Physical Chemistry I

Fill in the blanks $\boxed{1}$ to $\boxed{20}$ with appropriate words, numbers, or equations, and answer the following questions.

I − a

Consider describing the molecular orbital of the dihydrogen cation H_2^+ with the 1s atomic orbital of the hydrogen atom. The two hydrogen nuclei are denoted as A and B, and the wave functions of their 1s atomic orbitals are described by φ_A and φ_B, respectively. The wave function of the molecular orbital ψ is then described as a linear combination of φ_A and φ_B as

$$\psi = c_A \varphi_A + c_B \varphi_B$$

In the following we assume that the orbitals are all real functions, and use the following notations for the integrals

$$<\varphi_A \mid \varphi_B> = <\varphi_B \mid \varphi_A> = S$$

$$<\varphi_A \mid H \mid \varphi_A> = <\varphi_B \mid H \mid \varphi_B> = h_{AA}$$

and

$$<\varphi_A \mid H \mid \varphi_B> = <\varphi_B \mid H \mid \varphi_A> = h_{AB}\ .$$

Here H is the electronic Hamiltonian of the system (not including the nucleus-nucleus interaction), and the integrals S, h_{AA}, and h_{AB} are called $\boxed{1}$, $\boxed{2}$, and $\boxed{3}$, respectively. Using these notations, the electronic energy of the system, $E = <\psi \mid H \mid \psi>$, becomes $\boxed{4}$, and the $\boxed{5}$ condition, $<\psi \mid \psi> = 1$, is rewritten as $\boxed{6}$.

Next, since A and B are equivalent in the dihydrogen cation, c_A and c_B have the relations $\boxed{7}$ and $\boxed{8}$ for the bonding and antibonding orbitals, respectively. Using these relations, the wave functions of the bonding and antibonding orbitals, ψ_+ and ψ_-, become

$$\psi_+ = \boxed{9}$$

and

$$\psi_- = \boxed{10}\ ,$$

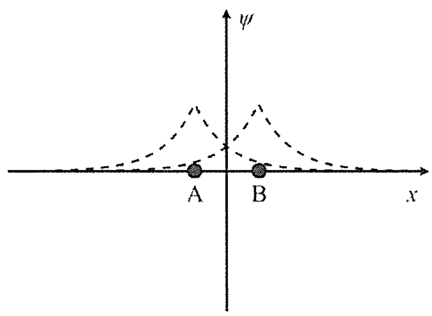
and the corresponding (orbital) energies E_+ and E_- are

$$E_+ = \boxed{11}$$

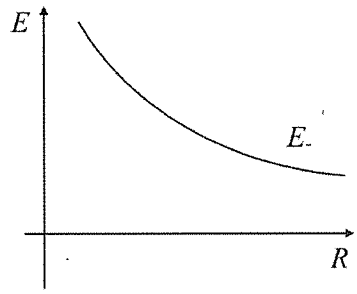
and

$$E_- = \boxed{12}\ .$$

(1) Draw the approximate bonding and antibonding orbitals of the dihydrogen cation H_2^+ along the x axis which connects the two nuclei (see figure on right). Here we assume that the hydrogen nuclei are at the equilibrium distance, and the 1s atomic orbitals of the hydrogen atoms are given in the right figure as dashed lines.



(2) The orbital energy of the antibonding orbital, E_-, can be described as a curve shown in the right figure. Here, R is the distance between the hydrogen nuclei. Draw a rough sketch of the energy curve for the bonding orbital, E_+.
(Copy the figure to your answer sheet and add the curve for E_+).



I − b

Next we use the results of the dihydrogen cation H_2^+ to estimate the energy of the hydrogen molecule H_2. For simplicity, here we ignore the electron-electron interaction, thus assume that the molecular orbitals and the orbital energies do not change. By denoting the bonding and antibonding orbitals as σ and σ*, respectively, and using the Pauli exclusion principle, the electron configuration of the hydrogen molecule in the ground state is described as $(\sigma)^{\boxed{13}}(\sigma^*)^{\boxed{14}}$, and the total electronic energy is given by $\boxed{15}$ using h_{AA}, h_{AB}, and S. Since the total electron energy is given by $2h_{AA}$ when the electrons are localized to each hydrogen atom, the delocalization energy will be given as $\boxed{16}$. In the singly excited electronic state of the hydrogen molecule, the electron configuration is $(\sigma)^{\boxed{17}}(\sigma^*)^{\boxed{18}}$ and the total electronic energy is given by $\boxed{19}$. Thus the excitation energy can be estimated to be $\boxed{20}$.

(1) Describe the Pauli exclusion principle.

(2) If we consider the electron spins, the total electronic wave function of the hydrogen, $\psi(1,2)$, can be described as a product of the bonding orbital wave function ψ_+ and the spin function as

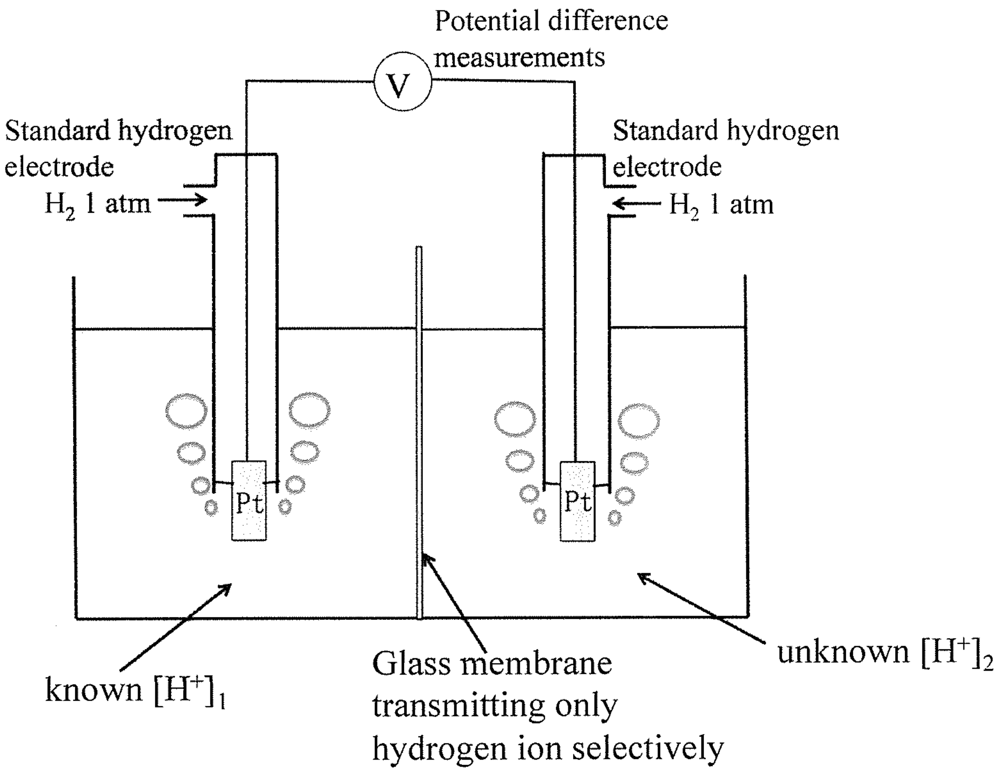
$$\psi(1,2) = \psi_+(1)\,\psi_+(2)\ \boxed{\quad A \quad}$$

Here 1 and 2 denote the electrons. Fill in $\boxed{A}$ with the spin term to complete the wave function. Use $\alpha(i)$ and $\beta(i)$ ($i = 1, 2$) for the spin functions of the electrons.

(3) In realistic hydrogen molecules, electron repulsion plays an important role. The strength of this repulsion is inversely proportional to the distance between the electrons. Using this fact, discuss how the total electronic energy and the electronic wave function change when the electron repulsion is taken into account.

Physical Chemistry II

Figure below shows a cell combining two standard hydrogen electrodes. A standard hydrogen electrode has a Pt plate that is immersed in the aqueous solution of the hydrogen ion of the concentration $[H^+]$ and is bubbled by hydrogen gas of 1 atm. The potential (E) of a standard hydrogen electrode is expressed by equation (1). Two electrodes are separated by a glass membrane transmitting only hydrogen ion selectively. Here, the solutions of left and right sides contain the hydrogen ion concentrations of known $[H^+]_1$ and unknown $[H^+]_2$, respectively. This cell acts as a pH sensor.



$$E = E_0 + \frac{RT}{F} \ln \left(\frac{[H^+]}{[P_{H_2}]^{1/2}} \right) \quad \text{(equation 1)}$$

Here, $[H^+]$ is the concentration of hydrogen ions which can be regarded as the activity of hydrogen ions, $[P_{H_2}]$ is the activity of standard hydrogen electrode, R is the gas constant (8.31 $JK^{-1}mol^{-1}$), T is the absolute temperature, and E_0 is the standard redox potential.

Answer the following questions. Numerical answers should have two significant figures. Use Avogadro's number N_A (6.02×10^{23} mol^{-1}) and the elementary electric charge e (1.60×10^{-19} C) if necessary.

II－a

Write the electrode reaction occurring at the standard hydrogen electrode.

II−b

Answer the name of equation (1).

II−c

Answer the name of constant F.

II−d

Write equation expressing F. Derive the value of constant F.

II−e

Standard hydrogen electrode immersed in the H^+ solution of the known concentration of $[H^+]_1$ shows an electrode potential of E_1, while standard hydrogen electrode immersed in the H^+ solution of the unknown concentration of $[H^+]_2$ shows an electrode potential of E_2. Formation of the concentration cell between left and right sides of the glass membrane induces the membrane potential $E_g = E_1 - E_2$. Express E_g by using $[H^+]_1$, $[H^+]_2$, R, T, and F.

II−f

Define pH using the concentration of hydrogen ions $[H^+]$.

II−g

Estimate the change of E_g in the mV unit when pH of the unknown solution is increased by 1 at room temperature (300 K). Use $\ln 10 = 2.30$ if necessary.