

Klausurtermin „Molekültheorie und Spektroskopie“:

Datum: *Mittwoch, 5. März 2014*
Zeit: *10:00 (s.t.)*
Raum: *G.10.02 Hörsaal 9*

Schriftliche Hilfsmittel sind ohne Einschränkung erlaubt.

Bitte einen Taschenrechner mitbringen.

Die Aufgabentexte werden in deutscher und englischer Sprache verfügbar sein.

Nuclear-motion wavefunction

describes vibrational and rotational motion.

Simplest approximation

$$\Psi_n = \Psi_{\text{vib}} \Psi_{\text{rot}}$$

Better approximation

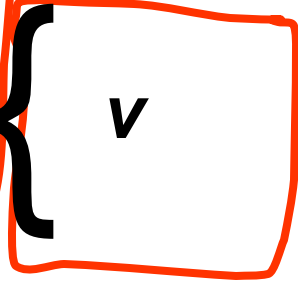
$$\Psi_n = \sum_p c_p \Psi_{\text{vib}}^{(p)} \Psi_{\text{rot}}^{(p)}$$

„Rotation-vibration“ interaction

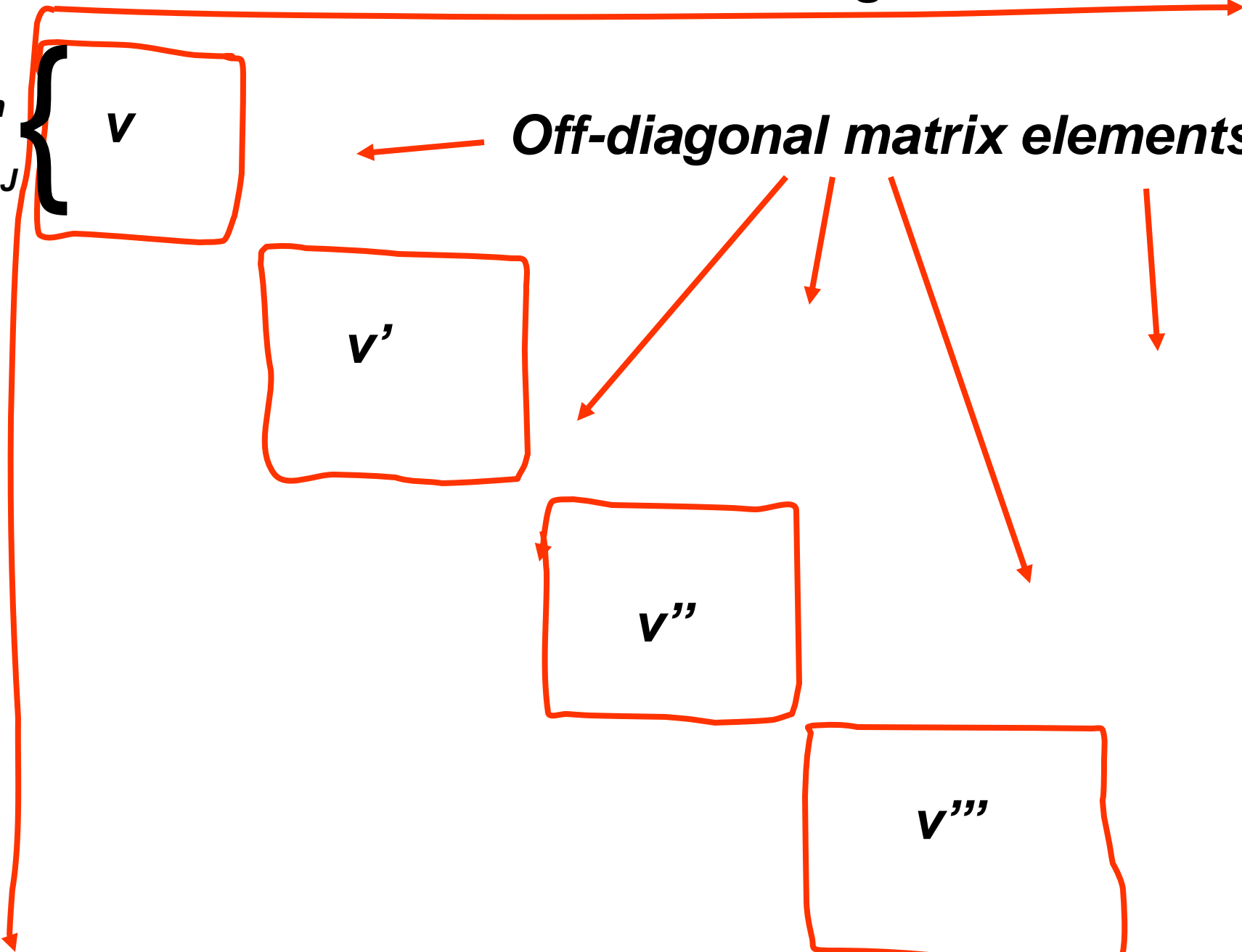
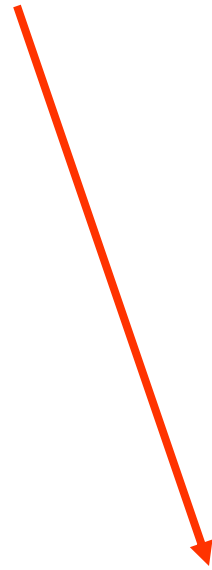
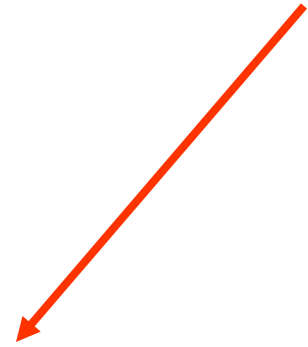
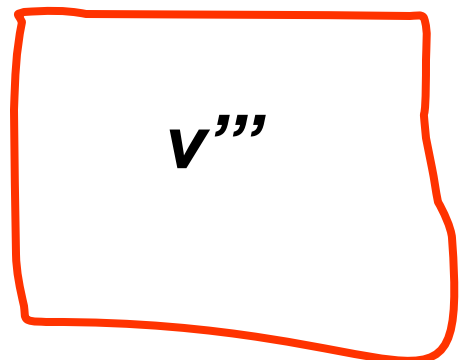
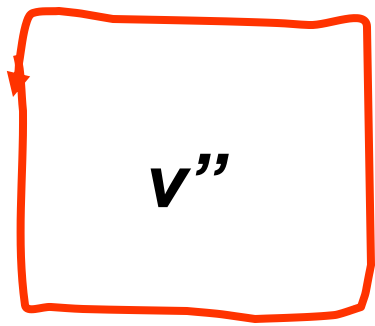
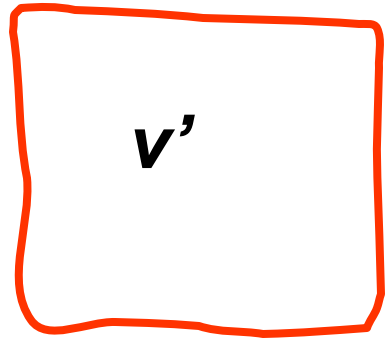
Matrix diagonalization

Hamiltonian matrix for a given J

*rotation
levels
 $k=-J$ to J*



Off-diagonal matrix elements



A variational calculation produces a list of numerical values for the molecular energies, intensities, and other properties if needed and programmed for a given electronic state of a given molecule.

Not so instructive for understanding molecules in general

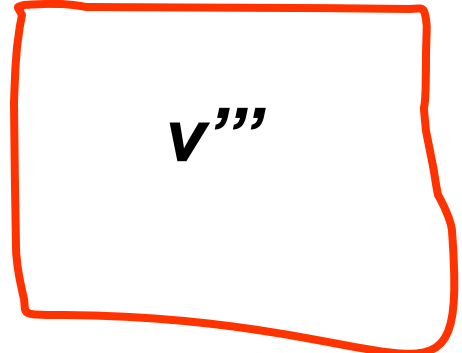
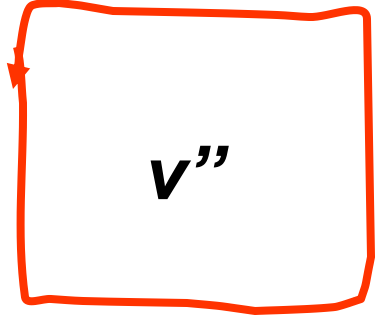
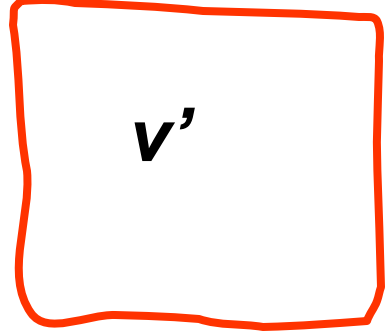
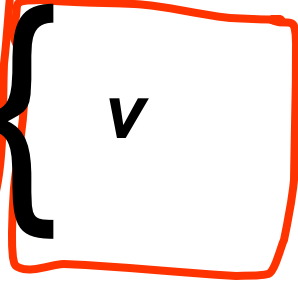
Traditionally (before powerful computers were available) the rotation-vibration Schrödinger equation was approximately solved with perturbation theory (Störungstheorie).

Not so accurate but instructive!

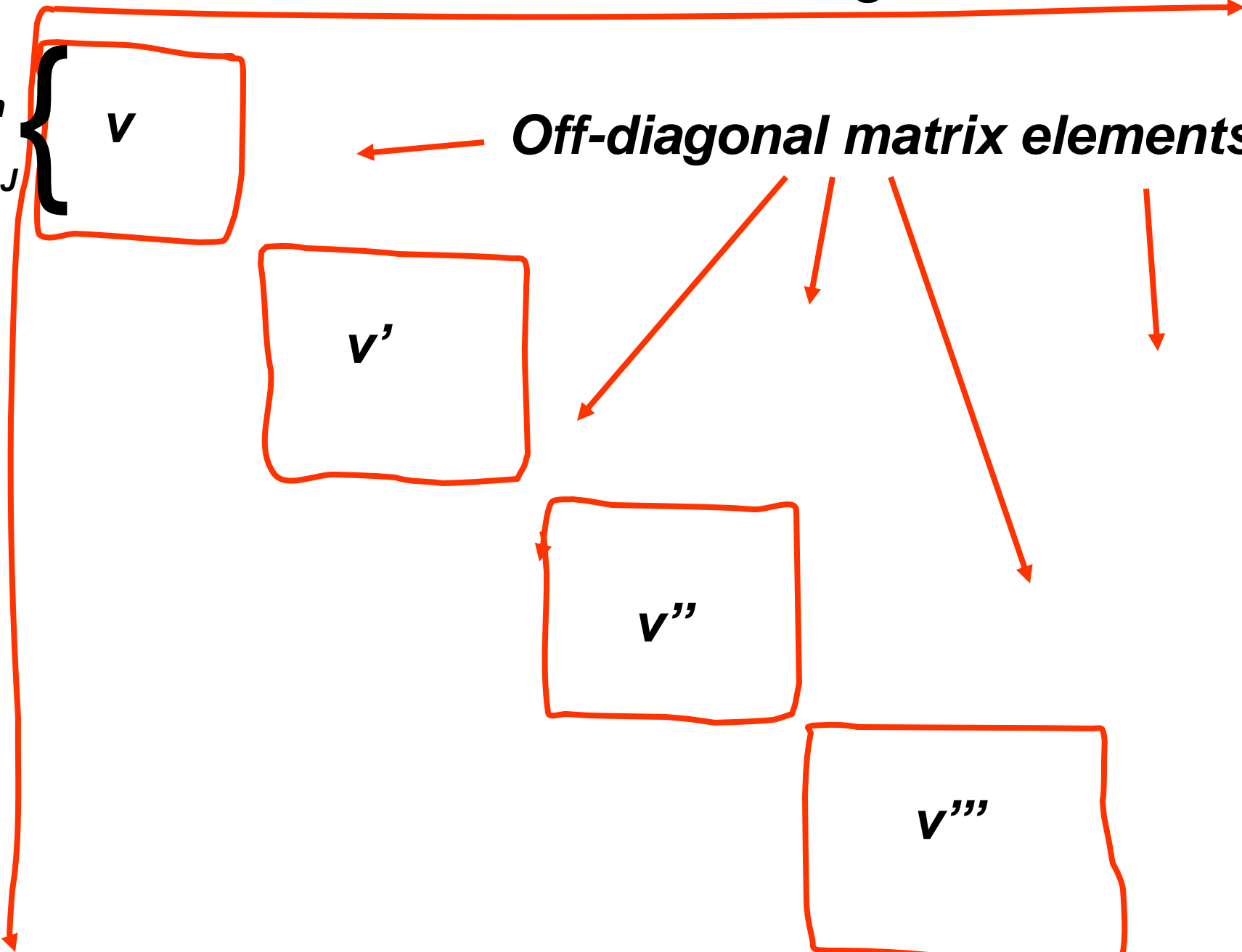
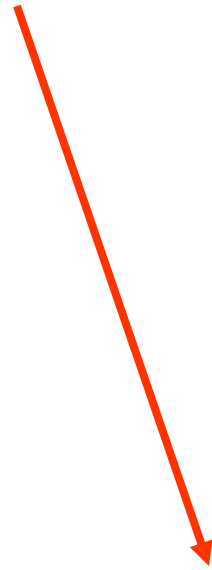
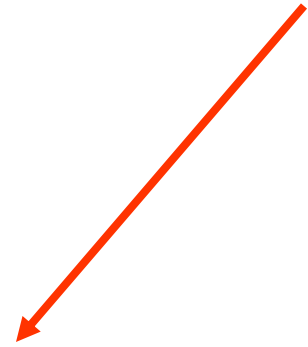
What is perturbation theory?

Hamiltonian matrix for a given J

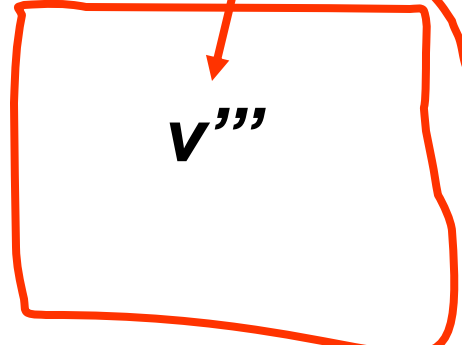
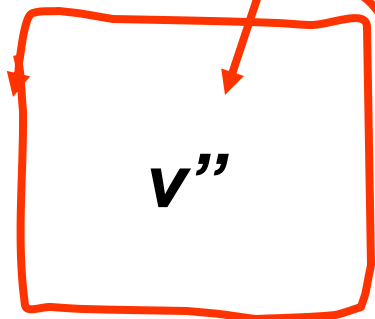
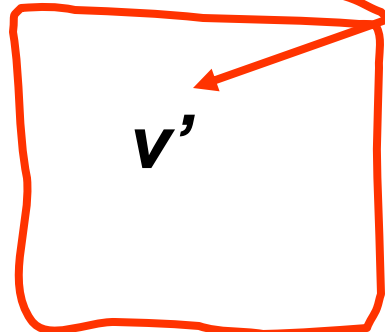
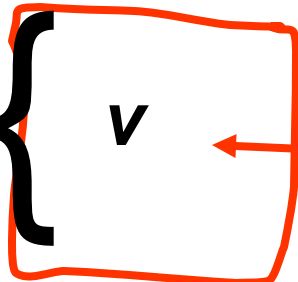
*rotation
levels
 $k=-J$ to J*



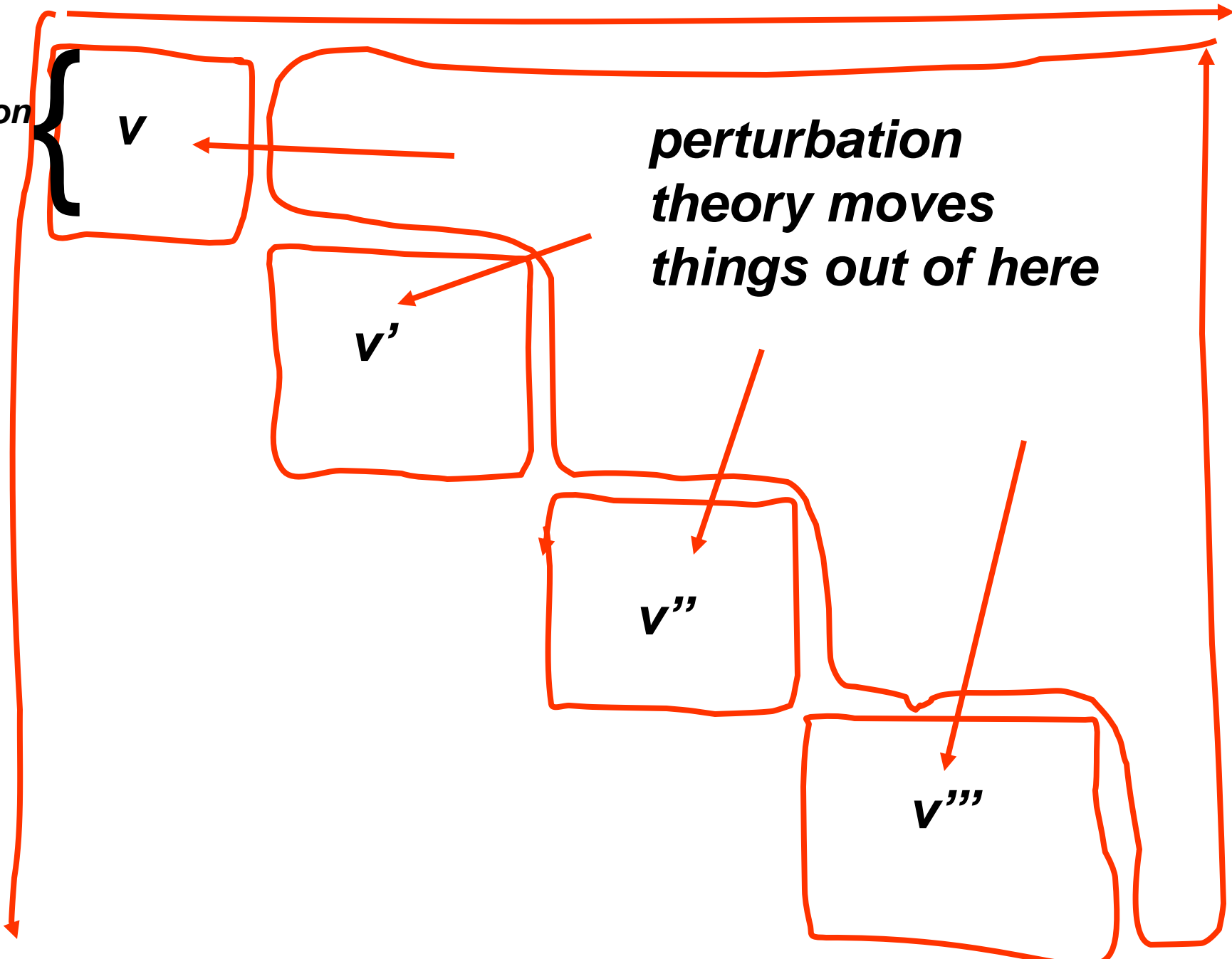
Off-diagonal matrix elements



*rotation
levels*



***perturbation
theory moves
things out of here***



2nd order perturbation theory expression for new matrix elements

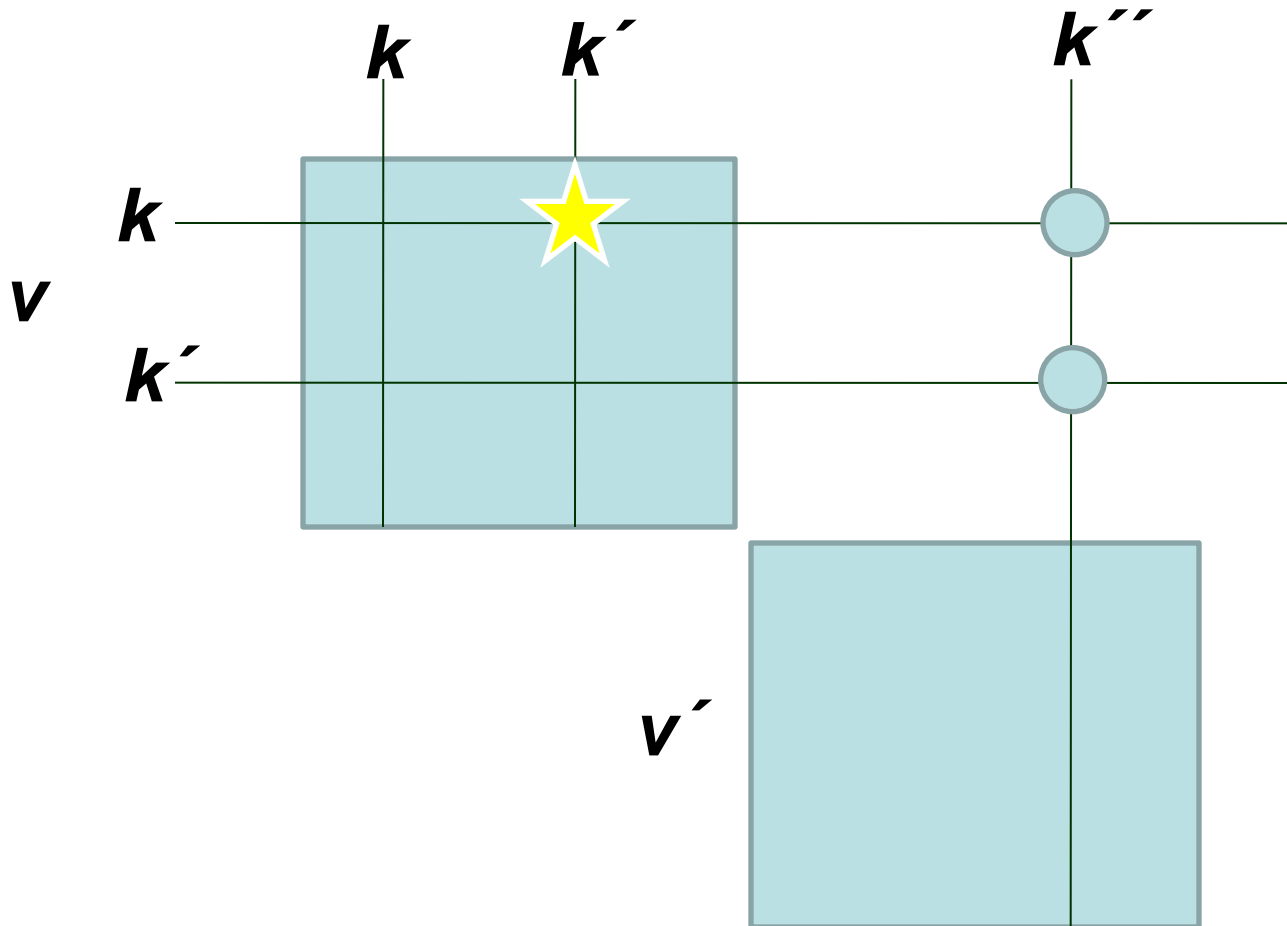
**One vibrational
block (labeled v)**

$$H(vk;vk') + \sum_{v' \neq v} \sum_{k''} \frac{H(vk;v'k'')H(v'k'';vk')}{E_v^0 - E_{v'}^0}$$

**rotational
levels**

**Energy difference
approximated to
vibrational energy
difference of v and v'**

Off diagonal MEs removed to 2nd order



$$H(vk;vk') + \sum_{v' \neq v} \sum_{k''} \frac{H(vk;v'k'')H(v'k'';vk')}{E_v^0 - E_{v'}^0}$$

2nd order perturbation theory produces corrections to the harmonic oscillator-rigid rotor energies

The correction terms are (mostly) small, at least at small values of J and K .

We list here the corrections obtained for different types of molecules.

Diatomic molecule

Harmonic oscillator/rigid rotor

$$E_{vJ}^{(0)} = \hbar \sqrt{\frac{k}{\mu}} \left(v + \frac{1}{2} \right) + \frac{\hbar^2}{2\mu r_e^2} J(J + 1).$$

$= hc \omega_e$ $= hc B_e$

„Improved theory“, $T_{vJ} = E_{vJ}/hc$

$$T_{vJ} = T_v + B_v J(J + 1) - D_v J^2(J + 1)^2 + \dots,$$

$$T_v = \omega_e \left(v + \frac{1}{2} \right) + \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \dots,$$

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right) + B^{(2)} \left(v + \frac{1}{2} \right)^2 + \dots,$$

$$D_v = D_e + D^{(1)} \left(v + \frac{1}{2} \right) + D^{(2)} \left(v + \frac{1}{2} \right)^2 + \dots,$$

Diatomic molecule

Higher order parameters can be derived in terms of low-order parameters by perturbation theory, for example the centrifugal distortion constant

$$D_e = \frac{1}{2h^2c^2\omega_e} \left[\frac{\hbar^2}{\mu r_e^3} \sqrt[4]{\frac{\hbar^2}{k\mu}} \right]^2$$

or

$$D_e = \frac{4B_e^3}{\omega_e^2} = \left(\frac{2B_e}{\omega_e} \right)^2 B_e.$$

Diatomic molecule

The expression for the energy of a diatomic molecule is sometimes written as the Dunham expansion

$$T_{vJ} = \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} Y_{jk} \left(v + \frac{1}{2} \right)^j J^k (J + 1)^k$$

The quantities Y_{jk} are called Dunham coefficients

$$Y_{10} = \omega_e$$

$$Y_{01} = B_e$$

$$Y_{11} = -\alpha_e \quad \text{etc}$$

Linear molecule

$$T_{VLJ\ell} = G_{VL} + F_{VJ\ell},$$

***v* quantum numbers**

***ℓ* quantum numbers**

$$= \sum_j \ell_j$$

$$G_{VL} = \sum_r \omega_r \left(v_r + \frac{d_r}{2} \right) + \sum_{r \leq r'} X_{rr'} \left(v_r + \frac{d_r}{2} \right) \left(v_{r'} + \frac{d_{r'}}{2} \right) + \sum_{j \leq j'} g_{jj'} \ell_j \ell_{j'}$$

$$F_{VJ\ell} = B_V [J(J+1) - \ell^2] - D_V [J(J+1) - \ell^2]^2 + H_V [J(J+1) - \ell^2]^3 + L_V [J(J+1) - \ell^2]^4 + \dots,$$

$$B_V = B_e - \sum_r \alpha_r \left(v_r + \frac{d_r}{2} \right) + \sum_{r \leq s} \gamma_{rs} \left(v_r + \frac{d_r}{2} \right) \left(v_s + \frac{d_s}{2} \right) + \dots, \quad \text{with similar expressions for } D_V, H_V, L_V, \dots$$

Symmetric top molecule (prolate)

$$T_{VLJk} = G_{VL} + F_{VLJk},$$

v quantum numbers

ℓ quantum numbers

$$G_{VL} = \sum_r \omega_r \left(v_r + \frac{d_r}{2} \right) + \sum_{r \leq r'} X_{rr'} \left(v_r + \frac{d_r}{2} \right) \left(v_{r'} + \frac{d_{r'}}{2} \right) + \sum_{j \leq j'} g_{jj'} \ell_j \ell_{j'}$$

$$\begin{aligned} F_{VLJk} &= B_V J(J+1) + (A_V - B_V) k^2 - 2 \sum_j \left(A \zeta_{ja,jb}^{(z)} \right)_V \ell_j k \\ &- D_J J^2 (J+1)^2 - D_{JK} J(J+1) k^2 - D_K k^4 \\ &+ \sum_j \eta_j^J \ell_j J(J+1) k + \sum_j \eta_j^K \ell_j k^3, \end{aligned}$$

Symmetric top molecule (prolate)

$$T_{VLJk} = G_{VL} + F_{VLJk},$$

***v* quantum numbers**

***ℓ* quantum numbers**

$$F_{VLJk} = B_V J(J+1) + (A_V - B_V) k^2 - 2 \sum_j \left(A \zeta_{ja,jb}^{(z)} \right)_V \ell_j k$$

$$- D_J J^2 (J+1)^2 - D_{JK} J(J+1) k^2 - D_K k^4$$

$$+ \sum_j \eta_j^J \ell_j J(J+1) k + \sum_j \eta_j^K \ell_j k^3,$$

$$B_V = B_e - \sum_r \alpha_r^{(B)} \left(v_r + \frac{d_r}{2} \right), \quad A_V = A_e - \sum_r \alpha_r^{(A)} \left(v_r + \frac{d_r}{2} \right),$$

$$\left(A \zeta_{ja,jb}^{(z)} \right)_V = A_e \zeta_{ja,jb}^{(z)} - \sum_r \alpha_r^{(A \zeta_j)} \left(v_r + \frac{d_r}{2} \right).$$

Symmetric top molecule (prolate)

The **centrifugal distortion terms** involving D_J , D_{JK} , D_K , η_j^J and η_j^K are all small, but the **Coriolis interaction term**

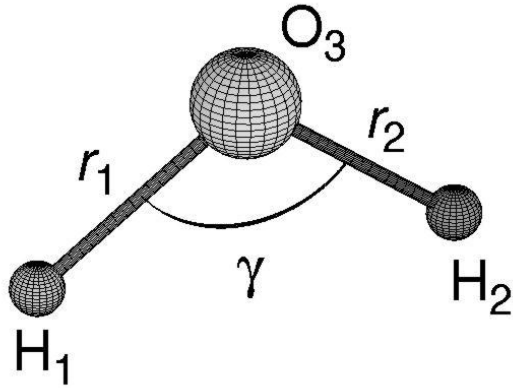
$$- 2 \sum_j \left(A \zeta_{ja,jb}^{(z)} \right)_V \ell_j k$$

has the same order of magnitude as

$$B_V J(J + 1) + (A_V - B_V) k^2$$

Example: ν_4 state of CH_3F , $v_4 = \ell_4 = 1$, all other v and ℓ quantum numbers = 0, $A_V = 5.1462 \text{ cm}^{-1}$, $B_V = 0.8524 \text{ cm}^{-1}$, $\left(A \zeta_{ja,jb}^{(z)} \right)_V = 0.2432 \text{ cm}^{-1}$.

Rigid asymmetric top



$$I_{aa}^e < I_{bb}^e < I_{cc}^e$$

$$A_e > B_e > C_e$$

General Hamiltonian

$$\hat{H}_{\text{rot}}^0 = \hbar^{-2}(A_e \hat{J}_a^2 + B_e \hat{J}_b^2 + C_e \hat{J}_c^2)$$

No simplification possible

- So what now ?

Rigid asymmetric top

Matrix diagonalization – Diagonalize asymmetric rotor

Hamiltonian in basis of $|J, k, m\rangle$ functions

$$\psi_{\text{rot}} = \sum_k c_k |J, k, m\rangle$$

Matrix elements:

$$\begin{aligned} H_{(J,k,m),(J,k,m)} &= \langle \psi_{J,k,m} | \widehat{H}_{\text{asymm}} | \psi_{J,k,m} \rangle = \langle J, k, m | \widehat{H}_{\text{asymm}} | J, k, m \rangle \\ &= \frac{\hbar^2}{4} \left\{ \left(\frac{1}{I_{xx}} + \frac{1}{I_{yy}} \right) [J(J+1) - k^2] + \frac{2k^2}{I_{zz}} \right\}, \end{aligned}$$

$$\begin{aligned} H_{(J,k,m),(J,k\pm 2,m)} &= \langle \psi_{J,k,m} | \widehat{H}_{\text{asymm}} | \psi_{J,k\pm 2,m} \rangle \\ &= \langle J, k, m | \widehat{H}_{\text{asymm}} | J, k \pm 2, m \rangle \\ &= \frac{\hbar^2}{8} \left(\frac{1}{I_{xx}} - \frac{1}{I_{yy}} \right) \sqrt{J(J+1) - k(k\pm 1)} \\ &\quad \times \sqrt{J(J+1) - (k\pm 1)(k\pm 2)}. \end{aligned}$$

Vibrating asymmetric top

Matrix diagonalization – Diagonalize vibrating-asymmetric-rotor

Hamiltonian in basis of $|J, k, m\rangle$ functions

$$\psi_{\text{rot}} = \sum_k c_k |J, k, m\rangle$$

The matrix elements are slightly more complicated than those of the rigid asymmetric top

Vibrating asymmetric top – matrix elements

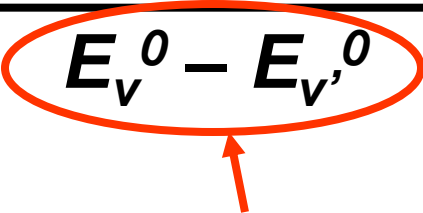
$$\begin{aligned}
 H'_{(J,k,m),(J,k,m)} &= \langle \psi_{J,k,m} | \widehat{H}_{\text{Watson}} | \psi_{J,k,m} \rangle = \langle J, k, m | \widehat{H}_{\text{Watson}} | J, k, m \rangle \\
 &= \frac{1}{2} (B_V + C_V) [J(J+1) - k^2] + A_V k^2 - \Delta_J J^2 (J+1)^2 \\
 &\quad - \Delta_{JK} J(J+1) k^2 - \Delta_K k^4 + \Phi_J J^3 (J+1)^3 + \Phi_{JK} J^2 (J+1)^2 k^2 \\
 &\quad + \Phi_{KJ} J(J+1) k^4 + \Phi_K k^6
 \end{aligned}$$

$$\begin{aligned}
 H'_{(J,k,m),(J,k\pm 2,m)} &= \langle \psi_{J,k,m} | \widehat{H}_{\text{Watson}} | \psi_{J,k\pm 2,m} \rangle \\
 &= \langle J, k, m | \widehat{H}_{\text{Watson}} | J, k \pm 2, m \rangle \\
 &= \left\{ \frac{1}{4} (B_V - C_V) - \delta_J J(J+1) - \frac{1}{2} \delta_K [(k \pm 2)^2 + k^2] + \phi_J J^2 (J+1)^2 \right. \\
 &\quad \left. + \frac{1}{2} \phi_{JK} J(J+1) [(k \pm 2)^2 + k^2] + \frac{1}{2} \phi_K [(k \pm 2)^4 + k^4] \right\} \\
 &\quad \times \sqrt{J(J+1) - k(k \pm 1)} \sqrt{J(J+1) - (k \pm 1)(k \pm 2)},
 \end{aligned}$$

where

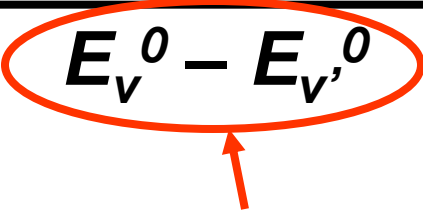
$$B_V = B_e - \sum_r \alpha_r^{(B)} \left(v_r + \frac{1}{2} \right) + \sum_{r \leq s} \gamma_{rs}^{(B)} \left(v_r + \frac{1}{2} \right) \left(v_s + \frac{1}{2} \right) + \dots, \quad \text{etc.}$$

2nd order perturbation theory expression for new matrix elements

$$H(vk;vk') + \sum_{v' \neq v} \sum_{k''} \frac{H(vk;v'k'')H(v'k'';vk')}{E_v^0 - E_{v'}^0}$$


*For the 2nd order perturbation theory to work **converge** well, this energy difference must be large compared to the numerator $H(vk;v'k'')H(v'k'';vk')$. Then the correction is small and 2nd order theory is OK.*

2nd order perturbation theory expression for new matrix elements

$$H(vk;vk') + \sum_{v' \neq v} \sum_{k''} \frac{H(vk;v'k'')H(v'k'';vk')}{E_v^0 - E_{v'}^0}$$


If the energy difference is small, i.e.

$$E_v^0 \approx E_{v'}$$

*there is a **RESONANCE***

rotation levels

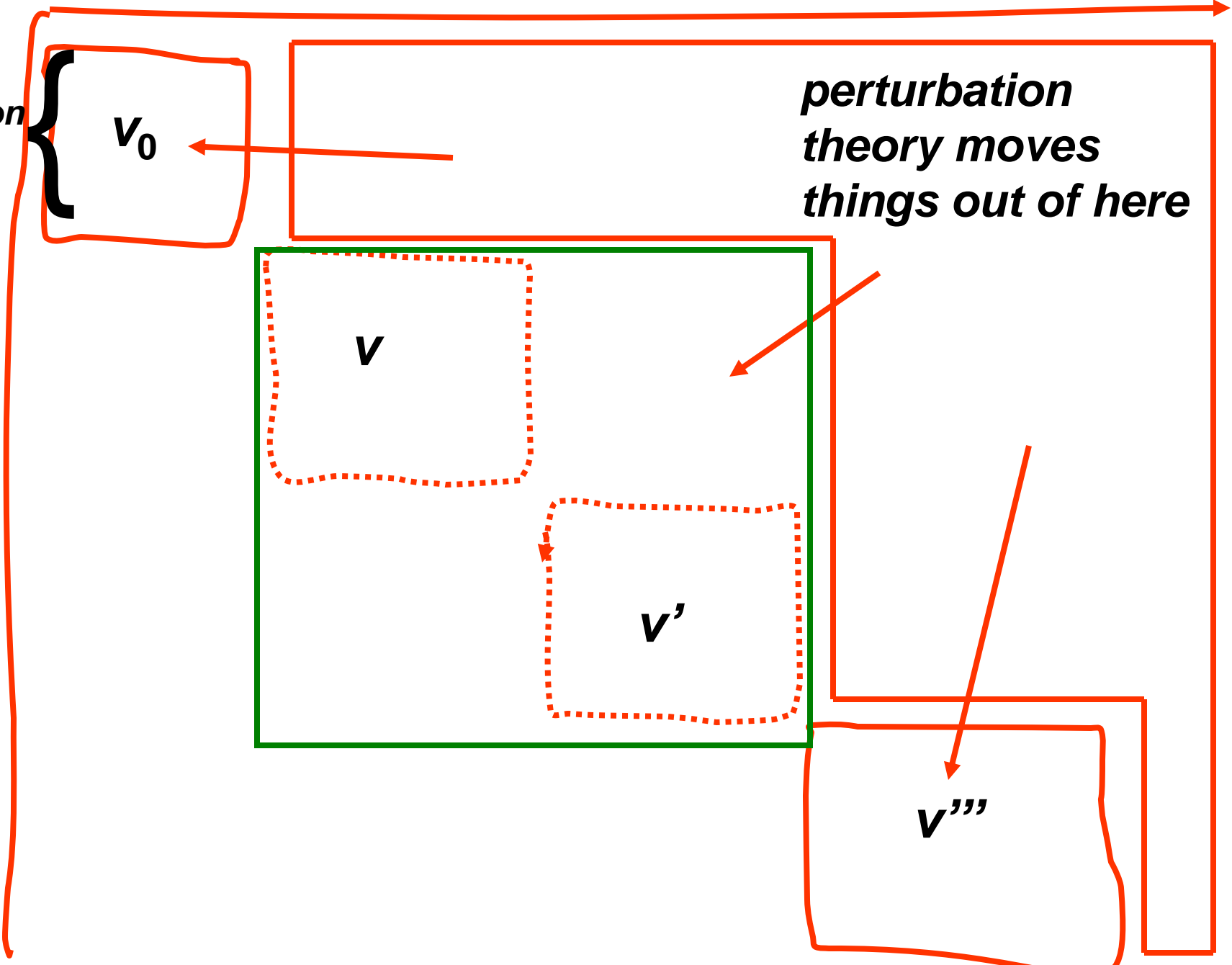
V_0

perturbation theory moves things out of here

V

V'

V'''



2nd order perturbation theory with a resonance

We modify the perturbation theory so that it does not try to remove matrix elements between v and v'

We must now diagonalize a matrix for v and v' simultaneously.

Famous example of resonance: ν_1
and $2\nu_2$ in CO_2

We modify the perturbation theory so that it does not try to remove matrix elements between ν and ν'

We must now diagonalize a matrix for ν and ν' simultaneously.

ν_1 and $2\nu_2$ in $^{12}\text{C}^{16}\text{O}_2$

Zero-order theory:

$$E_{\text{vib}} = \sum_r \omega_r \left(v_r + \frac{d_r}{2} \right)$$

$$\omega_1 = 1336.97 \text{ cm}^{-1} \quad \omega_2 = 667.19 \text{ cm}^{-1}$$

$$E(v_1=1, v_2=0, v_3=0) - E(v_1=0, v_2=0, v_3=0) \quad 1336.97 \text{ cm}^{-1}$$

$$E(v_1=0, v_2=2, v_3=0) - E(v_1=0, v_2=0, v_3=0) \quad 1334.38 \text{ cm}^{-1}$$

$$2.59 \text{ cm}^{-1}$$

RESONANCE!

ν_1 and $2\nu_2$ in $^{12}\text{C}^{16}\text{O}_2$

Zero-order vibrational energies:

$$E(\nu_1=1, \nu_2=0, \nu_3=0) - E(\nu_1=0, \nu_2=0, \nu_3=0) \quad 1336.97 \text{ cm}^{-1}$$

$$E(\nu_1=0, \nu_2=2, \nu_3=0) - E(\nu_1=0, \nu_2=0, \nu_3=0) \quad 1334.38 \text{ cm}^{-1}$$

Experimental values:

$$E(\nu_1=1, \nu_2=0, \nu_3=0) - E(\nu_1=0, \nu_2=0, \nu_3=0) \quad 1388.17 \text{ cm}^{-1}$$

$$E(\nu_1=0, \nu_2=2, \nu_3=0) - E(\nu_1=0, \nu_2=0, \nu_3=0) \quad 1285.40 \text{ cm}^{-1}$$

Deviations are due to the RESONANCE!

ν_1 and $2\nu_2$ in $^{12}\text{C}^{16}\text{O}_2$

Better theory: Treat the two states together as one matrix

$$\begin{pmatrix} E(1, 0^0, 0) & W \\ W & E(0, 2^0, 0) \end{pmatrix}$$

Off-diagonal matrix element W originates in higher-order potential energy terms neglected in the harmonic approximation

$$W = \left\langle 1, 0^0, 0 \left| \frac{1}{2} \phi_{122} q_1 (q_{2a}^2 + q_{2b}^2) \right| 0, 2^0, 0 \right\rangle \approx 50 \text{ cm}^{-1}.$$



The eigenvalues of the 2×2 matrix are close to the observed energy values.

This particular resonance is called a **Fermi** resonance

Whenever zero-order energies are close, resonances occur