



Anharmonic vibrational Møller-Plesset Perturbation Theories Using the Dyson Equation

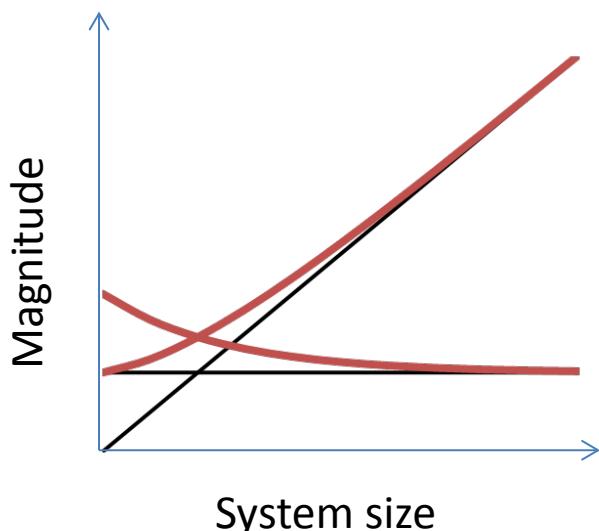
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Vibrational many-body methods

Diagrammatic representation of programmable equations

Electronic	Vibrational
MBPT2	VPT2 (Mills)
HF	VSCF (Bowman, Ratner and Gerber)
MP2	VMP2 (Norris, Ratner, and Roitberg)
CCSD	VCC (Christiansen)
CI	VCI (Bowman, Christoffel, and Tobin)



Extensive



Nonphysical



Intensive



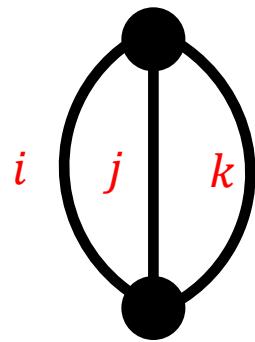
Nonphysical

(Goldstone, Proc. Roy. Soc. London A **1957**)

Diagrams

$$\hat{H} = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \sum_i F_{ii} Q_i^2 + \frac{1}{3!} \sum_{i,j,k} F_{ijk} Q_i Q_j Q_k + \frac{1}{4!} \sum_{i,j,k,l} F_{ijkl} Q_i Q_j Q_k Q_l + \dots$$


(normal coordinates)

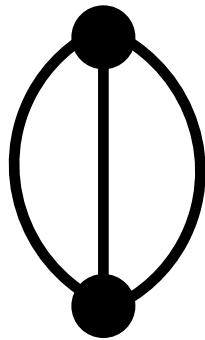


$$= \frac{1}{3!} \sum_{ijk} \frac{F_{ijk}^2 |\langle 0|Q_i|1\rangle|^2 |\langle 0|Q_j|1\rangle|^2 |\langle 0|Q_k|1\rangle|^2}{-\omega_i - \omega_j - \omega_k}$$

Diagrams

$$\hat{H} = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \sum_i F_{ii} Q_i^2 + \frac{1}{3!} \sum_{i,j,k} F_{ijk} Q_i Q_j Q_k + \frac{1}{4!} \sum_{i,j,k,l} F_{ijkl} Q_i Q_j Q_k Q_l + \dots$$


(normal coordinates)



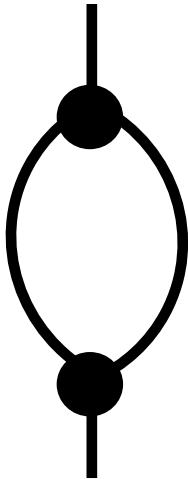
$\propto V^1$

Size-extensive
Total energy

Diagrams

$$\hat{H} = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \sum_i F_{ii} Q_i^2 + \frac{1}{3!} \sum_{i,j,k} F_{ijk} Q_i Q_j Q_k + \frac{1}{4!} \sum_{i,j,k,l} F_{ijkl} Q_i Q_j Q_k Q_l + \dots$$


(normal coordinates)



$$\propto V^0$$

Size-intensive
Frequency

VSCF and XVSCF

$$\hat{H} = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \sum_i F_{ii} Q_i^2 + \frac{1}{3!} \sum_{i,j,k} F_{ijk} Q_i Q_j Q_k + \frac{1}{4!} \sum_{i,j,k,l} F_{ijkl} Q_i Q_j Q_k Q_l + \dots$$


$$\left(-\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + U_i(Q_i) \right) \phi_i(Q_i) = \epsilon_i \phi_i(Q_i)$$

VSCF and XVSCF

$$\hat{H} = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \sum_i F_{ii} Q_i^2 + \frac{1}{3!} \sum_{i,j,k} F_{ijk} Q_i Q_j Q_k + \frac{1}{4!} \sum_{i,j,k,l} F_{ijkl} Q_i Q_j Q_k Q_l + \dots$$


$$\left(-\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + U_i(Q_i) \right) \phi_i(Q_i) = \epsilon_i \phi_i(Q_i)$$

$$U_i(Q_i) = U_i^{(0)} + U_i^{(1)} Q_i + \frac{1}{2} U_{ii}^{(2)} Q_i^2 + \frac{1}{6} U_{iii}^{(3)} Q_i^3 + \dots$$




VSCF and XVSCF

$$\hat{H} = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \sum_i F_{ii} Q_i^2 + \frac{1}{3!} \sum_{i,j,k} F_{ijk} Q_i Q_j Q_k + \frac{1}{4!} \sum_{i,j,k,l} F_{ijkl} Q_i Q_j Q_k Q_l + \dots$$

Keçeli and Hirata , J.
Chem. Phys. **2011**

$$\left(-\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + U_i(Q_i) \right) \phi_i(Q_i) = \epsilon_i \phi_i(Q_i)$$

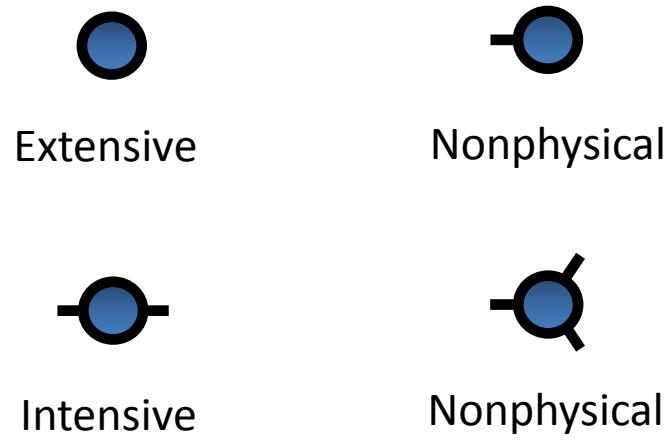
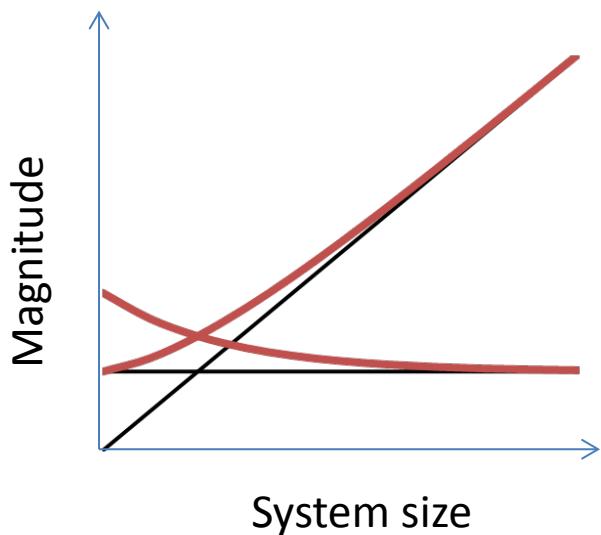
Hermes, Keçeli and Hirata,
J. Chem. Phys. **2012**

$$U_i(Q_i) = U_i^{(0)} + \cancel{U_i^{(1)} Q_i} + \frac{1}{2} U_{ii}^{(2)} Q_i^2 + \cancel{\frac{1}{6} U_{ill}^{(3)} Q_i^3} + \dots$$

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Vibrational perturbation theory

Obtaining anharmonic frequencies

$$\nu_v = E_v^{(0)} + E_v^{(1)} + E_v^{(2)} - E_0^{(0)} - E_0^{(1)} - E_0^{(2)}$$

Vibrational perturbation theory

Obtaining anharmonic frequencies

$$\nu_{\mathbf{v}} = E_{\mathbf{v}}^{(0)} + E_{\mathbf{v}}^{(1)} + E_{\mathbf{v}}^{(2)} - E_{\mathbf{0}}^{(0)} - E_{\mathbf{0}}^{(1)} - E_{\mathbf{0}}^{(2)}$$

$$E_s^{(2)} = \sum_{\mathbf{v} \neq \mathbf{s}} \frac{\left| \langle \Phi_s^{(0)} | \hat{H}_1 | \Phi_{\mathbf{v}}^{(0)} \rangle \right|^2}{E_s^{(0)} - E_{\mathbf{v}}^{(0)}}$$

Fermi, Darling-Dennison, *etc.* resonance

Vibrational perturbation theory

Obtaining anharmonic frequencies

$$\nu_{\nu} = E_{\nu}^{(0)} + E_{\nu}^{(1)} + E_{\nu}^{(2)} - E_{\mathbf{0}}^{(0)} - E_{\mathbf{0}}^{(1)} - E_{\mathbf{0}}^{(2)}$$

$$E_s^{(2)} = \sum_{\nu \neq s} \frac{\left| \langle \Phi_s^{(0)} | \hat{H}_1 | \Phi_{\nu}^{(0)} \rangle \right|^2}{E_s^{(0)} - E_{\nu}^{(0)}}$$

Fermi, Darling-Dennison, etc. resonance

Standard remedy: delete divergent terms in $E_s^{(2)}$ ("P-space") and...

Barone, *J. Chem. Phys.* **2005**

$$H_{\text{eff}} = \begin{pmatrix} \langle \Phi_{P1}^{(0)} | \hat{H}_{\text{eff}} | \Phi_{P1}^{(0)} \rangle & \langle \Phi_{P1}^{(0)} | \hat{H}_{\text{eff}} | \Phi_{P2}^{(0)} \rangle \\ \langle \Phi_{P1}^{(0)} | \hat{H}_{\text{eff}} | \Phi_{P2}^{(0)} \rangle & \langle \Phi_{P2}^{(0)} | \hat{H}_{\text{eff}} | \Phi_{P2}^{(0)} \rangle \end{pmatrix}$$

Selection of P-space:

Martin, Lee, Taylor, & François,
J. Chem. Phys. **1995**

Matthews & Stanton,
Mol. Phys. **2009**

Vibrational perturbation theory

In the spirit of size consistency...

$$\nu_v = E_v^{(0)} + E_v^{(1)} + E_v^{(2)} - E_0^{(0)} - E_0^{(1)} - E_0^{(2)}$$

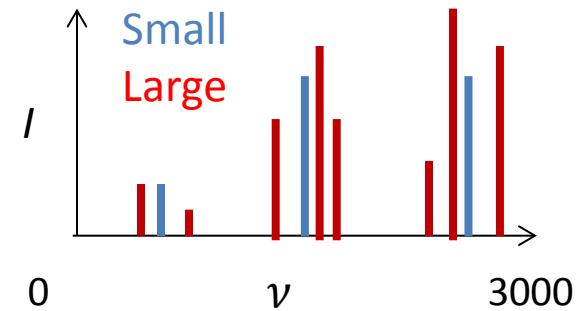
$$E_s^{(2)} = \sum_{v \neq s} \frac{\left| \langle \Phi_s^{(0)} | \hat{H}_1 | \Phi_v^{(0)} \rangle \right|^2}{E_s^{(0)} - E_v^{(0)}}$$

Size-intensive?



$$H_{\text{eff}} = \begin{pmatrix} \langle \Phi_{P1}^{(0)} | \hat{H}_{\text{eff}} | \Phi_{P1}^{(0)} \rangle & \langle \Phi_{P1}^{(0)} | \hat{H}_{\text{eff}} | \Phi_{P2}^{(0)} \rangle \\ \langle \Phi_{P2}^{(0)} | \hat{H}_{\text{eff}} | \Phi_{P1}^{(0)} \rangle & \langle \Phi_{P2}^{(0)} | \hat{H}_{\text{eff}} | \Phi_{P2}^{(0)} \rangle \end{pmatrix}$$

Size of P -space tends to grow with system size



Green's function

$$G_{ij}(t_2 - t_1) \equiv \langle \Phi_0 | T\{(a_i(t_2) + a_i^\dagger(t_2))(a_j(t_1) + a_j^\dagger(t_1))\} | \Phi_0 \rangle$$

Green's function

$$G_{ij}(t_2 - t_1) \equiv \langle \Phi_0 | T\{(a_i(t_2) + a_i^\dagger(t_2))(a_j(t_1) + a_j^\dagger(t_1))\} | \Phi_0 \rangle$$

Fourier transform



\hat{H}_0 : (effective) harmonic Hamiltonian

$$\begin{aligned} G_{ii}^{(0)}(\nu) = & \frac{1}{\nu - \omega_i + i\delta} \\ & + \frac{1}{-\nu - \omega_i + i\delta} \end{aligned}$$

Harmonic frequencies

Green's function

$$G_{ij}(t_2 - t_1) \equiv \langle \Phi_0 | T\{(a_i(t_2) + a_i^\dagger(t_2))(a_j(t_1) + a_j^\dagger(t_1))\} | \Phi_0 \rangle$$

Fourier transform

\hat{H} : full Hamiltonian

$$G_{ii}(\nu) = \sum_{\nu} \frac{|\langle \Phi_0 | (a_i + a_i^\dagger) | \Phi_{\nu} \rangle|^2}{\nu - (E_{\nu} - E_0) + i\delta} + \sum_{\nu} \frac{|\langle \Phi_0 | (a_i + a_i^\dagger) | \Phi_{\nu} \rangle|^2}{-\nu - \underbrace{(E_{\nu} - E_0)}_{\text{Exact frequencies}} + i\delta} \xrightarrow{\text{Intensities}}$$

\hat{H}_0 : (effective) harmonic Hamiltonian

$$G_{ii}^{(0)}(\nu) = \frac{1}{\nu - \omega_i + i\delta} + \frac{1}{-\nu - \underbrace{\omega_i}_{\text{Harmonic frequencies}} + i\delta}$$

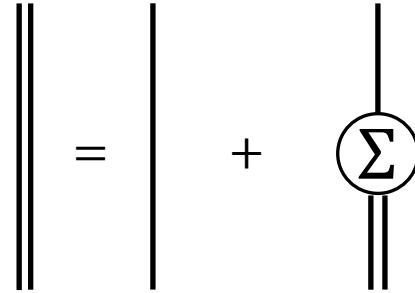
Harmonic frequencies

The Dyson equation

$$G_{ii}(\nu) = G_{ii}^{(0)}(\nu) + G_{ii}^{(0)}(\nu)\Sigma_{ii}(\nu)G_{ii}(\nu)$$

$$= \left\{ \left\{ G_{ii}^{(0)}(\nu) \right\}^{-1} - \Sigma_{ii}(\nu) \right\}^{-1}$$

$$= \frac{2\omega_i}{\nu^2 - \omega_i^2 - 2\omega_i\Sigma_{ii}(\nu)}$$

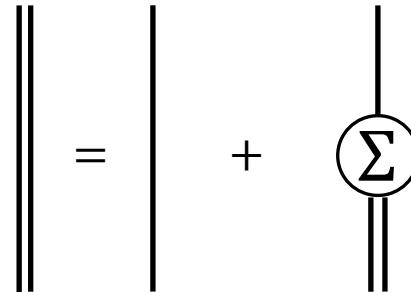


The Dyson equation

$$G_{ii}(\nu) = G_{ii}^{(0)}(\nu) + G_{ii}^{(0)}(\nu)\Sigma_{ii}(\nu)G_{ii}(\nu)$$

$$= \left\{ \left\{ G_{ii}^{(0)}(\nu) \right\}^{-1} - \Sigma_{ii}(\nu) \right\}^{-1}$$

$$= \frac{2\omega_i}{\nu^2 - \omega_i^2 - 2\omega_i\Sigma_{ii}(\nu)}$$



Dyson equation

$$\nu_\nu = \sqrt{\omega_i^2 + 2\omega_i\Sigma_{ii}(\nu_\nu)}$$

Self-consistent equation

RSPT

$$\begin{aligned} \nu_\nu &= E_\nu^{(0)} + E_\nu^{(1)} + E_\nu^{(2)} \\ &\quad - E_0^{(0)} - E_0^{(1)} - E_0^{(2)} \end{aligned}$$

Simple sum

Potentially divergent terms

The Dyson self-energy

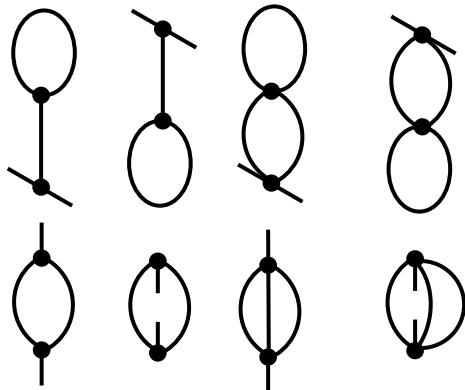
$$\Sigma_{ii}(\nu) = \Sigma_{ii}^{(1)}(\nu) + \Sigma_{ii}^{(2)}(\nu) + \Sigma_{ii}^{(3)}(\nu) + \dots$$

$$\Sigma_{ii}^{(1)}(\nu) =$$



$$|| = | + |\Sigma|$$

$$\Sigma_{ii}^{(2)}(\nu) =$$



The Dyson self-energy

$$\Sigma_{ii}(\nu) = \Sigma_{ii}^{(1)}(\nu) + \Sigma_{ii}^{(2)}(\nu) + \Sigma_{ii}^{(3)}(\nu) + \dots$$

$$\Sigma_{ii}^{(1)}(\nu) = \text{Diagram: A loop with a dot at the top-left vertex} = \frac{1}{2} \sum_j F_{iijj} (2^2 \omega_i \omega_j)^{-1}$$
$$\Sigma_{ii}^{(2)}(\nu) = \text{Diagram: A row of four connected loops with dots at the top-left vertices. The first two loops are vertical, and the last two are horizontal. The second loop has a small branch line extending from its top-right vertex. The third loop has a small branch line extending from its bottom-right vertex. The fourth loop has a small branch line extending from its top-right vertex. Below this row is another row of four similar diagrams, rotated 180 degrees. The first two loops are vertical, and the last two are horizontal. The second loop has a small branch line extending from its bottom-right vertex. The third loop has a small branch line extending from its top-right vertex. The fourth loop has a small branch line extending from its bottom-right vertex. The two rows are vertically aligned. To the right of the second row is a plus sign (+). To the right of the plus sign is a diagram: a vertical line with a circle containing the Greek letter Sigma (\Sigma) at the top vertex. The line continues downwards through the circle to another vertical line at the bottom vertex. This represents the full Dyson equation: } \parallel = \parallel + \text{Diagram: A vertical line with a circle containing the Greek letter Sigma (\Sigma) at the top vertex. The line continues downwards through the circle to another vertical line at the bottom vertex. This represents the full Dyson equation: }$$

The Dyson self-energy

$$\Sigma_{ii}(\nu) = \Sigma_{ii}^{(1)}(\nu) + \Sigma_{ii}^{(2)}(\nu) + \Sigma_{ii}^{(3)}(\nu) + \dots$$

$$\Sigma_{ii}^{(1)}(\nu) = \text{Diagram: A loop with a dot at the top-left vertex and a line extending downwards from the bottom-right vertex.} = \frac{1}{2} \sum_j F_{iijj} (2^2 \omega_i \omega_j)^{-1}$$

$$\Sigma_{ii}^{(2)}(\nu) = \begin{array}{c} \text{Diagram: A vertical line with a loop attached to its middle, ending in a dot at the top.} \\ \text{Diagram: A vertical line with a loop attached to its middle, ending in a dot at the bottom.} \\ \text{Diagram: Two loops connected by a vertical line, ending in a dot at the top.} \\ \text{Diagram: Two loops connected by a vertical line, ending in a dot at the bottom.} \\ \text{Diagram: A vertical line with a loop attached to its middle, ending in a dot at the top-left vertex and a line extending downwards from the bottom-right vertex.} \\ \text{Diagram: A vertical line with a loop attached to its middle, ending in a dot at the bottom-left vertex and a line extending upwards from the top-right vertex.} \\ \text{Diagram: A vertical line with a loop attached to its middle, ending in a dot at the top-left vertex and a line extending upwards from the top-right vertex.} \\ \text{Diagram: A vertical line with a loop attached to its middle, ending in a dot at the bottom-left vertex and a line extending downwards from the bottom-right vertex.} \end{array}$$

$$\text{Diagram: Three parallel vertical lines.} = \text{Diagram: A single vertical line.} + \text{Diagram: A vertical line with a circle containing the symbol } \Sigma \text{ attached to it.}$$

cf. Barone & Minichino *J. Mol. Struct. (Theochem)* **1995**

$$\text{Diagram: A loop with a dot at the top-left vertex and a line extending downwards from the bottom-right vertex.} = \frac{1}{2} \sum_{jk} \frac{F_{ijk}^2 (2^3 \omega_i \omega_j \omega_k)^{-1}}{\nu - \omega_j - \omega_k}$$

Connection to VPT2 frequencies

$$E(\nu) = V_{\text{ref}} + \chi_0 + \sum_i \omega_i \left(\nu_i + \frac{1}{2} \right) + \sum_{i \leq j} \chi_{ij} \left(\nu_i + \frac{1}{2} \right) \left(\nu_j + \frac{1}{2} \right)$$

$$\Sigma_{ii}^{(\nu)}(\nu) = \quad \text{Diagram 1} \quad + \quad \text{Diagram 2} \quad + \quad \text{Diagram 3} \quad + \quad \text{Diagram 4} \quad + \quad \text{Diagram 5}$$

$$\Sigma_{ii}^{(\nu)}(\underline{\omega_i}) = 2\chi_{ii} + \frac{1}{2} \sum_{j \neq i} \chi_{ij}$$

VPT2 correction to fundamental frequency

Two perturbation theories

XVH

$$\hat{H}_0: \bullet | \quad \Sigma_{ii}(\nu) = \bullet \circ + \dots$$

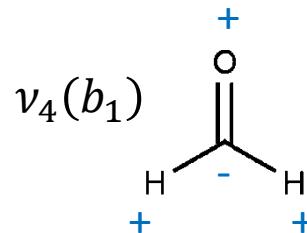
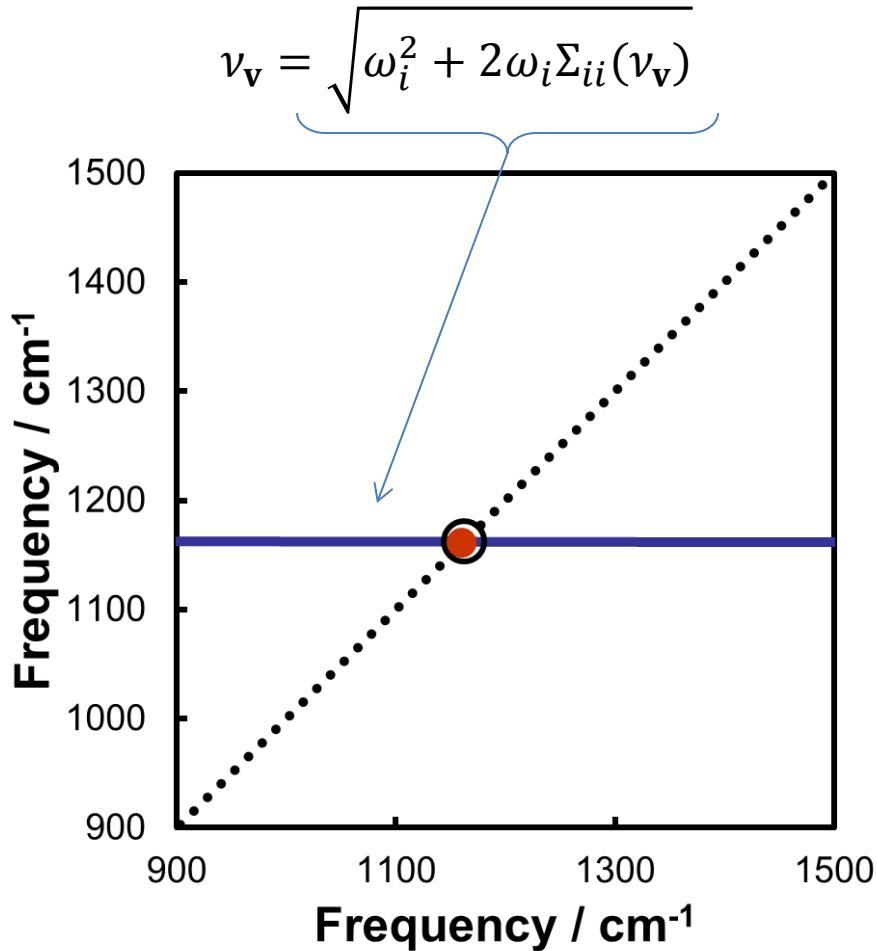
The diagram shows the free Hamiltonian \hat{H}_0 as a vertex with a vertical line and a dot. The self-energy $\Sigma_{ii}(\nu)$ is shown as a sum of diagrams: a single loop, a loop with a vertical line, a loop with a diagonal line, a loop with a horizontal line, and a loop with two diagonal lines.

XVMP

$$\hat{H}_0: \bullet | + \bullet \circ \quad \Sigma_{ii}(\nu) = \bullet \circ + \dots$$

The diagram shows the free Hamiltonian \hat{H}_0 as a sum of a vertex with a vertical line and a dot, and a vertex with a vertical line and a loop. The self-energy $\Sigma_{ii}(\nu)$ is shown as a sum of diagrams: a loop with a vertical line, a loop with a diagonal line, a loop with a horizontal line, and a loop with two diagonal lines. The last term in the self-energy series is labeled "(part)".

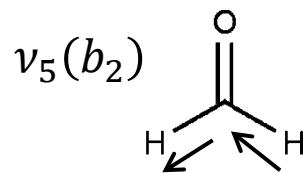
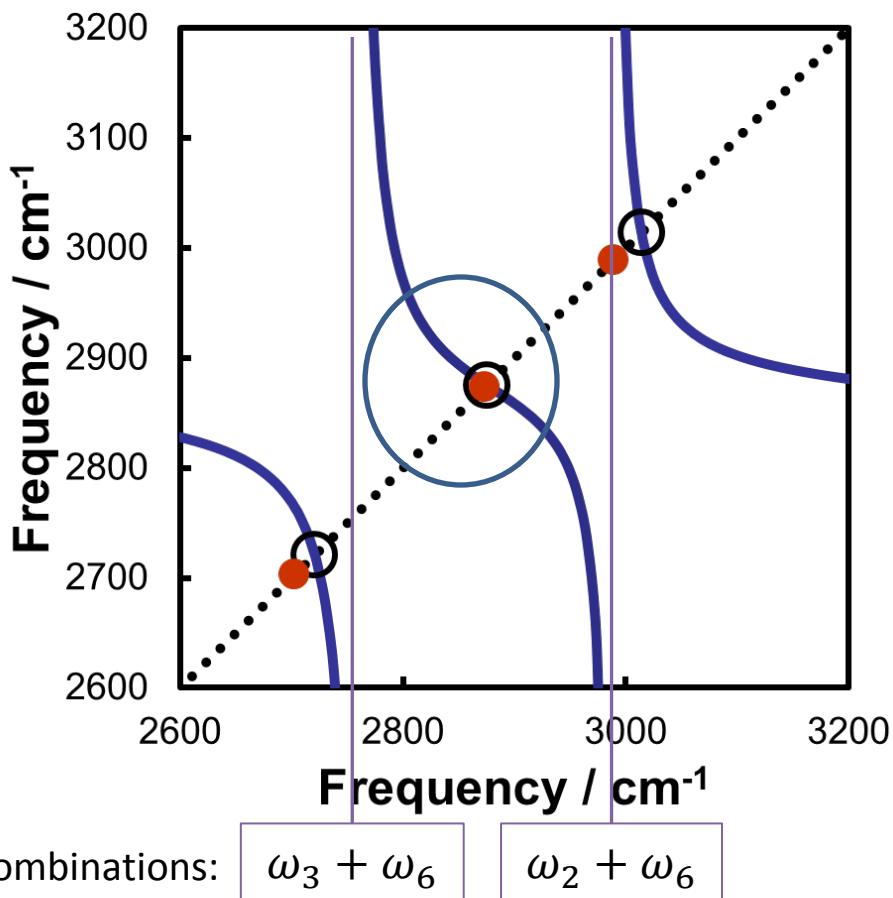
Formaldehyde, no resonance



VCI	1161 cm^{-1}
VMP2	$+2.1 \text{ cm}^{-1}$
XVH2	$+5.0 \text{ cm}^{-1}$
XVMP2	$+1.6 \text{ cm}^{-1}$

Formaldehyde, resonance

$$\nu_v = \sqrt{\omega_i^2 + 2\omega_i\Sigma_{ii}(\nu_v)}$$



VCI	2873 cm^{-1}
VMP2	$+691 \text{ cm}^{-1}$
XVH2	$+11 \text{ cm}^{-1}$
XVMP2	$+2.1 \text{ cm}^{-1}$

Intensity

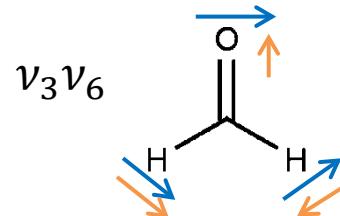
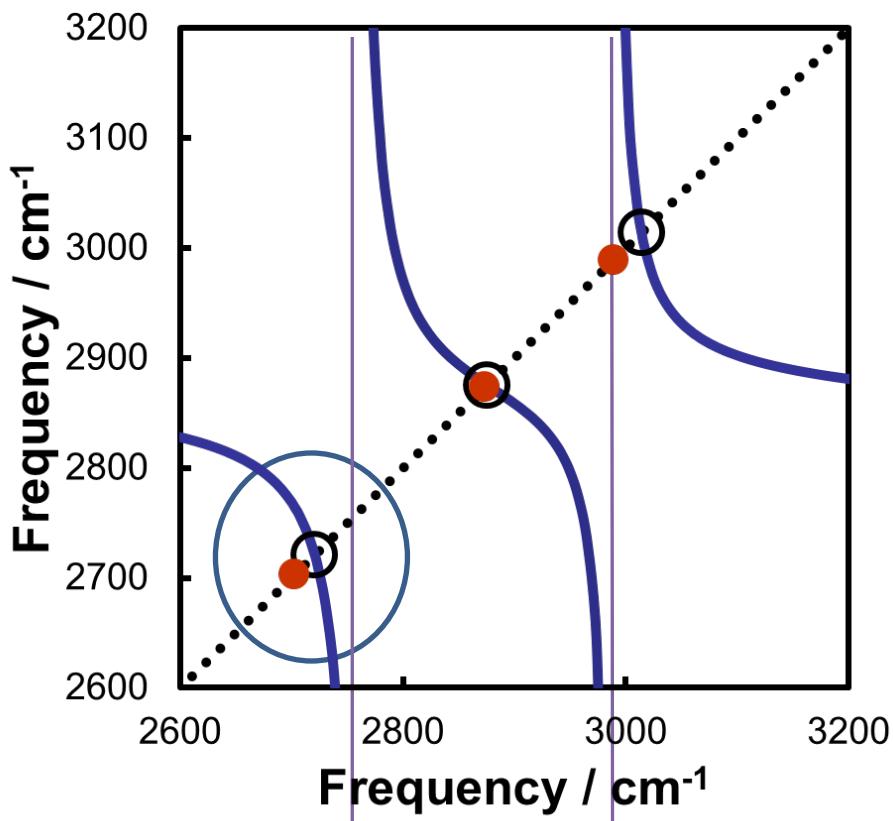
VCI: 0.47

XVH2: 0.52

XVMP2: 0.62

Formaldehyde, resonance

$$\nu_v = \sqrt{\omega_i^2 + 2\omega_i\Sigma_{ii}(\nu_v)}$$



VCI	2703 cm^{-1}
XVH2	$+47 \text{ cm}^{-1}$
XVMP2	$+18 \text{ cm}^{-1}$

Intensity

VCI: 0.17

XVH2: 0.42

XVMP2: 0.24

Conclusion

- Diagonalization-free method for multi-configuration excited states
- Møller-Plesset partitioning based on XVSCF
- Only defined for a Taylor-series PES in normal coordinates
 cf. Fortenberry, Huang, Yachmenev, Thiel, Lee, *Chem. Phys. Lett.* **2013**
- Not exact for Morse oscillator (although reduces to VPT2)
 cf. Matthew, Vázquez, Stanton, *Mol. Phys.* **2007**
- **Further work:** application to solids at finite temperature;
 automatic generation of high-order diagrams

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