NAME: AZERBAIJAN
Score /20
[Numbers without decimal points are to be considered infinitely precise. Show reasonable significant figures and proper units. In particular, use generally accepted units for various quantities. Do not write on back.]

1. (10 points) For the following questions, fill in the blanks with a proper word or phrase.

The Maxwell-Boltzmann distribution function appropriately applies only to ideal (noniteracting) gases.

At any temperature, the root-mean-square speed of a gas obeying the Maxwell-Boltzmann distribution law is the largest of the three named speeds.

In a gaseous mixture of argon and krypton, which kind of molecule has more kinetic energy per molecule at $25^{\circ} \mathrm{C}$, on average, assuming both argon and krypton obey the Maxwell-Boltzmann distribution?
They are the same.

The relations for the simple kinetic theory of the viscosity of a gas assumes that the gases are in laminar flow.

The accepted unit of viscosity coefficient is the poise, even though it is a non-SI unit.
2. (4 points) A solution of sucrose in water is held at $20^{\circ} \mathrm{C}$ in a narrow capillary, so that the sucrose molecules are constrained to move in one dimension only. How far will the average sucrose molecule move in 5.67 seconds? (That is, what is the root-mean-square distance for that time?)
For one-dimensional diffusion,

$$
<x^{2}>=2 D t
$$

Hence, for sucrose (with the diffusion coefficient taken from Table 9.1 of the handbook:

$$
\Delta x=\sqrt{\left\langle x^{2}\right\rangle}=\sqrt{2 D t}=\sqrt{2\left(0.46 \times 10^{-9} \mathrm{~m}^{2} \mathrm{~s}^{-1}\right)(5.67 \mathrm{~s})}=7.2 \times 10^{-5} \mathrm{~m}
$$

Note the number of acceptable significant figures.
3. ( 6 points) Calculate the sedimentation coefficient of hemoglobin (molar mass of $68 \mathbf{~ k g ~ m o l}^{-1}$ ) at $\mathbf{2 0 ^ { \circ }}{ }^{\circ} \mathrm{C}$ in water.

From the equation on page 9-6 of the handbook

$$
s=\frac{M D\left(1-V \rho_{0}\right)}{R T}
$$

On page 9-7 of the handbook, most of the necessary information is found in Table 9.6. The density of pure water at $20^{\circ} \mathrm{C}$ is found on Table 7.9 on page $7-7$ of the handbook. Substitution gives

$$
\begin{aligned}
& s=\frac{\left(68 \mathrm{~kg} \mathrm{~mol}^{-1}\right)\left(6.9 \times 10^{-11} \mathrm{~m}^{2} \mathrm{~s}^{-1}\right)\left(1-\left(0.749 \times 10^{-6} \mathrm{~m}^{3} \mathrm{~g}^{-1}\right)\left(998263 \mathrm{~g} \mathrm{~m}^{3}\right)\right)}{\left(8.3144349 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)(293.15 \mathrm{~K})} \\
&=\frac{\left(469.2 \times 10^{-11} \mathrm{~kg} \mathrm{~m}^{2} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}\right)(1-0.7477)}{2437.38 \mathrm{~kg} \mathrm{~m}^{2} \mathrm{~s}^{2} \mathrm{~mol}^{-1}}=4.857 \times 10^{-13} \mathrm{~s}=4.9 \mathrm{sV}
\end{aligned}
$$

Note that, since two of the input values were given only to two significant digits, the result is given only to two decimal places. (Answers from 4.85 sV to 4.95 sV should be considered correct.) The correct unit for sedimentation coefficient is the svedberg, not the second.

NAME: $\qquad$
BHUTAN
Score $\qquad$ /20
[Numbers without decimal points are to be considered infinitely precise. Show reasonable significant figures and proper units. In particular, use generally accepted units for various quantities.]

1. (8 points) For certain unusual reactions, the rate law is of zero order in the reactant, $A$, at least under some conditions. (a) Write an equation for the velocity, $v$, of such a reaction, assuming the rate constant is $k_{0}$.

$$
v=k_{0} C_{A}^{0}=k_{0}
$$

(b) Derive an equation for the time dependence of the reactant concentration, $C_{A}(t)$, assuming that the concentration at time $t=0$ is $C_{A}(0)$. [Note: the result of (b) cannot be correct if the result of (a) is incorrect.] (Show all mathematical work correctly.)

From the expression in (a), one may obtain the equation $v=-\frac{d C_{A}}{d t}=k_{0}$. Integration of this equation gives $\int_{C_{A(0)}}^{C_{A}(t)} d C_{A}=-k_{0} \int_{0}^{t} d t$. Carrying out the integral gives the equation we seek.

$$
C_{A}(t)=C_{A}(0)-k_{0} t
$$

2. (4 points) From data in the handbook, calculate the rate constant for the formation of hydrogen chloride by the gas-phase attack of chlorine atoms on dihydrogen at a temperature of $-33.97^{\circ} \mathrm{C}$, the temperature at which chlorine gas liquefies.

The information needed to answer this straightforward calculational question is found on Table 10.2 of the handbook. Using the information there and the Arrhenius equation gives

$$
\begin{aligned}
k(T) & =A \exp \left(-\frac{E_{a}}{R T}\right)=\left(8 \times 10^{13} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}\right) \exp \left(-\frac{23000 \mathrm{~J} \mathrm{~mol}^{-1}}{\left(8.3144349 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}\right)(239.18 \mathrm{~K})}\right) \\
& =7.5891 \times 10^{8} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}
\end{aligned}
$$

Note that it is assumed that $A$ and $E_{a}$ are infinitely accurate, since they are not given with a decimal point.
3. (8 points) The constant-volume decomposition of cyclobutane at $438^{\circ} \mathrm{C}$ by the reaction $\mathrm{C}_{4} \mathrm{H}_{8}(\mathrm{~g}) \rightarrow$ $2 C_{2} H_{4}(g)$ has a rate constant, $k\left(438{ }^{\circ} C\right)=2.48 \times 10^{-4} s^{-1}$. (For purposes of this question, you may assume that each component may be treated as an ideal gas.)
(a) What is the order of this reaction with respect to cyclobutane? $\qquad$
(b) In one sentence, explain how you concluded the order was what you stated in part (a).

There are two ways to know the order: (1) from the units of the rate constant, and (2) from the observation that this is essentially a decomposition. Either way to explain this is correct.
(c) If the initial pressure of cyclobutane in the containment vessel was exactly 1 bar, how long would it take for exactly half of the cyclobutane to be transformed into ethene?
$2.79 \times 10^{3} \mathrm{~s}$
(This is the half-life of this reaction.)
(d) At the point at which half of the cyclobutane has been converted to ethene, what is the total pressure in the vessel?
For every cyclobutane molecule lost, one gains two molecules of ethane. At a constant volume there is 0.5 bar of cyclobutane in the volume at this point, but 1 bar ( 0.5 bar x 2 ) of ethane. Hence, the total pressure when exactly half of the cyclobutane is reacted is $\mathbf{1 . 5} \mathbf{~ b a r}$.

NAME: DJIBOUTI
Score /20
[Numbers without decimal points are to be considered infinitely precise. Show reasonable significant figures and proper units. In particular, use generally accepted units for various quantities.]

1. (10 points) The chlorination of vinyl chloride, $C_{2} H_{3} C l+C l_{2} \quad \rightarrow \quad C_{2} H_{3} C l_{3}$ is believed to proceed by the following mechanism:

$$
\begin{gathered}
\mathrm{Cl}_{2} \xrightarrow{k_{1}} 2 \mathrm{Cl} \cdot \\
\mathrm{Cl} \cdot+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{Cl} \xrightarrow{k_{2}} \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{Cl}_{2} \\
{ }_{2} \mathrm{H}_{3} \mathrm{Cl}_{2} \cdot+\mathrm{Cl}_{2} \xrightarrow{k_{3}} \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{Cl}_{3}+\mathrm{Cl} \cdot \\
2 \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{Cl}_{2} \cdot \xrightarrow{k_{4}} \text { stable species }
\end{gathered}
$$

Derive the rate expression for the production of trichloroethane at steady state predicted by the mechanism.
The product is only created in step 3, so the rate of reaction is the rate of step 3: v= $=v_{3}$
To solve for this, however, one must use the steady-state approximation on intermediates. There are two intermediates, $\mathrm{Cl} \cdot$ and $C_{2} H_{3} C l_{2} \cdot$ (which in equations I write as $R \cdot$ ), which are assumed to be at steady state:

$$
\frac{d[C l \cdot]}{d t}=0 \text { and } \frac{d[R \cdot]}{d t}=0
$$

From the mechanism, these can be expressed in terms of the rates of the steps:

$$
\frac{d[c l \cdot]}{d t}=2 v_{1}-v_{2}+v_{3}=0 \text { and } \frac{d[R \cdot]}{d t}=v_{2}-v_{3}-2 v_{4}
$$

Adding these two equations together gives the result: $v_{1}=v_{4}$, which - by substitution of the expressions for these in terms of concentrations - gives the following result: $[R \cdot]=\sqrt{\frac{k_{1}}{k_{4}}}\left[C l_{2}\right]^{1 / 2}$.
Substitution of this value into the equation for the overall product creation gives the rate expression we seek:

$$
v=v_{3}=k_{3}[R \cdot]\left[C l_{2}\right]=k_{3} \sqrt{\frac{k_{1}}{k_{4}}}\left[C l_{2}\right]^{3 / 2}
$$

2. (10 points) Fill in the blank with the correct word or phrase to complete the statement.
i. Enzymes are protein molecules that serve as a catalyst in a wide variety of chemical reactions.
ii. Adsorption accompanied by dissociation of the adsorbate is a process referred to as chemisorption.
iii. Lindemann's mechanism provides an elegant example of the relationship between kinetics and reaction mechanisms for unimolecular reactions.
iv. Molecules that occupy the enzyme's active site are known as competitive inhibitors.
v. The Belousov-Zhabotinsky reaction is a classic example of an oscillating reaction.

NAME:
ERITREA
Score /20
[Numbers without decimal points are to be considered infinitely precise. Show reasonable significant figures and proper units. In particular, use generally accepted units for various quantities.]

1. (6 points) Consider the hydrogen atom which consists of a proton and an electron. Write down the classical Hamiltonian function for the hydrogen atom. [For this problem, the proton (of mass $M_{p}$ ) should be considered to be at a point $R_{p}$ (with co-ordinates relative to a cartesian system of $X_{p}, Y_{p}, Z_{p}$ ), and the electron position (of mass $m_{e}$ ) relative to the same co-ordinate system is at point $r_{e}$ (with co-ordinates $X_{e}$, $y_{e}, z_{e}$ ). The charge (in SI units) is e, and the charge on the electron is -e.]

One must find the contributions to the kinetic energy and the potential energy. Both the electron and proton are moving in this space, but the only potential energy is the Coulombic interaction between the two particles. Thus, the Hamiltonian function is

$$
H=T+V=T_{p}+T_{e}+V=\frac{P_{p}^{2}}{2 M_{p}}+\frac{p_{e}^{2}}{2 m_{e}}-\frac{e^{2}}{4 \pi \epsilon_{0}} \frac{1}{\left|\boldsymbol{R}_{\boldsymbol{p}}-\boldsymbol{r}_{e}\right|}
$$

2. (8 points) For the operators, determine the action on the operand: (Symbols other than $x$ and $\theta$ are to be considered constants.) In the last column, indicate whether the function is an eigenfuction of the operator.

| Operator | Operand | Result | Eigenfunction? |
| :---: | :---: | :---: | :---: |
| $\frac{d}{d x}$ | $A \exp (i Q x)$ | $i Q(A \exp (i Q x))$ | $\boxed{\text { Yes }} \square$ No |
| $\left(K+\frac{d}{d \theta}\right)$ | $A \exp \left(-\theta^{2} / 2\right)$ | $(K-\theta) A \exp \left(-\theta^{2} / 2\right)$ | $\square$ Yes $⿴$ No |

3. (6 points) For each statement below, fill in the appropriate word(s) to complete the sentence.
i. The equation $\exp (i \theta)=\cos (\theta)+i \sin (\theta)$ is known as Euler's relation.
ii. A plot of the kinetic energy of ejected electrons versus the frequency of light in an experiment to interrogate the photoelectric effect gives a method to determine Planck's constant.
iii. The term photon is generally used to describe the spatially localized packet of light.
iv. The two key properties that distinguish quantum physics from classical physics are quantization and wave-particle duality.
v. In the double-slit experiment, the alternation of maxima and minima is an indication of interference.
vi. The quantum theory is derived from the Hamiltonian description of classical mechanics.

NAME：
FIJI
Score 120
［Numbers without decimal points are to be considered infinitely precise．Show reasonable significant figures and proper units．In particular，use generally accepted units for various quantities．］

1．（ 6 points）Write out the simplest form of the commutator of each set of operators indicated．（Assume that $x$ and $y$ are independent variables．）

| Commutator | Simplest equivalent form |
| :---: | :---: |
| $\left[\frac{d}{d x}, x\right]$ | $\left[\frac{d}{d x}, x\right]=+1$ |
| $\left[\frac{\partial}{\partial x}, y\right]$ | $\left[\frac{\partial}{\partial x}, y\right]=0$ |
| $\left[y \frac{\partial}{\partial x}, x \frac{\partial}{\partial y}\right]$ | $\left[y \frac{\partial}{\partial x}, x \frac{\partial}{\partial y}\right]=y \frac{\partial}{\partial y}-x \frac{\partial}{\partial x}$ |

## 2．（9 points）Calculate the zero－point energy of an electron in a 1－D box that is 1 Angstrom unit long．

The formula for the energy for a particle in a one－dimensional box is found in the handbook on page 11－2．The value depends on the mass，the size of the box，and the quantum number．The zero－point energy is the energy of the lowest state，hence it is for $n=1$ ．So，the zero－point energy is given by the formula

$$
Z P E=E_{1}=\frac{h^{2}}{8 m a^{2}}=\frac{\left(6.6260693 \times 10^{-34} \mathrm{~J} \mathrm{~s}\right)^{2}}{8\left(9.1093826 \times 10^{-31} \mathrm{~kg}\right)\left(1 \times 10^{-10} \mathrm{~m}\right)^{2}}=6.0246666 \times 10^{-18} \mathrm{~J}
$$

3．（5 points）The following statements about quantum mechanics are all true．However，not all of these are postulates of quantum mechanics．Put a check in the YES box for each one that is a postulate of quantum mechanics．Put a check in the NO box if the statement is not one of the five postulates．

| Statement | Is it a postulate？ |  |
| :---: | :---: | :---: |
| For every observable of a system such as position，there exists a corresponding operator． | 区 YES | $\square$ NO |
| A wave function must be normalized for it to have meaning as the condition of a quantum system． | $\square \mathrm{YES}$ | 区 NO |
| The state of a quantum mechanical system is completely specified by a wave function． | 区 YES | $\square$ NO |
| A quantum mechanical system must always be in an eigenstate of the Hamiltonian operator． | $\square \mathrm{YES}$ | 区 NO |
| In any single measurement of an observable corresponding to an operator，the only values that will ever be measured are the eigenvalues of that operator． | 区 YES | $\square$ NO |

1．（6 points）The hydrogen atom＇s electronic energy levels can be explicitly determined through quantum mechanical methods，without any major approximation．Determine，as accurately as possible，the energy of the transition of lowest energy of the Lyman series（in $\mathrm{cm}^{-1}$ ）．

The energies of the electronic levels of a hydrogen－like atom are given by this formula from the handbook：
$E_{n}=-\frac{Z^{2} E_{h}}{2} \frac{1}{n^{2}}$ ，where $Z$ is the atomic number，$E_{h}$ is the Hartree energy，and $n$ is the principal quantum number of the state．The Lyman series involves transitions to（emission）or from（absorption）the state with $n=1$ ，and for hydrogen $Z=1$ ．． The quantum number of the other state increases in energy as $n$ is increased，so the lowest－energy transition involves states with $n=1$ and $n=2$ ．Therefore，the energy we seek is
$\Delta E=E_{2}-E_{1}=\left(-\frac{1^{2} E_{h}}{2} \frac{1}{2^{2}}\right)-\left(-\frac{1^{2} E_{h}}{2} \frac{1}{1^{2}}\right)=\frac{3 E_{h}}{8}=\left(\frac{3}{8}\right)\left(4.359744417 \times 10^{-18} \mathrm{~J}\right)=1.63490416 \times 10^{-18} \mathrm{~J}$
where the value of the Hartree energy was found from Table 1．3．But the problem requires that value must be in $\mathrm{cm}^{-1}$ ，not joules．Table 3.5 of the handbook has the needed information because it gives the Hartree energy in $\mathrm{cm}^{-1}$ ．

$$
\Delta E=\frac{3 E_{h}}{8}=\left(\frac{3}{8}\right)\left(219474.63 \mathrm{~cm}^{-1}\right)=8.2302986 \times 10^{4} \mathrm{~cm}^{-1}
$$

given to the accuracy allowed by the known precision of $E_{h}$ ．Other equivalent ways to obtain this energy include use of Rydberg＇s formula，with the precision of the value of Rydberg＇s constant determining the accuracy of the calculation． （Spectroscopic methods determine energies and fundamental constants with very high precision．）

2．（ 10 points）In the following table，put the letter of the phrase in Column B that most appropriately is connected to the word or phrase in Column A．

| Column A | Column B |
| :--- | :--- |
| ＿h＿Dipole approximation | a．Realistic anharmonic potential |
| ＿d＿Incoherent photon source | b．Random event related to the lifetime of the state |
| ＿c＿P branch | c．Lower－frequency part of an infrared spectrum |
| ＿g＿Raman spectroscopy | d．Light bulb |
| ＿b＿Spontaneous emission | e．Laser |
|  | f． Defined with respect to the lowest occupied level |
|  | g．Based on scattering of a photon |
|  | h． Assuming the electric field lies along an axis of a molecule |

3．（4 points）Indicate，for each diatomic molecule below whether it is predicted to show an infrared spectrum by checking the appropriate box．

| $\mathrm{H}_{2} \quad$ YYES | 区 No | $\mathrm{D}_{2} \quad$ प YES | 凶 No |
| :---: | :---: | :---: | :---: |
| HD ®yes | $\square$ No | CO 区 yes | $\square$ No |

Homonuclear diatomics like $\mathrm{H}_{2}$ and $\mathrm{D}_{2}$ have no permanent dipole moments．CO has a rather large permanent dipole moment．HD has a very weak dipole moment caused by the displacement of the center of mass from the exact center of the H－D bond．

NAME：
INDONESIA
Score $\qquad$ ／20

1．（7 points）For each of the following，indicate whether the function is an acceptable wave function for the helium atom．If it is acceptable，indicate the term symbol for which the wave function is appropriate．

| Wave Function | Is it acceptable？ | Term Symbol |
| :---: | :---: | :---: |
| $\psi_{1 s}(1) \psi_{2 s}(2) \alpha(1) \alpha(2)$ | $\square$ Yes 区 No |  |
| $\psi_{1 s}(1) \psi_{2 s}(2) \frac{1}{\sqrt{2}}\{\alpha(1) \beta(2)-\beta(1) \alpha(2)\}$ | $\square$ Yes 区 No |  |
| $\frac{1}{2}\left\{\psi_{1 s}(1) \psi_{2 p 0}(2)-\psi_{2 p 0}(1) \psi_{1 s}(2)\right\}\{\alpha(1) \beta(2)+\beta(1) \alpha(2)\}$ | $\boxed{\text { Yes } \quad \square \text { No }}$ | ${ }^{3} \mathrm{P}$ |
| $\frac{1}{2}\left\{\psi_{1 s}(1) \psi_{2 s}(2)+\psi_{2 s}(1) \psi_{1 s}(2)\right\}\{\alpha(1) \beta(2)-\beta(1) \alpha(2)\}$ | $\boxed{\text { Yes }} \square$ No | ${ }^{1} \mathrm{~S}$ |
| $\frac{1}{2}\left\{\psi_{1 p 0}(1) \psi_{2 s}(2)-\psi_{2 s}(1) \psi_{1 p 0}(2)\right\}\{\alpha(1) \beta(2)+\beta(1) \alpha(2)\}$ | $\square$ Yes 区 No |  |

2．（8 points）For each of the following atoms，write the ground－state configuration and the lowest－energy term that arises for that configuration．［HINT：Neglect spin－orbit coupling．］

| Atom | Ground－state Configuration | Lowest－energy Term |
| :---: | :---: | :---: |
| H | $(1 \mathbf{s})^{1}$ | ${ }^{2} \mathbf{S}$ |
| Be | $(1 \mathbf{s})^{2}(2 \mathrm{~s})^{2}$ | ${ }^{2} \mathbf{s}$ |
| F | $(1 \mathbf{s})^{2}(2 \mathbf{s})^{2}(2 \mathrm{p})^{5}$ | ${ }^{2} \mathbf{P}$ |
| Ne | $(1 \mathbf{s})^{2}(2 \mathbf{s})^{2}(2 \mathrm{p})^{6}$ | ${ }^{1} \mathbf{S}$ |

3．（ 5 points）Consider combining two quantum mechanical angular momenta．Indicate the possible values of the total angular momentum when combining these to create a total angular momentum．

| First Angular Momentum | Second Angular Momentum | Possible Values of Total A．M． |
| :---: | :---: | :---: |
| $L_{1}=2$ | $L_{2}=1$ | $L=1,2,3$ |
| $S_{1}=1 / 2$ | $S_{2}=1 / 2$ | $S=0,1$ |

NAME:

1. (10 points) The principal emission of the potassium atom is in the violet region of the spectrum. It consists of two closely spaced emission lines at wave lengths of 393.366 nm and 396.847 nm . Because potassium has a single electron outside of filled shells, its ground state is ${ }^{2} \mathbf{S}_{1 / 2}$. (a) The two transitions involve emission to take the atom to the ground state. From what two levels do these emissions arise?
$ـ^{2} \mathbf{P}_{1 / 2}$ $\qquad$ and $\qquad$ ${ }^{2} \mathbf{P}_{3 / 2}$ $\qquad$
(b) From these two emission lines, one may calculate a fundamental constant of the potassium atom. Carry out this calculation to determine this constant (in $\mathrm{cm}^{-1}$ ). [Be sure to specify your answer to the proper number of significant digits.]
The difference in energy of the two states is only the difference in the spin-orbit energies:

$$
\begin{aligned}
& E_{S O}\left({ }^{2} P_{3 / 2}\right)=\frac{\xi}{2}\left\{\frac{3}{2}\left(\frac{3}{2}+1\right)-1(1+1)-\frac{1}{2}\left(\frac{1}{2}+1\right)\right\}=\frac{\xi}{2} \\
& E_{S O}\left({ }^{2} P_{1 / 2}\right)=\frac{\xi}{2}\left\{\frac{1}{2}\left(\frac{1}{2}+1\right)-1(1+1)-\frac{1}{2}\left(\frac{1}{2}+1\right)\right\}=-\xi
\end{aligned}
$$

The energy difference between these two states is $\Delta E=3 \xi / 2$,

$$
\Delta E=\frac{1}{393.366 \times 10^{-7} \mathrm{~cm}}-\frac{1}{396.847 \times 10^{-7} \mathrm{~cm}}=222.989 \mathrm{~cm}^{-1}
$$

So, the spin-orbit coupling constant is $2 / 3$ of this value:

$$
\xi=148.660 \mathrm{~cm}^{-1}
$$

2. ( 10 points) In the table, match the phrase in column $A$ with the best phrase in column $B$ by placing the number in the blank beside the entry in column $A$. There is only one correct answer for each.

| Column A | Column B |
| :---: | :---: |
| _ 9__ Coulomb integral | 1. Asymmetric top spectroscopy. |
| 4__ Doppler shift | 2. S and T branches of the FTIR spectrum. |
| 5_ Hund's first rule | 3. $\int \psi_{1}^{*}\left(r_{1}\right) \psi_{1}^{*}\left(r_{2}\right) \frac{e^{2}}{4 \pi \varepsilon_{0}}\left(\frac{1}{r_{12}}\right) \psi_{2}\left(r_{1}\right) \psi_{2}\left(r_{2}\right) d^{2} r_{1} d^{3} r_{2}$ |
| 8__ Koopman's theorem | 4. An effect used to measure the speed at which stars and other radiating astronomical objects are moving relative to the Earth. |
| _10__ Raman effect | 5. Of the terms derived from a configuration, the term with highest spin multiplicity is of lowest energy. |
|  | 6. Has two degenerate modes of vibration. |
|  | 7. No matter what approximate wave function is substituted for the ground-state eigenfunction in Schroedinger's equation, the predicted approximate energy will always be greater than, or equal to, the true energy. |
|  | 8. The electron distribution in an atom is not affected by the removal of an electron in an ionization event. |
|  | 9. Quantum mechanical energy term to account for electron-electron repulsion. |
|  | 10. Scattering of light with frequency change. |

NAME:

1. ( 10 points) The hydrogen molecule ion (with nuclear centers $A$ and $B$ ) serves as the exemplary homonuclear diatomic molecule. For each one-electron LCAO molecular orbital listed in the table, indicate the appropriate molecular term symbol. ( $N$ is an appropriate normalization constant, in each case. You do not have to indicate whether the orbital is bonding or antibonding. )

| Molecular Orbital | Symmetry Symbol |
| :---: | :---: |
| $N\left(\Psi_{1 s, A}+\Psi_{1 s, B}\right)$ | $\sigma_{g}$ |
| $N\left(\Psi_{1 s, A}-\Psi_{1 s, B}\right)$ | $\sigma_{u}$ |
| $N\left(\Psi_{2 p_{0}, A}-\Psi_{2 p_{0}, B}\right)$ | $\sigma_{g}$ |
| $N\left(\Psi_{2 p_{1}, A}+\Psi_{2 p_{1}, B}\right)$ | $\pi_{u}$ |
| $N\left(\Psi_{2 p_{-1}, A}-\Psi_{2 p_{-1}, B}\right)$ | $\pi_{g}$ |

(1) One-electron orbitals are listed as lower case Greek letters. (2) Orbitals do not have spin; electrons have spin.
2. (10 points) In the table below, match the phrase in column $A$ with the phrase in column $B$ that best describes it.

| Column A | Column B |
| :--- | :--- |
| _c__ AO | (a) [bonding electrons - antibonding electrons]/2 |
| _e__ Basis functions | (b) A measure of the degree to which AOs have <br> nonzero values in the same region |
| _a_ Bond order | (c) Atomic orbital |
| _f__ Delocalization | (d) For a system subject to a Coulomb potential, the <br> average kinetic and potential energies are related. |
| _h_ Hartree-Fock method | (e) The set from which one forms MOs |
| _g_ Molecular configuration | (f) Extension of an MO over the whole molecule |
| _b_ Overlap integral | (g) Obtained by putting electrons into MOs, in order of <br> energy and obeying Hund's rule |
| _i_ Secular determinant | (h) A procedure to find the multiple-electron state due <br> to a mean-field approximation for electron repulsion. |
| ___ Symmetry designation | (i) Expression for finding the eigenvalues of the <br> Hamiltonian matrix |
| d_ Virial theorem | (j) Classification of a molecular orbital according to the <br> physical layout of the function |

1．（10 points）For the following homoatomic diatomic molecules，give the ground configuration and ground－state term symbol．

| Molecule | Configuration | Ground State Term |
| :---: | :---: | :---: |
| $\mathrm{H}_{2}$ | $\left(1 \sigma_{\mathrm{g}}\right)^{2}$ | ${ }^{1} \Sigma_{\mathrm{g}}{ }^{+}$ |
| $\mathrm{Li}_{2}$ | $\left(1 \sigma_{g}\right)^{2}\left(1 \sigma_{u}^{*}\right)^{2}\left(2 \sigma_{g}\right)^{2}$ | ${ }^{1} \Sigma_{g}{ }^{+}$ |
| $\mathrm{N}_{2}$ | $\left(1 \sigma_{g}\right)^{2}\left(1 \sigma_{u}^{*}\right)^{2}\left(2 \sigma_{g}\right)^{2}\left(2 \sigma u^{*}\right)^{2}\left(3 \sigma_{g}\right)^{2}(\pi u)^{4}$ | ${ }^{1} \Sigma_{g}{ }^{+}$ |
| $\mathrm{O}_{2}$ | $\left(1 \sigma_{g}\right)^{2}\left(1 \sigma_{u}^{*}\right)^{2}\left(2 \sigma_{g}\right)^{2}\left(2 \sigma_{u}^{*}\right)^{2}\left(3 \sigma_{g}\right)^{2}\left(\pi_{u}\right)^{4}\left(\pi_{g}^{*}\right)^{2}$ | ${ }^{3} \Sigma_{g}$ |
| $\mathrm{F}_{2}$ | $\left(1 \sigma_{g}\right)^{2}\left(1 \sigma_{u}^{*}\right)^{2}\left(2 \sigma_{g}\right)^{2}\left(2 \sigma_{u}^{*}\right)^{2}\left(3 \sigma_{g}\right)^{2}(\pi u)^{4}\left(\pi_{g}^{*}\right)^{4}$ | ${ }^{1} \Sigma_{g}{ }^{+}$ |

2．（6 points）Below are three UV absorption spectra from your textbook．What kind of system gives rise to each？

（a）＿atom $\qquad$
（b）＿diatomic molecule $\qquad$
（c）＿polyatomic molecule $\qquad$

3．（4 points）For a water molecule，which of these symmetry operations does the electron density of the molecule have？

| Symmetry property | Does water have this property？ |
| :---: | :---: |
| Horizontal reflection plane | $\square$ Yes 区 No |
| Vertical reflection plane | 区 Yes $\square$ No |
| Inversion center | $\square$ Yes 区 No |
| Rotation axis | 区 Yes $\square$ No |

