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1 Quantum Theory and the Electronic Structure of Atoms 2 Quantum numbers Quantum numbers are used to differentiate between electrons i. In quantum theory, each electron in an atom is assigned a set of four quantum numbers. ii. Three of these give the location of the electron, and the fourth gives the orientation of the electron within the orbital iii. Definitions of numbers 3 n=1 n=2 n=3 quantum numbers (n, l, ml, ms) principal quantum number ndistance of e- from the nucleus n=1 n=2 n=3 4 quantum numbers: (n, l, ml, ms)angular momentum quantum number l for a given value of n, l = 0, 1, 2, 3, … n-1 l = s orbital l = p orbital l = d orbital l = f orbital n = 1, l = 0 n = 2, l = 0 or 1 n = 3, l = 0, 1, or 2 Shape of the “volume” of space that the e- occupies 5 l = 0 (s orbitals) l = 1 (p orbitals) 6 l = 2 (d orbitals) 7 quantum numbers: (n, l, ml, ms)magnetic quantum number ml for a given value of l ml = -l, …., 0, …. +l if l = 1 (p orbital), ml = -1, 0, or 1 if l = 2 (d orbital), ml = -2, -1, 0, 1, or 2 orientation of the orbital in space 8 ml = -1, 0, or 1 3 orientations is space 9 ml = -2, -1, 0, 1, or 2 5 orientations is space 10 (n, l, ml, ms) spin quantum number ms ms = +½ or -½ ms = +½ ms = -½ 11 quantum numbers: (n, l, ml, ms)Existence (and energy) of electron in atom is described by its unique wave function y. Pauli exclusion principle - no two electrons in an atom can have the same four quantum numbers. Each seat is uniquely identified (E, R12, S8) Each seat can hold only one individual at a time 12 13 y = (n, l, ml, ½) or y = (n, l, ml, -½)quantum numbers: (n, l, ml, ms) Shell – electrons with the same value of n Subshell – electrons with the same values of n and l Orbital – electrons with the same values of n, l, and ml How many electrons can an orbital hold? If n, l, and ml are fixed, then ms = ½ or - ½ y = (n, l, ml, ½) or y = (n, l, ml, -½) An orbital can hold 2 electrons 14 How many 2p orbitals are there in an atom?If l = 1, then ml = -1, 0, or +1 2p 3 orbitals l = 1 How many electrons can be placed in the 3d subshell? n=3 If l = 2, then ml = -2, -1, 0, +1, or +2 3d 5 orbitals which can hold a total of 10 e- l = 2 15 16 The Energies of OrbitalsEnergy of orbitals in a single electron atom Energy only depends on principal quantum number n n=3 n=2 n=1 17 Energy of orbitals in a multi-electron atom Energy depends on n and ln=3 l = 2 n=3 l = 1 n=3 l = 0 n=2 l = 1 n=2 l = 0 n=1 l = 0 18 “Fill up” electrons in lowest energy orbitals (Aufbau principle)C 6 electrons B 5 electrons Be 4 electrons Li 3 electrons He 2 electrons ? ? H 1 electron B 1s22s22p1 Be 1s22s2 Li 1s22s1 He 1s2 H 1s1 19 The most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins (Hund’s rule). Ne 10 electrons F 9 electrons O 8 electrons N 7 electrons C 6 electrons C 1s22s22p2 N 1s22s22p3 O 1s22s22p4 F 1s22s22p5 Ne 1s22s22p6 20 Order of orbitals (filling) in multi-electron atom1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s 21 in the orbital or subshellElectron configuration is how the electrons are distributed among the various atomic orbitals in an atom. number of electrons in the orbital or subshell 1s1 principal quantum number n angular momentum quantum number l Orbital diagram 1s1 H 22 What is the electron configuration of Mg?Mg 12 electrons 1s < 2s < 2p < 3s < 3p < 4s 1s22s22p63s2 = 12 electrons Abbreviated as [Ne]3s2 [Ne] 1s22s22p6 What are the possible quantum numbers for the last (outermost) electron in Cl? Cl 17 electrons 1s < 2s < 2p < 3s < 3p < 4s 1s22s22p63s23p5 = 17 electrons Last electron added to 3p orbital n = 3 l = 1 ml = -1, 0, or +1 ms = ½ or -½ 23 24 25 26 27 28 We're fetching your file...Please wait a moment while we retrieve your file from its home on the internet Quantum Theory and the Electronic Structure of Atoms Chapter 6 February 14, 2005Properties of Waves Wavelength (l) is the distance between identical points on successive waves. Amplitude is the vertical distance from the midline of a wave to the peak or trough.Properties of Waves Frequency (n) is the number of waves that pass through a particular point in 1 second (Hz = 1 cycle/s). The speed (u) of the wave = l x nMaxwell (1873), proposed that visible light consists of electromagnetic waves. Electromagnetic radiation is the emission and transmission of energy in the form of electromagnetic waves. Speed of light (c) in vacuum = 3.00 x 108 m/s All electromagnetic radiation l x n = cA photon has a frequency of 6.0 x 104 Hz. Convert this frequency into wavelength (nm). Does this frequency fall in the visible region? l n Radio wave l x n = c l = c/n l = 3.00 x 108 m/s / 6.0 x 104 Hz l = 5.0 x 103 m l = 5.0 x 1012 nmMystery #1, “Black Body Problem”Solved by Planck in 1900 Energy (light) is emitted or absorbed in discrete units (quantum). E = h x n Planck’s constant (h) h = 6.63 x 10-34 J•sMystery #2, “Photoelectric Effect”Solved by Einstein in 1905 hn • Light has both: • wave nature • particle nature KE e- Photon is a “particle” of light hn = KE + BE KE = hn - BEWhen copper is bombarded with high-energy electrons, X rays are emitted. Calculate the energy (in joules) associated with the photons if the wavelength of the X rays is 0.154 nm. E = h x n E = h x c / l E = 6.63 x 10-34 (J•s) x 3.00 x 10 8 (m/s) / 0.154 x 10-9 (m) E = 1.29 x 10 -15 JLine Emission Spectrum of Hydrogen Atoms( ) En = -RH 1 n2 Bohr’s Model of the Atom (1913) • e- can only have specific (quantized) energy values • light is emitted as e- moves from one energy level to a lower energy level n (principal quantum number) = 1,2,3,… RH (Rydberg constant) = 2.18 x 10-18JE = hn E = hnni = 3 ni = 3 f i ni = 2 nf = 2 DE = RH i f ( ) ( ) ( ) Ef = -RH Ei = -RH nf = 1 nf = 1 1 1 1 1 n2 n2 n2 n2 Ephoton = DE = Ef - EiCalculate the wavelength (in nm) of a photon emitted by a hydrogen atom when its electron drops from the n = 5 state to the n = 3 state. Ephoton = DE = RH i f ( ) 1 1 n2 n2 Ephoton = 2.18 x 10-18 J x (1/25 - 1/9) Ephoton = DE = -1.55 x 10-19 J Ephoton = h x c / l l = h x c / Ephoton l= 6.63 x 10-34 (J•s) x 3.00 x 108 (m/s)/1.55 x 10-19J l=1280 nmWhy is e- energy quantized? De Broglie (1924) reasoned that e- is both particle and wave. 2pr = nll = h/mu u = velocity of e- m = mass of e-What is the de Broglie wavelength (in nm) associated with a 2.5 g Ping-Pong ball traveling at 15.6 m/s? l = h/mu h in J•s m in kg u in (m/s) l = 6.63 x 10-34 / (2.5 x 10-3 x 15.6) l = 1.7 x 10-32 m = 1.7 x 10-23 nmSchrodinger Wave Equation • In 1926 Schrodinger wrote an equation that described both the particle and wave nature of the e- • Wave function (Y) describes: • . energy of e- with a given Y • . probability of finding e- in a volume of space • Schrodinger’s equation can only be solved exactly for the hydrogen atom. Must approximate its solution for multi-electron systems.n=1 n=2 n=3 Schrodinger Wave Equation Y = fn(n, l, ml, ms) principal quantum number n n = 1, 2, 3, 4, …. distance of e- from the nucleusWhere 90% of the e- density is found for the 1s orbital e- density (1s orbital) falls off rapidly as distance from nucleus increasesSchrodinger Wave Equation Y = fn(n, l, ml, ms) angular momentum quantum number l for a given value of n, l= 0, 1, 2, 3, … n-1 l = 0 s orbital l = 1 p orbital l = 2 d orbital l = 3 f orbital n = 1, l = 0 n = 2, l = 0 or 1 n = 3, l = 0, 1, or 2 Shape of the “volume” of space that the e- occupies l = 0 (s orbitals) l = 1 (p orbitals)l = 2 (d orbitals)Schrodinger Wave Equation Y = fn(n, l, ml, ms) magnetic quantum number ml for a given value of l ml = -l, …., 0, …. +l if l = 1 (p orbital), ml = -1, 0, or1 if l = 2 (d orbital), ml = -2, -1, 0, 1, or2 orientation of the orbital in spaceml = -1 ml = 0 ml = 1 ml = -2 ml = -1 ml = 0 ml = 1 ml = 2Schrodinger Wave Equation Y = fn(n, l, ml, ms) spin quantum number ms ms = +½or -½ ms = +½ ms = -½Schrodinger Wave Equation Y = fn(n, l, ml, ms) Existence (and energy) of electron in atom is described by its unique wave function Y. Pauli exclusion principle - no two electrons in an atom can have the same four quantum numbers. Each seat is uniquely identified (E, R12, S8) Each seat can hold only one individual at a timeHow many electrons can an orbital hold? Schrodinger Wave Equation Y = fn(n, l, ml, ms) Shell – electrons with the same value of n Subshell – electrons with the same values of nandl Orbital – electrons with the same values of n, l, andml If n, l, and mlare fixed, then ms = ½ or - ½ Y = (n, l, ml, ½) or Y = (n, l, ml, -½) An orbital can hold 2 electronsHow many electrons can be placed in the 3d subshell? n=2 n=3 l = 1 l = 2 How many 2p orbitals are there in an atom? If l = 1, then ml = -1, 0, or +1 2p 3 orbitals If l = 2, then ml = -2, -1, 0, +1, or +2 3d 5 orbitals which can hold a total of 10 e-Energy of orbitals in a single electron atom ( ) En = -RH 1 n2 n=1 n=2 n=3 Energy only depends on principal quantum number nEnergy of orbitals in a multi-electron atom n=1 l = 0 n=2 l = 0 n=2 l = 1 n=3 l = 0 n=3 l = 1 n=3 l = 2 Energy depends on n and l? ? “Fill up” electrons in lowest energy orbitals (Aufbau principle) Li 3 electrons Be 4 electrons B 5 electrons C 6 electrons B 1s22s22p1 Be 1s22s2 Li 1s22s1 H 1 electron He 2 electrons He 1s2 H 1s1The most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins (Hund’s rule). C 6 electrons N 7 electrons O 8 electrons F 9 electrons Ne 10 electrons Ne 1s22s22p6 C 1s22s22p2 N 1s22s22p3 O 1s22s22p4 F 1s22s22p5Order of orbitals (filling) in multi-electron atom 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6sWhat is the electron configuration of Mg? What are the possible quantum numbers for the last (outermost) electron in Cl? Mg 12 electrons 1s < 2s < 2p < 3s < 3p < 4s 1s22s22p63s2 2 + 2 + 6 + 2 = 12 electrons Abbreviated as [Ne]3s2 [Ne] 1s22s22p6 Cl 17 electrons 1s < 2s < 2p < 3s < 3p < 4s 1s22s22p63s23p5 2 + 2 + 6 + 2 + 5 = 17 electrons Last electron added to 3p orbital n = 3 l = 1 ml= -1, 0, or +1 ms = ½ or -½Outermost subshell being filled with electrons2p 2p Paramagnetic Diamagnetic unpaired electrons all electrons paired 2. Rally coach Which level is the highest energy ,and why? 3. Bohr’s Model of the Atom Electrons can be only at a certain distances from the nucleus. Each distance equal to a certain quantity of energy that an electron can have. An electron that is as close to the nucleus as it can is in its lowest energy level, the farther an electron is from the nucleus , the higher the energy level that the electron occupies. 4. Bohr’s Model of the Atom The difference in energy between two energy levels is known as Quantum of energy. An electron can be in only one energy level or another not between energy levels. Normally if an electron is in a state of lowest possible energy , it is in a ground state 5. Now If the picture for the hydrogen atom, why the electron move to higher level in the excited state? 6. Bohr’s Model of the Atom Normally if an electron is in a state of lowest possible energy , it is in a groun -state . If an electron gains energy , it moves to an excited state. An electron in an excited state will release a specific quantity of energy as it quickly falls back to its ground state. The smaller the electron’s orbit, the lower the atom’s energy state, or energy level. Conversely, the larger the electron’s orbit, the higher the atom’s energy state, or energy level. Thus, a hydrogen atom can have many different excited states, although it contains only one electron. 7. Bohr’s Model of the Atom Bohr assigned a number, n called a quantum number, to each orbit. He also calculated the radius of each orbit. 8. The hydrogen line spectrum: Hydrogen atom has a single electron is in the n = 1 orbit. In the ground state, the atom does not radiate energy. When energy is added from an outside source, the electron moves to a higher-energy orbit, such as the n = 2 orbit Such an electron transition raises the atom to an excited state. When the atom is in an excited state, the electron can drop from the higher-energy orbit to a lower-energy orbit. As a result of this transition, the atom emits a photon equals the energy difference between the two levels. 9. ΔE How could we calculate the difference in energy between two energy levels ? 10. The hydrogen line spectrum: 11. The limits of Bohr’s model Bohr’s model failed to explain the spectrum of any other element. Did not fully account for the chemical behavior of atoms 12. The Quantum Mechanical Model of the Atom De Broglie : suggested that electrons have characteristics similar to those of waves. The Heisenberg uncertainty principle : impossible to know both the velocity and position of a particle at the same time The Schrödinger wave equation: The atomic model in which electrons are treated as waves is called the wave mechanical model or the quantum mechanical model of the atom. 13. Compare and contrast: Bohr’s model and the quantum mechanical model. quantum mechanical model Bohr’s model electron’s energy has certain values. electron’s energy has certain values. Did not describe the electron’s path around the nucleus described the electron’s path around the nucleus 14. Electron’s probable location Atomic Orbital is the area around the nucleus which describes the electron’s probable location. Atomic Orbital is like a cloud in which we could find the electron. Hydrogen’s Atomic Orbitals the orbital does not have an exact defined size Because the boundary of an atomic orbital is fuzzy, 15. Principal quantum number The quantum mechanical model assigns four quantum numbers The first one is the principal quantum number (n) indicates the relative size and energy of atomic orbitals. As n increases, the orbital becomes larger 16. Energy levels and sublevels Principal energy levels contain energy sublevels. Principal energy level 1 consists of a single sublevel. Principal energy level 2 consists of two sublevels. principal energy level 3 consists of three sublevels, and so on. Sublevels are labeled s , p , d , or f 17. 17 we have 4 atomic orbital S P d F All s orbitals are spherical. All p orbitals are dumbbell-shaped. Not all d or f orbitals have the same shape. Each orbital can contain, at most, two electrons. Shapes of orbitals Note that the number of orbitals of each sublevel is odd number So , S = 2 electrons P = 6 electrons d = 10 electrons F = 14 electrons 18. Maximum Number of Electrons In Each SublevelMaximum Number of Electrons In Each Sublevel Maximum Number Sublevel Number of Orbitals of Electrons s 1 2 p 3 6 d 5 10 f 7 14 19. First four energy levels The number of orbitals of each principal energy level equals n 2 1 Quantum Theory and the Electronic Structure of AtomsChemistry Fifth Edition Julia Burdge Lecture PowerPoints Chapter 6 Quantum Theory and the Electronic Structure of Atoms ©2020 McGraw-Hill Education. All rights reserved. Authorized only for instructor use in the classroom. No reproduction or further distribution permitted without the prior written consent of McGraw-Hill Education. 2 6.1 The Nature of Light 2 Properties of Waves Wavelength λ (lambda) is the distance between identical points on successive waves (for example, successive peaks or successive troughs). 3 6.1 The Nature of Light 3 Properties of Waves The frequency ν (nu) is the number of waves that pass through a particular point in 1 second. 4 6.1 The Nature of Light 4 Properties of Waves Amplitude is the vertical distance from the midline of a wave to the top of the peak or the bottom of the trough. 5 6.1 The Nature of Light 5 Properties of Waves The speed of light through a vacuum, c, is c = × 108 m /s. The speed, wavelength, and frequency of a wave are related by the equation c = λν where and ν are expressed in meters (m) and reciprocal seconds (s−1), respectively. 6 SAMPLE PROBLEM Setup One type of laser used in the treatment of vascular skin lesions is a neodymium-doped yttrium aluminum garnet or Nd:YAG laser. The wavelength commonly used in these treatments is 532 nm. What is the frequency of this radiation? Setup Solving for frequency gives = c/λ. 7 SAMPLE PROBLEM 6.1 Solution 8 Access the text alternative for these images6.1 The Nature of Light 6 Properties of Waves Access the text alternative for these images (knee joint X ray) ©kaling2100/Shutterstock; (MRI) ©Don Farrall/Getty Images 9 6.2 Quantum Theory 2 Quantization of Energy Planck gave the name quantum to the smallest quantity of energy that can be emitted (or absorbed) in the form of electromagnetic radiation. The energy E of a single quantum of energy is given by E = hν where h is called Planck’s constant and is the frequency of the radiation. The value of Planck’s constant is 6.63 × 10−34 J • s. 10 SAMPLE PROBLEM Setup How much more energy per photon is there in green light of wavelength 532 nm than in red light of wavelength 635 nm? Setup 11 SAMPLE PROBLEM 6.2 Solution 1The energy of a single photon with wavelength 532 nm is 3.74 × 10−19 J. Following the same procedure, the energy of a photon of wavelength 635 nm is 3.13 × 10−19 J. 12 SAMPLE PROBLEM 6.2 Solution 2Solution The difference between them is Therefore, a photon of green light (= 532 nm) has 6.1 × 10−20 J more energy than a photon of red light (= 635 nm). 13 6.3 Bohr’s Theory of the Hydrogen Atom 3©McGraw-Hill Education 14 6.3 Bohr’s Theory of the Hydrogen Atom 4Atomic Line Spectra Johannes Rydberg developed an equation that could calculate all the wavelengths of hydrogen’s spectral lines: In this equation, now known as the Rydberg equation, is the wavelength of a line in the spectrum; R∞ is the Rydberg constant (×107 m−1); and n1 and n2 are positive integers, where n2 > n1. 15 6.3 Bohr’s Theory of the Hydrogen Atom 5The Line Spectrum of Hydrogen According to the laws of classical physics, an electron moving in an orbit of a hydrogen atom would radiate away energy in the form of electromagnetic waves. Thus, such an electron would quickly spiral into the nucleus and annihilate itself with the proton. 16 6.3 Bohr’s Theory of the Hydrogen Atom 6The Line Spectrum of Hydrogen Bohr postulated that the electron in atomic hydrogen is allowed to occupy only certain orbits of specific energies. In other words, the energies of the electron are quantized. An electron in any of the allowed orbits will not radiate energy and therefore will not spiral into the nucleus. 17 6.3 Bohr’s Theory of the Hydrogen Atom 9The Line Spectrum of Hydrogen Conversely, radiant energy (in the form of a photon) is emitted when the electron moves from a higher-energy excited state to a lower-energy excited state or the ground state. 18 6.3 Bohr’s Theory of the Hydrogen Atom 10The Line Spectrum of Hydrogen ΔE = Ef − Ei 19 6.3 Bohr’s Theory of the Hydrogen Atom 11The Line Spectrum of Hydrogen 20 6.3 Bohr’s Theory of the Hydrogen Atom 13 21 SAMPLE PROBLEM Setup Calculate the wavelength (in nm) of the photon emitted when an electron transitions from the n = 4 state to the n = 2 state in a hydrogen atom. Setup According to the problem, the transition is from n = 4 to n = 2, so ni = 4 and nf = 2. The required constants are h = 6.63 × 10−34 J·s and c = 3.00 × 108 m/s. 22 SAMPLE PROBLEM 6.4 Solution 23 6.5 Quantum Mechanics 1 The Uncertainty Principle To describe the problem of trying to locate a subatomic particle that behaves like a wave, Werner Heisenberg formulated what is now known as the Heisenberg uncertainty principle: It is impossible to know simultaneously both the momentum p and the position x of a particle with certainty. Stated mathematically, 24 6.5 Quantum Mechanics 3 The Schrödinger Equation Erwin Schrödinger, using a complex mathematical technique, formulated an equation that describes the behavior and energies of submicroscopic particles in general. The Schrödinger equation requires advanced calculus to solve, and we will not discuss it here. The equation, however, incorporates both particle behavior, in terms of mass m, and wave behavior, in terms of a wave function ψ (psi), which depends on the location in space of the system (such as an electron in an atom). 25 6.5 Quantum Mechanics 4 The Schrödinger Equation The wave function itself has no direct physical meaning. However, the probability of finding the electron in a certain region in space is proportional to the square of the wave function, ψ2. The idea of relating ψ2 to probability stemmed from a wave theory analogy. 26 6.5 Quantum Mechanics 5 The Quantum Mechanical Description of the Hydrogen Atom The Schrödinger equation specifies the possible energy states the electron can occupy in a hydrogen atom and identifies the corresponding wave functions (ψ). These energy states and wave functions are characterized by a set of quantum numbers (to be discussed shortly), with which we can construct a comprehensive model of the hydrogen atom. 27 6.5 Quantum Mechanics 6 The Quantum Mechanical Description of the Hydrogen Atom The square of the wave function, ψ2, defines the distribution of electron density in three-dimensional space around the nucleus. Regions of high electron density represent a high probability of locating the electron. 28 6.5 Quantum Mechanics 7 The Quantum Mechanical Description of the Hydrogen Atom To distinguish the quantum mechanical description of an atom from Bohr’s model, we speak of an atomic orbital, rather than an orbit. An atomic orbital can be thought of as the wave function of an electron in an atom. When we say that an electron is in a certain orbital, we mean that the distribution of the electron density or the probability of locating the electron in space is described by the square of the wave function associated with that orbital. 29 6.6 Quantum Numbers Topics Principal Quantum Number (n)Angular Momentum Quantum Number (l) Magnetic Quantum Number (ml) Electron Spin Quantum Number (ms) 30 6.6 Quantum Numbers 1 Principal Quantum Number (n) In quantum mechanics, three quantum numbers are required to describe the distribution of electron density in an atom. These numbers are derived from the mathematical solution of Schrödinger’s equation for the hydrogen atom. 31 6.6 Quantum Numbers 2 Principal Quantum Number (n) The principal quantum number (n) designates the size of the orbital. The larger n is, the greater the average distance of an electron in the orbital from the nucleus and therefore the larger the orbital. n = 1, 2, 3, … 32 6.6 Quantum Numbers 3 Angular Momentum Quantum Number (l) The angular momentum quantum number (l) describes the shape of the atomic orbital. The values of l are integers that depend on the value of the principal quantum number, n. For a given value of n, the possible values of l range from 0 to n – 1. l 1 2 3 Orbital designation s p d f 33 6.6 Quantum Numbers 4 Angular Momentum Quantum Number (l) A collection of orbitals with the same value of n is frequently called a shell. One or more orbitals with the same n and l values are referred to as a subshell. For example, the shell designated by n = 2 is composed of two subshells: l = 0 and l = 1 (the allowed values of l for n = 2). These subshells are called the 2s and 2p subshells where 2 denotes the value of n, and s and p denote the values of l. 34 6.6 Quantum Numbers 5 Magnetic Quantum Number (ml) The magnetic quantum number (ml) describes the orientation of the orbital in space. Within a subshell, the value of ml depends on the value of l. For a certain value of l, there are (2l + 1) integral values of *ml* as follows: –l, …, 0 , …, +l 35 6.6 Quantum Numbers 6 TABLE 6.2 Allowed values of the Quantum Numbers n, l, and ml When n is l can be When l is ml can be 1 Only 0 2 0 or 1 -1, 0, or +1 3 0, 1, or 2 -2,-1, 0, +1, or +2 4 0, 1, 2,or 3 -2,-1, 0, +1,or +2 -3,-2,-1,0,+1,+2,or +3 . 36 6.6 Quantum Numbers 7 Magnetic Quantum Number (ml) 37 SAMPLE PROBLEM Setup What are the possible values for the magnetic quantum number (ml) when the principal quantum number (n) is 3 and the angular momentum quantum number (l) is 1? Setup The possible values of *ml* are –l, , 0, , +l. Solution The possible values of *ml* are –1, 0, and +1. 38 6.6 Quantum Numbers 8 Electron Spin Quantum Number (ms) Whereas three quantum numbers are sufficient to describe an atomic orbital, an additional quantum number becomes necessary to describe an electron that occupies the orbital. Electrons possess a magnetic field, as if they were spinning. 39 6.6 Quantum Numbers 9 Electron Spin Quantum Number (ms) To specify the electron’s spin, we use the electron spin quantum number (ms). Because there are two possible directions of spin, opposite each other, ms has two possible values: +1/2 and –1/2. Two electrons in the same orbital with opposite spins are referred to as “paired.” 40 6.6 Quantum Numbers 10 Electron Spin Quantum Number (ms) To summarize, we can designate an orbital in an atom with a set of three quantum numbers. These three quantum numbers indicate the size (n), shape (l), and orientation (ml) of the orbital. A fourth quantum number (ms) is necessary to designate the spin of an electron in the orbital. 41 6.7 Atomic Orbitals Topics s Orbitals p Orbitals d Orbitals and Other Higher-Energy Orbitals Energies of Orbitals 42 6.7 Atomic Orbitals 1 s Orbitals For any value of the principal quantum number (n), the value 0 is possible for the angular momentum quantum number (l), corresponding to an s subshell. Furthermore, when l = 0, the magnetic quantum number (ml) has only one possible value, 0, corresponding to an s orbital. Therefore, there is an s subshell in every shell, and each s subshell contains just one orbital, an s orbital. 43 6.7 Atomic Orbitals 2 44 6.7 Atomic Orbitals 3 s Orbitals All s orbitals are spherical in shape but differ in size, which increases as the principal quantum number increases. 45 6.7 Atomic Orbitals 4 p Orbitals When the principal quantum number (n) is 2 or greater, the value 1 is possible for the angular momentum quantum number (l), corresponding to a p subshell. And, when l = 1, the magnetic quantum number (ml) has three possible values: –1, 0, and +1, each corresponding to a different p orbital. 46 Access the text alternative for these images6.7 Atomic Orbitals 5 p Orbitals Therefore, there is a p subshell in every shell for which n 2, and each p subshell contains three p orbitals. These three p orbitals are labeled px , py , and pz . Access the text alternative for these images 47 6.7 Atomic Orbitals 6 p Orbitals These three p orbitals are identical in size, shape, and energy; they differ from one another only in orientation. Like s orbitals, p orbitals increase in size from 2p to 3p to 4p orbital and so on. 48 6.7 Atomic Orbitals 7 d Orbitals and Other Higher-Energy Orbitals When the principal quantum number (n) is 3 or greater, the value 2 is possible for the angular momentum quantum number (l), corresponding to a d subshell. When l = 2, the magnetic quantum number (ml) has five possible values, –2, –1, 0, +1, and +2, each corresponding to a different d orbital. 49 6.7 Atomic Orbitals 8 d Orbitals and Other Higher-Energy Orbitals 50 6.7 Atomic Orbitals 9 d Orbitals and Other Higher-Energy Orbitals All the 3d orbitals in an atom are identical in energy and are labeled with subscripts denoting their orientation with respect to the x, y, and z axes and to the planes defined by them. The d orbitals that have higher principal quantum numbers (4d, 5d, etc.) have shapes similar to those shown for the 3d orbitals . 51 6.8 Electron Configuration 1Energies of Atomic Orbitals in Many-Electron Systems The hydrogen atom is a particularly simple system because it contains only one electron. The electron may reside in the 1s orbital (the ground state), or it may be found in some higher-energy orbital (an excited state). With many-electron systems, we need to know the ground- state electron configuration—that is, how the electrons are distributed in the various atomic orbitals. 52 6.8 Electron Configuration 2Energies of Atomic Orbitals in Many-Electron Systems To do this, we need to know the relative energies of atomic orbitals in a many-electron system, which differ from those in a one-electron system such as hydrogen. In many-electron atoms, electrostatic interactions cause the energies of the orbitals in a shell to split. 53 6.8 Electron Configuration 3 54 6.8 Electron Configuration 4The Pauli Exclusion Principle According to the Pauli exclusion principle, no two electrons in the same atom can have the same four quantum numbers. If two electrons in an atom have the same n, l, and *m l* values (meaning that they occupy the same orbital), then they must have different values of ms; that is, one must have ms= –1/2 and the other must have ms = +1/2. 55 6.8 Electron Configuration 5The Pauli Exclusion Principle Because there are only two possible values for ms , and no two electrons in the same orbital may have the same value for ms , a maximum of two electrons may occupy an atomic orbital, and these two electrons must have opposite spins. Two electrons in the same orbital with opposite spins are said to have paired spins. 56 6.8 Electron Configuration 6The Pauli Exclusion Principle Orbital Notation and Orbital Diagrams 57 6.8 Electron Configuration 7The Aufbau Principle We can continue the process of writing electron configurations for elements based on the order of orbital energies and the Pauli exclusion principle. This process is based on the Aufbau principle, which makes it possible to “build” the periodic table of the elements and determine their electron configurations by steps. Each step involves adding one proton to the nucleus and one electron to the appropriate atomic orbital. 58 6.8 Electron Configuration 8The Aufbau Principle 1s22s1 1s22s2 1s22s22p1 59 6.8 Electron Configuration 9Hund’s Rule According to Hund’s rule, the most stable arrangement of electrons in orbitals of equal energy is the one in which the number of electrons with the same spin is maximized. 1s22s22p2 1s22s22p3 60 6.8 Electron Configuration 10Hund’s Rule 61 6.8 Electron Configuration 11General Rules for Writing Electron Configurations Electrons will reside in the available orbitals of the lowest possible energy. Each orbital can accommodate a maximum of two electrons. Electrons will not pair in degenerate orbitals if an empty orbital is available. Orbitals will fill in the order indicated in the following figure. 62 6.8 Electron Configuration 12Access the text alternative for these images 63 SAMPLE PROBLEM 6.9 StrategyWrite the electron configuration and give the orbital diagram of a calcium (Ca) atom (Z = 20). Strategy Use the general rules given and the Aufbau principle to “build” the electron configuration of a calcium atom and represent it with an orbital diagram. Setup Because Z = 20, we know that a Ca atom has 20 electrons. 64 SAMPLE PROBLEM 6.9 SolutionSolution Ca 1s2 2s2 2p6 3s2 3p6 4s2 Access the text alternative for these images 65 6.9 Electron Configurations and the Periodic Table 2 66 6.9 Electron Configurations and the Periodic Table 3 67 6.9 Electron Configurations and the Periodic Table 4Electron Configurations and the Periodic Table Anomalies 68 6.9 Electron Configurations and the Periodic Table 5Electron Configurations and the Periodic Table Anomalies The reason for these anomalies is that a slightly greater stability is associated with the half-filled (3d5) and completely filled (3d10) subshells. 1. Theodore L. Brown; H. Eugene LeMay, Jr.; and Bruce E. Bursten Electronic Structure of Atoms Chemistry, The Central Science, 10th edition Chapter 6 Electronic Structure of Atoms John D. Bookstaver St. Charles Community College St. Peters, MO ã 2006, Prentice Hall, Inc. 2. Electronic Structure of Atoms Waves • To understand the electronic structure of atoms, one must understand the nature of electromagnetic radiation. • The distance between corresponding points on adjacent waves is the wavelength (l). 3. Electronic Structure of Atoms Waves • The number of waves passing a given point per unit of time is the frequency (n). • For waves traveling at the same velocity, the longer the wavelength, the smaller the frequency. 4. Electronic Structure of Atoms Electromagnetic Radiation • All electromagnetic radiation travels at the same velocity: the speed of light (c), 3.00 ´ 108 m/s. • Therefore, c = ln 5. Electronic Structure of Atoms The Nature of Energy • The wave nature of light does not explain how an object can glow when its temperature increases. • Max Planck explained it by assuming that energy comes in packets called quanta. 6. Electronic Structure of Atoms The Nature of Energy • Einstein used this assumption to explain the photoelectric effect. • He concluded that energy is proportional to frequency: E = hn where h is Planck’s constant, 6.63 ´ 10−34 J-s. 7. Electronic Structure of Atoms The Nature of Energy • Therefore, if one knows the wavelength of light, one can calculate the energy in one photon, or packet, of that light: c = ln E = hn 8. Electronic Structure of Atoms The Nature of Energy Another mystery involved the emission spectra observed from energy emitted by atoms and molecules. 9. Electronic Structure of Atoms The Nature of Energy • One does not observe a continuous spectrum, as one gets from a white light source. • Only a line spectrum of discrete wavelengths is observed. 10. Electronic Structure of Atoms The Nature of Energy • Niels Bohr adopted Planck’s assumption and explained these phenomena in this way: 1. Electrons in an atom can only occupy certain orbits (corresponding to certain energies). 11. Electronic Structure of Atoms The Nature of Energy • Niels Bohr adopted Planck’s assumption and explained these phenomena in this way: 2. Electrons in permitted orbits have specific, “allowed” energies; these energies will not be radiated from the atom. 12. Electronic Structure of Atoms The Nature of Energy • Niels Bohr adopted Planck’s assumption and explained these phenomena in this way: 3. Energy is only absorbed or emitted in such a way as to move an electron from one “allowed” energy state to another; the energy is defined by E = hn 13. Electronic Structure of Atoms The Nature of Energy The energy absorbed or emitted from the process of electron promotion or demotion can be calculated by the equation: DE = −RH (1) nf 2 1 ni 2 - where RH is the Rydberg constant, 2.18 ´ 10−18 J, and ni and nf are the initial and final energy levels of the electron. 14. The Wave Nature of Matter • Louis de Broglie posited that if light can have material properties, matter should exhibit wave properties. • He demonstrated that the relationship between mass and wavelength was Electronic Structure of Atoms l = h mv 15. Electronic Structure of Atoms The Uncertainty Principle • Heisenberg showed that the more precisely the momentum of a particle is known, the less precisely is its position known: (Dx) (Dmv) ³ h 4p • In many cases, our uncertainty of the whereabouts of an electron is greater than the size of the atom itself! 16. Electronic Structure of Atoms Quantum Mechanics • Erwin Schrödinger developed a mathematical treatment into which both the wave and particle nature of matter could be incorporated. • It is known as quantum mechanics. 17. Electronic Structure of Atoms Quantum Mechanics • The wave equation is designated with a lower case Greek psi (y). • The square of the wave equation, y2, gives a probability density map of where an electron has a certain statistical likelihood of being at any given instant in time. 18. Electronic Structure of Atoms Quantum Numbers • Solving the wave equation gives a set of wave functions, or orbitals, and their corresponding energies. • Each orbital describes a spatial distribution of electron density. • An orbital is described by a set of three quantum numbers. 19. Principal Quantum Number, n • The principal quantum number, n, describes the energy level on which the orbital resides. • The values of n are integers ≥ 0. Electronic Structure of Atoms 20. Azimuthal Quantum Number, l • This quantum number defines the shape of the orbital. • Allowed values of l are integers ranging from 0 to n − 1. • We use letter designations to communicate the different values of l and, therefore, the shapes and types of orbitals. Electronic Structure of Atoms 22. Magnetic Quantum Number, ml • Describes the three-dimensional orientation of the orbital. • Values are integers ranging from -l to l: Electronic Structure of Atoms −l ≤ ml ≤ l. • Therefore, on any given energy level, there can be up to 1 s orbital, 3 p orbitals, 5 d orbitals, 7 f orbitals, etc. 23. Magnetic Quantum Number, ml • Orbitals with the same value of n form a shell. • Different orbital types within a shell are subshells. Electronic Structure of Atoms 24. Electronic Structure of Atoms s Orbitals • Value of l = 0. • Spherical in shape. • Radius of sphere increases with increasing value of n. 25. Electronic Structure of Atoms s Orbitals Observing a graph of probabilities of finding an electron versus distance from the nucleus, we see that s orbitals possess n−1 nodes, or regions where there is 0 probability of finding an electron. 27. Electronic Structure of Atoms d Orbitals • Value of l is 2. • Four of the five orbitals have 4 lobes; the other resembles a p orbital with a doughnut around the center. 28. Electronic Structure of Atoms Energies of Orbitals • For a one-electron hydrogen atom, orbitals on the same energy level have the same energy. • That is, they are degenerate. 29. Electronic Structure of Atoms Energies of Orbitals • As the number of electrons increases, though, so does the repulsion between them. • Therefore, in many-electron atoms, orbitals on the same energy level are no longer degenerate. 30. Electronic Structure of Atoms Spin Quantum Number, ms • In the 1920s, it was discovered that two electrons in the same orbital do not have exactly the same energy. • The “spin” of an electron describes its magnetic field, which affects its energy. 31. Electronic Structure of Atoms Spin Quantum Number, ms • This led to a fourth quantum number, the spin quantum number, ms. • The spin quantum number has only 2 allowed values: +1/2 and −1/2. 32. Electronic Structure of Atoms Pauli Exclusion Principle • No two electrons in the same atom can have exactly the same energy. • For example, no two electrons in the same atom can have identical sets of quantum numbers. 33. Electronic Structure of Atoms Electron Configurations • Distribution of all electrons in an atom • Consist of Number denoting the energy level 34. Electronic Structure of Atoms Electron Configurations • Distribution of all electrons in an atom • Consist of Number denoting the energy level Letter denoting the type of orbital 35. Electronic Structure of Atoms Electron Configurations • Distribution of all electrons in an atom. • Consist of Number denoting the energy level. Letter denoting the type of orbital. Superscript denoting the number of electrons in those orbitals. 36. Electronic Structure of Atoms Orbital Diagrams • Each box represents one orbital. • Half-arrows represent the electrons. • The direction of the arrow represents the spin of the electron. 37. Electronic Structure of Atoms Hund’s Rule “For degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized.” 38. Electronic Structure of Atoms Periodic Table • We fill orbitals in increasing order of energy. • Different blocks on the periodic table, then correspond to different types of orbitals. 39. Electronic Structure of Atoms Some Anomalies Some irregularities occur when there are enough electrons to half-fill s and d orbitals on a given row. 40. Electronic Structure of Atoms Some Anomalies For instance, the electron configuration for copper is [Ar] 4s1 3d5 rather than the expected [Ar] 4s2 3d4. 41. Electronic Structure of Atoms Some Anomalies • This occurs because the 4s and 3d orbitals are very close in energy. • These anomalies occur in f-block atoms, as well. Chapter 7; Electronic Structure of Atoms • Electromagnetic Radiation • Flame Test/ Emission Spectra • Quantized Energy Levels • Bohr Model/ Rydberg Equation • Principal Energy Levels, n • First Ionization Energy • 2nd , 3rd, 4th, etc Ionization EnergyChapter 7; Electronic Structureof Atoms • Sublevels (s, p, d, f) • Photoelectron Spectroscopy • Electron Configuration • Valence Electrons/ Core • Good/ Bad Point of Atom Model • Quantum Theory • Dual Nature of the Electron • Heisenberg Uncertainty PrincipleChapter 7; ElectronicStructure of Atoms • Quantum Numbers (n, l, ml, ms) • Oribtal Diagrams • Paramagnetism and DiamagnetismExperimental Evidence Line Spectra Ionization Energies Photoelectron Spectrum Intensity/detail of Line Spectra What it means Electrons in quanitized ‘n’ # electrons in each ‘n’ # electrons in each ‘n’ and each sublevel Indicates ‘n’ have sublevels associated with them Electronic Structure ModelElectronic StructureOrder of orbitals (filling) in multi-electron atom 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s 7.7What is the electron configuration of Mg? What is the electron configuration of Cl? Mg 12 electrons 1s < 2s < 2p < 3s < 3p < 4s 1s22s22p63s2 2 + 2 + 6 + 2 = 12 electrons Abbreviated as [Ne]3s2 [Ne] 1s22s22p6 Cl 17 electrons 1s < 2s < 2p < 3s < 3p < 4s 1s22s22p63s23p5 2 + 2 + 6 + 2 + 5 = 17 electrons 7.7Electron Configurations of Cations and Anions Of Representative Elements Na [Ne]3s1 Na+ [Ne] Atoms lose electrons so that cation has a noble-gas outer electron configuration. Ca [Ar]4s2 Ca2+ [Ar] Al [Ne]3s23p1 Al3+ [Ne] H 1s1 H- 1s2 or [He] Atoms gain electrons so that anion has a noble-gas outer electron configuration. F 1s22s22p5 F- 1s22s22p6 or [Ne] O 1s22s22p4 O2- 1s22s22p6 or [Ne] N 1s22s22p3 N3- 1s22s22p6 or [Ne] 8.2What neutral atom is isoelectronic with H- ? Na+: [Ne] Al3+: [Ne] F-: 1s22s22p6 or [Ne] O2-: 1s22s22p6 or [Ne] N3-: 1s22s22p6 or [Ne] Na+, Al3+, F-, O2-, and N3- are all isoelectronic with Ne H-: 1s2 same electron configuration as He 8.2Electron Configurations of Transition Metals • Completely filled or half-completely filled d-orbitals have a special stability • Some “irregularities” are seen in the electron configurations of transition and inner-transition metals.Fe: [Ar]4s23d6 Mn: [Ar]4s23d5 Fe2+: [Ar]4s03d6 or [Ar]3d6 Mn2+: [Ar]4s03d5 or [Ar]3d5 Fe3+: [Ar]4s03d5 or [Ar]3d5 Electron Configurations of Cations of Transition Metals When a cation is formed from an atom of a transition metal, electrons are always removed first from the ns orbital and then from the (n – 1)d orbitals. Order of filling; 3s