

Lecture 16

Identical Particles

16.1 Introduction

There are many systems in nature that are made of several particles of the same species. These particles all have the same mass, charge, and spin. For instance the electrons in an atom are identical particles. Identical particles cannot be distinguished by measuring their properties. This is also true for classical particles. In classical mechanics we can always follow the trajectory of each individual particle, i.e. their time evolution in space. The trajectories identify each particle in classical mechanics, making identical particles distinguishable.

In quantum mechanics the concept of trajectory does not exist and identical particles are *indistinguishable*. Let us consider for simplicity a system of two identical particles. The state of the system is described by a wave function:

$$\psi(\xi_1, \xi_2), \quad \xi = \{\underline{x}, \sigma\}, \quad (16.1)$$

where \underline{x} yields the position of the particle, and σ yields the z -component of the spin of the particle, if the latter is different from zero.

The state with the two particles exchanged is described by the wave function:

$$\psi(\xi_2, \xi_1). \quad (16.2)$$

If the two particles are identical, the two functions represent the *same* quantum state, and therefore:

$$\psi(\xi_1, \xi_2) = e^{i\alpha} \psi(\xi_2, \xi_1). \quad (16.3)$$

Repeating the exchange of the two particles we find:

$$e^{2i\alpha} = 1 \implies e^{i\alpha} = \pm 1. \quad (16.4)$$

Hence the wave function of a system of two identical particles must be either symmetric or antisymmetric under the exchange of the two particles.

The Spin-Statistics Theorem

Systems of identical particles with integer spin ($s = 0, 1, 2, \dots$), known as *bosons*, have wave functions which are symmetric under interchange of any pair of particle labels. The wave function is said to obey *Bose-Einstein* statistics.

Systems of identical particles with half-odd-integer spin ($s = \frac{1}{2}, \frac{3}{2}, \dots$), known as *fermions*, have wave functions which are antisymmetric under interchange of any pair of particle labels. The wave function is said to obey *Fermi-Dirac* statistics.

This law was discovered by Wolfgang Pauli and is supported by experimental evidence.

16.2 A first look at Helium

In the simplest model of the helium atom, the Hamiltonian is

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \frac{e^2}{4\pi\epsilon_0|r_1 - r_2|}$$

where

$$\hat{H}_i = \frac{\hat{p}_i^2}{2\mu} - \frac{2e^2}{4\pi\epsilon_0 r_i}$$

Note that it is *symmetric* under permutation of the indices 1 & 2 which label the two electrons. This must be the case if the two electrons are *identical* or *indistinguishable*: it cannot matter which particle we label 1 and which we label 2.

This observation is quite general: the same argument holds for identical particles other than electrons and can be extended to systems of more than two identical particles.

Let us write the symmetry condition concisely as:

$$\hat{H}(1, 2) = \hat{H}(2, 1)$$

Suppose that

$$\hat{H}(1, 2)\psi(1, 2) = E\psi(1, 2)$$

then interchanging the labels 1 & 2 gives

$$\hat{H}(2, 1)\psi(2, 1) = E\psi(2, 1)$$

but using the symmetry property of \hat{H} means that

$$\hat{H}(1, 2)\psi(2, 1) = E\psi(2, 1)$$

so we conclude that $\psi(1, 2)$ and $\psi(2, 1)$ are both eigenfunctions belonging to the *same* eigenvalue, E , as is any linear combination of $\psi(1, 2)$ and $\psi(2, 1)$. In particular, the normalised symmetric and antisymmetric combinations

$$\psi_{\pm} \equiv \frac{1}{\sqrt{2}}\{\psi(1, 2) \pm \psi(2, 1)\}$$

are eigenfunctions belonging to the eigenvalue, E .

If we introduce a particle interchange operator, P_{12} , with the property that

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

then the symmetric and antisymmetric combinations are eigenfunctions of P_{12} with eigenvalues ± 1 respectively:

$$P_{12}\psi_{\pm} = \pm\psi_{\pm}$$

Since ψ_{\pm} are simultaneous eigenfunctions of \hat{H} and P_{12} it follows that $[\hat{H}, P_{12}] = 0$, as you can easily verify from the above equations, and that the symmetry of the wavefunction is a constant of the motion.

16.3 Two-electron wave function

In the previous lecture, we constructed the states of the coupled representation for two spin- $\frac{1}{2}$ electrons, the three triplet states:

$$\begin{aligned}\chi_{1,1} &= \alpha_1\alpha_2 \\ \chi_{1,0} &= \frac{1}{\sqrt{2}}\{\alpha_1\beta_2 + \beta_1\alpha_2\} \\ \chi_{1,-1} &= \beta_1\beta_2\end{aligned}$$

and the singlet state:

$$\chi_{0,0} = \frac{1}{\sqrt{2}}\{\alpha_1\beta_2 - \beta_1\alpha_2\}$$

where we have used a simplified notation for the states of the coupled basis:

$$\chi_{s,m_s} \equiv |s, m_s, s_1, s_2\rangle.$$

Notice that the triplet states are *symmetric* under interchange of the labels 1 and 2, whereas the singlet state is *antisymmetric*. If we are to satisfy the Spin-Statistics Theorem, this has implications for the symmetry of the spatial wavefunctions that we combine with the spin functions to give the full wavefunction of the 2-electron system. The 2-electron wavefunction will have the general form

$$\Psi(1, 2) = \psi(r_1, r_2) \cdot \chi$$

The symmetry properties of the various factors are as follows:

	symmetry of χ_s	symmetry of ψ	symmetry of Ψ
$s = 0$ (singlet)	a	s	a
$s = 1$ (triplet)	s	a	a

Thus the spatial wavefunction must be *antisymmetric* if the two electrons are in a *spin triplet state* but *symmetric* if they are in a *spin singlet state*.

16.4 More on the He atom

Suppose for the moment that we neglect spin and also neglect the mutual Coulomb repulsion between the two electrons. That is, we treat the two electrons as moving independently in the Coulomb field of the nucleus. The Hamiltonian then reduces to

$$\hat{H} = \hat{H}_1 + \hat{H}_2 \quad \text{where} \quad \hat{H}_i = \frac{\hat{p}_i^2}{2\mu} - \frac{2e^2}{4\pi\epsilon_0 r_i}$$

We already know what the eigenfunctions and eigenvalues for \hat{H}_1 and \hat{H}_2 are, namely

$$\begin{aligned}\hat{H}_1 u_{n_1 \ell_1 m_1}(\underline{r}_1) &= E_{n_1} u_{n_1 \ell_1 m_1}(\underline{r}_1) \\ \hat{H}_2 u_{n_2 \ell_2 m_2}(\underline{r}_2) &= E_{n_2} u_{n_2 \ell_2 m_2}(\underline{r}_2)\end{aligned}$$

so it is easy to see that \hat{H} has eigenfunctions which are just products of the 1-electron eigenfunctions:

$$\begin{aligned}\hat{H} u_{n_1 \ell_1 m_1}(\underline{r}_1) u_{n_2 \ell_2 m_2}(\underline{r}_2) &\equiv (\hat{H}_1 + \hat{H}_2) u_{n_1 \ell_1 m_1}(\underline{r}_1) u_{n_2 \ell_2 m_2}(\underline{r}_2) \\ &= (E_{n_1} + E_{n_2}) u_{n_1 \ell_1 m_1}(\underline{r}_1) u_{n_2 \ell_2 m_2}(\underline{r}_2) \equiv E_n u_{n_1 \ell_1 m_1}(\underline{r}_1) u_{n_2 \ell_2 m_2}(\underline{r}_2)\end{aligned}$$

Thus the energy eigenvalues are given by

$$E_n = E_{n_1} + E_{n_2} \quad \text{where} \quad E_{n_i} = -\frac{\mu}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n_i^2}$$

The Ground State:

In this crude model the ground state energy is just

$$E_{n=1} = E_{n_1=1} + E_{n_2=1} = 2 E_{n_1=1}.$$

Setting $Z = 2$ in the Bohr formula thus yields for the ground state energy:

$$E_1 = 8 \times (-13.6 \text{ eV}) = -108.8 \text{ eV}$$

to be compared with the experimentally measured value of -78.957 eV .

The ground state spatial wavefunction has $n_1 = n_2 = 1$ and $\ell_1 = \ell_2 = m_1 = m_2 = 0$ and is thus

$$u_{100}(\underline{r}_1) u_{100}(\underline{r}_2).$$

Each electron is in a $1s$ state; we say that the *electronic configuration* is $(1s)^2$.

If we now worry about spin, we remember that the total wavefunction is a product of a spatial wavefunction and a spin wavefunction of the correct symmetry. But the spatial wavefunction is *symmetric* and can thus *only be combined with a spin singlet spin function* to give an overall antisymmetric 2-electron wavefunction;

$$\Psi(\text{ground state}) = u_{100}(\underline{r}_1) u_{100}(\underline{r}_2) \chi_{0,0}.$$

Notice that, since $\ell_1 = \ell_2 = 0$, the total orbital angular momentum quantum number of the ground state configuration is $\ell = \ell_1 + \ell_2 = 0$. Thus the ground state has zero orbital and spin angular momentum, and hence zero total angular momentum.

The First Excited States:

The first excited states correspond to one electron being excited to a $2s$ or $2p$ state, with the other remaining in a $1s$ state. The electronic configurations are denoted by $(1s)(2s)$ and $(1s)(2p)$ respectively. The (degenerate) energy eigenvalue can again be obtained from the Bohr formula with $Z = 2$:

$$E_{n=2} = E_{n_1=1} + E_{n_2=2} = E_{n_1=2} + E_{n_2=1} = 5 \times -13.6 \text{ eV} = -68.0 \text{ eV}$$

In this case it is possible to construct spatial wavefunctions which are either *symmetric* or *antisymmetric*. The overall antisymmetric combinations are then:

$$\begin{aligned} \Psi^{\text{singlet}}(1, 2) &= \frac{1}{\sqrt{2}} \{u_{100}(\mathbf{r}_1) u_{2\ell m_\ell}(\mathbf{r}_2) + u_{2\ell m_\ell}(\mathbf{r}_1) u_{100}(\mathbf{r}_2)\} \chi_{0,0} \\ \Psi^{\text{triplet}}(1, 2) &= \frac{1}{\sqrt{2}} \{u_{100}(\mathbf{r}_1) u_{2\ell m_\ell}(\mathbf{r}_2) - u_{2\ell m_\ell}(\mathbf{r}_1) u_{100}(\mathbf{r}_2)\} \chi_{1, m_s} \end{aligned}$$

16.5 Pauli exclusion principle

The results that we have just obtained for the independent particle approximation to the helium atom illustrate a more general result, related to the Spin-Statistics Theorem and known as *the Pauli Exclusion Principle* which states

No two identical fermions can be in the same quantum state

For example,

- in the ground state, we see that although both electrons have $n = 1$ and $\ell = m_\ell = 0$ i.e. both are in a $1s$ state, they are in a spin singlet state, which means that if one electron is in the spin state α , the other must be in the state β : the two electrons cannot have an identical set of quantum numbers; if both were in the spin state α , the 2-electron spin state would be a triplet state, which is ruled out by the Spin-Statistics Theorem;
- in any excited state, both electrons can be in the spin state α , corresponding to the triplet state, but then the spatial wavefunction is forced to be antisymmetric, so that the quantum numbers n, ℓ, m_ℓ , of the two electrons have to differ - otherwise the spatial wavefunction would vanish identically!

No such restriction applies to identical bosons; any number of identical bosons can occupy the same quantum state.

Note that the correlation between spin and statistics has been postulated in the nonrelativistic context used in this course. The spin-statistic theorem can actually be derived in a relativistic formulation of quantum mechanics. It is a consequence of the principles of special relativity, quantum mechanics, and the positivity of the energy.

16.6 Summary

As usual, we summarize the main concepts introduced in this lecture.

- Indistinguishable particles in quantum mechanics.
- Symmetry of the wave function, example of the He atom.
- Two-electron wave function, combining spin and spatial wave functions.
- More on the He atom.
- Pauli exclusion principle.

