MANY-ELECTRON ATOMS

The electrostatic Hamiltonian is

$$H = -\frac{\hbar^2}{2m^2}\sum_{j=1}^{N}\nabla_j^2 - \sum_{j=1}^{N}\frac{Ze^2}{r_j} + \sum_{j=1}^{N}\sum_{i<j}\frac{e^2}{r_{ij}}.$$

H is invariant under the exchange of electrons. P_{ij} interchanges the coordinates and spins of electrons i and j, e.g.

$$P_{12}\psi(1,2,3,\cdots,N) = \psi(2,1,3,\cdots,N).$$

P_{ij} is a symmetry operator, $[H, P_{ij}] = 0$. Since electrons are indistinguishable, this interchange cannot affect any physical property, including $|\psi|^2$. Therefore,

$$|P_{12}\psi(1,2,\cdots,N)|^2 = |\psi(1,2,\cdots,N)|^2, \text{ giving}$$

$$P_{12}\psi(1,2,\cdots,N) = \gamma\psi(1,2,\cdots,N),$$

where γ is a phase factor, $\gamma = e^{i\alpha}$, with α real. Applying P_{12} twice gives back the original function,

$$P_{12}^2\psi(1,2,\cdots,N) = \gamma^2\psi(1,2,\cdots,N) = \psi(1,2,\cdots,N),$$

so that $\gamma^2 = 1$ and $\gamma = \pm 1$. There is nothing in nonrelativistic quantum mechanics to tell us which is the correct sign. However, the two signs lead to very different physics. The most prominent example is that only particles with antisymmetric functions ($\gamma = -1$) obey the Pauli exclusion principle. Obviously, electrons fall into this category.

Particles with symmetric ψ ($\gamma = 1$) are called bosons, since they obey the Bose-Einstein statistics. These include photons and some elementary particles such as pions. They do not obey Pauli's principle, and many of them can live happily in the same level (the Bose-Einstein condensation at ultracold temperatures). Fermions (electrons, protons, neutrons) are particles obeying the Fermi-Dirac statistics. They have an antisymmetric function and obey Pauli. Relativistic quantum mechanics shows that bosons have integer spin (0,1,$\cdots$), while fermions have half-integer spin.

Model system: two identical particles in one dimension

This model, taken from the book by Morrison, Estle and Lane, demonstrates some of the prominent features of atomic systems, while not including all their complexities. The Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} + V(x_1) - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} + V(x_2) + V'(|x_1 - x_2|).$$

V is an attractive potential simulating the attraction to the nucleus, and V' is repulsive, similar to the interelectron repulsion. A perturbation approach is used, with

$$H^{(0)} = \sum_{i=1}^{2}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_i^2} + V(x_i)\right), \quad H^{(1)} = V'(|x_1 - x_2|).$$

We assume that the solutions of the one-particle equations are known,

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi_n^{(0)}(x) = E_n^{(0)}\psi_n^{(0)}(x),$$

so that the solutions of $H^{(0)}$ are

$$\psi_{n_1 n_2}^{(0)}(x_1 x_2) = \psi_{n_1}^{(0)}(x_1)\psi_{n_2}^{(0)}(x_2), \quad E_{n_1 n_2}^{(0)} = E_{n_1}^{(0)} + E_{n_2}^{(0)}.$$

$\psi^{(0)}_{n_1n_2}(x_1x_2)$ is neither symmetric nor antisymmetric under an interchange of x_1 and x_2. It is easy to write functions with the correct symmetry. For bosons,

$$^S\psi^{(0)}_{n_1n_2} = \frac{1}{\sqrt{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2) + \psi^{(0)}_{n_2}(x_1)\psi^{(0)}_{n_1}(x_2)\right],$$

and for fermions

$$^A\psi^{(0)}_{n_1n_2} = \frac{1}{\sqrt{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2) - \psi^{(0)}_{n_2}(x_1)\psi^{(0)}_{n_1}(x_2)\right].$$

If $n_1 = n_2$, the boson function only needs a different normalization, whereas the fermion function vanishes.

Bosons with zero spin

The zero-order function of the ground state is
$^S\psi^{(0)}_{11} = \psi^{(0)}_1(x_1)\psi^{(0)}_1(x_2)$. To first order,

$$E_{11} \approx 2E^{(0)}_1 + \langle {}^S\psi^{(0)}_{11}|V'(|x_1 - x_2|)\,{}^S\psi^{(0)}_{11}\rangle = 2E^{(0)}_1 + J_{11},$$

where the Coulomb integral

$$J_{nn'} \equiv \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^{(0)*}_n(x_1)\psi^{(0)*}_{n'}(x_2)V'\psi^{(0)}_n(x_1)\psi^{(0)}_{n'}(x_2)dx_1dx_2 =$$

$$= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi^{(0)}_n(x_1)|^2 V'(|x_1 - x_2|)|\psi^{(0)}_{n'}(x_2)|^2 dx_1dx_2.$$

The last step is allowed because V' is a multiplicative potential.

First excited state: in classical mechanics this state is twofold degenerate, since there is a function with boson 1 in $\psi^{(0)}_1$ and boson 2 in $\psi^{(0)}_2$ and another function with the two bosons exchanged. In quantum mechanics these two functions describe the same state, since identical particles are indistinguishable.

$$ {}^{S}\psi_{12}^{(0)} = \sqrt{\frac{1}{2}}\left[\psi_1^{(0)}(x_1)\psi_2^{(0)}(x_2) + \psi_1^{(0)}(x_2)\psi_2^{(0)}(x_1)\right] $$

$$E_{12} \approx E_1^{(0)} + E_2^{(0)} + \langle {}^{S}\psi_{12}^{(0)}|V'|{}^{S}\psi_{12}^{(0)}\rangle = E_1^{(0)} + E_2^{(0)} + J_{12} + K_{12},$$

where J is the Coulomb integral defined above and K is the exchange integral,

$$K_{nn'} \equiv \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi_n^{(0)*}(x_1)\psi_{n'}^{(0)*}(x_2)V'\psi_{n'}^{(0)}(x_1)\psi_n^{(0)}(x_2)dx_1dx_2.$$

The exchange integral has no classical analog. It appears because of the requirement that the wavefunction be symmetric.

For $V' > 0$ (repulsive potential) it can be shown that $J_{nn'} \geq K_{nn'} \geq 0$.

Two identical spin-1/2 fermions in one dimension

Here we must include the spin from the start. There will be four functions corresponding to fermions in orbitals $\psi_{n_1}^{(0)}, \psi_{n_2}^{(0)}$, differing by the spins:

$$ {}^{A}\psi_{n_1n_2++}^{(0)} = \sqrt{\frac{1}{2}}\left[\psi_{n_1}^{(0)}(x_1)\alpha(1)\psi_{n_2}^{(0)}(x_2)\alpha(2) - \psi_{n_2}^{(0)}(x_1)\alpha(1)\psi_{n_1}^{(0)}(x_2)\alpha(2)\right]$$

$$ {}^{A}\psi_{n_1n_2+-}^{(0)} = \sqrt{\frac{1}{2}}\left[\psi_{n_1}^{(0)}(x_1)\alpha(1)\psi_{n_2}^{(0)}(x_2)\beta(2) - \psi_{n_2}^{(0)}(x_1)\beta(1)\psi_{n_1}^{(0)}(x_2)\alpha(2)\right]$$

$$ {}^{A}\psi_{n_1n_2-+}^{(0)} = \sqrt{\frac{1}{2}}\left[\psi_{n_1}^{(0)}(x_1)\beta(1)\psi_{n_2}^{(0)}(x_2)\alpha(2) - \psi_{n_2}^{(0)}(x_1)\alpha(1)\psi_{n_1}^{(0)}(x_2)\beta(2)\right]$$

$$ {}^{A}\psi_{n_1n_2--}^{(0)} = \sqrt{\frac{1}{2}}\left[\psi_{n_1}^{(0)}(x_1)\beta(1)\psi_{n_2}^{(0)}(x_2)\beta(2) - \psi_{n_2}^{(0)}(x_1)\beta(1)\psi_{n_1}^{(0)}(x_2)\beta(2)\right]$$

These zero-order functions are degenerate, with energy $E^{(0)}_{n_1} + E^{(0)}_{n_2}$. Rather than solve 4×4 secular equations, we will look at the coupling of the two spins. $\vec{S} \equiv \vec{S}_1 + \vec{S}_2$ is an angular momentum. There exist therefore functions χ_{SM_S} which satisfy

$$S^2\chi_{SM_S} = S(S+1)\hbar^2\chi_{SM_S}, \quad S_z\chi_{SM_S} = M_S\hbar\chi_{SM_S}.$$

Since the vector addition of the two spins gives $|s_1 - s_2| \le S \le s_1 + s_2$, S can have the values 0 and 1. In all there will be 4 functions:

$$S = 0,\ M_S = 0; \quad S = 1,\ M_S = 1, 0, -1.$$

Since energies do not depend on M values, the 4 degenerate functions will split into two energy levels with degeneracy 1 (singlet) and 3 (triplet). This is indeed what happens in real system which resemble the model we are using. An example is the He atom in the $1s2s$ excited states, which appear as singlet and triplet.

We want to write the new functions $\psi^{(0)}_{n_1n_2SM_S}$ in terms of the old $\psi^{(0)}_{n_1n_2\pm\pm}$. Since $M_S = m_{s_1} + m_{s_2}$, two of the new functions can be written immediately,

$$\psi^{(0)}_{n_1n_211} = \psi^{(0)}_{n_1n_2++} \quad \text{and} \quad \psi^{(0)}_{n_1n_21-1} = \psi^{(0)}_{n_1n_2--}.$$

To find the two linear combinations of $\psi^{(0)}_{n_1n_2+-}$ and $\psi^{(0)}_{n_1n_2-+}$ ($M_S = 0$) which belong to $S = 1$ and $S = 0$, we apply S^- to $\psi^{(0)}_{n_1n_211}$:

$$S^-\psi^{(0)}_{n_1n_211} = \sqrt{2}\hbar\psi^{(0)}_{n_1n_210}$$

$$(S_1^- + S_2^-)\psi^{(0)}_{n_1n_2++} = \hbar(\psi^{(0)}_{n_1n_2+-} + \psi^{(0)}_{n_1n_2-+}).$$

From these equations we get

$$\psi^{(0)}_{n_1n_210} = \sqrt{\frac{1}{2}}\left(\psi^{(0)}_{n_1n_2+-} + \psi^{(0)}_{n_1n_2-+}\right).$$

The function for $S = 0, M_S = 0$ must be orthogonal, giving

$$\psi^{(0)}_{n_1n_200} = \sqrt{\frac{1}{2}}\left(\psi^{(0)}_{n_1n_2+-} - \psi^{(0)}_{n_1n_2-+}\right).$$

Using the definitions of $\psi^{(0)}_{n_1n_2\pm\pm}$ above we find

$$\psi^{(0)}_{n_1n_200} = \sqrt{\frac{1}{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2) + \psi^{(0)}_{n_2}(x_1)\psi^{(0)}_{n_1}(x_2)\right]\chi_{00}$$

$$\psi^{(0)}_{n_1n_21M_S} = \sqrt{\frac{1}{2}}\left[\psi^{(0)}_{n_1}(x_1)\psi^{(0)}_{n_2}(x_2) - \psi^{(0)}_{n_2}(x_1)\psi^{(0)}_{n_1}(x_2)\right]\chi_{1M_S}$$

The singlet spin function is $\chi_{00} = \sqrt{\frac{1}{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$.
The triplet functions are $\chi_{11} = \alpha(1)\alpha(2)$,
$\chi_{10} = \sqrt{\frac{1}{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)], \quad \chi_{1-1} = \beta(1)\beta(2)$.

Note that all the triplet functions have the same spatial part, which is different from that of the singlet. This means that the triplet functions have the same energy, again different from the singlet. All functions are antisymmetric under electron exchange. The triplet has a symmetric spin part and antisymmetric space part; the singlet has an antisymmetric spin part and symmetric space part. The energy difference between singlet and triplet is not caused by spin-spin interaction, which does not appear in our model. It results from the different symmetry of the spin functions, which leads to different space functions and different energy expressions.

Ground state ($n_1 = n_2 = 1$)

In this case all triplet functions vanish, and only the singlet remains, with the energy

$$E_{11} \approx 2E_1^{(0)} + J_{11} + K_{11}.$$

1st excited state ($n_1 = 1, n_2 = 2$)

To first order

$$E_{12} \approx E_1^{(0)} + E_2^{(0)} + \langle \psi_{12SM_S}^{(0)} | V' | \psi_{12SM_S}^{(0)} \rangle = E_1^{(0)} + E_2^{(0)} + J_{12} \pm K_{12},$$

where the + sign applies to the singlet and the − sign to the triplet. The energy of the triplet is lower. The reason: the spin function of the triplet is symmetric, so that the spatial part is antisymmetric. The function therefore vanishes for $x_1 = x_2$ and is small for $x_1 \approx x_2$ ("the Fermi hole"). If so, why are most molecular ground states singlets? Because most of them are closed shells, which give rise to singlets only. The ground state of He is $1s^2$, which is a singlet. The first excited state is $1s2s$, which has a singlet and a triplet state, with the triplet lower in energy.