Helium

Unlike hydrogen, where generalizations of simple Bohr theory were quite successful, the spectrum of helium presented intractable puzzles before the Pauli principle was discovered. The presence of two identical particles has a major impact on the spectrum of helium. We will give a discussion of the helium spectrum with the charge $+Ze$ nucleus treated as infinitely heavy, and ignoring fine structure. This simplified treatment is still adequate to investigate the major effects of particle identity. The Hamiltonian is independent of spin, and reads

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\vec{r_1} - \vec{r_2}|}.$$

The Hamiltonian is clearly invariant under the interchange in space of the two particles,

$$\vec{r_1} \leftrightarrow \vec{r_2}, \quad H \leftrightarrow H.$$

This means that solutions to the Schrödinger equation can be classified by evenness or oddness under particle spacial interchange, so we have either

$$\Psi_+(\vec{r_1}, \vec{r_2}) = \Psi_+(\vec{r_2}, \vec{r_1}),$$

or

$$\Psi_-(\vec{r_1}, \vec{r_2}) = -\Psi_-(\vec{r_2}, \vec{r_1}).$$

The Pauli principle can be satisfied with either of these spacial interchange types. Overall antisymmetry results when the spin wave function is correctly chosen.

A standard notation for spin states in the atomic physics literature is

$$\alpha(1) \ \text{ means } \ S_z(1) = \frac{1}{2} \ \text{ or } \ |\uparrow>,$$

and

$$\beta(1) \ \text{ means } \ S_z(1) = -\frac{1}{2} \ \text{ or } \ |\downarrow> .$$

The total spin for two spin 1/2 particles can be either 1 or 0. For the total spin 1 or triplet state we have

Triplet

$$|1,1> = \alpha(1)\alpha(2) = |\uparrow\uparrow>$$

$$|1,0> = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2)) = \frac{1}{\sqrt{2}}(|\uparrow\downarrow> + |\downarrow\uparrow>)$$

$$|1,-1> = \beta(1)\beta(2) = |\downarrow\downarrow>$$

and

Singlet

$$|0,0>=\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)-\beta(1)\alpha(2))=\frac{1}{\sqrt{2}}(|\uparrow\downarrow>-|\downarrow\uparrow>)$$

These states illustrate a general rule: Combining two equal spins (or angular momenta), the maximum spin is symmetric under interchange, the next lowest spin is anti symmetric, etc. So here the triplet state is symmetric under interchange of the spins of particle 1 and 2, while the single state is antisymmetric. With these two spin states in hand, along with Ψ_+, Ψ_-, we can construct states which are antisymmetric under interchange of 1 and 2. If the spin state is singlet the corresponding states are called "para," and if the spin state is triplet the state is called "ortho." Denoting the combination of a position vector $\vec{r}$, and a spin label m as ξ, we then have as allowed possibilities,

$$\Psi(\xi_1,\xi_2)=\left\{\begin{array}{cc}\Psi_+(\vec{r_1},\vec{r_2})|0,0> & para\\ \Psi_-(\vec{r_1},\vec{r_2})|1,S_z> & ortho\end{array}\right\},$$

so we either have symmetry in space, antisymmetry in spin, or vice versa.

The total orbital angular momentum is

$$\vec{L}=\vec{L}_1+\vec{L}_2,$$

and since the Hamiltonian is clearly rotationally invariant, we have that the total orbital angular momentum is conserved,

$$[\vec{L},H]=0$$

Likewise, the total spin is conserved, so we can classify states by their total orbital angular momentum and total spin. The notation used is as follows:

$$n^{2S+1}L,$$

where S is the total spin, L is the total orbital angular momentum, and n is a number ordering the states, so $n=1$ is the lowest state with a given set of quantum numbers, $n=2$ is next, and so on. So we may list the states of helium as follows:

Parahelium:

$$1^1S,\ \ 2^1S,\ldots$$
$$2^1P,\ \ 3^1P,\ldots$$

and

Orthohelium:

$$2^3S,\ \ 3^3S,\ldots$$
$$2^3P,\ \ 3^3P,\ldots$$

It turns out that insight can be obtained into the He spectrum by doing perturbation theory in the electron electron interaction. We break the Hamiltonian into two parts, H_0 and V, given by

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2}$$

$$V = \frac{1}{|\vec{r_1} - \vec{r_2}|}$$

For the ground state, it is clearly advantageous to put both electrons in the 100 state,

$$\Psi^{(0)}(1^1S) = \Psi_{100}(r_1)\Psi_{100}(r_2) = \frac{Z^3}{\pi}\exp(-Z(r_1 + r_2)$$

Along with this spacial wave function, the spin state is the antisymmetric single state. This is not written explicitly, and does not play a role in the matrix element. The unperturbed energy is just $E^{(0)} = Z^2 = 4$ for helium. The first order correction, $E^{(1)}$ is given by the matrix element of V in this state;

$$E^{(1)} =< \Psi^{(0)}(1^1S)|V|\Psi^{(0)}(1^1S) >=< \Psi^{(0)}(1^1S)|\frac{1}{|\vec{r_1} - \vec{r_2}|}|\Psi^{(0)}(1^1S) >$$

Writing out the matrix element we have

$$< \Psi^{(0)}(1^1S)|V|\Psi^{(0)}(1^1S) >=$$

$$\int d^3\vec{r_1}d^3\vec{r_2}\frac{Z^6}{\pi^2}\exp(-2Z(r_1 + r_2)\frac{1}{|\vec{r_1} - \vec{r_2}|} = \frac{5Z}{8}$$

The surprisingly simple answer $5Z/8$ can be obtained in either of two ways. One is to use the expansion

$$\frac{1}{|\vec{r_1} - \vec{r_2}|} = \frac{1}{r_>}\sum_l (\frac{r_<}{r_>})^l P_l(\hat{r_1}\cdot\hat{r_2}).$$

The other is by Fourier transform, where the following formulae are useful:

$$\frac{1}{r} = \int \frac{d^3\vec{k}}{(2\pi)^3}\frac{4\pi}{k^2}\exp(i\vec{k}\cdot\vec{r}),$$

and

$$\frac{8\pi\beta}{(k^2+\beta^2)^2} = \int d^3\vec{r}\exp(-i\vec{k}\cdot\vec{r})\exp(-\beta r)$$

Comparing to experiment for the ground state of helium and quadruply ionized carbon gives the following table:

	$E^{(0)}$	$E^{(0)}+E^{(1)}$	*experiment*
He	-4	-2.75	-2.904
C^{4+}	-36	-32.35	-32.41

We see that first order perturbation theory is rather reasonable, giving semi-quantitative results.

Going on to excited states, we list the spacial wave functions for the lowest lying excited state, giving para first, followed by ortho;

2^1S	$\frac{1}{\sqrt{2}}[\Psi_{100}(1)\Psi_{200}(2)+\Psi_{100}(2)\Psi_{200}(1)]$
2^1P	$\frac{1}{\sqrt{2}}[\Psi_{100}(1)\Psi_{21m}(2)+\Psi_{100}(2)\Psi_{21m}(1)]$
2^3S	$\frac{1}{\sqrt{2}}[\Psi_{100}(1)\Psi_{200}(2)-\Psi_{100}(2)\Psi_{200}(1)]$
2^3P	$\frac{1}{\sqrt{2}}[\Psi_{100}(1)\Psi_{21m}(2)-\Psi_{100}(2)\Psi_{21m}(1)]$

As in the case of the ground state, these spacial wave functions are accompanied by the corresponding spin wave functions, the singlet for para, or the triplet for ortho. In the table above, for the ortho case, $m=0,\pm 1$. We will concentrate on the $2S$ states, para and ortho. The treatment of $2P$ states is similar. For the para $2S$ state, we have

$$E^{(1)} =< 2^1S|\frac{1}{|\vec{r_1}-\vec{r_2}|}|2^1S >= J+K,$$

where the "direct integral" J is

$$J=\int d^3\vec{1}\, d^3\vec{2}\, |\Psi_{100}(\vec{1})|^2|\Psi_{200}(\vec{2})|^2\frac{1}{|\vec{1}-\vec{2}|},$$

and the "exchange integral" K is

$$K=\int d^3\vec{1}\, d^3\vec{2}\, \Psi^*_{100}(\vec{1})\Psi^*_{200}(\vec{2})\Psi_{100}(\vec{2})\Psi_{200}(\vec{1})\,\frac{1}{|\vec{1}-\vec{2}|}$$

The direct integral has a simple physical interpretation. It is the Coulomb energy between two charge distributions, one for the state Ψ_{100}, the other for Ψ_{200}. The exchange integral is a more subtle object, and is required to be present by the Pauli Principle. The formula for $E^{(1)}$ for the ortho $2S$ state can be expressed in terms of these same integrals.

$$< 2^3S|\frac{1}{|\vec{r_1}-\vec{r_2}|}|2^3S >= J-K$$

The integral J is obviously positive, and the integral K turns out also to be positive, which leads to the following:

$$J > 0, \quad K > 0, \quad \rightarrow E(2^1S) > E(2^3S)$$

In the table below, the experimental numbers are listed, which show that this prediction is correct.

state	*energy*
1^1S	-2.90
2^3S	-2.18
2^1S	-2.15

The fact that $E(2^1S) > E(2^3S)$ is a rather striking consequence of the antisymmetry of the overall wave function. It shows that even though the Hamiltonian is independent of spin, the energies of states depend on the fermionic nature of the wave function. This is why the spectrum of helium was a complete puzzle when attempts were made to explain it using so-called "old quantum theory."

Now before the inclusion of electron electron repulsion, the states 2^3S and 2^1S were degenerate, with a common energy of $-2.5\,a.u.$ We have seen previously that first order perturbation theory in the electron electron repulsion is reasonably accurate. Here we assume that perturbation theory is again semi-quantitative and use it to get an estimate of the direct and exchange integrals from experimental results. We have

$$2^1S, \quad J + K \sim (-2.15 + 2.50) = 0.35,$$

and

$$2^3S, \quad J + K \sim (-2.18 + 2.50) = 0.32$$

Combining these two results, we can estimate $J \sim 0.34$, and $K \sim 0.015$, so the exchange integral is much smaller than the direct integral. To summarize, the exchange integral, although small, is definitely non-zero, and is a direct result of the Pauli principle and spin 1/2, even though the Hamiltonian is independent of spin.