HW #6

1. Three-electron Atoms

(a)

We set up the Slater determinant for three electrons,

$$|1s^2\,2s\rangle = \frac{1}{\sqrt{3!}}\det\begin{pmatrix} |1s^\uparrow\rangle_1 & |1s^\uparrow\rangle_2 & |1s^\uparrow\rangle_3 \\ |1s^\downarrow\rangle_1 & |1s^\downarrow\rangle_2 & |1s^\downarrow\rangle_3 \\ |2s\rangle_1 & |2s\rangle_2 & |2s\rangle_3 \end{pmatrix}$$

Here, the subscripts refer to which electron out of three, and we did not specify the spin orientation of the electron in the $2s$ state because it is not relevant. The Slater determinant for the $1s^2\,2p$ configuration would be similar, except that there is an additional quantum number of $m_l = -1, 0, 1$ which is also not relevant for the calculations. By writing it out, I get

$$|1s^2\,2s\rangle = \frac{1}{\sqrt{6}}\left(|1s^\uparrow\,1s^\downarrow\,2s\rangle + |1s^\downarrow\,2s\,1s^\uparrow\rangle + |2s\,1s^\uparrow\,1s^\downarrow\rangle - |1s^\uparrow\,2s\,1s^\downarrow\rangle - |2s\,1s^\downarrow\,1s^\uparrow\rangle - |1s^\downarrow\,1s^\uparrow\,2s\rangle\right)$$

and

$$|1s^2\,2p\rangle = \frac{1}{\sqrt{6}}\left(|1s^\uparrow\,1s^\downarrow\,2p\rangle + |1s^\downarrow\,2p\,1s^\uparrow\rangle + |2p\,1s^\uparrow\,1s^\downarrow\rangle - |1s^\uparrow\,2p\,1s^\downarrow\rangle - |2p\,1s^\downarrow\,1s^\uparrow\rangle - |1s^\downarrow\,1s^\uparrow\,2p\rangle\right)$$

Here, the notation is

$|1s^\uparrow\,1s^\downarrow\,2p\rangle = |1s^\uparrow\rangle_1 \otimes |1s^\downarrow\rangle_2 \otimes |2p\rangle_3$ etc.

(b)

The expectation value of $H_0 = \sum_{i=1}^{3} \left(\frac{\vec{p}_i^{\,2}}{2m} - \frac{Z e^2}{r_i} \right)$ for the $1s^2\,2s$ configuration is

$\langle 1s^2\,2s \,|\, H_0 \,|\, 1s^2\,2s \rangle$

$= \frac{1}{6} \left(\langle 1s^\uparrow\,1s^\downarrow\,2s | + \langle 1s^\downarrow\,2s\,1s^\uparrow | + \langle 2s\,1s^\uparrow\,1s^\downarrow | - \langle 1s^\uparrow\,2s\,1s^\downarrow | - \langle 2s\,1s^\downarrow\,1s^\uparrow | - \langle 1s^\downarrow\,1s^\uparrow\,2s \,| \right)$
$H_0 \left(| 1s^\uparrow\,1s^\downarrow\,2s \rangle + | 1s^\downarrow\,2s\,1s^\uparrow \rangle + | 2s\,1s^\uparrow\,1s^\downarrow \rangle \right.$
$\left. - | 1s^\uparrow\,2s\,1s^\downarrow \rangle - | 2s\,1s^\downarrow\,1s^\uparrow \rangle - | 1s^\downarrow\,1s^\uparrow\,2s \rangle \right)$

Yuck! I hate *Mathematica*. The point here is that H_0 is a one-body operator. It picks up only one out of three electrons each time. For instance, if I calculate the term

$$\langle 1s^\uparrow\,1s^\downarrow\,2s \,|\, H_0 \,|\, 1s^\uparrow\,1s^\downarrow\,2s \rangle = \sum_{i=1}^{3} \left\langle 1s^\uparrow\,1s^\downarrow\,2s \left| \frac{\vec{p}_i^{\,2}}{2m} - \frac{Z e^2}{r_i} \right| 1s^\uparrow\,1s^\downarrow\,2s \right\rangle$$

$$= \left\langle 1s^\uparrow\,1s^\downarrow\,2s \left| \frac{\vec{p}_1^{\,2}}{2m} - \frac{Z e^2}{r_1} \right| 1s^\uparrow\,1s^\downarrow\,2s \right\rangle + \left\langle 1s^\uparrow\,1s^\downarrow\,2s \left| \frac{\vec{p}_2^{\,2}}{2m} - \frac{Z e^2}{r_2} \right| 1s^\uparrow\,1s^\downarrow\,2s \right\rangle + \left\langle 1s^\uparrow\,1s^\downarrow\,2s \left| \frac{\vec{p}_3^{\,2}}{2m} - \frac{Z e^2}{r_3} \right| 1s^\uparrow\,1s^\downarrow\,2s \right\rangle$$

In the first term, the second and third electrons are not affected by the operator and

$$\left\langle 1s^\uparrow\,1s^\downarrow\,2s \left| \frac{\vec{p}_1^{\,2}}{2m} - \frac{Z e^2}{r_1} \right| 1s^\uparrow\,1s^\downarrow\,2s \right\rangle$$

$$= \left(\left\langle 1s^\uparrow \right|_1 \otimes \left\langle 1s^\downarrow \right|_2 \otimes \langle 2s |_3 \right) \left(\frac{\vec{p}_1^{\,2}}{2m} - \frac{Z e^2}{r_1} \right) \left(| 1s^\uparrow \rangle_1 \otimes \left| 1s^\downarrow \right\rangle_2 \otimes \left| 2s \right\rangle_3 \right)$$

$$= \left\langle 1s^\uparrow \right|_1 \frac{\vec{p}_1^{\,2}}{2m} - \frac{Z e^2}{r_1} \left| 1s^\uparrow \right\rangle_1 \langle 1s^\downarrow |_2 \; | 1s^\downarrow \rangle_2 \; \langle 2s |_3 \; | 2s \rangle_3$$

$$= \left\langle 1s^\uparrow \left| \frac{\vec{p}^{\,2}}{2m} - \frac{Z e^2}{r} \right| 1s^\uparrow \right\rangle$$

In the last line, I used the fact that the single-particle states are properly normalized. The expectation value refers to only a single-particle state, and I dropped the particle index. Therefore,

$$\langle 1s^\uparrow\,1s^\downarrow\,2s \,|\, H_0 \,|\, 1s^\uparrow\,1s^\downarrow\,2s \rangle = \left\langle 1s^\uparrow \left| \frac{\vec{p}^{\,2}}{2m} - \frac{Z e^2}{r} \right| 1s^\uparrow \right\rangle + \left\langle 1s^\downarrow \left| \frac{\vec{p}^{\,2}}{2m} - \frac{Z e^2}{r} \right| 1s^\downarrow \right\rangle + \left\langle 2s \left| \frac{\vec{p}^{\,2}}{2m} - \frac{Z e^2}{r} \right| 2s \right\rangle$$

$$= E_{1s} + E_{1s} + E_{2s}$$

and hence the expectation value is simply the sum of single-particle energies. The same applies to all the diagonal pieces in the expectation value.

For the off-diagonal (the ket and the bra are different) pieces, we find, for example,

$$\left\langle 1s^\uparrow\,1s^\downarrow\,2s \left| \frac{\vec{p}_1^{\,2}}{2m} - \frac{Z e^2}{r_1} \right| 1s^\downarrow\,2s\,1s^\uparrow \right\rangle$$

$$= \left(\left\langle 1s^\uparrow \right|_1 \otimes \left\langle 1s^\downarrow \right|_2 \otimes \langle 2s |_3 \right) \left(\frac{\vec{p}_1^{\,2}}{2m} - \frac{Z e^2}{r_1} \right) \left(| 1s^\downarrow \rangle_1 \otimes \left| 2s \right\rangle_2 \otimes \left| 1s^\uparrow \right\rangle_3 \right)$$

$$= \left\langle 1s^\uparrow \right|_1 \frac{\vec{p}_1^{\,2}}{2m} - \frac{Z e^2}{r_1} \left| 1s^\downarrow \right\rangle_1 \langle 1s^\downarrow |_2 \; | 2s \rangle_2 \; \langle 2s |_3 \; | 1s^\uparrow \rangle_3$$

$$= 0$$

because of the orthogonality of single-particle states. Therefore, the expectation value of H_0 is given by the diagonal pieces only, and we find

$\langle 1s^2\,2s \,|\, H_0 \,|\, 1s^2\,2s \rangle$

$= \frac{1}{6} \left(\langle 1s^\uparrow\,1s^\downarrow\,2s \,|\, H_0 \,|\, 1s^\uparrow\,1s^\downarrow\,2s \rangle + \langle 1s^\downarrow\,2s\,1s^\uparrow \,|\, H_0 \,|\, 1s^\downarrow\,2s\,1s^\uparrow \rangle + \langle 2s\,1s^\uparrow\,1s^\downarrow \,|\, H_0 \,|\, 2s\,1s^\uparrow\,1s^\downarrow \rangle + \right.$
$\left. \langle 1s^\uparrow\,2s\,1s^\downarrow \,|\, H_0 \,|\, 1s^\uparrow\,2s\,1s^\downarrow \rangle + \langle 2s\,1s^\downarrow\,1s^\uparrow \,|\, H_0 \,|\, 2s\,1s^\downarrow\,1s^\uparrow \rangle + \langle 1s^\downarrow\,1s^\uparrow\,2s \,|\, H_0 \,|\, 1s^\downarrow\,1s^\uparrow\,2s \rangle \right)$

$\langle 1s^2\,2s\,|\,H_0\,|\,1s^2\,2s\rangle = E_{1s} + E_{1s} + E_{2s}$, just the sum of single-particle energies without any prefactor.

This is a general result for any Slater determinants if the operator is a "single-body operator".

(c)

The Coulomb potential is an example of a "two-body operator."
The expectation value of $\Delta H = \sum_{i<j}^{3} \frac{e^2}{r_{ij}} = \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}}$ for the $1s^2\,2s$ configuration is
$\langle 1s^2\,2s\,|\,\Delta H\,|\,1s^2\,2s\rangle$
$= \frac{1}{6}\left(\langle 1s^\uparrow\,1s^\downarrow\,2s\,| + \langle 1s^\downarrow\,2s\,1s^\uparrow\,| + \langle 2s\,1s^\uparrow\,1s^\downarrow\,| - \langle 1s^\uparrow\,2s\,1s^\downarrow\,| - \langle 2s\,1s^\downarrow\,1s^\uparrow\,| - \langle 1s^\downarrow\,1s^\uparrow\,2s\,|\right)$
$\Delta H\left(|\,1s^\uparrow\,1s^\downarrow\,2s\rangle + |\,1s^\downarrow\,2s\,1s^\uparrow\rangle + |\,2s\,1s^\uparrow\,1s^\downarrow\rangle\right.$
$\left. - |\,1s^\uparrow\,2s\,1s^\downarrow\rangle - |\,2s\,1s^\downarrow\,1s^\uparrow\rangle - |\,1s^\downarrow\,1s^\uparrow\,2s\rangle\right)$
For instance, if I calculate the term
$\langle 1s^\uparrow\,1s^\downarrow\,2s\,|\,\Delta H\,|\,1s^\uparrow\,1s^\downarrow\,2s\rangle = \left\langle 1s^\uparrow\,1s^\downarrow\,2s\,\middle|\,\frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}}\,\middle|\,1s^\uparrow\,1s^\downarrow\,2s\right\rangle$
$= \left\langle 1s^\uparrow\,1s^\downarrow\,2s\,\middle|\,\frac{e^2}{r_{12}}\,\middle|\,1s^\uparrow\,1s^\downarrow\,2s\right\rangle + \left\langle 1s^\uparrow\,1s^\downarrow\,2s\,\middle|\,\frac{e^2}{r_{13}}\,\middle|\,1s^\uparrow\,1s^\downarrow\,2s\right\rangle + \left\langle 1s^\uparrow\,1s^\downarrow\,2s\,\middle|\,\frac{e^2}{r_{23}}\,\middle|\,1s^\uparrow\,1s^\downarrow\,2s\right\rangle$
In the first term, the third electrons are not affected by the operator and
$\left\langle 1s^\uparrow\,1s^\downarrow\,2s\,\middle|\,\frac{e^2}{r_{12}}\,\middle|\,1s^\uparrow\,1s^\downarrow\,2s\right\rangle$
$= \left(\left\langle 1s^\uparrow\right|_1 \otimes \left\langle 1s^\downarrow\right|_2 \otimes \langle 2s|_3)\,\frac{e^2}{r_{12}}\,(|\,1s^\uparrow\rangle_1 \otimes \left|1s^\downarrow\right\rangle_2 \otimes \left|2s\right\rangle_3\right)$
$= \left\langle 1s^\uparrow\right|_1 \otimes \left\langle 1s^\downarrow\right|_2 \frac{e^2}{r_{12}} \left|1s^\uparrow\right\rangle_1 \otimes \left|1s^\downarrow\right\rangle_2 \langle 2s|_3\;|2s\rangle_3$
$= \left\langle 1s^\uparrow\right|_1 \otimes \left\langle 1s^\downarrow\right|_2 \frac{e^2}{r_{12}} \left|1s^\uparrow\right\rangle_1 \otimes \left|1s^\downarrow\right\rangle_2$
$= \left\langle 1s^\uparrow\,1s^\downarrow\,\middle|\,\frac{e^2}{r_{12}}\,\middle|\,1s^\uparrow\,1s^\downarrow\right\rangle$
Similarly with the other two terms. Therefore,
$\langle 1s^\uparrow\,1s^\downarrow\,2s\,|\,\Delta H\,|\,1s^\uparrow\,1s^\downarrow\,2s\rangle =$
$\left\langle 1s^\uparrow\right|_1 \otimes \left\langle 1s^\downarrow\right|_2 \frac{e^2}{r_{12}} \left|1s^\uparrow\right\rangle_1 \otimes \left|1s^\downarrow\right\rangle_2 + \left\langle 1s^\uparrow\right|_1 \otimes \left\langle 2s\right|_3 \frac{e^2}{r_{13}} \left|1s^\uparrow\right\rangle_1 \otimes \left|2s\right\rangle_3 + \left\langle 1s^\downarrow\right|_2 \otimes \left\langle 2s\right|_3 \frac{e^2}{r_{23}} \left|1s^\downarrow\right\rangle_2 \otimes \left|2s\right\rangle_3$
Because each term involves only two electrons, not three of them, we can relabel them so that the Coulomb potential always refers to "1" and "2",
$\langle 1s^\uparrow\,1s^\downarrow\,2s\,|\,\Delta H\,|\,1s^\uparrow\,1s^\downarrow\,2s\rangle =$
$\left\langle 1s^\uparrow\right|_1 \otimes \left\langle 1s^\downarrow\right|_2 \frac{e^2}{r_{12}} \left|1s^\uparrow\right\rangle_1 \otimes \left|1s^\downarrow\right\rangle_2 + \left\langle 1s^\uparrow\right|_1 \otimes \left\langle 2s\right|_2 \frac{e^2}{r_{12}} \left|1s^\uparrow\right\rangle_1 \otimes \left|2s\right\rangle_2 + \left\langle 1s^\downarrow\right|_1 \otimes \left\langle 2s\right|_2 \frac{e^2}{r_{12}} \left|1s^\downarrow\right\rangle_1 \otimes \left|2s\right\rangle_2$
and we write them in a simpler expression,
$\langle 1s^\uparrow\,1s^\downarrow\,2s\,|\,\Delta H\,|\,1s^\uparrow\,1s^\downarrow\,2s\rangle = \left\langle 1s^\uparrow\,1s^\downarrow\,\middle|\,\frac{e^2}{r_{12}}\,\middle|\,1s^\uparrow\,1s^\downarrow\right\rangle + \left\langle 1s^\uparrow\,2s\,\middle|\,\frac{e^2}{r_{12}}\,\middle|\,1s^\uparrow\,2s\right\rangle + \left\langle 1s^\downarrow\,2s\,\middle|\,\frac{e^2}{r_{12}}\,\middle|\,1s^\downarrow\,2s\right\rangle$
Namely the sum of all three combinations. The same applies to all the diagonal pieces in the expectation value, and they all give the same result. The contribution of all diagonal terms is hence
$\frac{1}{6}\left(\langle 1s^\uparrow\,1s^\downarrow\,2s\,|\,\Delta H\,|\,1s^\uparrow\,1s^\downarrow\,2s\rangle + \langle 1s^\downarrow\,2s\,1s^\uparrow\,|\,\Delta H\,|\,1s^\downarrow\,2s\,1s^\uparrow\rangle + \langle 2s\,1s^\uparrow\,1s^\downarrow\,|\,\Delta H\,|\,2s\,1s^\uparrow\,1s^\downarrow\rangle +\right.$
$\left.\langle 1s^\uparrow\,2s\,1s^\downarrow\,|\,\Delta H\,|\,1s^\uparrow\,2s\,1s^\downarrow\rangle + \langle 2s\,1s^\downarrow\,1s^\uparrow\,|\,\Delta H\,|\,2s\,1s^\downarrow\,1s^\uparrow\rangle + \langle 1s^\downarrow\,1s^\uparrow\,2s\,|\,\Delta H\,|\,1s^\downarrow\,1s^\uparrow\,2s\rangle\right)$
$= \langle 1s^\uparrow\,1s^\downarrow\,2s\,|\,\Delta H\,|\,1s^\uparrow\,1s^\downarrow\,2s\rangle$
$= \left\langle 1s^\uparrow\,1s^\downarrow\,\middle|\,\frac{e^2}{r_{12}}\,\middle|\,1s^\uparrow\,1s^\downarrow\right\rangle + \left\langle 1s^\uparrow\,2s\,\middle|\,\frac{e^2}{r_{12}}\,\middle|\,1s^\uparrow\,2s\right\rangle + \left\langle 1s^\downarrow\,2s\,\middle|\,\frac{e^2}{r_{12}}\,\middle|\,1s^\downarrow\,2s\right\rangle$
In general, there are $N!$ diagonal matrix elements which cancels the $\frac{1}{N!}$ normalization factor, and each term contributes ${}_N C_2$ pieces, one for each Coulomb term.

Unlike for the single-body operator, there are also the so-called "exchange terms" where two electrons are interchanged in the ket and the bra,
$-\langle 1s^\uparrow\,1s^\downarrow\,2s\,|\,\Delta H\,|\,1s^\uparrow\,2s\,1s^\downarrow\rangle$

$= -\left\langle 1\,s^\uparrow\ 1\,s^\downarrow\ 2\,s \,\middle|\, \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}} \,\middle|\, 1\,s^\uparrow\ 2\,s\ 1\,s^\downarrow \right\rangle$

$= -\left\langle 1\,s^\uparrow\ 1\,s^\downarrow\ 2\,s \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1\,s^\uparrow\ 2\,s\ 1\,s^\downarrow \right\rangle - \left\langle 1\,s^\uparrow\ 1\,s^\downarrow\ 2\,s \,\middle|\, \frac{e^2}{r_{13}} \,\middle|\, 1\,s^\uparrow\ 2\,s\ 1\,s^\downarrow \right\rangle - \left\langle 1\,s^\uparrow\ 1\,s^\downarrow\ 2\,s \,\middle|\, \frac{e^2}{r_{23}} \,\middle|\, 1\,s^\uparrow\ 2\,s\ 1\,s^\downarrow \right\rangle$

In the first term, the third electron is not affected by the operator, and the matrix element is proportional to $\langle 2\,s \,|\, 1\,s^\downarrow \rangle = 0$. The same is true also with the second term where the orthogonality of the second electron state makes it vanish. The only contribution comes from the third term. By going through the same steps as for the diagonal piece, we find

$-\langle 1\,s^\uparrow\ 1\,s^\downarrow\ 2\,s \,|\, \Delta H \,|\, 1\,s^\uparrow\ 2\,s\ 1\,s^\downarrow \rangle$

$= -\left\langle 1\,s^\uparrow\ 1\,s^\downarrow\ 2\,s \,\middle|\, \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}} \,\middle|\, 1\,s^\uparrow\ 2\,s\ 1\,s^\downarrow \right\rangle$

$= -\left\langle 1\,s^\downarrow\ 2\,s \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 2\,s\ 1\,s^\downarrow \right\rangle$

where the "2" and "3" are relabeled to "1" and "2". Out of $6 \times 5 = 30$ (or in general $N! \times (N! - 1)$) off-diagonal matrix elements, there are only $6 \times 3 = 18$ (or in general $N! \times {}_N C_2 = N!\,N(N-1)/2$) such terms. The overall $N!$ cancels $\frac{1}{N!}$ in the normalization factor.

On the other hand, when the ket and bra has more than two electrons interchanged, the orthogonality of the single-particle states makes them vanish. For example,

$-\langle 1\,s^\uparrow\ 1\,s^\downarrow\ 2\,s \,|\, \Delta H \,|\, 1\,s^\uparrow\ 2\,s\ 1\,s^\downarrow \rangle$

$= -\left\langle 1\,s^\uparrow\ 1\,s^\downarrow\ 2\,s \,\middle|\, \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}} \,\middle|\, 1\,s^\uparrow\ 2\,s\ 1\,s^\downarrow \right\rangle$

$= -\left\langle 1\,s^\uparrow\ 1\,s^\downarrow\ 2\,s \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1\,s^\uparrow\ 2\,s\ 1\,s^\downarrow \right\rangle - \left\langle 1\,s^\uparrow\ 1\,s^\downarrow\ 2\,s \,\middle|\, \frac{e^2}{r_{13}} \,\middle|\, 1\,s^\uparrow\ 2\,s\ 1\,s^\downarrow \right\rangle - \left\langle 1\,s^\uparrow\ 1\,s^\downarrow\ 2\,s \,\middle|\, \frac{e^2}{r_{23}} \,\middle|\, 1\,s^\uparrow\ 2\,s\ 1\,s^\downarrow \right\rangle$

In each term, there is one electron that is not affected by the operator that makes the matrix element vanish.

Therefore, the off-diagonal pieces contribute as

$-\left\langle 1\,s^\uparrow\ 1\,s^\downarrow \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1\,s^\downarrow\ 1\,s^\uparrow \right\rangle - \left\langle 1\,s^\uparrow\ 2\,s \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 2\,s\ 1\,s^\uparrow \right\rangle - \left\langle 1\,s^\downarrow\ 2\,s \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 2\,s\ 1\,s^\downarrow \right\rangle.$

The grand total is

$\langle 1\,s^2\ 2\,s \,|\, \Delta H \,|\, 1\,s^2\ 2\,s \rangle$

$= \left\langle 1\,s^\uparrow\ 1\,s^\downarrow \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1\,s^\uparrow\ 1\,s^\downarrow \right\rangle + \left\langle 1\,s^\uparrow\ 2\,s \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1\,s^\uparrow\ 2\,s \right\rangle + \left\langle 1\,s^\downarrow\ 2\,s \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1\,s^\downarrow\ 2\,s \right\rangle$

$-\left\langle 1\,s^\uparrow\ 1\,s^\downarrow \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1\,s^\downarrow\ 1\,s^\uparrow \right\rangle - \left\langle 1\,s^\uparrow\ 2\,s \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 2\,s\ 1\,s^\uparrow \right\rangle - \left\langle 1\,s^\downarrow\ 2\,s \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 2\,s\ 1\,s^\downarrow \right\rangle$

In general, the result for the two-body operators is given by the ${}_N C_2$ non-exhcnage and ${}_N C_2$ exchange terms, the latter with the negative signs.

Everthing is the same for $1\,s^2\ 2\,p$ configuration after changing $2\,s$ to $2\,p$.

(d)

Because the Coulomb potential does not affect the spins, the electron "1" in the ket and the bra must have the same spin to give a non-vanishing contribution, and the same for the electron "2". Therefore,

$\left\langle 1\,s^\uparrow\ 1\,s^\downarrow \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1\,s^\downarrow\ 1\,s^\uparrow \right\rangle = 0$

At this point, we have to decide if $2\,s$ electron is spin up or down. If it is spin up,

$\left\langle 1\,s^\downarrow\ 2\,s^\uparrow \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 2\,s^\uparrow\ 1\,s^\downarrow \right\rangle = 0.$

Therefore, the grand total is simplified to

$\langle 1s^2\, 2s \,|\, \Delta H \,|\, 1s^2\, 2s\rangle$
$= \left\langle 1s^\uparrow\, 1s^\downarrow \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1s^\uparrow\, 1s^\downarrow\right\rangle + \left\langle 1s^\uparrow\, 2s^\uparrow \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1s^\uparrow\, 2s^\uparrow\right\rangle$
$+\left\langle 1s^\downarrow\, 2s^\uparrow \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1s^\downarrow\, 2s^\uparrow\right\rangle - \left\langle 1s^\uparrow\, 2s^\uparrow \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 2s^\uparrow\, 1s^\uparrow\right\rangle$
Furthermore, the second and third terms here are the same. After using up all spin degrees of freedom, and expression simplifies to
$\langle 1s^2\, 2s \,|\, \Delta H \,|\, 1s^2\, 2s\rangle$
$= \left\langle 1s\, 1s \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1s\, 1s\right\rangle + 2\left\langle 1s\, 2s \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1s\, 2s\right\rangle - \left\langle 1s\, 2s \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 2s\, 1s\right\rangle$

(e)

We use the perturbation theory to work out the binding energy up to the first order in the Coulomb repulsion.

We make use of the identities
$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{r_<{}^l}{r_>{}^{l+1}} P_l(\cos\theta_{12})$
and
$P_l(\cos\theta_{12}) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_l^{m*}(\Omega_1)\, Y_l^m(\Omega_2)$.
The radial wave functions are
$R_{1s}(r) = a^{-3/2}\, 2\, e^{-r/a}$
$R_{2s}(r) = a^{-3/2}\, \frac{1}{\sqrt{2}} \left(1 - \frac{r}{2a}\right) e^{-r/2a}$
$R_{2p}(r) = a^{-3/2}\, \frac{\sqrt{6}}{12}\, \frac{r}{a}\, e^{-r/2a}$
Here, $a = a_B/Z$, where $a_B = \hbar^2/(m_e e^2)$.

■ $1s^2\, 2s$ configuration

We first study the $1s^2\, 2s$ configuration.
The one-body operator H_0 gives simply $E_{1s} + E_{1s} + E_{2s} = \frac{-9}{8}\, \frac{Z e^2}{a} = \frac{-9}{8}\, \frac{Z^2 e^2}{a_B}$.
Now we calculate the Coulomb repulsion terms. The first term is
$\left\langle 1s\, 1s \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1s\, 1s\right\rangle$
$= a^{-6} \int d\vec{x}_1 \int d\vec{x}_2\, \frac{e^2}{r_{12}} \left(2 e^{-r_1/a}\, Y_0^0(\Omega_1)\right)^2 \left(2 e^{-r_2/a}\, Y_0^0(\Omega_2)\right)^2$
Using the above identities, we find only $l = m = 0$ contributes,
$\left\langle 1s\, 1s \,\middle|\, \frac{e^2}{r_{12}} \,\middle|\, 1s\, 1s\right\rangle$
$= e^2 a^{-6} \int d\vec{x}_1 \int d\vec{x}_2\, \frac{1}{r_>}\, 4\pi\, Y_0^0(\Omega_1)\, Y_0^0(\Omega_2)$
$\left(2 e^{-r_1/a}\, Y_0^0(\Omega_1)\right)^2 \left(2 e^{-r_2/a}\, Y_0^0(\Omega_2)\right)^2$
$= e^2 a^{-6} \int r_1^2\, dr_1 \int r_2^2\, dr_2\, \frac{1}{r_>}\, 16\, e^{-2r_1/a}\, e^{-2r_2/a}$

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In[2]:= 2 Integrate[Integrate[16 r1^2 E^(-2 r1/a) r2^2 E^(-2 r2/a) 1/r1, {r2, 0, r1}, Assumptions → a > 0],
          {r1, 0, ∞}, Assumptions → a > 0]

Out[2]= 5 a^5 / 8
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Hence $\left\langle 1s\,1s \left| \frac{e^2}{r_{12}} \right| 1s\,1s \right\rangle = \frac{5}{8}\,\frac{e^2}{a}$.

The second term is
$\left\langle 1s\,2s \left| \frac{e^2}{r_{12}} \right| 1s\,2s \right\rangle = a^{-6} \int d\vec{x}_1 \int d\vec{x}_2\, \frac{e^2}{r_{12}} \left(2\,e^{-r_1/a}\, Y_0{}^0(\theta_1, \phi_1)\right)^2 \left(\frac{1}{\sqrt{2}}\,(1 - \frac{r_2}{2a})\, e^{-r_2/2a}\, Y_0{}^0(\theta_2, \phi_2)\right)^2$
Again only $l = m = 0$ contributes,
$\left\langle 1s\,2s \left| \frac{e^2}{r_{12}} \right| 1s\,2s \right\rangle$
$= e^2\, a^{-6} \int d\vec{x}_1 \int d\vec{x}_2\, \frac{1}{r_>}\, 4\pi\, Y_0{}^0(\theta_1, \phi_1)\, Y_0{}^0(\theta_2, \phi_2)\, \left(2\,e^{-r_1/a}\, Y_0{}^0(\theta_1, \phi_1)\right)^2 \left(\frac{1}{\sqrt{2}}\,(1 - \frac{r_2}{2a})\, e^{-r_2/2a}\, Y_0{}^0(\theta_2, \phi_2)\right)^2$
$= e^2\, a^{-6} \int r_1{}^2\, d r_1 \int r_2{}^2\, d r_2\, \frac{1}{r_>}\, 2\,(1 - \frac{r_2}{2a})^2\, e^{-2 r_1/a}\, e^{-r_2/a}$

```
In[3]:= Integrate[Integrate[2 r1^2 r2^2 1/r1 (1 - r2/(2 a))^2 E^(-2 r1/a) E^(-r2/a), {r2, 0, r1}, Assumptions → a > 0],
          {r1, 0, ∞}, Assumptions → a > 0] +
         Integrate[Integrate[2 r1^2 r2^2 1/r2 (1 - r2/(2 a))^2 E^(-2 r1/a) E^(-r2/a), {r1, 0, r2}, Assumptions → a > 0],
          {r2, 0, ∞}, Assumptions → a > 0]
```

Out[3]= $\frac{17\,a^5}{81}$

Hence $\left\langle 1s\,2s \left| \frac{e^2}{r_{12}} \right| 1s\,2s \right\rangle = \frac{17}{81}\,\frac{e^2}{a}$.

The third term is
$\left\langle 1s\,2s \left| \frac{e^2}{r_{12}} \right| 2s\,1s \right\rangle$
$= a^{-6} \int d\vec{x}_1 \int d\vec{x}_2\, \frac{e^2}{r_{12}}\, (2\,e^{-r_1/a}\, Y_0{}^0(\theta_1, \phi_1))$
$(2\,e^{-r_2/a}\, Y_0{}^0(\theta_2, \phi_2)) \left(\frac{1}{\sqrt{2}}\,(1 - \frac{r_1}{2a})\, e^{-r_1/2a}\, Y_0{}^0(\theta_1, \phi_1)\right) \left(\frac{1}{\sqrt{2}}\,(1 - \frac{r_2}{2a})\, e^{-r_2/2a}\, Y_0{}^0(\theta_2, \phi_2)\right)$
Again only the $l = m = 0$ piece contributes, and
$\left\langle 1s\,2s \left| \frac{e^2}{r_{12}} \right| 2s\,1s \right\rangle = e^2\, a^{-6} \int r_1{}^2\, d r_1 \int r_2{}^2\, d r_2\, \frac{1}{r_>}\, 2\, e^{-r_1/a}\, e^{-r_2/a} (1 - \frac{r_1}{2a})\, e^{-r_1/2a} (1 - \frac{r_2}{2a})\, e^{-r_2/2a}$

```
In[8]:= 2 Integrate[Integrate[r1^2 r2^2 1/r1 2 E^(-3 r1/(2 a)) E^(-3 r2/(2 a)) (1 - r1/(2 a)) (1 - r2/(2 a)),
          {r2, 0, r1}, Assumptions → a > 0], {r1, 0, ∞}, Assumptions → a > 0]
```

Out[8]= $\frac{16\,a^5}{729}$

Hence $\left\langle 1s\,2s \left| \frac{e^2}{r_{12}} \right| 2s\,1s \right\rangle = \frac{16}{729}\,\frac{e^2}{a}$.

Putting all three terms together,
$\langle 1s^2\, 2s \,|\, \Delta H \,|\, 1s^2\, 2s \rangle$
$= \frac{5}{8}\,\frac{e^2}{a} + 2\left(\frac{17}{81}\,\frac{e^2}{a}\right) - \frac{16}{729}\,\frac{e^2}{a} = \frac{5965}{5832}\,\frac{e^2}{a}$

```
In[10]:= 5/8 + 2 17/81 - 16/729
```

Out[10]= $\frac{5965}{5832}$

Finally, adding the one-body pieces, the total energy is
$E = -\frac{9}{8}\frac{Z e^2}{a} + \frac{5965}{5832}\frac{e^2}{a} = -\frac{9}{8}\frac{Z^2 e^2}{a_B} + \frac{5965}{5832}\frac{Z e^2}{a_B} = -193\,\text{eV}$
for $Z = 3$ and using $\frac{e^2}{2 a_B} = 13.7$ eV.

```
In[12]:= 2 * 13.7 * (-9/8 Z^2 + 5965/5832 Z) /. {Z → 3}

Out[12]= -193.35
```

■ $1 s^2\, 2 p$ configuration

We next study the $1 s^2\, 2 p$ configuration.
The one-body operator H_0 gives simply $E_{1s} + E_{1s} + E_{2p} = \frac{-9}{8}\frac{Z e^2}{a} = \frac{-9}{8}\frac{Z^2 e^2}{a_B}$. At this point, the energy is degenerate with the $1 s^2\, 2 s$ configuration.

Now we calculate the Coulomb repulsion terms. The first term is again the same as the $1 s^2\, 2 s$, $\left\langle 1s\, 1s \right| \frac{e^2}{r_{12}} \left| 1s\, 1s \right\rangle = \frac{5}{8}\frac{e^2}{a}$

The second term is
$\left\langle 1s\, 2p \right| \frac{e^2}{r_{12}} \left| 1s\, 2p \right\rangle = a^{-6} \int d\vec{x}_1 \int d\vec{x}_2 \frac{e^2}{r_{12}} (2 e^{-r_1/a} Y_0{}^0(\Omega_1))^2 \left| \frac{\sqrt{6}}{12} \frac{r_2}{a} e^{-r_2/2a} Y_1{}^m(\Omega_2) \right|^2$
Again only $l = m = 0$ contributes because the $d\,\Omega_1$ integration is trivial,
$\left\langle 1s\, 2s \right| \frac{e^2}{r_{12}} \left| 1s\, 2s \right\rangle$
$= e^2 a^{-6} \int d\vec{x}_1 \int d\vec{x}_2 \frac{1}{r_>} 4\pi Y_0{}^0(\Omega_1) Y_0{}^0(\Omega_2)$
$(2 e^{-r_1/a} Y_0{}^0(\Omega_1))^2 \left| \frac{\sqrt{6}}{12} \frac{r_2}{a} e^{-r_2/2a} Y_1{}^m(\Omega_2) \right|^2$
$= e^2 a^{-6} \int r_1{}^2 d r_1 \int r_2{}^2 d r_2 \frac{1}{r_>} \frac{1}{6} e^{-2 r_1/a} \frac{r_2{}^2}{a^2} e^{-r_2/a}$

```
In[17]:= Integrate[Integrate[1/6 r1^2 r2^2 1/r1 r2^2/a^2 E^(-2 r1/a) E^(-r2/a), {r2, 0, r1}, Assumptions → a > 0],
           {r1, 0, ∞}, Assumptions → a > 0] +
          Integrate[Integrate[1/6 r1^2 r2^2 1/r2 r2^2/a^2 E^(-2 r1/a) E^(-r2/a), {r1, 0, r2}, Assumptions → a > 0],
           {r2, 0, ∞}, Assumptions → a > 0]

Out[17]= 59 a^5/243
```

Hence $\left\langle 1s\, 2p \right| \frac{e^2}{r_{12}} \left| 1s\, 2p \right\rangle = \frac{59}{243}\frac{e^2}{a}$.

The third term is
$\left\langle 1s\, 2p \right| \frac{e^2}{r_{12}} \left| 2p\, 1s \right\rangle$
$= a^{-6} \int d\vec{x}_1 \int d\vec{x}_2 \frac{e^2}{r_{12}} (2 e^{-r_1/a} Y_0{}^0(\Omega_1)) (2 e^{-r_2/a} Y_0{}^0(\Omega_2))$
$\left(\frac{\sqrt{6}}{12} \frac{r_1}{a} e^{-r_1/2a} Y_1{}^m(\Omega_1)\right)^* \left(\frac{\sqrt{6}}{12} \frac{r_2}{a} e^{-r_2/2a} Y_1{}^m(\Omega_2)\right)$

In this case, only the $l = 1$ piece contributes, and

$\left\langle 1s\,2p \right| \frac{e^2}{r_{12}} \left| 2p\,1s \right\rangle$

$= e^2 a^{-6} \int d\vec{x}_1 \int d\vec{x}_2 \frac{r_<}{r_>^2} \frac{4\pi}{3} Y_1{}^m(\Omega_1) Y_1{}^{m*}(\Omega_2)$

$(2 e^{-r_1/a} Y_0{}^0(\Omega_1))(2 e^{-r_2/a} Y_0{}^0(\Omega_2))$

$\left(\frac{\sqrt{6}}{12} \frac{r_1}{a} e^{-r_1/2a} Y_1{}^m(\Omega_1)\right)^* \left(\frac{\sqrt{6}}{12} \frac{r_2}{a} e^{-r_2/2a} Y_1{}^m(\Omega_2)\right)$

$= e^2 a^{-6} \int r_1{}^2\, dr_1 \int r_2{}^2\, dr_2 \frac{r_<}{r_>^2} \frac{1}{18} e^{-r_1/a} e^{-r_2/a} \frac{r_1}{a} e^{-r_1/2a} \frac{r_2}{a} e^{-r_2/2a}$

```
In[24]:= 2 Integrate[Integrate[r1^2 r2^2 r2/r1^2 1/18 E^(-3 r1/(2 a)) E^(-3 r2/(2 a)) r1/a r2/a,
           {r2, 0, r1}, Assumptions -> a > 0], {r1, 0, ∞}, Assumptions -> a > 0]

Out[24]= 112 a^5 / 6561
```

Hence $\left\langle 1s\,2p \right| \frac{e^2}{r_{12}} \left| 2p\,1s \right\rangle = \frac{112}{6561} \frac{e^2}{a}$.

Putting all three terms together,

$\langle 1s^2\,2p \,|\, \Delta H \,|\, 1s^2\,2p \rangle$

$= \frac{5}{8} \frac{e^2}{a} + 2\left(\frac{59}{243} \frac{e^2}{a}\right) - \frac{112}{6561} \frac{e^2}{a} = \frac{57397}{52488} \frac{e^2}{a}$

```
In[27]:= 5/8 + 2 59/243 - 112/6561

Out[27]= 57397/52488
```

Finally, adding the one-body pieces, the total energy is

$E = -\frac{9}{8} \frac{Z e^2}{a} + \frac{57397}{52488} \frac{e^2}{a} = -\frac{9}{8} \frac{Z^2 e^2}{a_B} + \frac{57397}{52488} \frac{Z e^2}{a_B} = -188 \text{ eV}$

for $Z = 3$ and using $\frac{e^2}{2 a_B} = 13.7$ eV.

```
In[31]:= 2*13.7*(-9/8 Z^2 + 57397/52488 Z) /. {Z -> 3}

Out[31]= -187.537
```

Hence, $1s^2\,2p$ configuration is less bound than the $1s^2\,2s$ configuration.

(f)

The variational method requires only a small modification of the calculation done in (e). One has to be careful about Z' in the wave function and Z in the Hamiltonian.

The one-body part is obtained as
$\left\langle n\,l\,m \,\middle|\, \frac{\vec{p}^{\,2}}{2m} \,\middle|\, n\,l\,m \right\rangle = \frac{Z'^2 e^2}{2 n^2 a_B}$
and
$\left\langle n\,l\,m \,\middle|\, \frac{Z e^2}{r} \,\middle|\, n\,l\,m \right\rangle = -\frac{Z e^2}{n^2 a'} = -\frac{Z Z' e^2}{n^2 a_B}$.
Therefore,
$\langle 1s^2\,2s \,|\, H_0 \,|\, 1s^2\,2s\rangle = \langle 1s^2\,2p \,|\, H_0 \,|\, 1s^2\,2p\rangle$
$= \left(-2\left(Z Z' - \frac{Z'^2}{2}\right) - \frac{1}{2^2}\left(Z Z' - \frac{Z'^2}{2}\right)\right) \frac{e^2}{a_B} = \frac{-9}{8}\left(2 Z Z' - Z'^2\right) \frac{e^2}{a_B}$

On the other hand, the calculation of the Coulomb repulsion terms does not depend on the Z but only on Z'. Hence, for the $1s^2\,2s$ configuration,
$E = -\frac{9}{8}\left(2 Z Z' - Z'^2\right) \frac{e^2}{a} + \frac{5965}{5832} Z' \frac{e^2}{a}$
Now we vary Z' to minimize the energy,

```
In[36]:= Solve[D[-9/8 (2 Z Zp - Zp^2) + 5965/5832 Zp, Zp] == 0, Zp]

Out[36]= {{Zp -> (-5965 + 13122 Z)/13122}}

In[37]:= Simplify[-9/8 (2 Z Zp - Zp^2) + 5965/5832 Zp /. %[[1]]]

Out[37]= -(5965 - 13122 Z)^2/153055008

In[38]:= 2*13.7*% /. {Z -> 3}

Out[38]= -199.72
```

Therefore, the result is -200 eV and is lower than the perturbative result -193 eV.

Similarly for the $1s^2\,2p$ configuration,
$E = -\frac{9}{8}\left(2 Z Z' - Z'^2\right) \frac{e^2}{a} + \frac{57397}{52488} Z' \frac{e^2}{a}$

```
In[39]:= Solve[D[-9/8 (2 Z Zp - Zp^2) + 57397/52488 Zp, Zp] == 0, Zp]

Out[39]= {{Zp -> (-57397 + 118098 Z)/118098}}

In[40]:= Simplify[-9/8 (2 Z Zp - Zp^2) + 57397/52488 Zp /. %[[1]]]

Out[40]= -(57397 - 118098 Z)^2/12397455648
```

```
In[41]:= 2 * 13.7 * % /. {Z → 3}

Out[41]= -194.818
```

Even after the improvement by the variational method, which certainly is lower than the perturbative result -188 eV, but is still higher than that of the $1s^2\,2s$ configuration, -200 eV. In other words, the degeneracy between the $2s$ and $2p$ orbitals is resolved by the Coulomb repulsion, and the $2s$ orbital must be filled earlier than the $2p$ orbital, the standard result consistent with chemistry.

(g)

The ionization energy of Li is the energy required to remove an electron from Li to turn it into Li^+. Removing another electron turns it into Li^{++}, and so on. Therefore, the total binding energy of the lithium is

```
In[32]:= 5.39172 + 75.64018 + 122.45429

Out[32]= 203.486
```

Compared to the perturbative result, -193 eV, and the variational result, -200 eV, the experimental value is well reproduced, especially after the variational method.