

Final Exam, Phys. Chem. I B (AY2022)

Periods 7-8, Friday, July 29, 2022: Total 40 points

Unauthorized reproduction, copying, or posting to the Internet is strictly prohibited.

Instructions:

- (1) Closed-book exam: use pencils, erasers, and a ruler only.
- (2) Work individually on the exam: testing YOUR knowledge. Cheating on the exam shall result in *failing grades* for all the specialized courses enrolled during the Semester (both the First and Second Terms). Such a violation leads to disciplinary action as stipulated in the Student Disciplinary Regulations.
- (3) Answer the questions in the space provided after the questions. If you need more space to elaborate on your answer, use the blank side of the sheet also. The language for your answers is either *English* or *Japanese*. Write in print, please. Ensure that you include your student ID number and full name at the given spaces.
- (4) Show all your process as you solve the problems. Correct but incomplete attempts will obtain partial points, whereas answers without showing your work will not receive points.

受験上の注意 :

- (1) 資料持込み不可。鉛筆と消しゴムと定規だけ使用する。(2) 個人で取り組む。あなたの知識をみるテストです。不正行為をおこなった者は、今期(第1・第2タームとも)履修しているすべての専門教育科目の評価が「不可」となり、学生懲戒指針に基づき懲戒処分を受けます。(3) 自分の解答は質問の後の与えられたスペースに書く。スペースが足りない場合は用紙の裏面も用いてよい。解答のための言語は「英語または日本語」とする。日本語は楷書で英語はブロック体で書く。自分の学生番号と名前を指定の場所に忘れず書く。(4) 解答プロセスも残す。途中まで正しい答案には部分点を与えるが、答えだけの場合は得点とならない。

Use \hbar to denote Planck's constant divided by 2π . Possibly useful integrals are:

$$\int_0^{\infty} \exp(-\beta x^2) dx = \frac{1}{2} \sqrt{\frac{\pi}{\beta}}; \quad \int_0^{\infty} x^{2n} \exp(-\beta x^2) dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1}} \sqrt{\frac{\pi}{\beta^{2n+1}}};$$
$$\int_0^{\infty} x^n \exp(-\beta x) dx = \frac{n!}{\beta^{n+1}} \quad (\beta > 0; n, \text{ positive integer})$$

where $\exp(x) = e^x$. You may also find it useful to recall that the volume element is expressed in spherical coordinates as $d\tau = r^2 \sin \theta dr d\theta d\phi$.

Problem 1: (19 points)

Read the sentences below and answer the questions that follow.

Hydrogenic (or hydrogen-like) atoms (atomic number Z) are the most important systems in physical chemistry. Their one-electron wavefunctions are called atomic orbitals and are given by the product of radial and angular parts:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi).$$

The atomic orbitals are specified by three quantum numbers, which are designated n , l , and m_l by convention.

Some lower-order functions are

$$R_{1,0} = 2 \left(\frac{Z}{a}\right)^{\frac{3}{2}} \exp\left(-\frac{Zr}{a}\right), \quad R_{2,0} = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a}\right)^{\frac{3}{2}} \left(2 - \frac{Zr}{a}\right) \exp\left(-\frac{Zr}{2a}\right),$$

$$R_{2,1} = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a}\right)^{\frac{3}{2}} \frac{Zr}{a} \exp\left(-\frac{Zr}{2a}\right),$$

$$Y_{0,0} = \left(\frac{1}{4\pi}\right)^{\frac{1}{2}}, \quad Y_{1,0} = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos \theta, \quad Y_{1,\pm 1} = \mp \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin \theta \exp(\pm i\phi),$$

$$Y_{2,0} = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} (3 \cos^2 \theta - 1), \quad Y_{2,\pm 1} = \mp \left(\frac{15}{8\pi}\right)^{\frac{1}{2}} \cos \theta \sin \theta \exp(\pm i\phi),$$

(double signs in same order)

where a is the Bohr radius. The orbitals are practically identified by the name, such as the 1s and $2p_z$ orbitals.

The name of subshells comes from the study of atomic spectra. The atomic spectra arise from the transitions between the orbital energy levels. The transition probability is proportional to the absolute square of the transition dipole moment, $|\mu_{fi}|^2$, with

$$\mu_{fi} = \int \psi_f^* \hat{\mu} \psi_i d\tau = -e \int \psi_f^* \mathbf{r} \psi_i d\tau.$$

If $\mu_{fi} = 0$, the transition is ; if $\mu_{fi} \neq 0$, the transition is .

Question 1) What are the quantum numbers that uniquely specify the radial wavefunction $R(r)$? Give the proper names, *not* symbols. (Write your answer only.)

Question 2) Write all the possible combinations of the set (n, l, m_l) representing the 3d orbitals.

Question 3) Calculate the mean radius of the 2s orbital $\langle r \rangle_{2s}$.

Question 4) How many radial and angular nodes does the $2p_z$ orbital have? For your non-zero answers, find the position of each node.

Question 5) At what radius does the radial distribution function of the 1s orbital have the maximum?

(questions continue on next page)

(continued)

Question 6 Fill in the blanks A and B with words that are antonyms of each other. (Write your answer only.)

(Note) antonym = 反意語, 反对語

(Problem set continues on next page)

Problem 2: (14 points)

Read the sentences below and answer the questions that follow.

The Hamiltonian of two-electron atoms with atomic number Z (such as He and Li^+) is expressed as

$$\hat{H} = \hat{h}(1) + \hat{h}(2) + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad (\text{P2.1})$$

where

$$\hat{h}(j) = -\frac{\hbar^2}{2m_e} \nabla_j^2 - \frac{Ze^2}{4\pi\epsilon_0 r_j} \quad (j = 1, 2) , \quad (\text{P2.2})$$

m_e is the mass of an electron, ∇_j^2 the Laplacian for the electron j , r_j the distance between the nucleus and electron j , and r_{12} the distance between the electrons. Since Eq. (P2.2) is a one-electron operator, the equation

$$\hat{h}(j)\psi(j) = E(j)\psi(j) \quad (\text{P2.3})$$

is equivalent to the Schrödinger equation of hydrogenic atoms, with the lowest energy given by

$$E(j) = Z^2 E_H \quad (\text{P2.4})$$

where $\psi(j)$ is the normalized wavefunction for the ground state, and E_H indicates the ground-state energy of the hydrogen atom. Unfortunately, no analytical expression can be obtained for the orbitals and energies of the two-electron atoms, and we are forced to make approximations.

Entire wavefunctions including the electron spin are called A, which are expressed as the product of spatial and spin parts. For example, an appropriate expression for the helium atom in its ground state is written as the following Slater determinant,

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi(1)\alpha(1) & \psi(2)\alpha(2) \\ \psi(1)\beta(1) & \psi(2)\beta(2) \end{vmatrix} \quad (\text{P2.5})$$

where the label of electrons is indicated in parentheses.

Question 1) Suppose that the ground-state energy of the two-electron atom is evaluated by perturbation theory: (i) What is the reasonable choice of the unperturbed Hamiltonian, $\hat{H}^{(0)}$? (ii) Express the unperturbed energy $E_Z^{(0)}$ with E_H .

Question 2) When we evaluate the effect of terms that are not included in $\hat{H}^{(0)}$ by a first-order perturbation, write the integral showing the first-order perturbation energy, $E_Z^{(1)}$. No need to calculate your integral.

(questions continue on next page)

(continued)

Question 3) How does the ground-state energy change when we include the perturbation energy? Explain the reason for the answer.

Question 4) Fill in the blank A with suitable technical word(s). (Write your answer only.)

Question 5) Prove that the Slater determinant of Eq. (P2.5) satisfies the Pauli principle.

(Problem set continues on next page)

Student ID _____ Name (print) _____

Problem 3: (7 points)

Answer the following questions.

Question 1) For hydrogenic atoms, the 2s and 2p orbitals have the same energy, while for many-electron atoms, the energy is lower for the 2s orbital. Explain the reason by looking at the radial distribution functions.

Question 2) Describe the Aufbau principle that plays an essential role in determining the ground-state electron configuration of atoms.

END OF QUESTIONS

Check your work before submission.