Advanced Quantum Physics
Week 8

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Identical particles in quantum mechanics

I may want to say a bit more about trajectories and that macroscopic objects can still be distinguished from the trajectory even if they are identical.

Unlike macroscopic objects that can always be distinguished on the basis of their properties (e.g. their color, their shape, etc.) or from their trajectories, some fundamental quantum particles such as electrons are completely identical. This means that there is no intrinsic property that allows to distinguish them. Any two electrons have the same mass, same charge, same spin-1/2. As we will see, identical particles require a special treatment in quantum mechanics. More specifically, the wavefunction of several identical particles must have symmetry properties under the exchange of two particles.

The many-particle wavefunction

Let us imagine we have a quantum mechanical system with two particles. To simplify the notation, we suppose that they are only characterized by a position (we neglect e.g. spin degrees of freedom, etc.). The total wavefunction that described this system is a function $\Psi(\vec{r}_1, \vec{r}_2) \in \mathcal{L}^2(\mathbb{R}^3) \otimes \mathcal{L}(\mathbb{R}^3)$. The modulus square of this wavefunction $|\Psi(\vec{r}_1, \vec{r}_2)|^2$ expresses the probability to find the first particle at $\vec{r}_1$ if the second particle is at $\vec{r}_2$. If the two particles are distinguishable, for example an electron and a proton, the wavefunction does not need to have any particular symmetry under the exchange of the proton and the electron. In general we have $|\Psi(\vec{r}_1, \vec{r}_2)| \neq |\Psi(\vec{r}_2, \vec{r}_1)|$.

The situation is very different is the two particles are completely indistinguishable (for example two electrons). Any physical quantity computed from the state $\Psi(\vec{r}_1, \vec{r}_2)$ has to be the same if the two electrons are exchanged. Indeed, there is absolutely no way to tell the difference between a system with two electrons and the same system with the two electrons exchanged, precisely because they are identical. So when we are dealing with identical particles, we expect that $|\Psi(\vec{r}_1, \vec{r}_2)|^2 = |\Psi(\vec{r}_2, \vec{r}_1)|^2$. Or in other words, we

generally expect that $\Psi(\vec{r}_2, \vec{r}_1) = e^{i\alpha}\Psi(\vec{r}_1, \vec{r}_2)$. But because exchanging particles twice should bring you to the exact same state, one can expect to have

$$\Psi(\vec{r}_1, \vec{r}_2) = \pm\Psi(\vec{r}_2, \vec{r}_1) \qquad \text{identical particles}$$

Therefore, when dealing with identical particles, the wavefunction must be either symmetric or antisymmetric under the exchange of two particles.

The permutation operator

Let us formalize things and introduce the permutation operator $\hat{P}_{12}$ that exchanges particle 1 and particle 2.

$$\hat{P}_{12}\,|1:\psi_a\rangle \otimes |2:\psi_b\rangle = |1:\psi_b\rangle \otimes |2:\psi_a\rangle,$$

where $|1:\psi_a\rangle \otimes |2:\psi_b\rangle$ is a wavefunction describing the first particle in the state $|\psi_a\rangle$ and the second particle in the state $|\psi_b\rangle$. We clearly have the following properties for the permutation operator $\hat{P}_{12}$

- Involution: $\hat{P}_{12}^2 = \mathbb{1}$

- Hermitian: $\hat{P}_{12}^\dagger = \hat{P}_{12}$

- Unitary: $\hat{P}_{12}\hat{P}_{12}^\dagger = \hat{P}_{12}^\dagger\hat{P}_{12} = \mathbb{1}$

- Eigenvalues of $\hat{P}_{12}$ are ± 1

Using the permutation operator, we can rewrite the expected condition for the wavefunction of identical particles:

$$\hat{P}_{12}\,|1:\psi_a\rangle \otimes |2:\psi_b\rangle = \pm|1:\psi_a\rangle \otimes |2:\psi_b\rangle$$

We see that the wavefunction for identical particles must be an eigenvector of the permutation operator.

Time evolution

If we are considering two identical particles, the Hamiltonian that describes this system must be invariant under the exchange of the particles. We must therefore have

$$[\hat{\mathcal{H}}, \hat{P}_{12}] = 0$$

This means that also the evolution operator commutes with the permutation operator

$$[\hat{U}(t, t_0), \hat{P}_{12}] = 0$$

If at some time the system is described by a symmetric eigenstate of the permutation operator (with eigenvalue $+1$), then it will continue to be a symmetric eigenstate of $\hat{P}_{12}$ at later times. The same property is true for antisymmetric eigenstates.

It seems that at that stage we could conclude that a system of two identical particles must be described by either a symmetric or an antisymmetric wavefunction. This nevertheless comes with a contradiction. If the same system can in different conditions be either in a symmetric or in an antisymmetric wavefunction, one could imagine that it is possible to create a linear superposition of a symmetric and an antisymmetric state. That linear combination would not be an eigenstate of the permutation operator and contradicts our assumption $\hat{P}_{12}|1 : \psi_a\rangle \otimes |2 : \psi_b\rangle = \pm|1 : \psi_a\rangle \otimes |2 : \psi_b\rangle$. In order to avoid this contradiction, we have to postulate that some systems will always be in a symmetric state and some others always in an antisymmetric state!

The symmetry postulate and the spin-statistics theorem

The symmetry postulate states that all particles in nature belong to one of the two following categories

- **Bosons**: For these particles, the state of the system is described by a wavefunction that is *symmetric* under the exchange of two identical particles

$$\hat{P}_{12}|\Psi\rangle = |\Psi\rangle$$

  Examples of bosons are π mesons, photons, ...

- **Fermions**: For these particles, the state of the system is described by a wavefunction that is *antisymmetric* under the exchange of two identical particles

$$\hat{P}_{12}|\Psi\rangle = -|\Psi\rangle$$

  Examples of fermions are electrons, neutrinos, quarks, protons, neutrons, ...

You may notice in the examples above that particles with *integer spin are bosons*, while particles with *half-integer spin are fermions*. Under weak assumptions, this result can be proved. This is the so-called spin-statistics theorem.

An important consequence of the postulate is that two independent fermions cannot be in the same quantum state $|\psi\rangle$. Indeed, the generic wavefunction for two fermions must be antisymmetric and therefore always has the form

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\left(|1 : \psi_a\rangle \otimes |2 : \psi_b\rangle - |1 : \psi_b\rangle \otimes |2 : \psi_a\rangle\right)$$

If the fermions are in the same quantum state $|\psi\rangle$, we would have $|\psi\rangle = |\psi_a\rangle = |\psi_b\rangle$ and the wavefunction would be zero. The impossibility for two fermions to be in the same state is called the *Pauli exclusion principle*.

Composite particles

If several fermions and bosons are gathered together to form a composite particle, the latter can be seen as a single fermion or boson. To decide whether it is a boson or a fermion it is enough to use the spin-statistics theorem and see if the composite particle has half or integer spin. Recalling the rules of the addition of angular momentum, we see that a combination of several bosons will always have integer spin. Instead the combination of several fermions will have integer spin for an even number of fermions and half-integer spin for an odd number of fermions. To summarize

- A composite particle is a fermion if it contains an odd number of fermions. Otherwise it is a boson.

- Examples of fermionic composite particles are protons and neutrons (made of 3 quarks) while the α particle (2 protons and 2 neutrons) or the hydrogen atom (1 proton and 1 electron) are bosonic composite particles.

System of N independent particles

Let us consider a system of N quantum particles. As we have discussed earlier, it is in general very difficult, if not impossible, to solve the Schrödinger equation when the particles are interacting. A starting point is therefore often to solve the problem where we neglect the interactions between the particles and suppose they are independent. The solutions obtained like this provide a first approximation and can later be used as a platform to construct, e.g. a perturbation theory. So let us write the Hamiltonian of this non-interacting system. It is a sum of one-particle Hamiltonians

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2 + \cdots + \hat{\mathcal{H}}_N,$$

where $\hat{\mathcal{H}}_n = \mathbb{1} \otimes \cdots \otimes \hat{h} \otimes \cdots \otimes \mathbb{1}$ describes the action of the single-particle Hamiltonian $\hat{h}$ on the nth particle. The Hamiltonian $\hat{h}$ could e.g. be the Hamiltonian of an electron in a Coulomb potential or that of an electron in a periodic potential, etc. We suppose the eigenstates and eigenenergies of this single-particle Hamiltonian are known and given by

$$\hat{h}|\psi_\alpha\rangle = E_\alpha|\psi_\alpha\rangle$$

We can now try to write the N-particle eigenstates $|\Psi_{\alpha_1,...,\alpha_n}\rangle$ of the full Hamiltonian $\hat{\mathcal{H}}$. If the particles are distinguishable, this is easy and we would just write

$$|\Psi_{\alpha_1,...,\alpha_n}\rangle = |1 : \psi_{\alpha_1}\rangle \otimes |2 : \psi_{\alpha_2}\rangle \otimes \cdots \otimes |N : \psi_{\alpha_N}\rangle$$

It is an instructive exercise to check that this is indeed an eigenstate of $\hat{\mathcal{H}}$ with eigenenergy $E = E_{\alpha_1} + E_{\alpha_2} + \ldots + E_{\alpha_n}$

$$\hat{\mathcal{H}}|\Psi_{\alpha_1,...,\alpha_n}\rangle = (E_{\alpha_1} + E_{\alpha_2} + \ldots + E_{\alpha_n})|\Psi_{\alpha_1,...,\alpha_n}\rangle$$

Note that in the expression above, there is no constraint whatsoever on the α_n and some of them can be identical. Rather than writing the wavefunction explicitly, one can also use a graphical representation. For example, the wavefunction $|1 : \psi_2\rangle \otimes |2 : \psi_0\rangle \otimes |3 : \psi_3\rangle \otimes |4 : \psi_0\rangle$ could be represented by
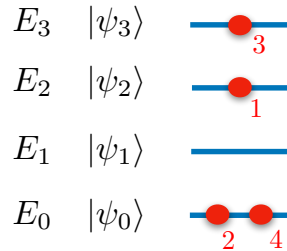
Looking at the figure, one can immediately read the eigenenergy of the state $E = 2E_0 + E_2 + E_3$.
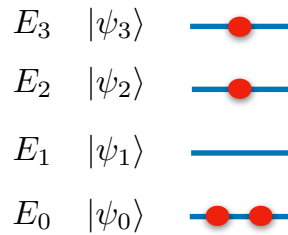
N independent bosons

The situation changes slightly if one considers a set of N identical bosons. In that case the eigenstates $|\Psi^{\text{bosons}}_{\alpha_1,...,\alpha_n}\rangle$ must have the property that they are symmetric under the exchange of any two bosons. More generally, if the bosons are exchanged according to some permutation $p = \{p(0),...,p(N)\}$ of $\{1,...,N\}$, the symmetry postulate imposes that

$$\hat{P}_p|\Psi^{\text{bosons}}_{\alpha_1,...,\alpha_N}\rangle = |\Psi^{\text{bosons}}_{\alpha_1,...,\alpha_N}\rangle \qquad \forall p,$$

where we introduced the permutation operator $\hat{P}_p$. Clearly the wavefunctions we wrote above for distinguishable particles does not have this property. On the other hand, if we start from the wavefunction $|1:\psi_{\alpha_1}\rangle\otimes|2:\psi_{\alpha_2}\rangle\otimes\cdots\otimes|N:\psi_{\alpha_N}\rangle$ and exchange two indices, say α_m and α_n, the new obtained state is still an eigenstate of the Hamiltonian with the same energy. Actually, any permutation of the indices α_n will create an eigenstate with the same energy. Therefore for a given set $\{\alpha_1,...,\alpha_N\}$, there are $N!$ states with the same energy $E = E_{\alpha_1} + ... + E_{\alpha_n}$. We just have to find a linear combination of these states that has the property to be symmetric under any permutation of bosons. Clearly, taking the sum of all the $N!$ degenerate states has this property. We can conclude that the eigenstates for N identical bosons have the form

$$|\Psi^{\text{bosons}}_{\alpha_1,...,\alpha_N}\rangle = \frac{C}{\sqrt{N!}} \sum_p \hat{P}_p |1:\psi_{\alpha_1}\rangle \otimes \cdots \otimes |N:\psi_{\alpha_n}\rangle$$

where the sum is over all permutations p of $\{1,...,N\}$ and C is a normalization constant. The reason for this normalization constant is that if some of the α_n's are the same, then some of the permutations yield the same state and therefore there will be less than $N!$ distinct states in the sum. The energy associated to this state is still $E = E_{\alpha_1} + \cdots + E_{\alpha_N}$. But with the symmetry constraint there is now only a single eigenstate for a given set of $\{\alpha_1,...,\alpha_N\}$, while there were many different degenerate eigenstates when we considered distinguishable particles. We can also use a graphical representation for bosons, but this time there are no labels on the particles because it is understood that the associated eigenstate is a sum over all permutations of labels. For example, the wavefunction $|\Psi^{\text{bosons}}_{0,0,2,3}\rangle$ can be represented as

N independent fermions

We now turn to the case of N independent fermions and look for the eigenstates $|\Psi^{\text{fermions}}_{\alpha_1,...,\alpha_N}\rangle$ of the Hamiltonian. This time the wavefunction must have the property that it is antisymmetric under the exchange of any two fermions. Generally this translates into the

condition

$$\hat{P}_p \,|\Psi^{\text{fermions}}_{\alpha_1,...,\alpha_N}\rangle = (-1)^p \,|\Psi^{\text{fermions}}_{\alpha_1,...,\alpha_N}\rangle,$$

where $(-1)^p$ is the signature of the permutation. The way to create such a wavefunction from the eigenstates $|\psi_\alpha\rangle$ is to construct what is known as a *Slater determinant*

$$|\Psi^{\text{fermions}}_{\alpha_1,...,\alpha_N}\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |1 : \psi_{\alpha_1}\rangle & |1 : \psi_{\alpha_2}\rangle & \ldots & |1 : \psi_{\alpha_N}\rangle \\ |2 : \psi_{\alpha_1}\rangle & |2 : \psi_{\alpha_2}\rangle & \ldots & |2 : \psi_{\alpha_N}\rangle \\ \vdots & \vdots & & \vdots \\ |N : \psi_{\alpha_1}\rangle & |N : \psi_{\alpha_2}\rangle & \ldots & |N : \psi_{\alpha_N}\rangle \end{vmatrix}$$

The eigenstates $|\Psi^{\text{fermions}}_{\alpha_1,...,\alpha_N}\rangle$ are expressed in terms of a determinant whose lines are associated to the different particles and the columns to the different α_n's. Exchanging two particles corresponds to exchanging two lines with brings a minus sign to the determinant and thus implements the symmetry postulate. Also, it is clear that all the α_n must be different, otherwise the matrix would have two identical lines and the determinant would vanish. This is just the Pauli exclusion principle. The eigenstate again has eigenvalue $E = E_{\alpha_1} + \ldots + E_{\alpha_n}$. It can also be represented graphically and just like for bosons there will be no labels on the particles as it is understood that the associated eigenstate is constructed with a Slater determinant. The only difference with bosons is that, in accordance with the Pauli exclusion principle, two particles cannot be on the same state. For example, the eigenstate $|\Psi^{\text{fermions}}_{0,2,3}\rangle$ would be represented by
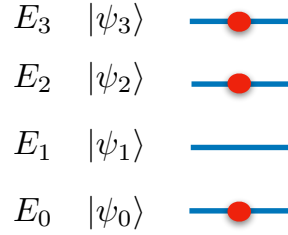
Ground-state for N independent identical particles

Using the results above, we can see how to construct the ground-state for a systems of identical particles. If we have a system of N bosons, the lowest energy state is obtained by having all bosons in the lowest energy level $|\psi_0\rangle$. The corresponding wavefunction is $|\Psi^{\text{bosons}}_{0,...,0}\rangle = |1 : \psi_0\rangle \otimes \cdots \otimes |N : \psi_0\rangle$. The ground-state energy is $E = N\,E_0$ and it is non-degenerate (unless the original energy E_0 was degenerate). For a system of N fermions, because two fermions cannot occupy the same quantum state, the ground-state is constructed by progressively filling states from the lowest level. The ground-state energy is $E = E_0 + \cdots + E_{N-1}$ and the associated eigenstate is $|\Psi^{\text{fermions}}_{0,1,...,N-1}\rangle$. Here is an illustration of the ground state for four bosons (on the left) and four fermions (on the right).

bosons   fermions
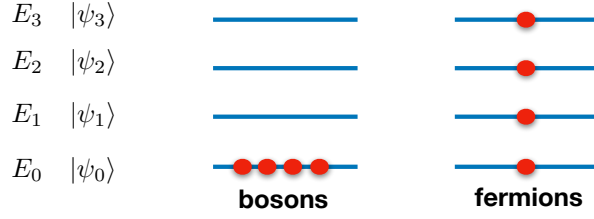
Space and spin wavefunctions

We have expressed the eigenstates of a set of independent particles in terms of the eigenstates $|\psi_\alpha\rangle$ of the single-particle Hamiltonian $\hat{h}$. Very often, the wavefunction will have a spatial part and a spin part. If we consider a particle with spin-1/2, the wavefunction could be written as

$$|\psi_\alpha\rangle = |\phi_\alpha\rangle \otimes |\sigma_\alpha\rangle,$$

where $|\sigma_\alpha\rangle = |1/2, \sigma_\alpha\rangle$ is the eigenstate of the $\hat{S}_z$ operator with eigenvalue $\sigma_\alpha\hbar$ and $|\phi_\alpha\rangle$ describes the spatial wavefunction. If the Hamiltonian is *spin-independent*, the eigenenergies will have a degeneracy, e.g. they would be twice degenerate for a spin-1/2. In that case, the states can be described by two equivalent representations, as shown here
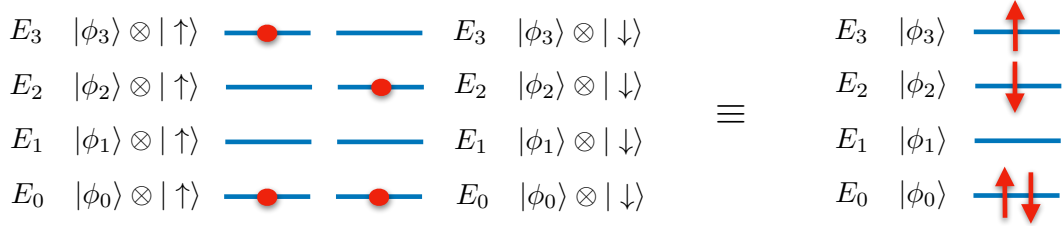
On the left, we use the same representation as above and there are two lines at every degenerate energy level, one for the $|\uparrow\rangle$ spin state and one for the $|\downarrow\rangle$ spin state. We are dealing with fermions, so only one particle can occupy a given level. On the right, the same state is represented but every energy level appears only once. The degeneracy is expressed by the possibility to put either an arrow up or an arrow down on the level. It is very common to see the representation on the right.

Factorizing the wavefunction for two independent electrons

Let us take the example of two independent electrons characterized by a spin-independent Hamiltonian. It could be the Hamiltonian for e.g. a helium atom where the Coulomb repulsion between the electrons is ignored. We want to write the wavefunction for a given eigenstate of the system. In this example, we will consider the eigenstate corresponding to having one electron in the ground state ϕ_0 and one electron in an excited state ϕ_1. The corresponding eigenenergy is $E = E_0 + E_1$ and it is four times degenerate. Because of this degeneracy, there are several ways to organize the four eigenstates. A possible approach is to start from the four representations

$$E_1 \quad |\phi_1\rangle$$
$$E_0 \quad |\phi_0\rangle$$

$$\frac{1}{\sqrt{2}}\Big(|\phi_0;\phi_1\rangle \otimes |\uparrow\uparrow\rangle \\ -|\phi_1;\phi_0\rangle \otimes |\uparrow\uparrow\rangle\Big)$$

$$\frac{1}{\sqrt{2}}\Big(|\phi_0;\phi_1\rangle \otimes |\uparrow\downarrow\rangle \\ -|\phi_1;\phi_0\rangle \otimes |\downarrow\uparrow\rangle\Big)$$

$$\frac{1}{\sqrt{2}}\Big(|\phi_0;\phi_1\rangle \otimes |\downarrow\uparrow\rangle \\ -|\phi_1;\phi_0\rangle \otimes |\uparrow\downarrow\rangle\Big)$$

$$\frac{1}{\sqrt{2}}\Big(|\phi_0;\phi_1\rangle \otimes |\downarrow\downarrow\rangle \\ -|\phi_1;\phi_0\rangle \otimes |\downarrow\downarrow\rangle\Big)$$

The Slater determinant is shown below every representation. We have found four eigenstates with the required antisymmetry under particles exchange:

1. $\frac{1}{\sqrt{2}}\Big(|\phi_0;\phi_1\rangle - |\phi_1;\phi_0\rangle\Big) \otimes |\uparrow\uparrow\rangle$

2. $\frac{1}{\sqrt{2}}\Big(|\phi_0;\phi_1\rangle \otimes |\uparrow\downarrow\rangle - |\phi_1;\phi_0\rangle \otimes |\downarrow\uparrow\rangle\Big)$

3. $\frac{1}{\sqrt{2}}\Big(|\phi_0;\phi_1\rangle \otimes |\downarrow\uparrow\rangle - |\phi_1;\phi_0\rangle \otimes |\uparrow\downarrow\rangle\Big)$

4. $\frac{1}{\sqrt{2}}\Big(|\phi_0;\phi_1\rangle - |\phi_1;\phi_0\rangle\Big) \otimes |\downarrow\downarrow\rangle$

These four states span the eigensubspace associate to the eigenenergy $E = E_0 + E_1$. They could for example be used to start the construction of a degenerate perturbation theory. Of course any linear combination of these states will still have the required antisymmetry. It turns out that there is a better choice for a basis of the eigensubspace. Indeed, while the first and fourth eigenstates above are factorized as the product of a spatial wavefunction and a spin part, this is not true for the second and third states. Instead, using the sum and the difference of these two states one obtains a new basis

1. $\frac{1}{\sqrt{2}}\Big(|\phi_0;\phi_1\rangle - |\phi_1;\phi_0\rangle\Big) \otimes |\uparrow\uparrow\rangle$

2. $\frac{1}{\sqrt{2}}\Big(|\phi_0;\phi_1\rangle + |\phi_1;\phi_0\rangle\Big) \otimes \frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\Big)$

3. $\frac{1}{\sqrt{2}}\Big(|\phi_0;\phi_1\rangle - |\phi_1;\phi_0\rangle\Big) \otimes \frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\Big)$

4. $\frac{1}{\sqrt{2}}\Big(|\phi_0;\phi_1\rangle - |\phi_1;\phi_0\rangle\Big) \otimes |\downarrow\downarrow\rangle$

Now all the states are written simply as the product of a spatial part multiplying a spin part. There are two groups of states. Three states are written as the product of an antisymmetric spatial wavefunction $\frac{1}{\sqrt{2}}\Big(|\phi_0;\phi_1\rangle - |\phi_1;\phi_0\rangle\Big)$ and a symmetric spin state. These three spin states are recognized as those that form the spin triplet with $S = 1$. The last state is written as the product of a symmetric spatial wavefunction $\frac{1}{\sqrt{2}}\Big(|\phi_0;\phi_1\rangle + |\phi_1;\phi_0\rangle\Big)$ multiplying an antisymmetric spin state. This is the spin singlet with $S = 0$. In short one can then write the four states as

$$|\phi_{\text{antisymmetric}}\rangle \otimes |\chi_{\text{triplet}}\rangle \qquad \text{3-fold degenerate}$$
$$|\phi_{\text{symmetric}}\rangle \otimes |\chi_{\text{singlet}}\rangle \qquad \text{non-degenerate}$$

Writing the states like this has several advantages. First of all, it is quite natural as the states are now classified according to quantum numbers corresponding to $\{\hat{\mathcal{H}}, \hat{S}^2, \hat{P}_{12}\}$. Another important advantage is that the matrix of an operator that does not involve spin operators will be diagonal in this basis, because the factorized spin states are all orthogonal. This property was not true for the first basis discussed above. As a result, perturbations will in general lift the degeneracy between these four states, by separating the spin triplet states (that remain degenerate) and the spin singlet state. Note that similar considerations can be carried over to systems of more than two electrons, but the construction is more delicate and is described by what is known as Young diagrams.

Physical consequences of particle statistics

There are many important consequences of the particle statistics. For example, the magnetic properties of atoms and Hund's rules, the relation between the electronic band structure of materials and their transport properties (conductors, semiconductors, band insulators), the very different specific heat of para- and orthohydrogen, etc. Here, we will discuss two examples where particles statistics plays a key role.

Hund's rules

Start from the two electron example above and discuss the rules.

Specific heat of para- and orthohydrogen

The specific heat of a gas of hydrogen molecules is very sensitive to the spin state of the two protons. If the two spin-1/2 protons bind into a spin singlet, the molecule is called parahydrogen; if they bind into a spin triplet the molecule is called orthohydrogen. The interaction energy between the two proton spins is completely negligible. The main difference between para- and orthohydrogen comes from the symmetry of the spatial wavefunction. Under the exchange of the two protons, the wavefunction must change sign. In parahydrogen, this means that the spatial wavefunction must be symmetric, while it is antisymmetric in orthohydrogen. Recalling that the parity of a state with angular momentum ℓ is $(-1)^\ell$, we see that parahydrogen must have ℓ even, while orthohydrogen will have odd ℓ. The rotational energy is given by $E = \hbar^2 \ell(\ell+1)/I$ with I the moment of inertia of the molecule. We therefore see that the two kinds of molecules will have a very different energy spectrum and thus a very different specific heat. This is a typical example where the spin state imposes a constraint on the spatial wavefunction and leads to qualitative differences.

The ideal Fermi gas

The ideal Fermi gas is another example, that is encountered very often, where particle statistics plays an instrumental role. It can be described by N independent fermions in a closed d-dimensional box of size L. The many-particle Hamiltonian for this system is simply

$$\hat{\mathcal{H}} = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m},$$

where m is the mass of the fermions. The eigenstates of the corresponding single-particle Hamiltonian are given by $\phi_{\vec{k}}(\vec{r}) = \frac{1}{L^{d/2}} e^{i\vec{k}\vec{r}}$, where $\vec{k}$ takes discrete values

$$\vec{k} = \frac{2\pi}{L}(n_1, n_2, \ldots, n_d) \qquad n_i \in \mathbb{Z}$$

The eigenenergies are $E_{\vec{k}} = k^2/2m$. The vector $\vec{k}$ can be used to represent an energy level. All possible states are then seen as the set of all $\vec{k}$ vectors in a d-dimensional space. In order to construct the ground-state, we must fill the states starting from the lowest energies, which means by filling those available states that have their associated $\vec{k}$ closest to the origin. When the N lowest energy levels have been filled, they reach an energy $E_F = \hbar^2 k_F^2/2m$ called the Fermi energy that is such that all states with $E < E_F$ are filled and all those with $E > E_F$ are empty. In three dimensions, the volume of the sphere of radius k_F is $4\pi k_F^3/3$. A quantum state is occupying a volume $(2\pi/L)^3$. There are therefore

$$N = \frac{4}{3}\pi k_F^3 \left(\frac{L}{2\pi}\right)^3$$

particles within the sphere. Introducing the particle density $n = N/L^3 = k_F^3/6\pi^2$ we see that the Fermi energy is related to n through

$$E_F = \frac{\hbar^2}{2m}\left(6\pi^2 n\right)^{\frac{2}{3}}$$

The total energy per unit volume is obtained by integrating the energy over all $\vec{k}$ inside the sphere

$$\frac{E_{\text{tot}}}{L^3} = \frac{1}{L^3}\int_0^{k_F} \frac{4\pi k^2 dk}{(2\pi L)^3}\frac{\hbar^2 k^2}{2m} = \frac{3}{5}nE_F$$

The ideal Bose gas

Maybe say something about BEC.