II CHAPTER: HYDROGEN ATOM, MOLECULE AND GAS

II.1 THE HYDROGEN ATOM

Hydrogen, with one proton and one electron, is the simplest atom. The state of the electron is described by Schrödinger´s equation

$$\left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{R}-\mathbf{r}) \right]\phi(\mathbf{r}) = \varepsilon\,\phi(\mathbf{r}) \qquad (\text{II.1}$$

where **R** indicates the position of the proton and **r** that of the electron. The potential V(**R** - **r**) is simply due to the Coulomb attraction between the proton and the electron, i.e.

$$\mathrm{V}(\mathbf{R}-\mathbf{r}) = \frac{-e^2}{4\pi\varepsilon_0|\mathbf{R}-\mathbf{r}|} \qquad (\text{II.2}$$

Equation II.1 is solved in essentially every book on Quantum Physics. We simply remind here that:

i. the energy levels are given by

$$\varepsilon_n = -\frac{m\,e^4}{8\varepsilon_0^2 h^2}\,\frac{1}{n^2} = -13.598\,\frac{1}{n^2}\ \text{in}\ [eV] \qquad (\text{II.3}$$

ii. the eigenstates $\phi_{n/m}$ depend on three quantum numbers (four, if one includes the electron spin) which are

n : the principal quantum number
l: the orbital angular momentum quantum number
m: the orbital magnetic quantum number (not to be confused with m, the mass of the electron

For a given n we have

$$l = 0,\ 1,\ \ldots.,\ n-1 \qquad (\text{II.4}$$

and

$$m = -l,\ -l+1,\ \ldots..,\ l-1,\ l \qquad (\text{II.5}$$

This implies that the energy level, ε_n is n^2-times degenerate. Remembering that the spin

of the electron is either +1/2 or - 1/2 we can thus accommodate $2n^2$ electrons in levels of energy ε_n. An easy way to remember these results is shown in Table II.1.

iii. Far from the nucleus all the wave functions decrease exponentially with the distance $|\mathbf{R}-\mathbf{r}|$ from the nucleus so that

$$\phi_{nlm}(r,\theta,\varphi) \propto e^{-\frac{|\mathbf{R}-\mathbf{r}|}{na_0}} \qquad \text{(II.6}$$

where $a_0 = \dfrac{\varepsilon_0 h^2}{\pi m e^2}$ (II.7

is the Bohr radius. It is equal to 0.529 Å (52.9 pm). Near the nucleus ϕ_{nlm} can exhibit nodes. These are, however, not of primary importance in condensed matter physics.

Table II.1: Energy levels of the hydrogen atom for the four lowest levels. For historical reasons a state with $l = 0$ is called a s-state, one with $l = 1$ a p-state, one with $l = 2$ a d-state and one with $l = 3$ a f-state.

n	ε_n (eV)	l=0	l=1	l=2	l=3	l=….	degeneracy
n							n^2
..	…..						…..
4	ε_4= -0.85	4s	4p	4d	4f		1+3+5+7 = 16
3	ε_3= -1.51	3s	3p	3d			1+3+5 = 9
2	ε_2= -3.40	2s	2p				1+3 = 4
1	ε_1= -13.6	1s					1

iv. The angular dependence of ϕ_{nlm} is, however, very important as it is responsible for the orientation of bonds in solids.

$$\phi_{n00}(r,\theta,\varphi) \propto 1 \qquad \text{(s-states)}$$

$$\phi_{n10}(r,\theta,\varphi) \propto \cos\theta \qquad \text{(p-states)}$$
$$\phi_{n1\pm1}(r,\theta,\varphi) \propto \sin\theta\, e^{\pm i\varphi}$$

$$\phi_{n20}(r,\theta,\varphi) \propto 3\cos^2\theta - 1$$
$$\phi_{n2\pm1}(r,\theta,\varphi) \propto \sin\theta\cos\theta\; e^{\pm i\varphi} \qquad \text{(d-states)}$$
$$\phi_{n2\pm2}(r,\theta,\varphi) \propto \sin^2\theta\; e^{\pm 2i\varphi}$$

Instead of working with complex wave functions, one can construct real ϕ´s by means of linear combinations. For example, $e^{i\varphi} + e^{-i\varphi} = 2\cos\varphi$ and $e^{i\varphi} - e^{-i\varphi} = 2\sin\varphi$.

For p-states we have then

$$\begin{aligned} \phi_{n10} &\propto \cos\theta \\ \phi_{n11} &\propto \sin\theta\,\sin\varphi \\ \phi_{n1-1} &\propto \sin\theta\,\cos\varphi \end{aligned} \qquad \text{(II.8}$$

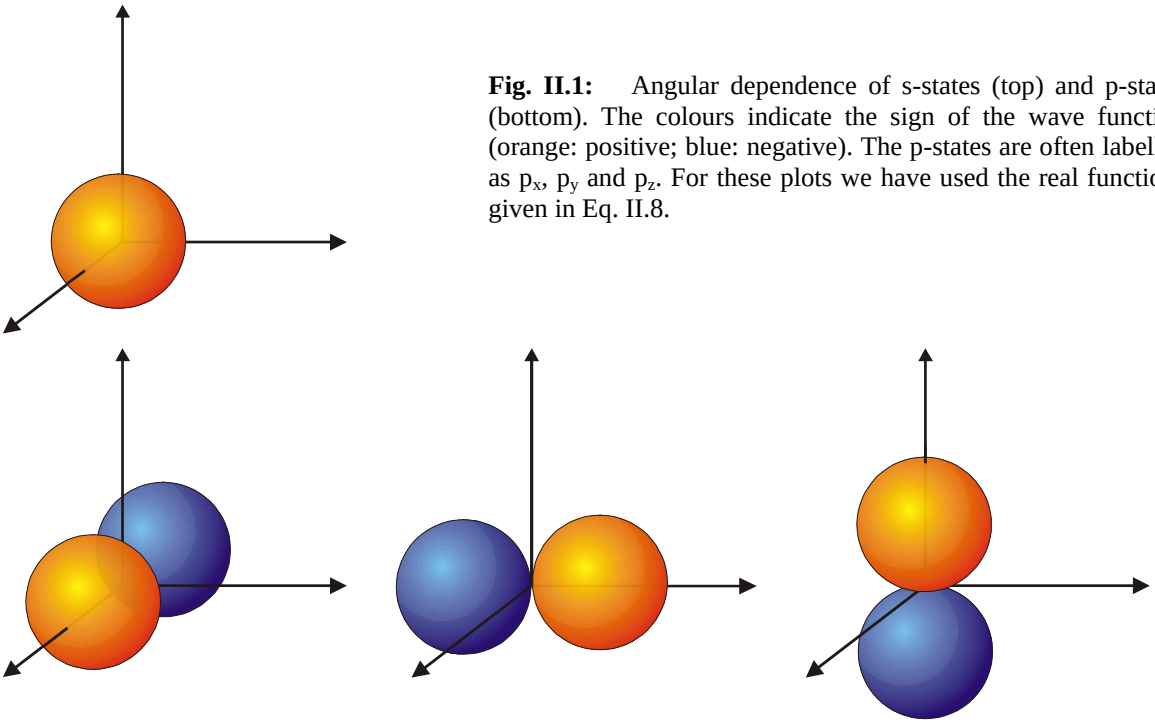


Fig. II.1: Angular dependence of s-states (top) and p-states (bottom). The colours indicate the sign of the wave function (orange: positive; blue: negative). The p-states are often labelled as p_x, p_y and p_z. For these plots we have used the real functions given in Eq. II.8.

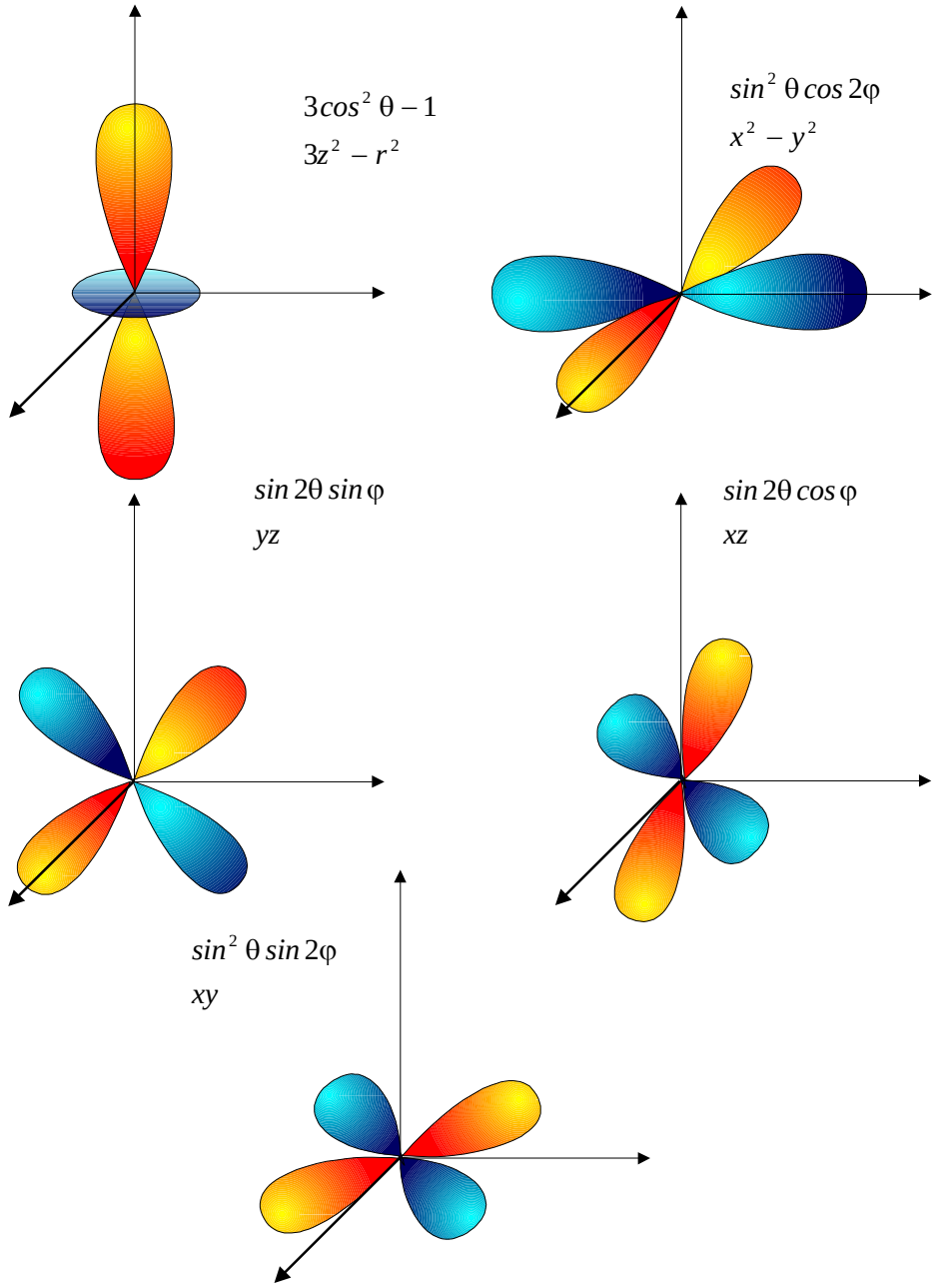


Fig. II.2: Angular dependence of d-states (l=2). The colours indicate the sign of the wave function. The polynomials indicated under the angular dependence of the d states are often used to label the d-states as $d_{3z^2-r^2}$, $d_{x^2-y^2}$, d_{xz}, d_{yz}, and d_{xy}. Note that $x = r\sin\theta\cos\varphi$, $y = r\sin\theta\sin\varphi$ and $x = r\cos\theta$

and for d-states we have

$$\begin{aligned}
\phi_{n2\,0} &\propto 3\cos^2\theta - 1 \\
\phi_{n2\,1} &\propto \sin 2\theta \sin\varphi \\
\phi_{n2-2} &\propto \sin 2\theta \cos\varphi \\
\phi_{n2\,2} &\propto \sin^2\theta \sin 2\varphi \\
\phi_{n2-2} &\propto \sin^2\theta \cos 2\varphi
\end{aligned} \qquad \text{(II.9}$$

It is noteworthy to point out that the angular part of the wave functions shown in Fig. II.1 and Fig. II.2 are very useful for the understanding, at least qualitatively, of the orientation of chemical bonds in molecules, of the properties of transition metals and the arrangement of H atoms in complex metal-hydride systems such as Mg_2NiH_4, Mg_2CoH_5, and Mg_2FeH_6. This will be discussed in the chapter on these hydrides.

II.2 THE HYDROGEN ISOTOPES

Beside Hydrogen H (also called **Protium)** made of 1 proton and 1 electron with an abundance of 99.985% one finds two other isotopes in nature: **Deuterium** D made of 1 proton, 1 neutron and 1 electron with an abundance of 0.015% and radioactive **Tritium** T made of 1 proton, 2 neutrons and 1 electron) with a radioactive decay time of 12.32 years. Tritium decays via β^--emission at 18.6 keV. The natural occurrence of Tritium is very low even compared to that of Deuterium. One deuterium per 6000 H atoms and one Tritium per 100 billion H atoms !

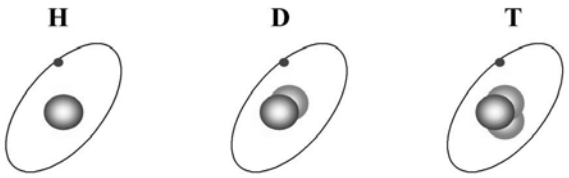


Fig. II.3: Schematic representation of H, D and T atoms.

Table II.2: Properties Hydrogen and its isotopes, Deuterium and Tritium (from Fukai [1])

Property	H	D	T
Nucleus			
Nuclear mass [m_P]	1.000	1.998	2.993
Nuclear spin [$h/2\pi$]	+½	+1	+½
Nuclear moment [μ_N]	2.79285	0.85744	2.97896
Atom			
Mass [g/mol]	1.007825	2.0140	3.01605
Ionisation energy [eV]	13.5989	13.6025	13.6038
Molecule			
Binding energy [eV]	4.748	4.748	-
Dissociation energy [eV]	4.478	4.556	4.59
Vibration energy [eV]	0.5160	0.3712	0.3402
Rotation energy [eV]	0.00732	0.00370	-
Critical point gas-liquid			
Temperature [K]	32.98	38.34	40.44
Pressure [Pa]	1.298×10^6	1.649×10^6	1.906×10^6
Triple point			
Temperature [K]	13.96	18.73	20.62
Pressure [Pa]	$7.20\cdot10^3$	17.15×10^3	21.60×10^3

Tritium is produced in nuclear reactors through neutron capture and is used in hydrogen atomic bombs, fluorescent paints and for the radioactive labelling of organic compounds. Tritium is not freely available and costs about 2$/Ci. Deuterium is not subject to special regulations and costs about 1$ per liter gas. The physical properties of the three isotopes are rather similar as can be seen in

II.3 THE H_2^+ MOLECULE

Consider two protons fixed at $\mathbf{R}_1$ and $\mathbf{R}_2$ and one electron at $\mathbf{r}$, i.e. a H_2^+-molecule as indicated in Fig. II.4.

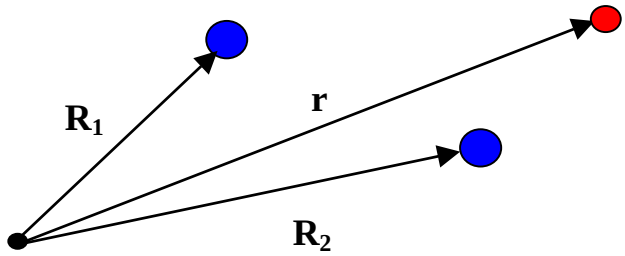


Fig. II.4: Position vectors used for the treatment of the H_2^+ molecule ion.

Then we have the following Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{R}_1-\mathbf{r}) + V(\mathbf{R}_2-\mathbf{r})\right]\varphi(\mathbf{r}) = \bar{\varepsilon}\,\varphi(\mathbf{r}) \qquad \text{(II.10}$$

As we are primarily interested in the state with lowest energy, the so-called ground state of the system, we try to find a solution of Eq. II.10 in the form of a linear combination of the ground state wave function $\phi_G(\mathbf{r})$ of the one electron - one proton problem (the previous H-problem; $\phi_G = \phi_{100}$). As here there are *two* protons we have to specify where ϕ_G is centred (at $\mathbf{R_1}$ or $\mathbf{R_2}$) so that $\phi_G(\mathbf{R_1 - r})$ and $\phi_G(\mathbf{R_2 - r})$ need to be considered. The linear combination is then

$$\varphi(\mathbf{r}) = a\,\phi_G(\mathbf{R}_1-\mathbf{r}) + b\,\phi_G(\mathbf{R}_2-\mathbf{r}) \qquad \text{(II.11}$$

As ϕ_G is a rapidly decreasing function of $|\mathbf{R - r}|$ (see Eq. II.6) we assume that

$$\int d^3r\;\phi_G{}^*(\mathbf{R}_1-\mathbf{r})\,\phi_G(\mathbf{R}_2-\mathbf{r}) \cong 0 \qquad \text{(II.12}$$

as long as the distance between the two protons, $|\mathbf{R_2} - \mathbf{R}_1|$ is not too small. In other words, we assume that the two states ϕ_G ($\mathbf{R}_1$ - $\mathbf{r}$) and ϕ_G ($\mathbf{R}_2$ - $\mathbf{r}$) are orthogonal.
As in the following part of this course we shall often encounter integrals, we introduce here the more compact notation

$$\int d^3r\ \Psi_1^*\hat{A}\ \Psi_2 \equiv \left\langle \Psi_1 \middle| \hat{A} \middle| \Psi_2 \right\rangle \qquad \text{(II.13}$$

where $\hat{A}$ is an operator. In the special case of Eq. II.12, $\hat{A} = 1$ and one writes simply

$$\int d^3r\ \phi_G^*(\mathbf{R}_1 - \mathbf{r})\,\phi_G(\mathbf{R}_2 - \mathbf{r}) \equiv \left\langle \phi_G(\mathbf{R}_1 - \mathbf{r}) \mid \phi_G(\mathbf{R}_2 - \mathbf{r}) \right\rangle \cong 0 \qquad \text{(II.14}$$

Note, however, that

$$\left\langle \phi_G(\mathbf{R}_i - \mathbf{r}) \middle| \phi_G(\mathbf{R}_i - \mathbf{r}) \right\rangle = 1 \qquad \text{(II.15}$$

because we choose ϕ_G ($\mathbf{R}_i$ - $\mathbf{r}$) to be normalised.

The standard way to solve Eq. II.10 proceeds in several steps that are used so often in condensed matter physics that we indicate them explicitly.

Step 1: Introduce the Ansatz (Eq. II.11) into Eq. II.10.
Step 2: Multiply both sides of the equation either by $\phi_{R1}^* \equiv \phi_G^*(\mathbf{R}_1 - \mathbf{r})$ or $\phi_{R2}^* \equiv \phi_G^*(\mathbf{R}_2 - \mathbf{r})$.Two relations are obtained.
Step 3: Integrate both relations over whole space and make use of the ortho-normalisation properties (I.13) and (I.14).

Introducing the following notations for simplification with $\mathbf{R_1}$=**L** and $\mathbf{R_2}$=**R**

$$\overline{H}_i \equiv -\frac{\hbar^2}{2m}\Delta + V(\mathbf{R}_i - \mathbf{r}) \qquad \text{(i=L, R)} \qquad \text{(II.16}$$

$$L \equiv \phi_G(\mathbf{L} - \mathbf{r}) \qquad \text{R} \equiv \phi_G(\mathbf{R} - \mathbf{r}) \qquad \text{(II.17}$$

$$V_L \equiv V(\mathbf{L} - \mathbf{r}) \qquad V_R \equiv V(\mathbf{R} - \mathbf{r}) \qquad \text{(II.18}$$

we obtain by following the three steps indicated above

$$a\left\langle L \middle| \overline{H}_L + V_R \middle| L \right\rangle + b\left\langle L \middle| \overline{H}_R + V_L \middle| R \right\rangle = \bar{\varepsilon}\left\langle L \middle| a\,L + b\,R \right\rangle \qquad \text{(II.19}$$

and

$$a\left\langle R \middle| \overline{H}_L + V_R \middle| L \right\rangle + b\left\langle R \middle| \overline{H}_R + V_L \middle| R \right\rangle = \bar{\varepsilon}\left\langle R \middle| a\,L + b\,R \right\rangle \qquad \text{(II.20}$$

In Eqs. II.19 and II.20 we have written the total Hamiltonian of Eq. II.10 as

$$\overline{H} = \overline{H}_L + V_R = \overline{H}_R + V_L \qquad \text{(II.21}$$

to explicitly make use of the fact that

$$\overline{H}_L\, L = \varepsilon_G\, L \qquad\qquad \overline{H}_R\, R = \varepsilon_G\, R \qquad \text{(II.22}$$

here ε_G = - 13.598 eV is the ground state energy of the hydrogen atom.

Defining

$$\langle L | V_R | L \rangle = \langle R | V_L | R \rangle \equiv -V \qquad \text{(II.23}$$

and

$$\langle L | V_L | R \rangle = \langle R | V_R | L \rangle \equiv -t \qquad \text{(II.24}$$

Eqs. II.19 and II.20 become simply

$$a(\varepsilon_G - V) - bt = \bar{\varepsilon}\, a \qquad \text{(II.25}$$

$$-at + b(\varepsilon_G - V) = \bar{\varepsilon}\, b \qquad \text{(II.26}$$

Note that because V_i are attractive potentials, the matrix elements in Eqs. II.23 and II.24 are negative. Thus V > 0 and t > 0.
In Fig. II.5 and Fig. II.6 we indicate which terms contribute to *V* and *t*. From these schematic pictures it is evident that *t* depends sensitively on the overlap of the wave functions ϕ_{R1} and ϕ_{R2}. This is the reason why *t* is called the overlap matrix element or overlap integral. When *t* is large the electron can easily tunnel from one atom to the other. When $t \to 0$ this is impossible and the electron remains permanently near one proton. The H_2^+-molecule is then, in fact, made of a neutral H atom and a lonely proton.

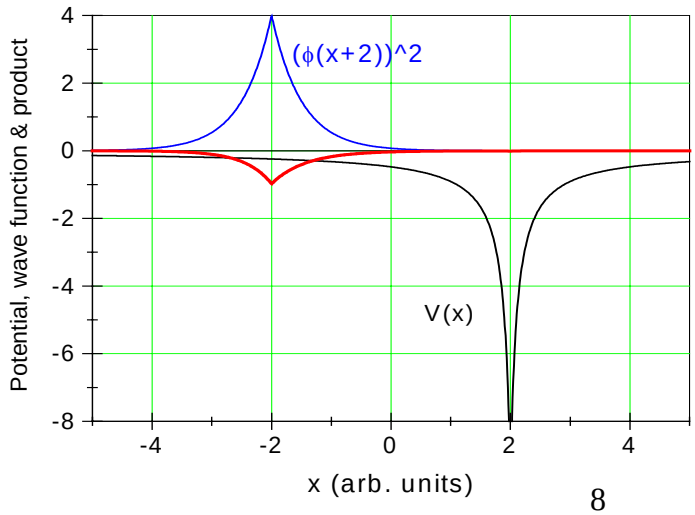


Fig. II.5: Contribution to the integral V. The blue curves indicate the square of the wave function and the black curve the potential. The red curve is the product which appears in the definition for V.

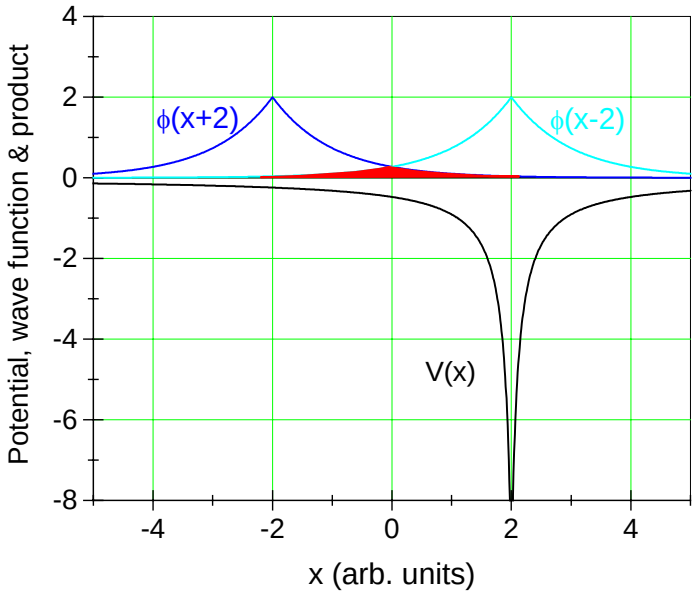


Fig. II.6: Contribution to the overlap integral t . The blue curves indicate the wave functions and the black curve the potential. The red region contributes most to the product that appears in the definition of t.

The two equations II.25 and II.26 form a system of equations that has a non-trivial solution ($a \neq 0$, $b \neq 0$) if the following determinant vanishes, i.e.

$$\begin{vmatrix} \varepsilon_G - V - \bar{\varepsilon} & -t \\ -t & \varepsilon_G - V - \bar{\varepsilon} \end{vmatrix} = 0 \qquad \text{(II.27}$$

This condition determines the eigenvalues of the problem. The determinant is equal to

$$\left[(\varepsilon_G - V) - \bar{\varepsilon}\right]^2 - t^2 = 0 \qquad \text{(II.28}$$

and, therefore,

$$\bar{\varepsilon} = (\varepsilon_G - V) \pm t \qquad \text{(II.29}$$

Note that as the Coulomb interaction is attractive both V and t are positive. Compared to the neutral H-atom in which the electron has an energy ε_G, in the H_2^+-molecule the energy of the electron is lowered by two terms:

- by $-V$ which is the Coulomb interaction energy of an electron, centred on proton "1", with proton "2"
- by $-t$ as a result of the possibility to tunnel from a state centred at proton "1" to a state centred at proton "2".

It is useful to get some intuition about this problem by actually calculating the states corresponding to the two eigenvalues in Eq. II.29.

For that we fill

$$\bar{\varepsilon}_+ = \varepsilon_G - V + t \qquad \text{(II.30}$$

in Eq. II.25 or II.26 and find that a = -b and

$$\varphi_+(r) = \frac{1}{\sqrt{2}}(L - R) \qquad \text{(II.31}$$

This is a state with a node halfway between the two protons. For the low energy state we have similarly, with

$$\bar{\varepsilon}_- = \varepsilon_G - V - t \qquad \text{(II.32}$$

$$\varphi_-(r)\frac{1}{\sqrt{2}}(L + R) \qquad \text{(II.33}$$

The square root comes from the normalisation of the wave functions φ_+ and φ_- . In Fig. II.7 we indicate schematically the change in energy of the electron when another proton is added to an hydrogen atom to form an H_2^+-molecule.

If one is interested in the total energy of the H_2^+-molecule one must include the Coulomb repulsion between the two protons into the Schrödinger equation (Eq.II.10). At large separation of the protons, the Coulomb repulsion between protons cancels to first order the electronic energy lowering –V. At very short separation of the protons their Coulomb repulsion gives a strongly positive contribution to the total energy. At intermediate proton separation, the total ground state energy is, however, still negative so that the H_2^+-molecule exists in nature.

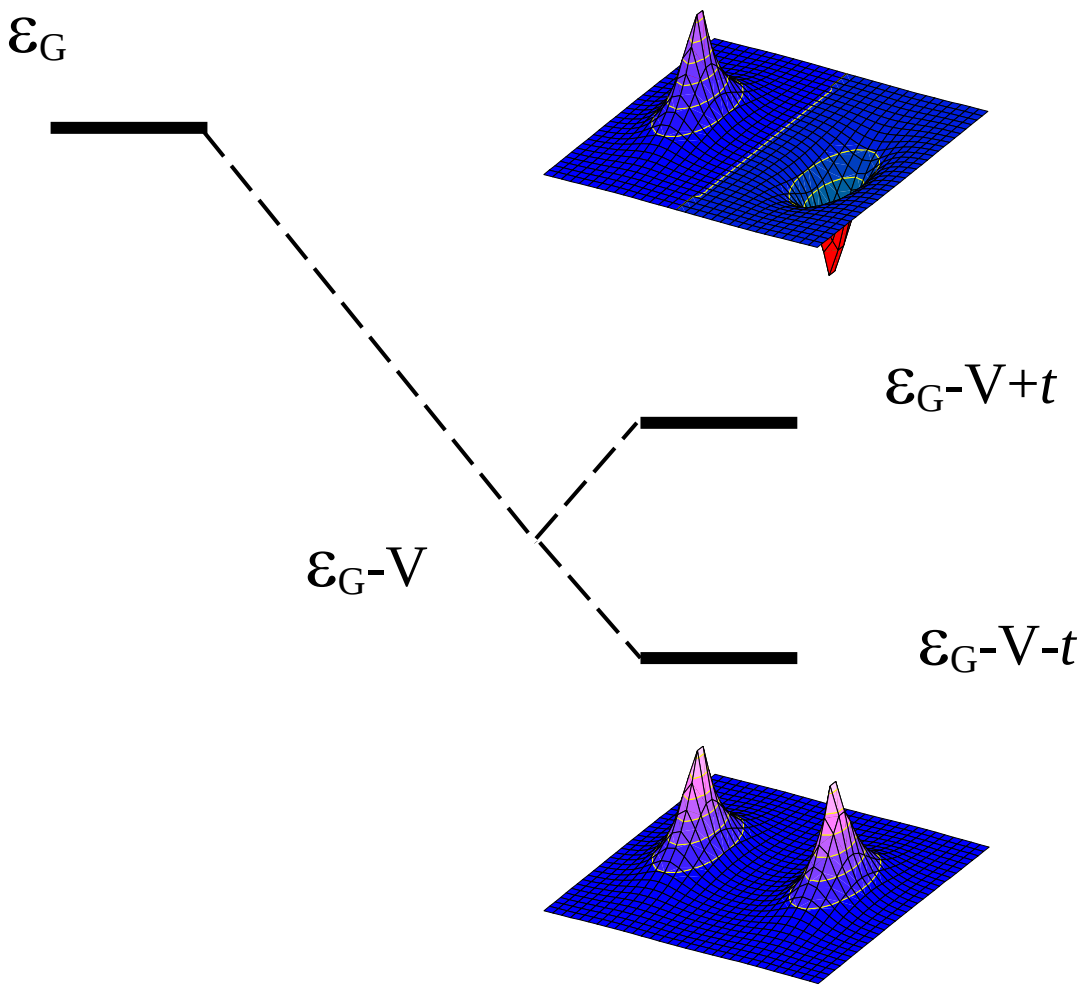


Fig. II.7: Effect of an approaching proton on the ground state of an hydrogen atom. The spatial spread of the wave functions φ_+ and φ_- is schematically indicated for the two levels (see Eqs.II.31 and 33). The lower state is called the **bonding** state. The upper state is called the **antibonding** state. Only the electronic terms are considered. The repulsive proton-proton interaction is not taken into account.

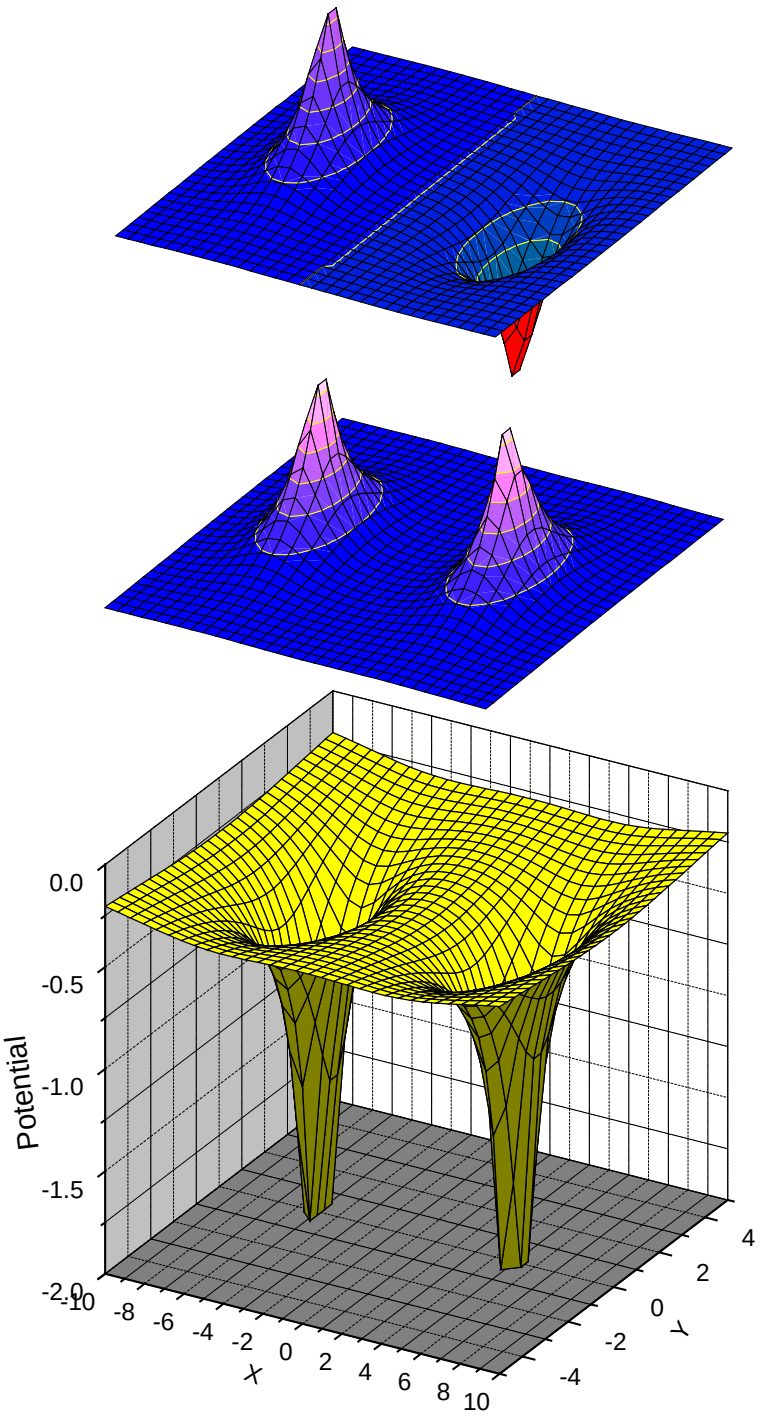


Fig. II.8: Bonding and antibonding states in a situation where both protons are far apart (at x = -5 and x = +5 in arbitrary units).

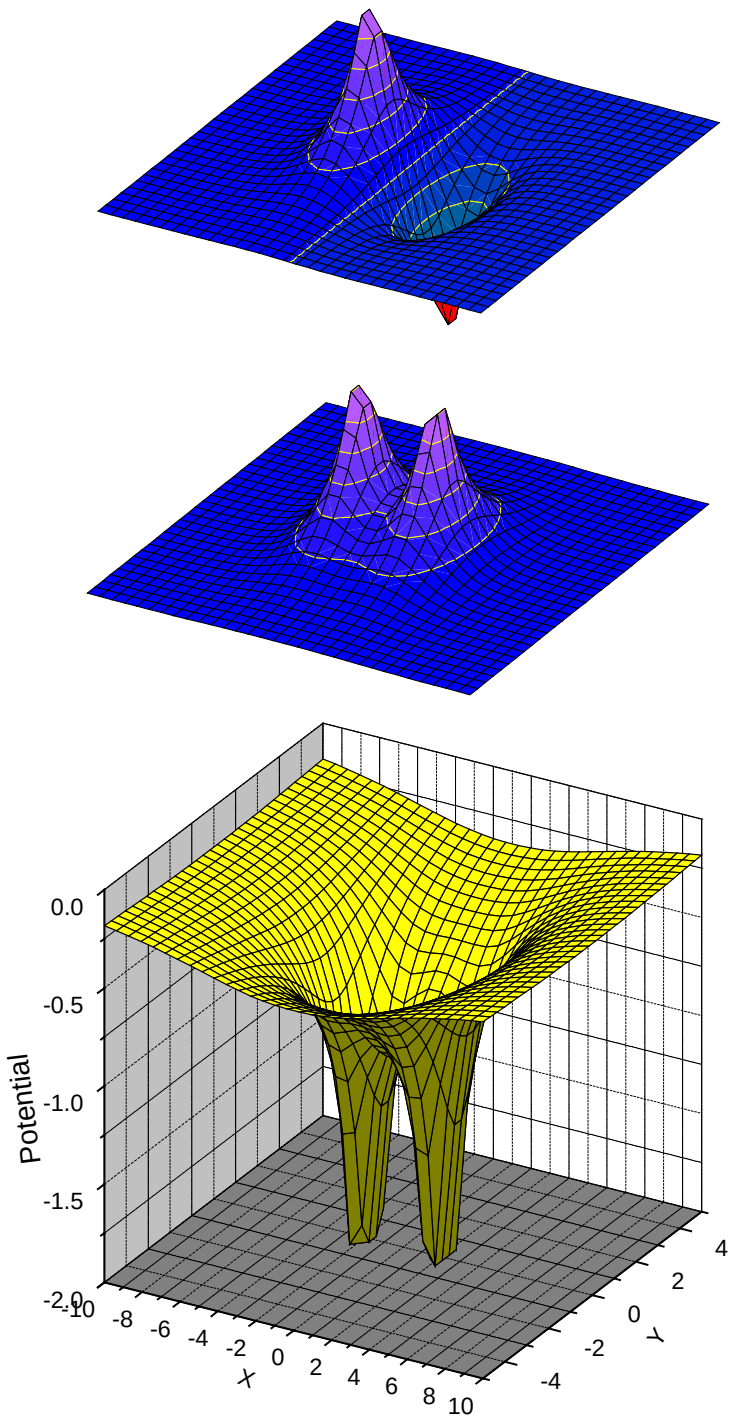


Fig. II.9: Bonding and antibonding states in a situation where both protons (at x = -2 and x = +2) are close to each other. Their overlap is then much larger than in Fig. II.8 and the electron can easily tunnel from one proton to the other. Note that the wave function of the antibonding state is strictly zero exactly halfway between the protons.

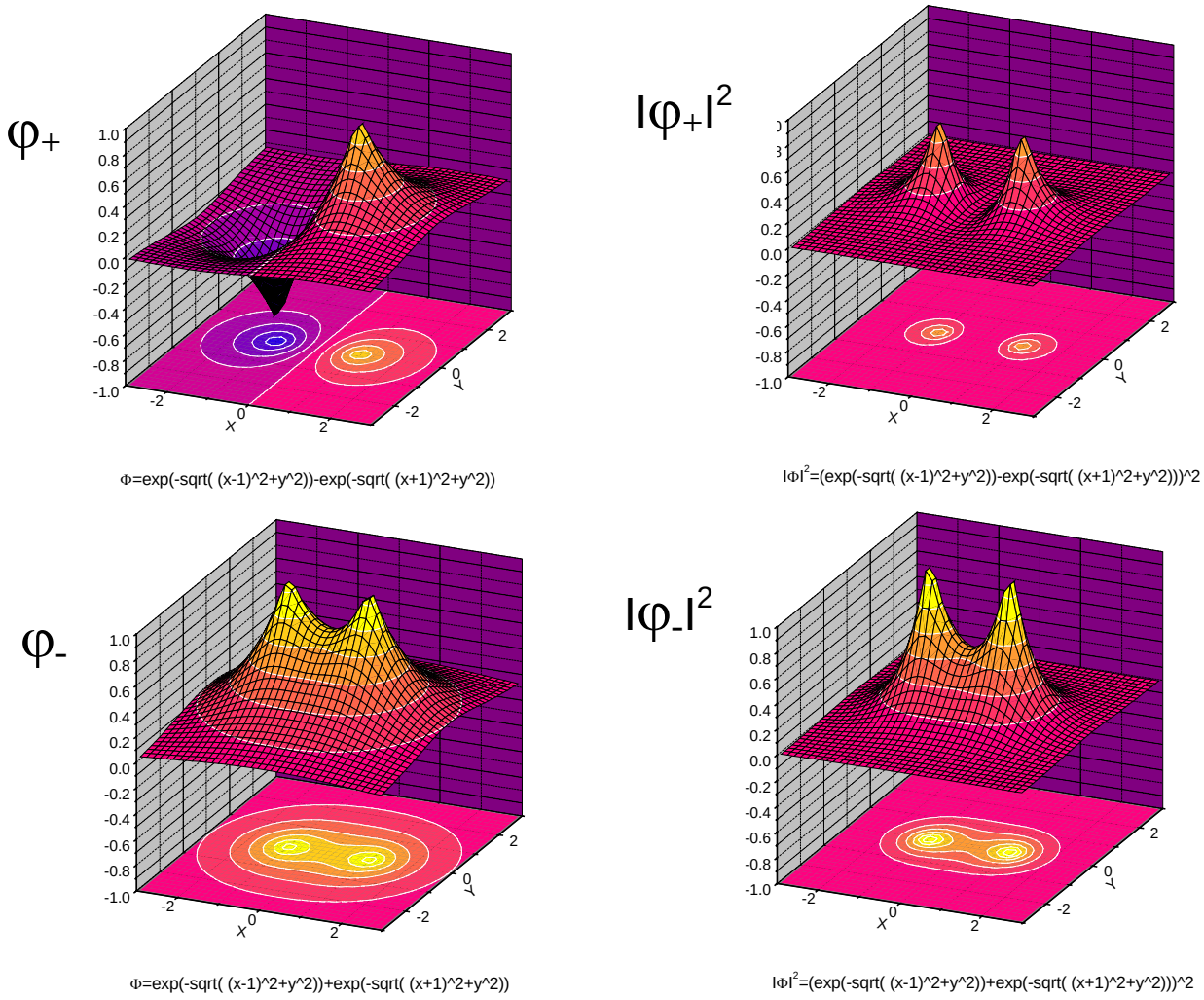


Fig. II.10: Schematic representation of the antibonding (top) and bonding (bottom) states of the H_2^+ molecule. On the left we indicate the wave functions and on the right the square of the wave functions. The functions actually plotted for the illustrations are indicated below each figure.

II.4 THE H_2 MOLECULE

The H_2 molecule consists of two electrons orbiting around two protons at position **L** and **R, L** and **R** standing for left and right.

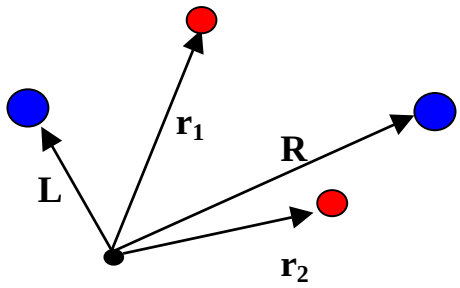


Fig. II.11: Definition of the coordinates chosen for the H_2 molecule. The protons are in blue and the electrons in red.

The Schrödinger equation of for the two electrons is

$$-\frac{\hbar^2}{2m}\Delta_1\Psi-\frac{\hbar^2}{2m}\Delta_2\Psi+\left(\begin{array}{l}-\dfrac{e^2}{4\pi\varepsilon_0|\mathbf{L}-\mathbf{r}_1|}-\dfrac{e^2}{4\pi\varepsilon_0|\mathbf{R}-\mathbf{r}_1|}\\ -\dfrac{e^2}{4\pi\varepsilon_0|\mathbf{L}-\mathbf{r}_2|}-\dfrac{e^2}{4\pi\varepsilon_0|\mathbf{R}-\mathbf{r}_2|}+\dfrac{e^2}{4\pi\varepsilon_0|\mathbf{r}_2-\mathbf{r}_1|}\end{array}\right)\Psi=E\Psi \quad (\text{II.34}$$

where the wave function depends on $\mathbf{r_1}$ and $\mathbf{r_2}$. For simplicity we write Eq.II.34 as

$$\left[T_1+V_L(1)+V_R(1)+T_2+V_R(2)+V_L(2)+V_{12}\right]\Psi=E\Psi \quad (\text{II.35}$$

with

$$V_L(i)=-\frac{e^2}{4\pi\varepsilon_0|\mathbf{L}-\mathbf{r}_i|} \qquad V_R(i)=-\frac{e^2}{4\pi\varepsilon_0|\mathbf{R}-\mathbf{r}_i|} \quad (\text{II.36}$$

and

$$V_{12}=-\frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_2-\mathbf{r}_1|} \quad (\text{II.37}$$

We construct a two-electron state from the atomic s-orbitals $\varphi(\mathbf{r}_i\text{-}\mathbf{L})$ and $\varphi(\mathbf{r}_i\text{-}\mathbf{R})$ which, for simplicity, shall be denoted below as L_i and R_i, respectively. There are six possible states

$$\begin{aligned}
\Phi_0 &= \frac{1}{\sqrt{2}}\left[L_1R_2 + L_2R_1\right]\times\left|\uparrow\downarrow - \downarrow\uparrow\right\rangle \\
\Phi_1^1 &= \frac{1}{\sqrt{2}}\left[L_1R_2 - L_2R_1\right]\times\left|\uparrow\uparrow\right\rangle \\
\Phi_1^0 &= \frac{1}{\sqrt{2}}\left[L_1R_2 - L_2R_1\right]\times\left|\uparrow\downarrow + \downarrow\uparrow\right\rangle \\
\Phi_1^{-1} &= \frac{1}{\sqrt{2}}\left[L_1R_2 - L_2R_1\right]\times\left|\downarrow\downarrow\right\rangle
\end{aligned} \qquad \text{(II.38}$$

$$\begin{aligned}
\Phi_L &= \left[L_1L_2\right]\times\left|\uparrow\downarrow - \downarrow\uparrow\right\rangle \\
\Phi_R &= \left[R_1R_2\right]\times\left|\uparrow\downarrow - \downarrow\uparrow\right\rangle
\end{aligned} \qquad \text{(II.39}$$

The three states Φ_0, Φ_L, Φ_R have zero total spin (S=0) while the states Φ_1^1, Φ_1^0, Φ_1^{-1} have total spin 1. The solution of the Schrödinger equation will be seeked in the form of a linear combination of these six wave functions, i.e.

$$\Psi = c_0\Phi_0 + c_1\Phi_1^1 + c_2\Phi_1^0 + c_3\Phi_1^{-1} + c_4\Phi_L + c_5\Phi_R \qquad \text{(II.40}$$

In building up the matrix equation for the coefficients c_i we need to calculate matrix elements of the form

$$\begin{aligned}
&\left\langle L_1R_2 \pm L_2R_1 \middle| L_1R_2 \pm L_2R_1\right\rangle \\
&\left\langle L_1R_2 \pm L_2R_1 \middle| L_1L_2\right\rangle \\
&\left\langle L_1R_2 \pm L_2R_1 \middle| R_1R_2\right\rangle \\
&\left\langle L_1L_2 \middle| R_1R_2\right\rangle
\end{aligned} \qquad \text{(II.41}$$

and

$$\begin{aligned}
&\left\langle L_1R_2 \pm L_2R_1 \middle| H \middle| L_1R_2 \pm L_2R_1\right\rangle \\
&\left\langle L_1R_2 \pm L_2R_1 \middle| H \middle| L_1L_2\right\rangle \\
&\left\langle L_1R_2 \pm L_2R_1 \middle| H \middle| R_1R_2\right\rangle \\
&\left\langle L_1L_2 \middle| H \middle| R_1R_2\right\rangle
\end{aligned} \qquad \text{(II.42}$$

We assume here again that the overlaps between L and R orbitals are such that

$$\langle L_1 | R_1 \rangle = \langle L_2 | R_2 \rangle = 0 \qquad \text{and} \qquad \langle L_1 | L_1 \rangle = \langle R_1 | R_1 \rangle = 1 \quad (\tag{II.43}$$

In the spirit of the so-called **Hubbard** approximation[2] we assume now that the Coulomb repulsion is only important when the two electrons are near the same proton. This implies that all matrix elements involving V_{12} vanish except

$$\langle L_1 L_2 | V_{12} | L_1 L_2 \rangle = \langle R_1 R_2 | V_{12} | R_1 R_2 \rangle = U \quad (\tag{II.44}$$

Introducing the notation

$$\begin{aligned} [T_i + V_R(i)] R_i &= \varepsilon_0 R_i \\ [T_i + V_L(i)] L_i &= \varepsilon_0 L_i \end{aligned} \tag{II.45}$$

$$\begin{aligned} \varepsilon_H &= \varepsilon_0 + \langle L_i | V_R(i) | L_i \rangle \\ \varepsilon_H &= \varepsilon_0 + \langle R_i | V_L(i) | R_i \rangle \end{aligned}$$

and

$$W = \langle L_i | V_L(i) | R_i \rangle = \langle L_i | V_R(i) | R_i \rangle \tag{II.46}$$

we obtain the following matrix

$$\begin{pmatrix} 2\varepsilon_H & 0 & 0 & 0 & \sqrt{2}W & \sqrt{2}W \\ 0 & 2\varepsilon_H & 0 & 0 & 0 & 0 \\ 0 & 0 & 2\varepsilon_H & 0 & 0 & 0 \\ 0 & 0 & 0 & 2\varepsilon_H & 0 & 0 \\ \sqrt{2}W & 0 & 0 & 0 & (2\varepsilon_H + U) & 0 \\ \sqrt{2}W & 0 & 0 & 0 & 0 & (2\varepsilon_H + U) \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \end{pmatrix} = E \begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \end{pmatrix} \tag{II.47}$$

There exists a non-trivial solution if the following determinant vanishes,

$$\begin{vmatrix} 2\varepsilon_H - E & 0 & 0 & 0 & \sqrt{2}W & \sqrt{2}W \\ 0 & 2\varepsilon_H - E & 0 & 0 & 0 & 0 \\ 0 & 0 & 2\varepsilon_H - E & 0 & 0 & 0 \\ 0 & 0 & 0 & 2\varepsilon_H - E & 0 & 0 \\ \sqrt{2}W & 0 & 0 & 0 & (2\varepsilon_H + U) - E & 0 \\ \sqrt{2}W & 0 & 0 & 0 & 0 & (2\varepsilon_H + U) - E \end{vmatrix} = 0 \tag{II.48}$$

There are three degenerate states with energy

$$E = 2\varepsilon_H \qquad \text{(II.49}$$

The other three states have an energy given by

$$\begin{vmatrix} (2\varepsilon_H - E) & \sqrt{2}W & \sqrt{2}W \\ \sqrt{2}W & (2\varepsilon_H + U - E) & 0 \\ \sqrt{2}W & 0 & (2\varepsilon_H + U - E) \end{vmatrix} = 0 \qquad \text{(II.50}$$

For a discussion of the behaviour of the roots of this equation we take the zero of energy as $2\varepsilon_H = 0$. Then,

$$\begin{vmatrix} (-E) & \sqrt{2}W & \sqrt{2}W \\ \sqrt{2}W & (U - E) & 0 \\ \sqrt{2}W & 0 & (U - E) \end{vmatrix} = 0 \qquad \text{(II.51}$$

with the secular equation

$$E(U - E)^2 + 4W^2(U - E) = 0 \qquad \text{(II.52}$$

The energy eigenvalues are

$$E_5 = \frac{U}{2} + \frac{1}{2}\sqrt{(U^2 + 16W^2)} \qquad \text{(-0.41, 0, 0, 0, -0.64, -0.64)} \qquad \text{(II.53}$$

$$E_0 = \frac{U}{2} - \frac{1}{2}\sqrt{(U^2 + 16W^2)} \qquad \text{(0.91, 0, 0, 0, -0.29, -0.29)} \qquad \text{(II.54}$$

and

$$E_4 = U \qquad \text{(0, 0, 0, 0, -0.71, 0.71)} \qquad \text{(II.55}$$

Furthermore there are the three states at $E_1=E_2=E_3=0$ corresponding to Eq. II.49 with our new choice of the energy zero. The values given in the parentheses are the eigenvectors (c_0, c_1, c_2, c_3, c_4, c_5) for a situation with U = 5 eV and W = $-\sqrt{2}$ eV. The corresponding energy levels are indicated in Fig. II.12. For clarity, we have also indicated the situation in absence of hybridisation, i.e. when W=0.

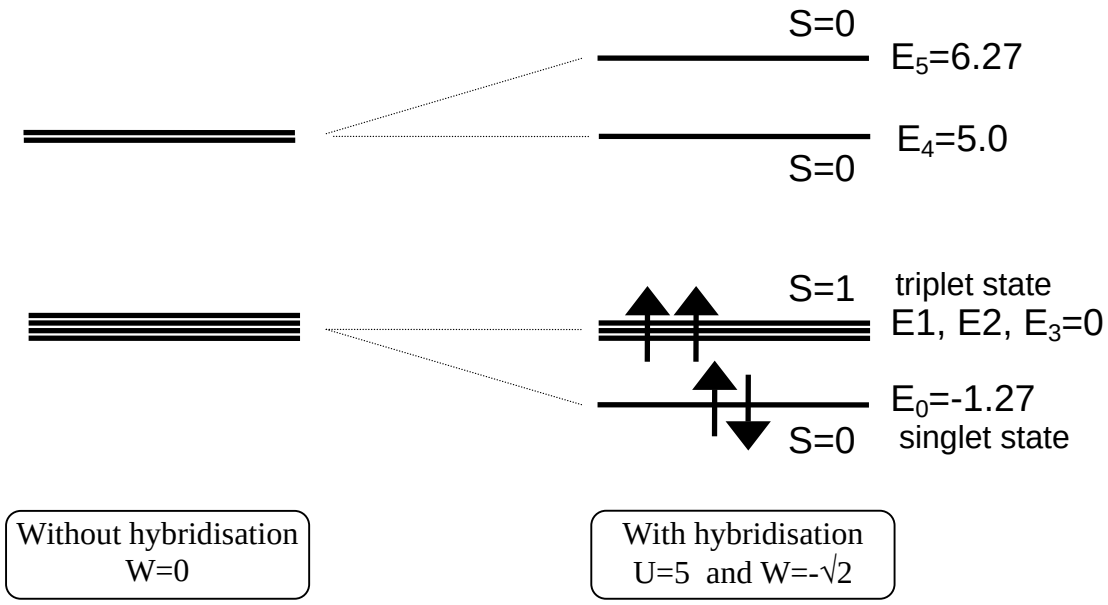


Fig. II.12: Influence of hybridisation on the total electronic energy of the H_2 molecule in the Hubbard approximation. The ground state is called the **bonding** state. Its total spin is S=0. The triplet state has S=1. The ground state is thus non-magnetic. The eigenvectors are given in Eqs.II.53-55.

The ground state has a lower energy when W≠0 than for a situation where hybridisation vanishes. This is expected since W≠0 corresponds to a situation where tunnelling of an electron from one hydrogen to the other is possible. This weaker localisation of the electrons in space leads to a lowering of their energy as a result of Heisenberg's uncertainty principle. The ground state having zero total spin is non-magnetic. The density of electrons does not vanish between the two protons as it does for the antisymmetric states with higher energies.

The dependence of the ground state energy (singlet state) as a function of the proton separation is indicated in
Fig. II.13. In contrast to the triplet state, the energy of the singlet state exhibits a minimum for a proton-proton separation of 0.74611 Å. The binding energy is then 4.52 eV. This implies that 2.26 eV are needed to break the H-H bond in the H_2 molecule. This corresponds to an energy of 218.1 kJ/molH since 1 eV=96.485 kJ/molH.

The different spin arrangements for the two states makes it possible to produce **atomic** hydrogen. For this one needs only to place hydrogen in a strong magnetic field that forces both spins to be parallel to each other. Silvera and Walraven[3] showed experimentally that atomic H with a density of 1.8×10^{14} atoms/cm^3 could be kept for more than 9 minutes at a temperature of 0.27 K in a magnetic field of 7 T. There are two types of hydrogen molecules in the singlet state that differ only through the value of the proton nuclear spin. This a direct consequence of the requirement that the total wave function of a system must be antisymmetric for the permutation of fermionic particles and symmetric for bosonic particles. This implies that the wave function of a H_2 (T_2) molecule must be antisymmetric for the permutation of the protons (tritons) and symmetric for the permutation of the deuterons in the D_2 molecule.

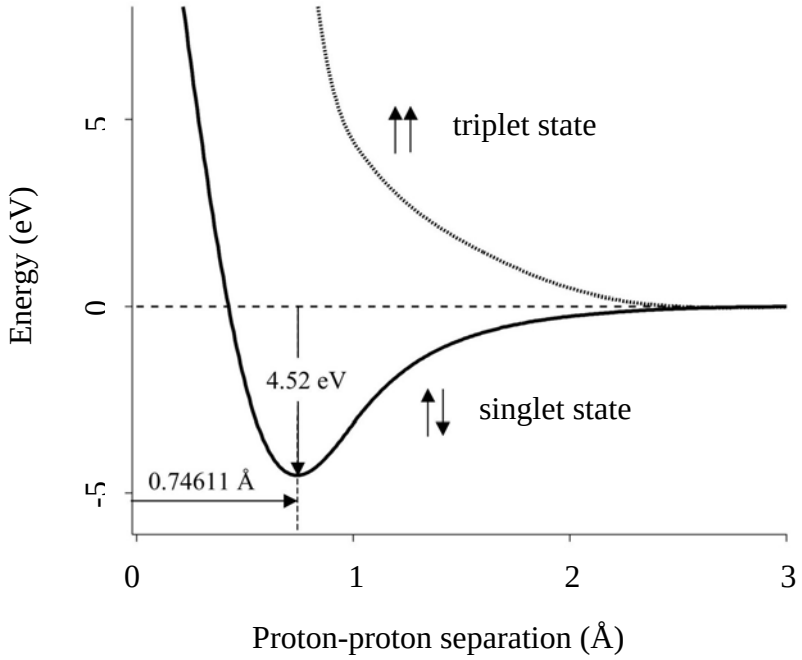


Fig. II.13:Bonding and antibonding states of the H_2 molecule. At large separation W is very small and the singlet and triplet states are degenerate (see Fig. II.12). The large increase at small proton-proton separation is due to their Coulomb repulsion.

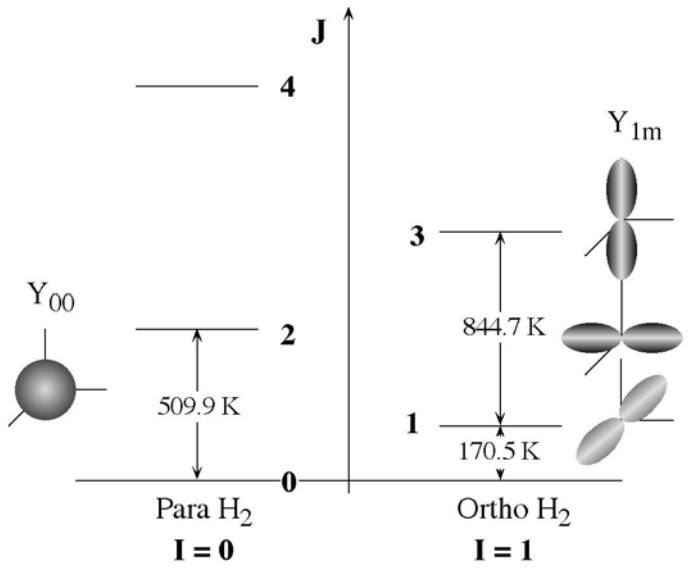


Fig. II.14. Energy and wave function for the rotation states of a Para- and Ortho-Hydrogen molecule. I is the nuclear spin and J the rotation quantum number. The nuclear spin I assumes the values 0 and 1 while J=0, 1, 2, ….

The $(2I+1)^2$ possible nuclear spin states for two identical particles with spin I are split into $(2I+1)\cdot(I+1)$ symmetric states and $(2I+1)\cdot I$ antisymmetric states with respect to the permutation of the particles. The nuclear spins must be coupled to the rotation degrees of freedom in such a way that the total wave function is antisymmetric for the permutation of the nuclei. This leads to two the two types of hydrogen: **Para- (I = 0)** and **Ortho-Hydrogen(I = 1)**. At room temperature normal hydrogen (n-H_2) consists of 25% Para-hydrogen and 75% Ortho-hydrogen. The melting and boiling points of para-hydrogen are approx. 0.1 K lower than that of normal hydrogen.

II.5 HYDROGEN GAS AND LIQUID

The interaction between H_2 molecules is rather weak compared to other gases and consequently the critical temperature is low (T_c = 33.0 K). At temperatures far above the critical point and at pressures lower than the critical pressure (p_c = 1.30 MPa, i.e. 13 bar) hydrogen gas behaves almost ideally and can be accurately described by the Van der Waals (1873) equation for n moles gas

$$\left(p+\frac{n^2}{V^2}\cdot a\right)\cdot\left(V-n\cdot b\right)=n\cdot R\cdot T \qquad \text{(II.56}$$

with R = 8.314 $JK^{-1}mol^{-1}$; a = 2.476×10^{-2} m^6Pamol^{-2} ; b = 2.661×10^{-5} m^3mol^{-1}.

Table II.3: Molar volume V, enthalpy H, Gibbs free energy G and entropy S for H_2 at T = 298 K as given by Hemmes et al.[4]

p [bar]	V [l·mol^{-1}]	H^0 [J·mol^{-1}]	G^0 [J·mol^{-1}]	S^0 [J·mol^{-1}K^{-1}]
1	24.94302	8506	-30724	130.77
2	12.48587	8507	-28994	125.00
5	5.00308	8510	-26704	117.38
10	2.50887	8515	-24968	111.61
20	1.26183	8526	-23224	105.84
50	0.51373	8560	-20895	98.18
100	0.26451	8620	-19091	92.37
200	0.14009	8747	-17210	86.52
500	0.006578	9176	-14450	82.63
1000	0.004098	9954	-11924	72.93

From the thermodynamic relation

$$\left(\frac{\partial G}{\partial p}\right)_T = V \qquad \text{(II.57}$$

we obtain, using the ideal gas relation pV = nRT , that

$$G = G^0 + RT \ln\left(\frac{p}{p^0}\right) \qquad \text{(II.58}$$

The Gibbs free energy and consequently, the chemical potential of H_2 gas, varies logarithmically with pressure. This is of course only true at low pressures. For real gases calculations with the Gibbs free energy are more transparent when a new quantity, the **fugacity f**, is introduced. The idea is to keep formally the same functional relation as for an ideal gas. We write

$$G_2 - G_1 = RT \int_{p_1}^{p_2} V dp = RT \ln\left(\frac{f_2}{f_1}\right) \qquad \text{(II.59}$$

with $\lim_{p\to 0}\left(\frac{f}{p}\right) = 1$ and

$$RT \ln\left(\frac{f}{p}\right) = \int_{p=0}^{p} \left(V - \frac{RT}{p}\right) \cdot dp \qquad \text{(II.60}$$

At low pressures, say up to 0.1 GPa, the fugacity is essentially equal to the pressure p. At higher pressures large deviations occur (see Fig. II.17).

The relation between pressure and volume for a real gas is often expressed in term of the so-called **virial coefficients** in the form

$$pV = nRT + B(T)\frac{n}{V} + C(T)\frac{n^2}{V^2} + ... \qquad \text{(II.61}$$

The virial-coefficients are in general depending on the gas and temperature and can be found in appropriate tables. For hydrogen gas one finds for 15 K < *T* < 400 K the following approximation[5] for the coefficient B(*T*):

$$B(T) = 15.4 - 9.0 \cdot \left(\frac{T}{T_0} - 1\right) - 0.2 \cdot \left(\frac{T}{T_0} - 1\right)^2 \text{ with } T_0 = 298.15 \text{ K} \qquad \text{(II.62}$$

It is well-known that the Van der Waals relation leads to p-V isotherms

$$p(V) = \frac{n \cdot R \cdot T}{V - n \cdot b} - a \cdot \frac{n^2}{V^2} \qquad \text{(II.63}$$

that are not everywhere physically meaningful. At low temperatures one can obtain negative pressures for a certain range of volumes. Furthermore, there are regions where the pressure increases with increasing volume. This is the signature of two coexisting (liquid-gas) phases. In

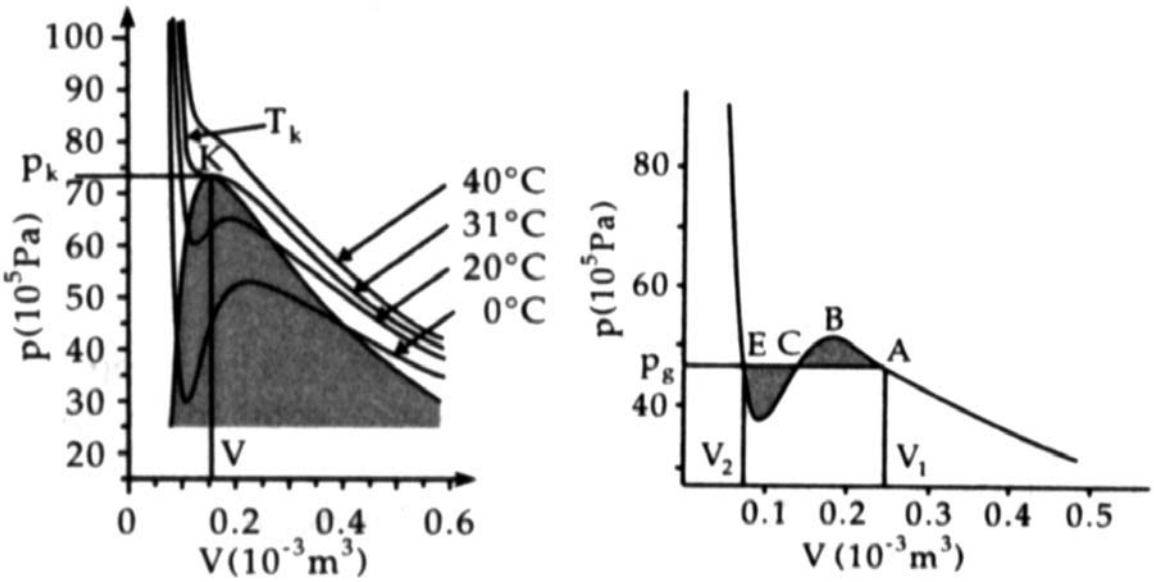


Fig. II.15: Pressure-volume (p-V) isotherms of a Van der Waals gas at four temperatures. In the right panel we illustrate Maxwell's construction. The areas of the shaded regions are equal.

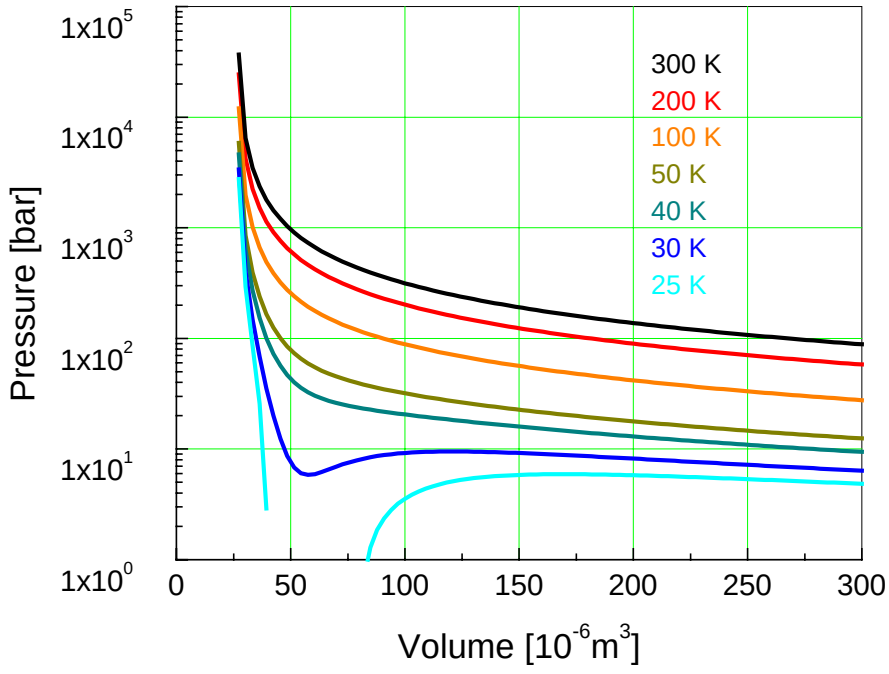


Fig. II.16: Vand der Waals isotherms for hydrogen at several temperatures.

the coexistence region pressure is constant and the value of the plateau pressure can be obtained by means of the so-called Maxwell construction as shown in Fig. II.15.
At the critical temperature T_k the p-V isotherms have a point of inflexion for a given value of the volume and pressure (V_k, p_k). Above the critical temperature we have always $dp/dV < 0$. The critical point is obtained by requiring both $dp/dV = 0$ and $d^2p/dV^2 = 0$. For a Van der Waals gas,

$$T_k = \frac{8a}{27Rb}, \qquad p_k = \frac{a}{27b^2}, \quad V_k = 3 \cdot b \tag{II.64}$$

In term of the reduced variables

$$\overline{p} = \frac{p}{p_k}, \quad \overline{V} = \frac{V}{V_k} \quad \overline{T} = \frac{T}{T_k} \tag{II.65}$$

one can cast the Van der Waals equation in the following general form

$$\left(\overline{p} + \frac{3}{\overline{V}^2}\right)\left(3\overline{V} - 1\right) = 8\overline{T} \tag{II.66}$$

Table II.4: Properties of hydrogen gas: some useful constants

Gas constant	4125	$J \cdot kg^{-1} K^{-1}$
Specific heat c_p at 293 K	14'266	$J \cdot kg^{-1} K^{-1}$
Density of gas	0.08988	$kg \cdot m^{-3}$
Density of liquid	70.8	$kg \cdot m^{-3}$
Critical point temperature T_k	33.25	$K\ kJ \cdot m^{-3}$
Critical point pressure p_k	13.07×10^5	Pa
Boiling point at normal pressure	20.28	K
Enthalpy of vaporisation ΔH_v	451.9	$kJ \cdot kg^{-1}$
Melting point at normal pressure T_m	14.1	K
Enthalpy of melting ΔH_m	58.6	$kJ \cdot kg^{-1}$

II.6 STATISTICAL TREATMENT OF HYDROGEN GAS

As found experimentally H_2 gas is very well described as an ideal Boltzmann gas for pressures smaller than 2400 Torr and temperatures higher than 120°C. In what follows we assume that according to Boltzmann's statistics the occupation number of a molecular energy level is much smaller than 1. This implies that the chance of finding two molecules in the same state is vanishingly small, and, from the general relation for the free energy

$$\mathrm{F} = -\mathrm{kT}\ln\sum_{\mathrm{n}} \exp\left(-\frac{E_n}{kT}\right) \tag{II.67}$$

where the sum is over all states of the gas containing N_{H_2} molecules, we find

$$\left(\sum_{\substack{n \\ states of the\ gas}} e^{-E_n/kT} \right) = \sum_n e^{-\sum_k \varepsilon_k/kT} = \left(\sum_{\substack{k \\ molecular\ energies}} e^{-\varepsilon_k/kT} \right)^{N_{H_2}} \frac{1}{N_{H_2}!} \qquad (\text{II.68}$$

where ε_k is the energy of the k-th molecule. The division by $N_{H_2}!$ is necessary because a given set of N_{H_2} energies $\left\{\varepsilon_1,...,\varepsilon_{N_{H_2}}\right\}$ does not define one state of the gas but $N_{H_2}!$ states which differ only by permutation of the molecules (one divides by $N_{H_2}!$ because all the ε_k are assumed to be different). From Eq.II.68 one obtains

$$F = -kTN_{H_2} \ln \sum_k e^{-\varepsilon_k/kT} + kT \ln N_{H_2}! \qquad (\text{II.69}$$

and using Stirling's formula

$$\ln N! \cong N \ln \frac{N}{e} \qquad (\text{II.70}$$

we have, simply

$$F = -kTN_{H_2} \ln \left(\frac{e}{N_{H_2}} \sum_k e^{-\varepsilon_k/kT} \right) \qquad (\text{II.71}$$

In the temperature and pressure ranges of interest the energy of a molecule is given by the following classical expression

$$\varepsilon = \varepsilon_b + \frac{\mathbf{p}^2}{2m} + \frac{\mathbf{M}^2}{2\Theta_{H_2}} \qquad (\text{II.72}$$

where ε_b is the binding energy of the H_2 molecule (as for the lattice gas we take the zero energy at the energy of an H-atom, i.e. a dissociated H_2 molecule), **M** is the angular momentum and Θ is the moment of inertia of the molecule. The classical limit of Eq.II.71 is

$$F = -kTN_{H_2} \ln \frac{e}{N_{H_2}} \frac{1}{(2\pi\hbar)^r} \int e^{-\varepsilon(\mathbf{p},\mathbf{q})/kT} \mathbf{dpdq} \qquad (\text{II.73}$$

where $\mathbf{dp}=dp_1,...,dp_r$ and $\mathbf{dq}=dq_1,...,dq_r$ where r is the number of degrees of freedom of the molecule. Without going into the details of the calculation of the integral in Eq.II.73 we arrive at

the following expression (see Landau-Lifschitz, Statistical Physics Chapter IV) for the free energy of a diatomic gas H_2

$$F_{H_2} = N_{H_2}\varepsilon_b + F_{translational} + F_{rotational}$$

$$= \left\{N_{H_2}\varepsilon_b\right\} + \left\{-N_{H_2}kT\ln\left[\frac{eV}{N_{H_2}}\left(\frac{m_{H_2}kT}{2\pi\hbar^2}\right)^{3/2}\right]\right\} + \left\{-N_{H_2}kT\ln\left(\frac{kT\Theta_{H_2}}{\hbar^2}\right)\right\} \qquad (\text{II.74})$$

from which we derive the chemical potential μ_{H_2}

$$\mu_{H_2} = \frac{\partial F_{H_2}}{\partial N_{H_2}} = \varepsilon_b - kT\ln\left[\frac{eV}{N_{H_2}}\left(\frac{m_{H_2}kT}{2\pi\hbar^2}\right)^{3/2}\right] + kT - kT\ln\left(\frac{kT\Theta_{H_2}}{\hbar^2}\right)$$
$$= \varepsilon_b - kT\ln\left[\frac{V}{N_{H_2}}kT\left(\frac{m_{H_2}kT}{2\pi\hbar^2}\right)^{3/2}\frac{\Theta_{H_2}}{\hbar^2}\right] \qquad (\text{II.75})$$

Remembering that for an ideal gas

$$pV = N_{H_2}kT \qquad (\text{II.76})$$

we can express μ_{H_2} as a function of p and T

$$\mu_{H_2}(p,T) = \varepsilon_b - kT\ln\left[\frac{\Theta_{H_2}(kT)^2}{p\hbar^5}\left(\frac{m_{H_2}kT}{2\pi}\right)^{3/2}\right] \qquad (\text{II.77})$$

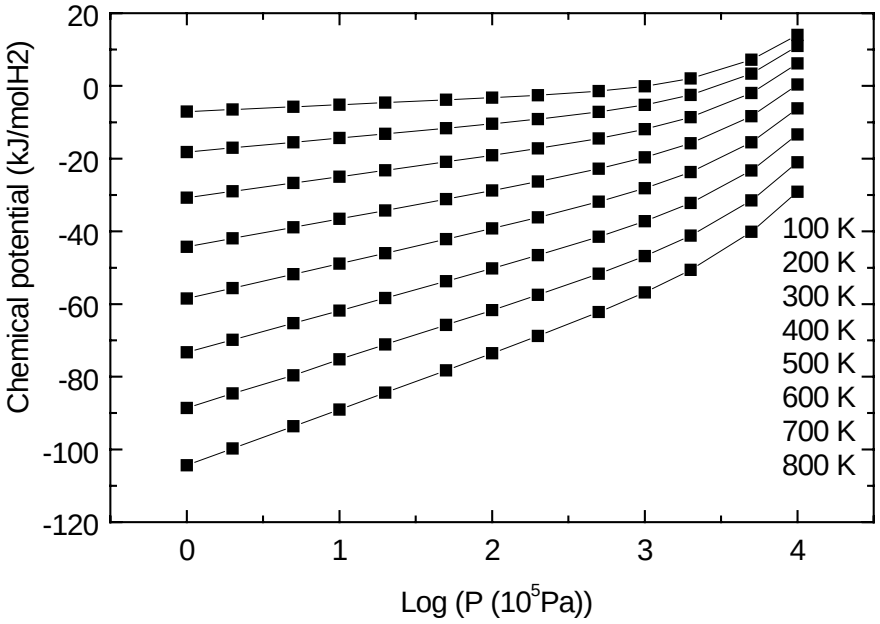
or

$$\mu_{H_2} = \varepsilon_b + kT\ln\left[\frac{p}{p_0(T)}\right] \qquad (\text{II.78})$$

with

$$p_0(T) = \left(\frac{(kT)^{7/2}\Theta_{H_2}m_{H_2}^{3/2}}{\hbar^5(2\pi)^{3/2}}\right) \qquad (\text{II.79})$$

Fig. II.17: Chemical potential μ_{H_2} of molecular hydrogen as a function of pressure for various temperatures. The values of other thermodynamic



functions can be found in Hemmes et al. At low pressures the chemical potential is clearly proportional to the logarithm of the pressure.

For hydrogen we have approximately

$$p_0(T) = \left(\frac{T}{9.13} \right)^{7/2} \qquad \text{(II.80}$$

with $p_0(T)$ expressed in bar and T in Kelvin .

II.7 SOLID HYDROGEN

At sufficiently low temperatures hydrogen becomes solid. Its melting line is given by[6]

$$p_m[MPa] = -51.49 + 0.1702 \times \left(T_m[K] + 9.689 \right)^{1.8077} \qquad \text{(II.81}$$

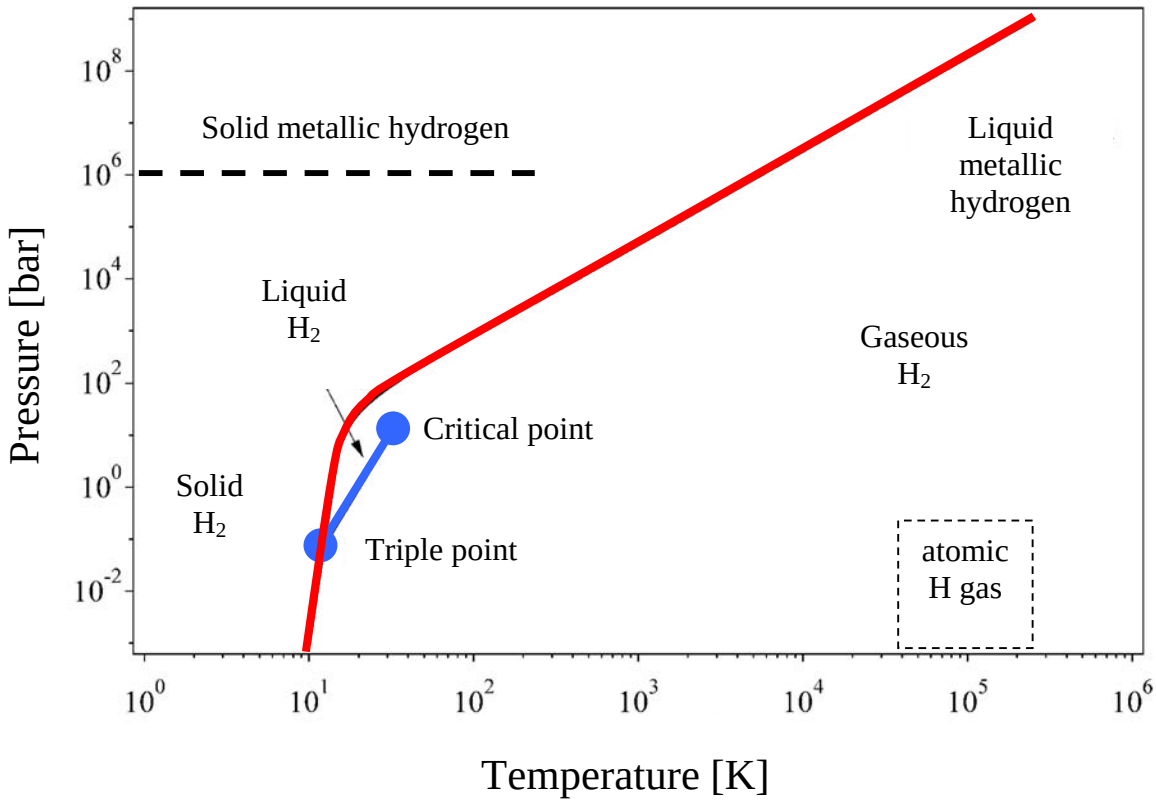


Fig. II.18: Schematic phase diagram of hydrogen

where p_m is the hydrogen vapour pressure and T_m the melting temperature. The melting temperature of hydrogen is about 4% lower than that of Deuterium.
Hydrogen (H_2, D_2) is a molecular solid that crystallises at low pressure in an hcp structure. The „spherical“ form (I = 0) (Para-Hydrogen and Ortho-Deuterium) remain in the hcp down to 0 K. The „non-spherical“ form (I = 1) (Ortho-Hydrogen and Para-Deuterium) transform below 3 K into a fcc structure.

One expects that molecular hydrogen transforms into an atomic metallic phase at very high pressures ($p > 10^6$ bar). Theoretical models predict metallisation pressures in the order 1.5×10^6 and 4×10^6 bar corresponding to hydrogen molar volumes between 2.4 and 2.0 cm^3mol^{-1}.

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