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 $\frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$)

length "1.248" means $1.248\,a_0$

measure energy in units of E_h (Hartree $\underbrace{2\cdot\frac{\overbrace{m_e e^4}}{32\pi^2\varepsilon_0^2\hbar^2}}_{2\times 13.6\,eV} = \frac{e^2}{4\pi\varepsilon_0 a_0}$)

energy "$-4E_h$" means -108.8 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, $a_0 = \dfrac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	5.2918×10^{-11} m
Energy	$\dfrac{m_e e^4}{16\pi^2\epsilon_0^2\hbar^2} = \dfrac{e^2}{4\pi\epsilon_0 a_0} = E_h$	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

<u>Example</u>: $\hat{H}_{(SI)} = \dfrac{-\hbar^2}{2m_e}\nabla^2_{\vec{r}} - \dfrac{e^2}{4\pi\varepsilon_0 r}$ (A1) Hamiltonian of <u>H-atom</u> in SI units

$$\nabla^2_{\vec{r}} = \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$$

<u>"Slow Motion"</u>

$$\hat{H}_{(SI)} = \underbrace{\frac{e^2}{4\pi\varepsilon_0 a_0}}\left[\frac{-\hbar^2}{2m_e}\frac{4\pi\varepsilon_0}{e^2 a_0}\cdot \overbrace{a_0^2\nabla^2_{\vec{r}}}^{\text{dimensionless}} - \overbrace{\frac{a_0}{r}}^{\text{dimensionless}}\right]$$

But $a_0 = \dfrac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$

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

<u>Define</u>: $\vec{r}\,' = \dfrac{\vec{r}}{a_0}$; $(x', y', z') = \left(\dfrac{x}{a_0}, \dfrac{y}{a_0}, \dfrac{z}{a_0}\right)$, $\quad \dfrac{\partial^2}{\partial x'^2}+\dfrac{\partial^2}{\partial y'^2}+\dfrac{\partial^2}{\partial z'^2} = a_0^2\left(\dfrac{\partial^2}{\partial x^2}+\dfrac{\partial^2}{\partial y^2}+\dfrac{\partial^2}{\partial z^2}\right)$

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

(save the prime)

measure energy in E_h

<u>"Fast Forward"</u>: Start from (A1), set $m_e = 1$, $e = 1$, $\hbar = 1$, $4\pi\varepsilon_0 = 1$,
then $\hat{H}^{(H\text{-atom})}_{\text{atomic units}} = -\frac{1}{2}\nabla^2_{\vec{r}} - \frac{1}{r}$ results! (A2)

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

Even the H-atom eigenstates look simpler

e.g. $\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$ (SI units) (H-atom ground state) $\text{Energy} = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}$

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

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

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

$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$ (SI units) (ground state) $\text{Energy} = -\frac{me^4 Z^2}{32\pi^2\varepsilon_0^2\hbar^2}$

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

In atomic units, the helium atom's Hamiltonian becomes

$$\hat{H}_{helium} = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + \frac{1}{|r_1 - r_2|}$$

$$= -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + \frac{1}{r_{12}} \quad \text{(atomic units)}$$

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

Rough estimate of ground state energy $= \left(-\frac{Z^2}{2}\right) + \left(-\frac{Z^2}{2}\right) \; (E_h) \; (\text{with } Z=2)$

$= -4 \quad (E_h)$

(which is -108.84 eV)