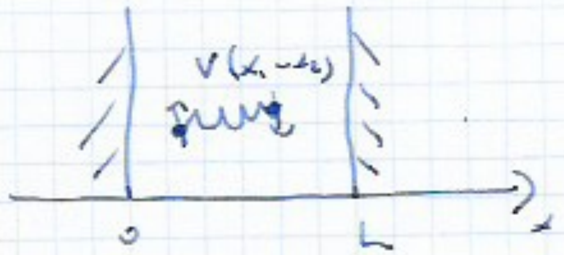
Two electrons in 1d infinite well with interaction



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

one-particle functions

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2$$

Spinor (spin functions)

$$\alpha = \uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \chi_+ \quad , \quad \beta = \downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \chi_-$$

spin orbitals

$$\phi_n(x_i) \uparrow(i) \quad \text{or} \quad \phi_n(x_i) \downarrow(i)$$

1) Ground state

Pauli principle

$$\boxed{|\phi_1(\cdot)\uparrow(\cdot), \phi_1(\cdot)\downarrow(\cdot)|}$$

$$\Psi_0(x_1\ x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(x_1)\uparrow(1) & \phi_1(x_1)\downarrow(1) \\ \phi_1(x_2)\uparrow(2) & \phi_1(x_2)\downarrow(2) \end{vmatrix} =$$

$$= \underbrace{\phi_1(x_1)\phi_1(x_2)}_{\text{symmetric orbital part}} \underbrace{\frac{1}{\sqrt{2}}\left[\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)\right]}_{\text{antisymmetric spin part - singlet}} \quad \begin{matrix} S^z = 0 \\ S^{tot} = 0 \end{matrix}$$

1st order perturbation

$$E_{11} = \frac{\pi^2\hbar^2}{2mL^2}(1^2+1^2) + \Delta E_{11} = \frac{\pi^2\hbar^2}{mL^2} + \Delta E_{11} \quad \left(> \frac{\hbar^2\pi^2}{mL^2} \text{ for repulsion}\right)$$

$$\Delta E_{11} = \int dx_1\, dx_2\, |\phi_1(x_1)|^2\, V(x_1-x_2)\, |\phi_1(x_2)|^2 \quad (>0 \text{ for repulsion})$$

$$\frac{1}{2}\left[\langle\uparrow\downarrow| - \langle\downarrow\uparrow|\right]\cdot\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right] = \frac{1}{2}\left[\langle\uparrow\downarrow|\uparrow\downarrow\rangle + \langle\downarrow\uparrow|\downarrow\uparrow\rangle\right] = 1$$

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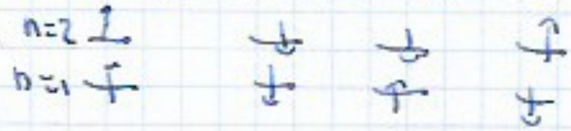
2) First excited state is 4 fold degenerate



$\boxed{\phi_1(--)\uparrow(--),\ \phi_2(--)\uparrow(--)}$

a)

$$\psi_1^a(x_1\ x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(x_1)\uparrow(1) & \phi_2(x_1)\uparrow(1) \\ \phi_1(x_2)\uparrow(2) & \phi_2(x_2)\uparrow(2) \end{vmatrix} =$$

$$= \underbrace{\frac{1}{\sqrt{2}}\left[\phi_1(x_1)\phi_2(x_2) - \phi_2(x_1)\phi_1(x_2)\right]}_{\text{antisymmetric orbital part}} \underbrace{\uparrow(1)\uparrow(2)}_{\substack{\text{symmetric} \\ \text{triplet} \\ \text{part}}} \qquad \begin{matrix} S^z = 1 \\ S^{tot} = 1 \end{matrix}$$

b)

$$\psi_1^b(x_1\ x_2) = \frac{1}{\sqrt{2}} \underbrace{\left[\phi_1(x_1)\phi_2(x_2) - \phi_2(x_1)\phi_1(x_2)\right]}_{\text{antisymmetric}} \underbrace{\downarrow(1)\downarrow(2)}_{\substack{\text{triplet} \\ \text{part}}} \qquad \begin{matrix} S^z = -1 \\ S_{tot} = 1 \end{matrix}$$

The next two situations $\overset{\downarrow}{\uparrow}$ $\overset{\downarrow}{\uparrow}$ are equivalent (electrons are indistinguishable) so we take symmetric and antisymmetric combinations of Slater determinants

$$\psi_1^c(x_1, x_2) = \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(x_1)\uparrow(1) & \phi_2(x_1)\downarrow(1) \\ \phi_1(x_2)\uparrow(2) & \phi_2(x_2)\downarrow(2) \end{vmatrix} + \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(x_1)\downarrow(1) & \phi_2(x_1)\uparrow(1) \\ \phi_1(x_2)\downarrow(2) & \phi_2(x_2)\uparrow(2) \end{vmatrix} \right)$$

$\boxed{\phi_1(..)\uparrow(..),\ \phi_2(..)\downarrow(..)}$ $\boxed{\phi_1(--)\downarrow(--),\ \phi_2(--)\uparrow(--)}$

$$= \underbrace{\frac{1}{\sqrt{2}}\left(\phi_1(x_1)\phi_2(x_2) - \phi_2(x_1)\phi_1(x_2)\right)}_{\text{antisymmetric orbital}} \frac{1}{\sqrt{2}} \underbrace{\left(\uparrow(1)\downarrow(2) + \downarrow(1)\uparrow(2)\right)}_{\substack{\text{symmetric spin} \\ \text{triplet}}} \qquad \begin{matrix} S^z = 0 \\ S^{tot} = 1 \end{matrix}$$

$$\Psi_1^{a}(x_1, x_2) = \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\left| \quad \right| - \frac{1}{\sqrt{2}}\left| \quad \right|\right) =$$

$$= \underbrace{\frac{1}{\sqrt{2}}\left(\phi_1(x_1)\phi_2(x_2) + \phi_1(x_2)\phi_2(x_1)\right)}_{\text{symmetric orbital}} \frac{1}{\sqrt{2}}\left(\underbrace{\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)}_{\text{antisymmetric spin singlet}}\right) \quad S^z = 0 \quad S^{tot} = 0$$

$$E_{12} = \frac{\pi^2\hbar^2}{2mL^2}(1^2 + 2^2) + \Delta E_{12} = \frac{5}{2}\frac{\pi^2\hbar^2}{mL^2} + \Delta E_{12}$$

ΔE_{12} depends on symmetry of orbital part

$$\Delta E_{a/b}^{sym} = \frac{1}{2}\int dx_1 \int dx_2 \, V(x_1 - x_2)\left[\phi_1(x_1)\phi_2(x_2) - \phi_2(x_1)\phi_1(x_2)\right]^* \cdot \left[\phi_1(x_1)\phi_2(x_2) - \phi_2(x_1)\phi_1(x_2)\right] =$$

$$= \frac{1}{2}\int dx_1 \int dx_2 \, V(x_1 - x_2)\Big[\,|\phi_1(x_1)|^2|\phi_2(x_2)|^2 + |\phi_2(x_1)|^2|\phi_1(x_2)|^2 - \phi_1^*(x_1)\phi_2^*(x_2)\phi_2(x_1)\phi_1(x_2) - \phi_2^*(x_1)\phi_1^*(x_2)\phi_1(x_1)\phi_2(x_2)\Big]$$

$$\Delta E_c^{sym} = \Delta E_{a/b}^{sym}$$

$$\Delta E_a^{ant} = \frac{1}{2}\int dx_1 \int dx_2 \, V(x_1 - x_2)\Big[\,|\phi_1(x_1)|^2|\phi_2(x_2)|^2 + |\phi_2(x_1)|^2|\phi_1(x_2)|^2 + \phi_1^*(x_1)\phi_2^*(x_2)\phi_2(x_1)\phi_1(x_2) + \phi_2^*(x_1)\phi_1^*(x_2)\phi_1(x_1)\phi_2(x_2)\Big]$$

For a contact interaction

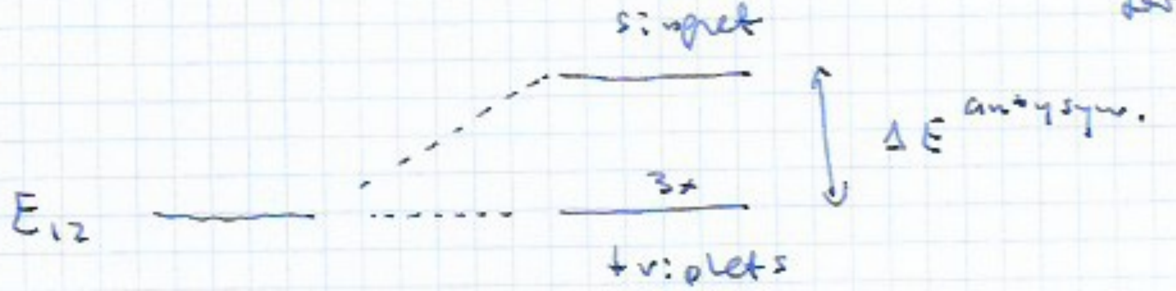
$$V(x_1 - x_2) = V_0 \, \delta(x_1 - x_2)$$

$$\Delta E^{sym} = \frac{2}{2} V_0 \int dx_1 \Big[|\phi_1(x_1)|^2 |\phi_2(x_1)|^2 - |\phi_1^*(x_1)|^2 |\phi_2(x_1)|^2 \Big] = 0$$

$$\Delta E^{antysym} = \frac{2}{2} V_0 \int dx_1 \Big(|\phi_1(x_1)|^2 |\phi_2(x_1)|^2 + |\phi_1(x_1)|^2 |\phi_2(x_1)|^2 \Big] =$$

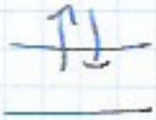
$$= 2 V_0 \int dx_1 |\phi_1(x_1)|^2 |\phi_2(x_1)|^2 > 0$$

for $V_0 > 0$



Exchange interaction ⇔ level splitting according to spin symmetry (singlet - triplet) due to an interaction and wave function antisymmetry.

3) Second excited state



$$\psi_2(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_2(x_1)\uparrow(1) & \phi_2(x_1)\downarrow(1) \\ \phi_2(x_2)\uparrow(2) & \phi_2(x_1)\downarrow(1) \end{vmatrix} =$$

$$= \underbrace{\phi_2(x_1)\,\phi_2(x_2)}_{\text{symmetric}} \frac{1}{\sqrt{2}} \Big[\underbrace{\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)}_{\text{singlet}} \Big]$$

$$E_{22} = \frac{\hbar^2 \pi^2}{2mL^2} \overset{=8}{(2^2+2^2)} + \Delta E_{22} = 4\frac{\hbar^2\pi^2}{mL^2} + \Delta E_{22}$$

$$\Delta E_{22} = \int dx_1 \int dx_2 \, |\phi_2(x_1)|^2 \, V(x_1 - x_2) \, |\phi_2(x_2)|^2 > 0$$

(as $V > 0$

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