

# The importance of constants

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Quantum Mechanics 1

September 22, 2008

- 1 Universal constants
- 2 The physics of molecules

# Outline

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# The physics of dimensional constants

Many dimensional constants correct our knowledge of basic physics.

- 1 The Joule's constant relates units of energy and heat. It tells us that these two notions are the same.
- 2 The speed of light in vacuum relates time and space. It says that these two quantities are not different. It also relates energy and mass.
- 3 Planck's constant relates energy and frequency (time). It tells us that energy is the same as frequency.

There are other fundamental dimensional constants, for example, the charge of the electron and its mass, which defy current understanding in terms of more basic phenomena

$$m_e = 9.109 \times 10^{-31} \text{ Kg}, \quad e = 1.602 \text{ C}.$$

# The meaning of dimensionless constants

Some dimensionless constants relate the scales of different phenomena. Among these are Avogadro's number,  $N_A \simeq 6.022 \times 10^{23}$ , which relates the fundamental scale of molecular phenomena to “accidental” human scales. For example, the proton mass is essentially

$$m_p = \frac{1 \text{ gm}}{N_A} = 1.67 \times 10^{-27} \text{ Kg.}$$

Most of the dimensionless constants discovered in the 18th and 19th centuries are of this kind. All of them can be simply rewritten in terms of  $N_A$ .

# Natural units

Natural units are those in which the dimensional constants are unity. Take Planck's relation in natural units,

$$E = \hbar\omega, \quad \hbar = 1.054589 \times 10^{-34} \text{ J/Hz} = 1.$$

One also has  $c = 2.998 \times 10^8 \text{ m/Hz} = 1$ . As a result, in natural units

$$1 = \hbar c = 3.16 \times 10^{-26} \text{ Jm} = 197 \text{ eVnm},$$

$$1 = \hbar = 6.58 \times 10^{-16} \text{ eV/Hz}.$$

where the latter units ( $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ , and  $1 \text{ nm} = 10^{-9} \text{ m}$ ) are chosen to be scales natural in the molecular domain. In applications to the thermodynamics of collections of molecules, it is also natural to set

$$k_B = 11 \times 10^3 \text{ K/ev} = 1.$$

# Fundamental constants

Some new constants can be found in natural units:

- ① The electron's Compton wavelength  $\lambda_e = \hbar/(m_e c) = 0.0004 \text{ nm}$ , is just the electron's mass in a different unit.
- ② The fine structure constant  $e^2/(\hbar c) = 1/137.036$ , is only the electron's charge in dimensionless (natural) units.
- ③ The Planck mass is Newton's gravitational constant in different units.

These are all fundamental: *i.e.*, we have no theory that predicts these values. There are also “non-fundamental” constants, *i.e.*, those for which we have theories. These are the constants at the molecular level,

- ① The Bohr radius of the Hydrogen atom  $\lambda_e/\alpha \simeq 0.053 \text{ nm}$ , can be derived in a quantum mechanical treatment of the hydrogen atom.
- ② The ionization energy of the Hydrogen atom  $\alpha^2 m_e c^2/2 \simeq 13.6 \text{ eV}$  can be derived through the quantum mechanics of the hydrogen atom.
- ③ The proton mass (and hence  $N_A$ ) is (expected to be) understood in terms of present day theory (quantum chromodynamics: QCD).

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# The physics of molecules

Classically, one could think of molecular excitations in terms of

- ① atoms connected rigidly together; in this case one could write a Hamiltonian for rotational motion:  $H = L^2/2I$ . What is the value of  $I$ ?
- ② atoms connected by springs; then one could write a Hamiltonian for vibrational motion:  $H = p^2/2m + m\omega^2 x^2$ . How big is  $\omega$ ?

Spectra of atoms show that the structure is more complicated. This was one of the points of origin of quantum mechanics. Now one knows that solely electrical forces determine the excitations of molecules, such as

- ① electronic excitations: single electron, multi-electron etc.
- ② tunnelling transitions of groups of nuclei and electrons
- ③ rotational motion involving all the nuclei and electrons together
- ④ vibrational motion involving all the nuclei and electrons together

# The ammonia molecule

- ➊ What is the energy of the lowest electronic excitation of the ammonia molecule?
- ➋ There could be vibrational states of the molecule in which the distance between the N nucleus and the centroid of the 3H nuclei change. What is the lowest excitation energy for these vibrations?
- ➌ What is the energy splitting between the two states of the N nucleus (symmetric on the two sides of the plane of 3H and antisymmetric)?
- ➍ What source did you use to find the above data (if it is a book or journal give the full reference; if it is a web site give the url)? How did you locate these sources? Why do you consider the source to be reliable?
- ➎ Present a model Hamiltonian for the two states of N (discussed in part c) in the basis in which it is on one side of the plane or the other. What are the values of the parameters in the model you have written down.

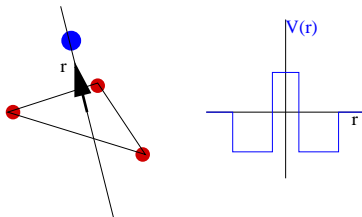
# Molecular spectra

- ❶ Electronic transitions: energies of eV to KeV (molecular orbitals and inner shell transitions). Photon frequencies from  $10^{15}$  Hz to  $10^{18}$  Hz, corresponding to wavelengths 100 nm to about 0.1 nm (visible to X-ray). They are naturally excited at temperatures of  $10^4$  to  $10^7$  K.
- ❷ Vibrational spectra correspond to wavelength between approximately 1 mm (microwave) and about 1000 nm (infrared), *i.e.*, to energies between  $10^{-4}$  eV and 0.1 eV. These levels are excited at temperatures of 1 K to 1000 K.
- ❸ Rotational spectra lie at wavelengths between 1 mm and 10 cm, and correspond to energies of  $10^{-4}$  and  $10^{-6}$  eV. These levels can be excited at temperatures of a few 10s of mK.
- ❹ The ammonia maser utilizes the tunnelling transition of the N atom in ammonia and yields a frequency of about 10 GHz, corresponding to an energy splitting of about  $10^{-6}$  eV or a temperature of about a mK.

# The physics of molecular spectra

- ❶ A rough understanding of the magnitude of electronic transitions will be obtained by solving the hydrogen atom problem: allowing us to write electronic energy levels in terms of  $\alpha$ ,  $m_e$  and  $Z$ . A more precise understanding needs to take into account electron-electron interactions and therefore solve more than the hydrogen atom.
- ❷ Rotational energy levels give information about the moment of inertia of molecules, and hence about molecular sizes. These can be determined approximately by solving the hydrogen problem, and then taking into account sizes of orbitals as a function of  $\alpha$ ,  $m_e$  and  $Z$ .
- ❸ Vibrational energy levels are essentially many-body problems in atomic physics, and need to take into account the distortion of atomic electrons in the presence of other atoms. A model computation could proceed by taking into account the long distance (cav der Waals) potential between nuclei.
- ❹ Tunnelling energy levels are also complex many body problems, which can be modelled simply by a model potential (see the next problem).

# A problem



As the N nucleus is placed at different points,  $r$ , along the line joining the two equilibrium positions, the energy is minimized at two symmetrically placed points (the equilibrium positions). When the nucleus is in the plane of the three H nuclei, electronic repulsion gives a local maximum in the potential. Far away, the potential increases, because electron delocalization (chemical bonding) is less effective. A model can be given in terms of piecewise constant potentials (as shown). Tune this model to reproduce the ammonia maser frequency. Which parts of the potential need to be fine tuned?