

Quantum Mechanics in Chemistry

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1 Light as a Particle

One of the most important and easily recognizable pieces of evidence for the particle nature of light comes from the photoelectric effect. When light is directed at a metal surface, electrons (called *photoelectrons*) are sometimes emitted. The assumption that light imparts energy as a continuous wave would lead to the conclusion that light of greater intensity would eject photoelectrons with a higher energy¹. However, the energy of the photoelectrons is instead found to depend on frequency. Furthermore, there is a threshold frequency below which no intensity of light can eject electrons. Einstein solved this problem by theorizing that light delivers energy in individual packets called *quanta*. He went on to describe the energy of one of these quanta:

$$E = hf$$

Where f is the frequency and h is Planck's constant, equal to $6.63 \times 10^{-34} \text{ J s}^{-1}$.

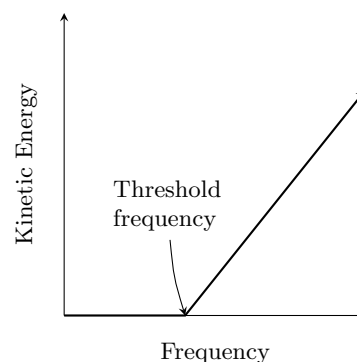


Figure 1: The relationship between frequency and the kinetic energy of photoelectrons in the photoelectric effect.

2 Electrons as Waves

While Louis de Broglie was studying theoretical quantum mechanics, he discovered that a useful relationship between photons and electrons could be drawn if the moving electron was assigned a wavelength, now called the *de Broglie wavelength*:

$$\lambda = \frac{h}{mv}$$

Where m is the mass of the electron and v is its translational velocity (mv is the translational momentum in Newtonian mechanics). While the full scope of the analogy de Broglie was able to draw is unimportant, one part is easy to see by equating two expressions of energy, the one obtained above and $E = mc^2$:

$$\begin{aligned} mc^2 &= hf \\ mc^2 &= \frac{hc}{\lambda} \\ \lambda &= \frac{h}{mc} \end{aligned}$$

In this equation, c is simply the speed of light; therefore, the resulting solution for λ is clearly analogous to the de Broglie wavelength above.

¹To determine the kinetic energy of ejected electrons, an external electric field is adjusted so that it exactly balances the force with which the electrons are ejected. The magnitude of the electric field needed can be used to calculate the energy in question.

3 The Bohr Hydrogen Atom

When the light given off by atoms excited by high temperatures or electric arcs is examined carefully, only certain discrete wavelengths of light are found. These wavelengths follow particularly nice patterns for the hydrogen atom. The Balmer series of emission lines, which are the lines in the visible spectrum, are shown below.

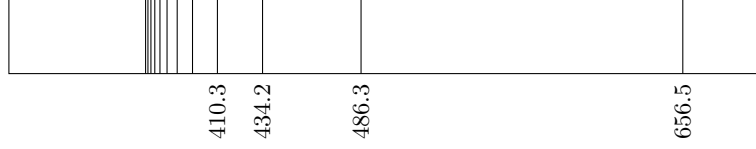


Figure 2: The Balmer series of the hydrogen atom. The wavelengths shown are in nanometers.

These discrete wavelengths of light can be converted to energy by using the formula above, $E = hf = \frac{hc}{\lambda}$. Sorting the emission lines from right to left and converting them to energy yields the relationship to the right.

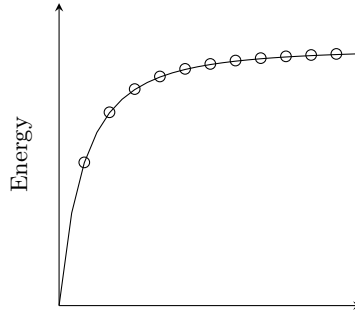


Figure 3: The Balmer series of the hydrogen atom. The wavelengths shown are in nanometers.

The fitted curve shown uses the relationship $E = 13.6(\frac{1}{4} - \frac{1}{n^2})\text{eV}$, where n is the index of the emission line starting from 3. Bohr was able to derive the physical meaning of this relationship by making only a single assumption about the behavior of electrons in atoms. He postulated that electrons occupy discrete energy levels, and that the angular momentum of electrons in the n th energy level is equal to $n\hbar$ (where \hbar is the reduced Planck constant, $\frac{h}{2\pi}$). From this starting point, the structure of a single-electron atom can be completely determined.

First, we know from classical mechanics that a mass m moving with velocity v in a circular path of radius r requires a centripetal force of magnitude $\frac{mv^2}{r}$ to keep it in its path. This force must be provided by the electrostatic interaction with the nucleus, as shown in Figure 4. We thus have

$$\begin{aligned}\frac{mv^2}{r} &= \frac{Ze^2}{r^2} \\ mv^2 &= \frac{Ze^2}{r}\end{aligned}$$

We can multiply both sides of this equation by mr^2 to obtain:

$$m^2v^2r^2 = Ze^2mr$$

The left side of this equation is simply the angular momentum (which is given by classical mechanics as mvr) squared. However, we also know from Bohr's postulate that the angular momentum is $n\hbar$. Substituting,

$$n^2\hbar^2 = Ze^2mr$$

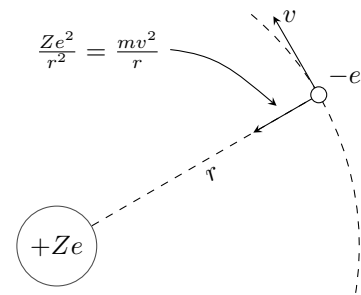


Figure 4: The Bohr model of the atom, in which an electron orbits in a fixed radius r due to the centripetal force provided by electrostatic interaction with the nucleus.

There is now only one unknown parameter, r . Solving for r yields:

$$r = \frac{n^2 \hbar^2}{Z m e^2} = \frac{n^2}{Z} \times 0.530 \text{ \AA}$$

We can use this along with Bohr's postulate to find velocity.

$$\begin{aligned} mvr &= n\hbar \\ v &= \frac{n\hbar}{mr} \\ v &= \frac{Ze^2}{n\hbar} = \frac{Z}{n} \times 2.188 \times 10^6 \text{ m s}^{-1} \end{aligned}$$

Finally, we can use the values of velocity and radius to compute the total energy, which is the sum of kinetic and potential energies.

$$\begin{aligned} E &= \frac{1}{2}mv^2 - \frac{Ze^2}{r} \\ E &= \frac{Z^2 e^4 m}{2n^2 \hbar^2} - \frac{Z^2 e^4 m}{n^2 \hbar^2} \\ E &= -\frac{Z^2 e^4 m}{2n^2 \hbar^2} = -\frac{Z^2}{n^2} \times 13.6 \text{ eV} \end{aligned}$$

For the hydrogen atom, subtracting the energy of the n^{th} and the 2^{nd} energy level gives:

$$E_p = 13.6 \left(\frac{1}{4} - \frac{1}{n^2} \right) \text{ eV}$$

This is exactly the equation that fit the energies of the hydrogen emission spectrum. This can be seen as a confirmation of Bohr's original postulate. Furthermore, by choosing levels other than the 2^{nd} for an electron to fall to (for example, the first), we can predict the existence of other hydrogen emission series following a similar pattern to the Balmer series above. Bohr did just this, and the existence of a hydrogen emission spectrum in the ultraviolet, called the Lyman series, was later discovered by Theodore Lyman. This series corresponds to electrons falling to the first energy level. The series for the 3^{rd} level is called the Paschen series.

4 The Multi-electron Atom

Although an electron alone in an atom can be fully characterized by its energy level n , more complicated atoms require more parameters. We call n the *total quantum number*, and it determines the energy and size of an electron orbital. The *angular momentum quantum number* l determines the value of the orbital angular momentum. It takes on values of 0, 1, 2, ..., $n - 1$. Often, the angular momentum quantum number is associated with a letter. The letters used are s, p, d, and f for 0, 1, 2, and 3 respectively (successive values of l are labeled alphabetically starting with g). The magnetic quantum number m_l has a more complicated physical interpretation: it is the value of the orbital angular momentum in a specified direction (such as the direction of a magnetic field). It takes on values of $-l, -l + 1, \dots, 0, 1, \dots, l$. There are therefore $2l + 1$ different values of m_l given a value of l . Finally, each electron can have two values of m_s , the magnetic spin number: $\pm \frac{1}{2}$.

In summary:

1. n = total quantum number : 0, 1, ...
2. l = angular momentum quantum number : 0, 1, ..., n
3. m_l = magnetic quantum number : $-l, -l + 1, \dots, 0, 1, \dots, l$
4. m_s = spin quantum number : $\pm \frac{1}{2}$

While we have already determined that the energy of an electron in an atom is dependent largely on n , there is also a less prominent but still significant dependence on l . This difference in energy between electrons with the same n value is somewhat challenging to compute; it is simpler to just present the final result. It is conveniently included in the familiar resource below.

It is not immediately obvious how the periodic table shows the relative energies of electron orbitals. To understand this, we first must count the number of orbitals for a given pair of n and l values. There are always two possible values of m_s , and m_l ranges from $-l$ to l , giving $2l + 1$ possible values. There are then $4l + 2$ available sets of quantum numbers for each fixed pair of n and l values; for increasing l , this is 2 electrons, 6 electrons, 10 electrons, 14 electrons, and so on. Now we can reexamine the periodic table, starting from the second period. We see a sequence of two elements, followed by a break and then a sequence of 6. The same is true of the third period. In the fourth period, the break is replaced by a sequence of 10 elements. In the sixth and seventh periods, the lanthanides and actinides respectively contribute a sequence of 14 elements each. There is a clear correspondence between the periodic table and quantum numbers. In fact, this is true in the first period as well; helium is shown separately from hydrogen because chemically it has the properties of the noble gases, but for purposes of electron configurations, it would be more reasonably placed next to hydrogen.

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principle.

This method of reasoning can be used to write electron configurations of neutral atoms. To write an electron configuration, we write the names of every occupied subshell followed by its occupancy in superscript. The simplest example is hydrogen; it has only a single electron in the 1s subshell. We write its electron configuration as $1s^1$. Similarly, simply by reading through the periodic table row by row, we can see that oxygen has 2 electrons in its 1s subshell, 2 electrons in its 2s subshell, and 4 electrons in its 2p subshell. We write this configuration as $1s^2 2s^2 2p^4$. The configuration of aluminum is similarly $1s^2 2s^2 2p^6 3s^2 3p^1$. These configurations can get rather long; to shorten them, we can take out the configuration of a noble gas and replace it with the symbol for the noble gas. For example, the configuration of aluminum can be rewritten as $[\text{Ne}]3s^2 3p^1$.

When dealing with d subshells, there are some exceptions to this rule. Half-filled subshells and filled subshells are relatively more stable than other partially filled subshells. Some transition metals will therefore “steal” an electron from the nearest s subshell to stabilize their d subshells. The elements that steal a single electron are: chromium, copper, niobium, molybdenum, ruthenium, rhodium, silver, platinum, and gold. Palladium is the only element which can steal both electrons from the s subshell; its configuration is $[\text{Kr}]4d^{10}$.

5 Box Notation and Magnetism

The notation used so far for writing electron configurations only takes the quantum numbers n and l into account; both magnetic numbers are disregarded. This is, in fact, illustrative of a physical reality: when an atom is not in the presence of a magnetic field, the values of m_l and m_s are inconsequential. However, in the presence of a magnetic field, the orientation of orbitals and the spin of the electrons within them determine the response of an atom to the field. We therefore need a way to determine how electrons arrange themselves into individual orbitals. To depict this, we use box notation:

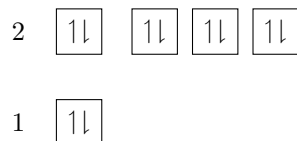


Figure 5: The electron configuration of neon.

This shows the 10 electrons in neon arranged into the 1s, 2s, and 2p subshells. We did not need any new information to construct this diagram, because the Pauli exclusion principle dictates that every electron must take on a different set of quantum numbers. With 10 electrons, and only 10 sets of quantum numbers to choose from without violating the Aufbau principle, there is no choice to be made. However, consider drawing the box notation for oxygen. Clearly, 2 electrons must be removed from the above diagram to bring the total down to only 8. According to the Aufbau principle, they should be removed from the highest energy level (much like deconstructing a pyramid starting with its top, or highest energy, blocks). We must decide whether two electrons in the same orbital (the same box, as depicted in this notation) should be removed, or whether they should be removed from different boxes. If they are in fact removed from different boxes, then we must further decide whether two electrons of opposing spin should be removed, or two electrons of the same spin. All of these decisions can be made using *Hund’s rule of maximum multiplicity*: electrons should be arranged so that the total spin is maximized. This yields the following configuration for oxygen, in which the total spin is maximized at $1 (\frac{1}{2} + \frac{1}{2})$.

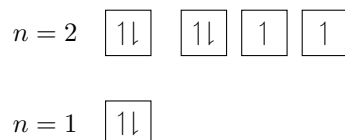


Figure 6: The electron configuration of oxygen, according to Hund’s rule.

We may now ask how a free oxygen atom would react to a magnetic field. According to the theory

of electromagnetism, a spinning electron has a permanent magnetic dipole, which can align with a magnetic field and be attracted to it. All atoms with unpaired electrons exhibit this effect, known as *paramagnetism*. Atoms with all electrons paired are called *diamagnetic*. Although intuitively diamagnetic materials would have no reaction to a magnetic field, there is a quantum effect whereby they create a magnetic field repelling an external magnetic field. Compounds can also be paramagnetic or diamagnetic, although determining which requires the use of more complex molecular orbital theory.