# Problem Set 3

## Physical Chemistry 2, Summer 2021

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1. **Radial part of hydrogen atom.** The radial equation of hydrogen atom is

$$-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2}+\left[-\frac{e^2}{4\pi\epsilon_0 r}+\frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2}\right]u=Eu$$

   (a) First, let's tidy up the notation. Define three variables:

$$\kappa\equiv\frac{\sqrt{-2m_eE}}{\hbar},\ \rho\equiv\kappa r,\ \rho_0\equiv\frac{m_ee^2}{2\pi\epsilon_0\hbar^2\kappa}$$

   Show that radial equation reduces into following form

$$\frac{d^2u}{d\rho^2}=\left[1-\frac{\rho_0}{\rho}+\frac{l(l+1)}{\rho^2}\right]u$$

   (b) Investigate asymptotic behavior at $\rho\to\infty$ and $\rho\to 0$. Show that $u(\rho)$ can be written, introducing new function $v(\rho)$.

$$u(\rho)=\rho^{l+1}e^{-\rho}v(\rho)$$

   (c) Show that

$$\rho\frac{d^2v}{d\rho^2}+2(l+1-\rho)\frac{dv}{d\rho}+[\rho_0-2(l+1)]v=0$$

   (d) Write down $v(\rho)$ as power series, $v(\rho)=\sum_{j=0}^{\infty}c_j\rho^j$. By substituting this relation, show that coefficients satisfy

$$c_{j+1}=\frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}c_j$$

   (d) Observe the form of coefficients at large $j$ limit. Show that the power series should terminate at some point. i.e., there exists an integer $N$ such that $c_{N-1}\neq 0$ and $c_N=0$. In that case,

$$2(N+l)-\rho_0=2n-\rho_0=0\quad\text{where}\quad n\equiv N+l$$

   also show that

$$E=-\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{1}{n^2}=\frac{E_1}{n^2}\ (n=1,2,\ldots)$$

   (e) Show that

$$\rho=\frac{r}{an}\text{ where }a=\frac{4\pi\epsilon_0\hbar^2}{m_ee^2}$$

   (f) From the recursion formula, find out the ground state wavefunction of hydrogen atom.

$$\psi_{100}(r,\theta,\phi)=R_{10}(r)Y_0^0(\theta,\phi)=\frac{1}{\sqrt{\pi a^3}}e^{-r/a}$$

   (g) From the recursion formula, determine $R_{20}(r)$ and $R_{21}(r)$.

2. **Griffiths, 4.15**

   (a) Find $\langle r\rangle$ and $\langle r^2\rangle$ for an electron in the ground state of hydrogen. Express answers in terms of the Bohr radius.

   (b) Find $\langle x\rangle$ and $\langle x^2\rangle$ for an electron in the ground state of hydrogen.

   (c) Find $\langle x^2\rangle$ in the state $n=2, l=1, m=1$.

3. **Griffiths, 4.16** What is the most probable value of $r$, in the ground state of hydrogen?

4. **Ladder operator method for angular momentum.**

   (a) Before we start, show that
   $$[L^2, \mathbf{L}] = 0$$
   Since they commute, **they share common set of eigenfunctions**. We will use this fact in further discussion.

   (b) Assume that $f$ is common eigenstate of $L^2$ and $L_z$.
   $$L^2 f = \lambda f,\ L_z f = \mu f$$
   Define following ladder operators:
   $$L_\pm \equiv L_x \pm i L_y$$
   Show that
   $$[L_z, \pm L_\pm] = \pm\hbar L_\pm,\ [L^2, L_\pm] = 0$$

   (c) Show that
   $$L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z$$

   (d) Show that
   $$L^2(L_\pm f) = \lambda(L_\pm f), \quad L_z(L_\pm f) = (\mu \pm \hbar)(L_\pm f)$$
   Therefore, $L_\pm$ raises and lowers the $z$-component of angular momentum, without changing the size of angular momentum vector.

   (e) Therefore, for a given value of $\lambda$, there must exist a *top rung*, since $z$-component of angular momentum cannot exceed the size of angular momentum.
   $$L_+ f_{\max} = 0,\ L_z f_{\max} = \hbar l f_{\max},\ L^2 f_{\max} = \lambda f_{\max}$$

   (f) By using result in (c), show that
   $$\lambda = \hbar^2 l(l+1)$$

   (g) Repeat the same argument as in (e) and (f), for the *bottom rung* of the ladder.
   $$L_- f_{\min} = 0,\ L_z f_{\min} = \hbar\bar{l} f_{\min},\ L^2 f_{\min} = \lambda f_{\min}$$
   Then show that
   $$\lambda = \hbar^2 \bar{l}(\bar{l} - 1), \quad \bar{l} = -l$$
   Therefore, the eigenvalues of $L_z$ are $m\hbar$ where $-l \le m \le l$. In summary,
   $$L^2 f_l^m = \hbar^2 l(l+1) f_l^m, \quad L_z f_l^m = \hbar m f_l^m$$
   In class, we wrote $f_l^m$ as $Y_l^m$, the spherical harmonics.

   (h) Show that
   $$L_+ f_l^m = \hbar\sqrt{(l-m)(l+m+1)} f_l^{m+1}$$
   $$L_- f_l^m = \hbar\sqrt{(l+m)(l-m+1)} f_l^{m-1}$$

5. **McQuarrie, 6-10.** Using explicit expressions for $Y_l^m$, show that

$$|Y_1^1|^2 + |Y_1^0|^2 + |Y_1^{-1}|^2 = \text{const.}$$

This is a special case of the general theorem

$$\sum_{m=-l}^{+l} |Y_l^m|^2 = \text{const.}$$

known as Unsöld's theorem. What is the physical significance of this result?

6. **McQuarrie, 6-29.** Let $\psi_1 = \psi_{210}$ and $\psi_2 = \psi_{211}$. What is the energy corresponding to $\psi = c_1\psi_1 + c_2\psi_2$ where $c_1^2 + c_2^2 = 1$? What does this result tell you about the uniqueness of the three $p$ orbitals?

7. **McQuarrie, 8-21.** Argue that the normalization constant of an $N \times N$ Slater determinant of orthonormal spin orbitals is $1/\sqrt{N!}$.

8. **Griffiths, 5.17.** Figure out the electron configurations of atomic number 1 to 36, and write down the ground state term symbols.

9. **Prove the variation theorem.** Given a system whose Hamiltonian operator $\hat{H}$ is time independent and whose lowest-energy eigenvalue is $E_0$, if $\phi$ is well-behaved function of the coordinates of the system's particles that satisfies the boundary conditions of the problem, then

$$\frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \geq E_0$$

10. **Linear variation functions.** Assume that $\{f_i\}_{i=1}^n$ are $n$ linearly independent functions. Let the trial function be

$$\phi = \sum_{i=1}^n c_i f_i$$

Show that energy eigenvalues are solution of secular equation, $\det(H_{ij} - ES_{ij}) = 0$ where $H$ and $S$ matrices are defined as in the lecture note.

11. **The virial theorem.** Consider a linear, time-independent operator $\hat{A}$.

   (a) Show that

$$\int \psi^* [\hat{H}, \hat{A}] \psi \, d\tau = 0$$

   (b) Define $\hat{A}$ as following:

$$\hat{A} = \sum_i \hat{x}_i \hat{p}_i \text{ where } \hat{\mathbf{x}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3)$$

   Show that

$$\left\langle \sum_i q_i \frac{\partial V}{\partial q_i} \right\rangle = 2 \langle T \rangle$$

   (c) A function $f(x_1, \ldots, x_j)$ of several variables is **homogeneous of degree** $n$ if it satisfies

$$f(\lambda x_1, \lambda x_2, \ldots, \lambda x_j) = \lambda^n f(x_1, x_2, \ldots, x_j)$$

   Prove the Euler theorem: if $f$ is homogeneous function of degree $n$, then

$$\sum_{k=1}^j x_k \frac{\partial f}{\partial x_k} = nf$$

   (d) From the Euler theorem, prove that $2\langle T \rangle = n \langle V \rangle$.

12. **Hellmann-Feynman theorem.** Consider a system with a time-independent Hamiltonian $\hat{H}$ that involves *parameters.*

$$\hat{H}\psi_n = E_n\psi_n$$

Assume that hamiltonian depends on the parameter $\lambda$. Then

$$\frac{\partial E_n}{\partial \lambda} = \frac{\partial}{\partial \lambda}\int \psi_n^* \hat{H}\psi_n \, d\tau$$

By expanding this term with chain rule, derive **Hellmann-Feynman theorem**.

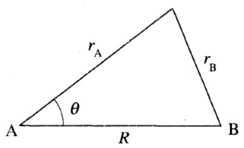
$$\frac{\partial E_n}{\partial \lambda} = \int \psi_n^* \frac{\partial \hat{H}}{\partial \lambda}\psi_n \, d\tau$$

13. **Levine, 14-37(a).** Apply the Hellmann-Feynman theorem with $Z$ as the parameter to find $\langle 1/r \rangle$ for the hydrogen-like atom bound states $\psi_{nlm}$.

14. **Levine, 14-38.** Use the Hellmann-Feynman theorem to find $\langle p_x^2 \rangle$ for the one-dimensional harmonic oscillator stationary states. Check that the result obtained agrees with the virial theorem.

15. **McQuarrie, 9-42.** In this problem, we evaluate the overlap integral using spherical coordinates centered on atom A.

$$S(R) = \frac{1}{\pi}\int d\mathbf{r}_A \, e^{-r_A}e^{-r_B} = \frac{1}{\pi}\int_0^\infty dr_A \, e^{-r_A}r_A^2 \int_0^{2\pi} d\phi \int_0^\pi d\theta \, sin\theta e^{-r_B}$$




(a) From the law of cosines, $r_B = (r_A^2 + R^2 - 2r_A R\cos\theta)^{1/2}$, evaluate

$$I_\theta = \int_0^\pi e^{-(r_A^2+R^2-2r_A R\cos\theta)^{1/2}} \sin\theta \, d\theta$$

Let $x = \cos\theta$ and $u = (r_A^2 + R^2 - 2r_A Rx)^{1/2}$.

(b) Substitute the result into $S(R)$ to get

$$S(R) = e^{-R}\left(1 + R + \frac{R^2}{3}\right)$$

16. **McQuarrie, 10-29.** Derive the Hückel theory secular determinant for benzene.

17. **McQuarrie, 10-30.** Calculate the Hückel $\pi$-electron energies of cyclobutadiene. Compare the stability of cyclobutadiene with that of two isolated ethene molecules. Has cyclobutadiene square-like geometry?

18. **McQuarrie, 10-32.** Calculate the $\pi$-electron energy levels and the total $\pi$-electron energy of bicyclobutadiene.

19. **McQuarrie, 10-37.** Using Hückel molecular-orbital theory, determine whether the linear state $(H - H - H^+)$ or the triangular state of $H_3^+$ is the more stable state.