量子化学作业 第七章 (2017-2018 学期)

1. Show that the substitution $R(r)Y_l^{m_l}(\theta,\phi)$ into Equation 7.7 yields Equation 7.10.

2. Referring to Table 7.2, show that $R_{10}(R)$ and $R_{20}(R)$ are orthonormal.

3. Show explicitly that

$$\hat{H}\psi = -\frac{m_e e^4}{8\varepsilon_0^2 h^2}\psi$$

for the ground state of a hydrogen atom.

4. By evaluating the appropriate integrals, compute $<r>$ in the 2*s*, 2*p*, and 3*s* states of the hydrogen atom; compare your results with Table 7.4 and the general formula

$$<r_{nl}>=\frac{a_0}{2Z}\left[3n^2-l(l+1)\right]$$

5. Show that the sum of the probability densities for the $n=3$ states of a hydrogen atom is spherically symmetric. Do you expect this to be true for all values of n? Explain.

6. What is the ratio of the ground-state energy of atomic hydrogen to that of atomic deuterium?

7. Superconducting magnets have magnetic field strengths of the order of 15 T. Calculate the magnitude of the splitting shown in Figure 7.9 for a magnetic field of 15 T. Compare your result with the energy difference between the unperturbed ls and 2p levels. Show that the three distinct transitions shown in Figure 7.9 lie very close together.

8. Show that the force acting upon a magnetic dipole moment in a magnetic field B_z that varies in the z direction is given by $F_z = m_z \partial B_z / \partial z$.

9. Extend Table 7.6 to the case $l = 4$. How many states are there?

10. Can you deduce a general formula for the total number of states for each value of l in Table 7.6?

11. Townsend (see end-of-chapter references) gives the following formula for the shift of a hydrogen atom energy level due to spin-orbit coupling:

$$\Delta E_{so} = \frac{m_e c^2 Z^4 \alpha^4}{4n^3(l+\frac{1}{2})l(l+1)} \times \begin{cases} l & j = l + \frac{1}{2} \\ -(l+1) & j = l - \frac{1}{2} \end{cases}$$

The only new quantity in this expression is a, which is called the *fine structure constant*, and is given by $e^2 / 4\pi\varepsilon_0 \hbar c$. Use this formula for ΔE_{so} to show that the difference in energy between two states with the same value of *n* and *l* is

$$\text{diff=} \frac{m_e c^2 Z^4 \alpha^4}{2n^3 l(l+1)} = \frac{5.8437 Z^4 cm^{-1}}{n^3 l(l+1)}$$

Calculate the difference in energies between the $2p\,^2\mathrm{P}_{1/2}$ and $2p\,^2\mathrm{P}_{3/2}$ states of a hydrogen atom and compare your results to what you obtain from Table 7.7. Do the same for the $3p\,^2\mathrm{P}_{1/2}$ and $3p\,^2\mathrm{P}_{3/2}$ states and the $4p\,^2\mathrm{P}_{1/2}$ and $4p\,^2\mathrm{P}_{1/2}$ states.

12. Use the equation of the previous problem to calculate the difference in energy between the $3d\,^2\mathrm{D}_{3/2}$ and $3d\,^2\mathrm{D}_{5/2}$ (原书写错，上一届助教注) states and the $4d\,^2\mathrm{D}_{3/2}$ and $4d\,^2\mathrm{D}_{5/2}$ states of a hydrogen atom. How about for the $4f\,^2\mathrm{F}_{5/2}$ and $4f\,^2\mathrm{F}_{7/2}$ states?

13. We'll see in Section 8.6 that the selection rule for electronic transitions in a hydrogen atom depends upon whether the integral $I = \langle n, l, m_l | z | n', l', m_l' \rangle$ is zero or nonzero. If $I = 0$, then the transition is forbidden; otherwise, it may occur. Show that $I = 0$ unless $\Delta l = \pm 1$ and $\Delta m_l = 0$. Do you find any restriction on Δn?