Vibrational Møller Plesset Perturbation Theory

Zero-th order Hamiltonian and Energy

$$\widehat{H}_0 = \sum_{i=1}^{f} \left[-\frac{1}{2}\frac{\partial^2}{\partial Q_i^2} + \bar{V}_i(Q_i) \right], \tag{1}$$

$$\Delta = \widehat{H} - \widehat{H}_0 = V^{nMR} - \sum_{i=1}^{f} \bar{V}_i \,, \tag{2}$$

$$E_{\boldsymbol{p}}^{(0)} = \langle \boldsymbol{p} | \widehat{H}_0 | \boldsymbol{p} \rangle = \sum_{i=1}^{f} \epsilon_{p_i}^{(i)} \,, \tag{3}$$

Perturbative expansion

$$\Psi_{\boldsymbol{p}} = \Psi_{\boldsymbol{p}}^{(0)} + \lambda \Psi_{\boldsymbol{p}}^{(1)} + \lambda^2 \Psi_{\boldsymbol{p}}^{(2)} + \cdots, \tag{4}$$

$$E_{\boldsymbol{p}} = E_{\boldsymbol{p}}^{(0)} + \lambda E_{\boldsymbol{p}}^{(1)} + \lambda^2 E_{\boldsymbol{p}}^{(2)} + \cdots, \tag{5}$$

1st-order energy

$$E_{\boldsymbol{p}}^{(1)} = \langle \boldsymbol{p} | \Delta | \boldsymbol{p} \rangle, \tag{6}$$

$$E_{\boldsymbol{p}}^{(0+1)} = \langle \boldsymbol{p} | \widehat{H}_0 + \Delta | \boldsymbol{p} \rangle = \langle \boldsymbol{p} | \widehat{H} | \boldsymbol{p} \rangle = E_{\boldsymbol{p}}^{\mathrm{VSCF}}, \tag{7}$$

VMP2 energy

$$E_{\boldsymbol{p}}^{\mathrm{VMP2}} = E_{\boldsymbol{p}}^{(0+1)} + E_{\boldsymbol{p}}^{(2)}, \tag{8}$$

$$E_{\boldsymbol{p}}^{(2)} = \sum_{\boldsymbol{q}\neq\boldsymbol{p}} \frac{\langle \boldsymbol{p}|\widehat{H}|\boldsymbol{q}\rangle\langle \boldsymbol{q}|\widehat{H}|\boldsymbol{p}\rangle}{E_{\boldsymbol{p}}^{(0)} - E_{\boldsymbol{q}}^{(0)}}, \tag{9}$$

$$= \sum_{l=1}^{n} \sum_{\boldsymbol{i}_l} \sum_{\boldsymbol{q}_{\boldsymbol{i}_l}\neq\boldsymbol{p}_{\boldsymbol{i}_l}} \frac{\left\langle \boldsymbol{p}\middle|\widehat{H}\middle|\boldsymbol{p}_{\boldsymbol{p}_{\boldsymbol{i}_l}}^{\boldsymbol{q}_{\boldsymbol{i}_l}}\right\rangle \left\langle \boldsymbol{p}_{\boldsymbol{p}_{\boldsymbol{i}_l}}^{\boldsymbol{q}_{\boldsymbol{i}_l}}\middle|\widehat{H}\middle|\boldsymbol{p}\right\rangle}{\delta\epsilon_{\boldsymbol{p}_{\boldsymbol{i}_l}}^{\boldsymbol{q}_{\boldsymbol{i}_l}}}, \tag{10}$$

$$N_{conf} = \sum_{l=1}^{n} N_{conf}^{(l)} = \sum_{l=1}^{n} \binom{f}{l} (M-1)^l, \tag{11}$$

VMP2-(k) energy

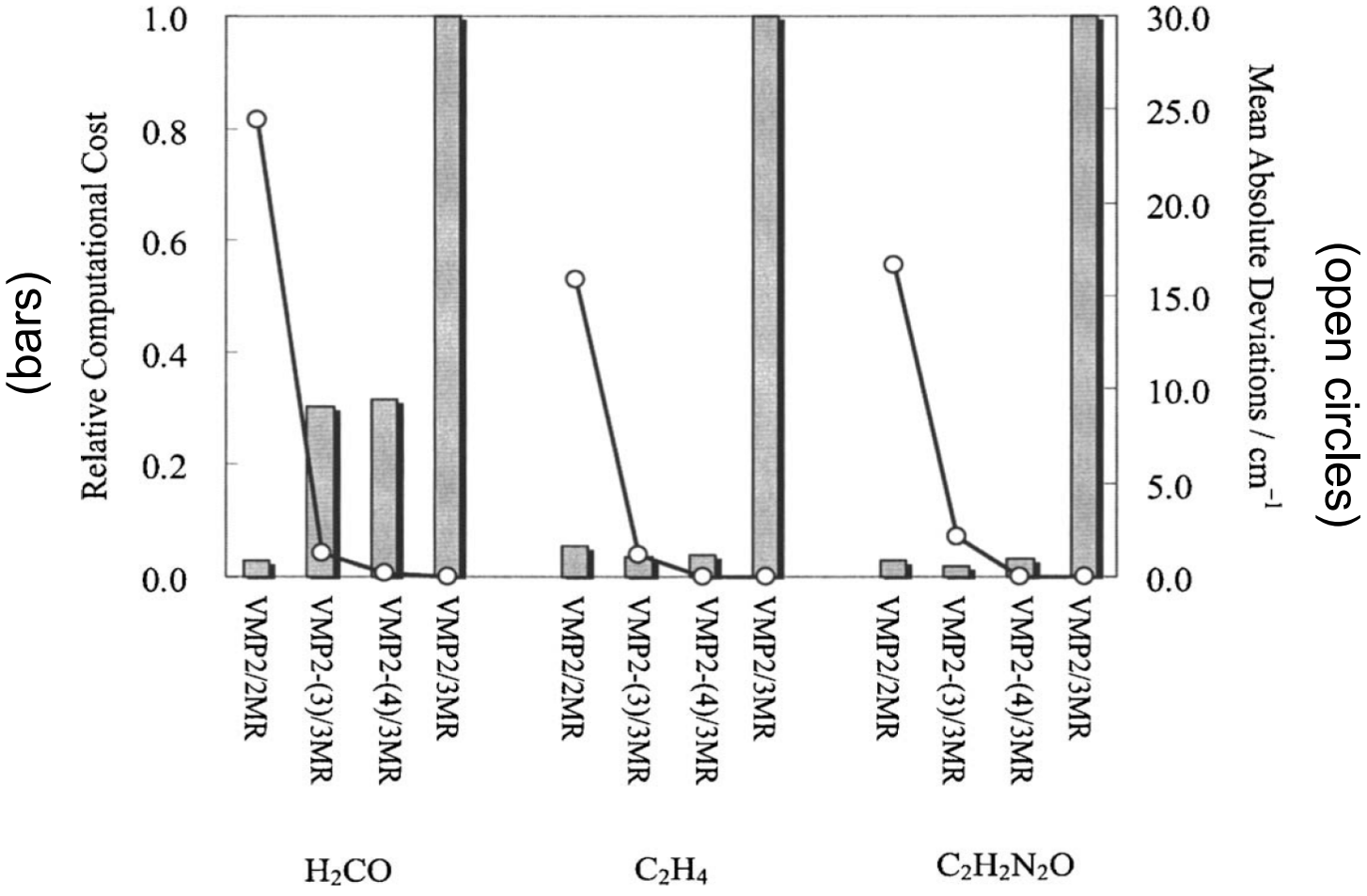
$$E_{\boldsymbol{p}}^{(2)} \simeq \sum_{l=1}^{n} \sum_{\lambda_{\boldsymbol{q}_{\boldsymbol{i}_l}\boldsymbol{p}_{\boldsymbol{i}_l}}\leq k} \frac{\left\langle \boldsymbol{p}\middle|\widehat{H}\middle|\boldsymbol{p}_{\boldsymbol{p}_{\boldsymbol{i}_l}}^{\boldsymbol{q}_{\boldsymbol{i}_l}}\right\rangle \left\langle \boldsymbol{p}_{\boldsymbol{p}_{\boldsymbol{i}_l}}^{\boldsymbol{q}_{\boldsymbol{i}_l}}\middle|\widehat{H}\middle|\boldsymbol{p}\right\rangle}{\delta\epsilon_{\boldsymbol{p}_{\boldsymbol{i}_l}}^{\boldsymbol{q}_{\boldsymbol{i}_l}}}, \tag{12}$$

$$N_{conf} = \sum_{l=1}^{n} \binom{f}{l}\binom{k}{l}, \tag{13}$$

# of configurations in the VMP2 summation.

	H_2CO	C_2H_4	$C_2H_2N_2O$
VMP2	21,500	226,600	465,500
VMP2-(3)	78	324	633
VMP2-(4)	240	1,065	2,178

(n = 3, M = 11)



K. Yagi, S. Hirata, and K. Hirao, JCP **127**, 034111 (2007).

Vibrational Quasi-degenerate Perturbation Theory

B. Kirtman, J. Chem. Phys. **49**, 3890 (1968).
I. Shavitt and L. T. Redmon, J. Chem. Phys. **73**, 5711 (1980).
K. Yagi, S. Hirata, and K. Hirao, PCCP **10**, 1781 (2008).

P and Q space

$$P = \sum_{\boldsymbol{p}} |\boldsymbol{p}\rangle\langle\boldsymbol{p}|\,, \tag{14}$$

$$Q = 1 - P = \sum_{\boldsymbol{q}} |\boldsymbol{q}\rangle\langle\boldsymbol{q}|\,, \tag{15}$$

Similarity transform

$$\hat{H}_{\mathrm{eff}} = U^{-1}\hat{H}U, \tag{16}$$

$$\left(\hat{H}_{\mathrm{eff}}\right)_D \equiv P\hat{H}_{\mathrm{eff}}P + Q\hat{H}_{\mathrm{eff}}Q, \tag{17}$$

$$\left(\hat{H}_{\mathrm{eff}}\right)_X \equiv P\hat{H}_{\mathrm{eff}}Q + P\hat{H}_{\mathrm{eff}}Q = 0. \tag{18}$$

Perturbative expansion

$$U = \sum_{n=1}^{\infty} U^{(n)}\,, \hat{H}_{\mathrm{eff}} = \sum_{n=1}^{\infty} \hat{H}_{\mathrm{eff}}^{(n)} \tag{19}$$

Approximate solution in the P space

$$\hat{H}_{\mathrm{eff}}^{(n)}\Psi_{\boldsymbol{p}}^{(n)} = E_{\boldsymbol{p}}^{(n)}\Psi_{\boldsymbol{p}}^{(n)} \tag{20}$$

1st-order QDPT = truncated VCI

$$\left\langle \boldsymbol{p}' \middle| \widehat{H}_{\text{eff}}^{(0+1)} \middle| \boldsymbol{p} \right\rangle = \langle \boldsymbol{p}' | \widehat{H} | \boldsymbol{p} \rangle, \tag{21}$$

2nd-order QDPT

$$\left\langle \boldsymbol{p}' \middle| \widehat{H}_{\text{eff}}^{(2)} \middle| \boldsymbol{p} \right\rangle = \sum_{\boldsymbol{q}} \frac{\langle \boldsymbol{p}' | \widehat{H} | \boldsymbol{q} \rangle \langle \boldsymbol{q} | \widehat{H} | \boldsymbol{p} \rangle}{2} \left\{ \frac{1}{E_{\boldsymbol{p}'}^{(0)} - E_{\boldsymbol{q}}^{(0)}} + \frac{1}{E_{\boldsymbol{p}}^{(0)} - E_{\boldsymbol{q}}^{(0)}} \right\}, \tag{22}$$

If P space component is only one (**p**), QDPT2 reduces to PT2,

$$\left\langle \boldsymbol{p} \middle| \widehat{H}_{\text{eff}}^{(2)} \middle| \boldsymbol{p} \right\rangle = \sum_{\boldsymbol{q} \neq \boldsymbol{p}} \frac{\langle \boldsymbol{p} | \widehat{H} | \boldsymbol{q} \rangle \langle \boldsymbol{q} | \widehat{H} | \boldsymbol{p} \rangle}{E_{\boldsymbol{p}}^{(0)} - E_{\boldsymbol{q}}^{(0)}}, \tag{23}$$

P and Q space construction based on λ_{pq}

K. Yagi and H. Otaki, JCP **140**, 084113 (2014).

Target state(s): **t**

$$A(\mathbf{t},k)=\{\mathbf{t}'\,|\,1\le\lambda_{\mathbf{tt}'}\le k\}.$$

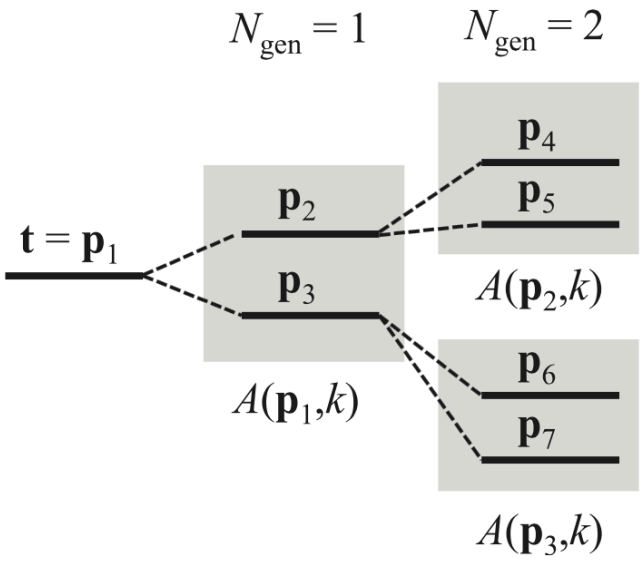


Figure 2. Illustration of *P* space construction algorithm.

P space (degenerate states)

1. For **p**' such that $\lambda_{pp'}\le k$,

   • Discard if $\left|E_{p}^{(0)}-E_{p'}^{(0)}\right|>pth0$, • Select if $\left|\frac{\langle p|\hat{H}|p'\rangle}{E_{p}^{(0)}-E_{p'}^{(0)}}\right|>pth1$,

2. Pruning based on VCI in P space

$$\Psi_{\mathbf{p}}^{\mathrm{VCI}}=\sum_{J}C_{\mathbf{pp}'}\Phi_{\mathbf{p}'}^{\mathrm{VSCF}}$$

   • if $\left|C_{\mathbf{pp}'}\right|<pth2$, then set $C_{\mathbf{pp}'}=0$

   • if $\left|C_{\mathbf{pp}'}\right|^2<pth3$, then discard **p**'

3. Repeat this procedure for N_{Gen} times.

Q space (non-degenerate states)

$$Q_{\mathbf{p}'\mathbf{p}}=A'(\mathbf{p},k)\cap A'(\mathbf{p}',k).$$

K. Yagi, S. Hirata, and K. Hirao, PCCP **10**, 1781 (2008).

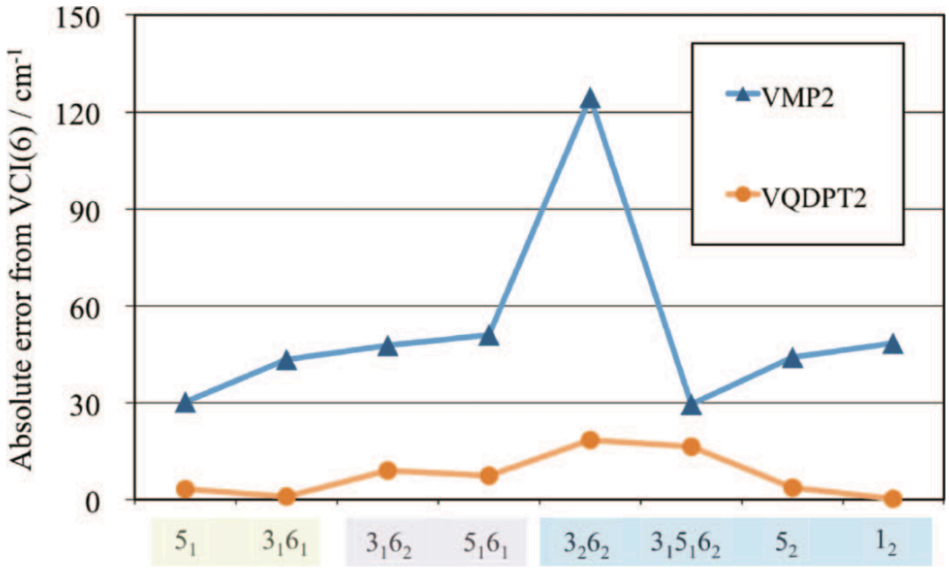
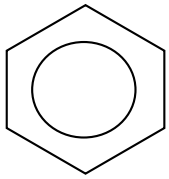
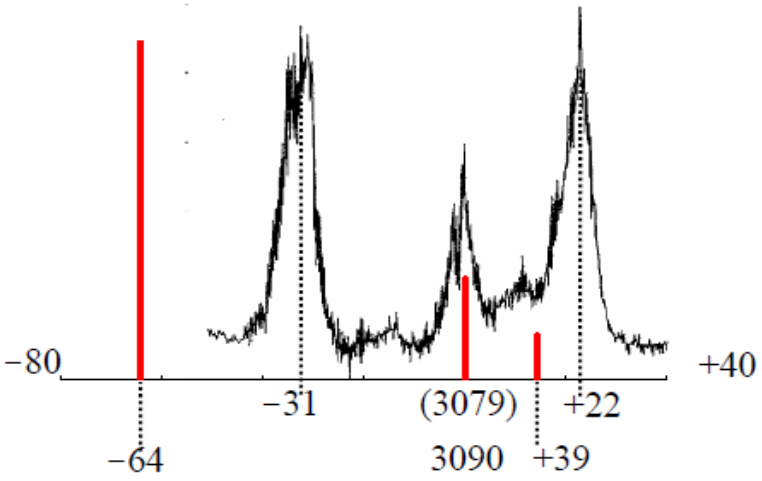


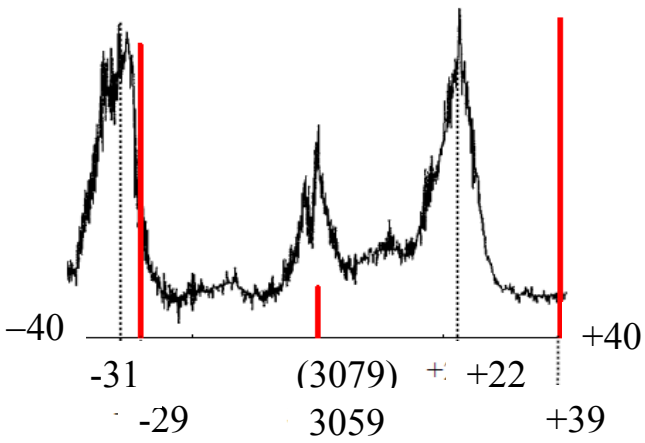
Figure 3. Plots of the error of VMP2 and VQDPT2 frequencies from VCI-(6) frequencies for the resonance states of H_2CO. VMP2 and VQDPT2 used $k = 4$ and $N_{gen} = 3$. The label i_n denote the n-th excited states of the i-th vibrational mode. The mode number is, 1: CH_2 symmetric stretch, 2: CO stretch, 3: CH_2 bending, 4: CH_2 wagging, 5: CH_2 anti-symmetric stretch, 6: CH_2 rocking.



$\nu_{12} \Leftrightarrow \nu_{13}+\nu_{16} \Leftrightarrow \nu_2+\nu_{13}+\nu_{18}$

(CH str.) (CCH bend) (Ring deformation)





QFF (B3LYP/cc-pVDZ)

Multiresolution PES