\[ H = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|r_1 - r_2|} \]

(ignoring fine structure, etc.), \( Z = 2 \).

Experimentally, \( E_{gs} = -78.975 \text{ eV} \).

\( 1E_{gs} \) is the energy necessary to remove both electrons to "infinity."

Theoretically, this problem cannot be solved exactly. It is an example of the 3-body problem, which generally can only be solved approximately.
Let's write \( H = H_0 + H_1 \),

with \( H_0 = -\frac{1}{2m} \left( \nabla_1^2 + \nabla_2^2 \right) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} \)

and \( H_1 = \frac{e^2}{r_1 - r_2} \).

We know the ground state of \( H_0 \); it is

\[
\Psi_0(r_1, r_2) = \chi_{100}(r_1) \chi_{100}(r_2)
\]

\[= \frac{Z^3}{\pi a^3} e^{-\frac{Z(r_1 + r_2)}{a}}, \]

where \( a = \frac{\hbar^2}{m_e e^2} \) is Bohr radius.

Note that since the spatial wavefunction is symmetric, the spin wavefunction must be antisymmetric \((S=0, \text{ singlet})\).
\[ \hat{H}_0 \Phi_0 = -2 \frac{Z^2 m e^4}{\varepsilon^4} \Phi_0 \]

\[ = 8 E_1 \Phi_0 \]

\[ 8 E_1 = -8 (13.6 \text{eV}) = -109 \text{eV} \]

Obviously, this is too low! That is not surprising, since we left out the electron-electron repulsion \[ \hat{H}_1 = \frac{e^2}{|r_1 - r_2|} \].

First-order nondegenerate perturbation theory:

\[ E_{gs} = 8 E_1 + \langle H_1 \rangle. \]

\[ \langle H_1 \rangle = \left( \frac{8 e}{\pi \alpha^3} \right)^2 \int e^{-4 (r_1 + r_2)/9} \frac{d^3 r_1 \, d^3 r_2}{|r_1 - r_2|} \]
\[ |\vec{r}_1 - \vec{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2} \]

Choosing \( \mathbf{z}_2 \)-axis to lie along \( \vec{r}_1 \), without loss of generality.

The \( \mathbf{r}_2 \)-integral is

\[ I_2 = \int \frac{e^{-4r_2/\rho}}{l^{3}r_2} \, d^3 r_2 \]

\[ = \int \frac{e^{-4r_2/\rho} r_2^2 \sin \theta_2 \, dr_2 \, d\theta_2 \, d\phi_2}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}} \]

The \( \phi_2 \)-integral gives \( 2\pi \); the \( \theta_2 \)-integral is
\[ I_2 = 4\pi \left( \frac{1}{r_1} \int_0^{r_1} e^{-4r_2/a} r_2^2 \, dr_2 + \int_{r_1}^{\infty} e^{-4r_2/a} r_2 \, dr_2 \right) \]

\[ = \frac{\pi a^3}{8r_1} \left( 1 - \left(1 + \frac{2r_1}{a}\right) e^{-4r_1/a} \right) \]
Thus

\[
\langle H_1 \rangle = \frac{8e^2}{\pi a^3} \int \left[ 1 - \left( 1 + \frac{2a}{r} \right) e^{-\frac{4r}{a}} \right] e^{-\frac{4r}{a}} \times r, \sin \theta, dr, d\theta, d\phi,
\]

\[
= 4\pi \left( \frac{8e^2}{\pi a^3} \right) \int_0^\infty \left[ r e^{-\frac{4r}{a}} - (r - \frac{2a^2}{r}) e^{-\frac{8r}{a}} \right] dr
\]

\[
= \frac{32e^2}{a^3} \frac{5a^2}{128} = \frac{5}{4} \frac{e^2}{a} = 34 \text{eV}
\]

The result of pert. th. is thus

\[
E_{gs} \simeq -\left( 8 - \frac{5}{2} \right) 13.6 \text{eV} = -\frac{11}{2} 13.6 \text{eV}
\]

\[
= -74.8 \text{eV}
\]

Not bad, compared to the exp. value \( E_{gs} = -79 \text{eV} \).
Note that 1st-order pert. thy overestimates $E_{gs}$. This is because

$$E_{gs}^{(0)} + E_{gs}^{(1)} = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | H_1 | \Phi_0 \rangle$$

$$= \langle \Phi_0 | H_1 | \Phi_0 \rangle \geq E_{gs}$$

by the variational principle.

Let's use the variational principle to improve our estimate of $E_{gs}$. Physically, each electron screens the nuclear electric field felt by the other. For example, if $r_2 \gg \frac{a}{2}$, it will see a Coulomb potential with $Z^* = 1$, not 2.
We can take screening into account in the variational wavefunction by replacing \( Z = \hat{Z} \) with an effective charge \( \hat{Z} < Z \). Try

\[
\Psi_0(r_1, r_2) = \frac{\hat{Z}}{\pi a^3} e^{-\frac{\hat{Z} (r_1 + r_2)}{a}}.
\]

Write:

\[
H = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) - \frac{\hat{Z} e^2}{r_1} - \frac{\hat{Z} e^2}{r_2} + \frac{\hat{Z}^2 e^2}{r_1} + \frac{\hat{Z}^2 e^2}{r_2} + \frac{e^2}{|r_1 - r_2|}.
\]

\[
\langle H \rangle = 2 (\hat{Z})^2 E_1 + 2 (\hat{Z} - \hat{Z}) \langle \frac{e^2}{r} \rangle + \langle \hat{H} \rangle
\]

\[
= 2 (\hat{Z})^2 E_1 - 4 (\hat{Z} - \hat{Z}) \hat{Z} E_1 + \frac{5 \hat{Z}}{8 a}
\]
\[ \langle H \rangle = \left[ 2(z^*)^2 - 4(z^*-2)z^* - \frac{5}{4} z^* \right] E_1 \]

\[ = \left[ -2(z^*)^2 + \frac{27}{4} z^* \right] E_1 \]

\[ \text{minimum:} \]

\[ 0 = \frac{\partial \langle H \rangle}{\partial z^*} = \left[ -4 z^* + \frac{27}{4} \right] E_1 \]

\[ z^* = \frac{27}{16} = 1.69 \]

Our bound is:

\[ E_{gs} \geq \frac{729}{128} E_1 = -77.5 \text{eV} \]

This is 3eV lower than 1st-order pert. theory, and only 1.5eV above the experimental value.