Statistical Molecular Thermodynamics

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Video 1.5

Atomic Energy Levels

How is energy stored in an atom?

Connecting *macroscopic* thermodynamics to a molecular understanding requires that we understand how energy is distributed on a *microscopic* scale.

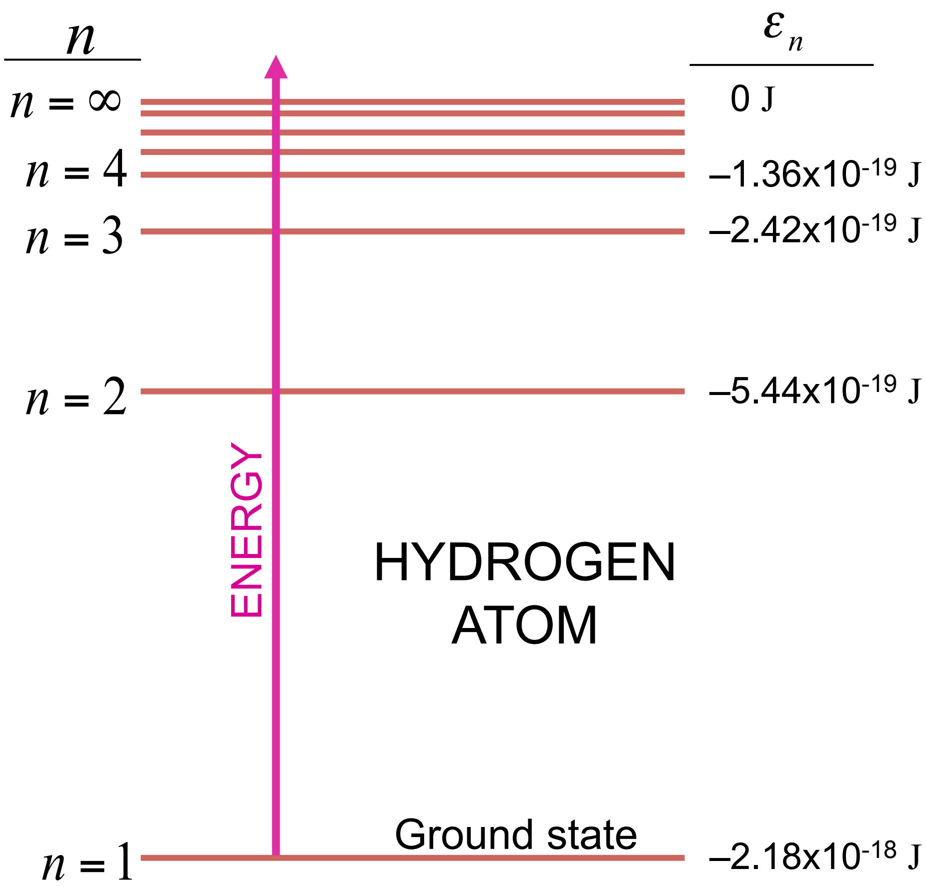
ATOMS

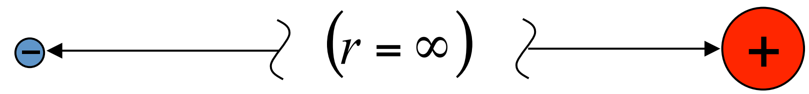
Electrons: Electronic energy. Changes in the kinetic and potential energy of one or more electrons associated with the nucleus.

Nuclear motion: Translational energy. The atom can move (translate) in space — kinetic energy only.

ELECTRONIC ENERGY LEVELS

THE HYDROGEN ATOM





Series limit ($n=\infty$), electron and proton are infinitely separated, i.e., there is *no interaction*.

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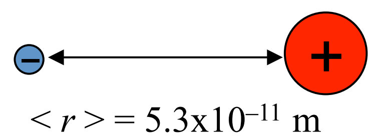
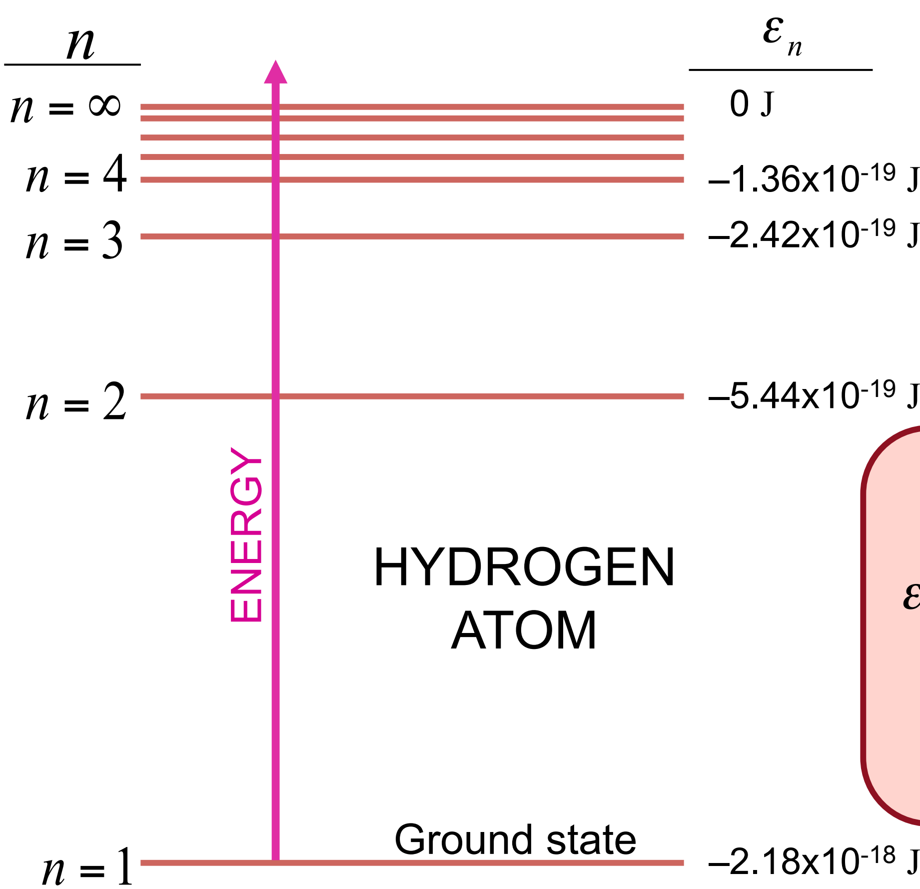
Ground state ($n=1$), average distance between electron and proton is $r = 5.3\text{x}10^{-11}$ m (1 bohr).



Electronic Energy levels

The Hydrogen Atom



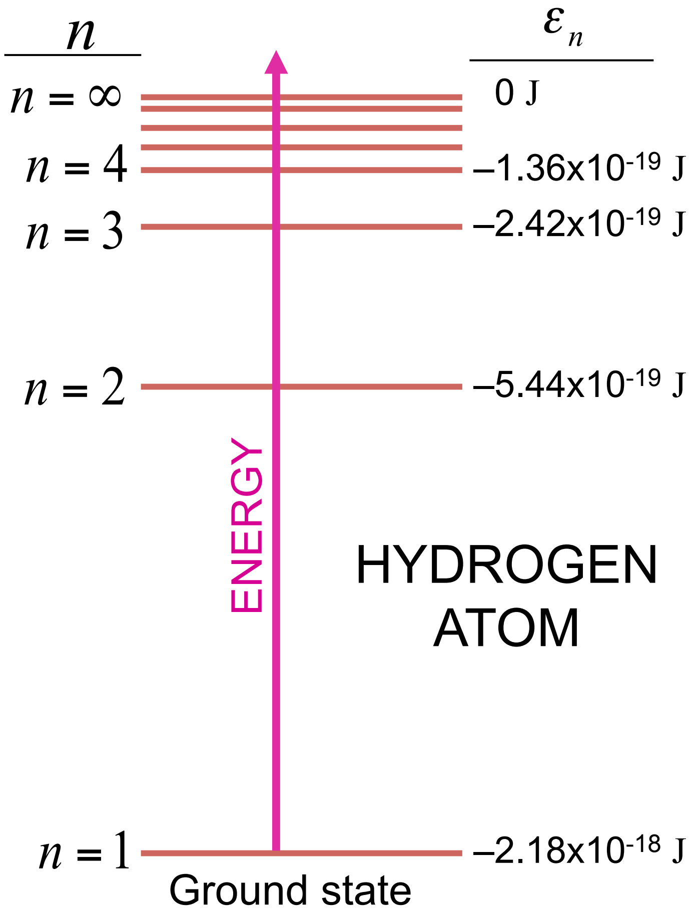
convert J to cm^{-1}

$$\varepsilon_n = -\frac{2.17869 \times 10^{-18}}{n^2}\ \text{J} = -\frac{109680}{n^2}\ \text{cm}^{-1}$$

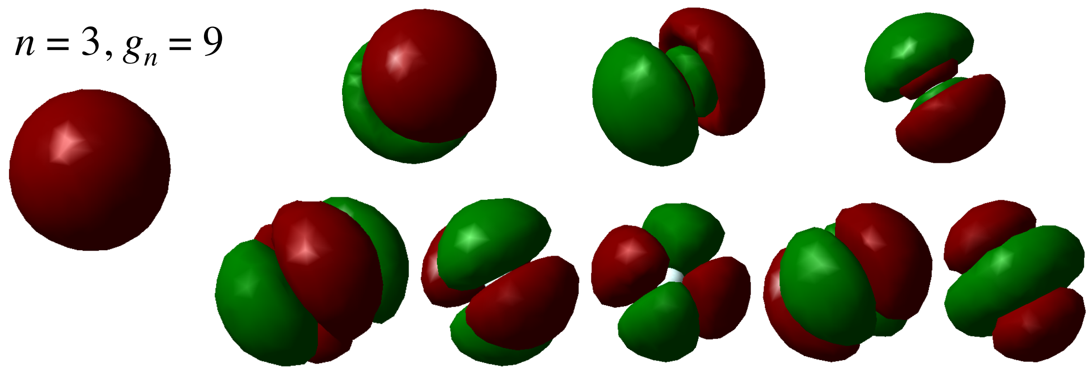
integer values ($n = 1, 2, 3, \ldots$)

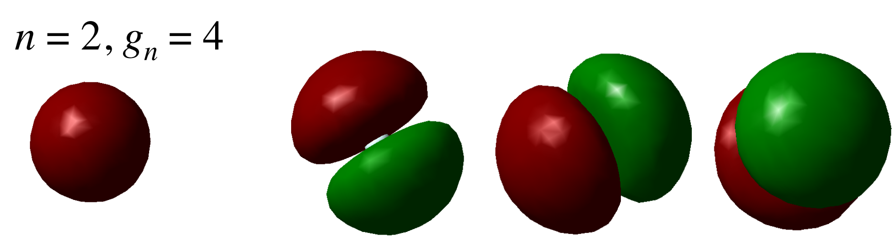
Wave Functions and Degeneracy

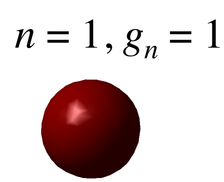
The Hydrogen Atom



Wave functions are atomic orbitals







The number of wave functions, or states, with the *same* energy is called the *degeneracy*, g_n.

Electronic Energy levels
Many-Electron Atoms

There is no simple formula for the electronic energy levels of atoms having more than one electron. Instead, we can refer to tabulated data:

TABLE 1.2
Data from "Moore's tables", listing the degeneracies and energies (in cm^{-1}) of the first few states of atomic sodium.

Electron configuration	Degeneracy	Energy/cm^{-1}
3*s*	2	0.00
3*p*	2	16 956.183
3*p*	4	16 978.379
4*s*	2	25 739.86
3*d*	6	29 172.855
3*d*	4	29 172.904
4*p*	3	30 266.88
4*p*	4	30 272.51
5*s*	2	33 200.696
4*d*	6	34 548.754
4*d*	4	34 548.789

[a]From C.E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. Circ. No. 467 (US Government Printing Office, Washington, DC, 1949).

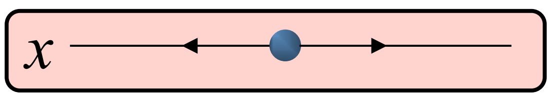
For electronic energy levels, there is usually a very large gap from the ground state to the first excited state. As a result, we will see that, at "reasonable" temperatures, we will seldom need to consider any states above the ground state when computing "partition functions".

Translational energy levels

In addition to electronic energy, atoms have translational energy.

To find the allowed translational energies we solve the Schrödinger equation for a particle of mass m in a box of variable side lengths.

In 1D, motion is along the x dimension and the particle is constrained to the interval $0 \le x \le a$

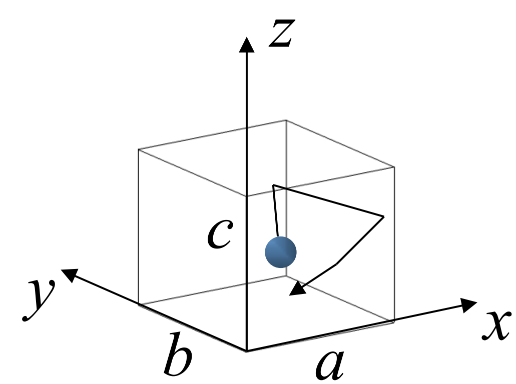


$$\varepsilon_n = \frac{n^2 h^2}{8ma^2} \qquad n = 1,2,3,\cdots$$

The allowed states are *non-degenerate*, i.e., $g_n = 1$ for all values of n.

In 3D,

$$\varepsilon_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \qquad \begin{aligned} n_x &= 1,2,3,\cdots \\ n_y &= 1,2,3,\cdots \\ n_z &= 1,2,3,\cdots \end{aligned}$$



States *can be degenerate*. E.g., if $a = c$ then the two *different states* $(n_x = 1, n_y = 1, n_z = 2)$ and $(n_x = 2, n_y = 1, n_z = 1)$ have the *same energy*.