APPENDIX H

Optimal Wave Function for the Hydrogen-Like Atom

In several instances, we encounter the problem of the mean value of the Hamiltonian for the hydrogen-like atom (atomic units 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, θ, ϕ are the spherical coordinates of the electron (and the position of the nucleus is fixed in the origin).

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

$$\varepsilon(\Phi) = \left\langle \Phi \middle| \hat{H} \middle| \Phi \right\rangle,$$

requires calculation of the mean value of the kinetic energy:

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

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

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

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 the spherical coordinates

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\sin\theta\frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2}, \tag{H.1}$$

Ideas of Quantum Chemistry, Second Edition. http://dx.doi.org/10.1016/B978-0-444-59436-5.00028-3

and in view of the fact that Φ is spherically symmetric (it depends on r only),

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

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

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

Quite similarly, the second integral gives

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

Therefore, finally,

$$\varepsilon = \frac{1}{2}c^2 - Zc. \tag{H.3}$$

We may want to use the variational method of 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 Φ. We may treat c as such a parameter. Hence, minimizing ε, we force $\frac{\partial\varepsilon}{\partial c} = 0$, and therefore, $c_{opt} = Z$. Note that in this particular case, the following is true:

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

$$-\frac{\bar{V}}{\bar{T}} = 2, \tag{H.4}$$

which is called the *virial theorem*.