

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.73 Quantum Mechanics I
Fall, 2002

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Problem Set #4

DUE: At the start of Lecture on Friday, October 4.

Reading: CTDL, pages 94-144.

Problems:

1. RKR and Franck-Condon. Use Robert LeRoy's programs!
<http://theochem.uwaterloo.edu/~leroy/>

For CO, consider the $A^1\Pi$ and $X^1\Sigma^+$ electronic states. The molecular constants (in cm^{-1} units) are:

	<u>$X^1\Sigma^+$</u>	<u>$A^1\Pi$</u>
Y_{00}	0.190	-0.554
Y_{10}	2169.814	1518.24
Y_{20}	-13.288	-19.40
Y_{30}	0.01051	0.766
Y_{01}	1.931281	1.6115
Y_{11}	-0.017504	-0.02325
Y_{21}	5.487×10^{-7}	0.00159
$\mu = 6.85620871 \text{ amu}$		$D_0^0(X) = 89462 \text{ cm}^{-1}$
$T_e = 65075.77 \text{ cm}^{-1}$		$D_0^0(A) = (89462 - 64748) \text{ cm}^{-1} = 24714 \text{ cm}^{-1}$
$R_e(X) = 0.1128323 \text{ nm}$		$R_e(A) = 0.12353 \text{ nm}$

- A. Determine the RKR $V(x)$ potential energy curves for the CO $X^1\Sigma^+$ and $A^1\Pi$ electronic states. Use the following $G(v)$ and $B(v)$ functions

$$G(v) = Y_{00} + Y_{10}(v + 1/2) + Y_{20}(v + 1/2)^2 + Y_{30}(v + 1/2)^3$$

$$B(v) = Y_{01} + Y_{11}(v + 1/2) + Y_{21}(v + 1/2)^2$$

as input to RKR. Ask RKR to calculate turning points for $-1/2 \leq v < 15$ in steps of 0.25.

- B. Calculate overlap integrals, $\langle v' | v'' \rangle$, and Franck Condon factors for all transitions between $v'' = 0$ of the X-state to $0 \leq v' \leq 15$ of the A-state. The Franck-Condon factor is

$$q_{v'v''} = |\langle v' | v'' \rangle|^2$$

where q is the F-C factor, v' and v'' are respectively the vibrational quantum numbers for the upper (A) and lower (X) electronic states.

- C. Sketch what the A–X absorption spectrum would look like. Consider that initially only $v'' = 0$ is populated and represent each vibrational band as a vertical line, at the frequency of the $v' \leftarrow v'' = 0$ transition, with height equal to the F-C factor. [This cartoon of the spectrum ignores the rotational structure of each vibrational band.]
- D. Now create a wavepacket in the $A^1\Pi$ state by using a 1fs laser pulse, centered at $\sim 72,000 \text{ cm}^{-1}$, to *in effect* transfer the $v'' = 0$ wavefunction onto the upper potential. A 1fs pulse has a Fourier Transform width of $\sim 15,000 \text{ cm}^{-1}$.

$$\Psi(x, 0) = \sum_{v'=0,15} \langle v' | v'' = 0 \rangle \psi_{v'}(x) \quad [x = R - R_e]$$

- (i) Plot $|\Psi(x, 0)|^2$ vs. x . Compare it to $|\psi_{v''=0}(x)|^2$.
- (ii) Calculate $\langle E \rangle = E_0$, $\langle x \rangle = x_0$, and $\langle p \rangle = p_0$ at $t = 0$ for this wavepacket. You are going to have to ask LeRoy's programs to calculate a lot (136 each for E , x , and p) of integrals of the form $\langle v_i | \mathbf{H} | v_j \rangle$, $\langle v_i | \mathbf{x} | v_j \rangle$, and $\langle v_i | \mathbf{p} | v_j \rangle$. If this turns out to be too difficult, use harmonic oscillator selection rules ($\Delta v = \pm 1$ for \mathbf{x} and \mathbf{p} , $\Delta v = 0$ for \mathbf{H}) and scaling rules ($\langle v + 1 | \mathbf{x} | v \rangle = (v + 1)^{1/2} \langle 1 | \mathbf{x} | 0 \rangle$ and similarly for \mathbf{p}).

- (iii) Why is $p_0 \approx 0$? Why is $\langle x \rangle_0 \approx R_e(X) - R_e(A) = -0.0107\text{nm}$? Why is $E_0 \approx 65,076 + V_A(R = R_e(X))$?
- (iv) The classical Franck-Condon principle requires that, because an electronic transition is “instantaneous”, the nuclear coordinates and momenta do not change, $\Delta R = 0$ and $\Delta P = 0$. The $\Delta R = 0$ rule requires transitions to be vertical and the $\Delta P = 0$ rule is nearly equivalent to a requirement that strong transitions be from turning point to turning point (where $p(x_{\pm}) = 0$). This means that you can determine E_0 and $\langle x \rangle_0$ from a simple potential curve diagram rather than the lengthy calculation you have done in part D(ii). Compare the values of E_0 and $\langle x \rangle_0$ obtained from the potential curve diagram to those you obtained in a rigorous calculation.

E. Now set up

$$\Psi(x, t) = \sum_{v'=0,15} \langle v' | v''=0 \rangle \psi_{v'}(x) e^{-iE_{v'}t/\hbar}$$

for the wavepacket in part D. You have already calculated $\langle v' | v''=0 \rangle$ in part B. Be sure to retain the signs of the overlap integrals.

- (i) Compute and plot $\langle x \rangle_t$, $\langle p \rangle_t$.
- (ii) What does your plot of $\langle x \rangle_t$ tell you about the width of the upper potential, $V_A(x)$, at $\langle E \rangle_0$? [NOTE that $\langle E \rangle_t = \langle E \rangle_0 = E_0$!] What does it tell you about the shape of $V_A(x)$? What does the maximum value of $\langle p \rangle_t$ tell you about the depth of $V_A(x)$ (i.e. the energy of the minimum of $V_A(x)$)?
- (iii) $\langle x \rangle_t$ and $\langle p \rangle_t$ are not observable directly in a simple time-domain experiment. However, the average oscillation period of $\langle x \rangle_t$ of the wavepacket is easily measurable. Compare the oscillation period, T , defined as $\langle x \rangle_0 = \langle x \rangle_T$, to $\rho(E_0)/c$, where $\rho(E_0)$ is the density of states at E_0 in units of $1/\text{cm}^{-1}$ and c is the speed of light in units of cm/sec . You can obtain $\rho(E_0)$ from $\left. \frac{dG(v)}{dv} \right|_{v=v(E_0)}$ and $v(E_0)$ is obtained from

$$E_{\text{vib}} = E_0 - T_e = G(v(E_0)).$$

- F. Plot the survival probability of your wavepacket

$$P(t) = |\langle \Psi(x,t) | \Psi(x,0) \rangle|^2.$$

You should see a series of partial rephasings, each one smaller than the previous one. Why? Will the system ever rephase nearly perfectly to $P(t) \approx 1.0$? If so, can you predict when this will occur?

- G. There is a lot of useful information in $P(t)$. The initial rate of decay of $P(t)$ is related to $\left. \frac{dV(x)}{dx} \right|_{x=x_0}$ because the force on the wavepacket is -1 times the gradient of $V(x)$. In order to relate the initial decay rate of $P(t)$, via classical mechanics, to the gradient of the potential at x_0 , we need to define a semi-classical length of the wavepacket so that we can imagine the wavepacket moving away from perfect overlap with itself at $t = 0$ and use this to define a time-dependent overlap probability. Use the distance of the first internal node of $\psi_{v(E_0)}(x)$ from x_0 as this wavepacket length. What is the value of $P(t)$ when a classical mechanical particle has moved from x_0 to the position of the first node of $\psi_{v(E_0)}(x)$. You can approximate $V(x)$ as linear at x_0 . This provides a universal relationship between $\left. \frac{dV}{dx} \right|_{x_0}$ and the decay rate of $P(t)$. Using this relationship, the slope of an excited potential curve may be experimentally determined at $R_c(x)$ from the observed $\left. \frac{dP}{dt} \right|_{t=0}$.

- H. The ratio of $P(t)$ values at the second and first partial recurrences of the wavepacket, $P(T_2)/P(T_1)$, provides information about the ratio of the anharmonicity of the potential to the average vibrational frequency at E_0 . For a $G(v)$ function truncated to

$$G(v) = Y_{10}(v + 1/2) + Y_{20}(v + 1/2)^2$$

$$\rho(v) = Y_{10} + 2Y_{20}(v + 1/2).$$

Thus, for a wavepacket with average excitation energy E_0 , $P(T_2)/P(T_1)$ is going to be related to the ratio

$$\frac{\left. \frac{d^2G}{dv^2} \right|_{v=v(E_0)}}{\left. \frac{dG}{dv} \right|_{v=v(E_0)}} \approx \frac{2Y_{20}}{Y_{10} + 2Y_{20}(v + 1/2)}.$$

Since you determine $Y_{10} + 2Y_{20}[v(E_0) + 1/2]$ from the oscillation period of $P(t)$ determined in part E(iii), you can determine the anharmonicity constant from $P(T_2)/P(T_1)$. From the known values of Y_{10} , Y_{20} , and $v(E_0)$ and your empirical value for $P(T_2)/P(T_1)$, obtain a value for the universal proportionality factor relating $P(T_2)/P(T_1)$ to Y_{10} and Y_{20} .

- I. What would $|\Psi(x,0)|^2$ look like if you had started the system initially in $v'' = 1$ instead of $v'' = 0$? Would this two-lobed initial preparation make $P(t)$ have a more complicated appearance? Explain. Speculate about the evolution of $|\Psi(x,t)|^2$ for such a preparation. [HINT: think in terms of two wavepackets, each with its own values of $\langle x \rangle_0$, $\langle p \rangle_0$, and $\langle E \rangle_0$.] Can you guess what these initial values are and how the center position and momentum of these two wavepackets would sample $V_A(x)$?
2. CTDL, page 203, #1. This is a beautiful introduction to “density matrices”.