Physics 452: Notes on Atomic Units

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We will want to solve the Schrödinger equation using a computer:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi\,.$$

Before starting, we wish to scale the variables to make them dimensionless and of convenient size. Motivated by the hydrogen atom, let's arbitrarily choose to scale distance by the Bohr radius so that

$$\vec{r}\,' = \frac{1}{a_o}\vec{r}\,,\text{ and } \nabla'^2 \equiv a_o^2\nabla^2 = a_o^2\frac{\partial^2}{\partial x^2} + a_o^2\frac{\partial^2}{\partial y^2} + a_o^2\frac{\partial^2}{\partial z^2} = \frac{\partial^2}{\partial x'^2} + \frac{\partial^2}{\partial y'^2} + \frac{\partial^2}{\partial z'^2}\,.$$

Then the equation becomes

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2a_o^2 m}\nabla'^2\psi + V\psi \Rightarrow i\frac{a_o^2 m}{\hbar}\frac{\partial\psi}{\partial t} = -\frac{1}{2}\nabla'^2\psi + \frac{a_o^2 m}{\hbar^2}V\psi\,.$$

This motivates us to make the following scalings on time and energy:

$$t' \equiv \frac{\hbar}{a_o^2 m}t = \frac{t}{2.41\times 10^{-17}\,\text{s}}\,,\text{ and } V' = \frac{a_o^2 m}{\hbar^2}V = \frac{V}{27.3\text{ eV}}\,.$$

Where we have entered the Bohr radius as

$$a_o \equiv \frac{4\pi\varepsilon_o\hbar^2}{e^2 m} = 5.28\times 10^{-11}\,\text{m}\,.$$

Thus, the Schrodinger equation looks like

$$i\frac{\partial\psi}{\partial t'} = -\frac{1}{2}\nabla'^2\psi + V'\psi\,.$$

We could stop here, but sometimes the potential contains other kinds of variables. Therefore, it may be interesting to scale these other variables explicitly rather than simply scaling the potential as a whole. A frequently used potential is

$$V = \frac{-e^2}{4\pi\varepsilon_o r} - e\vec{E}\cdot\vec{r}\sin(\omega t)\,.$$

The potential converted to the new system is

$$V' = -\frac{e^2 m}{4\pi\varepsilon_o \hbar^2}\frac{a_o^2}{r} - \frac{e a_o^3 m}{\hbar^2}\vec{E}\cdot\frac{\vec{r}}{a_o}\sin(\omega t)\,.$$

The potential can then be written as

$$V' = -\frac{1}{r'} - \vec{E}'\cdot\vec{r}\,'\sin(\omega' t')\,,$$

as long as we make the following definitions:

$$\vec{E}' \equiv \frac{e a_o^3 m}{\hbar^2}\vec{E} = \frac{\vec{E}}{5.17\times 10^{11}\,\mathrm{N/C}} \text{ and } \omega' = \frac{a_o^2 m}{\hbar}\omega \equiv \left(2.41\times 10^{-17}\,\mathrm{s}\right)\omega\,.$$

The laser intensity (linearly polarized) that corresponds to an atomic unit of field is

$$\frac{1}{2}\varepsilon_o c\left(5.17\times 10^9\,\mathrm{V/cm}\right)^2 = 3.55\times 10^{16}\,\mathrm{W/cm^2}\,.$$

This intensity is referred to as one unit of atomic intensity (i.e. $I' = I/3.55\times 10^{16}\,\mathrm{W/cm^2}$). Nevertheless, this transformation is artificial since we have already developed transformations that can apply to energy, time, and length (i.e. everything which is present in $\mathrm{W/cm^2}$). If this is done, the result is inconsistent with the transformation defined above. In other words, we artificially set the atomic unit of intensity to be that at which the field has one atomic unit.