量子化学作业　　第十章（2017-2018 学期）

（第九章光谱部分）

1. Determine the term symbols associated with an np^1 electron configuration. Show that these term symbols are the same as for an np^5 electron configuration.

2. Given that the electron configuration of a zirconium atom is $[\mathrm{Kr}]4d^2 5s^2$, what is the ground-state term symbol for Zr?

（第十章）

1. The overlap integral, Equation 10.13c(Page 507 of the textbook), and other integrals that arise in two-center systems like H_2^+ are called *two-center integrals*. Two-center integrals are most easily evaluated by using a coordinate system called *elliptical coordinates*. In this coordinate system (Figure 10.4)(Page 503 of the textbook), there are two fixed points separated by a distance R. A point P is given by the three coordinates

$$\lambda = \frac{r_A + r_B}{R}$$

$$\mu = \frac{r_A - r_B}{R}$$

and the angle ϕ, which is the angle that the (r_A, r_B, R) triangle makes about the interfocal axis. The differential volume element in elliptical coordinates

$$d\mathbf{r} = \frac{R^3}{8}(\lambda^2 - \mu^2)d\lambda d\mu d\phi$$

is

Given the above definitions of λ, μ and ϕ, show that

$$1 \le \lambda < \infty \qquad -1 \le \mu \le 1 \qquad 0 \le \phi \le 2\pi$$

Now use elliptical coordinates to evaluate the overlap integral (Equation 10.13c):

$$\begin{aligned} S &= \int d\mathbf{r} 1s_A 1s_B \\ &= \frac{Z^3}{\pi}\int d\mathbf{r}\; e^{-Zr_A} e^{-Zr_B} \end{aligned}$$

2. Show that

$$\langle \hat{T} \rangle = \left\langle \psi_+ \middle| -\frac{1}{2}\nabla^2 \middle| \psi_+ \right\rangle = \frac{\frac{1}{2} - \frac{S}{2} - K}{1+S}$$

$$\langle \hat{V} \rangle = \left\langle \psi_+ \middle| -\frac{1}{r_A} \middle| \psi_+ \right\rangle + \left\langle \psi_+ \middle| -\frac{1}{r_B} \middle| \psi_+ \right\rangle + \left\langle \psi_+ \middle| \frac{1}{R} \middle| \psi_+ \right\rangle = \frac{-1 + J + 2K}{1+S} + \frac{1}{R}$$

3. Instead of just minimizing $E_+(\zeta, R)$ numerically, we can do it analytically. Use Equation 10.33(Page 518 of the textbook) to show that the optimum value of ζ as a function of $\omega=\zeta R$ is given by

$$\zeta = \frac{-V_+(\omega) - \omega \dfrac{dV_+(\omega)}{d\omega}}{2T_+(\omega) + \omega \dfrac{dT_+(\omega)}{d\omega}}$$

4. In this problem, we shall prove that $\zeta \to 2$ as $R \to 0$, as shown in Figure 10.16(Page 519 of the textbook). First show that

$$S(\omega) = 1 - \frac{1}{6}\omega^2 + O(\omega^3)$$

$$J(\omega) = -1 + \frac{2}{3}\omega^2 + O(\omega^3)$$

$$K(\omega) = -1 + \frac{\omega^2}{2} + O(\omega^3)$$

as $R \to 0$. Now show that

$$T_+(\omega) = \frac{1}{2} - \frac{\omega^2}{6} + O(\omega^3)$$

$$V_+(\omega) = \frac{1}{\omega} - 2 + \frac{2}{3}\omega^2 + O(\omega^3)$$

Substitute these results into ζ in Problem 3 to obtain

$$\zeta = 2 - \frac{2\omega^2}{3} + O(\omega^3)$$

5. Show that ψ given by Equation 10.38(Page 526 of the textbook) is an eigenfunction of $\hat{S}_z = \hat{S}_{z1} + \hat{S}_{z2}$ with $S_z = 0$.

6. In this problem, we shall prove that if an Hermitian operator $\hat{F}$ commutes with $\hat{H}$, then matrix elements of $\hat{H}$, $H_{ij} = <\psi_i|H|\psi_j>$, between states with different eigenvalues of $\hat{F}$ vanish. For simplicity, we prove this only for nondegenerate states. Let $\hat{F}$ be an operator that commutes with $\hat{H}$, and let its eigenvalues and eigenfunctions be denoted by λ and ψ_λ, respectively. Show that

$$\left[\hat{H},\hat{F}\right]_{\lambda\sigma} = \left\langle \psi_\lambda \left| \left[\hat{H},\hat{F}\right] \right| \psi_\sigma \right\rangle = (\sigma-\lambda) H_{\lambda\sigma}$$

Now argue that $H_{\lambda\sigma}=0$ unless $\lambda=\sigma$. For degenerate states, it is possible to take linear combinations of the degenerate eigenfunctions and carry out a similar proof.

7. Show that the normalization condition for Equation 10.64(Page 538 of the textbook) is $c_1^2+2c_1c_2S_{AB}+c_2^2=1$, where S_{AB} is the overlap integral involving ϕ_A and ϕ_B.