Atomic units

Atomic units (**au** or **a.u.**) form a system of natural units which is especially convenient for atomic physics calculations. There are two different kinds of atomic units, **Hartree atomic units**[1] and **Rydberg atomic units**, which differ in the choice of the unit of mass and charge. This article deals with **Hartree atomic units**, where the numerical values of the following four fundamental physical constants are all unity by definition:

- Electron mass m_e;
- Elementary charge e;
- Reduced Planck's constant $\hbar = h/(2\pi)$;
- Coulomb's constant $k_\mathrm{e} = 1/(4\pi\epsilon_0)$.

In Hartree units, the speed of light is approximately 137. Atomic units are often abbreviated "a.u." or "au", not to be confused with the same abbreviation used also for astronomical units, arbitrary units, and absorbance units in different contexts.

Contents

Use and notation

Atomic units, like SI units, have a unit of mass, a unit of length, and so on. However, the use and notation is somewhat different from SI.

Suppose a particle with a mass of m has 3.4 times the mass of electron. The value of m can be written in three ways:

- "$m = 3.4~m_\mathrm{e}$". This is the clearest notation (but least common), where the atomic unit is included explicitly as a symbol.[2]
- "$m = 3.4~\mathrm{a.u.}$" ("a.u." means "expressed in atomic units"). This notation is ambiguous: Here, it means that the mass m is 3.4 times the atomic unit of mass. But if a length L were 3.4 times the atomic unit of length, the equation would look the same, "$L = 3.4~\mathrm{a.u.}$" The dimension needs to be inferred from context.[2]
- "$m = 3.4$". This notation is similar to the previous one, and has the same dimensional ambiguity. It comes from formally setting the atomic units to 1, in this case $m_\mathrm{e} = 1$, so $3.4~m_\mathrm{e} = 3.4$.[3][4]

Fundamental atomic units

These four fundamental constants form the basis of the atomic units (see above). Therefore, their numerical values in the atomic units are unity by definition.

Fundamental atomic units

Dimension	Name	Symbol/Definition	Value in SI units[5]
mass	electron rest mass	m_e	9.109 382 91(40) × 10^{-31} kg
charge	elementary charge	e	1.602 176 565(35) × 10^{-19} C
action	reduced Planck's constant	$\hbar = h/(2\pi)$	1.054 571 726(47) × 10^{-34} J·s
electric constant^{-1}	Coulomb force constant	$k_\mathrm{e} = 1/(4\pi\epsilon_0)$	8.987 551 787 3681 × 10^{9} kg·m^3·s^{-2}·C^{-2}

Related physical constants

Dimensionless physical constants retain their values in any system of units. Of particular importance is the fine-structure constant $\alpha = \dfrac{e^2}{(4\pi\epsilon_0)\hbar c} \approx 1/137$. This immediately gives the value of the speed of light, expressed in atomic units.

Some physical constants expressed in atomic units

Name	Symbol/Definition	Value in atomic units
speed of light	c	$1/\alpha \approx 137$
classical electron radius	$r_\mathrm{e} = \dfrac{1}{4\pi\epsilon_0}\dfrac{e^2}{m_\mathrm{e} c^2}$	$\alpha^2 \approx 5.32 \times 10^{-5}$
proton mass	m_p	$m_\mathrm{p}/m_\mathrm{e} \approx 1836$

Derived atomic units

Below are given a few derived units. Some of them have proper names and symbols assigned, as indicated in the table. k_B is the Boltzmann constant.

Derived atomic units

Dimension	Name	Symbol	Expression	Value in SI units	Value in more common units
length	bohr	a_0	$4\pi\epsilon_0\hbar^2/(m_\mathrm{e}e^2) = \hbar/(m_\mathrm{e}c\alpha)$	5.291 772 1092(17) × 10^{-11} m[6]	0.052 917 721 092(17) nm = 0.529 177 210 92(17) Å
energy	hartree	E_h	$m_\mathrm{e}e^4/(4\pi\epsilon_0\hbar)^2 = \alpha^2 m_\mathrm{e}c^2$	4.359 744 17(75) × 10^{-18} J	27.211 385 eV = 627.509 kcal·mol^{-1}
time			$\hbar/E_\mathrm{h}$	2.418 884 326 505(16) × 10^{-17} s	
velocity			$a_0E_\mathrm{h}/\hbar = \alpha c$	2.187 691 2633(73) × 10^{6} m·s^{-1}	
force			E_h/a_0	8.238 7225(14) × 10^{-8} N	82.387 nN = 51.421 eV·Å^{-1}
temperature			$E_\mathrm{h}/k_\mathrm{B}$	3.157 7464(55) × 10^{5} K	
pressure			$E_\mathrm{h}/{a_0}^3$	2.942 1912(19) × 10^{13} Pa	
electric field			$E_\mathrm{h}/(ea_0)$	5.142 206 52(11) × 10^{11} V·m^{-1}	5.142 206 52(11) GV·cm^{-1} = 51.422 0652(11) V·Å^{-1}
electric potential			E_h/e	2.721 138 505(60) × 10^{1} V	
electric dipole moment			ea_0	8.478 353 26(19) × 10^{-30} C·m	2.541 746 D
Magnetic field (SI)			$\frac{\hbar}{ea_0^2}$	2.35 × 10^{5} T	2.35 × 10^{9} G
Magnetic dipole moment (SI)			$\frac{e\hbar}{2m_e}$		2 (Bohr magneton)
Magnetic field (cgs)			$\frac{e}{a_0^2c}$	1.72 × 10^{3} T	1.72 × 10^{7} G
Magnetic dipole moment (cgs)			$\frac{e\hbar}{2m_ec}$		

SI and Gaussian-CGS variants, and magnetism-related units

There are two common variants of atomic units, one where they are used in conjunction with SI units for electromagnetism, and one where they are used with Gaussian-CGS units.[7] Although the units written above are the same either way (including the unit for electric field), the units related to magnetism are not. In the SI system, the atomic unit for magnetic field is

$$1 \text{ a.u.} = \frac{\hbar}{ea_0^2} = 2.35 \times 10^5 \text{ T} = 2.35 \times 10^9 \text{ G},$$

and in the Gaussian-cgs unit system, the atomic unit for magnetic field is

$$1 \text{ a.u.} = \frac{e}{a_0^2c} = 1.72 \times 10^3 \text{ T} = 1.72 \times 10^7 \text{ G}.$$

(These differ by a factor of α.)

Other magnetism-related quantities are also different in the two systems. An important example is the Bohr magneton: In SI-based atomic units,[8]

$$\mu_\mathrm{B} = \frac{e\hbar}{2m_\mathrm{e}} = 1/2 \text{ a.u.}$$

and in Gaussian-based atomic units,[9]

$$\mu_\mathrm{B} = \frac{e\hbar}{2m_\mathrm{e}c} = \alpha/2 \approx 3.6 \times 10^{-3} \text{ a.u.}$$

Bohr model in atomic units

Atomic units are chosen to reflect the properties of electrons in atoms. This is particularly clear from the classical Bohr model of the hydrogen atom in its ground state. The ground state electron orbiting the hydrogen nucleus has (in the classical Bohr model):

- Orbital velocity = 1
- Orbital radius = 1
- Angular momentum = 1
- Orbital period = 2π
- Ionization energy = ½
- Electric field (due to nucleus) = 1
- Electrical attractive force (due to nucleus) = 1

Non-relativistic quantum mechanics in atomic units

The Schrödinger equation for an electron in SI units is

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(\mathbf{r},t) + V(\mathbf{r})\psi(\mathbf{r},t) = i\hbar\frac{\partial\psi}{\partial t}(\mathbf{r},t).$$

The same equation in **au** is

$$-\frac{1}{2}\nabla^2\psi(\mathbf{r},t) + V(\mathbf{r})\psi(\mathbf{r},t) = i\frac{\partial\psi}{\partial t}(\mathbf{r},t).$$

For the special case of the electron around a hydrogen atom, the Hamiltonian in SI units is:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r},$$

while **atomic units** transform the preceding equation into

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}.$$

Comparison with Planck units

Both Planck units and au are derived from certain fundamental properties of the physical world, and are free of anthropocentric considerations. It should be kept in mind that au were designed for atomic-scale calculations in the present-day universe, while Planck units are more suitable for quantum gravity and early-universe cosmology. Both au and Planck units normalize the reduced Planck constant. Beyond this, Planck units normalize to 1 the two fundamental constants of general relativity and cosmology: the gravitational constant G and the speed of light in a vacuum, c. Atomic units, by contrast, normalize to 1 the mass and charge of the electron, and, as a result, the speed of light in atomic units is a large value, $1/\alpha \approx 137$. The orbital velocity of an electron around a small atom is of the order of 1 in atomic units, so the discrepancy between the velocity units in the two systems reflects the fact that electrons orbit small atoms much slower than the speed of light (around 2 orders of magnitude slower).

There are much larger discrepancies in some other units. For example, the unit of mass in atomic units is the mass of an electron, while the unit of mass in Planck units is the Planck mass, a mass so large that if a single particle had that much mass it might collapse into a black hole. Indeed, the Planck unit of mass is 22 orders of magnitude larger than the au unit of mass. Similarly, there are many orders of magnitude separating the Planck units of energy and length from the corresponding atomic units.

See also

- Natural units
- Planck units
- Various extensions of the CGS system to electromagnetism.

Notes and references

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External links

- CODATA Internationally recommended values of the Fundamental Physical Constants. (http://physics.nist.gov/cuu/Constants/index.html)