SLATER DETERMINANTS

Finding ψ's that satisfy the Pauli Principle can be hard.

P.P = $\boxed{\psi(2,1) = -\psi(1,2)}$] ψ is antisymmetric under e^- exchange.

The point of a Slater Determinant is to make ψ's that satisfy the P.P.

Recall the Orbital Approximation: $\psi(1,2,3...) = \psi(1)\psi(2)\psi(3)...$ ← e^- in their own separate orbital

Furthermore: $\psi(1) = \phi(r)\chi(\alpha)$ ← spin part. Spin is up (α) or down (β)

spatial part (i.e. s/p/d/f)

called a "spin orbital" ← Total ψ

This is also an approximation that is crap for heavy atoms.

Say I have 2 e^- in a molecular orbital, $\psi(1,2)$. How do I combine the two ~~...~~ spin orbitals? E.g. $\psi(1,2) = \psi_1(1)\,\psi_2(2) = \phi_{1s}(1)\,\phi_{1s}(2)\,\chi_1(a)\,\chi_2(\beta)$

If the spatial part ϕ is the same (i.e. both in an s orbital or whatever), then I can see if this ψ satisfies the P.P:

$$\psi(1,2) = -\phi_{1s}(1)\,\phi_{1s}(2)\,\chi_1(a)\,\chi_2(\beta)$$

$$\psi(2,1) = \phi_{1s}(2)\,\phi_{1s}(1)\,\chi_2(a)\,\chi_1(\beta)$$

] $\psi(2,1) \neq -\psi(1,2)$ UNACCEPTABLE!

So the simple combination didn't work. Lets try a more complex linear combination:

Normalisation constant.

$$\psi(1,2) = \frac{1}{\sqrt{2}}\left[\psi_1(1)\,\psi_2(2) - \psi_1(2)\,\psi_2(1)\right] = \frac{1}{\sqrt{2}}\left[\phi_{1s}(1)\phi_{1s}(2)\chi_1(\alpha)\chi_2(\beta) - \phi_{1s}(2)\,\phi_{1s}(1)\,\chi_2(\alpha)\,\chi_1(\beta)\right]$$

$$\psi(1,2) = \frac{1}{\sqrt{2}}\left[\phi_{1s}(1)\,\phi_{1s}(2)\left[\chi_1(a)\chi_2(\beta) - \chi_2(\alpha)\chi_1(\beta)\right]\right]$$

Does it satisfy P.P? $-\psi(2,1) = \frac{-1}{\sqrt{2}}\left[\phi_{1s}(2)\,\phi_{1s}(1)\left[\chi_2(a)\chi_1(\beta) - \chi_1(\alpha)\chi_2(\beta)\right]\right] = \psi(1,2)$

→ Yes it does! Check it yourself and see!

We could write the acceptable combination as a determinant:

$$\psi(1,2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_1(1) & \psi_2(1) \\ \psi_1(2) & \psi_2(2)\end{vmatrix} = \frac{1}{\sqrt{2}}\left[\psi_1(1)\,\psi_2(2) - \psi_2(1)\,\psi_1(2)\right]$$

This is a Slater Determinant - automatically generates ψ's that satisfy the Pauli Principle. Nice!