Final Exam, Phys. Chem. I B, 2nd Term of AY2021

Wednesday, August 4, 2021: Total score of 50 pts

Instructions:

(1) You are supposed to work individually on the exam: do not ask anyone else; do not cheat or cooperate among the students for the exam. 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.

(2) You should answer the questions on given paper sheets from the exam paper. The language for your answers is either *English* or *Japanese*. Ensure that you include your student ID number and full name at the beginning of each answer sheet.

(3) 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.

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

$$\int_0^\infty \exp(-\beta x^2)\,\mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{\beta}}; \quad \int_0^\infty x^{2n}\exp(-\beta x^2)\,\mathrm{d}x = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}}\sqrt{\frac{\pi}{\beta^{2n+1}}};$$

$$\int_0^\infty x^n \exp(-\beta x)\,\mathrm{d}x = \frac{n!}{\beta^{n+1}} \quad (\beta > 0; n, \text{positive integer})$$

You may also find it useful to recall that the volume element is expressed in spherical polar coordinates as $\mathrm{d}\tau = r^2 \sin\theta\, \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi$.

Problem 1: (5 pts)

Calculate the ratio of zero-point vibrational energies of $^{1}H^{35}Cl$ and $^{2}D^{35}Cl$, $E_0(HCl):E_0(DCl)$, assuming that the molecules are harmonic oscillators and that the force constants are the same. Here the superscript on the left of each element indicates the mass number. (You can use a calculator to obtain the value. Express the result to two significant figures（有効数字２桁）.)

Problem 2: (8 pts)

Describe the way to determine the bond length r of diatomic molecules from their microwave spectra assuming that the three-dimensional rigid rotor model is a good approximation. The energy of the rotor is expressed as

$$E_l = \frac{\hbar^2}{2I} l(l+1)$$

where l and I are the angular momentum quantum number and the moment of inertia of a diatomic molecule, respectively.

Problem 3: (18 pts)

The hydrogen atom (atomic number $Z = 1$) is the most informative example in quantum chemistry. When the Schrödinger equation is solved for the hydrogen atom, the wavefunctions obtained are called atomic orbitals and are expressed as the product of radial and angular parts:

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

Some lower-order functions are

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

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

$$Y_{0,0} = \left(\frac{1}{4\pi}\right)^{\frac{1}{2}}, \quad Y_{1,0} = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\theta, \quad Y_{1,\pm1} = \mp\left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta \exp(\pm i\phi),$$

$$Y_{2,0} = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} (3\cos^2\theta - 1), \quad Y_{2,\pm1} = \mp\left(\frac{15}{8\pi}\right)^{\frac{1}{2}} \cos\theta \sin\theta \exp(\pm i\phi),$$

where a is the Bohr radius. It turns out that three quantum numbers are necessary to specify each atomic orbital. The quantum numbers are, by convention, designated n, l, and m_l. The principal quantum number, n, determines the energy and size of the orbital. The orbitals with the same value of n are said to belong to the same *shell* of the atom. The mean radius of an electron from the nucleus increases with the value of n.

Question 1) Following the sentences about the principal quantum number, describe the physical significance of the other two quantum numbers.

Question 2) Justify the underlined portion by calculating the mean radius $\langle r \rangle$ of the 1s and 2s orbitals.

Question 3) How many radial and angular nodes are there for the $2p_z$ orbital? For your non-zero answers, find the position of each node.

Problem 4: (16 pts)

The Hamiltonian of a hydrogenic (or hydrogen-like) atom with atomic number Z is expressed as

$$\hat{h}(j) = -\frac{\hbar^2}{2m_e}\nabla_j^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_j} \quad (j, \text{ label of the electron})$$

where m_e is the mass of an electron, ∇_j^2 the Laplacian for the electron j, e the elementary charge, ε_0 the vacuum permittivity, and r_j the distance of the electron j from the nucleus. The normalized eigenfunction of the Hamiltonian corresponding to the ground state is given by

$$\psi(j) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \exp(-Zr_j/a_0)$$

with the energy eigenvalue of

$$E_1(Z;j) = -\frac{e^2}{8\pi\varepsilon_0 a_0}Z^2$$

where a_0 is the Bohr radius.

Question 1) What is the expression for the ground-state energy of the helium ion He^+?

Question 2) Write down the Hamiltonian of a two-electron atom with atomic number Z. Use r_{12} for the separation between the two electrons.

Question 3) If the ground-state energy of the two-electron atom is evaluated by perturbation theory, what is the reasonable choice of the unperturbed Hamiltonian, $\hat{H}^{(0)}$? Also, express the unperturbed energy $E_Z^{(0)}$ with $E_1(Z;j)$.

Question 4) Write out the integral indicating the first-order perturbation energy $E_Z^{(1)}$. No need to evaluate the integral.

Question 5) Taking the effect of the perturbation into account, does the ground-state energy of the two-electron atom increase or decrease from that for the unperturbed system? Explain the reason for the answer.

Problem 5: (3 pts)

The electron configuration of the chromium atom is: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$. Give a reasonable interpretation on the abnormality in the electron configuration.

END OF QUESTIONS

Check your work before submission.