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2.5: Quantum Mechanics and the Atom

Key Concept Video Quantum Mechanics and the Atom: Orbitals and Quantum Numbers

As we have seen, the position and velocity of the electron are complementary properties—if we know one accurately, the other becomes indeterminate. Since velocity is directly related to energy (recall that kinetic energy equals $\frac{1}{2}mv^2$), position and *energy* are also complementary properties—the more we know about one, the less we know about the other. Many of the properties of an element, however, depend on the energies of its electrons. In the following paragraphs, we describe the probability distribution maps for electron states in which the electron has well-defined energy, but not well-defined position. In other words, for each of these states, we can specify the *energy* of the electron precisely, but not its location at a given instant. Instead, the electron's position is described in terms of an **orbital**, a probability distribution map showing where the electron is likely to be found. Since chemical bonding often involves the sharing of electrons between atoms (see Section 4.2), the spatial distribution of atomic electrons is important to bonding.

These states are known as energy *eigenstates*.

The mathematical derivation of energies and orbitals for electrons in atoms comes from solving the *Schrödinger* equation for the atom of interest. The general form of the Schrödinger equation is:

[Math Processing Error]

The symbol H stands for the Hamiltonian operator, a set of mathematical operations that represents the total energy (kinetic and potential) of the electron within the atom. The symbol E is the actual energy of the electron. The symbol ψ is the **wave function**, a mathematical function that describes the wavelike nature of the electron. A plot of the wave function squared represents an orbital, a probability density distribution map of the electron.

An operator is different from a normal algebraic entity. An operator transforms one mathematical function into another. For example, d/dx is an operator that means “take the derivative of.” When d/dx operates on a function (such as x^2), it returns another function ($2x$).

The symbol ψ is the Greek letter psi, pronounced “sigh.”

Solutions to the Schrödinger Equation for the Hydrogen Atom

When the Schrödinger equation is solved, it yields many solutions—many possible wave functions. The wave functions themselves are fairly complicated mathematical functions, and we do not examine them in detail in this book. Instead, we will introduce graphical representations (or plots) of the orbitals that correspond to the wave functions. Each orbital is specified by three interrelated **quantum numbers**: n ,

the **principal quantum number**, ℓ , the **angular momentum quantum number** (sometimes called the *azimuthal quantum number*); and m_ℓ , the **magnetic quantum number**. These quantum numbers all have integer values, as had been hinted at by both the Rydberg equation and Bohr's model. A fourth quantum number, m_s , the **spin quantum number**, specifies the orientation of the spin of the electron. We examine each of these quantum numbers individually.

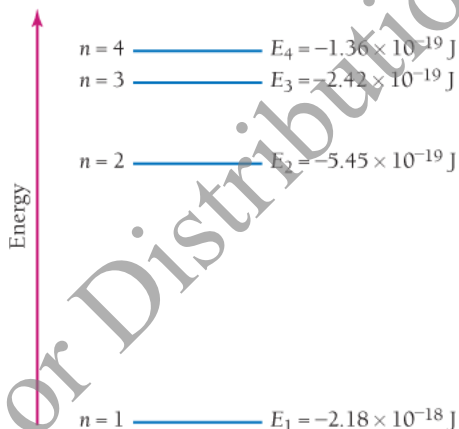
The Principal Quantum Number (n)

The principal quantum number is an integer that determines the overall size and energy of an orbital. Its possible values are 1, 2, 3, and so on. For the hydrogen atom, the energy of an electron in an orbital with quantum number n is given by:

$$E_n = -2.18 \times 10^{-18} \text{ J} / n^2$$

[Math Processing Error]

The energy is negative because the electron's energy is lowered (made more negative) by its interaction with the nucleus (see the description of Coulomb's law in Section 3.3). The constant, R_H , is the Rydberg constant for hydrogen times Planck's constant times the speed of light. Notice that orbitals with higher values of n have greater (less negative) energies, as shown in the energy level diagram at left. Notice also that, as n increases, the spacing between the energy levels becomes smaller.



The Angular Momentum Quantum Number (ℓ)

The angular momentum quantum number is an integer that determines the shape of the orbital. We consider these shapes in Section 2.6. The possible values of ℓ are 0, 1, 2, ..., $n-1$. In other words, for a given value of n , ℓ can be any integer (including 0) up to $n-1$. For example, if $n=2$, then the only possible value of ℓ is 0; if $n=3$, the possible values of ℓ are 0 and 1. In order to avoid confusion between n and ℓ , values of ℓ are often assigned letters as follows:

Value of ℓ	Letter Designation
$\ell = 0$	s
$\ell = 1$	p
$\ell = 2$	d
$\ell = 3$	f

The values of l beyond 3 are designated with letters in alphabetical order so that $l = 4$ is designated g , $l = 5$ is designated h , and so on.

Conceptual Connection 2.4 The Relationship between n and l

The Magnetic Quantum Number

The magnetic quantum number is an integer that specifies the orientation of the orbital. We will consider these orientations in Section 2.6. The possible values of m_l are the integer values (including zero) ranging from $-l$ to $+l$. For example, if $l = 0$, then the only possible value of m_l is 0; if $l = 1$, the possible values of m_l are -1 , 0, and $+1$; if $l = 2$, the possible values of m_l are -2 , -1 , 0, $+1$, $+2$, and so on.

Conceptual Connection 2.5 The Relationship between l and m_l

The Spin Quantum Number

The spin quantum number specifies the orientation of the spin of the electron. **Electron spin** is a fundamental property of an electron (like its negative charge). One electron does not have more or less spin than another—all electrons have the same amount of spin. The orientation of the electron's spin is quantized, with only two possibilities that we can call spin up and spin down. The spin quantum becomes important in Section 3.3 when we begin to consider how electrons occupy orbitals. For now, we will focus on the first three quantum numbers.

The idea of a “spinning” electron is something of a metaphor. A more correct way to express the same idea is to say that an electron has inherent angular momentum.

Each specific combination of the first three quantum numbers (n , l , and m_l) specifies one atomic orbital. For example, the orbital with $n = 1$, $l = 0$, and $m_l = 0$ is known as the $1s$ orbital. The 1 in $1s$ is the value of n , and the s specifies that $l = 0$. There is only one $1s$ orbital in an atom, and its m_l value is zero. Orbitals with the same value of n are said to be in the same **principal level** (or **principal shell**). Orbitals with the same value of n and l are said to be in the same **sublevel** (or **subshell**). The diagram at right shows all of the orbitals, each represented by a small square, in the first three principal levels.

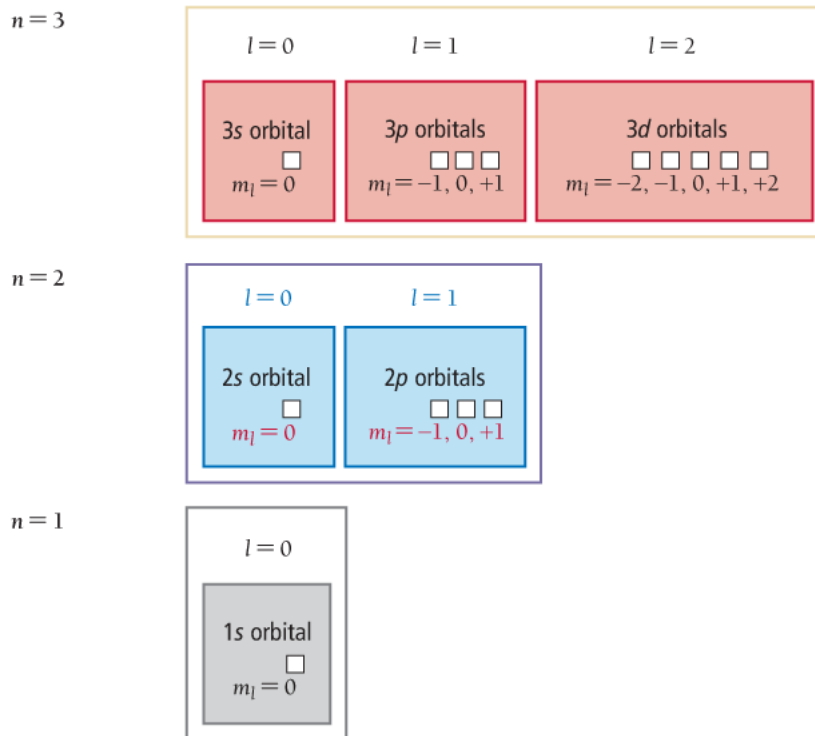
For example, the $n = 2$ level contains the $2s$ and $2p$ sublevels. Within the $n = 2$ level, the $2s$ sublevel—called the $2s$ sublevel—contains only one orbital (the $2s$ orbital), with $m_l = 0$. The $2p$ sublevel—called the $2p$ sublevel—contains three $2p$ orbitals, with $m_l = -1, 0, +1$.

In general, notice the following:

- The number of sublevels in any level is equal to n , the principal quantum number. Therefore, the $n = 1$ level has one sublevel, the $n = 2$ level has two sublevels, etc.
- The number of orbitals in any sublevel is equal to $2l + 1$. Therefore, the s sublevel ($l = 0$) has one orbital, the p sublevel ($l = 1$) has three orbitals, the d sublevel ($l = 2$) has five orbitals, etc.
- The number of orbitals in a level is equal to n^2 . Therefore, the $n = 1$ level has one orbital, the $n = 2$ level has four orbitals, the $n = 3$ level has nine orbitals, etc.

Principal level
(specified by n)

Sublevel
(specified by l)



Example 2.5 Quantum Numbers I

What are the quantum numbers and names (for example, 2s, 2p) of the orbitals in the [Math Processing Error] principal level? How many [Math Processing Error] orbitals exist?

SOLUTION

First determine the possible values of l (from the given value of n). Then determine the possible values of [Math Processing Error] for each possible value of l . For a given value of n , the possible values of l are 0, 1, 2,..., [Math Processing Error]. [Math Processing Error]; therefore [Math Processing Error], 1, 2, and 3

For a given value of l , the possible values of [Math Processing Error] are the integer values including zero ranging from $-l$ to $+l$. The name of an orbital is its principal quantum number (n) followed by the letter corresponding to the value l . The total number of orbitals is given by [Math Processing Error].

l	Possible m_l Values	Orbital name(s)
0	0	4s (1 orbital)
1	-1, 0, +1	4p (3 orbitals)
2	-2, -1, 0, +1, +2	4d (5 orbitals)
3	-3, -2, -1, 0, +1, +2, +3	4f (7 orbitals)

$$\text{Total number of orbitals} = 4^2 = 16$$

FOR PRACTICE 2.5 List the quantum numbers associated with all of the 5d orbitals. How many 5d orbitals exist?

Example 2.6 Quantum Numbers II

These sets of quantum numbers are each supposed to specify an orbital. One set, however, is erroneous. Which one and why?

- [Math Processing Error]
- [Math Processing Error]
- [Math Processing Error]
- [Math Processing Error]

SOLUTION

Choice (d) is erroneous because, for [Math Processing Error], the possible values of [Math Processing Error] are only -1 , 0 , and $+1$.

FOR PRACTICE 2.6 Each set of quantum numbers is supposed to specify an orbital. However, each set contains one quantum number that is not allowed. Replace the quantum number that is not allowed with one that is allowed.

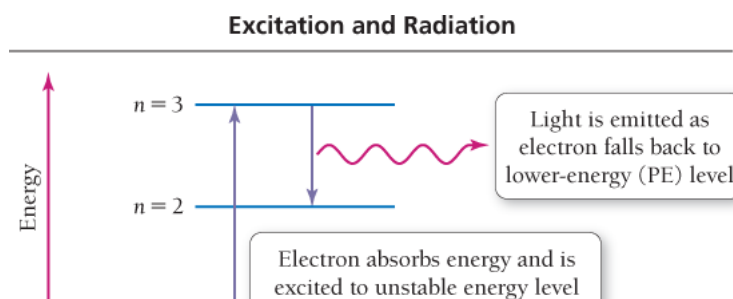
- [Math Processing Error]
- [Math Processing Error]
- [Math Processing Error]

Atomic Spectroscopy Explained

Quantum theory explains the atomic spectra of atoms discussed in Section 2.3. Each wavelength in the emission spectrum of an atom corresponds to an electron *transition* between quantum-mechanical orbitals. When an atom absorbs energy, an electron in a lower-energy orbital is *excited* or promoted to a higher-energy orbital, as shown in Figure 2.21. In this new configuration, however, the atom is unstable, and the electron quickly falls back or *relaxes* to a lower-energy orbital. As it does so, it releases a photon of light containing an amount of energy precisely equal to the energy difference between the two energy levels. We saw previously (see Equation 2.6) that the energy of an orbital with principal quantum number n is given by [Math Processing Error], where [Math Processing Error]. Therefore, the difference in energy between the two levels [Math Processing Error] and [Math Processing Error] is given by [Math Processing Error].

Figure 2.21 Excitation and Radiation

When an atom absorbs energy, an electron can be excited from an orbital in a lower-energy level to an orbital in a higher-energy level. The electron in this “excited state” is unstable, however, and relaxes to a lower-energy level, releasing energy in the form of electromagnetic radiation.



$$n = 1$$

If we substitute the expression for E_n into the expression for ΔE , we get the following expression for the change in energy that occurs in an atom when an electron changes energy levels:

The Rydberg equation, $\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$, can be derived from the relationships just covered. We leave this derivation to an exercise (see Problem 2.96).

[2.7]

ΔE

For example, suppose that an electron in a hydrogen atom relaxes from an orbital in the $n = 5$ level to an orbital in the $n = 2$ level. Then ΔE , the energy difference corresponding to the transition from $n = 5$ to $n = 2$, is determined as follows:

ΔE

The energy carries a negative sign because the atom *emits* the energy as it relaxes from $n = 5$ to $n = 2$. Since energy must be conserved, the exact amount of energy emitted by the atom is carried away by the photon:

ΔE

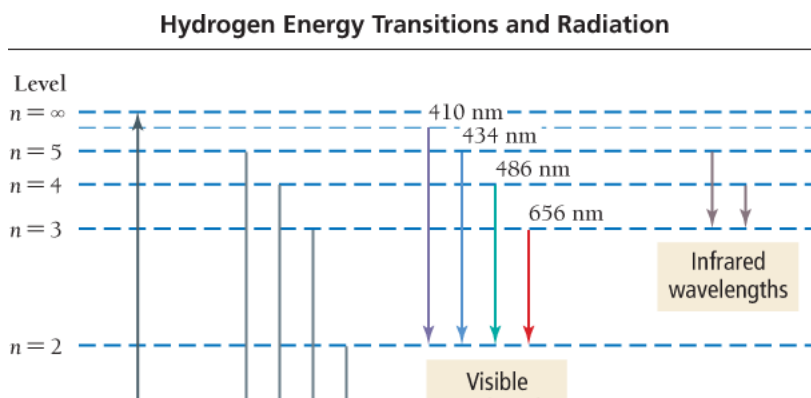
This energy determines the frequency and wavelength of the photon. Since the wavelength of the photon is related to its energy as $E = hc/\lambda$, we calculate the wavelength of the photon as:

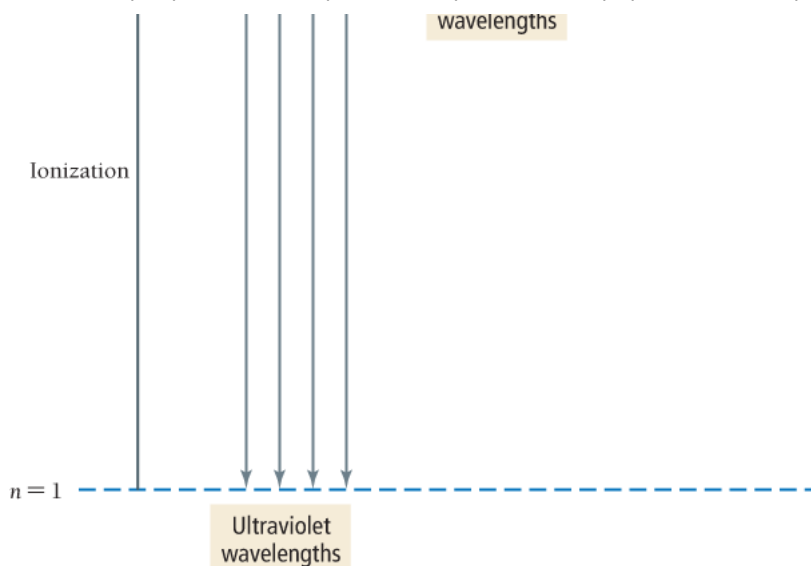
λ

Consequently, the light emitted by an excited hydrogen atom as it relaxes from an orbital in the $n = 5$ level to an orbital in the $n = 2$ level has a wavelength of 434 nm (violet). Similarly, we can calculate the light emitted due to a transition from $n = 4$ to $n = 2$ to be 486 nm (green). Notice that transitions between orbitals that are further apart in energy produce light that is higher in energy, and therefore shorter in wavelength, than transitions between orbitals that are closer together. Figure 2.22 shows several of the transitions in the hydrogen atom and their corresponding wavelengths.

Figure 2.22 Hydrogen Energy Transitions and Radiation

An atomic energy level diagram for hydrogen, showing some possible electron transitions between levels and the corresponding wavelengths of emitted light.





Conceptual Connection 2.6 Emission Spectra

Example 2.7 Wavelength of Light for a Transition in the Hydrogen Atom

Determine the wavelength of light emitted when an electron in a hydrogen atom makes a transition from an orbital in [Math Processing Error] to an orbital in [Math Processing Error].

SORT You are given the energy levels of an atomic transition and asked to find the wavelength of emitted light.

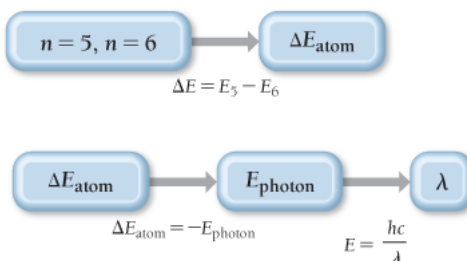
GIVEN: [Math Processing Error]

FIND: λ

STRATEGIZE In the first part of the conceptual plan, calculate the energy of the electron in the [Math Processing Error] and [Math Processing Error] orbitals using Equation 2.6 and subtract to find [Math Processing Error].

In the second part, find [Math Processing Error] by taking the negative of [Math Processing Error], and then calculating the wavelength corresponding to a photon of this energy using Equation 2.3. (The difference in sign between [Math Processing Error] and [Math Processing Error] applies only to emission. The energy of a photon must always be positive.)

CONCEPTUAL PLAN



RELATIONSHIPS USED

[Math Processing Error]

SOLVE Follow the conceptual plan. Begin by calculating [Math Processing Error].

SOLUTION

[Math Processing Error]

Calculate [Math Processing Error] by changing the sign of [Math Processing Error].

[Math Processing Error]

Solve the equation relating the energy of a photon to its wavelength for λ . Substitute the energy of the photon and calculate λ .

[Math Processing Error]

CHECK The units of the answer (m) are correct for wavelength. The magnitude is reasonable because [Math Processing Error] m is in the infrared region of the electromagnetic spectrum. You know that transitions from [Math Processing Error] or [Math Processing Error] to [Math Processing Error] lie in the visible region, so it makes sense that a transition between levels of higher n value (which are energetically closer to one another) would result in light of longer wavelength.

FOR PRACTICE 2.7 Determine the wavelength of the light absorbed when an electron in a hydrogen atom makes a transition from an orbital in which [Math Processing Error] to an orbital in which [Math Processing Error].

FOR MORE PRACTICE 2.7 An electron in the [Math Processing Error] level of the hydrogen atom relaxes to a lower-energy level, emitting light of [Math Processing Error]. Find the principal level to which the electron relaxed.

Interactive Worked Example 2.7 Wavelength of Light for a Transition in the Hydrogen Atom

Not for Distribution

Not for Distribution

Not for Distribution

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