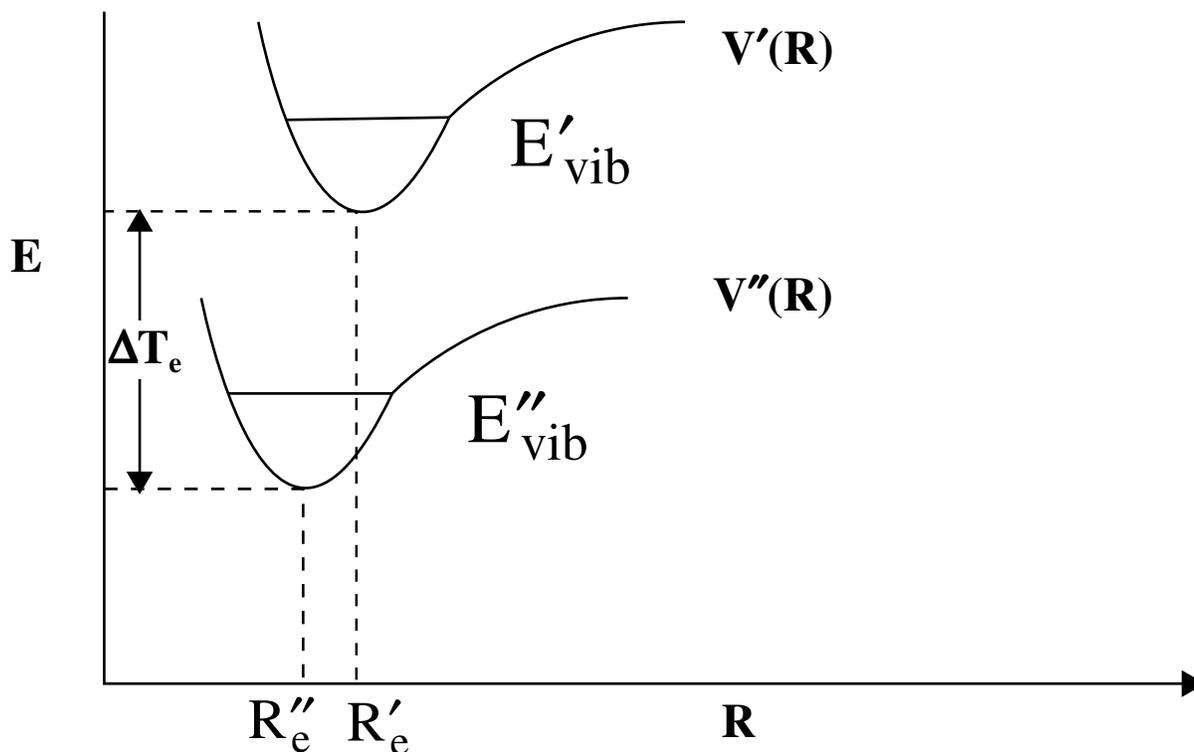


5.74 RWF Lecture #10 Supplement

Stationary Phase for Vibration-Electronic Spectra

Consider two electronic potential energy curves



The classical Franck-Condon principle specifies $\Delta R = 0$, $\Delta P = 0$. If $\Delta P = 0$, then the kinetic energy, $KE(R)$, must also be unchanged upon excitation

$$KE'(R) = E'_{\text{vib}} - V'(R)$$

$$KE''(R) = E''_{\text{vib}} - V''(R)$$

thus

$$E'_{\text{vib}} - E''_{\text{vib}} = V'(R) - V''(R)$$

which can only be satisfied at special values of R , each of which is a **stationary phase** point.

The choice of transition frequency from a given vibrational level of either the lower or upper electronic state determines the stationary phase point. This is the R -value (or R -values) at which the transition occurs and the region where a piece of the initial state wavefunction is transferred onto the final state potential.

The transition frequency

$$h\nu = \Delta T_e + E'_{\text{vib}} - E''_{\text{vib}} = \Delta T_e + V'(R) - V''(R)$$

$$\underbrace{h\nu - \Delta T_e}_{\substack{\text{specified by} \\ \text{the experimentalist}}} = \underbrace{V'(R) - V''(R)}_{\text{General requirement}} = \underbrace{V'(R_{sp}) - V''(R_{sp})}_{\text{satisfied at } R_{sp}}$$

R_{sp} may be swept through a small region of the initial state vibrational wavefunction by systematic variation of the center frequency of the probe laser, ν . As R_{sp} sweeps through lobes of the initial state wavefunction, the transition amplitude increases and decreases. The maximum transition amplitude is obtained when R_{sp} is at the maximum of the outermost lobe of the vibrational wavefunction (because the outer turning point is always softer than the inner turning point).

A similar Franck-Condon-like principle applies to Rydberg-Rydberg transitions

$$V_\ell(r) = -\frac{1}{r} + \frac{\ell(\ell+1)}{2\mu r^2}$$

$$\mu \approx m_e \equiv 1$$

$$V_{\ell+1}(r) - V_\ell(r) = \frac{\ell+1}{r^2}$$

$$\Delta E_{n'n''} = hc\mathfrak{R} \left[\frac{1}{n''^2} - \frac{1}{n'^2} \right] = hc\mathfrak{R} \left[\frac{n'^2 - n''^2}{n''^2 n'^2} \right]$$

In Rydberg units $hc\mathfrak{R} = 1$

$$n' = n'' + m$$

$$\frac{n'^2 - n''^2}{n''^2 n'^2} = \frac{n''^2 + 2mn'' + m^2 - n''^2}{n''^2(n''^2 + 2n''m + m^2)}$$

Two useful limits:

- (1) $m \gg n''$ (excitation from low- n'' initial state)
 $\Delta E_{n'n''} = hc\mathfrak{R}n''^{-2}$
- (2) $m \ll n''$ (transition between high Rydberg states)
 $\Delta E_{n'n''} = hc\mathfrak{R} 2mn''^{-3}$

Stationary phase requires

$$\Delta E_{n'n''} = V_{\ell+1}(r_{sp}) - V_{\ell}(r_{sp}) = \frac{\ell + 1}{r_{sp}^2}$$

$$\text{Case (1)} \quad r_{sp} = \left[\frac{(\ell + 1)n''^2}{hc\mathfrak{R}} \right]^{1/2}$$

$$\text{Case (2)} \quad r_{sp} = \left[\frac{(\ell + 1)n''^3}{mhc\mathfrak{R}} \right]^{1/2}$$

Case (1) shows that r_{sp} is small (inside the core) when n'' is small and m is large. High- n wavepackets are launched from inside the core.

$$\text{let } n'' = 1, \ell = 0, r_{sp} = 1a_0 \quad (1a_0 = 0.529\text{\AA}).$$

Case (2) implies that r_{sp} can be very large. The r_{sp} lies near the outer turning point of the lower state.

$$n'' = 4, \ell = 3, m = 1 \quad (5g \leftarrow 4f)$$

$$r_{sp} = 16a_0$$

You should verify that there is no stationary phase point for $n = 5, \ell = 2 \leftarrow n = 4, \ell = 3$! All upward (i.e. $\Delta n > 0$) Rydberg-Rydberg transitions have a strong $\Delta \ell = +1$ propensity rule.

By adjusting n'' and n' (via choice of initial state and center transition frequency), one can build a Rydberg wavepacket that looks like the inner or outer lobe of the initial n'', ℓ'' eigenstate. Simple physical pictures are based on this!

Heller's Fractionation Index

This provides a simple measure of how strongly a single bright state gets diluted into a bath of dark states.

Three cases:

- 1) You have an \mathbf{H}^{eff} and can look at all of the eigenvectors.

Suppose $|\psi_B^{(0)}\rangle$ is bright and $\{|\psi_{Di}^{(0)}\rangle \quad 1 \leq i \leq N\}$ are dark. The eigenvectors are

$$|\psi_j\rangle = \sum_{i=1}^N c_i^j |\psi_{Di}^{(0)}\rangle + \underbrace{\left(1 - \sum_i |c_i^j|^2\right)^{1/2}}_{\beta_j} |\psi_B^{(0)}\rangle$$

The relative intensities of transitions into the $N + 1$ mixed eigenstates $|\psi_j\rangle$ are given by $|\beta_j|^2$.

Heller's fractionation index, for the Bright state, B , is

$$f_B = \sum_{j=1}^{N+1} \beta_j^4.$$

If all eigenstates have equal shares of the Bright state character (strong-mixing limit)

$$|\beta_j| = (N + 1)^{-1/2}$$

$$f_B = \left[(N + 1)^{-1/2} \right]^4 (N + 1) = (N + 1)^{-1}$$

which implies that the single Bright state is delocalized into $N + 1$ states, N of which are dark.

Alternatively, you can ask how fractionated a single eigenstate is with respect to the zero-order basis in which it is expressed.

$$f_j = \left[\sum_{i=1}^N (c_i^j)^4 \right] + \beta_j^4$$

This fractionation index depends on the choice of basis set, just as the Bright state fractionation index is determined by the specific basis set to which the Bright state belongs.

2. An eigenstate-resolved spectrum.

Heller's fractionation index is, where I_i is the relative intensity of the i -th line,

$$f = \frac{\sum_{i=1}^N I_i^2}{\left(\sum_{i=1}^N I_i \right)^2}.$$

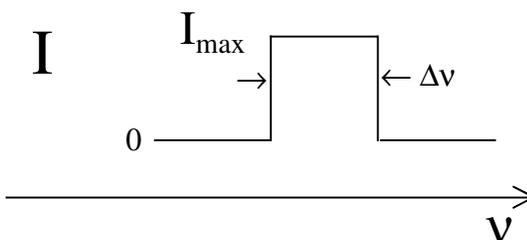
As for the eigenvector fractionation, if each line has equal intensity, $I_i = 1/N$, and

$$f = \frac{\sum_{i=1}^N N^{-2}}{\left(\sum_{i=1}^N N^{-1} \right)^2} = \frac{N(N^{-2})}{(N \cdot N^{-1})^2} = \frac{1}{N}.$$

So we get the same result for the maximally fractionated (small f) limit, regardless of whether we look at eigenvectors or eigenstate-resolved transition intensities.

3. A continuous spectrum.

For simplicity, consider $I(\nu)$ as a single rectangular feature,



$$f = \frac{\int I^2 d\nu}{\left(\int I d\nu\right)^2} = \frac{I_{\max}^2 \Delta\nu}{(I_{\max} \Delta\nu)^2} = \frac{1}{\Delta\nu}.$$

The stronger the mixing of the Bright state with the continuum bath, the broader is the spectrum.

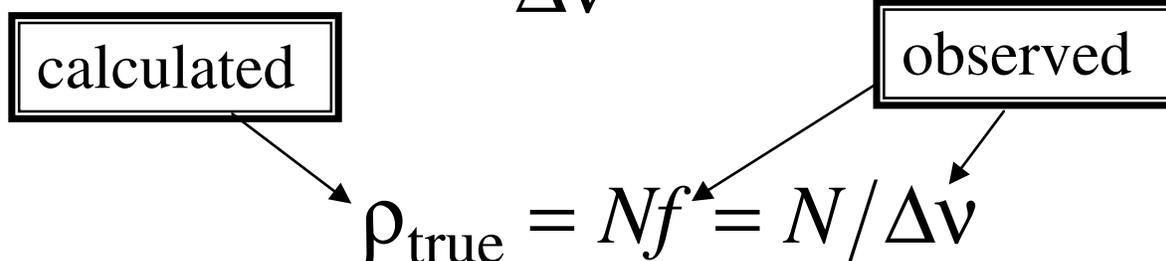
This can be converted to an eigenstate dilution factor merely by assuming that the density of states, $\rho(\nu)$, is independent of frequency.

$$\rho = \frac{\# \text{ states}}{\delta\nu} = \frac{N}{\Delta\nu}.$$

width of one "state"

Thus, in the limit of maximum fractionation within $\Delta\nu$,

$$f = \frac{1}{\Delta\nu} = \rho/N$$



The fractionation index tells us what fraction of symmetry and energetically accessible state or phase space is accessed by our pluck.

$$\text{Fraction of space accessed} = \frac{1}{Nf}$$

when $f = 1/N$, the fraction accessed = 1 (all of it!)

when $f = 1$, the fraction accessed = $1/N$.
