

## Chapter 5

# Central concepts related to symmetry and gauge-invariance

Symmetries, conservation laws, and gauge-theories are crucial in many branches of physics. It is important to have a clear idea of what is meant by these concepts and why they are so powerful. Below, we provide an introduction to them.

### 5.1 The Pauli principle and the spin-statistics theorem

Particles which have the same mass, charge, and spin in quantum mechanics, such as electrons, are considered to be identical. This means that they cannot be distinguished. Unlike in classical physics, where the trajectory of identical particles can be followed (making them in principle distinguishable), there is no such concept of a trajectory in QM and we thus have no way of distinguishing between *e.g.* two electrons.

Consider a state consisting of two particles. The state of the system is described by the total wavefunction  $\Psi(\xi_1, \xi_2)$  where  $\xi = (\mathbf{r}, \sigma)$  is the coordinate for the position  $\mathbf{r}$  and  $z$ -component of the spin of each particle (assuming that the particle has spin - otherwise, the  $\sigma$  can simply be dropped). If the two particles are truly identical, then we should not be able to distinguish physically the state  $\Psi(\xi_2, \xi_1)$  from the above. This means that

$$|\Psi(\xi_1, \xi_2)|^2 = |\Psi(\xi_2, \xi_1)|^2 \quad (5.1)$$

which in turn means that

$$\Psi(\xi_1, \xi_2) = e^{i\theta} \Psi(\xi_2, \xi_1). \quad (5.2)$$

By repeating the argument, we see that  $e^{i\theta} = \pm 1$ . The wavefunction describing two identical particles must thus be either symmetric or antisymmetric under exchange of the two particles, a statement which is described by the following theorem.

**Spin-statistics theorem:** systems of identical particles that have integer spin (bosons) must have a total wavefunction that is symmetric under exchange of any two particles. The wavefunction is said to obey Bose-Einstein statistics.

Conversely, systems of identical particles that have half-integer spin (fermions) must have a

total wavefunction that is antisymmetric under exchange of any two particles. In statistical mechanics, it is the Fermi-Dirac distribution function which governs the distribution of fermions: the latter are thus stated to obey Fermi-Dirac statistics.

Consider now fermions for concreteness. A two-electron wavefunction will have the general form

$$\Psi(\xi_1, \xi_2) = \psi(\mathbf{r}_1, \mathbf{r}_2) \times \chi(\sigma_1, \sigma_2) \quad (5.3)$$

as long as we can neglect spin-orbit coupling - otherwise, the orbital  $\psi$  and spin  $\chi$  part cannot generally be factorized in this manner. There are two ways in which we can make the total wavefunction  $\Psi$  antisymmetric under exchange of  $\xi_1$  and  $\xi_2$ . One is that the spatial part  $\psi(\mathbf{r}_1, \mathbf{r}_2)$  is symmetric under  $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$  whereas the spin part is antisymmetric. The spin part must then be a singlet state  $\uparrow\downarrow - \downarrow\uparrow$ . The other possibility is that the spatial part is antisymmetric under exchange of the spatial coordinates, whereas the spin part is symmetric. The spin part is then in a triplet state  $\uparrow\uparrow, \downarrow\downarrow, \uparrow\downarrow + \downarrow\uparrow$ .

From the above considerations follows the so-called Pauli exclusion principle.

**Pauli principle:** no two fermions can be in exactly the same quantum state.

The state where the spatial part is symmetric (with the two electrons being in the same spatial quantum state) simultaneously as the spin part is symmetric (the spin of the two electrons is the same) is not allowed, which means that at least one quantum number must be different for the electrons (either a quantum number characterizing the spatial state or the spin quantum number).

### 5.1.1 Range of Pauli principle

Does the Pauli principle apply to any two electrons in the universe? Yes, the Pauli principle has an infinite range. However, it only has a practical consequence when the two electrons are close enough so that there is an overlap between their wavefunctions.

We know now that a wavefunction describing two electrons must be antisymmetric in their coordinates, including position. Neglect spin in what follows for brevity of notation. If we have two electrons 1 and 2 belonging to an atom where the eigenfunctions are labelled  $\psi_j$  where  $j$  is a quantum number describing the state, we can then antisymmetrize the total wavefunction in the following way to describe the total state:

$$\Psi(1, 2) = \psi_n(\mathbf{r}_1)\psi_m(\mathbf{r}_2) - \psi_m(\mathbf{r}_1)\psi_n(\mathbf{r}_2). \quad (5.4)$$

where  $(n, m)$  are a set of quantum numbers describing the state and  $(1, 2)$  describes the electron coordinates. Clearly, the above satisfies  $\Psi(1, 2) = -\Psi(2, 1)$ . The generalization of this to  $N$  fermions is called a Slater determinant. We see from this expression that the two electrons should not be able to reside in exactly the same type of state  $\psi_n$ , even if they have different positions, because the wavefunction then vanishes:

$$\psi_n(\mathbf{r}_1)\psi_n(\mathbf{r}_2) - \psi_n(\mathbf{r}_2)\psi_n(\mathbf{r}_1) = 0. \quad (5.5)$$

It is important to distinguish such a scenario from a case where two electrons belong to different atoms separated in space. In that case, these electrons can be in the same quantum state because

their wavefunctions are separated in space and thus centered around different points (the core of each atom). Let the separation distance between the atoms be  $\mathbf{R}$ . Then, their wavefunction is

$$\Psi(1, 2) = \psi_n(\mathbf{r}_1)\psi_m(\mathbf{r}_2 - \mathbf{R}) - \psi_m(\mathbf{r}_1 - \mathbf{R})\psi_n(\mathbf{r}_2) \quad (5.6)$$

Now, we see that even if  $m = n$ , the wavefunction does not vanish. It only vanishes if  $n = m$  and  $\mathbf{r}_1 = \mathbf{r}_2$ : the electrons cannot be at exactly the same position and in the same quantum state. This is the basic principle behind ferromagnetism: since electrons cannot be at the same position when they are in the same quantum state (both spins pointing in the same direction), they avoid the Coulomb interaction and lower the energy of the system.

A final note concerns Eq. (5.3). In light of how we wrote the antisymmetric wavefunction Eq. (5.4), one might be tempted to write a general two-electron wavefunction including spin on the form

$$\Psi(\xi_1, \xi_2) = \psi_n(\mathbf{r}_1)\chi(\sigma_1)\psi_m(\mathbf{r}_2)\chi(\sigma_2) - \psi_m(\mathbf{r}_1)\chi(\sigma_1)\psi_n(\mathbf{r}_2)\chi(\sigma_2) \quad (5.7)$$

by simply multiplying each wavefunction with a spin-part. However, we see that  $\chi(\sigma_1)\chi(\sigma_2)$  can be factored out in the above equation, meaning that only an equal spin triplet state could be adequately described in this way since  $\chi(\sigma_1)\chi(\sigma_2)$  is symmetric under the exchange  $\sigma_1 \leftrightarrow \sigma_2$ . Thus, Eq. (5.3) is more general.

### 5.1.2 Exchange energy from the Pauli principle: a quantum phenomenon

As mentioned previously, the antisymmetrization of the wavefunction has consequences when there is an overlap between the wavefunctions of the two quantum states  $\psi_n$  and  $\psi_m$ . To see this, consider as an example a Helium-like system where two electrons interact both with a nucleus  $Z$  and with each other. The total Hamiltonian is then

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12} = \left( -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} \right) + \left( -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2} \right) + \frac{e^2}{4\pi\epsilon_0 r_{12}}. \quad (5.8)$$

The expectation value for the energy is then

$$\langle E \rangle = \int \int \Psi(1, 2)^* \hat{H} \Psi(1, 2) d^3 r_1 d^3 r_2 \quad (5.9)$$

where  $\Psi(1, 2)$  is the wavefunction describing the two electrons. We know that this spatial part can be either symmetric or antisymmetric, depending on the spin state of the electrons. Let us therefore account for both possibilities by writing

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} [\psi_n(\mathbf{r}_1)\psi_m(\mathbf{r}_2) \pm \psi_m(\mathbf{r}_1)\psi_n(\mathbf{r}_2)] \quad (5.10)$$

so that the  $\pm$  corresponds to a singlet/triplet state. We don't need to write out the spin part explicitly because the Hamiltonian does not depend explicitly on spin, and thus this part plays no role in evaluating  $\langle E \rangle$ . However - it is important to emphasize that the *spin statistics* nevertheless will be seen to play a crucial role in that it determines the  $\pm$  sign of the spatial part.

Inserting the above wavefunction into the expectation value, we obtain

$$\langle E \rangle = E_1 + E_2 + E_{12} \quad (5.11)$$

where  $E_{12}$  is the e-e Coulomb repulsion energy

$$E_{12} = \int \int \Psi(1, 2)^* \frac{e^2}{4\pi\epsilon_0 r_{12}} \Psi(1, 2) d^3r_1 d^3r_2. \quad (5.12)$$

Interestingly, the Coulomb energy can be further divided into two parts:

$$E_{12} = D_{nm} \pm J_{nm} \quad (5.13)$$

by inserting  $\Psi(1, 2)$ , namely the direct Coulomb energy  $D_{nm}$  and the *exchange energy*  $J_{nm}$ :

$$\begin{aligned} D_{nm} &= \frac{e^2}{4\pi\epsilon_0} \int \int \psi_n^*(\mathbf{r}_1) \psi_m^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_n(\mathbf{r}_1) \psi_m(\mathbf{r}_2) d^3r_1 d^3r_2, \\ J_{nm} &= \frac{e^2}{4\pi\epsilon_0} \int \int \psi_n^*(\mathbf{r}_1) \psi_m^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_m(\mathbf{r}_1) \psi_n(\mathbf{r}_2) d^3r_1 d^3r_2. \end{aligned} \quad (5.14)$$

To get this, we used that  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| = r_{21}$ . The direct Coulomb energy probes the repulsion due to an electron density at  $\mathbf{r}_1$  and at  $\mathbf{r}_2$ . In the exchange energy integral, one instead effectively measures the overlap between the states  $\psi_n$  and  $\psi_m$  for the electrons 1 and 2, respectively, weighted by  $1/r_{12}$  (the separation distance between the electrons). Its existence is a direct consequence of the fact that the wavefunction is a superposition of states. Moreover, it is seen that if the wavefunctions  $\psi_n$  and  $\psi_m$  have no overlap, meaning that one is zero when the other is non-zero for all positions  $\mathbf{r}$ , the exchange integral  $J_{nm} \rightarrow 0$ . This is in contrast to the Coulomb term  $D_{nm}$

If  $J_{nm} > 0$ , it means that the energy of the system is minimized in the triplet configuration [the - sign in Eq. (5.13)]. Physically, this means that by aligning the spins of the electrons, they can maximize their separation distance and thus reducing the Coulomb repulsion energy. If  $J_{nm} < 0$ , the energy of the system is minimized in the singlet configuration. The exchange energy term is a purely quantum mechanical effect with no classical analogue.

### The ground-state of a two-electron system with spin-independent $\hat{H}$ is always spin-singlet

It is shown in the textbook "Theory of magnetism" by Mattis that the ground-state (lowest energy level) of a two-fermion system with spin-independent Hamiltonian is always spin-singlet. We give this proof below.

However, we also note in passing that a simple two-fermion model can still give a ferromagnetic exchange interaction if one considers wavefunctions which are in an excited state and uses *e.g.* first-order perturbation theory. This is for instance the case for the He-example considered above. If one of the electrons is in the 1s ( $n = 1$ ) state and the other is in an  $n > 1$  state where  $n$  is the principal quantum number, then one can show that the triplet configuration for the electrons always has lower energy than the singlet configuration. This is demonstrated by evaluating the exchange integrals for the two configurations. However, the ground-state for He must be a spin-singlet state, just like for the  $H_2$  molecule. When one considers *three or more electrons*, the ground-state can be ferromagnetic.

Therefore, we can state that simple two-fermion models can yield ferromagnetic coupling when using perturbation theory, but never in the ground-state: it will always be antiferromagnetically (singlet) coupled. We now give the proof for the latter statement following the textbook by D. C. Mattis.

*Proof:* Consider the two-fermion Schrödinger equation:

$$H\Psi(1, 2) = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2)\Psi(1, 2) + V(r_1, r_2)\Psi(1, 2) = E\Psi(1, 2). \quad (5.15)$$

Here,  $1 = (r_1, s_1)$  and similarly for 2. The Hamiltonian is not separable, i.e.  $H \neq H_1 + H_2$ . Therefore, the solution  $\Psi$  cannot be a product of one-body eigenfunctions and the energy eigenvalues  $E$  cannot be written as the sum of the individual particles' energies.

We note that if spin does not explicitly enter in  $H$ , we can consider a simpler eigenvalue problem

$$H\Phi(r_1, r_2) = E\Phi(r_1, r_2) \quad (5.16)$$

where all spin labels have been removed, so that  $\Phi$  is the spatial part of the wavefunction. If  $H$  is invariant under the interchange of spatial coordinates as it should be for identical particles. Moreover, we take  $\Phi$  to be real without loss of generality since the wavefunction of the time-independent Schrödinger equation (for a stationary solution) can always be chosen to be real. Due to the overall antisymmetry of the wavefunction dictated by the Pauli principle,  $\Phi(r_1, r_2)$  is *either* symmetric or antisymmetric under permutation of  $r_1$  and  $r_2$ . The belonging spin-part is then singlet or triplet. Let us moreover define a node as a point where a function crosses zero. Under these circumstances, we may state generally that:

*The ground-state wavefunction will be a nodeless, symmetric function  $\Phi$ . It is also unique (non-degenerate). Therefore, by the Pauli principle, the spin-part of the total particle wavefunction  $\Psi$  must be antisymmetric and singlet.*

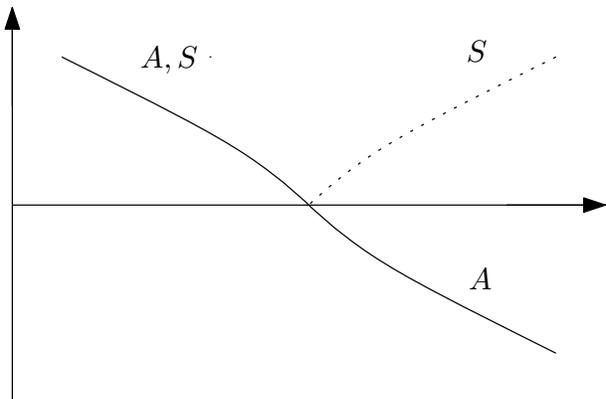
To see this, we use the principle of contradiction. Let us assume that the ground state is antisymmetric and see if there is some inconsistency. Suppose that the antisymmetric eigenstate  $A(\mathbf{r}_1, \mathbf{r}_2) = -A(\mathbf{r}_2, \mathbf{r}_1)$  is unique and corresponds to the lowest energy eigenvalue  $E_0$ . Its exact energy is:

$$E_0 = \frac{\int [\frac{\hbar^2}{2m}|\nabla_1 A(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\nabla_2 A(\mathbf{r}_1, \mathbf{r}_2)|^2 + V(\mathbf{r}_1, \mathbf{r}_2)A^2(\mathbf{r}_1, \mathbf{r}_2)] d^3r_1 d^3r_2}{\int A^2(\mathbf{r}_1, \mathbf{r}_2) d^3r_1 d^3r_2}. \quad (5.17)$$

Here, we used a partial integration to bring the  $\nabla^2$  term to a  $|\nabla|^2$  term, which can be done since the surface term must vanish for a normalizable wavefunction. This wavefunction has nodes whenever  $\mathbf{r}_1 = \mathbf{r}_2$  since it is antisymmetric:  $A(\mathbf{r}_1, \mathbf{r}_1) = 0$ .

Consider now instead a symmetric wavefunction  $S(\mathbf{r}_1, \mathbf{r}_2) = |A(\mathbf{r}_1, \mathbf{r}_2)|$ . This symmetric state cannot be an eigenstate of  $H$  for the following reason. In the perpendicular direction to the nodal surfaces defined by  $A = 0$ , the derivatives of  $S$  are discontinuous since  $S$  has a cusp at those surfaces. Thus,  $S$  has a discontinuous normal derivative to the nodal surface. But cusps are not allowed in the eigenfunction if the potential that enters the SE is non-singular. This can be seen by considering in 1D  $\psi'' = (V - E)\psi$  which shows that if  $V$  is non-singular,  $\psi''$  cannot be singular and hence  $\psi'$  cannot be discontinuous (*e.g.* derivative of step-function is Dirac delta).

The situation is illustrated in the figure below where  $A$  and  $S$  are plotted along a direction normal to a nodal surface of  $A$ .



If such an  $S(\mathbf{r}_1, \mathbf{r}_2)$  is used to calculate the expectation value of  $H$ , we obtain a "variational" energy  $E_S$  which has to be higher than the ground-state since  $S(r_1, r_2)$  does not satisfy the Schrödinger equation. Now, the variational energy obtained using  $S$  as a trial function is by definition given by:

$$E_S = \frac{\int [\frac{\hbar^2}{2m} |\nabla_1 S(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\nabla_2 S(\mathbf{r}_1, \mathbf{r}_2)|^2 + V(\mathbf{r}_1, \mathbf{r}_2) S^2(\mathbf{r}_1, \mathbf{r}_2)] d^3 r_1 d^3 r_2}{\int S^2(\mathbf{r}_1, \mathbf{r}_2) d^3 r_1 d^3 r_2}. \quad (5.18)$$

This is true despite the fact that  $\nabla S$  is not defined at the nodal surfaces defined by  $A(\mathbf{r}_1, \mathbf{r}_2) = 0$ , i.e. a 5-dimensional surface, for the following reason. We have that  $|\nabla A|^2 = |\nabla|A||^2 = |\nabla S|^2$  everywhere *except* at the cusp points where  $\nabla S$  is discontinuous in the direction normal to the surface. So why have we written the integral above over the entire region of space, i.e. integrating over all values of  $\mathbf{r}_1$  and  $\mathbf{r}_2$ ? Shouldn't we exclude the nodal surfaces?

Yes, we should, but here is the point: the contribution to the integral from those surfaces is exactly zero. This can be understood by noting that the contribution to an  $n$ -dimensional integral from a  $(n - 1)$ -dimensional surface is zero. Consider for instance the 1D integral  $\int_a^b f(x) dx$ . The contribution to this integral from one single point (0-dim surface) is zero since the point has no width. The only exception would be if the integrand is a Dirac  $\delta$ -function at that point, but that is not the case for the system we consider: the normal derivative is discontinuous and not singular at the nodal surface. Similarly, consider a 2D integral  $\int \int f(x, y) dx dy$ . The contribution to this integral from a single curve  $y = y(x)$  is zero, because the area of a 1D curve is zero. We can now generalize this all the way up to 6 dimensions. Just like a 2D surface has zero volume (in 3D), a 5D surface has zero volume in 6D and does not contribute to the integral.

Therefore, we have proven that

$$E_S = E_0. \quad (5.19)$$

But according to what we just stated concerning the variational principle,  $E_S > E_0$ . Yet the above equation shows that  $E_S = E_0$ . This is inconsistent and proves that an antisymmetric state  $A$  cannot be the ground state.

We close by mentioning that by similar argumentation one shows that the symmetric state of lowest energy, the true ground state, is nodeless. In that case, if we first assume that the true ground state is a nodeless function  $F$ , then the absolute value of  $F$  is either  $+F$  or  $-F$  and hence no contradiction appears when using the variational energy for  $|F|$ . Moreover, since two nodeless states cannot be orthogonal and the eigenfunctions of  $H$  should form an orthonormal complete set, the ground state

of the two-electron is non-degenerate and unique.

The take-home message here is then that even if  $\hat{H}$  is spin-independent, the energy of the system depends on the spin-configuration of the particles.