

Multi-Electron Wavefunctions

For atoms with more than one electron, the wavefunction depends on the spatial and spin coordinates of each electron. eg- for a two-electron system:

$$\Psi(r_1, s_1; r_2, s_2; t)$$

The wavefunction also depends on time.

Electrons are necessarily indistinguishable. So if we swap spin and position of two electrons, all measurable quantities should remain unchanged.

$$\Rightarrow |\Psi(r_1, s_1; r_2, s_2; t)|^2 = |\Psi(r_2, s_2; r_1, s_1; t)|^2$$

Consider an operator whose effect swaps two electrons. When the operator \hat{O} acts on a wavefunction with two electrons, it can only produce the same wavefunction with an unknown phase change. Acting twice produces the initial wavefunction with same initial phase.

$$\text{so } \hat{O}\Psi = \lambda\Psi \quad \hat{O}\hat{O}\Psi = \hat{O}\lambda\Psi = \lambda(\lambda\Psi) = \lambda^2\Psi = \Psi$$

$$\Rightarrow \lambda^2 = 1$$

λ here is the eigenvalue of particle exchange.

If it is +1, the particles are called bosons.

If it is -1, the particles are called fermions.

Relativistic QM tells us we get +1 for integer spin particles and -1 for half integer spin particles.

So the electrons give -1 and are fermions.

Now let's think about two more operators. One operator that exchanges position of two electrons but not spin. And another that exchanges spin of two electrons but not position.

We find that to a good level of approximation, neither of these operators change the Hamiltonian, so they both commute with the Hamiltonian. We can thus write energy eigenstates which are also eigenstates of the operators. As with the particle exchange operator, applying either operator twice must give the initial wavefunction, so eigenvalues must be ± 1 . We find if the position swap operator has $+1$, the spin swap operator must have -1 and vice versa.

It is convenient to use single-electron orbitals as a complete set of states, i.e. quantum numbers n, m . So for our two electron atom, energy eigenstates are:

these are just the 1 we had in angular mom. section. Using m for second electron

$$\Psi(\zeta_1, s_1; \zeta_2, s_2; t) = \sum_{n, m, s_1, s_2} a_{n, m, s_1, s_2} \Psi_n(\zeta_1) \Psi_m(\zeta_2) |s_1\rangle |s_2\rangle$$

We said that with some approximation, these are also eigenstates of the spatial exchange and spin exchange operators. The approximation we make is to ignore interaction between spins and positions. We can factorise the above into the eigenstates of the two operators:

$$\Psi(\zeta_1, s_1; \zeta_2, s_2; t) = \sum_{n, m} a_{n, m} \Psi_n(\zeta_1) \Psi_m(\zeta_2) \sum_{s_1, s_2} b_{s_1, s_2} |s_1\rangle |s_2\rangle$$

$$\text{i.e. } a_{n, m, s_1, s_2} = a_{n, m} b_{s_1, s_2}$$

so $|b_{s_1, s_2}|^2$ is probability of electrons having spin s_1, s_2

$|a_{n, m}|^2$ is probability of electrons being in orbitals n, m

Spin-States of Multi-Electron Systems

For a two electron system, the complete basis of spin states is:

$$|\uparrow\rangle|\uparrow\rangle \quad |\uparrow\rangle|\downarrow\rangle \quad |\downarrow\rangle|\uparrow\rangle \quad |\downarrow\rangle|\downarrow\rangle$$

However, these states are not all eigenstates of the spin exchange operator.

A complete set which are eigenstates of the spin exchange operator is:

$$|\uparrow\rangle|\uparrow\rangle \quad \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle) \quad \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle) \quad |\downarrow\rangle|\downarrow\rangle$$

The first three have eigenvalue $+1$ under spin exchange operator (called even) and the last one has -1 (called odd).

So, using our approximation from the previous page, the first three have -1 under spatial exchange operator and the last one has $+1$.

The total spin is the vector sum of the spins of each electron.

$$\underline{\hat{S}} = \underline{\hat{S}}_1 + \underline{\hat{S}}_2$$

As with spin itself, we cannot simultaneously know every component of the total spin vector, but we can know \hat{S}^2 and one component, say \hat{S}_z .

The operator for z component of total spin is the sum of the z components of the individual spins:

$$\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z}$$

We can therefore work out a quantum number associated with the z component of the total spin for each of the four spin states we listed.

eg. for $|\uparrow\rangle|\uparrow\rangle$:

$$\begin{aligned}\hat{S}_z |\uparrow\rangle|\uparrow\rangle &= (\hat{S}_{1z} + \hat{S}_{2z}) |\uparrow\rangle|\uparrow\rangle = \hat{S}_{1z} |\uparrow\rangle|\uparrow\rangle + |\uparrow\rangle \hat{S}_{2z} |\uparrow\rangle \\ &= \hbar |\uparrow\rangle|\uparrow\rangle\end{aligned}$$

We say that this is quantum number 1. The other states have quantum numbers 0, 0, -1 in that order.