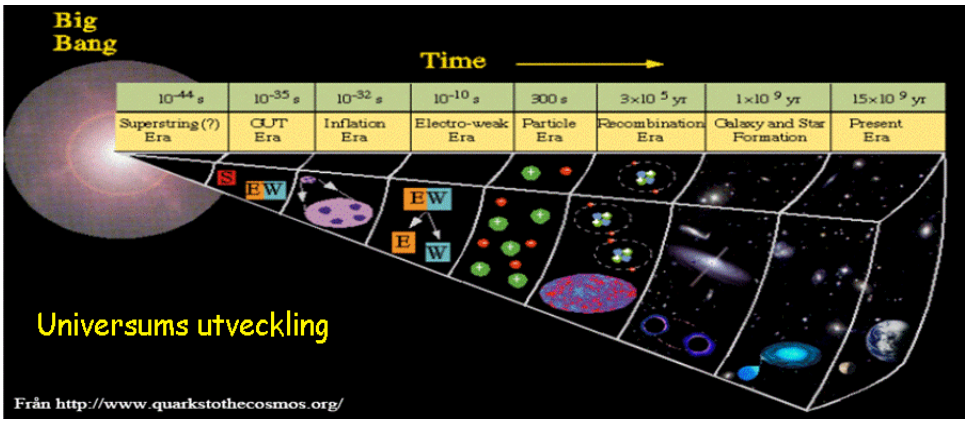
Appendix. Atoms and Molecule



Contents. These chapters are from the course SK180N Modern Physics

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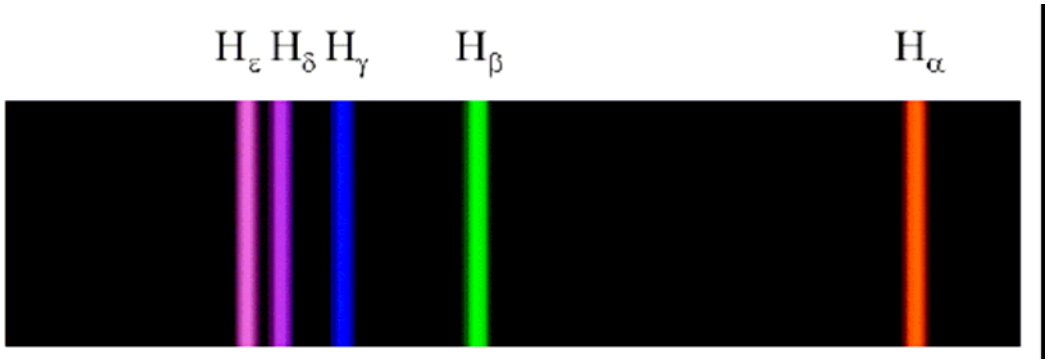
Chapter 10.3

The atom

10.3.1 Introduction

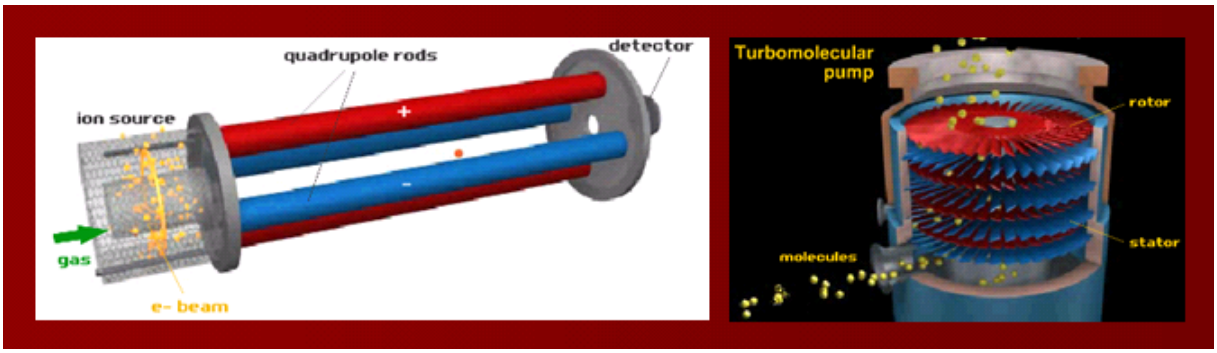
The spectroscopy showed that each element has a characteristic spectrum. For some elements (hydrogen, some alkali metals) the spectral series were very regular, and the series easily recognizable.
Balmer found for the visible wavelengh of the hydrogen spectrum that

$$\lambda_m = const\frac{m^2}{m^2-2^2} \text{ where } m = 3,4,5,\ldots$$



The Balmer series of atomic hydrogen

Encouraged by Planck's success with the quantisation phenomenon, Bohr's theory for hydrogen theory for hydrogen was presented 1913. It means that in a bound (atomic) system the energy is quantised. The systems possible energy levels can be described by an energy formula, where (in the simplest model) each level can be assed with *one* quantum number *n*. The absorption of electromagnetic radiation or through collisions with surrounding atoms, kinetic energy is transferred to the electron, leading to the *excitation* of the atom; the opposite de-excitation process takes place under photon emission. Around a proton with charge e^+ an electron with opposite charge is orbiting. The proton mass is around 1836 times heavier than the electron, why in the simplest description the electron is moving in a circular orbit around the (infinitely heavy) proton.
By the use of mass spectrometers the different elements masses could be determined in detail. Below is shown a modern mass spectrometer, a so-called mass quadrupole with great selectivity.



10.3.2 Bohr's three postulates

- 1. The electron orbits in stabile orbits without radiating energy.
- 2. When the electron jumps from one stabile orbit to another it absorbs or emits energy according to $E_i - E_f = hf_{if}$
- 3. The integral of the electrons momentum *p* around the electrons orbit is equal to an integer of Planck's constant *h*.

$$\oint pds = nh$$

Postulate 3) gives, since *p* is constant along the orbit

$$\oint pds = p\oint ds = p \cdot 2\pi r = nh$$

dvs $mvr = nh/2\pi$

Newton's second law in the *r*-direction gives

$$e^2/4\pi\varepsilon_0 r^2 = mv^2/r$$

If we eliminate v from these two equations and solve for r (depending on the integer n), we get:

$$r_n = n^2\ \varepsilon_0 h^2/(me^2\pi)$$

The electrons energy, E, without taking the rest mass into account, is the sum of the kinetic and potential energy:

$$E = \tfrac{1}{2}\, mv^2 - e^2/4\pi\varepsilon_0 r = \tfrac{1}{2}\, mv^2 - mv^2 = -\tfrac{1}{2}\, mv^2 = -e^2/8\pi\varepsilon_0 r$$

(The energy < 0 since the electron is *bound*)

Put in the expression for r_n and solve for E (that depends on the integer n)

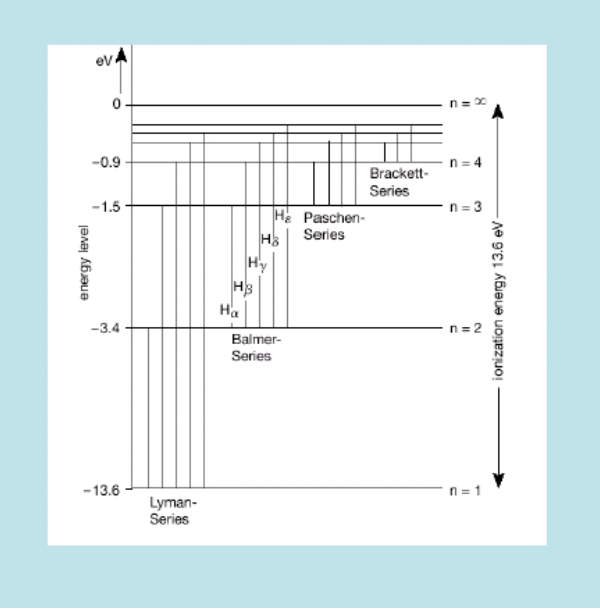
$$E_n = -me^4/(8\varepsilon_0 h^2\ n^2)$$

We see that the energy is quantised and besides negative. The quantum number n is called the principle quantum number and can have the values 1, 2, 3,…

10.3.3 Energy levels

Matter consists of atoms and each atom consists of a small but heavy nucleus and an electron cloud. Every electron has an accurate energy. Every atom has many different energy levels. Every excited atom gets rid of its excess energy. Then, an electron jumps from one orbit with higher energy to an orbit with lower energy and the excess energy is emitted as a photon. The energy difference between two levels is $E_m - E_n$.

$$E_m - E_n = -me^4/8\varepsilon_0 h^2\ (1/m^2 - 1/n^2) = -13{,}61\ eV\ (1/m^2 - 1/n^2)$$



Energy level diagram of atomic hydrogen

Thus, we can calculate the energy of the absorbed photon that is absorbed/emitted in connection with the electronic transition.

$$\Delta E = hf = \frac{hc}{\lambda}$$

Since we have the energy expression for the levels and the photon energy we can derive how the wavelength λ depends on the quantum numbers *m* and *n*:

$$\Delta E = E_m - E_n = -\frac{me^4}{8\varepsilon_0^2 h^2}\cdot\frac{1}{m^2} - \left(-\frac{me^4}{8\varepsilon_0^2 h^2}\cdot\frac{1}{n^2}\right)$$

$$\frac{hc}{\lambda} = -\frac{me^4}{8\varepsilon_0^2 h^2}\cdot\frac{1}{m^2} - \left(-\frac{me^4}{8\varepsilon_0^2 h^2}\cdot\frac{1}{n^2}\right) = k\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

$$\frac{1}{\lambda} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

$R = 1.097\text{x}10^7\ \text{m}^{-1}$ is called the Rydberg constant.
The expression gives the transitions wavelength if you know the quantum numbers *m* and *n*.

Example
What wavelength do we get if an electron jumps from *m*=2 till *n*=1 in atomic hydrogen?
The formula for the wavelength gives

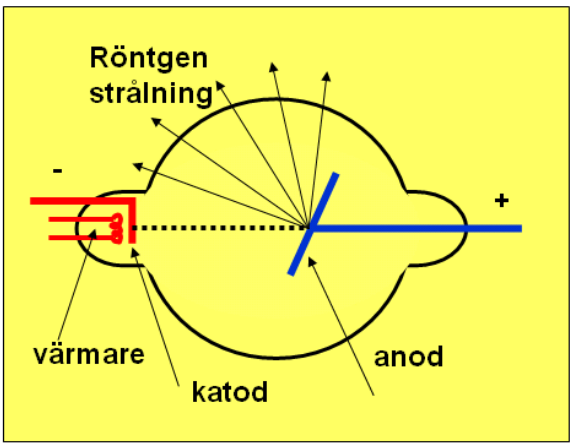
$$\frac{1}{\lambda} = 1{,}097\times10^7\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = 1{,}097\times10^7\left(1 - 1/4\right) = 1{,}097\times10^7\,\frac{3}{4}$$

$$\lambda = \frac{4}{3\times1{,}097\times10^7}\,m \approx 121{,}5\,nm$$

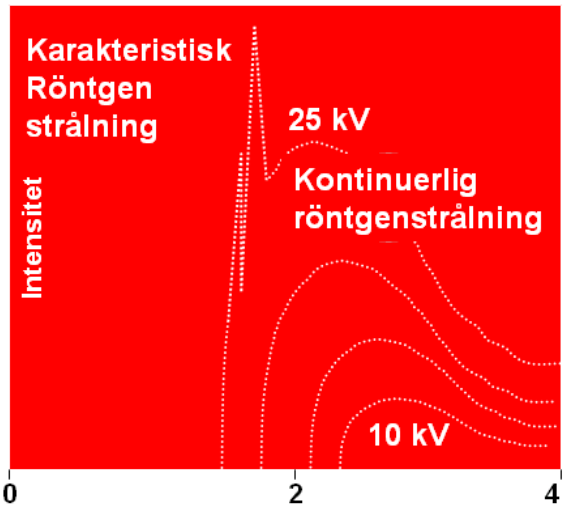
The spectral line 121.5 nm is also called the $\text{Lyman}_{\text{alfa}}$ or L_α that also can be seen in the solar spectrum. It has a short wavelength and can be found in the so-called VUV-region, Vacuum-Ultra-Violet region.

10.3.4 X-ray spectra

Let us in detail study the radiation from a X-ray tube that has been described in section 3.2. The tube is connected to a high voltage from about 10 kV to around 30 kV. The material of the anode consists of an element that can stand high temperatures, as tungsten (Wolfram) or Molybdenum. One heats the cathode in order to easily get free electrons that can be accelerated towards the anode.



The radiation consists of two types, the characteristic radiation and the continuous radiation or Bremsstrahlung (From German breaking radiation). We can study the spectrum of the figure below where several X-ray spectra are shown for different acceleration voltages.



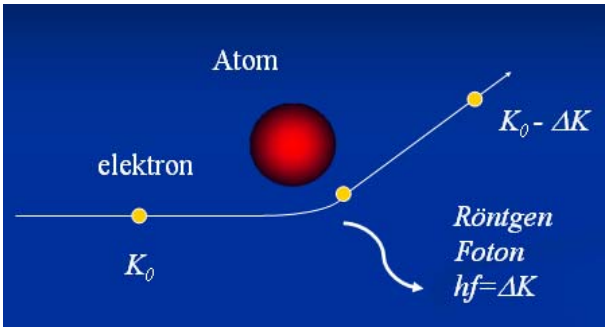
The Bremsstrahlung can be explained by scattering theory. When an electric charge is accelerated, radiation is emitted, just as in an antenna. At the bending of electric charges or free electrons they will be accelerated and will emit X-ray radiation. The radiation with the shortest wavelength or with the highest energy is obtained when all of the electrons energy is transformed to photon energy. We can easily calculate the frequency and wavelength for this radiation, i.e. , f_c and λ_c:

$$hf_c = eV$$

With the equation $c = f\lambda$ we get

$$\lambda_c = \frac{c}{f_c} = \frac{c}{eV/h} = \frac{hc}{eV}$$

From this, the shortest wavelength, we will then have a continuous spectrum of Bremsstrahlung that can be illustrated with the figure below.



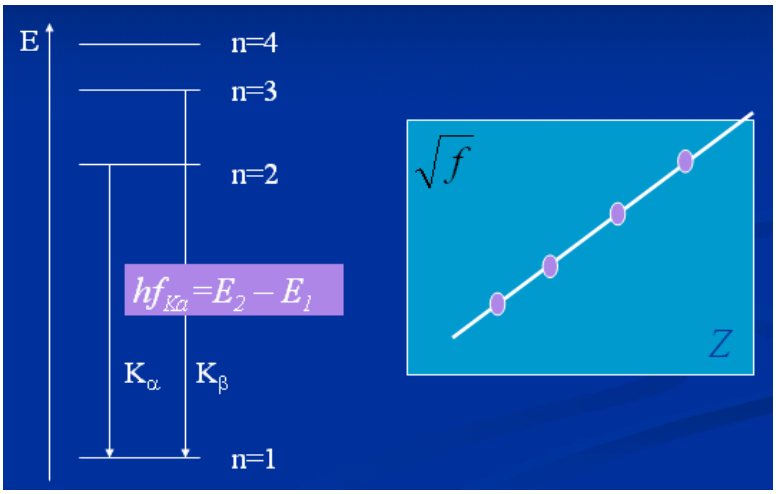
Example
Calculate the shortest wavelength we get if the acceleration voltage is 20 kV.
With the formula for the cut-off wavelength we get:

$$\lambda_c = \frac{hc}{eV} = \frac{6{,}63\times10^{-34}\times3{,}00\times10^{8}}{1{,}60\times10^{-19}\times20\times10^{3}}m = 62\,pm$$

X-ray or Röntgen's pictures
These are Wilhelm Röntgen's own pictures of his wife's hand from 1895.

Wilhelm K. Röntgen 1845-1923

Moseley diagram
When one examined the peaks of the X-ray spectrum for different anode materials one could see that the peaks corresponded to electronic transitions and photon emission from the materials inner shells. The big peak of the spectrum is called K_α and the one at shorter wavelength K_β, which means an electron jumps to the K-shell, illustrated in the figure below. One systematically examined K_α and K_β radiation for various elements with different atomic numbers, Z (proton number). Making a diagram where one puts the square root of the frequency of the radiation $f^{1/2}$ against Z one gets a straight line, like in the figure below, which is called a Moseley diagram:



We can try to see if we with the quantum mechanics atomic model can obtain this linear expression. We can formulate the energy expression for an element with atomic number Z (in the *eV* unit):

$$E_n = -\frac{13{,}6(Z-1)^2}{n^2}\ eV$$

$$hf = E_2 - E_1 = \frac{-13{,}6(Z-1)^2}{2^2} - \frac{-13{,}6(Z-1)^2}{1^2} = 10{,}2(Z-1)^2\,eV$$

Here, we have multiplied the expression for the hydrogen atom with the factor $(Z\text{-}1)^2$ describing how the energy levels are influenced by heavier elements. The charge squared found in the expression can be explained by the fact that the expression for the potential energy of the atom for hydrogen is e^2, why we for heavier elements should have Z^2. When we study how the inner shell electrons are influenced, we just eliminate this charge and that gives the remaining charge *Z-1*, which we then just, take the square of. The formula does not hold for hydrogen, but for heavier elements.

Let us continue and solve the frequency out of the energy expression:

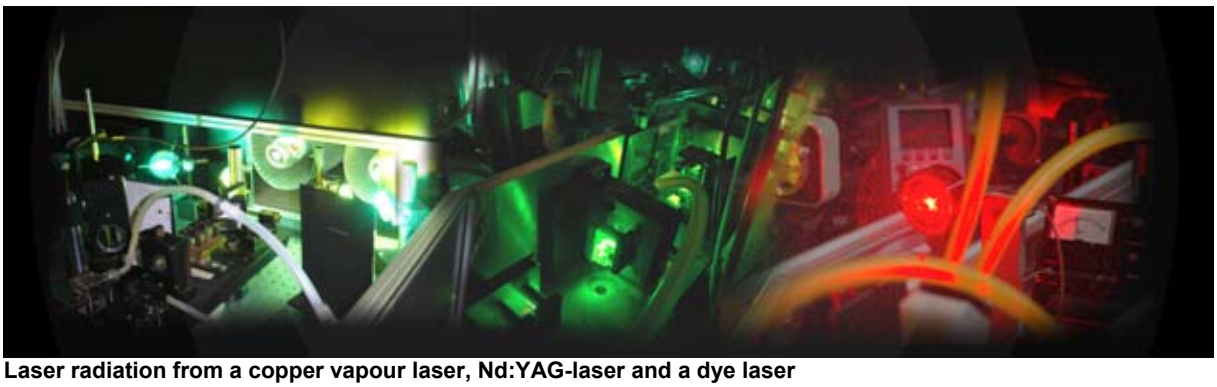
$$= \frac{hf}{h} = 2{,}46\times10^{15}(Z-1)^2\,Hz$$

now see that the frequency is proportional against $(Z\text{-}1)^2$ and takes the square root of the expression:

$$\sqrt{f} = C(Z-1) = CZ - C$$

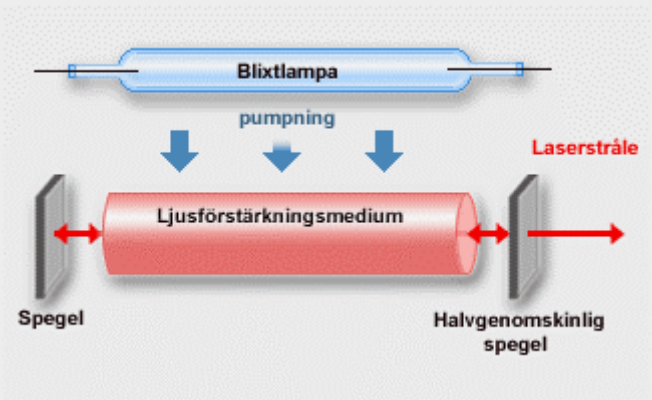
This equation describes the same straight line as in the Mosley diagram!

10.3.5 Lasers



Laser radiation from a copper vapour laser, Nd:YAG-laser and a dye laser

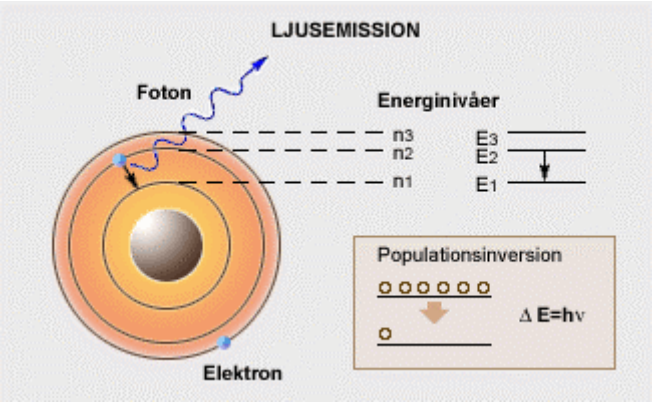
How does a laser work?



A laser is a light source where one for instance has a gas (or another suitable medium) contained in a cavity held between two mirrors. If you excite the medium with energy of the form of a light flash or electronically, the medium will transfer its excess energy into photons that will pass back and forth between the mirrors. In this way the light will be coherent. The light will also have just one wavelength (most often).

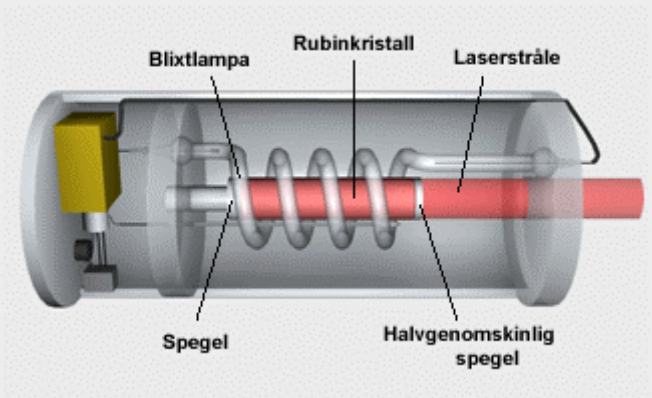
10.3.6 Light amplification by stimulated emission

Excited atoms will normally emit uncoherent light in random emission or spontaneous emission. The light will also be emitted randomly in direction. However, an excited atom can be forced to emit light in one specific direction by the phenomenon stimulated emission. One important factor for this process to occur is that there are more excited atoms of a sample than atoms in the ground state, i.e. we have a so-called inverted population. When a lamp has transferred energy to the atoms in one flash, which is called optical pumping, some atoms are excited. These atoms will return to their ground state in some nanoseconds and emit one photon each. However, if the excited atom is influenced by a photon of the same energy that corresponds to the transition in question, the atom will emit a photon in the same direction as the incoming photon. Thus, we will have two photons with the same energy or wavelength. If there are many excited atoms they will be influenced to emit the same types of photons in the same direction. We will now have many coherent photons and this phenomenon is called stimulated emission.



When all, or almost all, excited atoms have emitted photons we will have a device with high intensity where all photons have the same wavelength. If one of the mirrors of the cavity has a transparency of around 4%, this will result in a beam of light escaping from the cavity. We have now a laser beam. Laser stands for light amplified by stimulated emission of radiation.

The first laser was the Ruby laser that is shown below and Theodor Maiman built it in 1960.



10.4 Molecules

10.4.1 Introduction

In this section we will discuss what kinds of forces binding atoms together to form molecules. There are in general two kinds of cases. In most un-organic molecules, they are held together by *ionic bonds* but concerning the organic molecules and some un-organic they are held together by *covalent* bonds. Besides, there are other types of bonds like the so-called *Van der Waals bonds*. We will discuss the ionic bonds of the diatomic molecule NaCl and covalent bonds of the simplest of all molecules, the hydrogen molecule, H_2. When you study spectra from molecules and compare with atoms, one finds that molecular spectra a rich of spectral lines and also more complex than atomic spectra. The electronic distribution around the molecules is of course more complex, even though the nuclei are at rest relative each other. However, this is not the case. The nuclei both rotate around their common centre of gravity and vibrate relative each other, and this gives rise to both rotational energy and vibrational energy and also quantised rotational and vibrational energy levels. Transitions between these levels give rise to rotational and vibrational spectral lines. Also transitions between rotational level of excited states and for example the ground electronic states give rise to rotational spectra. A molecule thus gives much more spectral lines rich compared to atomic spectra. We will also discuss how to gain information of different parameters in the study of molecular spectra, such as dissociation energies etc.

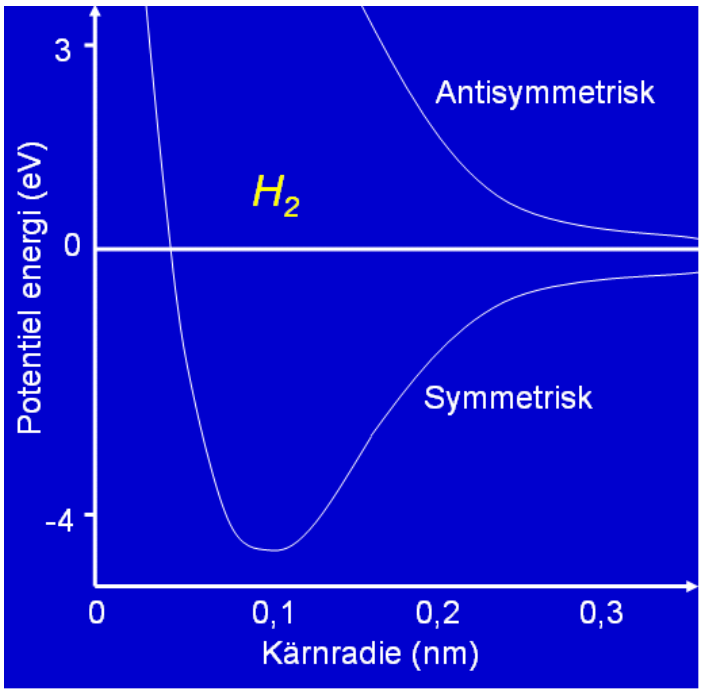
10.4.2 Ionic bonds

A good example of a molecule that has an ionic bond is NaCl. If you calculate the total energy of the sodium and the chlorine atoms at a large distance from each other and compare with the NaCl-molecules energy, one finds that it is less than the Na and Cl atomic energy. This makes the molecule stable and keeps it held together. Let us perform this calculation. $_{11}$Na has 11 electrons, that is 1 electron more than the rare gas helium (electron configuration $1s^2 2s^2 2p^6$) why it has a 3s electron in its outer shell, that is easy to remove. Na-atom can be ionised if you add 5.1 eV getting the ion Na^+. We can say that the *ionisation energy* is 5.1 eV for Na. The chlorine atom $_{17}$Cl has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^5$. The outer 3p shell lacks an electron and it is easy to capture an electron. If an electron gets in the neighbourhood of a Cl-atom it can be captured in that shell making the ion to form Cl^-. Cl^- has 3.8 eV less energy than the Cl

atom and is more stabile. The ionisation of takes of 5.1 eV but if we let the Na-electron join the Cl^- ion we gain 3.8 eV, why the difference only will be 5.1 – 3.8 eV = 1.3 eV. We have thus formed a diatomic molecule with less energy than the energies of the two separate atoms, why it is stabile.

10.4.3 Covalent bonding and the H_2 molecule

The hydrogen molecule is stabile, which is not caused by ion bonding since it is needed 13,6 eV to ionise atomic hydrogen. H^- might be formed, but the electron affinity is small, around 0,7 eV. This is the reason for H^+ and H^- at any distance from each other not can have less energy than two H-atoms have together. However, a stabile H_2 molecule can be explained by quantum mechanics and the Schrödinger equation. When solving the Schrödinger equation for the hydrogen molecule, one gets two solutions. One solution is symmetric and one anti-symmetric. Before letting the two hydrogen atoms move closer to each other they both have their *1s* level with the same energy. Together we have two electrons, but if the inner shells would be filled, there would be space for four electrons. When the two atoms are brought together the two *1s* levels are split into two levels, one symmetric and one anti-symmetric level as can be seen in the figure. The symmetric can have two electrons, as well as the anti-symmetric. The symmetric gets a minimum at the nuclear distance 0.074 nm. In covalent bonds two atoms together own an electron pair that in general move in the area between the two nuclei in this way bonding the molecule together. Looking at larger molecules one observes that the valence electrons are the ones participating in the interaction.



Energy diagram for the H_2-molecule

Thus, the covalent bond is of quantum mechanical character but is also responsible for the built-up of certain crystals.

10.4.4 Molecular energy

Let us start to discuss diatomic molecules, which also can be regarded as model molecules for polyatomic molecules. The molecule has several different types of energies. It can, just as the atom, be electronically excited, or by photons, just as the atom is excited between the atomic shells. A molecule can also rotate, vibrate and bend. All these energy forms are quantised. When the molecule both vibrates and rotates, complicated spectra appears, that gives information about how the energy of the molecule is built.

10.4.4.1Vibrational energy

Let us start with a diatomic molecule where the distance between the nuclei is r_0. We can then express the potential energy of the molecule as a Taylor series around r_0 and gets:

$$V(r) = V(r_0) + (r - r_0)\frac{dV}{dr} + \frac{(r - r_0)^2}{2!}\frac{d^2V}{dr^2} + \frac{(r - r_0)^3}{3!}\frac{d^3V}{dr^3} + \ldots$$

Since the molecule has a minimum in potential energy, the first derivative must be $\frac{dV}{dr} = 0$ in that point. The second term of the expression above must then be zero. If we truncate the series omitting higher order terms we obtain:

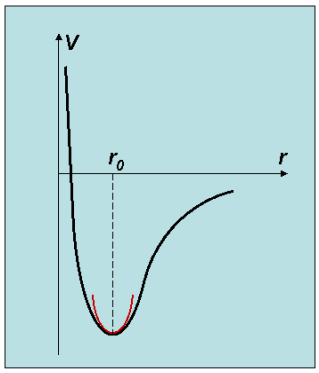
$$V(r) = V(r_0) + \frac{1}{2}\frac{d^2V}{dr^2}(r - r_0)^2$$

where we can compare with the harmonic oscillator for a spring, where the spring constant is k. The potential energy can be derived using Hooke's law:

$$V(r) = V(r_0) + \frac{1}{2}k(r - r_0)^2$$

The spring constant for the system will become $k = \frac{d^2V}{dr^2}$

The energy expression is called the parabolic approximation for molecular energies and is shown in the figure below together with a normal potential energy curve for a diatomic molecule:



Energy diagram for a diatomic molecule
as a function of the nuclear *r*.
The parabolic approximation is also shown.

If we put the systems reduced mass to μ we immediately get the angular frequency of the molecular system to

$$\omega = \sqrt{\frac{k}{\mu}}$$

A diatomic molecule with the masses m_1 and m_2 and μ stands for the reduced mass and is

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

In the Schrödinger equation we can put the potential energy of the system to

$$V(r) = V(r_0) + \frac{1}{2}k(r - r_0)^2$$

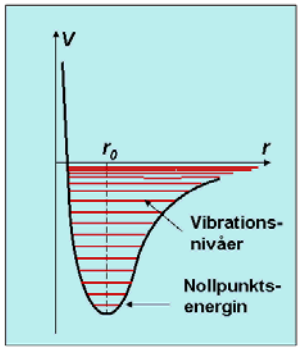
After some derivations one then obtains the following expressions for the molecular vibrational levels just as we made the derivation of the hydrogen atomic levels:

$$E_v = \left(\upsilon + \frac{1}{2}\right)\hbar\omega$$

where **υ = 0, 1, 2, …**which is called the **vibrational quantum number.**

and $\hbar = \frac{h}{2\pi}$. We have found that the molecular energy also is quantised. For $\upsilon = 0$ we get $E_0 = \frac{\hbar\omega}{2}$ also called the zero point energy showing that the molecular energy not is zero in its lowest position, but just $\frac{\hbar\omega}{2}$. With the condition $c = \nu\lambda$ and the expression for the spectroscopic wavenumber $\sigma = \frac{1}{\lambda}$ we get $\hbar\omega = \frac{h\omega}{2\pi} = \frac{h2\pi\nu}{2\pi} = h\frac{c}{\lambda} = hc\sigma$. In many spectroscopic cases one often uses the unit cm^{-1} in order to describe the energies. For a transition σ is directly proportional against the energy. You just invert the wavelength and get the wavenumber σ. For instance a laser excitation of a molecule with the wavenumber 15 000 cm^{-1} corresponds to the wavelength of λ = 1/15 000 cm = 670 nm in the red wavelength region.

With the energy expression we can describe the vibrational levels in an energy diagram for a diatomic molecule as shown in the figure below. The distance between the levels

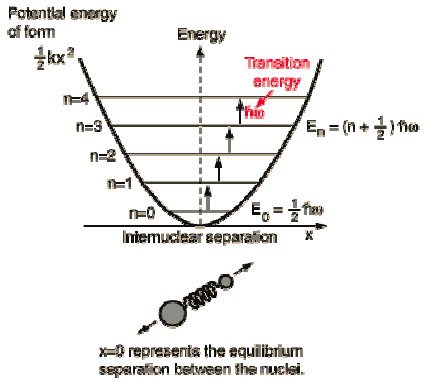


Energidiagram med vibrationsnivåer

will be smaller the higher up i the energy level diagram since the higher order terms show up. A more adequate picture we get if we use the following energy expression:

$$E_v = \omega_e\left(\upsilon+\frac{1}{2}\right)+\omega_e x_e\left(\upsilon+\frac{1}{2}\right)^2$$

Here ω_e stands for the vibrational constant and $\omega_e x_e$ is the first higher order term that corresponds to the centrifugal distortion when the molecule both rotates and vibrates. Within spectroscopy both constants are given in the unit cm^{-1}.

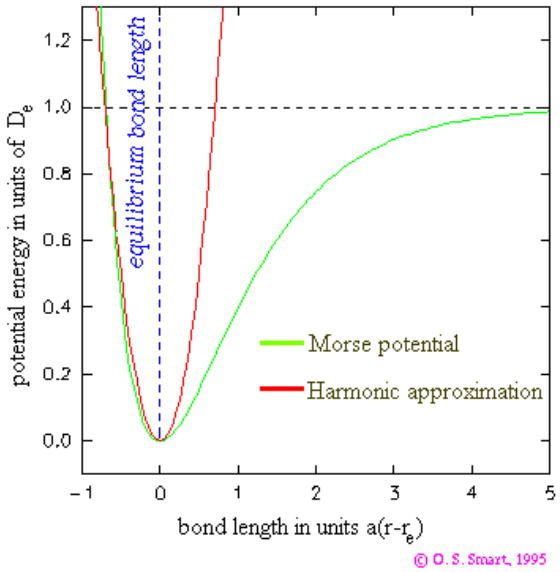


The Morse potential

To regard a molecular vibration as a harmonic oscillator is only the first order approximation. But reality does not look directly as we have foreseen. For example there is a limit for how high the potential energy can reach. Finally, the two atoms will be separated. Another possibility is to use the so called Morse-potential:

$$V = D_e\left(1-e^{a(r_e-r)}\right)^2$$

Here D_e is the dissociation energy and r_e is the internuclear equilibrium distance. In the figure below one can see both models. The harmonic oscillator is a good approximation at smaller distances between the nuclei, but is unreasonable for grater separation distances. The harmonic oscillator model does not take into account the breakage of the bond for larger distances. In the diagram we have put the energy as a function of the internuclear distance.



10.4.4.2 Rotational energy

Rotational spectra of molecules appear in the microwave region. A molecules complete spectrum has its origin in the electronic transitions of the molecule, the molecular vibrations and rotations. If we compare the order of the different types of transitions we can generalize as follows:

1. The distance between rotational levels of a molecule is normally around 10^{-3} eV, and the transitions between rotational energy levels lay in the wavelength region around 0.1 nm to 1 cm.
2. The energy differences of vibrational energy levels is some 100 times greater, that is around 0.1 eV and one finds radiation transitions between 1 μm to 0.1 nm.
3. The electronic transitions of a molecule have the largest energy and the difference between the levels is around 1 eV or more. The wavelengths we observe are often seen in the visible and in the UV-region.

We can describe the rotation by applying a simple mechanical model an suppose we have a diatomic molecule consisting of atoms with masses m_1 and m_2. The molecule rotates freely around their center of mass. Let us suppose the distance between the atoms is r and the distance from the center of mass to atom 1 is r_1 and to atom 2, r_2.
The moment of inertia (I) of the molecule is

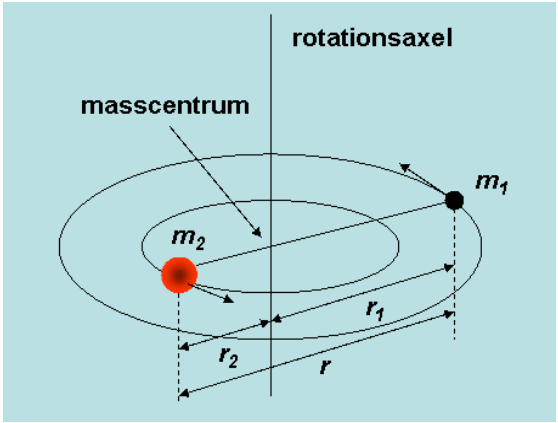
$$I = m_1 r_1^2 + m_2 r_2^2$$

With the equation $m_1 r_1 = m_2 r_2$ we can rewrite the moment of inertia as:

$$I = \frac{m_1 m_2}{m_1 + m_2}(r_1 + r_2)^2 = \mu r^2$$

Here μ is the reduced mass and $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$

In the figure below, we observe the system where the atoms rotate around the center of mass.



A rotating molecule with masses m_1 and m_2.

A particle with mass *m* and velocity ***v***, that is with momentum $\boldsymbol{p} = \mathbf{m}\boldsymbol{v}$ has the angular momentum $\boldsymbol{L} = \boldsymbol{r}\,x\,\boldsymbol{p}$ with respect to a point at a distance of ***r*** from the point. By using the Schrödinger equation for a diatomic molecule, which we regard as two particles moving around the center of mass, we can calculate the energy Eigenvalues for the system. We use the momentum operator $\boldsymbol{p}_{op} = -\, i\hbar\nabla$. With $\boldsymbol{L} = \boldsymbol{r}\,x\,\boldsymbol{p}$ we get the operator in the z-direction to

$$L_z = xp_y - yp_x = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}) = -i\hbar\frac{\partial}{\partial \phi}$$

Here, we have moved from Cartesian coordinates to polar coordinates just as we did when solving the Schrödinger equation from the beginning for hydrogen. If we do the same in both x and y-direction we can evaluate the L^2 operator, that becomes:

$$L^2 = L_x^2 + L_y^2 + L_z^2 = -\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{\hbar^2}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \equiv \Omega$$

When an operator operates on a function we obtain an Eigenvalue. Let us examine what happens when we operate with L^2 on the wave function ψ so that we get an equation of the form:

Operator ψ = konstant ψ

Here the operator can be L_x, L_y, L_z and L^2. If we assume the wavefunction has the form as earlier:

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

It is most simple to operate with the L_z operator, which we derived to be $L_z = -\hbar\frac{\partial}{\partial\phi}$. We thus obtain

$$-\hbar\frac{\partial}{\partial\phi}\left[R(r)\Theta(\theta)\Phi(\phi)\right] = \hbar m_l\left[R(r)\Theta(\theta)\Phi(\phi)\right]$$

Since we only operate on $\Phi(\phi)$ we can neglect $R(r)$ and $\Theta(\theta)$ why we get

$$\frac{d\Phi}{d\phi} = im_l\Phi$$

This first order differential equation has the solution $\Theta(\phi) = \sqrt{2\pi}e^{im\phi}$
Here $|m| = 0,1,2,3,...$ why the function $\Phi(\phi)$ only can assume one value if the angle ϕ is changed by 2π. This is why we directly get an Eigenvalue for the L_z operator:

$$L_z = m_l\hbar$$

, so the quantum number m_l gives one z-component of the angular momentum to an electron of the state *n, m, m_l.* The same holds for a molecule since the derivation was the same.

If we suppose that $\Omega\left[R(r)\Theta(\theta)\Phi(\phi)\right] = b\left[R(r)\Theta(\theta)\Phi(\phi)\right]$
Here *b* is the Eigenvalue of the equation. As we did earlier we can neglect R(r) since the operator Ω does not operate on R(r). After division with $\hbar^2\Theta\Phi$ and with the equation

$$\frac{\partial^2\Phi}{\partial\phi^2} = -m_l^2\Phi$$

, which we know it has the solutions $\sqrt{2\pi}e^{im_l\phi}$ only when $m_l = o,\pm1,\pm2,...\pm l$.
In the Schrödinger equation we got

$$-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{d\Theta}{\partial\theta}\right)+\frac{m_l{}^2}{\sin^2\theta} = konst = l(l+1)$$

The reason for choosing the constants value to *l(l+1)* is just to make the expressions simpler, so we can derive integer quantum numbers, just as we did in the case of the hydrogen atom. Here we see that one has a solution if *l* = 0 or a positive integer greater than or equal to $|m_l|$. Otherwise there is no simple solution.

Thus, we have got $L^2 = \hbar^2 l(l+1)$
and $L = \hbar\sqrt{l(l+1)}$

The quantum number *l* determines the size of the total angular momentum.
With a simple mechanical model for the rotational energy, $E = \frac{L^2}{2I}$ we observe that it is quantised and that it can only have values according to:

$$E_l = \frac{L^2}{2I} = \frac{\hbar^2 l(l+1)}{2I} = \frac{\hbar^2 l(l+1)}{2\mu r^2}$$ där *l* = 0, 1, 2, ,…

The quantity $\frac{\hbar^2}{2I} = B$

is called the *rotational constant*. The *B-value* is given in the energy unit cm^{-1} in scientific literature. The allowed transitions of a diatomic molecule are separated by an interval of *2B,* which can be seen in molecular spectra. If we can define a spectral line it is also possible to calculate the moment of inertia and the separation distance between the atoms (bond length). If the moment of inertia has been determined we can directly determine the B-value:

$$B = \frac{\hbar}{4\pi cI}$$

The quantised rotational energy can be derived in a similar way, and is within molecular spectroscopy given as a function of the rotational quantum number *J* according

$$F(J) = \frac{E_J}{hc} = BJ(J+1)$$

For a stabile diatomic molecule the so-called selection rules gives the possible rotational transitions $\Delta J = \pm 1$. For molecules like HCl and CO, the transitions occur at lower energies since the centrifugal force prolongs the molecule and makes the moment of inertia large. In the expression above, we have to add terms describing the prolongation, namely $DJ^2(J+1)^2$ etc.
If you travel upwards in the energy diagram, the energy levels will become closer to each other. One says that the Born-Oppenheimer approximation does not hold anymore. The *B*-value will be reduced and we can write:

$$B_\upsilon = B_e - \alpha\left(\upsilon + \frac{1}{2}\right)$$

där α [cm^{-1}] är en konstant.

Let us now summarize and describe the total energy, $T(\upsilon,J)$, for a diatomic molecule with both contributions, the rotational as well as the vibrational part:

$T(\upsilon,J) = G(\upsilon) + F(J)$

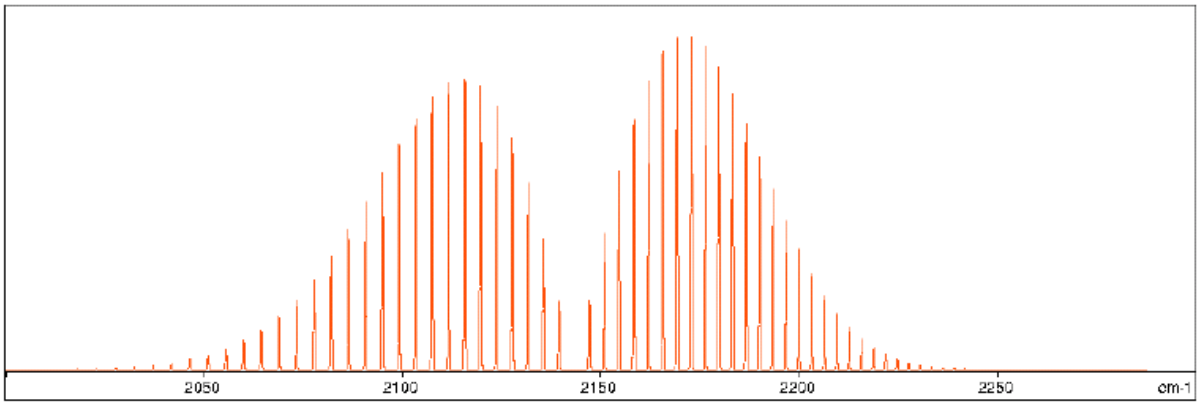
10.4.5 Molecular spectra

The normal observed molecular spectrum includes vibrational-, rotational- or electronic transitions. For a diatomic molecule the electronic states can be represented in a diagram of potential energy as a function of the internuclear distance. Electronic transitions correspond to nearly vertical lines on such a plot, since the transition occurs rapidly why the internuclear distance does not change especially much during the process. Vibrational transitions occur between vibrational levels of the same electronic level. Also rotational transitions appear on a common vibrational level, even though there are examples of combinations of vibrational-and rotational transitions for light molecules.

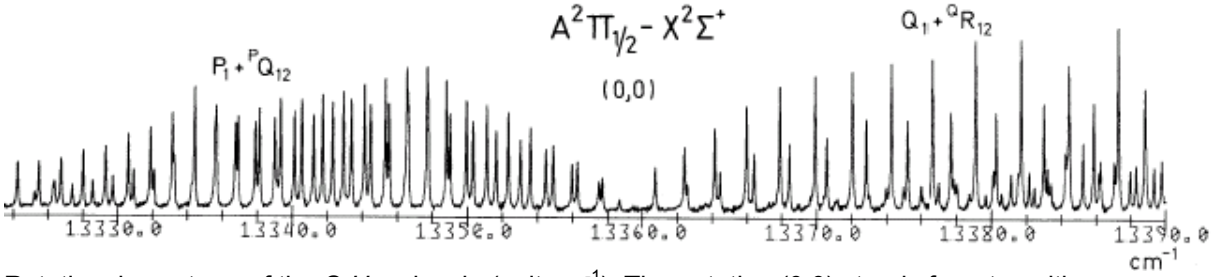
10.4.6 Rotational spectra

Electromagnetic radiation can excite the rotational levels of the molecule if it has an electric dipole moment. The field influences the molecule and the spectra of rotational transitions lay typically in the microwave region of the electromagnetic spectrum. The transitions between vibrational levels give rise to larger energy differences. In general the energy of a vibrational

level is round 0.1eV while the rotational transitions are at least two orders of magnitude smaller, around 10^{-3} eV for rotational transitions.
Let us study the CO-molecule where the fundamental band can be found in the infrared wavelength region around 2100 cm^{-1} or 5 μm. The spectrum is symmetric around its center, the so called zero gap:



The CO-molecules infrared spectrum between 2000-2300 cm^{-1}, around 5 μm.



Rotational spectrum of the *SrH* molecule (unit cm^{-1}). The notation (0,0) stands for a transition between υ = 0 of the excited level to the υ = 0 of the ground level. P, Q and R are notations for rotational transitions of rotational spectra.

As a conclusion, we can say that the key word in modern physics is quanta and quantum physics. We have achieved discrete levels for electronic, vibrational and rotational energies. Classically we would have got continous spectrum, making it impossible to study these rotational and vibrational spectra

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10.4.2 Ionic bond
10.4.3 Covalent bond

10.4.4 Molecular energy
10.4.5 Rotational energy
10.4.6 Molecular spectra
10.4.7 Rotational spectra

Learning goals
Determine the wavelengths of transitions of the hydrogen atom with Balmer's formula
Describe Bohr's three postulates and its consequences
Determine energies of hydrogen and hydrogen like atoms
Describe X-ray spectra
Determine the cut-off wavelength
Describe Mosely diagrams
Discuss the laser principle
Discuss different types of molecular bonds
Calculate vibrational energies at different quantum numbers
Give an overview of how the rotational energies appear
Calculate rotational energies for different quantum numbers

Advices for learning
Think of how one with the Balmer formula just could calculate wavelengths
With Bohr's postulat the Balmer formula could be explained
Characteristic X-ray spectra could be explained with Bohr's model
Study the principle of the laser and the requirements for lasing
Be observant for different types of molecular bonds
Compare atoms and molecules with respect to energy calculations

Readings
- Thornton, Rex, Modern Physics, Saunders
- Krane, Modern Physics, Wiley
- Beiser, Concepts of Modern Physics, McGraw-Hill
- Serway, Moses, Moger, Modern Physics, Saunders
- Eisberg, Resnick, Quantum Physics of Atoms, Molecules, Solids and Particles, Wiley
- Blatt, Modern Physics, McGraw-Hill
- Halliday and Resnick, Fundamentals of Physics, Wiley
- Blatt, Modern Physics, McGraw-Hill
- Benson, University physics, Wiley

WEB-readings
- http://hyperphysics.phy-astr.gsu.edu/hbase/hph.html
- http://nobelprize.org/nobel_prizes/physics/laureates/1901/rontgen-bio.html
- http://nobelprize.org/nobel_prizes/physics/laureates/1910/waals-bio.html
- http://nobelprize.org/nobel_prizes/physics/laureates/1922/bohr-bio.html