Vibrational SCF and Correlation Theories with Optimized Coordinates

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Vibrational Structure Theory

- Molecular Hamiltonian and Schrödinger equation

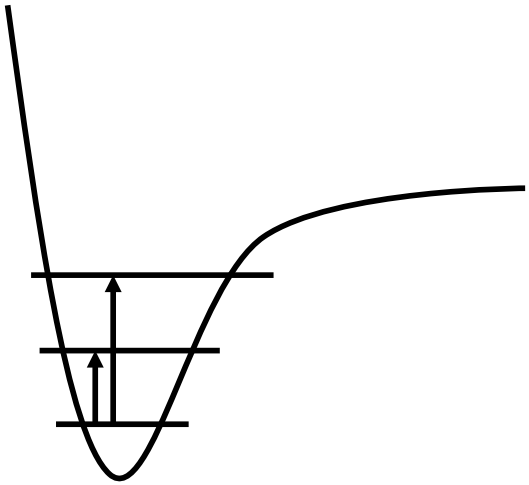
$$\left[\hat{T}_N + \hat{T}_E + \hat{V}_N + \hat{V}_E + \hat{V}_{NE}\right]\Phi_n = E_n\Phi_n$$

- Born-Oppenheimer approx.

$$\Phi_n \cong \Phi_n^{(N)}\Phi_n^{(E)}$$

$$\left[\hat{T}_E + \hat{V}_E + \hat{V}_{NE}\right]\Phi_{n_E}^{(E)} = E_{Nn_E}^{(E)}\Phi_{n_E}^{(E)}$$

$$\left[\hat{T}_N + \hat{V}_N + E_{Nn_E}^{(E)}\right]\Phi_{n_N}^{(N)} = E_{n_N n_E}\Phi_{n_N}^{(N)}$$



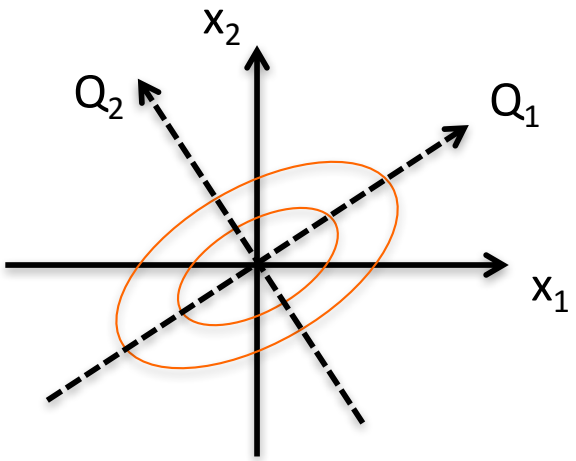
- Vibrational Schrödinger equation

$$\left[\hat{T}_V + \hat{T}_{RV} + V\right]\Phi_{n_v}^{(V)} = E_{n_v n_E}\Phi_{n_v}^{(V)}$$

In practice, we choose a set of coordinates to represent the vibrational SE.

Normal Coordinates

- Obtained by diagonalizing the mass-weighted Hessian

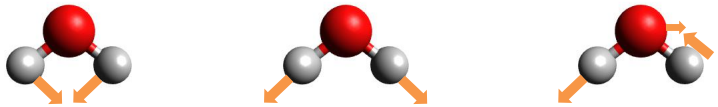


$$V = c_{11}\, x_1^2 + c_{22}\, x_2^2 + c_{12}\, x_1 x_2$$

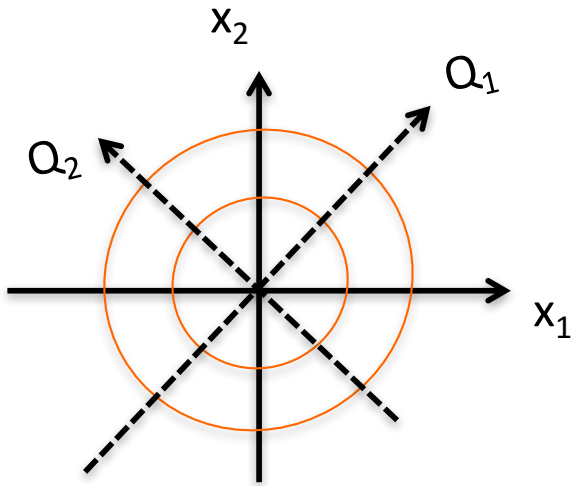
$$\downarrow$$

$$V = c'_{11}\, Q_1^2 + c'_{22}\, Q_2^2$$

(ex) Normal coordinates of a water molecule



- Normal coordinates tend to be delocalized



$V = c_{11}\, x_1^2 + c_{22}\, x_2^2 + c_{12}\, x_1 x_2$ with $c_{11} \approx c_{22} >> c_{12}$

$\text{HO-(CH}_2\text{)}_n\text{-OH}$ $\text{HO-(CH}_2\text{)}_n\text{-OH}$

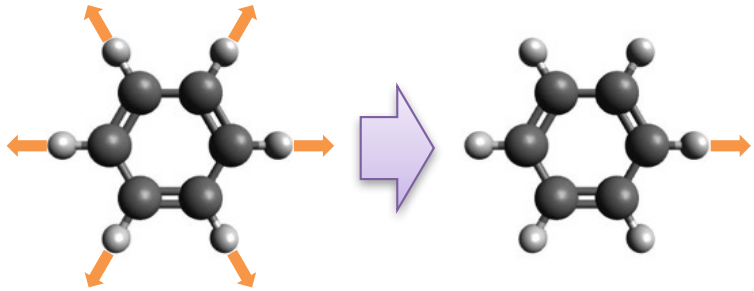
$$\downarrow \quad \phi = \tan^{-1}\left(\frac{c_{12}}{c_{11} - c_{22}}\right) \approx \frac{\pi}{4}$$

$$V = c'_{11}\, Q_1^2 + c'_{22}\, Q_2^2$$

$\text{HO-(CH}_2\text{)}_n\text{-OH}$ $\text{HO-(CH}_2\text{)}_n\text{-OH}$

Normal vs Local modes

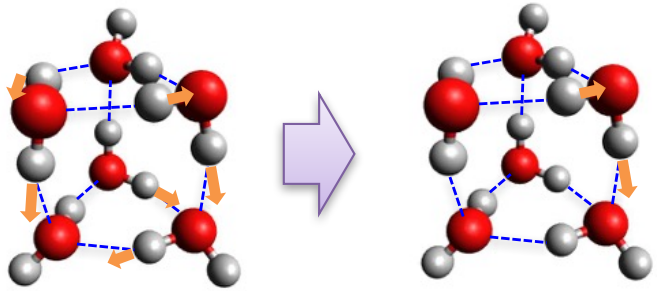
- **Local** XH stretching modes



Henry (1977)

Child & Halonen (1984)

- **Local** monomer model



Wang & Bowman (2010)

- **Localized** mode

Jacob & Reiher (2009)

However, there is no guarantee that local is better than normal...

What is the mathematical definition of **"good"** coordinates?
How can we frame the physical ground?

Optimized-Coordinate Vibrational SCF

Thompson & Truhlar (1982); Bačić, Gerber & Ratner (1986); Bowman, Zuniga, Wierzbicki (1988)
Yagi, Keçeli & Hirata (2012)

VSCF wavefunction: $$\Phi_{\mathbf{0}}(\tilde{\mathbf{Q}}) = \prod_{i=1}^{f} \phi_0^{(i)}(\tilde{Q}_i)$$

VSCF equation: $$\left[-\frac{1}{2}\frac{\partial^2}{\partial Q_i^2} + \left\langle \prod_{j\neq i}^{f} \phi_{n_j}^{(j)} \middle| V \middle| \prod_{j\neq i}^{f} \phi_{n_j}^{(j)} \right\rangle \right] \phi_{n_j}^{(i)}(\tilde{Q}_i) = \varepsilon_{n_j}^{(i)} \phi_{n_j}^{(i)}(\tilde{Q}_i)$$

- $\phi_m^{(i)} = \sum_{n=1}^{M} C_{nm} \chi_n^{(i)}$: modal coefficients
- $\tilde{Q}_s = \sum_{i=1}^{f} U_{is} Q_i,$: transformation matrix

✔ Harmonic potential → Normal coordinates
✔ Non-interacting systems → Local coordinates

Jacobi Sweep Algorithm

Yagi, Keçeli & Hirata (2012), Yagi & Otaki (2014),
Thomsen, Yagi & Christiansen (2014).

Successive 2x2 rotations:

$$\mathbf{U} = \mathbf{U}^{(1)}\mathbf{U}^{(2)}\cdots\mathbf{U}^{(n)},$$

Selection of pairs:

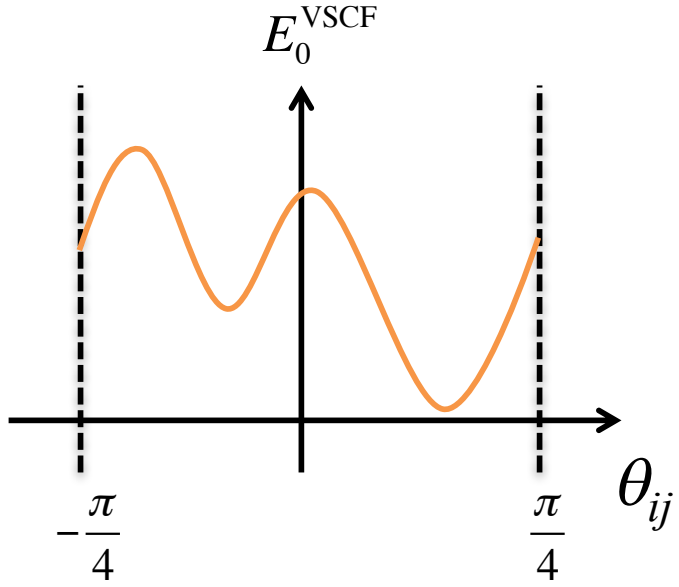
$$\eta_{st} = \sqrt{\frac{(c_{ss} - c_{tt})^2 + c_{st}^2}{c_{ss} + c_{tt}}}$$

- Loop over sweep
  - Loop over mode pairs : **in parallel**

    Numerically find the best θ_{ij}

  - End loop

  check convergence
- End of sweep

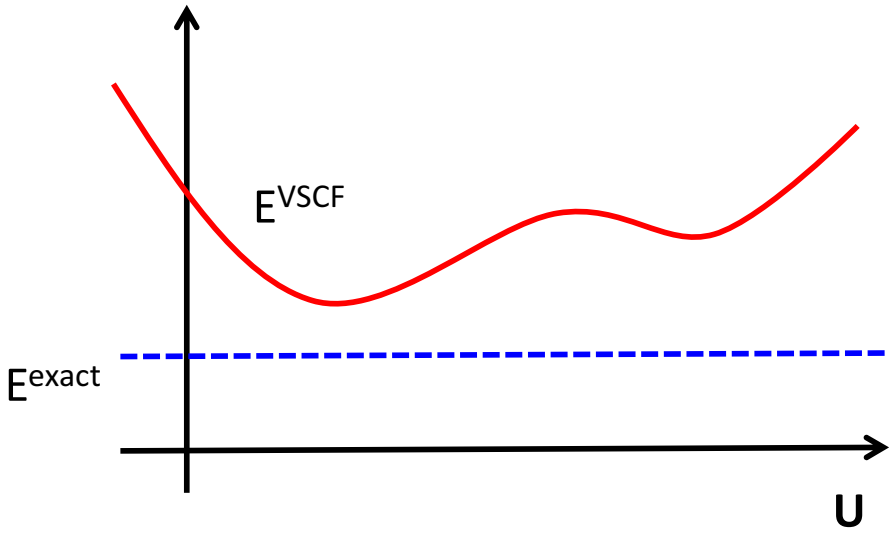


Total # of VSCF calc. = $N_{\mathrm{sweep}} \times N_{\mathrm{pair}} \times 10$

Invariance of the Hamiltonian

Yagi, Keçeli & Hirata (2012)

$$H(\mathbf{Q}) = -\frac{1}{2}\sum_{i=1}^{f}\frac{\partial^2}{\partial Q_i^2} + V(\mathbf{Q})$$



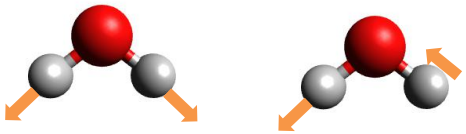
✕ *n*MR expansion

$$V(\mathbf{Q}) = \sum_{i=1}^{f} V_i(Q_i) + \sum_{i>j}^{f} V_{ij}(Q_i,Q_j) + \sum_{i,j,k=1}^{f} V_{ijk}(Q_i,Q_j,Q_k) + \cdots$$

○ Taylor expansion

$$V(\mathbf{Q}) = V_0 + \sum_{i=1}^{f} c_i Q_i + \frac{1}{2}\sum_{i,j=1}^{f} c_{ij} Q_i Q_j + \frac{1}{3!}\sum_{i,j,k=1}^{f} c_{ijk} Q_i Q_j Q_k + \cdots$$

Water

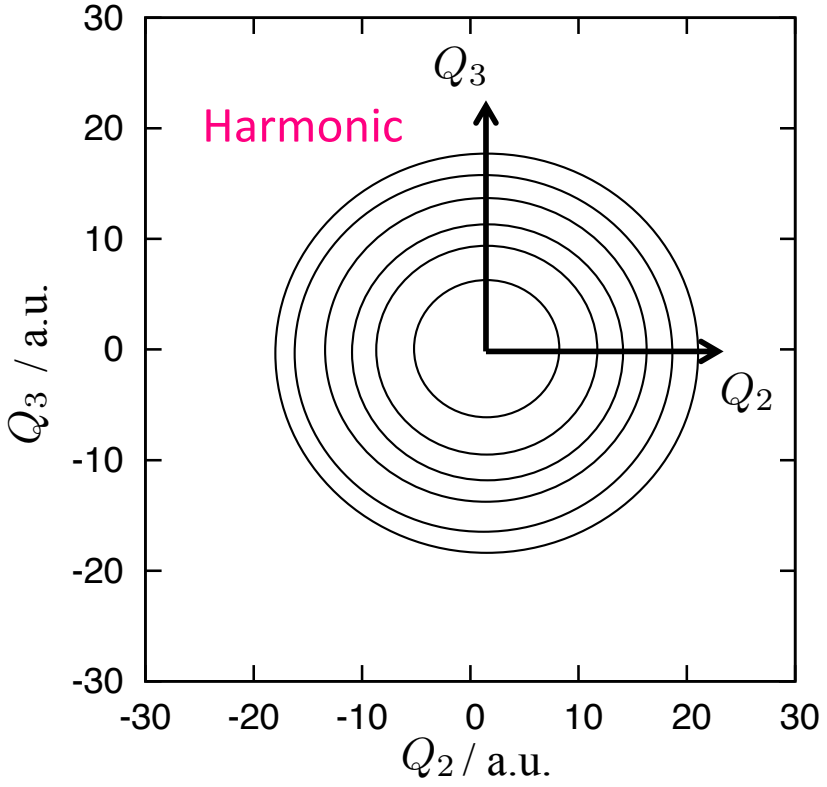


Q_2 Q_3

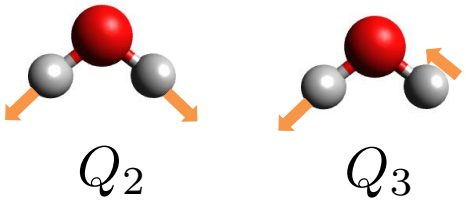
normal

$$V = \frac{1}{2}(\omega_2^2 Q_2^2 + \omega_3^2 Q_3^2)$$

Onigiri

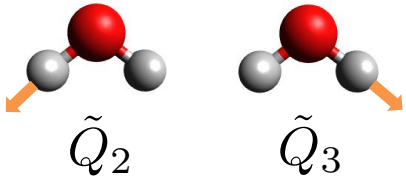


Water



normal

Variationally minimize
the VSCF energy

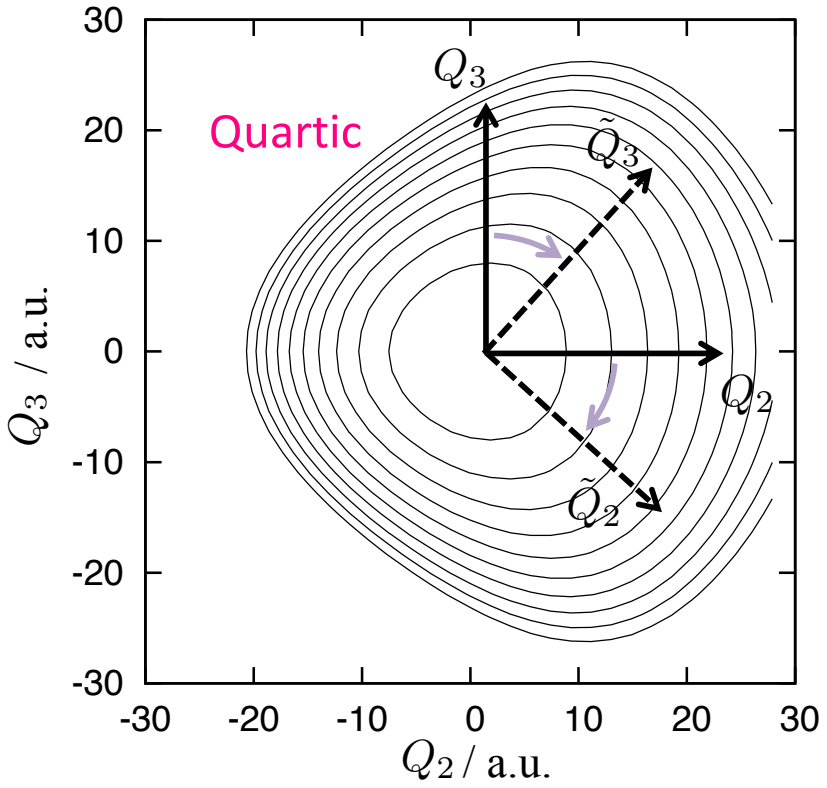


optimized

Child & Halonen, (1984)
Jensen, (2000)

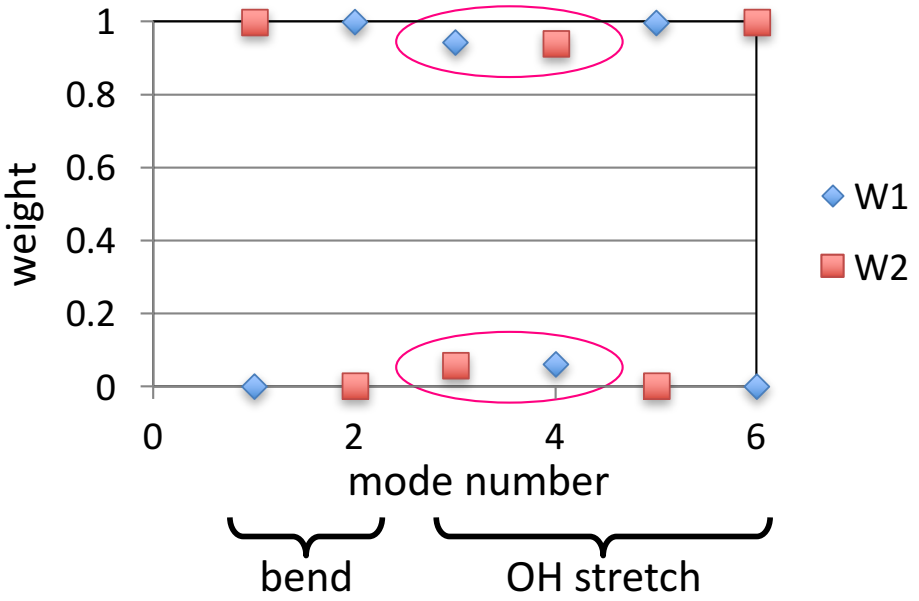
$$V = \frac{1}{2}(\omega_2^2 Q_2^2 + \omega_3^2 Q_3^2)$$
$$+c_{233} Q_2 Q_3^2 + c_{223} Q_2^2 Q_3$$
$$+c_{2233} Q_2^2 Q_3^2$$
$$+c_{2223} Q_2^3 Q_3 + c_{2333} Q_2 Q_3^3$$

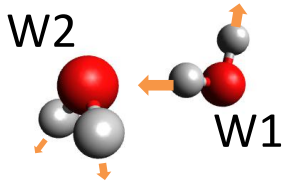
Onigiri



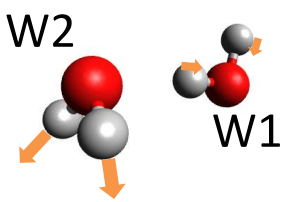
Water dimer

Normal coordinates



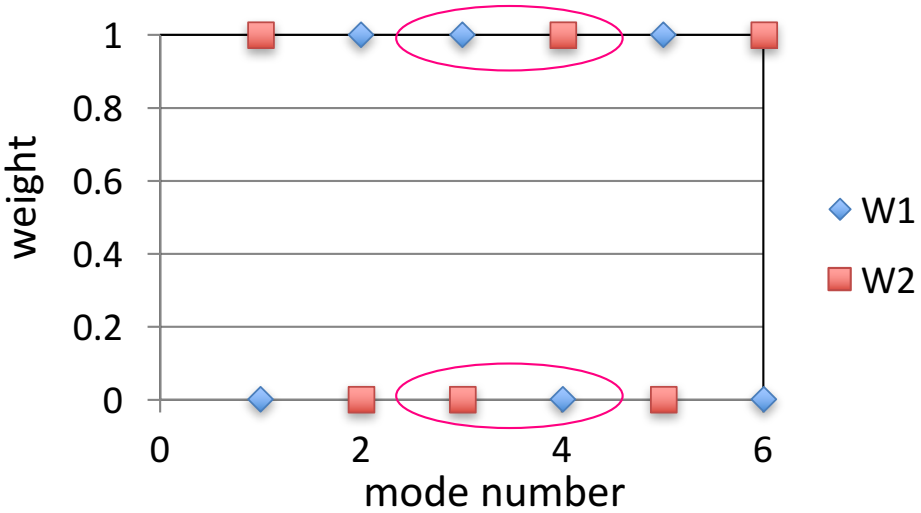


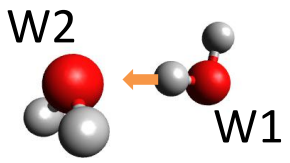
Q_3 : 3783 cm^{-1}



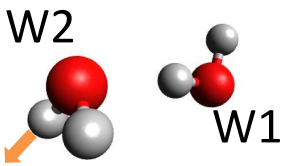
Q_4 : 3836 cm^{-1}

Optimized coordinates





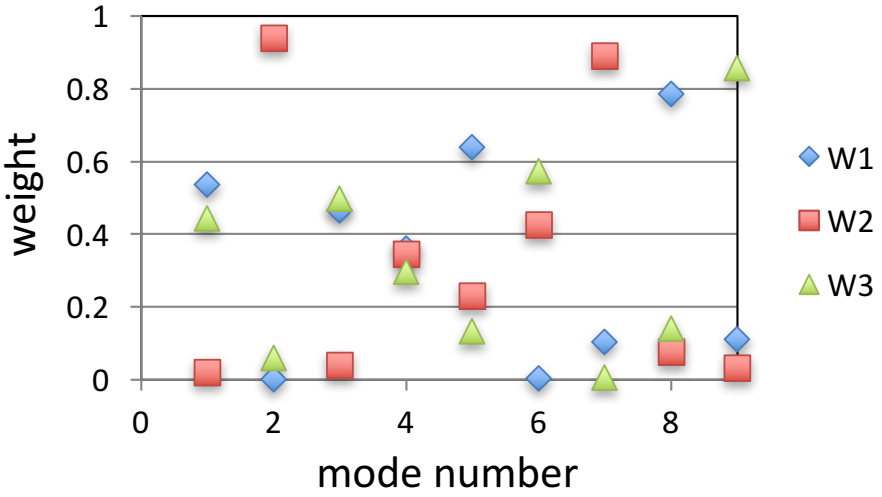
$\tilde{Q}_3$: 3807 cm^{-1}



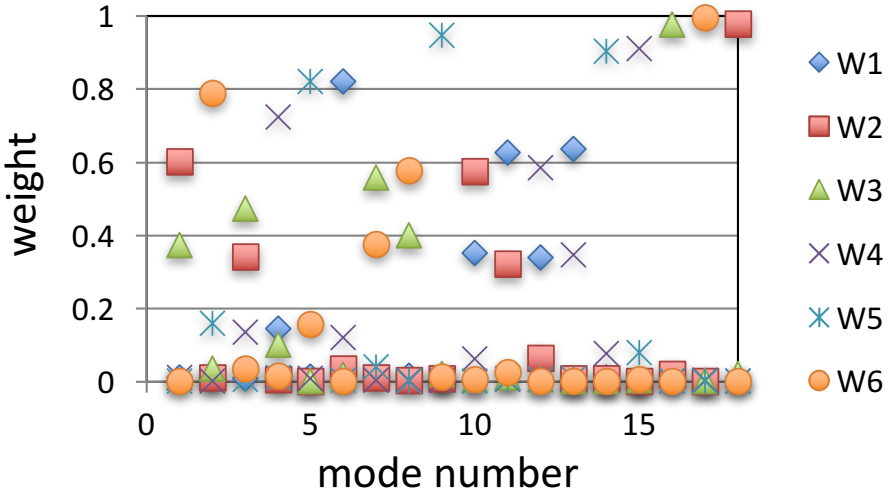
$\tilde{Q}_4$: 3892 cm^{-1}

Water trimer and hexamer

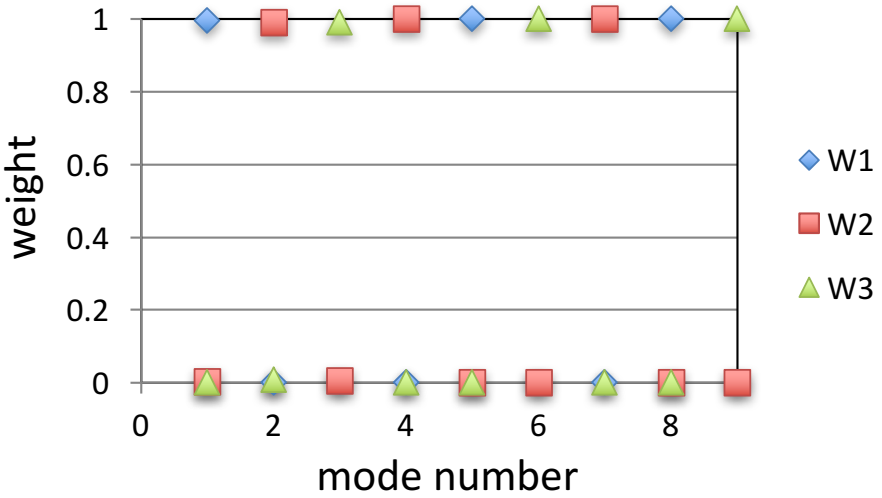
Normal coordinates



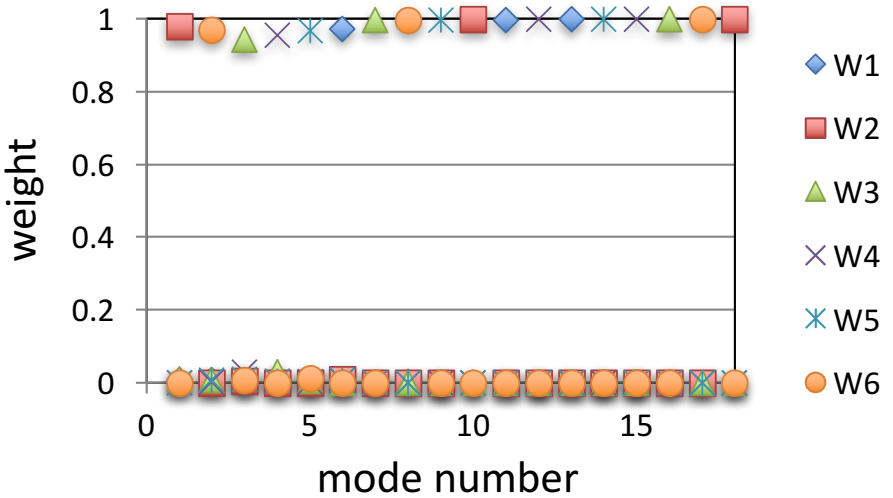
Normal coordinates



Optimized coordinates

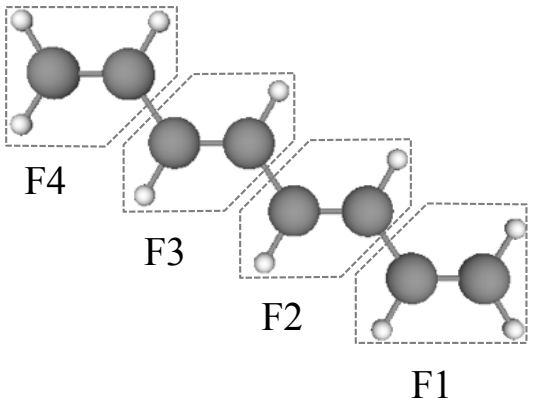


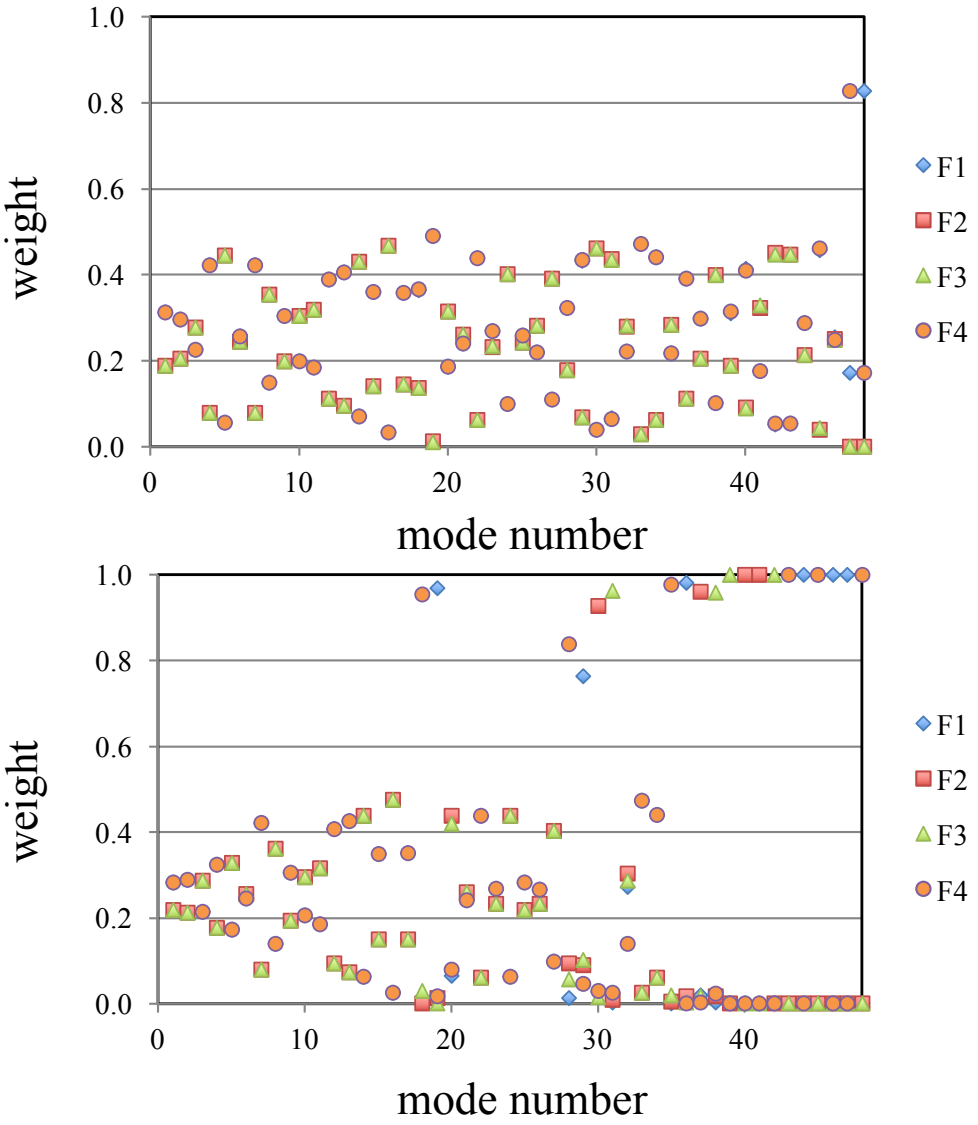
Optimized coordinates



Intramolecular vibration is localized to each water molecule

Octatetraene





C-H and C=C stretch are localized,
yet the scheletal vibration remain delocalized.

On the concept of vibrational modes

The term, “vibrational modes”, is used without discreminating:

- The representative molecular motion
  = separability of the system
- The assignment of the vibrational bands
  = character of the eigenstates

In the harmonic potential, normal coordinates satisfy these two.

oc-VSCF enhance the separability of the system, but does not necessarily characterize the eigenstates.

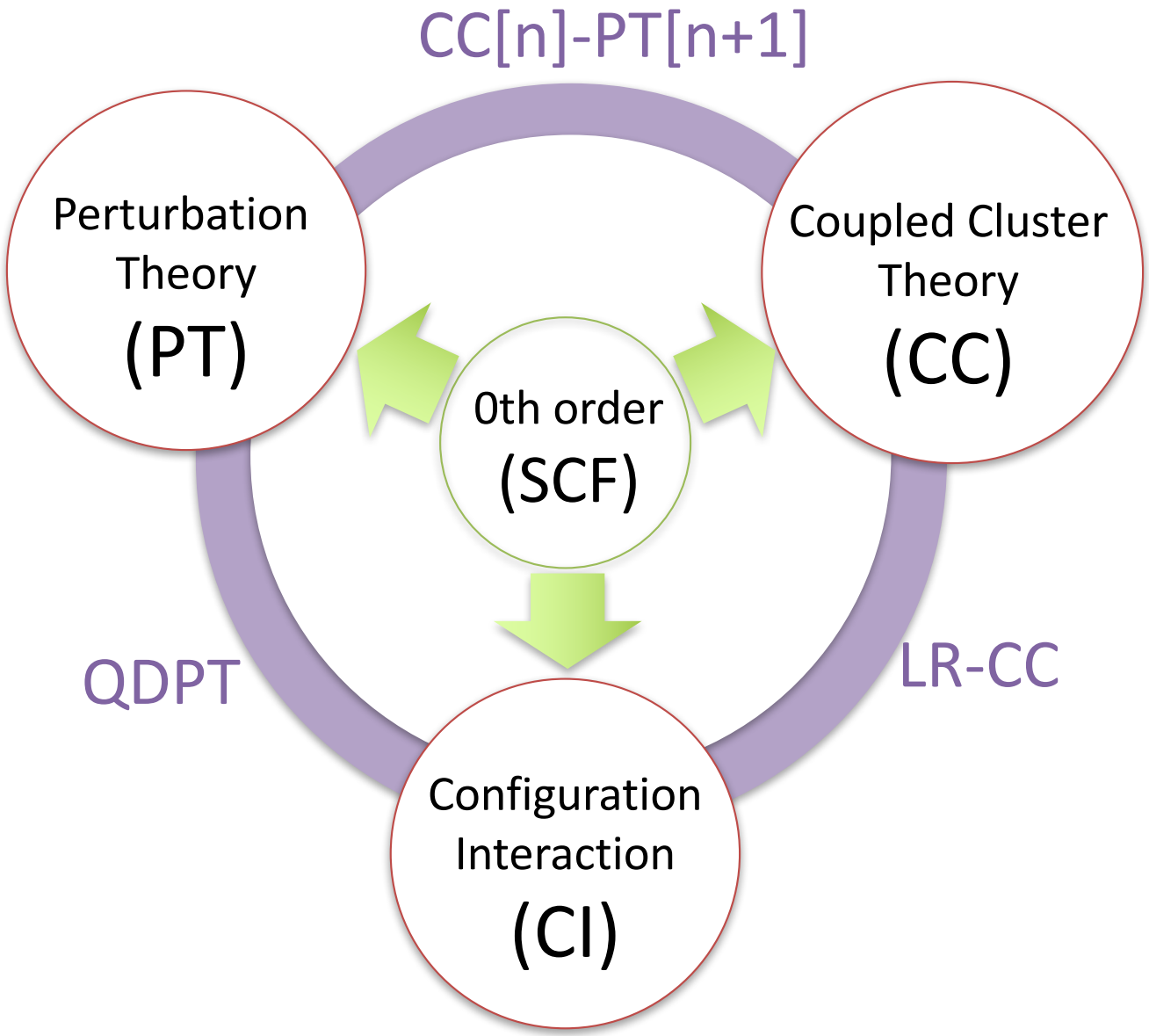
Therefore, the correlation levels of calculations is necessary for quantinative purposes.

Optimized Coordinate
Vibrational Self-consistent Field Method
(oc-VSCF)

Vibrational correlation theories
with optimized coordinates

Summary and Outlook

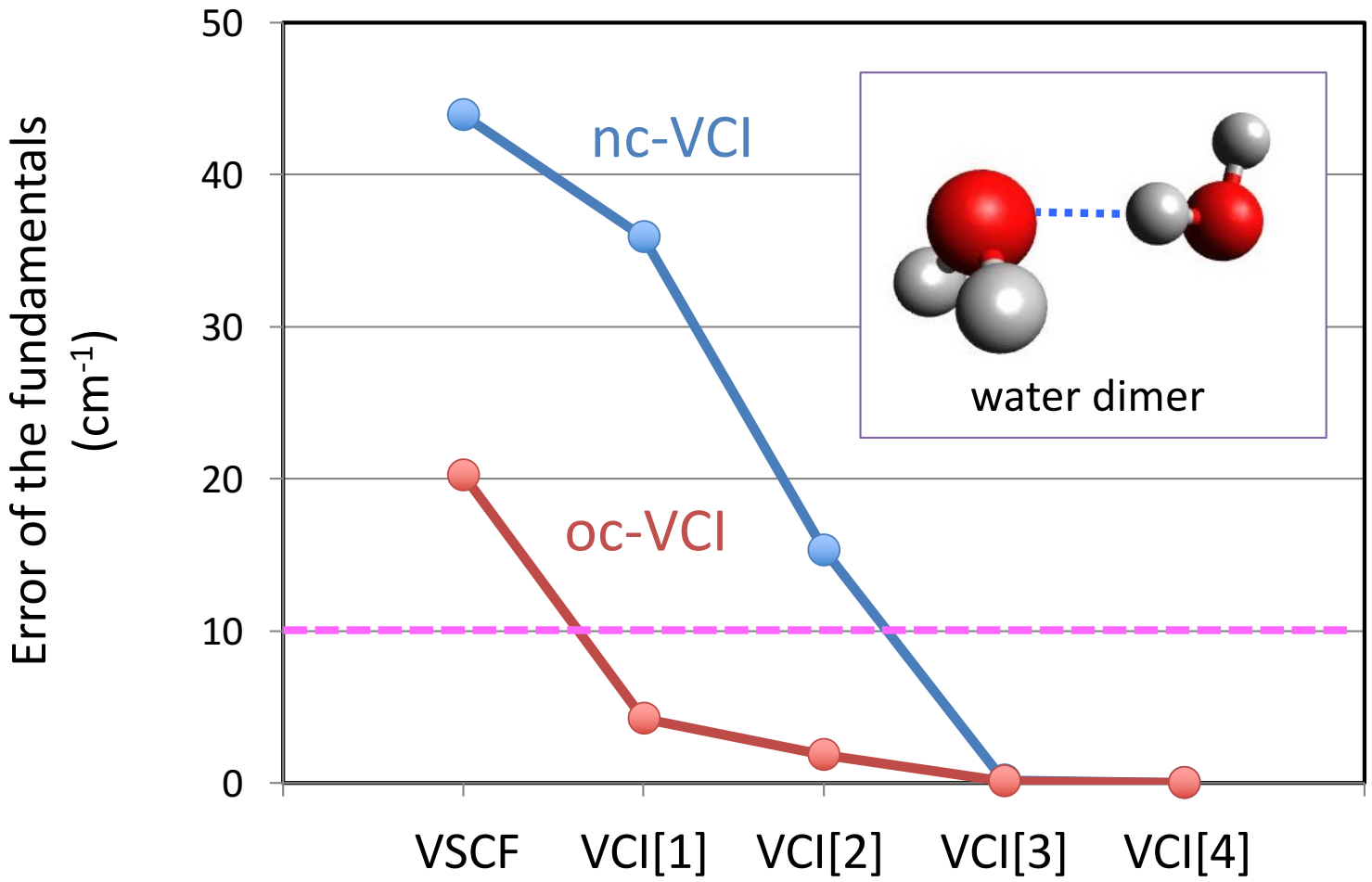
Quantum Many-Body Theories



Many-body expansion starting from the oc-VSCF solution

oc-VCI applied to water dimer

Yagi, Keçeli & Hirata, JCP (2012)

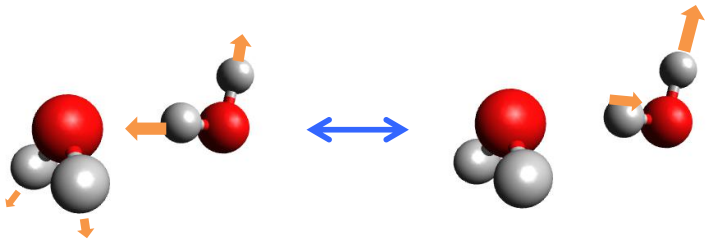


oc-VCI is 30,000 times faster than nc-VCI

Force constants

	Normal coord.[a]	Optimized coord.[b]
Off-diagonal (coupling) constants		
c'_{st}	0.0	
c'_{stt}		
c'_{sst}		
c'_{sttt}		
c'_{sstt}		
c'_{ssst}		

units in cm^{-1}

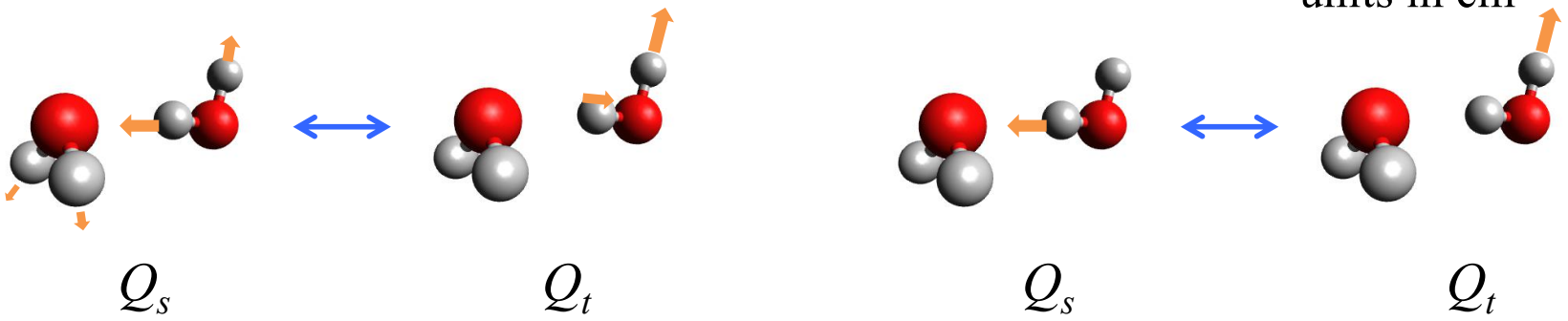


Q_s Q_t

Force constants

	Normal coord.[a]	Optimized coord.[b]
Off-diagonal (coupling) constants		
c'_{st}	0.0	103.7
c'_{stt}	−564.8	−7.4
c'_{sst}	−246.0	−16.8
c'_{sttt}	−59.5	−0.9
c'_{sstt}	87.1	−0.8
c'_{ssst}	61.4	4.5

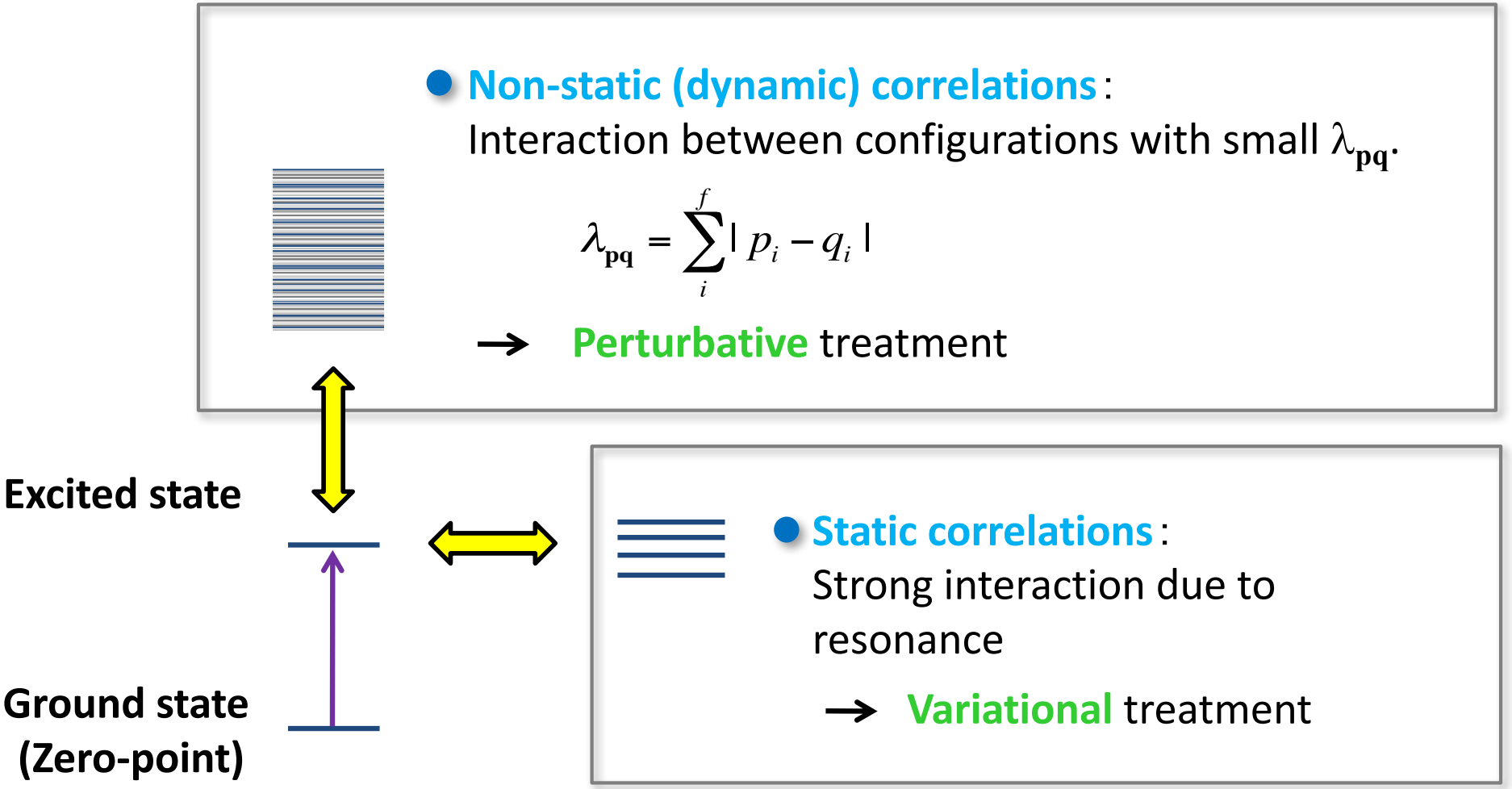
units in cm^{-1}



The reduction of anharmonic coupling enhances the quality of VSCF wavefunction

Vibrational Quasi-Degenerate PT

Yagi, Hirata, Hirao, PCCP (2008).



The two types of correlations are incorporated in a balanced way

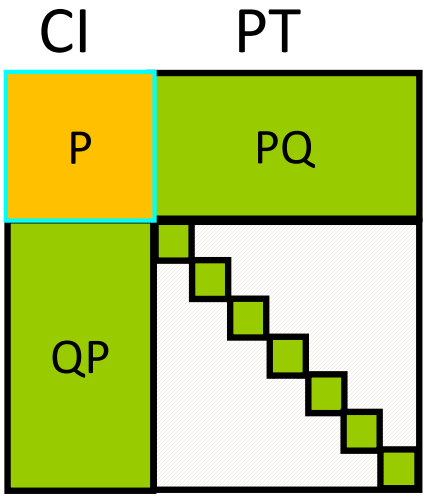
Quasi-degenerate PT

B. Kirtman, J. Chem. Phys. **49**, 3890 (1968).
I. Shavitt and L. T. Redmon, J. Chem. Phys. **73**, 5711 (1980).

The effective Hamiltonian:

$$\langle m|H_{\text{eff}}^{(0+1)}|n\rangle = \langle m|H|n\rangle,$$

$$\langle m|H_{\text{eff}}^{(2)}|n\rangle = \sum_q \frac{\langle m|H|q\rangle\langle q|H|n\rangle}{2}\left\{\frac{1}{E_m^{(0)}-E_q^{(0)}}+\frac{1}{E_n^{(0)}-E_q^{(0)}}\right\},$$



→ Diagonalization of $H_{\text{eff}}^{(0\text{-}2)}$ yeilds the energy and wave function.

→ In case of no-degeneracy,

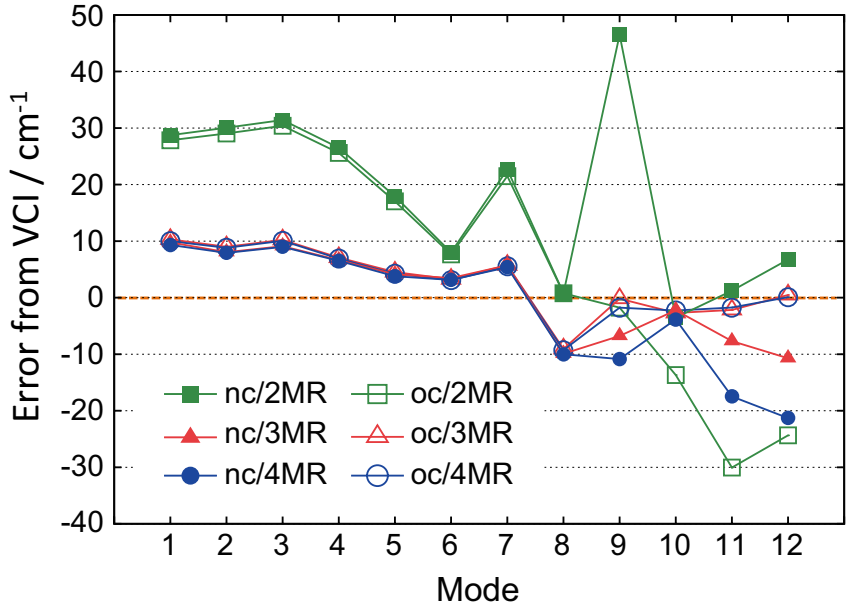
$$\langle n|H_{\text{eff}}^{(2)}|n\rangle = \sum_q \frac{\langle n|H|q\rangle\langle q|H|n\rangle}{E_n^{(0)}-E_q^{(0)}}, \qquad \text{(PT2)}$$

P and Q space is efficiently constructed based on $\lambda_{\mathbf{pq}}$

oc-VQDPT2

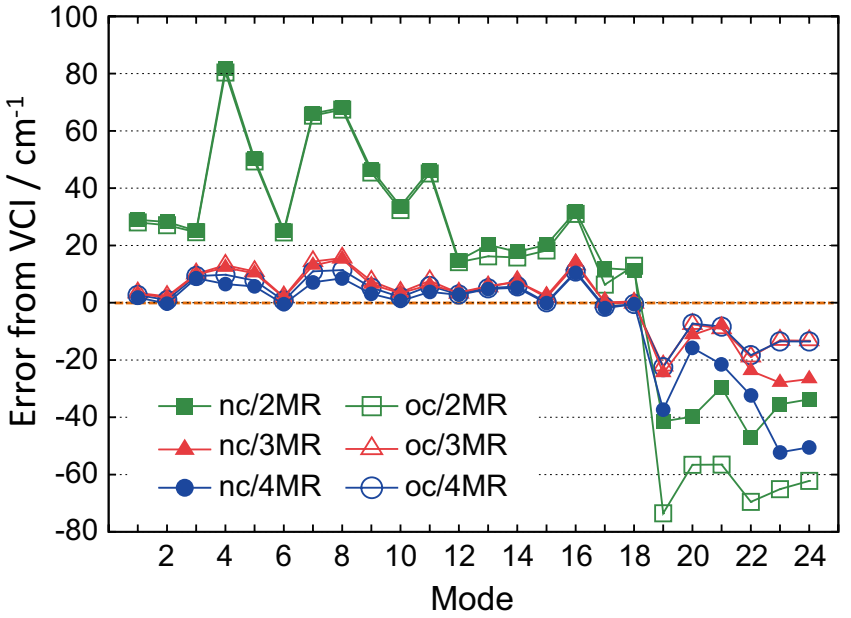
Yagi & Otaki (2014).

(a) C_2H_4



	2MR	3MR	4MR
nc	14.5	6.9	13.4
oc	17.5	**1.4**	**1.5**

(b) C_4H_6



	2MR	3MR	4MR
nc	37.9	20.3	35.0
oc	63.9	**14.0**	**13.9**

oc-VQDPT2 converge smoothly with respect to the order of mode coupling