# Chapter 7. Exercises

1. Assume that each circular Bohr orbit for an electron in a hydrogen atom contains an integer number of de Broglie wavelengths, $n = 1, 2, \ldots$. Show that the orbital angular momentum must then be quantized. Bohr's formula for the hydrogen energy levels follows from this.

2. Based on your knowledge of the first few hydrogenic eigenfunctions, deduce general formulas, in terms of n and ℓ, for: (i) the number of radial nodes in an atomic orbital; (ii) the number of angular nodes; (iii) the total number of nodes.

3. Calculate the wavelength of the Lyman alpha transition $(1s \leftarrow 2p)$ in atomic hydrogen and in He^+. Express the results in both nm and cm^{-1}.

4. Determine the maximum of the radial distribution function for the ground state of hydrogen atom. Compare this value with the corresponding radius in the Bohr theory.

5. The following reaction might occur in the interior of a star:

$$He^{++} + H \rightarrow He^+ + H^+$$
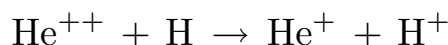
Calculate the electronic energy change (in eV). Assume all species in their ground states.

6. Which of the following operators is *not* equal to the other four: (i) $\partial^2/\partial r^2$ (ii) $r^{-2}\,\partial/\partial r\, r^2\,\partial/\partial r$ (iii) $r^{-1}\,\partial^2/\partial r^2\, r$ (iv) $(r^{-1}\,\partial/\partial r\, r)^2$ (v) $\partial^2/\partial r^2 + 2r^{-1}\partial/\partial r$.

7. Calculate the expectation values of r, r^2 and of r^{-1} in the ground state of the hydrogen atom. Give results in atomic units.

8. Calculate the expectation values of potential and kinetic energies for the $1s$ state of of a hydrogenlike atom.

9. Verify that the $3d_{xy}$ orbital given in the table is a normalized eigenfunction of the hydrogenlike Schrödinger equation.

10. Show that the function

$$\psi(r, \theta, \phi) = \text{const} \left[1 - r \sin^2(\theta/2)\right] e^{-r/2}$$

is a solution of the Schrödinger equation for the hydrogen atom and find the corresponding eigenvalue (in atomic units).

11. For the ground state of a hydrogenlike atom, calculate the radius of the sphere enclosing 90% of the electron probability in the $1s$ state of hydrogen atom. (This involves a numerical computation with successive approximations.)

12. Consider as a variational approximation to the ground state of the hydrogen atom the wavefunction $\psi(r) = e^{-\alpha r}$. Calculate the corresponding energy $E(\alpha)$ then optimize with respect to the parameter α. Compare with the exact solution.

13. The electron-spin resonance hyperfine splitting for atomic hydrogen is given by

$$\Delta \nu = 532.65 \left\{ \frac{8\pi}{3} |\psi(0)|^2 + \left\langle \frac{3\cos^2 \theta - 1}{r^3} \right\rangle \right\} \text{MHz}$$

Calculate $\Delta \nu$ for the $1s$ and for the $2p_0$ states. The result is in MHz when the bracketed terms are expressed in atomic units. (Hint: In the expectation value, do the integral over angles first.)

Chapter 7. Solutions

1. De Broglie wavelength $\lambda = h/p$ with $L = r\,p$. Circumference of orbit $2\pi r = n\lambda$, an integer number of wavelengths. This implies $L = nh/2\pi = n\hbar$.

2. $n - \ell - 1$ radial nodes, ℓ angular nodes, $n - 1$ total nodes.

3. The best formula to use is

$$\frac{1}{\lambda} = Z^2 R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where R is the Rydberg constant, 109678 cm^{-1}. For hydrogen, $1/\lambda = R(1/1^2 - 1/2^2) = 82258.5\,\text{cm}^{-1}$, $\lambda = 121.6\,\text{nm}$. For helium, $1/\lambda = 4\,R(1/1^2 - 1/2^2) = 329034\,\text{cm}^{-1}$, $\lambda = 30.39\,\text{nm}$.

4. Find the maximum of $D_{1s}(r) = 4\pi r^2 \left[\psi_{1s}(r) \right]^2 = \text{const}\, r^2\, e^{-2Zr}$. Set $dD/dr = 0$, giving $r_{\text{max}} = 1/Z\ (= a_0/Z)$, same as Bohr radius for $1s$ orbit.

5. He^{++} and H$^+$ are bare nuclei so their electronic energies equal zero. He$^+$ and H are hydrogenlike so their $1s$ energies equal $-Z^2/2$. Thus $\Delta E = -4/2 + 1/2 = -3/2$ hartrees $= -40.8$ eV.

6. (i). The other four operators are equal.

7.
$$\langle r \rangle = \int_0^\infty \psi_{1s}(r)\, r\, \psi_{1s}(r)\, 4\pi r^2\, dr = \frac{3}{2} \quad \left(= \frac{3}{2} a_0 \right)$$

$$\langle r^2 \rangle = \int_0^\infty \psi_{1s}(r)\, r^2\, \psi_{1s}(r)\, 4\pi r^2\, dr = 3 \quad \left(= 3a_0^2 \right)$$

$$\langle r^{-1} \rangle = \int_0^\infty \psi_{1s}(r)\, r^{-1}\, \psi_{1s}(r)\, 4\pi r^2\, dr = 1 \quad \left(= \frac{1}{a_0} \right)$$

8. Average potential energy:

$$< V > = \int_0^\infty \psi_{1s}(r) \left(-\frac{Z}{r} \right) \psi_{1s}(r)\, 4\pi r^2\, dr = -Z^2$$

Average kinetic energy:

$$< T > = \int_0^\infty \psi_{1s}(r) \left(-\frac{1}{2}\nabla^2 \right) \psi_{1s}(r)\, 4\pi r^2\, dr = Z^2/2$$

More simply, since total energy $E_{1s} = -Z^2/2$, $\langle T \rangle = E_{1s} - \langle V \rangle$. Note that $\langle V \rangle = -2\langle T \rangle$, consistent with the virial theorem.

9. For an easier exercise, do the $2p_z$ orbital instead.

10. You should find that this function solves the Schrödinger equation with $E = -Z^2/8$, i.e., $n = 2$. For normalization

$$\text{const} = \frac{Z^{3/2}}{4\sqrt{\pi}}$$

Noting that $\sin^2(\theta/2) = (1 - \cos\theta)/2$, the function is found to be an *s-p* hybrid orbital:

$$\psi = \frac{1}{\sqrt{2}} \left(\psi_{2s} + \psi_{2pz} \right)$$

11. Solve for R:

$$\int_0^R |\psi_{1s}(r)|^2 \, 4\pi r^2 \, dr = 0.9$$

or easier

$$\int_R^\infty |\psi_{1s}(r)|^2 \, 4\pi r^2 \, dr = 0.1$$

We find, using integral table,

$$4 \int_R^\infty r^2 \, e^{-2r} \, dr = e^{2R} \left(1 + 2R + 2R^2\right) = 0.1$$

Solving numerically, $R = 2.6612 a_0 = 1.41$ Å.

12. Let $\psi(r) = e^{-\alpha r}$. Then

$$E(\alpha) = \frac{\int_0^\infty e^{-\alpha r} \left(-\frac{1}{2}\nabla^2 - Z/r\right) e^{-\alpha r} 4\pi r^2 \, dr}{\int_0^\infty e^{-2\alpha r} 4\pi r^2 \, dr} = \frac{1}{2}\alpha^2 - Z\alpha$$

$E'(\alpha) = 0$ for minimum, giving $\alpha = Z$. Thus $\psi(r) = e^{-Zr}$ and $E = -Z^2/2$, which in this exceptional case equal the exact eigenfunction and eigenvalue.