

# Vibrational Coupled Cluster Theory

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LC\*TC

**Lundbeck Foundation**  
Center for Theoretical Chemistry



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Center for Oxygen  
Microscopy and imaging

# Molecular Quantum Mechanics

$$H \Psi = E \Psi$$

**Born-Oppenheimer approximation:**

$$H_{el} \Psi_{el} = E_{el} \Psi_{el}$$

$$(T_n + E_{el}) \Psi_n = E \Psi_n$$

$$\Psi = \Psi_{el} \Psi_n$$

One cannot stop molecules moving!

Accurate calculations requires us to consider nuclear motion!

The calculational perspective:

For electrons there are many standard theoretical methods, many computer programs, and much to choose from and build upon.

Quantum Mechanics for the motion of the nuclei? Less widespread.

# Molecular Quantum Mechanics

$$H_{el} \Psi_{el} = E_{el} \Psi_{el}$$

$$(T_n + E_{el}) \Psi_n = E \Psi_n$$

$$\Psi = \Psi_{el} \Psi_n$$

Three issues:

1. Accuracy/efficient of individual points (ES theory)
2. From the ability to calculate individual points to the potential energy surface
3. Wave function for nuclear motion.

My primary focus here: Explicit wave function methods.

??

??

Computational Scaling: Exponential  $\Rightarrow$  Polynomial  $\Rightarrow$  Linear

Coupled Cluster is the accurate approach for electronic correlation.

Could it also be the case for nuclear motion?

# Schedule

- Some Key-issues and background
  - PES
  - Second Quantization
  - VSCF
- Vibrational Coupled Cluster (VCC)
  - Theory
  - The models
  - Benchmarks
  - Implementation
- Response Theory
  - Spectra
  - The Lanczos method
- Summary

# What are we looking at?

System

M coupled distinguishable modes, index m

$q_m$

Coordinates (normal or other)

$\phi_{s_m}^m(q_m)$

Orthonormal one-mode basis functions

$$|\mathbf{s}\rangle = \prod_{m=1}^M \phi_{s_m}^m(q_m)$$

Hartree-Products: M-mode basis

$$|\Psi\rangle = \sum_{\mathbf{s}} C_{\mathbf{s}} |\mathbf{s}\rangle$$

Total wave function

$H$

Hamiltonian operator depending on

$$q_m, \frac{\partial}{\partial q_m}$$

# The Hamiltonian

$$H = T + V(q_1, q_2, q_3, \dots, q_M)$$

“Many-Body” Expansion  $V^{(1)}, V^{(2)}, V^{(3)}, \dots, V^{(M)}$

$$\bar{V}^{m_1}(q_{m_1}) = V(q_1 = 0, \dots, 0, q_{m_1}, 0, \dots, q_M = 0)$$

$$\bar{V}^{m_1, m_2}(q_{m_1}, q_{m_2}) = V(0, \dots, q_{m_1}, \dots, q_{m_2}, 0, \dots, 0) - V(0, \dots, q_{m_1}, \dots, 0) - V(0, \dots, q_{m_2}, \dots, 0)$$

$$\bar{V}^{\mathbf{m}_n}(q_{m_1}, \dots, q_{m_n}) = V^{\mathbf{m}_n}(q_{m_1}, \dots, q_{m_n}) - \dots$$

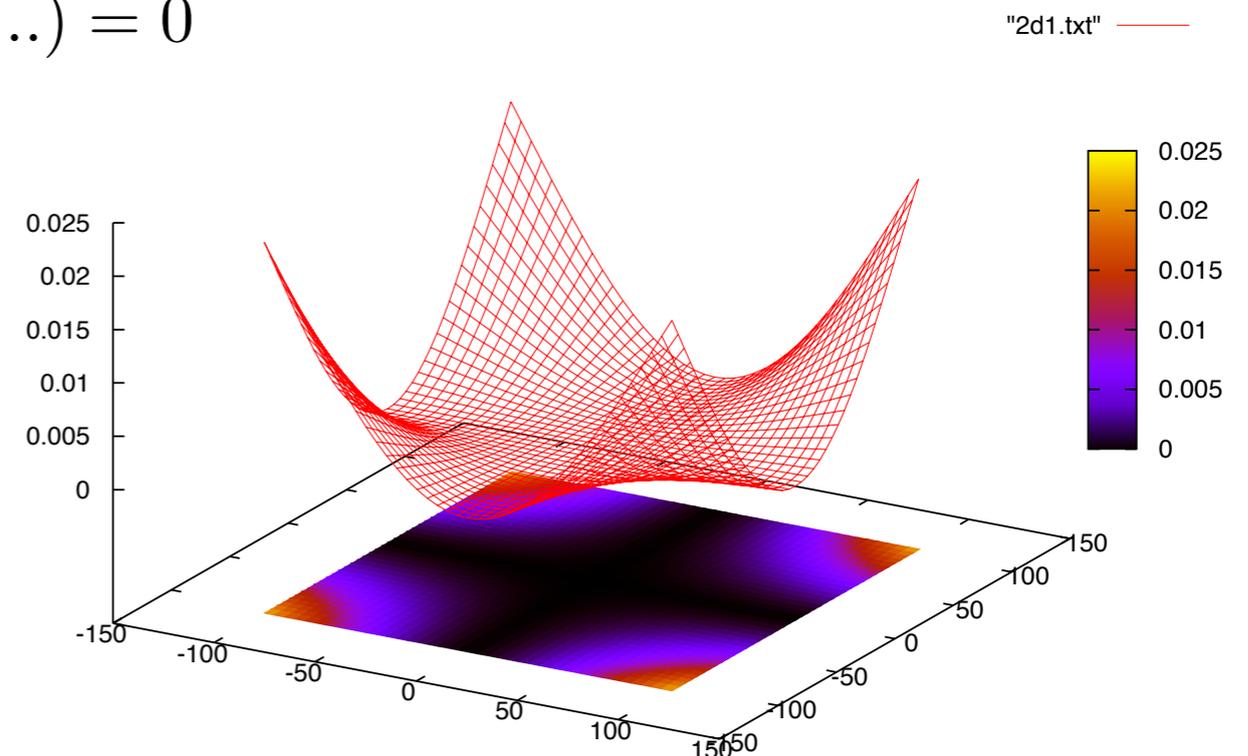
$$\bar{V}^{\mathbf{m}_n}(\dots, q_i = 0, \dots) = 0$$

Two-mode coupling example:

Hope decay of importance:  
one-mode, two-mode, three-mode....

**N-mode representation, Carter, Bowman, and coworkers**

**Pair-coupling: Gerber and coworkers**



# The Hamiltonian

$$H = T + V(q_1, q_2, q_3, \dots, q_M)$$

Generally

$$V = \sum_{\mathbf{m}_n \in \text{MCR}\{\mathbf{V}\}} \bar{V}^{\mathbf{m}_n}(q_{m_1}, \dots, q_{m_n})$$

$$\mathbf{m}_n = (m_1, m_2, \dots, m_n)$$

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$N_{ppd}^M$

# The Hamiltonian

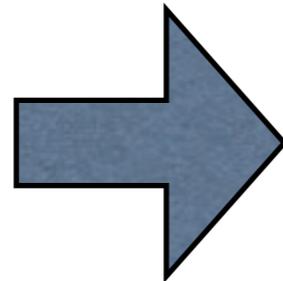
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$$N_{ppd}^M$$



$$\sum_{n=1}^{N_{maxc}} \binom{M}{n} N_{ppd}^n$$

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In practice: generate grid for each coupling (man-made or automatic).  
Then represented in terms of a product of one-mode operators.

Automized using energy derivatives and adaptive build up:  
Adaptive Density Guided Approach (ADGA)

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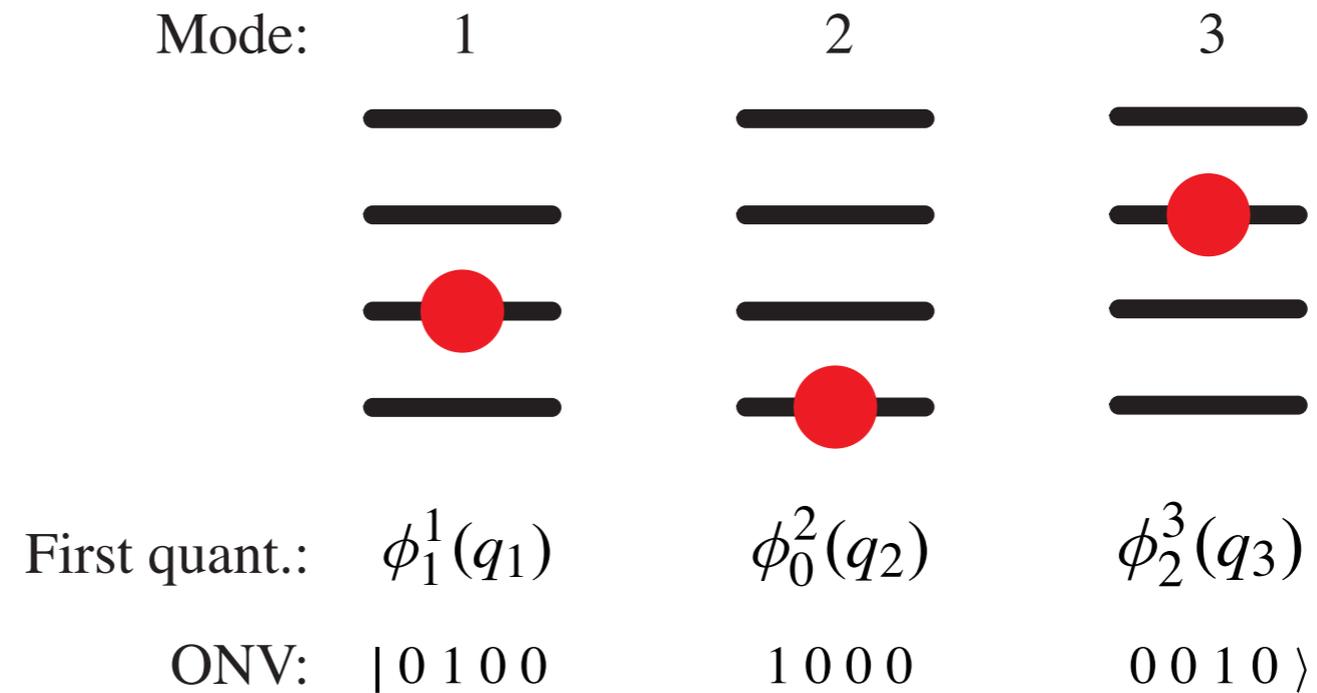
In practice: generate grid for each coupling (man-made or automatic).  
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$$H = \sum_t^{N_t} c_t \prod_{m \in \mathbf{m}^t} h^{m,t}$$

Automized using energy derivatives and adaptive build up:  
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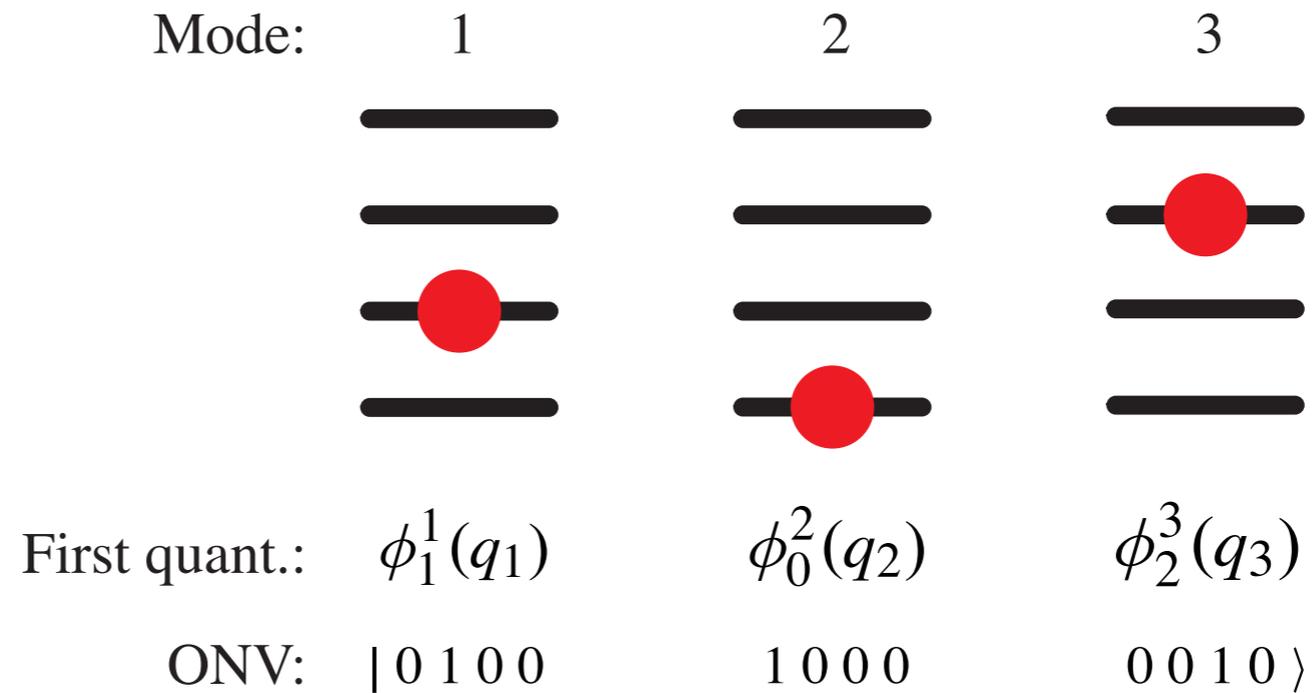
# Second Quantization

Hartree product represented by occupation number vector



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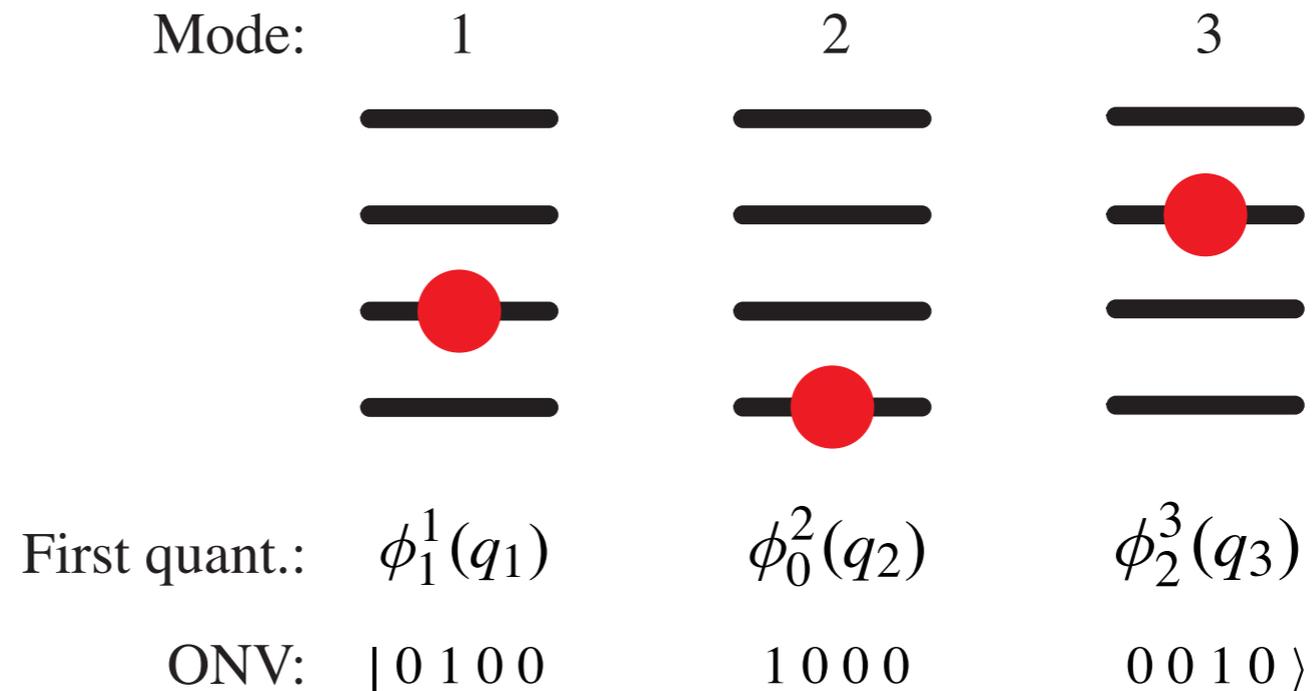


Creation / annihilation operators

$$\begin{aligned}
 a_r^{m\dagger} |\dots 0000 \dots\rangle &= |\dots 0010 \dots\rangle \\
 a_r^m |\dots 0010 \dots\rangle &= |\dots 0000 \dots\rangle
 \end{aligned}$$

# Second Quantization

Hartree product represented by occupation number vector



Creation / annihilation operators

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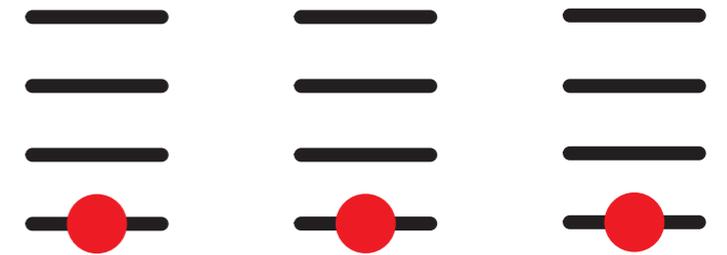
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# Second Quantization

Reference state:

$$|\Phi_{\mathbf{i}}\rangle = \prod_m a_{i_m}^{m\dagger} |\text{vac}\rangle$$

$\uparrow$   
(0, 0, 0)



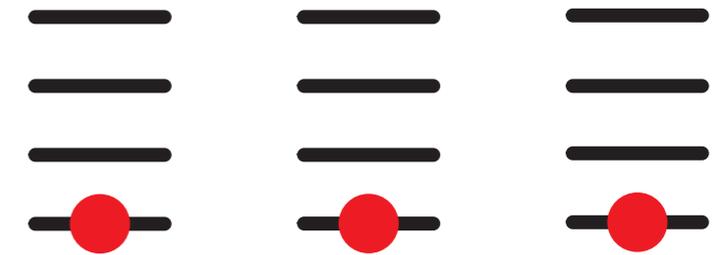
SQ forms for other types of operators can easily be made

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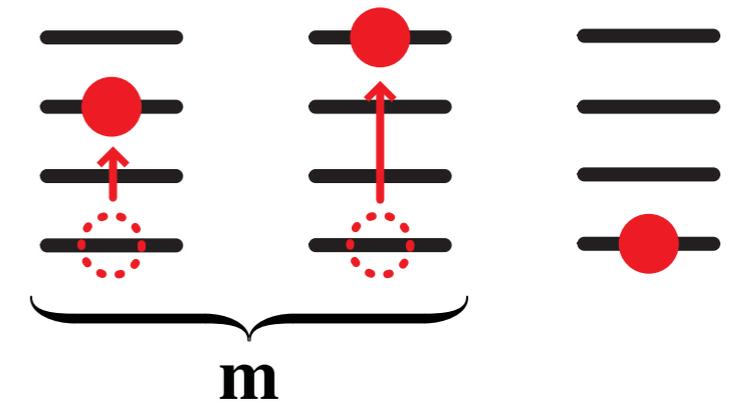
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Excitation operators:

$$\tau_{\mu}^{\mathbf{m}} = \prod_{m \in \mathbf{m}} a_{a_m}^{m\dagger} a_{i_m}^m$$

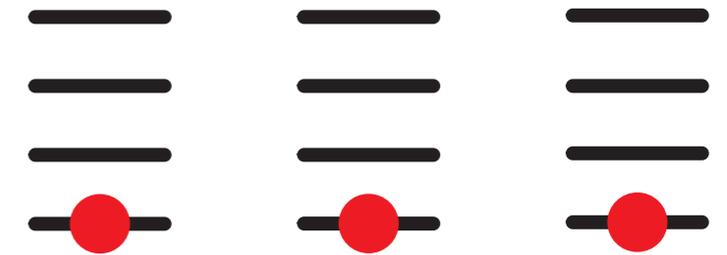


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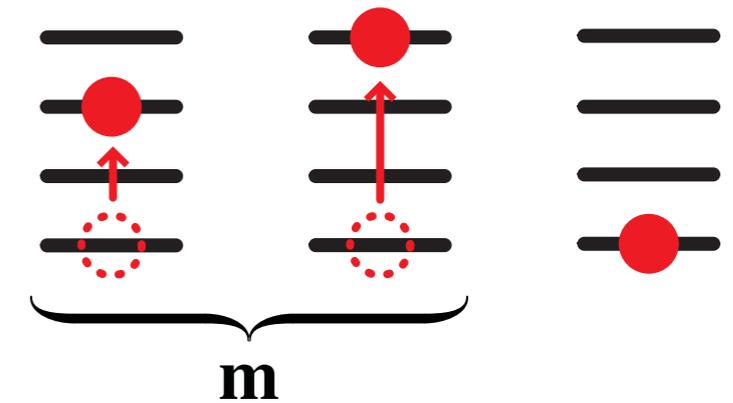
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$H$  assumed to be a sum of products, e.g.

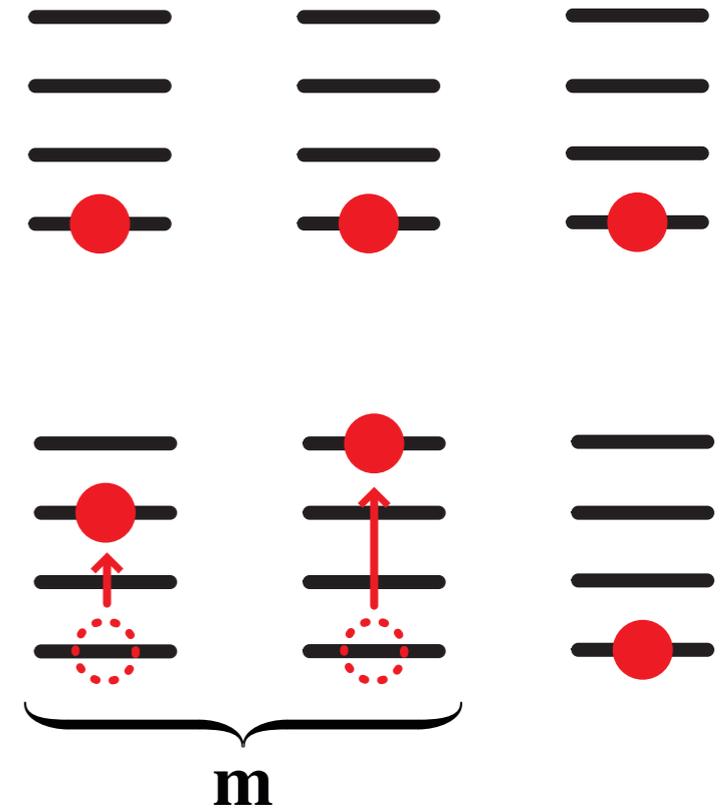
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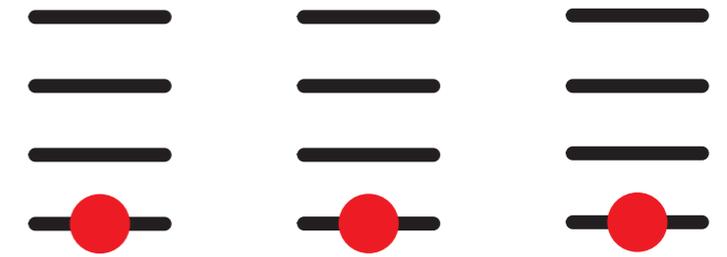
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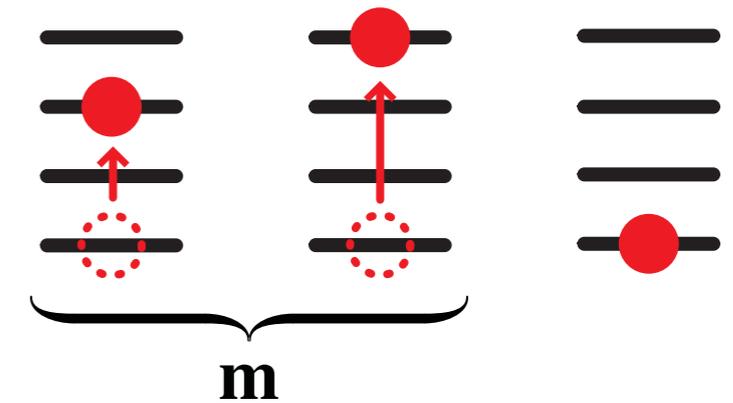
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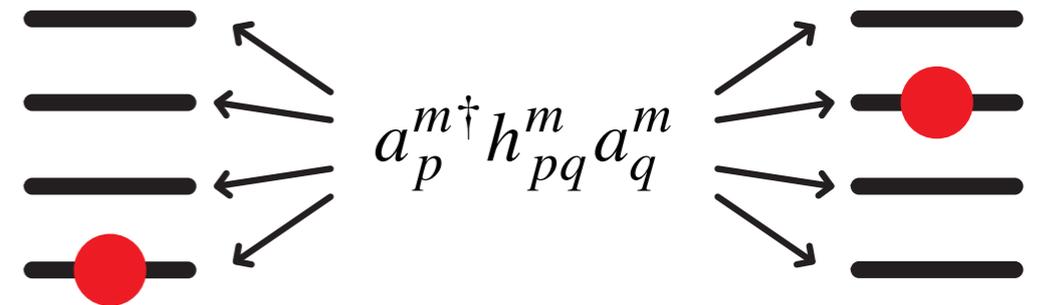
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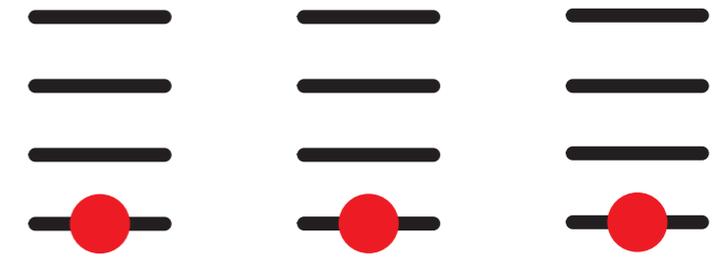
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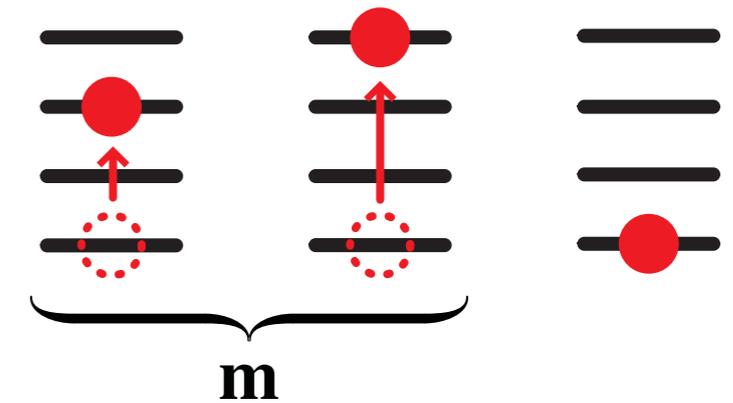
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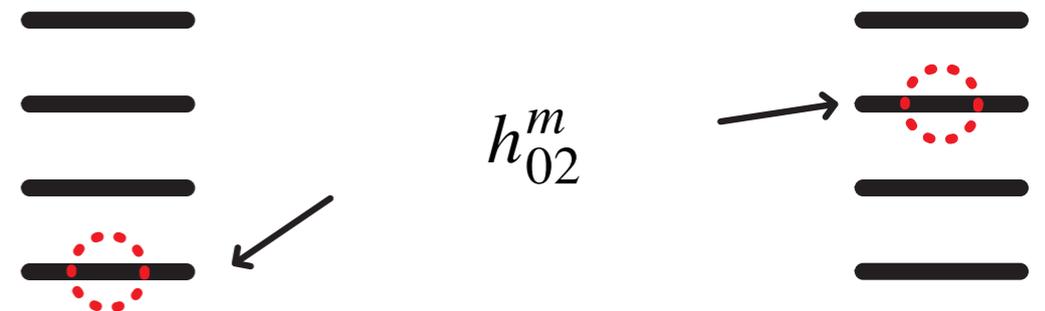
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SQ forms for other types of operators can easily be made

# Second Quantization

- One-to-one correspondence between “first-quantization” and second quantization
- Both WFs and operators represented in terms of creation and annihilation operators with welldefined algebraic properties

$$[a_{p_m}^m, a_{q_m}^{m\dagger}] = \delta_{mm'} \delta_{p_m q_m}$$

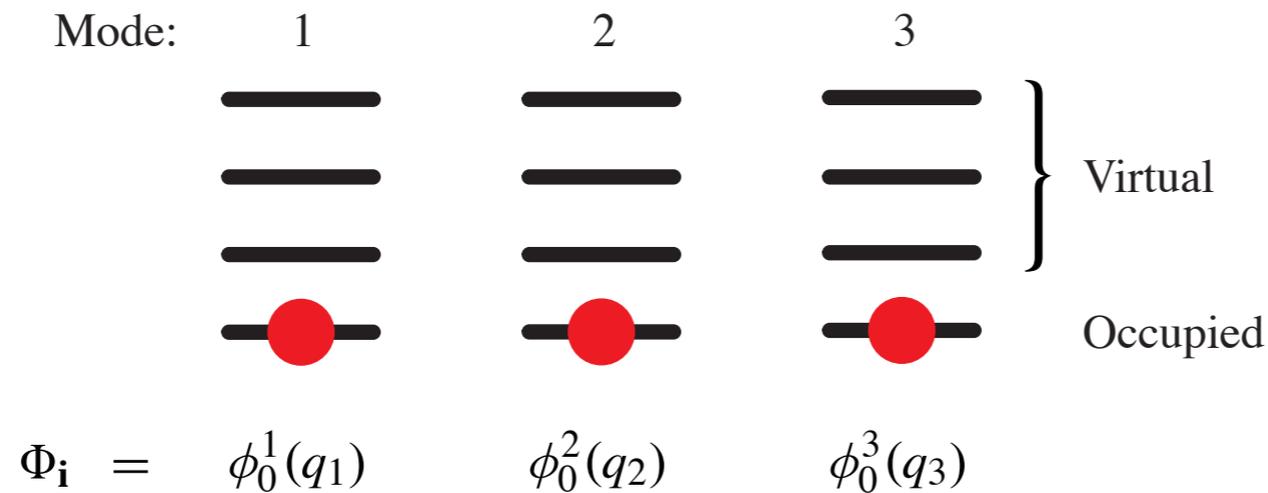
$$[a_{p_m}^{m\dagger}, a_{q_m}^{m\dagger}] = [a_{p_m}^m, a_{q_m}^m] = 0$$

- Formulation
- Inspiration

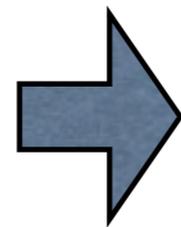
# Vibrational Self Consistent Field

Ansatz: Wave function is a single Hartree-Product

$$|\Phi_{\mathbf{i}}(q_1, q_2, \dots, q_M)\rangle = \prod_{m=1}^M \phi_{i_m}(q_m) \quad |\Phi_{\mathbf{i}}\rangle = \prod_{m=1}^M a_{i_m}^\dagger |\text{vac}\rangle$$



Variational principle



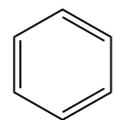
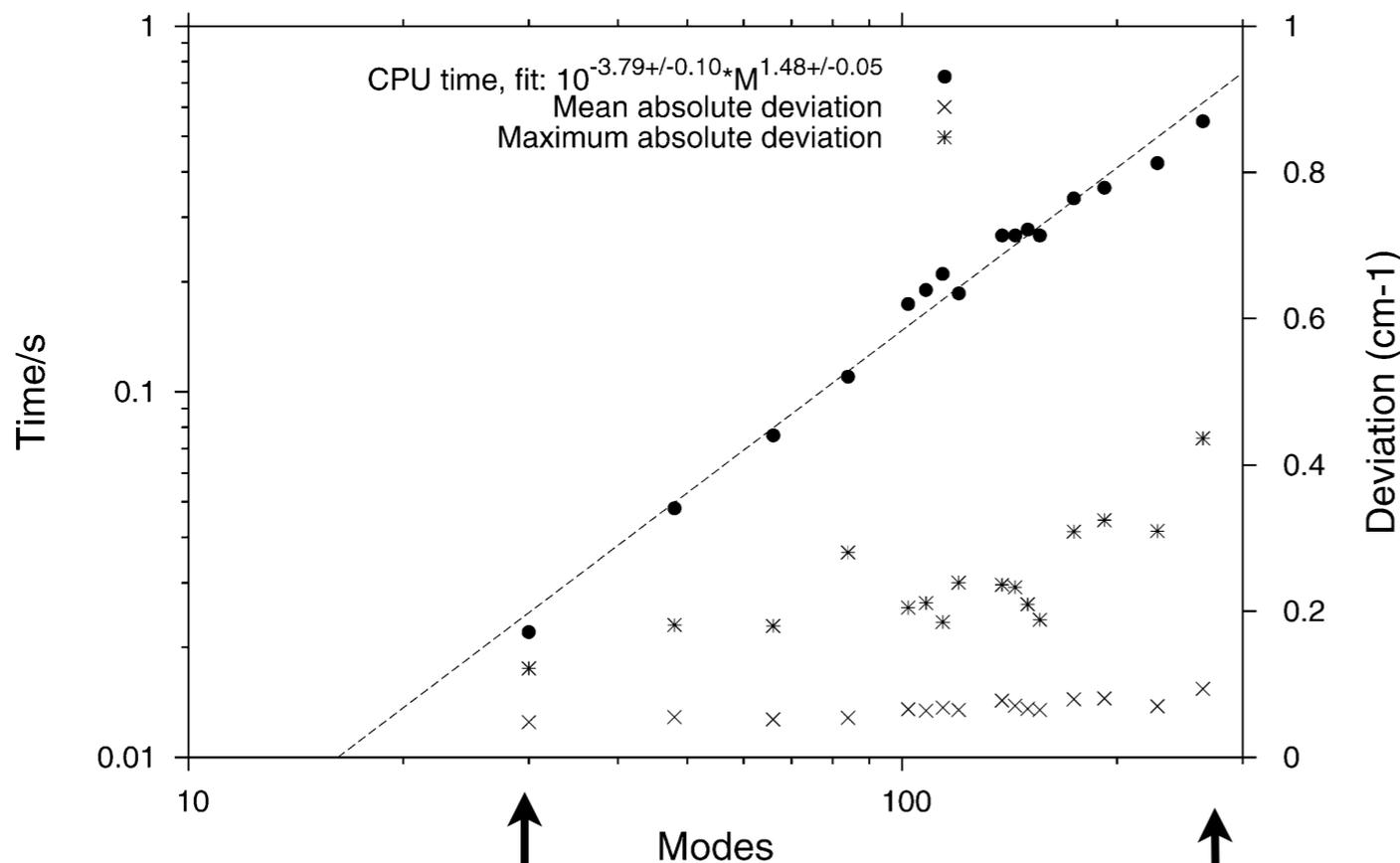
Self-Consistent-Field eqs.

$$\hat{F}^m \phi^m = \epsilon \phi^m$$

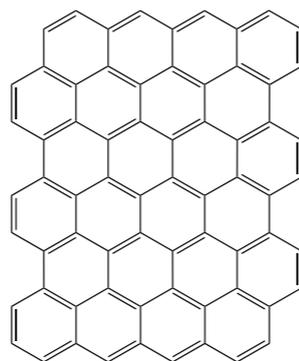
$$\hat{F}^m = \langle \Phi_{\mathbf{i}} | H | \Phi_{\mathbf{i}} \rangle^{(-m)}$$

# VSCF can be fast!

CPU-time: log-log plot.



2M PES, PAHs



VSCF scaling per iteration per state and with  $nM$  coupling potential:

$$M^n$$

$$\hat{F}^m \phi^m = \epsilon \phi^m$$



Build mean-field.

Watch out to include only terms that really couple something.

JCTC, 2010

# Vibrational Correlation

- VSCF: Fast but not accurate enough
- Mean field theory
- Defines a correlation problem
- VCI: Vibrational configuration Interaction:  
Linear expansion in Hartree-Products
- FVCI: Full VCI  
the exact limit

# Wave Function approaches - VSCF flavoured

- VSCF: Vibrational Self Consistent Field
- VCI: Vibrational Configuration Interaction  
Bowman and co-workers (1979), Rauhut (2004), ... many other .....
- VMP: Vibrational Møller-Plesset perturbation theory  
Gerber and co-workers (1996) (cc-VSCF = VMP2).  
OC (higher-order).
- VCC: Vibrational coupled cluster theory  
Second quantization & Response theory  
OC(2004), Seidler and OC (2007-...)
- VMCSCF: Vibrational Multi-configurational self-consistent-field  
Rauhut (2010)
- MCTDH: Multi-configurational Time-dependent Hartree  
Meyer, Cederbaum, Manthe (1990 - )
- Quasi-degeneration perturbation theory  
Yagi, Hirata, Hirao
- Selection schemes:  
Yagi, Benoit, Rauhut, ....

# Vibrational Coupled Cluster Theory

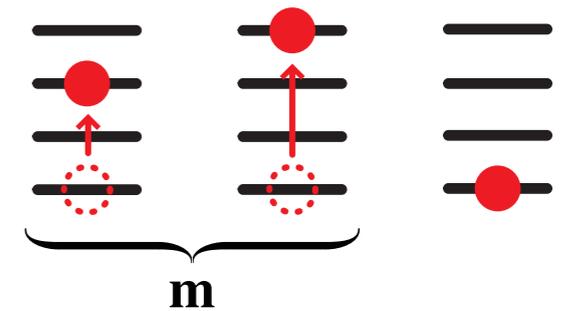
Exponential parameterization:

$$|\text{VCC}\rangle = \exp(T)|\Phi_{\mathbf{i}}\rangle$$

Cluster operator:

$$T = \sum_{\mathbf{m}} \sum_{\mu^{\mathbf{m}}} t_{\mu^{\mathbf{m}}} \tau_{\mu^{\mathbf{m}}}$$

amplitudes
excitation operators



TISE:

$$\exp(-T)H \exp(T)|\Phi_{\mathbf{i}}\rangle = E|\Phi_{\mathbf{i}}\rangle$$

Projection:

$$e_{\mu^{\mathbf{m}}} = \langle \mu^{\mathbf{m}} | \exp(-T)H \exp(T)|\Phi_{\mathbf{i}}\rangle = 0$$

$$E = \langle \Phi_{\mathbf{i}} | H \exp(T)|\Phi_{\mathbf{i}}\rangle$$

VCC[n]

truncate at n-th level coupling

# VCC II

VCC equations:

$$e_{\mu^{\mathbf{m}}} = \langle \mu^{\mathbf{m}} | \exp(-T) H \exp(T) | \Phi_{\mathbf{i}} \rangle = 0$$
$$E = \langle \Phi_{\mathbf{i}} | H \exp(T) | \Phi_{\mathbf{i}} \rangle$$

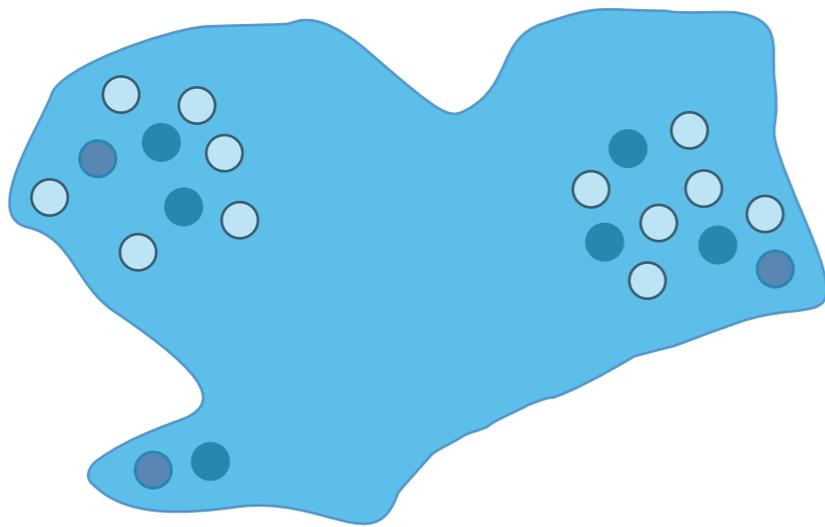
# VCC II

VCC equations:

$$e_{\mu^{\mathbf{m}}} = \langle \mu^{\mathbf{m}} | \exp(-T) H \exp(T) | \Phi_{\mathbf{i}} \rangle = 0$$

$$E = \langle \Phi_{\mathbf{i}} | H \exp(T) | \Phi_{\mathbf{i}} \rangle$$

A molecule



$$T = \sum_{\mathbf{m} \in \text{MCR}[T]} \sum_{\mu^{\mathbf{m}}} t_{\mu^{\mathbf{m}}} \tau_{\mu^{\mathbf{m}}}$$

“Standard”: Excitation level truncation  
Open possibility to design on MCR[T]

VCC[1]   VCC[2]   VCC[3]   VCC[4]   VCC[5]   ...  
(VCCSD)

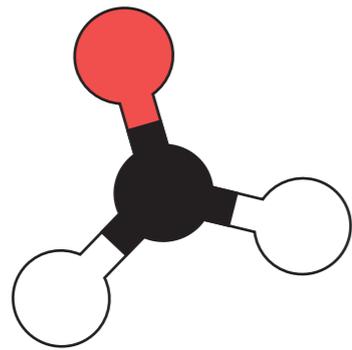
# Comments

- Well-defined in SQ
- Similar to electronic structure theory??
  - Yes - at some intermediate level.
  - Not in the basic theory: SQ and H different
  - Not in practice
- Different from Boson CC
  - also different from Durga Prasad's vibrational boson CC (and earlier ID-method of Bishop). (Banik et al. JCP 2008).
  - Ladder operators, not based on VSCF. Restricted to HO.
- The cure to everything??
  - Only an efficient computational correlation approach
  - When you are converged you are converged

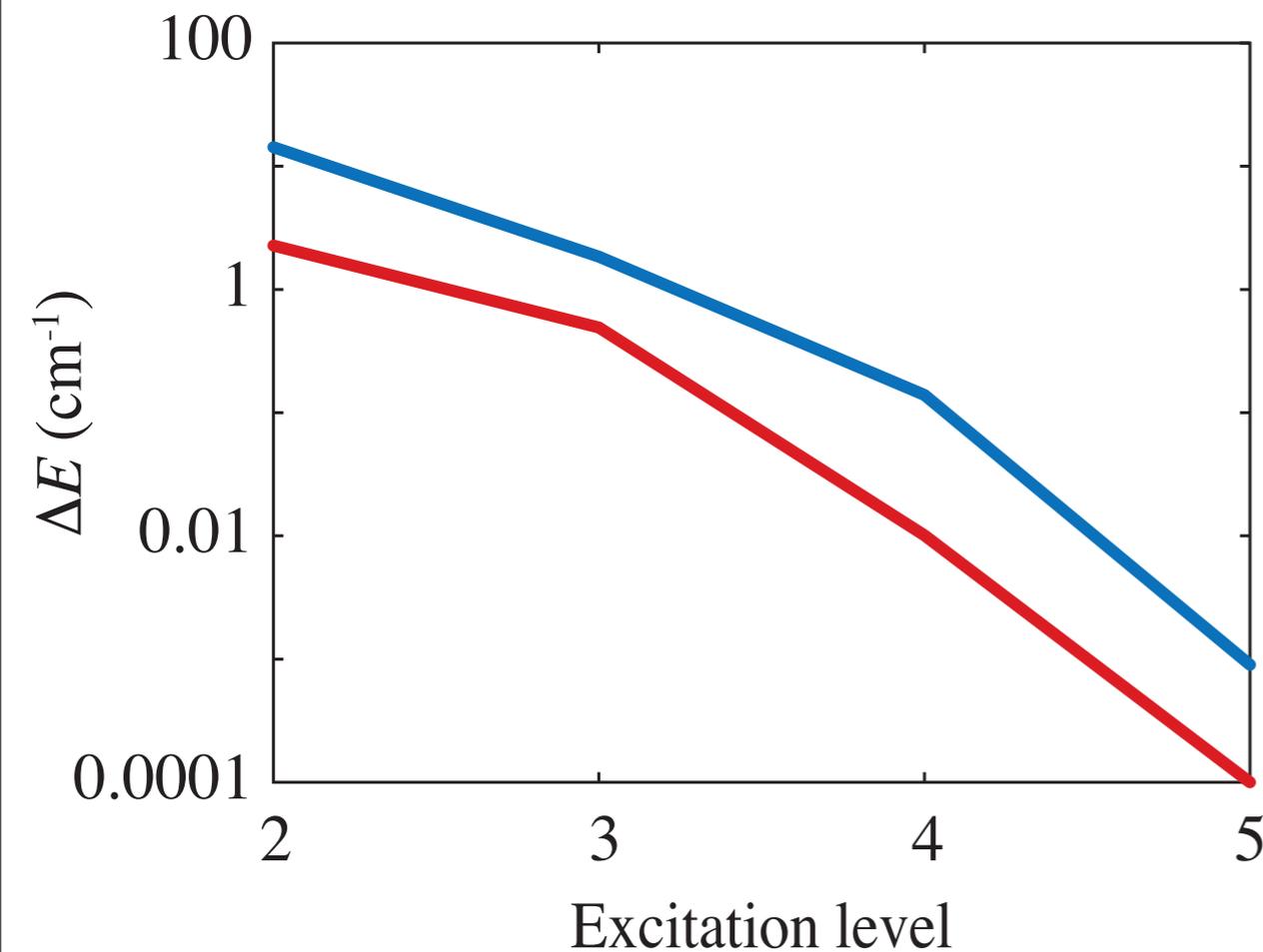
# Benchmark Calculations:

$\Delta E$  relative to FVCI for Fundamentals

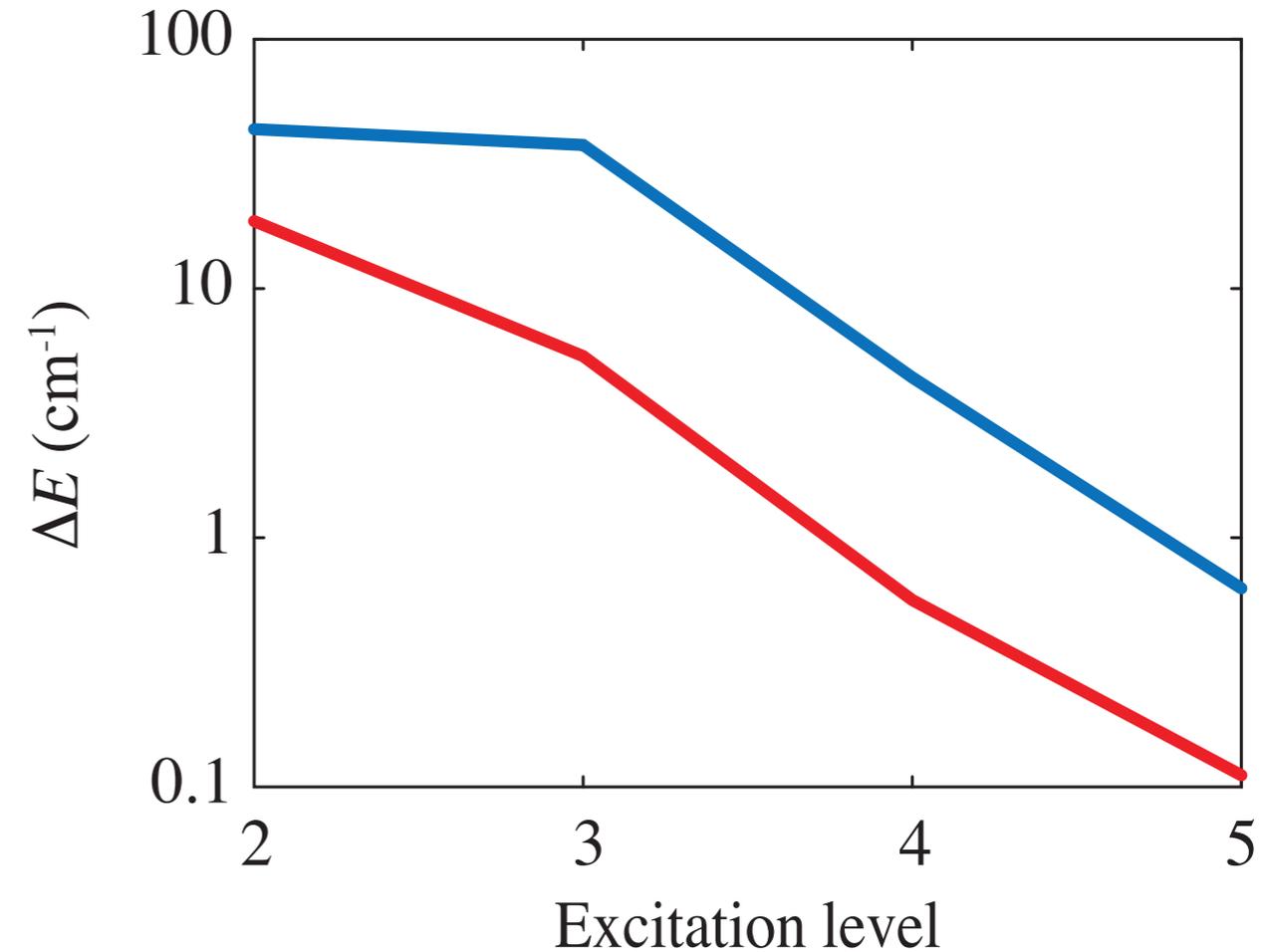
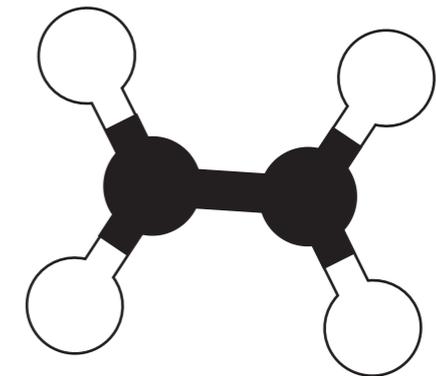
## Formaldehyde 4M potential



VCI ——— (blue line)  
VCC ——— (red line)



## Ethylene 3M potential



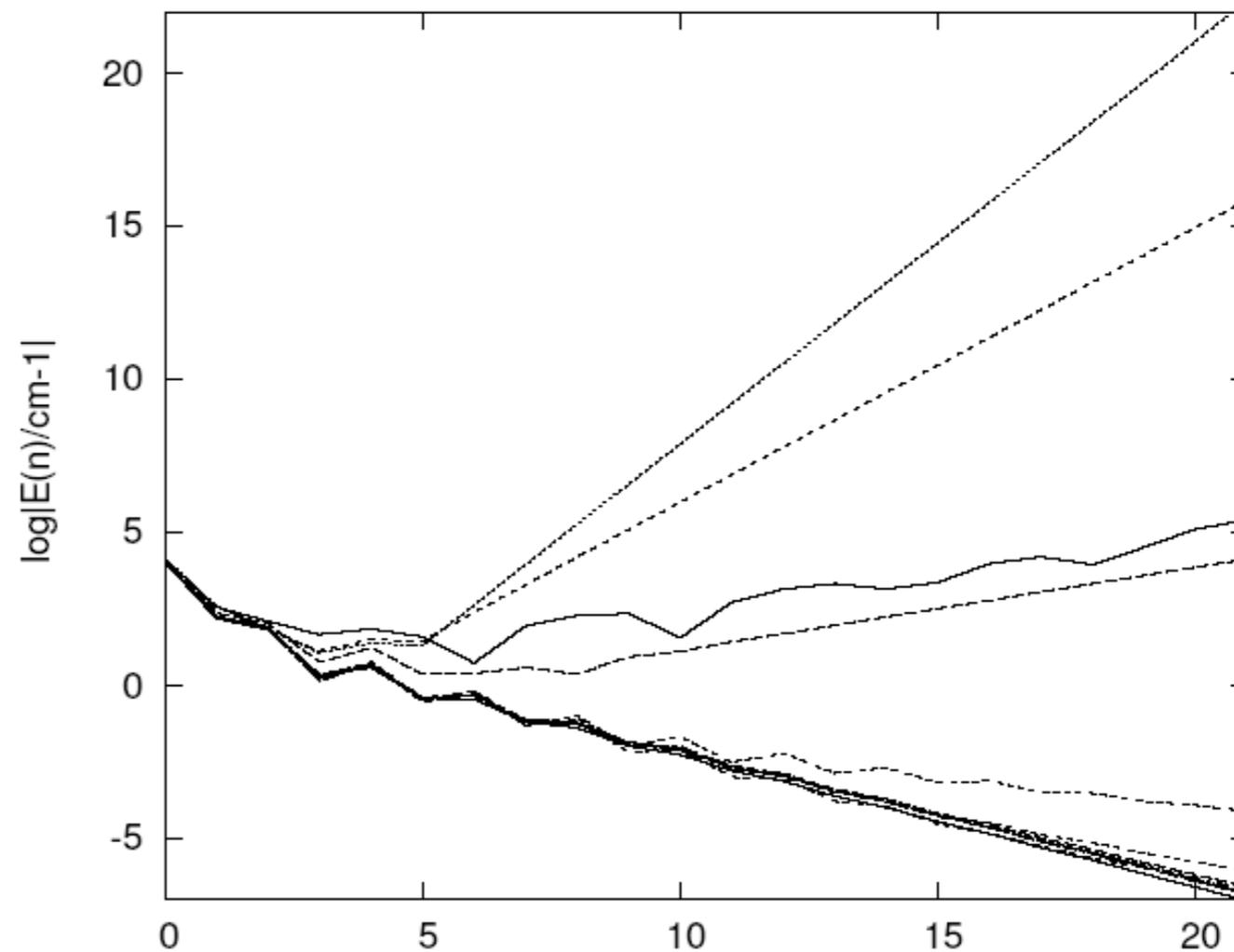
# Vibrational Møller Plesset (VMP)

$$H = H_0 + U = \sum_m F^{m,i} + U$$

Expand in power of  $U \Rightarrow$  VMP2, VMP3, VMP4, etc....

VMP energies as function  
of order for ethylene  
fundamentals

VMP arbitrary order  
implementation



	Variational	Size-consistent	Convergent
VMP	No	Yes	No
VCI	Yes	No	Yes
VCC	No	Yes	Yes

# The challenge of implementing VCC:

## One of 39 pages of equations for VCC[3] with H3

$$\begin{aligned}
 & - \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad c_{m_0 m_1 m_2} \cdot t^{m_0 m_1} \cdot i_{m_1 m_2} \cdot t_{m_0}^{m_2} \quad M^3 O^3 N^3 \\
 & + \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad \{m_2\} [c_{m_1 m_2 m_3}, t_{m_3}^{m_2}]_{\{m_1\}} \cdot t^{m_0 m_1} \cdot i_{m_1 m_2} \quad M^3 O^2 N^3 \\
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 & - \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad [c_{m_1 m_2 m_3}, i_{m_3}]_{\{m_1 m_2\}} \cdot t^{m_0 m_1} \cdot m_2 t_{m_1} \quad M^3 O^2 N^3 \\
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 & + \frac{1}{6} [ [ [ H_3, T_2 ], T_2 ], T_2 ] \\
 & + \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad [c_{m_0 m_1 m_3}, t_{m_3}^{m_2}]_{\{m_0 m_1\}} \cdot t_{m_1}^{m_0} \cdot t_{m_0}^{m_1} \quad M^3 O^2 N^3 \\
 & - \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad c_{m_0 m_1 m_2} \cdot t_{m_1}^{m_0} \cdot t_{m_2}^{m_1} \cdot t_{m_0}^{m_2} \quad M^3 O^3 N^3 \\
 & + \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad \{m_2\} [c_{m_1 m_2 m_3}, t_{m_3}^{m_2}]_{\{m_1\}} \cdot t_{m_1}^{m_0} \cdot t_{m_2}^{m_1} \quad M^3 O^2 N^3 \\
 & - \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad \{m_1\} [\{m_1\} [c_{m_1 m_3 m_4}, t_{m_3}^{m_1}]_{\{m_4\}}, t_{m_4}^{m_2}]_{\{m_2\}} \cdot t_{m_1}^{m_0} \quad M^3 O N^3 \\
 & + \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad [ [ [ c_{m_3 m_4 m_5}, t_{m_3}^{m_0} ]_{\{m_4 m_5\}}, t_{m_4}^{m_1} ]_{\{m_5\}}, t_{m_5}^{m_2} ]_{\{m_0\} \{m_1\} \{m_2\}} \quad M^3 N^3 \\
 & + \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad [c_{m_0 m_1 m_3}, t_{m_3}^{m_2}]_{\{m_0 m_1\}} \cdot t^{m_0 m_1} \cdot t_{m_0 m_1} \quad M^3 O^2 N^3 \\
 & - \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad c_{m_0 m_1 m_2} \cdot t^{m_0 m_1} \cdot t_{m_1 m_2} \cdot t_{m_0}^{m_2} \quad M^3 O^3 N^3 \\
 & + \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad \{m_2\} [c_{m_1 m_2 m_3}, t_{m_3}^{m_2}]_{\{m_1\}} \cdot t^{m_0 m_1} \cdot t_{m_1 m_2} \quad M^3 O^2 N^3 \\
 & + \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad \{m_1\} [c_{m_0 m_1 m_3}, t_{m_1 m_3}]_{\{m_0\}} \cdot t^{m_0 m_1} \cdot t_{m_0}^{m_2} \quad M^3 O N^3 \\
 & - \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad \{m_1\} [\{m_1\} [c_{m_1 m_3 m_4}, t_{m_1 m_3}]_{\{m_4\}}, t_{m_4}^{m_2}]_{\{m_2\}} \cdot t^{m_0 m_1} \quad M^3 N^3 \\
 & + \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad \{m_2\} [c_{m_1 m_2 m_3}, t_{m_2 m_3}]_{\{m_1\}} \cdot t^{m_0 m_1} \cdot t_{m_1}^{m_2} \quad M^3 O N^3 \\
 & - \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad [c_{m_1 m_3 m_4}, t_{m_3 m_4}]_{\{m_1\}} \cdot t^{m_0 m_1} \cdot t_{m_1}^{m_2} \quad M^3 O N^3 \\
 & + [ [ H_3, T_2 ], T_3 ] \\
 & - \mathcal{D}_{m_0 m_1 m_2}^{m'_0 m'_1 m'_2} \quad \{m_1\} [c_{m_0 m_1 m_3}, t_{m_3}^{m_1 m_2}]_{\{m_0\}} \cdot m_0 t_{m_1} \quad M^3 O^2 N^3
 \end{aligned}$$

# Automatic Derivation of VCC

## 1. Computer derives detailed equations

BCH Commutator expansion, SQ algebra, long lists involving contractions between integrals and amplitudes

## 2. Identify computational convenient form

Find intermediates. Rearrange for minimal operation count.

## 3. Process the resulting lists of terms and intermediates

Computational scaling: VCI and VCC similar scaling

	VCC[2]	VCC[3]	VCC[4]	VCC[5]	VCC[6]
H2	M <sup>3</sup>	M <sup>4</sup>	M <sup>5</sup>	M <sup>6</sup>	M <sup>7</sup>
H3	M <sup>3</sup>	M <sup>4</sup>	M <sup>5</sup>	M <sup>6</sup>	M <sup>7</sup>
H4	M <sup>4</sup>	M <sup>5</sup>	M <sup>6</sup>	M <sup>7</sup>	M <sup>8</sup>
H5	M <sup>5</sup>	M <sup>6</sup>	M <sup>6</sup>	M <sup>7</sup>	M <sup>8</sup>

P Seidler and O Christiansen J. Chem. Phys. **131**, 234109 (2009)

# Automatic Derivation

## BCH expansion

$$\begin{aligned} e_{\mu^{\mathbf{m}}} &= \langle \mu^{\mathbf{m}} | \exp(-T) H \exp(T) | \Phi_{\mathbf{i}} \rangle \\ &= \langle \mu^{\mathbf{m}} | H + [H, T] + \frac{1}{2} [[H, T], T] + \frac{1}{6} [[[H, T], T], T] + \dots | \Phi_{\mathbf{i}} \rangle \end{aligned}$$

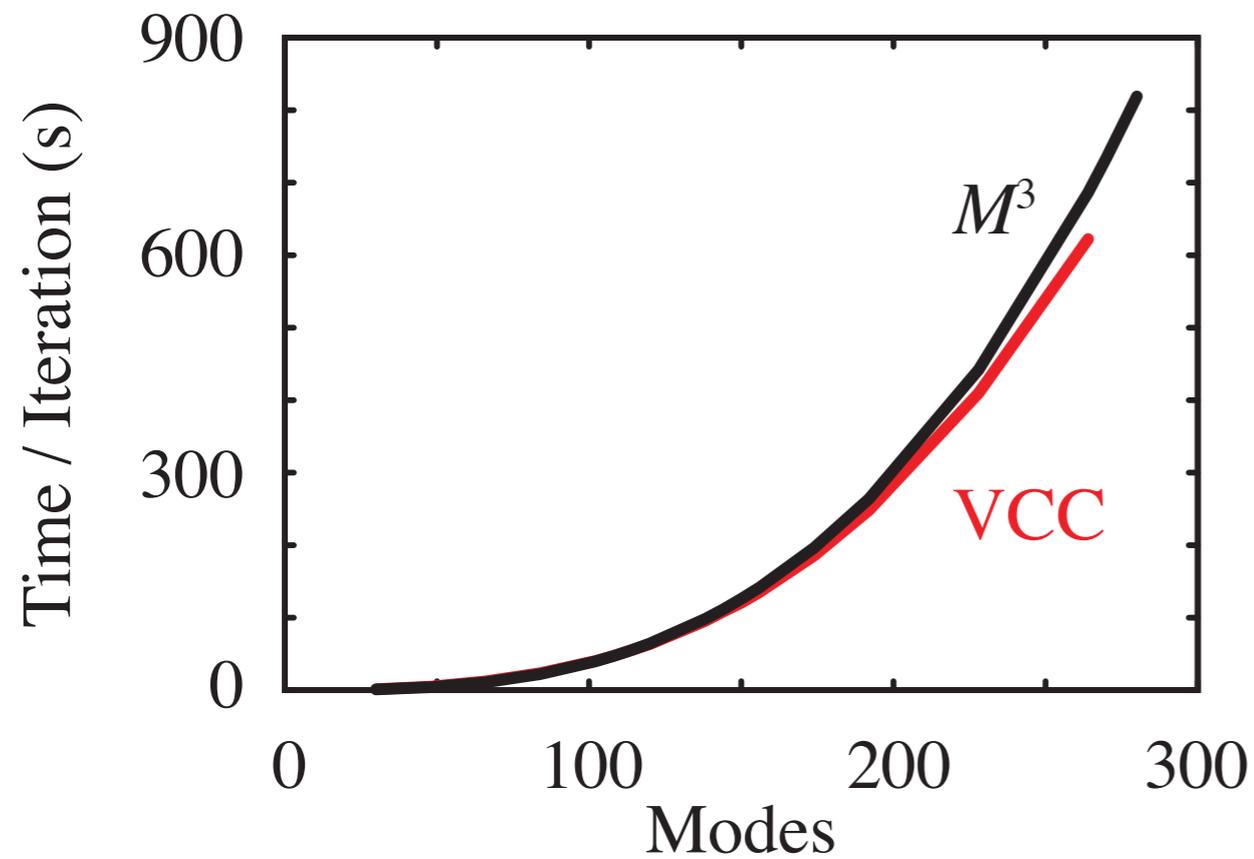
## Commutator expansion

$$[[H_3, T_1], T_2] = H_3 T_1 T_2 - T_1 H_3 T_2 - T_2 H_3 T_1 + T_1 T_2 H_3$$

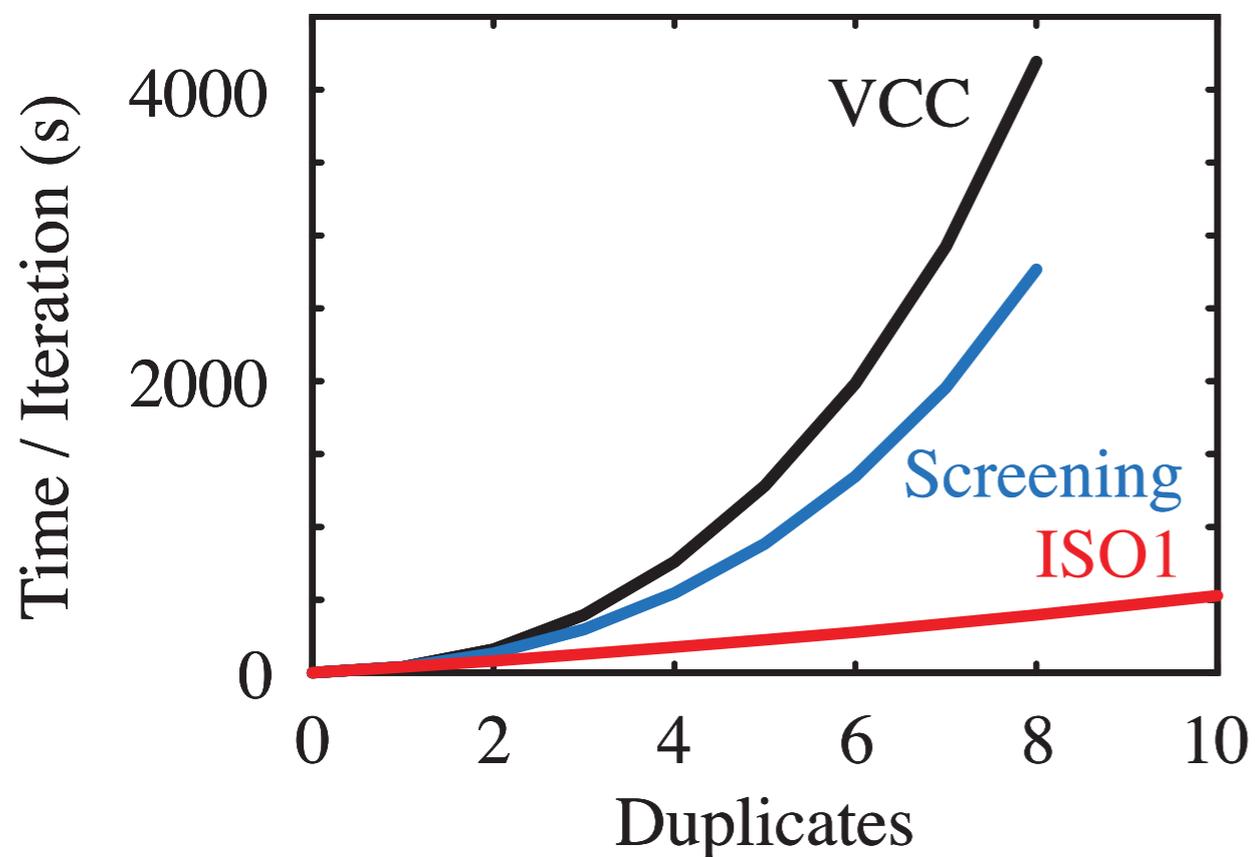
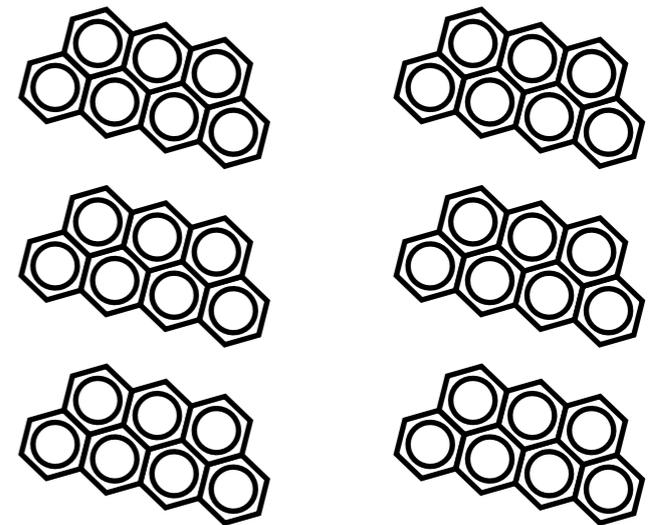
## Evaluation of matrix elements

$$e_{\mu^{\mathbf{m}}} \leftarrow \langle \mu^{\mathbf{m}} | T_1 H_3 T_2 | \Phi_{\mathbf{i}} \rangle$$

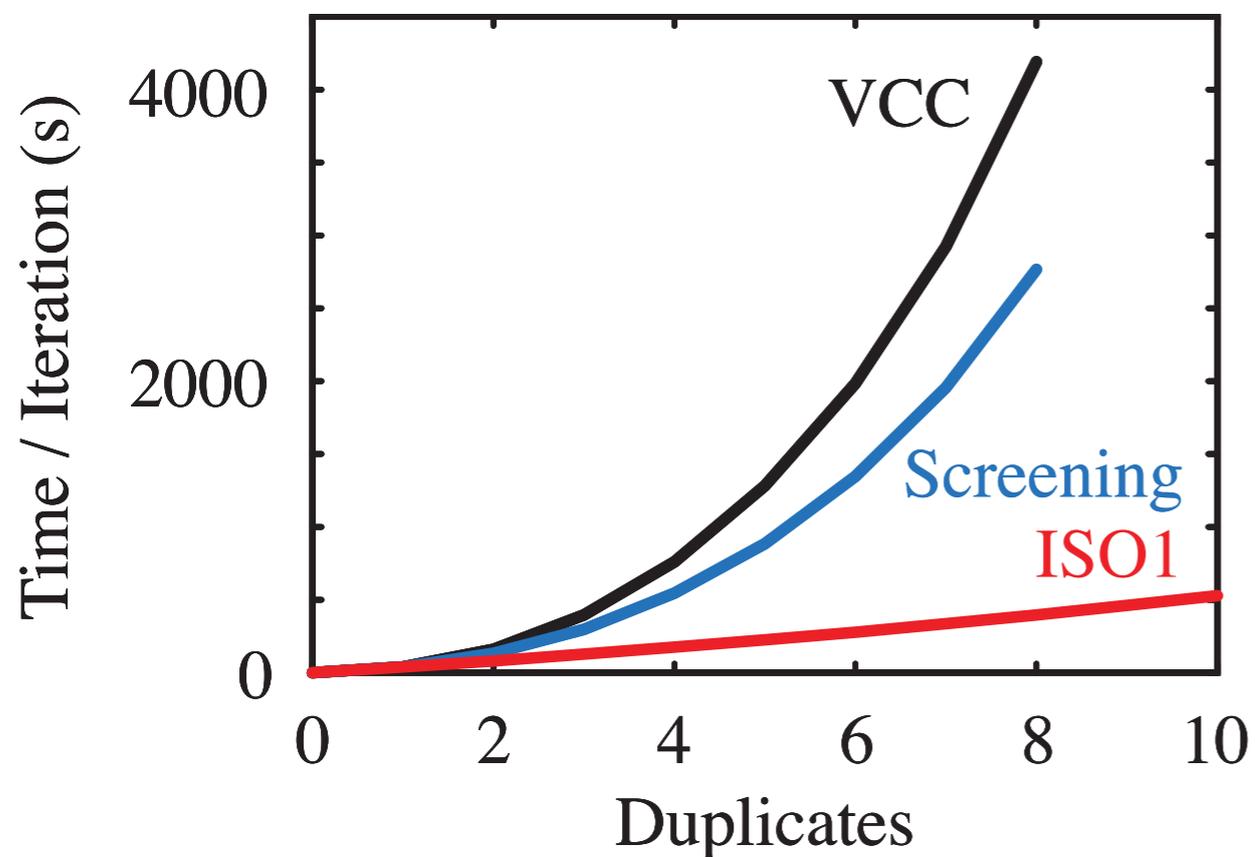
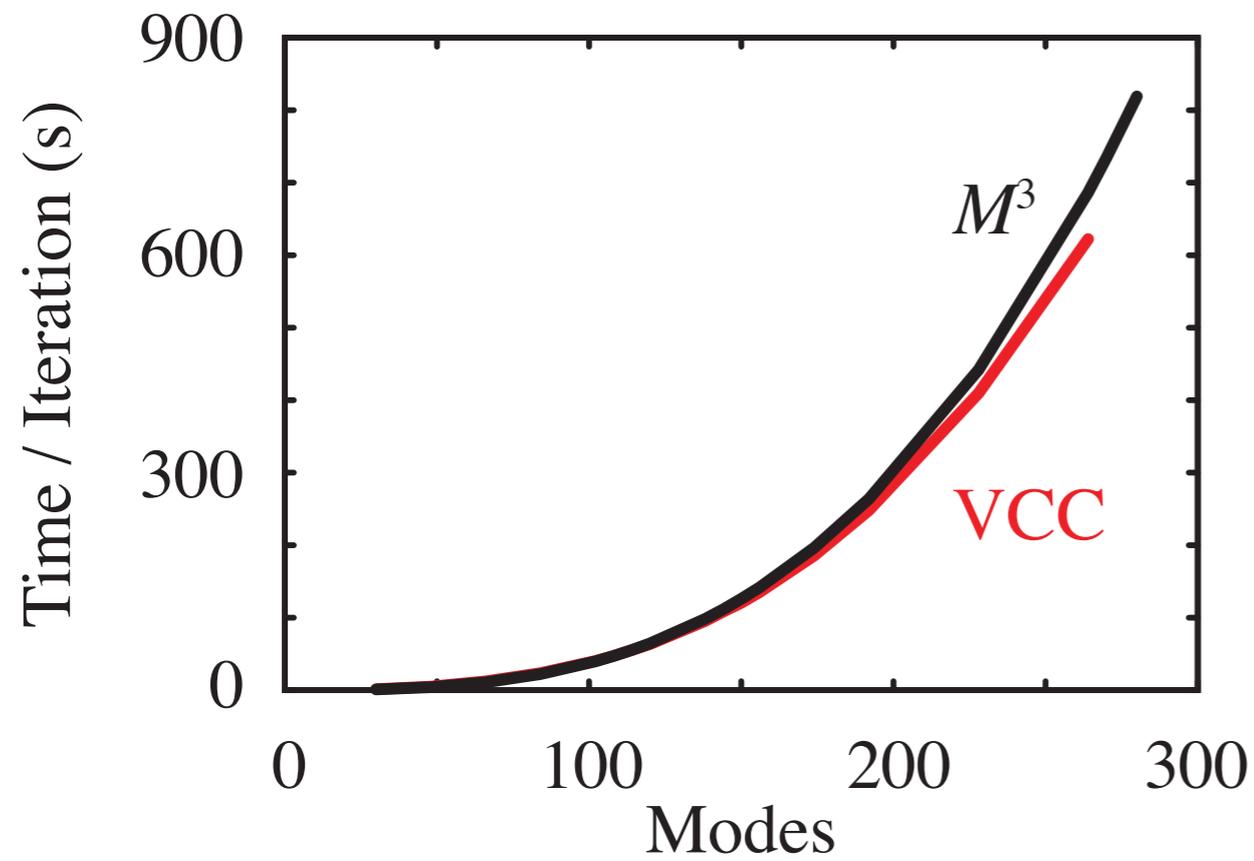
# VCC scaling illustrations



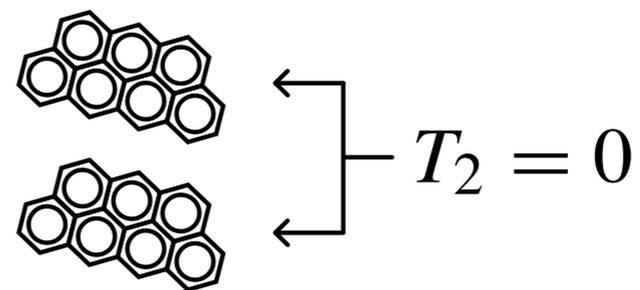
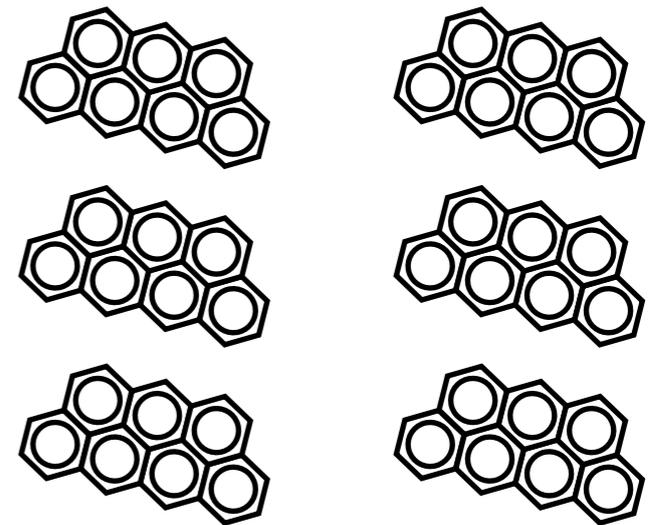
VCC[2]  
2M PES  
PAHs



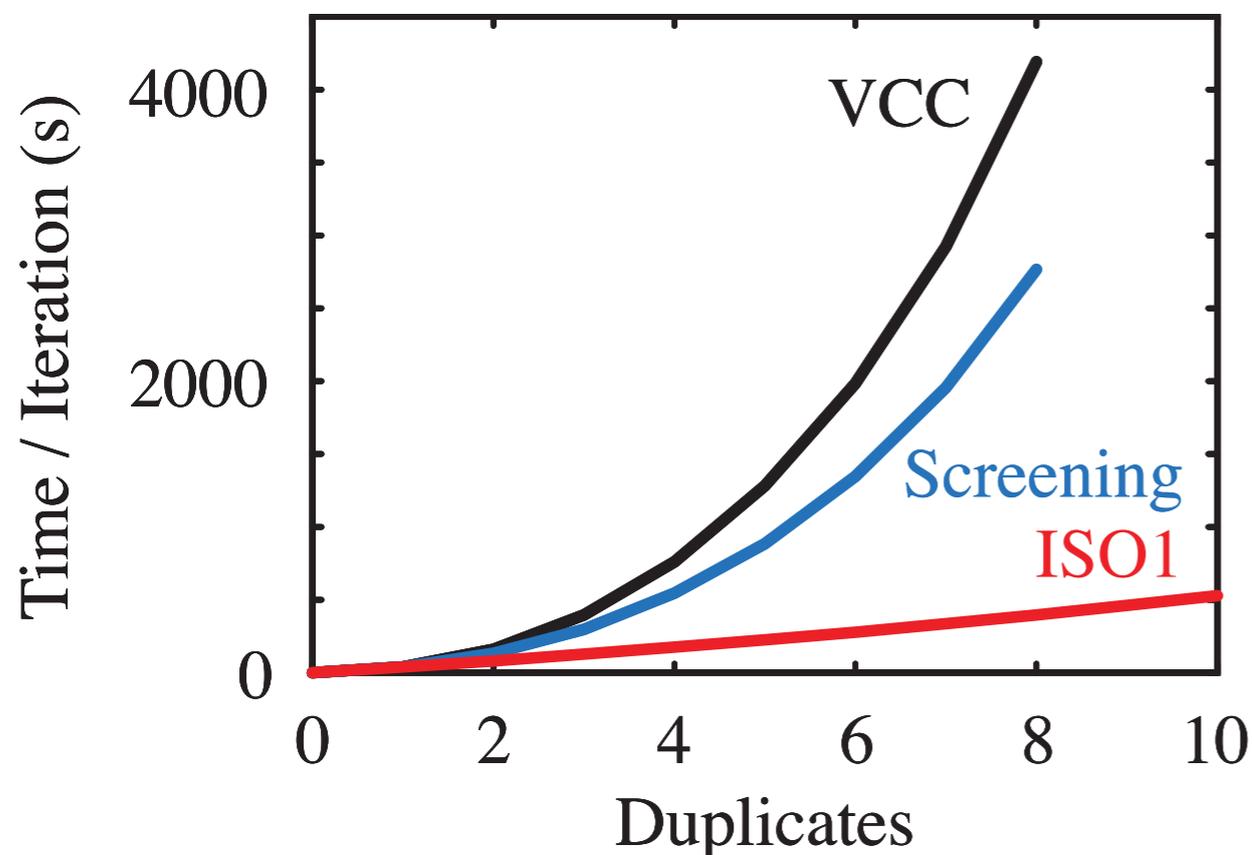
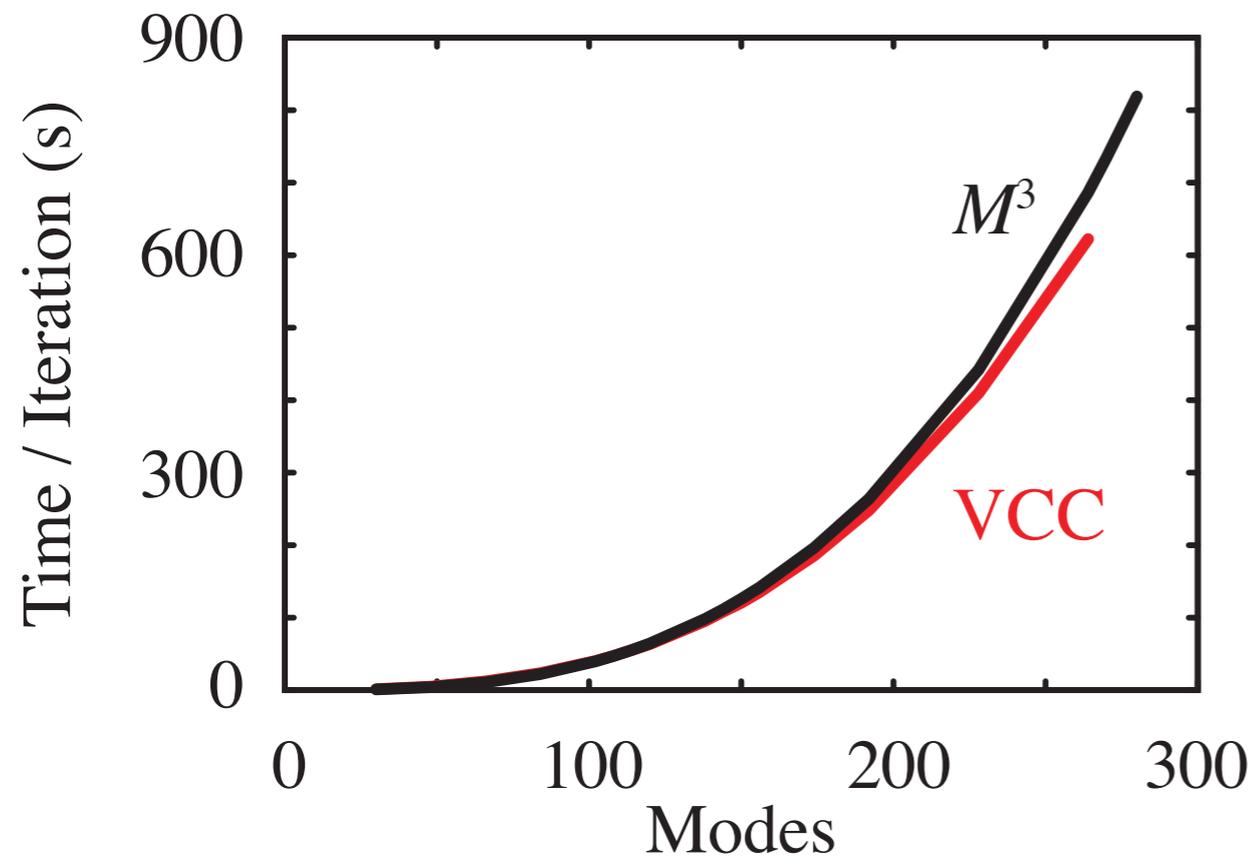
# VCC scaling illustrations



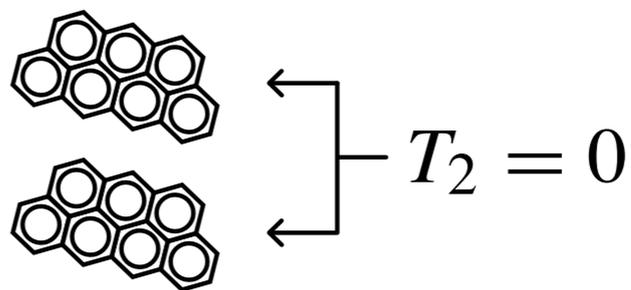
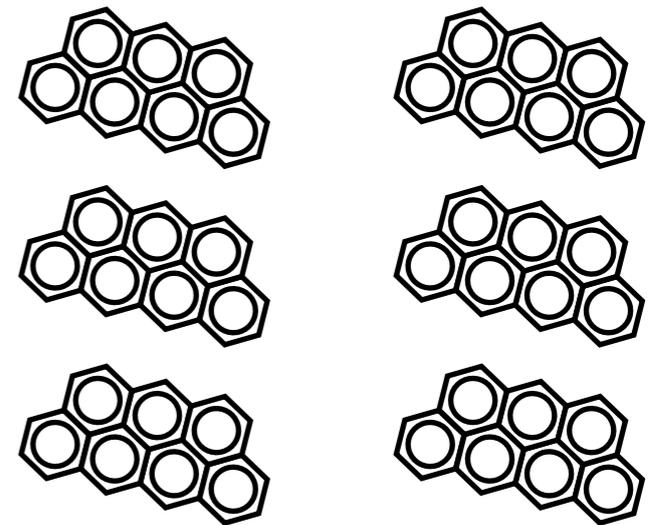
VCC[2]  
2M PES  
PAHs



# VCC scaling illustrations



VCC[2]  
2M PES  
PAHs



$$T = \sum_{\mathbf{m} \in \text{MCR}[T]} T^{\mathbf{m}}$$

# VCC cost reductions

- ⦿ Now: General and “fast” - difficult to develop but now we have a general framework.
- ⦿ Shown only a glimpse of the theory and details
- ⦿ Further avenues to explore
  - ➡ Parallelization (partly there).
  - ➡ Exploit sparsity and structure in various ways
  - ➡ Define other models and reduction tricks

# Additional CC-models: VCC[2pt3]

Full 2M, approximate 3M

$$H = F^{(0)} + U_2^{(1)} + U_3^{(2)}$$

$$F^{(0)} = H_1 + F_2 + F_3$$

$$U_2^{(1)} = H_2 - F_2$$

$$U_3^{(2)} = H_3 - F_3$$

Tildes: T1 similarity transf.

# Additional CC-models: VCC[2pt3]

Full 2M, approximate 3M

$$H = F^{(0)} + U_2^{(1)} + U_3^{(2)}$$

$$F^{(0)} = H_1 + F_2 + F_3$$

$$U_2^{(1)} = H_2 - F_2$$

$$U_3^{(2)} = H_3 - F_3$$

3M equations

Tildes: T1 similarity transf.

$$\begin{aligned} e_{\mu_3} = & \langle \mu_3 | [F, T_3]^{(2)} + \tilde{U}_3^{(2)} + [\tilde{U}_2^{(1)}, T_2]^{(2)} + [\tilde{U}_3^{(2)}, T_2]^{(3)} + [\tilde{U}_2^{(1)}, T_3]^{(3)} + [\tilde{U}_3^{(2)}, T_3]^{(4)} \\ & + \frac{1}{2} [[\tilde{U}_2^{(1)}, T_2], T_2]^{(3)} + \frac{1}{2} [[\tilde{U}_3^{(2)}, T_2], T_2]^{(4)} + [[\tilde{U}_2^{(1)}, T_2], T_3]^{(4)} \\ & + [[\tilde{U}_3^{(2)}, T_2], T_3]^{(5)} + \frac{1}{2} [[\tilde{U}_3^{(2)}, T_3], T_3]^{(6)} + \frac{1}{6} [[[\tilde{U}_3^{(2)}, T_2], T_2], T_2]^{(5)} | \Phi_i \rangle \end{aligned}$$

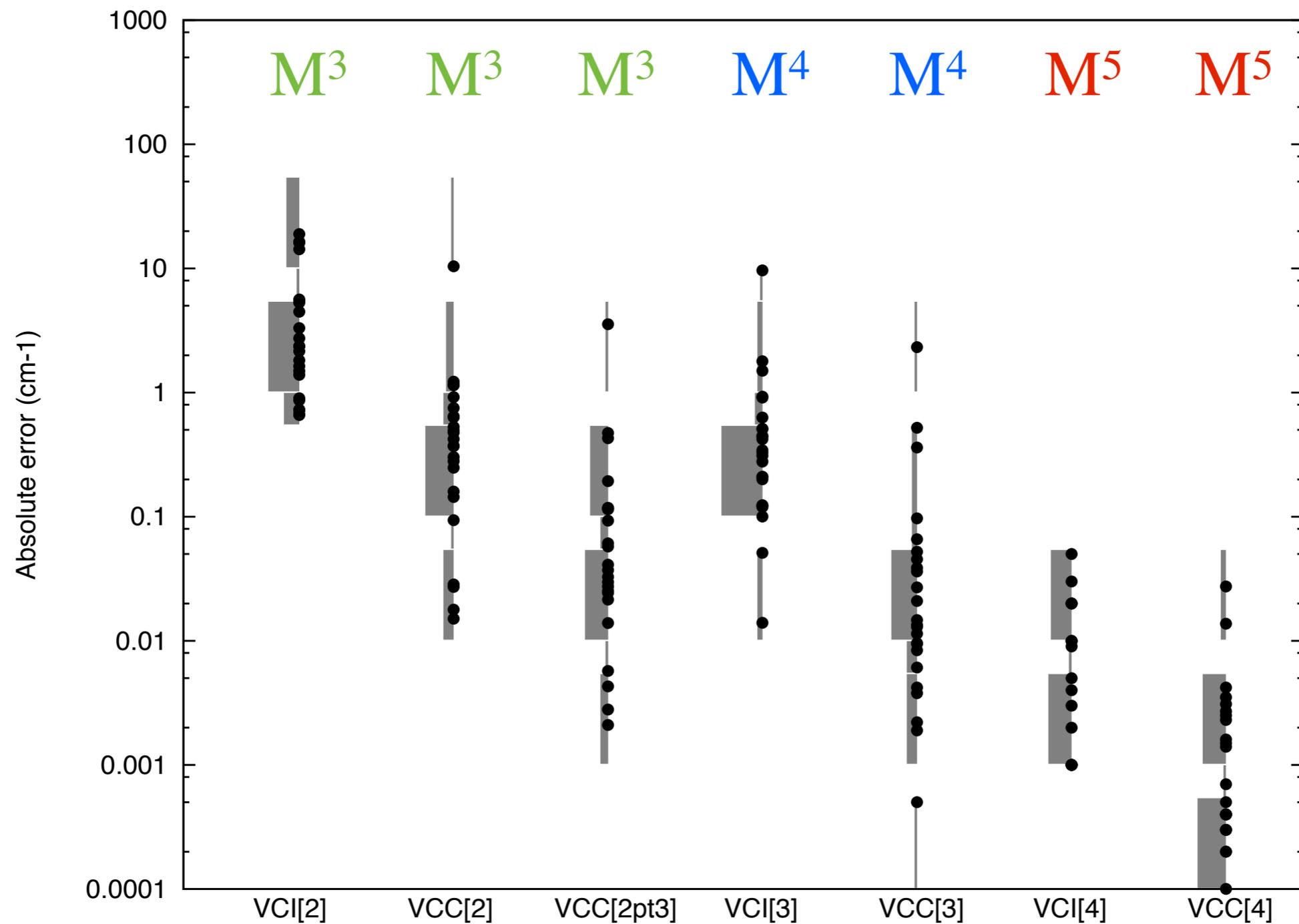
VCC[2pt3]/H3  $M^3$  scaling as compared to VCC[3]/H3  $M^4$

JCP,2009

# VCC[2pt3]

Benchmarks: H<sub>2</sub>CO, SOCl<sub>2</sub>, HFCO, CCl<sub>2</sub>O

Fundamentals



# VCC can be combined with vibrational Møller-Plesset theory

A hierarchy with modest increase in complexity:

VCC[2]

VCC[2pt3]

VCC[3]

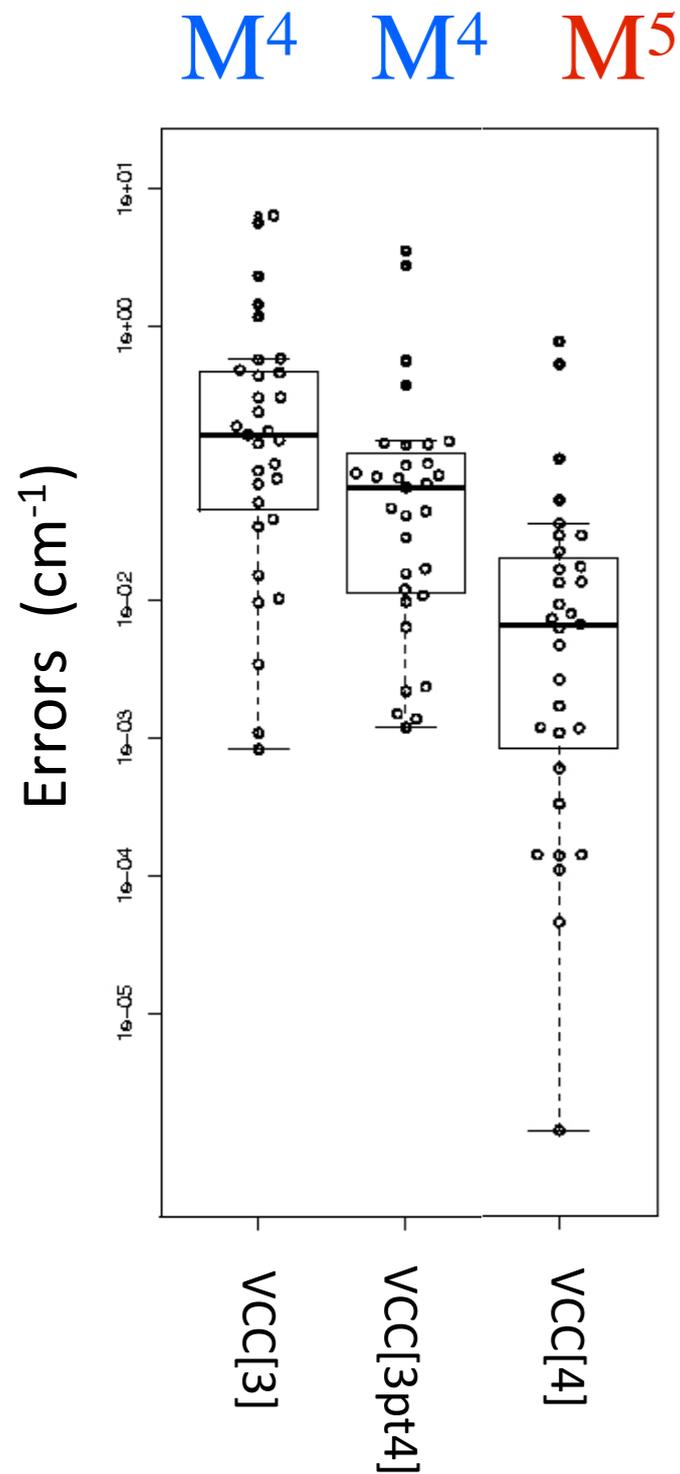
VCC[3pt4]

VCC[4]

...

VCC[n-pt-(n+1)]: same parameters as VCC[n+1] but only the most important (in terms of VMP order) are included among the terms not already in VCC[n].

# VCC[3pt4]



Deviation from VCC[4]: ethylenoxide

VCC[3pt4] <b>M<sup>4</sup></b>	VCI[4] <b>M<sup>5</sup></b>
3,8	12,0
-1,5	31,9
0,2	1,9
0,2	1,7
0,1	2,3

Zocante et al. JCP 2012

# Response Theory

$$H_0 \rightarrow H_0 + V^t$$

$$\Psi \rightarrow \Psi(t)$$

$$\langle \Psi(t) | X | \Psi(t) \rangle = \langle \Psi | X | \Psi \rangle + \text{response}$$

general operators

## Linear response function (LRF)

$$\langle\langle X; Y \rangle\rangle_\omega^\gamma = \sum_{k \neq 0} \left[ \frac{\langle \Psi_0 | X | \Psi_k \rangle \langle \Psi_k | Y | \Psi_0 \rangle}{\omega + i\gamma - \omega_k} - \frac{\langle \Psi_0 | Y | \Psi_k \rangle \langle \Psi_k | X | \Psi_0 \rangle}{\omega + i\gamma + \omega_k} \right]$$

external frequency

damping

Excitation frequency

Studying the response of the ground state can be used to study excited states:  
From Linear response function: One-Photon Spectra  
From higher order response function: Two-photon spectra

# From response functions to spectra

$$\text{LRF: } \langle\langle X; Y \rangle\rangle_{\omega}^{\gamma} = \sum_{k \neq 0} \left[ \frac{\langle \Psi_0 | X | \Psi_k \rangle \langle \Psi_k | Y | \Psi_0 \rangle}{\omega + i\gamma - \omega_k} - \frac{\langle \Psi_0 | Y | \Psi_k \rangle \langle \Psi_k | X | \Psi_0 \rangle}{\omega + i\gamma + \omega_k} \right]$$

1. Let  $\gamma \rightarrow 0$ . Then there are poles at  $\omega \rightarrow \omega_k$ .

$$\lim_{\omega \rightarrow \omega_f} (\omega - \omega_f) \langle\langle Y; Y \rangle\rangle_{\omega}^{\gamma=0} = |\langle \Psi_0 | Y | \Psi_f \rangle|^2$$

$\Psi_{exact}(t) \rightarrow \langle\langle Y; Y \rangle\rangle_{\omega}^{\gamma, \text{exact}} \rightarrow \text{Exact spectra}$

$\Psi_{approx}(t) \rightarrow \langle\langle Y; Y \rangle\rangle_{\omega}^{\gamma, \text{approx}} \rightarrow \text{Approx. spectra}$

Idea: 0. Determine reference state by the approach  
1. Calculate excited state by equations found from a formal analysis of the approximate response function

# Time-dependent VCC

Exponential parameterization:

$$|\text{VCC}\rangle = \exp(-iF(t)) \exp(T(t)) |\Phi_i\rangle$$

Time-dep. amplitudes

Time-dep. generalized phase factor

Projection of the time-dependent Schrödinger equation:

$$i\hbar \dot{\mu}^{\mathbf{m}} = \langle \mu^{\mathbf{m}} | \exp(-T) H \exp(T) | \Phi_{\mathbf{i}} \rangle$$

Perturbation expansion, Fourier components, ....

Derive ....

# VCC - Linear response function

$$\langle\langle Y; Y \rangle\rangle_{\omega} = \{ \eta^Y (t^Y(\omega + i\gamma) + t^Y(-\omega - i\gamma)) + \mathbf{F} t^Y(-\omega - i\gamma) t^Y(\omega + i\gamma) \}$$
$$(\mathbf{A} - \omega \mathbf{1}) t^Y(\omega) = -\xi^Y$$

Sum over states  $\Rightarrow$  solve linear equations

$$A_{\mu_i \nu_j} = \langle \mu_i | \exp(-T) [H, \tau_{\nu_j}] | CC \rangle$$

$$\xi_{\mu_i}^Y = \langle \mu_i | \exp(-T) Y | CC \rangle$$

$$\eta_{\nu_j}^Y = \langle \Lambda | [Y, \tau_{\nu_j}] | CC \rangle$$

$$F_{\mu_i \nu_j} = \langle \Lambda | [[H, \tau_{\mu_i}], \tau_{\nu_j}] | CC \rangle$$

....

Dont worry too much  
about the details here.

# VCC response excitation energies

A. Excited state equations through pole-search:

$$A_{\mu_i \nu_j} = \langle \mu_i | \exp(-T) [H, \tau_{\nu_j}] \exp(T) | \Phi_i \rangle$$

$$A_{\mu_i \nu_j} = \langle \mu_i | \exp(-T) H \exp(T) | \nu_j \rangle - \delta_{\mu_i, \nu_j} E_{VCC}$$

Asym. VCC Jacobian

$$\mathbf{A}R = \omega R$$

Huge A matrix never constructed explicitly

Iterative techniques:

Davidson, Olsen, - well-separated states

Lanczos

Require transformations with Jacobian

Same spirit for implementation as described previously

# From response functions to spectra

$$\text{LRF: } \langle\langle X; Y \rangle\rangle_{\omega}^{\gamma} = \sum_{k \neq 0} \left[ \frac{\langle \Psi_0 | X | \Psi_k \rangle \langle \Psi_k | Y | \Psi_0 \rangle}{\omega + i\gamma - \omega_k} - \frac{\langle \Psi_0 | Y | \Psi_k \rangle \langle \Psi_k | X | \Psi_0 \rangle}{\omega + i\gamma + \omega_k} \right]$$

2. For finite  $\gamma$  the imaginary part gives a Lorentzian broadened spectrum

$$\text{Im}[\langle\langle Y; Y \rangle\rangle_{\omega}^{\gamma}] = - \sum_{k \neq 0} |\langle \Psi_0 | Y | \Psi_k \rangle|^2 \left( \frac{\gamma}{(\omega - \omega_k)^2 + \gamma^2} - \frac{\gamma}{(\omega + \omega_k)^2 + \gamma^2} \right)$$

$$\lim_{\gamma \rightarrow 0} \text{Im}[\langle\langle Y; Y \rangle\rangle_{\omega}^{\gamma}] = - \sum_{k \neq 0} \pi |\langle \Psi_0 | Y | \Psi_k \rangle|^2 (\delta(\omega - \omega_k) - \delta(\omega + \omega_k))$$

Use response function analogy with exact theory:

$$\Psi_{exact}(t) \rightarrow \langle\langle Y; Y \rangle\rangle_{\omega}^{\gamma, \text{exact}} \rightarrow \text{Exact spectra (broadened)}$$

$$\Psi_{approx}(t) \rightarrow \langle\langle Y; Y \rangle\rangle_{\omega}^{\gamma, \text{approx}} \rightarrow \text{Approx. spectra (broadened)}$$

# Spectra and states

- Challenge: The number of states increases wildly with the number of degrees of freedom
- Their nature can be hard to predict
- Calculating all the states explicitly becomes impossible
- Can we work around this?
- Do we need all states explicitly?

# Idea: use directly damped response functions themselves to get absorption.

Linear response functions determine the absorption spectrum defined as

$$\sigma_X^\gamma(\omega) = -\omega \operatorname{Im} \langle \langle X; X \rangle \rangle_\omega^\gamma$$

VCI wave function  $\rightarrow$  VCI response function  $\rightarrow$  VCI spectrum

VCC wave function  $\rightarrow$  VCC response function  $\rightarrow$  VCC spectrum

VCI & VCC response functions have been derived and implemented.

# How solved in practice?

## I. Lanczos iteration

$$C(\omega) = \mathbf{U}^T (\mathbf{A} - \omega \mathbf{1})^{-1} \mathbf{V}$$
$$= \mathbf{u} \mathbf{v} \mathbf{u}^T (\mathbf{A} - \omega \mathbf{1})^{-1} \mathbf{v}$$

Contribution to response functions for VCI / VCC

Asymmetric matrix Lanczos iteration on response A matrix:

$$\mathbf{q}_1 = \mathbf{v} \quad \mathbf{p}_1 = \mathbf{u}$$

$$\beta_j \mathbf{q}_{j+1} = \mathbf{r}_j = (\mathbf{A} - \alpha_j) \mathbf{q}_j - \gamma_{j-1} \mathbf{q}_{j-1}$$

$$\gamma_j \mathbf{p}_{j+1} = \mathbf{s}_j = (\mathbf{A}^T - \alpha_j) \mathbf{p}_j - \beta_{j-1} \mathbf{p}_{j-1}$$

$$\alpha_j = \mathbf{p}_j^T \mathbf{A} \mathbf{q}_j$$

$$1 = \mathbf{p}_{j+1}^T \mathbf{q}_{j+1} = \left( \frac{\mathbf{s}_j}{\gamma_j} \right) \left( \frac{\mathbf{r}_j}{\beta_j} \right)$$

$$\mathbf{T}^{(k)} = \begin{pmatrix} \alpha_1 & \gamma_1 & 0 & 0 & 0 & 0 & 0 \\ \beta_1 & \alpha_2 & \gamma_2 & 0 & 0 & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \gamma_{k-1} \\ 0 & \cdot & \cdot & \cdot & 0 & \beta_{k-1} & \alpha_k \end{pmatrix}$$

NB Focus is not on Lanczos as eigensolver, but on building a space for accurate calculation of a matrix functions. Note start guess.

## 2. Complex equation solvers: - another time

# The moments of the spectra converge with increasing Lanczos iterations

$$[\sigma_X(\omega)]_n = \int_0^\infty \sigma_X(\omega) \omega^n d\omega$$

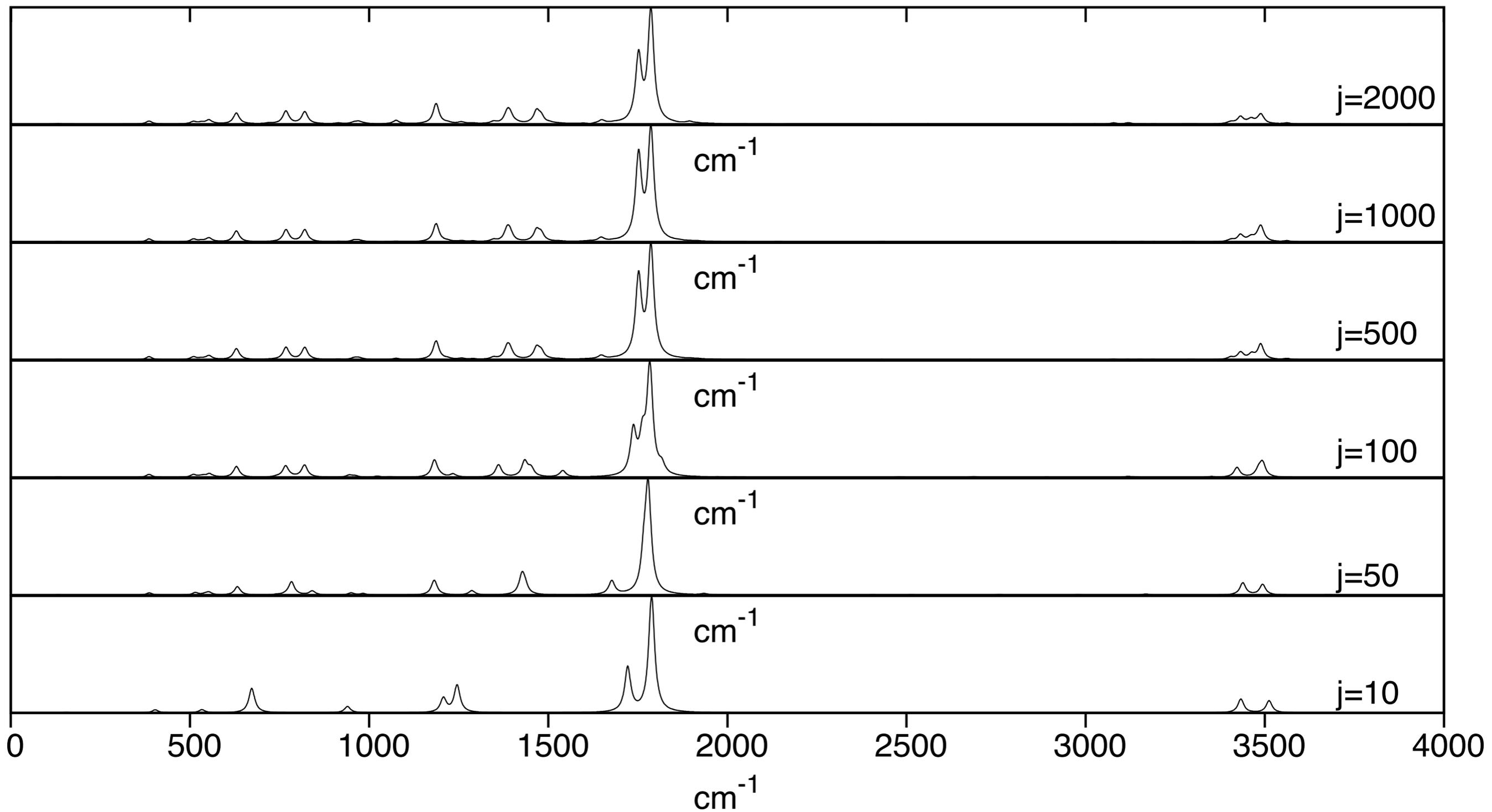
“Exact” spectrum

$$[\sigma_X^{(j)}(\omega)]_n = \int_0^\infty \sigma_X^{(j)}(\omega) \omega^n d\omega$$

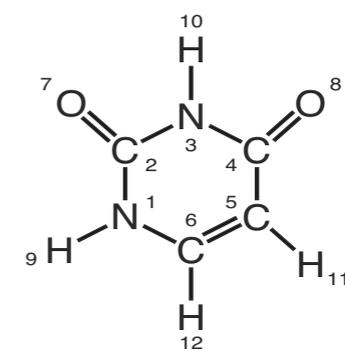
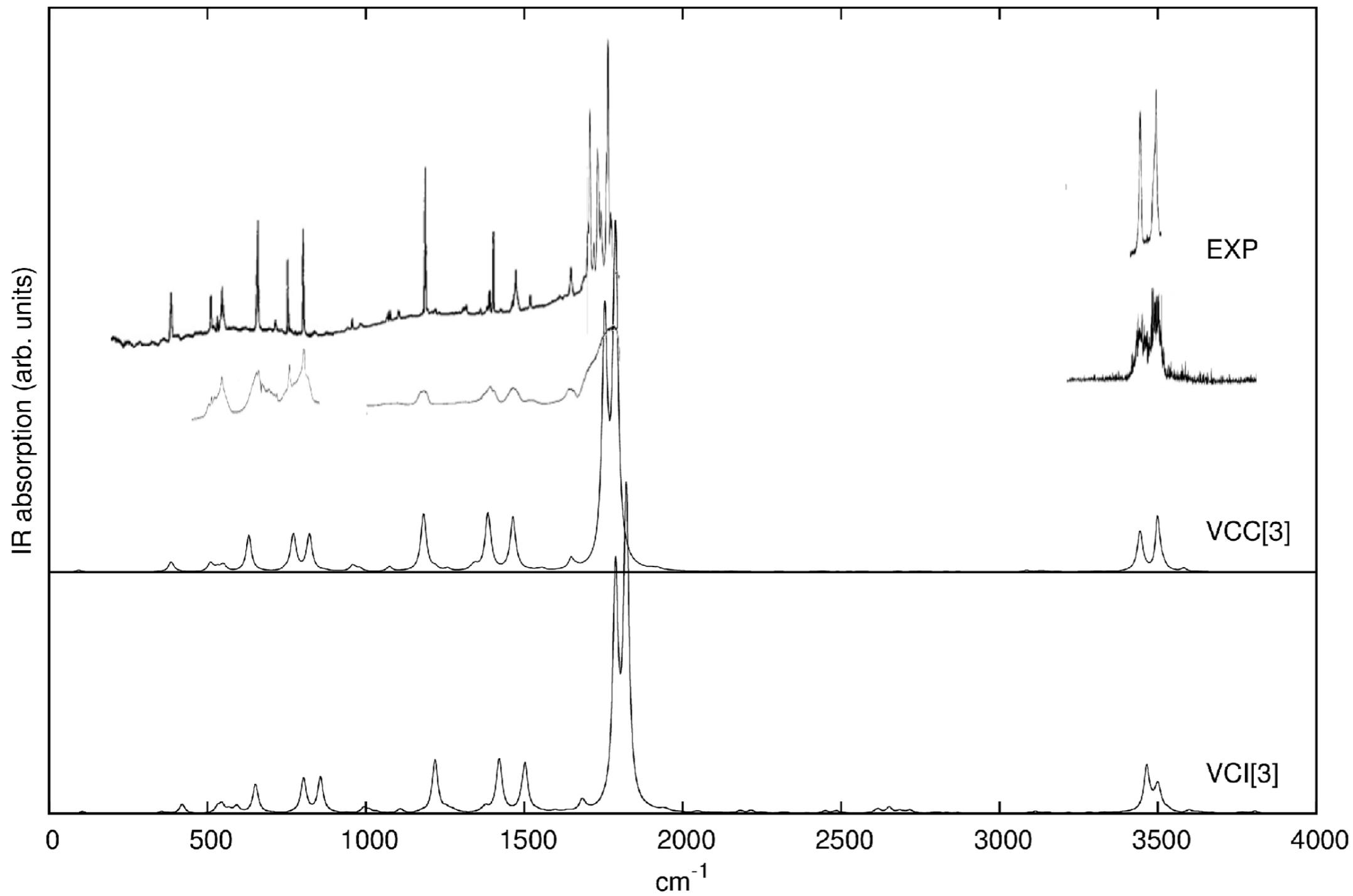
The Lanczos spectrum truncated at j-th step.

$$[\sigma_X(\omega)]_n = [\sigma_X^{(j)}(\omega)]_n \quad 0 \leq n \leq 2j - 3$$

# Uracil convergence for VCC[2]



# Uracil



Thomsen et al. JCP 2012  
PES:ADGA, 2M,RI-MP2/TZVPP

# Summary

VCC the accurate choice at given excitation level  
→ theoretically attractive (size-consistency)

VCC can be made computationally competitive

Automatic derivation and implementation of equations

→ General VCC response theory now possible.

→ Approximate VCC models easily implemented and tested.

Direct calculation of spectra/properties - important for larger systems defining an important role of “damped” response theory.

# MidasCpp

## Molecular Interactions, Dynamics and Simulations Chemistry Program Package in C++

Potential energy and property surface generation:

Static and dynamic grids, ADGA (Adaptive Density-Guided Approach)

Derivative based/Interpolation etc., Interfaces to various electronic structure programs

Wave functions:

VSCF, VMP $n$ , VCI, VCC

+ Response Theory

+ Temperature

+ Properties