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.

\[
\Phi_n \cong \Phi_n^{(N)} \Phi_n^{(E)}
\]

\[
\left[ \hat{T}_E + \hat{V}_E + \hat{V}_{NE} \right] \Phi_n^{(E)} = E_n^{(E)} \Phi_n^{(E)}
\]

\[
\left[ \hat{T}_N + \hat{V}_N + E_n^{(E)} \Phi_n^{(N)} = E_n \Phi_n^{(N)}
\]

Vibrational Schrödinger equation

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

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

\[ V = c_{11} x_1^2 + c_{22} x_2^2 + c_{12} x_1 x_2 \quad \text{with} \quad c_{11} \approx c_{22} \gg c_{12} \]

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

\[ V = c'_{11} Q_1^2 + c'_{22} Q_2^2 \]
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: \[ \Phi_0(\tilde{Q}) = \prod_{i=1}^{f} \phi_0^{(i)}(\tilde{Q}_i) \]

VSCF equation:
\[
\begin{align*}
-\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + \left\langle \prod_{j \neq i}^{f} \phi_n^{(j)} \bigg| V \bigg| \prod_{j \neq i}^{f} \phi_n^{(j)} \right\rangle \phi_n^{(i)}(\tilde{Q}_i) &= \epsilon_n^{(i)} \phi_n^{(i)}(\tilde{Q}_i) \\
\end{align*}
\]

\[ \phi_m^{(i)} = \sum_{n=1}^{M} C_{nm} \chi_n^{(i)} \] : modal coefficients

\[ \tilde{Q}_s = \sum_{i=1}^{f} U_{is} Q_i, \] : transformation matrix

- Harmonic potential
- Non-interacting systems

\[ \rightarrow \] Normal coordinates
\[ \rightarrow \] Local coordinates
Jacobi Sweep Algorithm


Successive 2x2 rotations:

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

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 $\theta_{ij}$

End loop

check convergence

End of sweep

Total # of VSCF calc. = $N_{\text{sweep}} \times N_{\text{pair}} \times 10$
Invariance of the Hamiltonian

Yagi, Keçeli & Hirata (2012)

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

- **nMR expansion**
  \[ V(Q) = \sum_{i=1}^{f} V_i(Q_i) + \sum_{i>j}^{f} V_{ij}(Q_i, Q_j) + \sum_{i,j,k=1}^{f} V_{ijk}(Q_i, Q_j, Q_k) + \cdots \]

- **Taylor expansion**
  \[ V(Q) = V_0 + \sum_{i=1}^{f} c_i Q_i + \frac{1}{2} \sum_{i,j=1}^{f} c_{ij} Q_i Q_j + \frac{1}{3!} \sum_{i,j,k=1}^{f} c_{ijk} Q_i Q_j Q_k + \cdots \]
Water

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

Onigiri
Water

\[ V = \frac{1}{2} (\omega_2^2 Q_2^2 + \omega_3^2 Q_3^2) + c_{233} Q_2 Q_3^2 + c_{223} Q_2^2 Q_3 + c_{223} Q_2^2 Q_3^2 + c_{223} Q_2^3 Q_3 + c_{233} Q_2 Q_3^3 \]

Variationally minimize the VSCF energy


Onigiri
Water dimer

Normal coordinates

Optimized coordinates
Water trimer and hexamer

Normal coordinates

Optimized coordinates

Intramolecular vibration is localized to each water molecule
Octatetraene

C-H and C=C stretch are localized, yet the skeletal vibration remain delocalized.
On the concept of vibrational modes

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

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

Vibrational correlation theories
with optimized coordinates

Summary and Outlook
Quantum Many-Body Theories

CC[n]-PT[n+1]

Perturbation Theory (PT)

Coupled Cluster Theory (CC)

0th order (SCF)

Configuration Interaction (CI)

QDPT

LR-CC

Many-body expansion starting from the oc-VSCF solution
oc-VCI applied to water dimer

Yagi, Keçeli & Hirata, JCP (2012)

Error of the fundamentals (cm⁻¹)

oc-VCI is 30,000 times faster than nc-VCI
## Force constants

<table>
<thead>
<tr>
<th>Off-diagonal (coupling) constants</th>
<th>Normal coord. (^a)</th>
<th>Optimized coord. (^b)</th>
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<tbody>
<tr>
<td>(c'_{st})</td>
<td></td>
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<tr>
<td>(c'_{stt})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c'_{sst})</td>
<td></td>
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</tr>
<tr>
<td>(c'_{ssst})</td>
<td></td>
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</tbody>
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units in cm\(^{-1}\)

\(^a\) ZPE 9352.8 (26.2) 9352.8 (26.2) 9326.9 (0.3) 9326.6 (0.0) 93

\(^b\) \(\hat{\eta}_{1}\) and \(\hat{\eta}_{2}\) correspond to a and b, respectively.
## Force constants

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<tr>
<td>(c'_{st})</td>
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<td>(c'_{ssst})</td>
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The reduction of anharmonic coupling enhances the quality of VSCF wavefunction.
Vibrational Quasi-Degenerate PT


- **Non-static (dynamic) correlations**: Interaction between configurations with small $\lambda_{pq}$.
  $$\lambda_{pq} = \sum_{i} |p_i - q_i|$$
  → **Perturbative** treatment

- **Static correlations**: Strong interaction due to resonance
  → **Variational** treatment

The two types of correlations are incorporated in a balanced way
Quasi-degenerate PT


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 \( H_{\text{eff}}^{(0-2)} \) yields the energy and wave function.

→ In case of no-degeneracy,

\[
\langle n | H_{\text{eff}}^{(2)} | n \rangle = \sum_q \frac{\langle n | H | q \rangle \langle q | H | n \rangle}{E_n^{(0)} - E_q^{(0)}},
\]  \hspace{1cm} (PT2)

P and Q space is efficiently constructed based on \( \lambda_{pq} \)
oc-VQDPT2

Yagi & Otaki (2014).

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<th>2MR</th>
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<th>4MR</th>
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<tbody>
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<tr>
<td>oc</td>
<td>63.9</td>
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<td>13.9</td>
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oc-VQDPT2 converge smoothly with respect to the order of mode coupling