

## H. OPTIMAL WAVE FUNCTION FOR A HYDROGEN-LIKE ATOM

In several contexts we encounter the problem of the mean value of the Hamiltonian for a hydrogen-like atom (the a.u. are used throughout)

$$\hat{H} = -\frac{1}{2}\Delta - \frac{Z}{r}$$

with the normalized function

$$\Phi(r, \theta, \phi; c) = \sqrt{\frac{c^3}{\pi}} \exp(-cr),$$

where  $r, \theta, \phi$  are the spherical coordinates of the electron (the position of the nucleus is fixed at the origin).

Calculation of the mean value of the Hamiltonian, i.e. the mean value of the energy

$$\varepsilon(\Phi) = \langle \Phi | \hat{H} | \Phi \rangle$$

requires calculation of the mean value of the kinetic energy:

$$\bar{T} = \left\langle \Phi \left| -\frac{1}{2}\Delta \right| \Phi \right\rangle$$

and the mean value of the potential energy (Coulombic attraction of an electron by a nucleus of charge  $Z$ )

$$\bar{V} = -Z \left\langle \Phi \left| \frac{1}{r} \right| \Phi \right\rangle.$$

Therefore,

$$\varepsilon = \bar{T} + \bar{V}.$$

First, the Laplacian  $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$  may be expressed in spherical coordinates

$$\Delta = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}, \quad (\text{H.1})$$

and in view of the fact that  $\Phi$  is spherically symmetric (it only depends on  $r$ )

$$\begin{aligned}
 \left\langle \Phi \left| -\frac{1}{2}\Delta \right| \Phi \right\rangle &= -\frac{1}{2} \left\langle \Phi \left| \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right| \Phi \right\rangle \\
 &= -\frac{1}{2} \frac{c^3}{\pi} (-c) \left[ \int_0^\infty r^2 \left[ \frac{2}{r} - c \right] \exp(-2cr) dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \right] \\
 &= \frac{1}{2} c^4 \left[ \int_0^\infty [2r - cr^2] \exp(-2cr) dr \right] \\
 &= 2c^4 \left[ 2 \int_0^\infty r \exp(-2cr) dr - c \int_0^\infty r^2 \exp(-2cr) dr \right] \\
 &= 4c^4 (2c)^{-2} - 2c^5 2(2c)^{-3} = c^2 - \frac{1}{2}c^2 = \frac{1}{2}c^2,
 \end{aligned}$$

where we have used (this formula is often exploited throughout the book)

$$\int_0^\infty r^n \exp(-\beta r) dr = n! \beta^{-(n+1)}. \quad (\text{H.2})$$

Similarly the second integral gives

$$\begin{aligned}
 -Z \left\langle \Phi \left| \frac{1}{r} \right| \Phi \right\rangle &= -Z \frac{c^3}{\pi} \left[ \int_0^\infty r \exp(-2cr) dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \right] \\
 &= -4Zc^3 (2c)^{-2} = -Zc.
 \end{aligned}$$

Therefore, finally

$$\varepsilon = \frac{1}{2}c^2 - Zc. \quad (\text{H.3})$$

We may want to use the variational method for finding the ground-state wave function. In this method we minimize the mean value of the Hamiltonian with respect to parameters in the variational function  $\Phi$ . We may treat  $c$  as such a parameter. Hence, minimizing  $\varepsilon$  we force  $\frac{\partial \varepsilon}{\partial c} = 0$ , and therefore  $c_{\text{opt}} = Z$ . Note that in this particular case:

- Such a value of  $c$  gives the *exact* ground-state of the hydrogen-like atom from the variational function.
- The ground-state energy computed with  $c_{\text{opt}} = Z$  gives  $\varepsilon = \frac{1}{2}Z^2 - ZZ = -\frac{1}{2}Z^2$ , which is the *exact* ground-state energy.
- The quantity  $-\frac{\bar{V}}{T} = \frac{Zc}{\frac{1}{2}c^2} = 2\frac{Z}{c}$ . For  $c = c_{\text{opt}} = Z$  we have what is called the *virial theorem*

virial theorem

$$-\frac{\bar{V}}{\bar{T}} = 2. \quad (\text{H.4})$$