Engel 10.30

**Problem.** Follow the instructions provided and derive the energy formula Engel shows for the excited $1s^1\ 2s^1$ of He.

**Answer.** Engel's instructions are straightforward (I hope). The following comments are designed to get you over any "sticky" points.

**a.** Engel says "expand eq. 10.27" to obtain the sum of three integrals shown. Eq. 10.27 has the following form:

$$\int \psi \left[ \hat{H}_1 + \hat{H}_2 + \frac{\text{const}}{r_{12}} \right] \psi \ d\tau_1 \ d\tau_2$$

This can be re-written as

$$\int \psi \hat{H}_1 \psi \ d\tau_1 + \int \psi \hat{H}_2 \psi \ d\tau_2 + \int \psi \left[ \frac{\text{const}}{r_{12}} \right] \psi \ d\tau_1 \ d\tau_2$$

Sticky point: notice the index of integration is different for each integral. I think the book is wrong. As Engel writes it, the integration index matches the electron coordinates contained in the operator, but not the wave function. The wave function is a function of the coordinates of electron 1 and electron 2 in all three integrals, so I think the correct integrals are:

$$\int \psi \hat{H}_1 \psi \ d\tau_1 \ d\tau_2 + \int \psi \hat{H}_2 \psi \ d\tau_1 \ d\tau_2 + \int \psi \left[ \frac{\text{const}}{r_{12}} \right] \psi \ d\tau_1 \ d\tau_2$$

The last step of **part a** is to insert the definition of $\psi$ wherever the wave function appears (note: the definition of $\psi$ is already used in eq. 10.27).

**b.** First, we simplify the integrals containing the one-electron energy operators, $\hat{H}_1$ and $\hat{H}_2$. We accomplish this by using Engel's reminder: $\psi$ is constructed from hydrogen atom eigenfunctions. Therefore,

$$\hat{H}_1 \psi = \hat{H}_1 \left[ \frac{1}{\sqrt{2}} \left( 1\ s(1) \ 2\ s(2) + 2\ s(1) \ 1\ s(2) \right) \right]$$

$$= \frac{1}{\sqrt{2}} \left[ \left( \hat{H}_1 \ 1\ s(1) \right) \ 2\ s(2) + \left( \hat{H}_1 \ 2\ s(1) \right) \ 1\ s(2) \right]$$

$$= \frac{1}{\sqrt{2}} \left[ \left( E_{1s} + 1\ s(1) \right) \ 2\ s(2) + \left( E_{2s} + 2\ s(1) \right) \ 1\ s(2) \right]$$

and

$$\psi \hat{H}_1 \psi = \frac{1}{2} \times \left[ 1\ s(1) \ 2\ s(2) + 2\ s(1) \ 1\ s(2) \right] \times \left[ E_{1s} + 1\ s(1) \ 2\ s(2) + E_{2s} + 2\ s(1) \ 1\ s(2) \right]$$

$$= \frac{1}{2} \times \left[ E_{1s} + 1\ s(1)^2 + E_{2s} + 2\ s(1)^2 + (E_{1s} + E_{2s})(1\ s(1) \ 2\ s(1) \ 1\ s(2) \ 2\ s(2)) \right]$$
\[
\psi \hat{H}_1 \psi \, d\tau_1 \, d\tau_2 = \frac{1}{2} \times [E_{1s} \int 1 \, s(1)^2 \, d\tau_1 \int 2 \, s(2)^2 \, d\tau_2 + E_{2s} \int 2 \, s(1)^2 \, d\tau_1 \int 1 \, s(2)^2 \, d\tau_2 \\
+ (E_{1s} + E_{2s}) \int 1 \, s(1) \, 2 \, s(1) \, d\tau_1 \int 1 \, s(2) \, 2 \, s(2) \, d\tau_2]
\]

\[= \frac{1}{2} \times [E_{1s} + E_{2s}]\]

Look at the sum of integral products just before the final line. Any integral that contains the square of a hydrogen eigenfunction equals one because these orbitals have been normalized. Any integral that contains the product of different eigenfunctions equals zero because these orbitals are orthogonal. Therefore, the first integral product turns into one, the second integral product turns into one, and the third vanishes.

The same arithmetic applies to \( \hat{H}_2 \) and this adds another \( \frac{1}{2} \times [E_{1s} + E_{2s}] \) to the energy, so that the two one-electron integrals are replaced by \( E_{1s} + E_{2s} \).

c. Now we expand the two-electron integral from part a. Nothing vanishes because the \( \frac{1}{r_{12}} \) term in the integral prevents us from breaking the two-electron integral into a product of one-electron integrals. All we can do is rename the integrals.

\[
\begin{align*}
\int \psi \left[ \frac{\text{const}}{r_{12}} \right] \psi \, d\tau_1 \, d\tau_2 &= \int \left[ \frac{1}{\sqrt{2}} \left( 1 \, s(1) \, 2 \, s(2) + 2 \, s(1) \, 1 \, s(2) \right) \right] \left[ \frac{\text{const}}{r_{12}} \left[ \frac{1}{\sqrt{2}} \left( 1 \, s(1) \, 2 \, s(2) + 2 \, s(1) \, 1 \, s(2) \right) \right] \right] \, d\tau_1 \, d\tau_2 \\
&= \frac{\text{const}}{2} \times \left[ \int 1 \, s(1) \, 2 \, s(2) \, \frac{1}{r_{12}} \, 1 \, s(1) \, 2 \, s(2) + \int 1 \, s(1) \, 2 \, s(2) \, \frac{1}{r_{12}} \, 2 \, s(1) \, 1 \, s(2) + \int 2 \, s(1) \, 1 \, s(2) \, \frac{1}{r_{12}} \, 1 \, s(1) \, 2 \, s(2) + \int 2 \, s(1) \, 1 \, s(2) \, \frac{1}{r_{12}} \, 2 \, s(1) \, 1 \, s(2) \right] \\
&= \frac{\text{const}}{2} \times \left[ \int 1 \, s(1)^2 \, \frac{1}{r_{12}} \, 2 \, s(2)^2 + \int 1 \, s(1) \, 2 \, s(2) \, \frac{1}{r_{12}} \, 2 \, s(1) \, 1 \, s(2) + \int 2 \, s(1)^2 \, \frac{1}{r_{12}} \, 1 \, s(2)^2 \right]
\end{align*}
\]

Sticky point: the first and third integrals have the same value (it can't matter which function I assign to electron 1 and which function I assign to electron 2), therefore I can combine them ...

\[
= \text{const} \int 1 \, s(1)^2 \, \frac{1}{r_{12}} \, 2 \, s(2)^2 + \text{const} \int 1 \, s(1) \, 2 \, s(2) \, \frac{1}{r_{12}} \, 2 \, s(1) \, 1 \, s(2)
\]

\[= J + K\]