

Appendix A : Atomic Units

- Can simplify equations without carrying constants around

Idea: Make quantities dimensionless (no units)

- How? Measure quantities in units of a known constant

e.g. measure masses in units of m_e (electron mass)

mass "4" means $4m_e$

measure charges in units of e (electron charge)

charge "-2" means $-2e$

measure length in units of a_0 (Bohr radius $\frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$)

length "1.248" means $1.248a_0$

measure energy in units of E_h (Hartree $\frac{2 \cdot m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} = \frac{e^2}{4\pi\epsilon_0 a_0}$)

energy "-4 E_h " means -108.8 eV $2 \times 13.6 \text{ eV}$

scales set by
hydrogen atom results

Why?
Typical of all atoms
(and molecules)

Atomic Units and Their SI Equivalents [Taken from: McQuarrie "Quantum Chemistry"]

Property	Atomic unit	SI equivalent
Mass	Mass of an electron, m_e	9.1094×10^{-31} kg
Charge	Charge on a proton, e	1.6022×10^{-19} C
Angular momentum	Planck constant divided by 2π , \hbar	1.0546×10^{-34} J·s
Length	Bohr radius, $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	5.2918×10^{-11} m
Energy	$\frac{m_e e^4}{16\pi^2\epsilon_0^2\hbar^2} = \frac{e^2}{4\pi\epsilon_0 a_0} = E_h$	4.3597×10^{-18} J
Permittivity	$\kappa_0 = 4\pi\epsilon_0$	1.1127×10^{-10} C ² ·J ⁻¹ ·m ⁻¹

What for?

- Simplify equations and results
- understand literature (journal articles)
- Communicate with professionals

Example: $\hat{H}_{(SI)} = \frac{-\hbar^2}{2m_e} \nabla_{\vec{r}}^2 - \frac{e^2}{4\pi\epsilon_0 r}$ (A1) Hamiltonian of H-atom in SI units

\uparrow
 $(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})$

"Slow Motion"

$$\hat{H}_{(SI)} = \frac{e^2}{4\pi\epsilon_0 a_0} \left[\frac{-\hbar^2}{2m_e} \frac{4\pi\epsilon_0}{e^2 a_0} \cdot \overbrace{a_0^2 \nabla_{\vec{r}}^2}^{\text{dimensionless}} - \frac{a_0}{r} \right]$$

$$= E_h \left[-\frac{1}{2} a_0^2 \nabla_{\vec{r}}^2 - \frac{1}{\left(\frac{r}{a_0}\right)} \right]$$

But $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$

Define: $\vec{r}' = \frac{\vec{r}}{a_0}$; $(x', y', z') = \left(\frac{x}{a_0}, \frac{y}{a_0}, \frac{z}{a_0}\right)$, $\frac{\partial^2}{\partial x'^2} + \frac{\partial^2}{\partial y'^2} + \frac{\partial^2}{\partial z'^2} = a_0^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$

$$\hat{H}_{\text{atomic units}} = \frac{\hat{H}_{(SI)}}{E_h} = -\frac{1}{2} \nabla_{\vec{r}'}^2 - \frac{1}{r'} = \underbrace{-\frac{1}{2} \nabla_{\vec{r}}^2 - \frac{1}{r}}_{\text{look simpler! (H-atom Hamiltonian)}} \quad \text{(A2) (save the prime)}$$

measure energy in E_h \nearrow

"Fast Forward": Start from (A1), set $m_e=1$, $e=1$, $\hbar=1$, $4\pi\epsilon_0=1$, then $\hat{H}_{\text{atomic units}}^{(H\text{-atom})} = -\frac{1}{2} \nabla_{\vec{r}}^2 - \frac{1}{r}$ results! (A2)

$$\hat{H}_{\text{atomic units}}^{(\text{H-atom})} = -\frac{1}{2} \nabla^2 - \frac{1}{r}$$

Even the H-atom eigenstates look simpler

e.g. $\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$ Energy = $-\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2}$
(SI units) (H-atom ground state)

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} e^{-r} \quad \text{(atomic units) (look simpler)}$$
Energy = $-\frac{1}{2} (E_h)$

Hydrogen-like ions: one electron + (+Ze) nucleus charge

$$\hat{H}_{\text{atomic unit}} = -\frac{1}{2} \nabla^2 - \frac{Z}{r} \quad \text{atomic number (just a number)}$$

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \quad \text{(SI units) (ground state)}$$
Energy = $-\frac{m_e Z^2 e^4}{32\pi^2 \epsilon_0^2 \hbar^2}$

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} Z^{3/2} e^{-Zr} \quad \text{(atomic units) (look simpler)}$$
Energy = $-\frac{Z^2}{2} (E_h)$

In atomic units, the helium atom's Hamiltonian becomes

$$\begin{aligned}\hat{H}_{\text{helium}} &= -\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} - \frac{1}{2} \nabla_2^2 - \frac{2}{r_2} + \frac{1}{|r_1 - r_2|} \\ &= -\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} - \frac{1}{2} \nabla_2^2 - \frac{2}{r_2} + \frac{1}{r_{12}} \quad (\text{atomic units})\end{aligned}$$

Note: r_{12} = distance between
electron 1 and electron 2
in units of a_0

If $\left(\frac{1}{r_{12}}\right)$ (el-el interaction) is ignored, problem becomes separate problems of electrons 1 & 2

$$\begin{aligned}\text{Rough estimate of ground state energy} &= \left(-\frac{Z^2}{2}\right) + \left(-\frac{Z^2}{2}\right) \quad (E_h) \quad (\text{with } Z=2) \\ &= -4 \quad (E_h)\end{aligned}$$

(which is -108.84 eV)