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In practice this means we minimize the value of the Hamiltonian expectation value to achieve this upper bound.

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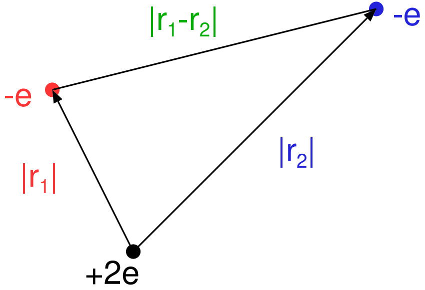
Helium atom

The helium atom is an ideal application of the variational principle. The full Hamiltonian includes an electron-electron interaction which we ignored when we first discussed it



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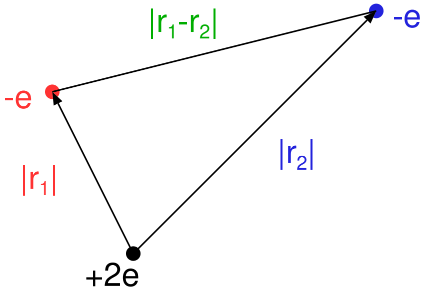

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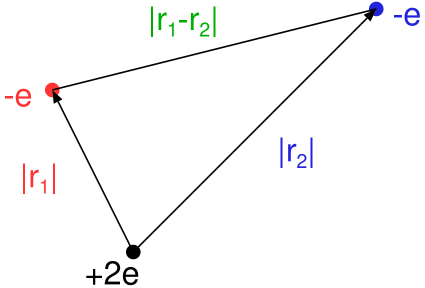

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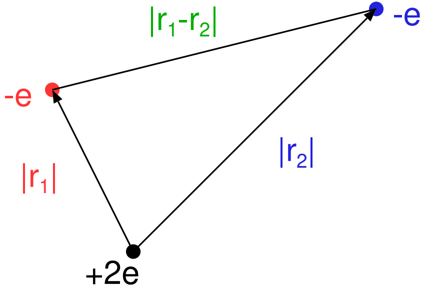

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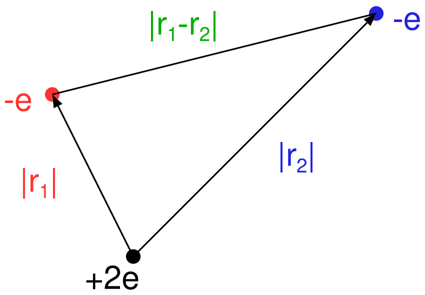

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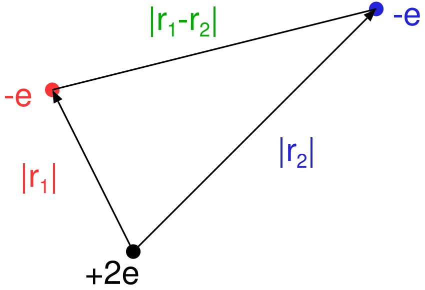

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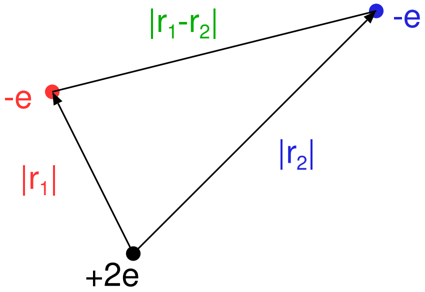

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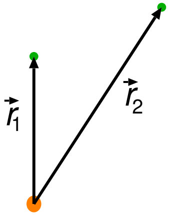

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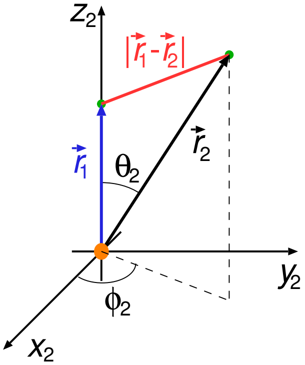

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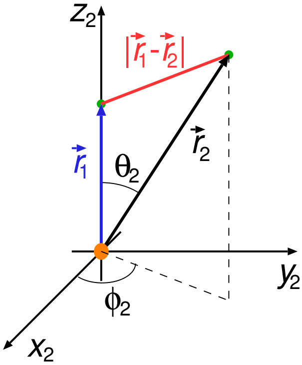

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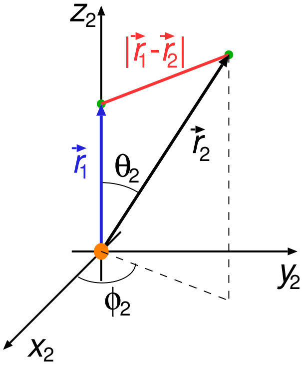

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$$I_\theta = \int_0^\pi \frac{\sin\theta_2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}}\, d\theta_2 = \left. \frac{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}}{r_1\, r_2} \right|_0^\pi$$

The r_2 integral

$$\langle V_{ee} \rangle = \left(\frac{e^2}{4\pi\epsilon_0}\right)\left(\frac{8}{\pi a^3}\right)^2 \int \frac{e^{-4r_1/a}\, e^{-4r_2/a}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}}\, d^3\vec{r}_1\, d^3\vec{r}_2$$

the $\vec{r}_2$ integral then can be evaluated

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The r_2 integral

The r_2 integral is thus split into two parts

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The r_2 integral

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$$I_2 = 4\pi \left(\frac{1}{r_1} \int_0^{r_1} r_2^2 \, e^{-4r_2/a} \, dr_2 + \qquad\qquad \right)$$

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$$I_2 = 4\pi \left(\frac{1}{r_1} \int_0^{r_1} r_2^2 \, e^{-4r_2/a} \, dr_2 + \int_{r_1}^{\infty} r_2 \, e^{-4r_2/a} \, dr_2 \right)$$

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$$I_{red} = -\left(\frac{a}{4}\right) r_2^2 e^{-4r_2/a} \Big|_0^{r_1}$$

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$$I_{red} = -\left(\frac{a}{4}\right) r_2^2 e^{-4r_2/a} \Big|_0^{r_1} + 2\left(\frac{a}{4}\right) \int_0^{r_1} r_2 e^{-4r_2/a}\, dr_2$$

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$$\begin{aligned} I_{red} &= \; - \left(\frac{a}{4}\right) r_2^2 e^{-4r_2/a} \Big|_0^{r_1} + 2 \left(\frac{a}{4}\right) \int_0^{r_1} r_2 e^{-4r_2/a} \, dr_2 \\ &= - \left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a} - 2 \left(\frac{a}{4}\right)^2 r_2 e^{-4r_2/a} \Big|_0^{r_1} + 2 \left(\frac{a}{4}\right)^2 \int_0^{r_1} e^{-4r_2/a} \, dr_2 \end{aligned}$$

The r_2 integral

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&= -\left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^2 r_2 e^{-4r_2/a}\Big|_0^{r_1} + 2\left(\frac{a}{4}\right)^2 \int_0^{r_1} e^{-4r_2/a}\, dr_2 \\
&= -\left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^2 r_1 e^{-4r_1/a}
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$$I_2 = 4\pi \left(\frac{1}{r_1} \int_0^{r_1} r_2^2 \, e^{-4r_2/a} \, dr_2 + \int_{r_1}^{\infty} r_2 \, e^{-4r_2/a} \, dr_2 \right)$$

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&= -\left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^2 r_2 e^{-4r_2/a} \Big|_0^{r_1} + 2\left(\frac{a}{4}\right)^2 \int_0^{r_1} e^{-4r_2/a} \, dr_2 \\
&= -\left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^2 r_1 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^3 e^{-4r_1/a} + 2\left(\frac{a}{4}\right)^3
\end{aligned}$$

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&= -\left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^2 r_1 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^3 e^{-4r_1/a} + 2\left(\frac{a}{4}\right)^3 \\
I_{blue} &=
\end{aligned}$$

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&= - \left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a} - 2 \left(\frac{a}{4}\right)^2 r_2 e^{-4r_2/a} \Big|_0^{r_1} + 2 \left(\frac{a}{4}\right)^2 \int_0^{r_1} e^{-4r_2/a} \, dr_2 \\
&= - \left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a} - 2 \left(\frac{a}{4}\right)^2 r_1 e^{-4r_1/a} - 2 \left(\frac{a}{4}\right)^3 e^{-4r_1/a} + 2 \left(\frac{a}{4}\right)^3 \\
I_{blue} &= \, - \left(\frac{a}{4}\right) r_2 e^{-4r_2/a} \Big|_{r_1}^{\infty}
\end{aligned}$$

The r_2 integral

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&= -\left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^2 r_1 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^3 e^{-4r_1/a} + 2\left(\frac{a}{4}\right)^3 \\
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&= -\left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^2 r_2 e^{-4r_2/a} \Big|_0^{r_1} + 2\left(\frac{a}{4}\right)^2 \int_0^{r_1} e^{-4r_2/a} \, dr_2 \\
&= -\left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^2 r_1 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^3 e^{-4r_1/a} + 2\left(\frac{a}{4}\right)^3 \\
I_{blue} &= -\left(\frac{a}{4}\right) r_2 e^{-4r_2/a} \Big|_{r_1}^{\infty} + \left(\frac{a}{4}\right) \int_{r_1}^{\infty} e^{-4r_2/a} \, dr_2 = +\left(\frac{a}{4}\right) r_1 e^{-4r_1/a}
\end{aligned}$$

The r_2 integral

The r_2 integral is thus split into two parts

$$I_2 = 4\pi \left(\frac{1}{r_1} \int_0^{r_1} r_2^2 \, e^{-4r_2/a} \, dr_2 + \int_{r_1}^{\infty} r_2 \, e^{-4r_2/a} \, dr_2 \right)$$

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&= -\left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^2 r_2 e^{-4r_2/a} \Big|_0^{r_1} + 2\left(\frac{a}{4}\right)^2 \int_0^{r_1} e^{-4r_2/a} \, dr_2 \\
&= -\left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^2 r_1 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^3 e^{-4r_1/a} + 2\left(\frac{a}{4}\right)^3 \\
I_{blue} &= -\left(\frac{a}{4}\right) r_2 e^{-4r_2/a} \Big|_{r_1}^{\infty} + \left(\frac{a}{4}\right) \int_{r_1}^{\infty} e^{-4r_2/a} \, dr_2 = +\left(\frac{a}{4}\right) r_1 e^{-4r_1/a} + \left(\frac{a}{4}\right)^2 e^{-4r_1/a}
\end{aligned}$$

The r_2 integral

$$I_2 = 4\pi \left[\frac{1}{r_1} \int_0^{r_1} r_2^2 \, e^{-4r_2/a} \, dr_2 + \int_{r_1}^{\infty} r_2 \, e^{-4r_2/a} \, dr_2 \right]$$

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&= 4\pi \left[\frac{1}{r_1} \left(-\left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^2 r_1 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^3 e^{-4r_1/a} + 2\left(\frac{a}{4}\right)^3 \right) \right. \\
&\qquad \left. + \left(\frac{a}{4}\right) r_1 e^{-4r_1/a} + \left(\frac{a}{4}\right)^2 e^{-4r_1/a} \right]
\end{aligned}
$$

The r_2 integral

$$
\begin{aligned}
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&= 4\pi \left[\frac{1}{r_1} \left(\cancel{-\left(\frac{a}{4}\right) r_1^2 e^{-4r_1/a}} - 2\left(\frac{a}{4}\right)^2 r_1 e^{-4r_1/a} - 2\left(\frac{a}{4}\right)^3 e^{-4r_1/a} + 2\left(\frac{a}{4}\right)^3 \right) \right. \\
&\qquad \left. + \cancel{\left(\frac{a}{4}\right) r_1 e^{-4r_1/a}} + \left(\frac{a}{4}\right)^2 e^{-4r_1/a} \right]
\end{aligned}
$$

The r_2 integral

$$I_2 = 4\pi \left[\frac{1}{r_1} \int_0^{r_1} r_2^2 \, e^{-4r_2/a} \, dr_2 + \int_{r_1}^{\infty} r_2 \, e^{-4r_2/a} \, dr_2 \right]$$

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

$$\left. + \left(\frac{a}{4}\right) r_1 e^{-4r_1/a} + \left(\frac{a}{4}\right)^2 e^{-4r_1/a} \right]$$

$$I_2 = 4\pi \left[-\left(\frac{a}{4}\right)^2 e^{-4r_1/a} - \frac{2}{r_1}\left(\frac{a}{4}\right)^3 e^{-4r_1/a} + \frac{2}{r_1}\left(\frac{a}{4}\right)^3 \right]$$

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$$= 4\pi \frac{2a^3}{64 r_1} \left[-\frac{r_1}{2}\left(\frac{4}{a}\right) e^{-4r_1/a} - e^{-4r_1/a} + 1 \right]$$

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$$= 4\pi\frac{2a^3}{64r_1}\left[-\frac{r_1}{2}\left(\frac{4}{a}\right) e^{-4r_1/a} - e^{-4r_1/a} + 1\right] = \frac{\pi a^3}{8r_1}\left[1 - \left(1 + \frac{2r_1}{a}\right) e^{-4r_1/a}\right]$$

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An improved helium atom energy

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- Helium atom review

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- Helium atom review
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