Atomic Structure

Atomic structure, as we will consider it here, relates most closely to atoms as they exist in isolation. In isolation means single atoms (or ions) that are not bonded to other atoms. Since relatively little of the matter on our planet exists in this form (Inert gasses like helium and neon are examples of matter that does exist in a monoatomic state.), you might wonder why I am asking you to learn about it. The reason is that atomic structure, particularly the structure of atomic orbitals, is a bit simpler than molecular structure. If we learn the basics of atomic structure first, it is easier to study molecular structure.

The subatomic particles that are of most interest to us in CHM 109 are protons (p^+), neutrons (n), and electrons (e^-). p^+ and n have approximately equal mass (close to 1.0 atomic mass unit [amu] each), while electrons each weigh about one-two thousandth of an amu. Protons and electrons have charges that are equal in magnitude but opposite in sign, but neutrons have no charge. Other particles such as positrons (e^+ or β^+) are important in some areas of medicine (PET scans), but we will not have time to consider them in any detail. Further, while we will learn that neutrons are very important components of the nucleus, we will consider only their effect on atomic weight, nuclear stability, and relationship to atomic energy in CHM 109. Our main interest this semester will be on p^+, because they determine elemental identity, and e^-. We will be particularly interested in the outermost e^-, because they are involved in ion formation and the interactions associated with forming and breaking covalent bonds. These latter processes are central to the chemistry of living things, and a major focus of the course.

How are the three main subatomic particles arranged to form matter? The p^+ and n are bound by very high energy interactions in a very small space called the nucleus (plural: nuclei) which is located in the center of the atom. (Based on your previous knowledge of how charged particles interact, is there something about nuclear structure that is unsettling?) The e^- exist in clearly defined spaces with known shapes outside of the nucleus. Because almost all of the mass of an atom is present in the nucleus I tend to look at the nuclei as (more or less fixed) reference points of atoms, and the e^- are bound to but moving around these reference points. Two ways to view the structure of a ^{4}He (said "helium four") atom are shown in Figure 1. The 4 indicates the *mass number* of the atom, which is the sum of the number of $p^+ + n$. The elemental identity is determined by the number of p^+, which for He is always 2. The *atomic number* of He is therefore 2. For the Bohr model, it may be useful to view the

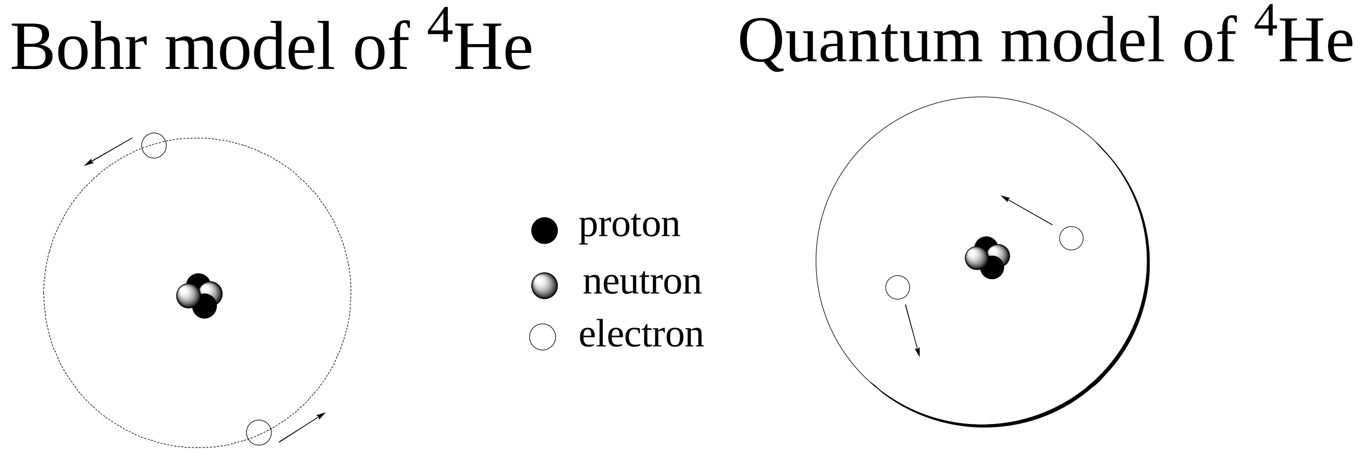


Figure 1. Two ways of looking at the structure of a ^{4}He atom.

nucleus like the sun and the electrons moving in *orbits* nucleus like planets move around the sun in our solar system. In the quantum model, the electrons are confined to a spherical space called an *orbit*<u>*al*</u>. The electrons in the quantum model should be viewed both as particles (that are moving so fast that they blur out) and as waves. (Viewing matter as a wave makes my head hurt!) An orbital may contain either 1 or 2 electrons. An orbital containing 2 electrons is said to be full, and that arrangement is sometimes more stable than an orbital with just one electron in it.

Students are sometimes bothered by the fact that there is more than one way to look at a problem. However, it is useful to do this to solve problems, both in biochemistry and in life in general. In the case of atomic structure, the quantum model tends to provide much better predictions to most chemistry problems, and it therefore the model we used most of the time. The mathematics behind the derivation of the shape and size or orbitals is relatively complex, and we will not deal with that. We will however, need to know the names, shapes/sizes, and energies of the different orbitals that are important in biochemistry.

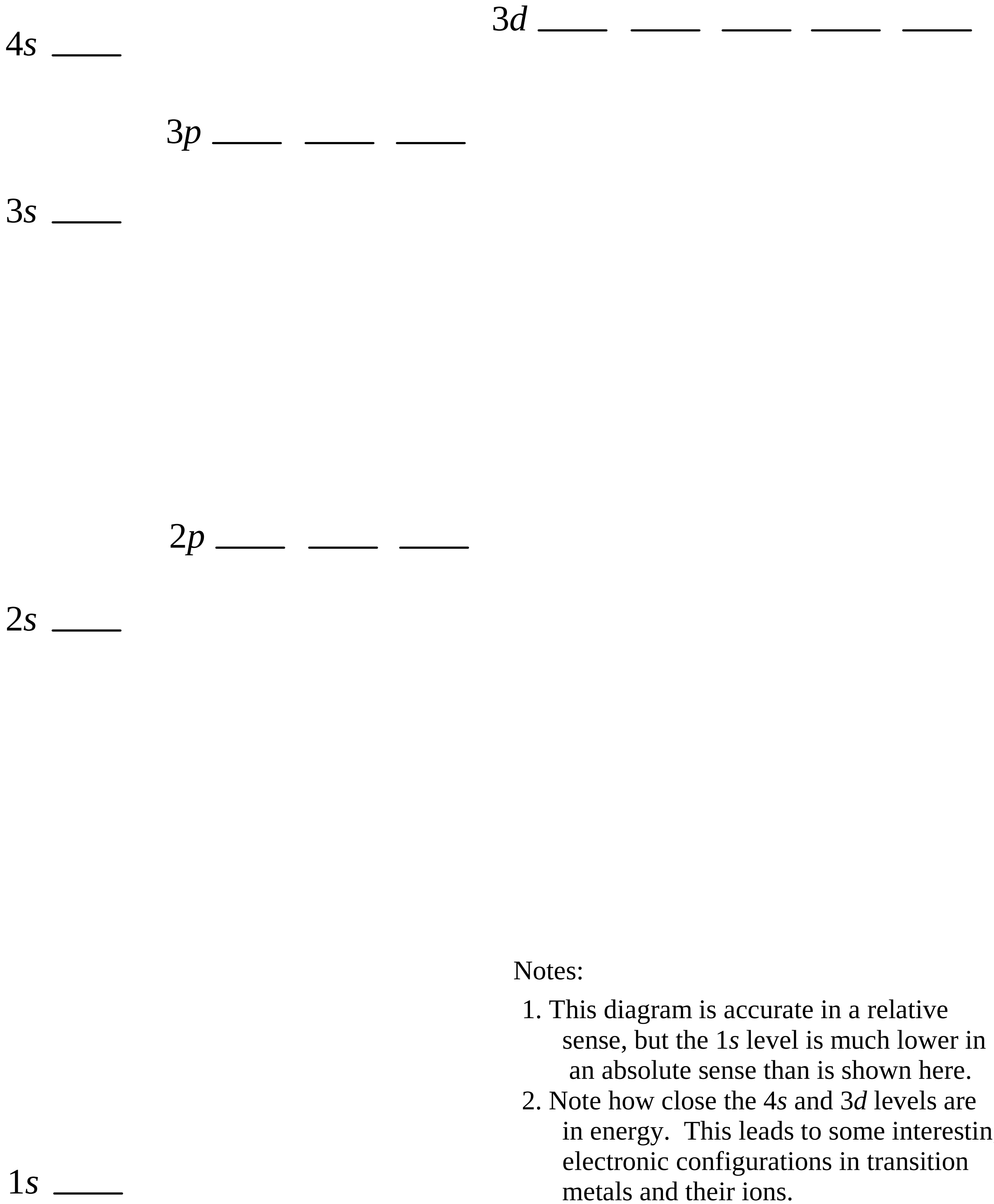
Names: The orbitals names include a principal quantum number (1, 2, 3, *etc.*) and a lower case letter. For the quantum number 1, there is only one type of orbital. It is called 1*s*. At each higher quantum number, a new type of orbital appears. At the 2 level, there is one *s* orbital (called 2*s*) and three *p* orbitals (usually called $2p_x$, $2p_y$, and $2p_z$). The new type of orbital that occurs at the 3 level is the *d* orbital, and there are 5 of them at each new level. As before, the 3 level also contains one 3*s* and three 3*p* orbitals. The new orbital type at the 4 level is *f*, and there are 7 of them. The *f* orbitals are seldom of interest in biochemical systems, and we therefore will not spend time on them in CHM 109.

Shapes: The s orbitals have one (for our purposes) spherical lobe, and increase in size at each higher principal quantum number. That is, the 2*s* orbital is larger than the 1*s* orbital, and so on. Each of the 2*p* orbitals has 2 lobes, and like the *s* orbitals, they increase in size with increasing principal quantum number. The shapes of the d orbitals are more complicated. At this point, I refer you to Dr. Winter's Orbitron (http://winter.group.shef.ac.uk/orbitron/) to get a better feel for the shapes and sizes of the orbitals. Look at orbitals up to 3*d*, and then go to the lower left side of the page to look at the sp^2 and sp^3 *hybrid* orbitals, which are important for understanding the molecular structure of biological molecules containing C, N, and O.

Energies: Electrons occupy the lowest energy orbitals first. When a low energy orbital is full (2 e^- per orbital) then the next higher energy orbital is filled, and so on. The filling pattern is very simple at first: *1s* ➔ *2s* ➔ *2p* ➔ *3s* ➔ *3p*. You might expect that 3d would come next. However, generally speaking, the *4s* orbital fills first, then the *3d*s. (In reality, it is even more complicated, with the 4s orbital filling, and then sometimes emptying, as the *3d* orbitals fill.) A general orbital energy diagram is shown on p. 3 that contains orbitals up through 4*s*3*d*. Page 4 shows an orbital diagram that has been filled in to represent a sulfur atom. The vertical arrows in the diagram represent electrons, and the direction the arrow is pointing indicates that the electron spin is up or down. We will not consider electron spin in CHM 109.

The energies we have described here with energy level diagrams and electronic configurations (see bottom of p. 4) refer to *ground state* arrangements. Ground state means the lowest energy in which the system can exist. Some important processes in biochemistry involve absorption of energy and the associated elevation of electrons to higher energy levels. Two examples of this are the light reactions of photosynthesis in green plants (and algae) the absorption of ultraviolet (UV) light by DNA in skin cells prior to thymine dimer formation (a potential precursor to formation of skin cancer).

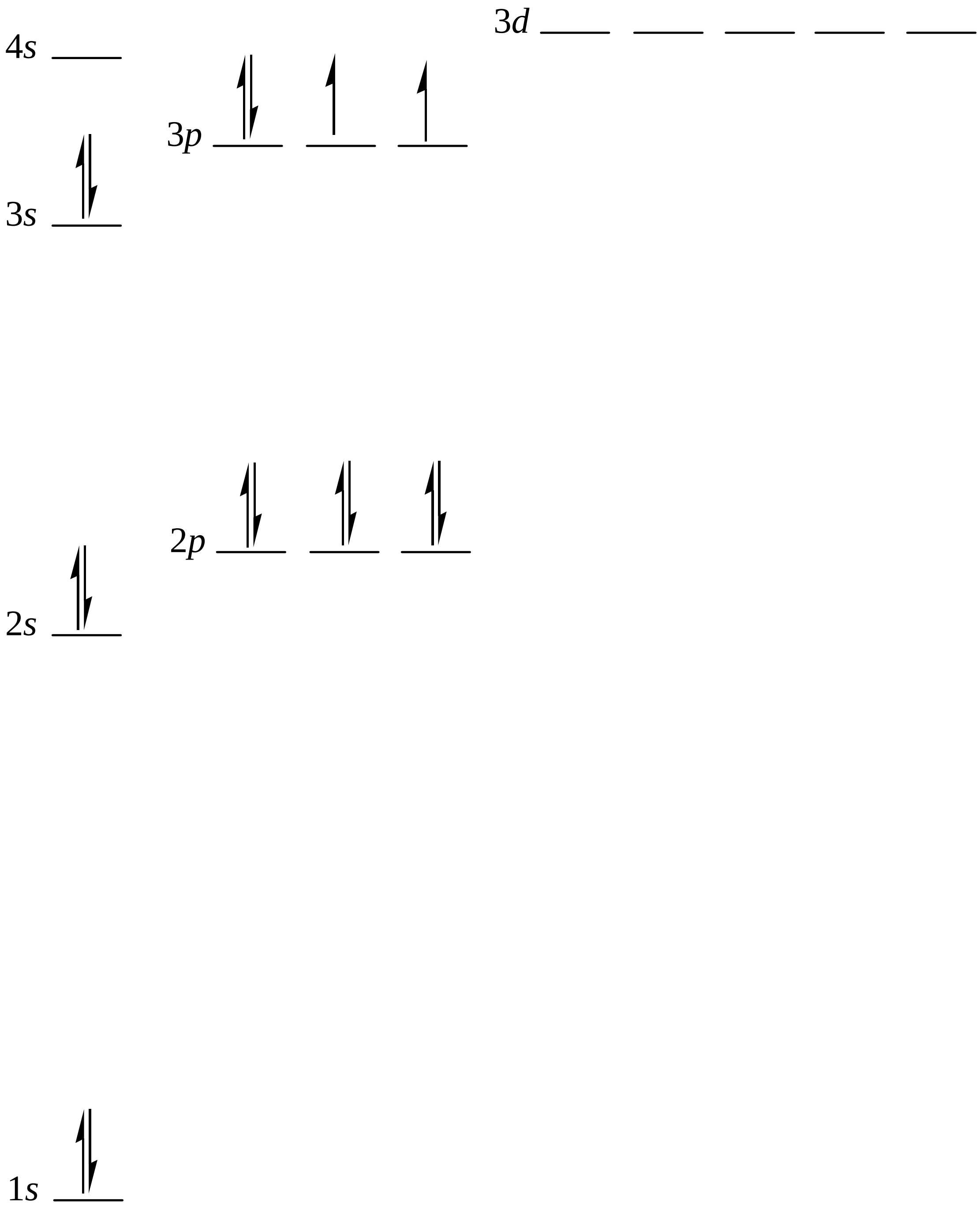
Orbital Energies



Notes:

1. This diagram is accurate in a relative sense, but the 1*s* level is much lower in an absolute sense than is shown here.
2. Note how close the 4*s* and 3*d* levels are in energy. This leads to some interesting electronic configurations in transition metals and their ions.

Sulfur Orbital Filling Pattern



The electronic configuration for a sulfur atom is $1s^2 2s^2 2p^6 3s^2 3p^4$.