Consider an electronic system with the following eigenstates.

$|0\rangle = (1,0,0,0)$ no electrons
$|1\rangle = (0,1,0,0)$ one electron in state ϕ_1
$|2\rangle = (0,0,1,0)$ one electron in state ϕ_2
$|3\rangle = (0,0,0,1)$ two electrons, one in state ϕ_1, one in state ϕ_2

Let electron states ϕ_n be modeled by a one dimensional box of length L.

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

Let $|\xi\rangle$ be a state vector.

$$|\xi\rangle = c_0|0\rangle + c_1|1\rangle + c_2|2\rangle + c_3|3\rangle, \quad \langle\xi|\xi\rangle = 1$$

Let us determine matrix $\hat{E}$ such that the expected energy $\langle E\rangle$ is

$$\langle E\rangle = \langle\xi|\hat{E}|\xi\rangle$$

Matrix $\hat{E}$ is the sum of kinetic energy $\hat{K}$ and potential energy $\hat{V}$.

$$\hat{E} = \hat{K} + \hat{V}$$

Matrix $\hat{K}$ is computed from eigenvalues of the box model.

$$\hat{K} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & E_1 & 0 & 0 \\ 0 & 0 & E_2 & 0 \\ 0 & 0 & 0 & E_1 + E_2 \end{pmatrix}, \quad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

Matrix $\hat{V}$ has one entry due to Coulomb interaction in the two electron state.

$$\hat{V} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \langle V\rangle \end{pmatrix}$$

Let $\psi(x,y)$ be the antisymmetrized wavefunction of the two electrons.

$$\psi(x,y) = \frac{\phi_1(x)\phi_2(y) - \phi_1(y)\phi_2(x)}{\sqrt{2}}$$

The expected potential energy is

$$\langle V \rangle = \frac{e^2}{4\pi\epsilon_0} \int_0^L \int_0^L \psi^*(x,y) \left(\frac{1}{|x-y|} \right) \psi(x,y)\, dx\, dy$$

Let us now choose $L = 10^{-9}$ meters and compute numerical values.

$$\hat{K} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0.38\,\text{eV} & 0 & 0 \\ 0 & 0 & 1.50\,\text{eV} & 0 \\ 0 & 0 & 0 & 1.88\,\text{eV} \end{pmatrix}$$

Computing $\langle V \rangle$ by numerical integration we have

$$\hat{V} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 4.67\,\text{eV} \end{pmatrix}$$

Hence

$$\hat{E} = \hat{K} + \hat{V} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0.38\,\text{eV} & 0 & 0 \\ 0 & 0 & 1.50\,\text{eV} & 0 \\ 0 & 0 & 0 & 6.55\,\text{eV} \end{pmatrix}$$

The expected energy is

$$\langle E \rangle = \langle \xi | \hat{E} | \xi \rangle = 0.38\, c_1^* c_1 + 1.50\, c_2^* c_2 + 6.55\, c_3^* c_3$$

For a state $|\xi\rangle$ with uniform probability distribution $c_i^* c_i = \frac{1}{4}$ we have

$$\langle E \rangle = \tfrac{1}{4}(0.38 + 1.50 + 6.55) = 2.11\,\text{eV}$$