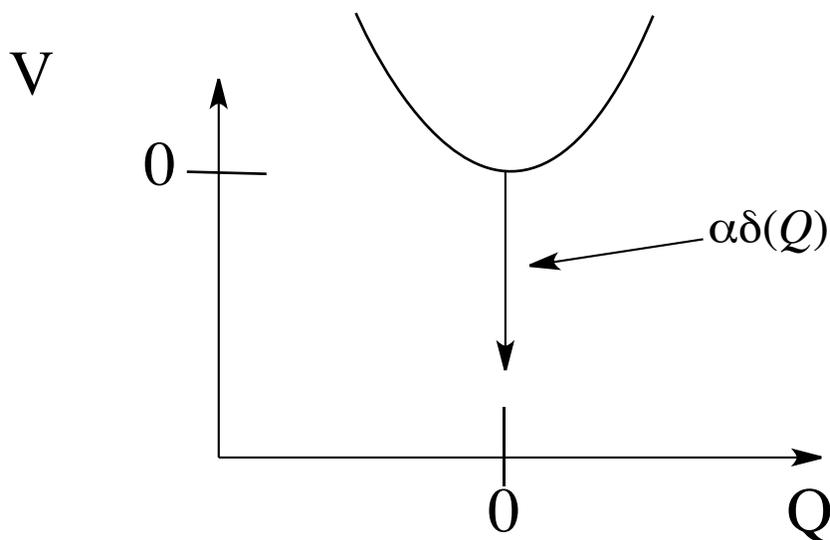MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.61 Physical Chemistry
Fall, 2017

Professor Robert W. Field

FINAL EXAMINATION ANSWERS

Monday, December 18

I.   Effect of a δ-Function at Q = 0   (30 points + 5) on the Energy Levels of a Harmonic Oscillator

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dQ^2} + \frac{1}{2}kQ^2 - \alpha\delta(Q); \quad \alpha > 0$$

$$V(Q) = \frac{1}{2}kQ^2 - \alpha\delta(Q) \text{ looks like this:}$$

A. (6 points)   Without doing any calculation, which energy levels are unaffected by the $-\alpha\delta(Q)$ term?

The odd-v levels (odd symmetry) have a node at $Q = 0$. They are not affected by the $\delta(Q)$ delta-function.

B. (6 points)   Without doing any calculation, are the energy levels that are affected by the $-\alpha\delta(Q)$ term shifted up or down?

The δ-function acts as an extra well, resulting in a stabilization of all of the odd-v/odd-symmetry levels. Another way of answering is that the $E_v^{(1)} = H_{vv}^{(1)}$ term is negative for all odd-v levels, therefore all of these states are lowered in energy. Another answer is that all non-zero matrix elements of $H_{v,v-1}^{(1)}$, appear with a negative energy denominator in

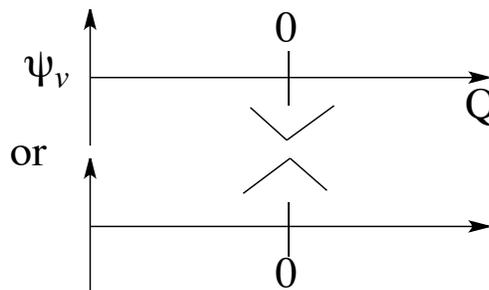$$E_i^{(2)} = \sum_{j \neq i} \frac{\left(H_{ij}\right)^2}{E_i^{(0)} - E_j^{(0)}} \ .$$

C. (6 points)   Without doing any calculation, among the levels that are affected by the $-\alpha\delta(Q)$ term, is the magnitude of the energy shift larger or smaller for a low-v vs. a high-v level?

The energy shift is larger for a low-v level than for a high-v level. This is a general rule for tunneling. Then there is another way of answering. The diagonal and off-diagonal elements of $\alpha\delta(Q)$ are $\dfrac{\alpha^2 |\psi_v(0)\psi_{v'}(0)|^2}{E_v^{(0)} - E_{v'}^{(0)}}$. Since the perturbation term depends on the value of $\psi_{\text{odd-}v}(0)\psi_{\text{odd-}v'}(0)$ and the HO wavefunction have a decreasing with-v amplitude at $Q = 0$ because the kinetic energy and classical |momentum| is largest at $Q = 0$. The $\psi_v(0)$ values decrease with v, so the level shift decreases with v.

D. (12 points)   It is possible to show that $-\alpha\delta(Q)$ causes a discontinuity of $\dfrac{d\psi_v}{dQ}$

at $Q = 0$

$$\left.\frac{d\psi_v}{dQ}\right|_{+0} - \left.\frac{d\psi_v}{dQ}\right|_{-0} = -\frac{2\mu}{\hbar^2}\alpha\psi_v(0)$$

This looks like

Based on the v-dependent magnitude of $\psi_v(Q)$ at $Q = 0$ for the even-v states, justify your answer to part **C**. There are two ways to justify your answer to part **C**: (1) using perturbation theory, or (2) by adjusting the phase of the energy-shifted $\psi_v(Q)$ at the turning points $[Q_\pm,$ where $E_v = V(Q_\pm)]$ so that $\psi(\pm \infty) = 0$.

Your justification of your answer to part **C** should be based on how

the magnitude of the discontinuity in $\dfrac{d\psi}{dQ}$ at $Q = 0$ affects the size of

the energy level shift relative to the energy of the vth harmonic

oscillator level, $\omega_e(v + 1/2)$.

The answers involving perturbation theory have been stated in Part **C**. The answer that deals explicitly with the discontinuity of the derivative of ψ at $Q = 0$ is based on the requirement that $\psi_v(\pm\infty) = 0$. This is achieved when $\psi_v(Q_\pm)$ and $\delta\psi_v \big| \delta Q \big|_{Q=Q_\pm}$ [$Q_\pm$ are the turning points, where $E_v = V(Q_\pm)$] have the unique correct value so that $\psi_v(Q_\pm)$ can satisfy the $Q = \pm\infty$ boundary condition. The $-\alpha\delta(Q)$ form creates a cusp in $\psi_v(\text{odd-}v)$ that has the form of too much accumulation of phase at $E_v^{(0)}$ that is corrected by lowering the energy, thereby removing the extra accumulated phase. If we had a $+\alpha\delta(Q)$ perturbation, the opposite behavior of too little accumulated phase would result and the energy must be increased to compensate.

    E. (5 points *extra credit*)

Derive the equation in part **D** for the discontinuity of $\dfrac{d\psi_v}{dQ}$ by

integrating the Schrödinger equation

$$\lim_{\varepsilon \to 0} \int_{-\varepsilon}^{+\varepsilon} (H\psi - E\psi)\,dQ = 0 \,.$$

$$H\psi = -\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dQ^2} + \frac{1}{2}kQ^2\psi - \alpha\delta(Q)\psi$$

$$(H\psi - E\psi) = 0$$

$$\int_{-\varepsilon}^{\varepsilon} (H\psi - E\psi)\,dQ = 0$$

$$\lim_{Q=|\varepsilon|\to 0} \frac{1}{2}kQ^2\psi = 0$$

$$\lim_{Q=|\varepsilon|\to 0} \alpha\delta(Q)\psi(Q) = \alpha\psi(0)$$

$$\int_{-\varepsilon}^{+\varepsilon} \left[-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dQ^2} - \alpha\psi(0)d - E\psi(0) \right] dQ = 0$$

$$\qquad\qquad\qquad\quad \downarrow \qquad\quad \downarrow$$
$$\qquad\qquad\qquad\quad 0 \qquad\quad 0$$
$$\qquad\quad \psi \text{ is continuous} \quad E \text{ is finite}$$

$$\int_{-\varepsilon}^{+\varepsilon} -\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dQ^2}\,dQ = -\frac{\hbar^2}{2\mu}\left[\frac{d\psi}{dQ}\right]_{-\varepsilon}^{+\varepsilon}$$

II.   Derivation of One Part of the Angular   (25 points) Momentum Commutation Rule

A.   (5 points)   Show that $\left[\hat{A}\hat{B},\hat{C}\right] = \hat{A}\left[\hat{B},\hat{C}\right] + \left[\hat{A},\hat{C}\right]\hat{B}$.

Show [AB,C] = A[B,C] + [A,C]B

A[B,C] = ABC − ACB

[A,C]B = ACB − CAB

A[B,C] + [A,C]B = ABC − CAB

[AB,C] = ABC − CAB

    Q.E.D.

B.   (20 points)

$$\vec{\mathbf{L}} = \vec{\mathbf{r}} \times \vec{\mathbf{p}} = \begin{pmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{pmatrix} = \hat{i}\left(yp_z - zp_y\right) - \hat{j}\left(xp_z - zp_x\right) + \hat{k}\left(xp_y - yp_x\right) \tag{1}$$

$$\left[\mathbf{x},\mathbf{p}_x\right] = i\hbar \tag{2}$$

$$\left[\mathbf{L}_x,\mathbf{L}_y\right] = +i\hbar\mathbf{L}_z \tag{3}$$

    Use equations (1) and (2) to derive equation (3).

$\left[L_x, L_y\right] = +i\hbar L_z$

$L_x = yp_z - zp_y$

$L_y = -xp_z + zp_x$

$L_z = xp_y - yp_x$

$\left[yp_z - zp_y, -xp_z + zp_x\right] = -\left[yp_z, xp_z\right] + \left[yp_z, zp_x\right] + \left[zp_y, xp_z\right] - \left[zp_y, zp_x\right]$

$$= 0 + \left[yp_z, zp_x\right] + \left[zp_y, xp_z\right] + 0$$

$$= y\left[p_z, z\right]p_x + p_y\left[z, p_z\right]x = -i\hbar yp_x + i\hbar p_y x$$

$$= i\hbar\left(p_y x - yp_x\right)$$

Thus $[L_x, L_y] = i\hbar L_z$.

III. Some Perturbation Theory   (25 points)

All electronic properties of a molecule are parametrically dependent on the displacement coordinate, $\mathbf{Q}$. This is part of the Born-Oppenheimer Approximation. We are interested in how the Q-dependence of the generic "A" property is encoded in the E_{vJ} energy levels.

Molecular Constants:

$$E_{vJ}/hc = \omega_e(v+1/2)+\left[B_e - \alpha_e(v+1/2)\right]J(J+1) \tag{1}$$

$$+\left[A_e - \alpha_A(v+1/2) - A_J J(J+1) + A_D J^2(J+1)^2\right]$$

$\mathbf{Q}$ Dependence: $\mathbf{H}/hc = \omega_e(v+1/2)+B(\mathbf{Q})J(J+1)+A(\mathbf{Q})$ $\tag{2}$

$$\mathbf{Q} = \left[\frac{\hbar}{4\pi c\mu\omega_e}\right]^{1/2}\left(\mathbf{a}+\mathbf{a}^\dagger\right) \qquad \left(\omega_e \text{ is in cm}^{-1} \text{ units}\right) \tag{3}$$

$$B(\mathbf{Q}) = B_e\left[1 - 2\mathbf{Q}/R_e + \ldots\right] \qquad \left(B_e \text{ is in cm}^{-1} \text{ units}\right) \tag{4}$$

$$A(\mathbf{Q}) = A_e + \frac{\partial A}{\partial Q}\mathbf{Q} \qquad \left(A_e \text{ is in cm}^{-1} \text{ units}\right) \tag{5}$$

$$\mathbf{H}^{(0)}/hc = \omega_e(v+1/2)+B_e J(J+1)+A_e \tag{6}$$

$$\mathbf{H}^{(1)}/hc = \mathbf{Q}\left[-2\left(B_e/R_e\right)J(J+1)+\frac{\partial A}{\partial Q}\right] \tag{7}$$

Compute the $\mathbf{H}^{(1)}_{v,v+1}$ and $\mathbf{H}^{(1)}_{v,v-1}$ matrix elements and use them to derive the term in $E^{(2)}_{vJ}$ that has the $J(J+1)$ dependence on the J quantum numbers. This is the A_J term in Equation (1).

We need to apply NDPT to $\mathbf{H}^{(1)}$

$\mathbf{H}^{(1)} \propto Q$ and the selection rule for Q is $\Delta v = \pm 1$, so there is no $\mathbf{H}^{(1)}_{v,v} = E^{(1)}_v$ contribution.

$$E_{vJ} = E^{(0)}_{vJ} + 0 + \sum_{v'=v\pm 1}\frac{\left|H_{vv'}\right|^2}{E^{(0)}_{vJ} - E^{(0)}_{v^{-1}J}}$$

$$\left(H^{(1)}_{vv'}\right)^2 = \left(Q_{v,v\pm 1}\right)^2\left[-2\left(B_e/R_e\right)J(J+1)+\frac{\partial A}{\partial Q}\right]^2$$

$$Q^2_{v,v+1} = \left[\frac{\hbar}{4\pi c\mu\omega_e}\right](v+1)$$

$$E^{(0)}_{vJ} - E_{v+1,J} = hc\left[-\omega_e\right]$$

$$Q^2_{v,v-1} = \left[\frac{\hbar}{4\pi c\mu\omega_e}\right]v$$

$$E^{(0)}_{vJ} - E^{(0)}_{v-1,J} = hc\omega_e$$

Put it all together

Answer to Problem III (continued)

$$E_v^{(2)} = \left[\frac{\hbar}{4\pi c\mu\omega_e}\right]\left(-2\left(B_e/R_e\right)J(J+1) + \frac{\partial A}{\partial Q}\right)^2\left[\frac{v+1}{-\hbar c\omega_e} + \frac{v}{\hbar c\omega_e}\right]$$

$$= \left[\frac{\hbar}{4\pi c\mu\omega_e}\right]\left(-2\left(B_e/R_e\right)J(J+1) + \frac{\partial A}{\partial Q}\right)^2\left(-\frac{1}{\hbar c\omega_e}\right)$$

The only term that depends on $J(J + 1)$ is the cross term in the middle factor

$$\left[+4\left(B_e/R_e\right)J^2(J+1)^2 + \left(\frac{\partial A}{\partial Q}\right)^2 - 4\left(\frac{B_e}{R_e}\right)\frac{\partial A}{\partial Q}J(J+1)\right]$$

$$\underset{\text{cross term}}{}$$

$$-A_J = \left[\frac{\hbar}{4\pi c\mu\omega_e}\right]\left[-4\left(B_e/R_e\right)\frac{\partial A}{\partial Q}\right]\left[-\frac{1}{\hbar c\omega_e}\right]$$

IV. IR Spectroscopy Under a Deadline   (50 points)

You have a contract with the Army Research Office (ARO) to determine the equilibrium bond length (r_e), vibrational frequency (ω_e), and electric dipole moment (μ_{e1}) of the electronic ground state of TAt (tritium astatide). Your contract terminates tomorrow and you must write a final report today. Last night, on your desperate final attempt to record the vibration-rotation spectrum of TAt in an electric field of 100,000 Volts/cm, you obtained a spectrum unlike any you had observed previously. You suspect that this spectrum is that of the TAt $v = 1 \leftarrow v = 0$ transition, but you have no additional scheduled experimental time on the hyper-IPECAC facility, which is the only Astatine source ($^{210}At_{85}$ has a half life of 8.3 hours) in the world that is capable of generating the At flux needed for your experiment. Therefore you must write your final report to ARO without doing any further experiments to verify whether your spectrum is that of TAt or some other molecule. The likely other molecules include At_2, T_2, HAt, DAt, HT, and DT (you may ignore all other possibilities here). Your continued funding by ARO depends on the timely submittal of your report, but your career depends on its correctness.

One of your research assistants has provided you with the following possibly useful information:

Atomic Weight			Ionization Potentials		
H	1.00782		H	109,677.581 cm^{-1}	
D	2.01410		F	140,553.5 cm^{-1}	
T	3.01605		Cl	104,991 cm^{-1}	
At	210.0		Br	95,550 cm^{-1}	
			I	84,340 cm^{-1}	
			At	unknown	

"Covalent Radius"		"Ionic Radius"	
H	0.32Å	H$^-$	2.08Å
F	0.72Å	F$^-$	1.36Å
Cl	0.99Å	Cl$^-$	1.81Å
Br	1.14Å	Br$^-$	1.95Å
I	1.33Å	I$^-$	2.16Å
At	1.45Å	At$^-$	unknown

Ground State

		ω_e	R_e	μ_e
HF	$^1\Sigma$	4138.32 cm^{-1}	0.9168 Å	1.8262 Debye
HCl	$^1\Sigma$	2990.95 cm^{-1}	1.2746 Å	1.1085 Debye
HBr	$^1\Sigma$	2648.98 cm^{-1}	1.4144 Å	0.8265 Debye
HI	$^1\Sigma$	2309.01 cm^{-1}	1.6092 Å	0.4477 Debye
HAt	unknown	------	------	-------
F_2	$^1\Sigma_g$	916.64 cm^{-1}	1.4119 Å	-------
Cl_2	$^1\Sigma_g$	559.72 cm^{-1}	1.9879 Å	-------

Br$_2$	$^1\Sigma_g$	325.321 cm^{-1}	2.2811 Å	-------
I$_2$	$^1\Sigma_g$	214.50 cm^{-1}	2.6663 Å	-------
At$_2$	unknown	-------	--------	-------
H$_2$	$^1\Sigma_g$	4401.21 cm^{-1}	0.7414 Å	-------

Some useful conversion formulas (B_e is in cm^{-1}, μ is in atomic mass units, and R_e is in Å, and 1 cm $= 10^8$Å):

$$\text{Reduced Mass} \qquad \mu(XY) = \frac{M_X M_Y}{M_X + M_Y}(\text{amu}) \qquad \omega_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad (\text{cm}^{-1})$$

$$B_e = \frac{1.6858 \times 10^{-15}}{\mu R_e^2} \qquad (\text{cm}^{-1})$$

In the absence of an electric field, the vibrational rotational energy is given by:

$$E_{vJ}/hc = \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + [B_e - \alpha_e(v+1/2)]J(J+1). \quad (\text{cm}^{-1})$$

Before analyzing your spectrum and writing your report to ARO, it would be a good idea to make some predictions about the spectroscopic properties of TAt.

PLEASE NOTE: Many parts of this question can be answered even if you are unable to answer an earlier part.

    A. (4 points)   Use the properties of related atoms and molecules to estimate R_e and ω_e for TAt. Specify the basis for the relationships that you are exploiting.

There are two ways to estimate R_e and ω_e for TAt. One is to use some form of linear extrapolation. The other is to use isotope-substitution relationships of TAt to HAt.

There are no molecular constants for HAt, so you need to get clever. Use linear extrapolation to get from HI to HAt and then use isotope relationships to get from HAt to TAt.

For ω_e and R_e	ω_e(HCl) – ω_e(HBr)	R_e(HCl) – R_e(HBr)
	342 cm^{-1}	–0.140Å
	ω_e(HBr) – ω_e(HI)	R_e(HBr) – R_e(HI)
	339 cm^{-1}	–0.195
estimate	ω_e(HAt) =	R_e(HAt)
	2309 – 336 = 1973	1.609 + 0.250 = 1.859Å

Isotope ratio for ω_e: $\dfrac{\omega_e^h}{\omega_e^\ell} = \left(\dfrac{\mu^\ell}{\mu^h}\right)^{1/2} = \left(\dfrac{\frac{(210)(1)}{211}}{\frac{(210)(3)}{214}}\right) = 0.581$,   and for R_e: $\dfrac{R_e^h}{R_e^\ell} = 1$

ω_e(TAt) $\approx$ (0.581)1973 cm^{-1} = 1146 cm^{-1}
R_e(TAt) $\approx$ 1.859Å = 1.859 $\times$ 10^{-8} cm

B. (6 points)   Compute B_e from your estimated r_e. Let $\alpha_e \approx 0$ and $\omega_e x_e \approx 0$ and calculate the frequencies (in cm^{-1}) of the 3 lowest-J transitions in the P branch and in the R branch of the $v = 1 \leftarrow v = 0$ rotation-vibration band. The P(J) line is the $J - 1 \leftarrow J$ transition and the R(J) line is the $J + 1 \leftarrow J$ transition. The lowest possible J-value in a $^1\Sigma$ state is $J = 0$.

$$B_e = \frac{1.6858 \times 10^{-15}}{(\mu)(1.859 \times 10^{-8})^2} = \frac{1.6858 \times 10^{-15}}{(2.94)(3.45 \times 10^{-16})}$$

$$\mu = \frac{(3)(210)}{213} = 2.94$$

$B_e = 1.862$

$$P(J) = \omega_e + B'(J-1)(J) - B''(J)(J+1)$$
$$= (B' - B'')J^2 - B'J - B''J$$
$$\approx 0J^2 - 2BJ$$

$$R(J) = \omega_e + B'(J+1)(J+2) - B''(J)(J+1)$$
$$= (B' - B'')J^2 + 3B'J + 2B' - B''J$$
$$\approx 0J^2 + 2B'J + 2B'$$

$R(0)$	$\omega_e +$	$2B$	1136.92
$R(1)$	$\omega_e +$	$4B$	1133.34
$R(2)$	$\omega_e +$	$6B$	1129.70
$P(0)$	ω_e	$-2B$	1122.24
$P(1)$	ω_e	$-4B$	1118.42
$P(2)$	ω_e	$-6B$	1114.54

From these assignments, we get
$$2B_e \approx 1136.92 - 1133.34 = 3.58 \text{ cm}^{-1}$$
$$B_e = 1.79 \text{ cm}^{-1}$$
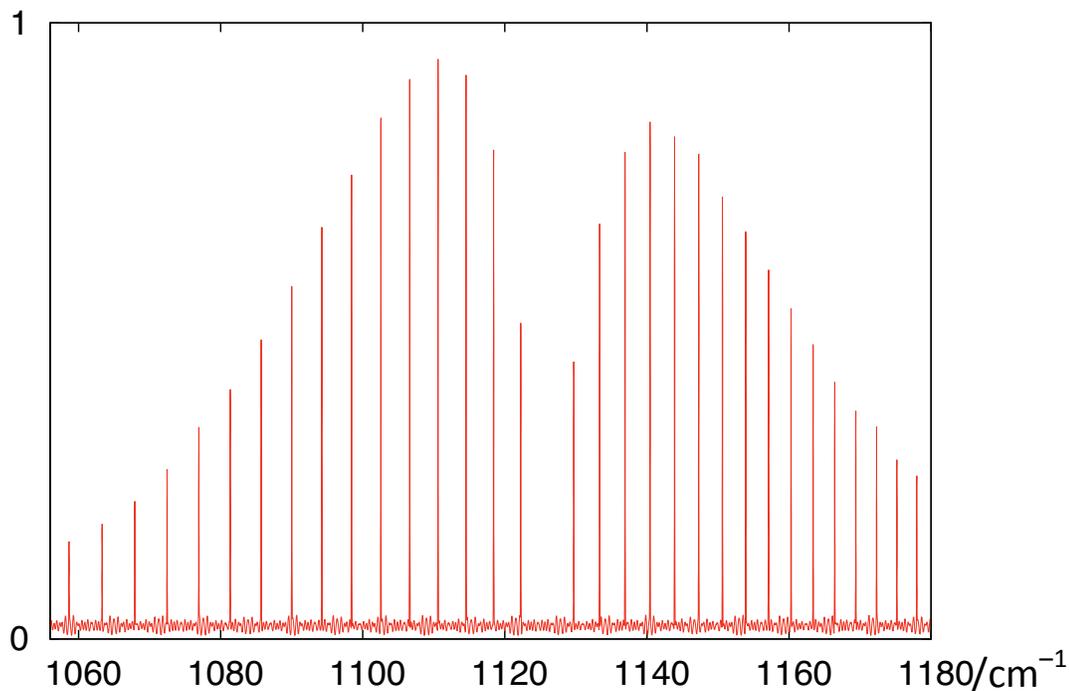$$\omega_e \approx 1136.92 - 3.58 = 1133.34 \text{ cm}^{-1}$$

These are very close to the predicted values
$$\omega_e = 1146 \text{ cm}^{-1} \qquad B_e = 1.862 \text{ cm}^{-1}$$

Looks good for assignment as TAt.

C. (4 points)   Estimate the electric dipole moment, μ_{el}, for TAt, in Debye units. Do you expect the T or the At atom to have a net positive charge? Why?

Your record of the infrared spectrum *below* for what (you hope) is TAt is:

You identify the following lines from the spectrum (all in cm^{-1}):
    1058.66, 1063.32, 1067.92, 1072.46, 1076.93, 1081.35, 1085.71, 1090.01, 1094.25,
    1098.43, 1102.55, 1106.61, 1110.60, 1114.54, 1118.42, 1122.24, 1129.70, 1133.34,
    1136.92, 1140.44, 1143.89, 1147.29, 1150.63, 1153.91, 1157.13, 1160.29, 1163.39,
    1166.43, 1169.40, 1172.32, 1175.18, 1177.98

To estimate μ(TAt) we expect it to be the same as for HAt which we can guestimate by linear extrapolation from HCl, HBr, and HI.

μ(HCl) – μ(HBr)   1.1085D – 0.8265D = 0.282 Debye
μ(HBr) – μ(HI)   0.8265D – 0.4477D = 0.379 Debye

μ(HAt) ≈ 0.4477 – 0.379 – 0.097 ≈ 0.

μ for TAt is likely to be near zero. There is no way to predict whether T or At will have a net positive charge.

D. (10 points)   Assign a few lines of the rotation-vibration spectrum. Two or three lines each in the R and P branches will be sufficient. Assume $\alpha_e \approx 0$ and $\omega_e x_e \approx 0$ and use your assigned lines to determine ω_e and B_e. Could this be TAt?

I have given the low-J assignments in the answer to Part **C**. The key feature to notice is the "zero-gap" between the lines at 1122.24 and 1129.70 cm^{-1}. This gap identifies the lowest-J lines in the R and P branches. It also tells us that the transition is $^1\Sigma$ - $^1\Sigma$, not $^1\Pi$ - $^1\Pi$. The zero gap would be larger for a $^1\Pi$ - $^1\Pi$ transition. There would also be a moderately strong $Q(1)$ line near the middle of the zero-gap.

Looking good for TAt.

E. (4 points)   Which of the molecules At_2, T_2, HAt, DAt, HT, and DT are expected to have electric dipole allowed rotation-vibration spectra? If you are undecided about HT and DT, state your reasons for and against.

HAt, DAt will definitely have a strong electric dipole allowed transition.

At_2 and T_2 definitely will not have any dipole allowed transition.

HT and DT will have a very weak dipole allowed transition, but it will have very large ω_e and B_e constants.

The center of electron charge will not quite coincide with the center of mass. The molecule rotates about the center of mass. There will be a small rotating electric dipole.

F. (4 points)   What is the the minimum necessary spectroscopic information that could be useful in showing that your observed spectrum is **not** due to any of the molecules from part **E** that have an allowed rotation-vibration spectrum? Could your spectrum be due to any of the other likely candidate molecules?

The rotational and vibrational constants for the observed transition are too small for the molecule to be HAt or DAt. This is a huge effect.

The rotational and vibrational constants for HT and DT are vastly too large for a plausible assignment of the observed spectrum to HT or DT. The Stark effect will also be very, very small for HT and DT.

The dipole moment for the putative TAt spectrum will be small, much smaller due to that for TI or DI.

The small μ_e will be an excellent confirmation of the TAt assignment.

For Question IV.G: The $v = 1 \leftarrow v = 0$ spectrum consists of a series of absorption lines following the selection rule $\Delta J = \pm 1$ (R and P branches). In the absence of an external electric field, all $2J + 1$ $M_J$components of each J-level are *exactly degenerate* and the spectrum consists of simple R and P "lines". When a 10^5 V/cm electric field is applied, a new term is added to the Hamiltonian:

$$\widehat{\mathbf{H}}^{\text{Stark}} = \boldsymbol{\varepsilon} \cdot \boldsymbol{\mu} .$$

If this field lies along the laboratory Z-direction, the M_J-degeneracy is lifted. The **only non-zero** integrals involving the Stark-effect Hamiltonian are

$$\int \phi_{J,M_J}^{*} \widehat{\mathbf{H}}^{\text{Stark}} \phi_{J-1,M_J} d\tau = \mathbf{H}_{J,M;J-1,M}^{\text{Stark}} = f \; \mu_{el} \varepsilon_Z \left[\frac{J^2 - M^2}{4J^2 - 1} \right]^{1/2}$$

$$\int \phi_{J,M_J}^{*} \widehat{\mathbf{H}}^{\text{Stark}} \phi_{J+1,M_J} d\tau = \mathbf{H}_{J,M;J+1,M}^{\text{Stark}} = f \; \mu_{el} \varepsilon_Z \left[\frac{(J+1)^2 - M^2}{(2J+1)(2J+3)} \right]^{1/2}$$

where f is a constant, the value of which depends on the units used. If μ_{el} is in Debye (D), ε_z is in Volts/cm, and $\mathbf{H}_{JM;J\pm1,M}^{\text{Stark}}$ is desired in cm^{-1}, the conversion factor is $f = 1.6794 \times 10^{-5}$ [(V/cm)D]$^{-1}$.

At E = 10^5 V/cm, the lines at 1129.70 and 1122.24 cm^{-1} each split into two components separated by 9.0×10^{-3} cm^{-1}. The lines at 1133.34 and 1118.42 cm^{-1} broaden slightly, but no splitting is resolvable. The electric field has no perceptible effect on all of the remaining lines. **See next page for Question IV.G.**

G. (10 points)   Calculate the Stark splitting for a generic diatomic molecule in $J = 1$ of a $^1\Sigma^+$ electronic state. The $M_J = 0$ component is pushed down by $J = 2$, $M_J = 0$ and pushed up by $J = 0$, $M_J = 0$. The $M_J = +1$ and $M_J = -1$ levels are both shifted downward by the same amount by their interaction with $J = 2$, $M_J = 1$, and $M_J = -1$, but there exist no $J = 0$, $M_J = \pm 1$ levels to push these $J = 2$, $J_M = \pm 1$ levels up. Use second-order perturbation theory to express the energy shifts in terms of μ_{el} and B_e (specifically, μ_{el}^2 / B times some J-dependent factors).

The 1129.70 line is R(0) and the 1122.24 line is P(1). One expects both of these lines to split into 2 components because $J = 1$ splits and $J = 0$ only shifts. The 1133.34 line is R(1) and the 1118.42 line is P(2). both of these lines will split into more than 2 components (draw a level diagram) and the Stark splittings of $J = 2$ will be much smaller than in $J = 1$ because of the larger energy denominator for the second-order Stark shift in $J = 2$.

Stark effect for $J = 1$ of a $^1\Sigma^+$ state: $\Delta M = 0$ selection rule for F-field in z-direction.
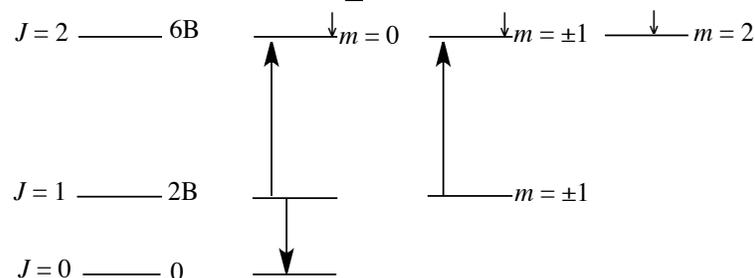
E-field in Z-direction

$$\langle m = 0, J = 0 | \mathbf{H}^{\text{Stark}} | m = 0, J = 1 \rangle = f\mu_{el}\varepsilon_Z \left[\frac{1 - 0}{4 - 1} \right]^{1/2}$$

$$\langle m = 0, J = 1 | \mathbf{H}^{\text{Stark}} | m = 0, J = 2 \rangle = f\mu_{el}\varepsilon_Z \left[\frac{4 - 0}{16 - 1} \right]^{1/2}$$

$$\langle m = \pm 1, J = 1 | \mathbf{H}^{\text{Stark}} | m = \pm 1, J = 2 \rangle = f\mu_{el}\varepsilon_Z \left[\frac{4 - 1}{16 - 1} \right]^{1/2}$$

$0 \quad f^2\mu^2\varepsilon_Z^2 \left[+(1/3)^{1/2}/2B - (4/15)^{1/2}/4B \right]$

$\pm 1 \quad f^2\mu_{el}^2\varepsilon_Z^2 \left[-(3/15)^{1/2}/4B \right]$

$0 \quad f^2\mu_{el}^2\varepsilon_Z^2 \dfrac{[1/3]^{1/2}}{-2B}$

m

$f = (1.6794 \times 10^{-5}) \, [\text{V/cm} \cdot \text{D}]^{-1}$

$\varepsilon = 1 \times 10^5 \, \text{V/cm}$

$J = 1, m = 0 \quad (1.6794 \times 10^{-5})^2 (10^5)^2 \mu^2$

$J = 1, m = \pm 1$

H. (5 points)   Interpret the observed Stark effect and use it to estimate μ_{el}.

The results summarized in **IV.G** are consistent with a barely observable splitting of 9×10^{-3} cm^{-1} in $J = 1$.

This splitting yields $\mu_{el} =$

I. (3 points)   Does the observed Stark effect determine the sign of μ_{el}?

The Stark splitting is a second-order effect and samples only $(\mu_{el})^2$. It cannot yield the sign of μ_{el}.

V.   From $\Psi(x,t)$ to $\rho(t)$ **(35 points)**

$$\Psi(x,t) = c_1(t)\psi_1(x) + c_2(t)\psi_2(x) + c_3(t)\psi_3(x) + c_4(t)\psi_4(x)$$

where $\{\psi_n\}$ are eigenfunctions of a time-independent $\mathbf{H}^{(0)}$. E_n is the eigen-energy associated with the ψ_n eigenfunction

$$|\Psi\rangle \equiv |\mathbf{c}\rangle = \begin{pmatrix} c_1(t) \\ c_2(t) \\ c_3(t) \\ c_4(t) \end{pmatrix}$$

A. (6 points)   Evaluate the following objects in terms of the $\{c_n(t)\}$ and $\{c_n^*(t)\}$.

(i) (2 points) $\langle \mathbf{c}|\mathbf{c}\rangle$

$\langle \mathbf{c}|\mathbf{c}\rangle = \sum_i c_i^* c_i$ a real and positive number.

(ii) (4 points) $|\mathbf{c}\rangle\langle\mathbf{c}|$

$$|\mathbf{c}\rangle\langle\mathbf{c}| = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} \begin{pmatrix} c_1^* & c_2^* & c_3^* & c_4^* \end{pmatrix} = \begin{pmatrix} c_1^*c_1 & c_1c_2^* & c_1c_3^* & c_1c_4^* \\ c_2c_1^* & c_2^*c_2 & c_2c_3^* & c_2c_4^* \\ c_3c_1^* & c_3c_2^* & c_3^*c_3 & c_3c_4^* \\ c_4c_1^* & c_4c_2^* & c_4c_3^* & c_4^*c_4 \end{pmatrix}$$

B. (3 points)   What is an object like $|\mathbf{c}\rangle\langle\mathbf{c}|$ called?

$|\mathbf{c}\rangle\langle\mathbf{c}|$ is called the "density matrix". It denoted as ρ or ρ_c.

C. (4 points)   If $\Psi(x,t)$ is normalized to 1, what combination of $\{c_n(t)\}$ and $\{c_n^*(t)\}$ must be equal to 1?

$\int \Psi^*(x,t)\Psi(x,t)dt = 1$ requires that $\left[c_1c_1^* + c_2c_2^* + c_3c_3^* + c_4c_4^* \right] = 1$.

D. (5 points)   Some notation: $|n\rangle = \psi_n(x)$, i.e. $|3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}$

(i)   (3 points) Evaluate $\langle 3|\mathbf{c}\rangle\langle\mathbf{c}|4\rangle$.

$$\langle 3|\mathbf{c}\rangle = \begin{pmatrix} 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = c_3$$

$$\langle \mathbf{c}|4\rangle = \begin{pmatrix} c_1^* & c_2^* & c_3^* & c_4^* \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = c_4^*$$

$$\langle 3|\mathbf{c}\rangle\langle\mathbf{c}|4\rangle = c_3 c_4^*$$

(ii)   (2 points) What is the relationship of $\langle 3|\mathbf{c}\rangle\langle\mathbf{c}|4\rangle$ to
$$\langle 4|\mathbf{c}\rangle\langle\mathbf{c}|3\rangle ?$$

ρ is Hermitian, this means $\rho^\dagger = \rho$

$$\langle 3|\mathbf{c}\rangle\langle\mathbf{c}|4\rangle = \left[\langle 4|\mathbf{c}\rangle\langle\mathbf{c}|3\rangle\right]^*$$

For questions **E**, **F**, and **G**, simplify to a 2-state system:
$$\Psi(x,t) = c_1 e^{-iE_1 t/\hbar}\psi_1(x) + c_2 e^{-iE_2 t/\hbar}\psi_2(x)$$

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad\qquad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\mathbf{H}|1\rangle = E_1|1\rangle \qquad\qquad \mathbf{H}|2\rangle = E_2|2\rangle$$

E. (6 points)   At $t = 0$, $\Psi(x,0) = |1\rangle$.

(i)   (2 points) Write an expression for $\Psi(x,t)$.

$$\Psi(x,t) = c_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-iE_1 t/\hbar} + c_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{-iE_2 t/\hbar}$$

(ii)   (2 points) Write an expression for $\rho(t)$.

$$\rho(t) = \begin{pmatrix} c_1 c_1^* & c_1 c_2^* e^{i(E_2 - E_1)t/\hbar} \\ c_1^* c_2 e^{-i(E_2 - E_1)t/\hbar} & c_2 c_2^* \end{pmatrix}$$

(iii)   (2 points) Is ρ time-dependent when the system is in a single energy eigenstate?

If $c_1 = 1, c_2 = 0$ or $c_1 = 0, c_2 = 1$ then ρ is time-independent because the off-diagonal elements are zero and the only time-dependence resides in the off-diagonal elements of ρ.

F. (3 points)   Suppose we apply a pulse that terminates at $t = 0$. This pulse results in a flip angle of $\pi/2$ at ω_{12}. Then $\Psi(x,0) = 2^{-1/2} |1\rangle + 2^{-1/2} |2\rangle$.

(i)   (1 points) Give an expression for $\Psi(x,t)$.

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

or

$$= 2^{-1/2} \left[\begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-iE_1 t/\hbar} + \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{-iE_2 t/\hbar} \right]$$

(ii)   (2 points) Write an expression for $\rho(t)$.

$$\rho(t) = \begin{pmatrix} \dfrac{1}{2} & \dfrac{1}{2} e^{-i(E_1 - E_2)t/\hbar} \\ \dfrac{1}{2} e^{+i(E_1 - E_2)t/\hbar} & \dfrac{1}{2} \end{pmatrix}$$

G. (8 points)   When $\Psi(x,t)$ involves a superposition of energy eigenstates:

(i)   (2 points) Are the population terms (diagonal elements) of $\boldsymbol{\rho}$ time-dependent?

The diagonal terms are independent of time.

(ii)   (3 points) Are the coherence terms (off-diagonal elements) of $\boldsymbol{\rho}$ time-dependent?

The off-diagonal (coherence) terms are time-dependent.

(iii) (3 points) If a ρ_{ij} term is time-dependent, at what frequency does it oscillate?

If ρ_{ij} is time-dependent, it oscillates at $\omega_{ij} = \left(E_i - E_j\right)/\hbar$.

VI. Semi-classical Calculation of   (35 points) Vibrational Overlap Integrals in the Diabatic Representation
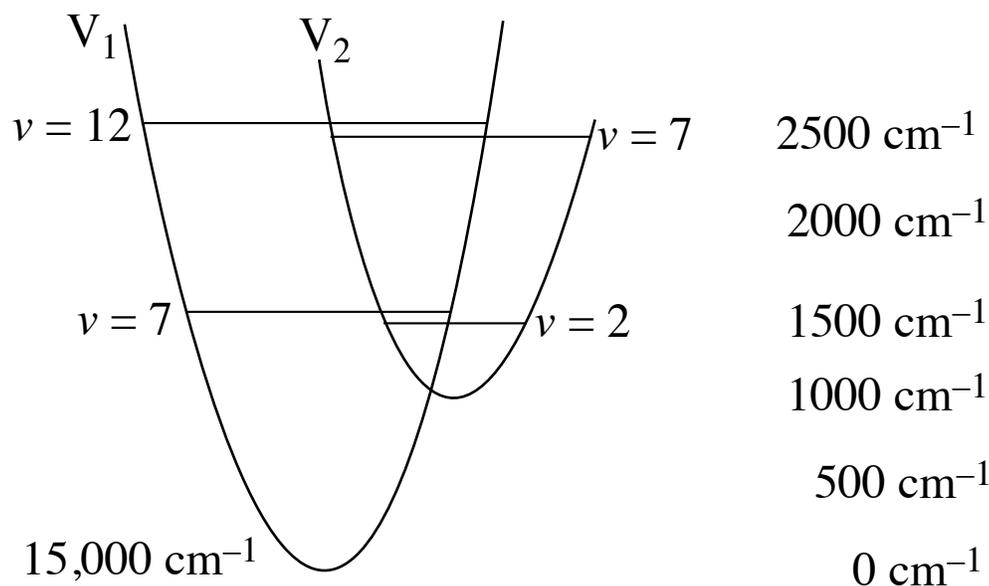
Diabatic potential energy curves can cross. Near-degenerate vibrational states of two crossing diabatic curves, $V_1(R)$ and $V_2(R)$, interact with each other with an interaction matrix element

$$\left\langle e_1, v_1 \middle| \mathbf{H}^{el}(R) \middle| e_2, v_2 \right\rangle = \left\langle e_1 \middle| \mathbf{H}^{el}(R_c) \middle| e_2 \right\rangle \left\langle v_1 \middle| v_2 \right\rangle$$

where

$$\left\langle e_1 \middle| \mathbf{H}^{el}(R_c) \middle| e_2 \right\rangle \equiv H_{12}^{el}(R_c)$$

and R_c is the internuclear distance at which $V_1(R)$ intersects $V_2(R)$. For this problem, V_1 and V_2 are *both* harmonic and *both* have the same value of $\omega_e = 200$ cm^{-1}

$$V_1(R)/hc = 15{,}000 \text{ cm}^{-1} + \frac{1}{2}k\left(R - R_{e1}\right)^2$$

$$V_2(R)/hc = 16{,}000 \text{ cm}^{-1} + \frac{1}{2}k\left(R - R_{e2}\right)^2$$

$k = \omega_e^2 \mu$ (μ is the reduced mass)

$\omega_e = 200$ cm^{-1}

R_c is chosen so that $v_1 = 7$ is near degenerate with $v_2 = 2$ and $v_1 = 12$ is near degenerate with $v_2 = 7$.

The stationary phase point, R_{sp}, is the value of R at which the classical mechanical momentum on V_1 is the same as that on V_2.

A. (5 points)   What is the relationship between R_{sp} nd R_c for the $v_1 = 7$, $v_2 = 2$ pair of levels *and* for the $v_1 = 12$, $v_2 = 7$ pair of levels?

$$R_{sp} (v_1 = 7, v_2 = 2) =$$

$$R_{sp} (v_1 = 12, v_2 = 7) =$$

The stationary phase point for two near-degenerate levels is the curve-crossing point, R_c.

$R_{sp} = R_c$ for both ($v_1 = 7$ and $v_2 = 2$) and ($v_1 = 12$ and $v_2 = 7$).

B. (8 points)

(i)   (5 points) What is the distance between nodes on either side of R_c at $v_1 = 7$ and at $v_2 = 2$? Use the deBroglie relationship between $\lambda(R)$ and the classical mechanical momentum, $p_v(R)$. Express $p_v(R)$ in terms of $\left(E_v - V\left(R_{sp}\right)\right)$ and μ, the reduced mass.

$$\lambda(R) = h/p(R)$$

$$p_v(R) = \left[2\mu\left(E_v - V(R)\right)\right]^{1/2}$$

Distance between nodes is $1/2\ \lambda(R)$.

$$\frac{1}{2}\lambda(R) = \frac{1}{2}\frac{h}{\left[2\mu\left(E_v - V\left(R_c\right)\right)\right]^{1/2}}$$

(ii)   (3 points) Is this node-spacing the same for $v_1 = 12$ and $v_2 = 7$?

For near-degenerate vibrational levels, e.g. $v_1 = 7$ and $v_2 = 2$, $[E_v - V(R_c)]$ is the same, so the node to node distance is the same.

C. (5 points)   For a harmonic oscillator with $\omega_e = 200$ cm^{-1}, what is the vibrational level-independent oscillation period? Express your answer in symbols (ω_e, h, c, etc.).

If $\omega_e = 200$ cm^{-1}

$$hc\omega_e = E_v - E_{v-1}$$

$$\tau = \frac{h}{\Delta E} = \frac{1}{c\omega_e} = \frac{1}{\left(3\times 10^{10}\ \text{cm/s}\right)\left(200\ \text{cm}^{-1}\right)} = \frac{1}{6\times 10^{12}\ \text{s}^{-1}} = 1.67\times 10^{-13}\ s$$

D. (10 points)

(i)   (3 points) What is the probability (expressed in terms of ω_e, h, and $p_v(R)$) of finding the classical oscillator with momentum $p > 0$ between the R_c-centered pair of nodes for $v_1 = 7$ on V_1? [HINT: use semi-classical expressions for wavelength and velocity.]

We want the ratio: $\dfrac{\text{node-to-node time}}{\tau/2}$. Velocity is p/μ, so node-to-node time is $\dfrac{\frac{1}{2}\lambda}{p/\mu}$

For $v_1 = 7$: we want

$$E(v_1 = 7) - V_1(R_c) = hc\left[\left(15{,}000 \text{ cm}^{-1} + (7.5)200\right)\left(-15{,}000 - \frac{1}{2}k\left(R_c - R_{el}\right)^2\right)\right].$$

(ii)   (2 points) Is this probability different from that for $v_2 = 2$ on V_2?

The probabilities are identical because $p_{E_{v_2=2}}(R_c)$ and $\lambda_{E_{v_2=2}}(R_c)$ are the same as $p_{E_{v_1=7}}(R_c)$ and $\lambda_{E_{v_1=7}}(R_c)$.

(iii)   (2 points) How is $\int_{R_c-\lambda/4}^{R_c+\lambda/4}\left|\psi_v(R)\right|^2 dR$ related to the probability in part **D(i)**?

$\int_{R_c-\lambda/4}^{R_c+\lambda/4}\left|\psi_v(R)\right|^2 dR$ is the node-to-node probability in Part **D(i)**.

(iv)   (3 points) Estimate the $\langle v_1 = 7 | v_2 = 2 \rangle$ overlap integral.

$\left|\langle v_1 = 7 | v_2 = 2 \rangle\right|^2$ is the node-to-node probability in the R_c region. This is true because the $\langle v_1 = 7 | v_2 = 2 \rangle$ integral accumulates in the $R = R_c$ node-to-node region.

$$\langle v_1 = 7 | v_2 = 2 \rangle = \left[\int_{R_c-\lambda/4}^{R_c+\lambda/4}\left|\psi_v(R)\right|^2 dR\right]^{1/2}$$

E. (7 points)   Estimate the ratio

$$\frac{\langle v_1 = 12 | v_2 = 7 \rangle}{\langle v_1 = 7 | v_2 = 2 \rangle}$$

$$\left[\text{HINT:} \ \ \frac{p_{v_1=12}^2 (R_c)}{p_{v_1=7}^2 (R_c)} = \frac{1500 \ \text{cm}^{-1}}{500 \ \text{cm}^{-1}} \right]$$

We have two stationary phase regions centered at R_c and with the same distance between nodes. The harmonic oscillator period does not depend on v.

However, the velocity in the $v_1 = 12$, $v_2 = 7$ region is larger than that in the $v_1 = 7$, $v_2 = 2$ region.

$$\frac{p_{v_1=12}^2 (R_c)}{2\mu} = \frac{(2500-1000)^2 \, hc}{2\mu}$$

$$\frac{p_{v_2=7}^2 (R_c)}{2\mu} = \frac{(2500-1000)^2 \, hc}{2\mu}$$

However,

$$\frac{p_{v_1=7}^2 (R_c)}{2\mu} = \frac{(1500-1000)^2 \, hc}{2\mu}$$

$$\frac{p_{v_2=2}^2 (R_c)}{2\mu} = \frac{(1500-1000)^2 \, hc}{2\mu}$$

$$\frac{p_{v_1=12}^2 (R_c)}{p_{v_1=7}^2 (R_c)} = \frac{(1500)^2}{(500)^2}$$

Thus $\dfrac{\langle v_1 = 12 | v_2 = 7 \rangle}{\langle v_1 = 7 | v_2 = 2 \rangle} = \dfrac{1500}{500}$!

Have a Wonderful Holiday Break!!!

USEFUL CONSTANTS and FORMULAS

$1mW = 10^{-3}W = 10^{-3}$ J s^{-1}	$1nm = 10^{-9}m$	$1eV = 1.602 \times 10^{-19}$ J
$h = 6.63 \times 10^{-34}$ J s	$\hbar = 1.05 \times 10^{-34}$ J s	$c = 3.0 \times 10^{8}$ m s^{-1}
$hc = 2.0 \times 10^{-25}$ J m	$m_e = 9.11 \times 10^{-31}$ kg	$e = 1.602 \times 10^{-19}$ C
$\lambda\nu = c$	$\varepsilon_0 = 8.854 \times 10^{-12}$ Cs^2 kg^{-1}m^{-3}	$E = h\nu \qquad \lambda = h/p$
$\ell_n = mr\nu = n\hbar$	$r_n = n^2 a_0$	$a_0 = 5.29 \times 10^{-11}$ m
$\omega = 2\pi c\overline{\omega} = \left[k/\mu\right]^{1/2}$	$c = 3 \times 10^{10}$ cm/s	$x(t) = \sin \omega t$
$E_v = hc\,\overline{\omega}\ (v + 1/2)$		

$$\mathbf{x} = \left[\frac{\hbar}{4\pi c\mu\overline{\omega}}\right]^{1/2} (\mathbf{a}+\mathbf{a}^{\dagger}) \qquad \mathbf{p} = \left[\hbar\pi c\mu\overline{\omega}\right]^{1/2} i(\mathbf{a}^{\dagger} - \mathbf{a})$$

Particle in a box

$$E_n = \frac{n^2\hbar^2}{8ma^2} = \frac{n^2\hbar^2\pi^2}{2ma^2} \qquad \psi_n\left(0 \le x \le a\right) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right)$$

Harmonic Oscillator

$$E_n = \left(n+\frac{1}{2}\right)h\nu = \left(n+\frac{1}{2}\right)\hbar\omega \qquad \alpha = \frac{\sqrt{k\mu}}{\hbar} = \frac{\mu\omega}{\hbar} \qquad \tilde{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}, \quad V = \frac{1}{2}\mu\omega^2 x^2$$

$$\int_{-\infty}^{\infty} e^{-\alpha x^2}dx = \sqrt{\frac{\pi}{\alpha}} \qquad \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2}dx = \sqrt{\frac{\pi}{\alpha}}\frac{1}{2\alpha}$$

$$\int_{-\infty}^{\infty} x^{2n} e^{-\alpha x^2}dx = 2\frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{\alpha}}$$

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \qquad\qquad \psi_1(x) = \frac{1}{\sqrt{2}}\left(\frac{\alpha}{\pi}\right)^{1/4}\left(2\alpha^{1/2}x\right)e^{-\alpha x^2/2}$$

$$\psi_2(x) = \frac{1}{\sqrt{8}}\left(\frac{\alpha}{\pi}\right)^{1/4}\left(4\alpha x^2 - 2\right)e^{-\alpha x^2/2}$$

$$\psi_3(x) = \frac{1}{\sqrt{48}}\left(\frac{\alpha}{\pi}\right)^{1/4}\left(8\alpha^{3/2}x^3 - 12\alpha^{1/2}x\right)e^{-\alpha x^2/2}$$

Raising and lowering operators

$$\hat{\mathbf{a}} = \left(\frac{\mu\omega}{2\hbar}\right)^{1/2}\left(\hat{\mathbf{x}} + i\frac{\hat{\mathbf{p}}}{\mu\omega}\right) \qquad \hat{\mathbf{a}}^{\dagger} = \left(\frac{\mu\omega}{2\hbar}\right)^{1/2}\left(\hat{\mathbf{x}} - i\frac{\hat{\mathbf{p}}}{\mu\omega}\right)$$

$$\hat{\mathbf{x}} = \left(\frac{\hbar}{2\mu\omega}\right)\left(\hat{\mathbf{a}}^{+} + \hat{\mathbf{a}}^{-}\right) \qquad \hat{\mathbf{p}} = i\left(\frac{\hbar\mu\omega}{2}\right)\left(\hat{\mathbf{a}}^{+} - \hat{\mathbf{a}}^{-}\right)$$

$$\hat{\mathbf{a}}^{+}\left|\psi_{n}\right\rangle = \hat{\mathbf{a}}^{+}\left|n\right\rangle = \sqrt{n+1}\left|\psi_{n+1}\right\rangle = \sqrt{n+1}\left|n+1\right\rangle$$

$$\hat{\mathbf{a}}^{-}\left|\psi_{n}\right\rangle = \hat{\mathbf{a}}^{-}\left|n\right\rangle = \sqrt{n}\left|\psi_{n-1}\right\rangle = \sqrt{n}\left|n-1\right\rangle$$

$$\hat{\mathbf{a}}^{+} = \mathbf{a}^{\dagger}, \qquad \mathbf{a}^{-} = \mathbf{a} \qquad \text{(notation)}$$

Hydrogen atom

Three-dimensional operators in spherical coordinates

$$\hat{\mathbf{H}}(r,\theta,\phi) = -\frac{\hbar^{2}}{2\mu}\left[\frac{1}{r^{2}}\frac{\partial}{\partial r}\left(r^{2}\frac{\partial}{\partial r}\right) + \frac{1}{r^{2}\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^{2}\sin^{2}\theta}\frac{\partial^{2}}{\partial\phi^{2}}\right] + V(r,\theta,\phi)$$

$$\hat{L}^{2} = -\hbar^{2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^{2}\theta}\frac{\partial^{2}}{\partial\phi^{2}}\right] \qquad \hat{L}_{z} = -i\hbar\frac{\partial}{\partial\phi}$$

$$U = \frac{-Ze^{2}}{4\pi\varepsilon_{0}r}, \quad E_{n} = \frac{-Z^{2}e^{2}}{8\pi\varepsilon_{0}a_{0}n^{2}} = \frac{-Z^{2}}{2n^{2}}\text{(atomic units)} \ \ n = 1,2,3,\ldots, \quad a_{0} = \frac{4\pi\varepsilon_{0}\hbar^{2}}{\mu e^{2}}$$

Radial integrals

$$\int_{0}^{\infty} x^{n}e^{x/a}dx = n!a^{n+1}$$

H atom spatial wavefunctions (where $\sigma = Zr/a_{0}$. In atomic units $a_{0} = 1$ and $\sigma = Zr$.)

$n = 1$	$\ell = 0$	$m = 0$	$\psi_{100} = \psi_{1s} = \dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z}{a_{0}}\right)^{3/2}e^{-\sigma}$
$n = 2$	$\ell = 0$	$m = 0$	$\psi_{200} = \psi_{2s} = \dfrac{1}{\sqrt{32\pi}}\left(\dfrac{Z}{a_{0}}\right)^{3/2}(2-\sigma)e^{-\sigma/2}$
	$\ell = 1$	$m = 0$	$\psi_{210} = \psi_{2p_{z}} = \dfrac{1}{\sqrt{32\pi}}\left(\dfrac{Z}{a_{0}}\right)^{3/2}\sigma e^{-\sigma/2}\cos\theta$
	$\ell = 1$	$m = \pm 1$	$\psi_{21\pm1} = \dfrac{1}{\sqrt{64\pi}}\left(\dfrac{Z}{a_{0}}\right)^{3/2}\sigma e^{-\sigma/2}\sin\theta e^{\pm i\phi}$
$n = 3$	$\ell = 0$	$m = 0$	$\psi_{300} = \dfrac{1}{81\sqrt{3\pi}}\left(\dfrac{Z}{a_{0}}\right)^{3/2}(27-18\sigma+2\sigma^{2})e^{-\sigma/3} = \psi_{3s}$

Perturbation Theory

$$\widehat{\mathbf{H}} = \widehat{\mathbf{H}}^{(0)} + \widehat{\mathbf{H}}^{(1)} \qquad \psi_n = \psi_n^{(0)} + \psi_n^{(1)} \qquad E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)}$$

$$E_n^{(1)} = \int \psi_n^{(0)*} \widehat{\mathbf{H}}^{(1)} \psi_n^{(0)} d\tau = \left\langle \psi_n^{(0)*} \middle| \widehat{\mathbf{H}}^{(1)} \middle| \psi_n^{(0)} \right\rangle$$

$$\psi_n^{(1)} = \sum_{j \neq n} \frac{\int \psi_j^{(0)*} \widehat{\mathbf{H}}^{(1)} \psi_n^{(0)} d\tau}{E_n^{(0)} - E_j^{(0)}} \psi_j^{(0)} = \sum_{j \neq n} \frac{\left\langle \psi_j^{(0)*} \middle| \widehat{\mathbf{H}}^{(1)} \middle| \psi_n^{(0)} \right\rangle}{E_n^{(0)} - E_j^{(0)}} \psi_j^{(0)}$$

$$E_n^{(2)} = \sum_{j \neq n} \frac{\widehat{H}_{nj}^{(1)} \widehat{H}_{jn}^{(1)}}{E_n^{(0)} - E_j^{(0)}} = E_n^{(2)} = \sum_{j \neq n} \frac{\left\langle n \middle| \widehat{\mathbf{H}}^{(1)} \middle| j \right\rangle \left\langle j \middle| \widehat{\mathbf{H}}^{(1)} \middle| n \right\rangle}{E_n^{(0)} - E_j^{(0)}}$$

Spin operators

$$\mathbf{S}_i = \frac{h}{2}\sigma_i \qquad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\hat{\mathbf{S}}_+ = h\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad \hat{\mathbf{S}}_- = h\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

$$\hat{\mathbf{S}}_\pm = \hat{\mathbf{S}}_x \pm i\hat{\mathbf{S}}_y$$

$$\left| \pm x \right\rangle = \frac{1}{\sqrt{2}} \left(\left| +z \right\rangle \pm \left| -z \right\rangle \right) \qquad \left| \pm y \right\rangle = \frac{1}{\sqrt{2}} \left(\left| +z \right\rangle \pm i \left| -z \right\rangle \right)$$

$$\left| +n \right\rangle = \cos(\theta/2) \left| +z \right\rangle + e^{i\phi} \sin(\theta/2) \left| -z \right\rangle$$

$$\left| -n \right\rangle = \sin(\theta/2) \left| +z \right\rangle - e^{i\phi} \cos(\theta/2) \left| -z \right\rangle$$

Turning points of $V(x)$:

$$V\left(x_\pm(v) \right) = E(v)$$

$$E(v) = hc\overline{\omega}(v + 1/2) = \frac{1}{2} k \left[x_\pm(v) \right]^2$$

5.61 Physical Chemistry
Fall 2017