

Section 5 Exercises, Problems, and Solutions

Exercises:

1. Time dependent perturbation theory provides an expression for the radiative lifetime of an excited electronic state, given by τ_R :

$$\tau_R = \frac{3\hbar^4 c^3}{4(E_i - E_f)^3 |\mu_{fi}|^2},$$

where i refers to the excited state, f refers to the lower state, and μ_{fi} is the transition dipole.

a. Evaluate the z-component of the transition dipole for the $2p_z \rightarrow 1s$ transition in a hydrogenic atom of nuclear charge Z , given:

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}, \text{ and } \psi_{2p_z} = \frac{1}{4\sqrt{2}} \left(\frac{Z}{a_0}\right)^{5/2} r \cos\theta e^{-Zr/2a_0}.$$

Express your answer in units of ea_0 .

b. Use symmetry to demonstrate that the x- and y-components of μ_{fi} are zero, i.e.

$$\langle 2p_z | e x | 1s \rangle = \langle 2p_z | e y | 1s \rangle = 0.$$

c. Calculate the radiative lifetime τ_R of a hydrogenlike atom in its $2p_z$ state. Use the relation $e^2 = \frac{\hbar^2}{m_e a_0}$ to simplify your results.

2. Consider a case in which the complete set of states $\{ |k\rangle \}$ for a Hamiltonian is known.

a. If the system is initially in the state m at time $t=0$ when a constant perturbation V is suddenly turned on, find the probability amplitudes $C_k^{(2)}(t)$ and $C_m^{(2)}(t)$, to second order in V , that describe the system being in a different state k or the same state m at time t .

b. If the perturbation is turned on adiabatically, what are $C_k^{(2)}(t)$ and $C_m^{(2)}(t)$?

Here, consider that the initial time is $t_0 \rightarrow -\infty$, and the potential is $V e^{-\lambda t}$, where the positive parameter λ is allowed to approach zero $\lambda \rightarrow 0^+$ in order to describe the adiabatically (i.e., slowly) turned on perturbation.

c. Compare the results of parts a. and b. and explain any differences.

d. Ignore first order contributions (assume they vanish) and evaluate the transition rates $\frac{d}{dt} |C_k^{(2)}(t)|^2$ for the results of part b. by taking the limit $\lambda \rightarrow 0^+$, to obtain the adiabatic results.

3. If a system is initially in a state m , conservation of probability requires that the total probability of transitions out of state m be obtainable from the decrease in the probability of being in state m . Prove this to the lowest order by using the results of exercise 2, i.e.

$$\text{show that: } |C_m|^2 = 1 - \sum_k |C_k|^2.$$

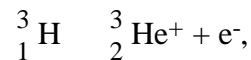
$$\sum_k |C_k|^2$$

Problems:

1. Consider an interaction or perturbation which is carried out suddenly (instantaneously, e.g., within an interval of time t which is small compared to the natural period ω_{nm}^{-1} corresponding to the transition from state m to state n), and after that is turned off adiabatically (i.e., extremely slowly as $V \propto e^{-t}$). The transition probability in this case is given as:

$$T_{nm} = \frac{|\langle n|V|m\rangle|^2}{\hbar^2 \omega_{nm}^2}$$

where V corresponds to the maximum value of the interaction when it is turned on. This formula allows one to calculate the transition probabilities under the action of sudden perturbations which are small in absolute value whenever perturbation theory is applicable. Let's use this "sudden approximation" to calculate the probability of excitation of an electron under a sudden change of the charge of the nucleus. Consider the reaction:



and assume the tritium atom has its electron initially in a $1s$ orbital. a. Calculate the transition probability for the transition $1s \rightarrow 2s$ for this reaction using the above formula for the transition probability.

b. Suppose that at time $t = 0$ the system is in a state which corresponds to the wavefunction ψ_m , which is an eigenfunction of the operator H_0 . At $t = 0$, the sudden change of the Hamiltonian occurs (now denoted as H and remains unchanged). Calculate the same $1s \rightarrow 2s$ transition probability as in part a., only this time as the square of the magnitude of the coefficient, $A_{1s,2s}$ using the expansion:

$$\psi(r,0) = \psi_m(r) = \sum_n A_{nm} \psi_n(r), \text{ where } A_{nm} = \int \psi_m(r) \psi_n^*(r) d^3r$$

Note, that the eigenfunctions of H are ψ_n with eigenvalues E_n . Compare this "exact" value with that obtained by perturbation theory in part a.

2. The methyl iodide molecule is studied using microwave (pure rotational) spectroscopy. The following integral governs the rotational selection rules for transitions labeled $J, M, K \rightarrow J', M', K'$:

$$I = \langle D_{M'K'}^{J'} | \mu | D_{MK}^J \rangle.$$

The dipole moment μ lies along the molecule's C_3 symmetry axis. Let the electric field of the light define the lab-fixed Z -direction.

a. Using the fact that $\cos \theta = D_{00}^{1*}$, show that

$$I = 8 \mu^2 (-1)^{M+K} \begin{matrix} J' & 1 & J \\ M & 0 & M \end{matrix} \begin{matrix} J' & 1 & J \\ K & 0 & K \end{matrix} \begin{matrix} M'M \\ K'K \end{matrix}$$

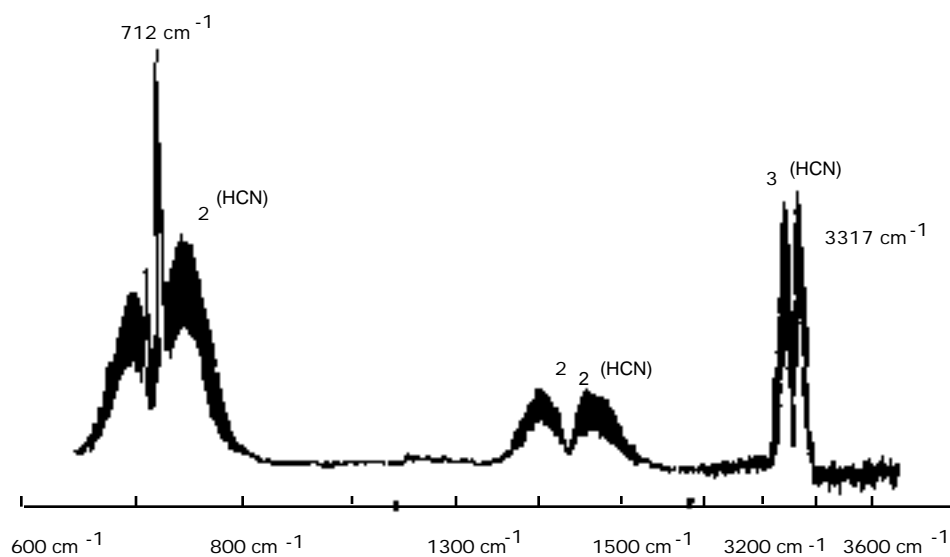
b. What restrictions does this result place on $J = J' - J$? Explain physically why the K quantum number can not change.

3. Consider the molecule BO .

a. What are the total number of possible electronic states which can be formed by combination of ground state B and O atoms?

- b. What electron configurations of the molecule are likely to be low in energy? Consider all reasonable orderings of the molecular orbitals. What are the states corresponding to these configurations?
- c. What are the bond orders in each of these states?
- d. The true ground state of BO is 2 . Specify the +/- and u/g symmetries for this state.
- e. Which of the excited states you derived above will radiate to the 2 ground state? Consider electric dipole, magnetic dipole, and electric quadrupole radiation.
- f. Does ionization of the molecule to form a cation lead to a stronger, weaker, or equivalent bond strength?
- g. Assuming that the energies of the molecular orbitals do not change upon ionization, what are the ground state, the first excited state, and the second excited state of the positive ion?
- h. Considering only these states, predict the structure of the photoelectron spectrum you would obtain for ionization of BO.

4.



The above figure shows part of the infrared absorption spectrum of HCN gas. The molecule has a CH stretching vibration, a bending vibration, and a CN stretching vibration.

- Are any of the vibrations of linear HCN degenerate?
- To which vibration does the group of peaks between 600 cm^{-1} and 800 cm^{-1} belong?
- To which vibration does the group of peaks between 3200 cm^{-1} and 3400 cm^{-1} belong?
- What are the symmetries (, ,) of the CH stretch, CN stretch, and bending vibrational motions?
- Starting with HCN in its 0,0,0 vibrational level, which fundamental transitions would be infrared active under parallel polarized light (i.e., z-axis polarization):

- i. 000 001?
- ii. 000 100?
- iii. 000 010?

f. Which transitions would be active when perpendicular polarized light is used?
 g. Why does the 712 cm⁻¹ transition have a Q-branch, whereas that near 3317 cm⁻¹ has only P- and R-branches?

Solutions

Exercises:

1. a. Evaluate the z-component of μ_{fi} :

$$\mu_{fi} = \langle 2p_z | e r \cos \theta | 1s \rangle, \text{ where } 1s = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}, \text{ and } 2p_z = \frac{1}{4\sqrt{2}} \left(\frac{Z}{a_0} \right)^{5/2} r \cos \theta e^{-Zr/2a_0}.$$

$$\begin{aligned} \mu_{fi} &= \frac{1}{4\sqrt{2}} \left(\frac{Z}{a_0} \right)^{5/2} \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \langle r \cos \theta e^{-Zr/2a_0} | e r \cos \theta e^{-Zr/a_0} \rangle \\ &= \frac{1}{4\sqrt{2}} \left(\frac{Z}{a_0} \right)^4 \langle r \cos \theta e^{-Zr/2a_0} | e r \cos \theta e^{-Zr/a_0} \rangle \\ &= \frac{e}{4\sqrt{2}} \left(\frac{Z}{a_0} \right)^4 \int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} r^2 e^{-Zr/2a_0} e^{-Zr/a_0} \cos^2 \theta \\ &= \frac{e}{4\sqrt{2}} \left(\frac{Z}{a_0} \right)^4 \int_0^\infty r^4 e^{-3Zr/2a_0} dr \int_0^\pi \sin \theta \cos^2 \theta d\theta \end{aligned}$$

Using integral equation 4 to integrate over r and equation 17 to integrate over θ we obtain:

$$\begin{aligned} &= \frac{e}{4\sqrt{2}} \left(\frac{Z}{a_0} \right)^4 \frac{4!}{3Z^5} \frac{-1}{3} \int_0^\pi \cos^3 \theta d\theta \\ &= \frac{e}{4\sqrt{2}} \left(\frac{Z}{a_0} \right)^4 \frac{2^5 a_0^5 4!}{3^5 Z^5} \frac{-1}{3} ((-1)^3 - (1)^3) \\ &= \frac{e}{\sqrt{2}} \frac{2^8 a_0}{3^5 Z} = \frac{ea_0}{Z} \frac{2^8}{\sqrt{2} 3^5} = 0.7449 \frac{ea_0}{Z} \end{aligned}$$

b. Examine the symmetry of the integrands for $\langle 2p_z | e^x | 1s \rangle$ and $\langle 2p_z | e^y | 1s \rangle$. Consider reflection in the xy plane:

Function	Symmetry
$2p_z$	-1
x	+1
1s	+1
y	+1

Under this operation the integrand of $\langle 2p_z | e^x | 1s \rangle$ is $(-1)(1)(1) = -1$ (it is antisymmetric) and hence $\langle 2p_z | e^x | 1s \rangle = 0$.

Similarly, under this operation the integrand of $\langle 2p_z | e^y | 1s \rangle$ is $(-1)(1)(1) = -1$ (it is also antisymmetric) and hence $\langle 2p_z | e^y | 1s \rangle = 0$.

$$c. \quad R = \frac{3\hbar^4 c^3}{4(E_i - E_f)^3 |\mu_{fi}|^2},$$

$$E_i = E_{2p_z} = -\frac{1}{4} Z^2 \frac{e^2}{2a_0}$$

$$E_f = E_{1s} = -Z^2 \frac{e^2}{2a_0}$$

$$E_i - E_f = \frac{3}{8} \frac{e^2}{a_0} Z^2$$

Making the substitutions for $E_i - E_f$ and $|\mu_{fi}|$ in the expression for R we obtain:

$$R = \frac{3\hbar^4 c^3}{4 \left(\frac{3}{8} \frac{e^2}{a_0} Z^2 \right)^3 \left(\frac{ea_0}{Z} \frac{2^8}{\sqrt{2} 3^5} \right)^2},$$

$$= \frac{3\hbar^4 c^3}{4 \frac{3^3}{8^3} \frac{e^6}{a_0^3} Z^6 \frac{e^2 a_0^2}{Z^2} \frac{2^{16}}{(2)3^{10}}},$$

$$= \frac{\hbar^4 c^3 3^8 a_0}{e^8 Z^4 2^8},$$

Inserting $e^2 = \frac{\hbar^2}{m_e a_0}$ we obtain:

$$R = \frac{\hbar^4 c^3 3^8 a_0 m_e^4 a_0^4}{\hbar^8 Z^4 2^8} = \frac{3^8 c^3 a_0^5 m_e^4}{2^8 \hbar^4 Z^4}$$

$$= 25.6289 \frac{c^3 a_0^5 m_e^4}{\hbar^4 Z^4}$$

$$= 25,6289 \frac{1}{Z^4} \times \frac{(2.998 \times 10^{10} \text{ cm sec}^{-1})^3 (0.529177 \times 10^{-8} \text{ cm})^5 (9.109 \times 10^{-28} \text{ g})^4}{(1.0546 \times 10^{-27} \text{ g cm}^2 \text{ sec}^{-1})^4}$$

$$= 1.595 \times 10^{-9} \text{ sec} \times \frac{1}{Z^4}$$

So, for example:

Atom	R
H	1.595 ns
He ⁺	99.7 ps
Li ⁺²	19.7 ps
Be ⁺³	6.23 ps
Ne ⁺⁹	159 fs

2. a. $H = H_0 + H'(t)$, $H'(t) = V(t)$, $H_0 \psi_k = E_k \psi_k$, $E_k = E_k/\hbar$

$$i\hbar \frac{d}{dt} \psi = H \psi$$

let $\psi(r,t) = \sum_j c_j(t) \psi_j e^{-i E_j t/\hbar}$ and insert into the above expression:

$$i\hbar \sum_j \dot{c}_j \psi_j e^{-i E_j t/\hbar} - \sum_j c_j E_j \psi_j e^{-i E_j t/\hbar} = i\hbar \sum_j c_j(t) e^{-i E_j t/\hbar} (H_0 + H'(t)) \psi_j$$

$$i\hbar \sum_j \dot{c}_j \psi_j e^{-i E_j t/\hbar} + \sum_j c_j E_j \psi_j e^{-i E_j t/\hbar} - \sum_j c_j E_j \psi_j e^{-i E_j t/\hbar} - \sum_j c_j H'(t) \psi_j e^{-i E_j t/\hbar} = 0$$

$$i\hbar \sum_j \dot{c}_j \langle m | \psi_j \rangle - \sum_j c_j \langle m | H'(t) | \psi_j \rangle e^{-i E_j t/\hbar} = 0$$

$$i\hbar \dot{c}_m e^{-i E_m t/\hbar} = \sum_j c_j H'_{mj} e^{-i E_j t/\hbar}$$

So,

$$c_m = \frac{1}{i\hbar} \sum_j c_j H'_{mj} e^{-i(E_j - E_m)t/\hbar}$$

Going back a few equations and multiplying from the left by ψ_k instead of ψ_m we obtain:

$$i\hbar \sum_j \dot{c}_j \langle k | \psi_j \rangle - \sum_j c_j \langle k | H'(t) | \psi_j \rangle e^{-i E_j t/\hbar} = 0$$

$$i\hbar \dot{c}_k e^{-i E_k t/\hbar} = \sum_j c_j H'_{kj} e^{-i E_j t/\hbar}$$

So,

$$c_k = \frac{1}{i\hbar} \sum_j c_j H'_{kj} e^{-i(jk)t}$$

Now, let:

$$c_m = c_m^{(0)} + c_m^{(1)} + c_m^{(2)} + \dots$$

$$c_k = c_k^{(0)} + c_k^{(1)} + c_k^{(2)} + \dots$$

and substituting into above we obtain:

$$c_m^{(0)} + c_m^{(1)} + c_m^{(2)} + \dots = \frac{1}{i\hbar} \sum_j [c_j^{(0)} + c_j^{(1)} + c_j^{(2)} + \dots] H'_{mj} e^{-i(jm)t}$$

first order:

$$c_m^{(0)} = 0 \quad c_m^{(0)} = 1$$

second order:

$$c_m^{(1)} = \frac{1}{i\hbar} \sum_j c_j^{(0)} H'_{mj} e^{-i(jm)t}$$

(n+1)st order:

$$c_m^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{mj} e^{-i(jm)t}$$

Similarly:

first order:

$$c_k^{(0)} = 0 \quad c_k^{(0)} = 0$$

second order:

$$c_k^{(1)} = \frac{1}{i\hbar} \sum_j c_j^{(0)} H'_{kj} e^{-i(jk)t}$$

(n+1)st order:

$$c_k^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{kj} e^{-i(jk)t}$$

So,

$$c_m^{(1)} = \frac{1}{i\hbar} c_m^{(0)} H'_{mm} e^{-i(mm)t} = \frac{1}{i\hbar} H'_{mm}$$

$$c_m^{(1)}(t) = \frac{1}{i\hbar} \int_0^t dt' V_{mm} = \frac{V_{mm}t}{i\hbar}$$

and similarly,

$$c_k^{(1)} = \frac{1}{i\hbar} c_m^{(0)} H'_{km} e^{-i(km)t} = \frac{1}{i\hbar} H'_{km} e^{-i(km)t}$$

$$c_k^{(1)}(t) = \frac{1}{i\hbar} \int_0^t dt' V_{km} e^{-i(km)t'} = \frac{V_{km}}{i\hbar} [e^{-i(km)t} - 1]$$

$$c_m^{(2)} = \frac{1}{i\hbar} \sum_j c_j^{(1)} H'_{mj} e^{-i(\epsilon_j - \epsilon_m)t}$$

$$c_m^{(2)} = \sum_j \frac{1}{i\hbar} \frac{V_{jm}}{\hbar} [e^{-i(\epsilon_j - \epsilon_m)t} - 1] H'_{mj} e^{-i(\epsilon_j - \epsilon_m)t} + \frac{1}{i\hbar} \frac{V_{mm}t}{\hbar} H'_{mm}$$

$$c_m^{(2)} = \sum_j \frac{1}{i\hbar} \frac{V_{jm}V_{mj}}{\hbar} \int_0^t dt' e^{-i(\epsilon_j - \epsilon_m)t'} [e^{-i(\epsilon_j - \epsilon_m)t'} - 1] - \frac{V_{mm}V_{mm}}{\hbar^2} \int_0^t t' dt'$$

$$= \sum_j \frac{V_{jm}V_{mj}}{\hbar^2} \int_0^t dt' [1 - e^{-i(\epsilon_j - \epsilon_m)t'}] - \frac{|V_{mm}|^2}{\hbar^2} \frac{t^2}{2}$$

$$= \sum_j \frac{V_{jm}V_{mj}}{\hbar^2} t - \frac{e^{-i(\epsilon_j - \epsilon_m)t} - 1}{-i(\epsilon_j - \epsilon_m)} - \frac{|V_{mm}|^2}{\hbar^2} \frac{t^2}{2}$$

$$= \sum_j \frac{V_{jm}V_{mj}}{\hbar^2} (e^{-i(\epsilon_j - \epsilon_m)t} - 1) + \sum_j \frac{V_{jm}V_{mj}}{\hbar^2} t - \frac{|V_{mm}|^2}{2\hbar^2} t^2$$

Similarly,

$$c_k^{(2)} = \frac{1}{i\hbar} \sum_j c_j^{(1)} H'_{kj} e^{-i(\epsilon_j - \epsilon_k)t}$$

$$= \sum_j \frac{1}{i\hbar} \frac{V_{jm}}{\hbar} [e^{-i(\epsilon_j - \epsilon_m)t} - 1] H'_{kj} e^{-i(\epsilon_j - \epsilon_k)t} +$$

$$\frac{1}{i\hbar} \frac{V_{mm}t}{\hbar} H'_{km} e^{-i(\epsilon_m - \epsilon_k)t}$$

$$c_k^{(2)}(t) = \sum_j \frac{V_{jm}V_{kj}}{\hbar^2} \int_0^t dt' e^{-i(\epsilon_j - \epsilon_k)t'} [e^{-i(\epsilon_j - \epsilon_m)t'} - 1]$$

$$- \frac{V_{mm}V_{km}}{\hbar^2} \int_0^t t' dt' e^{-i(\epsilon_m - \epsilon_k)t'}$$

$$= \sum_j \frac{V_{jm}V_{kj}}{\hbar^2} \frac{e^{-i(\epsilon_j - \epsilon_m)t} - 1}{-i(\epsilon_j - \epsilon_m)} - \frac{e^{-i(\epsilon_m - \epsilon_k)t} - 1}{-i(\epsilon_m - \epsilon_k)}$$

$$- \frac{V_{mm}V_{km}}{\hbar^2} e^{-i(\epsilon_m - \epsilon_k)t} \frac{t}{-i(\epsilon_m - \epsilon_k)} - \frac{1}{-(i(\epsilon_m - \epsilon_k))^2} t$$

$$= \sum_j \frac{V_{jm}V_{kj}}{\hbar^2} \frac{e^{-i(\epsilon_j - \epsilon_m)t} - 1}{\epsilon_j - \epsilon_m} - \frac{e^{-i(\epsilon_m - \epsilon_k)t} - 1}{\epsilon_m - \epsilon_k}$$

$$\begin{aligned}
& + \frac{V_{mm}V_{km}}{\hbar^2} e^{-i(mk)t} \frac{t}{i} - \frac{1}{mk} \frac{t}{0} \\
= & \sum_j \frac{V_{jm}V_{kj}}{E_m - E_j} \frac{e^{-i(mk)t} - 1}{E_m - E_k} - \frac{e^{-i(jk)t} - 1}{E_j - E_k} \\
& + \frac{V_{mm}V_{km}}{\hbar(E_m - E_k)} e^{-i(mk)t} \frac{t}{i} - \frac{1}{mk} + \frac{1}{mk}
\end{aligned}$$

So, the overall amplitudes c_m , and c_k , to second order are:

$$\begin{aligned}
c_m(t) = & 1 + \frac{V_{mm}t}{i\hbar} + \sum_j \frac{V_{jm}V_{mj}}{i\hbar(E_m - E_j)} t + \\
& \sum_j \frac{V_{jm}V_{mj}}{\hbar^2(E_m - E_j)^2} (e^{-i(jm)t} - 1) - \frac{|V_{mm}|^2 t^2}{2\hbar^2} \\
c_k(t) = & \frac{V_{km}}{(E_m - E_k)} [e^{-i(mk)t} - 1] + \\
& \frac{V_{mm}V_{km}}{(E_m - E_k)^2} [1 - e^{-i(mk)t}] + \frac{V_{mm}V_{km}}{(E_m - E_k)} \frac{t}{i\hbar} e^{-i(mk)t} + \\
& \sum_j \frac{V_{jm}V_{kj}}{E_m - E_j} \frac{e^{-i(mk)t} - 1}{E_m - E_k} - \frac{e^{-i(jk)t} - 1}{E_j - E_k}
\end{aligned}$$

b. The perturbation equations still hold:

$$c_m^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{mj} e^{-i(jm)t} ; c_k^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{kj} e^{-i(jk)t}$$

So, $c_m^{(0)} = 1$ and $c_k^{(0)} = 0$

$$c_m^{(1)} = \frac{1}{i\hbar} H'_{mm} t$$

$$c_m^{(1)} = \frac{1}{i\hbar} \int_0^t V_{mm} dt' e^{-i(mm)t'} = \frac{V_{mm}e^{-i(mm)t}}{i\hbar}$$

$$c_k^{(1)} = \frac{1}{i\hbar} H'_{km} e^{-i(mk)t}$$

$$\begin{aligned}
c_k^{(1)} = & \frac{1}{i\hbar} \int_0^t V_{km} dt' e^{-i(mk)t'} = \frac{V_{km}}{i\hbar(-i(mk))} [e^{-i(mk)t} - 1] \\
= & \frac{V_{km}}{E_m - E_k + i\hbar} [e^{-i(mk)t} - 1]
\end{aligned}$$

$$c_m^{(2)} = \sum_j \frac{1}{i\hbar} \frac{V_{jm}}{E_m - E_j + i\hbar} e^{-i(mj)t} V_{mj} e^{-i(jm)t} +$$

$$\begin{aligned}
c_m^{(2)} &= \int_j^m \frac{1}{i\hbar} \frac{V_{jm}V_{mj}}{E_m - E_j + i\hbar} e^{2t} dt' - \frac{|V_{mm}|^2}{\hbar^2} e^{2t} dt' \\
&= \int_j^m \frac{V_{jm}V_{mj}}{i\hbar^2 (E_m - E_j + i\hbar)} e^{2t} dt' - \frac{|V_{mm}|^2}{2\hbar^2} e^{2t} \\
c_k^{(2)} &= \int_j^m \frac{1}{i\hbar} \frac{V_{jm}}{E_m - E_j + i\hbar} e^{-i(mj+\dots)t} H'_{kj} e^{-i(jk)t} + \\
&\quad \frac{1}{i\hbar} \frac{V_{mm}}{\hbar} e^{-i(mk)t} H'_{km} e^{-i(mk)t} \\
c_k^{(2)} &= \int_j^m \frac{1}{i\hbar} \frac{V_{jm}V_{kj}}{E_m - E_j + i\hbar} e^{-i(mk+2)\dots t} dt' - \\
&\quad \frac{V_{mm}V_{km}}{\hbar^2} e^{-i(mk+2)\dots t} dt' \\
&= \int_j^m \frac{V_{jm}V_{kj} e^{-i(mk+2)\dots t}}{(E_m - E_j + i\hbar)(E_m - E_k + 2i\hbar)} - \frac{V_{mm}V_{km} e^{-i(mk+2)\dots t}}{i\hbar (E_m - E_k + 2i\hbar)}
\end{aligned}$$

Therefore, to second order:

$$\begin{aligned}
c_m(t) &= 1 + \frac{V_{mm}e^{-t}}{i\hbar} + \int_j^m \frac{V_{jm}V_{mj}}{i\hbar^2 (E_m - E_j + i\hbar)} e^{2t} \\
c_k(t) &= \frac{V_{km}}{i\hbar(-i(mk+\dots))} [e^{-i(mk+\dots)t}] \\
&\quad + \frac{V_{jm}V_{kj} e^{-i(mk+2)\dots t}}{j (E_m - E_j + i\hbar)(E_m - E_k + 2i\hbar)}
\end{aligned}$$

c. In part a. the $c^{(2)}(t)$ grow linearly with time (for $V_{mm} = 0$) while in part b. they remain finite for $t > 0$. The result in part a. is due to the sudden turning on of the field.

$$\begin{aligned}
d. |c_k(t)|^2 &= \frac{V_{jm}V_{kj} e^{-i(mk+2)\dots t}}{j (E_m - E_j + i\hbar)(E_m - E_k + 2i\hbar)}^2 \\
&= \frac{V_{kj}V_{kj}'V_{jm}V_{j'm} e^{-i(mk+2)\dots t} e^{i(mk+2)\dots t}}{jj' (E_m - E_j + i\hbar)(E_m - E_j' - i\hbar)(E_m - E_k + 2i\hbar)(E_m - E_k - 2i\hbar)}
\end{aligned}$$

$$= \frac{V_{kj}V_{kj}V_{jm}V_{jm} e^{4t}}{jj' [(E_m-E_j)(E_m-E_j)+i\hbar (E_j-E_j')+\hbar^2 2]((E_m-E_k)^2+4\hbar^2 2)}$$

$$\frac{d}{dt} |c_k(t)|^2 = \frac{4 V_{kj}V_{kj}V_{jm}V_{jm}}{jj' [(E_m-E_j)(E_m-E_j)+i\hbar (E_j-E_j')+\hbar^2 2]((E_m-E_k)^2+4\hbar^2 2)}$$

Now, look at the limit as 0^+ :

$$\frac{d}{dt} |c_k(t)|^2 \rightarrow 0 \text{ when } E_m = E_k$$

$$\lim_{0^+} \frac{4}{((E_m-E_k)^2+4\hbar^2 2)} (E_m-E_k)$$

So, the final result is the 2nd order golden rule expression:

$$\frac{d}{dt} |c_k(t)|^2 \frac{2}{\hbar} (E_m-E_k) \lim_{0^+} \frac{V_{jm}V_{kj}}{j (E_j - E_m - i\hbar)}$$

3. For the sudden perturbation case:

$$|c_m(t)|^2 = 1 + \sum_j \frac{V_{jm}V_{mj}}{(E_m - E_j)^2} [e^{-i(jm)t} - 1 + e^{i(jm)t} - 1] + O(V^3)$$

$$|c_m(t)|^2 = 1 + \sum_j \frac{V_{jm}V_{mj}}{(E_m - E_j)^2} [e^{-i(jm)t} + e^{i(jm)t} - 2] + O(V^3)$$

$$|c_k(t)|^2 = \frac{V_{km}V_{mk}}{(E_m - E_k)^2} [-e^{-i(km)t} - e^{i(km)t} + 2] + O(V^3)$$

$$1 - \sum_k |c_k(t)|^2 = 1 - \sum_k \frac{V_{km}V_{mk}}{(E_m - E_k)^2} [-e^{-i(km)t} - e^{i(km)t} + 2] + O(V^3)$$

$$= 1 + \sum_k \frac{V_{km}V_{mk}}{(E_m - E_k)^2} [e^{-i(km)t} + e^{i(km)t} - 2] + O(V^3)$$

to order V^2 , $|c_m(t)|^2 = 1 - \sum_k |c_k(t)|^2$, with no assumptions made regarding V_{mm} .

k

For the adiabatic perturbation case:

$$|c_m(t)|^2 = 1 + \sum_j \frac{V_{jm}V_{mj}e^{2t}}{i\hbar^2 (E_m - E_j + i\hbar)} + \frac{V_{jm}V_{mj}e^{2t}}{-i\hbar^2 (E_m - E_j - i\hbar)} + O(V^3)$$

$$= 1 + \sum_j \frac{1}{i\hbar^2} \frac{1}{(E_m-E_j+i\hbar)} - \frac{1}{(E_m-E_j-i\hbar)} V_{jm}V_{mj}e^{2t} + O(V^3)$$

$$= 1 + \sum_j \frac{1}{i\hbar^2} \frac{-2i\hbar}{(E_m-E_j)^2+\hbar^2 2} V_{jm}V_{mj}e^{2t} + O(V^3)$$

$$= 1 - \sum_{j \neq m} \frac{V_{jm} V_{mj} e^{2i t}}{(E_m - E_j)^2 + \hbar^2} + O(V^3)$$

$$|c_k(t)|^2 = \frac{V_{km} V_{mk}}{(E_m - E_k)^2 + \hbar^2} e^{2i t} + O(V^3)$$

to order V^2 , $|c_m(t)|^2 = 1 - \sum_k |c_k(t)|^2$, with no assumptions made regarding V_{mm} for this case as well.

Problems:

1. a. $T_{nm} = \frac{|\langle n|V|m\rangle|^2}{\hbar^2 \omega_{nm}^2}$

evaluating $\langle 1s|V|2s\rangle$ (using only the radial portions of the 1s and 2s wavefunctions since the spherical harmonics will integrate to unity) where $V = (e^2/r)$:

$$\langle 1s|V|2s\rangle = \int_0^\infty 2 \frac{Z}{a_0} \frac{3}{2} e^{-Zr/a_0} \frac{1}{r} \frac{1}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/2a_0} r^2 dr$$

$$\langle 1s|V|2s\rangle = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \int_0^\infty r e^{-3Zr/2a_0} dr - \frac{Zr^2}{2a_0} e^{-3Zr/2a_0} dr$$

Using integral equation 4 for the two integrations we obtain:

$$\langle 1s|V|2s\rangle = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \left[\frac{1}{3Z/2} - \frac{Z}{2a_0} \frac{2}{3Z/3} \right]$$

$$\langle 1s|V|2s\rangle = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \left[\frac{2^2 a_0^2}{3^2 Z^2} - \frac{2^3 a_0^2}{3^3 Z^2} \right]$$

$$\langle 1s|V|2s\rangle = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \frac{(3)2^2 a_0^2 - 2^3 a_0^2}{3^3 Z^2} = \frac{8Z}{\sqrt{2} 27 a_0}$$

Now,

$$E_n = -\frac{Z^2 e^2}{n^2 2a_0}, E_{1s} = -\frac{Z^2 e^2}{2a_0}, E_{2s} = -\frac{Z^2 e^2}{8a_0}, E_{2s} - E_{1s} = \frac{3Z^2 e^2}{8a_0}$$

So,

$$T_{nm} = \frac{\left(\frac{8Z}{\sqrt{2} 27 a_0}\right)^2}{\frac{3Z^2}{8a_0} \frac{2}{2}} = \frac{2^6 Z^2 2^6 a_0^2}{(2) 3^8 a_0^2 Z^4} = \frac{2^{11}}{3^8 Z^2} = 0.312 \text{ (for } Z = 1)$$

b. $m(r) = 1s = 2 \frac{Z}{a_0} \frac{3}{2} e^{-Zr/a_0} Y_{00}$

The orthogonality of the spherical harmonics results in only s-states having non-zero values for A_{nm} . We can then drop the Y_{00} (integrating this term will only result in unity) in determining the value of $A_{1s,2s}$.

$$\psi_{2s}(r) = \frac{1}{\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} \left(1 - \frac{Zr}{2a_0} \right) e^{-\frac{Zr}{2a_0}}$$

Remember for $1s$ $Z = 1$ and for $2s$ $Z = 2$

$$A_{nm} = \int_0^\infty \frac{1}{\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-\frac{Zr}{a_0}} \frac{1}{\sqrt{2}} \left(\frac{Z+1}{a_0} \right)^{3/2} \left(1 - \frac{(Z+1)r}{2a_0} \right) e^{-\frac{(Z+1)r}{2a_0}} r^2 dr$$

$$A_{nm} = \frac{2}{\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} \left(\frac{Z+1}{a_0} \right)^{3/2} \int_0^\infty e^{-\frac{(3Z+1)r}{2a_0}} \left(1 - \frac{(Z+1)r}{2a_0} \right) r^2 dr$$

$$A_{nm} = \frac{2}{\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} \left(\frac{Z+1}{a_0} \right)^{3/2} \int_0^\infty r^2 e^{-\frac{(3Z+1)r}{2a_0}} dr - \frac{(Z+1)r^3}{2a_0} e^{-\frac{(3Z+1)r}{2a_0}} dr$$

Evaluating these integrals using integral equation 4 we obtain:

$$A_{nm} = \frac{2}{\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} \left(\frac{Z+1}{a_0} \right)^{3/2} \left[\frac{2}{\frac{(3Z+1)^3}{2a_0}} - \frac{Z+1}{2a_0} \frac{(3)(2)}{\frac{(3Z+1)^4}{2a_0}} \right]$$

$$A_{nm} = \frac{2}{\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} \left(\frac{Z+1}{a_0} \right)^{3/2} \left[\frac{2^4 a_0^3}{(3Z+1)^3} - (Z+1) \frac{(3)2^4 a_0^3}{(3Z+1)^4} \right]$$

$$A_{nm} = \frac{2}{\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} \left(\frac{Z+1}{a_0} \right)^{3/2} \frac{-2^5 a_0^3}{(3Z+1)^4}$$

$$A_{nm} = -2 \frac{[2^3 Z(Z+1)]^{3/2}}{(3Z+1)^4}$$

The transition probability is the square of this amplitude:

$$T_{nm} = -2 \frac{[2^3 Z(Z+1)]^{3/2}}{(3Z+1)^4} = \frac{2^{11} Z^3 (Z+1)^3}{(3Z+1)^8} = 0.25 \text{ (for } Z = 1\text{)}.$$

The difference in these two results (parts a. and b.) will become negligible at large values of Z when the perturbation becomes less significant as in the case of $Z = 1$.

2. \hat{z} is along Z (lab fixed), and $\hat{\mu}$ is along z (the C-I molecule fixed bond). The angle between Z and z is θ :

$$\hat{z} \cdot \hat{\mu} = \mu \cos \theta = \mu D_{00}^{1*}(\theta)$$

So,

$$\begin{aligned} I &= \langle D_{M'K'}^{J'} | \hat{z} \cdot \hat{\mu} | D_{MK}^J \rangle = \langle D_{M'K'}^{J'} | \mu D_{00}^{1*} | D_{MK}^J \rangle \sin \theta \int d\Omega \\ &= \mu \langle D_{M'K'}^{J'} | D_{00}^{1*} | D_{MK}^J \rangle \sin \theta \int d\Omega \end{aligned}$$

Now use:

$$D_{M'n'}^{J'*} D_{00}^{1*} = \sum_{jmn} \langle J'M'10|jm\rangle^* D_{mn}^{j*} \langle jn|J'K'10\rangle^*$$

to obtain:

$$I = \mu \sum_{jmn} \langle J'M'10|jm\rangle^* \langle jn|J'K'10\rangle^* D_{mn}^{j*} D_{MK}^J \sin^2 \theta \, d\theta \, d\phi$$

Now use:

$$D_{mn}^{j*} D_{MK}^J \sin^2 \theta \, d\theta \, d\phi = \frac{8}{2J+1} \int J_j M_m \, n,$$

to obtain:

$$\begin{aligned} I &= \mu \frac{8}{2J+1} \sum_{jmn} \langle J'M'10|jm\rangle^* \langle jn|J'K'10\rangle^* \int J_j M_m \, n \\ &= \mu \frac{8}{2J+1} \langle J'M'10|JM\rangle \langle JK|J'K'10\rangle. \end{aligned}$$

We use:

$$\langle JK|J'K'10\rangle = \sqrt{2J+1} (-i)^{(J'-1+K)} \begin{matrix} J' & 1 & J \\ & K' & 0 & K \end{matrix}$$

and,

$$\langle J'M'10|JM\rangle = \sqrt{2J+1} (-i)^{(J'-1+M)} \begin{matrix} J' & 1 & J \\ & M' & 0 & M \end{matrix}$$

to give:

$$\begin{aligned} I &= \mu \frac{8}{2J+1} \sqrt{2J+1} (-i)^{(J'-1+M)} \begin{matrix} J' & 1 & J \\ & M' & 0 & M \end{matrix} \sqrt{2J+1} (-i)^{(J'-1+K)} \begin{matrix} J' & 1 & J \\ & K' & 0 & K \end{matrix} \\ &= \mu 8^2 (-i)^{(J'-1+M+J'-1+K)} \begin{matrix} J' & 1 & J \\ & M' & 0 & M \end{matrix} \begin{matrix} J' & 1 & J \\ & K' & 0 & K \end{matrix} \\ &= \mu 8^2 (-i)^{(M+K)} \begin{matrix} J' & 1 & J \\ & M' & 0 & M \end{matrix} \begin{matrix} J' & 1 & J \\ & K' & 0 & K \end{matrix} \end{aligned}$$

The 3-J symbols vanish unless: $K' + 0 = K$ and $M' + 0 = M$.

So,

$$I = \mu 8^2 (-i)^{(M+K)} \begin{matrix} J' & 1 & J \\ & M & 0 & M \end{matrix} \begin{matrix} J' & 1 & J \\ & K & 0 & K \end{matrix} M'M K'K.$$

b. $\begin{matrix} J' & 1 & J \\ & M & 0 & M \end{matrix}$ and $\begin{matrix} J' & 1 & J \\ & K & 0 & K \end{matrix}$ vanish unless $J' = J + 1, J, J - 1$
 $J = \pm 1, 0$

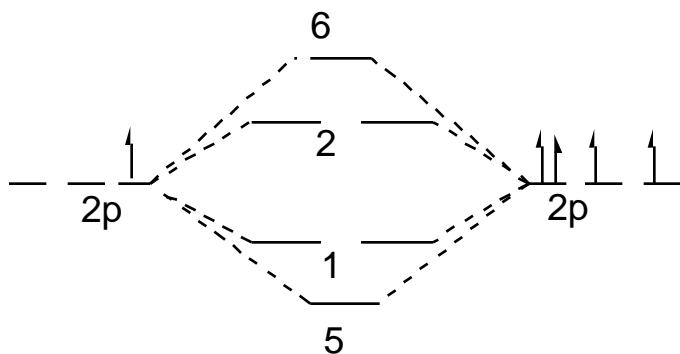
The K quantum number can not change because the dipole moment lies along the molecule's C_3 axis and the light's electric field thus can exert no torque that twists the molecule about this axis. As a result, the light can not induce transitions that excite the molecule's spinning motion about this axis.

3. a. B atom: $1s^2 2s^2 2p^1$, 2P ground state $L = 1, S = \frac{1}{2}$, gives a degeneracy $((2L+1)(2S+1))$ of 6.

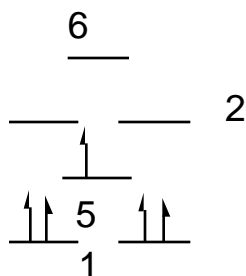
O atom: $1s^2 2s^2 2p^4$, 3P ground state $L = 1, S = 1$, gives a degeneracy $((2L+1)(2S+1))$ of 9.

The total number of states formed is then $(6)(9) = 54$.

b. We need only consider the p orbitals to find the low lying molecular states:



Which, in reality look like this:



This is the correct ordering to give a $^2 +$ ground state. The only low-lying electron configurations are $1^3 5^2$ or $1^4 5^1$. These lead to $^2 -$ and $^2 +$ states, respectively.

c. The bond orders in both states are $2\frac{1}{2}$.

d. The $^2 -$ is + and g/u cannot be specified since this is a heteronuclear molecule.

e. Only one excited state, the $^2 -$, is spin-allowed to radiate to the $^2 +$. Consider symmetries of transition moment operators that arise in the E1, E2 and M1 contributions to the transition rate

Electric dipole allowed: z^+ , x, y^- , the $^2 -$ $^2 +$ is electric dipole allowed via a perpendicular band.

Magnetic dipole allowed: R_z^- , $R_{x,y}^+$, the $^2 -$ $^2 +$ is magnetic dipole allowed.

Electric quadrupole allowed: x^2+y^2, z^2^+ , xy, yz^- , x^2-y^2, xy^- the $^2 -$ $^2 +$ is electric quadrupole allowed as well.

f. Since ionization will remove a bonding electron, the BO^+ bond is weaker than the BO bond.

g. The ground state BO^+ is 1^+ corresponding to a 1^4 electron configuration. An electron configuration of $1^3 5^1$ leads to a $^3 -$ and a $^1 -$ state. The $^3 -$ will be lower in energy. A $1^2 5^2$ configuration will lead to higher lying states of $^3 -$, $^1 -$, and $^1 +$.

h. There should be 3 bands corresponding to formation of BO^+ in the $^1 +$, $^3 -$, and $^1 -$ states. Since each of these involves removing a bonding electron, the Franck-Condon integrals will be appreciable for several vibrational levels, and thus a vibrational progression should be observed.

4. a. The bending (ν_2) vibration is degenerate.

b. $\text{H}-\text{C}-\text{N}$

bending fundamental

c. $\text{H}-\text{C}-\text{N}$

stretching fundamental

d. CH stretch (ν_3 in figure) is ν_3 , CN stretch is ν_1 , and HCN (ν_2 in figure) bend is ν_2 .

e. Under z (ν_2) light the CN stretch and the CH stretch can be excited, since $\nu_0 = 0$, $\nu_1 = 1$ and z provides coupling.

f. Under x,y (ν_2) light the HCN bend can be excited, since $\nu_0 = 0$, $\nu_1 = 1$ and x,y provides coupling.

g. The bending vibration is active under (x,y) perpendicular polarized light. $J = 0, \pm 1$ are the selection rules for ν_2 transitions. The CH stretching vibration is active under (z) \parallel polarized light. $J = \pm 1$ are the selection rules for ν_3 transitions.