Appendix

A. Hartree Atomic Units

In this book we employ a system of atomic units, usually referred to as Hartree's system. This is based on the following units:

		Dimension
e	the absolute value of the electric charge of the electron	[A s]
m	the rest mass of the electron	[kg]
$\hbar$	Planck's constant divided by 2π	[kg m^2/s]
$4\pi\varepsilon_0$	4π times the permittivity of vacuum	[A^{2}s^4/kg m^3]

The dimensions in SI units of the basic quantities are shown in square brackets. Other atomic units can be obtained by combining these quantities to give the correct dimension.

The first Bohr radius

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \tag{A.1}$$

has the dimension [m], and, hence, it is the atomic unit of length.

The fine-structure constant

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 c\hbar}, \tag{A.2}$$

where c is the velocity of light in vacuum, is a pure number ($\approx 1/137$). This means that αc is the atomic unit of velocity, or that the velocity of light is approximately 137 atomic units.

In spectroscopy, the energy is often expressed in terms of

$$hcR_\infty = \frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2}, \tag{A.3}$$

where R_∞ is the Rydberg constant for infinite nuclear mass. In atomic units this has the value of 1/2, so the atomic energy unit is

$$\boxed{1\mathrm{H} = 2hcR_\infty \approx 27.2\ \mathrm{eV}}\,. \tag{A.4}$$

This unit is nowadays often referred to as the *Hartree unit*.

The Rydberg constant itself has the dimension [m^{-1}], and its value in atomic units is $\alpha/4\pi$ (h has the value of 2π). This leads to the relation

$$R_\infty = \frac{\alpha}{4\pi a_0}, \tag{A.5}$$

which is easily checked by means of the complete expressions.

The Bohr magneton

$$\mu_B = \frac{e\hbar}{2m}$$

has the value 1/2 in atomic units, so the unit for magnetic moment is $2\mu_B$. (It should be observed that the expression $e\hbar/2mc$ used in older literature for the Bohr magneton is based on a *mixed* unit system and therefore does not have the correct dimension.)

From the relation

$$\mu_0\varepsilon_0 = 1/c^2 ,$$

where μ_0 is the permeability of vacuum, we find that

$$\frac{\mu_0}{4\pi} = \frac{1}{4\pi\varepsilon_0 c^2}$$

has the value α^2 in atomic units.

B. States and Operators

B.1 Representation of Physical States

The state of a physical system is in the time-independent Schrödinger formalism represented by a wave function $\Psi^a(\boldsymbol{r})$, where $\boldsymbol{r}$ stands for the space and spin coordinates of all the particles. In the *Dirac notation* such a state is represented by a *ket*, or *ket vector*, $|\Psi^a\rangle$. The corresponding complex conjugate function $\Psi^a(\boldsymbol{r})^*$ is represented in Dirac's notation by a *bra*, or *bra vector*, $\langle\Psi^a|$.

The *scalar product* of two functions, $\Psi^a(\boldsymbol{r})$ and $\Psi^b(\boldsymbol{r})$, is in the Dirac and Schrödinger notations

$$\langle\Psi^a|\Psi^b\rangle = \int \Psi^a(\boldsymbol{r})^*\Psi^b(\boldsymbol{r})d\boldsymbol{r} . \tag{B.1}$$

This represents an *integration* over all space coordinates and a *summation* over all spin coordinates. If the scalar product is zero, the functions are *orthogonal*. The function Ψ^a is *normalized*, if $\langle\Psi^a|\Psi^a\rangle = 1$. It follows directly from (B.1) that