

G. Atomic and Subatomic Physics

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Chapter 21. Atoms and Molecules

Chapter Introduction

A. Why?

It is important to understand how large bodies interact with each other, but we cannot feel we understand our environment without some knowledge of atoms and molecules, including how they hold together and react. The atomic-molecular model of matter is at the heart of any explanation of why things happen, and, as is well-known, the fields of chemistry and biology are entry gates to engineering, medicine, geology, and many other areas of study.

B. What to Look For

Early speculation on atomic structure envisioned atoms that could be treated as hard spheres or the equivalent. That didn't work, and we know that the important properties of atoms are their internal structures and the shapes of the molecules formed from them. Thus an understanding of those internal structures, and how they may be deduced, is critically important. Most of that information has come to us from studies of how electromagnetic radiation interacts with atoms and molecules, through the various branches of *spectroscopy*.

C. Pre-Test for Prior Comprehension

- a. Why are lines belonging to the “sharp” series sharper (*i.e.*, narrower) than lines belonging to the “diffuse” series?
- b. Why were planetary models of the atom initially discarded as unsatisfactory?
- c. Why was Rutherford justifiably surprised by the result of his scattering measurements?
- d. Why is the “pure vibration” (*Q* branch) missing for diatomic rotation-vibration spectra?
- e. How many vibrational modes are expected for H₂S (a bent molecule)?
- f. How does an atomic orbital differ from an atomic electronic orbit?
- g. Which is more important in finding the minimum energy of an atomic system: lowering kinetic energy or lowering potential energy?

D. Inquiry Question(s)

If the Bohr model for hydrogen is adjusted for a doubly-charged nucleus and two electrons, including the electron-electron repulsion, what general change in characteristics of orbits and ionization energy should be expected? Could the model be extended to include more than two electrons (in different energy states)?

Is the (average) location of electrons, *e.g.*, in diatomic molecules, important enough (in determining potential energy) to explain the general properties of the energy states of the molecules, or is there another parameter, or quality, that is more important in determining molecular stability?

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Short Answers to Pre-Test Questions

a. Lines of the *sharp* series are characterized by states with $L = 0$, so there is no splitting between levels of different angular momentum values. Lines of the *diffuse* series involve states of $L = 2$, and thus are split among $2 \times 2 + 1 = 5$ energy levels, appearing therefore as a broad line.

b. An electron in a planetary orbit is constantly accelerated and therefore would be expected to radiate away its energy and collapse into the center.

c. The ratio of the mass of electrons to the mass of an α particle is almost $1/8000$, or roughly that of a letter-sized sheet of tissue paper to a 15" (diameter) shell. Thus electrons can't scatter α particles through large angles!

d. A diatomic molecule cannot rotate about its axis of symmetry because the rotational energy steps are too large.

e. $3N - 6$ (total number of degrees of freedom - 3 rotations - 3 translations) = $3 \times 3 - 6 = 3$.

f. An orbital is a time-average description of electron density, as contrasted with an orbit that purports to describe the time dependence of electron motion about the nucleus.

g. A decrease in average kinetic energy represents an *increase* in electron energy, whereas a decrease in electron potential energy corresponds to an equivalent decrease in energy (toward more stability).

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In ancient Greece, some argued that a drop of water could, in principle, be divided *ad infinitum*. Others argued that there must be some limit at which the particles were no longer divisible. Apparently no one suggested that the ultimate indivisible particles (Greek *atoms*) would be something other than water. More recently, Galileo, Newton, and Bernoulli were among those who assumed the existence of what we now call atoms and molecules. By the 19th century, the "hard sphere" model was known to *not* fit experimental evidence and there was no good alternative. It was not until Einstein's analysis of Brownian motion in the first decade of the 20th century that important skeptical scientists were convinced such particles were more than a convenient model. Nevertheless, important theoretical and experimental studies in the 19th century laid the groundwork for breakthrough discoveries relating to molecules, atoms, and nuclei in the 20th century.

We have seen already that classical mechanics is no longer sufficient when examining molecules and smaller particles even though the results for small particles are often tantalizingly close to what we might expect for classical objects. We follow the usual custom of discussing small systems with classical descriptions as far as we can, calling attention to the deviations from classical behavior. Yet we must recognize that this method, which gives us a readily recognizable and understandable description, quickly takes us beyond the point at which we can justify, or prove the validity of, the classical model.

21.1 Atomic States

Understanding atomic states began in the 19th century with observations and classification, but little in the way of explanation. This was followed by a false start, applying classical mechanics with some arbitrary conjectures to obtain a quantitative fit of energies for the hydrogen

atom, and a second false start that unlocked the door to quantum mechanics. For every atom other than hydrogen, exact analytical solutions cannot be found, but various approximation methods give values of energies that are arbitrarily close and adequate for most purposes.

21.1.1. *Empirical Description.* The most striking features of atomic emission spectra are the very sharp lines and the very large number of lines that can be observed. It seemed clear that something(s) inside the atom participated in harmonic oscillations. Stoney suggested in 1874 there must be a small natural unit of electricity and proposed the name *electron* in 1891. Crookes recognized that a stream of particles, of uncertain character, streamed from the negative electrode of his evacuated tubes. By 1897 J.J. Thomson had shown these *cathode rays* consisted of negatively charged particles, or electrons, and measured the ratio of their charge to their mass, which was only about 1/1835 compared to the hydrogen atom. Combining the small mass per electron and the apparently very large number of oscillators present in each atom, it was conjectured by the turn of the century that there were thousands of electrons in each atom.

Lines emitted by metallic elements were found to fit several distinct series. For hydrogen, the series were designated as Lyman, Balmer, Paschen, Brackett, and Pfund,¹ all fitting the general formula with integers n_1 and n_2 ,

$$\nu = R \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

with $n_2 = 1, 2, 3, 4,$ or $5,$ respectively, and $n_1 > n_2.$

For the alkali metals, there is a substantial splitting of the hydrogen series to form new series. What would have been the Lyman series is now called the *principal* series. A portion of what would have been the Paschen series now becomes the *fundamental* series.

The principal series is the only one usually observed in absorption. The fundamental series was the lowest-frequency series recognized. What would have been the Balmer series becomes two series, called the *sharp* series and the *diffuse* series, indicating the general appearances of the lines in each. The names would have little significance now except that the letter designations, *s*, *p*, *d*, and *f*, have been carried over to most applications that involve designation of angular momentum values of 0, 1, 2, and 3, respectively.

21.1.2. *Rutherford's Nucleus.* When electrons were accepted as a constituent of atoms, the obvious explanation seemed to be a planetary model, with electrons orbiting about a positive charge. However, such a model was unsatisfactory because electrons in orbits are continuously accelerated, and would therefore radiate electromagnetic energy, according to Maxwell's

¹ Theodore Lyman (1874-1954); Johann Balmer (1825-1898, Swiss mathematician; Friedrich Paschen (1865-1947); Frederick Brackett (1896-1988); and August Pfund (1879-1949).

equations, losing energy and spiraling into the nucleus in a fraction of a second. J.J. Thomson² therefore proposed a semi-rigid atom, with electrons embedded in positive charge, free to oscillate about their equilibrium positions, somewhat like cherries embedded in Jello. He called it a *plum pudding* model, after the raisins in a well-known English dish of the times, no longer common.

Rutherford,³ then at Manchester, devised an experiment to confirm the plum pudding model. Carried out in his laboratory by Geiger and Marsden, the experiment allowed fast-moving alpha particles (helium nuclei) emitted by radioactive sources to pass through very thin gold foil. Because the mass of the electron was very small compared to the alpha particles, only small deflections could be expected (*e.g.*, on the order of magnitude of 1/100 degree), but these should have provided information on the spatial distribution of electrons in the “pudding”. The surprising finding was that some of the alpha particles were deflected through large angles.⁴

The conclusion that followed was that there must be a concentration of mass within the atom, in what became known as the atomic nucleus. That contradicted Thomson’s model, but was validated by many later experiments.

21.1.3. *Bohr’s Model.* A young post-doctoral student from Denmark, Niels Bohr (1885-1962), working with Rutherford and Thomson in 1911-13, undertook to find an explanation, taking into consideration the work of Planck and Einstein. He returned to the abandoned planetary model⁵ for the hydrogen atom, adding the arbitrary assumption that the electrons did not radiate as they were accelerated in their orbits. Applying an argument similar to that of Planck, he proposed that only certain orbits were stable, and these had energies such that between any two, $\Delta E/h$ would give the frequency of one of the observed lines of the hydrogen spectrum. The method proved spectacularly successful in quantitatively predicting the positions of the lines of the hydrogen spectrum.

By contrast, Bohr’s model proved quite unsatisfactory in other respects. It predicted a planar atom and, especially for the ground state and some excited states, a fixed radius of the electron in orbit. Its predictions for the helium atom, and heavier atoms, were not even close to experimental

² Joseph John Thomson (1856-1940) third Cavendish Professor at Cambridge (following Maxwell and Rayleigh).

³ Ernest Rutherford (1871-1937), student under Thomson at Cambridge, professor at McGill (Montreal), then Manchester, then succeeded Thomson at Cambridge (1919).

⁴ Rutherford expressed himself dramatically in reporting their results. “It was quite the most incredible event that ever happened to me in my life. It was almost as incredible as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you.”

⁵ Hantaro Nagaoka (Imperial University, Tokyo) had proposed (*Phil. Mag.* VII, 445-455 (1904)) a model for the atom that resembled Saturn. Electrons moving in a common circular orbit, with equal-angle spacing, about a positively charged nucleus, provides short-term stability, but is subject to “long term” decay by radiative loss.

values.⁶

On the other hand, as we can see now, the circular orbit with $n = 1$ did predict the correct uncertainty in average position, $\langle x \rangle$, and in average momentum, $\langle p_x \rangle$. It also provided a labeling scheme for the hydrogen energy states that with only minor modification has been retained to the present and carried over to more complex atoms. The *principal* quantum number, n , determined the semi-major axis of the elliptical orbit (half the total length of the orbit), and thus the averaged distance of the electron from the nucleus, and hence the energy of the electron. A second quantum number, l (equal to Bohr's k , minus 1) gave the angular momentum of the electron in its orbit. When measuring atomic properties, the experimental apparatus (or sometimes a property of the atom) defines a unique direction, which we may call the z axis. A so-called *magnetic* quantum number, m , describes the projection of l on the z axis. Thus if the angular momentum is fully about the z axis, $m = l$; if the angular momentum is perpendicular to the z axis, $m = 0$; and in general, $m = 0, \pm 1, \pm 2, \text{etc.}$ up to l .

Soon after Bohr's model was introduced, it was extended, by Arnold Sommerfeld (1868-1951), to include relativistic corrections to the orbits. This effectively introduced a fourth quantum number, corresponding to the addition of time as a fourth dimension. This fourth quantum number became known as the *spin* quantum number, because it described an intrinsic angular momentum of the electron,⁷ $s \hbar$, apart from the orbital angular momentum, $l \hbar$, and its projected values, $m \hbar$.

About the same time, studies of molecular vibrational spectra discovered the fine structure associated with rotations and, from Planck's methods, explained the primary features of the energy levels of rotational states, based on angular momentum properties.

21.1.4. *DeBroglie Waves*. Planck and, especially, Einstein had shown that electromagnetic waves have some properties of particles. It was also recognized that electrons in atoms were described by integers, as were rotating molecules. Integers were known to be characteristic of harmonic equations. Thus deBroglie,⁸ starting on a doctoral thesis, saw that waves seemed to

⁶ In retrospect, we can see that Bohr's heavier atoms gave wrong energies because he failed to incorporate the effects of electron-electron repulsions. With such repulsion terms included, the energies are correct but any remaining semblance of physical reality is lost. See R.P. Bauman and J.P. Considine, "Derivation of Interelectronic Screening Parameters from Statistical Considerations", *J. Chem. Phys.* **34**, 1388-1391 (1961); J.P. Considine and R.P. Bauman, "Screening Parameters for Two-, Three-, and Four-Electron Systems", *J. Chem. Phys.* **38**, 1278-1281 (1963).

⁷ The spin angular momentum is actually $(s(s + 1))^{1/2} \hbar$, but the projected spin angular momentum about the z axis is $s \hbar$. Thus s and m are similar, in some respects, to the molecular rotational quantum number K (sec. 10.5; 21.2.1).

⁸ Prince Louis-Victor de Broglie (1892-1987) submitted his doctoral thesis in 1924 on *Researches on the Quantum Theory*. (He was the son of the Duc de Broglie; his older brother,

have properties associated with particles, but particles were exhibiting properties normally associated with waves. The question was what sort of frequency might be associated with a free particle, such as an electron.

Einstein had given the energy of a particle as

$$E = m c^2$$

but he had also given the equation

$$E = h \nu$$

Could these be combined to find ν ? The frequency would then be

$$\nu = \frac{m c^2}{h}$$

For an electron at rest, the calculated frequency is about 1.2×10^{20} Hz, but there was not then (and is still not, today) any experiment that would allow detection of such a frequency. Therefore deBroglie sought to calculate a wavelength for an electron, anticipating that a wavelength might be measurable.

He associated the *group speed* of the electron with the apparent speed of the particle, then calculated by means of some equations of optics the *phase speed*, and from the phase speed and frequency he calculated a wavelength,⁹ which gave the value

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

where p is the ordinary momentum, $p = m u$, of the electron.

Curiously, deBroglie's derivation, based on special relativity, appeared to fit several problems, but only in the non-relativistic limit. Searching for a test of his model, deBroglie proposed that Bohr's model of the hydrogen atom could be explained by fitting an integral number of electron wavelengths into the length of a circular orbit. However, the fit is fortuitous, of little or no value, for the hydrogen atom is not planar and it is not momentum, p , that is constant for the electron but L , the angular momentum, and r is not a constant.

Nevertheless, what might be called a successful failure provided an important clue to Schroedinger and to Heisenberg as they developed a more powerful theory for the behavior of small systems, which became known as *wave mechanics* or, as it is more commonly known today, *quantum mechanics*. A copy of de Broglie's thesis had been sent to Einstein, who saw some merit to the speculations and encouraged its acceptance. In 1927, Davisson and Germer observed diffraction of electrons in crystals, and in 1929, de Broglie received the Nobel prize for this work.

Maurice, was also a physicist.)

⁹ L. de Broglie, *Matter and Light* (New York; Dover Publications, Inc.).

Some aspects of deBroglie waves are carried over into quantum mechanics.

21.2 Molecular Rotations and Vibrations

A molecule, consisting of two or more atoms bound together, would be expected to have several recognizable forms of motion, other than translation of the entire molecule. The molecule should rotate; it should vibrate; and we may appropriately expect the inner parts — the electrons coupled to the nuclei — to have excited states. We discuss rotations and vibrations first, then the electronic states of atoms and molecules.

21.2.1. *Rotations.* We saw in sec. 10.5 that molecules do rotate, but only with certain possible energies. Any linear molecule can rotate *only* about an axis perpendicular to its symmetry axis (*i.e.*, similar to a twirling baton), with possible energy values

$$E_{\text{rot}} = h \nu = J(J + 1) hc B \quad J = 0, 1, 2, \dots$$

where we loosely associate ν with a rotation frequency of the molecule. (The frequency absorbed is not E/h , but $\Delta E/h$.)

Is it permissible to have $J = 0$, and hence no rotational motion? The conjugate variables that appear in Heisenberg's uncertainty principle, applied to rotations, are the angular momentum $L = I \omega$, and the rotational position, θ , which can vary from $\theta = 0$ to $\theta = 2\pi$. If we have *no* information about θ , then it is possible to have $L = 0$ and hence $J = 0$.

Indeed, we must have zero rotational energy of a linear molecule (including a diatomic molecule or a single atom) about any axis for which the moment of inertia is vanishingly small. The quantization condition (see sec. 10.5) gives a coefficient, A , of the rotational quantum number about the symmetry axis, K , of

$$A = \frac{h}{8\pi c I_a}$$

which is extremely large when I_a is very small. Hence the minimum rotational energy,

$$E_{\text{rot}, A} = hcK^2 A$$

would be prohibitively large if K were non-zero (sec. 10.5).

Non-linear symmetric rotors (molecules with a single three-fold or higher axis of symmetry) may have a value of the A (or C) constant that is quite large (*e.g.*, ethane, C_2H_6) or very small (*e.g.*, hexachloroethane, C_2Cl_6), giving rotational energies (hcK^2A) far apart or close together, compared to the $J(J + 1) hcB$ levels.

Rotational levels of linear molecules,¹⁰ such as HCl, absorb energy at a frequency given by

¹⁰ If the molecule has a center of symmetry, such as Cl_2 , or acetylene, C_2H_2 or $H-C \equiv C-H$, some levels are missing. This complication need not concern us here.

$$\begin{aligned}
 \Delta E &= h \nu = J'(J' + 1) h cB - J''(J'' + 1) h cB \\
 &= (J'' + 1)(J'' + 2) h cB - J''(J'' + 1) h cB \\
 &= 2(J'' + 1) h cB \\
 &= 2J' h cB
 \end{aligned}$$

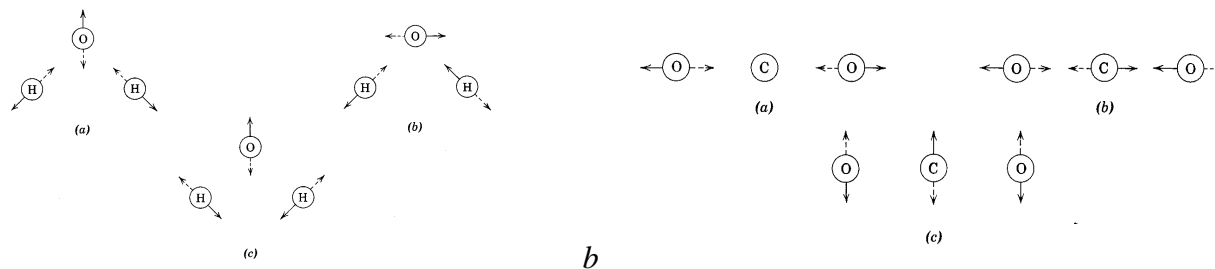
because absorption of a photon increases the angular momentum by one unit; $J' = J'' + 1$.

Associating the frequency of rotation with the frequency of radiation absorbed gives a (semi-classical) rotation frequency. However, only in the limit of very large moments of inertia, and therefore very high rotational quantum numbers, is the frequency of absorption exactly equal to the rotation frequency.

Molecular rotational energies, or frequencies, typically fall in the far infrared region, or beyond, in the microwave region. Wavenumbers ($\sigma = 1/\lambda = E/hc$) are typically below $10^4 \text{ m}^{-1} = 100 \text{ cm}^{-1}$.

21.2.2. *Molecular Vibrations.* To specify the locations of the N atoms of a molecule requires $3N$ coordinates. Of these, 3 are required to describe the motion of the center of mass and 3 are required for the rotational orientations (or only 2 if the molecule is linear). The remaining $3N - 6$ (or $3N - 5$) variables, or *degrees of freedom*, describe vibrations of the molecule.

The water molecule, with $N = 3$ atoms, has three independent, or *normal*, modes of vibration, as shown in Figure 21.1: a symmetric stretch, an asymmetric stretch, and a bending mode. Each of the three atoms requires 3 coordinates to specify its position in space, or a total of $3N = 9$ coordinates. Of these, 3 describe the location of the center of mass of the molecule and 3 describe the rotation of the molecule about its center of mass, leaving $3N - 6 = 3$ coordinates to describe vibrations.



a

Figure 21.1. Vibrational modes of a) water (symmetric stretch, antisymmetric stretch, and bending modes), and b) CO₂ (symmetric stretch, antisymmetric stretch, and bending modes).

Because carbon dioxide is linear, it does not have sufficient energy to rotate about its axis. It has only two, equivalent, rotational modes, about axes perpendicular to the linear axis. Thus subtracting 3 coordinates for location of the center of mass and only 2 for rotations about the center of mass, we find $3N - 5 = 4$ coordinates to describe the vibrations. It has a symmetric stretch, an asymmetric stretch, and two, equivalent, bending modes, for a total of 4 vibrations.

Each vibration has an energy, specified by a vibrational quantum number v , and vibrational frequency ν , of

$$E = (v + \frac{1}{2})h\nu = (v + \frac{1}{2})hc\sigma$$

A harmonic oscillator can only change vibrational state by one step, $\Delta v = \pm 1$, for which the energy change is

$$\Delta E = h\nu = hc\sigma$$

We associate the frequency of radiation absorbed or emitted with the classical vibration frequency, and only for the $\Delta v = \pm 1$ is there agreement of the exciting radiation frequency and the (classical) vibration frequency. In the simple case of a diatomic molecule,

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where μ is the *reduced mass*,

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

Calculations of vibration frequencies of polyatomic molecules are more complex, because they must take into consideration all masses and force constants in the molecule, but purely classical models work extremely well for predicting molecular vibration frequencies.

Vibrations typically fall in the infrared region, in the range from about $10^4 \text{ m}^{-1} = 100 \text{ cm}^{-1}$ to about $4 \times 10^5 \text{ m}^{-1} = 4000 \text{ cm}^{-1}$.

21.2.3. Rotations Plus Vibrations. A photon carries one unit of angular momentum, associated with its “spin”. When the photon is absorbed (or emitted) the absorber must change its angular momentum by one unit (\hbar) to satisfy the law of conservation of angular momentum. The angular momentum of a molecule may increase, $\Delta J = + 1$; decrease, $\Delta J = - 1$; or change in direction by vector addition of one unit of angular momentum to the original angular momentum, $\Delta J = 0$ (if $J \neq 0$ and the molecule is not linear). Therefore, when a molecule absorbs a photon that raises its vibrational level ($\Delta v = + 1$), it must also change its rotational state.

For carbon monoxide, CO, with a rotational constant, B , of 1.92 cm^{-1} , the pure rotational spectrum consists of evenly spaced lines, starting at 3.84 cm^{-1} , or 2.6 mm , in the microwave region. As we saw in section 10.5.2 (Figures 10.8, 10.9), the rotation-vibration spectrum is centered about the vibrational frequency, with “side bands” arising from changes in rotational state during the vibrational absorption.

Non-linear molecules (except spherical rotors), show three rotational branches. The *P* branch falls below ν_0 , the vibrational frequency, and corresponds to $\Delta J = - 1$. The *Q* branch falls at ν_0 , corresponding to $\Delta J = 0$. The *R* branch is above ν_0 , corresponding to $\Delta J = + 1$. The *Q* branch is missing for linear molecules and, for a different reason, for spherical rotors (sec. 10.5).

21.3 Electronic States of Atoms

Electrons, like other spin $\frac{1}{2}$ particles (protons, neutrons, and neutrinos, among others) belong to a general class of particles known as *fermions*. If there are n electrons, in the potential field of

a nucleus, for example, the state function for the n electrons may be approximated by a product of n one-electron functions.¹¹ *Such one-electron functions were given the name orbitals by Mulliken.*¹² They are generally represented by the Greek symbol ψ (psi).

Wolfgang Pauli (1900-1958) proposed in 1925 that for any n -electron state function (or a state function for any other fermions), if two of the identical particles are interchanged, the state function will change sign. It follows that no two fermions can be in identical states. This is the basis of the Aufbau principle, the rule for “building up” atomic states from the simpler states of the hydrogen atom.

Functions that describe the single electron in a hydrogen atom can be found analytically. These functions are a very poor approximation for electrons in a polyelectronic atom. On the other hand, the *symmetry properties* of the hydrogenic orbitals make them quite satisfactory for counting electron states.

Thus, for helium, we approximate the ground state by placing two electrons in identical orbitals, which are the hydrogen atom ground-state orbital. We then avoid the problem of identical states by giving the helium electrons different spin quantum numbers (one $+ \frac{1}{2}$, the other $- \frac{1}{2}$). An orbital times a spin function is called a *spinorbital*. The two electrons in helium are in identical orbitals, but different spinorbitals, and thus different states.

There are only two spinorbitals in the hydrogen atom with principal quantum number $n = 1$ (and only one of these is occupied in hydrogen). There are eight spinorbitals (generally unoccupied in hydrogen) with $n = 2$, so we can describe elements 3 through 10 (Li through Ne, in the periodic table) as having 2 electrons in $n = 1$ states and up to 8 electrons in $n = 2$ states.

The 2 electrons in $n = 1$ states and 2 of the electrons in $n = 2$ states have no angular momentum, other than spin. Borrowing terminology from 19th century spectroscopy, such states are called *s* states (associated with the *sharp* series of lines).¹³ The orbitals are spherically symmetric, with no dependence on angle. The other six electrons in $n = 2$ states each have angular momentum of one unit, which may be oriented in space with projection on the z axis (experimental apparatus axis) of $l_z = -1$, $l_z = 0$, or $l_z = +1$. Each of the orbitals may be assigned either $s = -\frac{1}{2}$ or $s = +\frac{1}{2}$.

The Aufbau principle is based on the symmetries of atomic states, based on the geometric

¹¹ A better approximation is a linear combination of products of n one-electron functions, which does not change the argument of this section. Taking the linear combination gives a more accurate representation, and more accurate energy, compensating for electron-electron interactions that cannot otherwise be calculated. This energy correction is therefore generally called *correlation energy*.

¹² Note that an orbital is a time-independent function that describes the time-average density of the electron in space. It does not resemble an orbit, which describes position *vs.* time for a classical particle.

¹³ An *s* state (one electron) or an *S* state (multiple electrons, or not specifically electronic) is a state with no angular momentum. The notation must be distinguished from the quantum number *s* (or *S* for multiple electrons) that designates the spin quantum number.

properties associated with the four quantum numbers, n , l , m , and s . It does not pretend to estimate the energies of the states. We can, nevertheless, get quite reasonable estimates of comparative energies through a “back-door” strategy.

Consider only the energy of the outermost, or most easily removed, electron. This is the (first) ionization energy ($I.E.$) for the atom. If it were not for electron-electron repulsions, adding to the nuclear charge (or better, the charge of an atomic kernel — the nucleus plus all the “inner” electrons) should increase the amount of energy required to pull off an outer electron by the square of the (net) charge.¹⁴

We throw in two empirical rules. Because of electron-electron repulsions, the net increase with kernel charge is linear *unless* two electrons are going into the same orbital. If they *do* go into the same orbital, the ionization energy (whether for atoms or molecules) is lowered by about 1 to 3 eV.

Now we can construct the graph of ionization energies shown in Figure 21.2 (experimental values, with lines added). Helium ($Z = 2$) should have twice the *ionization energy* of H ($Z = 1$), except that both electrons go into the same orbital, so the *ionization energy* is 2 eV less than twice (24.6 and 13.6 eV). The pattern repeats for Li and Be (5.4 eV and 9.3 eV or a deficit of 1.5 eV). Then B, C, and N are linear because each new electron goes into a new orbital. Similarly, O, F, and Ne are linear but the line is displaced downward.

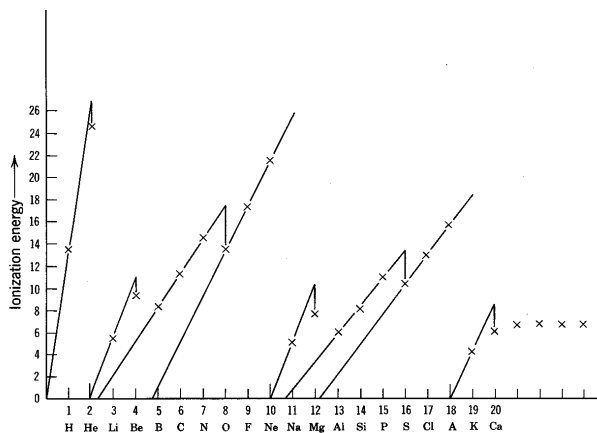


Figure 21.2. First ionization energies vs. atomic number.

The pattern repeats for the next set, Na to Ar. Then for the transition metals (Ca to Cu), electrons are inserted at intermediate levels¹⁵ so the outermost electrons, and hence the *ionization*

¹⁴ Comparing He^+ with H, for example, the helium radius is $1/Z (= 1/2)$ the hydrogen radius, increasing the energy by a factor of Z , apart from the factor of Z because of the greater central charge of Coulomb’s law. So the $I.E.$ of He^+ is four times as great as for H (54.4 eV vs. 13.6 eV).

¹⁵ The quantum numbers n_i are the primary determinant of energy for hydrogen orbitals because n is the best guide for determining average distance of the electron from the nucleus. Close encounters correspond to low energy (stable); remoteness corresponds to high energy (less

energy, remains roughly constant, before picking up the earlier pattern.

Note that electron-electron repulsions are important in determining energy states of the atoms. There are no mysterious “attractions” associated with filled or half-filled shells.

We can, however, see that we are accumulating too many restrictions, or quantum numbers. Any N electrons must have $4N$ degrees of freedom, or quantum numbers. These are the $4N$ values of n , l , m , and s (arising, essentially, from x , y , z , and t). But every atom (and even filled or half-filled shells) has additional requirements:

- total energy (no longer solely dependent on n)
- total angular momentum, J
- total orbital angular momentum, L
- total projection of orbital angular momentum, M
- total spin angular momentum, S
- plus the
- $4n$ orbital quantum numbers ($n_i, l_i, (m_l)_i, s_i$)

all linked by equations such as

$$\begin{aligned}L &= \sum l_i \\M &= \sum (m_l)_i \\S &= \sum s_i \\J &= L + S \quad \text{or} \\j_i &= l_i + s_i \quad \text{and } J = \sum j_i\end{aligned}$$

Clearly we are well beyond our allotment of $4n$ quantum numbers.

We are not about to drop these multiple quantum numbers, because they are so convenient in labeling atomic electronic states. What we must do is recognize that many of the quantum numbers we assign are far from rigorous descriptions of the electronic states.

An important property of quantum numbers is that they provide a guide to *selection rules*. A selection rule is a rule that tells us what transitions are possible (under specified conditions, such as by absorption of radiation). Each selection rule reflects an underlying constraint on changes of state, because of symmetries and/or conservation laws. For example, a photon has an angular momentum (projection) of \hbar . Therefore, an atom that absorbs, or emits, a photon must change (vector) angular momentum by one unit, or \hbar . Absorption and emission processes can almost always be described as involving (primarily) one electron. Therefore an electron involved in absorption or emission must undergo a change of orbital angular momentum described by $\Delta l = \pm 1$ (although if $l > 0$, the angular momentum may be only reoriented — $\Delta l = 1, \Delta m_l = \pm 1, \Delta l = 0$). Similarly, because electronic spin interacts extremely weakly with anything else (and has no direct effect on energy except as a minute correction), a very good rule is $\Delta s = 0$ for any process (Table

stable). We might expect, therefore, that as the charge on the nucleus increases (from + 1 in hydrogen to + Z in an atom of atomic number Z), the energies of electronic states would be affected. Especially, those states for which the electrons come closest to the nucleus, or spend more time passing through the nucleus, would be most affected. Thus it should not be surprising, as we go to high Z , that the sublevels ($l = 0, 1, 2, 3 \dots$ called s, p, d, f, ... levels) get shifted relative to each other. You can see this effect by looking at tables that give energies of electronic states in atoms.

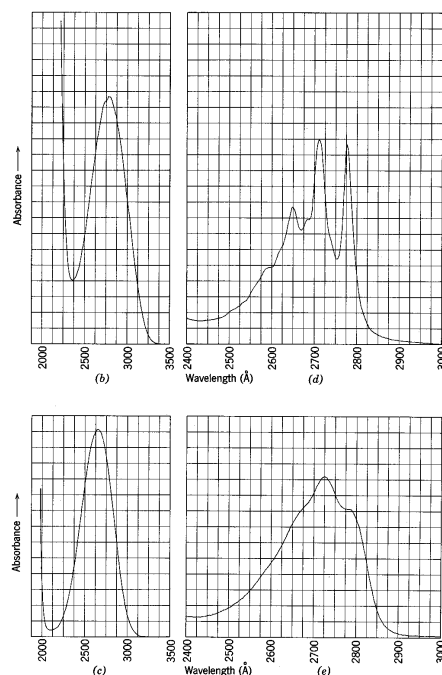
1).

What happens, then, in complex atoms when s_l is no longer a good quantum number for electrons? We find transitions such as the very strong ultraviolet line emitted by Hg at 254 nm, which is conventionally described as a “forbidden” change in state of the mercury electron involving $\Delta s = 1$. In other words, even when the quantum numbers are not valid, they may be satisfactory labels for keeping track of states, but selection rules based on them will be violated because they no longer describe the underlying principles, such as conservation of momentum.

Table 1.		Selection Rules
Rule		Basis of rule
$\Delta l = \pm 1$		Absorption or emission of a photon changes angular momentum by one unit, \hbar .
$\Delta l = 0$	if $l > 0$	Change of (vector) l by one unit may leave magnitude of l unchanged.
$\Delta s = 0$		“Spin” does not interact with external fields, so s does not change.

21.3.1. *Electronic Absorption in Molecules.* Atoms and molecules contain electrons, each of which must be in a different electronic state. These electrons may be excited into higher-energy states. The energies required are occasionally as low as the near infrared (roughly 4000 cm^{-1} , or a wavelength of $2.5 \mu\text{m}$, up to the visible region, 800 nm), but more typically they fall in the visible region or, especially, in the ultraviolet (Figure 21.3).

Figure 21.3. Ultraviolet absorption spectra of acetone in b) cyclohexane and in c) water, and of phenol ($\phi\text{-OH}$) in d) cyclohexane and in 95% ethanol. Note the effect of the “chromophores” $\text{C}=\text{O}$ and ϕ (benzene ring, or phenyl group) is to move the absorption into the near ultraviolet (280 and 260 nm and near 270 nm). Note also that a polar solvent shifts and/or broadens the absorption band of the polar absorbers.



There are no simple rules for electronic absorption bands, comparable to $\Delta J = 0, \pm 1$ or $\Delta v = 0, \pm 1$. On the other hand, most molecules show no more than one or a very few electronic absorption bands in the near ultraviolet and visible regions. Electronic absorption bands are typically very broad. Although they include changes of rotational and vibrational states, usually



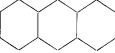
no structure is apparent in the electronic absorption from such causes, especially in condensed phases.

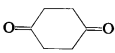
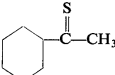
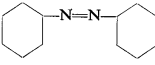
All molecules absorb at higher frequencies, with wavelengths below about 200 nm. Because oxygen and nitrogen absorb strongly there, as do most window and prism materials, measurements must be carried out in evacuated systems. Experiments there are much more difficult in this "vacuum ultraviolet" region. Furthermore, there is so much very strong absorption that it is not easy to identify materials by absorption patterns in this high-energy region.

Until approximately the middle of the 20th century, analysis of ultraviolet and visible absorption spectra was based very largely on empirical interpretation. Especially for recognition of compounds from their electronic absorption spectra, the primary effort was toward prediction of where compounds would absorb, which also aided in predicting colors of compounds from their structures.

A convenient simplification of electronic absorption spectra is the description in terms of *chromophores* (color bearers), small parts of molecules that cause color by absorption in the visible region or that absorb in the nearby ultraviolet region. A few common chromophores are listed in Table 20.1. Nearby *auxochromes*, which do not, themselves, give rise to absorption bands at wavelengths above 300 nm, may lower the excited states associated with the absorption frequency, and thus increase the wavelength of absorption.

Table 20.1.

Chromophores and Auxochromes ^a				
Group	Example	σ (10^3 cm^{-1}); λ (\AA)	a (L/mole-cm)	
C=C	<chem>H2C=CH2</chem>	55	1825	250
		57.3	1744	16,000
		58.6	1704	16,500
C≡C	<chem>H-C#C-CH2-CH3</chem>	62	1620	10,000
		58	1720	2500
C=O	<chem>H2CO</chem>	34	2950	10
		54	1850	strong
C=S	<chem>CH3-C(=S)-CH3</chem>	22	4600	weak
		36	2775	10
-NO ₂	<chem>CH3-NO2</chem>	47.5	2100	10,000
-N=N-	<chem>CH3-N=N-CH3</chem>	28.8	3470	15
		> 38.5	< 2600	strong
		39	2550	200
		50	2000	6300
		55.5	1800	100,000
-Cl	<chem>CH3Cl</chem>	58	1725	—
-Br	<chem>CH3Br</chem>	49	2040	1800
-I	<chem>CH3I</chem>	38.8	2577	—
		49.7	2010	1200
-OH	<chem>CH3OH</chem>	55	1830	200
		67	1500	1900
-SH	<chem>C2H5SH</chem>	43	2320	160
-NH ₂	<chem>CH3NH2</chem>	46.5	2150	580
		52.5	1905	3200
-S-	<chem>CH3-S-CH3</chem>	44	2280	620
		46.5	2150	700
C=C-C=C	<chem>H2C=CH-CH=CH2</chem>	49.3	2030	2300
		48	2090	25,000
		32	3110	250
		37	2700	5000
		45	2210	100,000
		28	3600	6000
		40	2500	150,000

Group	Example	σ (10^3 cm^{-1}); λ (\AA)	a (L/mole-cm)	
		23	4400	20
		34	3000	1000
		40	2500	15,000
C=C-C=O	<chem>H2C=C-C(=O)-H</chem>	30	3330	20
		47.5	2100	12,000
		16.5	6000	—
		22.5	4400	500
		31	3200	20,000
		43	2300	10,000

^a Band positions and especially band intensities must be regarded as approximate. Values are taken largely from Kamlet and Ungade, *Organic Electronic Spectral Data*, Interscience, New York, 1960, or from F. A. Matsen, ref. 47.

From R.P. Bauman, *Absorption Spectroscopy*.

21.3.2. *Inner-electron Absorption and Scattering.* Most energy states of the inner electrons in atoms are little changed when the atoms join to form molecules. These unchanging states give rise to absorption in the x-ray region, beyond the vacuum ultraviolet, roughly below 10 nm, or 100 Å.¹⁶

Instead of giving sharp or broad absorption bands, as for molecular electronic, vibrational, and rotational absorption, x-rays give essentially no absorption up to a critical energy, or *absorption edge*, then give strong absorption that falls off as energy increases further. The resultant appearance is as shown in Figure 21.4. These absorption edges are labeled consecutively as K, L, M, ... or, taking into consideration the splitting of these edges, as K_{α} , K_{β} , etc. The K series would be identical with the Lyman series for hydrogen, but for heavier atoms the electron falls from a (filled) L shell, $n = 2$, to an empty spot in the K shell, $n = 1$, to give the K_{α} line in emission, or from the (filled) M shell, $n = 3$, to an empty spot in the K shell to give the K_{β} line, and so forth. In emission, these lines can be quite sharp and are called *characteristic lines* of the element. (They usually appear with a broad background arising from the rapid deceleration of free electrons incident on the material, called *bremstrahlung*, or “braking radiation”).

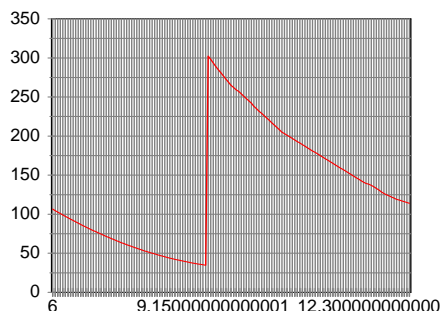


Figure 21.4. X-ray absorption vs. energy. Absorption edge: absorption coefficient against x-ray energy. Absorption drops sharply at the absorption edge, and more slowly as x-ray energy increases above the edge.

X-rays are only weakly refracted, so they are separated by means of gratings, which must have extremely close spacings. In 1912 it was recognized by von Laue¹⁷ that crystals have the proper spacings to act as gratings for x-rays. Studies of crystal structure by x-ray diffraction were

¹⁶ All atoms are roughly 1 Å in diameter, which makes the older ångstrom unit occasionally convenient. 1 Å = 1×10^{-10} m. The unit is named for Anders Jonas Ångström (1814-1874). The inconvenient Å symbol was retained on the basis of the observation that Å is separated from A in the Swedish phone book.

¹⁷ Max von Laue (1879-1960) contributed in many areas of physics, including relativity, superconductivity, and the history of physics, as well as crystallography, for which he received the Nobel Prize in 1914.

undertaken by Bragg.¹⁸ Furthermore, because the spacings in the crystals depend on the crystal structure, the diffraction from crystals is a powerful analytical tool to determine the crystal material or to find the spacings between atoms in the crystal.

The reflection of optical gratings is from grooves in an aluminum surface. The reflection, or scattering, of x-rays from a crystal is by the electrons. With careful mathematical analysis of that scattering, a plot of electron density in the crystal may be obtained. Positively charged nuclei are located in regions of maximum electron density, so the electron-density plot gives the locations of the atoms, and hence the crystal structure, including bond lengths and angles in molecular crystals.

21.4 Formation of Molecules

When two atoms approach, the electron shells tend to repel each other. Under some circumstances, however, the electrons may rearrange to give an attraction. For example, consider the simplest case of two protons and one electron, $H + H^+$, as shown in Figure 21.5.

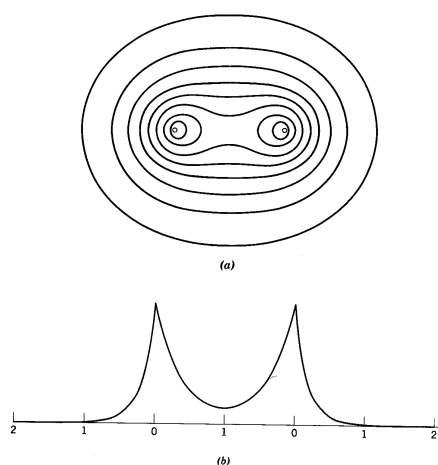


Figure 21.5. Electron density for H_2^+ . a. Contour lines for electronic wave function plotted against distance along internuclear axis.

See Bates, Ledsham, and Stewart, *Phil. Trans. Roy. Soc.* **A246**, 215 (1953).

Because electrons are constantly moving, changing positions and velocities, it is only possible to calculate average, time-independent properties of electronic systems such as atoms and molecules. Thus it might seem that we cannot understand anything of atomic or molecular structure without detailed analysis by quantum mechanics.

Actually we can get a good start toward understanding how atoms combine to form

¹⁸ Sir William Bragg (1862-1942) learned the trade of instrument maker soon after graduating from Cambridge. In 1912 he designed and built an x-ray diffraction instrument which he applied to the diffraction of x-rays by crystals. His son, William Lawrence Bragg, tested and amended von Laue's proposal and the two explored crystal structures with this technique. They shared the Nobel Prize in 1915.

molecules. We have three powerful tools available that allow us to carry out a partial analysis *as if* the electrons obeyed laws of classical mechanics and electrostatics.

First, it might be expected that if something happens quickly, the effect on slower processes will primarily be the time-averaged effect of the rapid process. This is confirmed by a theorem called the *Born-Oppenheimer approximation*. The nuclei are large enough that they may usually be considered stationary as the electrons move rapidly about them. Thus the nuclei effectively see only time-averaged positions of electrons.

Second, Coulomb's law is valid in quantum mechanics. If we know where an electron is at some instant (and the locations of other charges), we know the instantaneous value of V , the potential energy. If we know how the electrons move (*i.e.*, their time-average locations) we can evaluate the time-average value of the potential energy, V .

Third, the virial theorem (considered in secs. 10.1 & 12.4.5) is applicable in quantum mechanics as well as in classical mechanics. It tells us that if the potential energy depends on a position coordinate, q , in the form $V \sim q^n$, then the time-average values of potential and kinetic energies satisfy the equation

$$\langle T \rangle = \frac{n}{2} \langle V \rangle$$

Because Coulomb's law is applicable in quantum mechanics, $V \sim q^{-1}$, so $n = -1$ for Coulombic interactions and

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle$$

and because

$$\langle T \rangle + \langle V \rangle = E$$

it follows that

$$\langle T \rangle = -E$$

and

$$\frac{1}{2} \langle V \rangle = E$$

Thus, if we know $\langle V \rangle$, we know $\langle T \rangle$ and, more important, we know $\langle E \rangle$.

Putting this information together, we see that, if the single electron is, on the average, outside the two nuclei, the potential energy will contain a (large) nuclear-nuclear repulsion, a nuclear-electron attraction (comparable to that of the H atom), and a very small nuclear-electron attraction (long distance). The system lowers its potential energy by increasing the proton-proton distance, so it is unstable.

If, by contrast, the electron is between the two nuclei, there are two proton-electron attraction terms in the potential energy and a smaller proton-proton repulsion (at a greater distance). The system should be stable, and indeed H_2^+ is stable.

Although proton-proton distances change, also, adding another electron between the nuclei

increases the proton-electron attraction terms roughly by two while adding an electron-electron repulsion term. Thus H_2 is also stable, but not twice as stable as H_2^+ . A third electron added could not go into the same energy level, so it would have to go outside, making the system less stable.

An electron in a chemical bond may have angular momentum about the nuclear-nuclear axis, in which case it would be called a p state, or it may have zero angular momentum about the axis, which would be called an s state; except it has been found more helpful to distinguish molecular states from atomic states, so the molecular states are labeled π (angular momentum of ± 1 along the axis) or σ (zero angular momentum along the axis). A σ state may hold 2 electrons, a normal single bond, whereas a π bond may hold 4 electrons (two in each angular momentum state), giving a double bond.

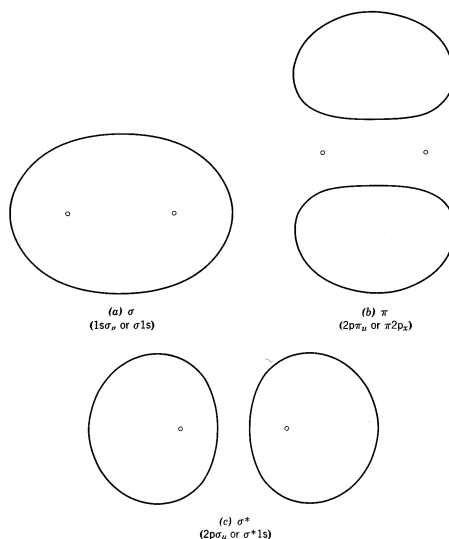


Figure 21.6. Bonding (σ and π) and anti-bonding (σ) orbitals. See Bates *et al.*, *loc. cit.*

Electron states may be classified as occupying *bonding orbitals* (as in Figure 21.6a and b), *antibonding orbitals* (Figure 21.6c), or *non-bonding orbitals*. The non-bonding orbitals typically describe inner electrons that contribute to the stability of the individual atoms but have little or no measurable effect on the stability of the chemical bond. If we count the number of electrons in bonding orbitals and subtract the number in antibonding orbitals, we get the *net* number of bonding electrons. The observed (classical) force constant of the chemical bond in representative diatomic molecule states, plotted against net number of bonding electrons ($\pm \frac{1}{2}$ electron, to recognize the approximations involved), gives the relationship shown in Figure 21.7. Note that changing the nuclei (*e.g.*, from C, N, or O to Li, Na, or Cs) also changes the bond energies significantly.

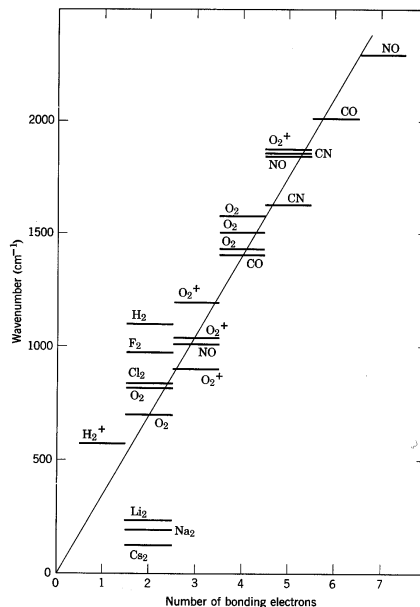


Figure 21.7. Observed wavenumber for vibrational transitions, corrected for mass effect, plotted against net number of bonding electrons for various diatomic molecules. R.P. Bauman, *Absorption Spectroscopy*, Wiley, 1962, p. 288.

Electron spin has no appreciable effect on energies. The energies of interaction between electron spin and orbitals are very small. It might therefore appear that spin would be unimportant and could be ignored. On the contrary, it is helpful for describing electronic states for two reasons.

First of all, because electron spins do not significantly interact with their surroundings, the spins remain constant. This makes them nearly indelible labels and thus important for labeling electronic states. You may find it helpful to think of spin as something like a uniform, which doesn't directly affect the play on the field but helps identify the players and indirectly determines what positions they may play. Second, no two electrons can be in the same state. Therefore no more than two electrons can share the same orbital, or time-average spatial distribution, and then only if their spin quantum numbers are different. Thus the spin label helps to determine how many electrons can go into bonding, non-bonding, and antibonding states.

We have discussed atomic and molecular states in the approximation of one-electron wave functions, called orbitals. All electrons within the atom or molecule are indistinguishable. Exchanging the states of any two electrons changes the sign of the (unobservable) state function, ψ , leaving all probabilities, proportional to ψ^2 (or better, to the product of the state function and its complex conjugate, $\psi^*\psi$), unchanged. Thus the fiction of N electrons, each in a unique state, is only a first approximation.

21.5 The Variation Principle, or How We Know Energy Values

To obtain good values for energies, after calculating expected one-electron state functions, it is necessary to take into consideration the repulsions between electrons as they move with respect to each other. This we cannot do directly because we have no information on instantaneous positions of the electrons.

We conclude the discussion of atomic and molecular structures by giving away an important secret. For the types of problems of interest, it is possible to choose an arbitrary function as an approximation to the solution and calculate what the answer would be if this were the correct function. Then we change the function a little and recalculate the answer. If we have set the problem up correctly (employing rules of the *calculus of variations* or, more explicitly, the *Rayleigh-Ritz* principle), the lower of the two values will be closer to the true value. (Wouldn't it be nice if you could always do two calculations and know which of the two answers was better?)

There is no need to stop with two answers. We can set up the problem so that there are one or more variables, or parameters, that can be arbitrarily changed and which will accordingly change the trial function. Then calculus allows us to choose the value of a parameter that gives the extreme value (in this case, a minimum value) for the answer. Carried to a logical conclusion, we set up equations to calculate the energy of a system consisting of nuclei and electrons. We may choose a set of possible solution functions that make up a "complete set", meaning that *any* function may be written by choosing the proper combination of members of that set. (The sine and cosine functions are one example of a complete set. With certain well-known restrictions,

any function may be written as a sum of sine and cosine functions, a procedure called *Fourier analysis*.)

The standard example of application of the variation method is calculation of the energy of the helium atom, where the electron-electron interaction makes the problem fundamentally insoluble. By putting together a mix of functions (*e.g.*, the hydrogen-atom one-electron functions) we may calculate the energy of the helium atom as accurately as we may wish. The “trial function” we end up with may be not nearly as good as the energy value we calculate, but we can assume if the trial function gives a good energy value, it cannot be too far off from the “true” description of the atom.

One limitation of the variation method is that it only gives the minimum energy value. For the helium atom, this would be the ground state. But we can select our trial functions by other criteria. For example, we can choose only functions that satisfy certain symmetry conditions. Then the energy we calculate will be the lowest energy for a state of that symmetry. Because different atomic (and/or molecular) states have different symmetry properties, this allows us to calculate a large number of “lowest energy” states. Other similar tricks allow calculations of additional states, such as the requirement that the various states must be orthogonal. (That is, there must be no tendency for the helium atom, or other structure, to spontaneously change from one state to another, which means the different states must be mathematically independent, or perpendicular to each other.)

With such techniques we can indirectly take into consideration the average effects of the instantaneous electron-electron repulsions, or the *electron correlation energy*. Extremely accurate energies can be calculated with these techniques and powerful computers. We then have no information about states of individual electrons but good information on the time-average electron spatial densities, which is all we can hope to acquire.

We do not wish to enter into a discussion of mathematical methods or proofs. The point is simply that we can do much better in calculating energies of atomic and molecular states than our state of knowledge of fundamental principles would seem to permit. That, in turn, provides more understanding of the nature of the real states, which has provided a quite complete picture of how atoms and molecules are assembled without being able to do exact calculations from first principles.

Chapter Summary

Firm information about atoms and molecules is little more than a century old. Much of the understandings originated with spectroscopy, which provided information on the presence of electrons in atoms and on the energies involved. Thomson measured the ratio of e/m for the electron. Rutherford demonstrated the presence of a dense nucleus. Bohr found a model for the hydrogen atoms that has provided important labels for electronic states. Quantum mechanics provided an understanding of the fundamental rules for formation of atoms and molecules and for rotational and vibrational states of molecules. Electronic states in atoms and molecules are now well understood despite the mathematical difficulties.

Chapter 22. Subatomic Structure and Reactions

Nuclei and particles smaller than nuclei have been a primary center of research during the past century. Initially, the discoveries seemed to fall into a reasonably neat pattern. Then, as energies of experiments became greater, more and more particles were discovered, with no apparent systematic connection between them. Eventually, toward the end of the century, theories were proposed that not only explained the many particles, and their properties, but predicted new particles, which were subsequently found with the expected masses and other properties. We cannot explore the topic in depth but will give some of the highlights of the discovery process and some generalizations concerning what was discovered.

22.1 Synoptic History of Subatomic Particles

Understanding of subatomic particles has a short history, developed over little more than a century. A synopsis of the major developments can be quite brief. Although not complete, these high points lay out the principal stages of understanding.

22.1.1. *Electron*. In 1874, G. Johnstone Stoney (1826-1911) suggested the need for a fundamental quantity of electricity, for which he proposed (in 1891) the name *electron*. Stoney based his analysis on Faraday's electrolysis experiments and the value of 96,500 C/g for production of hydrogen. He combined this with an estimate of 10^{25} for Avogadro's number to predict a charge on the electron of about 10^{-20} C (compared to the present best value of 1.6×10^{-19} C). He pointed out that the quantity e was one of three constants clearly provided by nature (along with c and G , the speed of light in vacuum and Newton's gravitational constant)

J.J. Thomson, working in 1897 in the Cavendish Laboratory at Cambridge University (endowed, by Cavendish relatives, with money inherited from Henry Cavendish) showed that cathode rays were the subatomic negative charges proposed by Stoney. Thomson found the ratio of charge to mass, e/m , to be about 1.76×10^{11} C/kg. Because the mass of the electron was so small compared to atomic masses, and because so many oscillator frequencies were observed in the spectra of atoms, it was concluded that there were probably thousands of electrons in each atom, but "the electrons responsible for the radiation are probably few and not directly involved in the structure of the atom."¹

¹ A. Schuster, "Spectroscopy", in *Encyclopedia Britannica, eleventh edition, Cambridge, England, 1911*. Sir Arthur Schuster (1851-1934) was professor of mathematics, then professor of physics at Manchester (1881-1888 and 1888-1907), knighted in 1920.

22.1.2. *Stability of the Atom.* Models of the atom were severely restricted by two constraints. Earnshaw's theorem² demonstrates that no static arrangement of electrical charges can be stable, in the absence of externally applied forces. Maxwell's equations show that any accelerated charge will radiate energy, and therefore an atom with accelerated electrons (as in any solar model) must collapse in a small fraction of a second.

22.1.3. *The Nucleus.* Rutherford, at Manchester, devised a test to confirm Thomson's plum pudding model of the atom. Astonishingly, they found quite large deflections, quite inconsistent with Thomson's model.

The necessary conclusion was that most of the mass of the atom was concentrated into a small, dense volume, which was called the *nucleus*. To explain the density of nuclei, it was supposed that they were constructed of relatively heavy particles, now called *protons*, each proton with a mass comparable to an entire hydrogen atom, and each with a positive charge equal in magnitude to the charge on an electron. To balance mass and charge properties, the number of protons was taken to be equal to the mass number (integral approximation to the atomic mass), with a number of electrons in the nucleus equal to the difference between the mass number and the atomic number. The accompanying electrons outside the nucleus, equal in number to the atomic number, gave the atom no net charge. The model was incomplete and failed to explain most of the known properties of the atoms.

22.1.4. *Mass and Energy.* In 1905-6, in a comparatively little-noted portion of his papers on relativity, Einstein provided an explanation for the non-integral masses of atoms. Because the mass was a measure of the energy of the nucleus, and particles coming together to form the nucleus interacted and thus gave up or acquired energy in various amounts, the resultant energy, and mass, of each nucleus depended on characteristics other than simply the number of particles.

22.1.5. *Bohr's Model.* Bohr proposed that Maxwell's equations did not apply to the accelerated electrons and borrowed Planck's equation, $\Delta E = h \nu$, to give the frequency of emission equal to the *change* of energy of an electron moving between fixed orbits. His model fit very closely to the observed spectrum of hydrogen, but failed to explain spectra of other atoms or other known properties of the hydrogen atom.

Sommerfeld showed that Bohr's model could be solved relativistically, yielding elliptical orbits and better agreement with the hydrogen spectrum, including a small splitting of levels. In 1925, Goudsmit and Uhlenbeck³ proposed that the splitting observed in the hydrogen spectrum could be explained by assigning to the electron an additional property, an angular momentum, or

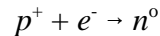
² Samuel Earnshaw (1805-1888). In 1839 he presented a paper at the Cambridge Philosophical Society in which he pointed out that because electrical, magnetic, and gravitational forces obey inverse square force laws, there can be no point of stable equilibrium for such charges, or force centers (*Trans. Camb. Phil. Soc.* 7, pp. 97-112 (1842)).

³ Samuel Goudsmit (1902-1978) and George Uhlenbeck (1900-1988) met while working under Paul Ehrenfest in Leiden.

spin, of $\frac{1}{2} \hbar$. Later, from the work of Dirac and Pauli (1900-1958), it was understood that the relativistic description added a fourth coordinate (time, in addition to the three spatial coordinates), which was the property most closely related to the spin. Electrons (and other “fermions”) can have only a single electron at a time in any given *state* (defined by the values of the four quantum numbers, with respect to any given reference frame).

22.1.6. *Quantum Mechanics*. In 1925, Heisenberg and Schroedinger,⁴ following different mathematical paths, found mathematical representations known as *quantum mechanics* (or sometimes *wave mechanics*) that could reconcile experimental values with the requirements of Heisenberg’s (1927) *uncertainty principle* and thus bring observations of atomic and many subatomic particles into agreement with theory. A model for atoms was soon devised, based on quantum mechanics, which replaced the unsatisfactory Bohr model.

22.1.7. *Neutron*. The development of quantum mechanics and the uncertainty principle showed that although electrons may pass freely through nuclei, they cannot be bound within a nucleus because the confinement in position, Δx , gives too great an uncertainty in momentum, Δp_x , to permit confinement. Fermi proposed, in 1920, the existence of a heavy, neutral particle, which was labeled the *neutron*. The neutron took the place of the proton + electron combination previously assigned to the nucleus to satisfy requirements of mass and charge. The reaction



may occur (in either direction), but only under certain conditions (and requires the emission of a neutrino, considered below).

The proton and the neutron are commonly referred to, collectively, as *nucleons*. They are members of a class of particles known as *baryons*, or “heavy particles”.

22.1.8. *Positrons and Anti-Particles*. In Dirac’s 1928 analysis of the relativistic motion of the electron, he found, in addition to the small splitting of levels already detected experimentally, the possibility of a “negative energy” or “negative mass” state of an electron, which could also be explained as a positive charge state of the electron. (The equation for electron energy came out of the relativistic solution as E^2 , and Dirac recognized that both positive and negative values of the square root were therefore indicated.) Dirac initially concluded that the particle described was the proton, then recognized that it must be an as-yet undetected particle with mass equal to the electron mass.

Carl Anderson (1905-1991) found experimental verification of the *positron* in 1932. It may be described as having the same mass as the electron but opposite charge. It is now recognized as a member of a class of particles known as *antiparticles*, associated with nearly all “normal” particles.

Feynman later showed that an alternative model of the positron is an ordinary electron that has been scattered backward in time. Such a process appears, initially, to violate the concept of causality, but such violations are not consequential *if* they happen with a short enough time

⁴ Werner Heisenberg (1901-1976); Erwin Schroedinger (1887-1961).

interval, for which the uncertainties in energy, time, and other variables fall within the zone prescribed by the uncertainty principle.

Any particle may combine with its antiparticle, in the presence of one or more other particles to satisfy requirements of conservation of momentum as well as conservation of energy, to produce photons, typically gamma particles, with energy equal to $h\nu/c^2$ and with one unit of angular momentum. Similarly, photons, of sufficient energy and in the presence of other particles to balance conservation-law requirements, can produce a pair of particles, consisting of a particle and its anti-particle. Best known of these is the production, from a 1.02 MeV gamma, of one electron and one positron, or the reverse process, the annihilation reaction in which an electron and a positron produce a pair of gammas, each with energy of 0.51 MeV.

22.1.9. *Neutrinos.* Certain nuclei are known to emit electrons, or β particles (historically called β rays). When the properties of the emitted electrons were compared to the changes in energy of the nuclei, it was found there were apparent discrepancies. The conservation laws for energy, momentum, and angular momentum, all seemed to be violated in these decay processes.

In 1930, Pauli argued that the conservation laws could be satisfied in beta decay if an additional particle, called a *neutrino*, were emitted along with the electron. The neutrino could have variable energy, little or no rest mass, no charge, and a spin of $\frac{1}{2} \hbar$. In 1956 (long after the existence of the neutrino was well accepted), Cowan and Reines gave experimental confirmation of its existence. More recently, studies of neutrinos have shown that they are a family of related particles, which have a very small but non-zero mass. These neutrinos change into each other during flight.

22.2 Nuclear Forces, Wells, and Barriers

In previous chapters, we have considered many different types of forces: gravitational, frictional, van der Waals, electrostatic, and magnetic, among others. Upon further examination it has been found that all but the first (gravitational) are examples of a single force, which may be called the electromagnetic force. The forces holding molecules together, and keeping molecules apart, all arise from the interactions between charged particles, static or moving with respect to each other. Both the familiar gravitational force and the electromagnetic force have infinite range, falling off only as the inverse square of the distance.

Study of properties of nuclei and their emissions has led to the discovery of two additional types of force. The “weak” force, which is responsible for the process of β decay, has been shown to be related in a fundamental way to the electromagnetic force, although in practice they are quite different. (The force is sometimes called the “electroweak” force.)

The radius of a nucleus, of mass number A , may be approximated as

$$r = r_0 A^{1/3}$$

with $r_0 = 1.5 \times 10^{-15}$ m. The force primarily responsible for holding nuclei together has been labeled the “strong” force. The strong force differs in having a very short range (roughly on the order of 10^{-14} m). It is an attractive force between nucleons.

One can see the importance of a different kind of force when you consider that a typical

nucleus, such as copper, has 29 protons brought together within a radius of about 6×10^{-15} m. The 35 neutrons may be considered as moderators, or “go-betweens”, to prevent the protons from fighting each other off. The attractions between nucleons would not be sufficient, if all the nucleons were protons, to hold the nucleus together, but 35 neutrons + 29 protons give sufficient attraction to overcome the repulsions of the 29 protons. As the number of protons increases, the number of neutrons must increase even faster, but too many neutrons can also lead to instability. The most stable nuclei fall near the “line of stability” shown in Figure 22.1.

There are significant variations from this extremely simple model. For example, “even-even” nuclei, with even numbers of protons and even numbers of neutrons, tend to be more stable than otherwise expected. Such differences have been explained with a *shell model*, somewhat like the model for electrons in atoms, or with the *liquid drop model*, particularly helpful in explaining how a nucleus will break up under stress.

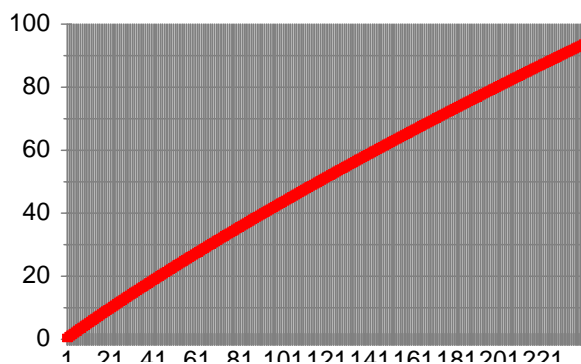
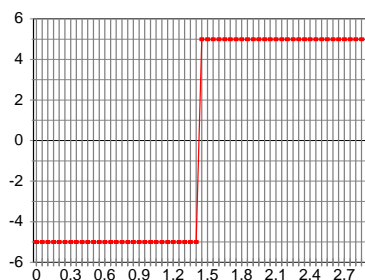


Figure 22.1. Line of stability. Atomic number Z (ordinate) vs. mass number A (abscissa). As the number of neutrons falls farther above or below the line of maximum stability, the nucleus becomes less energetically stable. Note that the line is nonlinear, requiring more neutrons at higher A or Z values.⁵



⁵ The curve is the line $Z = 66.7A/(A^{2/3} + 132)$. After D. Halliday, *Introductory Nuclear Physics*, Wiley, New York; p. 294.

Figure 22.2. Potential energy varies with radius, which in one-dimensional cross section gives a square potential well for particles within a nucleus.

With this simplified model of the nucleus, we may envision a set of nucleons sharing the space in a *square well*, such as that shown in Figure 22.2.⁶ Outside the nucleus the potential falls according to Coulomb's inverse square law. However, there are several additional characteristics that contribute to complexity of nuclei.

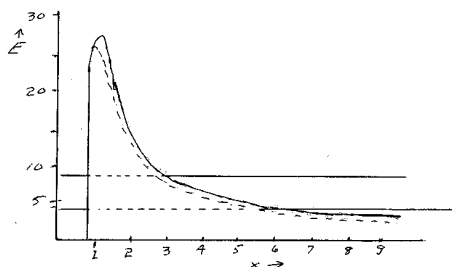


Figure 22.3. Alpha-particle tunneling out of a nucleus through a Coulomb barrier. Energy, E , of the alpha, relative to the nucleus, vs. position, x (in 10^{-15} m). For uranium (alpha energy 4.25 MeV) the process is very slow, requiring on the order of 10^9 y. Polonium has almost an identical barrier (dashed line) but the alpha energy of about 9 MeV allows tunneling in roughly 10^{-6} s. Tunneling probability depends exponentially on the area above the energy level of the particle.

22.2.1. *Tunneling.* Given a well of the form shown in Figure 22.3, it seems clear that any particles (such as an α — two protons plus two neutrons) could only escape from the nucleus if it had energy A , sufficient to pass over the barrier. It would then appear outside the nucleus with this energy. In fact, α particles are observed coming from certain nuclei with energies such as that of level B . We must conclude that the α particle has passed through the barrier, rather than over it. We call the process *tunneling*.

Tunneling probability may be approached by considering that the greater the *area* of barrier above the level of the particle (*e.g.*, above energy level B , in cross-section view), the less likely it is for a particle to tunnel through the barrier. In fact, the probability falls off exponentially with the area. The farther the particle energy is below the top of the barrier, and the wider the barrier, the smaller the probability of the particle escaping through the barrier. We may simply chalk this up to one of the surprising vagaries of quantum mechanics, or we may examine it more carefully and see that the result is less surprising than we might have anticipated.

⁶ The well is called square because a plane cutting through the center gives the square (or actually rectangular) cross-section shown in the figure. The actual well, in two dimensions, would be a cylindrical well. In three dimensions it would have spherical symmetry. Rather than the inverse-square dependence on distance that applies to electrons in atoms, the energy levels in nuclei arise from a combination of electrical repulsions and the attractive strong force and are better approximated by Bessel functions.

The question becomes, what is the probability that, on any given venture to the barrier, the particle may be able to get through. The probability need not be high because the frequency of striking the barrier is high.

We also must take into consideration the nature of the barrier. One cannot construct a classical barrier with quantum particles. In classical mechanics we envision an impenetrable barrier as a permanent structure, somewhat like a line of fence posts, or a solid wall, anchored in place. With quantum particles, a better analogy would be a set of roving patrols at the border, each of which moves about randomly. Then even if the patrols are usually close together, there is a finite probability that, at any given moment, there may be a sufficient gap to allow an oncoming particle to slip through. We would then say the particle has tunneled through the barrier.

However, any measurement of position and momentum is subject to sufficient uncertainty that we can never demonstrate that the particle was certainly within the barrier region with an energy less than that required to pass over the barrier. Given the limitations on our ability to measure instantaneous properties of the system, it is prudent to accept the mathematical description as a measure of the probability of “tunneling through” the barrier.

22.2.2. *Radioactive decay.* We cannot go into all the rules of nuclear structure, but will note a few guideposts. Usually, more than one number of neutrons can be combined with some specific number of protons to form a stable structure. Because the number of protons determines the number of electrons and their arrangement around the nucleus, all atoms with the same number of protons have essentially identical chemical properties (and nearly identical rates of reaction, with only slight variations because of differences in mass). Thus all atoms, with the same number of protons, appear in the same place in the Periodic Table, and are therefore called *isotopes* (“same place”). Different isotopes may, however, have different properties for radioactive decay and nuclear reactions because the nuclei are different.

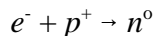
As the number of protons in the nucleus increases, an increasing number of neutrons is necessary to achieve stability, but too many neutrons will also decrease the stability. The α particle (He nucleus), an even-even nucleus, is exceptionally stable. The line of stability curves upward, but isotopes are less stable as they deviate from the line of stability.

When a nucleus becomes unstable, one (or more) of several possibilities may be expected.

1. Two protons and two neutrons may clump together and escape from the nucleus as an α particle. This is likely primarily for heavy nuclei. Then, because the nucleus was originally richer in neutrons than protons, and has lost two p and two n , the nucleus now is comparatively even richer in neutrons, which can lead to catastrophic failure (fission) or to a more minor adjustment.

2. If the nucleus has too many neutrons, relative to protons, a neutron may lose an electron which then escapes as a β particle, leaving behind a proton. A neutrino (or an anti-neutrino) is also ejected. Loss of an electron changes the charge on the nucleus, increasing the atomic number by one unit.

3. If the nucleus has too few neutrons, relative to protons, a positron ($\beta^+ = e^+$) may be ejected (with a neutrino). Alternatively, especially in heavy elements for which the nuclear charge is large and therefore the inner electron states lie close to the nucleus, an inner electron (from the K shell) may be captured by the nucleus,



reducing the atomic number by one.

4. If the nucleus is inherently stable except that it has excess energy (perhaps as a consequence of one of the processes just considered), the nucleus may eject energy in the form of a γ particle (also called γ rays, or photons), a higher-energy equivalent of an x-ray. Such a photon carries energy $h\nu$ as well as mass, $h\nu/c^2$.

5. For very heavy nuclei, instability may lead to fission of the nucleus into at least two parts, with generally some smaller fragments, such as α particles, emitted as well. Because the two major fragments formed are now much too rich in neutrons, some free neutrons are expected.

6. Reverse processes may occur, as well, when outside particles strike the nucleus. Of particular importance is neutron capture. This is much more likely when the neutrons have very low kinetic energies, comparable to thermal energies (kT , with T approximately room temperature). Neutrons emitted by one nucleus, generally carrying large kinetic energies, may be *thermalized* by letting them bounce off other light nuclei (such as hydrogen, deuterium, or carbon), sharing excess energy with these other nuclei. The thermalized neutrons may then be absorbed by a heavy nucleus, leading to fission and the release of more neutrons. Under proper conditions, this may give a steady release of energy, sufficient to drive heat engines that in turn drive generators to produce electric power. Under other conditions (with other mixes of nuclei), the process of fission may be so fast that it produces a major explosion (commonly described, somewhat inappropriately, as an “atomic” bomb).

7. Because very light nuclei, such as hydrogen and deuterium, are less stable than heavier nuclei (especially α particles), it is possible to combine the very light nuclei to produce heavier nuclei, with the release of very large amounts of energy. This *fusion* process has been accomplished under extreme conditions, by heating the reactive components suddenly to a very high temperature at very high densities, driven by a localized fission reaction. Attaining conditions of high temperature and high density sufficient to react the light nuclei under controlled conditions suitable for power production has been a goal of research and development for some decades, but thus far usually “a few months” (at least) from practical accomplishment.

Two advantages of the fusion reaction are the plentiful supply of reactants and the comparative absence of “dirty” products. The seas hold enormous quantities of water, so that even if we choose deuterium, which is a very small component of ordinary water, there is still far more deuterium than we might need for such a process. The reaction products of fusion are not reactive, so there is no inherent problem of radioactive waste disposal. On the other hand, any container for a fusion reaction will be bombarded with high-energy particles, and will develop some consequent radioactivity, so there will always be some disposal and shielding problems.

22.3 Global Warming

Modern civilization faces several continuing problems, other than those rooted in political conflicts. Many parts of the world have a shortage of clean water. Undeveloped parts of the world typically lack the fertilizers necessary to produce adequate food, and most of the world faces an increasing shortage of fuel for transportation, for manufacturing, for heating, lighting, and cooling, and for other “creature comforts”. Underlying all of these is the need for energy sources (interpreted in the sense of high free energy or energy with low entropy). Given adequate energy, essentially all the *technical* problems are soluble.

Potable water may be produced almost anywhere in the world by processes that are well understood and tested. Given adequate energy, liquid fuels may be produced from widely available resources by the Fischer-Tropsch synthesis, the reaction of hydrogen and carbon monoxide to form hydrocarbons, or synthetic gasoline. Fertilizer, to replace the naturally occurring substances removed by growing crops, primarily requires high energy expenditures.

On the other hand, a few decades ago there was great concern among professional and amateur environmentalists about the total energy release on Earth. The concern was that as fuel, of any type, is consumed, more energy is released, and much of this “waste heat” does not (over the short term) escape the surface layers of the atmosphere. Thus increased energy release calls for mechanisms for disposing of excess energy (not yet defined). While such mechanisms are, or can be, readily available, there is real question as to whether we want to undertake any major process of cooling the Earth before we understand the implications of such a change. We do not, yet, know whether the net effect of increasing the thermal energy of the Earth and its environment is good or bad — certainly it can be helpful in some local situations and times and disconcerting at other places and times. In the past, the Earth has been much warmer than at present, and has been much cooler than at present, but the overall effect on civilization is still conjectural. The only certainty seems to be that people will complain about existing conditions, but resist strongly any change in those conditions (*e.g.*, warming, or cooling, or change in precipitation).

The geologic record shows clearly there have been extended warm periods (including the Medieval Warm Period, centered around roughly 1000 A.D.) when Greenland acquired its name and, especially obvious, cool periods, including the major ice ages that brought glaciers across the northern portion of the United States as well as briefer periods such as the “Little Ice Age”. There is, as yet, no consensus on the cause of these very substantial changes in climate. Even the Little Ice Age (*ca.* 1600 ± 300) was characterized by wide-spread flooding, famine, and changes in glaciation and sea ice, although the present indications are that the global temperature change was less than 1°C. (Was the Little Ice Age driven by a temperature change, or was it driven by another factor that overcame the Earth’s inherent temperature stability?) For lack of contrary information, it is generally assumed the thermal flow from the center of the Earth is constant with time (but measurements are limited to a fleeting moment of geologic time).

Nor is there a consensus on whether we have fully emerged from the Little Ice Age, or where we are in the larger Ice Age cycle — are we still warming from the last major glaciation period or have we begun the following cooling stage toward the next major ice age? Even a brief examination of records will confirm that it is not possible to draw valid conclusions about climate change from current weather, any more than one can predict weather from knowledge of climate.

One part of the theory of climate change is well developed. It is well known that there are three substantial sources of energy input to the surface of the Earth. Some comes from internal radioactivity and, especially locally, significant energy comes from human activities, but more comes from the Sun. Energy from the Sun peaks in the visible region, which passes largely unattenuated through the atmosphere. When this energy is absorbed and re-emitted, it is released primarily in the infrared region (“heat waves”), and there are many components of the atmosphere that absorb infrared radiation, including water, carbon dioxide, and methane. Thus, as was explained in the 19th century, light entering a greenhouse through the glass roof cannot leave the

greenhouse because the glass absorbs infrared radiation and thus the greenhouse is warmed. Early in the 20th century it was shown that real greenhouses are adequately warmed even if the glass roof is replaced by an infrared transmitter (silica), so the “greenhouse effect” is *not* the explanation of greenhouse warming. This is strongly confirmed by the marked rise in atmospheric CO₂ over the last century, with little or no change in *global* surface temperatures. (NASA satellite studies have shown little or no change in global temperatures; less than 1°C over the last century.) The long-term effects of high atmospheric CO₂ appear predictable. Plant growth will be stimulated, storage of carbon in forests and other plants will be increased, and carbonates on the sea floor will increase. Such effects have slow rates for reaching equilibrium. Current habits of our civilization do not encourage the trend toward long-term equilibrium. There is a net conversion of stored carbon (in forests and petroleum) to carbon dioxide. To date, serious proposals for reducing “greenhouse gases” have been only proposals to limit, slightly, the rate of growth⁷ of these gases in the atmosphere, with no possibility, or suggestion, of returning levels to those of any earlier period. Thus no “cure” has been seriously proposed, by scientists or by politicians.

Nevertheless, it seems desirable to decrease the levels of atmospheric “greenhouse gases”, especially because we have too few clues concerning the intermediate term effects of such gases. Many of the predictions, such as increased snowfall in arctic regions because of ocean warming, have already proved to be invalid. Water levels have fallen drastically, and risen again, without apparent cause (recently in Lake Michigan).

The *only* known source of adequate energy that does not entail an increasing rate of increases in greenhouse gases is nuclear power (fission and, potentially, fusion). At the time of this writing, a substantial portion of the electric power produced in many countries comes from nuclear reactors. These have the clear advantage of much smaller fuel needs, eliminating mining and transportation of very large quantities of fuel (*e.g.*, coal and oil), processes that have a very poor track record in terms of safety and destruction of local environments. Nuclear reactors have the advantage of not producing greenhouse gases, nor do they produce the more dangerous contaminants (particulates, toxic metals, and nitrogen oxides, especially) associated with current practices of burning coal and petroleum. The safety record of nuclear reactors (even including one or two clearly foolish “cost-saving” designs and inadequately supervised “experiments”, such as Chernobyl) has been astoundingly good compared to the alternative power plants we have chosen to live with.

The one “unresolved” problem of nuclear reactors, as commonly described in popular literature, is the disposal of radioactive waste materials, but this is a problem with known technical solutions. The problem is exacerbated, in the minds of the public, by combining two types of waste. There are comparatively large quantities of low-level waste, which will not bother anyone more than a short distance away (such as a kilometer). There are small amounts of high-level nuclear waste, which would be dangerous if allowed, in concentrated form, to reach population centers. Too often, the volume of low-level waste is superimposed on a discussion of the effects of high-level waste. Some of this misinformation is malicious, but most is a

⁷ Again, we have confusion between speed and acceleration, or a function and its derivative. Decreasing the slope will not decrease the function.

consequence of well-intentioned ignorance.

Background nuclear radiation, especially from rocks and arriving from outer space, is easily measured.⁸ If all radioactive waste were widely distributed (*e.g.*, by distributing it in the oceans), there would be no detectable increase in background radiation. The preferred solution, however, is to isolate the wastes in underground cavities shown to be stable and not subject to water leakage. Under such conditions, the measurable radiation in any area inhabited by human beings will be undetectable with customary detectors.

The greatest unresolved problem of nuclear power is that certain types of reactors are inherently better than others because, while providing power, they produce their own fuel from plentiful natural materials. These reactors also are capable of producing the forms of unstable nuclei that can be made into bombs (after concentration processes). Thus some of the more responsible countries have chosen to avoid these reactors for power, whereas less responsible countries prefer these *breeder reactors*. Such problems are political rather than scientific and do not have easy technical solutions.

22.4 Nuclear Reactions

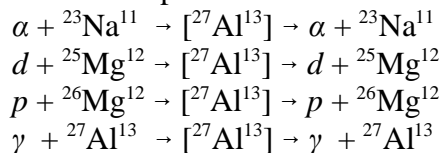
Some nuclear processes, which are typically labeled as *radioactivity*, occur spontaneously. A nucleus may be unstable to the point that, given enough time (perhaps microseconds, or years, or thousands of years, all very long compared to nuclear time scales), the nucleus spontaneously emits a particle or may even break up. However, many nuclear processes are initiated by an outside disturbance, such as a projectile from outer space or from a nearby unstable nucleus or from an accelerator.

22.4.1. *Notation.* Any atomic nucleus is called a *nuclide*. Nuclides are represented by the symbol of the element, preceded by the integral approximation to the atomic mass (the number of protons plus neutrons), called the *mass number*, A . Thus normal hydrogen is ${}^1\text{H}$, normal helium is ${}^4\text{He}$, *etc.* Although the element uniquely specifies the atomic number, it is sometimes helpful to add the atomic number, Z , as a right superscript. (Not everyone remembers off hand that vanadium is number 23, or that technetium is element number 43.) Thus we may have ${}^7\text{Li}^3$, ${}^{27}\text{Al}^{13}$,

⁸ Background radiation is substantially higher in commercial airplanes flying at altitudes on the order of 30,000 ft and it is higher in communities such as New York City, sitting on granite. The effects of background radiation are more easily studied in seven western states (roughly along the Rocky Mountains), where exposures are 50 to 100% higher, but cancer deaths (the primary concern) are 15% less, than in other states. Any residual effects (favorable or unfavorable) for these low levels of radioactivity are so statistically improbable that it has not been possible to do more than guess at the magnitude, or even the sign, of the health effects of these exposures. For facts and figures on radiation and health, see John Lenihan, *The Good News About Radiation*, Cogito Books, Madison, Wisconsin, 1993. See also Sohei Kondo, *Health Effects of Low-level Radiation*, Kinki University Press, Osaka, Japan; Medical Physics Publishing, Madison, Wisconsin, 1993. It is worth mentioning that genetic effects predicted by some for offspring of survivors of Hiroshima and Nagasaki have not shown up in studies by Japanese or American researchers.

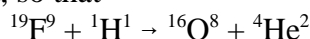
and $^{238}\text{U}^{92}$. Nevertheless, the symbols are typically read *as if* they were written C^{12} and C^{13} , putting the element = atomic number = name first, followed by the mass number.

Many possibilities exist for choice of projectile plus choice of target nuclide. For example,⁹ there are several ways of producing the excited state of ^{27}Al , which we represent in square brackets, $[^{27}\text{Al}^{13}]$. Also, there are several products obtainable from $[^{27}\text{Al}^{13}]$.

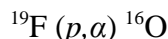


The compound nucleus, $[^{27}\text{Al}^{13}]$, does not remember how it was formed, so any of the processes on the left, forming $[^{27}\text{Al}^{13}]$, may lead to any of the processes on the right (or to $n + {}^{26}\text{Al}^{13}$). In these reactions, α of course represents an α particle, d represents a deuteron (proton plus neutron, or the nucleus of $^2\text{H}^1 = \text{deuterium}$), p represents a proton, and γ represents a gamma, or photon.

The notation may be condensed, so that



may be written in the more compact form



22.4.2. *Energy Balance.* If the rest masses of the particles involved in a nuclear reaction are known, the change in rest mass,

$$\Delta E = \left\{ \sum_i m_{R,i} - \sum_i m_{P,i} \right\} c^2$$

tells whether the reaction process is *exoergic*, giving off energy, or *endoergic*, taking up energy. If exoergic, extra energy appears on the right hand side initially as kinetic energy of the products. If endoergic, extra energy must have been supplied to the reactants, probably as kinetic energy of a projectile. This energy difference is often called the Q value for the reaction, because the extra energy may be transferred to the surroundings as thermal energy (although it need not be a reversible thermal energy transfer).

The same method could be applied to any process, such as a chemical reaction. For example, we could take the masses of products and subtract the masses of reactants for a chemical reaction such as



but the lack of sensitivity of apparatus for determining mass would undoubtedly tell us that the reaction (which is quite exothermic) had a ΔE of 0 MeV. The experimental value is 284 kJ/mol (CO or CO_2), which would be 2.95 eV (per molecule), or a mass difference of 5.25×10^{-36} kg.

22.5 Structures of Nuclear Particles

At one time it was argued that an electron must have at least a certain minimum size. Thus

⁹ D. Halliday, *Nuclear Physics*, Wiley, New York, 1950.

the inherent angular momentum, or “spin”, of an electron was envisioned as a physical rotation of the electron. More recent experiment and theory describes the electron as a true point particle, with no internal structure.

Along with the electron, a companion particle, now called a *muon*, was discovered, with a rest mass about 250 times that of the electron. More recently, a third particle, the *tau* particle, has been predicted and detected, with rest mass nearly 3500 times that of the electron. It was also found that the neutrino, with rest mass zero, or nearly zero, is really three different particles, one a companion to the electron, another a companion to the muon, and the third a companion to the tau. Thus there are altogether six particles in this set, all of which were called *leptons* (light particles), because the masses (except for the tau) are small compared to the proton and neutron. Each lepton has a corresponding antiparticle (hence 12 distinguishable particles in all).

In addition to the leptons, many heavier particles have been found. One could write down a very large number of conceivable reactions involving nuclei and these subnuclear particles. Only some of these conceivable reactions satisfy the conservation laws — conservation of energy and conservation of angular momentum, but also conservation laws specific to the subnuclear particles. These restrictions are expressed by *selection rules*. But there are other guides, as well. For example, a general rule is that reactions involving large energy changes, if otherwise allowed, tend to happen rapidly as compared to processes involving small energy differences. (Note that this is the reverse of what one might expect. “Easy” (small ΔE) things take longer than “hard” (large ΔE) things.)

A major breakthrough in the theory of subnuclear particles was the recognition that there are smaller particles, called *quarks*, with electric charges that are fractions of the “basic” charge, *i.e.*, $\pm 1/3 e$ and $\pm 2/3 e$. Theoretical analysis suggests that there should be six such particles, analogous to the six leptons. Each quark has its corresponding antiquark.

The quarks are fermions, exhibiting several underlying properties previously unknown. These properties were given somewhat fanciful names as they were discovered. We will initially choose letter labels.

Two of the quarks might be considered basic. We label them, quite arbitrarily, *d* and *u*, with electric charge of $- 1/3 e$ (< 0) and $+ 2/3 e$ (> 0) and rest masses about 700 times that of the electron. These quarks can combine to give protons and neutrons.

$$\begin{array}{ll} d + 2 u = p & \text{Electric charge: } - 1/3 + 2(+2/3) = + 1 \\ 2d + u = n^0 & \text{Electric charge: } 2(- 1/3) + 2/3 = 0 \end{array}$$

An extensive search for free quarks proved fruitless. Current understanding is that the forces between quarks *increase* with distance between the particles (somewhat like an unbreakable spring binding two masses), so that quarks never exist outside their “cocoon”.

To explain the full “zoo” of subnuclear particles, and the selection rules governing their reactions, it then became necessary to postulate four additional quarks, which we label *b*, *c*, and *s*, *t*. These have rest masses of approximately 10,000, 3000, 1000, and nearly 350,000 times that of the electron, and have charges, like the *d* and *u* quarks, of $- 1/3$, $+ 2/3$, $- 1/3$, and $+ 2/3$ times *e*, respectively.

Quarks may combine in other combinations. A quark and an antiquark give particles called

mesons (intermediate mass). In particular, $u + \text{anti } d$ gives π^+ and $\text{anti } u + d$ gives π^- , each called a *pion*. An s or $\text{anti } s$ with d , u , or $\text{anti } u$ gives the set of K particles, or *kaons*. Combinations of three quarks give other *hadrons*, besides the proton and neutron. There is a great deal of symmetry in the scheme as presently understood, and predictions of missing particles have led to their subsequent discovery, with the properties as predicted.¹⁰

Nevertheless, it was soon found necessary to add one more property, which has been labeled as *color*, with three choices (labeled, not too surprisingly, as *red*, *green*, and *blue*). One quark of a meson is of a certain color and the other is the anticolor, so mesons are *colorless*. The three quarks of a hadron must each have different color, because quarks, being fermions, are subject to the Pauli exclusion principle concerning the exchange of equivalent particles.

22.6 Forces and Particles

It is not difficult to imagine a particle passed from one object to another exerting a repulsive force on each. It is more difficult to conceive of particles exerting attractive forces on the emitting and absorbing objects. No good classical models exist for the mechanism of attraction by means of such virtual particles. Yet as we have seen, most forces we encounter are either traceable to electromagnetic forces or gravitational forces, and both are now attributed to *carrier particles*.

The photon is created and destroyed by electromagnetic interactions and is now considered to be the carrier of the electromagnetic force. Imagine a charged particle emitting photons that are subsequently reabsorbed without ever having been detected by external apparatus. Such photons are called *virtual*. The gravitational force is similarly ascribed to particles called *gravitons*, which have not yet been detected but are believed probable.

The strong force is believed to be exerted, or *mediated*, by mesons, and in particular by the pions. Additional particles, W and Z, are associated with the weak (often called “electroweak”) interaction of β decay. New particles, called *gluons*, are postulated for interactions between quarks.

If violations of conservation of energy, for example, are not detectable, then they are of no consequence to the law of conservation of energy. Because the virtual particles exist for very short periods of time, they “fly under the radar” of the conservation laws, governed by the uncertainty principle and special relativity. It appears they violate conservation laws, but we can never catch them doing so.

The speed of such particles must be less than, or at most equal to, the speed of light in vacuum, and therefore the *range*, over which they can act, must be no more than c times the lifetime. From the uncertainty principle in the form $\Delta E \Delta \tau \geq h/4\pi$, we find the maximum range of a particle of rest mass m_o to be

$$\text{Range} = c \Delta \tau = \frac{c \frac{\hbar}{2}}{m_o c^2} \approx \frac{\hbar}{m_o c}$$

¹⁰ The d and u quarks are generally known as *down* and *up*. The others have been labeled as *bottom* or *beauty*, as *charm*, as *sideways* or *strange*, and as *top* or *truth*. The names clearly have no significance except to distinguish one from another.

Thus a massive virtual particle can have only a short range, whereas the photon, with zero rest mass, has an infinite range. From such considerations it was possible to predict the rest mass of the mesons and other particles, such as W and Z, before they were observed, based on known properties of the forces they mediate.

22.7 Accelerators

Early studies of nuclear structure were severely limited by the rare occurrence of high-energy events. Some of these came from natural radioactive decay of nuclei of uranium, radium, thorium, and other very heavy elements. Many came from *cosmic rays*, the particles primarily created in the outer reaches of the atmosphere by high-energy particles coming from the Sun.

A succession of developments led to *accelerators*, devices that could accelerate charged particles to high speeds and therefore high energies. An early version was the Cockcroft-Walton accelerator, which charged a set of capacitors in parallel, then reconnected them in series to get voltage multiplication. Similar results may be achieved with suitably isolated transformers in series. Charged particles traveled through an evacuated tube from one voltage extreme to the other.

About the same time, Robert Van de Graaff (1901-1967) combined the principles of the electrostatic generator, devised by Kelvin, and Faraday's ice pail experiment, to obtain a high voltage electrostatic accelerator. Charge was transferred, by a metallic comb, to a moving belt which passed inside a metallic dome. Work must be done to move the charged belt through the opening into the dome, which is accomplished by the motor driving the belt. Inside the dome, charge can be transferred to the inside of the conducting dome (across zero potential difference). The charge then moves to the outside of the dome, adding to the charge already there. By this means potential differences of several million volts may be obtained. The Van de Graaff generator gives precise voltage control. By placing two such generators in tandem, the available voltage may be doubled, reaching 40 MeV in practice.

Most modern accelerators are built on the concept of the cyclotron, developed by E.O. Lawrence. A charged particle moving perpendicular to the magnetic lines of force in a uniform magnetic field travels in a circle at the cyclotron resonance frequency, $\omega = 2\pi\nu = qB/m$ (sec. 16.4). The particle travels within a conducting metallic "pill box", so that it is not subject to any electrical fields, except that the pill box is divided in half, to form two "D"s, and an electrostatic potential is placed between the two D's. As the particle travels from one D to the other, it is accelerated. Then the potential is reversed, while the particle is inside and thus protected from the electric fields. When the particle reaches the separation, it is therefore accelerated again, and this process may be continued, reaching very high speeds and energies of the accelerated particle.

The limitation to the cyclotron energy arises from relativistic effects. As the speed increases, the mass increases, changing the cyclotron frequency for the particle. Thus above a certain energy, the particle tends to get slightly out of phase and is no longer properly accelerated. Variations of the cyclotron design to accommodate for relativistic effects operate in pulses, with ramped frequencies to accommodate the changing masses. They include the *betatron* and the *synchrotron*.

An alternative accelerator design is the linear accelerator, which produces an electromagnetic wave moving through a series of conducting chambers. The electrons “surf” on the electromagnetic wave, moving before the wave like a surfer on the leading edge of a breaking water wave. By proper design of the chambers, the speed of the electromagnetic wave may be controlled, such that the wave speed increases along the tube, thus allowing the electron (or other charged particle) to accelerate while remaining on the leading edge of the traveling wave.

Additional performance is achieved by designing two accelerators, or accelerating paths, that lead one beam directly into an oncoming beam. The energy of collision is the sum of the energies of the two beams, which because of relativistic effects is much more effective than increasing the energy of a single beam. Intersecting beams double the (relative) speeds, corresponding to an increase in collision energy by much more than a factor of two. New accelerators are more or less constantly under construction to give higher energies of collision events, enabling the exploration of higher-energy events and thus new particles and interactions.

Particle accelerators have found wide applications, in medicine (especially for treatment of cancer), in production of radioactive isotopes, and for production of high intensity radiation (particularly from synchrotrons) for application to other types of studies.

Chapter Summary

A summary review is given of electrons, atoms, the nucleus, special relativity's contributions to mass and energy, quantum mechanics, other particles and anti-particles, nuclei and their potential wells and stability, nuclear energy and reactions, and nuclear forces and particles.