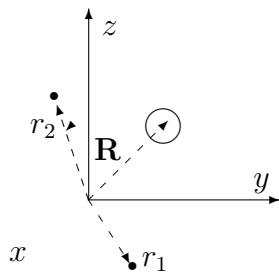


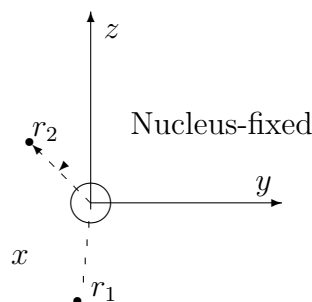
Lecture 22: Helium Atom‡

Read McQuarrie: Chapter 7.9, 9.1–9.5

Now that we have treated the Hydrogen-like atoms in some detail, we now proceed to discuss the next-simplest system: the Helium atom. In this situation, we have two electrons – with coordinates r_1 and r_2 – orbiting a nucleus with charge $Z = 2$ located at the point \mathbf{R} . Now, for the hydrogen atom we were able to ignore the motion of the nucleus by transforming to the center of mass. We then obtained a Schrödinger equation for a single effective particle – with a reduced mass that was very close to the electron mass – orbiting the origin. It turns out to be fairly difficult to transform to the center of mass when dealing with three particles, as is the case for Helium.



However, because the nucleus is much more massive than either of the two electrons ($M_{\text{Nuc}} \approx 7000m_e$) it is a very good approximation to assume that the nucleus sits at the center of mass of the atom. In this approximate set of COM coordinates, then, $\mathbf{R}=0$ and the electron coordinates r_1 and r_2 measure the distance between each electron and the nucleus. Further, we feel justified in separating the motion of the nucleus (which will roughly correspond to rigidly translating the COM of the atom) from the relative motion of the electrons orbiting the nucleus within the COM frame. Thus, in what follows, we focus **only on the motion of the electrons** and ignore the motion of the nucleus.



We will treat the quantum mechanics of multiple particles (1, 2, 3...) in much the same way as we described multiple dimensions. We will invent operators $\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{r}}_3, \dots$ and associated momentum operators $\hat{\mathbf{p}}_1, \hat{\mathbf{p}}_2, \hat{\mathbf{p}}_3, \dots$. The operators for a given particle (i) will be assumed to commute with all operators associated with any other particle (j):

$$[\hat{\mathbf{r}}_1, \hat{\mathbf{p}}_2] = [\hat{\mathbf{p}}_2, \hat{\mathbf{r}}_3] = [\hat{\mathbf{r}}_2, \hat{\mathbf{r}}_3] = [\hat{\mathbf{p}}_1, \hat{\mathbf{p}}_3] = \dots \equiv 0$$

Meanwhile, operators belonging to the same particle will obey the normal commutation relations. Position and momentum along a given axis do not commute:

$$[\hat{x}_1, \hat{\mathbf{p}}_{x_1}] = i\hbar \quad [\hat{y}_1, \hat{\mathbf{p}}_{y_1}] = i\hbar \quad [\hat{z}_1, \hat{\mathbf{p}}_{z_1}] = i\hbar$$

‡Lecture Notes originally written by Professor Troy Van Voorhis

while all components belonging to different axes commute:

$$\hat{x}_1 \hat{y}_1 = \hat{y}_1 \hat{x}_1 \quad \hat{\mathbf{p}}_{z1} \hat{y}_1 = \hat{y}_1 \hat{\mathbf{p}}_{z1} \quad \hat{\mathbf{p}}_{z1} \hat{\mathbf{p}}_{x1} = \hat{\mathbf{p}}_{x1} \hat{\mathbf{p}}_{z1} \quad \text{etc.}$$

As you can already see, one of the biggest challenges to treating multiple electrons is the explosion in the number of variables required!

In terms of these operators, we can quickly write the Hamiltonian for the Helium atom:

$$\hat{\mathbf{H}} \equiv \frac{\hat{\mathbf{p}}_1^2}{2m_e} + \frac{\hat{\mathbf{p}}_2^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{\hat{\mathbf{r}}_1} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{\hat{\mathbf{r}}_2} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|}$$

Kinetic Energy
of Electron 1
Nucleus-Electron 1
Attraction
Electron-Electron
Repulsion

Kinetic Energy
of Electron 2
Nucleus-Electron 2
Attraction

This Hamiltonian looks very intimidating, mainly because of all the constants (e , m_e , ϵ_0 ; etc.) that appear in the equation. It is therefore much simpler to work everything out in **atomic units**:

$$\begin{aligned} \hat{\mathbf{H}} &\equiv \frac{\hat{\mathbf{p}}_1^2}{2} + \frac{\hat{\mathbf{p}}_2^2}{2} - \frac{Z}{\hat{\mathbf{r}}_1} - \frac{Z}{\hat{\mathbf{r}}_2} + \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} \\ &= \frac{\nabla_1^2}{2} + \frac{\nabla_2^2}{2} - \frac{Z}{\hat{\mathbf{r}}_1} - \frac{Z}{\hat{\mathbf{r}}_2} + \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} \end{aligned}$$

Once Schrödinger had solved the Hydrogen atom, it was generally believed that the solution of the Helium atom would follow not long afterward. However, scientists have tried for decades to solve this three body problem without succeeding. Very, very accurate approximations were developed, but no exact solutions were found. As it turns out, even with the simplifications described above it is **impossible** to determine the eigenstates of the Helium atom. This situation is common in chemistry, as most of the problems we are interested in cannot be solved exactly. We therefore must resort to making approximations, as we will do throughout the remainder of this course.

Non-Interacting Electron Approximation

For Helium, the first thing we notice is that the Hamiltonian becomes separable if we neglect the electron-electron repulsion term:

$$H_{\text{ind}} = \frac{\nabla_1^2}{2} + \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} = \underbrace{\frac{\nabla_1^2}{2} - \frac{Z}{r_1}}_{\text{Electron 1}} + \underbrace{\frac{\nabla_2^2}{2} - \frac{Z}{r_2}}_{\text{Electron 2}} = H_1 + H_2$$

Thus, if we neglect the interaction between the electrons, the Hamiltonian reduces to the sum of two hydrogenic atom Hamiltonians (with $Z = 2$). We have experience with Hamiltonians of this form. For example, if we had a 2D Harmonic oscillator, we would write

$$H_{\text{ind}} = \frac{1}{2} \frac{\partial^2 \psi}{\partial x^2} + \frac{1}{2} \omega_x^2 x^2 + \frac{1}{2} \frac{\partial^2}{\partial y^2} + \frac{1}{2} \omega_y^2 y^2 = H_x + H_y.$$

Here the Hamiltonian separates into two 1D Harmonic oscillators and we can immediately write the wavefunctions as products of the 1D oscillator eigenfunctions:

$$\psi_{n_x n_y}(x, y) = \psi_{n_x}(x) \psi_{n_y}(y)$$

with energies that are the sum of the energies of the two oscillators

$$E_{n_x n_y} = \omega_x \left(n_x + \frac{1}{2} \right) + \omega_y \left(n_y + \frac{1}{2} \right)$$

By analogy (Hamiltonians Add \rightarrow Wavefunctions Multiply \rightarrow Energies Add), we can immediately write the correct form for the eigenfunctions of this non-interacting electron Hamiltonian above:

$$\psi_{n_1 \ell_1 m_1 m_{s1}; n_2 \ell_2 m_2 m_{s2}}(\mathbf{r}_1, \boldsymbol{\sigma}_1; \mathbf{r}_2, \boldsymbol{\sigma}_2) = \psi_{n_1 \ell_1 m_1 m_{s1}}(\mathbf{r}_1, \boldsymbol{\sigma}_1) \psi_{n_2 \ell_2 m_2 m_{s2}}(\mathbf{r}_2, \boldsymbol{\sigma}_2)$$

Here we have introduced a few notation conventions that it is important to spell out. First, we begin here the convention that Capital Greek letters will be used for wavefunctions that involve more than one-electron (like the wave function for Helium) while lower case Greek letters will be used for one-electron functions (like the Hydrogen orbitals). Second, we have introduced the quantum number m_s to tell us the **spin** of a given electron. This concept was introduced for the Hydrogen atom, but will become increasingly important in what follows. By convention, we denote $m_s = +\frac{1}{2}$ by “ α ” and $m_s = -\frac{1}{2}$ by “ β ”. We have further invented a coordinate, $\boldsymbol{\sigma}$, that covers the spin degree of freedom for the electron. Thus, the normalization and orthogonality conditions for α and β can be written:

$$\int \alpha^*(\boldsymbol{\sigma}) \alpha(\boldsymbol{\sigma}) d\boldsymbol{\sigma} = \int \beta^*(\boldsymbol{\sigma}) \beta(\boldsymbol{\sigma}) d\boldsymbol{\sigma} = 1 \quad \int \alpha^*(\boldsymbol{\sigma}) \beta(\boldsymbol{\sigma}) d\boldsymbol{\sigma} = \int \beta^*(\boldsymbol{\sigma}) \alpha(\boldsymbol{\sigma}) d\boldsymbol{\sigma} = 0$$

Wave functions that depend on both space and spin (like the one above) are just shorthand for products of (space part) \times (spin part). For example:

$$\psi_{3s\alpha}(r, \boldsymbol{\sigma}) \equiv \psi_{3s}(r) \alpha(\boldsymbol{\sigma})$$

In addition to knowing the wave functions, the separability of the Hamiltonian allows us to immediately write the energies as well:

$$E_{n_1, n_2} = E_{n_1} + E_{n_2} = \frac{Z^2}{2m_1^2} + \frac{Z^2}{2m_2^2}$$

where we have made use of atomic units ($\hbar = m_e = e = 4\pi\epsilon_0 = 1$) to simplify our energy expression. Thus, by neglecting the electron repulsion (an approximation) we move from a problem that is impossible to solve to one that we can easily solve.

However, the outstanding question is: how good is this approximation? The easiest way to test this is to look at the ground state. This involves putting both electrons in the 1s orbital:

$${}_{1s;1s}(\mathbf{r}_1, \boldsymbol{\sigma}_1; \mathbf{r}_2, \boldsymbol{\sigma}_2) = {}_{100}(\mathbf{r}_1, \boldsymbol{\sigma}_1) {}_{100}(\mathbf{r}_2, \boldsymbol{\sigma}_2)$$

This wave function has an energy

$$E_{11} = \frac{Z^2}{2} + \frac{Z^2}{2} = Z^2 = 4 \text{ a.u.} = 108.8 \text{ eV.}$$

How good is this result? Well, we can determine the ground state energy of Helium by removing one electron to create He^+ and then removing the second to create He^{2+} . As it turns out, the first electron takes 24.6 eV to remove and the second takes 54.4 eV to remove, which means the correct ground state energy is 79.0 eV. So our non-interacting electron picture is off by 30 eV, which is a lot of energy. To give you an idea of how much energy that is, you should note that a typical covalent chemical bond is worth about 5 eV of energy. So totally neglecting the electron interaction is not a very good approximation.

Independent Electron Approximation

Two steps:

- * antisymmetrization
- * include interaction term

So what can we do to improve this approximation? Well, first we note that there is a fundamental rule about electronic wave functions that is violated by the independent particle wave functions. We first note that all fundamental particles can be divided into two classes:

fermions, which have half integer spin, and **bosons**, which have integer spin. Thus, electrons, for example, are fermions because they have spin-1/2. Meanwhile, a photon is a boson because photons have spin-1. There is a very powerful theorem concerning wave functions for identical fermions or bosons.

Spin Statistics Theorem: Any wave function that describes multiple identical **fermions** must be **antisymmetric** upon exchange of the electrons. Any wave function that describes multiple identical **bosons** must be **symmetric** upon exchange of the particles.

The proof of this theorem is well beyond the scope of this course. For the present, we will take it as another postulate of quantum mechanics. The result is that any wavefunction we build for electrons must be antisymmetric. It is easy to show that the product wavefunction described above is **not antisymmetric**. To test antisymmetry, all we have to do is recall that, since the electrons are identical, the labels “1” and “2” are arbitrary. By swapping these labels we can’t possibly change the outcome of any measurement. Upon interchanging the labels “1” and “2”, an antisymmetric wavefunction will give the same wavefunction back times a minus sign. However, our proposed wavefunction does not do this:

$${}_{1s\alpha}(\mathbf{r}_1, \boldsymbol{\sigma}_1) {}_{1s}(\mathbf{r}_2, \boldsymbol{\sigma}_2) \xrightarrow[1 \text{ and } 2]{\text{interchange}} {}_{1s\alpha}(\mathbf{r}_2, \boldsymbol{\sigma}_2) {}_{1s}(\mathbf{r}_1, \boldsymbol{\sigma}_1) \neq - {}_{1s\alpha}(\mathbf{r}_1, \boldsymbol{\sigma}_1) {}_{1s}(\mathbf{r}_2, \boldsymbol{\sigma}_2)$$

This is a problem, because we said that all electron wavefunctions must be antisymmetric under exchange. We can fix this problem by taking the “ \pm ” combination of the wavefunction we proposed and its exchange partner:

$${}_{1s\alpha;1s}(\mathbf{r}_1, \boldsymbol{\sigma}_1; \mathbf{r}_2, \boldsymbol{\sigma}_2) \equiv \frac{1}{\sqrt{2}} [{}_{1s\alpha}(\mathbf{r}_1, \boldsymbol{\sigma}_1) {}_{1s}(\mathbf{r}_2, \boldsymbol{\sigma}_2) - {}_{1s\alpha}(\mathbf{r}_2, \boldsymbol{\sigma}_2) {}_{1s}(\mathbf{r}_1, \boldsymbol{\sigma}_1)]$$

where the leading factor of $1/\sqrt{2}$ ensures that the new wavefunction is normalized. We check that this is antisymmetric:

$$\begin{aligned} {}_{1s\alpha;1s}(\mathbf{r}_1, \boldsymbol{\sigma}_1; \mathbf{r}_2, \boldsymbol{\sigma}_2) &\equiv \frac{1}{\sqrt{2}} [{}_{1s\alpha}(\mathbf{r}_1, \boldsymbol{\sigma}_1) {}_{1s}(\mathbf{r}_2, \boldsymbol{\sigma}_2) - {}_{1s\alpha}(\mathbf{r}_2, \boldsymbol{\sigma}_2) {}_{1s}(\mathbf{r}_1, \boldsymbol{\sigma}_1)] \\ &\stackrel{1 \leftrightarrow 2}{\rightarrow} \frac{1}{\sqrt{2}} [{}_{1s\alpha}(\mathbf{r}_2, \boldsymbol{\sigma}_2) {}_{1s}(\mathbf{r}_1, \boldsymbol{\sigma}_1) - {}_{1s\alpha}(\mathbf{r}_1, \boldsymbol{\sigma}_1) {}_{1s}(\mathbf{r}_2, \boldsymbol{\sigma}_2)] \\ &= \frac{1}{\sqrt{2}} [{}_{1s\alpha}(\mathbf{r}_1, \boldsymbol{\sigma}_1) {}_{1s}(\mathbf{r}_2, \boldsymbol{\sigma}_2) - {}_{1s\alpha}(\mathbf{r}_2, \boldsymbol{\sigma}_2) {}_{1s}(\mathbf{r}_1, \boldsymbol{\sigma}_1)] \\ &= - {}_{1s\alpha;1s}(\mathbf{r}_1, \boldsymbol{\sigma}_1; \mathbf{r}_2, \boldsymbol{\sigma}_2) \end{aligned}$$

Does this new wavefunction give a better energy? As it turns out, this change by itself does nothing for the energy prediction. The new wavefunction is a linear combination of two degenerate eigenstates of the **non-interacting electron** Hamiltonian. As we learned before, any sum of degenerate eigenstates is also an eigenstate with the same eigenvalue. So, while

quantum mechanics says we have to make the wavefunction antisymmetric, antisymmetry *by itself* does not affect our energy for Helium.

The simplest way for us to improve our estimate of the helium ground state energy is to consider not the *eigenvalues* of our approximate Hamiltonian with our approximate eigenfunctions, but instead look at the **average energy** of our approximate function with the exact Hamiltonian. That is to say, a better approximation to the energy can be obtained from

$$\langle \hat{\mathbf{H}} \rangle = \int \psi_{1s\alpha;1s}^* \hat{H} \psi_{1s\alpha;1s} d\tau_1 d\tau_2$$

where $d\tau_1 = d\mathbf{r}_1 d\tau_1$ and similarly for $d\tau_2$. We refer to this picture as an **independent electron approximation**. Within the wavefunction the electrons behave as if they do not interact, because we have retained the separable form. However, in computing the energy, we recover these interactions in an approximate way by computing the average energy, *including the interaction*.

We can simplify the average energy pretty quickly:

$$\begin{aligned} & \int \psi_{1s\alpha;1s}^* \left(\hat{\mathbf{H}}_1 + \hat{\mathbf{H}}_2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \psi_{1s\alpha;1s} d\tau_1 d\tau_2 \\ \Rightarrow & \int \psi_{1s\alpha;1s}^* \left(2 + 2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \psi_{1s\alpha;1s} d\tau_1 d\tau_2 \\ \Rightarrow & -4 \int \psi_{1s\alpha;1s}^* \psi_{1s\alpha;1s} d\tau_1 d\tau_2 + \int \psi_{1s\alpha;1s}^* \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{1s\alpha;1s} d\tau_1 d\tau_2 \\ \Rightarrow & -4 + \int \frac{|\psi_{1s\alpha;1s}|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\tau_1 d\tau_2. \end{aligned}$$

We thus have for the average energy:

$$\langle \hat{\mathbf{H}} \rangle = -4 + \int \frac{|\psi_{1s\alpha;1s}|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\tau_1 d\tau_2.$$

The first term is simply the non-interacting electron energy from above. The second term is the **average value** of the electron-electron repulsion. Because the integrand is strictly positive (as one would expect for electron repulsion) this new term will only increase the average energy, which is a good thing, since our non-interacting picture gave an energy that was 30 eV too small! We can further expand the repulsion term based on the antisymmetric form of the wavefunction. First, we note that we can factorize the antisymmetric wavefunction

into a space part times a spin part:

$$\begin{aligned} & \frac{1}{\sqrt{2}} [\text{}_{1s\alpha}(\mathbf{r}_1, \boldsymbol{\sigma}_1) \text{}_{1s}(\mathbf{r}_2, \boldsymbol{\sigma}_2) \text{}_{1s\alpha}(\mathbf{r}_2, \boldsymbol{\sigma}_2) \text{}_{1s}(\mathbf{r}_1, \boldsymbol{\sigma}_1)] \\ & \Rightarrow \frac{1}{\sqrt{2}} [\text{}_{1s}(\mathbf{r}_1)\alpha(\boldsymbol{\sigma}_1) \text{}_{1s}(\mathbf{r}_2) (\boldsymbol{\sigma}_2) \text{}_{1s}(\mathbf{r}_2)\alpha(\boldsymbol{\sigma}_2) \text{}_{1s}(\mathbf{r}_1) (\boldsymbol{\sigma}_1)] \\ & \Rightarrow \underbrace{\text{}_{1s}(\mathbf{r}_1) \text{}_{1s}(\mathbf{r}_2)}_{\text{space}(\mathbf{r}_1, \mathbf{r}_2)} \underbrace{\frac{1}{\sqrt{2}} [\alpha(\boldsymbol{\sigma}_1) (\boldsymbol{\sigma}_2) (\boldsymbol{\sigma}_1)\alpha(\boldsymbol{\sigma}_2)]}_{\text{spin}(\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2)} \end{aligned}$$

With these definitions, it is easy to verify that the space and spin wavefunctions are individually normalized. Note, in the absence of a magnetic field, you will always be able to write the eigenfunctions of the Hamiltonian in this form because \mathbf{H} is separable into a space and spin part

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_{\text{space}} + \hat{\mathbf{H}}_{\text{spin}},$$

with the expectation value of the spin part being (trivially) zero. As a result, eigenfunctions of \mathbf{H} will always be products of a space part and a spin part as above. With this space/spin separation in hand, we can simplify the repulsion term:

$$\begin{aligned} & \int \frac{|\text{}_{1s\alpha;1s}|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\tau_1 d\tau_2 = \int \frac{|\text{space} \text{spin}|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 d\boldsymbol{\sigma}_1 d\boldsymbol{\sigma}_2 \\ & = \int \frac{|\text{space}(\mathbf{r}_1, \mathbf{r}_2)|^2 |\text{spin}(\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 d\boldsymbol{\sigma}_1 d\boldsymbol{\sigma}_2 \\ & = \int |\text{spin}(\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2)|^2 d\boldsymbol{\sigma}_1 d\boldsymbol{\sigma}_2 \int \frac{|\text{space}(\mathbf{r}_1, \mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ & = \int \frac{|\text{space}(\mathbf{r}_1, \mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned}$$

The evaluation of this 6 dimensional integral is very tedious (cf. McQuarrie problems 8-39 and 8-40) but the result is that

$$\int \frac{|\text{space}|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = \frac{5Z}{8} = \frac{5}{4} \text{a.u.} = +34 \text{ eV}$$

Adding this average repulsion term to our non-interacting energy gives a ground state estimate of $108.8 \text{ eV} + 34 \text{ eV} = 142.8 \text{ eV}$, which is only 4 eV off of the correct energy. The energy is still not very accurate, but at least we are making progress.

As we have seen already, the independent electron picture is not all that accurate for describing atoms. However, chemists are very pragmatic and realize that the ease of solving

non-interacting problems is extremely valuable and, as we will soon see, it gives us a picture (molecular orbital theory) that allows us to describe a wide range of chemistry. Therefore, chemists are extremely reluctant to abandon an independent particle picture. Instead, a great deal of work has gone into making more accurate models based on independent particles — either by making more sophisticated corrections like the one above or by coming up with a different non-interacting Hamiltonian that gives us a better independent particle model. We will spend the next several lectures discussing the qualitative features of electronic structure and bonding that come out of this picture.

EXCITED STATES

Thus far, we have focused on the ground state of the Helium atom. Before moving on to talk about many-electron atoms, it is important to point out that we can describe many more properties of the system using the same type of approximation. By using the same independent particle prescription we can come up with wave functions for excited states and determine their energies, their dependence on electron spin, etc. by examining the wave functions themselves. That is to say, there is much we can determine from simply looking at without doing any significant computation.

We will use the excited state $1s2s$ configuration of Helium as an example. For the ground state we had:

$$\begin{array}{c} \uparrow \\ \uparrow \\ \downarrow \\ \downarrow \end{array} \begin{array}{c} \uparrow \\ \downarrow \end{array} \Rightarrow \frac{\text{space}(\mathbf{r}_1, \mathbf{r}_2)}{1s(\mathbf{r}_1) \ 1s(\mathbf{r}_2)} \times \frac{\text{spin}(\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2)}{\frac{1}{\sqrt{2}} [\alpha(\boldsymbol{\sigma}_1) \ (\boldsymbol{\sigma}_2) \ (\boldsymbol{\sigma}_1)\alpha(\boldsymbol{\sigma}_2)]}$$

In constructing excited states it is useful to use **stick diagrams** to describe **electronic configurations**. Then there are four different configurations we can come up with:

1. $\left[\begin{array}{c} 2s \uparrow \rightarrow \\ 1s \uparrow \rightarrow \end{array} \right.$?	?
2. $\left[\begin{array}{c} 2s \uparrow \rightarrow \\ 1s \downarrow \rightarrow \end{array} \right.$?	?
3. $\left[\begin{array}{c} 2s \downarrow \rightarrow \\ 1s \uparrow \rightarrow \end{array} \right.$?	?
4. $\left[\begin{array}{c} 2s \downarrow \rightarrow \\ 1s \downarrow \rightarrow \end{array} \right.$?	?

Where the question marks indicate that we need to determine the space and spin wave functions that correspond to these stick diagrams. It is fairly easy to make a reasonable guess for each configuration. For example, in the first case we might write down a wave function like:

$${}_{1s\alpha}(\mathbf{r}_1, \boldsymbol{\sigma}_1) {}_{2s\alpha}(\mathbf{r}_2, \boldsymbol{\sigma}_2) = {}_{1s}(\mathbf{r}_1) {}_{2s}(\mathbf{r}_2)\alpha(\boldsymbol{\sigma}_1)\alpha(\boldsymbol{\sigma}_2)$$

However, we immediately note that this wave function is not antisymmetric. We can perform the same trick as before to make an antisymmetric wave function out of this:

$$\begin{aligned} &\Rightarrow \frac{1}{\sqrt{2}} [{}_{1s}(\mathbf{r}_1) {}_{2s}(\mathbf{r}_2)\alpha(\boldsymbol{\sigma}_1)\alpha(\boldsymbol{\sigma}_2) \quad {}_{1s}(\mathbf{r}_2) {}_{2s}(\mathbf{r}_1)\alpha(\boldsymbol{\sigma}_2)\alpha(\boldsymbol{\sigma}_1)] \\ &\Rightarrow \frac{1}{\sqrt{2}} [\underbrace{{}_{1s}(\mathbf{r}_1) {}_{2s}(\mathbf{r}_2) \quad {}_{1s}(\mathbf{r}_2) {}_{2s}(\mathbf{r}_1)}_{\text{space}} \quad \underbrace{\alpha(\boldsymbol{\sigma}_2)\alpha(\boldsymbol{\sigma}_1)}_{\text{spin}}] \end{aligned}$$

Applying the same principle to the $1s \uparrow 2s \downarrow$ configuration gives us a bit of trouble:

$$\Rightarrow \frac{1}{\sqrt{2}} [{}_{1s}(\mathbf{r}_1) {}_{2s}(\mathbf{r}_2)\alpha(\boldsymbol{\sigma}_1)\alpha(\boldsymbol{\sigma}_2) \quad {}_{1s}(\mathbf{r}_2) {}_{2s}(\mathbf{r}_1)\alpha(\boldsymbol{\sigma}_2) (\boldsymbol{\sigma}_1)] \neq \text{space spin}$$

Hence, the pure $\uparrow\downarrow$ configuration can't be separated in terms of a space part and a spin part. We find a similar result for $1s \downarrow 2s \uparrow$:

$$\Rightarrow \frac{1}{\sqrt{2}} [{}_{1s}(\mathbf{r}_1) {}_{2s}(\mathbf{r}_2) (\boldsymbol{\sigma}_1)\alpha(\boldsymbol{\sigma}_2) \quad {}_{1s}(\mathbf{r}_2) {}_{2s}(\mathbf{r}_1) (\boldsymbol{\sigma}_2)\alpha(\boldsymbol{\sigma}_1)] \neq \text{space spin}$$

Since we know the wave function *should* separate, we have a problem. The solution comes in realizing that for an open shell configuration like this one, the $1s \uparrow 2s \downarrow$ and $1s \downarrow 2s \uparrow$ states

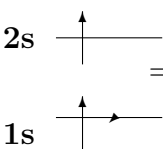
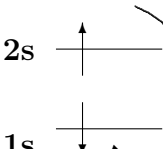
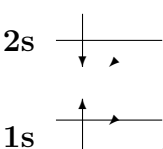
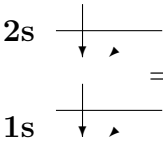
are degenerate eigenstates and so we can make any linear combinations of them we like and we'll still obtain an eigenstate. If we make the “+” and “-” combinations of $1s \uparrow 2s \downarrow$ and $1s \downarrow 2s \uparrow$ we obtain:

$$\begin{aligned} \Rightarrow & \frac{1}{\sqrt{2}} [\underbrace{1s(1) 2s(2)}_{\text{space}} \alpha(1) \underbrace{(2)}_{\text{spin}} \quad \underbrace{1s(2) 2s(1)}_{\text{space}} \alpha(2) \underbrace{(1)}_{\text{spin}}] \\ & \pm \frac{1}{\sqrt{2}} [\underbrace{1s(1) 2s(2)}_{\text{space}} \underbrace{(1) \alpha(2)}_{\text{spin}} \quad \underbrace{1s(2) 2s(1)}_{\text{space}} \underbrace{(2) \alpha(1)}_{\text{spin}}] \end{aligned}$$

four additive terms

$$\Rightarrow \frac{1}{\sqrt{2}} [\underbrace{1s(1) 2s(2)}_{\text{space}} \mp \underbrace{1s(2) 2s(1)}_{\text{space}}] \frac{1}{\sqrt{2}} [\underbrace{\alpha(1) (2) \pm \alpha(2) (1)}_{\text{spin}}]$$

also four additive terms, which separates nicely. Performing similar manipulations for the $\uparrow\uparrow$ configuration and taking care to make sure that all of our spatial and spin wavefunctions are individually normalized allows us to complete the table we set out for the $1s2s$ excited states:

	$\text{space}(\mathbf{r}_1, \mathbf{r}_2)$	\times	$\text{spin}(\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2)$
1		$\Rightarrow \frac{1}{\sqrt{2}} [$	$1s(\mathbf{r}_1) 2s(\mathbf{r}_2) \quad 1s(\mathbf{r}_2) 2s(\mathbf{r}_1)] \times \alpha(\boldsymbol{\sigma}_1) \alpha(\boldsymbol{\sigma}_2)$
2		$\frac{1}{\sqrt{2}} [$	$1s(\mathbf{r}_1) 2s(\mathbf{r}_2) + 1s(\mathbf{r}_2) 2s(\mathbf{r}_1)] \times \frac{1}{\sqrt{2}} [\alpha(\boldsymbol{\sigma}_1) (\boldsymbol{\sigma}_2) \quad (\boldsymbol{\sigma}_1) \alpha(\boldsymbol{\sigma}_2)]$
and			
3		$\frac{1}{\sqrt{2}} [$	$1s(\mathbf{r}_1) 2s(\mathbf{r}_2) \quad 1s(\mathbf{r}_2) 2s(\mathbf{r}_1)] \times \frac{1}{\sqrt{2}} [\alpha(\boldsymbol{\sigma}_1) (\boldsymbol{\sigma}_2) + (\boldsymbol{\sigma}_1) \alpha(\boldsymbol{\sigma}_2)]$
4		$\Rightarrow \frac{1}{\sqrt{2}} [$	$1s(\mathbf{r}_1) 2s(\mathbf{r}_2) \quad 1s(\mathbf{r}_2) 2s(\mathbf{r}_1)] \times (\boldsymbol{\sigma}_1) (\boldsymbol{\sigma}_2)$

We notice several things about these wave functions:

- While the overall wave function is always antisymmetric by construction, *the spatial part can be either antisymmetric* (cases 1, 3 and 4) *or symmetric* (case 2). This effect

is compensated for in the spin part, which can also be antisymmetric (case 2) or symmetric (cases 1,3 and 4). The resulting wave function always has a symmetric part times an antisymmetric part, resulting in an antisymmetric wave function.

- The spin part of Case 2 is exactly the same as the spin part of the ground state of the helium atom. Thus, just as we thought of the electrons in the ground state as being “paired“, we say **the electrons in Case 2 are paired**.
- The spatial parts of three of the states above (cases 1,3 and 4) are the same. Case 2 has a different spatial part. Because the Hamiltonian only depends on spatial variables and not spin, we immediately conclude that states 1,3 and 4 will be degenerate — even when we take into account the electron-electron interaction. State 2, however, will generally have a different energy once we account for interactions. In common spectroscopic parlance the three degenerate states are called a **triplet** and the unique state is called a **singlet**. Further, because these states arise from degenerate spin states, they are called singlet and triplet spin states

Energies of Singlet and Triplet States

As we showed above, we expect the singlet and triplet states to have different energies once electron repulsion is taken into account. Which one will be lower? To decide this, we note that the triplet spatial wavefunction is zero when the two electrons are at the same position:

$$\mathbf{r}_1 = \mathbf{r}_2 \implies T = \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_1) \psi_{2s}(\mathbf{r}_1) - \psi_{1s}(\mathbf{r}_1) \psi_{2s}(\mathbf{r}_1)] = 0$$

whereas the singlet wavefunction is non-zero:

$$\mathbf{r}_1 = \mathbf{r}_2 \implies S = \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_1) \psi_{2s}(\mathbf{r}_1) + \psi_{1s}(\mathbf{r}_1) \psi_{2s}(\mathbf{r}_1)] = \sqrt{2} \psi_{1s}(\mathbf{r}_1) \psi_{2s}(\mathbf{r}_1) \neq 0.$$

Because the electrons repel each other more when they are close to one another, we therefore expect the singlet to have more electron-electron repulsion and a higher energy. This rule turns out to hold quite generally and is called Hund’s first rule: **for degenerate non-interacting states, the configuration with highest spin multiplicity lies lowest in energy**. Hund actually has three rules (of which this is the first) concerning the ordering of degenerate noninteracting states. The others will not be discussed here, but see McQuarrie Section 9.11-9.12 for more on this topic.

So we expect the triplet to be lower. How much lower? To answer this question, we have to compute the average energies of the singlet and triplet wavefunctions. *Recall that the spin*

part never matters for the energy:

$$\begin{aligned} \int \hat{\mathbf{H}} \, d\mathbf{r}d\boldsymbol{\sigma} &= \int \int \hat{\mathbf{H}}_{\text{space}} \, d\mathbf{r} \int \int \hat{\mathbf{H}}_{\text{spin}} \, d\boldsymbol{\sigma} = \int \int \hat{\mathbf{H}}_{\text{space}} \, d\mathbf{r} \int \int \mathbf{1} \, d\boldsymbol{\sigma} \\ &= \int \int \hat{\mathbf{H}}_{\text{space}} \, d\mathbf{r} \end{aligned}$$

The influence of the spin wave function is only indirect: if the spin part is antisymmetric (e.g. singlet) then the spatial part must be symmetric and *vice versa*. To simplify our algebra, it is convenient to create the obvious shorthand notation:

$$\begin{aligned} T &= \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_1) \psi_{2s}(\mathbf{r}_2) - \psi_{1s}(\mathbf{r}_2) \psi_{2s}(\mathbf{r}_1)] \equiv \frac{1}{\sqrt{2}} (1s2s - 2s1s) \\ S &= \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_1) \psi_{2s}(\mathbf{r}_2) + \psi_{1s}(\mathbf{r}_2) \psi_{2s}(\mathbf{r}_1)] \equiv \frac{1}{\sqrt{2}} (1s2s + 2s1s) \end{aligned}$$

where we just need to remember that the first function in a product will be the one that has electron “1” while the second will have electron “2”. Proceeding then:

$$\begin{aligned} E_{S/T} &= \iint \psi_{S/T}^* \hat{\mathbf{H}}_{S/T} \psi_{S/T} \, d\mathbf{r}_1 d\mathbf{r}_2 = \frac{1}{2} \iint (1s2s \pm 2s1s)^* (\hat{\mathbf{h}}_1 + \hat{\mathbf{h}}_2 + \hat{V}_{12}) (1s2s \pm 2s1s) \, d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{2} \iint (1s2s \pm 2s1s)^* \left(E_{1s} + E_{2s} + \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right) (1s2s \pm 2s1s) \, d\mathbf{r}_1 d\mathbf{r}_2 \\ &= E_{1s} + E_{2s} + \frac{e^2}{8\pi\epsilon_0} \iint (1s2s \pm 2s1s)^* \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} (1s2s \pm 2s1s) \, d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned}$$

On the second line, we have used the fact that both S and T are eigenstates of the *independent particle Hamiltonian* (that is, \mathbf{h}_1 and \mathbf{h}_2 are hydrogenic Hamiltonians and $1s$ and $2s$ are hydrogenic orbitals). On the third line, we have taken the independent particle energy outside the integral because S and T are normalized. Thus, we see that the average energy takes on the familiar form of (non-interacting energy)+(interactions). The interaction term can be simplified further:

$$\begin{aligned} &\frac{e^2}{8\pi\epsilon_0} \iint (1s2s \pm 2s1s)^* \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} (1s2s \pm 2s1s) \, d\mathbf{r}_1 d\mathbf{r}_2 \quad (4 \text{ terms}) \\ \implies &\frac{e^2}{8\pi\epsilon_0} \iint [1s^* 2s^* \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} 1s2s \pm 1s^* 2s^* \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} 2s1s \pm 2s^* 1s^* \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} 1s2s \\ &\quad + 2s^* 1s^* \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} 2s1s] \, d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned}$$

We note that the first and last terms are the same if we just *interchange the dummy integration variables* (and recall that all the orbitals are real, so that we can drop the complex conjugation):

$$\begin{aligned} \frac{e^2}{4\pi\epsilon_0} \iint 1s^*(1)2s^*(2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} 1s(1)2s(2) d\mathbf{r}_1 d\mathbf{r}_2 \\ \xrightarrow{1 \leftrightarrow 2} \frac{e^2}{4\pi\epsilon_0} \iint 1s^*(2)2s^*(1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} 1s(2)2s(1) d\mathbf{r}_2 d\mathbf{r}_1 \\ = \frac{e^2}{4\pi\epsilon_0} \iint 2s^*(1)1s^*(2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} 2s(1)1s(2) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned}$$

Note the tie lines: $e(1)$ is in $2s$ and $e(2)$ is in $1s$. Meanwhile the second and third terms are also the same:

$$\begin{aligned} \frac{e^2}{4\pi\epsilon_0} \iint 1s^*(1)2s^*(2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} 1s(2)2s(1) d\mathbf{r}_1 d\mathbf{r}_2 \\ \xrightarrow{1 \leftrightarrow 2} \frac{e^2}{4\pi\epsilon_0} \iint 1s^*(2)2s^*(1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} 1s(1)2s(2) d\mathbf{r}_2 d\mathbf{r}_1 \\ = \frac{e^2}{4\pi\epsilon_0} \iint 2s^*(1)1s^*(2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} 1s(1)2s(2) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned}$$

Note the different arrangement of the tie lines: $e(1)$ is in $1s$ on left and $2s$ on the right. These integrals are called **Coulomb** (J) and **exchange** (K) integrals, respectively. Both are positive numbers (because they arise from electron *repulsion*). The Coulomb integral is so named because we can re-write it as

$$J = \frac{e^2}{4\pi\epsilon_0} \iint \frac{|1s(1)|^2 |2s(2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2.$$

The first factor in the numerator is the *probability* of finding a $1s$ electron at a point \mathbf{r}_1 , while the second is the *probability* of finding a $2s$ electron at a point \mathbf{r}_2 . Since the electron is charged, each of these probabilities reflects the appropriate *charge density* at the points \mathbf{r}_1 and \mathbf{r}_2 , and J reflects the *classical electrostatic repulsion* between these two densities. Thus, J accounts for the classical repulsion between the $1s$ and $2s$ electrons (according to Coulomb's law).

Meanwhile, K is completely quantum mechanical in nature. This exchange interaction results from the fact that the electrons are indistinguishable and the wavefunction is antisymmetric. Notice that, if we had not antisymmetrized our wavefunctions, the spatial part would have just been a direct product $1s2s$ instead of the symmetric/antisymmetric $1s2s \pm 2s1s$ combinations we obtained for the singlet and triplet. In the former case, the electrons are being treated as distinguishable (e.g. electron "1" is always $1s$ while electron

“2” is always 2s) and the exchange term disappears from the energy:

$$\frac{1}{2} \iint (1s2s \pm 2s1s)^* \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} (1s2s \pm 2s1s) d\mathbf{r}_1 d\mathbf{r}_2$$

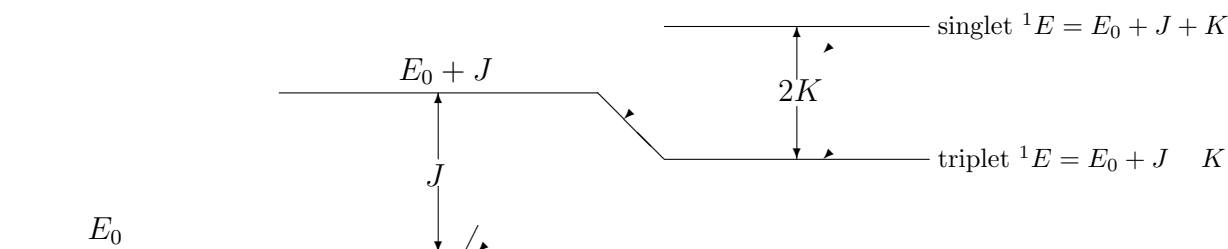
$$\text{distinguishable} \rightarrow \iint 1s^* 2s^* \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} 1s 2s d\mathbf{r}_1 d\mathbf{r}_2.$$

Clearly exchange — which arises from the cross terms on the LHS — is absent on the RHS. Thus, the K integrals only arise when we have terms in the wavefunction where two electrons have exchanged places. Hence the name “exchange.” It is important to note that, next to the Pauli exclusion principle, this is the largest impact that antisymmetry has on chemistry. It can be rigorously proved that $J > K$ always (i.e. no matter what functional form the 1s and 2s wavefunctions have).

Thus, in terms of J and K the energies of the singlet and triplet states become:

$$E_{S/T} = E_{1s} + E_{2s} + J_{1s2s} \pm K_{1s2s}.$$

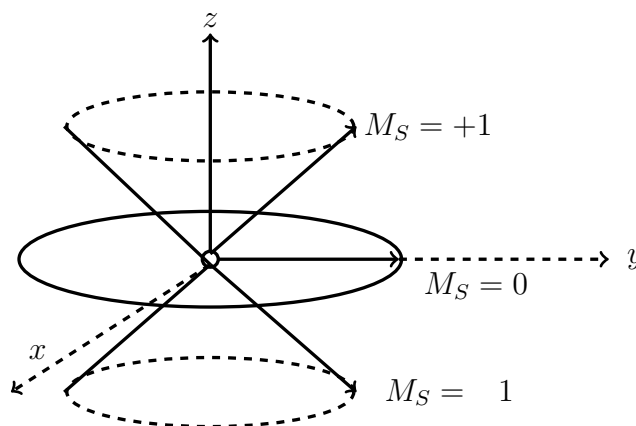
Thus we see that, as expected, the singlet state is higher in energy than the triplet. In fact, we can even give a numerical estimate for the splitting by evaluating K_{12} . Plugging in the forms of the 1s and 2s orbitals of helium and doing the integrals, we obtain $K_{12} = 32/729 = 1.2$ eV and a splitting of $2K_{12} = 2.4$ eV. The latter is quite a bit larger than the experimental singlet-triplet splitting in helium, which comes out to only 0.8 eV. Once again, we see the independent particle model gives us a *qualitatively correct* picture (i.e. the sign of the splitting is correct and of the right order of magnitude) but we fail to obtain quantitative results. We therefore arrive at the following qualitative picture of the 1s2s excited state of Helium:



In other chemistry courses you may have been taught that there are only two spin states for a pair of electrons: $\uparrow\downarrow$ and $\uparrow\uparrow$. The former represented the singlet state and the latter the triplet state. You were told to think of the singlet electrons as being “paired” and the triplets as being “unpaired.” However, how do these strange spin states we’ve derived connect with the “paired” and “unpaired” ideas? To answer this question, first of all we should note that neither of the antiparallel states we’ve derived is strictly $\uparrow\downarrow$. Instead, they look like $\uparrow\downarrow \pm \downarrow\uparrow$, with $\uparrow\downarrow - \downarrow\uparrow$ being the singlet and $\uparrow\downarrow + \downarrow\uparrow$ being part of the triplet. The idea that the singlet state is $\downarrow\uparrow$ is a white lie that you were told in order to simplify the arguments: as long as the subtle difference between $\downarrow\uparrow$ and $\uparrow\downarrow - \downarrow\uparrow$ isn’t important, we can get away with explaining much (though not all) chemistry by treating the singlet state as $\uparrow\downarrow$.

In the more precise picture we've derived here, **the spin part of the wavefunction determines whether the electrons are paired or not**. An electron pair has the characteristic spin part $\alpha\beta - \beta\alpha$. That is to say, paired electrons form a singlet. Spin parts that look like $\alpha\alpha$, $\alpha\beta + \beta\alpha$, or $\beta\beta$ are unpaired triplet configurations. As we have seen above, **pairing two electrons raises the energy through the exchange integral**. In some situations, this is called the "pairing energy." The counterintuitive thing that we have to re-learn is that $\alpha\beta + \beta\alpha$ does not describe an electron pair. In every way it behaves like $\alpha\alpha$ or $\beta\beta$: the energies are the same and (as you may show on the homework) the eigenvalues of $\widehat{S}_{\text{total}}^2$ are the same. This idea really does not fit into the simple qualitative picture of triplet states being $\uparrow\uparrow$,

but it is nonetheless true. The fact that there are three components of the triplet state is not a coincidence. As you will show, the eigenvalues of $\widehat{S}_{\text{total}}^2$ for the triplet states are all $2\hbar^2$, which is consistent with a total spin of $S = 1$, because the eigenvalues of $\widehat{S}_{\text{total}}^2$ would then be $\hbar^2 S(S + 1) = 2\hbar^2$. This picture is also consistent with the idea that, if we add two spins with $s = \frac{1}{2}$ parallel to one another, we should get a total S of $S = \frac{1}{2} + \frac{1}{2} = 1$. Given this picture, we note that the three triplet states would then correspond to the three possible z -projections of spin. That is to say the three triplet



states should have $M_S = +1, 0$ and -1 , respectively. This gives us at least some qualitative picture of what the $\alpha\beta + \beta\alpha$ state means and why it corresponds to unpaired electrons. In the $\alpha\beta + \beta\alpha$ state the spins are oriented parallel to each other, but they are both oriented perpendicular to the z -axis, so that on average you will always find one spin-up and one spin-down along z . This is a very simple example of the addition of angular momentum, a topic which is covered in much greater depth in McQuarrie.

Consider also the use of S_{\pm} to obtain all of the M_S eigenstates of a two-electron state.

$$\begin{aligned}
 S_{\pm} |SM_S\rangle &= \hbar[S(S+1) - M_S(M_S \pm 1)]^{1/2} |SM_S \pm 1\rangle \\
 S_{-} |1\ 1\rangle &= \hbar[2 - 0]^{1/2} |1\ 0\rangle \\
 S_{-} |1\ 0\rangle &= \hbar[2 - 0]^{1/2} |1\ -1\rangle \\
 S_{-} |1\ -1\rangle &= 0 \\
 S_{+} |0\ 0\rangle &= 0
 \end{aligned}$$

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