\[ (M2) F_i = \int \left( \sum_{r_2} \left( r_2 \right)^4 \left( \phi \right)^4 \right) \, r_1 \cos \theta \, r_2 \, dR \, d\phi \, d\theta \]

\[ r_1, \quad \nu = 1 \pm 1 \text{ depends only on } r_1, r_2 \text{ not } \theta, \phi \]

\[ (M2) F_i = \int \left( \sum_{r_2} \left( r_2 \right)^4 \left( \phi \right)^4 \right) \, r_1 \cos \theta \, r_2 \, dR \, d\phi \, d\theta \]

2nd integral = 0 only when \( \Delta J = 1 \pm 1 \); \( M = M' \) in diatomics with \( \Lambda \neq 0 \); \( \Delta J = 0 \) transitions are allowed
b) Vibrational Transitions

\[ \nu_i = \nu_{e_i} + \nu_S \ \text{and} \ \nu_f = \nu_{e_f} + \nu_S + \Delta \nu \]
Assume Harmonic oscillator

\[ J' = J + 1; M' = M \ (z=\text{polarized light}) \]

Restrictions on \( \nu' \):

Evaluate \( \int_{R_i}^{R_f} \left[ \int_N^{R_f} \psi_{e' \nu' \lambda'} \psi_{e \nu \lambda} \right] \psi_{e' \nu' \lambda'} \psi_{e \nu \lambda} \ dx \ dt \)

\[ \psi(R) \rightarrow \text{permanent dipole as a function of} \ R \]

Expand \( \psi(R) \) about \( R_e \)

\[ \psi(R) \equiv \psi(R_e) + \frac{1}{R_e} \frac{d}{dR} \bigg|_{R=R_e} (R-R_e) \]

\[ M_f \propto \int_{R_i}^{R_f} \left( \psi(R_e) + \frac{1}{R_e} \frac{d}{dR} \bigg|_{R=R_e} (R-R_e) \right) \nu_i \ dx \]

No contribution from \( \psi(R_e) \) (\( \nu_i, \nu_f \) orthogonal)

\[ M_f \propto \frac{d}{dR} \bigg|_{R=R_e} \int_{R_i}^{R_f} (R-R_e) \nu_i \ dx \]

Only heteronuclear diatomics have rotational, vibrational spectra

c) Electronic Transitions

\[ \nu_i = \nu_{e_i} + \nu \ \text{and} \ \nu_f = \nu_{e_f} + \nu \]

\[ \int_{R_i}^{R_f} \left[ \int_N^{R_f} \psi_{e' \nu' \lambda'} \psi_{e \nu \lambda} \right] \psi_{e' \nu' \lambda'} \psi_{e \nu \lambda} \ dx \ dt \]

Inner integral: electronic transition. Dipole \( M \)

\( M \) to only if \( \nu' = \nu \) or \( \nu' = \nu + 1 \) (Electronic selection rule)
Restrictions on \( v' \)?

Assume \( M_{f}^{p} \text{ = Const} \) (Franck-Condon Approx.)

Left with \( M_{f}^{p} \int \psi_{v}^{*} \psi_{v} \, dR \) - Vibrational Overlap Integral

These vibrational wavefunctions do not have to be orthogonal because they are associated with different electronic states.

\[
|M_{f}^{p}|^2 \times |\int \psi_{v}^{*} \psi_{v} \, dR|^2 \quad \text{Franck-Condon Factor}
\]

Determines vibrational structure of electronic transitions

Two cases:

1. \( E_{v'}(R) = E_{0}(R) + T_{e} \) electronic term value

2. U.V. wavefunction in upper, lower states about \( \int \psi_{v}^{*} \psi_{v} \, dR = 0 \) only when \( v' = v \)
Absorption Spectra

a) Rotational Spectra: $\Delta J = 1$ (P-Branch only)
   \[ E(1+1) - E(1) = 2B_c \]

b) Vibrational: $\Delta N = 1$  $\Delta J = \pm 1$ (P-Branch)
   \[ E(2) - E(1) = B_c \]

Lower State $E_{\text{ud}} = \hbar \omega (v + \frac{1}{2}) + B_c J(J+1)$
Upper State $E_{\text{us}} = \hbar \omega (v + \frac{3}{2}) + B_c (J+1)(J+2)$

Transition Energies:
\[ R(J) = \hbar \omega_c + 2B_c (J+1) \]
\[ P(J) = \hbar \omega_c - 2B_c J \]
Gap of UB between $P(0)$, $P(1)$ for transitions

This race is definitely necessary.