle interchange. This state vector must include both the spatial and spin parts. If both particles are in the same single-particle spatial state ($n_\text{a} = n_\text{b}$), then only a symmetric spatial state is allowed. We know that the spin triplet state $\left|1M\right\rangle$ is symmetric and the singlet state $\left|00\right\rangle$ is antisymmetric. Thus the allowed states are

$$\begin{aligned}\left|\psi_{n_a n_a}^{SA}\right\rangle &= \left|n_a n_a\right\rangle\left|00\right\rangle\\ \left|\psi_{n_a n_b}^{SA}\right\rangle &= \frac{1}{\sqrt{2}}\left[\left|n_a n_b\right\rangle+\left|n_b n_a\right\rangle\right]\left|00\right\rangle\\ \left|\psi_{n_a n_b}^{AS}\right\rangle &= \frac{1}{\sqrt{2}}\left[\left|n_a n_b\right\rangle-\left|n_b n_a\right\rangle\right]\left|1M\right\rangle\end{aligned}$$

In the ground state, both fermions occupy the lowest single particle spatial state, so only the singlet state is allowed:

$$\begin{aligned}&\left|\psi_{00}^{SA}\right\rangle=\left|n_a=0,n_b=0\right\rangle\left|00\right\rangle\\ &E_{ground}=\hbar\omega\end{aligned}$$

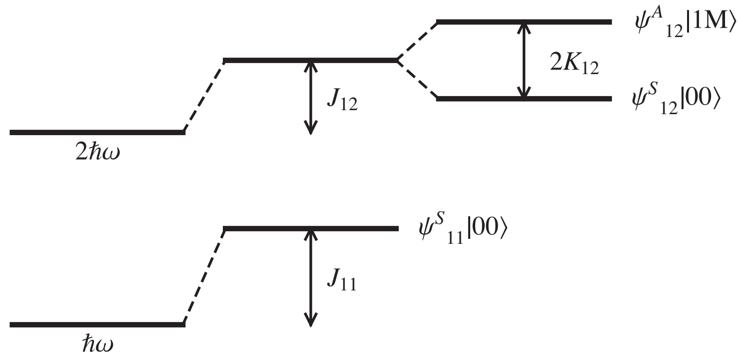
The ground state is nondegenerate.

The first excited state has one particle in the single-particle ground state ($n_a = 0$) and one in the first excited single-particle state ($n_b = 1$) and both singlet and triplet states are allowed:

$$\left|\psi_{01}^{SA}\right\rangle = \frac{1}{\sqrt{2}}\left[\left|n_a = 0, n_b = 1\right\rangle + \left|n_b = 1, n_a = 0\right\rangle\right]\left|00\right\rangle$$
$$\left|\psi_{01}^{AS}\right\rangle = \frac{1}{\sqrt{2}}\left[\left|n_a = 0, n_b = 1\right\rangle - \left|n_b = 1, n_a = 0\right\rangle\right]\left|1M\right\rangle$$
$$E_{excited} = 2\hbar\omega$$

There are four possible configurations for this situation, so the state is four-fold degenerate.

b) If we now let the two particles interact via $H' = \frac{1}{2}\alpha\left(x_1 - x_2\right)^2$, then the additional potential energy changes the energy of each state. Treating the new interaction as a perturbation, we must find the matrix elements of this perturbation. Any spatial perturbation is diagonal with respect to the spin parts. Because this interaction is proportional to the square of the particle separation, nearby particles have less interaction energy and distant particles have more interaction energy. Analogous to the square well case shown in Figs. 13.3 and 13.4, the symmetric spatial state (associated with the spin singlet) has reduced particle separation and hence smaller interaction energy. On the contrary, the antisymmetric spatial wavefunction (associated with the spin triplet) has increased particle separation and hence larger interaction energy. Thus the spin triplet states are shifted up more than the spin singlet state, as shown below:



13.12 For the symmetric triplet spin state, the spatial wave function is antisymmetric

$$\left|\psi_{12}^{AS}\right\rangle \doteq \psi_{12}^{A}\left(x_1, x_2\right)\left|1M\right\rangle = \frac{1}{\sqrt{2}}\left[\varphi_1\left(x_1\right)\varphi_2\left(x_2\right) - \varphi_2\left(x_1\right)\varphi_1\left(x_2\right)\right]\left|1M\right\rangle$$

The resultant first-order energy correction is

$$\begin{aligned} E_{12}^{(1)} &= \left\langle\psi_{12}^{A}\right|H'\left|\psi_{12}^{A}\right\rangle\left\langle 1M \mid 1M\right\rangle = \left\langle\psi_{12}^{A}\right|V_{\text{int}}\left(x_1 - x_2\right)\left|\psi_{12}^{A}\right\rangle \\ &= \tfrac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[\varphi_1^*\left(x_1\right)\varphi_2^*\left(x_2\right) - \varphi_1^*\left(x_2\right)\varphi_2^*\left(x_1\right)\right]V_{\text{int}}\left(x_1 - x_2\right) \\ &\qquad\qquad \left[\varphi_1\left(x_1\right)\varphi_2\left(x_2\right) - \varphi_1\left(x_2\right)\varphi_2\left(x_1\right)\right]dx_1 dx_2 \end{aligned}$$

Multiplying out the terms gives four integrals

$$\begin{aligned}
E_{12}^{(1)} = \tfrac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\varphi_1(x_1)|^2 |\varphi_2(x_2)|^2 V_{\text{int}}(x_1 - x_2)\, dx_1\, dx_2 \\
+\tfrac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\varphi_1(x_2)|^2 |\varphi_2(x_1)|^2 V_{\text{int}}(x_1 - x_2)\, dx_1\, dx_2 \\
-\tfrac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \varphi_1^*(x_1)\varphi_2^*(x_2)\varphi_1(x_2)\varphi_2(x_1) V_{\text{int}}(x_1 - x_2)\, dx_1\, dx_2 \\
-\tfrac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \varphi_1^*(x_2)\varphi_2^*(x_1)\varphi_1(x_1)\varphi_2(x_2) V_{\text{int}}(x_1 - x_2)\, dx_1\, dx_2
\end{aligned}$$

Now swap the integration dummy variables x_1 and x_2 in the 2nd and 4th integrals to show that the 1st and 2nd integrals are equal, as are the 3rd and 4th, (see Problem 13.10) resulting in

$$\begin{aligned}
E_{12}^{(1)} &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\varphi_1(x_1)|^2 V_{\text{int}}(x_1 - x_2) |\varphi_2(x_2)|^2\, dx_1\, dx_2 \\
&\quad -\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \varphi_1^*(x_1)\varphi_2^*(x_2) V_{\text{int}}(x_1 - x_2)\varphi_1(x_2)\varphi_2(x_1)\, dx_1\, dx_2 \\
&= J_{12} - K_{12}
\end{aligned}$$

13.13 a) The $n_a = 1$ electron is in the 1*s* state and so has $\ell_a = 0$, while the $n_b = 2$ electron could be in the 2*s* state or in the 2*p* state and so has $\ell_b = 0$ or 1. Both electrons have $s_i = 1/2$. Thus we get total $L = 0$ in the 1*s*2*s* state and total $L = 1$ in the 1*s*2*p* state, and total $S = 0, 1$ in both cases. When we add L and S to get J, we get the following results:

1*s*2*s*: $L = 0$ -> $J = L + S = S = 0,1$
-> states are $^3S_1$ 3 states
$^1S_0$ 1 state

1*s*2*p*: $L = 1$ -> $J = L + S = 1 + 0 = 1$ or $1 + 1 = 0, 1, 2$
-> states are $^1P_1$ 3 states
$^3P_2$ 5 states
$^3P_1$ 3 states
$^3P_0$ 1 states

b) This gives a total of 16 states

c) The hydrogenic energy levels are

$$E_n = -\frac{Z^2}{2n^2}\alpha^2 mc^2 = -\frac{Z^2}{n^2} 13.6eV$$

For the two electrons we thus get:

$$E_{n_1n_2} = -\frac{Z^2}{2n_a^2}\alpha^2mc^2 - \frac{Z^2}{2n_b^2}\alpha^2mc^2 = -Z^2 13.6eV\left(\frac{1}{n_a^2}+\frac{1}{n_b^2}\right)$$
$$E_{12} = -2^2\times 13.6eV\left(\frac{1}{1}+\frac{1}{4}\right) = -13.6eV\times 4\times\frac{5}{4} = -13.6eV\times 5 = -68.0eV$$

d) The electrons interact through the Coulomb force and so repel each other and create higher energy, or less binding. Thus we expect the energy levels to go up. How much they go up depends on the overlap of the electron density in the different states. The calculation is done in Problem 13.15. The total wave function must be antisymmetric with respect to exchange of the two particles, which means we must combine antisymmetric spatial wave functions with symmetric spin wave functions and vice versa. Since the spin wave functions are antisymmetric for singlet states and symmetric for triplet states, we get two possibilities for each configuration (*s* or *p*):

$$\left|\psi^{SA}_{1s,2\ell}\right\rangle = \left|\psi^{S}_{1s,2\ell}\right\rangle\left|00\right\rangle \doteq \frac{1}{\sqrt{2}}\left[\psi_{100}(\mathbf{r}_1)\psi_{2\ell m}(\mathbf{r}_2)+\psi_{100}(\mathbf{r}_2)\psi_{2\ell m}(\mathbf{r}_1)\right]\left|00\right\rangle$$
$$\left|\psi^{AS}_{1s,2\ell}\right\rangle = \left|\psi^{A}_{1s,2\ell}\right\rangle\left|1M\right\rangle \doteq \frac{1}{\sqrt{2}}\left[\psi_{100}(\mathbf{r}_1)\psi_{2\ell m}(\mathbf{r}_2)-\psi_{100}(\mathbf{r}_2)\psi_{2\ell m}(\mathbf{r}_1)\right]\left|1M\right\rangle$$

Since the antisymmetric spatial wave function is zero when $\mathbf{r}_1 = \mathbf{r}_2$, there is less overlap in that state and hence less electron repulsion, leading to a smaller upward shift. Hence the spin triplet states are shifted up less than the spin singlet states. It turns out (see Problem 13.15) that the $1s2p$ levels are shifted upward more than the $1s2s$ levels because there is greater overlap and hence greater electronic repulsion. This gives the energy level structure shown in Fig. 13.9.

13.14 The direct integral in the ground state of helium is

$$E^{(1)}_{1s,1s} = \iint \psi^*_{100}(\mathbf{r}_1)\psi^*_{100}(\mathbf{r}_2)\frac{e^2}{4\pi\varepsilon_0\left|\mathbf{r}_1-\mathbf{r}_2\right|}\psi_{100}(\mathbf{r}_2)\psi_{100}(\mathbf{r}_1)\,d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

The ground state wave function is

$$\psi_{100}(r,\theta,\phi) = \sqrt{\frac{Z^3}{\pi a_0^3}}\,e^{-Zr/a_0}$$

Use the spherical harmonic addition theorem

$$\frac{1}{\left|\mathbf{r}_1-\mathbf{r}_2\right|} = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\frac{4\pi}{2\ell+1}\frac{r_<^{\ell}}{r_>^{\ell+1}}Y_\ell^{m*}(\theta_1,\phi_1)\,Y_\ell^{m}(\theta_2,\phi_2)$$

where $r_>$ stands for the larger of the two distances r_1 and r_2, and $r_<$ the smaller . Putting this all together gives

$$E_{1s,1s}^{(1)} = \frac{Z^6 e^2}{4\pi^3 \varepsilon_0 a_0^6} \iint e^{-2Zr_1/a_0} e^{-2Zr_2/a_0} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell+1} \frac{r_<^\ell}{r_>^{\ell+1}} Y_{\ell m}^*(\theta_1,\phi_1)\, Y_{\ell m}(\theta_2,\phi_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2$$
$$= \frac{Z^6 e^2}{4\pi^3 \varepsilon_0 a_0^6} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell+1} \iint e^{-2Z(r_1+r_2)/a_0} \frac{r_<^\ell}{r_>^{\ell+1}} Y_{\ell m}^*(\theta_1,\phi_1) Y_{\ell m}(\theta_2,\phi_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

Recall that $Y_0^0(\theta,\phi) = 1/\sqrt{4\pi}$ and separate the integrals to get

$$E_{1s,1s}^{(1)} = \frac{Z^6 e^2}{4\pi^3 \varepsilon_0 a_0^6} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{(4\pi)^2}{2\ell+1} \int_0^\infty \int_0^\infty e^{-2Z(r_1+r_2)/a_0} \frac{r_<^\ell}{r_>^{\ell+1}} r_1^2\, dr_1 r_2^2\, dr_1$$
$$\times \int Y_\ell^{m*}(\theta_1,\phi_1) Y_0^{0*}(\theta_1,\phi_1) d\Omega_1 \int Y_0^{0*}(\theta_2,\phi_2) Y_\ell^m(\theta_2,\phi_2) d\Omega_2$$

The spherical harmonics are orthonormal, so the angular integrals require that $\ell = 0$ and $m = 0$, giving

$$E_{1s,1s}^{(1)} = \frac{4Z^6 e^2}{\pi \varepsilon_0 a_0^6} \int_0^\infty \int_0^\infty e^{-2Z(r_1+r_2)/a_0} \frac{1}{r_>} r_1^2\, dr_1 r_2^2\, dr_2$$
$$= \frac{4Z^6 e^2}{\pi \varepsilon_0 a_0^6} \int_0^\infty e^{-2Zr_1/a_0} r_1^2\, dr_1 \left[\frac{1}{r_1} \int_0^{r_1} e^{-2Zr_2/a_0} r_2^2\, dr_2 + \int_{r_1}^\infty e^{-2Zr_2/a_0} \frac{1}{r_2} r_2^2\, dr_2 \right]$$
$$= \frac{4Z^6 e^2}{\pi \varepsilon_0 a_0^6} \int_0^\infty e^{-2Zr_1/a_0} r_1^2\, dr_1 \left[\begin{array}{l} \frac{1}{r_1}\left(\frac{a_0}{4Z^3}\right)\left(a_0^2 - e^{-2Zr_1/a_0}\left\{a_0^2 + 2a_0 r_1 Z + 2r_1^2 Z^2\right\}\right) \\ +\left(\frac{a_0}{4Z^2}\right) e^{-2Zr_1/a_0}\left\{a_0 + 2r_1 Z\right\} \end{array} \right]$$
$$= \frac{Z^3 e^2}{\pi \varepsilon_0 a_0^5} \left[\begin{array}{l} \int_0^\infty \left(a_0^2 e^{-2Zr_1/a_0} - e^{-4Zr_1/a_0}\left\{a_0^2 + 2a_0 r_1 Z + 2r_1^2 Z^2\right\}\right) r_1\, dr_1 + \\ +\int_0^\infty e^{-4Zr_1/a_0}\left(a_0 Z + 2r_1 Z^2\right) r_1^2\, dr_1 \end{array} \right]$$
$$= \frac{Z^3 e^2}{\pi \varepsilon_0 a_0^5} \left[\frac{a_0^4}{4Z^2} - \frac{a_0^4}{16Z^2} - \frac{a_0^4}{16Z^2} - \frac{3a_0^4}{64Z^2} + \frac{a_0^4}{32Z^2} + \frac{3a_0^4}{64Z^2} \right]$$
$$= \frac{5Ze^2}{32\pi \varepsilon_0 a_0} = \frac{5}{8}\left(\frac{Ze^2}{4\pi \varepsilon_0 a_0}\right)$$

Numerically, we get

$$E_{1s,1s}^{(1)} = \frac{5}{8} Z \left(\frac{e^2}{4\pi \varepsilon_0 a_0}\right) = \frac{5}{8} 2(2Ryd) = \frac{5}{2} 13.6eV = 34eV$$

13.15. We will need the following. Note that the wave functions are for hydrogen-like states with $Z = 2$.

$$R_{10}(r) = \frac{4\sqrt{2}}{a_0^{\frac{3}{2}}} e^{-\frac{2r}{a_0}}$$

$$R_{20}(r) = \frac{2}{(a_0)^{\frac{3}{2}}}\left(1 - \frac{r}{a_0}\right) e^{-\frac{r}{a_0}}$$

$$R_{21}(r) = \frac{2}{\sqrt{3}(a_0)^{\frac{3}{2}}} \frac{r}{a_0} e^{-\frac{r}{a_0}}$$

$$\frac{1}{|\vec{\mathbf{r}}_1 - \vec{\mathbf{r}}_2|} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell+1} \frac{r_<^\ell}{r_>^{\ell+1}} Y_\ell^{m*}(\theta_1,\phi_1) Y_\ell^m(\theta_2,\phi_2)$$

$$\int x e^{-x} dx = -xe^{-x} - e^{-x}$$

$$\int x^2 e^{-x} dx = -x^2 e^{-x} - 2xe^{-x} - 2e^{-x}$$

$$\int x^3 e^{-x} dx = -x^3 e^{-x} - 3x^2 e^{-x} - 6xe^{-x} - 6e^{-x}$$

$$\int x^4 e^{-x} dx = -x^4 e^{-x} - 4x^3 e^{-x} - 12x^2 e^{-x} - 24xe^{-x} - 24e^{-x}$$

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

The integrals we want are:

$$J_{2\ell} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi_{100}(\vec{\mathbf{r}}_1)|^2 |\psi_{2\ell m}(\vec{\mathbf{r}}_2)|^2 \frac{e^2}{|\vec{\mathbf{r}}_1 - \vec{\mathbf{r}}_2|} d^3r_1 d^3r_2$$

$$K_{2\ell} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi_{100}^*(\vec{\mathbf{r}}_1)\psi_{2\ell m}^*(\vec{\mathbf{r}}_2) \frac{e^2}{|\vec{\mathbf{r}}_1 - \vec{\mathbf{r}}_2|} \psi_{100}(\vec{\mathbf{r}}_2)\psi_{2\ell m}(\vec{\mathbf{r}}_1) d^3r_1 d^3r_2$$

First look at J and put in the expansion for the particle separation:

$$\begin{aligned} J_{2\ell_1} &= e^2 \iint |\psi_{100}(\vec{\mathbf{r}}_1)|^2 |\psi_{2\ell_1 m_1}(\vec{\mathbf{r}}_2)|^2 \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell+1}\frac{r_<^\ell}{r_>^{\ell+1}} Y_\ell^{m*}(\theta_1,\phi_1) Y_\ell^m(\theta_2,\phi_2) d^3r_1 d^3r_2 \\ &= e^2 \iint |R_{10}(r_1)|^2 |R_{2\ell_1}(r_2)|^2 |Y_0^0(\theta_1,\phi_1)|^2 |Y_{\ell_1}^{m_1}(\theta_2,\phi_2)|^2 \\ &\qquad \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell+1}\frac{r_<^\ell}{r_>^{\ell+1}} Y_\ell^{m*}(\theta_1,\phi_1) Y_\ell^m(\theta_2,\phi_2) dr_1 dr_2 d\Omega_1 d\Omega_2 \end{aligned}$$

Note that the angular integral for particle 1 collapses the sums:

$$\int \left|Y_0^0(\theta_1,\phi_1)\right|^2 Y_\ell^{m*}(\theta_1,\phi_1)\,d\Omega_1 = \int Y_0^{0*}(\theta_1,\phi_1)Y_0^0(\theta_1,\phi_1)Y_\ell^{m*}(\theta_1,\phi_1)\,d\Omega_1$$
$$= \frac{1}{\sqrt{4\pi}}\int Y_0^0(\theta_1,\phi_1)Y_\ell^{m*}(\theta_1,\phi_1)\,d\Omega_1 = \frac{1}{\sqrt{4\pi}}\delta_{\ell 0}\delta_{m0}$$

This makes the angular integral for particle 2 simpler

$$\int \left|Y_{\ell_1}^{m_1}(\theta_2,\phi_2)\right|^2 Y_0^0(\theta_2,\phi_2)\,d\Omega_2 = \int Y_{\ell_1}^{m_1*}(\theta_2,\phi_2)Y_{\ell_1}^{m_1}(\theta_2,\phi_2)Y_0^0(\theta_2,\phi_2)\,d\Omega_2$$
$$= \frac{1}{\sqrt{4\pi}}\int Y_{\ell_1}^{m_1*}(\theta_2,\phi_2)Y_{\ell_1}^{m_1}(\theta_2,\phi_2)\,d\Omega_2 = \frac{1}{\sqrt{4\pi}}$$

This gives

$$J_{2\ell} = e^2\iint \left|R_{10}(r_1)\right|^2\left|R_{2\ell}(r_2)\right|^2\frac{1}{r_>}r_1^2r_2^2\,dr_1dr_2$$
$$= e^2\int_0^\infty \left|R_{10}(r_1)\right|^2 r_1^2dr_1\left[\frac{1}{r_1}\int_0^{r_1}\left|R_{2\ell}(r_2)\right|^2 r_2^2\,dr_2 + \int_{r_1}^\infty \frac{1}{r_2}\left|R_{2\ell}(r_2)\right|^2 r_2^2\,dr_2\right]$$

Now put in the radial wave functions and change variables ($x = 2r_2/a_0$) to make the integrals simpler:

$$J_{20} = e^2\int_0^\infty \frac{32}{a_0^3}e^{-\frac{4r_1}{a_0}}r_1^2dr_1\left[\frac{1}{r_1}\int_0^{r_1}\frac{4}{a_0^3}\left(1-\frac{2r_2}{a_0}+\frac{r_2^2}{a_0^2}\right)e^{-\frac{2r_2}{a_0}}r_2^2\,dr_2 + \int_{r_1}^\infty \frac{1}{r_2}\frac{4}{a_0^3}\left(1-\frac{2r_2}{a_0}+\frac{r_2^2}{a_0^2}\right)e^{-\frac{2r_2}{a_0}}r_2^2\,dr_2\right]$$
$$= e^2\int_0^\infty \frac{32}{a_0^3}e^{-\frac{4r_1}{a_0}}r_1^2dr_1\left[\frac{1}{r_1}\int_0^{r_1}\frac{4}{a_0^3}\left(r_2^2-\frac{2r_2^3}{a_0}+\frac{r_2^4}{a_0^2}\right)e^{-\frac{2r_2}{a_0}}\,dr_2 + \int_{r_1}^\infty \frac{4}{a_0^3}\left(r_2-\frac{2r_2^2}{a_0}+\frac{r_2^3}{a_0^2}\right)e^{-\frac{2r_2}{a_0}}\,dr_2\right]$$
$$= e^2\int_0^\infty \frac{32}{a_0^3}e^{-\frac{4r_1}{a_0}}r_1^2dr_1\left[\frac{1}{r_1}\int_0^{\frac{2r_1}{a_0}}\frac{1}{2}\left(x^2-x^3+\tfrac{1}{4}x^4\right)e^{-x}\,dx + \int_{\frac{2r_1}{a_0}}^\infty \frac{1}{a_0}\left(x-x^2+\tfrac{1}{4}x^3\right)e^{-x}\,dx\right]$$
$$= e^2\int_0^\infty \frac{32}{a_0^3}e^{-\frac{4r_1}{a_0}}r_1^2dr_1\left[\begin{array}{l}\dfrac{1}{2r_1}\left[\begin{array}{l}-x^2e^{-x}-2xe^{-x}-2e^{-x}+x^3e^{-x}+3x^2e^{-x}+6xe^{-x}+6e^{-x}\\ -\frac{1}{4}x^4e^{-x}-x^3e^{-x}-3x^2e^{-x}-6xe^{-x}-6e^{-x}\end{array}\right]_0^{\frac{2r_1}{a_0}}\\ +\dfrac{1}{a_0}\left[\begin{array}{l}-xe^{-x}-e^{-x}+x^2e^{-x}+2xe^{-x}+2e^{-x}\\ -\frac{1}{4}x^3e^{-x}-\frac{3}{4}x^2e^{-x}-\frac{3}{2}xe^{-x}-\frac{3}{2}e^{-x}\end{array}\right]_{\frac{2r_1}{a_0}}^\infty\end{array}\right]$$
$$= e^2\int_0^\infty \frac{32}{a_0^3}e^{-\frac{4r_1}{a_0}}r_1^2dr_1\left[\begin{array}{l}\dfrac{1}{r_1}\left[-\frac{1}{8}x^4e^{-x}-\frac{1}{2}x^2e^{-x}-xe^{-x}-e^{-x}\right]_0^{\frac{2r_1}{a_0}}\\ +\dfrac{1}{a_0}\left[-\frac{1}{4}x^3e^{-x}+\frac{1}{4}x^2e^{-x}-\frac{1}{2}xe^{-x}-\frac{1}{2}e^{-x}\right]_{\frac{2r_1}{a_0}}^\infty\end{array}\right]$$

Now put in limits and change variables again, still using x ($x = r_1/a_0$).

$$J_{20} = 32e^2 \int_0^\infty e^{-4x} x^2 dx \left[\begin{array}{l} \frac{1}{xa_0}\left[-2x^4e^{-2x} - 2x^2e^{-2x} - 2xe^{-2x} - e^{-2x} + 1\right] \\ + \frac{1}{a_0}\left[2x^3e^{-2x} - x^2e^{-2x} + xe^{-2x} + \tfrac{1}{2}e^{-2x}\right] \end{array} \right]$$

$$= \frac{32e^2}{a_0} \int_0^\infty e^{-4x} dx \left[\begin{array}{l} \left[-2x^5e^{-2x} - 2x^3e^{-2x} - 2x^2e^{-2x} - xe^{-2x} + x\right] \\ + \left[2x^5e^{-2x} - x^4e^{-2x} + x^3e^{-2x} + \tfrac{1}{2}x^2e^{-2x}\right] \end{array} \right]$$

$$= \frac{32e^2}{a_0} \int_0^\infty e^{-4x} dx \left[-x^4e^{-2x} - x^3e^{-2x} - \tfrac{3}{2}x^2e^{-2x} - xe^{-2x} + x\right]$$

$$= \frac{32e^2}{a_0} \int_0^\infty \left[xe^{-4x} - x^4e^{-6x} - x^3e^{-6x} - \tfrac{3}{2}x^2e^{-6x} - xe^{-6x}\right] dx$$

$$= \frac{32e^2}{a_0}\left[\frac{1!}{4^2} - \frac{4!}{6^5} - \frac{3!}{6^4} - \frac{3}{2}\frac{2!}{6^3} - \frac{1!}{6^2}\right] = \frac{32e^2}{a_0}\left[\frac{1}{16} - \frac{1}{2^2 3^4} - \frac{1}{2^3 3^3} - \frac{1}{2^3 3^2} - \frac{1}{2^2 3^2}\right]$$

$$= \frac{e^2}{a_0}\left[2 - \frac{8}{3^4} - \frac{4}{3^3} - \frac{4}{3^2} - \frac{8}{3^2}\right] = \frac{e^2}{a_0}\left[\frac{162}{81} - \frac{8}{81} - \frac{12}{81} - \frac{108}{81}\right] = \frac{e^2}{a_0}\frac{34}{81}$$

Do the same for the $2p$ state

$$J_{21} = e^2 \int_0^\infty \frac{32}{a_0^3} e^{-\frac{4r_1}{a_0}} r_1^2 dr_1 \left[\frac{1}{r_1}\int_0^{r_1} \frac{4}{3a_0^3}\left(\frac{r_2^2}{a_0^2}\right) e^{-\frac{2r_2}{a_0}} r_2^2\, dr_2 + \int_{r_1}^\infty \frac{1}{r_2}\frac{4}{3a_0^3}\left(\frac{r_2^2}{a_0^2}\right) e^{-\frac{2r_2}{a_0}} r_2^2\, dr_2 \right]$$

$$= 32e^2 \int_0^\infty \frac{1}{a_0^3} e^{-\frac{4r_1}{a_0}} r_1^2 dr_1 \left[\frac{4}{3r_1}\frac{1}{2^5}\int_0^{\frac{2r_1}{a_0}} x^4 e^{-x}\, dx + \frac{4}{3a_0}\frac{1}{2^4}\int_{\frac{2r_1}{a_0}}^\infty x^3 e^{-x}\, dx \right]$$

$$= 32e^2 \int_0^\infty \frac{1}{a_0^3} e^{-\frac{4r_1}{a_0}} r_1^2 dr_1 \left[\begin{array}{l} \frac{4}{3r_1}\frac{1}{2^5}\left[-x^4e^{-x} - 4x^3e^{-x} - 12x^2e^{-x} - 24xe^{-x} - 24e^{-x}\right]_0^{\frac{2r_1}{a_0}} \\ + \frac{4}{3a_0}\frac{1}{2^4}\left[-x^3e^{-x} - 3x^2e^{-x} - 6xe^{-x} - 6e^{-x}\right]_{\frac{2r_1}{a_0}}^\infty \end{array} \right]$$

$$J_{21} = 32e^2 \int_0^\infty e^{-4x} x^2 dx \left[\begin{array}{l} \frac{2}{3xa_0}\left[-x^4 e^{-2x} - 2x^3 e^{-2x} - 3x^2 e^{-2x} - 3xe^{-2x} - \frac{3}{2}e^{-2x} + \frac{3}{2}\right] \\ + \frac{2}{3a_0}\left[+x^3 e^{-2x} + \frac{3}{2}x^2 e^{-2x} + \frac{3}{2}xe^{-2x} + \frac{3}{4}e^{-2x}\right] \end{array} \right]$$

$$= 32e^2 \int_0^\infty e^{-4x} dx \left[\begin{array}{l} \frac{2}{3a_0}\left[-x^5 e^{-2x} - 2x^4 e^{-2x} - 3x^3 e^{-2x} - 3x^2 e^{-2x} - \frac{3}{2}xe^{-2x} + \frac{3}{2}x\right] \\ + \frac{2}{3a_0}\left[+x^5 e^{-2x} + \frac{3}{2}x^4 e^{-2x} + \frac{3}{2}x^3 e^{-2x} + \frac{3}{4}x^2 e^{-2x}\right] \end{array} \right]$$

$$= \frac{2^6 e^2}{3a_0} \int_0^\infty e^{-4x} dx \left[-\frac{1}{2}x^4 e^{-2x} - \frac{3}{2}x^3 e^{-2x} - \frac{9}{2}x^2 e^{-2x} - \frac{3}{2}xe^{-2x} + \frac{3}{2}x\right]$$

$$= \frac{2^5 e^2}{3a_0} \int_0^\infty \left[3xe^{-4x} - x^4 e^{-6x} - 3x^3 e^{-6x} - 9x^2 e^{-6x} - 3xe^{-6x}\right] dx$$

$$= \frac{2^5 e^2}{3a_0}\left[3\frac{1!}{4^2} - \frac{4!}{6^5} - 3\frac{3!}{6^4} - 9\frac{2!}{6^3} - 3\frac{1!}{6^2}\right] = \frac{2^5 e^2}{a_0}\left[\frac{1}{2^4} - \frac{1}{2^2 3^5} - \frac{1}{2^3 3^3} - \frac{1}{2^3 3^2} - \frac{1}{2^2 3^2}\right]$$

$$= \frac{2e^2}{a_0}\left[1 - \frac{4}{3^5} - \frac{2}{3^3} - \frac{2}{3^2} - \frac{4}{3^2}\right] = \frac{4e^2}{a_0}\left[\frac{243}{243} - \frac{4}{243} - \frac{18}{243} - \frac{54}{243} - \frac{108}{243}\right] = \frac{e^2}{a_0}\frac{118}{243}$$

Now look at K and put in the expansion for the particle separation:

$$K_{2\ell_1} = e^2 \iint \psi_{100}^*(\vec{\mathbf{r}}_1)\psi_{2\ell_1 m_1}^*(\vec{\mathbf{r}}_2)\psi_{100}(\vec{\mathbf{r}}_2)\psi_{2\ell_1 m_1}(\vec{\mathbf{r}}_1)$$
$$\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell+1}\frac{r_<^\ell}{r_>^{\ell+1}} Y_\ell^{m*}(\theta_1,\phi_1) Y_\ell^m(\theta_2,\phi_2)\, d^3r_1 d^3r_2$$

$$= e^2 \iint R_{10}(r_1) R_{2\ell_1}(r_2) R_{10}(r_2) R_{2\ell_1}(r_1) Y_0^{0*}(\theta_1,\phi_1) Y_{\ell_1}^{m_1 *}(\theta_2,\phi_2) Y_0^0(\theta_2,\phi_2) Y_{\ell_1}^{m_1}(\theta_1,\phi_1)$$
$$\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell+1}\frac{r_<^\ell}{r_>^{\ell+1}} Y_\ell^{m*}(\theta_1,\phi_1) Y_\ell^m(\theta_2,\phi_2)\, dr_1 dr_2 d\Omega_1 d\Omega_2$$

Note that the angular integral for particle 1 collapses the sums:

$$\int Y_0^{0*}(\theta_1,\phi_1) Y_{\ell_1}^{m_1}(\theta_1,\phi_1) Y_\ell^{m*}(\theta_1,\phi_1)\, d\Omega_1 = \frac{1}{\sqrt{4\pi}} \int Y_{\ell_1}^{m_1}(\theta_1,\phi_1) Y_\ell^{m*}(\theta_1,\phi_1)\, d\Omega_1 = \frac{1}{\sqrt{4\pi}}\delta_{\ell\ell_1}\delta_{mm_1}$$

The angular integral for particle 2 gives the same result

$$\int Y_{\ell_1}^{m_1 *}(\theta_2,\phi_2) Y_0^0(\theta_2,\phi_2) Y_\ell^m(\theta_2,\phi_2)\, d\Omega_2 = \frac{1}{\sqrt{4\pi}} \int Y_{\ell_1}^{m_1 *}(\theta_2,\phi_2) Y_\ell^m(\theta_2,\phi_2)\, d\Omega_2 = \frac{1}{\sqrt{4\pi}}\delta_{\ell\ell_1}\delta_{mm_1}$$

This gives

$$K_{2\ell} = \frac{e^2}{2\ell+1}\iint R_{10}(r_1)R_{2\ell}(r_2)R_{10}(r_2)R_{2\ell}(r_1)\frac{r_<^\ell}{r_>^{\ell+1}}r_1^2r_2^2dr_1dr_2$$

$$= \frac{e^2}{2\ell+1}\int_0^\infty R_{10}(r_1)R_{2\ell}(r_1)r_1^2dr_1\left[\frac{1}{r_1^{\ell+1}}\int_0^{r_1} r_2^\ell R_{2\ell}(r_2)R_{10}(r_2)r_2^2\,dr_2 + r_1^\ell\int_{r_1}^\infty \frac{1}{r_2^{\ell+1}}R_{2\ell}(r_2)R_{10}(r_2)r_2^2\,dr_2\right]$$

Now put in the radial functions and proceed as before.

$$K_{20} = e^2\int_0^\infty R_{10}(r_1)R_{20}(r_1)r_1^2dr_1\left[\frac{1}{r_1}\int_0^{r_1} R_{20}(r_2)R_{10}(r_2)r_2^2\,dr_2 + \int_{r_1}^\infty \frac{1}{r_2}R_{20}(r_2)R_{10}(r_2)r_2^2\,dr_2\right]$$

$$= e^2\int_0^\infty \frac{8\sqrt{2}}{a_0^3}\left(1-\frac{r_1}{a_0}\right)e^{-\frac{3r_1}{a_0}}r_1^2dr_1\left[\frac{1}{r_1}\int_0^{r_1}\frac{8\sqrt{2}}{a_0^3}\left(1-\frac{r_2}{a_0}\right)e^{-\frac{3r_2}{a_0}}r_2^2\,dr_2 + \int_{r_1}^\infty\frac{1}{r_2}\frac{8\sqrt{2}}{a_0^3}\left(1-\frac{r_2}{a_0}\right)e^{-\frac{3r_2}{a_0}}r_2^2\,dr_2\right]$$

$$= 2^7e^2\int_0^\infty \frac{1}{a_0^3}\left(1-\frac{r_1}{a_0}\right)e^{-\frac{3r_1}{a_0}}r_1^2dr_1\left[\frac{1}{r_1}\left(\frac{1}{3}\right)^3\int_0^{\frac{3r_1}{a_0}}\left(x^2-\frac{x^3}{3}\right)e^{-x}\,dx + \frac{1}{a_0}\left(\frac{1}{3}\right)^2\int_{\frac{3r_1}{a_0}}^\infty\left(x-\frac{x^2}{3}\right)e^{-x}\,dx\right]$$

$$K_{20} = 2^7e^2\int_0^\infty \frac{1}{a_0^3}\left(1-\frac{r_1}{a_0}\right)e^{-\frac{3r_1}{a_0}}r_1^2dr_1\left[\begin{array}{l}\frac{1}{r_1}\left(\frac{1}{3}\right)^3\left[\begin{array}{l}-x^2e^{-x}-2xe^{-x}-2e^{-x}\\ +\frac{1}{3}x^3e^{-x}+x^2e^{-x}+2xe^{-x}+2e^{-x}\end{array}\right]_0^{\frac{3r_1}{a_0}}\\ +\frac{1}{a_0}\left(\frac{1}{3}\right)^2\left[-xe^{-x}-e^{-x}+\frac{1}{3}x^2e^{-x}+\frac{2}{3}xe^{-x}+\frac{2}{3}e^{-x}\right]_{\frac{3r_1}{a_0}}^\infty\end{array}\right]$$

$$= 2^7e^2\int_0^\infty \frac{1}{a_0^3}\left(1-\frac{r_1}{a_0}\right)e^{-\frac{3r_1}{a_0}}r_1^2dr_1\left[\begin{array}{l}\frac{1}{r_1}\left(\frac{1}{3}\right)^3\left[\frac{1}{3}x^3e^{-x}\right]_0^{\frac{3r_1}{a_0}}\\ +\frac{1}{a_0}\left(\frac{1}{3}\right)^2\left[\frac{1}{3}x^2e^{-x}-\frac{1}{3}xe^{-x}-\frac{1}{3}e^{-x}\right]_{\frac{3r_1}{a_0}}^\infty\end{array}\right]$$

$$= 2^7e^2\int_0^\infty(1-x)e^{-3x}x^2dx\left[\begin{array}{l}\frac{1}{xa_0}\frac{1}{3}\left[x^3e^{-3x}\right]\\ +\frac{1}{a_0}\left(\frac{1}{3}\right)^3\left[-9x^2e^{-3x}+3xe^{-3x}+e^{-3x}\right]\end{array}\right]$$

$$= \frac{2^7e^2}{3^3a_0}\int_0^\infty(1-x)e^{-6x}\left(3x^3+x^2\right)dx = \frac{2^7e^2}{3^3a_0}\int_0^\infty e^{-6x}\left(-3x^4+2x^3+x^2\right)dx$$

$$= \frac{2^7e^2}{3^3a_0}\left[-3\frac{4!}{6^5}+2\frac{3!}{6^4}+\frac{2!}{6^3}\right] = \frac{2^7e^2}{3^3a_0}\left[-\frac{1}{2^23^3}+\frac{1}{2^23^3}+\frac{1}{2^23^3}\right] = \frac{2^5e^2}{3^6a_0} = \frac{e^2}{a_0}\frac{32}{729}$$

$$K_{21} = \frac{e^2}{3}\int_0^\infty R_{10}(r_1)R_{21}(r_1)r_1^2 dr_1\left[\frac{1}{r_1^2}\int_0^{r_1} r_2 R_{21}(r_2)R_{10}(r_2)r_2^2\,dr_2 + r_1\int_{r_1}^\infty \frac{1}{r_2^2}R_{21}(r_2)R_{10}(r_2)r_2^2\,dr_2\right]$$

$$= \frac{e^2}{3}\int_0^\infty \frac{8\sqrt{2}}{\sqrt{3}a_0^3}\frac{r_1}{a_0}e^{-\frac{3r_1}{a_0}}r_1^2 dr_1\left[\frac{1}{r_1^2}\int_0^{r_1} r_2\frac{8\sqrt{2}}{\sqrt{3}a_0^3}\frac{r_2}{a_0}e^{-\frac{3r_2}{a_0}}r_2^2\,dr_2 + r_1\int_{r_1}^\infty \frac{1}{r_2^2}\frac{8\sqrt{2}}{\sqrt{3}a_0^3}\frac{r_2}{a_0}e^{-\frac{3r_2}{a_0}}r_2^2\,dr_2\right]$$

$$= \frac{2^7 e^2}{3^2}\int_0^\infty \frac{1}{a_0^3}\frac{r_1}{a_0}e^{-\frac{3r_1}{a_0}}r_1^2 dr_1\left[\frac{a_0}{r_1^2}\left(\frac{1}{3}\right)^5\int_0^{\frac{3r_1}{a_0}} x^4 e^{-x}\,dx + \frac{r_1}{a_0^2}\left(\frac{1}{3}\right)^3\int_{\frac{3r_1}{a_0}}^\infty xe^{-x}\,dx\right]$$

$$K_{21} = \frac{2^7 e^2}{3^2}\int_0^\infty \frac{1}{a_0^3}\frac{r_1}{a_0}e^{-\frac{3r_1}{a_0}}r_1^2 dr_1\left[\begin{array}{l}\frac{a_0}{r_1^2}\left(\frac{1}{3}\right)^5\left[-x^4e^{-x} - 4x^3e^{-x} - 12x^2e^{-x} - 24xe^{-x} - 24e^{-x}\right]_0^{\frac{3r_1}{a_0}} \\ +\frac{r_1}{a_0^2}\left(\frac{1}{3}\right)^2\left[-xe^{-x} - e^{-x}\right]_{\frac{3r_1}{a_0}}^\infty\end{array}\right]$$

$$= \frac{2^7 e^2}{3^3}\int_0^\infty x^3 e^{-3x}dx\left[\begin{array}{l}\frac{1}{x^2 a_0}\left[-x^4e^{-3x} - \frac{4}{3}x^3e^{-3x} - \frac{4}{3}x^2e^{-3x} - \frac{8}{9}xe^{-3x} - \frac{8}{27}e^{-3x} + \frac{8}{27}\right] \\ +\frac{x}{a_0}\left[xe^{-3x} + \frac{1}{3}e^{-3x}\right]\end{array}\right]$$

$$= \frac{2^7 e^2}{3^3}\int_0^\infty e^{-3x}dx\left[\frac{1}{a_0}\left[-x^4e^{-3x} - \frac{4}{3}x^3e^{-3x} - \frac{8}{9}x^2e^{-3x} - \frac{8}{27}xe^{-3x} + \frac{8}{27}x\right]\right]$$

$$= \frac{2^7 e^2}{3^3 a_0}\int_0^\infty\left[\frac{8}{27}xe^{-3x} - x^4e^{-6x} - \frac{4}{3}x^3e^{-6x} - \frac{8}{9}x^2e^{-6x} - \frac{8}{27}xe^{-6x}\right]dx$$

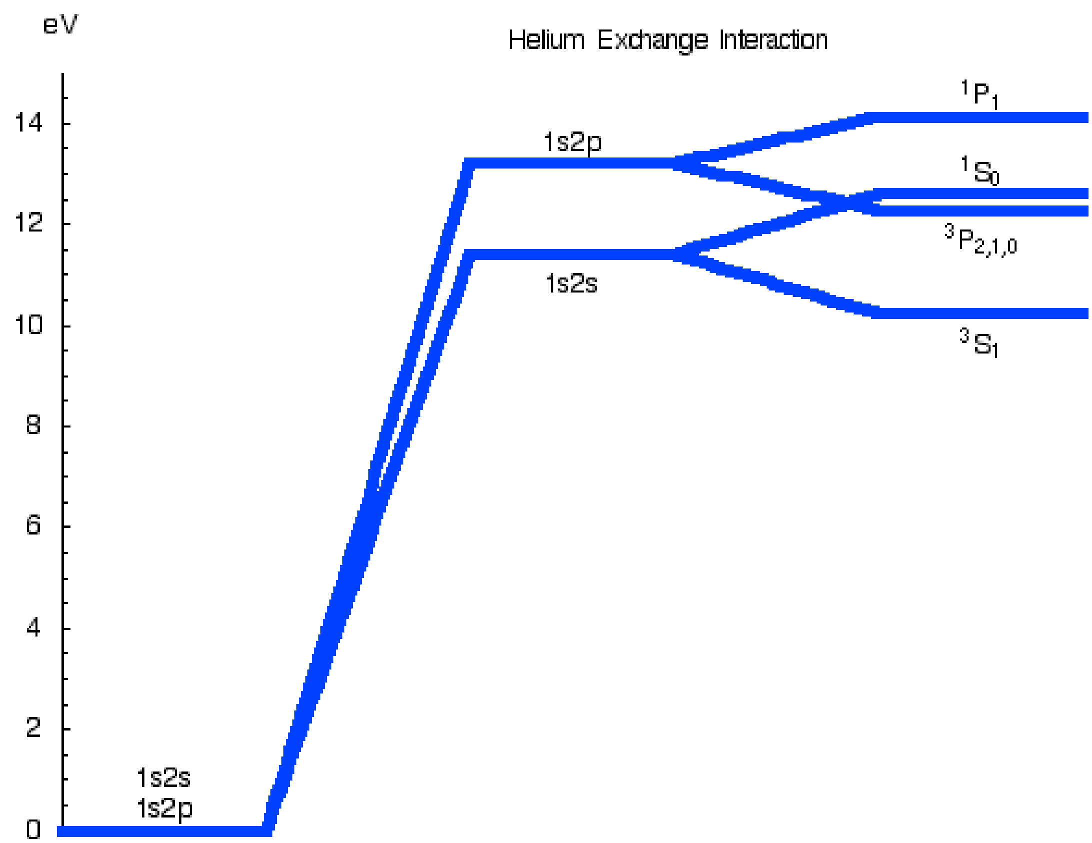
$$= \frac{2^7 e^2}{3^3 a_0}\left[\frac{2^2}{3^3}\frac{1!}{3^3} - \frac{4!}{6^5} - \frac{2^2}{3^1}\frac{3!}{6^4} - \frac{2^3}{3^2}\frac{2!}{6^3} - \frac{2^3}{3^3}\frac{1!}{6^2}\right]$$

$$= \frac{2^7 e^2}{3^8 a_0}\left[8 - \frac{3}{4} - \frac{3}{2} - 2 - 2\right] = \frac{2^7 e^2}{3^8 a_0}\left[\frac{7}{4}\right] = \frac{e^2}{a_0}\frac{224}{6561}$$

To summarize, we get : (putting in numbers (e^2/a_0 = 27.2 eV))

$$\boxed{\begin{array}{l} J_{20} = \frac{e^2}{a_0}\frac{34}{81} = 11.42\,eV \\ J_{21} = \frac{e^2}{a_0}\frac{118}{243} = 13.21\,eV \\ K_{20} = \frac{e^2}{a_0}\frac{32}{729} = 1.19\,eV \\ K_{21} = \frac{e^2}{a_0}\frac{224}{6561} = 0.93\,eV \end{array}}$$

These give the energy level structure shown below. This is not the final answer, since we are ignoring screening of nucleus, which is more effective for *p* states, hence lowering their binding and shifting them higher, so that *s* and *p* states do not overlap.



13.16 The molecular state $\left|\psi_{1s}^{g}\right\rangle$ is

$$\left|\psi_{1s}^{g}\right\rangle_1 \doteq \frac{1}{\sqrt{2}}\left[\psi_{1s}\left(\mathbf{r}_{1A}\right)+\psi_{1s}\left(\mathbf{r}_{1B}\right)\right]$$

The H_2 spatial state that is antisymmetric with respect to electron exchange when both electrons are in the $\left|\psi_{1s}^{g}\right\rangle$ one-electron ground state would be

$$\begin{aligned}\left|\psi_{1s,1s}^{A}\right\rangle &= \left(\left|\psi_{1s}^{g}\right\rangle_1\left|\psi_{1s}^{g}\right\rangle_2-\left|\psi_{1s}^{g}\right\rangle_2\left|\psi_{1s}^{g}\right\rangle_1\right)\\ &\doteq \frac{1}{2}\left[\psi_{1s}\left(\mathbf{r}_{1A}\right)+\psi_{1s}\left(\mathbf{r}_{1B}\right)\right]\left[\psi_{1s}\left(\mathbf{r}_{2A}\right)+\psi_{1s}\left(\mathbf{r}_{2B}\right)\right]\\ &\quad -\frac{1}{2}\left[\psi_{1s}\left(\mathbf{r}_{2A}\right)+\psi_{1s}\left(\mathbf{r}_{2B}\right)\right]\left[\psi_{1s}\left(\mathbf{r}_{1A}\right)+\psi_{1s}\left(\mathbf{r}_{1B}\right)\right]\end{aligned}$$

Expanding all the terms gives

$$\begin{aligned}\left|\psi^{A}_{1s,1s}\right\rangle &\doteq \frac{1}{2}\left[\psi_{1s}(\mathbf{r}_{1A})\psi_{1s}(\mathbf{r}_{2A})+\psi_{1s}(\mathbf{r}_{1A})\psi_{1s}(\mathbf{r}_{2B})+\psi_{1s}(\mathbf{r}_{1B})\psi_{1s}(\mathbf{r}_{2A})+\psi_{1s}(\mathbf{r}_{1B})\psi_{1s}(\mathbf{r}_{2B})\right]\\
&\qquad -\frac{1}{2}\left[\psi_{1s}(\mathbf{r}_{2A})\psi_{1s}(\mathbf{r}_{1A})+\psi_{1s}(\mathbf{r}_{2A})\psi_{1s}(\mathbf{r}_{1B})+\psi_{1s}(\mathbf{r}_{2B})\psi_{1s}(\mathbf{r}_{1A})+\psi_{1s}(\mathbf{r}_{2B})\psi_{1s}(\mathbf{r}_{1B})\right]\\
&\doteq \frac{1}{2}\left[\psi_{1s}(\mathbf{r}_{1A})\psi_{1s}(\mathbf{r}_{2A})+\psi_{1s}(\mathbf{r}_{1A})\psi_{1s}(\mathbf{r}_{2B})+\psi_{1s}(\mathbf{r}_{1B})\psi_{1s}(\mathbf{r}_{2A})+\psi_{1s}(\mathbf{r}_{1B})\psi_{1s}(\mathbf{r}_{2B})\right]\\
&\qquad -\frac{1}{2}\left[\psi_{1s}(\mathbf{r}_{1A})\psi_{1s}(\mathbf{r}_{2A})+\psi_{1s}(\mathbf{r}_{1A})\psi_{1s}(\mathbf{r}_{2B})+\psi_{1s}(\mathbf{r}_{1B})\psi_{1s}(\mathbf{r}_{2A})+\psi_{1s}(\mathbf{r}_{1B})\psi_{1s}(\mathbf{r}_{2B})\right]\\
&= 0\end{aligned}$$

13.17 a) The two fermions are non-interacting, so the Hamiltonian is separable in the coordinates x_1 and x_2. This means that the two-particle (space) wave function is a product of the single-particle space wave functions and the energy is the sum of the two single-particle energies.

$$E_{n_a n_b} = n_a^2 \frac{\hbar^2\pi^2}{2mL^2} + n_b^2 \frac{\hbar^2\pi^2}{2mL^2}$$

The lowest energy configuration is that where both particles occupy the single particle ground state (and this is OK with respect to the symmetrization postulate as explained in (b)) so that the ground state energy, which is independent of the spin state, is

$$E_{11} = 2\frac{\hbar^2\pi^2}{2mL^2}$$

b) The total state vector of the two-fermion system must be antisymmetric under particle interchange. Because both fermions occupy the lowest spatial state, the spatial wave function cannot be antisymmetric [or it would be zero by Eq. (13.22)], so it must be symmetric. Thus the spin part must be antisymmetric, which is the singlet spin state of Eq. (13.24):

$$\begin{aligned}\left|\psi^{SA}_{11}\right\rangle &\doteq \psi^{S}_{11}(x_1,x_2)\left|00\right\rangle\\
&\doteq \frac{1}{\sqrt{2}}\varphi_1(x_1)\varphi_1(x_2)\big(\left|+-\right\rangle - \left|-+\right\rangle\big)\\
&\doteq \frac{1}{\sqrt{2}}\frac{2}{L}\sin\left(\frac{\pi x_1}{L}\right)\sin\left(\frac{\pi x_2}{L}\right)\big(\left|+-\right\rangle - \left|-+\right\rangle\big)\end{aligned}$$

c) The first excited state has one particle in the single-particle ground state (n_a =1) and one in the first excited single-particle state (n_b = 2). Using the result from (a), we have

$$E_{12} = \left(1^2+2^2\right)\frac{\hbar^2\pi^2}{2mL^2} = 5\frac{\hbar^2\pi^2}{2mL^2}$$

d) The total state vector of the two-fermion system must be antisymmetric under particle interchange, so the possible configurations are (i) the antisymmetric singlet spin state $|00\rangle$ multiplied by the symmetric space state:

$$\begin{aligned}
\left|\psi_{12}^{SA}\right\rangle &\doteq \psi_{12}^{S}(x_1,x_2)|00\rangle \\
&\doteq \frac{1}{2}\left\{\varphi_1(x_1)\varphi_2(x_2)+\varphi_1(x_2)\varphi_2(x_1)\right\}\left(|+-\rangle - |-+\rangle\right) \\
&\doteq \frac{1}{L}\left\{\sin\left(\frac{\pi x_1}{L}\right)\sin\left(\frac{2\pi x_2}{L}\right)+\sin\left(\frac{\pi x_2}{L}\right)\sin\left(\frac{2\pi x_1}{L}\right)\right\}\left(|+-\rangle - |-+\rangle\right)
\end{aligned}$$

and (ii) the symmetric triplet spin state $|1M\rangle$ multiplied by the antisymmetric space state:

$$\begin{aligned}
\left|\psi_{12}^{AS}\right\rangle &\doteq \psi_{12}^{A}(x_1,x_2)|1M\rangle \\
&\doteq \frac{1}{\sqrt{2}}\left\{\varphi_1(x_1)\varphi_2(x_2)-\varphi_1(x_2)\varphi_2(x_1)\right\}|1M\rangle \\
&\doteq \frac{\sqrt{2}}{L}\left\{\sin\left(\frac{\pi x_1}{L}\right)\sin\left(\frac{2\pi x_2}{L}\right)-\sin\left(\frac{\pi x_2}{L}\right)\sin\left(\frac{2\pi x_1}{L}\right)\right\}\begin{cases} |++\rangle \\ \frac{1}{\sqrt{2}}\left(|+-\rangle - |-+\rangle\right) \\ |--\rangle \end{cases}
\end{aligned}$$

e) The four possible states for this energy level have the same energy because the Hamiltonian is independent of the total spin of the system and the particles do not interact. Therefore the first excited state is four-fold degenerate.

f) If we now let the two particles interact via their Coulomb repulsion, then the additional Coulomb potential energy changes the energy of the state. Treating the new interaction as a perturbation, we then must find the matrix elements of this perturbation. Any spatial perturbation is diagonal with respect to the spin parts. As we found in Fig. 13.6, the singlet and triplet excited states are both pushed up by the Coulomb repulsion. The symmetric spatial state (associated with the spin singlet) has greater particle overlap and hence greater Coulomb repulsion. On the contrary, the antisymmetric spatial wavefunction (associated with the spin triplet) is zero when $x_1 = x_2$, leading to less spatial overlap and hence less electron repulsion. Hence the spin triplet states are shifted up less than the spin singlet state.