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CHEMISTRY 444, SPRING, 2019 (19S)

Circle Section Number: **10 11**

Final Examination, May 24, 2019

Answer each question in the space provided; use back of page if extra space is needed. Answer questions so the grader can READILY understand your work; only work on the exam sheet will be considered. Write answers, where appropriate, with reasonable numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge.

1. (10 points) From the words phrases in column B, select the best match for each phrase in column A and put its letter in the adjacent blank. There is only one best match for each phrase.

Column A	Column B
<u> i </u> Proportionality constant between the gradient and the flux of a quantity	a) Activated complex
<u> c </u> Situation in which a gas has layers where each layer moves at a constant speed	b) Brownian motion
<u> h </u> Settling of dense particles in a solution subject to a force field such as gravity	c) Laminar flow
<u> j </u> Probability that a gas particle has a velocity in a given range	d) Lindemann's mechanism
<u> b </u> Apparently random motion of a particle in solution	e) Lotka-Volterra mechanism
<u> g </u> Stoichiometric quantity of reactant involved in an elementary step in a reaction mechanism	f) Michaelis-Menten mechanism
<u> d </u> Explanation of unimolecular reaction with a collision-induced reactive species	g) Molecularity
<u> a </u> Maximum in energy along the path between reactants and products	h) Sedimentation
<u> e </u> Description of an oscillating chemical reaction	i) Transport coefficient
<u> f </u> Description of the reactivity of an enzyme	j) Velocity distribution function

**DO NOT WRITE
IN THIS SPACE**

p. 1 _____ /10

p. 2 _____ /10

p. 3 _____ /15

p. 4 _____ /10

p. 5 _____ /10

p. 6 _____ /10

p. 7 _____ /10

p. 8 _____ /15

p. 9 _____ /10

p. 10 _____ /10

p. 11 _____ /15

p. 12 _____ /10

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p. 13 _____ /10
(Extra credit)

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TOTAL PTS
(out of 135)

2. (10 points) Engel and Reid report the diffusion coefficient of pure argon at 298.15 K and 1.00 atmosphere to be $1.100 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. Assuming that argon is an ideal gas, determine the viscosity of argon at 298.15 K, expressed in the appropriate unit.

Using kinetic theory, the relationship between the ideal-gas viscosity and kinetic parameters of a pure substance is

$$\eta = \frac{1}{2} \rho \langle v \rangle \lambda$$

where ρ is the density, $\langle v \rangle$ is the average speed, and λ is the mean-free path. Similarly, from your handbook, the diffusion coefficient, D , in a pure ideal gas is given by kinetic theory

$$D = \frac{1}{2} \langle v \rangle \lambda$$

By comparison, one sees that there is a simple relationship between the diffusion coefficient and the viscosity of an ideal gas

$$\eta = \rho D$$

To calculate the density, one may use the ideal-gas equation:

$$\rho = \frac{n}{V} M = \frac{PM}{RT}$$

where M is the molar mass. Thus, one may calculate the density of argon:

$$\rho = \frac{(101325 \text{ Pa})(0.039948 \text{ kg})}{(8.314474 \text{ J/K})(298.15 \text{ K})} = 1.6328 \text{ kg m}^{-3}$$

Putting this result into the equation derived above, one determines the corresponding viscosity. [Note that viscosity should be appropriately expressed in poise (or some unit derived from a poise; in this case, micropoise or millipoise is appropriate).]

$$\eta = (1.6328 \text{ kg m}^{-3})(1.100 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}) = 1.796 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1} = 1.796 \times 10^{-4} \text{ poise} = 179.6 \mu\text{P}$$

The reported experimental value of the viscosity of argon under these conditions is $227 \mu\text{P}$. Not perfect agreement, but close.

One could also obtain an answer using the following equation from your handbook for an ideal gas.

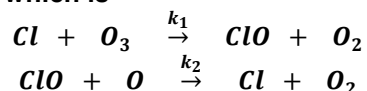
$$\eta = \sqrt{\frac{mk_b T}{6\pi\sigma_{AA}^2}}$$

This method requires one to find the cross-section, $\sigma_{AA} = \pi r_A^2 = \pi(d_A/2)^2$. One could use the Lennard-Jones coefficient for d_A as an estimate of the diameter of an argon atom. The result in this case is

$$\eta = 395 \mu\text{P}$$

A third method a student may think of is use of the Stokes-Einstein equation. The Stokes-Einstein equation is derived for a particle moving in a solvent and, consequently, this method is not applicable to the current problem of a pure gas phase. Applying it (incorrectly) to the ideal-gas phase mentioned in this problem, the result is $\eta = 1.12 \mu\text{P}$, which is off from the known experimental value by at least a factor of 100. Using the Stokes-Einstein equation is a major error, because assuming it applies to gases is not correct.

3. (15 points) In the 1970s, there was strong interest in the study of reactions that transform ozone into dioxygen in the stratosphere by the reaction $O_3 + O \rightarrow 2 O_2$. A reaction studied by Rowland and Molina is catalyzed by chlorinated species, the mechanism of which is



(a) What are the reactive species in this mechanism? [Failure to indicate the proper reactive species means the whole problem will be graded as incorrect. Thus, the answer to part (a) must be correct to receive any points.]

The reactive species do not appear in the overall reaction, so both Cl and ClO must be reactive species.

(b) Write an equation for the steady-state approximation. [This section has meaning only if the answer to section (a) is correct.]

There are two ways to write the steady-state approximation, but they are the same equation. Either one or both is considered correct.

$$\frac{d[Cl]}{dt} = 0 = -k_1[Cl][O_3] + k_2[ClO][O]$$

And

$$\frac{d[ClO]}{dt} = 0 = k_1[Cl][O_3] - k_2[ClO][O]$$

(c) Solve for the rate law at steady state in terms of the total concentration of chlorine present

$$[Cl]_{tot} = [ClO] + [Cl]$$

and the reactants. [Note: this part requires that part (b) be correct to receive credit.]

From the steady-state approximation,

$$[Cl] = \frac{k_2[ClO][O]}{k_1[O_3]}$$

But the total amount of chlorine is $[Cl]_{total} = [Cl] + [ClO]$, which gives a connection between these two species. Combining these equations gives

$$[ClO] = \frac{[Cl]_{tot}}{1 + \frac{k_2[O]}{k_1[O_3]}} \quad \text{and} \quad [Cl] = \left(\frac{k_2[O]}{k_1[O_3]} \right) \left(\frac{1}{1 + \frac{k_2[O]}{k_1[O_3]}} \right) [Cl]_{tot}$$

The rate of the reaction is given by

$$v = v_1 + v_2 = k_1[Cl][O_3] + k_2[ClO][O]$$

The result of substitution from above gives

$$v = k_1[O_3] \left(\frac{k_2[O]}{k_1[O_3]} \right) \left(\frac{1}{1 + \frac{k_2[O]}{k_1[O_3]}} \right) [Cl]_{tot} + \left(\frac{k_2[O]}{1 + \frac{k_2[O]}{k_1[O_3]}} \right) [Cl]_{tot} = 2 \frac{k_1 k_2 [O_3][O]}{k_1[O_3] + k_2[O]} [Cl]_{tot}$$

This reaction has been discussed in detail on pages 968 and 969 of your textbook.

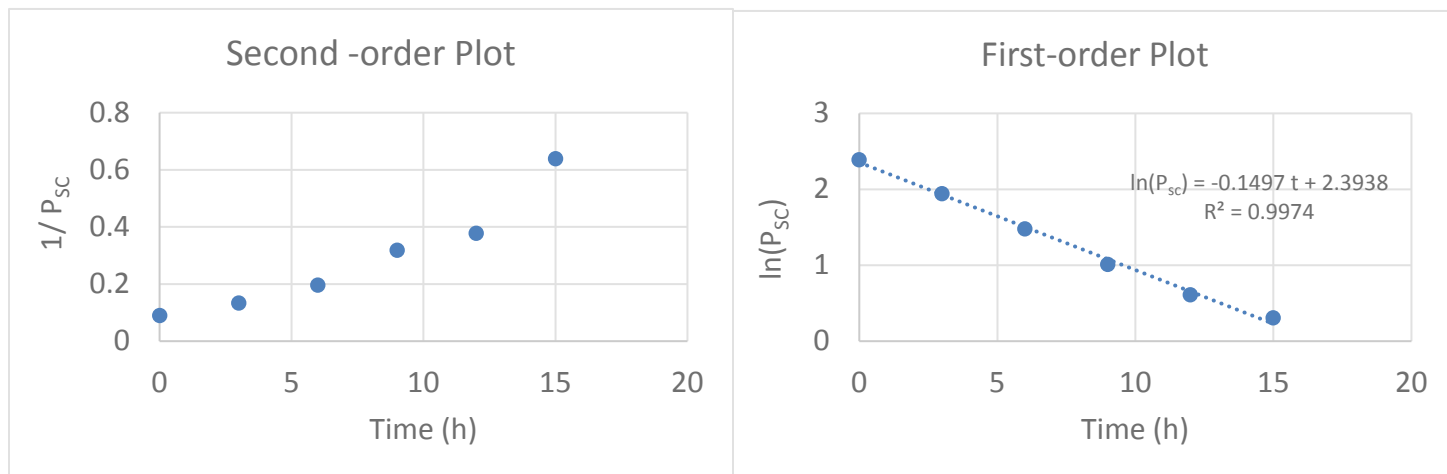
4. (10 points) The gas-phase decomposition of sulfuryl chloride produces sulfur dioxide and chlorine by the reaction



This reaction can be monitored by measuring the total pressure as a function of time. The total pressure in an experiment as a function of time is given in the table for one particular experiment. (a) Using these data in plots, determine whether the reaction is first order or second order. Explain how you know that. (b) Determine the rate constant under the conditions of this experiment. (Be sure to label all graphs properly and carefully.)

Time (h)	P_{total} (kPa)
0	11.12
3	14.58
6	17.37
9	19.06
12	20.03
15	20.79

One must plot the appropriate function of the concentration (partial pressure) of SO_2Cl_2 versus time to find which is linear in time. First, one must find the partial pressure of SO_2Cl_2 , which can be shown to be $P_{\text{SC}}(t) = 2P_{\text{total}}(0) - P_{\text{total}}(t)$. Finding this for each time, one may plot either the logarithm or the inverse, to see which is linear in time.



From these plots, it is obvious that the reaction is first-order in SO_2Cl_2 (as might have been expected given that this is a decomposition of a rather unstable molecule).

(b) The slope of the first-order plot gives the rate constant. $k = 0.1497 \text{ h}^{-1}$

5. (10 points) Determine whether the function given in each part is an eigenfunction of the operator. If it is an eigenfunction, give the eigenvalue of that function. [No credit without a mathematical demonstration; show all work. a , n , and π are constants.]

(a) $\hat{O} = -i\hbar \frac{d}{dx}$ and $f = \sin\left(\frac{n\pi x}{a}\right)$ Eigenfunction? Yes No

$$-i\hbar \frac{d}{dx} \sin\left(\frac{n\pi x}{a}\right) = \frac{i\hbar n\pi}{a} \cos\left(\frac{n\pi x}{a}\right)$$

(b) $\hat{O} = -\hbar^2 \frac{d^2}{dx^2}$ and $f = \sin\left(\frac{n\pi x}{a}\right)$ Eigenfunction? Yes No

$$-\hbar^2 \frac{d^2}{dx^2} \sin\left(\frac{n\pi x}{a}\right) = \left(\frac{n\pi}{a}\right) \hbar^2 \frac{d}{dx} \cos\left(\frac{n\pi x}{a}\right) = \left(\frac{n\pi}{a}\right)^2 \hbar^2 \sin\left(\frac{n\pi x}{a}\right)$$

Eigenvalue is $\left(\frac{n\pi}{a}\right)^2 \hbar^2 = \frac{n^2 \hbar^2}{4a^2}$

(c) $\hat{O} = x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y}$ and $f = x^2 y^2$ Eigenfunction? Yes No

$$\left(x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y}\right) x^2 y^2 = x \frac{\partial x^2 y^2}{\partial x} + y \frac{\partial x^2 y^2}{\partial y} = 2x^2 y^2 + 2x^2 y^2 = 4x^2 y^2$$

Eigenvalue is 4.

(d) $\hat{O} = a$ and $f = x + y$ Eigenfunction? Yes No

$$a(x + y) = a(x + y)$$

Eigenvalue is a .

(e) $\hat{O} = \frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta}\right)$ and $f = \cos\theta$ Eigenfunction? Yes No

$$\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta}\right) \cos\theta = \frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\cos\theta}{d\theta}\right) = \frac{-1}{\sin\theta} \frac{d\sin^2\theta}{d\theta} = \frac{-2}{\sin\theta} \sin\theta \cos\theta = -2\cos\theta$$

Eigenvalue is -2.

6. (10 points) In the table below, give the letter of the phrase or word in column B that best describes the word or phrase in column A best and most completely.

Column A	Column B
__g__ Band gap	a. Travel past an energy barrier higher than the total energy of the particle
__d__ Complete set	b. Wave functions describing a many-electron system must change sign under interchange of any two electrons
__e__ Heisenberg's principle	c. Electron-electron repulsion is treated in a mean-field approximation
__j__ Hermitian operator	d. All possible solutions of Schroedinger's equation for a particular potential-energy operator
__a__ Tunneling	e. Position and momentum of a particle can never be determined simultaneously with infinite accuracy
	f. Measured results correspond to elements of reality.
	g. Energy range for which there are no allowed states
	h. The lowest-energy term of the ground configuration has the highest spin multiplicity
	i. Overlap of wave functions on adjacent atoms
	j. Has real eigenvalues only

7. (10 points) For the following approximate orbital for the radial part of the ground state of the hydrogen-atom:

$$R(r) = A \exp(-cr^2/a_0^2)$$

A is a normalization constant, c is a constant, and a_0 is the Bohr radius. Determine the normalization constant for this radial part of the wave function over the range of r.

The normalization requires the following integral to be 1.

$$\int_0^{\infty} R^2 r^2 dr = 1 = A^2 \int_0^{\infty} r^2 \exp(-2cr^2/a_0^2) dr$$

One may evaluate the integral from the integral table in the handbook, which gives

$$A^2 \left(\frac{a_0^2}{8c} \right) \sqrt{\frac{\pi a_0^2}{2c}} = 1$$

Solution of this equation gives

$$A = \frac{1}{\sqrt{a_0^3}} \sqrt[4]{\frac{128c^3}{\pi}}$$

8. (15 points) Fill in the table below. All atoms should be considered to be in the ground configurations. Give all possible values of S and L. Give the ground-state term (only) in the last column.

Atom	Configuration	S	L	Term symbols
H	$(1s)^1$	1/2	0	$^2S_{1/2}$
He	$(1s)^2$	0	0	1S_0
O	$(1s)^2(2s)^2(2p)^4$	0 or 1	0, 1, or 2	3P_2
F	$(1s)^2(2s)^2(2p)^5$	1/2	1	$^2P_{3/2}$

9. (10 points) W. G. Brown (Phys. Rev. 1931, 37, 1007 – 1008.) studied the electronic spectrum of Br₂ vapor. He reports the following parameters of the ground and first excited states. As accurately as you can, calculate the energy (in cm⁻¹) of electronic excitation accompanied by a transition from the lowest vibrational state (n = 0) of the ground state to the first excited vibrational state (n = 1) of the first excited electronic state of Br₂. (For purposes of this question, you may neglect any contributions from rotational transitions.)

Electronic level	D ₀ /eV	ω _e /cm ⁻¹	x _e ω _e /cm ⁻¹
Ground state	0	323.86	1.150
First excited state	0.464	165.39	1.579

The difference in D₀ is the transition energy in going from the ground electronic level to the first excited electronic level, with the system starting in the vibrational state with n_l = 0 and ending in the vibrational state of the excited state with n_u = 0.

However, the energy of transition sought here is that difference in electronic energy plus the difference in vibrational energy between the n_u = 0 and n_u = 1 vibrational levels of the excited state.

$$\Delta E = \Delta E_{elect} + \Delta E_{vib} = D_{0,u} - D_{0,l} + E_{vib,u}(n=1) - E_{vib,u}(n=0)$$

Thus, one must calculate the additional energy to promote the system from n_u = 0 to n_u = 1 from information in the table. In symbols, this energy difference is

$$\begin{aligned} E_{vib,u}(n=1) - E_{vib,u}(n=0) &= \left(1 + \frac{1}{2}\right) \omega_{e,u} - \left(1 + \frac{1}{2}\right)^2 x_{e,u} \omega_{e,u} - \left(\frac{1}{2}\right) \omega_{e,u} + \left(\frac{1}{2}\right)^2 x_{e,u} \omega_{e,u} \\ &= \omega_{e,u} - 2x_{e,u} \omega_{e,u} \end{aligned}$$

Substituting values from the table, one obtains the extra vibrational energy, correct through second order.

$$\begin{aligned} E_{vib,u}(n=1) - E_{vib,u}(n=0) &= \frac{3}{2} 165.39 \text{ cm}^{-1} - \frac{9}{4} (1.579 \text{ cm}^{-1}) - \frac{1}{2} (165.39 \text{ cm}^{-1}) + \frac{1}{4} (1.579 \text{ cm}^{-1}) \\ &= 165.39 \text{ cm}^{-1} - 2(1.579 \text{ cm}^{-1}) = 162.232 \text{ cm}^{-1} \end{aligned}$$

D_{0,u} - D_{0,l} is, of course, 0.464 eV. One must convert this to cm⁻¹ to answer the question, which can be done by using the conversion factor in Table 3.5 of the handbook. And, finally the additionally vibrational excitation energy found above is added to give the predicted energy requested in the question.

$$\Delta E = 0.464 \text{ eV} (8065.54 \text{ cm}^{-1}/\text{eV}) + 162.232 \text{ cm}^{-1} = 3904.643 \text{ cm}^{-1}$$

10. (10 points) According to a compilation of work functions of metals by Herbert B. Michaelson in *The Handbook of Chemistry and Physics*, the work function of lead is 4.25 eV (from Eastman, D. E. *Phys. Rev. B* 1970, 2, 1 – 2.). What is the minimum frequency of light required to observe the photoelectric effect in lead?

The photoelectric effect will just barely be observed when the energy of the incident light is equal to the work function. First, let's convert this energy to joules using Table 3.5 of the handbook.

$$E_{mol} = 4.25 \text{ eV} (96.4853 \text{ J mol}^{-1}) = 410.06 \text{ kJ mol}^{-1}$$

But we need the energy per atom. This value we obtain by dividing this molar quantity by Avogadro's number.

$$E_{molecule} = \frac{410.06 \text{ kJ mol}^{-1}}{6.02211415 \times 10^{23} \text{ molecule mol}^{-1}} = 6.809 \times 10^{-19} \text{ J molecule}^{-1}$$

This is the minimum energy of a photon to remove the electron, but we know a formula that relates the energy of a photon to its frequency, Planck's formula, and so:

$$\nu = \frac{E}{h} = \frac{6.809 \times 10^{-19} \text{ J}}{6.62607015 \times 10^{-34} \text{ J s}} = 1.028 \times 10^{15} \text{ Hz}$$

One may also determine the wavelength (not asked for in this question) of this light:

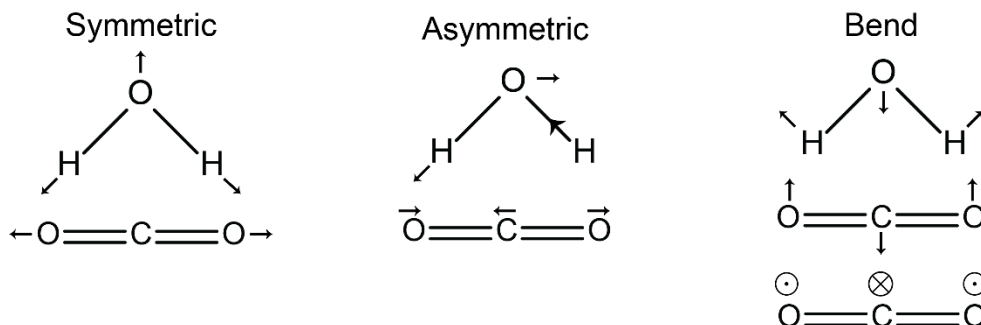
$$\lambda = \frac{c}{\nu} = \frac{2.99792458 \times 10^8 \text{ m s}^{-1}}{1.028 \times 10^{15} \text{ Hz}} = 2.916 \times 10^{-7} \text{ m} = 291.6 \text{ nm}$$

This light falls in the ultraviolet region of the spectrum, as one might expect.

11. (15 points) Fill in the blanks in the table below. All molecules are in their ground-state configurations, unless stated. In the term symbols, you must indicate the symmetry under reflection in the σ plane only for $^1\Sigma$ terms and symmetry under inversion for ALL terms. If more than one term corresponds to the same configuration, indicate the lowest-energy term according to the Hund's rules by circling this term.

Molecule	Configuration	S	Λ	List all term symbols. Circle the lowest energy term for multiple terms.
H ₂	$1\sigma_g^2$	0	0	$^1\Sigma_g^+$
First excited state of H ₂	$1\sigma_g^1 1\sigma_u^{*1}$	0 or 1	0	$^3\Sigma_u^-$, $^1\Sigma_u$
O ₂	$1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4 3\sigma_g^{*2} 1\pi_g^{*2}$	0 or 1	0 or 2	$^1\Sigma_g^+$, $^3\Sigma_g^-$, $^1\Delta_g$

12. (10 points). Given the normal modes shown in the following figure, decide which of the normal modes of CO_2 and H_2O are infrared-active. Among these, also specify which modes will be Raman-active. (The motion of the atoms in the second of the doubly degenerate bending mode for CO_2 is identical to the first, but is perpendicular to the plane of the page.)



H_2O symmetric is infrared active
 H_2O asymmetric is infrared active
 H_2O bend is infrared active
 CO_2 symmetric is Raman active
 CO_2 asymmetric is infrared active
 CO_2 bend is infrared active

13. (10 points, extra credit) Roughly speaking, quantum mechanics is relevant when the de Broglie wave length of the particle (h/p) in question is greater than the characteristic size of the system (d).

(a) For a system in thermal equilibrium, write down the thermal average de Broglie wave length.

From page 8-2 in the handbook we know that, for a system in equilibrium, the average kinetic energy is given by $3k_B T/2$, therefore

$$\frac{\langle p^2 \rangle}{2m} = \frac{3}{2} k_B T$$

Therefore, a typical de Broglie wavelength ($\lambda = h/\langle p \rangle$) is

$$\lambda = \frac{h}{\sqrt{3mk_B T}}$$

(b) The lattice spacing in a typical solid is around $d \sim 0.3$ nm. Estimate the temperature below which the unbound electrons in a solid are quantum mechanical.

Quantum mechanics is relevant when $\lambda = h/(\sqrt{3mk_B T}) > d$, which implies that the system temperature T must be

$$T < \frac{h^2}{3mk_B d^2}$$

$$T < \frac{(6.6260693 \times 10^{-34} \text{ J s})^2}{3(9.1093826 \times 10^{-31} \text{ kg})(1.3806505 \times 10^{-23} \text{ J/K})(3 \times 10^{-10} \text{ m})^2} = 1.293 \times 10^5 \text{ K}$$

Therefore, the electrons in a solid are *always* predicted to behave quantum mechanically under conditions typically found.

(c) Below what temperature are the nuclei in a solid quantum mechanical? Use silicon as an example. (The mass of a Si nucleus is $\sim 4.6833 \times 10^{-26}$ kg.)

$$T < \frac{(6.6260693 \times 10^{-34} \text{ J s})^2}{3(4.6833 \times 10^{-26} \text{ kg})(1.3806505 \times 10^{-23} \text{ J/K})(3 \times 10^{-10} \text{ m})^2} = 2.51 \text{ K}$$

Therefore, the nuclei are generally **not** quantum mechanical at temperatures we investigate.