Ay126: Helium

S. R. Kulkarni

April 10, 2021

The spectrum of Helium has no resemblance to that of Hydrogen or the Alkali elements. The spin of electrons played a major role in deciphering the Helium spectrum.To give you a sense of the complexity of the Helium atom I provide in Figure 1, in advance of the rest of the text, the Grotrian diagram for Helium.

1 The potential energy of the Helium atom

Let us start with the ground state of Helium. The ionization potential of HeI is $24.59\,\mathrm{eV}$. The ionization potential of HeII is

$$I(\mathrm{He}^+, 1s) = -\frac{Z^2}{2n^2} = 4 \times 13.6 = 2\,\mathrm{Hartree} \text{ for } n = 1 \tag{1}$$

Thus $24.59 + 54.42\,\mathrm{eV} = 79.02\,\mathrm{eV} = 2.804\,\mathrm{Hartree}$[1] is released when a Helium atom is formed from an alpha particle and two electrons. Inversely, the potential energy of the electronic system of the Helium atom is $2.8\,\mathrm{Hartree}$.

Following the QM solution for the Hydrogen atom the *ab initio* calculation of this potential energy was seen as an extremely goal. For a minute let us agree to ignore the electrostatic repulsion of the two electrons. Then each electron sees a nuclear charge of $Z = 2$ and the potential energy for each electron is $2\,\mathrm{Hartree}$ and thus the total potential energy of the electronic system is $-4\,\mathrm{Hartree}$ which is in clear disagreement with the experimental value of $-2.8\,\mathrm{Hartree}$. There are two factors we have ignored: the repulsion between the two electrons and the screening of the positively charged nucleus by each electron.

1.1 Perturbation Method

The Schrodinger equation for Helium is

$$\left(-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} - E \right)\psi(\mathbf{r_1}, \mathbf{r_2}). \tag{2}$$

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[1] A Hartree is a unit of energy used in atomic physics. It is the potential energy of the Hydrogen electron of the Hydrogen atom (but without the finite nuclear mass correction). It is about $27.2\,\mathrm{eV}$
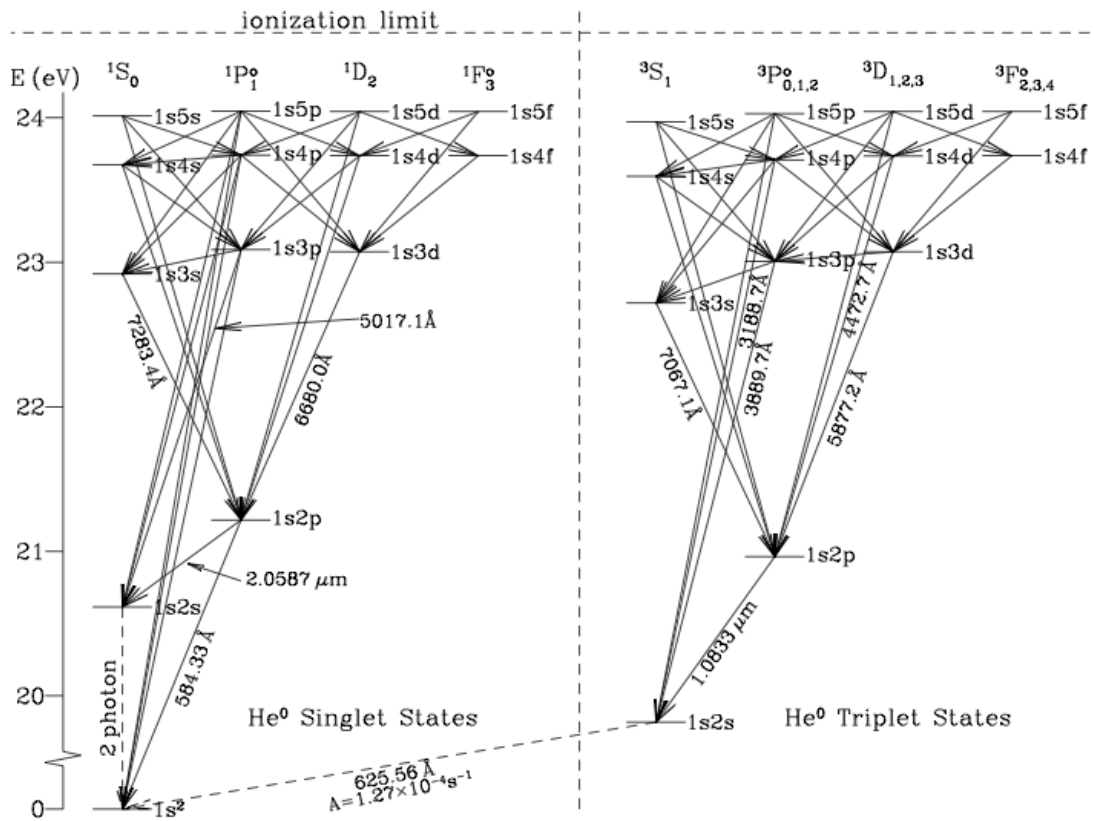
Figure 14.3 Radiative decay pathways for He^0 (see text). Selected lines are labeled by vacuum wavelength.

Figure 1: Grotrian diagram for Helium atom along with prominent lines.

There is no analytical solution even for $N = 2$ (Helium atom). The perturbation method consists of rewriting the Hamiltonian with two components: the principal and the perturbation. The solution for the principal is obtained and the resulting wave-function applied to the perturbation to compute the correction to the eigen-energies. In this case, the principal Hamiltonian is

$$H = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} \tag{3}$$

and the perturbation is

$$H' = \frac{e^2}{r_{12}}. \tag{4}$$

We have an exact solution for the principal Hamiltonian, say, for the ground state, $\psi(r_1, r_2) = \psi_{1s}(r_1) \times \psi 1s(r_2)$. In this case, resulting energy eigenvalue is simply the $E_1 = E_2 = -2$ Hartree. Using the wave function for the principal Hamiltonian we compute the energy eigenvalue of the perturbing Hamiltonian:

$$E' = \int \psi(r_1, r_2) H' \psi(r_1, r_2) dv_1 dv_2 \tag{5}$$

This yields, $+34$ eV$=1.25$ Hartree and thus the total energy is -2.75 Hartree or -75 eV which should be compared with the experimental value of -79 eV or -2.804 Hartree.

1.2 Variational Method

In the above scheme we did not allow for screening of the nucleus by the electrons. This leads us to the "variational" method, a technique common in QM. Specifically, here, we set Z in the wave-function to α. We know that α has be less than two to account for screening. Repeat the above exercise and then choose the value of α that minimizes the total energy, $E_1 + E_2 + E'$ (this exercise has been assigned as a homework problem).

2 Including Spin

Including the spin leads to a spin-orbital:

$$\phi(1) = \psi_{1s}(1)\alpha(1)$$

(for, say, spin up in a $1s$ orbit) and $\phi(2) = \psi_{1s}\beta(1)$ for spin up in a $1s$ orbit. The wave function for the entire atom/ion is

$$\psi(r_1, r_2, ..., r_N) = \phi_1(r_1)\phi_2(r_2)...\phi_N(r_N). \tag{6}$$

There are two important issues that must be addressed. The above formulation for ψ implicitly assumes that electrons are distinguishable and each electron is thus assigned to

3

its own orbital. However, electrons are not distinguishable and so this formulation for the wave function of the entire system is suspect. Next, Pauli's principle is <u>Wave functions are anti-symmetric with respect to interchange of identical Fermions.</u>

Let us return back to the Helium atom. Since the two electrons are not distinguishable we can confidently state that

$$|\psi(1,2)|^2 = |\psi(2,1)|^2. \tag{7}$$

There are two possibilities that satisfy the above equation. The symmetric solution is

$$\psi(1,2) = +\psi(2,1) \tag{8}$$

whereas the anti-symmetric solution is

$$\psi(1,2) = -\psi(2,1). \tag{9}$$

Next, noting that the spin-orbital is a product of spin wave function and spatial wave-function, the requirement of Pauli would **require** that one of the wave functions (spin or spatial) be symmetric and the other anti-symmetric.

Thus within the orbital approximation, a two-electron wave function which obeys the Pauli Principle can be written as

$$\psi(1,2) = \frac{1}{\sqrt{2}}\Big[\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)\Big] = -\psi(2,1). \tag{10}$$

Thus if $\phi_a = \phi_b$ then $\Psi(1,2) = 0$. Thus Pauli's principle leads to the usual statement *No two electrons can occupy the same spin orbital.* A spin orbital has four quantum numbers $(n, l, m_l$ and $m_s)$ and thus the conclusion is that no two spin orbitals can have the same set of four quantum numbers.

2.1 Spin wave functions

We start with the following pairs: $\alpha(1)\alpha(2)$ (the spins of both electrons is up), $\beta(1)\beta(2)$ (both spins are down), $\alpha(1)\beta(2)$ and $\alpha(2)\beta(1)$. While the first two wave functions enjoy symmetry upon exchange of the particles (a requirement given that particles are not distinguishable) the latter do not. So we must reformulate the last two paired wave functions. After some thought we get the following:

$$\sigma_{0,0} = \frac{1}{\sqrt{2}}\Big(\alpha(1)\beta(2) - \alpha(2)\beta(1)\Big) \tag{11}$$

$$\sigma_{1,1} = \alpha(1)\alpha(2) \tag{12}$$

$$\sigma_{1,0} = \frac{1}{\sqrt{2}}\Big(\alpha(1)\beta(2) + \alpha(2)\beta(1)\Big) \tag{13}$$

$$\sigma_{1,-1} = \beta(1)\beta(2) \tag{14}$$

The first one is anti-symmetric and has a net spin of zero, $S = 0$ ("singlet") The next three are symmetric have have $S = 1$ with projected values of $1, 0, -1$ ("triplet").

3 The Spectrum of Helium

As can be seen from Figure 1 Helium exhibits two systems each consisting of their own SPD families. On the left side we have the "Singlet" family (sometimes called as "para[dox]") and on the right side we have the "Triplet" family (old usage, "ortho[dox]"). Transitions involving levels one from each side appear to be forbidden. For instance, the A coefficient for the transition $(625\,\text{Å})$ of 1s2s (ground state) to 1s1s (ground state) is $1.27 \times 10^{-4}\,\text{s}^{-1}$

3.1 Ground State

For the ground state of Helium we assume that both electrons are in the ground state. The spatial part of the wave-function is thus $\psi_{1s}(1)\psi_{1s}(2)$. Given Pauli's principle we are forcecd to choose the anti-symmetric spin-state, $\sigma_{0,0}$. The, resulting wavefunction, $\psi_{1s}(1)\psi_{1s}(2)\sigma_{0,0}$ is the ground state and the first level of the Singlet family (see Figure 1).
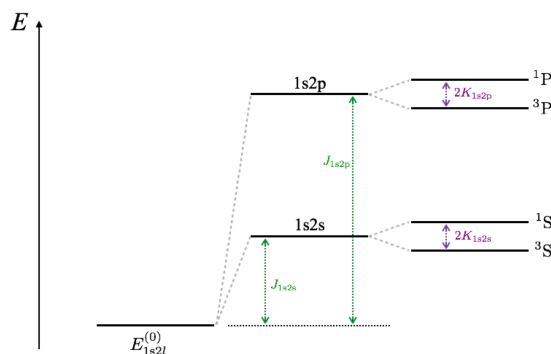

Figure 2: Excited states of Helium, $1s, 2s$ and $1s, 2p$.

3.2 Excited States

The first excited state is one electron in $1s$ and the other[2] is $2s$. Given two distinct quantum numbers there are two possible spatial wave-functions, one symmetric and the other anti-symmetric:

$$\psi_s = \frac{1}{\sqrt{2}}\Big[\psi_{1s}(\psi_{nl}(2) + \psi_{2s}(2)\psi_{1s}(1)\Big] \tag{15}$$

$$\psi_a = \frac{1}{\sqrt{2}}\Big[\psi_{1s}(1)\psi_{1s}(2) - \psi_{2s}(2)\psi_{1s}(1)\Big]. \tag{16}$$

In order to form the spin orbitals we pair the spatially symmetric wave function with the anti-symmetric spin function ("Singlet" series) and the spatially anti-symmetric wave

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[2]It has to be $2s$ since we know that $2s$ orbital penetrates more than $2p$.

function with the three symmetric spin functions ("Triplet" series). These wave functions are then used with the perturbed Hamiltonian, H' to derive the eigen-energies. The general result for an excited level of the sort $1s, nl$ is

$$E^{\pm}_{1s,nl} = E^0_{1s,nl} + J \pm K \tag{17}$$

$$J = \int |\psi_{1s}(r_1)|^2 \frac{1}{r_{12}} |\psi_{nl}(r_2)|^2 dv_1 dv_2 \tag{18}$$

$$K = \int \psi^*_{1s}(r_1)\psi^*_{nl}(r_2) \frac{1}{r_{12}} \psi_{1s}(r_2)\psi_{nl}(r_2) dv_1 dv_2 \tag{19}$$

where $E^0_{1s,nl}$ is the eigen-energy of the unperturbed Hamiltonian. Here, J is the "direct integral" and represents the Coulomb interaction between the two charges. K is the "exchange integral" and represents quantum interference. See Figure 2.

Figure 3 shows the relative importance of these two "perturbations" (but for $4p4d$). Notice that the spin-spin correlation energy is much greater than that of the electrostatic repulsion which is greater than the spin-orbit coupling.
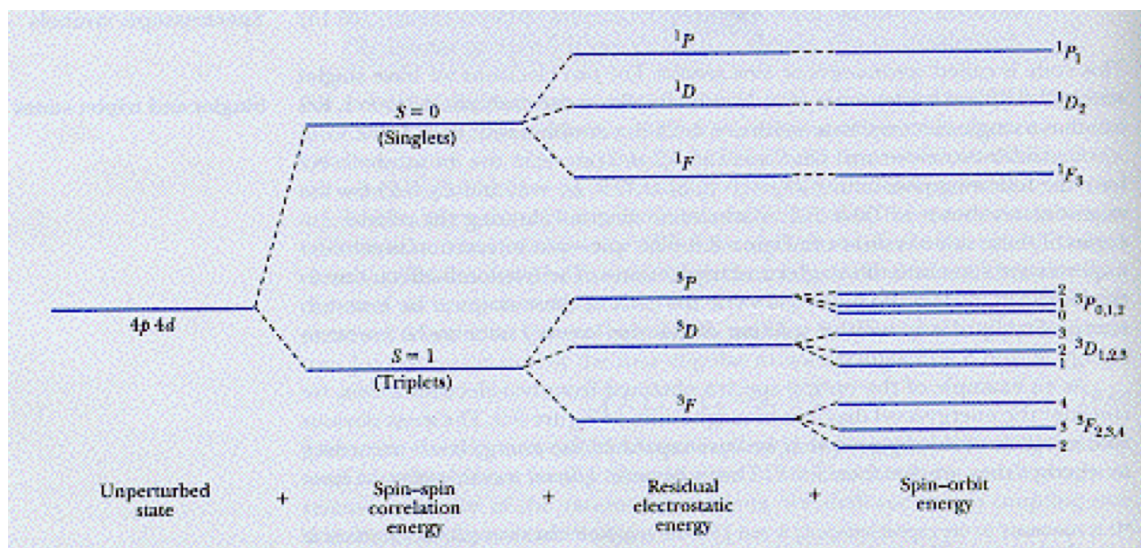

Figure 3: The relative importance of various effects which lead to "perturbation" of the energy levels expected in a purely radial model: spin-spin repulsion (Pauli exclusion principle), electron-electron repulsion and spin-orbit coupling. This is an illustrative figure and not a calculation.