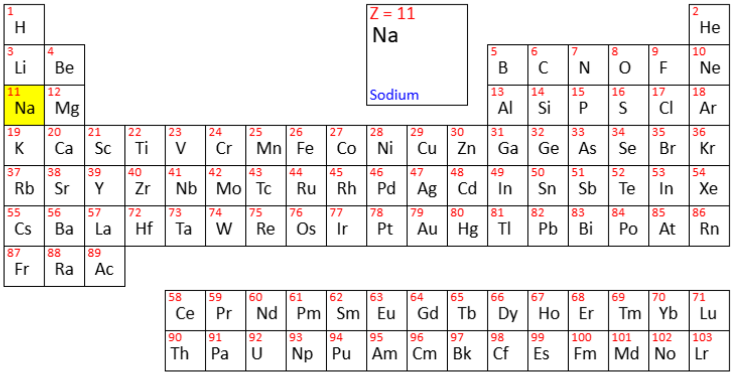
Modern Physics

Multi-electron Atoms



Hartree Approximation

The idea in this approximation is that each electron occupies a specific state with definite energy given by a wavefunction $\psi_k(\vec{r}_k,\sigma_k)$. Each wavefunction is an eigenvector solution to Schrödinger's equation of a spherical potential created by the nucleus and the other electrons.

If the electrons were distinguishable the wavefunction for the atom would be the product of these individual functions:

$$\psi_1(\vec{r}_1,\sigma_1)\psi_2(\vec{r}_2,\sigma_2)\ldots\psi_N(\vec{r}_N,\sigma_N)$$

However, since electrons are Fermions, the wavefunction needs to be antisymmetric. When exchanging two electrons the function needs to change sign. One way to construct such an antisymmetric wave function is with the Slater determinant:

$$\psi=\begin{vmatrix}\psi_1(\vec{r}_1,\sigma_1) & \psi_1(\vec{r}_2,\sigma_2) & \ldots & \psi_1(\vec{r}_N,\sigma_N)\\ \psi_2(\vec{r}_1,\sigma_1) & \psi_2(\vec{r}_2,\sigma_2) & \ldots & \psi_2(\vec{r}_N,\sigma_N)\\ \ldots & \ldots & \ldots & \ldots\\ \psi_N(\vec{r}_1,\sigma_1) & \psi_N(\vec{r}_2,\sigma_2) & \ldots & \psi_N(\vec{r}_N,\sigma_N)\end{vmatrix}$$

Notice that this automatically implies the Pauli Exclusion Principle. If any of the electrons occupied the same state as another electron, the determinant would vanish. Pauli had already determined this principle based on the understanding of the periodic table.

One detail about the periodic table is that originally Pauli thought that each angular quantum number ℓ admitted $2\ell+1$ states because the projection on the z-axis (L_z) has to be quantized from $-\ell$ to $+\ell$, but to get the periods right, the number has to be $2(2\ell+1)$. Where is the factor of 2 coming from? Pauli introduced an additional quantum number with only two possible values, which was later understood to be the spin.