1) General Hamiltonian for 'n' electron with nuclear charge 'Z'

$$\hat{H} = -\frac{\hbar^2}{2m_N}\hat{\nabla}_N^2 - \frac{\hbar^2}{2m_e}\sum_i \hat{\nabla}_i^2 - \frac{Ze^2}{4\pi\epsilon_0}\sum_i \frac{1}{r_i} + \frac{1}{4\pi\epsilon_0}\sum_i \sum_{j(>i)} \frac{e^2}{r_{ij}}$$

2) Orbital approximation $\Rightarrow$ Many electron eigenfunction can be expressed as product of one electron eigenfunctions

$$\psi(r_1, r_2, r_3 \ldots) = \phi(r_1)\phi(r_2)\phi(r_3)\ldots$$

N.B. This wavefunction, as a result of approximation, is no longer an eigenfunction of $\hat{H}$ as the Hamiltonian contains operator contributing electron-electron repulsion. This wavefunction can be used to obtain expectation value of energy but not the eigenvalue.

$$\hat{H} = \hat{H}_1 + \hat{H}_2 \ldots + \hat{H}_n + \boxed{\sum_i \sum_{j(>i)} \frac{1}{r_{ij}}} \Rightarrow$$ We are not neglecting inter-electronic repulsion.

for a $2e^-$ system, say

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}$$

$$\langle \psi^* | \hat{H} | \psi \rangle = \langle \phi_1^* | \hat{H}_1 | \phi_1 \rangle + \langle \phi_2^* | \hat{H}_2 | \phi_2 \rangle + \underbrace{\langle \phi_1^* \phi_2^* | \frac{1}{r_{12}} | \phi_1 \phi_2 \rangle}_{\text{inter-electronic repulsion contribution}}$$

3) 2-e spin functions $\alpha(1)\beta(2)$ or $\beta(1)\alpha(2)$ is $\boxed{\text{not}}$ acceptable as it violates the condition of indistinguishibility of fermions.

The following Slater determinant is $\boxed{\text{not a valid}}$ wavefunction as it specifies the spin of electron in respective orbitals i.e. 'α' state in 2s orbital & 'β' state 3s orbital. It's an example of breach of indistinguishibility condition.

4) Excited state of He atom $\Rightarrow 1s^1 2s^1$

- spin wavefunction $\Rightarrow$

① $\alpha(1)\alpha(2)$ ② $\beta(1)\beta(2)$

③ $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\beta(1)\alpha(2)]$ ④ $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\beta(1)\alpha(2)]$

①, ②, ③ $\Rightarrow$ symmetric ④ $\Rightarrow$ antisymmetric.

- Total wavefunction $\Rightarrow$

spatial part :

$$\phi_s = \frac{1}{\sqrt{2}}(1s(1)\,2s(2) + 1s(2)\,2s(1))$$

$$\phi_{as} = \frac{1}{\sqrt{2}}(1s(1)\,2s(2) - 1s(2)\,2s(1))$$

To make the total wavefunction antisymmetric,

$$\psi_1 = \phi_s \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad \psi_{2,3,4} = \phi_{as}\begin{cases}\alpha(1)\alpha(2)\\ \beta(1)\beta(2)\\ \frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\beta(1)\alpha(2))\end{cases}$$

$$\Psi_1 = \frac{1}{\sqrt{2}}\left[1s(1)2s(2) + 1s(2)2s(1)\right]\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]$$

$$= \frac{1}{2}\left[1s(1)\alpha(1)2s(2)\beta(2) - 1s(1)\beta(1)2s(2)\alpha(2) + 1s(2)\beta(2)2s(1)\alpha(1) - 1s(2)\alpha(2)2s(1)\beta(1)\right]$$

$$= \frac{1}{2}\left[\left\{1s(1)\alpha(1)2s(2)\beta(2) - 1s(2)\alpha(2)2s(1)\beta(1)\right\} \mp \left\{1s(1)\beta(1)2s(2)\alpha(2) - 1s(2)\beta(2)2s(1)\alpha(1)\right\}\right]$$

$$= \frac{1}{2}\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix} - \frac{1}{2}\begin{vmatrix} 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\beta(2) & 2s(2)\alpha(2) \end{vmatrix}$$

$$\Psi_2 = \frac{1}{\sqrt{2}}\left[1s(1)2s(2) - 1s(2)2s(1)\right]\alpha(1)\alpha(2)$$

$$= \frac{1}{\sqrt{2}}\left[1s(1)\alpha(1)2s(2)\alpha(2) - 1s(2)\alpha(2)2s(1)\alpha(1)\right]$$

$$= \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix}$$

$$\Psi_3 = \frac{1}{\sqrt{2}}\left[1s(1)2s(2) - 1s(2)2s(1)\right]\cancel{\alpha}\beta(1)\beta(2)$$

$$= \frac{1}{\sqrt{2}}\left[1s(1)\beta(1)2s(2)\beta(2) - 1s(2)\beta(2)2s(1)\beta(1)\right]$$

$$= \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\beta(1) & 2s(1)\beta(1) \\ 1s(2)\beta(2) & 2s(2)\beta(2) \end{vmatrix}$$

$$\psi_4 = \frac{1}{\sqrt{2}}\left[1s(1)2s(2) - 1s(2)2s(1)\right]\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right]$$

$$= \frac{1}{2}\left[1s(1)\alpha(1)2s(2)\beta(2) + 1s(1)\beta(1)2s(2)\alpha(2) - 1s(2)\beta(2)2s(1)\alpha(1) - 1s(2)\alpha(2)2s(1)\beta(1)\right]$$

$$= \frac{1}{2}\left[\{1s(1)\alpha(1)2s(2)\beta(2) - 1s(2)\alpha(2)2s(1)\beta(1)\} + \{1s(1)\beta(1)2s(2)\alpha(2) - 1s(2)\beta(2)2s(1)\alpha(1)\}\right]$$

$$= \frac{1}{2}\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix} + \frac{1}{2}\begin{vmatrix} 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\beta(2) & 2s(2)\alpha(2) \end{vmatrix}.$$

(5) As per the condition, spin wavefunction will be $= \alpha(1)\alpha(2)$

$$\hat{S}^2_{tot} = (\hat{S}_1 + \hat{S}_2)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2(\hat{S}_{1x}.\hat{S}_{2x} + \hat{S}_{1y}.\hat{S}_{2y} + \hat{S}_{1z}.\hat{S}_{2z}).$$

$$= \hat{S}_{1x}^2 + \hat{S}_{1y}^2 + \hat{S}_{1z}^2 + \hat{S}_{2x}^2 + \hat{S}_{2y}^2 + \hat{S}_{2z}^2 + 2(\hat{S}_{1x}.\hat{S}_{2x} + \hat{S}_{1y}.\hat{S}_{2y} + \hat{S}_{1z}.\hat{S}_{2z}).$$

Now,

$$\hat{S}_{1x}^2\,\alpha(1)\alpha(2) = \hat{S}_{1x}\left(\frac{\hbar}{2}\right)\beta(1)\alpha(2) = \frac{\hbar^2}{4}\alpha(1)\alpha(2)\ \left[= \hat{S}_{2x}^2\alpha(1)\alpha(2)\right]$$

$$\hat{S}_{1y}^2\,\alpha(1)\alpha(2) = \hat{S}_{1y}\left(\frac{i\hbar}{2}\right)\beta(1)\alpha(2) = -\frac{\hbar^2}{4}\alpha(1)\alpha(2)\ \left[= \hat{S}_{2y}^2\alpha(1)\alpha(2)\right]$$

$$\hat{S}_{1z}^2\,\alpha(1)\alpha(2) = \hat{S}_{1z}\frac{\hbar}{2}\alpha(1)\alpha(2) = \frac{\hbar^2}{4}\alpha(1)\alpha(2)\ \left[= \hat{S}_{2z}^2\alpha(1)\alpha(2)\right]$$

$$\hat{S}_{1x}\cdot\hat{S}_{1y}\,\alpha(1)\alpha(2) = \frac{\hbar}{2}\beta(1)\cdot\frac{\hbar}{2}\beta(2) = \frac{\hbar^2}{4}\beta(1)\beta(2)$$

$$\hat{S}_{1y}\cdot\hat{S}_{2y}\,\cancel{\beta(1)}\alpha(1)\alpha(2) = -\frac{i\hbar}{2}\beta(1)\cdot\left(-\frac{i\hbar}{2}\right)\beta(2) = -\frac{\hbar^2}{4}\beta(1)\beta(2)$$

$$\hat{S}_{1z}\cdot\hat{S}_{2z}\,\alpha(1)\alpha(2) = \left(\frac{\hbar}{2}\right)\alpha(1)\left(\frac{\hbar}{2}\right)\alpha(2) = \frac{\hbar^2}{4}\alpha(1)\alpha(2)$$

$$\hat{S}^2_{tot}\,\alpha(1)\alpha(2)$$

$$= \left[\cancel{\frac{\hbar^2}{4}} \cancel{-\frac{\hbar^2}{4}} + \frac{\hbar^2}{4} + \cancel{\frac{\hbar^2}{4}} \cancel{-\frac{\hbar^2}{4}} + \frac{\hbar^2}{4}\right]\alpha(1)\alpha(2)$$

$$+2\left[\cancel{\frac{\hbar^2}{4}\beta(1)\beta(2)} \cancel{-\frac{\hbar^2}{4}\beta(1)\beta(2)} + \frac{\hbar^2}{4}\alpha(1)\alpha(2)\right]$$

$$= \left[\frac{2\hbar^2}{4} + \frac{2\hbar^2}{4}\right]\alpha(1)\alpha(2)$$

$$= \underline{\hbar^2}\,\alpha(1)\alpha(2)$$

$\therefore$ Hence, the wavefunction is an eigenfunction of $\hat{S}^2_{total}$