The helium atom Hamiltonian is given by

\[ H_{\text{He}} = -\frac{\hbar^2}{2M_{\text{He}^{++}}} \nabla_{\text{He}^{++}}^2 - \frac{\hbar^2}{2m_e} \left[ \nabla_{e_1}^2 + \nabla_{e_2}^2 \right] - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \]

where the notation is defined in the drawing. There are nine degrees of freedom.

**APPROXIMATIONS ARE REQUIRED!!!**

1. First we separate out the center of mass motion. This gets rid of 3 degrees of freedom, but the attractive forces along \( r_1 \) and \( r_2 \) are not central forces. For that matter, neither is the electron-electron repulsion along \( r_{12} \). More approximations are required
2. Let \( M_{\text{He}^+} = \infty \). Namely, place the center of mass on the nucleus. When we rearrange, then

\[
\hat{\mathcal{H}}_{\text{He}} \equiv \left( -\frac{\hbar^2}{2m_e} \nabla_{e_1}^2 - \frac{2e^2}{r_1} \right) + \left( -\frac{\hbar^2}{2m_e} \nabla_{e_2}^2 - \frac{2e^2}{r_2} \right) + \frac{e^2}{r_{12}}
\]

**STILL NOT SEPARABLE!**

The problem of course is the \( e^2/r_{12} \) term, which couples the two electrons. Without it, this would be two separable central field problems. The energy would be the sum of two separate one electron ion energies, and the wave function would be a product of two separate one electron ion wavefunctions.

3. **Drop the \( r_{12} \) term!** This is equivalent to letting \( r_{12} = \infty \), a rather dumb approximation. (Note that the separation to follow in the notes would work equally well if \( r_{12} \) were simply a constant. In fact we would be much better off for chemical purposes by letting it be a few \( a_0 \).)
Now the helium Hamiltonian is separable, and looks like two independent He$^+$ problems. We know the energies and wavefunctions for He$^+$, and the $Z^2$ scaling in the energy expression. There will be 6 quantum numbers: $n_1, n_2, \ell_1, \ell_2, m_{\ell_1}$ and $m_{\ell_2}$.

$$E_{n_1,n_2} = \frac{4e^2}{2a_0} \left[ \frac{1}{n_1^2} + \frac{1}{n_2^2} \right]$$

$n_1 = 1,2,3,...$

$n_1 = 1,2,3,...$

with state function $\psi_{He}$ given by the product

$$\psi_{He} = R_{n_1,\ell_1}(r_1) Y_{\ell_1,m_1}(\theta_1,\phi_1) R_{n_2,\ell_2}(r_2) Y_{\ell_2,m_2}(\theta_2,\phi_2).$$

A commonly employed notation is $\psi_{He} = \psi_{n_1,\ell_1,m_1}(1) \psi_{n_2,\ell_2,m_2}(2)$

Instead of the three 1-electron quantum numbers, we might also just use the orbital designation, 1s, 2pz, etc. Thus the He ground state wave function is given by $\psi_{He} = \psi_{1s}(1) \psi_{1s}(2)$

NOTATION: The subscript indicates the state, and the value in parentheses the identity of the electron.
This is real progress!! We have found the following for He. It breaks into two independent He$^+$ problems with:

- 6 quantum numbers
- orbitals -- they are the He$^+$ orbitals we know
- energies
- angular momentum quantized
- wavefunction is product of two He$^+$ wavefunctions

Let's make comparisons of our result with experiment, the real world!

### Ionization Potential of He

<table>
<thead>
<tr>
<th>Reaction</th>
<th>IP</th>
</tr>
</thead>
<tbody>
<tr>
<td>He → He$^+$ + e</td>
<td>IP(He) = 24.6 eV</td>
</tr>
<tr>
<td>He$^+$ → He$^{++}$ + e</td>
<td>IP(He$^+$) = 54.4 eV</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Total Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>He → He$^{++}$ + 2e</td>
<td>Total energy(He) = 78.98 eV</td>
</tr>
</tbody>
</table>

How does our calculation compare with experiment??
Calculations of He and He$^+$ Ionization Potentials

The result for $IP(He^+)$ is $2^2 \times 13.6$ eV = 54.4 eV, exact, as we expect for a one electron ion.

\[ He^+ \rightarrow He^{++} + e \]

$IP(He^+) = 54.4$ eV

For $IP(He)$, we calculate the energy required to move one of the two electrons infinitely far away, leaving the other electron in the $n=1$ state. We obtain this result from $E(1,1) - E(1,\infty)$, giving

\[ IP(He) = 54.4 \text{ eV} \]

and the total energy, $He \rightarrow He^{++} + 2e$, $E_{\text{tot,He}} = 108.8 \text{ eV}$

The calculated He ionization energy is in error by ~30 eV or ~ 600 kcal/mol! This is much too large an error to be chemically useful.

Since we cannot solve the problem exactly, we begin to develop approximation methods. First, however, some issues that arise from multiple electrons
New Issues for Multi-electron Atoms

We shall discuss the various approximation methods shortly, but first we will deal with new issues arising from the presence of more than one electron.

These issues concern the nature of "intrinsic electron spin" and modifications to the wave function required by the presence of identical particles.

With these two pieces of information, we then encounter the Pauli Exclusion Principle, and complete our arsenal of tools required to build up atomic structure.

Various approximation methods can calculate the energy of the helium ground state, 1s², to arbitrary accuracy. We have seen no problems until we either think about helium excited states or realize that our knowledge to date would predict a 1s³ ground state for Li.

OOPS! Houston, there is a problem!
Stern-Gerlach Experiment and Electron Spin

The Stern-Gerlach experiment showed that a beam of one electron atoms (Ag) were deflected into two groups by an inhomogeneous magnetic field. The presence of any deflection indicates some magnetic property. The expected result was that the magnetic field would split the beam up into its $(2\ell + 1)$ components, corresponding to the spatial orientations of $L$ in the magnetic field. The observation of two components indicates that there is a magnetic effect with $\ell = 1/2$! This will be seen to be the electron spin magnetic moment.

The intrinsic electron spin arises naturally in a relativistic formulation of quantum mechanics, but in a non-relativistic form, we must introduce an additional postulate concerning spin.
We postulate the existence of spin angular momentum operators, $\hat{S}_x, \hat{S}_y, \hat{S}_z, \hat{S}^2$, completely analogous to the angular momentum operators, $\hat{L}_x, \hat{L}_y, \hat{L}_z, \hat{L}^2$. i.e.,

\[ [\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z \text{ and cyclic permutations} \]

\[ [\hat{S}_z, \hat{S}^2] = 0 \text{ as well as for the other components.} \]

The spin eigenvalues are postulated to have similar properties:

<table>
<thead>
<tr>
<th>Operator</th>
<th>Eigenvalues</th>
<th>Quantum Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\hat{S}^2$</td>
<td>$s(s+1)\hbar^2$</td>
<td>$s = 0, 1/2, 1, 3/2, 2, \ldots$</td>
</tr>
<tr>
<td>$\hat{S}_z$</td>
<td>$m_s \hbar$</td>
<td>$m_s = -s, -s+1, \ldots s$</td>
</tr>
</tbody>
</table>

The quantum number $s$ is called the spin of the particle. Experimentally, we find that elementary particles possess only a single value of spin.
In other words, spin is an intrinsic property of a particle.

Consider electrons with $s = 1/2$. The only possible eigenvalue of $\hat{S}^2$ is \( \frac{1}{2} \left( \frac{1}{2} + 1 \right) \hbar^2 = \frac{3}{4} \hbar^2 \).

Thus we have that the magnitude of the electron spin angular momentum is exactly \( \frac{\sqrt{3}}{2} \hbar \).

The possible eigenvalues for $\hat{S}_z$ and the spin eigenfunctions are given below.

<table>
<thead>
<tr>
<th>$\hat{S}_z$ Eigenvalue</th>
<th>$\hat{S}^2$ Eigenvalue</th>
<th>Eigenfunction</th>
</tr>
</thead>
<tbody>
<tr>
<td>((1/2)\hbar)</td>
<td>((3/4)\hbar^2)</td>
<td>$\alpha$(up)</td>
</tr>
<tr>
<td>(- (1/2)\hbar)</td>
<td>((3/4)\hbar^2)</td>
<td>$\beta$(down)</td>
</tr>
</tbody>
</table>
What do we know about the spin functions? They form a complete, orthonormal set spanning spin space.

\[ \langle \alpha | \alpha \rangle = 1 \]

Thus \( \langle \beta | \beta \rangle = 1 \)
\( \langle \alpha | \beta \rangle = 0 \)

where the integration is over "spin coordinates". The physical picture is as follows:

There is also a spin magnetic moment \( \mu \) associated with the electron, given by \( \mu = g_e \frac{e}{2m_e c} \bar{S} \) in the absence of an external magnetic field.
The term $g_e$ is $2.0023 \ldots$ and is known as the $g$-factor of the free electron. It is this magnetic moment that caused the silver atom beam to split up into two components. The two spin states are degenerate in the H atom.

Since the electron spin did not appear in the one electron Hamiltonian, the spin part is separable and the wavefunctions now have a fourth quantum number and are given by the product of a space part and a spin part.

$$\psi_{n,\ell,m,n_m} = \psi_{n,\ell,m,\alpha} \text{ or } \psi_{n,\ell,m,\beta}$$

These functions are frequently called spin-orbitals and written $1s\alpha$, $3p_z\beta$ etc.

We now have a $2n^2$ energy degeneracy for the H atom wavefunctions with orthogonality conditions $\langle \psi_{n,\ell,m,\alpha} | \psi_{n,\ell,m,\beta} \rangle = 0$ and similar relations.

The major chemical consequences of spin are only apparent after we learn how to modify the multi electron wave function to account for the inherent indistinguishability of identical particles.