

Lecture notes 6

6. Atoms and molecules

“Lecture notes” 6 — **Atoms and molecules** — covers the last part of this course. It is a continuation of Lecture notes 5.

6.1 From the Coulomb potential to atoms

Section 6.1 — “From the Coulomb potential to atoms” — is a translation of notes written by Hemmer, and covers some of the contents in his chapters 8 and 9.

We have solved the Schrödinger equation for one particle in a Coulomb potential, and we have seen how the results can be applied to the two-particle system of a hydrogen atom (using the reduced mass).

For an atom with Z electrons and a nucleus it is a simple matter to write down the time-independent Schrödinger equation. The wave function depends on $Z + 1$ vector coordinates, $\psi(\vec{r}_1, \dots, \vec{r}_Z, \vec{R})$, and the classical energy function (the Hamilton function) consists of the kinetic energy, the Coulomb attraction between the nucleus and the electrons and the Coulomb repulsion between each pair of electrons. The Hamiltonian operator is then readily obtained by replacing the kinetic terms by the corresponding operators.

It is, however, very difficult to solve this equation. This can only be done approximately, and it is also difficult to obtain accurate approximate solutions. Here, we shall confine ourselves to sketch the outline of how this is done. We start by discussing some principal features of many-particle systems.

6.1.1 Identical particles, symmetry, the Pauli principle and spin

a. Electrons are fermions

In classical mechanics, we can in principle always distinguish between particles, and follow their individual trajectories (orbits) as functions of time. We also imagine that this can be done without disturbing the particle. This is not so in quantum mechanics: Firstly, there are no well-defined classical orbits (as we have already seen). Secondly, it is in principle impossible to distinguish between identical particles like e.g. two electrons (except when they are very far apart).

The latter principle has important and experimentally verifiable consequences. It means, among other things, that the spectra of many-electron atoms are quite different from what they would be if it were possible to distinguish between the electrons. One of the consequences of this principle is **Pauli’s exclusion principle**, which is the main cornerstone when it comes to understand the periodic system. As we shall see, the exclusion principle is intimately connected with the indistinguishability of identical particles.

For two identical and indistinguishable particles, the numbering of their coordinates has no physical significance. Thus, there is no physical difference between $\Psi(1, 2)$ and the

state $\Psi(2, 1)$, where the coordinates of the two particles have been interchanged. We must therefore have

$$|\Psi(1, 2)|^2 = |\Psi(2, 1)|^2.$$

This means that the two functions can only differ by a phase factor:

$$\Psi(1, 2) = e^{i\alpha}\Psi(2, 1),$$

where α is real.

In nature there are only two alternatives. The two-particle state is either symmetric or antisymmetric with respect to interchange of the particle coordinates:

$$\Psi(2, 1) = \begin{cases} +\Psi(1, 2) & : \text{ bosons} \\ -\Psi(1, 2) & : \text{ fermions} \end{cases} \quad (\text{T6.1})$$

Particles with symmetric wave functions are called **bosons**, particles with antisymmetric wave functions are called **fermions**. And, what is very important for us: *Electrons are fermions*, and must therefore be described by states which are antisymmetric with respect to interchange of the particle indices.

b. Pauli's exclusion principle

To see how the Pauli principle follows for identical fermions, let us consider two particles 1 and 2 which do not interact with each other, in an external potential $V(\mathbf{r})$, so that the Hamiltonian is a sum of one-particle contributions,

$$\widehat{H}_{\text{tot}} = \widehat{H}(1) + \widehat{H}(2) \quad \left(\widehat{H}(n) \equiv -\frac{\hbar^2}{2m}\nabla_n^2 + V(\mathbf{r}_n), \quad n = 1, 2 \right).$$

Then the product of two one-particle states,

$$\psi_i(1)\psi_j(2), \quad \text{or} \quad \psi_i(2)\psi_j(1), \quad (\text{T6.2})$$

where ψ_i and ψ_j are two arbitrary eigenstate solutions of the one-particle Schrödinger equation $\widehat{H}\psi_n = E_n\psi_n$, will be a solution of the time-independent Schrödinger equation for the two particles. Both the product functions (T6.2) have the same energy eigenvalue $E_i + E_j$. In the case where the two particles are *not* identical, both these product functions are acceptable as eigenfunctions. If the particles are identical, on the other hand, none of them is acceptable, because the symmetry requirement (T6.1) is not satisfied. However, this disease can be cured. Since both the product functions have the same energy, we can form a symmetric linear combination

$$\psi_S(1, 2) = \frac{1}{\sqrt{2}} [\psi_i(1)\psi_j(2) + \psi_j(1)\psi_i(2)] \quad (\text{T6.3})$$

which satisfies the symmetry requirement $\psi(2, 1) = \psi(1, 2)$ for bosons. The factor $1/\sqrt{2}$ ensures that this wave function is normalized. Similarly we can construct an antisymmetric linear combination

$$\psi_A(1, 2) = \frac{1}{\sqrt{2}} [\psi_i(1)\psi_j(2) - \psi_j(1)\psi_i(2)] \quad (\text{T6.4})$$

which satisfies the antisymmetry requirement $\psi(2, 1) = -\psi(1, 2)$ for fermions.

Here we can now see that if the two one-particle states are *the same*, (that is, $i = j$), then in the fermion case we have $\psi_A(1, 2) = 0$; there is no such two-particle wave function where the two fermions are in the same one-particle state. This is an example of Pauli's exclusion principle:

$$\boxed{\text{Two fermions can not occupy the same one-particle state.}} \quad (\text{T6.5})$$

For more than two identical fermions this can be generalized: We start by noting that the above two-fermion state (T6.4) with the correct antisymmetry can be written as a determinant:

$$\psi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_i(1) & \psi_i(2) \\ \psi_j(1) & \psi_j(2) \end{vmatrix}. \quad (\text{T6.6})$$

An obvious generalization gives for Z fermions the following antisymmetric state, constructed in terms of the one-particle states $\psi_1, \psi_2, \dots, \psi_Z$:

$$\psi(1, 2, \dots, Z) = \frac{1}{\sqrt{Z!}} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \dots & \psi_1(Z) \\ \psi_2(1) & \psi_2(2) & \dots & \psi_2(Z) \\ \dots & \dots & \dots & \dots \\ \psi_Z(1) & \psi_Z(2) & \dots & \psi_Z(Z) \end{vmatrix}. \quad (\text{T6.7})$$

This state is called a **Slater determinant** and has the following properties:

- It is antisymmetric: If we interchange two of the particle indices (coordinates), e.g. 1 and 2, the new determinant will be equal to the old one, except that two columns have been interchanged. Such an interchange gives a minus sign.
- If two of the one-particle states are equal, $\psi_1 = \psi_2$ for example, then two of the lines of the determinant will be equal. A determinant with two equal lines is equal to zero. Thus we recover the exclusion principle: Two fermions can not occupy the same one-particle state.

A small exercise: Show that the functions

$$\psi_{\pm} = \frac{1}{\sqrt{2}} [\psi_{\alpha}(\mathbf{r}_1)\psi_{\beta}(\mathbf{r}_2) \pm \psi_{\alpha}(\mathbf{r}_2)\psi_{\beta}(\mathbf{r}_1)]$$

are normalized, when ψ_{α} and ψ_{β} are orthonormal.

c. Spin

The electron – and many other particles – have intrinsic angular momenta \mathbf{S} , called **spin**. The spin has angular-momentum properties equal to those studied previously for the orbital angular momentum \mathbf{L} . Contrary to the orbital angular-momentum quantum number l which is always an integer, the **spin angular-momentum quantum number** (called s) equals $\frac{1}{2}$ for the electron. This means that the eigenvalue of \mathbf{S}^2 is $s(s+1)\hbar^2 = \frac{1}{2}(\frac{1}{2}+1)\hbar^2 = \frac{3}{4}\hbar^2$, and that the eigenvalues of S_z equal $m_s\hbar$ with $m_s = -\frac{1}{2}$ or $m_s = \frac{1}{2}$. Thus the *size* of the spin

is fixed (contrary to the orbital angular momentum \mathbf{L}), and the spin has only two possible “orientations”. There are only two different eigenstates for the spin, which we can denote by χ_{m_s} , that is, $\chi_{-1/2}$ (“spin down”, $S_z = -\frac{1}{2}\hbar$) and $\chi_{+1/2}$ (“spin up”, $S_z = +\frac{1}{2}\hbar$). These can be taken to be orthonormalized, so that $\langle \chi_m, \chi_{m'} \rangle = \delta_{mm'}$.

A small exercise: What is $|\mathbf{S}|$ for a spin- $\frac{1}{2}$ particle? What is it for a particle with spin 1?

One more: What are the values that can be measured for S_z for a particle with spin $\frac{1}{2}$? What are the angles between \mathbf{S} and the z -axis corresponding to these measured values of S_z ? [Hint: See page 14 in Lecture notes 5.]

To describe the quantum-mechanical state of an electron completely, we have to use a “state function” which contains information not only on the *whereabouts* of the electron but also on the direction of its spin. In the absence of a magnetic field, the classical energy function and hence the Hamiltonian will be approximately independent of the spin direction. Simplifying slightly, we may then describe a one-particle state of an electron as a product of a spatial wave function (orbital) and the spin state χ . As an example,

$$\psi_{i,+1/2}(1) \equiv \psi_i(\mathbf{r}_1)\chi_{+1/2}(1)$$

describes a state where particle number 1 is in the spatial one-particle orbital $\psi_i(\mathbf{r})$ with $S_z = +\frac{1}{2}\hbar$.

Here, we can now note that the two-particle state

$$\psi(1, 2) = \psi_i(\mathbf{r}_1)\psi_i(\mathbf{r}_2) \cdot \frac{1}{\sqrt{2}} \left[\chi_{+1/2}(1)\chi_{-1/2}(2) - \chi_{-1/2}(1)\chi_{+1/2}(2) \right]$$

satisfies the antisymmetry requirement, although both electron 1 and electron 2 are in the same orbital $\psi_i(\mathbf{r})$. The “moral” is that the Pauli principle allows two electrons (but not more) to be in the same orbital, provided that the two spins are in the antisymmetric spin state

$$\chi_A(1, 2) = \frac{1}{\sqrt{2}} \left[\chi_{+1/2}(1)\chi_{-1/2}(2) - \chi_{-1/2}(1)\chi_{+1/2}(2) \right].$$

In this state the two spins actually are antiparallel, or opposite, as we say. This state is called the **singlet spin state**.

6.1.2 Atoms

a. Atoms without electron-electron interaction

Let us for a moment *neglect the repulsion* between the electrons, and let us also for simplicity suppose that the nucleus is at rest. (The latter is an excellent assumption for a heavy atom.) Then the Hamiltonian for an atom with atomic number Z is

$$\widehat{H} = \sum_{k=1}^Z \left[-\frac{\hbar^2}{2m} \nabla_k^2 - \frac{Ze^2}{4\pi\epsilon_0 r_k} \right].$$

Because this Hamiltonian consists of independent additive contributions, the Schrödinger equation $\widehat{H}\psi(\mathbf{r}_1, \dots, \mathbf{r}_Z) = E\psi$ will have solutions in terms of products of one-particle states:

$$\psi_{n_1 l_1 m_1}(\mathbf{r}_1) \psi_{n_2 l_2 m_2}(\mathbf{r}_2) \cdots \psi_{n_Z l_Z m_Z}(\mathbf{r}_Z).$$

Here, the one-particle states $\psi_{nlm}(\mathbf{r})$ are solutions of the Schrödinger equation for an electron in the Coulomb potential $-Ze^2/4\pi\epsilon_0 r$. The ground state for this atom (the state with the lowest possible total energy) is obtained by letting the electrons occupy the one-particle states with the lowest energies, with two electrons with opposite spins in each orbital.

Here we remember that the spectrum of the Coulomb potential is simple, as shown in the figure. We also remember that the degeneracy of level number n is n^2 .

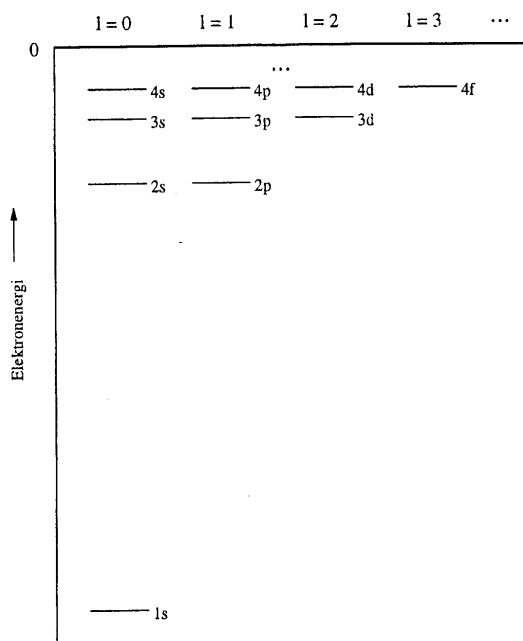


Fig. 1 One-particle states in the Coulomb potential.

This way we have two electrons in the lowest level, 8 in level no 2, etc, and $2n^2$ in level no n . Thus, in a world with no repulsion between the electrons, atoms with $Z = 2$ (helium), 10 (neon), 28 (nickel), ... would be exceptionally stable. (To change the state we would have to elevate an electron to the next level.)

As we all know, these elements are not the most stable ones. The reason of course is that we can *not* neglect the repulsion between the electrons:

b. The effective potential

A given electron will in reality feel a potential $V(\mathbf{r})$ which is weaker than the Coulomb attraction from the nucleus, due to the repulsion from the other $Z - 1$ electrons. If we pull this electron far out from the rest of the atom, it will “see” a net charge e and feel a net attractive potential $-e^2/4\pi\epsilon_0 r$, which is much weaker than the potential from the nucleus alone, $-Ze^2/4\pi\epsilon_0 r$.

In order to improve on the above (unsuccessful) model, we now approximate the atom as a system of Z independent electrons in an **effective** potential $V(\mathbf{r})$.

The question is how to find this effective potential $V(\mathbf{r})$, which in addition to the attraction from the nucleus shall take into account the average repulsion from the other electrons. If electron number i is in a one-particle state (orbital) $\psi_i(\mathbf{r})$, the corresponding charge density $-e|\psi_i(\mathbf{r}_i)|^2$ gives a contribution to the potential felt by the other electrons. The potential felt by electron number k thus is the sum of the nuclear attraction and the repulsion from the other electrons:

$$V(\mathbf{r}_k) = -\frac{Ze^2}{4\pi\epsilon_0 r_k} + \sum_{i(\neq k)} \int \frac{e^2 |\psi_i(\mathbf{r}_i)|^2}{4\pi\epsilon_0 |\mathbf{r}_k - \mathbf{r}_i|} d^3 r_i. \quad (\text{T6.8})$$

The wave function for electron number k thus satisfies a Schrödinger equation with the following potential:

$$\left[-\frac{\hbar^2}{2m} \nabla_k^2 + V(\mathbf{r}_k) \right] \psi_k(\mathbf{r}_k) = \epsilon_k \psi_k(\mathbf{r}_k). \quad (\text{T6.9})$$

Of course, from the outset we do not know the orbitals ψ_i in the expression for the potential energy. So what we have to do is so seek a **self consistent** set of orbitals, so that when they are inserted into the expression for the potential, they reproduce themselves as solutions. In practice, such a selfconsistent set of orbitals is found by iteration: A “start potential” is chosen. Using this potential, a set of orbitals is calculated. From these orbitals a new and improved potential is calculated (based on the Z states with lowest energies), and then used to obtain improved orbitals, etc. this procedure is repeated until a self consistent solution is obtained. In order to simplify the calculations, the effective potential is averaged over angles in each step of the iteration. This calculation scheme is called the **Hartree method**.

The Pauli principle is taken into account in that all the electrons are in separate one-particle states (two in each orbital, with opposite spins). In the scheme described above, we have “forgotten” to antisymmetrize with respect to interchange of particle coordinates. This can be done, and then results in somewhat modified equations which are known as the **Hartree-Fock equations**.

The main point in these methods is that we are describing the atomic structure in terms of orbitals based on a spherically symmetric effective potential $V(r)$. As you will understand, the detailed form of this potential (for a given atom) can only be found by the use of a fairly complicated numerical procedure. However, some of the main features of such potentials can be deduced rather easily:

With the (approximately) spherical effective potential, an electron will at a distance r from the nucleus feel the Coulomb force from the nuclear charge Ze and from that part of the “electronic cloud” which is inside a sphere with radius r . For *large* r , the total charge inside this sphere is approximately equal to $Ze - e(Z - 1) = e$. So, for large r the nuclear charge is almost completely “shielded” by the other $Z - 1$ electrons. If our electron moves inwards towards the nucleus, it will experience a force which gradually approaches the unscreened Coulomb force due to the nucleus, $-Ze^2/(4\pi\epsilon_0 r^2)$. Thus we can state that for large r the effective potential is approximately given by

$$V(r_k) \approx -\frac{e^2}{4\pi\epsilon_0 r_k}.$$

For small r , close to the nucleus, on the other hand, it follows from (T6.8) that

$$V(r_k) \approx -\frac{Ze^2}{4\pi\epsilon_0 r_k} + \frac{e^2}{4\pi\epsilon_0} \sum_{i \neq k} \int \frac{|\psi(\mathbf{r}_i)|^2}{r_i} d^3r_i = -\frac{Ze^2}{4\pi\epsilon_0 r_k} + \frac{e^2}{4\pi\epsilon_0} (Z-1) \langle 1/r \rangle,$$

where $\langle 1/r \rangle$ is the average of $1/r$ for the other electrons. Note that the (constant) second term on the right side corresponds to the work done by electron number k against the repulsive force from the other electrons if it travels from $r = \infty$ to $r = r_k \approx 0$.

Since the effective potential deviates from the pure $1/r$ form of the Coulomb potential, we can also state that the l -degeneracy will disappear, as discussed in Lecture notes 5. Thus the energy levels E_{nl} will depend both on n and l . We use the same notation ns , np , nd , ... for the levels as before. The ordering of these levels is not obvious. The positions of the lowest levels are shown in figure 2. We note that the principal quantum number n alone does not specify the energy, as it does for the hydrogen atom. The quantum number n now stands for $l + 1 + n_r$, where the radial quantum number n_r is the number of nodes of the radial function. As mentioned in Lecture notes 5, it turns out that the energy increases with l for a fixed n .

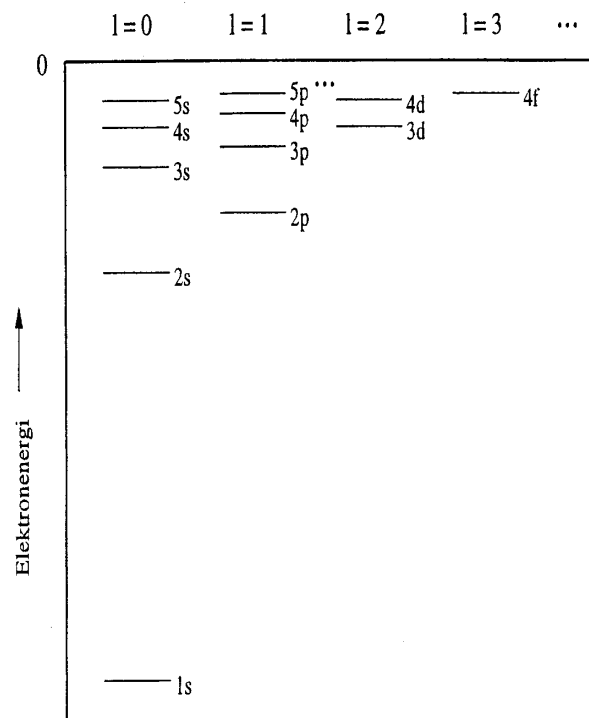


Fig. 2 Sequence of orbitals.

Note that the $4s$ level not only is lower than $4p$ and $4d$, but is even slightly lower than $3d$. Similarly the $5s$ level is slightly lower than $4d$ and $4f$. In fact, $4f$ is even higher than $6s$.

A small exercise: In the treatment of hydrogenlike atoms, we usually take the nucleus to be pointlike, calculating with a perfect Coulomb potential. Why is this a very good approximation, that is, why is the finite size of the nucleus of so little

importance in atomic physics? [Hint: The nuclear radii are given approximately by $A^{1/3} \cdot 10^{-15}$ m, where A is the nucleon number. Is it very probable to find an electron inside the nuclear radius, or what do you think? Note that “outside” the nucleus, the electron “sees” the field of a point charge.]

c. Electron configurations

The electron configuration of the ground state of an atom follows from the above sequence of energy levels, and is shown for the first 20 elements in the table below. The number of electrons in each level is shown as an upper index, so that $3s^2$ means that there are two electrons in the $3s$ orbital.

A small exercise: Two neutral atoms have the electron configurations

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5 \quad \text{and} \quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2.$$

What are the atomic numbers, and which elements are these? [See, e.g., Zumdahl.]

Z		Configuration
1	H	$1s^1$
2	He	$1s^2$
3	Li	$1s^2 2s^1$
4	Be	$1s^2 2s^2$
5	B	$1s^2 2s^2 2p^1$
6	C	$1s^2 2s^2 2p^2$
7	N	$1s^2 2s^2 2p^3$
8	O	$1s^2 2s^2 2p^4$
9	F	$1s^2 2s^2 2p^5$
10	Ne	$1s^2 2s^2 2p^6$

Z		Konfigurasjon
11	Na	$1s^2 2s^2 2p^6 3s^1 \equiv [Ne] 3s^1$
12	Mg	$1s^2 2s^2 2p^6 3s^2$
13	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$
14	Si	$1s^2 2s^2 2p^6 3s^2 3p^2$
15	P	$1s^2 2s^2 2p^6 3s^2 3p^3$
16	S	$1s^2 2s^2 2p^6 3s^2 3p^4$
17	Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$
18	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$
19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
20	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

The maximal number of electrons in a given level nl is $2(2l + 1)$; this is due to the m -degeneracy $2l + 1$ (which is common for all spherically symmetric potentials) and an extra factor 2 corresponding to the two spin directions. Elements for which all these degenerate states are occupied (that is, elements with “closed sub-shells”) are specially stable, because the energy difference to the next level is pretty large.

Based on this qualitative discussion we can understand some of the most important properties of the periodic system, like: (i) Elements with similar electron configurations for the most energetic levels have similar chemical properties, (ii) Noble gases (apart from helium) have a filled outer p -shell. Because the energy difference to the next d or s level is large, the electron configuration is not easily changed, and (iii) The elements with the largest chemical activity are those with one loosely bound (valence) electron in addition to filled shells, or elements which lack one electron in the outer shell.

In addition to this crude picture there are details, like the fact that an atom with two outer p -shell electrons prefers that these occupy two different p orbitals. We like to think that this is because the average distance between the electrons is largest when they occupy two different orbitals. (Carbon is an example.)

Some comments:

- The sizes of the atoms are not very different. (See e.g. Zumdahl.) This is due to the fact that when Z increases, and more orbitals are filled, the size of a given orbital (like those in the $2s$ and $2p$ subshells) shrinks. Cf the hydrogenlike atom, for which the size of an orbital scales with the factor $1/Z$.
- The ionization energy (the energy required to remove one electron from the atom) does not vary terribly much for the different elements. It lies in the range 5–15 eV. However, there are *some* differences: large ionization energy for noble gases, small ionization energy for alkali metals, with one valence electron outside closed shells.
- There is no limitation in principle on the number of sub-shells and orbitals that could be occupied by electrons. The reason that there are only about one hundred stable elements is that nuclei with larger Z are not stable.
- Last but not least, it should be noted that quantum mechanics gives a complete description, both qualitatively and quantitatively, of the chemical properties of the elements and their spectra.

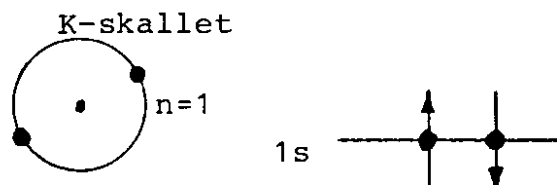
6.2 The periodic system

Let us consider more closely

6.2.1 The build-up of the elements

Helium ($Z = 2$)

In the ground state, both electrons occupy the $1s$ orbital. To satisfy the Pauli principle, the electrons have opposite spins. We note that the $1s$ orbital (also called the $1s$ shell or the K-shell) is now filled. This electron configuration is denoted by $1s^2$. Symbolically:



The ionization energy (that is, the energy which is required to remove one electron, also called the first ionization potential) is very large, 24.6 eV. Helium therefore (practically speaking) does not react (form compounds) with other atoms. It is the least reactive of all elements, occurs as a one-atomic gas, and condenses at a temperature as low as 4.2 K.

With one electron removed the helium ion is a hydrogenlike atom, where the electron has the ground-state energy

$$-\frac{1}{2}(2\alpha)^2 mc^2 \approx 4 \cdot (13.6 \text{ eV}) = -54.4 \text{ eV}.$$

This means that the average binding energy of the two electrons in the neutral helium atom is

$$\frac{1}{2}(24.6 + 54.4)\text{eV} = 39.5 \text{ eV}.$$

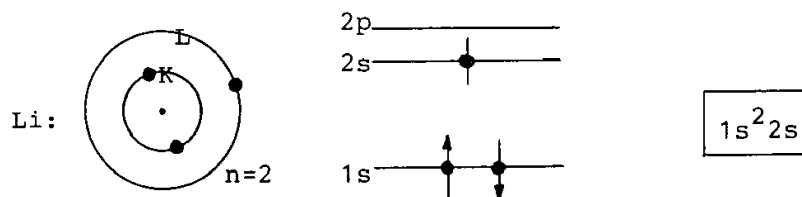
The fact that this average binding energy lies *between* the binding energies of hydrogen (13.6 eV) and He^+ (54.4 eV) is not very strange. If we follow one of the electrons and remember the above discussion of the “central-field approximation”, then this electron will “see” a force which is for *small* r approximately equal to the Coulomb force from the nucleus (with a charge $2e$). For *large* r , the nuclear charge is partly shielded by the charge of the other electron, and our electron will feel the force from a charge $\approx 2e - e = 1e$. “On the average” each of the electrons will thus roughly speaking feel that they are moving in the field of an “effective” charge which lies somewhere between $2e$ and $1e$. Based on the formula for the energy of a hydrogenlike atom, we can define an “effective charge number” Z_{eff} by setting

$$39.5 \text{ eV} = \frac{1}{2}(Z_{\text{eff}}\alpha)^2 mc^2.$$

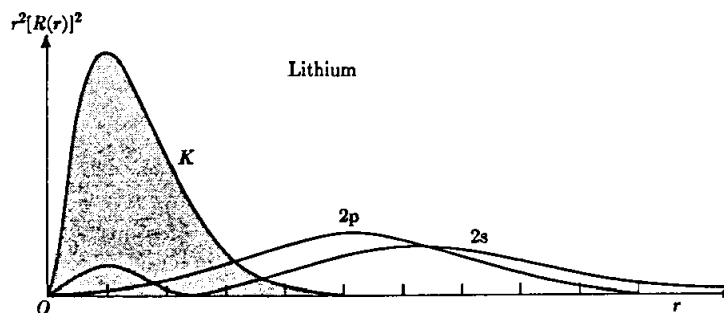
The result, $Z_{\text{eff}} \approx 1.7$, is a rough measure of how much the two $1s$ electrons shield for each other.

Lithium ($Z = 3$)

Two of the three electrons here fill the K-shell ($1s$). According to the exclusion principle, the third electron then has to go to the next lowest energy level, where it occupies one of the eight states of the L-shell ($n = 2$). The L-shell contains two sub-shells, the $2s$ orbital ($l = 0$) with two states, and the three $2p$ orbitals ($l = 1$) with six states. For hydrogen the two $2s$ states and the six $2p$ states were degenerate (l -degeneracy). For heavier atoms, where the effective potential deviates from the Coulomb form ($1/r$), there is no l -degeneracy, and the energies E_{nl} in general increase with l . In the ground state of Li, the third electron will therefore choose to be in a $2s$ state, so that the configuration of the ground state is $1s^2 2s$:



The figure shows the radial densities $P_{nl}^{\text{rad}}(r)$, for the two electrons in the K-shell and for the $2s$ and $2p$ states. These radial densities are qualitatively similar to those of the corresponding states of hydrogen, but the “scale” is of course diminished. The two $1s$ -electrons in the K-shell of lithium “see” an effective charge somewhere between 2 and 3, so that the “radius” of this K-shell is between 2 and 3 times smaller than the “radius” of the $1s$ orbital of hydrogen.



The sum of the radial densities of the $2s$ and $1s$ states gives the total radial electron density. As you can see, the $2s$ density overlaps with that of the K-shell. Therefore, the notion of “shells” should not be taken too literally.

The ionization energy required to remove the $2s$ electron turns out to be 5.4 eV. Repeating the rough argument above, we can then state that this electron experiences an effective attractive charge Z_{eff} given by

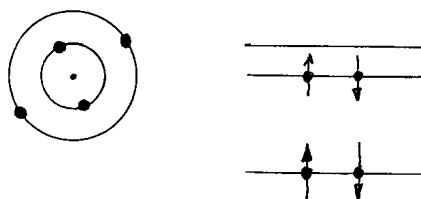
$$5.4 \text{ eV} = \frac{1}{2}(Z_{\text{eff}}\alpha)^2 \frac{mc^2}{2^2}, \quad \text{that is, } Z_{\text{eff}} \approx 1.26.$$

The moral is that when the last electron (here number 3) is forced by the Pauli principle to reside alone in an outer shell (here the L-shell), then the “overlap” with other shells is fairly small, so that the effective charge Z_{eff} and hence the binding energy are small.

The modest ionization energy of 5.4 eV implies that the lithium atom easily “gives away” the $2s$ electron. The ionization energy of the *next* electron (the so-called second ionization potential), on the other hand, is very high, 75.6 eV, that is, even higher than the first ionization potential of helium, which was 24.6 eV. (Note that the Li^+ ion is distinguished from the helium atom only by an extra proton charge in the nucleus.) Chemically, lithium therefore behaves as an element with **valence 1**.

A small exercise: What is the binding energy of the electron in the Li^{++} ion?
[Hint: Li^{++} has only one electron.]

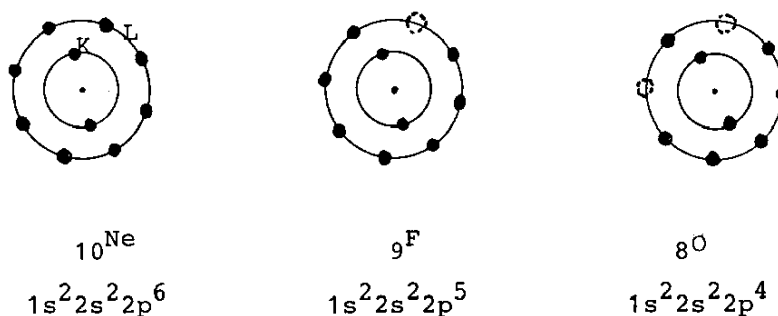
Beryllium ($Z = 4$)



Here the configuration is $1s^2 2s^2$. The ionization energy (the first ionization potential) is 9.3 eV, which is what is required to remove one electron. To remove one more costs an additional 18.2 eV. Thus the average binding energy of the two $2s$ electrons is about 13.7 eV. This corresponds to an average charge number slightly larger than 2. Again we can state that the two electrons will partly shield the nucleus for each other, but this to a certain extent compensated by the fact that part of the time these electrons are moving so close to the nucleus that they feel a charge larger than $2e$. This explains why the effective charge number here is larger than 2.

Boron, carbon, nitrogen, oxygen, fluorine, neon ($Z = 5 - 10$)

For these elements the six orbitals of the $2p$ subshell are filled successively. As Z is increased from 5 to 10, these orbitals are gradually bound more closely to the nucleus. For neon, for which both the K- and L-shells are completely filled, we find an ionization energy which is almost as high as for helium (21.6 eV). This means that the neon atom does not give away an electron to other atoms. Like helium, it also rarely forms a negative ion (with an extra electron). In other words, its electron affinity is very small. (An extra electron would have to be in a $3s$ state. Since the $3s$ orbital overlaps very little with the K- and L-shells, an extra ($3s$) electron would see an effective charge very close to zero.)



Flourine, on the other hand, with its nine electrons has one unoccupied $2p$ state in the L-shell. This state overlaps considerably with the other five $2p$ states, in the sense that if a tenth electron is placed in this state, it will experience a considerable effective attractive charge. This is reflected by the fact that fluorine has a considerable electron affinity: When a free electron is “captured” by a fluorine atom forming an F^- ion, the energy released is 3.6 eV. Thus fluorine has the valence -1 .

Oxygen, with the configuration $1s^2 2s^2 2p^4$, has two unoccupied $2p$ states. This atom therefore readily forms compounds where it “borrows” two electrons from the other atoms (example: H_2O), and thus has the valence -2 .

Note that the full shells of neon imply a spherically symmetric charge distribution. For a subshell (n, l) where all the states are occupied we have

$$\sum_m |\psi_{nlm}|^2 = [R_{nl}]^2 \sum_m |Y_{lm}(\theta, \phi)|^2, \quad (\text{T6.10})$$

where the sum over m in general can be shown to be equal to $(2l + 1)/4\pi$, and thus is independent of θ and ϕ .

A small exercise: Check that this is satisfied for the set $Y_{10}, Y_{1,\pm 1}$, and for the alternative set

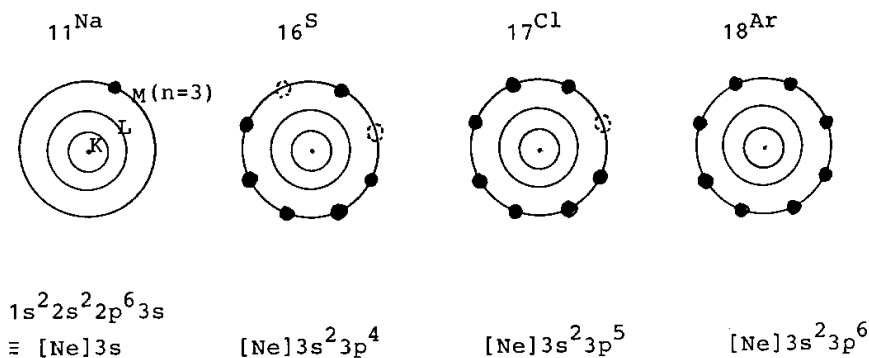
$$Y_{pz} \equiv Y_{10} = \sqrt{\frac{3}{4\pi}} \frac{z}{r}, \quad Y_{px} = \sqrt{\frac{3}{4\pi}} \frac{x}{r}, \quad Y_{py} = \sqrt{\frac{3}{4\pi}} \frac{y}{r}.$$

This is part of the reason that the central-field approximation (discussed in section 6.1.2) works so well, particularly for heavy atoms, where the majority of the electrons occupy filled shells.

6.2.2 The periodic system. Chemical properties

Sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, argon ($Z = 11 - 18$)

Here, the two $3s$ states and the $3p$ states are filled successively, in the same manner as the filling of the $2s$ and $2p$ orbitals were filled for the sequence lithium – argon. We can therefore repeat the above story for these elements:



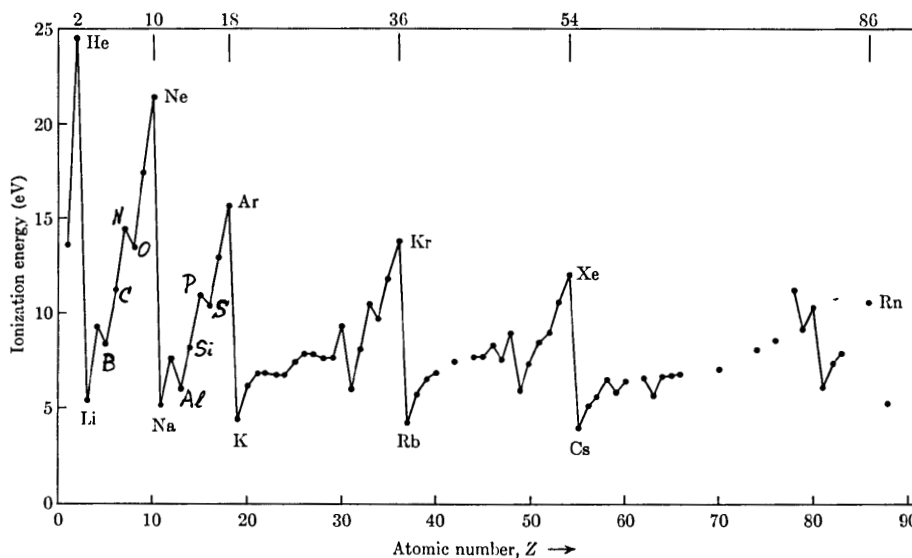
The eleventh electron of sodium sits alone in the M-shell ($n = 3$), in a $3s$ state. Sodium therefore has valence 1, like lithium. For argon — the last elements in this sequence — the sub-shells $3s$ and $3p$ are full, and we encounter yet another noble gas, with a particularly stable electron configuration. Chlorine and sulphur lack respectively one and two electrons to have a full $3p$ shell, and therefore have respectively valences -1 and -2 , like fluorine and oxygen.

The chemical properties of the elements sodium – argon are in general very similar to those of lithium – neon. The reason is that these properties are determined primarily by the wave functions of the outer electrons. The outer parts of these wave functions for e.g. lithium and sodium are very similar. [The $3s$ electron in sodium “sees” the effective charge of the nucleus and the K and L electrons, which is close to $11e - 10e = e$, that is, roughly equal to the effective charge “seen” by the $2s$ electron in lithium.]

For increasing atomic numbers, one finds several such sequences of elements. Thus the chemical properties vary in a periodic manner. This periodic pattern is called the **periodic system**, and is shown in the table below. The columns in this table contain **groups** of elements with similar chemical properties. The *lines* in the table are called **periods**.

1s	1	H																	2	He																																							
2s	3	Li	4	Be																																																							
3s	11	Na	12	Mg																																																							
4s	19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	$4s^1 3d^5$	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	$4s^1 3d^{10}$	30	Zn																																	
5s	37	Rb	38	Sr	39	Y	40	Zr	41	Nb	$5s^1 4d^4$	42	Mo	43	Tc	44	Ru	$5s^1 4d^7$	45	Rh	$5s^1 4d^8$	46	Pd	$5s^0 4d^{10}$	47	Ag	$5s^1 4d^{10}$	48	Cd																														
6s	55	Cs	56	Ba	57	La	Lanthanides	72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	$6s^1 5d^9$	79	Au	$6s^1 5d^{10}$	80	Hg																																
7s	87	Fr	88	Ra	89	Ac	Actinides																																																				
	s^1	s^2																	p^1	p^2	p^3	p^4	p^5	p^6																																			
																	5	B	6	C	7	N	8	O	9	F	10	Ne																															
																	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar																															
																	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr																															
																	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe																															
																	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn																															
																	6p																																										
																	7p																																										
																	4f	58	Ce	$5d^0 4f^2$	59	Pr	$5d^0 4f^3$	60	Nd	$5d^0 4f^4$	61	Pm	$5d^0 4f^5$	62	Sm	$5d^0 4f^6$	63	Eu	$5d^0 4f^7$	64	Gd	$5d^0 4f^7$	65	Tb	$5d^0 4f^9$	66	Dy	$5d^0 4f^{10}$	67	Ho	$5d^0 4f^{11}$	68	Er	$5d^0 4f^{12}$	69	Tm	$5d^0 4f^{13}$	70	Yb	$5d^0 4f^{14}$	71	Lu	$5d^1 4f^{14}$
																	5f	90	Th	$6d^2 5f^0$	91	Pa	$6d^1 5f^2$	92	U	$6d^1 5f^3$	93	Np	$6d^1 5f^4$	94	Pu	$6d^1 5f^6$	95	Am	$6d^1 5f^7$	96	Cm	$6d^1 5f^7$	97	Bk	$6d^1 5f^8$	98	Cf	$6d^0 5f^{10}$	99	Es	$6d^0 5f^{11}$	100	Fm	$6d^0 5f^{12}$	101	Md	$6d^0 5f^{13}$	102	No	$6d^0 5f^{14}$	103	Lw	$6d^1 5f^{14}$
																	f^1	f^2	f^3	f^4	f^5	f^6	f^7	f^8	f^9	f^{10}	f^{11}	f^{12}	f^{13}	f^{14}																													

The periodicity is reflected in several properties of the atoms, like e.g. the atomic radii (see Zumdahl), the electron affinity (Zumdahl) and the ionization energies. The figure shows the ionization energy as a function of the atomic number Z .

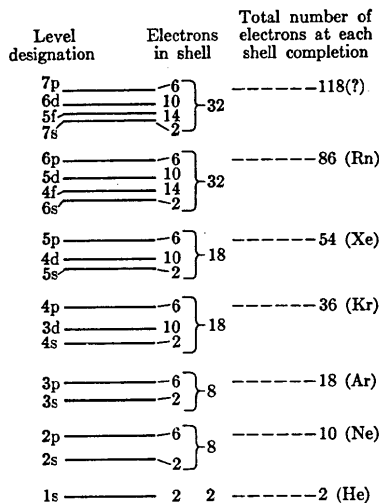


Potassium ($Z = 19$), etc

For potassium, one would naively expect to find the last electron in a $3d$ orbital. However, as shown in the table, it actually occupies a $4s$ state, so that potassium chemically belongs to the group of **alkali metals** (lithium, sodium, potassium, rubidium, cesium, ..). The reason is that the $3d$ orbitals, due to the high angular momentum ($l = 2$), in fact have a higher

energy than the 4s level, even if the latter has a higher principal quantum number ($n = 4$, and radial quantum number $n_r = n - l - 1 = 3$).

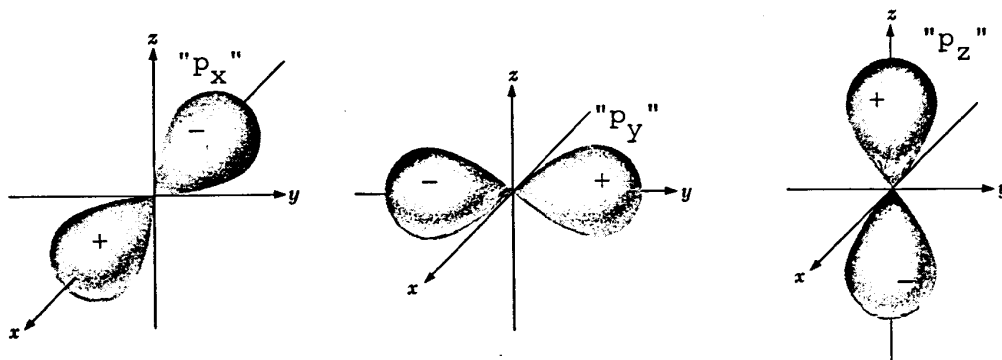
The filling sequence of the periodic system is determined by the following schematic display of the energy levels:



Here, we note that the 4s, 3d and 4p orbitals can accommodate altogether $2 \cdot 1 + 2 \cdot (2 \cdot 2 + 1) + 2 \cdot (2 \cdot 1 + 1) = 2 + 10 + 6 = 18$ electrons. The successive filling of these states corresponds to the fourth period of the periodic system. The fifth period has the same length, since it corresponds to the successive filling of the 5s, 4d and 5p subshells. Period number six, on the other hand, contains as many as 32 elements. This period corresponds to the successive filling of 6s, 5d, 4f (the lanthanides) and 6p (altogether $2 + 10 + 14 + 6 = 32$).

The periods of 2, 8, 8, 18, 18 and 32 are also evident in the diagram showing the ionization energies.

Let us focus in particular on the ionization energies for the elements from boron to neon, which correspond to the successive filling of the six 2p states. Here, one would perhaps expect that the ionization energy should increase for each step, being smallest for boron with only one 2p electron, and largest for neon which has a full 2p shell. This is what we would expect naively, but as shown in the diagram the steady increase is “broken” by oxygen, for which the last electron is more weakly bound than we would expect. To understand this, we take as our starting point boron, where the single 2p electron can choose between six possible states — two spin directions combined with three spatial 2p orbitals, which differ from each other only by their angular dependence. For the latter we can use the three functions Y_{p_x} , Y_{p_y} and Y_{p_z} mentioned above. Which one we choose is of no importance physically, since the orientation of the axes is quite arbitrary.



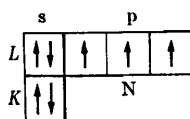
Next let us consider carbon, with *two* $2p$ electrons, and imagine that one of these chooses a state with the orbital angular function Y_{p_z} . The question then is: Which state will the other $2p$ electron choose? If we think a little beyond the central-field approximation, and consider the Coulomb repulsion between the two electrons, it seems clear that the electron will find it an advantage to choose one of the other orbitals, e.g. a p_x orbital. The two electrons will then on the average be farther away from each other than they would be if they were both in the same orbital ψ_{2p_z} (with opposite spins). The “moral” is as always: The ground state is the configuration with the lowest possible total energy.

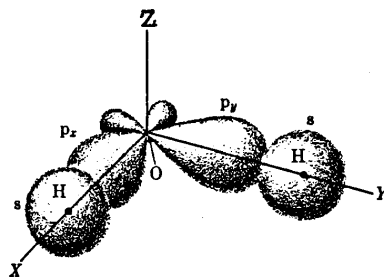
Following the same line of thought, we would expect that the three $2p$ electrons of nitrogen choose one orbital each (ψ_{2p_x} , ψ_{2p_y} and ψ_{2p_z}), and that turns out to be the case.¹

For the next element, oxygen, we have four $2p$ electrons, three of which can of course choose to be in separate $2p$ orbitals. The fourth electron, however, has to be in the same orbital as one of the first three. Between these two electrons in the same orbital we must assume that the repulsion is somewhat larger than between electrons in different orbitals. This will increase the total energy a little more than in the previous steps, and possibly is the explanation of the fact that the ionization energy of oxygen is slightly smaller than for nitrogen; cf the diagram.

Based on these arguments we can also try to understand the structure of H_2O . Oxygen lacks two electrons to have a full $2p$ shell. Suppose that the two unoccupied states in the $2p$ subshell is one in $2p_x$ and one in $2p_y$. In forming the water molecule, the oxygen atom tries to fill these vacancies by “borrowing” the two electrons of the two hydrogen atoms (at least part of the time). From this argument, we should expect a structure where the two protons and the oxygen nucleus make an angle close to 90 degrees. Experimentally this angle is about 104.5 degrees.

¹At the same time it turns out that the three spins of the $2p$ electrons are parallel. Thus, it is an experimental fact that the atoms in the ground state prefer a maximal resulting spin, This is one the so-called **Hund’s rules**. Illustration for nitrogen:





This deviation can be understood from the fact that the two protons, which part of the time are “stripped” of their electrons, experience repulsion. The total energy will therefore be minimal when the angle mentioned is somewhat larger than 90 degrees.

6.3 Molecules and solids

Molecules and solids are stable configurations of two or more atoms. From chemistry we know that the about one hundred elements can be combined to a vast number of molecules, with different composition, form, size and other properties. These molecules are the building blocks of innumerable inorganic and organic compounds.

The study of molecules raises many interesting questions: What makes the atoms stay together? Should we consider the molecule as an aggregate of atoms, or is it more fruitful to consider it as a collection of nuclei and electrons, where an electron is free to move anywhere in the collective field from the nuclei and the other electrons.

The answer to the last question is both yes and no. Thus, when e.g. two atoms form a two-atomic molecule, we make no big mistake in assuming that the inner electrons of each atom are so strongly bound to their respective nuclei that their states are approximately the same as when the two atoms are separated. For the outer electrons, however, this picture becomes wrong. For these we have to take into account that they are moving in the combined field of two ions lying fairly close together. The wave functions (**molecular orbitals**) for these outer electrons therefore become very different from atomic orbitals.²

We shall see that these differences for the outer electrons also answers the first question, about what binds together the atoms, which from the outset are neutral particles. The binding mechanisms can be divided crudely into two types, **ionic binding** and **covalent binding**.

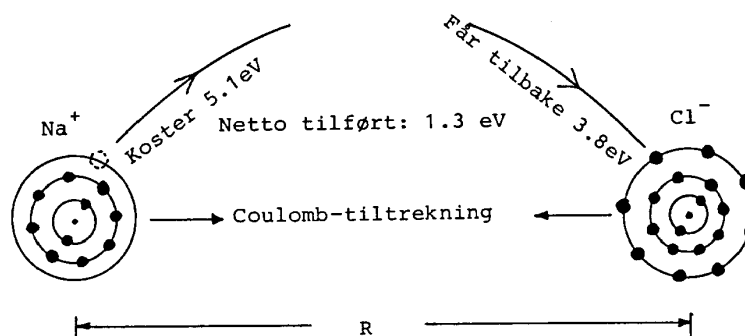
6.3.1 Ionic binding

Ionic binding typically occurs in salts like NaCl (common kitchen salt) and LiF (lithium fluoride). To understand why a sodium atom and a chlorine atom find it energetically favourable

²In principle, *all* the electrons move in molecular orbitals, as we shall see in the “chemical part” of this course. But as mentioned above, this is most important for the outer electrons, and one makes no big mistake by neglecting it for the inner electrons.

to form a molecule, we shall try to apply classical electrostatic energy considerations, where our starting point is a neutral sodium atom isolated by a large distance from a neutral chlorine atom.

We remember that chlorine is one electron short of having a full $3p$ shell (M-shell), while sodium has a single electron in the M-shell. It costs only 5.1 eV (the ionization energy) to remove this electron from the isolated sodium atom. This electron can be offered to the chlorine atom, which gladly accepts it and “pays” 3.8 eV for it. (This means that the 3.8 eV is released when the free electron and the chlorine atom form a Cl^- ion. This is the electron affinity of chlorine.) Thus the net cost of changing the two isolated neutral atoms into two isolated ions is $5.1 \text{ eV} - 3.8 \text{ eV} = 1.3 \text{ eV}$, when the distance R between them is kept large.



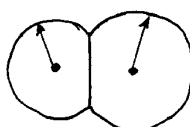
This expense is compensated, and more than that, if we let the two ions (Na^+ and Cl^-) merge into a molecule: With an experimental equilibrium distance of $R_0 \approx 2.5 \text{ \AA}$ between the two nuclei, the energy released because of the Coulomb attraction will be of the order of

$$V(\infty) - V(R_0) = \frac{e^2}{4\pi\epsilon_0 R_0} = \frac{\hbar^2}{2ma_0^2} \frac{2a_0}{R_0} \approx 13.6 \text{ eV} \cdot \frac{2 \cdot 0.53}{2.5} \approx 5.8 \text{ eV}.$$

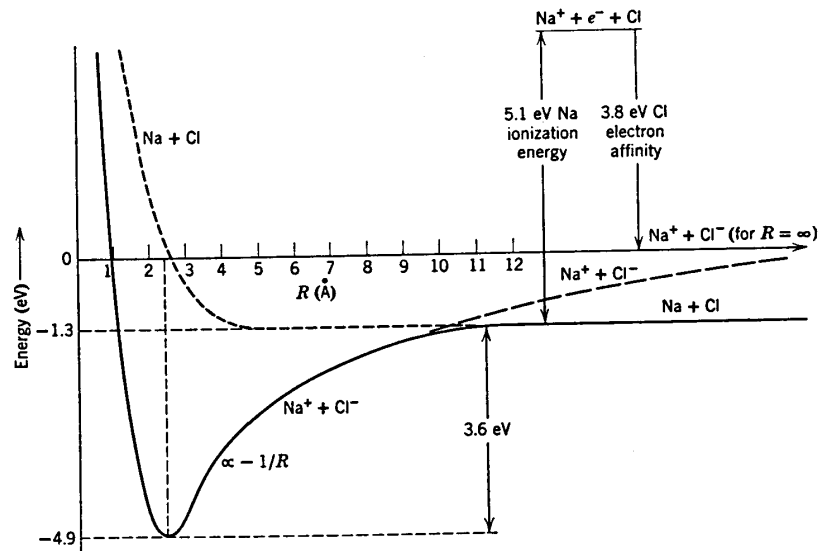
This simple estimate indicates that the net energy released in the formation of an NaCl molecule from the two neutral atoms is approximately $5.8 \text{ eV} - 1.3 \text{ eV} = 4.5 \text{ eV}$.

Experimentally, one finds that the binding energy is 3.6 eV. The main reason that the above estimate does not quite agree with the experimental value lies in what happens when the two ions (which at large distances are spherically symmetric) come into contact with each other and come close to the equilibrium distance. Then the two “electron clouds” start to “overlap”. Because of the Pauli principle, some of the electrons are then pushed away from the region of overlap. Otherwise the electron density in this overlap region would become higher than in the neighbourhood. The electrons which are pushed away, must find a new place, farther away from the nuclei than they would otherwise prefer.³ This costs energy. As a result, the total force between the two ions no longer is given by the Coulomb

³This can be compared with what happens when two soap bubbles come into contact (without merging into a single bubble); then the radii increase, because the total volume is approximately constant.



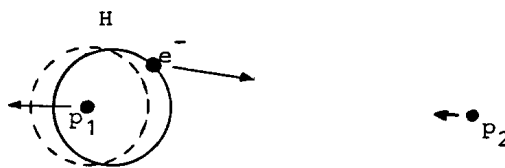
force ($-e^2/4\pi\epsilon_0 R^2$), but decreases towards zero when R decreases towards the equilibrium distance R_0 , and even becomes repulsive if we try to make R smaller than R_0 . A reasonably realistic potential corresponding to this force is shown in the figure. (See the curve marked $\text{Na}^+ + \text{Cl}^-$.)



6.3.2 Covalent binding

The most prominent form of covalent bindings is that found in the so-called homonuclear molecules, like H_2 , O_2 , N_2 etc. Here, the two atoms take part in the binding on an equal footing. Ionic binding is therefore completely excluded in these cases.

We shall try to understand the nature of the covalent binding by considering the simplest of all the examples, which is that of the hydrogen molecule ion H_2^+ , composed of two protons and one electron.



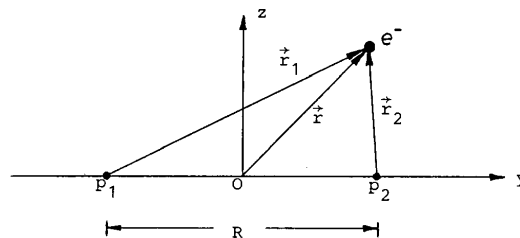
A simple way of considering this binding is to think of the H_2^+ ion as a proton (p_2) bound to a hydrogen atom (p_1, e^-). If we start out with the proton p_2 and the hydrogen atom very far away from each other, there will then be a negligible force between them, because the hydrogen atom is neutral and spherically symmetric (so that it has e.g. no dipole moment). If we let the proton p_2 approach the atom, however, we understand that the electric field surrounding p_2 will polarize the hydrogen atom, meaning that the electron e^- is pulled slightly *towards* p_2 , while the proton p_1 is pushed slightly *away*. On the average, the attractive force on e^- therefore becomes slightly larger than the repulsive force on p_1 . Thus we get a resulting attraction between the proton p_2 and the hydrogen atom, analogous to the force between a point charge and an electric dipole. This force increases with decreasing distance, also because the polarization of the atom increases. This increase continues until p_2 enters

the “electron cloud” of the hydrogen atom. Then the repulsion between p_1 and p_2 will at last become so large that the resulting force becomes zero. The equilibrium distance between the two protons turns out to be 1.06 \AA , and the binding energy is 2.65 eV (which is the energy required to remove p_2 from H_2^+ again).

At this equilibrium distance, we must expect to find a certain enhancement of the probability density of the electron (and hence also of its “charge density”) in the region between the protons. Thus, in a way it is the electron that keeps the two protons together.

To improve on this semiclassical description, we have to treat the problem using quantum mechanics. Instead of talking about a hydrogen atom and a proton, it is then most rewarding to regard the problem as one in which the electron is moving in the total potential due to the two protons:

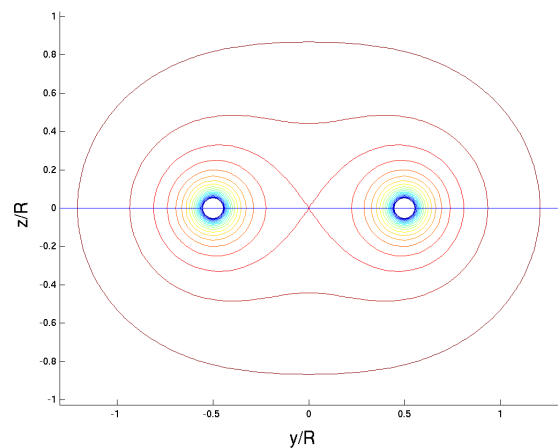
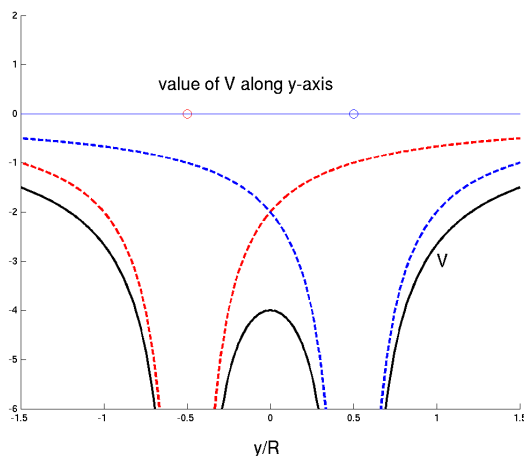
$$V(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right).$$



Suppose that the protons are kept at rest at a fixed distance R . By solving the time-independent Schrödinger equation for the electron, it is then possible to find the energy for a given type of wave function. This energy will depend on R . The total energy of this three-particle system then is

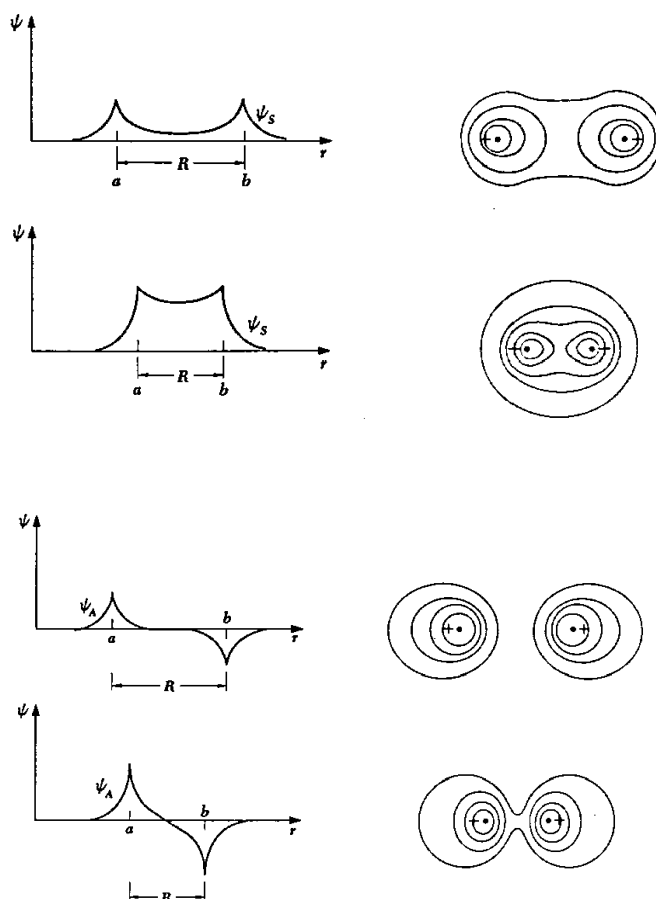
$$E_{\text{tot}}(R) = E(R) + \frac{e^2}{4\pi\epsilon_0 R},$$

where the last term represents the repulsion between the two protons. If this sum has a minimum for a certain distance R_0 , and if this minimal value $E_{\text{tot}}(R_0)$ is smaller than -13.6 eV (which is the energy of the electron in the isolated hydrogen atom), then we have a stable state for H_2^+ .



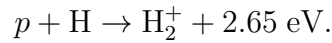
To actually solve the Schrödinger equation for the potential $V(\mathbf{r})$ above is fairly complicated. Presently we must therefore content ourselves with a *qualitative* discussion. If we choose our coordinate system as suggested above, with the two protons on the y -axis, equally far away from the origin, we understand that the potential will be symmetric with respect to the xz -plane (which is perpendicular to the paper plane). The figure on the left above shows how $V(\mathbf{r}) = V(x, y, z)$ then varies along the y -axis. (In units of $e^2/(4\pi\epsilon_0 R)$ the potential along the y -axis is given by $-1/|y/R + 0.5| - 1/|y/R - 0.5|$.) The dashed lines show the separate contributions from the two protons. The solid lines show the resulting potential, which is seen to be significantly deeper than the contribution from either of the protons. The figure on the right shows equi-potential curves in the yz -plane. By rotating these around the y -axis, we obtain equi-potential *surfaces*.

The states with the lowest energies in this potential will have $L_y = 0$, so that they are rotationally symmetric about the y -axis. Because the *potential* is symmetric with respect to the xz -plane, such a rotationally symmetric state must then be either symmetric or antisymmetric with respect to the xz -plane. This is illustrated in the figures below, which suggest how the wave functions (that is, the molecular orbitals) for the lowest symmetric and the lowest antisymmetric state behave along the y -axis, for two different proton-proton distances R .

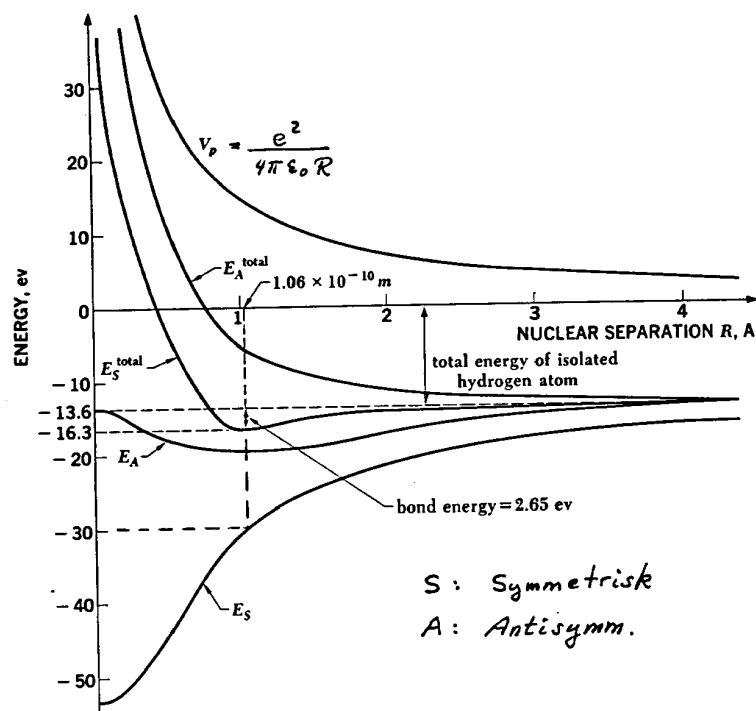


The “contour maps” on the right in these figures illustrate the behaviour of the wave functions in a plane through the y -axis. Note that the probability of finding the electron in the region *between* the two protons is largest for the symmetric state (because the antisymmetric is zero in the xz -plane, which is then a nodal plane for this state).

The curves in the diagram below show the electron energy $E(R)$ and the total energy $E_{\text{tot}}(R)$ as functions of the distance R between the two protons. For the symmetric state one finds that E_{tot} has a minimum of -16.3 eV for $R = R_0 = 1.06 \text{ \AA}$, in agreement with the experimental results. Remembering that the energy of the electron in the isolated hydrogen atom is -13.6 eV, we understand that this result implies that the binding energy of H_2^+ is 2.65 eV (which is the value mentioned above);



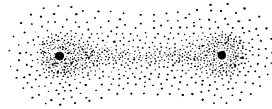
For the antisymmetric state, on the other hand, one does not find a minimum. This simply means that an electron in such an antisymmetric state is not able to keep the three particles in H_2^+ together; the antisymmetric molecular orbital is a *non-bonding* orbital.



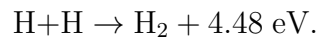
At the equilibrium distance $R_0 = 1.06 \text{ \AA} (\approx 2a_0)$, the repulsion between the two protons corresponds to a positive potential energy of 13.6 eV. What still makes H_2^+ more stable than an isolated hydrogen atom and a proton, is that the energy E_S of the electron in the symmetric molecular orbital is as low as -29.9 eV.

This is more than twice as low as in the limit $R \rightarrow \infty$. In this limit, E , $\langle K \rangle$ and $\langle V \rangle$ are the same as for the electron in the isolated hydrogen atom, namely $E = -13.6$ eV, $\langle K \rangle = -E = 13.6$ eV and $\langle V \rangle = 2E = -27.2$ eV. (Note that this holds both for the symmetric and the antisymmetric state, in the limit $R \rightarrow \infty$.) It can be shown that the relations $\langle K \rangle = -E$ and $\langle V \rangle = 2E$ hold also at the equilibrium distance, $R = R_0 \approx 1.06 \text{ \AA}$. Thus we can state that when R is decreased from ∞ to R_0 , then $\langle V \rangle$ has “grown” from $2 \cdot (-13.6 \text{ eV}) = -27.2 \text{ eV}$ to $2 \cdot (-29.9 \text{ eV}) = -59.8 \text{ eV}$ (and also the kinetic energy $\langle K \rangle$ has in fact increased, from 13.6 eV to 29.9 eV). This strong increase of $\langle V \rangle$ takes place because the electron here is moving in the much deeper total potential from the two protons (see the potential figure above). Note also that in the symmetric state

a considerable fraction of the “probability cloud” is found in the region between the two protons, where the electron feels the attraction from both protons.



The conclusion is that the covalent binding is due to the fact that the resulting potential is so deep that the energy (of the **bonding** molecular orbital) becomes *more than low enough* to compensate for the repulsion between the nuclei. Based on these considerations for H_2^+ , we can also understand qualitatively the binding in the neutral hydrogen molecule, H_2 . Here, the exclusion principle allows both electrons to be in the symmetric (bonding) molecular orbital, with opposite spins. This gives a stronger binding than in H_2^+ , with an equilibrium distance $R_0 \approx 0.74 \text{ \AA}$ and a binding energy which is almost twice as large:



More generally, we can state that the covalent binding between two atoms (with one unpaired electron each) is caused by the two electrons sharing a molecular orbital, with opposite spins.

A small exercise: Consider an H_2^+ -like system, where one electron is moving in the potential from two protons (p_1 and p_2) which we imagine are being kept fixed at a distance R . Let ψ_1 and ψ_2 be $1s$ orbitals (hydrogen orbitals) centered respectively around p_1 and p_2 , so that $(\widehat{K} + V_1)\psi_1 = E_1^{\text{H}}\psi_1$ and $(\widehat{K} + V_2)\psi_2 = E_1^{\text{H}}\psi_2$. Here, V_1 corresponds to the Coulomb force between the electron and p_1 (and V_2 corresponds to the Coulomb force between the electron and p_2), and $E_1^{\text{H}} \approx -\frac{1}{2}\alpha^2 m_e c^2 (\approx -13.6 \text{ eV})$.

a. First, suppose that the distance R between p_1 and p_2 is much larger than the Bohr radius a_0 , and argue that the linear combinations $\psi_{\pm} \equiv (\psi_1 \pm \psi_2)/\sqrt{2}$ are approximate eigenfunctions of the Hamiltonian $\widehat{H} = \widehat{K} + V_1 + V_2$ for the H_2^+ -like system. Hint: Show that $\widehat{H}\psi_{\pm} \approx E_1^{\text{H}}\psi_{\pm}$, because $V_2\psi_1$ and $V_1\psi_2$ both are small when R is large.

b. Then suppose that R is forced to be much *smaller* than a_0 , so that the system becomes approximately hydrogenlike, with a “nucleus” with charge $2e$. What is then the ground-state energy?

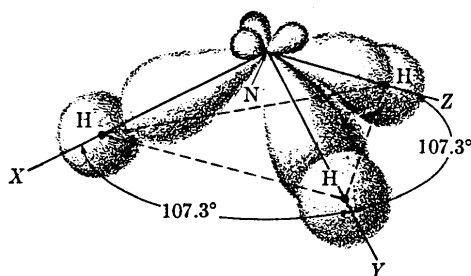
c. Suppose now that R is arbitrary, and imagine a coordinate system with the z -axis along the line connecting p_1 and p_2 and with the origin at the midpoint of this line. Explain why \widehat{L}_z , \widehat{H} and the parity operator \mathcal{P} all commute. Hint: Convince yourself that the potential $V = V_1 + V_2$ is independent of the azimuthal angle ϕ .

d. Show that the linear combinations ψ_{\pm} above are eigenfunctions of both \mathcal{P} and \hat{L}_z and state what the eigenvalues are.

In a two-atomic molecule consisting of two different atoms, one of these can be more attractive for the bonding electrons than the other. There is therefore not always a sharp distinction between pure covalent bindings (like those in H_2 , O_2 , etc) and pure ionic bindings (like that in NaCl).

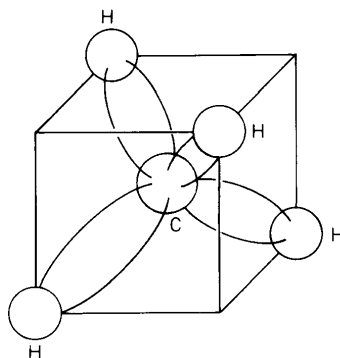
It should also be noted that atoms with several unpaired electrons can form compounds with several covalent bonds. An example is N_2 , where the three unpaired electrons of the nitrogen atom allows the molecule to form three bonding pairs, in three different molecular orbitals. This molecule therefore is very strongly bound. Another example is oxygen. This atom has two unpaired electrons, which can take part in two covalent bonds, like those found in H_2O .

As already discussed, this leads to a definite geometry for the water molecule. A similar effect is observed for the ammonia molecule NH_3 , where the three protons and the nitrogen nucleus form a pyramid, as indicated in the figure.



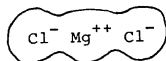
This geometry can be “understood” starting with the three orbitals ψ_{2p_x} , ψ_{2p_y} and ψ_{2p_z} of nitrogen. The reason that the angles of the molecule are larger than 90 degrees again is that the three protons, which part of the time are “stripped” of their electrons, repulse each other. The “moral” is as always that a molecule in its ground state chooses a configuration that minimizes the energy.

A third example is methane, CH_4 , which is treated in one of the exercises. Here, each of the four hydrogen electrons shares a molecular orbital with a carbon electron. It turns out that the configuration which minimizes the energy contains four molecular orbitals which have a certain similarity with the the four sp^3 orbitals of the $2p$ level of hydrogen (studied in the exercise). In this configuration, the “equilibrium positions” of the four protons constitute a regular tetrahedron, with the characteristic angles of 109.5 degrees:



This type of “directed” chemical bonding is characteristic for many carbon compounds (like e.g. diamond; see below).

This form of “directed” bonding does *not* occur when the binding is pure ionic. An example is magnesium chloride, MgCl_2 , which can be regarded as $\text{Cl}^- \text{Mg}^{++} \text{Cl}^-$, where all the three ions have full shells and therefore from the outset have spherical charge distributions. When these ions form a molecule, we would expect that the two negative chlorine ions prefer to stay as far away from each other as possible, that is, to form a linear molecule. This is what actually happens.



In this chapter we have so far neglected the motion of the *nuclei* in the molecules. Firstly, the molecules can *vibrate* around their equilibrium positions, which they are in fact obliged to do, because of the uncertainty principle. For a two-atomic molecule we have seen that the vibrational degree of freedom can be treated approximately as a harmonic oscillation; cf the exercise where we found that the “amplitudes” of the vibration are small compared to the equilibrium distances between the nuclei. For molecules containing more than two atoms, there will be several vibrational modes (corresponding to stretching, bending, torsion, etc). In addition the molecules can of course rotate, when in the gaseous phase. Also the rotational degree of freedom is quantized; cf the quantization of the rigid rotator.

6.3.3 Binding in solids

In solids, we can distinguish between four main types of binding: molecular binding, ionic binding, covalent binding and metal binding.

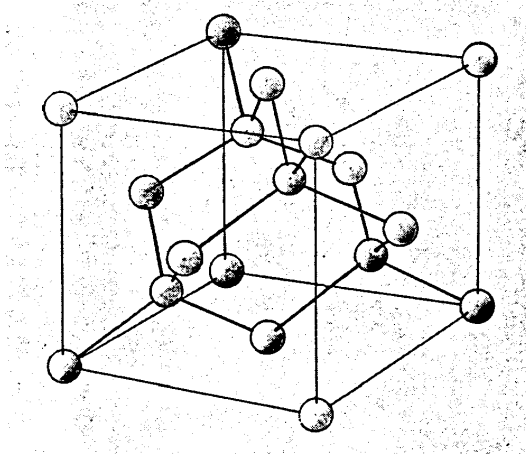
Molecular binding occurs in compounds where the molecules retain most of their individuality and interact only very weakly with neighbour molecules. This requires that the molecules have zero electric dipole moment and no unpaired electrons which could give rise to covalent bonds. Examples are the noble gases (with one-atomic “molecules”) and compounds like CH_4 , Cl_2 , I_2 , CO_2 etc, which all occur as gases at normal temperature and pressure. The bindings are so weak that the boiling and melting points lie close to the absolute zero. Most extreme in this respect is helium, which has a boiling point of 4.2 K, and which does not freeze at all, not even at zero degrees Kelvin. To obtain solid helium we need a pressure of 20 atmospheres at $T = 0$.

To understand that there can be any force at all between these molecules, we must take into account that the motion of the electrons cause fluctuations of the charge distributions. These fluctuations will give rise to fluctuating electric dipole moments (with zero average). These dipole moments will polarize the neighbour molecules, and cause an attractive so-called van der Waals force between the molecules. This force is very weak and decreases with the distance as R^{-7} . This type of binding is also called a **van der Waals binding**.

Ionic binding occurs e.g. in kitchen salt, NaCl . The crystal then consists of a densely packed structure of alternating Na^+ and Cl^- ions, which from the outset have spherical “charge clouds”. The ions therefore are packed together much like two kinds of spheres, where each ion tries to be surrounded by as many ions of the other kind as possible, and as

closely as possible. What is the most stable structure (geometry) depends on the relative size of the two ion types. Ionic bindings are very strong, corresponding to high melting temperatures. Because of the filled electronic shells there are no free electrons. These salts therefore are electric insulators.

Covalent binding occurs e.g. in diamond, where each carbon atom forms four covalent bonds with neighbour atoms. As shown in the figure, we again have the tetrahedral structure, where each carbon atom is bound to four neighbours.



This binding is very strong, and makes diamond a very hard material, with an extremely high melting point. “Covalent” compounds are electric insulators, because all the outer electrons are “confined” in their bonds.

Metal binding occurs in its most typical form in the alkali metals Li, Na, etc. As we remember, these have one loosely bound (valence) electron, which is easily released. In the metal, the positive ions form a crystal structure, while the valence electrons move more or less as free particles inside the metal. (It is common to call the collection of valence electrons an almost “free electron gas”.) This way the “free” electrons have much place at their disposal, like particles in a macroscopic box. Many of these electrons can then have rather low kinetic energies, and this is possibly part of the explanation of the fact that the metal is more stable (has a lower total energy) than the collection of isolated metal atoms. We note that the metal binding is analogous to the covalent binding, in the sense that the valence electrons are shared by *all* the atoms of the crystal.

The “freedom” of the valence electrons means that the metal has a high electric conductivity. The valence electrons are therefore also called **conductance electrons**.