17.4: Atomic Units

The electronic Hamiltonian is expressed, in this Section, in so-called atomic units (aus)

$$H_e = \sum \left[-\frac{1}{2}\nabla_j^2 - \sum_a \frac{Z_a}{r_{j,a}} \right] + \sum_{j<k} \frac{1}{r_{r,k}}.$$

These units are introduced to remove all $\hbar, \mathrm{e}, \text{and } \mathrm{m}_e$ factors from the equations.

To effect this unit transformation, one notes that the kinetic energy operator scales as r_j^{-2} whereas the coulombic potentials scale as r_j^{-1} and as $r_{j,k}^{-1}$. So, if each of the distances appearing in the cartesian coordinates of the electrons and nuclei were expressed as a unit of length a_0 multiplied by a dimensionless length factor, the kinetic energy operator would involve terms of the form $\left(-\frac{\hbar^2}{2(a_0)^2 m_e}\right)\nabla_j^2$, and the coulombic potentials would appear as $\frac{Z_a e^2}{(a_0) r_{j,a}}$ and $\frac{e^2}{(a_0) r_{j,k}}$. A factor of $\frac{e^2}{a_0}$ (which has units of energy since a_0 has units of length) can then be removed from the coulombic and kinetic energies, after which the kinetic energy terms appear as $-\frac{\hbar^2}{2(e^2 a_0) m_e}\nabla_j^2$ and the potential energies appear as $\frac{Z_a}{r_{j,a}}$ and $\frac{1}{r_{k,j}}$. Then, choosing $a_0 = \frac{\hbar^2}{e^2 m_e}$ changes the kinetic energy terms into $-\frac{1}{2}\nabla_j^2$; as a result, the entire electronic Hamiltonian takes the form given above in which no e^2, me, or $\hbar^2$ factors appear. The value of the so-called Bohr radius $a_0 = \frac{\hbar^2}{e^2 m_e}$ is 0.529 Å, and the so-called Hartree energy unit $\frac{e^2}{a_0}$, which factors out of H_e, is 27.21 eV or 627.51 kcal/mol.