

Consider an electronic system with the following eigenstates.

$$\begin{aligned} |0\rangle &= (1, 0, 0, 0) && \text{no electrons} \\ |1\rangle &= (0, 1, 0, 0) && \text{one electron in state } \phi_1 \\ |2\rangle &= (0, 0, 1, 0) && \text{one electron in state } \phi_2 \\ |3\rangle &= (0, 0, 0, 1) && \text{two electrons, one in state } \phi_1, \text{ one in state } \phi_2 \end{aligned}$$

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.

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

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

$$\psi(x, y) = \frac{1}{\sqrt{2}} (\phi_1(x)\phi_2(y) - \phi_1(y)\phi_2(x))$$

Then

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

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 V 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

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