Anharmonic vibrational Møller-Plesset Perturbation Theories Using the Dyson Equation

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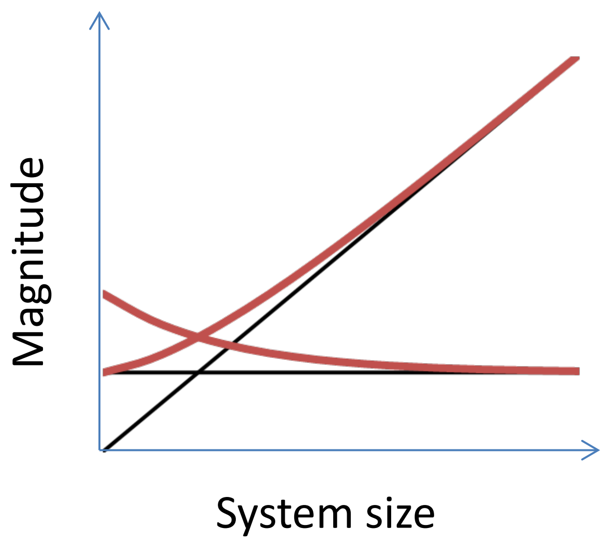
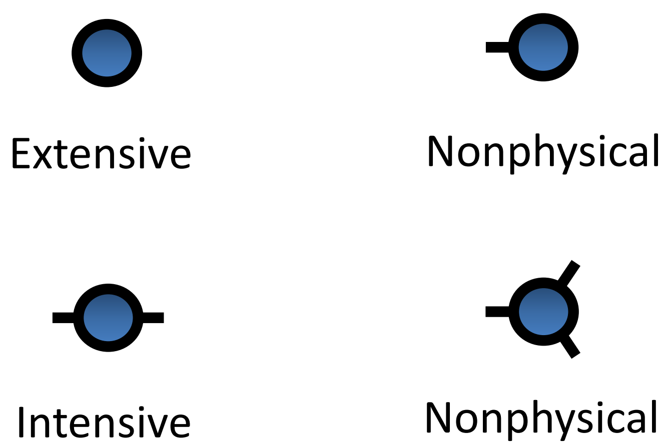
Vibrational many-body methods

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)

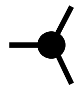


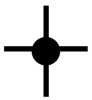


(Goldstone, Proc. Roy. Soc. London A **1957**)

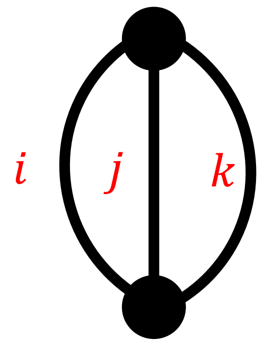
Diagrams

$$\hat{H} = -\frac{1}{2}\sum_{i}\frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\sum_{i} F_{ii}Q_i^2 + \frac{1}{3!}\sum_{i,j,k} F_{ijk}Q_iQ_jQ_k + \frac{1}{4!}\sum_{i,j,k,l} F_{ijkl}Q_iQ_jQ_kQ_l + \cdots$$





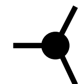
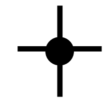
(normal coordinates)



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

Diagrams

$$\hat{H} = -\frac{1}{2}\sum_{i}\frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\sum_{i} F_{ii}Q_i^2 + \frac{1}{3!}\sum_{i,j,k} F_{ijk}Q_iQ_jQ_k + \frac{1}{4!}\sum_{i,j,k,l} F_{ijkl}Q_iQ_jQ_kQ_l + \cdots$$

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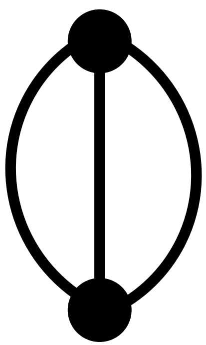
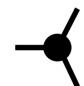


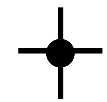
$\propto V^1$

Size-extensive
Total energy

Diagrams

$$\hat{H} = -\frac{1}{2}\sum_{i}\frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\sum_{i} F_{ii}Q_i^2 + \frac{1}{3!}\sum_{i,j,k} F_{ijk}Q_iQ_jQ_k + \frac{1}{4!}\sum_{i,j,k,l} F_{ijkl}Q_iQ_jQ_kQ_l + \cdots$$





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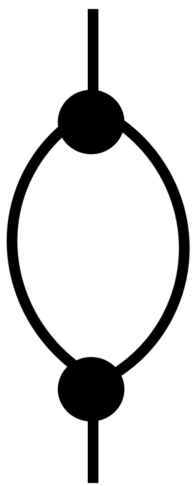
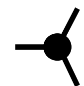


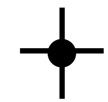
$\propto V^0$

Size-intensive
Frequency

VSCF and XVSCF

$$\hat{H} = -\frac{1}{2}\sum_{i}\frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\sum_{i} F_{ii}Q_i^2 + \frac{1}{3!}\sum_{i,j,k} F_{ijk}Q_iQ_jQ_k + \frac{1}{4!}\sum_{i,j,k,l} F_{ijkl}Q_iQ_jQ_kQ_l + \cdots$$

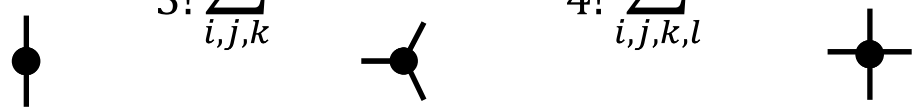




$$\left(-\frac{1}{2}\frac{\partial^2}{\partial Q_i^2} + U_i(Q_i)\right)\phi_i(Q_i) = \epsilon_i\phi_i(Q_i)$$

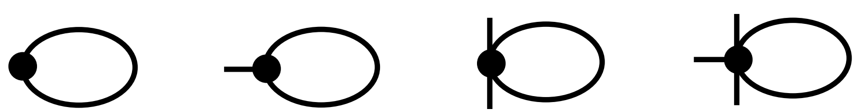
VSCF and XVSCF

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



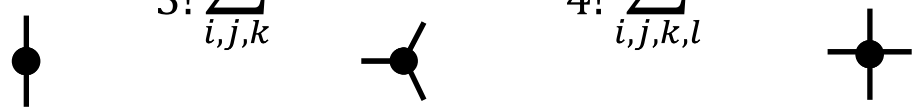
$$\left(-\frac{1}{2}\frac{\partial^2}{\partial Q_i^2} + U_i(Q_i)\right)\phi_i(Q_i) = \epsilon_i\phi_i(Q_i)$$

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



VSCF and XVSCF

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

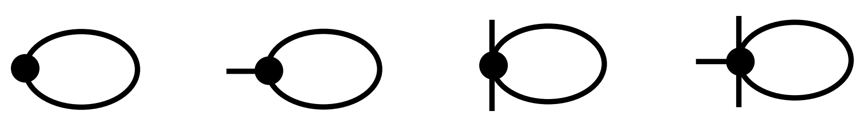


Keçeli and Hirata , *J. Chem. Phys.* **2011**

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

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

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



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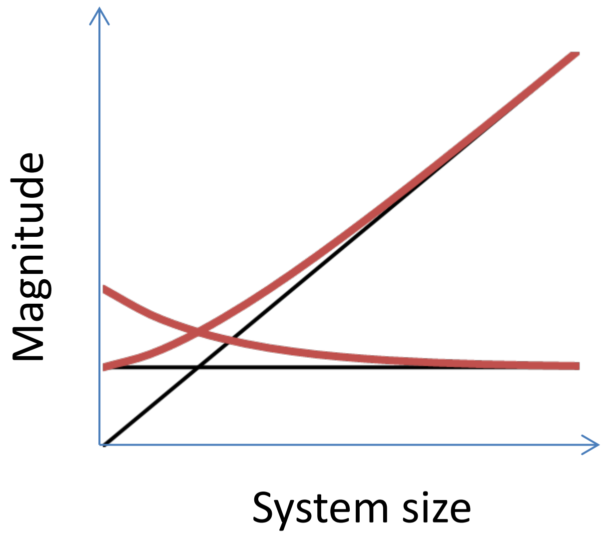

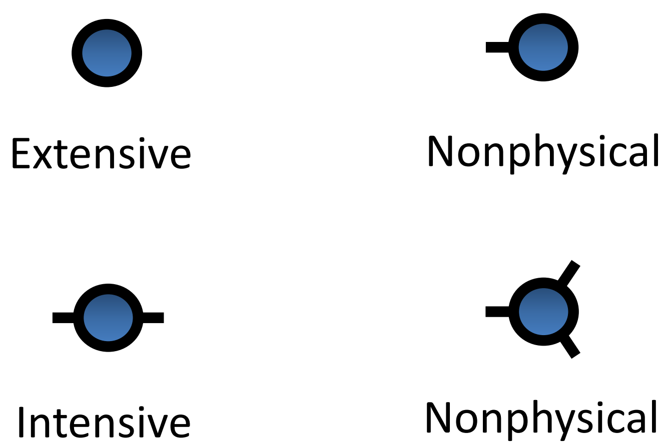

Vibrational perturbation theory

Obtaining anharmonic frequencies

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

Vibrational perturbation theory

Obtaining anharmonic frequencies

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

$$E_{\boldsymbol{s}}^{(2)} = \sum_{\boldsymbol{v} \neq \boldsymbol{s}} \frac{\left| \left\langle \Phi_{\boldsymbol{s}}^{(0)} \middle| \hat{H}_1 \middle| \Phi_{\boldsymbol{v}}^{(0)} \right\rangle \right|^2}{\underbrace{E_{\boldsymbol{s}}^{(0)} - E_{\boldsymbol{v}}^{(0)}}_{\text{Fermi, Darling-Dennison, } etc.\text{ resonance}}}$$

Vibrational perturbation theory

Obtaining anharmonic frequencies

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

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Standard remedy: delete divergent terms in $E_{\boldsymbol{s}}^{(2)}$ ("***P***-space") and…

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

$$\boldsymbol{H}_{\text{eff}} = \begin{matrix} \left\langle \Phi_{\boldsymbol{P1}}^{(0)} \middle| \hat{H}_{\text{eff}} \middle| \Phi_{\boldsymbol{P1}}^{(0)} \right\rangle & \left\langle \Phi_{\boldsymbol{P1}}^{(0)} \middle| \hat{H}_{\text{eff}} \middle| \Phi_{\boldsymbol{P2}}^{(0)} \right\rangle \\ \left\langle \Phi_{\boldsymbol{P1}}^{(0)} \middle| \hat{H}_{\text{eff}} \middle| \Phi_{\boldsymbol{P2}}^{(0)} \right\rangle & \left\langle \Phi_{\boldsymbol{P2}}^{(0)} \middle| \hat{H}_{\text{eff}} \middle| \Phi_{\boldsymbol{P2}}^{(0)} \right\rangle \end{matrix}$$

Selection of ***P***-space:

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

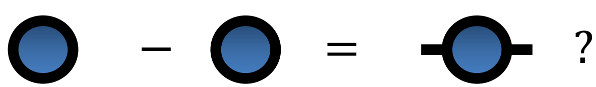
Matthews & Stanton, *Mol. Phys.* **2009**

Vibrational perturbation theory

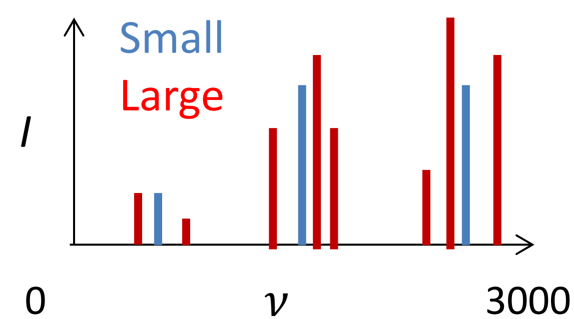
In the spirit of size consistency…

$$\nu_{\boldsymbol{v}} = \underbrace{E_{\boldsymbol{v}}^{(0)} + E_{\boldsymbol{v}}^{(1)} + E_{\boldsymbol{v}}^{(2)} - E_{\mathbf{0}}^{(0)} - E_{\mathbf{0}}^{(1)} - E_{\mathbf{0}}^{(2)}}_{\text{Size-intensive?}}$$

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



$$\boldsymbol{H}_{\text{eff}} = \underbrace{\begin{matrix} \left\langle \Phi_{\boldsymbol{P1}}^{(0)} \middle| \hat{H}_{\text{eff}} \middle| \Phi_{\boldsymbol{P1}}^{(0)} \right\rangle & \left\langle \Phi_{\boldsymbol{P1}}^{(0)} \middle| \hat{H}_{\text{eff}} \middle| \Phi_{\boldsymbol{P2}}^{(0)} \right\rangle \\ \left\langle \Phi_{\boldsymbol{P1}}^{(0)} \middle| \hat{H}_{\text{eff}} \middle| \Phi_{\boldsymbol{P2}}^{(0)} \right\rangle & \left\langle \Phi_{\boldsymbol{P2}}^{(0)} \middle| \hat{H}_{\text{eff}} \middle| \Phi_{\boldsymbol{P2}}^{(0)} \right\rangle \end{matrix}}_{\text{Size of } \boldsymbol{P}\text{-space tends to grow with system size}}$$



Green's function

$$G_{ij}(t_2 - t_1) \equiv \langle \Phi_{\mathbf{0}} | T\{(a_i(t_2) + a_i^\dagger(t_2))(a_j(t_1) + a_j^\dagger(t_1))\} | \Phi_{\mathbf{0}} \rangle$$

Green's function

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Fourier transform

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

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

Green's function

$$G_{ij}(t_2 - t_1) \equiv \langle \Phi_{\mathbf{0}} | T\{(a_i(t_2) + a_i^\dagger(t_2))(a_j(t_1) + a_j^\dagger(t_1))\} | \Phi_{\mathbf{0}} \rangle$$

Fourier transform

$\hat{H}$: full Hamiltonian

$$G_{ii}(\nu) = \sum_{\boldsymbol{v}} \frac{\left| \langle \Phi_{\mathbf{0}} | (a_i + a_i^\dagger) | \Phi_{\boldsymbol{v}} \rangle \right|^2}{\nu - (E_{\boldsymbol{v}} - E_{\mathbf{0}}) + i\delta} + \sum_{\boldsymbol{v}} \frac{\left| \langle \Phi_{\mathbf{0}} | (a_i + a_i^\dagger) | \Phi_{\boldsymbol{v}} \rangle \right|^2}{-\nu - \underbrace{(E_{\boldsymbol{v}} - E_{\mathbf{0}})}_{\text{Exact frequencies}} + i\delta}$$

Intensities

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

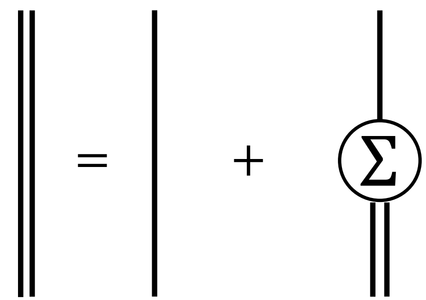
$$G_{ii}^{(0)}(\nu) = \frac{1}{\nu - \omega_i + i\delta} + \frac{1}{-\nu - \underbrace{\omega_i}_{\text{Harmonic frequencies}} + i\delta}$$

The Dyson equation

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

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

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



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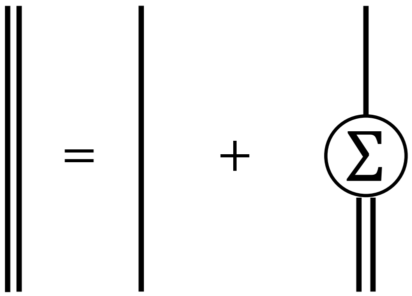
$$= \left\{ \left\{ G_{ii}^{(0)}(\nu) \right\}^{-1} - \Sigma_{ii}(\nu) \right\}^{-1}$$

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



Dyson equation

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

Self-consistent equation

RSPT

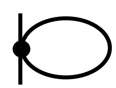
$$\nu_{\boldsymbol{v}} = E_{\boldsymbol{v}}^{(0)} + E_{\boldsymbol{v}}^{(1)} + E_{\boldsymbol{v}}^{(2)} - E_{\boldsymbol{0}}^{(0)} - E_{\boldsymbol{0}}^{(1)} - E_{\boldsymbol{0}}^{(2)}$$

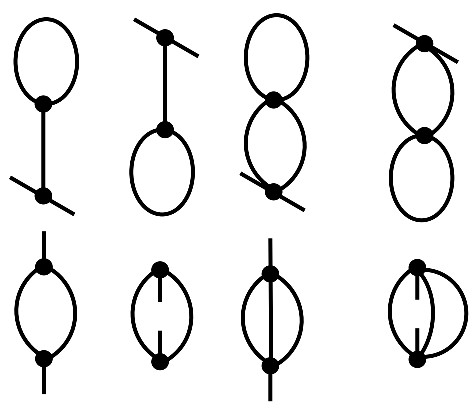
Simple sum

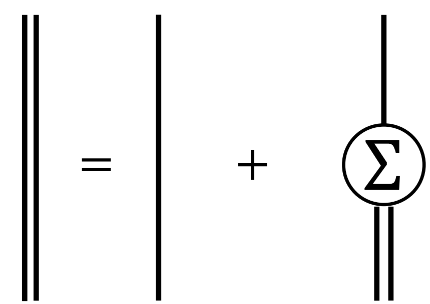
Potentially divergent terms

The Dyson self-energy

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

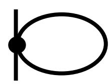
$\Sigma_{ii}^{(1)}(\nu) =$ 

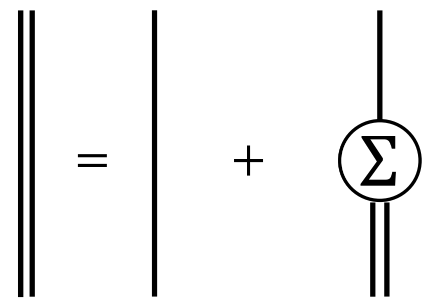
$\Sigma_{ii}^{(2)}(\nu) =$ 



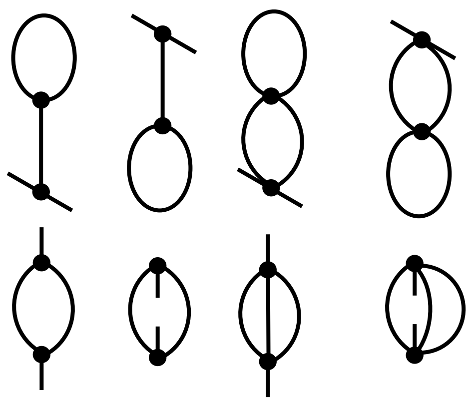
The Dyson self-energy

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

$\Sigma_{ii}^{(1)}(\nu) =$  $= \dfrac{1}{2}\displaystyle\sum_{j} F_{iijj}\left(2^2\omega_i\omega_j\right)^{-1}$

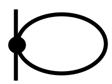


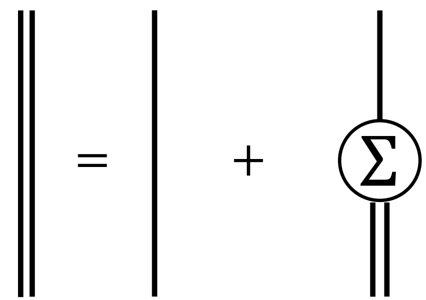
$\Sigma_{ii}^{(2)}(\nu) =$

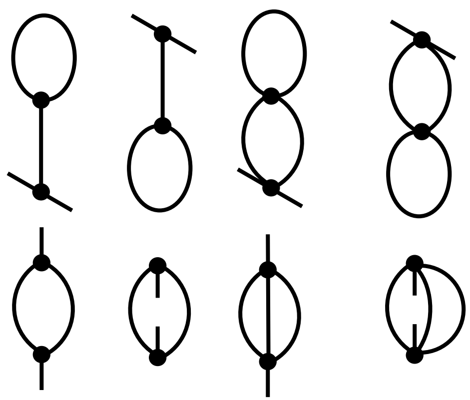


The Dyson self-energy

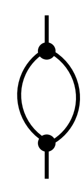
$$\Sigma_{ii}(\nu) = \Sigma_{ii}^{(1)}(\nu) + \Sigma_{ii}^{(2)}(\nu) + \Sigma_{ii}^{(3)}(\nu) + \cdots$$

$\Sigma_{ii}^{(1)}(\nu) =$  $= \dfrac{1}{2}\sum_{j} F_{iijj}\left(2^2\omega_i\omega_j\right)^{-1}$



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

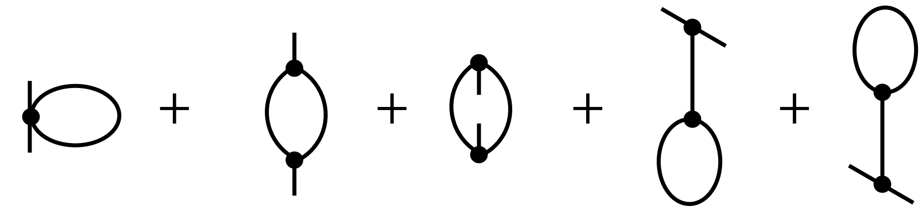
cf. Barone & Minichino *J. Mol. Struct. (Theochem)* **1995**

 $= \dfrac{1}{2}\sum_{jk} \dfrac{F_{ijk}^2\left(2^3\omega_i\omega_j\omega_k\right)^{-1}}{\nu - \omega_j - \omega_k}$

Connection to VPT2 frequencies

$$E(\boldsymbol{v}) = V_{\mathrm{ref}} + \chi_0 + \sum_i \omega_i \left(v_i + \frac{1}{2}\right) + \sum_{i \le j} \chi_{ij} \left(v_i + \frac{1}{2}\right)\left(v_j + \frac{1}{2}\right)$$

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



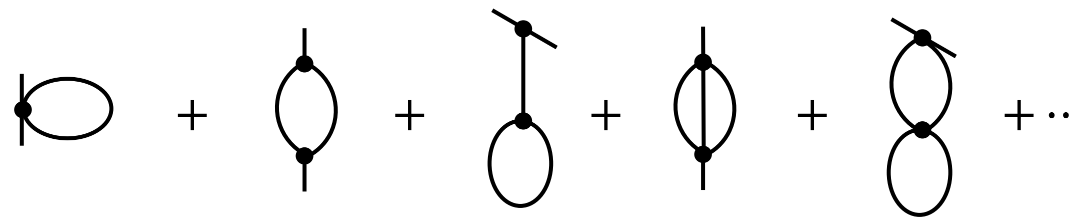
$$\Sigma_{ii}^{(v)}\underline{(\omega_i)} = 2\chi_{ii} + \frac{1}{2}\sum_{j \ne i} \chi_{ij}$$

VPT2 correction to fundamental frequency

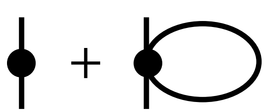
Two perturbation theories

XVH

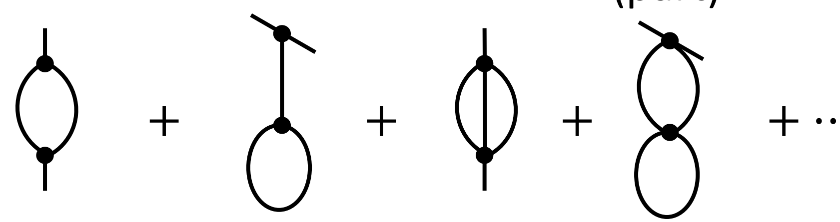
$\hat{H}_0$: 

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

XVMP

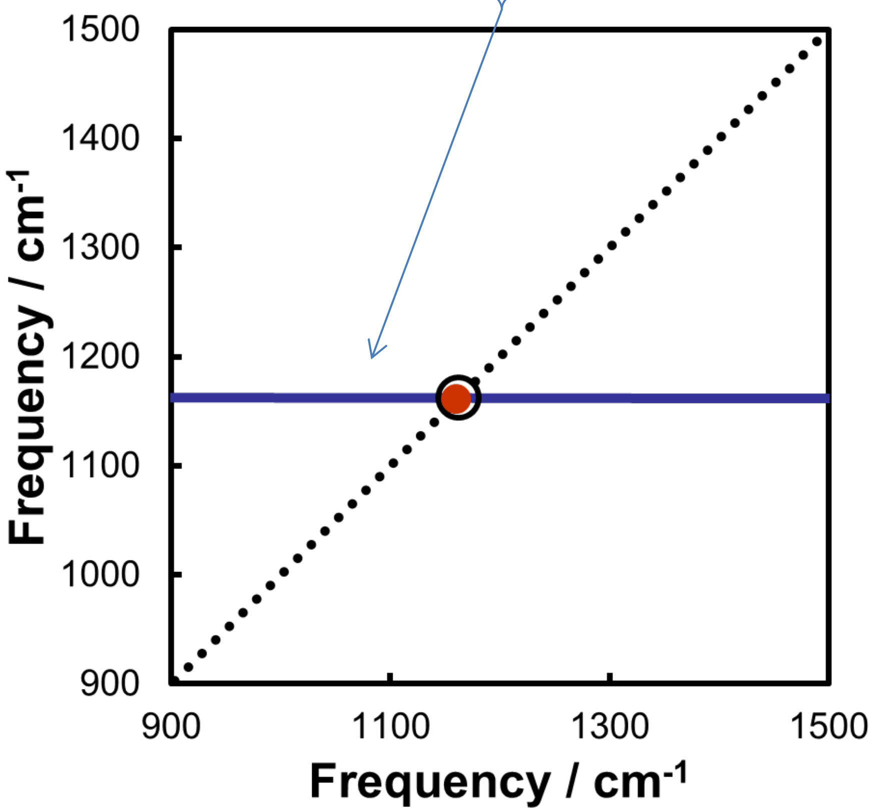
$\hat{H}_0$: 

(part)

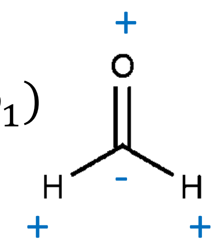
$\Sigma_{ii}(\nu) =$ 

Formaldehyde, no resonance

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



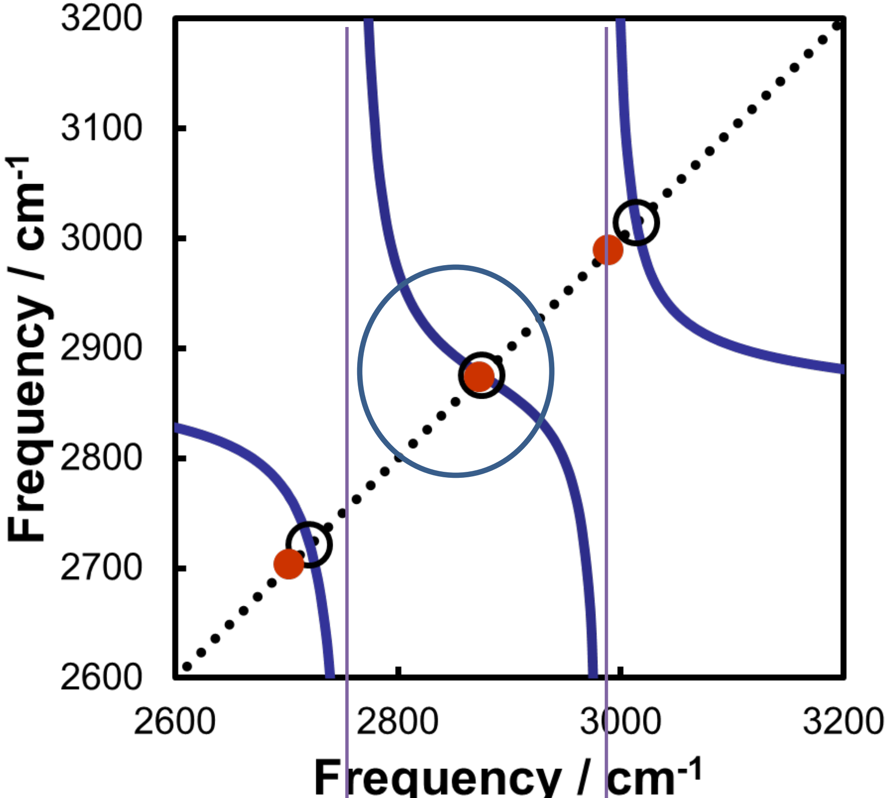
$\nu_4(b_1)$



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

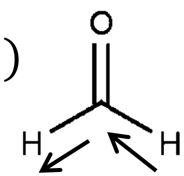
Formaldehyde, resonance

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



Combinations: $\omega_3 + \omega_6$ $\omega_2 + \omega_6$

$\nu_5(b_2)$



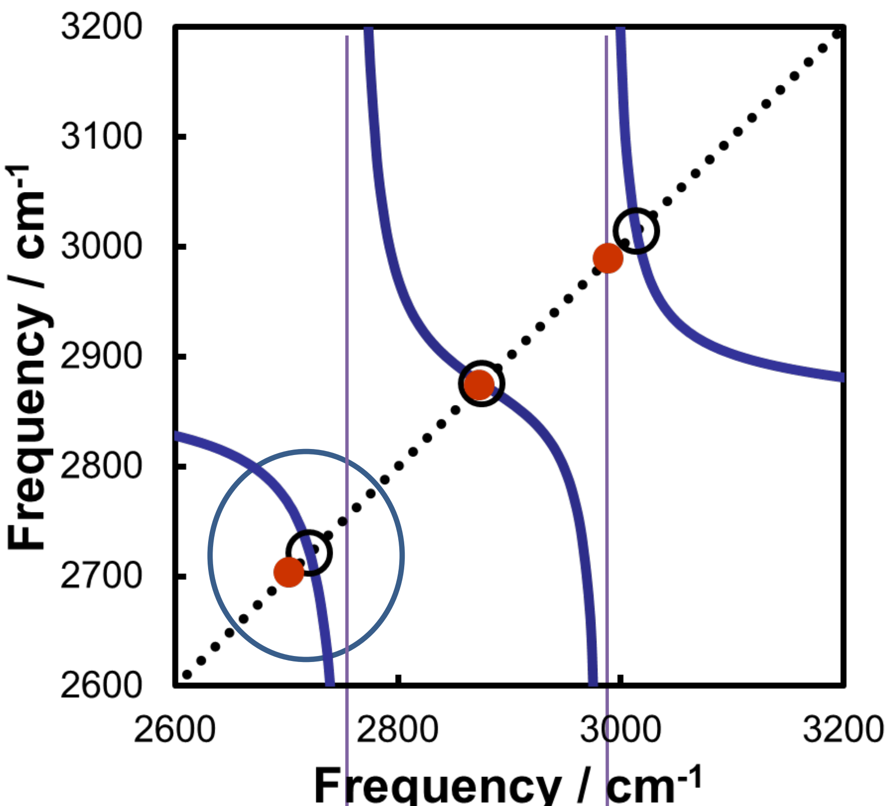
VCI	2873 cm^{-1}
VMP2	+691 cm^{-1}
XVH2	+11 cm^{-1}
XVMP2	+2.1 cm^{-1}

Intensity

VCI: 0.47
XVH2: 0.52
XVMP2: 0.62

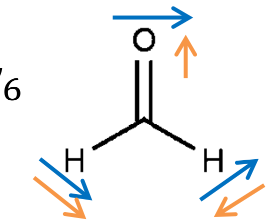
Formaldehyde, resonance

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



Combinations: $\boxed{\omega_3 + \omega_6}$ $\boxed{\omega_2 + \omega_6}$

$\nu_3\nu_6$



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