Atoms

The exact solution of the SE for multielectron systems cannot be found easily. Some qualitative features, however, can be deduced by considering a model in which electrons do not interact, e.g. $V_{ij}(r_{ij}) = 0$

Let us consider helium and assume infinite nuclear mass:

$$\hat{H} = \underbrace{\left[-\frac{\hbar^2}{2m_n}\nabla_n^2\right]}_{0 \text{ if } m_n=\infty} + \underbrace{\left[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{r_1}\right] + \left[-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{r_2}\right]}_{H_1 + H_2} + \underbrace{\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}}_{\text{ignore}}$$

The approximate solution is then

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{n\ell m}(\vec{r}_1)\,\psi_{n'\ell'm'}(\vec{r}_2)$$

where $\psi_{n\ell m}$ are hydrogen-like wave functions $(Z=2)$

The total energy of such state is

$$E = Z^2(E_n + E_{n'}) \quad \text{where} \quad E_n = \frac{-13.6\text{ eV}}{n^2}$$

For the ground state

$$\psi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3}\, e^{-\frac{2(r_1+r_2)}{a}}$$

Since the electrons are fermions the total wave function (including spin variables) must be anti-symmetric. This can be achieved by making the spin part of it antisymmetric and leaving the spatial part symmetric: If for hydrogen-like ion we have

$\psi = \psi_{n\ell m}(\vec{r})\,\chi(\vec{s})$ where χ is either $\chi_\downarrow$ or $\chi_\uparrow$

then

$$\psi(\vec{r}_1, \vec{s}_1, \vec{r}_2, \vec{s}_2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(r_2)\,\underbrace{\frac{1}{\sqrt{2}}\left[\chi_{\uparrow}(1)\,\chi_{\downarrow}(2) - \chi_{\downarrow}(1)\,\chi_{\uparrow}(2)\right]}_{\text{singlet spin state}}$$

If we recall addition of agular momenta, for $s_1 = \frac{1}{2}$ and $s_2 = \frac{1}{2}$ we get four possibilities to form eigenstates of S and M: The Clebsch-Gordan coefficients are trivial to obtain. Here are the eigenstates:

$$\left.|S=0, M=0\rangle = \frac{1}{\sqrt{2}}\left[|\tfrac{1}{2}\rangle|-\tfrac{1}{2}\rangle - |-\tfrac{1}{2}\rangle|\tfrac{1}{2}\rangle\right]\right\}\text{ singlet state}$$

$$\left.\begin{aligned} |S=1, M=-1\rangle &= |-\tfrac{1}{2}\rangle|\tfrac{1}{2}\rangle \\ |S=1, M=+1\rangle &= |\tfrac{1}{2}\rangle|\tfrac{1}{2}\rangle \\ |S=1, M=0\rangle &= \frac{1}{\sqrt{2}}\left[|\tfrac{1}{2}\rangle|-\tfrac{1}{2}\rangle + |-\tfrac{1}{2}\rangle|\tfrac{1}{2}\rangle\right] \end{aligned}\right\}\text{ triplet state}$$

The ground state of He is indeed a singlet one. The excited states (again, here we ignore the interaction between electrons) can be constructed in different ways. The first way is to have asymmetric spatial part and antisymmetric spin part. The second way is opposite: antisymmetric spatial part and symmetric spin part. Such combinations (more exactly states) are called parahelium and orthohelium respectively. The antisymmetric spatial part can be written as

$$\frac{1}{\sqrt{2}}\left[\psi_{nem}(\vec{r}_1)\,\psi_{n'e'm'}(\vec{r}_2) - \psi_{n'e'm'}(\vec{r}_1)\,\psi_{nem}(\vec{r}_2)\right]$$

We can consider larger atoms (i.e. atom with more electrons) much in the same way as we did He. If we ignore mutual repulsion of electrons they will occupy one-particle hydrogen-like states ψ_{nlm} (with a particular nuclear charge Z). If electrons were bosons they would all sit in the ground state ψ_{100}. However the Pauli principle allows only two electrons to occupy each hydrogen-like state. For any given n there are n^2 hydrogen-like orbitals. Thus $2n^2$ is the number of electrons that can be accomodated for each n value. These electrons form shells.

n	# electrons $= 2n^2$	possible angular momenta, ℓ
1	2	$\ell=0$
2	8	$\ell=0$, $\ell=1$
3	18	$\ell=0$, $\ell=1$, $\ell=2$

In each shell an electron has a particular value of ℓ and m. For historical reasons $\ell=0$ electrons are called s-electrons, $\ell=1$ electrons are called p-electrons, $\ell=2$ are called d-electrons, and so on (s, p, d, f, g, i, k, ...)

The filling of orbitals is usually given by configuration:

$$(1s)^2(2s)^2(2p)^2$$ ← how many (1 or 2)

The total angular momentum of all electrons, L, can be determined by adding sequentially the angular momenta of individual electrons, l_i. Shells that are completely filled carry no angular momentum

For each state of an atom we can also add individual spins of all electrons. Then L and S can be added, too, This will give a quantity called the total momentum: $\vec{J} = \vec{L} + \vec{S}$. Sets of states with particular L, S, and J values are usually denoted by the so called term symbols:

$$^{2S+1}L_J^{(e,o)}$$

where e or o stands for parity (even or odd).