NAME: Jack Decker   Score 20/20

[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. (4 points) Without doing any calculations, for a pure gas that obeys the Boltzmann distribution, put the following parameters in order of increasing magnitude: $\langle v \rangle$, v_{mp}, and v_{rms}. [Indicate the relative order with the "less than" sign (<).]

$$v_{mp} \; < \; \langle v \rangle \; < \; v_{rms}$$

2. (6 points) In pure water at 25°C, on average how far does a water molecule move (in three dimensions) in one millisecond by diffusion?

From the Handbook, one may find that, in three dimensions, $< r^2 > \; = \; < x^2 > \; + < y^2 > \; + < z^2 > = \; 6Dt$
From this equation one obtains, from the data in the Handbook, the result:

$$r_{rms} \; = \; \sqrt{6Dt} \; = \; \sqrt{6\,(2.26 \times 10^{-9}\, m^2\, s^{-1})(1 \times 10^{-3}\, s)} \; = \; 3.68 \times 10^{-6}\, m \; = \; 3.68 \times 10^{-4}\, cm$$

3. (10 points)
    a. (5 points) A standard rotary pump is capable8 of producing a vacuum on the order of 10^{-3} Torr. What is the single-particle collisional frequency and mean free path for N_2 at this pressure and 310 K?

From the handbook one can derive,

$$z_{11} = \sigma \langle v \rangle n^* = \frac{P_1 N_A}{RT} \sigma \sqrt{2} \left(\frac{8RT}{\pi M_1} \right)^{\frac{1}{2}}$$

$$= \frac{0.13\, \text{Pa} \; \cdot \; 6.023 \times 10^{23} \text{mol}^{-1}}{8.314\, J\, K^{-1} \text{mol}^{-1} \; \cdot \; 310\, K} \cdot 0.44 \times 10^{-18} m^2 \; \cdot 1.4142 \; \cdot \left(\frac{8 \cdot 8.314\, J\, K^{-1}\, \text{mol}^{-1} \cdot 310\, K}{3.1416 \; \cdot \; 0.028\, kg\, \text{mol}^{-1}} \right)^{\frac{1}{2}}$$

$$= 9.1 \times 10^3 s^{-1}$$

Mean-free path can be obtained from,

$$\lambda = \frac{1}{\sqrt{2} \sigma n^*} = \frac{1}{\sqrt{2} \sigma} \left(\frac{RT}{PN_A} \right) = 0.053\, m$$

    b. (5 points) A cryogenic pump can produce a vacuum on the order of 10^{-10} Torr. What is the collisional frequency and mean free path for N_2 at this pressure and 78.15 K?

$$z_{11} = \sigma \langle v \rangle n^* = \frac{P_1 N_A}{RT} \sigma \sqrt{2} \left(\frac{8RT}{\pi M_1} \right)^{\frac{1}{2}}$$

$$= \frac{1.3 \times 10^{-8}\, \text{Pa} \; \cdot \; 6.023 \times 10^{23} \text{mol}^{-1}}{8.314\, J\, K^{-1} \text{mol}^{-1} \; \cdot \; 78.15\, K} \cdot 0.44 \times 10^{-18} m^2 \; \cdot 1.4142 \; \cdot \left(\frac{8 \cdot 8.314\, J\, K^{-1}\, \text{mol}^{-1} \cdot 78.15\, K}{3.1416 \; \cdot \; 0.028\, kg\, \text{mol}^{-1}} \right)^{\frac{1}{2}}$$

$$= 1.82 \times 10^{-3} s^{-1}$$

Mean-free path can be obtained from,

$$\lambda = \frac{1}{\sqrt{2} \sigma n^*} = \frac{1}{\sqrt{2} \sigma} \left(\frac{RT}{PN_A} \right) = 1.3 \times 10^5\, m$$

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[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 reaction A + B → products is run in an equimolar mixture of A and B. At the end of one minute 70% of the A reactant remains unreacted. How much A will remain unreacted at the end of two minutes if:

(a) **(3 points)** The reaction is first order in A and zero order in B.

$$\frac{dA}{dt} = k[A]^1[B]^0$$

$$[A] = A_0 e^{-kT}, [A] = [B]$$

$$\frac{[A]_{1 \text{ minute}}}{[A]_0} = 0.7 = e^{-k \cdot 60 \text{ sec}}$$

$$\frac{\ln 0.7}{60 \text{ sec}} = -k$$

$$\frac{[A]_{2 \text{ min}}}{[A]_0} = e^{-k \cdot 120 \text{ sec}} = e^{-2 \cdot \ln 0.7} = 0.7^2$$

$$\frac{[A]_{2min}}{[A]_0} = (0.7)^2 = 0.49$$

(b) **(3 points)** The reaction is first order in B and zero order in A.

$$\frac{dA}{dt} = k[A]^0[B]^1 = k[B] = k[A]$$

$$\frac{[A]_{2min}}{[A]_0} = 0.49 \text{ as above}$$

(c) **(4 points)** The reaction is one-half order in A and one-half order in B.

$$\frac{d[A]}{dt} = k[A]^{1/2}[B]^{1/2} = k[A]^1$$

$$\frac{[A]_{2min}}{[A]_0} = 0.49$$

2. (**5 points**) At 552.3 K , the rate constant for the thermal decomposition of SO_2Cl_2 is 1.02×10^{-6} s^{-1}. If the activation energy is 210 kJ mol^{-1}, calculate the Arrhenius preexponential factor and determine the rate constant at 310 K.

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right)$$

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[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.]

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$-13.7957 = \ln A - \frac{210\ kJ\ \text{mol}^{-1}}{552.3\ K \cdot 8.3144349\ J\ K^{-1} mol^{-1}}$$

$$A = 7.402 \times 10^{13}$$

$$k(310K) = 7.402 \times 10^{13} \cdot \exp\left(\frac{210\ kJ\ \text{mol}^{-1}}{310\ K \cdot 8.3144349\ J\ K^{-1} mol^{-1}}\right)$$

$$= 3.06 \times 10^{-22} s^{-1}$$

3. (**5 points**) From data in the Handbook, estimate the second-order rate constant for the destruction of ozone (O_3) by nitric oxide (NO) at room temperature (298.15 K).

The Arrhenius parameters for this reaction are found in Table 10.2 on page 10-2. Using Arrhenius's equation,

$$k(T) = A\ exp\left(-\frac{E_a}{RT}\right)$$

$$k(298.15K) = 7.9 \times 10^{11} cm^3 mol^{-1} s^{-1}\ exp\left(-\frac{10.5 \times 10^3 J\ mol^{-1}}{8.3144349\ J\ mol^{-1} K^{-1}(298.15K)}\right)$$

$$= 1.14 \times 10^{10} cm^3 mol^{-1} s^{-1}$$

NAME: Jack Decker   Score 20/20

[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**) Consider the reversible reaction $A \leftrightarrow B + C$, with a forward rate of k_f and a reverse rate of k_r. A temperature jump experiment is performed where the relaxation time constant is measured to be 310 μs, resulting in an equilibrium where $K_{eq} = 0.70$ with $[A]_{eq} = 0.20$ M.

    a. (**3 points**) Calculate the relaxation time of the reaction.

    Assuming the following rate law:

    $$\frac{d[A]}{dt} = -k_f[A] + k_r[B][C] = 0$$

    The post-jump equilibrium concentrations with respect to the initial concentrations and concentration shift are:

    $$[A] - \zeta = [A]_{eq}$$
    $$[B] + \zeta = [B]_{eq}$$
    $$[C] + \zeta = [C]_{eq}$$

    Therefore, the differential rate expression for the concentration shift, ζ, is:

    $$\frac{d\zeta}{dt} = -k_f([A]_{eq} + \zeta) + k_r([B]_{eq} - \zeta)([C]_{eq} - \zeta)$$
    $$= -k_f([A]_{eq} + \zeta) + k_r([B]_{eq}[C]_{eq} - \zeta[B]_{eq} - \zeta[C]_{eq} + \zeta^2)$$

    Neglecting terms of order ζ^2, and knowing that $-k_f[A]_{eq} + k_r[B]_{eq}[C]_{eq} = 0$

    $$\frac{d\zeta}{dt} = -\left(k_f + k_r([B]_{eq} + [C]_{eq})\right) \cdot \zeta$$

    Thus the relaxation time is,

    $$\tau = \left(k_f + k_r([B]_{eq} + [C]_{eq})\right)^{-1}$$

    b. (**3 points**) Calculate the equilibrium concentrations for $[B]_{eq}$ and $[C]_{eq}$.

    The equilibrium constant is given by,

    $$K = \frac{k_f}{k_r} = \frac{[B]_{eq}[C]_{eq}}{[A]_{eq}} = 0.7$$

    If we assume $[B]_0 = [C_0]$, then $[B]_{eq} = [C]_{eq}$, and

    $$0.7 = \frac{x^2}{0.2} \rightarrow x = 0.374M = [B]_{eq} = [C]_{eq}$$

    c. (**4 points**) Obtain the rate constants for the reaction.

    From the equilibrium constant we know that $k_f = 0.7k_r$. Therefore,

    $$\tau = \left(k_f + k_r([B]_{eq} + [C]_{eq})\right)^{-1}$$
    $$310 \times 10^{-6}s = \frac{1}{k_f + k_r(0.374 + 0.374)}$$

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[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.]

$$310 \times 10^{-6}s = \frac{1}{0.7\,k_r + k_r(0.748)}$$

$$310 \times 10^{-6}s = \frac{1}{k_r(1.448)}$$

$$k_r = 2200\ s^{-1}, k_f = 0.7 \times k_r = 1500\ M^{-1}s^{-1}$$

2. (**6 points**)
   a. A black body is an object capable of emitting and absorbing all wavelengths of radiation.
   b. The photoelectric effect establishes that electromagnetic radiation consists of particles.
   c. Wave-particle duality is the recognition that the concepts of particle and wave blend together.
3. (**4 points**) What did Einstein postulate to explain that the kinetic energy of the emitted electrons in the photoelectric effects depends on the frequency? How does this postulate differ from the predictions of classical physics?

Einstein postulated that the energy of light depends on the frequency, whereas in classical theory, the energy depends only on the intensity and is independent of the frequency. He further postulated that the energy of light could only be an integral multiple of $h\nu$.

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[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)** A ground state H atom absorbs a photon and makes a transition to the *n=4* energy level. It then emits a photon of frequency $1.598×10^{14}$ s^{-1}. What is the final energy and *n* value of the atom?

From page 12-1 in the handbook, we know that for a Hydrogen-like atom

$$E_n = -\frac{Z^2 E_h}{2} \cdot \frac{1}{n^2} = -\frac{m_e e^4}{8\epsilon_0^2 h^2} \cdot \frac{1}{n^2}, n = 1,2,3, \dots$$

$$E_n = -\frac{9.109 \times 10^{-31} \text{ Kg} \cdot (1.6022 \times 10^{-19}\text{C})^4}{8 \cdot (8.85419 \times 10^{-12}\text{C}^2\text{J}^{-1}\text{m}^{-1})^2 (6.62607 \times 10^{-34} \text{ J} \cdot \text{s})^2} \cdot \frac{1}{n^2}$$

$$E_n = -2.179 \times 10^{-18}\text{J} \cdot \frac{1}{n^2}$$

Evaluating for $n = 1,2,3,4$, we obtain:

$$E_1 = -2.179 \times 10^{-18}\text{J}$$
$$E_2 = -5.448 \times 10^{-19}\text{J}$$
$$E_3 = -2.421 \times 10^{-19}\text{J}$$
$$E_4 = -1.362 \times 10^{-19}\text{J}$$

$$E_{\text{final}} = E_4 - h\nu = -1.362 \times 10^{-19} \text{ J} - 6.62607 \times 10^{-34} \text{ J s} \cdot 1.598 \times 10^{14}\text{s}^{-1}$$
$$= -2.421 \times 10^{-19} \text{ J}$$

Therefore, the atom is in the *n=3* energy level.

2. **(6 points)** For the following operators, determine the action on the operand: (Symbols other than x, y, and θ are to be considered constants.)

Operator	Operand	Result
$\dfrac{d^2}{dx^2}$	$A \sin\left(\dfrac{n\pi}{a}x\right)$	$-\left(\dfrac{n^2\pi^2}{a^2}\right) A \sin\left(\dfrac{n\pi}{a}x\right)$
$y + \dfrac{d}{dy}$	$A \exp(iQy)$	$(y + iQ) A \exp(iQy)$
$\left(\theta + \dfrac{d}{d\theta}\right)$	$A \exp(-\theta^2/2)$	0

3. **(6 points)** A particle is attached to a solid surface by a spring with an asymmetric spring constant. The result is a potential energy of the form:

$$V(x) = \frac{k}{2}x^2 + Ax^3$$

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[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.]

where $x = r - r_{eq}$, and k and A are constants that describe the strength of the interaction. If the particle has a mass m, write out a complete, correct expression for the Hamiltonian operator.

$$\widehat{H} \;=\; T + V \;=\; -\frac{\left(\frac{h}{2\pi}\right)^2}{2m}\frac{d^2}{dx^2} \;+\; \frac{k}{2}x^2 \;+\; Ax^3$$

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[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) A particle in a 1D box has as its initial wave function an even mixture of the first two stationary states $\Psi(x,0) = A[\psi_1(x) + \psi_2(x)]$.

    a.   Normalize $\Psi(x,0)$.

    First we calculate $|\Psi|^2$,

$$|\Psi|^2 = \Psi^*\Psi = |A|^2(\psi_1^* + \psi_2^*)(\psi_1 + \psi_2) = |A|^2[\psi_1^*\psi_1 + \psi_1^*\psi_2 + \psi_2^*\psi_1 + \psi_2^*\psi_2]$$

Since the functions $\psi_{i,i\in 1,2}$, are stationary states of the 1D particle in a box, then they define an orthonormal basis set. The latter implies that $\int \psi_i^*\psi_j dx = 0$ if $i \neq j$, and $\int \psi_i^*\psi_j dx = 1$ if $i = j$. Therefore,
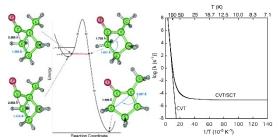
$$1 = \int |\Psi|^2 dx = 2|A|^2 \rightarrow A = 1/\sqrt{2}$$

    b.   (**6 bonus points**) Find $\Psi(x,t)$ and $|\Psi(x,t)|^2$, and show that having normalized Ψ at $t = 0$, it stays normalized. Let $\omega = \pi^2\hbar/2ma^2$.

$$\Psi(x,t) = \frac{1}{\sqrt{2}}\left[\psi_1 e^{-iE_1 t/\hbar} + \psi_2 e^{-iE_2 t/\hbar}\right], \left(\frac{E_n}{\hbar} = n^2\omega\right)$$

$$= \frac{1}{\sqrt{2}}\sqrt{\frac{2}{a}}\left[sin\left(\frac{\pi}{a}x\right)e^{-i\omega t} \ sin\left(\frac{2\pi}{a}x\right)e^{-i4\omega t}\right]$$

$$= \frac{1}{\sqrt{a}}e^{-i\omega t}\left[sin\left(\frac{\pi}{a}x\right) + sin\left(\frac{2\pi}{a}x\right)e^{-3i\omega t}\right].$$

$$|\Psi(x,t)|^2 = \frac{1}{a}\left[sin^2\left(\frac{\pi}{a}x\right) + sin\left(\frac{\pi}{a}x\right)sin\left(\frac{2\pi}{a}x\right)\left(e^{-3i\omega t + e^{3i\omega t}}\right) + sin^2\left(\frac{2\pi}{a}\right)\right]$$
$$= \frac{1}{a}\left[sin^2\left(\frac{\pi}{a}x\right) + sin^2\left(\frac{2\pi}{a}x\right) + 2 \ sin\left(\frac{\pi}{a}x\right)sin\left(\frac{2\pi}{a}x\right)cos(3\omega t)\right].$$

2.   **(6 points)** The figure (**left**) shows the ring expansion reactions of 1-methylcyclobutylhalocarbene, specifically fluorocarbene → fluorocyclopentene.

    a.   **(3 points)** Explain the origin of the lower energy pathway.

        At low temperatures, as indicated in the schematic and by the Arrhenius plot, a lower energy pathway is present. The lower energy pathway appears due to quantum tunneling. Due to quantum tunneling the potential barrier, is overpassed by the wave-like electrons, which are not trapped in the local minima, like a classical particle would be.

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[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.]

b. **(3 points)** Classically the low-temperature reaction-rate depends exponentially on the height of the potential energy barrier. Write the expression for the energy height of the barrier.

The activation energy for the reaction is proportional to the height of the potential energy barrier V_0. Let the total energy of the electrons in the system be described by E. Then the activation energy associated to the reaction rate will be proportional to the square root of the difference between the potential energy and the total energy of the electrons, thus

$$E_a \propto \sqrt{\hbar^2/2m(V_0 - E)}$$

3. **(6 points)** Evaluate the commutator $[\hat{x}, \hat{p}_x^2]$ by applying the operators to an arbitrary function $f(x)$.

$$[\hat{x}, \hat{p}_x^2] = \hat{x}\hat{p}_x[\hat{p}_x f(x)] - \hat{p}_x[\hat{p}_x \hat{x} f(x)]$$

$$= -\hbar^2 x \frac{d^2 f(x)}{dx^2} + \hbar^2 \frac{d}{dx}\left(\frac{d[xf(x)]}{dx}\right)$$

$$= -\hbar^2 x \frac{d^2 f(x)}{dx^2} + \hbar^2 \frac{d}{dx}\left(f(x) + x\frac{df(x)}{dx}\right)$$

$$= -\hbar^2 x \frac{d^2 f(x)}{dx^2} + \hbar^2 \left(\frac{df(x)}{dx} + \frac{df(x)}{dx} + x\frac{d^2 f(x)}{d^2}\right)$$

$$= +2\hbar^2 \frac{df(x)}{dx}$$

$$[\hat{x}, \hat{p}_x^2] = 2\hbar^2 \frac{d}{dx}$$

Name: _____

1. (8 points) In a vibrational spectroscopy experiment a strong absorption of infrared radiation is observed for $^{19}F^{35}Cl$. What vibrational frequency, in cm^{-1}, would you expect the absorbance to occur? Using the harmonic oscillator approximation, estimate the force constant k for this molecule.

> **Solution:** The molecular constants for several diatomic molecules are provided in Table 12.1 in the handbook. Therefore, the vibrational frequency for $^{19}F^{35}Cl$ employing a harmonic oscillator model is $\omega_e/(2\pi c) = 793.2$ cm^{-1}. Thus,
>
> $$\begin{aligned} \omega_e &= 2\pi c(793.2 \text{ cm}^{-1}) \\ &= 2\pi \cdot 2.99 \times 10^8 \frac{m}{s} \cdot 79320 \text{ m}^{-1} \\ &= 1.49 \times 10^{14} s^{-1} \end{aligned} \tag{1}$$
>
> The corresponding force constant k can be estimated using $\omega_e = \sqrt{k/\mu}$, where $\mu = m_A m_B/(m_A + m_B)$. Therefore,
>
> $$\begin{aligned} k = \omega_e^2 \mu &= (1.49 \times 10^{14} s^{-1})^2 \cdot \frac{(18.99840 \text{ g mol}^{-1}) \cdot (34.96885 \text{ g mol}^{-1})}{18.99840 \text{ g mol}^{-1} + 34.96885 \text{ g mol}^{-1}} \\ &= 2.22 \times 10^{28} s^{-2} \cdot 12.3103 \frac{g}{mol} \cdot \frac{1 \text{ Kg}}{1000 \text{ g}} \cdot \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} \\ &= 454 \text{ Kg s}^{-2} = 454 \text{ N m}^{-1} \end{aligned} \tag{2}$$

2. (5 points) Based on the spectral energy select the associated spectroscopy.

   (a) (1 point) Spectral energy: $E = 1.24 \times 10^{-6}$ ev.
   ◯ Vibrational spectroscopy   ◯ Electronic spectroscopy   ◯ Rotational spectroscopy   √ **NMR**

   (b) (1 point) Spectral energy: $E = 1.24 \times 10^{-4}$ ev.
   ◯ Vibrational spectroscopy   ◯ Electronic spectroscopy   √ **Rotational spectroscopy**
   ◯ NMR

   (c) (1 point) Spectral energy: $E = 0.124$ ev.
   √ **Vibrational spectroscopy**   ◯ Electronic spectroscopy   ◯ Rotational spectroscopy
   ◯ NMR

   (d) (1 point) Spectral energy: $E = 1.87$ ev.
   ◯ Vibrational spectroscopy   √ **Electronic spectroscopy**   ◯ Rotational spectroscopy
   ◯ NMR

   (e) (1 point) Spectral energy: $E = 24.97$ ev.
   ◯ Vibrational spectroscopy   √ **Electronic spectroscopy**   ◯ Rotational spectroscopy
   ◯ NMR

3. (7 points) Transition series

   (a) (4 points) Which transition gives rise to the highest frequency spectral line in the Lyman series?

Solution: The transition $n \to 1$ to $n \to \infty$, effectively the dissociation limit, will have the highest frequency for the Lyman series.

(b) (3 points) Which transition gives rise to the highest frequency spectral line in the Balmer series?

Solution: The transition $n \to 2$ to $n \to \infty$, will have the highest frequency for the Balmer series.

Name: _____

1. (10 points) The ground state of dysprosium (element 66, in the 6th row of the periodic Table). is listed as $^5I_8$. What are the total spin, total orbit, and grand total angular momentum quantum numbers? Suggest a *likely* electron configuration for dysprosium.

> **Solution:** The total spin, total orbit and grand total angular momentum are
>
> $$S=2; L=6; J=8$$
>
> A likely electron configuration is given by a definite part for 36 electrons and a likely part for 30 electrons.
> $$\underbrace{(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10}(4s)^2(4p)^6}_{\text{definite 36 electrons}}\underbrace{(4d)^{10}(5s)^2(5p)^6(4f)^{10}(6s)^2}_{\text{likely 30 electrons}}.$$

2. (10 points) Ions with a single electron such as He^+, Li^{2+}, and Be^{3+} are described by the H atom wave functions with Z/a_0 substituted for $1/a_0$, where Z is the nuclear charge. The 1s wave function becomes $\Psi(r) = \frac{1}{\sqrt{\pi}}(Z/a_0)^{3/2}e^{-Zr/a_0}$. Using the latter, calculate the total energy for the 1s state in He^+, Li^{2+}, and Be^{3+} by substitution in the Schrödinger equation.

> **Solution:** We substitute in the radial equation
>
> $$-\frac{\hbar^2}{2m_e r^2}\frac{d}{dr}\left[r^2\frac{dR(r)}{dr}\right] + \left[\frac{\hbar^2 l(l+1)}{2m_e r^2} - -\frac{Ze^2}{4\pi\epsilon_0 r}\right]R(r) = ER(r)$$
>
> $$\frac{\hbar^2}{2m_e r^2}\frac{d}{dr}\left[r^2\frac{d1/\sqrt{\pi}(Z/a_0)^{3/2}e^{-Zr/a_0}}{dr}\right] - +\left[\frac{\hbar^2 0(0+1)}{2m_e r^2} - -\frac{Ze^2}{4\pi\epsilon_0 r}\right]1/\sqrt{\pi} - (Z/a_0)^{3/2}e^{-Zr/a_0} =$$
>
> $$\left(\frac{\hbar}{\sqrt{\pi}}(Z/a_0)^{5/2}e^{-Zr/a_0} - \frac{e^2}{4\pi\sqrt{\pi}\epsilon_0 r}(Z/a_0)^{3/2}e^{-Zr/a_0}\right) - -\frac{\hbar^2}{2\sqrt{\pi}m_e}(Z/a_0)^{7/2}e^{-Zr/a_0} =$$
>
> Using the relation $a_0 = \frac{\epsilon_0 h^2}{\pi m_e e^2}$,
>
> $$\frac{1}{\sqrt{\pi}}(Z/a_0)^{3/2}\left[\left(\frac{Z}{4\pi}\frac{e^2}{\epsilon_0 r} - \frac{Ze^2}{4\pi\epsilon_0 r}\right)e^{-Zr/a_0} - \frac{\hbar^2}{2m_e}(Z/a_0)^2 e^{-Zr/a_0}\right] = ER(r)$$
>
> $$-\frac{1}{\sqrt{\pi}}(Z/a_0)^{3/2}\frac{\hbar}{2m_e}(Z/a_0)^2 e^{-Zr/a_0} = -\frac{1}{\sqrt{\pi}}(Z/a_0)^{3/2}\frac{Z^2 e^2}{8\pi\epsilon_0 a_0}e^{-Zr/a_0} = ER(r)$$
>
> $$\frac{-Z^2 e^2}{8\pi\epsilon_0 a_0}\Psi(r) = ER(r)$$
>
> Therefore $\Psi(r)$ is an eigenfunction with the value $-\frac{Z^2 e^2}{8\pi\epsilon_0 a_0}$. Thus the energies are,
>
> $$E_{He^+} = -\frac{4e^2}{8\pi\epsilon_0 a_0} = 8.72 \times 10^{-18}\text{ J}$$
>
> $$E_{Li^{2+}} = -\frac{9e^2}{8\pi\epsilon_0 a_0} = 19.61 \times 10^{-18}\text{ J}$$
>
> $$E_{He^{3+}} = -\frac{16e^2}{8\pi\epsilon_0 a_0} = 34.87 \times 10^{-18}\text{ J}$$

3. (10 points (bonus)) Is $\Psi(1,2) = 1s(1)\alpha(1)1s(2)\beta(2) + 1s(2)\alpha(2)1s(1)\beta(1)$ an eigenfunction of the operator $\hat{S}_z = \hat{S}_{z1} + \hat{S}_{z2}$? If so, what is its eigenvalue M_S?

Solution:

$$\hat{S}_Z[1s(1)\alpha(1)1s(2)\beta(2) + 1s(2)\alpha(2)1s(1)\beta(1)]$$
$$= (\hat{S}_{z1} + \hat{S}_{z2})[1s(1)\alpha(1)1s(2)\beta(2) + 1s(2)\alpha(2)1s(1)\beta(1)]$$
$$= \frac{\hbar}{2}[1s(1)\alpha(1)1s(2)\beta(2) - 1s(2)\alpha(2)1s(1)\beta(1)]$$
$$+ \frac{\hbar}{2}[-1s(1)\alpha(1)1s(2)\beta(2) + 1s(2)\alpha(2)1s(1)]\beta(1)]$$
$$= \frac{\hbar}{2}(0)$$

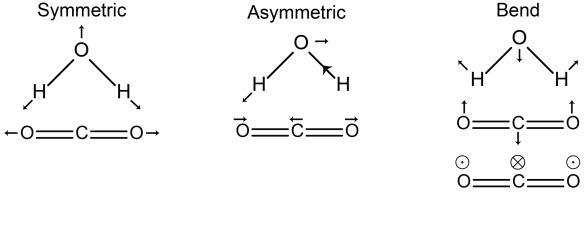The function is an eigenfunction of $\hat{S}_z$ with eigenvalue $M_S = 0$.

Answer the questions in the spaces provided. If you run out of room for an answer, continue on the back of the page. Numbers without decimal points are to be considered infinitely precise. Show reasonable significant figures and proper units.

Name: _____

1. (10 points) Match each of the concepts on the left with its specific mathematical formulation.

A. Photo electron emission   __C__ $H = \frac{4\pi^2 A}{h} \mathbf{I} \cdot \mathbf{S}$
B. Spin magnetic resonance   __E__ $\mathbf{M} = \chi \mathbf{B}$
C. Hyperfine coupling   __B__ $\hat{H}_Z = -g\mu_B B_0 \hat{S}_Z$
D. Zeeman effect   __A__ $E_{\text{kinetic}} = h\nu - E_{\text{binding}}$
E. Magnetic susceptibility   __D__ $H_Z = -\mu \cdot \mathbf{B}$

2. (6 points) Given the normal modes shown in the following figure, decide which of the normal modes of CO_2 and H_2O have a nonzero dynamical dipole moment and are therefore infrared active. The motion of the atoms in the second of the two doubly degenerate bend modes for CO_2 is identical to the first but is perpendicular to the plane of the page.

Symmetric   Asymmetric   Bend

H_2O symmetric **Active** H_2O asymmetric **Active** H_2O bend **Active**
CO_2 symmetric **Inactive** CO_2 asymmetric **Active** CO_2 bend **Active**

Solution: All three vibrational modes of water will lead to a change in the dipole moment and are therefore infrared active. The symmetric strech of carbon will not lead to a change in the dipole moment and is not infrared active. The other two modes will lead to a change in the dipole moment and are infrared active.

3. (6 points (bonus)) For the six modes in problem 2, decide which are Raman inactive.

H_2O symmetric **Inactive** H_2O asymmetric **Inactive** H_2O bend **Inactive**
CO_2 symmetric **Active** CO_2 asymmetric **Inactive** CO_2 bend **Inactive**

4. For a given molecule:

   (a) (2 points) Why would you observe a pure rotational spectrum in the microwave region?

> **Solution:** A ppure rotational spectrum is observed in the microwave region because the photon energy is insufficient to cause vibrational excitations.
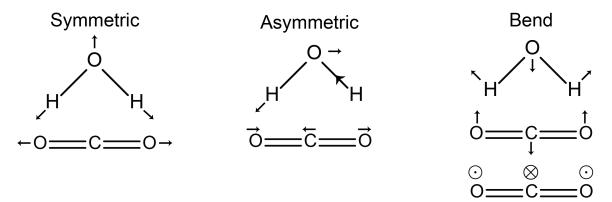
(b) (2 points) Why would you observe a rotational-vibrational spectrum in the infrared region?

> **Solution:** A rotational-vibrational spectrum is observed in the infrared region because absorption of an infrared photon can cause all excitations whose energies are equal to or less than the photon energy.

Answer the questions in the spaces provided. If you run out of room for an answer, continue on the back of the page. Numbers without decimal points are to be considered infinitely precise. Show reasonable significant figures and proper units.

Name: _____

1. (10 points) Match each of the concepts on the left with its specific mathematical formulation.

   A. Photo electron emission   __C__ $H = \frac{4\pi^2 A}{h}\mathbf{I}\cdot\mathbf{S}$
   B. Spin magnetic resonance   __E__ $\mathbf{M} = \chi\mathbf{B}$
   C. Hyperfine coupling   __B__ $\hat{H}_Z = -g\mu_B B_0 \hat{S}_Z$
   D. Zeeman effect   __A__ $E_{\text{kinetic}} = h\nu - E_{\text{binding}}$
   E. Magnetic susceptibility   __D__ $H_Z = -\mu\cdot\mathbf{B}$

2. (6 points) Given the normal modes shown in the following figure, decide which of the normal modes of CO_2 and H_2O have a nonzero dynamical dipole moment and are therefore infrared active. The motion of the atoms in the second of the two doubly degenerate bend modes for CO_2 is identical to the first but is perpendicular to the plane of the page.

> **Solution:** All three vibrational modes of water will lead to a change in the dipole moment and are therefore infrared active. The symmetric strech of carbon will not lead to a change in the dipole moment and is not infrared active. The other two modes will lead to a change in the dipole moment and are infrared active.

3. (a) (2 points) Why would you observe a pure rotational spectrum in the microwave region?

> **Solution:** A ppure rotational spectrum is observed in the microwave region because the photon energy is insufficient to cause vibrational excitations.

(b) (2 points) Why would you observe a rotational-vibrational spectrum in the infrared region?

> **Solution:** A rotational-vibrational spectrum is observed in the infrared region because absorption of an infrared photon can cause all excitations whose energies are equal to or less than the photon energy.

4. (20 points (bonus)) Suppose the Hamiltonian H, for a particular quantum system, is a function of some parameter λ; let $E_n(\lambda)$ and $\Psi_n(\lambda)$ be the eigenvalues and eigenfunctions of $H(\lambda)$. The **Feynman-Hellman** theorem states that $\frac{\partial E_n}{\partial \lambda} = \langle \psi_n | \frac{\partial H}{\partial \lambda} | \psi_n \rangle$.

   (a) (10 points) Prove the Feynmann-Hellmann theorem. Hint: Use first-order perturbation theory.

   Solution: Let the unperturbed Hamiltonean be $H(\lambda_0)$, for some fixed value λ_0. Now tweak λ to $\lambda_0 + d\lambda$. The perturbing Hamiltonian is $H' = H(\lambda_0 + d\lambda) - H(\lambda_0) = (\partial H/\partial \lambda)d\lambda$. The change in energy is given by applying first-order perturbation theory:

   $$dE_n = E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle = \langle \psi_n | \frac{\partial H}{\partial \lambda} \psi_n | \rangle d\lambda \Rightarrow \frac{\partial E}{\partial \lambda} = \langle \psi_n | \frac{\partial H}{\partial \lambda} | \psi_n \rangle. \tag{1}$$

   (b) (10 points) Apply the Feynmann-Hellmann theorem to the one-dimensional harmonic oscillator using $\lambda = \omega$.

   Solution: $E_n = (n + \frac{1}{2})\hbar\omega$; $H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$.

   $$\frac{\partial E_n}{\partial \omega} = (n + \frac{1}{2})\hbar; \frac{\partial H}{\partial \omega} = m\omega x^2 \tag{2}$$

   Therefore by applying the FH theorem,

   $$\left(n + \frac{1}{2}\right)\hbar = \langle n|m\omega x^2|n\rangle. \tag{3}$$

   But the potential energy for a harmonic oscillator is given by $V = \frac{1}{2} = m\omega^2 x^2$, therefore

   $$\langle V \rangle = \langle n|\frac{1}{2}m\omega^2 x^2|n\rangle = \frac{1}{2}\omega(n + \frac{1}{2})\hbar \Rightarrow \langle V \rangle = \frac{1}{2}(n + \frac{1}{2})\hbar\omega. \tag{4}$$