

V25.0109: General Chemistry I (Honors)

Notes for Lecture 9

I. ELECTRON SPIN

The quantum numbers n, l, m are not sufficient to fully characterize the physical state of the electrons in an atom. In 1926, Otto Stern and Walther Gerlach carried out an experiment that could not be explained in terms of the three quantum numbers n, l, m and showed that there is, in fact, another quantum-mechanical degree of freedom that needs to be included in the theory.

The experiment is illustrated in the figure below:

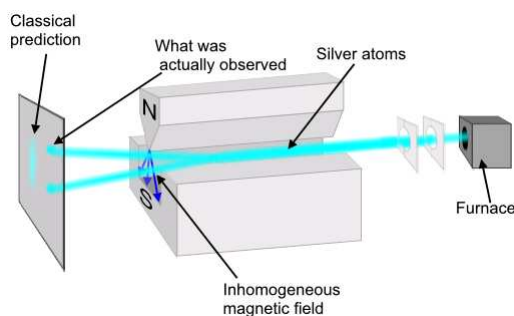


FIG. 1. The Stern-Gerlach apparatus.

A beam of atoms (e.g. hydrogen or silver atoms) is sent through a spatially inhomogeneous magnetic field with a definite field gradient toward one of the poles. It is observed that the beam splits into two beams as it passes through the field region.

It is known that a current loop in a nonuniform magnetic field experiences a net force. This is illustrated below:

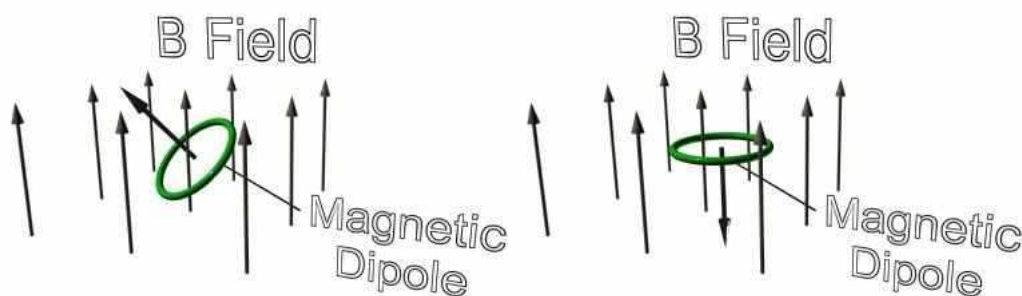


FIG. 2. A current loop in a magnetic field.

This force arises from an energy E given by

$$E = -\mathbf{M} \cdot \mathbf{B}$$

where \mathbf{M} is called the *magnetic moment* of the current loop. A current loop, as the figure suggests, is caused by circulating charges. A circulating particle has an associated angular momentum \mathbf{L} . If the charge of the particle is q and its mass is m , then the magnetic moment is given by

$$\mathbf{M} = \frac{q}{2mc} \mathbf{L}$$

The fact that the beam splits into 2 beams suggests that the electrons in the atoms have a degree of freedom capable of coupling to the magnetic field. That is, an electron has an *intrinsic magnetic moment* \mathbf{M} arising from a degree of freedom that has no classical analog. The magnetic moment must take on only 2 values according to the Stern-Gerlach experiment. The intrinsic property that gives rise to the magnetic moment must have some analog to an angular momentum and hence, must be a property that, unlike charge and mass, which are simple numbers, is a *vector property*. This property is called the *spin*, \mathbf{S} , of the electron. As the expression above suggests, the intrinsic magnetic moment \mathbf{M} of the electron must be proportional to the spin

$$\mathbf{M} = \gamma \mathbf{S}$$

In quantum mechanics, spin share numerous features in common with angular momentum, which is why we represent it as a vector. In particular, spin is quantized, i.e. we have certain allowed values of spin. Like angular momentum, the value of the magnitude squared S^2 of spin is fixed, and one of its components S_z is as well. For an electron, the allowed values of S_z are

$$S_z \longrightarrow m_s \hbar \quad m_s = -\frac{1}{2}, \frac{1}{2}$$

while S^2 has just one value $3\hbar^2/4$, corresponding to a general formula $s(s+1)\hbar^2$, where $s = 1/2$. For this reason, the electron is called a *spin-1/2* particle. The formula $s(s+1)\hbar^2$ is generally valid for any spin- s particle. The constant γ is called the *spin gyromagnetic ratio*

$$\gamma = -\frac{ge}{2m_e c}$$

where $g = 2$ for electrons. Note that $\gamma < 0$.

For an electron in a *uniform* magnetic field \mathbf{B} , the energy is determined by the spin \mathbf{S} :

$$E = -\gamma \mathbf{S} \cdot \mathbf{B}$$

If we choose the uniform field \mathbf{B} to be along the z -direction $\mathbf{B} = (0, 0, B)$, then

$$E = -\gamma B S_z$$

Since $\gamma < 0$, we see that the lowest energy configuration has \mathbf{S} antiparallel to \mathbf{B} . Given the two values of S_z , we have two allowed energies or two energy levels corresponding to the two values of m_s :

$$E_{1/2} = -\frac{\gamma B \hbar}{2} \quad E_{-1/2} = \frac{\gamma B \hbar}{2}$$

Using the given expression for γ , which is negative, we obtain the two energy levels

$$E_{1/2} = \frac{eB\hbar}{2m_e c} \quad E_{-1/2} = -\frac{eB\hbar}{2m_e c}$$

Unlike position and momentum, which have clear classical analogs, spin does not. But if we think of spin in pseudo-classical terms, we can think of a spinning charged particle, which is similar to a loop of current. Thus, if the particle spins about the z -axis, then \mathbf{S} points along the z -axis. Since the spinning charge is negative, the left-hand rule can be applied. When the fingers of the left hand curl in the direction of the spin, the thumb points in the direction of the spin. A spinning charge produces a magnetic field similar to that of a tiny bar magnet. In this case, the spin vector \mathbf{S} points toward the south pole of the bar magnet. Now if the spinning particle is placed in a magnetic field, it tends to align the spin vector in the opposite to the magnetic field lines, as the figure above suggests.

Now, when the electron is placed in a nonuniform magnetic field, with the field increasing in strength toward the north pole of the field source, the spin-up ($m_s = 1/2$) electrons have their bar-magnet poles oriented such that the south pole points toward the north pole of the field source, and these electrons will be attracted toward the region of

stronger field. The spin-down ($m_s = -1/2$) electrons have their bar-magnet north poles oriented toward the north pole of the field source and will be repelled to the region of weaker field, thus causing the beam to split as observed in the Stern-Gerlach experiment.

The implication of the Stern-Gerlach experiment is that we need to include a fourth quantum number, m_s in our description of the physical state of the electron. That is, in addition to give its principle, angular, and magnetic quantum numbers, we also need to say if it is a spin-up electron or a spin-down electron.

Note that we have added spin into the our quantum theory as a kind of *a posteriori* consideration, which seems a little contrived. In fact, the existence of the spin degree of freedom can be derived in a very natural way in the relativistic version of quantum mechanics, where it simply pops out of the relativistic analog of the Schrödinger equation, known as the *Dirac equation*.

II. SPIN WAVE FUNCTIONS

So far, we have not explicitly considered the spin of the electrons. For the next type of approximation we will consider, the so-called *valene bond approximation*, we will need to consider spin explicitly. As we have already seen in the case of the hydrogen atom, the wave functions of an electron depend on the coordinates $\mathbf{r} = (x, y, z)$ or (r, ϕ, θ) and on the z -component of spin S_z (the total spin $|\mathbf{S}|$ is fixed). While the coordinates can be anything, the spin S_z can only take on two values $\hbar/2$ and $-\hbar/2$. Recall that these lead to the two values of the spin quantum number $m_s = \pm 1/2$. The value $m_s = 1/2$ is what we call the “spin-up” state and $m_s = -1/2$ is what we call “spin-down”.

We now define the spin wave functions. The spin-up wave function is denoted

$$\psi_{1/2}(S_z) = \psi_{\uparrow}(S_z)$$

Since S_z can take on only two values $\pm\hbar/2$, the spin wave function only have two values:

$$\psi_{\uparrow}(\hbar/2) = 1 \quad \psi_{\uparrow}(-\hbar/2) = 0$$

The meaning of this wave function is that when the electron is in the spin-up state, the probability that a measurement of S_z will yield the value $\hbar/2$ is $P(S_z = \hbar/2) = |\psi_{\uparrow}(\hbar/2)|^2 = 1$ and the probability that its value will be $-\hbar/2$ is 0. Similarly, the spin-down wave function is

$$\psi_{-1/2}(S_z) = \psi_{\downarrow}(S_z)$$

where

$$\psi_{\downarrow}(\hbar/2) = 0 \quad \psi_{\downarrow}(-\hbar/2) = 1$$

so that the probability that a measurement of S_z yields the value $-\hbar/2$ is 1 and that its value is $\hbar/2$ is 0. Note that the spin wave functions are normalized, meaning that they satisfy

$$\sum_{S_z=-\hbar/2}^{\hbar/2} |\psi_{m_s}(S_z)|^2 = 1$$

and they are orthogonal, meaning that they satisfy

$$\sum_{S_z=-\hbar/2}^{\hbar/2} \psi_{\uparrow}(S_z)\psi_{\downarrow}(S_z) = 0$$

Now, for a hydrogen atom, there are four quantum numbers, n, l, m, m_s , and the wave function depends on four coordinates, r, θ, ϕ, s_z . While r, θ, ϕ are continuous, s_z takes on only two values. The wave function can be expressed as a simple product

$$\psi_{nlmm_s}(r, \theta, \phi, s_z) = \psi_{nlm}(r, \theta, \phi) \psi_{m_s}(s_z)$$

As a shorthand notation, we can generally represent the complete set of spatial and spin coordinates with a vector \mathbf{x} . The spatial coordinates can be r, θ, ϕ or x, y, z or any other set of spatial coordinates useful for a given problem. For the hydrogen atom, using this notation, we would write

$$\psi_{nlmm_s}(\mathbf{x}) = \psi_{nlm}(r, \theta, \phi) \psi_{m_s}(s_z)$$

III. MANY-ELECTRON ATOMS

The hydrogen atom is the *only* atom for which exact solutions of the Schrödinger equation exist. For any atom that contains two or more electrons, no solution has yet been discovered (so no solution for the helium atom exists!) and we need to introduce approximation schemes.

Let us consider the helium atom. The nucleus has a charge of $+2e$, and if we place the nucleus at the origin, there will be an electron at a position \mathbf{r}_1 with spin $s_{z,1}$ and an electron at position \mathbf{r}_2 and spin $s_{z,2}$. As usual, we consider the nucleus to be fixed. The classical energy is then

$$\frac{|\mathbf{p}_1|^2}{2m_e} + \frac{|\mathbf{p}_2|^2}{2m_e} + \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{2}{|\mathbf{r}_1|} - \frac{2}{|\mathbf{r}_2|} \right] = E$$

Note that E is not simply a sum of terms for electron 1 and electron 2, $E \neq \varepsilon_1 + \varepsilon_2$. Therefore, it is not possible to write the wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ as a simple product of the form $\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)$, nor is it even possible to use the special form we introduced for identical particles

$$\frac{1}{\sqrt{2}} [\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) - \psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_1)]$$

because these simple products are not correct solutions to the Schrödinger equation.

This means that the wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ depends on the full set of 6 coordinates $x_1, y_1, z_1, x_2, y_2, z_2$ or $r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2$ if spherical coordinates are used, and 2 spin coordinates $s_{z,1}, s_{z,2}$, and that this dependence is not simple! In fact, as the number of electrons increases, the number of variables on which Ψ depends increases as well. For an atom with M electrons, the wave function Ψ depends on $3M$ coordinates! Thus, it is clear that the wave function for a many-electron atom is a very unwieldy object!

As a side bar, we note that the 1998 Nobel prize in chemistry was awarded to Walter Kohn for the development of an extremely elegant theory of electronic structure known as *density functional theory*. In this theory, it is shown that the wave function Ψ , which depends on $3M$ coordinates, can be replaced by a much simpler object called the electron density denoted $\rho(\mathbf{r}) = \rho(x, y, z)$. This object depends on only three variables for a system of *any* number of electrons. In density functional theory, it is shown that *any* physical quantity can be computed from this electron density $\rho(\mathbf{r})$.

Consider now an imaginary form of helium in which the two electrons do not interact. For this simplified case, the energy is simply

$$\begin{aligned} E &= \frac{|\mathbf{p}_1|^2}{2m_e} + \frac{|\mathbf{p}_2|^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0} \left[\frac{2}{|\mathbf{r}_1|} + \frac{2}{|\mathbf{r}_2|} \right] \\ &= \left[\frac{|\mathbf{p}_1|^2}{2m_e} - \frac{2e^2}{4\pi\epsilon_0|\mathbf{r}_1|} \right] + \left[\frac{|\mathbf{p}_2|^2}{2m_e} - \frac{2e^2}{4\pi\epsilon_0|\mathbf{r}_2|} \right] \\ &= \varepsilon_1 + \varepsilon_2 \end{aligned}$$

In this case, the wave function could be expressed as an antisymmetric product as we did above, and the energy would just be the sum of the energies of two electrons interacting with a nucleus of charge $+2e$. We would need two quantum numbers n_1 and n_2 for this, and from our study of hydrogen-like atoms, the energy would be

$$E_{n_1 n_2} = -\frac{4}{n_1^2} - \frac{4}{n_2^2}$$

in Rydbergs. This comes from the fact that the energy of one electron interacting with a nucleus of charge $+Ze$ is $E_n = -Z^2/n^2$ in Rydbergs. So, the ground-state energy ($n_1 = 1, n_2 = 1$) would be -8 Ry. In real helium, the electron-electron Coulomb repulsion $e^2/(4\pi\epsilon_0 r_{12})$ increases the ground state energy above this value (the experimentally measured ground-state energy is -5.8 Ry). The tendency is for the electrons to arrange themselves such that the Coulomb repulsion is as small as possible.

A. Hartree-Fock theory

For the helium atom, what happens if we try to use a product form as a “guess” wave function? Ignoring spin for the moment, we take as a guess of the solution for the ground-state wave function

$$\Psi_g(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)]$$

Then we know from problem set #4 that the corresponding guess of the ground-state energy

$$E_g = \int \Psi_g \hat{H} \Psi_g dV_1 dV_2 > E_0$$

where E_0 is the true ground-state energy. Here, dV_1 and dV_2 are the volume elements of electron 1 and electron 2, respectively, and \hat{H} is the Hamiltonian

$$\hat{H} = \hat{K}_1 + \hat{K}_2 + \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{2}{|\mathbf{r}_1|} - \frac{2}{|\mathbf{r}_2|} \right]$$

That is, we know that this guess is *not* correct, however, we can try to optimize the form of the functions $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$ so as to make E_g as small as possible, thereby making it approach E_0 .

If we do this, we find that $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$ satisfy a set of 2 coupled Schrödinger-like equations and that the potential energy V in each equation corresponds to what the electron would experience if we averaged over all possible positions of the other electron (think back to the classical shell model!).

If we solve these equations, we find that both $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$ bear a strikingly resemblance to the hydrogenic function $\psi_{100}(r, \phi, \theta) = \psi_{1s}(r, \theta, \phi)$, the $1s$ wave function. The difference, however, is that it decays a little faster, as if its Z value were between 1 and 2. In fact, the value one obtains from an actual calculation is $Z \approx 1.69$. We will denote this as $\psi_{1s(Z)}(r, \theta, \phi)$. We can imagine one of the electrons as “occupying” the state $\psi_1(\mathbf{r})$ and the other as “occupying” the state $\psi_2(\mathbf{r})$, but of course, we cannot say which electron is in which state, which is why we need the above form of the guess wave function. We also obtain two energies ϵ_1 and ϵ_2 that are close in energy but that the energies are lower than the energy E_1 of the hydrogen atom.

Now, we see the problem with ignoring spin. If ψ_1 and ψ_2 are both $\psi_{1s(Z)}$, then the guess wave function becomes

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

However, if we multiply the spatial wave functions by spin wave functions, then the two orbitals we obtain are

$$\psi_1(\mathbf{x}) = \psi_{1s(Z)}(\mathbf{r})\psi_{\uparrow}(s_z), \quad \psi_2(\mathbf{x}) = \psi_{1s(Z)}(\mathbf{r})\psi_{\downarrow}(s_z)$$

Thus, if we substitute this into the expression for $\Psi_g(\mathbf{x}_1, \mathbf{x}_2)$, we find that we can factor out $\psi_{1s(Z)}(\mathbf{r}_1)\psi_{1s(Z)}(\mathbf{r}_2)$ and we are left with the antisymmetric combination of spin wave functions. The only possibility for the combination of spin wave functions leads to

$$\Psi_g(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \psi_{1s(Z)}(\mathbf{r}_1)\psi_{1s(Z)}(\mathbf{r}_2) [\psi_{\uparrow}(s_{z,1})\psi_{\downarrow}(s_{z,2}) - \psi_{\downarrow}(s_{z,2})\psi_{\uparrow}(s_{z,1})]$$

Note that another possible spin wave function would be $[\psi_{\uparrow}(s_{z,2})\psi_{\downarrow}(s_{z,1}) - \psi_{\uparrow}(s_{z,1})\psi_{\downarrow}(s_{z,2})]/\sqrt{2}$ however, this is different from the above wave function by an overall minus sign and is, therefore, not actually different.

As another shorthand notation, we can use symbols “1” and “2” to represent any of the variables of electrons 1 and 2. Thus, the guess wave functions can be represented simply as

$$\begin{aligned}\psi_g(1,2) &= \frac{1}{\sqrt{2}} [\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)] \\ &= \frac{1}{\sqrt{2}} \psi_{1s(Z)}(1)\psi_{1s(Z)}(2) [\psi_{\uparrow}(1)\psi_{\downarrow}(2) - \psi_{\uparrow}(2)\psi_{\downarrow}(1)]\end{aligned}$$

Given that the spin wave functions are rather simple, we can focus on the spatial parts of the wave functions in the proceeding discussion. For short, we denote the electronic configuration as $1s^2$.

The lowest HF energy obtained for helium, $\varepsilon_1 \approx -2.83\text{Ry}$. Note how close this is to the formula $-Z^2/n^2$ for $n = 1$ with $Z = 1.69$! The next energy ε_2 is only slightly large than this value, so we see that $\varepsilon_1 \approx \varepsilon_2$, but strictly $\varepsilon_1 < \varepsilon_2$.

Now, if we followed the same thing for lithium, we would obtain a set of 3 orbitals $\psi_1(\mathbf{r})$, $\psi_2(\mathbf{r})$ and $\psi_3(\mathbf{r})$, where ψ_1 and ψ_2 resemble $\psi_{100}(r, \phi, \theta)$ and ψ_3 resembles $\psi_{200}(r, \phi, \theta)$ but again, all of these orbitals decay faster than their counterparts for the hydrogen atom. The calculation gives an effective value of $Z \approx 2.64$. Thus, multiplying these by spin wave functions, we would obtain the three HF orbitals as

$$\begin{aligned}\psi_1(\mathbf{x}) &= \psi_{1s(Z)}\psi_{\uparrow}(s_z) \\ \psi_2(\mathbf{x}) &= \psi_{1s(Z)}\psi_{\downarrow}(s_z) \\ \psi_3(\mathbf{x}) &= \psi_{2s(Z)}\psi_{\uparrow}(s_z)\end{aligned}$$

We would denote the electronic configuration as $1s^2 2s^1$. Here, we find $\varepsilon_1 \approx \varepsilon_2$, and $\varepsilon_3 > \varepsilon_1, \varepsilon_2$. Strictly, $\varepsilon_1 < \varepsilon_2 < \varepsilon_3$. The total HF energy for the ground state is -14.86 Ry, while the experimental value is -14.96 Ry. Note that if we neglected the electron-electron repulsion, the energy would be

$$E_{n_1 n_2 n_3} = -\frac{9}{n_1^2} - \frac{9}{n_2^2} - \frac{9}{n_3^2}$$

with $n_1 = n_2 = n_3 = 1$, which gives -27 Ry.

For Beryllium, we would obtain four orbitals, two of which resemble 1s orbitals and two of which resemble 2s orbitals. Again, these decay as if they have an effective Z value between 3 and 4. We can, therefore, represent these orbitals as

$$\begin{aligned}\psi_1(\mathbf{x}) &= \psi_{1s(Z)}\psi_{\uparrow}(s_z) \\ \psi_2(\mathbf{x}) &= \psi_{1s(Z)}\psi_{\downarrow}(s_z) \\ \psi_3(\mathbf{x}) &= \psi_{2s(Z)}\psi_{\uparrow}(s_z) \\ \psi_4(\mathbf{x}) &= \psi_{2s(Z)}\psi_{\downarrow}(s_z)\end{aligned}$$

We would denote the electronic configuration as $1s^2 2s^2$.

For Boron, we would obtain 5 orbitals, two of which would resemble 1s, two would resemble 2s, and the fifth would resemble a $2p_x$ orbital. Again, all of these would decay as if they have an effective Z between 4 and 5. We can thus represent the 5 orbitals as

$$\begin{aligned}\psi_1(\mathbf{x}) &= \psi_{1s(Z)}\psi_{\uparrow}(s_z) \\ \psi_2(\mathbf{x}) &= \psi_{1s(Z)}\psi_{\downarrow}(s_z) \\ \psi_3(\mathbf{x}) &= \psi_{2s(Z)}\psi_{\uparrow}(s_z) \\ \psi_4(\mathbf{x}) &= \psi_{2s(Z)}\psi_{\downarrow}(s_z) \\ \psi_5(\mathbf{x}) &= \psi_{2p_x(Z)}\psi_{\uparrow}(s_z)\end{aligned}$$

and denote the electronic configuration as $1s^2 2s^2 2p_x^1$. Here the HF energies would follow the pattern $\varepsilon_1 \approx \varepsilon_2$, $\varepsilon_3 \approx \varepsilon_4$, $\varepsilon_3, \varepsilon_4 > \varepsilon_1, \varepsilon_2$, and $\varepsilon_5 > \varepsilon_3, \varepsilon_4$. Strictly, $\varepsilon_1 < \varepsilon_2 < \varepsilon_3 < \varepsilon_4 < \varepsilon_5$.

For carbon, we obtain 6 orbitals, and this time, the 6th orbital does not resemble $2p_x$ but rather $2p_y$. Hence, we would represent the 6 orbitals as

$$\begin{aligned}\psi_1(\mathbf{x}) &= \psi_{1s(Z)}\psi_{\uparrow}(s_z) \\ \psi_2(\mathbf{x}) &= \psi_{1s(Z)}\psi_{\downarrow}(s_z) \\ \psi_3(\mathbf{x}) &= \psi_{2s(Z)}\psi_{\uparrow}(s_z) \\ \psi_4(\mathbf{x}) &= \psi_{2s(Z)}\psi_{\downarrow}(s_z) \\ \psi_5(\mathbf{x}) &= \psi_{2p_x(Z)}\psi_{\uparrow}(s_z) \\ \psi_6(\mathbf{x}) &= \psi_{2p_y(Z)}\psi_{\uparrow}(s_z)\end{aligned}$$

These all decay as if they had an effective Z value between 5 and 6. The HF energies follow the pattern $\varepsilon_1 \approx \varepsilon_2$, $\varepsilon_3 \approx \varepsilon_4$, $\varepsilon_5 \approx \varepsilon_6$, $\varepsilon_3, \varepsilon_4 > \varepsilon_1, \varepsilon_2$, and $\varepsilon_5, \varepsilon_6 > \varepsilon_3, \varepsilon_4$. Note that for Boron and Carbon, the energies of the $2p$ orbitals are larger than for the $2s$ orbitals, which is not the case for hydrogen. The electronic configuration would be $1s^2 2s^2 2p_x 2p_y^1$.

For Nitrogen, the 7th orbital would resemble a $2p_z$ orbital, and we would just add $\psi_7(\mathbf{x}) = \psi_{2p_z(Z)}\psi_{\uparrow}(s_z)$. Now, for oxygen, the 8th orbital again resembles a $2p_x$ orbital, and we would add this to the list but with a down spin wave function $\psi_8(\mathbf{x}) = \psi_{2p_x(Z)}\psi_{\downarrow}(s_z)$. For oxygen, we find that the 5-8 HF energies are approximately equal, $\varepsilon_5 \approx \varepsilon_6 \approx \varepsilon_7 \approx \varepsilon_8$, although strictly $\varepsilon_5 < \varepsilon_6 < \varepsilon_7 < \varepsilon_8$.

These examples illustrate a more general procedure known as *Hartree-Fock* theory or the *Hartree-Fock approximation* (named after Douglas Hartree and Vladimir Fock) developed in 1930. Hartree-Fock (HF) theory makes several important assumptions:

1. The guess wave function is always composed of combinations of products of single-electron functions $\psi_1(\mathbf{r})$, $\psi_2(\mathbf{r})$,... that properly account for the identical nature of the electrons.
2. When the shapes of these functions are optimized, each electron is subject to an effective potential V that is generated by averaging over the positions of all the other electrons. For the i th electron, V depends only on \mathbf{r}_i .
3. For an atom, V depends only on the magnitude $|\mathbf{r}_i|$, which means that the effective potential is spherically symmetric.

If an atom has M electrons, then HF theory yields M functions $\psi_1(\mathbf{r}), \dots, \psi_M(\mathbf{r})$ and M energies $\varepsilon_1, \dots, \varepsilon_M$. These energies are all negative, $\varepsilon_i < 0$, and they are ordered such that

$$\varepsilon_1 < \varepsilon_2 < \dots < \varepsilon_M$$

We will give a physical interpretation of these energies shortly.

So how do we calculate probabilities in HF theory? What we are interested in is the probability of finding one of the M electrons in a small volume dV about the point \mathbf{r} independent of the positions of the remaining $M - 1$ electrons. This probability is given in terms of the electron density introduced earlier. That is

$$P(\text{electron is in } dV \text{ about } \mathbf{r}) = \rho(\mathbf{r})dV$$

and the electron density can be computed from the squares of the HF orbitals:

$$\rho(\mathbf{r}) = \sum_{i=1}^M \psi_i^2(\mathbf{r})$$

This is the same density that lead to the chemistry Nobel prize!

To give an idea of how well HF theory can predict the ground state energies of several atoms, consider the table below (all energies are in Ry):

Atom	HF Energy	Experiment
He	- 5.72	-5.80
Li	- 14.86	-14.96
Ne	- 257.10	-257.88
Ar	- 1053.64	-1055.20

The HF theory motivates the so-called “aufbau” principle for expressing/building up electron configurations in atoms. “Aufbau” is German for “building up” (*Aufbauen* = “to build up”). We see that the HF orbitals are ordered according to their energies and that as the energy increases, their shapes follow the “ladder” of wave functions of the hydrogen atom. Thus, as we consider atoms with more and more electrons, we simply have to “occupy” more of the HF orbitals in order of increasing energy. Since groups of these orbitals are close in energy, there are two rules we need to introduce for this procedure of occupying orbitals:

1. *Pauli exclusion principle*: No two electrons in an atom can have the same set of quantum numbers.
2. *Hund’s rule*: When electrons are added to a set of HF orbitals of approximately equal energy, a single electron enters each orbital before a second one can enter any orbital. The lowest energy configuration is always the one with parallel spins.

Now, let us apply these rules to fill the orbitals in the first row elements (which are all we care about for the next two chapters). The filling will refer to the figure below:

	1s	2s	2p _x	2p _y	2p _z
H: 1s ¹	↑	—	—	—	—
He: 1s ²	↑↓	—	—	—	—
Li: 1s ² 2s ¹	↑↓	↑	—	—	—
Be: 1s ² 2s ²	↑↓	↑↓	—	—	—
B: 1s ² 2s ² 2p _x ¹	↑↓	↑↓	↑	—	—
C: 1s ² 2s ² 2p _x ¹ 2p _y ¹	↑↓	↑↓	↑	↑	—
N: 1s ² 2s ² 2p _x ¹ 2p _y ¹ 2p _z ¹	↑↓	↑↓	↑	↑	↑
O: 1s ² 2s ² 2p _x ² 2p _y ¹ 2p _z ¹	↑↓	↑↓	↑↓	↑	↑
F: 1s ² 2s ² 2p _x ² 2p _y ² 2p _z ¹	↑↓	↑↓	↑↓	↑↓	↑
Ne: 1s ² 2s ² 2p _x ² 2p _y ² 2p _z ²	↑↓	↑↓	↑↓	↑↓	↑↓

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FIG. 3. Table of electronic configurations

Starting with hydrogen ($Z = 1$), HF theory gives the exact answer because the H atom is exactly soluble. Thus, we generate the exact function $\psi_{100}(r, \phi, \theta)$, and we put the one electron into this orbital for the ground state. We write this as

$$1s^1$$

For Helium ($Z = 2$), HF theory is no longer exact, however as we discussed, HF theory gives two orbitals $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$, both of which resemble ψ_{100} (but decays a little faster). The energies ϵ_1 and ϵ_2 are also very similar. Thus, we regard these orbitals as having roughly the same energy, and we place one electron into ψ_1 and one into ψ_2 . We regard this as placing two electrons into the single orbital ψ_{100} and assigning the electrons the same set of H-like quantum numbers n, l, m . To be consistent with Pauli's exclusion principle, they need to have one quantum number that is different, so we assign one electron $m_s = 1/2$ and the other $m_s = -1/2$ (see figure). We write the electron configuration as

$$1s^2$$

signifying that two electrons occupy the ψ_{100} orbital (although in reality, they occupy two different orbitals that happen to be very similar to each other).

For Lithium ($Z = 3$), HF theory yields three orbitals ψ_1 , ψ_2 , and ψ_3 . The first two closely resemble ψ_{100} , while the third resembles ψ_{200} . HF theory also yields three energies ϵ_1 , ϵ_2 and ϵ_3 with $\epsilon_1 \approx \epsilon_2$ and $\epsilon_3 > \epsilon_2 > \epsilon_1$. Each electron occupies an HF orbital, but we regard this as two electrons in a ψ_{100} orbital and the third in a ψ_{200} orbital (see figure). We write this as

$$1s^2 2s^1$$

Note that it takes two electrons to fill the 1s orbital, after which we move to a 2s-like orbital. In this case, we say that the 1s electrons form a *closed shell*, since we have now moved on to a different value of n , i.e., $n = 2$. The 2 1s electrons are called *core electrons* and the 2s electron is called a *valence electron*.

Coming to Beryllium ($Z = 4$), we have 4 HF orbitals, two of which resemble ψ_{100} and two of which resemble ψ_{200} , so we imagine that an electron in each HF orbital is equivalent to 2 in the ψ_{100} and 2 in the ψ_{200} . In each pair, the electrons have opposite spins to be consistent with the Pauli exclusion principle. We write this as

$$1s^2 2s^2$$

Now, we have two core electrons and two valence electrons.

For Boron ($Z = 5$), there are 5 HF orbitals. ψ_1 and ψ_2 resemble ψ_{100} , ψ_3 and ψ_4 resemble ψ_{200} , and ψ_5 resembles ψ_{21m} , i.e. a generic p -orbital (we do not specify m because the direction of the orbital does not matter). The energies are ordered such that $\epsilon_1 \approx \epsilon_2$, $\epsilon_3 \approx \epsilon_4$. Interestingly, ϵ_5 is larger than all of these and not close to ϵ_4 . Unlike in hydrogen, where orbitals with the same n but different values of l have the same energy, here orbitals with the same n but different values of l have different energies. Thus, ψ_5 is at a higher energy. Hence, when we fill, we start with 1s, then 2s and finally 2p. We can choose any of the 2p orbitals, so we just start with $2p_x$. We thus write the electronic configuration as

$$1s^2 2s^2 2p_x^1$$

For carbon ($Z = 6$), the situation is much the same. However, here we have ψ_5 and ψ_6 both with p -like character and similar in energy. Here, however, we need Hund's rule. We first put a spin-up electron in the $2p_x$ orbital and then another spin-up electron in the $2p_y$ orbital. The electronic configuration is

$$1s^2 2s^2 2p_x^1 2p_y^1$$

For nitrogen ($Z = 7$), we would place a spin-up electron in the $2p_z$ orbital and write $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. When we get to oxygen ($Z = 8$), we have now placed one electron in each of the three p -like orbitals. We now have to return to

p_x and place another electron in it, which will now be spin-down to be consistent with the Pauli exclusion principle. Its electronic configuration is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$. For fluorine ($Z = 9$), it is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$. Finally, when we get to Neon ($Z = 10$), we have $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$, which we can write simply as $1s^2 2s^2 2p^6$. With Neon, as with Helium, we have completed a shell, and the next HF orbital will be like ψ_{300} and have a higher energy, thereby starting the next shell. Thus, we see that for Neon, 8 electrons are needed to complete a shell, the 2 2s electrons and the 6 2p electrons. The fact that 8 electrons close a shell for Neon lend this atom special stability and make it highly unreactive.

IV. PROBING ENERGY LEVELS AND THE KOOPMANS APPROXIMATION

Quantum theory successfully predicts the shell structure of atoms and can explain the observed features of the periodic table (see end of chapter 5). The shell structure and the ionization energies of atoms can be probed by a technique known as photoelectron spectroscopy.

The technique works very much like the photoelectric effect in metals except that we use incident EM radiation (usually X-rays or UV rays) to knock electrons out of individual atoms, thereby leading to measures of the ionization energies. In this method, the ionization energy IE plays the same role as the work function of a metal.

Suppose a photon of energy $h\nu$ strikes an atom or cation in order to probe one of the ionization energies IE_i . The electron will be ejected from the atom or ion and have a residual kinetic energy $p^2/2m_e$. Thus, by energy conservation

$$h\nu = IE_i + \frac{p^2}{2m_e}$$

Given the experimental numbers, we can compare the measured ionization energies to the orbital energies generated in a HF calculation. We find a very interesting result. If the energies are ordered according to $\varepsilon_1 < \varepsilon_2 < \dots < \varepsilon_M$, then the first ionization energy IE_1 is approximately equal to the negative of the highest HF energy $-\varepsilon_M$:

$$IE_1 \approx -\varepsilon_M$$

Similarly, the second ionization energy has the property

$$IE_2 \approx -\varepsilon_{M-1}$$

Finally, the M th ionization energy IE_M satisfies

$$IE_M \approx -\varepsilon_1$$

These relations are known as *Koopmans's approximation*.

The essential approximations made in these relations are, firstly, the approximations inherent in the HF theory. But beyond this, it is also assumed that the energies do not change much as the electrons are sequentially stripped out of the atom. Obviously, these energies *should* change, as the screening and repulsion effects of the other electrons is reduced, and the electrons are drawn closer to the positively charged nucleus, but the effects are small. This type of approximation is known as the *frozen core approximation*.