

9 Indistinguishable Particles and Exchange

Quantum mechanics allows us to predict the results of experiments. If we conduct an experiment with indistinguishable particles a correct quantum description cannot allow anything which distinguishes between them. For example, if the wavefunctions of two particles overlap, and we detect a particle, which one is it? The answer to this is not only that we don't know, but that we can't know. Quantum mechanics can only tell us the probability of finding *a* particle in a given region. The wavefunction must therefore describe *both* particles. The Schroedinger equation is then:

$$\left[-\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + V(\mathbf{r}_1) + V(\mathbf{r}_2) \right] \Phi(\mathbf{r}_1, \mathbf{r}_2) = E\Phi(\mathbf{r}_1, \mathbf{r}_2)$$

where the subscripts label each particle, and there are six coordinates, three for each particle. Φ is a wave in six dimensions which contains the information we can measure: the probability of finding particles at \mathbf{r}_1 and \mathbf{r}_2 , but *not* what we can't measure: which particle is which.

What basis states would be appropriate for Φ ? An *approximation* is to use a product such as $\Phi(\mathbf{r}_1, \mathbf{r}_2) = |a(\mathbf{r}_1)b(\mathbf{r}_2)\rangle$ where $a(\mathbf{r}_1)$ and $b(\mathbf{r}_2)$ are one-particle wavefunctions of atoms 1 and 2. This allows us to separate the two particle equation into two one particle equations:

$$\left[\frac{-\hbar^2}{2m}\nabla_1^2 + V(r_1) \right] |a(\mathbf{r}_1)\rangle = E_1 |a(\mathbf{r}_1)\rangle; \quad \left[\frac{-\hbar^2}{2m}\nabla_2^2 + V(r_2) \right] |b(\mathbf{r}_2)\rangle = E_2 |b(\mathbf{r}_2)\rangle$$

provided that the particles do not interact (n.b ∇_1^2 does not act on $b(\mathbf{r}_2)$).

Unfortunately, by doing this we have introduced unphysical *labels* to the indistinguishable particles. And this is wrong: the effect of it is that the particles do not interfere with each other because they are in different dimensions (six dimensional space - remember?). When we construct a two-particle wavefunction out of two one-particle wavefunctions we must ensure that the probability density (the *measurable* quantity $|\Phi|^2$) is independent of the *artificial* labels.

9.1 The exchange operator and Pauli's exclusion principle

We introduce the *exchange operator* \hat{P}_{12} : an operator which permutes the labels of the particles. This is a rather strange operator, because it only changes the *unphysical* labels which we have attached to the one-particle wavefunctions in order to make the maths more easy. For a meaningful solution we must have a wavefunction which has a probability amplitude unchanged by \hat{P}_{12} : it must be symmetric or antisymmetric with respect to exchange: $|\Phi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \pm |\Phi(\mathbf{r}_2, \mathbf{r}_1)\rangle$.

Physical solutions must be eigenfunctions of \hat{P}_{12} with eigenvalues $+1$ (bosons) or -1 (fermions). Also, any physically meaningful Hamiltonian must commute with \hat{P}_{12} , otherwise \hat{H} and \hat{P}_{12} could not have common eigenfunctions and the system could not remain in an eigenstate of exchange.

A simple product wavefunction $|a(\mathbf{r}_1)b(\mathbf{r}_2)\rangle$ does not satisfy this (unless $a = b$). A linear combination of all permutations is required, for two particles:

$$|\Phi^-\rangle = |a(\mathbf{r}_1)b(\mathbf{r}_2) - a(\mathbf{r}_2)b(\mathbf{r}_1)\rangle / \sqrt{2}$$

$$|\Phi^+\rangle = C_{ab}|a(\mathbf{r}_1)b(\mathbf{r}_2) + a(\mathbf{r}_2)b(\mathbf{r}_1)\rangle + C_{aa}|a(\mathbf{r}_2)a(\mathbf{r}_1)\rangle + C_{bb}|b(\mathbf{r}_2)b(\mathbf{r}_1)\rangle$$

where the C_{ab} terms are expansion and normalisation parameters. Note that the antisymmetric combination cannot include terms where both particles are in the same state, but there are three possibilities for the symmetric state. Although any linear combinations of C_{ab} C_{bb} and $C_{aa} = 1$ are possible, C_{bb} and C_{aa} correspond to different configurations and are usually set to zero.

Notice that if $a = b$, then $|\Phi^-\rangle = 0$. Thus there is no possible antisymmetric combination involving identical states, i.e. two fermions cannot be in the same quantum state: the Pauli exclusion principle.

9.2 Two indistinguishable particles with spin 1/2

If we have two identical fermions of spin 1/2, confined in the same region, what is the appropriate wavefunction? In the scattering case we could measure spins far from the interaction, and if we knew that the total spins is conserved, spins can be associated with each particle. In the bound state we cannot tell which particle we are measuring, so the ket must contain both spin and spatial wavefunctions of both particles.

Assuming the spins do not interact, we can separate the two-particle spin wavefunction into $\sigma(1, 2) = \sigma_1\sigma_2$. We also know the appropriate one particle basis states $\uparrow_1, \downarrow_1, \uparrow_2, \downarrow_2$, where \uparrow_1 represents ‘‘particle 1’’ in spinor state $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$. The combinations for indistinguishable particles are then:

$$\uparrow_1\uparrow_2, \quad \downarrow_1\downarrow_2, \quad (\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2)/\sqrt{2}, \quad (\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)/\sqrt{2}$$

Operating on these with \hat{P}_{12} yields eigenvalues 1, 1, 1 and -1 respectively. $\mathbf{S}^2 = S(S + 1)$ yields 2, 2, 2 and 0, S_z yields 1,-1,0 and 0. Thus the demands of indistinguishability couples the spins of two identical particles into a triplet ($S=1$) and a singlet ($S=0$). The spin-1 vector has three possible M_s component values - hence the triplet.

9.3 The exchange interaction

The *overall* wavefunction describing fermions must be antisymmetric with respect to exchange, i.e. $\hat{P}_{12}|\Phi\rangle = -|\Phi\rangle$. Therefore in an atom or molecule where Φ includes both spin and spatial parts, the spin and spatial parts of a fermionic wavefunction have opposite exchange symmetry.

Spin must be considered even if the energy (Coulomb potential) depends explicitly only on the spatial part. The expectation value of the potential energy is different for symmetric and anti-symmetric spatial combinations. Using $|\Phi^\pm\rangle$ from above (with $C_{ab} = 1$).

$$\langle\Phi^\pm|\hat{V}|\Phi^\pm\rangle = \langle a(\mathbf{r}_1)b(\mathbf{r}_2)|V(r)|a(\mathbf{r}_1)b(\mathbf{r}_2)\rangle \pm \langle a(\mathbf{r}_1)b(\mathbf{r}_2)|V(r)|a(\mathbf{r}_2)b(\mathbf{r}_1)\rangle$$

The first term is called the direct interaction and the second term is known as the exchange interaction: a measurable contribution to the energy comparable in size to the first, which has no classical analogue.

9.4 Spins and Exchange

Now notice something strange. The exchange interaction has split the $\mathbf{S}=1$ states from the $\mathbf{S}=0$ states. We could write the potential as $\hat{V} = J_{nl} - (2\hat{\mathbf{S}} - 1)K_{nl}$, even though the Hamiltonian does not act on the spin! This is because the sign of the exchange integral depends on the (anti)symmetry of the spatial wavefunction. Thus we can write the matrix element as

$$\langle\Phi|J_{nl} - (2S - 1)K_{nl}|\Phi\rangle$$

This ‘exchange interaction’ appears to depend on the spin - the triplet states have lower energy than the singlet (this is one of *Hund’s rules* for determining energy levels in atoms). It is this type of exchange force which keeps spins aligned in a ferromagnet, not the magnetic interaction itself.

9.5 Wavefunction for many spin one-half particles

The exchange arguments for two-particle systems can be extended to many particle systems: The indistinguishable wavefunction consists of all possible permutations of the product of one electron wavefunctions. For the symmetric case $\hat{P}_{nm}\Phi = \Phi$, a product of these permutations will suffice. For the antisymmetric case, the correct form turns out to be given by the determinant of a matrix:

$$\Phi = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \phi_a(1) & \phi_b(1) & \dots & \phi_N(1) \\ \phi_a(2) & \phi_b(2) & \dots & \phi_N(2) \\ \dots & \dots & \dots & \dots \\ \phi_a(N) & \phi_b(N) & \dots & \phi_N(N) \end{pmatrix}$$

This is called a *Slater Determinant*. For fermions, where $\hat{P}_{nm}\Phi = -\Phi$ the Slater Determinant obeys the Pauli exclusion principle: if any two of the one-particle wavefunctions were identical ($\phi_n = \phi_m$), then the wavefunction would be the determinant of a matrix with two identical rows, i.e. zero.

Note also that $\langle \Phi | \hat{H} | \Phi \rangle$ has many more exchange terms than direct ones.

9.6 Helium

Helium is the simplest system for which we are unable to accurately calculate the energy.

For a single electron moving in the field of a helium nucleus, the spatial wavefunctions are similar to those of hydrogen $|u_{nlm}\rangle$.

When a second electron is added, a reasonable basis set is exchange-symmetrised wavefunctions consisting of spin states multiplying hydrogenic spatial parts:

$$(u_{nlm}(\mathbf{r}_1)u_{n'l'm'}(\mathbf{r}_2) \pm u_{n'l'm'}(\mathbf{r}_1)u_{nlm}(\mathbf{r}_2))$$

Since the overall wavefunction must be antisymmetric, the singlet (exchange-antisymmetric) spin states must combine with symmetric spatial states, and the triplet (exchange-symmetric) spin states must combine with antisymmetric spatial states.

If both electrons were in the same spatial state, the antisymmetric spatial wavefunction would be:

$$|(a(\mathbf{r}_1)a(\mathbf{r}_2) - a(\mathbf{r}_2)a(\mathbf{r}_1))\rangle = 0$$

Hence there is no triplet for the ground state.

9.7 Electron-electron interaction - ground state by perturbation theory

The hydrogen wavefunctions are only a choice of basis set: the hydrogenic potential ignores the electron-electron repulsion. A simple approach is to treat this as a perturbation and to use degenerate perturbation theory.

The perturbing potential is just $V = e^2/4\pi\epsilon_0 r_{12}$ where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. The unperturbed spatial ground state is just a product of the hydrogenic ones with $Z=2$ for helium:

$$u_{100}(r_1)u_{100}(r_2) = \frac{Z^3}{\pi a_0^3} e^{-Zr_1/a_0} e^{-Zr_2/a_0}$$

so by perturbation theory, the energy shift due to this potential is given by:

$$\langle u_{100}(r_1)u_{100}(r_2) | e^2/4\pi\epsilon_0 r_{12} | u_{100}(r_1)u_{100}(r_2) \rangle$$

The electron-electron repulsion is over 30% of the unperturbed energy ($4Z\mu e^4/\hbar^2$), so perturbation theory may seem inappropriate. Strictly, it isn't even the right integral, as it neglects correlation. But in fact the value of this integral is $5Z\mu e^4/8\hbar^2$ within 5% of the actual energy.

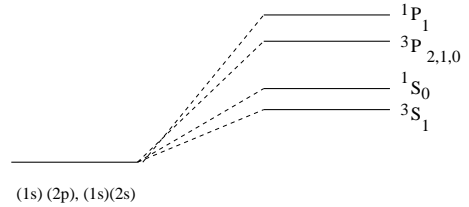
Note also that the radial wavefunctions are different for 2s and 2p, so the electron-electron interaction splits the degeneracy between 1s2s and 1s2p configurations.

9.8 Multiplicity and Degeneracy of Excited States

Ignoring electron-electron interaction, all 1s2s and 1s2p states have the same energy. The perturbation ($e^2/4\pi\epsilon_0 r_{12}$) lifts that degeneracy, and we can treat it with degenerate perturbation theory. Rather than evaluating the integral in the 4x4 matrix exactly, we can use a physical argument: ($e^2/4\pi\epsilon_0 r_{12}$) is not an external potential, and so applies no net torque or force on the electrons. The perturbation cannot change the angular momentum, so it cannot mix states with different l or m . The theta integral will be $\delta_{ll'}$, and the phi integral $\delta_{mm'}$, total angular momentum remains a good quantum number: $L=0(1s2s)$ or $L=1(1s2p)$. Since the 2s state has finite probability of being at the nucleus, and the 2p has zero probability of being there, the 2s state is less well *screened* from the nuclear charge by the 1s and will have lower energy.

For a given spatial excited state the possible normalised spin wavefunction combinations, consistent with the anti-symmetry requirement are a spin triplet and a spin singlet.

$$\begin{aligned}\Phi_3 &= (\phi_{nlm,n'l'm'} - \phi_{n'l'm',nlm})(\uparrow\uparrow)/\sqrt{2} \\ & (\phi_{nlm,n'l'm'} - \phi_{n'l'm',nlm})(\downarrow\downarrow)/\sqrt{2} \\ & (\phi_{nlm,n'l'm'} - \phi_{n'l'm',nlm})(\uparrow\downarrow + \downarrow\uparrow)/2 \\ \Phi_1 &= (\phi_{nlm,n'l'm'} + \phi_{n'l'm',nlm})(\uparrow\downarrow - \downarrow\uparrow)/2\end{aligned}$$



Where $|\phi_{nlm,n'l'm'}\rangle$ represents electron 1 in a hydrogenic state with quantum numbers n, l and m and electron 2 with n', l' , and m' . The subscripts on the Φ label spin *multiplicity* ($2S+1$)

Again whole effect of the potential is contained in the spatial part, the spin integral will be $\delta_{\sigma\sigma'}$. so off-diagonal matrix elements are all zero. We need to evaluate

$$J_{nl} = \langle \phi_{nlm,n'l'm'} | (e^2/4\pi\epsilon_0 r_{12}) | \phi_{nlm,n'l'm'} \rangle - \text{the } \textit{direct} \text{ integral.}$$

$$K_{nl} = \langle \phi_{nlm,n'l'm'} | (e^2/4\pi\epsilon_0 r_{12}) | \phi_{n'l'm',nlm} \rangle - \text{the } \textit{exchange} \text{ integral.}$$

with which perturbation theory gives an energy shift in the $1s^1 2s^1$ state of:

$$\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} (\langle \phi_{100,200} | 1/r_{12} | \phi_{100,200} \rangle + \langle \phi_{200,100} | 1/r_{12} | \phi_{200,100} \rangle \pm \langle \phi_{100,200} | 1/r_{12} | \phi_{200,100} \rangle \pm \langle \phi_{200,100} | 1/r_{12} | \phi_{100,200} \rangle)$$

where the + applies to the singlet state and the - to the triplet. The direct integral, electron-electron repulsion, increases the energy, but the exchange integral can either increase or decrease energy.

Thus the energy levels are split by different direct interactions into $L=0$ and $L=1$ and again through exchange interaction into singlet and triplet. The final degeneracies of states with one electron excited to $n=2$ are 3,1,9 and 3. The spectroscopic notation in the figure gives the quantum numbers as: $(nl)(n'l')^{2S+1}L_J$

Again, the most useful quantum number labels are the total spin and angular momentum: we could write the perturbation energy as $\Delta E = J_{nl} - (2S - 1)K_{nl}$, even though the perturbing potential does not act on the spin. The 'exchange force' selects preferred spin state via the requirement of overall antisymmetry.