

Chapter 1: Review of atomic physics

Hydrogen

The simplest atom is hydrogen; it consists of one proton and one electron. The Hamiltonian for a hydrogen atom is,

$$H_{total}^H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}. \quad (1)$$

Here m is the mass of an electron, e is the elementary charge, ϵ_0 is the permittivity constant, and \hbar is the reduced Planck's constant. Hydrogen is the only atom for which the eigenstates can be found analytically. The first few eigenstates are,

$$\begin{aligned} \psi_{1s} &= \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{r}{a_0}\right), \\ \psi_{2s} &= \frac{1}{4\sqrt{2\pi a_0^3}} \left(2 - \frac{r}{a_0}\right) \exp\left(-\frac{r}{2a_0}\right), \\ \psi_{2px} &= \frac{1}{4\sqrt{2\pi a_0^3}} \frac{r}{a_0} \exp\left(-\frac{r}{2a_0}\right) \sin\theta \cos\varphi, \\ \psi_{2py} &= \frac{1}{4\sqrt{2\pi a_0^3}} \frac{r}{a_0} \exp\left(-\frac{r}{2a_0}\right) \sin\theta \sin\varphi, \\ \psi_{2pz} &= \frac{1}{4\sqrt{2\pi a_0^3}} \frac{r}{a_0} \exp\left(-\frac{r}{2a_0}\right) \cos\theta. \end{aligned} \quad (2)$$

Here a_0 is the Bohr radius. The energies of the eigenstates can be determined by calculating the expectation value,

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2 n^2} = -\frac{13.6}{n^2} eV, \quad (3)$$

where n is the principle quantum number.

Helium

Helium has two electrons and a positively charged nucleus with a charge of $2e$. The Hamiltonian for helium is,

$$H_{total}^{He} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}. \quad (4)$$

The first term is the kinetic energy of electron 1, the second term is the kinetic energy of electron 2, the third term is the attractive Coulomb interaction between electron 1 and the nucleus, the fourth term is the attractive Coulomb interaction between electron 2 and the nucleus, and the last term is the repulsive electron-electron interaction. The eigenstates of this Hamiltonian are two-electron wavefunctions that depend on the positions of both electrons $\Psi(\vec{r}_1, \vec{r}_2)$. It is not possible to find a simple analytic expression for this two-electron wavefunction.

To simplify this problem, the electron-electron interactions are neglected resulting in the reduced Hamiltonian for helium,

$$H_{red}^{He} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2}. \quad (5)$$

The Schrödinger equation for this reduced Hamiltonian is,

$$-\frac{\hbar^2}{2m}\nabla_1^2\Psi - \frac{\hbar^2}{2m}\nabla_2^2\Psi - \frac{2e^2}{4\pi\epsilon_0 r_1}\Psi - \frac{2e^2}{4\pi\epsilon_0 r_2}\Psi = E\Psi. \quad (6)$$

This can be solved by the separation of variables. Assume that Ψ can be written as a product of two functions, $\Psi(\vec{r}_1, \vec{r}_2) = \phi_m(\vec{r}_1)\phi_n(\vec{r}_2)$. Substitute this form into the Schrödinger equation and divide by Ψ . The resulting terms can be rearranged so that all terms that depend on \vec{r}_1 can be put on the left side of the = sign and all terms that depend on \vec{r}_2 can be put on the right side of the = sign. Since a function of \vec{r}_1 cannot be equal to a function of \vec{r}_2 for all \vec{r}_1 and \vec{r}_2 , both sides of the equation must be equal to a constant. Let's call the constant E' . The separated equations are,

$$\begin{aligned} -\frac{\hbar^2}{2m}\nabla_1^2\phi_m(\vec{r}_1) - \frac{2e^2}{4\pi\epsilon_0|\vec{r}_1|}\phi_m(\vec{r}_1) &= (E - E')\phi_m(\vec{r}_1), \\ -\frac{\hbar^2}{2m}\nabla_2^2\phi_n(\vec{r}_2) - \frac{2e^2}{4\pi\epsilon_0|\vec{r}_2|}\phi_n(\vec{r}_2) &= E'\phi_n(\vec{r}_2). \end{aligned} \quad (7)$$

Both of these equations are nearly the same as the Schrödinger equation for hydrogen. A difference is that the Coulomb term is a factor of 2 greater than for hydrogen because of the $+2e$ charge of the helium nucleus. Nevertheless, slightly modified hydrogen wavefunctions called the atomic orbitals solve these equations.

Atomic orbitals

The first few atomic orbitals are,

$$\begin{aligned} \phi_{1s}^Z &= \sqrt{\frac{Z^3}{\pi a_0^3}} \exp\left(-\frac{Zr}{a_0}\right), \\ \phi_{2s}^Z &= \frac{1}{4}\sqrt{\frac{Z^3}{2\pi a_0^3}} \left(2 - \frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right), \\ \phi_{2px}^Z &= \frac{1}{4}\sqrt{\frac{Z^3}{2\pi a_0^3}} \frac{Zr}{a_0} \exp\left(-\frac{Zr}{2a_0}\right) \sin\theta \cos\varphi, \\ \phi_{2py}^Z &= \frac{1}{4}\sqrt{\frac{Z^3}{2\pi a_0^3}} \frac{Zr}{a_0} \exp\left(-\frac{Zr}{2a_0}\right) \sin\theta \sin\varphi, \\ \phi_{2pz}^Z &= \frac{1}{4}\sqrt{\frac{Z^3}{2\pi a_0^3}} \frac{Zr}{a_0} \exp\left(-\frac{Zr}{2a_0}\right) \cos\theta, \end{aligned} \quad (8)$$

where the superscript Z is the charge of the nucleus. For helium, $Z = 2$. These solutions are used extensively to describe the quantum states of atoms, molecules, and solids. The energies of the atomic orbitals are,

$$E = -\frac{Z^2 m e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} = -\frac{13.6 Z^2}{n^2} eV. \quad (9)$$

Many-electron wavefunctions

At this point it is necessary to discuss the properties of many-electron wavefunctions. This is because many-electron wavefunctions must satisfy an additional condition beyond being solutions to the Schrödinger equation: they must also be antisymmetric. A many-electron wavefunction must change sign when any two electrons are exchanged.

$$\Psi(\vec{r}_1, \dots, \vec{r}_j, \dots, \vec{r}_k, \dots, \vec{r}_j, \dots, \vec{r}_k) = -\Psi(\vec{r}_1, \dots, \vec{r}_k, \dots, \vec{r}_j, \dots, \vec{r}_k). \quad (10)$$

Many-electron wavefunctions are often written as products of atomic orbitals where it is necessary to include the spin in these products. The complete wavefunction of an electron is a product of a spatial part and a spin part. This is called a spin orbital. There are two spin orbitals for each of the atomic orbitals. The first few spin orbitals are,

$$\phi_{1s} \uparrow, \phi_{1s} \downarrow, \phi_{2s} \uparrow, \phi_{2s} \downarrow, \dots \quad (11)$$

Here the up and down arrows denote the spin of the spin orbitals. A many-electron wavefunction can be written as an antisymmetrized product of spin orbitals.

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \mathcal{A} \phi_{1s} \uparrow \phi_{1s} \downarrow \dots \phi_N \uparrow. \quad (12)$$

Here \mathcal{A} is the antisymmetrizing operator.

Slater determinants

One way to ensure the antisymmetry of the wavefunction is to construct a Slater determinant.

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{1s} \uparrow(\vec{r}_1) & \phi_{1s} \downarrow(\vec{r}_1) & \dots & \phi_N \uparrow(\vec{r}_1) \\ \phi_{1s} \uparrow(\vec{r}_2) & \phi_{1s} \downarrow(\vec{r}_2) & \dots & \phi_N \uparrow(\vec{r}_2) \\ \vdots & \vdots & & \vdots \\ \phi_{1s} \uparrow(\vec{r}_N) & \phi_{1s} \downarrow(\vec{r}_N) & \dots & \phi_N \uparrow(\vec{r}_N) \end{vmatrix}. \quad (13)$$

The rows in a Slater determinant are labeled by the electrons and the columns are labeled by the spin orbitals. If any two rows of a matrix are exchanged, the determinant changes sign. Therefore a Slater determinant always satisfies the antisymmetry condition.

If any two columns of the matrix are identical, the determinant is zero. This is an expression of the Pauli exclusion principle. No two electrons can occupy the same spin orbital. For notational convenience, a Slater determinant is often expressed in Dirac notation,

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = |\phi_{1s} \uparrow, \phi_{1s} \downarrow, \dots, \phi_N \uparrow\rangle. \quad (14)$$

The first spin orbital becomes the first column of the Slater determinant. The second spin orbital becomes the second column of the Slater determinant, and so forth. The order of the spin orbitals is important since exchanging the columns of the Slater determinant changes the sign of the wave function.

Returning to helium, the ground state of helium has two electrons in 1s orbitals. The two-electron ground state wavefunction is,

$$\Psi_0^{\text{He}}(\vec{r}_1, \vec{r}_1) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^{\text{He}} \uparrow(\vec{r}_1) & \phi_{1s}^{\text{He}} \downarrow(\vec{r}_1) \\ \phi_{1s}^{\text{He}} \uparrow(\vec{r}_2) & \phi_{1s}^{\text{He}} \downarrow(\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \phi_{1s}^{\text{He}}(\vec{r}_1) \phi_{1s}^{\text{He}}(\vec{r}_2) (\uparrow\downarrow - \downarrow\uparrow). \quad (15)$$

This is an exact solution to $H_{\text{red}}^{\text{He}}$ with an energy that can be determined from Eq. (9) to be -108.8 eV. A much better estimation for the energy can be obtained by numerically evaluating the energy using $H_{\text{total}}^{\text{He}}$ which includes the electron-electron interactions.

$$E_0^{\text{He}} \approx \frac{\langle \Psi_0^{\text{He}} | H_{\text{total}}^{\text{He}} | \Psi_0^{\text{He}} \rangle}{\langle \Psi_0^{\text{He}} | \Psi_0^{\text{He}} \rangle}. \quad (16)$$

This evaluates to -77.49 eV which is close to the actual ground state energy of -78.99 eV.

The first excited state of helium has one electron in a 1s orbital and one electron in a 2s orbital. There are four possible spin configurations for this state: $\uparrow\uparrow$, $\downarrow\downarrow$, $\downarrow\uparrow$, and $\uparrow\downarrow$. When the energy of these four states are evaluated using the reduced Hamiltonian (5), the energies of all four states are the same. Using Eq. (9), the energy of the first excited state is -68 eV.

However, when the energy of the four states is evaluated using the total Hamiltonian (4) which includes the electron-electron interactions, three of the states have the same energy but the fourth one has a different energy. The three states with the same energy are called the triplet state. The fourth state with a different energy is called a singlet.

Singlet and triplet states

The first excited state of helium has one electron in a 1s orbital and one electron in a 2s orbital. There are four possible spin configurations for this state: $\uparrow\uparrow$, $\downarrow\downarrow$, $\downarrow\uparrow$, and $\uparrow\downarrow$. The corresponding wavefunctions are,

$$\begin{aligned} \Psi_{\uparrow\uparrow} &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^{\text{He}} \uparrow(\vec{r}_1) & \phi_{2s}^{\text{He}} \uparrow(\vec{r}_1) \\ \phi_{1s}^{\text{He}} \uparrow(\vec{r}_2) & \phi_{2s}^{\text{He}} \uparrow(\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_{1s}^{\text{He}}(\vec{r}_1) \phi_{2s}^{\text{He}}(\vec{r}_2) - \phi_{2s}^{\text{He}}(\vec{r}_1) \phi_{1s}^{\text{He}}(\vec{r}_2)) \uparrow\uparrow, \\ \Psi_{\downarrow\downarrow} &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^{\text{He}} \downarrow(\vec{r}_1) & \phi_{2s}^{\text{He}} \downarrow(\vec{r}_1) \\ \phi_{1s}^{\text{He}} \downarrow(\vec{r}_2) & \phi_{2s}^{\text{He}} \downarrow(\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_{1s}^{\text{He}}(\vec{r}_1) \phi_{2s}^{\text{He}}(\vec{r}_2) - \phi_{2s}^{\text{He}}(\vec{r}_1) \phi_{1s}^{\text{He}}(\vec{r}_2)) \downarrow\downarrow, \\ \Psi_{\uparrow\downarrow} &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^{\text{He}} \uparrow(\vec{r}_1) & \phi_{2s}^{\text{He}} \downarrow(\vec{r}_1) \\ \phi_{1s}^{\text{He}} \uparrow(\vec{r}_2) & \phi_{2s}^{\text{He}} \downarrow(\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_{1s}^{\text{He}}(\vec{r}_1) \uparrow \phi_{2s}^{\text{He}}(\vec{r}_2) \downarrow - \phi_{2s}^{\text{He}}(\vec{r}_1) \downarrow \phi_{1s}^{\text{He}}(\vec{r}_2) \uparrow), \\ \Psi_{\downarrow\uparrow} &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^{\text{He}} \downarrow(\vec{r}_1) & \phi_{2s}^{\text{He}} \uparrow(\vec{r}_1) \\ \phi_{1s}^{\text{He}} \downarrow(\vec{r}_2) & \phi_{2s}^{\text{He}} \uparrow(\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_{1s}^{\text{He}}(\vec{r}_1) \downarrow \phi_{2s}^{\text{He}}(\vec{r}_2) \uparrow - \phi_{2s}^{\text{He}}(\vec{r}_1) \uparrow \phi_{1s}^{\text{He}}(\vec{r}_2) \downarrow). \end{aligned} \quad (17)$$

The first two wavefunctions, $\Psi_{\uparrow\uparrow}$ and $\Psi_{\downarrow\downarrow}$, have an antisymmetric orbital component and a symmetric spin component. It is not possible to directly separate the last two wavefunctions, $\Psi_{\uparrow\downarrow}$ and $\Psi_{\downarrow\uparrow}$, into a product of an orbital component and a spin component but they can be transformed to a wavefunction with an antisymmetric orbital component and a symmetric spin component,

$$\Psi_{\uparrow\downarrow+\downarrow\uparrow} = \frac{1}{2}(\Psi_{\uparrow\downarrow} + \Psi_{\downarrow\uparrow}) = \frac{1}{\sqrt{2}}((\phi_{1s}^{\text{He}}(\vec{r}_1)\phi_{2s}^{\text{He}}(\vec{r}_2) - \phi_{2s}^{\text{He}}(\vec{r}_1)\phi_{1s}^{\text{He}}(\vec{r}_2))(\uparrow\downarrow + \downarrow\uparrow)), \quad (18)$$

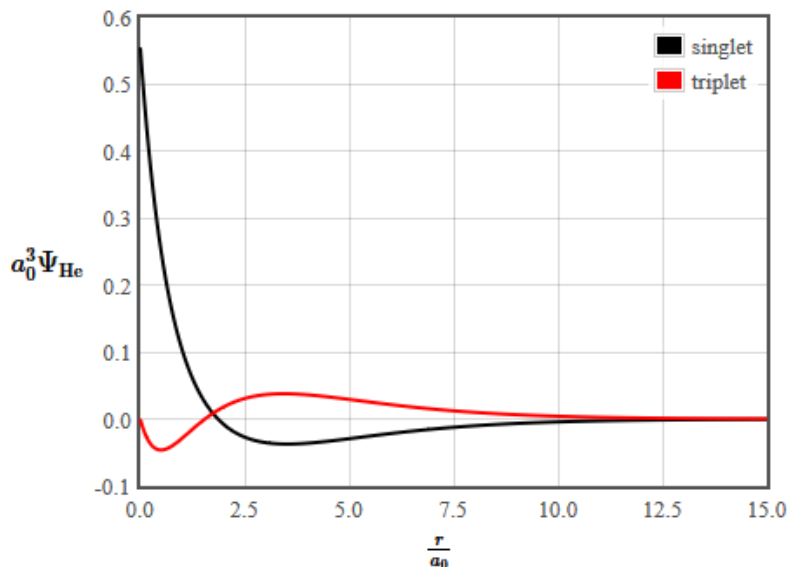
and a wavefunction with a symmetric orbital component and an antisymmetric spin component,

$$\Psi_{\uparrow\downarrow-\downarrow\uparrow} = \frac{1}{2}(\Psi_{\uparrow\downarrow} - \Psi_{\downarrow\uparrow}) = \frac{1}{\sqrt{2}}((\phi_{1s}^{\text{He}}(\vec{r}_1)\phi_{2s}^{\text{He}}(\vec{r}_2) + \phi_{2s}^{\text{He}}(\vec{r}_1)\phi_{1s}^{\text{He}}(\vec{r}_2))(\uparrow\downarrow - \downarrow\uparrow). \quad (19)$$

The wavefunctions $\Psi_{\uparrow\uparrow}$, $\Psi_{\downarrow\downarrow}$, $\Psi_{\uparrow\downarrow+\downarrow\uparrow}$, and $\Psi_{\uparrow\downarrow-\downarrow\uparrow}$ span the same space of functions that the wavefunctions $\Psi_{\uparrow\uparrow}$, $\Psi_{\downarrow\downarrow}$, $\Psi_{\uparrow\downarrow}$, and $\Psi_{\downarrow\uparrow}$ do so either set can be used to describe the first excited state of helium. We will work with the set of wavefunctions: $\Psi_{\uparrow\uparrow}$, $\Psi_{\downarrow\downarrow}$, $\Psi_{\uparrow\downarrow+\downarrow\uparrow}$, and $\Psi_{\uparrow\downarrow-\downarrow\uparrow}$.

The orbital components of wavefunctions $\Psi_{\uparrow\uparrow}$, $\Psi_{\downarrow\downarrow}$, and $\Psi_{\uparrow\downarrow+\downarrow\uparrow}$ are antisymmetric and are all identical, only their spin components are different. Spin does not appear in the total Hamiltonian so the energies of these three states must be the same. These three form the triplet state.

The energy of wavefunction $\Psi_{\uparrow\downarrow-\downarrow\uparrow}$, the singlet, evaluates to be higher than the other three. This is because the antisymmetric orbital wavefunction is zero when $\vec{r}_1 = \vec{r}_2$ so the electron-electron repulsion is smaller for the antisymmetric orbital wavefunction.



Plots of the single and triplet wavefunction assuming that the 2s electron sees an effective

nuclear charge of $Z_{\text{eff}}=1.15$.

$H_{\text{red}}^{\text{He}}$	$H_{\text{total}}^{\text{He}}$	exact
<u>1s¹2s¹ -68 eV</u>	<u>1s¹2s¹ -55.98 eV</u> <u>1s¹2s¹ -58.19 eV</u>	<u>1s¹2s¹ 2¹S -58.37 eV singlet</u> <u>1s¹2s¹ 2¹S -59.16 eV triplet</u>
	<u>1s² -77.49 eV</u>	<u>1s² 1¹S -78.99 eV singlet</u>
<u>1s² -108.8 eV</u>		

Three energy diagrams for helium. On the left are the energies of the atomic orbitals evaluated with $H_{\text{red}}^{\text{He}}$. In the center are the energies of the atomic orbitals evaluated with $H_{\text{total}}^{\text{He}}$. On the right are the true eigen energies for helium.

Exchange energy

Consider the energy difference between the singlet state and the triplet state.

$$\Delta E = \langle \Psi_{\uparrow\downarrow-\downarrow\uparrow} | H_{\text{total}}^{\text{He}} | \Psi_{\uparrow\downarrow-\downarrow\uparrow} \rangle - \langle \Psi_{\uparrow\uparrow} | H_{\text{total}}^{\text{He}} | \Psi_{\uparrow\uparrow} \rangle \quad (20)$$

Substituting in the symmetric orbital component for $\Psi_{\uparrow\downarrow-\downarrow\uparrow}$ and the antisymmetric orbital component for $\Psi_{\uparrow\uparrow}$ yields,

$$\begin{aligned} \Delta E = & \frac{1}{2} \langle \phi_{1s}^{\text{He}}(\vec{r}_1) \phi_{2s}^{\text{He}}(\vec{r}_2) + \phi_{2s}^{\text{He}}(\vec{r}_1) \phi_{1s}^{\text{He}}(\vec{r}_2) | H_{\text{total}}^{\text{He}} | \phi_{1s}^{\text{He}}(\vec{r}_1) \phi_{2s}^{\text{He}}(\vec{r}_2) + \phi_{2s}^{\text{He}}(\vec{r}_1) \phi_{1s}^{\text{He}}(\vec{r}_2) \rangle \\ & - \frac{1}{2} \langle \phi_{1s}^{\text{He}}(\vec{r}_1) \phi_{2s}^{\text{He}}(\vec{r}_2) - \phi_{2s}^{\text{He}}(\vec{r}_1) \phi_{1s}^{\text{He}}(\vec{r}_2) | H_{\text{total}}^{\text{He}} | \phi_{1s}^{\text{He}}(\vec{r}_1) \phi_{2s}^{\text{He}}(\vec{r}_2) - \phi_{2s}^{\text{He}}(\vec{r}_1) \phi_{1s}^{\text{He}}(\vec{r}_2) \rangle. \end{aligned} \quad (21)$$

After some algebra, this reduces to,

$$\begin{aligned} \Delta E = & \langle \phi_{1s}^{\text{He}}(\vec{r}_1) \phi_{2s}^{\text{He}}(\vec{r}_2) | H_{\text{total}}^{\text{He}} | \phi_{1s}^{\text{He}}(\vec{r}_2) \phi_{2s}^{\text{He}}(\vec{r}_1) \rangle \\ & + \langle \phi_{1s}^{\text{He}}(\vec{r}_2) \phi_{2s}^{\text{He}}(\vec{r}_1) | H_{\text{total}}^{\text{He}} | \phi_{1s}^{\text{He}}(\vec{r}_1) \phi_{2s}^{\text{He}}(\vec{r}_2) \rangle. \end{aligned} \quad (22)$$

The difference in energy only depends on matrix elements where the electrons at \vec{r}_1 and \vec{r}_2 get exchanged in the $\langle \psi |$ and the $|\psi \rangle$. For this reason, ΔE is called the exchange energy.

More accurate calculations

To determine the states of helium more accurately, we can look for better atomic orbitals. The atomic orbitals that we have used so far neglect the electron-electron interactions. The electrons will partially screen the positive nucleus so the true wavefunction will have a larger diameter than the one that was calculated neglecting the electron-electron interactions. This suggests that we use an atomic orbital of the form,

$$\sqrt{\frac{Z_e^3}{\pi a_0^3}} \exp\left(-\frac{Z_e r}{a_0}\right), \quad (23)$$

where Z_e is the effective charge of the nucleus. The energy of the helium ground state is minimized for $Z_e = 1.69$. There are a number of numerical techniques like the Hartree Fock method or density functional theory that can be used to find better atomic orbitals. It is known, however, that the true ground state of any interacting electron system cannot be written in terms of products of atomic orbitals because it will include factors like $(\vec{r}_1 - \vec{r}_2)^2$ which cannot be written as a product of two functions like $\phi_m(\vec{r}_1)\phi_n(\vec{r}_2)$. Calculating the true wavefunctions that are not written as atomic orbitals is a very computationally intensive process.

When a magnetic field is applied, a term must be added to the Hamiltonian that couples to the spin. The ground state has zero magnetic moment so its energy does not change in a magnetic field. The triplet state splits into three energy levels due to the Zeeman effect. There are also some small details in atomic spectra like the spin-orbit interaction, and the hyperfine interaction that will not be discussed further here.

Configuration	Term	J	Level (cm^{-1})	Ref.
$1s^2$	$1S$	0	0.000	M02
$1s2s$	$3S$	1	159855.9745	M02
$1s2s$	$1S$	0	166277.4403	M02
$1s2p$	$3P^\circ$	2	169086.7666	M02
		1	169086.8430	M02
		0	169087.8309	M02
$1s2p$	$1P^\circ$	1	171134.8970	M02
$1s3s$	$3S$	1	183236.7918	M02
$1s3s$	$1S$	0	184864.8294	M02
$1s3p$	$3P^\circ$	2	185564.5620	M02
		1	185564.5840	M02
		0	185564.8547	M02
$1s3d$	$3D$	3	186101.5463	M02
		2	186101.5488	M02
		1	186101.5930	M02
$1s3d$	$1D$	2	186104.9668	M02
$1s3p$	$1P^\circ$	1	186209.3651	M02
$1s4p$	$1P^\circ$	1	191492.7120	M02
He II ($2S_{1/2}$)	Limit		198310.6691	M02

The energy levels for He from physics.nist.gov

Many-electron atoms

The Hamiltonian for an atom with many electrons is,

$$H_{\text{total}} = - \sum_i^N \frac{\hbar^2}{2m} \nabla_i^2 - \sum_i^N \frac{Ze^2}{4\pi\epsilon_0|\vec{r}_i|} + \sum_{ij} \frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|}. \quad (24)$$

The first sum are the kinetic energies of the electrons, the second sum are the attractive Coulomb interactions between the electrons and the nucleus, the third sum are the repulsive electron-electron interactions. It is not possible to find simple analytic expressions for the eigenfunctions of this Hamiltonian. To make progress, we neglect the electron-electron interactions. This results in the reduced Hamiltonian.

$$H_{\text{red}} = - \sum_i^N \frac{\hbar^2}{2m} \nabla_i^2 - \sum_i^N \frac{Ze^2}{4\pi\epsilon_0|\vec{r}_i|}. \quad (25)$$

The reduced Hamiltonian can be solved by the separation of variables. The eigenfunctions of the reduced Hamiltonian are antisymmetrized products of atomic orbitals For instance, the ground state configuration of beryllium is $1s^22s^2$. The antisymmetrized four-electron wave function for the ground state is,

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4) = \frac{1}{\sqrt{4!}} \begin{vmatrix} \phi_{1s} \uparrow(\vec{r}_1) & \phi_{1s} \downarrow(\vec{r}_1) & \phi_{2s} \uparrow(\vec{r}_1) & \phi_{2s} \downarrow(\vec{r}_1) \\ \phi_{1s} \uparrow(\vec{r}_2) & \phi_{1s} \downarrow(\vec{r}_2) & \phi_{2s} \uparrow(\vec{r}_2) & \phi_{2s} \downarrow(\vec{r}_2) \\ \phi_{1s} \uparrow(\vec{r}_3) & \phi_{1s} \downarrow(\vec{r}_3) & \phi_{2s} \uparrow(\vec{r}_3) & \phi_{2s} \downarrow(\vec{r}_3) \\ \phi_{1s} \uparrow(\vec{r}_4) & \phi_{1s} \downarrow(\vec{r}_4) & \phi_{2s} \uparrow(\vec{r}_4) & \phi_{2s} \downarrow(\vec{r}_4) \end{vmatrix}. \quad (26)$$

This is an exact solution to the reduced Hamiltonian with an energy that is the sum of $-Z^213.6/n^2$ for the four atomic orbitals. The energy of the ground state wave function of beryllium evaluated in the reduced Hamiltonian is -544 eV.

A better estimation for the ground state energy can be made by evaluating the energy of this wavefunction in the total Hamiltonian which includes the electron-electron interactions. This requires some effort to calculate since the determinant of a 4×4 matrix has 24 terms and each of these must be integrated over the x-, y-, and z-components of the four electrons. Thus we have 24 twelve-dimensional integrals to evaluate.

The many electron wave functions of the other elements can be constructed in a similar manner. There are some anomalies in the table of electron configurations.

For instance, nickel has 28 electrons and an electron configuration of $1s^22s^22p^63s^23p^63d^84s^2$ while copper has 29 electrons and an electron configuration of $1s^22s^22p^63s^23p^63d^{10}4s^1$. The electrons fill the 4s shell in nickel but in copper one of these electrons is removed from the 4s shell.

The mysteries of how the electron shells fill can be explained by the Schrdinger equation. To find the ground state electron configuration of copper, guess a some candidate configurations with 29 electrons such as $1s^22s^22p^63s^23p^63d^{10}4s^1$ and $1s^22s^22p^63s^23p^63d^94s^2$, construct the corresponding many-electron wave functions and evaluate their energies using the total Hamiltonian. The electron configuration with the lowest energy is the one that will be observed.

It becomes increasing difficult to evaluate the energies of many-electron wavefunctions

as the number of electrons increases. This is because the determinant of an $N \times N$ matrix has $N!$ terms.

For gold with 79 electrons, there are $79! = 8.94 \times 10^{116}$ 237-dimensional integrals that need to be evaluated. Fortunately it is usually only necessary to include the valence electrons in the calculation.

Slater's rules

To get the size of the atomic orbitals correct, Slater proposed a set of rules that tell you what effective nuclear charge Z_{eff} should be used to take the screening of the core electrons into account. The effective charge for the first few atomic orbitals are given in the table below.

Effective Nuclear Charge Z_{eff}

	1s	2s,2p
H	1	
He	1.7	
Li	2.7	1.3
Be	3.7	1.95
B	4.7	2.6
C	5.7	3.25
N	6.7	3.9
O	7.7	4.55
Cl	8.7	5.2
Ne	9.7	5.85