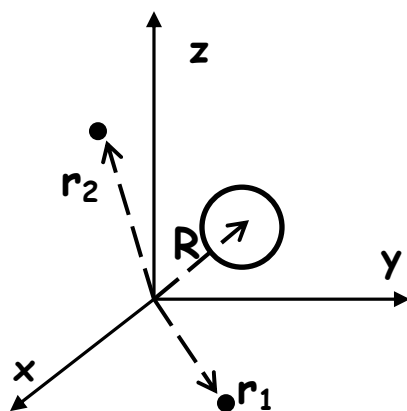


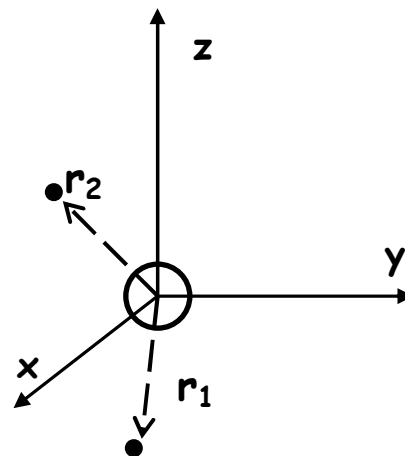
HELIUM ATOM

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 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 ($M_{\text{Nuc}} \approx 7000 m_{\text{el}}$) 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, $R=0$ 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 $\hat{r}_1, \hat{r}_2, \hat{r}_3, \dots$ and associated momentum operators $\hat{p}_1, \hat{p}_2, \hat{p}_3, \dots$. The operators for a given particle (i) will be assumed to commute with all operators associated with any other particle (j):

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

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

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

while all components belonging to different axes commute:

$$\hat{x}_1 \hat{y}_1 = \hat{y}_1 \hat{x}_1 \quad \hat{p}_{z_1} \hat{y}_1 = \hat{y}_1 \hat{p}_{z_1} \quad \hat{p}_{z_1} \hat{p}_{x_1} = \hat{p}_{x_1} \hat{p}_{z_1} \quad \text{etc.}$$

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 down the Hamiltonian for the Helium atom:

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

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. These constants result from our decision to use SI units (meter, gram, second) to express our lengths, masses and energies. This approach is quite awkward when the typical mass we're dealing with is 10^{-28} grams, the typical distance is 10^{-10} meters and the typical energy unit is 10^{-18} Joules. It is therefore much simpler to work everything out in what are called **atomic units**. In this system of units we choose our unit of mass to be equal to the electron mass, m_e , our unit of charge to be equal to the electron charge, e , and our unit of angular momentum to be \hbar . Further, we choose to work in electrostatic units, so that the permittivity of free space ($4\pi\epsilon_0$) is also 1. The result of these four choices is twofold. First of all, the Hamiltonian of the Helium atom (and indeed of any atom or molecule) simplifies greatly because all the constants are unity and can be omitted in writing the equations:

$$\hat{H} \equiv \frac{\hat{\mathbf{p}}_1^2}{2} + \frac{\hat{\mathbf{p}}_2^2}{2} - \frac{Z}{\hat{r}_1} - \frac{Z}{\hat{r}_2} + \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|}$$

$$= -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{\hat{r}_1} - \frac{Z}{\hat{r}_2} + \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|}$$

This will greatly simplify our algebra in the future and we will typically use atomic units from this point forward. The second benefit of this choice of units is that now our units of energy, mass, distance, angular momentum, etc. are of the appropriate size for dealing with atoms and molecules:

Atomic units and their SI equivalents		
Quantity	Natural unit	SI equivalent
Electron mass	$m = 1$	9.11×10^{-31} kg
Charge	$ e = 1$	1.06×10^{-19} C
Angular momentum	$\hbar = 1$	1.05×10^{-34} J · s
Permittivity	$\kappa_0 = 4\pi\epsilon_0 = 1$	1.11×10^{-10} C ² · J ⁻¹ · m ⁻¹
Length	$\kappa_0 \hbar^2 / me^2 = a_0 = 1$ (bohr) (Bohr radius)	5.29×10^{-11} m
Energy	$me^4 / \kappa_0^2 \hbar^2 = e^2 / \kappa_0 a_0 = 1$ (hartree) (twice the ionization energy of H)	4.36×10^{-18} J = 27.2 eV
Time	$\kappa_0^2 \hbar^3 / me^4 = 1$ (period of an electron in the first Bohr orbit)	2.42×10^{-17} s
Speed	$e^2 / \kappa_0 \hbar = 1$ (speed of an electron in the first Bohr orbit)	2.19×10^6 m/s
Electric potential	$me^3 / \kappa_0^2 \hbar^2 = e^2 / \kappa_0 a_0 = 1$ (potential of an electron in the first Bohr orbit)	27.21 V
Magnetic dipole moment	$e\hbar/m = 1$ (twice a Bohr magneton)	1.85×10^{-23} J · T ⁻¹

Thus, so long as we work consistently in atomic units, we will tend to find energies that are of order unity, distances that are of order unity, momenta that are of order unity ... without having to keep track of so much scientific notation.

Once Schrodinger 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 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:

$$\hat{H}_{ind} = \frac{\nabla_1^2}{2} + \frac{\nabla_2^2}{2} - \frac{Z}{\hat{r}_1} - \frac{Z}{\hat{r}_2} = \underbrace{\frac{\nabla_1^2}{2} - \frac{Z}{\hat{r}_1}}_{\text{Electron One}} + \underbrace{\frac{\nabla_2^2}{2} - \frac{Z}{\hat{r}_2}}_{\text{Electron Two}} \equiv \hat{H}_1 + \hat{H}_2$$

Thus, if we neglect the interaction between the electrons, the Hamiltonian reduces to the **sum of two hydrogenic atom Hamiltonians** (with $Z=2$). Based on our experience with separable Hamiltonians in the past (Hamiltonians Add \rightarrow Wavefunctions Multiply \rightarrow Energies Add), we can immediately write down the correct form for the eigenfunctions and eigenvalues of this Hamiltonian:

$$\Psi_{n_1 l_1 m_1 s_1; n_2 l_2 m_2 s_2}(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) = \psi_{n_1 l_1 m_1 s_1}(\mathbf{r}_1, \sigma_1) \psi_{n_2 l_2 m_2 s_2}(\mathbf{r}_2, \sigma_2)$$

$$E_{n_1 n_2} = E_{n_1} + E_{n_2} = -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2}$$

where, in the second line, 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 already solve easily.

However, the outstanding question is: how good is this approximation? The easiest way to test this is to look at the ground state. According to the Pauli exclusion principle, we can't put two electrons in the same state. However, as we learned in freshman chemistry, we can put one electron in 1s with spin up and the other in 1s with spin down:

$$\Psi_{1s\alpha; 1s\beta}(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) = \psi_{100\alpha}(\mathbf{r}_1, \sigma_1) \psi_{100\beta}(\mathbf{r}_2, \sigma_2)$$

This wavefunction 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 24.2 eV to remove and the second takes 54.4 eV to remove, which means the correct ground state energy is 78.8 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

So how can we go about improving this approximation? Well, first we note 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:

$$\begin{aligned} \psi_{1s\alpha}(\mathbf{r}_1, \sigma_1) \psi_{1s\beta}(\mathbf{r}_2, \sigma_2) &\xrightarrow{\substack{\text{Interchange} \\ 1 \text{ and } 2}} \psi_{1s\alpha}(\mathbf{r}_2, \sigma_2) \psi_{1s\beta}(\mathbf{r}_1, \sigma_1) \\ &\neq -\psi_{1s\alpha}(\mathbf{r}_1, \sigma_1) \psi_{1s\beta}(\mathbf{r}_2, \sigma_2) \end{aligned}$$

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

$$\Psi_{1s\alpha;1s\beta}(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) \equiv \frac{1}{\sqrt{2}} (\psi_{1s\alpha}(\mathbf{r}_1, \sigma_1) \psi_{1s\beta}(\mathbf{r}_2, \sigma_2) - \psi_{1s\alpha}(\mathbf{r}_2, \sigma_2) \psi_{1s\beta}(\mathbf{r}_1, \sigma_1))$$

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

$$\begin{aligned} \Psi_{1s\alpha;1s\beta}(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) &\equiv \frac{1}{\sqrt{2}} (\psi_{1s\alpha}(\mathbf{r}_1, \sigma_1) \psi_{1s\beta}(\mathbf{r}_2, \sigma_2) - \psi_{1s\alpha}(\mathbf{r}_2, \sigma_2) \psi_{1s\beta}(\mathbf{r}_1, \sigma_1)) \\ &\xrightarrow{1 \leftrightarrow 2} \frac{1}{\sqrt{2}} (\psi_{1s\alpha}(\mathbf{r}_2, \sigma_2) \psi_{1s\beta}(\mathbf{r}_1, \sigma_1) - \psi_{1s\alpha}(\mathbf{r}_1, \sigma_1) \psi_{1s\beta}(\mathbf{r}_2, \sigma_2)) \\ &= -\frac{1}{\sqrt{2}} (\psi_{1s\alpha}(\mathbf{r}_1, \sigma_1) \psi_{1s\beta}(\mathbf{r}_2, \sigma_2) - \psi_{1s\alpha}(\mathbf{r}_2, \sigma_2) \psi_{1s\beta}(\mathbf{r}_1, \sigma_1)) \\ &= -\Psi_{1s\alpha;1s\beta}(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) \end{aligned}$$

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 independent 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 got from

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

where $d\tau_1 = d\mathbf{r}_1 d\sigma_1$ 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 fold these interactions back in in an approximate way by computing the average energy *including the interaction*.

We can simplify the average energy pretty quickly:

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

We thus have for the average energy:

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

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 raise the average energy, which is a good thing, since our non-interacting picture gave an energy that was 30 eV too low! 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:

$$\begin{aligned} & \frac{1}{\sqrt{2}} (\psi_{1s\alpha}(\mathbf{r}_1, \sigma_1) \psi_{1s\beta}(\mathbf{r}_2, \sigma_2) - \psi_{1s\alpha}(\mathbf{r}_2) \psi_{1s\beta}(\mathbf{r}_1, \sigma_1)) \\ \Rightarrow & \frac{1}{\sqrt{2}} (\psi_{1s}(\mathbf{r}_1) \alpha(\sigma_1) \psi_{1s}(\mathbf{r}_2) \beta(\sigma_2) - \psi_{1s}(\mathbf{r}_2) \alpha(\sigma_2) \psi_{1s}(\mathbf{r}_1) \beta(\sigma_1)) \\ \Rightarrow & \underbrace{\psi_{1s}(\mathbf{r}_1) \psi_{1s}(\mathbf{r}_2)}_{\Psi_{space}(\mathbf{r}_1, \mathbf{r}_2)} \underbrace{\frac{1}{\sqrt{2}} (\alpha(\sigma_1) \beta(\sigma_2) - \beta(\sigma_1) \alpha(\sigma_2))}_{\Psi_{spin}(\sigma_1, \sigma_2)} \end{aligned}$$

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 H is separable into a space and spin part

$$\hat{H} = \hat{H}_{space} + \hat{H}_{spin}$$

With the spin part being (trivially) zero. As a result, eigenfunctions of 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:

$$\begin{aligned} \int \frac{|\Psi_{1s\alpha;1s\beta}|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\tau_1 d\tau_2 &= \int \frac{|\Psi_{space} \Psi_{spin}|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 d\sigma_1 d\sigma_2 = \int \frac{|\Psi_{space}(\mathbf{r}_1, \mathbf{r}_2)|^2 |\Psi_{spin}(\sigma_1, \sigma_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 d\sigma_1 d\sigma_2 \\ &= \int |\Psi_{spin}(\sigma_1, \sigma_2)|^2 d\sigma_1 d\sigma_2 \int \frac{|\Psi_{space}(\mathbf{r}_1, \mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &\stackrel{1}{=} \int \frac{|\Psi_{space}(\mathbf{r}_1, \mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned}$$

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

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

Adding this average repulsion term to our non-interacting energy gives a ground state estimate of $-108.8 \text{ eV} + 34 \text{ eV} = -74.8 \text{ eV}$, which is only 4 eV off of the correct energy. The energy is still not very close, 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.