Hydrogen atom, molecule and gas: a reminder

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Short review of quantum mechanics

- Hydrogen
  - Hydrogen atom
  - Hydrogen molecule ion (H_2^+)
  - Hydrogen molecule (H_2)
- Hydrogen gas and liquid
- Solid hydrogen

Short review of quantum mechanics

- Hydrogen
  - Hydrogen atom
    - The Schrödinger equation
    - The angular part
    - The radial part
    - The angular and radial parts together

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Schrödinger equation

$$-\frac{\hbar^2}{2m}\Delta\Psi(r,\vartheta,\varphi)-\frac{e^2}{4\pi\varepsilon_o r}\Psi(r,\vartheta,\varphi)=E\Psi(r,\vartheta,\varphi)$$

$$\Delta=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right)+\frac{1}{r^2\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}$$

Separation of variables

$$\Psi(r,\vartheta,\varphi)=R(r)\Theta(\vartheta)\Phi(\varphi)$$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+r^2\frac{2m}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_o r}\right)+$$

$$+\frac{1}{\Theta}\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial\Theta}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}=0$$

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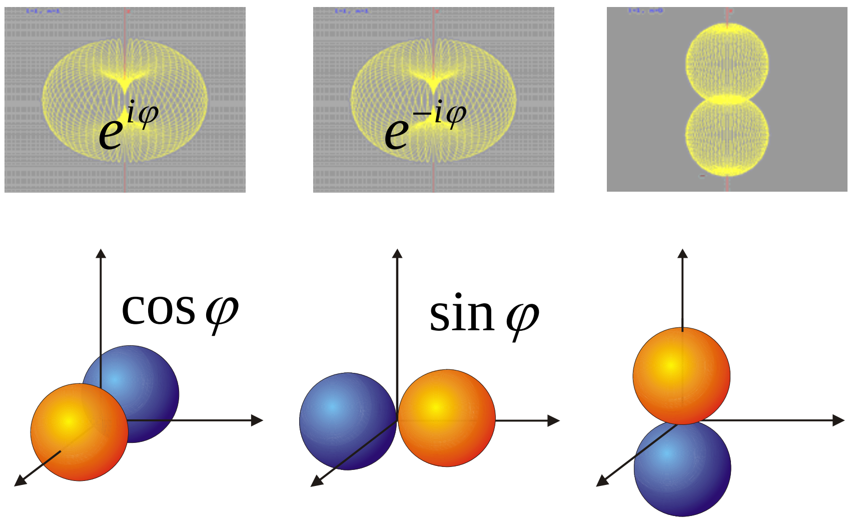
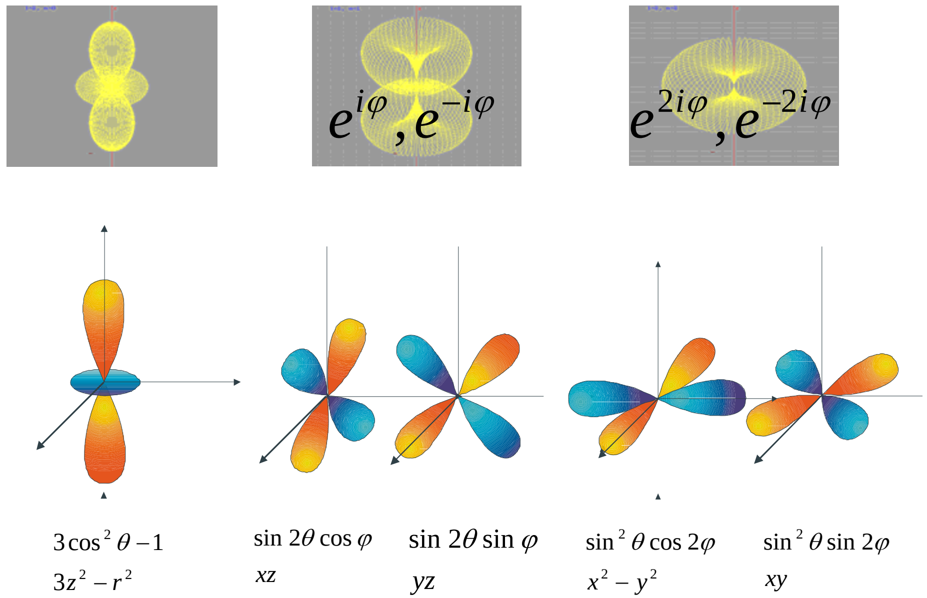
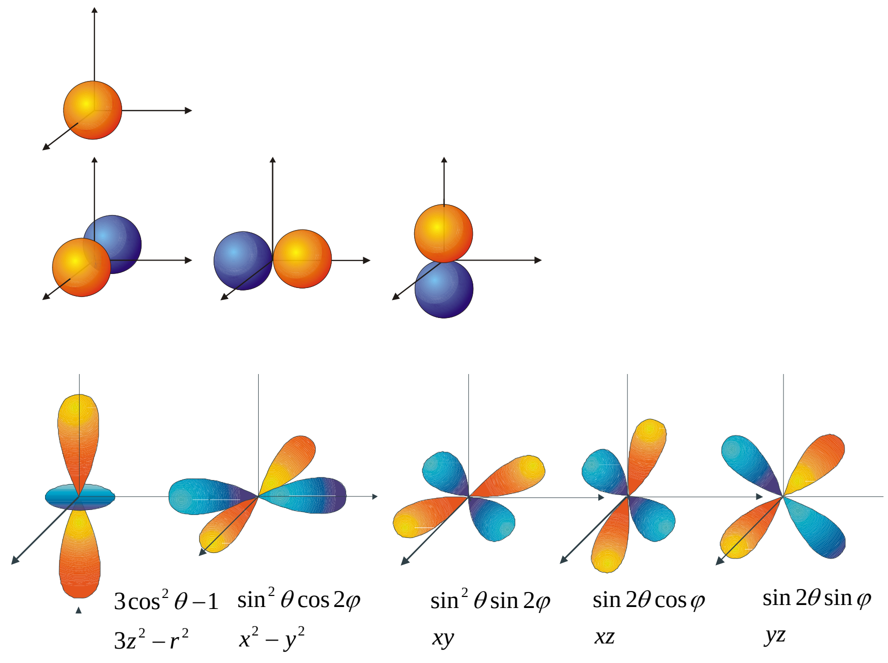
L=1, m=1 | L=1, m=-1 | L=1, m=0







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The radial part

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+r^2\frac{2m}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_o r}\right)+$$
$$+\frac{1}{\Theta}\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial\Theta}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}=0$$

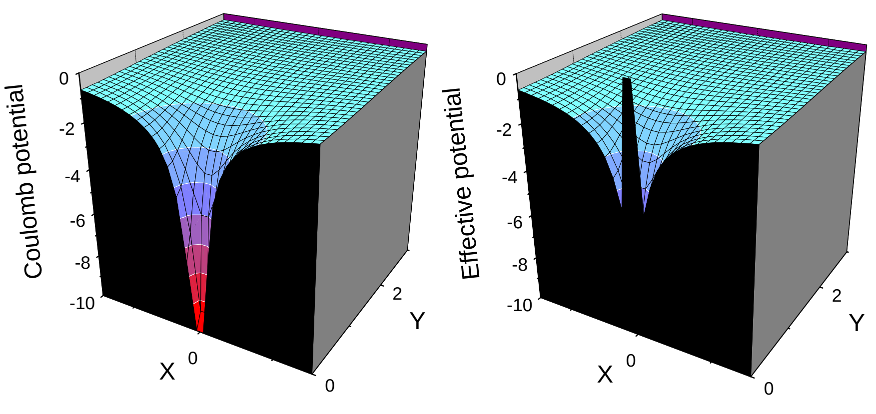
$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+r^2\frac{2m}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_o r}\right)-l(l+1)=0$$

L-dependent effective potential

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left(-\frac{e^2}{4\pi\varepsilon_o r}+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right)R(r)=ER(r)$$

Effective Hydrogen atom potential

L=0 L≠0



Degeneracy of energy levels in the hydrogen atom

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

Wave functions $R_{n,l}$

$$R_{1,0}(r) = \left(\frac{1}{a_0}\right)^{3/2} 2 e^{-\frac{r}{a_0}}$$

$$R_{2,0}(r) = \left(\frac{1}{2a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$$

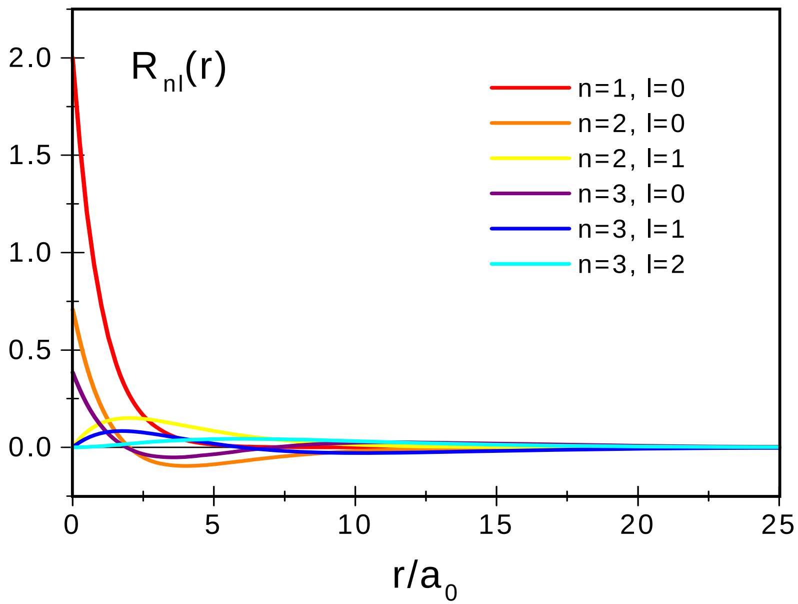
$$R_{2,1}(r) = \left(\frac{1}{2a_0}\right)^{3/2} \left(\frac{1}{\sqrt{3}} \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$$

$$R_{3,0}(r) = \left(\frac{1}{3a_0}\right)^{3/2} 2\left(1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}\left(\frac{r}{a_0}\right)^2\right) e^{-\frac{r}{3a_0}}$$

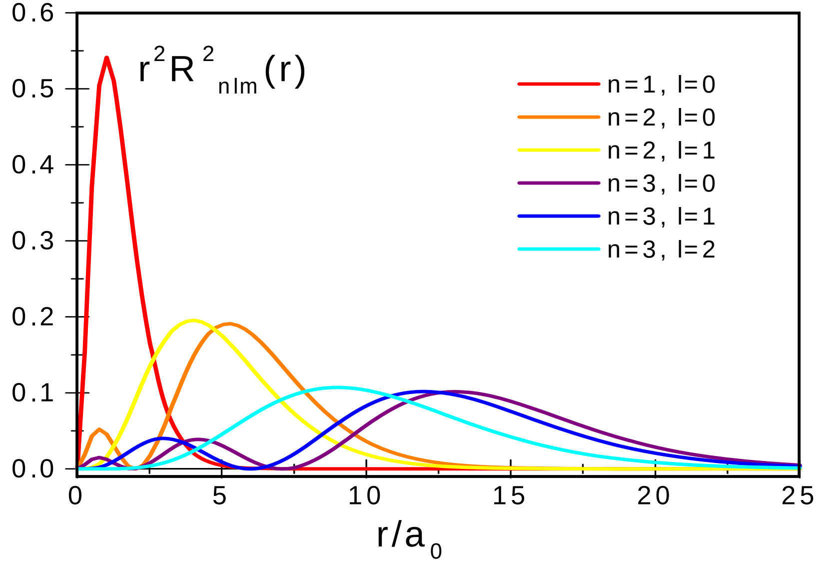
$$R_{3,1}(r) = \left(\frac{1}{3a_0}\right)^{3/2} \left(\frac{8}{9\sqrt{2}}\right)\left(\frac{r}{a_0}\right)\left(1 - \frac{r}{6a_0}\right) e^{-\frac{r}{3a_0}}$$

$$R_{3,2}(r) = \left(\frac{1}{3a_0}\right)^{3/2} \left(\frac{4}{27\sqrt{10}}\right)\left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{3a_0}}$$

Wave functions



The radial probability distribution



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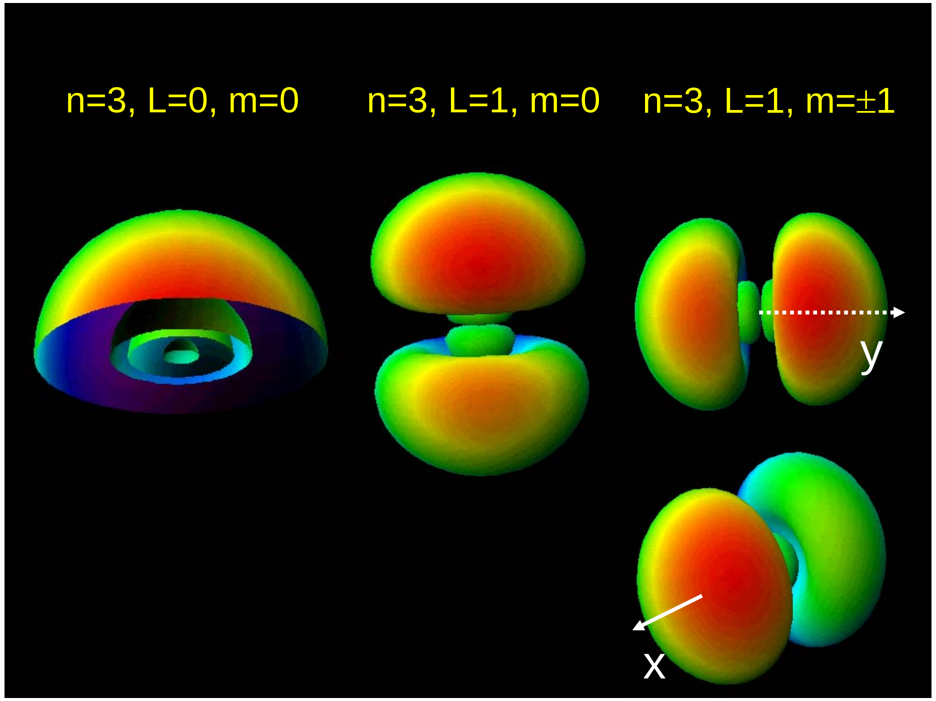

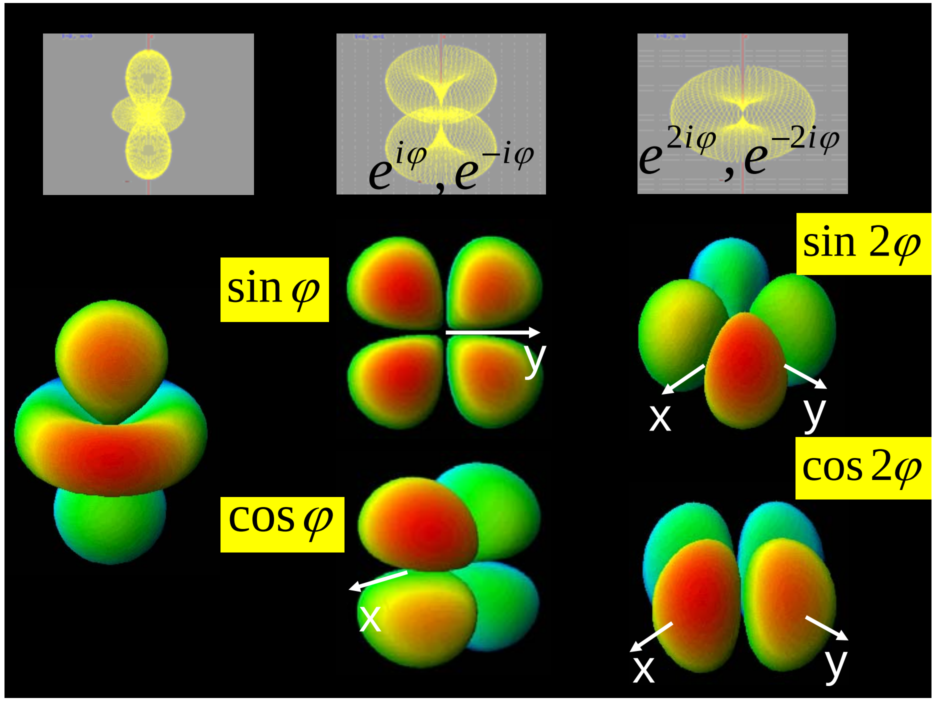

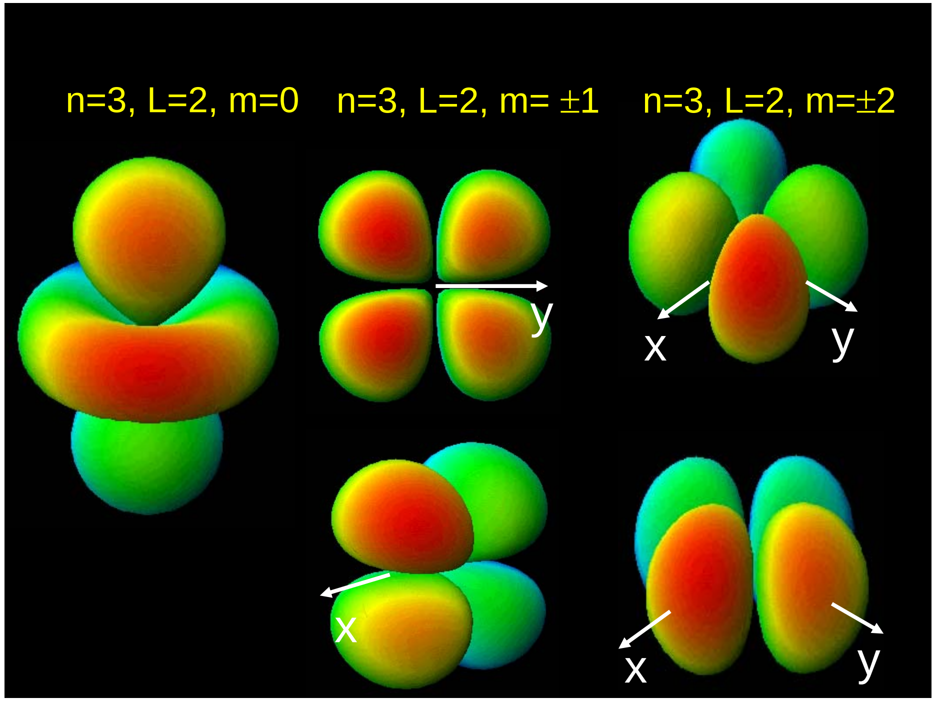

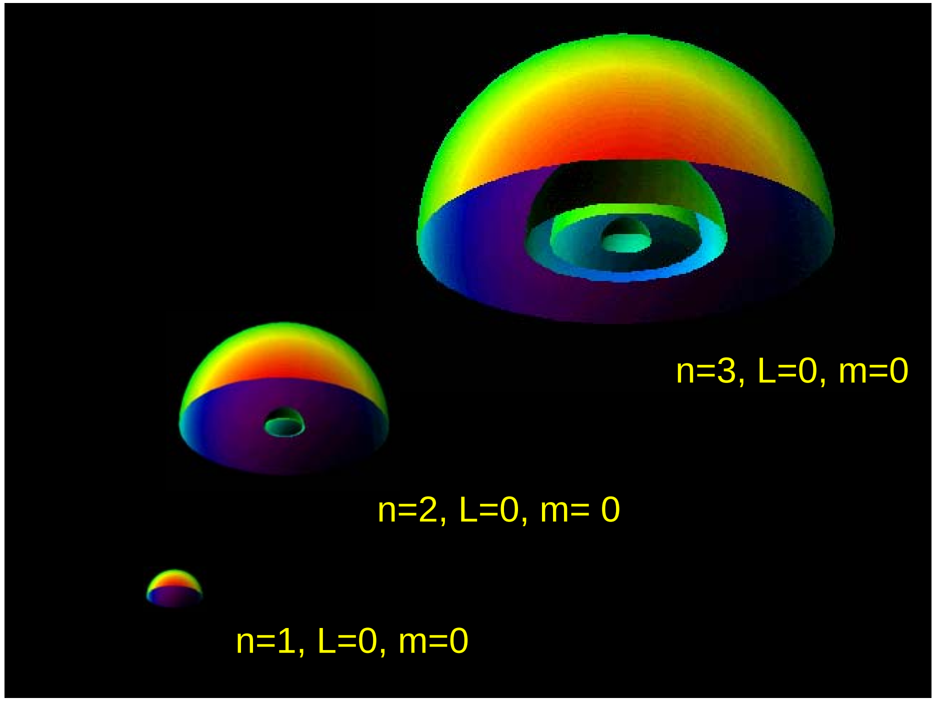

Orbital Viewer Program

Physical properties of hydrogen isotopes

	H	D	T
Nucleus			
Nuclear mass [m_p]	1.000	1.998	2.993
Nuclear spin [h/2π]	+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

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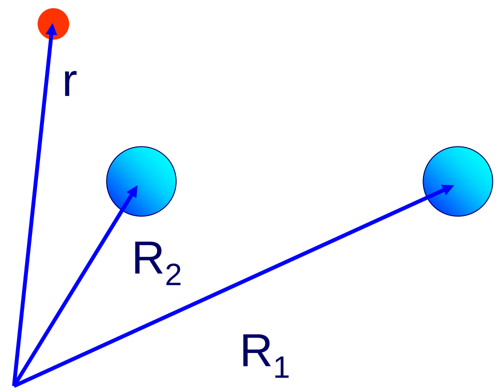
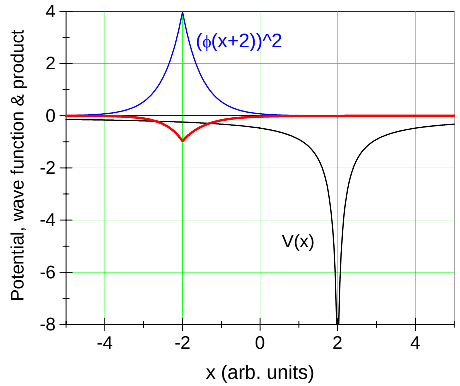
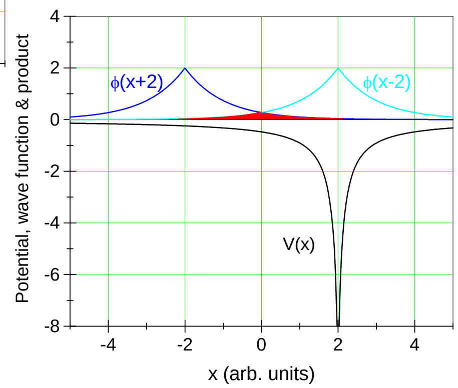
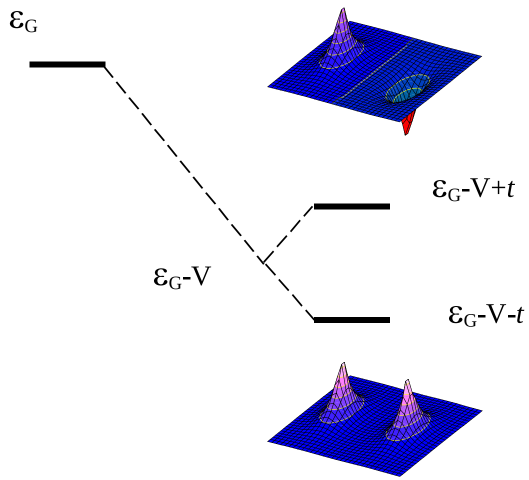
The H_2^+ molecule



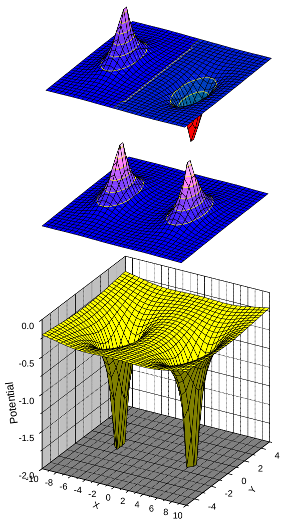


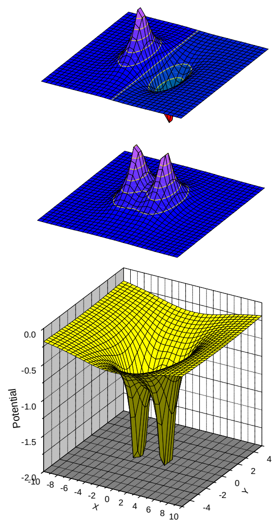


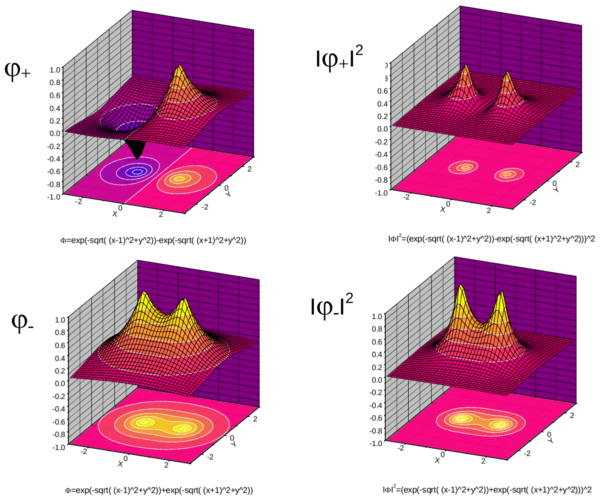
Bonding and antibonding state



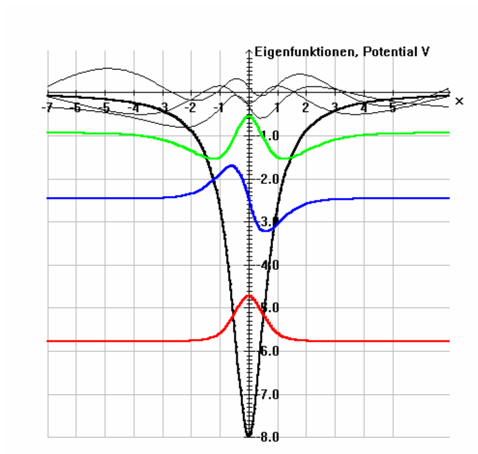
Influence of p-p separation

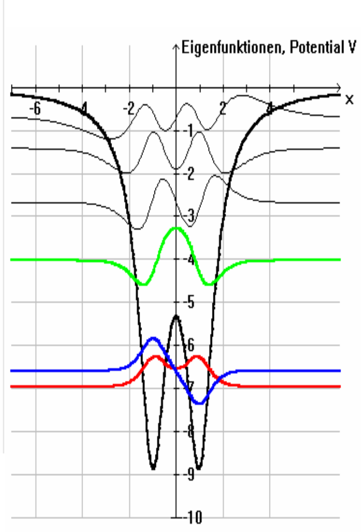






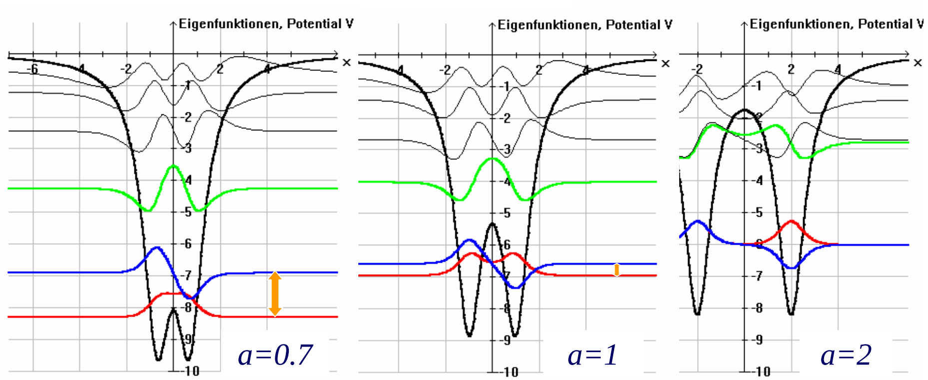
1- and 2-atom electron states





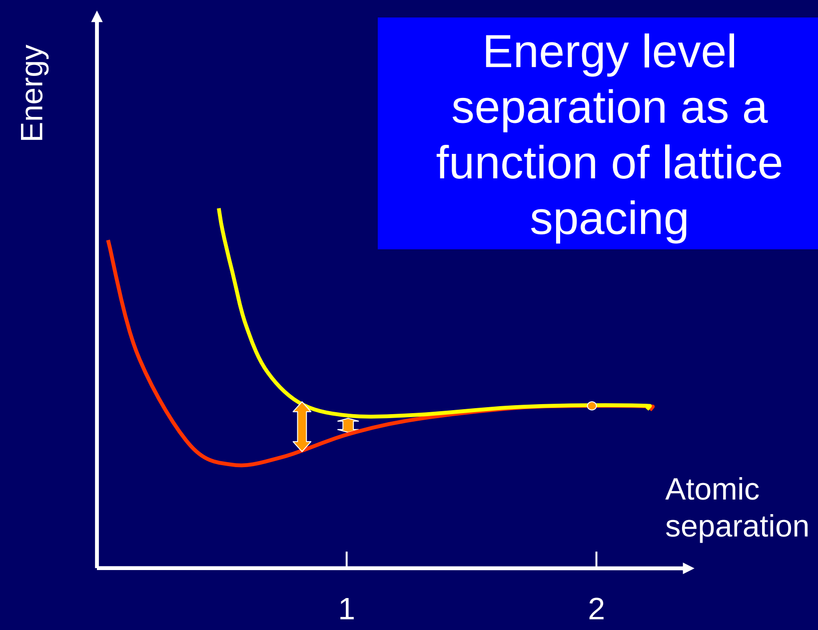
$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi-\frac{4}{x^2+0.5}\Psi=E\Psi$$

Effect of lattice spacing on electron states

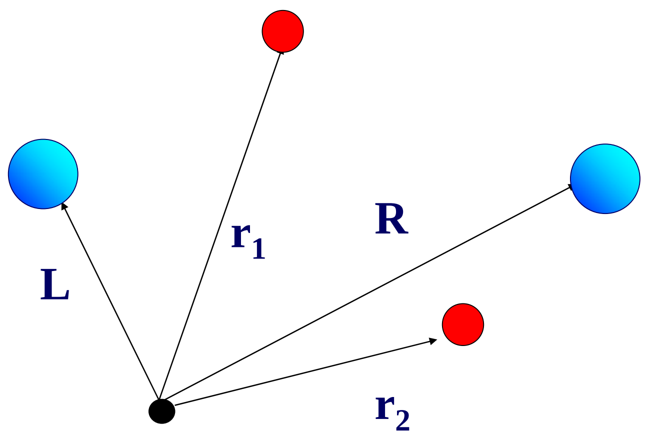


$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi-\frac{4}{(x-a)^2+0.5}\Psi-\frac{4}{(x+a)^2+0.5}\Psi=E\Psi$$

Energy level separation as a function of lattice spacing



The H_2 molecule



The Schrödinger equation

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

Two-electron states from atomic s-states:

$$\Phi_0=\frac{1}{\sqrt{2}}[L_1R_2+L_2R_1]\times|\uparrow\downarrow-\downarrow\uparrow\rangle$$

$$\Phi_1^1=\frac{1}{\sqrt{2}}[L_1R_2-L_2R_1]\times|\uparrow\uparrow\rangle$$

$$\Phi_1^0=\frac{1}{\sqrt{2}}[L_1R_2-L_2R_1]\times|\uparrow\downarrow+\downarrow\uparrow\rangle$$

$$\Phi_1^{-1}=\frac{1}{\sqrt{2}}[L_1R_2-L_2R_1]\times|\downarrow\downarrow\rangle$$

$$\Phi_L=[L_1L_2]\times|\uparrow\downarrow-\downarrow\uparrow\rangle$$

$$\Phi_R=[R_1R_2]\times|\uparrow\downarrow-\downarrow\uparrow\rangle$$

The Hubbard approximation

All matrix elements are 0 except for the two electrons on the same proton, i.e. $\langle L_1L_2|V_{12}|L_1L_2\rangle=\langle R_1R_2|V_{12}|R_1R_2\rangle=U$

$$\Phi_0=\frac{1}{\sqrt{2}}[L_1R_2+L_2R_1]\times|\uparrow\downarrow-\downarrow\uparrow\rangle$$

$$\Phi_1^1=\frac{1}{\sqrt{2}}[L_1R_2-L_2R_1]\times|\uparrow\uparrow\rangle$$

$$\Phi_1^0=\frac{1}{\sqrt{2}}[L_1R_2-L_2R_1]\times|\uparrow\downarrow+\downarrow\uparrow\rangle$$

$$\Phi_1^{-1}=\frac{1}{\sqrt{2}}[L_1R_2-L_2R_1]\times|\downarrow\downarrow\rangle$$

$$\Phi_L=[L_1L_2]\times|\uparrow\downarrow-\downarrow\uparrow\rangle$$

$$\Phi_R=[R_1R_2]\times|\uparrow\downarrow-\downarrow\uparrow\rangle$$

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

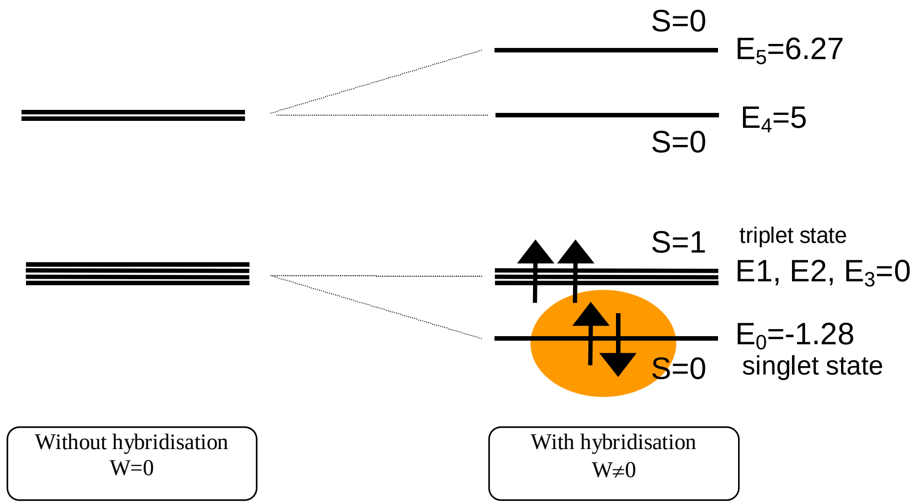
Energy eigenvalues

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

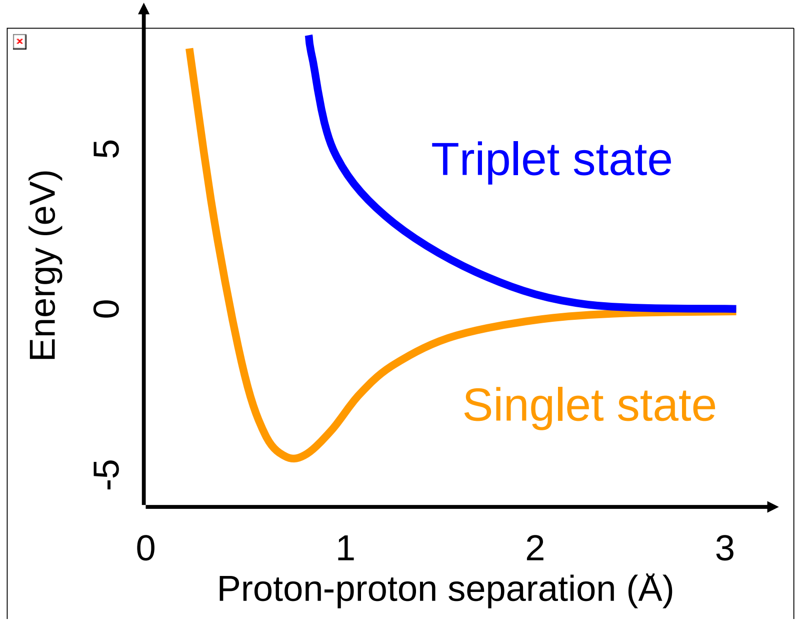
A non-trivial solution exists only if the determinant vanishes:

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

The H_2-molecule within the Hubbard approximation (U=5)



Singlet and triplet state of the H_2 molecule



Hydrogen

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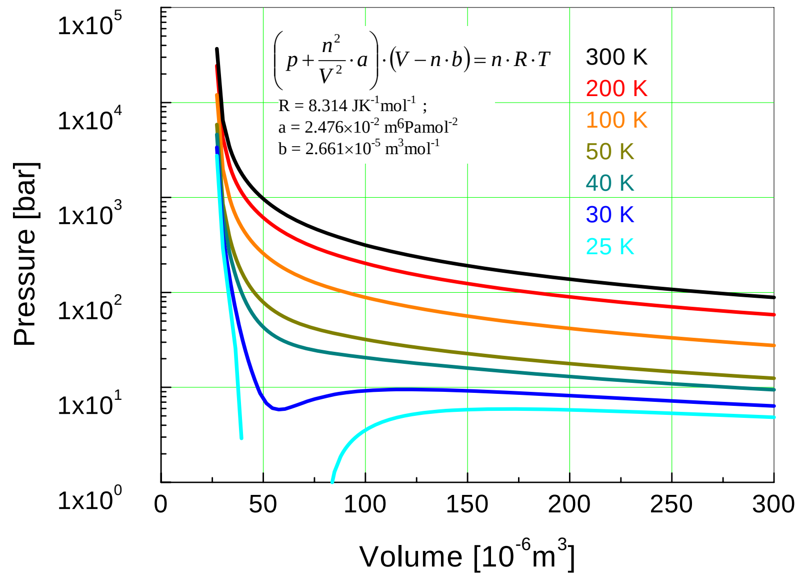
Van der Waals isotherms of hydrogen

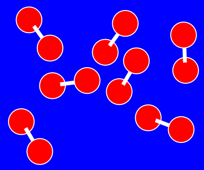


Useful values for hydrogen

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 Critical point pressure p_k	33.25 13.07×10^5	K kJ·m^{-3} 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	$kJ \cdot kg^{-1}$

Statistical physics of the hydrogen gas

$$F = -kT \ln \sum_n \exp\left(-\frac{E_n}{kT}\right)$$



over all states of the gas containing N_H molecules.

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

where ε_k is the energy of the k-th molecule.

$$F = -kTN_{H_2} \ln \sum_k e^{-\varepsilon_k / kT} + kT \ln N_{H_2}!$$

Using Stirling's formula

$$\ln N! \cong N \ln \frac{N}{e}$$

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

$$\varepsilon = \varepsilon_b + \frac{\mathbf{p}^2}{2m} + \frac{\mathbf{M}^2}{2\Theta_{H_2}}$$

ε_b is the binding energy of the H_2 molecule
M is the angular momentum and
Θ is the moment of inertia of the molecule.
The classical limit

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

where **dp**=$dp_1,\ldots,dp_r$ and **dq=**$dq_1,\ldots,dq_r$ where r is the number of degrees of freedom of the molecule.

The free energy of a diatomic gas H_2

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

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

$$+ \left\{-N_{H_2}kT\ln\left(\frac{kT\Theta_{H_2}}{\hbar^2}\right)\right\}$$

from which we derive the chemical potential μ_{H_2}

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

$$- kT\ln\left(\frac{kT\Theta_{H_2}}{\hbar^2}\right)$$

$$= \varepsilon_b - kT\ln\left[\frac{V}{N_{H_2}}\, kT\left(\frac{m_{H_2}kT}{2\pi\hbar^2}\right)^{3/2}\frac{\Theta_{H_2}}{\hbar^2}\right]$$

For an ideal gas $pV = N_{H_2}kT$

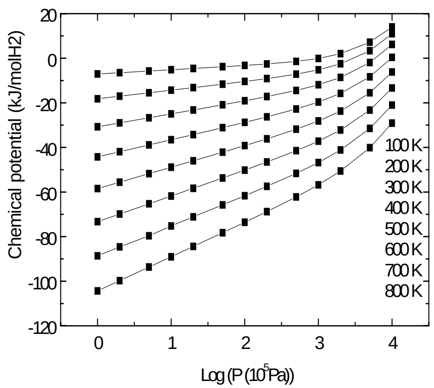
$$\mu_{H_2}(p,T) = \varepsilon_b - kT\ln\left[\frac{\Theta_{H_2}(kT)^2}{p\hbar^5}\left(\frac{m_{H_2}kT}{2\pi}\right)^{3/2}\right]$$

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

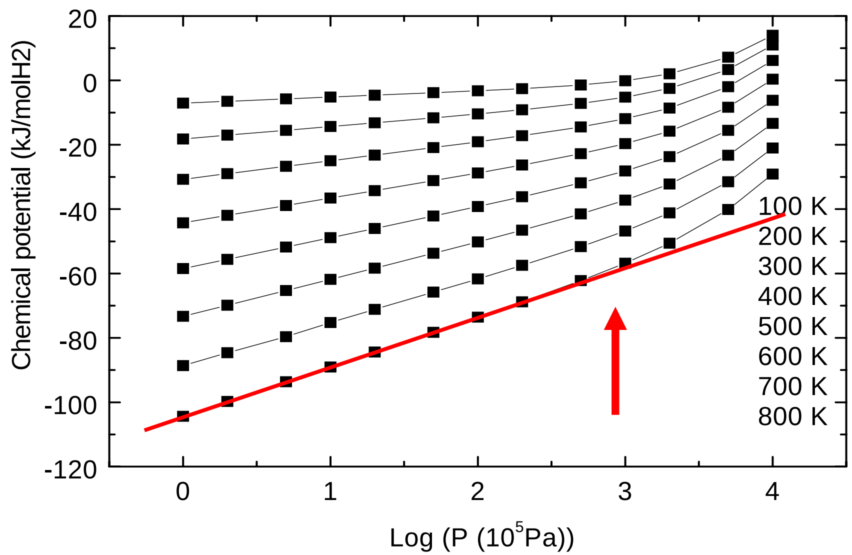
$$\mu_{H_2} = \varepsilon_b + kT\ln\left[\frac{p}{p_0(T)}\right]$$

with

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



Chemical potential of hydrogen



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