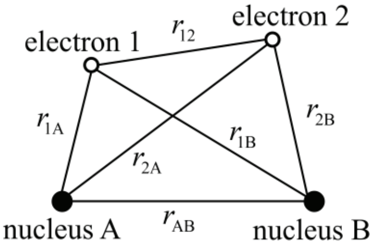
Physical Chemistry I

Answer the following questions on quantum chemistry of a hydrogen molecule.

I-a Choose the appropriate terms to fill in the blanks ①–⑧ from A–J in the following sentences. The following figure shows the coordinates of the hydrogen molecule.

A. mean field, B. atomic orbitals, C. atoms, D. nuclei–electrons,
E. molecular orbital, F. electrons, G. Born–Oppenheimer, H. nuclei,
I. Schrödinger, J. kinetic energy



The Hamiltonian $\hat{H}_{\mathrm{Total}}$ of a hydrogen molecule is written as

$$\hat{H}_{\mathrm{Total}} = \hat{T}_{\mathrm{n}} + \hat{T}_{\mathrm{e}} + \hat{V}_{\mathrm{nn}} + \hat{V}_{\mathrm{ne}} + \hat{V}_{\mathrm{ee}}$$

The ① operators for the nuclei and electrons are represented as

$$\hat{T}_{\mathrm{n}} = -\frac{\hbar^2}{2M}\left(\Delta_{\mathrm{A}} + \Delta_{\mathrm{B}}\right) \text{ and } \hat{T}_{\mathrm{e}} = -\frac{\hbar^2}{2m}\left(\Delta_1 + \Delta_2\right),$$

respectively. M and m are the masses of the nucleus and electron, respectively. Δ_1 is the differential operator (Laplacian) with respect to the spatial coordinates of electron 1. The other terms in the Hamiltonian are

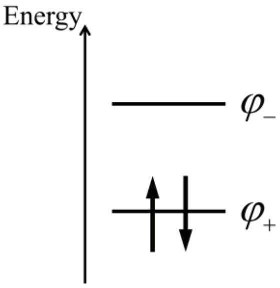
$$\hat{V}_{\mathrm{nn}} = \frac{e^2}{4\pi\varepsilon_0 r_{\mathrm{AB}}},\ \hat{V}_{\mathrm{ne}} = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{1\mathrm{A}}} + \frac{1}{r_{1\mathrm{B}}} + \frac{1}{r_{2\mathrm{A}}} + \frac{1}{r_{2\mathrm{B}}}\right),\ \hat{V}_{\mathrm{ee}} = \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

where e is the elementary charge, $\hbar = h/2\pi$ is the reduced Planck constant, h is the Planck constant, ε_0 is the permittivity of vacuum. $\hat{V}_{\mathrm{nn}}$ represents the interaction between ②. $\hat{V}_{\mathrm{ne}}$ shows the interaction between ③. $\hat{V}_{\mathrm{ee}}$ is the interaction between ④. We assume that electronic wavefunction Ψ does not depend on the velocities of the nuclei. Under this ⑤ approximation, the ⑥ equation is expressed as follows, using the Hamiltonian $\hat{H} = \hat{T}_{\mathrm{e}} + \hat{V}_{\mathrm{nn}} + \hat{V}_{\mathrm{ne}} + \hat{V}_{\mathrm{ee}}$ without $\hat{T}_{\mathrm{n}}$:

$$\hat{H}\Psi = E\Psi$$

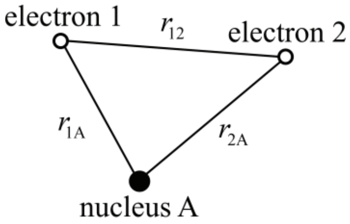
where E is the energy of the hydrogen molecule. The ⑥ equation can be approximately solved by representing individual molecular orbitals as a linear combination of ⑦, *i.e.*, by the ⑧ method.

I-b Using the 1s atomic orbitals of a hydrogen atom, a ground state calculation of the hydrogen molecule was performed with the ⑧ method, yielding two molecular orbitals (φ_+ and φ_-). The ground-state electronic configuration, considering electron spins, is shown in the right figure. Illustrate all other possible configurations based on the Pauli exclusion principle.



We will calculate the ground-state energies of a multi-electron atom and a diatomic molecule. The computational method used in Question I-b cannot accurately calculate the energy (E_{limit}) of a hydrogen molecule in the dissociation limit where the molecule separates into two hydrogen atoms. When using the normalized atomic orbital $a(1) = \sqrt{\sigma^3/\pi}\exp(-\sigma r_{1\text{A}})$ (where σ is a parameter and $r_{1\text{A}}$ is the distance between nucleus A and electron 1), the calculated E_{limit} becomes the average of the energies of the ionic (H^+ + H^-) and non-ionic (H + H) hydrogen molecules in the dissociation limit. On the other hand, the exact E_{limit} is the sum of the energies of the two non-ionic hydrogen atoms (H). Answer the following questions.

I-c Write down the Hamiltonian $\hat{H}$ for the hydrogen anion, H^-, under the $\boxed{⑤}$ approximation from Question I-a. The figure on the right shows the coordinates of H^-. Refer to $\hat{H}$ given in Question I-a.



I-d We will calculate the energy of H^-, E_{hydride}, using atomic orbital *a* and $\hat{H}$ obtained in I-c. Assuming that the normalized electronic wavefunction of H^- is $\Psi = a(1)a(2)$, E_{hydride} is expressed by Equation 1:

$$E_{\text{hydride}} = \iint \Psi \hat{H} \Psi dv_1 dv_2 = \iint a(1)a(2)\hat{H}a(1)a(2)dv_1 dv_2 \quad \text{(Equation 1)}$$

Using the results of the full-space integrals below, $E_{\text{hydride}} = \sigma^2 - 11\sigma/8$ (Equation 2) can be obtained in the atomic unit. Show the calculation process from Equation 1 to Equation 2. In the atomic units, for $\hat{H}$, $m = 1$; $e = 1$; $\hbar = 1$; $1/4\pi\varepsilon_0 = 1$.

$$\iint a(1)a(2)\left(-\frac{1}{2}\Delta_1\right)a(1)a(2)dv_1 dv_2 = \frac{\sigma^2}{2}, \ -\iint a(1)a(2)\frac{1}{r_{1\text{A}}}a(1)a(2)dv_1 dv_2 = -\sigma,$$

$$\iint a(1)a(2)\frac{1}{r_{12}}a(1)a(2)dv_1 dv_2 = \frac{5\sigma}{8}$$

I-e Calculate the energy of the ionic hydrogen molecule in the dissociation limit (H^+ + H^-) assuming the parameter σ for the atomic orbital *a* is 1. The atomic unit of energy is Hartree. The energy of hydrogen cation H^+ is 0.0000 Hartree. Furthermore, assuming the energy of the hydrogen atom H is −0.5000 Hartree, show the error of the calculated E_{limit} relative to the exact E_{limit}. Show the calculation results with two decimal places.

I-f Determine the parameter σ for the atomic orbital *a* and calculate the energy of H^- based on the variational principle. Show the calculation results with two decimal places.

(The end)

Physical Chemistry II

The following text describes the electronic spectra of polyatomic molecules in solution:

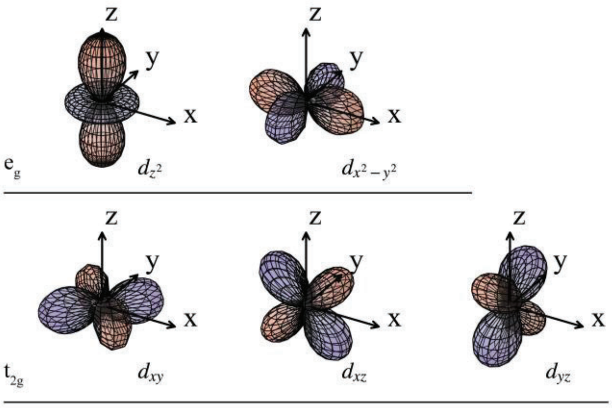
II-a Fill in the blanks ①–⑧ using the following terms in the box:

> Internal conversion, mirror image relation, spin–orbit interaction, vibrational, Stokes shift, intersystem crossing, Stark effect, Zeeman splitting, fluorescence, phosphorescence, solvation

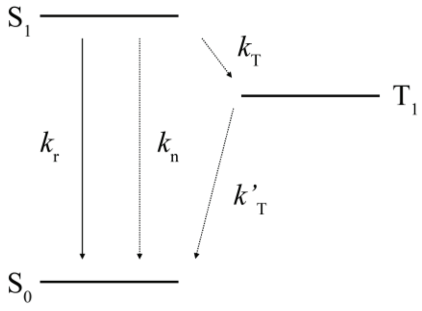
"In solution, singlet polyatomic molecules often show multiple peaks in their absorption spectra upon electronic transitions. This is due to the ① excitation that occurs simultaneously with the electronic transitions, and the resulting structure is called a ① structure. The excited molecule undergoes various relaxation processes to reach the most stable excited singlet state, and eventually returns to the ground state by emitting ②. When comparing the absorption and ② spectra, a shift in the peak wavelength is observed, which is known as the ③ and results from energy dissipation caused by ④. Furthermore, the absorption and ② spectra are often in a ⑤ with each other, particularly in small molecules with little structural change. Additionally, the excited molecule may undergo non-radiative transition to a triplet state and then emit ⑥ when returning to the ground state. A transition between states with different spin multiplicities is called ⑦ and can occur in the presence of ⑧."

II-b Explain the Laporte selection rule known for electronic transitions in centrosymmetric systems. Also, indicate which of the following transitions is allowed, assuming the parity of electronic states is given as g: even, u: odd:
(i) g → g (ii) g → u (iii) u → g

II-c As shown in the figure on the right, in octahedral d-metal complexes such as $[Ti(OH_2)_6]^{3+}$, the five d orbitals split into two sets, e_g and t_{2g}. Illustrate this splitting using the ligand field splitting parameter Δ_o.



II-d For d–d transitions in transition metal complexes, which geometry—tetrahedral or octahedral—exhibits stronger transition intensities? Explain the reason.



Chlorophyll (Chl) molecules play essential roles in photosynthesis such as light absorption and energy transfer. Chl can be extracted by soaking leaves in ethanol. Its measured emission lifetime is $\tau_0 = 1.0$ ns ($= 1.0 \times 10^{-9}$ s). After excitation, the relevant processes involve the following rate constants: emission from the singlet state (k_r), non-radiative relaxation (k_n), transition to the triplet state (k_T), and non-radiative relaxation from the triplet state (k'_T). Give your answers with two significant digits.

II-e Assume steady-state light excitation. When the number of absorbed photons is $I_{abs} = 3.0\times10^{17}$ photons·m^{-2}·s^{-1} and the number of emitted photons is $v = 6.0\times10^{16}$ photons·m^{-2}·s^{-1}, calculate the emission quantum yieldφ_0.

II-f Express the generation and decay rate of [Chl*] (the excited singlet-state concentration of chlorophyll) using the I_{abs} and the above rate constants.

II-g Using the steady-state approximation and the relationships $1/\tau_0 = (k_r + k_n + k_T)$ and $v = k_r$ [Chl*], estimate k_r.

II-h Chlorophyll extracted in ethanol exhibits emission, while leaves show almost no emission under illumination. This is because light energy absorbed by Chl is quenched by protein complexes called reaction centers (RC), which perform photoelectric conversion. This quenching reaction can be simply expressed as:

$$\text{Chl* + RC} \rightarrow \text{Chl + RC*}$$

If the rate constant of this reaction is $k_{RC} = 1.0\times10^{11}$ L mol^{-1} s^{-1}, estimate the RC concentration required to reduce the emission quantum yield to 0.01. You may use φ_0 in the absence of RC.

II-i In actual leaves, emission is barely observed even though the RC concentration is relatively low. This is because excitation energy transfer occurs sequentially from one Chl to another (here denoted Chl*b* and Chl*a*), efficiently concentrating energy at the reaction center:

$$\text{Chl}b\text{* + Chl}a \rightarrow \text{Chl}b\text{ + Chl}a\text{*}$$

The efficiency of this energy transfer (ET) is given by the inter-molecular distance r and the Förster radius R_0:

$$E_T = \frac{R_0^6}{R_0^6 + r^6}$$

Calculate the energy transfer efficiency when $R_0 = 6.0$ nm and $r = 3.0$ nm.

(End)