Atomic units (Notes by E. Koch)

For practical calculations of electronic structure the standard SI units are not particularly convenient, since the fundamental constants appearing in the Schrödinger equation have quite extreme numerical values [1]:

$$\begin{array}{rlll} \hbar & = 1.054\cdot 10^{-34} & \mathrm{m^2\,kg/s} & [L^2MT^{-1}] \\ m_e & = 9.109\cdot 10^{-31} & \mathrm{kg} & [M] \\ e & = 1.602\cdot 10^{-19} & \mathrm{C} & [Q] \\ 4\pi\epsilon_0 & = 1.113\cdot 10^{-10} & \mathrm{s^2\,C^2\,/\,m^3\,kg} & [L^{-3}M^{-1}T^2Q^2] \end{array}$$

We therefore would like to introduce a new set of units, the atomic time unit t_0, the length unit a_0, the mass unit m_e, and the charge unit e, such that the fundamental constants listed above have the numerical values 1 in these units. Thus the new units are defined by the system of equations

$$\begin{array}{rl} \hbar & = 1\; a_0^2\, m_e/t_0 \\ m_e & = 1\; m_e \\ e & = 1\; e \\ 4\pi\epsilon_0 & = 1\; t_0^2\, e^2\,/\,a_0^3\, m_e \end{array}$$

Solving we find the *atomic units* (a.u.):

$$\begin{array}{rlll} a_0 = & 4\pi\epsilon_0\hbar^2\,/\,m_e e^2 & \approx 5.2918\cdot\; 10^{-11}\mathrm{m} & \text{Bohr radius} \\ m_e = & & \approx 9.1095\cdot 10^{-31}\mathrm{kg} & \text{electron mass} \\ t_0 = & (4\pi\epsilon_0)^2\hbar^3\,/\,m_e e^4 & \approx 2.4189\cdot\; 10^{-17}\mathrm{s} & \\ e = & & \approx 1.6022\cdot\; 10^{-19}\mathrm{C} & \text{elementary charge} \end{array}$$

With these base units it is then easy to express derived units in a.u. Remembering, for example, that a Joule expressed in terms of the SI base units is J=kg m^2/s^2, the atomic unit of energy is given by

$$E_H = \frac{m_e a_0^2}{t_0^2} = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$$

which is called a *Hartree*. Since the energy is a central quantity, we give some useful conversions: 1 Ha $\approx$ 27.2 eV and 1 eV $\approx 1.6\,10^{-19}$ J.

With the choice of setting the numerical values of $\hbar$, m_e, e, and $4\pi\epsilon_0$ to unity in atomic units, we have completely determined the new units, and thus there is no more freedom to set the numerical value of other constants to one. So, e.g., it is not possible to also set c to one in atomic units (then the above system of equations for determining m_e, a_0, t_0 and e would be overdetermined). Instead we find for the numerical value of c in atomic units

$$c\,\frac{t_0}{a_0} = \frac{4\pi\epsilon_0\hbar c}{e^2} = \alpha^{-1} \approx 137\;,$$

i.e., one over the fine structure constant.

References

[1] A list of the latest "CODATA internationally recommended values of the fundamental physical constants" can, e.g., be found at the National Institute of Standards: `http://physics.nist.gov/cuu`.