

Permutation symmetry

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1 The spin-statistics theorem

Bosons are particles which obey Bose-Einstein statistics. This is the usual thermal distribution, particles with low energy being favored and the number in higher energy states tapering quickly as the energy exceeds the average. For a nondegenerate bosonic state, the expected number of particles in energy state E_i is

$$n_i(E_i) = \frac{1}{e^{(E_i - \mu)/kT} - 1}$$

There is no limit on the magnitude of n_i . By contrast, fermions are particles which obey Fermi-Dirac statistics, given for large numbers of fermions by

$$\langle n_i(E_i) \rangle = \frac{1}{e^{(E_i - \mu)/kT} + 1}$$

with the restriction of the exclusion principle, that no two fermions may occupy the same state at the same time. This means that we must always have $\langle n_i(E_i) \rangle \leq 1$.

In quantum field theory it is possible to prove that particles with integer spin $(0, 1, 2, \dots)$ must be bosons and particles with half-integer spin $(\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots)$ must be fermions.

It is also found in quantum field theory that fermion fields must always *anticommute*. For two fermion fields,

$$u_1 u_2 = -u_2 u_1$$

While arising from other considerations, antisymmetry under pairwise exchange enforces the exclusion principle, since for two particles in the same state, $u_1(x) = u_2(x) = u(x)$, the relation $u_1 u_2 = -u_2 u_1$ implies $u(x) = 0$.

2 A two-electron states

In hydrogen, we saw that the wave function was made up of a product of three parts,

$$\begin{aligned} \Psi &= \psi(r) \otimes |l, m_l\rangle \otimes \left| \frac{1}{2}, m_s \right\rangle \\ &= \psi(\mathbf{x}) \left| \frac{1}{2}, m_s \right\rangle \end{aligned}$$

describing the radial wave function, the orbital angular momentum state and the spin state.

Electrons are identical particles, and the combined state for multiple electrons must include terms for every possible interchange of pairs. Thus, while a two-electron state is built from products of 1-particle states, where

$$\psi_A(\mathbf{x}_1) \left| \frac{1}{2}, m_{s1} \right\rangle_A \psi_B(\mathbf{x}_2) \left| \frac{1}{2}, m_{s2} \right\rangle_B$$

describes particle A at position \mathbf{x}_1 with spin component m_{s1} and particle B at position \mathbf{x}_2 with spin component m_{s2} , we must also include a term $\psi_A(\mathbf{x}_2) \left| \frac{1}{2}, m_{s2} \right\rangle_A \psi_B(\mathbf{x}_1) \left| \frac{1}{2}, m_{s1} \right\rangle_B$ where the positions and spins are interchanged. The spin-statistics theorem tells us that the total wave function, $\Phi(\mathbf{x}_1, \mathbf{x}_2) \chi(m_{s1}, m_{s2})$ must be antisymmetric under the interchange of the identical electrons.

The total spin wave function is the combination of two spin- $\frac{1}{2}$ states,

$$\left| \frac{1}{2}, m_{s1} \right\rangle_A \left| \frac{1}{2}, m_{s2} \right\rangle_B$$

and we know how to add these. If the spins align, we have a triplet state, $\chi_{triplet} = |1, m\rangle$:

$$\begin{aligned} |1, 1\rangle &= \left| \frac{1}{2}, \frac{1}{2} \right\rangle_A \left| \frac{1}{2}, \frac{1}{2} \right\rangle_B \\ |1, 0\rangle &= \frac{1}{\sqrt{2}} \left(\left| \frac{1}{2}, -\frac{1}{2} \right\rangle_A \left| \frac{1}{2}, \frac{1}{2} \right\rangle_B + \left| \frac{1}{2}, \frac{1}{2} \right\rangle_A \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_B \right) \\ |1, -1\rangle &= \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_A \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_B \end{aligned}$$

while the remaining combination is a singlet:

$$\chi_{singlet} = |0, 0\rangle = \frac{1}{\sqrt{2}} \left(\left| \frac{1}{2}, -\frac{1}{2} \right\rangle_A \left| \frac{1}{2}, \frac{1}{2} \right\rangle_B - \left| \frac{1}{2}, \frac{1}{2} \right\rangle_A \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_B \right)$$

Notice that the triplet is symmetric under the interchange of particles, $A \Leftrightarrow B$, while the singlet is antisymmetric.

Similarly, the spatial wave function of the state may be symmetric,

$$\psi_A(\mathbf{x}_1) \psi_B(\mathbf{x}_2) + \psi_A(\mathbf{x}_2) \psi_B(\mathbf{x}_1)$$

or antisymmetric

$$\psi_A(\mathbf{x}_1) \psi_B(\mathbf{x}_2) - \psi_A(\mathbf{x}_2) \psi_B(\mathbf{x}_1)$$

The total state is therefore either

$$\frac{1}{\sqrt{2}} [\psi_A(\mathbf{x}_1) \psi_B(\mathbf{x}_2) + \psi_A(\mathbf{x}_2) \psi_B(\mathbf{x}_1)] |0, 0\rangle$$

or

$$\frac{1}{\sqrt{2}} [\psi_A(\mathbf{x}_1) \psi_B(\mathbf{x}_2) - \psi_A(\mathbf{x}_2) \psi_B(\mathbf{x}_1)] |1, m\rangle$$

to have the right total symmetry.

3 Example: Helium

For Helium, the spatial Hamiltonian is

$$\begin{aligned} \hat{H} &= \frac{\hat{\mathbf{p}}_1^2}{2m} + \frac{\hat{\mathbf{p}}_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \\ &= \hat{H}_0 + \frac{e^2}{r_{12}} \end{aligned}$$

where the potential terms give the potential energy due to the nucleus at position \mathbf{x}_1 , the nuclear potential energy at position \mathbf{x}_2 and finally the potential between the two electrons. We start by ignoring the interaction

of the two electrons and just looking at \hat{H}_0 , which is just the sum of two hydrogenic Hamiltonians. For this we have the simple products of hydrogen solutions with the product of the electric charges replaced by $2e^2$:

$$\psi_{total}(\mathbf{x}_1, \mathbf{x}_2) = \psi_{nlm}(\mathbf{x}_1) \psi_{nlm}(\mathbf{x}_2)$$

For the ground state, this is necessarily symmetric so the spin state must be the (antisymmetric) singlet,

$$\chi_{singlet} = |0, 0\rangle$$

from above,

$$\Psi = \psi_{100}(\mathbf{x}_1) \psi_{100}(\mathbf{x}_2) \chi_{singlet}$$

For one electron in an excited state this becomes either

$$\begin{aligned} \Psi &= \frac{1}{\sqrt{2}} (\psi_{100}(\mathbf{x}_1) \psi_{nlm}(\mathbf{x}_2) + \psi_{100}(\mathbf{x}_2) \psi_{nlm}(\mathbf{x}_1)) \chi_{singlet} \\ &= \psi_{sym}(\mathbf{x}_1, \mathbf{x}_2) \chi_{singlet} \end{aligned}$$

or

$$\begin{aligned} \Psi &= \frac{1}{\sqrt{2}} (\psi_{100}(\mathbf{x}_1) \psi_{nlm}(\mathbf{x}_2) - \psi_{100}(\mathbf{x}_2) \psi_{nlm}(\mathbf{x}_1)) \chi_{triplet} \\ &= \psi_{antisym}(\mathbf{x}_1, \mathbf{x}_2) \chi_{triplet} \end{aligned}$$

Now consider excited states, with the interaction term included as a perturbation. The perturbation energy takes the form

$$\begin{aligned} \Delta E_{\pm} &= \left\langle \frac{e^2}{r_{12}} \right\rangle_{\pm} = \frac{1}{2} \int d^3x_1 d^3x_2 \frac{e^2}{r_{12}} |(\psi_{100}(\mathbf{x}_1) \psi_{nlm}(\mathbf{x}_2) \pm \psi_{100}(\mathbf{x}_2) \psi_{nlm}(\mathbf{x}_1))|^2 \\ &= \frac{1}{2} \int d^3x_1 d^3x_2 \frac{e^2}{r_{12}} ((\psi_{100}(\mathbf{x}_1) \psi_{nlm}(\mathbf{x}_2) \pm \psi_{100}(\mathbf{x}_2) \psi_{nlm}(\mathbf{x}_1)) (\psi_{100}^*(\mathbf{x}_1) \psi_{nlm}^*(\mathbf{x}_2) \pm \psi_{100}^*(\mathbf{x}_2) \psi_{nlm}^*(\mathbf{x}_1))) \\ &= \frac{1}{2} \int d^3x_1 d^3x_2 \frac{e^2}{r_{12}} (\psi_{100}(\mathbf{x}_1) \psi_{nlm}(\mathbf{x}_2) \psi_{100}^*(\mathbf{x}_1) \psi_{nlm}^*(\mathbf{x}_2) + \psi_{100}(\mathbf{x}_2) \psi_{nlm}(\mathbf{x}_1) \psi_{100}^*(\mathbf{x}_2) \psi_{nlm}^*(\mathbf{x}_1)) \\ &\quad \pm \frac{1}{2} \int d^3x_1 d^3x_2 \frac{e^2}{r_{12}} (\psi_{100}(\mathbf{x}_2) \psi_{nlm}(\mathbf{x}_1) \psi_{100}^*(\mathbf{x}_1) \psi_{nlm}^*(\mathbf{x}_2) + \psi_{100}(\mathbf{x}_1) \psi_{nlm}(\mathbf{x}_2) \psi_{100}^*(\mathbf{x}_2) \psi_{nlm}^*(\mathbf{x}_1)) \\ &= \int d^3x_1 d^3x_2 \frac{e^2}{r_{12}} |\psi_{100}(\mathbf{x}_1)|^2 |\psi_{nlm}(\mathbf{x}_2)|^2 \\ &\quad \pm \int d^3x_1 d^3x_2 \frac{e^2}{r_{12}} \psi_{100}(\mathbf{x}_2) \psi_{100}^*(\mathbf{x}_1) \psi_{nlm}(\mathbf{x}_1) \psi_{nlm}^*(\mathbf{x}_2) \end{aligned}$$

The highest contribution to the energy comes from the plus sign, since the second integral turns out to be positive,

$$\Delta E_+ > \Delta E_-$$

Since ΔE_+ arises with the electrons in a symmetric state. As a result the electrons of the symmetric spatial configuration will be in the singlet spin state,

$$\Psi_+ = \psi_{sym}(\mathbf{x}_1, \mathbf{x}_2) \chi_{singlet} \quad \text{parahelium}$$

while the electrons in the lower energy state will be in the triplet configuration,

$$\Psi_- = \psi_{antisym}(\mathbf{x}_1, \mathbf{x}_2) \chi_{triplet} \quad \text{orthohelium}$$

These states are called parahelium and orthohelium, respectively. Parahelium states always have higher energy than orthohelium states.