# Notes for Lectures in Quantum Mechanics [1]

# A First Look at the He Atom Energy Levels

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October 27, 2021

[1] Updated:Jul 12 , 2021; Ver 0.x

# Overview

§1. Approximate Space Wave Function

§2. Singlet and Triplet States of Helium Atom

§3. Singlet States Have Higher Coulomb Energy

# He Atom Hamiltonian

As an example of system of two identical particles we shall discuss He atom. The Hamiltonian for He atom is given by

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

If the electrostatic interaction, $e^2/|\vec{r}_1 - \vec{r}_2|$, between the two electrons is neglected as a first approximation, the Hamiltonian becomes a sum of two hydrogen atom like Hamiltonians. In this approximation the electronic states are described by quantum numbers $(n_1, l_1, m_1)$ and $(n_2, l_2, m_2)$ for the two electrons. Let $u_1, u_2$ denote corresponding $H$-atom wave functions.

# Approximate Space Wave Function

The space part of the wave function for the two electrons will be product wave function $u_1(\vec{r}_1)u_2(\vec{r}_2)$, which must be properly symmetrized or anti-symmetrized as discussed below.

In very many situations the total wave function is a product of a part describing space properties and a spin wave function. Thus we write

$$\Phi_{\text{total}} = \psi_{\text{space}}(\vec{r}_1, \vec{r}_2)\chi_{spin}(m_1, m_2)$$

where $m_1, m_2$ refer to the spin variables for the two electrons.

# Singlet and Triplet States of Helium ... 1/2

As each electron carries spin 1/2, the total spin can take values 1 (triplet) and 0 (singlet). The values of total spin determines the symmetry property of spin wave function under an exchange of spin variables. It is known that spin wave function must be symmetric for $S = 1$ and antisymmetric for $S = 0$ states. The requirement that total wave function be antisymmetric (for two *electron* systems) fixes the symmetry property of the space part of the wave function as summarized in the table given below.

| Spin State | Total Spin | Spin wave function | Space wave function |
|---|---|---|---|

# Singlet and Triplet States of Helium ... 2/2

Therefore, out of the two combinations for the space wave function

$$\psi_{\pm}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left( u_1(\vec{r}_1) u_2(\vec{r}_2) \pm u_1(\vec{r}_2) u_2(\vec{r}_1) \right)$$

the symmetric combination $\psi_+$ should be used for the singlet states ($S = 0$) and the antisymmetric combination $\psi_-$ should be used for triplet states ($S = 1$). The ground state corresponds to $n_1 = n_2 = 1$ $l_1 = l_2 = 0$ $m_1 = m_2 = 0$ and the antisymmetric combination $\psi_-$ vanishes. Only the symmetric combination is nonzero. Thus the ground state is a singlet state; the same is true of all other states corresponding to electrons having identical $(n, l, m)$ quantum numbers.

# Singlet States have Higher Coulomb Energy

When the two electron states correspond to different $(n, l, m)$ quantum numbers, both symmetric and antisymmetric combinations $\psi_{\pm}(\bar{r}_1, \bar{r}_2)$ are possible. However, the antisymmetric combination $\psi_{\pm}(\vec{r}_1, \vec{r}_2)$ vanishes when $\vec{r}_1 = \vec{r}_2$. Therefore, the probability that the two electrons will be found close to each other will be small for $\psi_-$ ( for triplet states, known as *ortho helium*) and large for $\psi_+$ (singlet states, known as *para helium*). Since the Coulomb interaction between two electrons is positive and is large when their separation is small, total Coulomb energy will be higher in singlet states as compared to its value in the triplet state. These qualitative predictions are in agreement with the experimental results on energy the spectrum of He atom.