

IDENTICAL PARTICLES

Atoms:

A neutral atom, of atomic number Z , consists of a heavy (assumed stationary) nucleus, with electric charge Ze , surrounded by Z electrons (mass m and charge $-e$).

The Hamiltonian for this system is:

$$\hat{H} = \sum_{j=1}^Z \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right\} + \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq k}^Z \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|}$$

The term in curly brackets represents the kinetic plus potential energy of the j th electron, in the electric field of the nucleus.

The second sum (which runs over all values of j and k except $j = k$) is the potential energy associated with the mutual repulsion of the electrons (the factor of $1/2$ in front corrects for the fact that the summation counts each pair twice).

The problem is to solve Schrödinger's equation for the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)$:

$$\hat{H}\psi = E\psi,$$

This cannot be solved exactly, except for the very simplest case, $Z = 1$ (hydrogen). We must resort to elaborate approximation methods (you will study them in QM II).

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Helium:

After hydrogen, the simplest atom is helium ($Z = 2$).

The Hamiltonian consists of two hydrogenic Hamiltonians (with nuclear charge $2e$), one for electron 1 and one for electron 2, together with a final term describing the repulsion of the two electrons.

$$\hat{H} = \left\{ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|},$$

It is this last term that causes all the trouble.

If we simply *ignore* it, the Schrödinger equation separates, and the solutions can be written as products of *hydrogen* wave functions:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{n\ell m}(\mathbf{r}_1) \psi_{n'\ell' m'}(\mathbf{r}_2),$$

only with half the Bohr radius and four times the Bohr energies.

The total energy would be:

$$E = 4(E_n + E_{n'}),$$

where: $E_n = -13.6/n^2$ eV.

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Helium:

The ground state would be:

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a},$$

and its energy would be:

$$E_0 = 8 (-13.6 \text{ eV}) = -109 \text{ eV}.$$

Because ψ_0 is a symmetric function, the spin state has to be *antisymmetric*, so the ground state of helium should be a *singlet* configuration, with the spins “oppositely aligned.”

The *actual* ground state of helium is indeed a singlet, but the experimentally determined energy is -78.975 eV , so the agreement is not very good as we ignored electron–electron repulsion, which is certainly *not* a small contribution.

The excited states of helium consist of one electron in the hydrogenic ground state, and the other in an excited state:

$$\psi_{n\ell m} \psi_{100}$$

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Helium:

If we try to put *both* electrons in excited states, one immediately drops to the ground state, releasing enough energy to knock the other one into the continuum ($E > 0$), leaving you with a helium *ion* (He^+) and a free electron.

We can construct both symmetric and antisymmetric combinations. The former go with the *antisymmetric* spin configuration (the singlet)—they are called **parahelium**—while the latter require a *symmetric* spin configuration (the triplet)—they are known as **orthohelium**.

The ground state is necessarily parahelium; the excited states come in both forms.

Because the symmetric spatial state brings the electrons closer together, we expect a higher interaction energy in parahelium, and indeed, it is experimentally confirmed that the parahelium states have somewhat higher energy than their orthohelium counterparts.

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Helium:

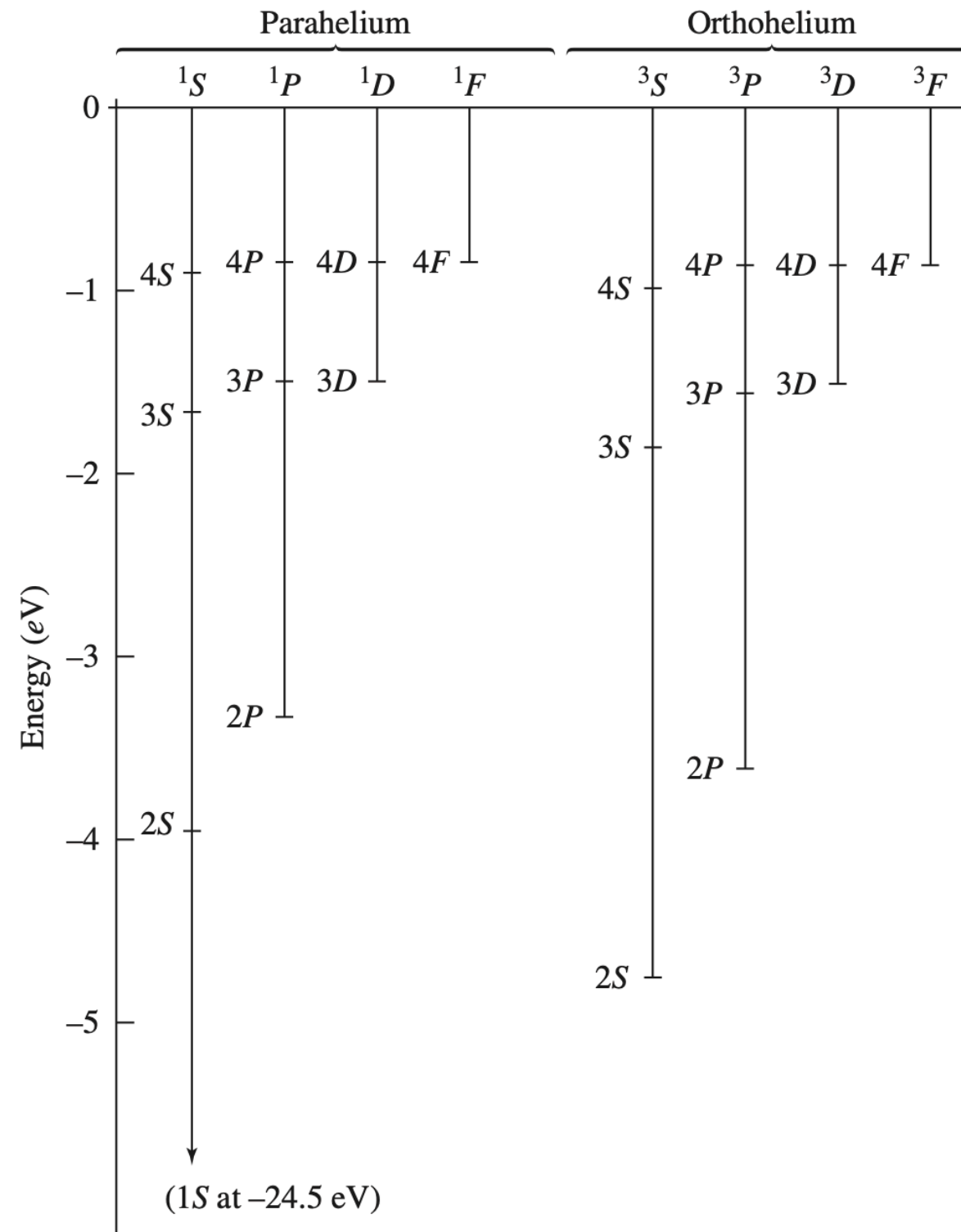


Figure 5.1: Energy level diagram for helium (the notation is explained in Section 5.2.2). Note that parahelium energies are uniformly higher than their orthohelium counterparts. The numerical values on the vertical scale are relative to the ground state of ionized helium (He^+): $4 \times (-13.6) \text{ eV} = -54.4 \text{ eV}$; to get the *total* energy of the state, subtract 54.4 eV.