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:

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

The approximate solution is then

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

where ψ_{nlm} are hydrogen-like wave functions $(Z=2)$

The total energy of such state is

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

For the ground state $\psi_{100} = \frac{Z^{3/2}}{\sqrt{\pi}\, a^{3/2}} e^{-\frac{Zr}{a}}$

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

Since the electrons are fermions the total wave function (including spin variables) must be antisymmetric. 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

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

then

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

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:

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

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

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 a symmetric 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

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

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 $\psi_{n\ell m}$ (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 $(s, p, d, f, g, i, k, \dots)$

The filling of orbitals is usually given by configuration:

$$(\underset{\underset{n}{\uparrow}}{1}\underset{\underset{\ell}{\nwarrow}}{s})^2(2s)^2(2p)^2 \longleftarrow \text{how many (1 or 2)}$$

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

For states of atoms we can also add individual spins of all electrons. This will give the total spin, S. Then $\vec{L}$ and $\vec{S}$ can be added too. The resulting angular momentum is called the total angular momentum J:

$$\vec{J} = \vec{L} + \vec{S}$$

Sets of states with particular values of L, S, and J are usually denoted using term symbols (atomic terms). They have the form

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

where $2S+1 = \varkappa$ is called multiplicity, L denotes the total angular momentum (S for $L=0$, P for $L=1$, D for $L=2$, F for $L=3$ and so on). For example, the term corresponding to the ground state of carbon atom (electronic configuration $(1s)^2(2s)^2(2p)^2$) is $^3P_0^e$, For the ground state of nitrogen we have $^4S^o_{3/2}$. The first excited state of nitrogen is $^2D^o_{5/2}$. The superscript e or o stands for even or odd states with respect to spatial reflection of all particles.

The term symbols for the ground states of atoms can be determined using Hund's rules (established empirically). There are three of them:

1. For a given electron configuration, the highest multiplicity term corresponds to the lowest energy.
2. For a given multiplicity, the term with the largest L corresponds to the lowest energy.
3. For a given term ^{x}L with the outermost subshell half-filled or less, the level with the lowest J value lies lowest in energy. If the outermost subshell is more than half-filled the level with the highest J value lies lowest.