Vibrational Coupled Cluster Theory

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SOLIDUM PETIT IN PROFUNDIS · UNIVERSITAS ARHUSIENSIS ·

Center for Oxygen Microscopy and imaging

Molecular Quantum Mechanics

$$H\,\Psi = E\,\Psi$$

Born-Oppenheimer approximation:

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

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

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

Computational Scaling: Exponential $\overset{??}{\Rightarrow}$ Polynomial $\overset{??}{\Rightarrow}$ Linear

Coupled Cluster is the accurate approach for electronic correlation.
Could it also be the case for nuclear motion?
Can one automize the whole process?

If time allows

- The key-steps in solving the nuclear motion problem
  - PES
  - WF
- Vibrational Coupled Cluster (VCC)
  - Theory
  - Benchmarks
  - Implementation
- Response Theory
  - Spectra
  - The Lanzcos method for calculating response functions
- Summary

What are we looking at?

System	M coupled distinguishable modes, index m
q_m	Coordinates (normal)
$\phi_{s_m}^m(q_m)$	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/Watsonian

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

Potential Coupling Expansion $\boldsymbol{V}^{(1)}, \boldsymbol{V}^{(2)}, \boldsymbol{V}^{(3)}, ..., \boldsymbol{V}^{(M)}$

More generally $$V = \sum_{\mathbf{m_n} \in \mathbf{MCR\{V\}}} \bar{V}^{\mathbf{m_n}}(q_{m_1}, .., q_{m_n})$$

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

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$$N_{ppd}^{M}$$

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

$$N_{ppd}^{M} \quad \Rightarrow \quad \sum_{n=1}^{N_{maxc}} \left(\begin{array}{c} M \\ n \end{array} \right) N_{ppd}^{n}$$

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$$N_{ppd}^{M} \quad \Rightarrow \quad \sum_{n=1}^{N_{maxc}} \left(\begin{array}{c} M \\ n \end{array} \right) N_{ppd}^{n}$$

In practice: generate grid for each coupling (man-made or automatic).
Then represent that in terms of a product of one-mode operators:
Product of polynomials.
We have automized that, adaptive density-guided approach (ADGA),
using derivatives, etc.

Static and Adaptive PES construction

- Static: Define grid apriori
- Iterative: some error control and adaption
- Aim? V - or rather E, Ψ
- ADGA: adaptive density-guided approach

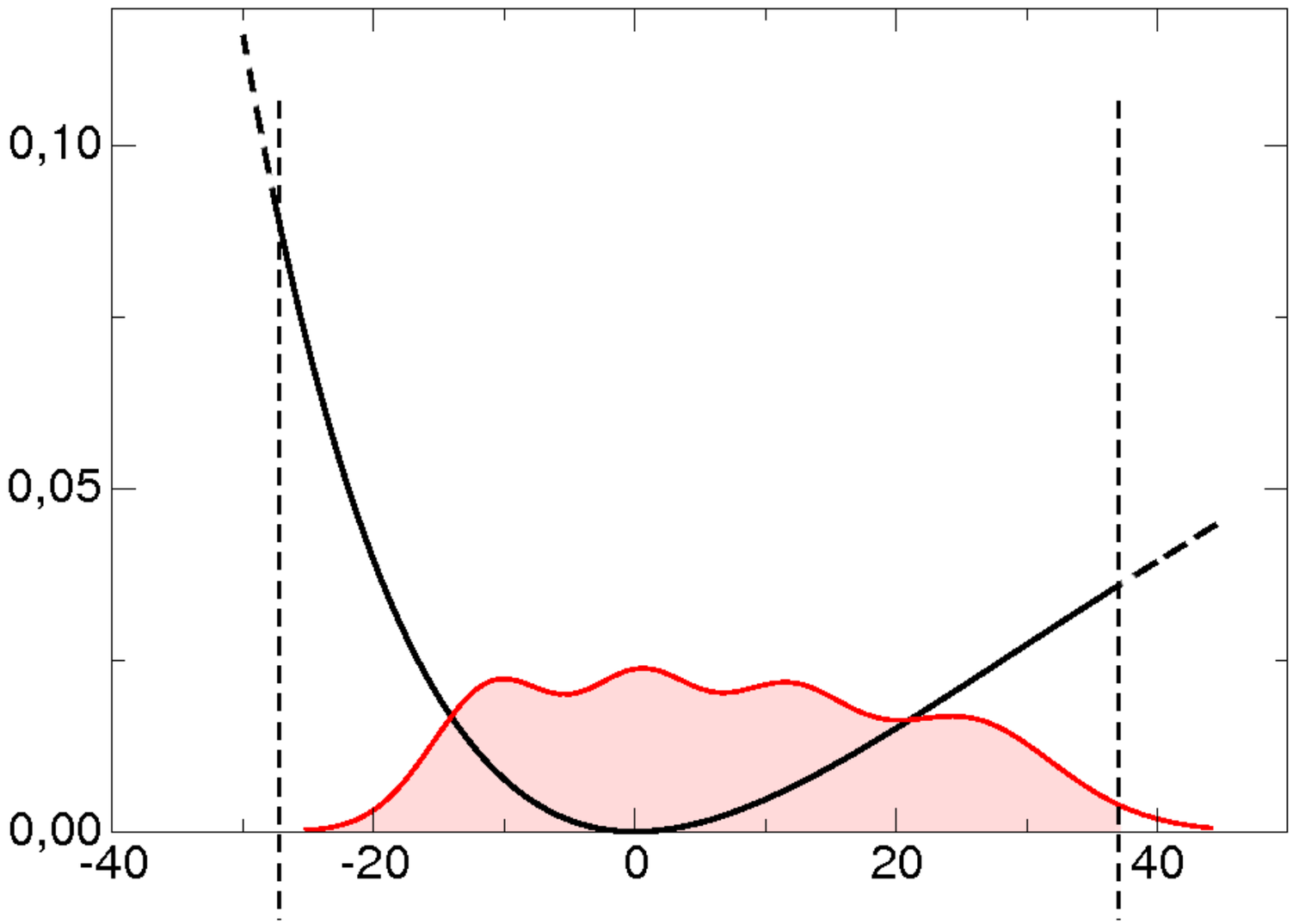
Use one-mode densities to determine:

Boundaries

Grid mesh

Average density (VSCF)

$$\rho(q_m)_{av} = \frac{\sum_{i^m}^{N} |\phi_{i^m}^{m}(q_m)|^2}{N}$$



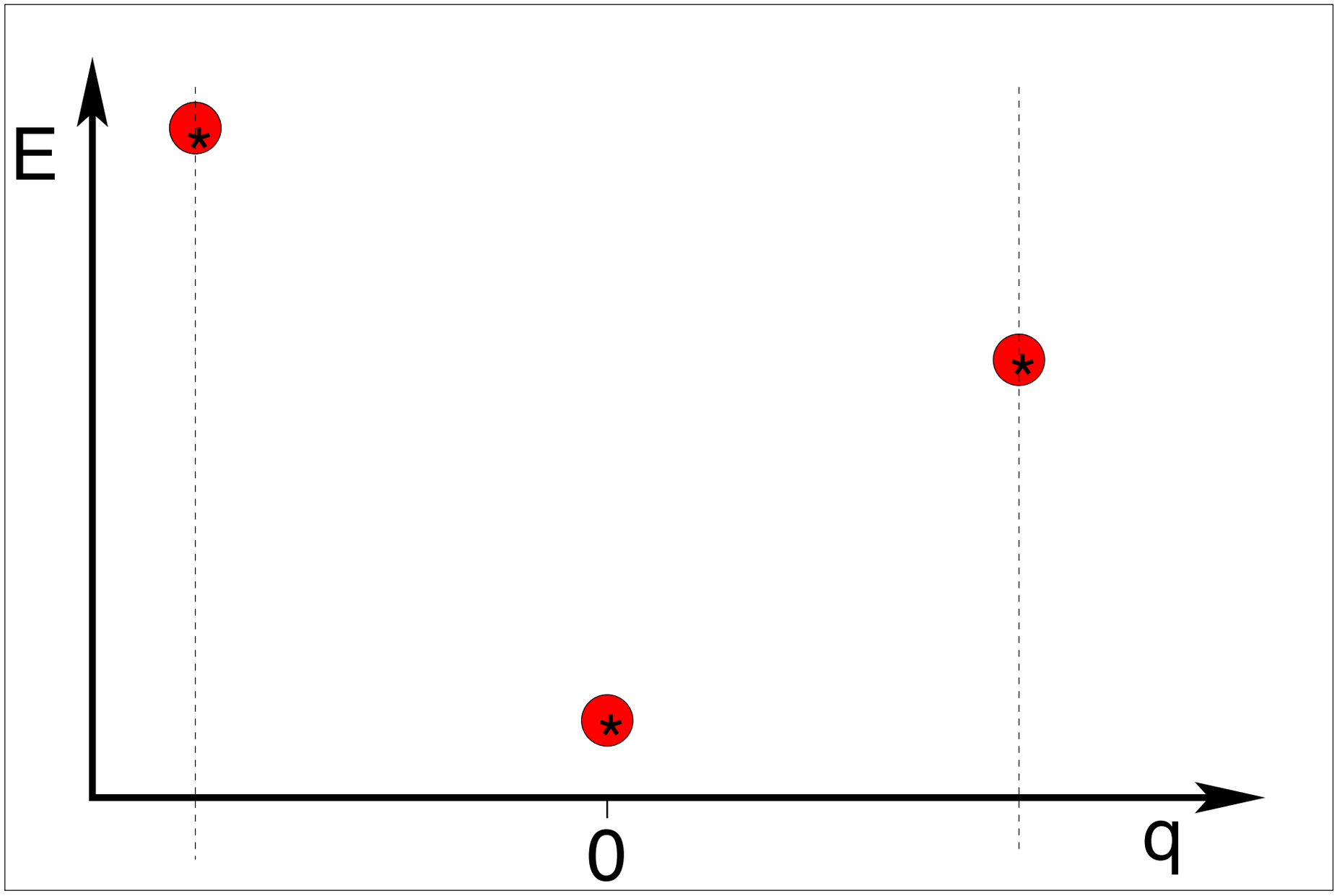
ADGA - test quantity

$$\int_I \rho(q_m)\, V(q_m) dq_m$$

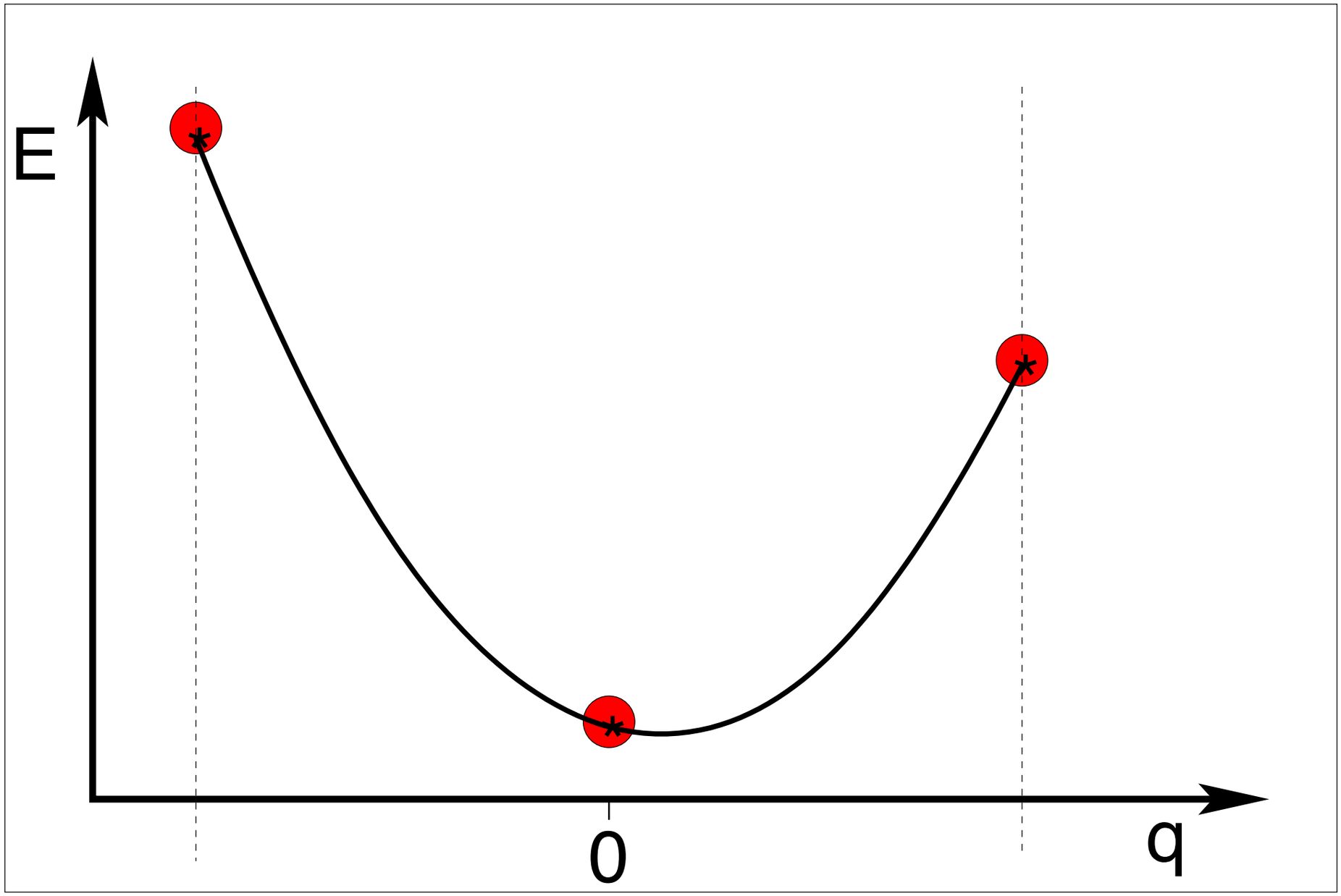
Balances potential and wave function

Energy contribution from interval

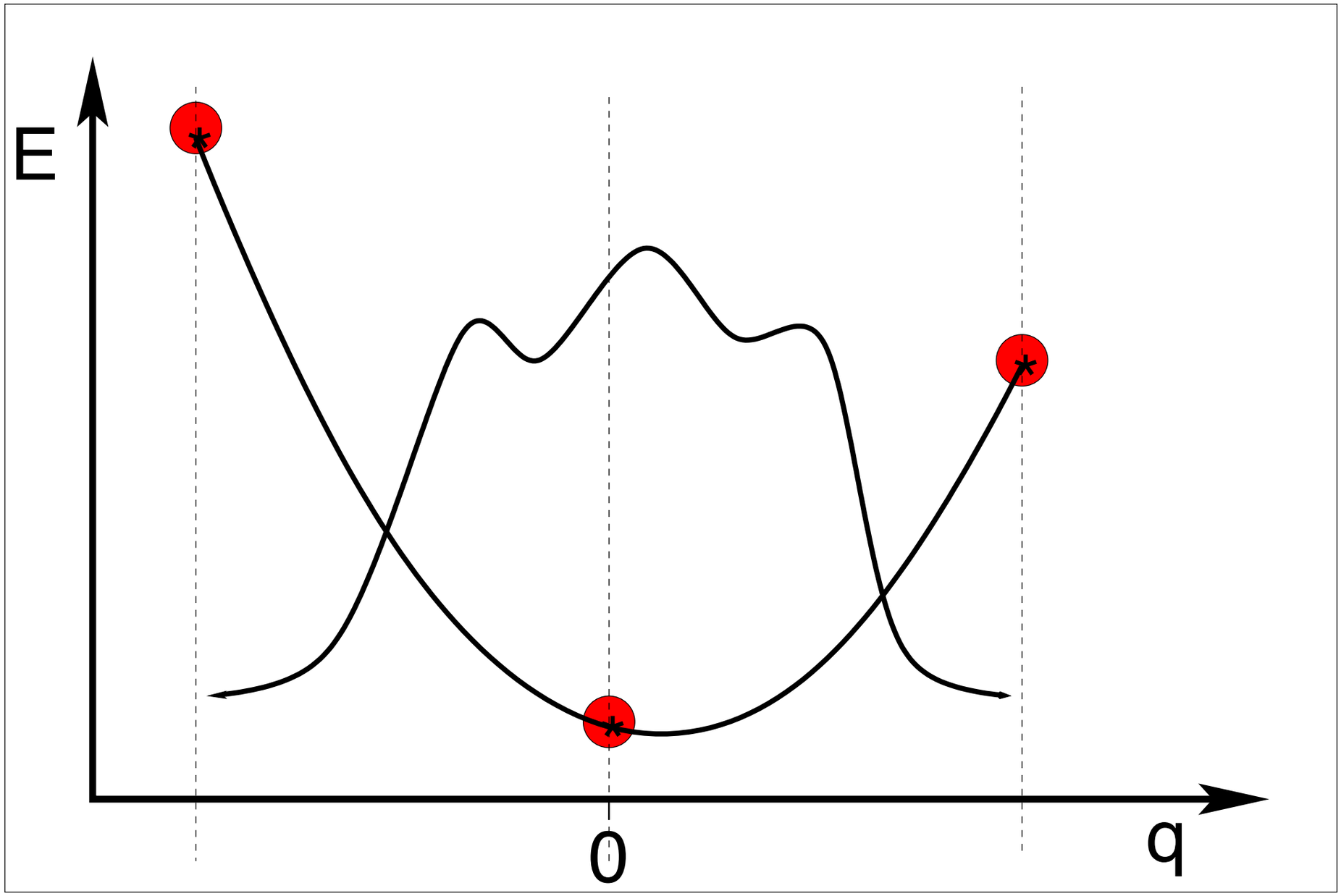
ADGA



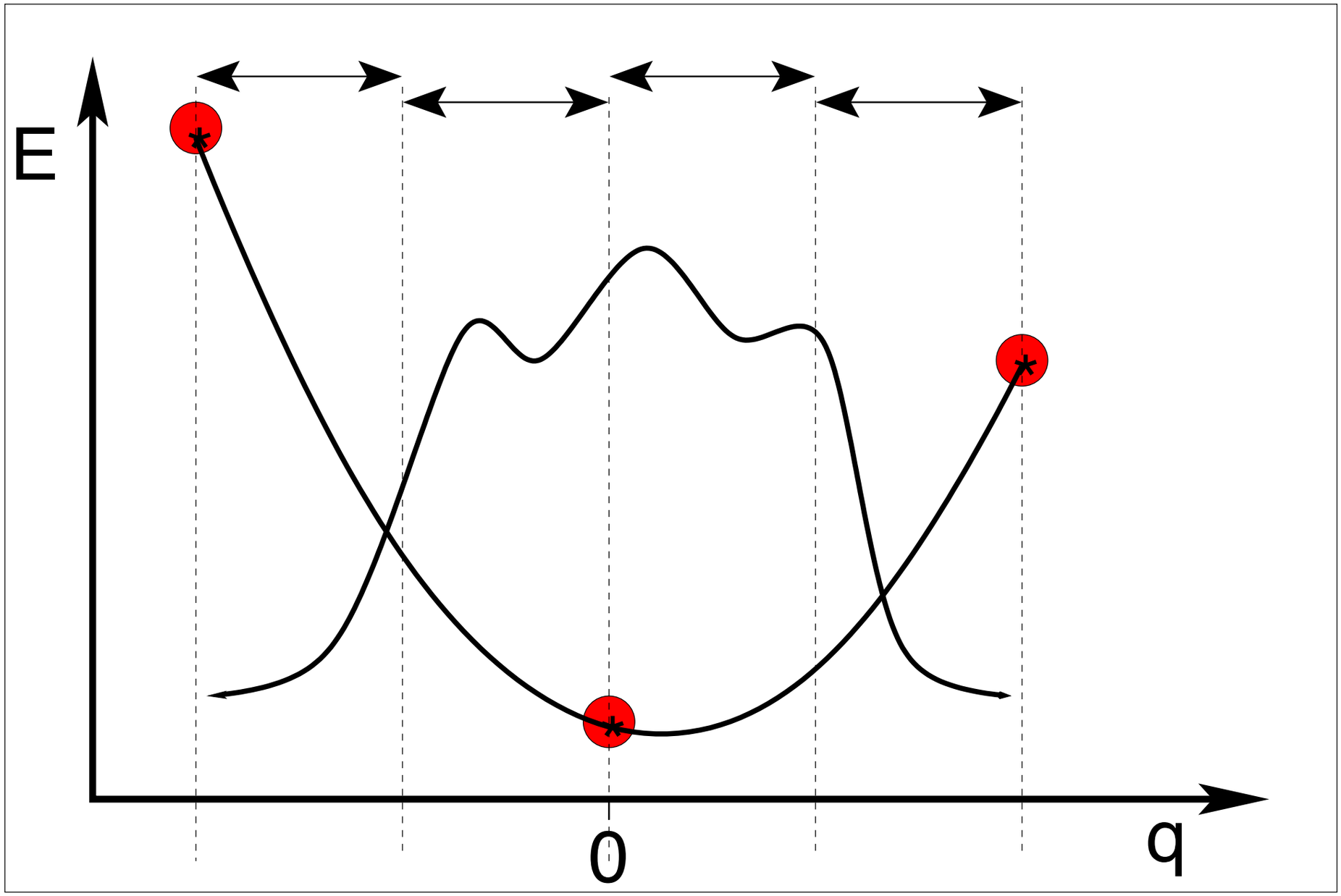
ADGA



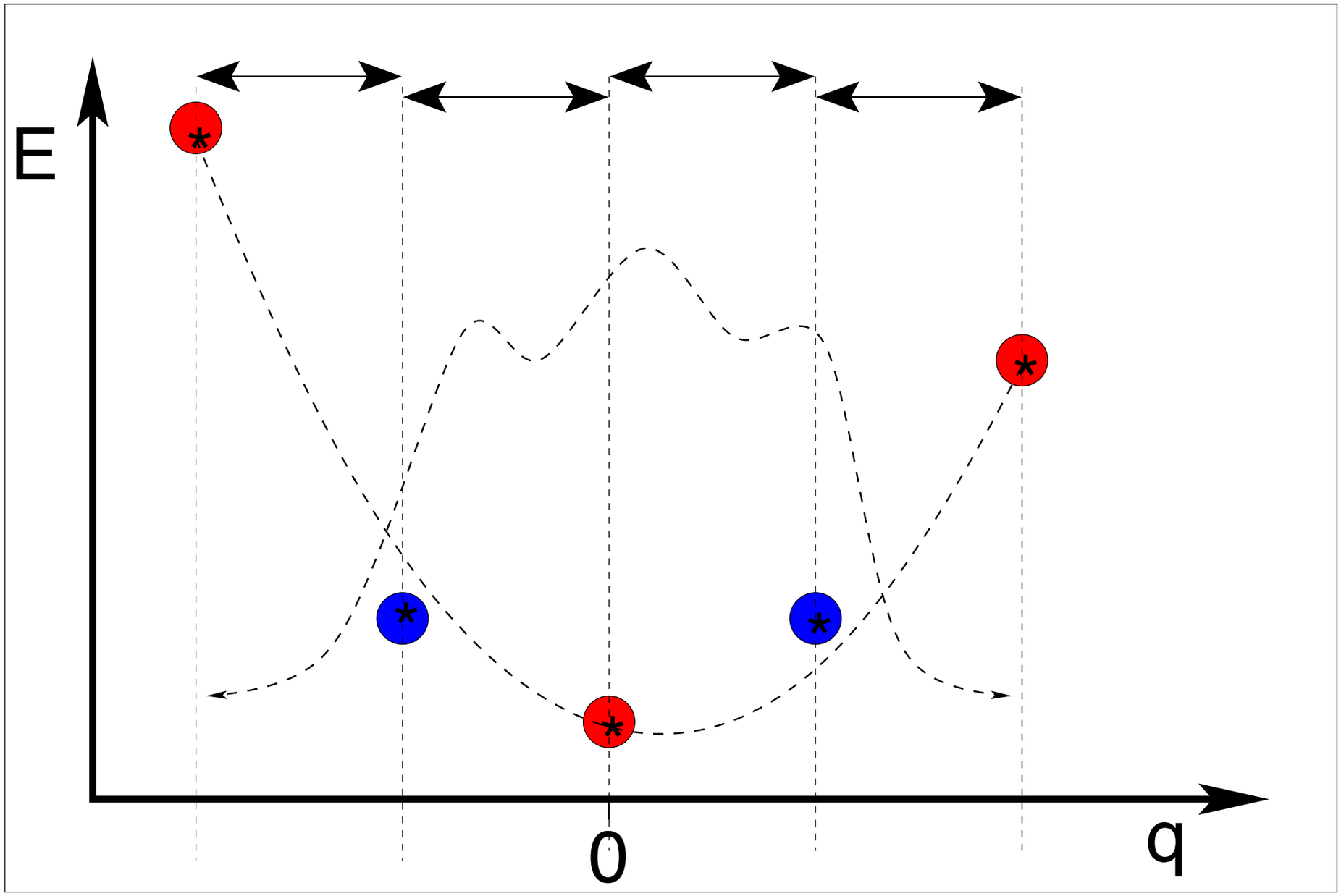
ADGA



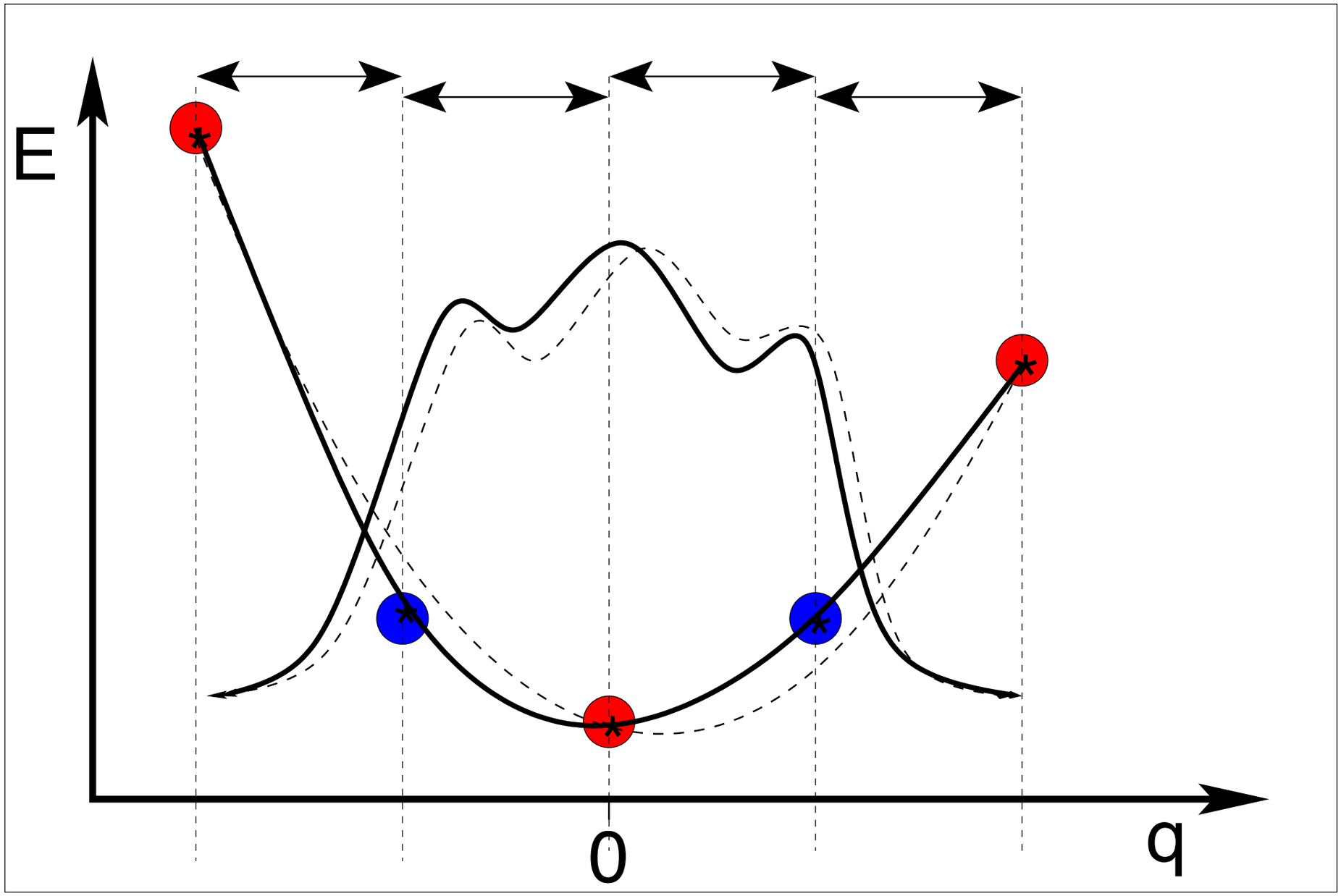
ADGA



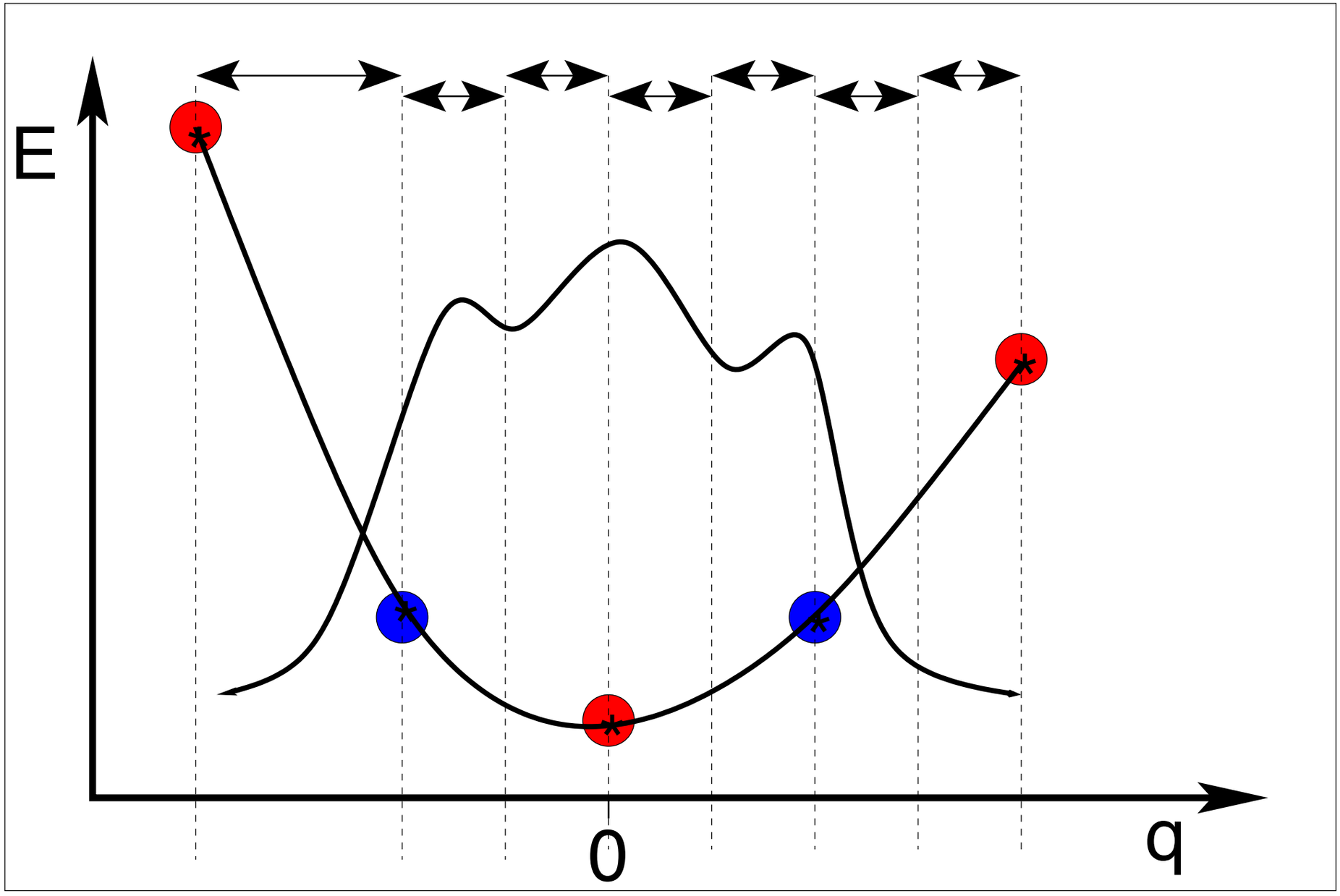
ADGA



ADGA



ADGA



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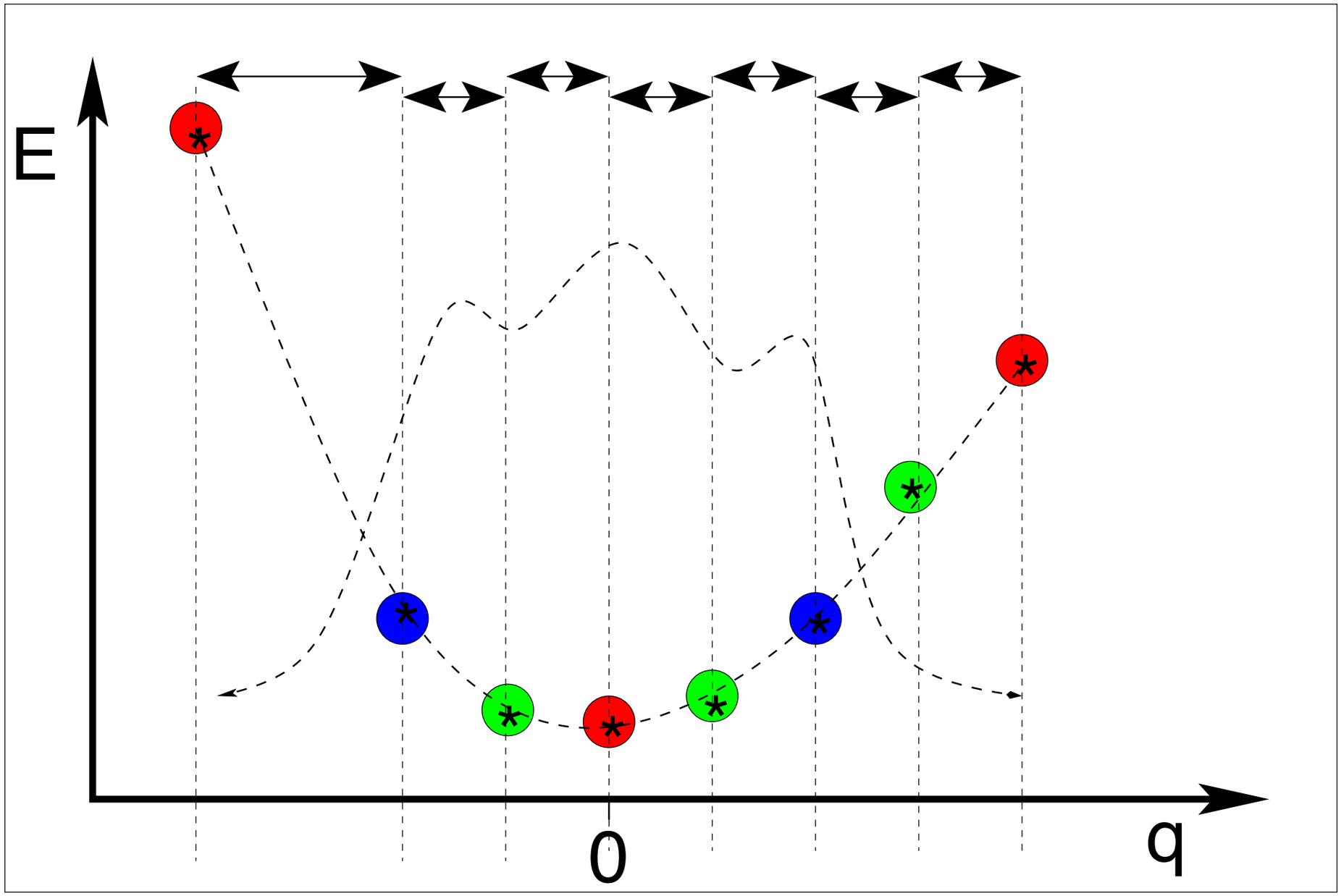
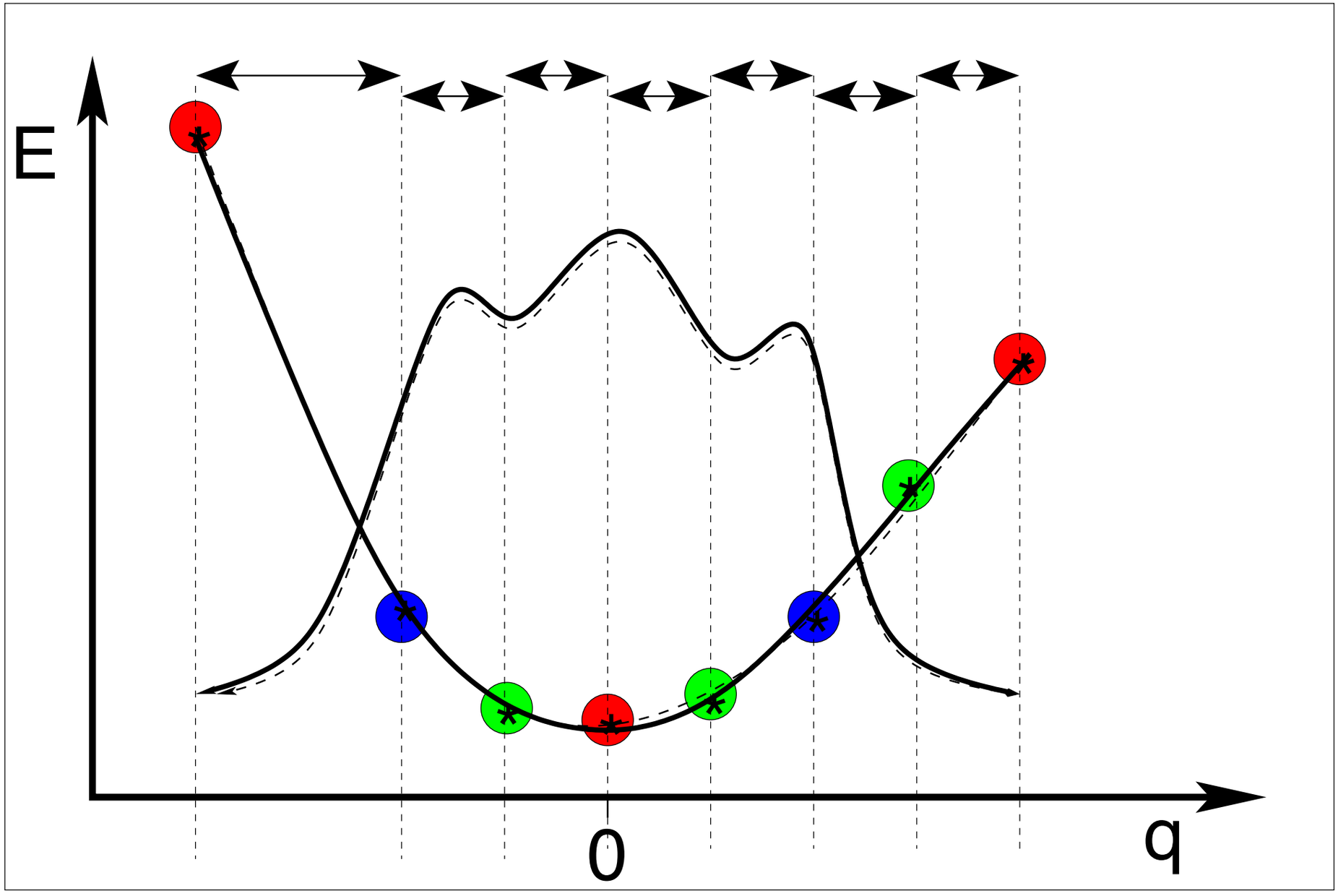
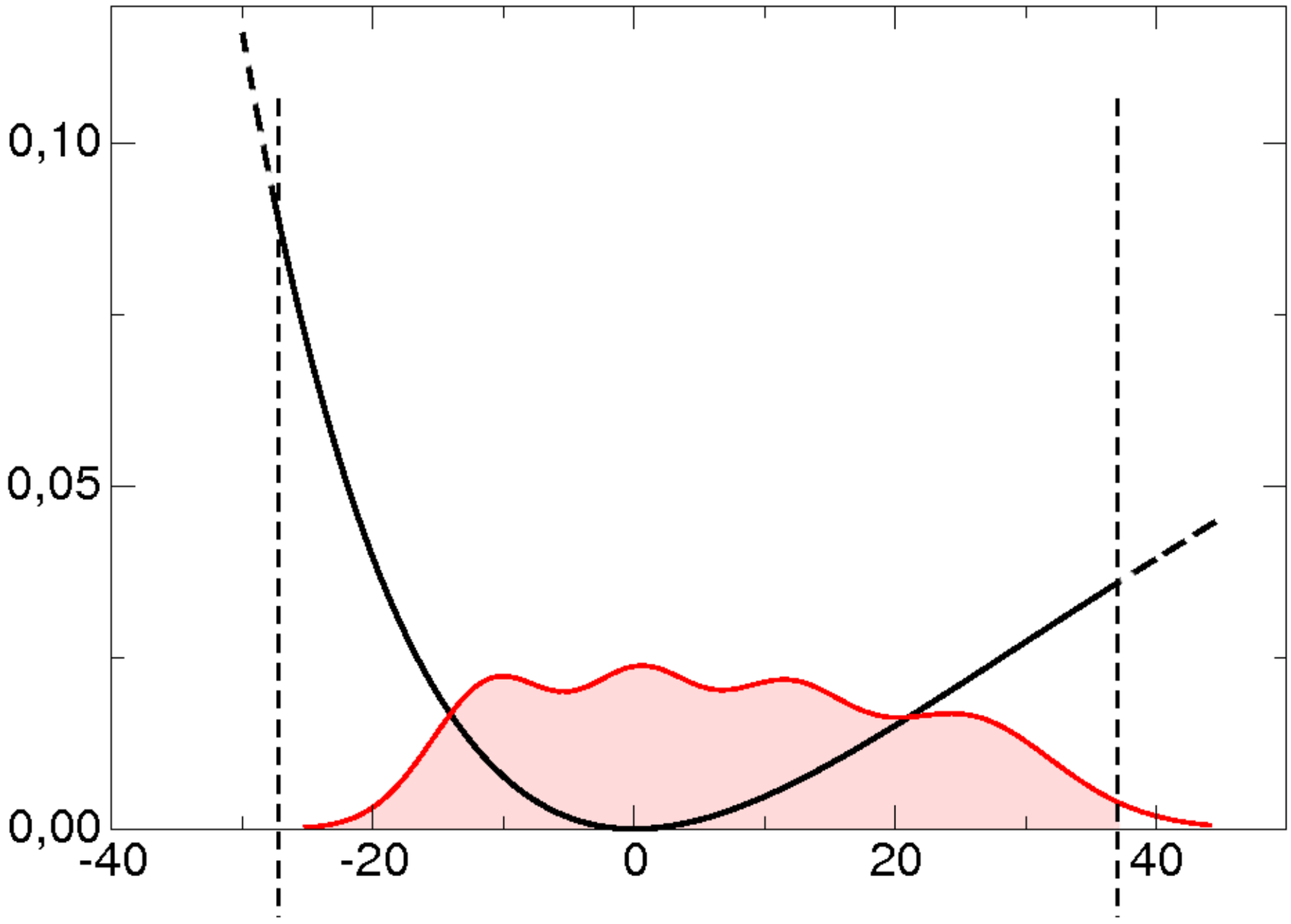


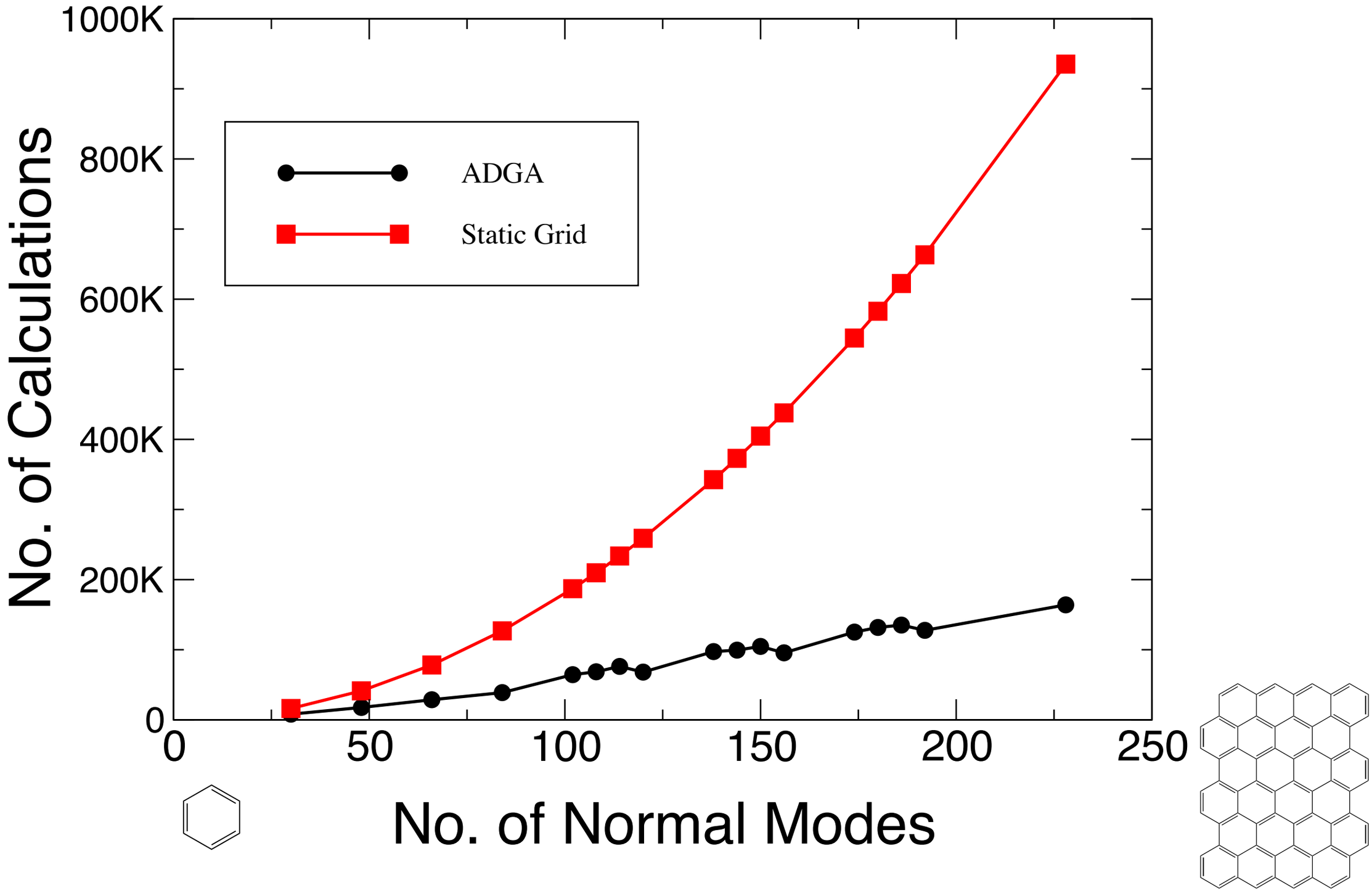
ADGA



Boundaries



PAH example, 2M PES



Summary: PES

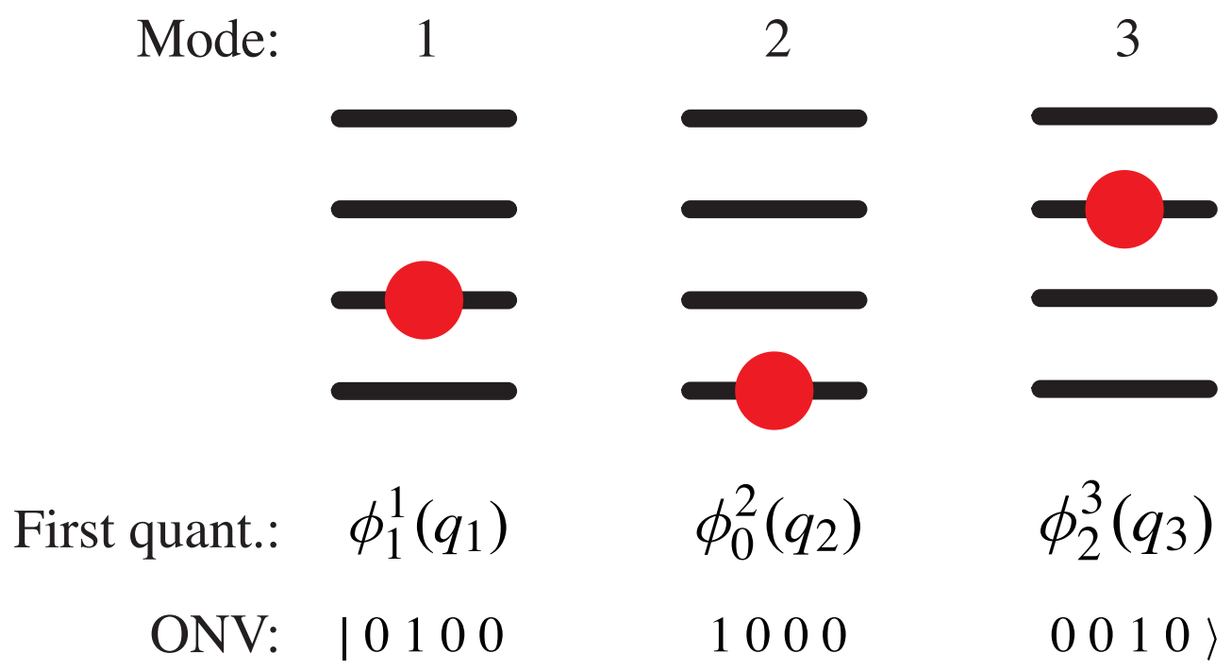
ADGA: Adaptive Density Guided Approach
→ Black box & Adaptive
→ Reduced cost & Scaling

We are addressing the scaling of the construction of the PES through a combination of:

→ ADGA: Adaptive Density Guided Approach
→ Derivative information
→ Multi-level approaches
→ automatic a priori neglect of mode combinations

Second Quantization

Hartree product represented by occupation number vector



OC, JCP, 2004.

Second Quantization

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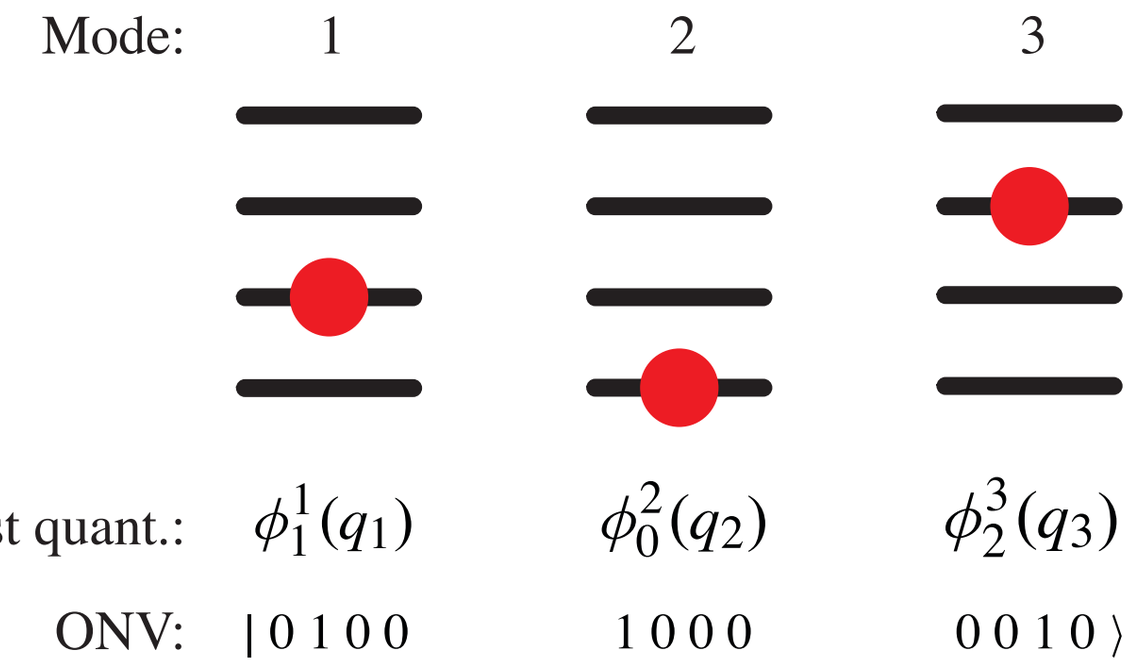


Creation / annihilation operators

$$a_r^{m\dagger}|\ldots 0000\ldots\rangle = |\ldots 0010\ldots\rangle$$
$$a_r^{m}|\ldots 0010\ldots\rangle = |\ldots 0000\ldots\rangle$$

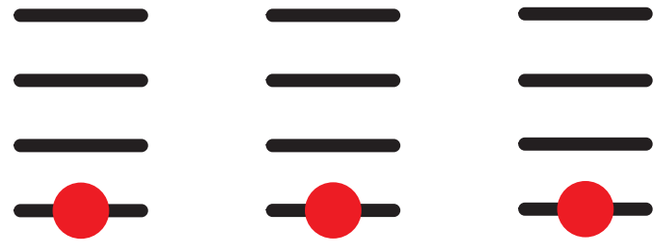
OC, JCP, 2004.

Second Quantization

Reference state: $|\Phi_{\mathbf{i}}\rangle = \prod_{m} a_{i_m}^{m\dagger} |\mathrm{vac}\rangle$

$\uparrow$

$(0, 0, 0)$



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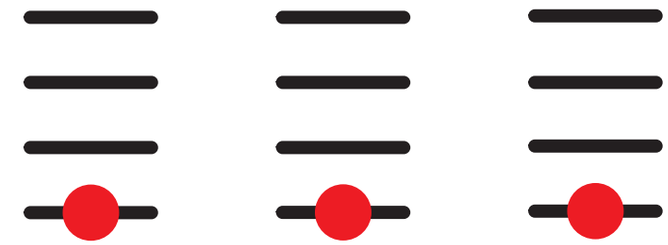
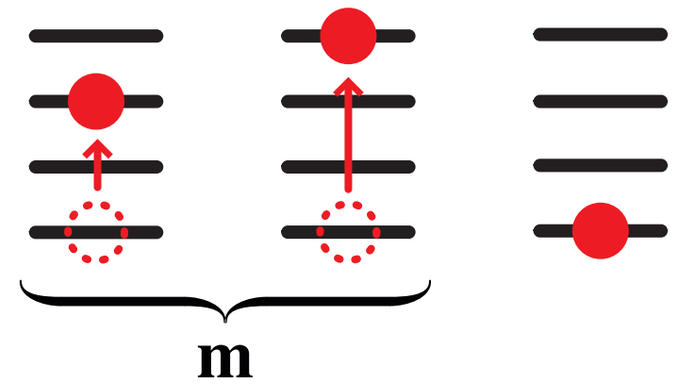
$\mathbf{i} \uparrow (0,0,0)$



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



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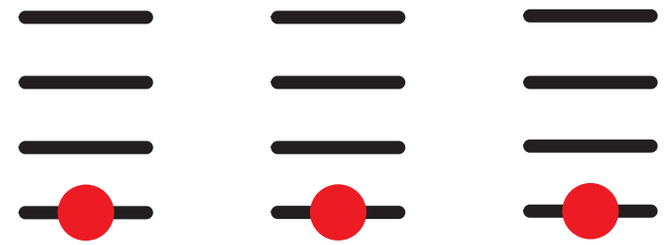
$\mathbf{i}$ (0, 0, 0)



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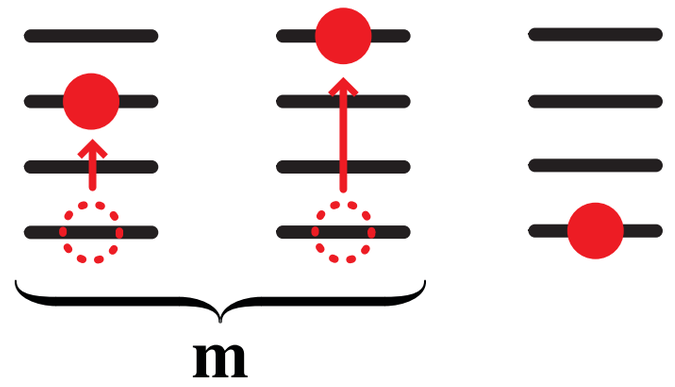

H assumed to be a sum of products, e.g. $h^1 h^2 h^3 = q_1 q_2 q_3^2$

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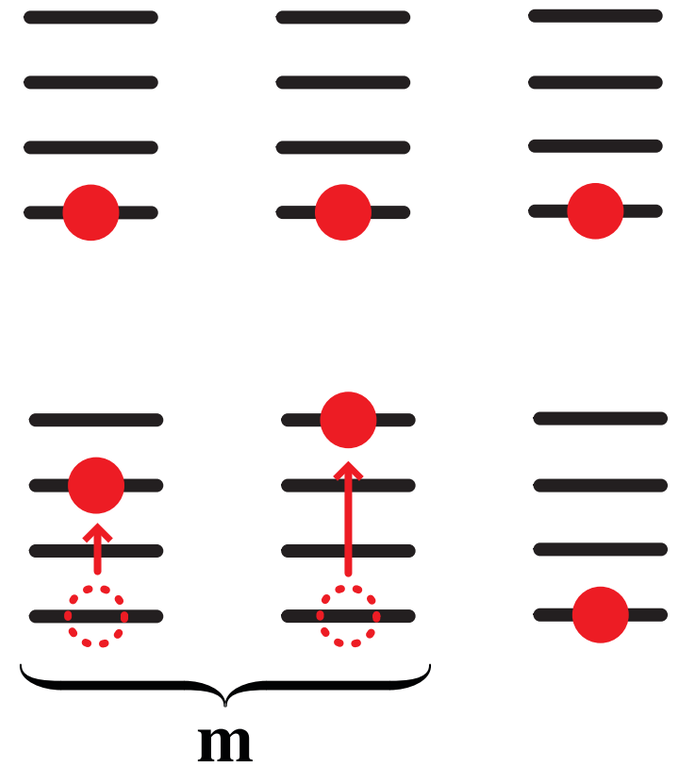

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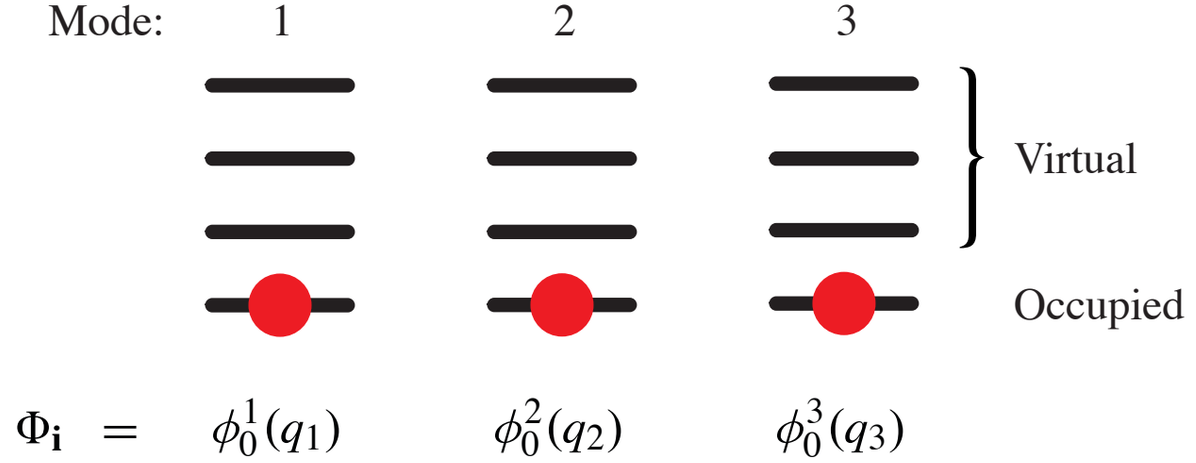
$$H = \sum_t^{N_t} c_t \prod_{m \in \mathbf{m}^t} \sum_{p,q} h_{pq}^{mo} a_p^{m\dagger} a_q^m$$

Vibrational Self Consistent Field

Ansatz: Wave function is a single Hartree-Product

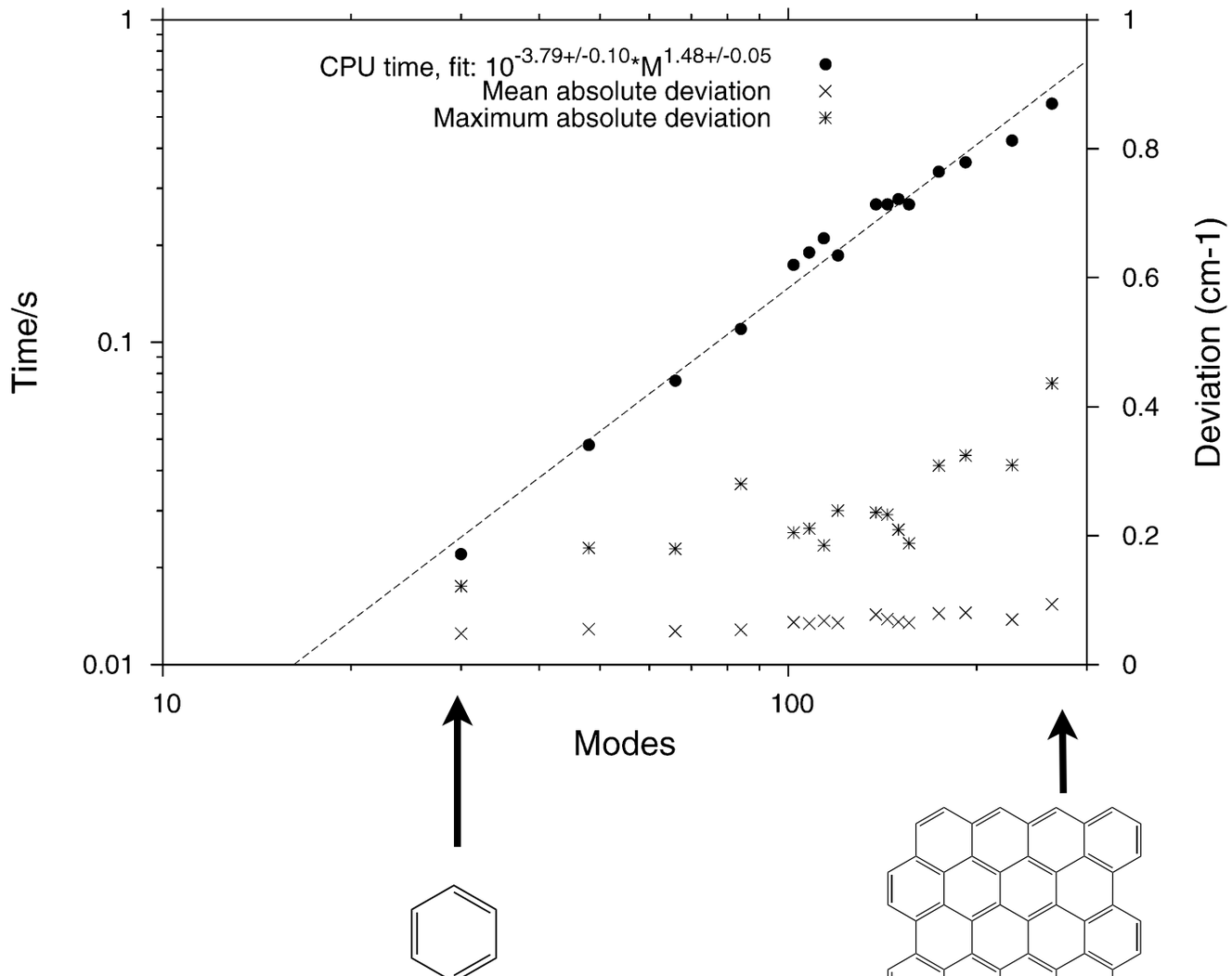
$$|\Phi_{\mathbf{i}}(q_1, q_2, ...q_M)\rangle = \prod_{m=1}^{M} \phi_{i_m}(q_m) \qquad |\Phi_{\mathbf{i}}\rangle = \prod_{m=1}^{M} a^{\dagger}_{i_m} |\mathrm{vac}\rangle$$

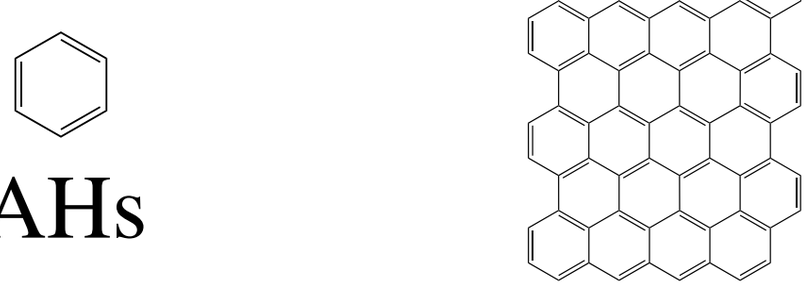


Variational principle → Self-Consistent-Field eqs.

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 really coupling something.

JCTC, 2010

Vibrational Correlation

- VSCF: Mean field theory.
  - Provides a reasonable set of one-mode functions
    - Defines a correlation problem.
- VCI: Linear expansion in Hartree-Products
- FVCI: given basis, the exact solution.

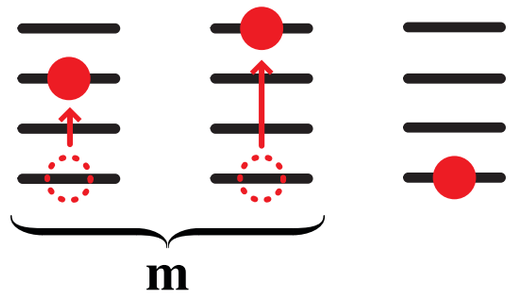
Vibrational Coupled Cluster Theory

Exponential parameterization: $|\mathrm{VCC}\rangle = \exp(T)|\Phi_\mathbf{i}\rangle$

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 response theory - first encounter

Ground state: solve non-linear t-eqs.
Excited states: Response theory

$$A_{\mu^{\mathbf{m}}\nu^{\mathbf{m}'}} = \frac{\partial}{\partial t_{\nu^{\mathbf{m}'}}} \langle \mu^{\mathbf{m}} | \exp(-T) H \exp(T) | \Phi_i \rangle$$

Asym VCC jacobian

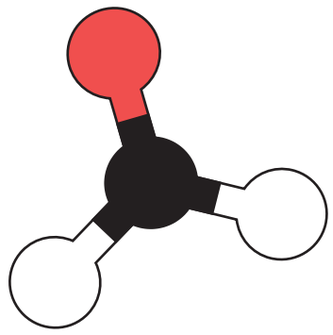
$$\mathbf{A}R = \omega R$$

All equations solved by iterative techniques:
Huge A matrix never constructed explicitly
Olsen (Davidson) algorithms ++
Doable, far from being generally easy!

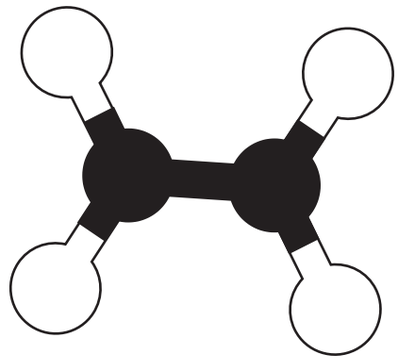
Benchmark Calculations:

ΔE relative to FVCI for Fundamentals

Formaldehyde 4M potential

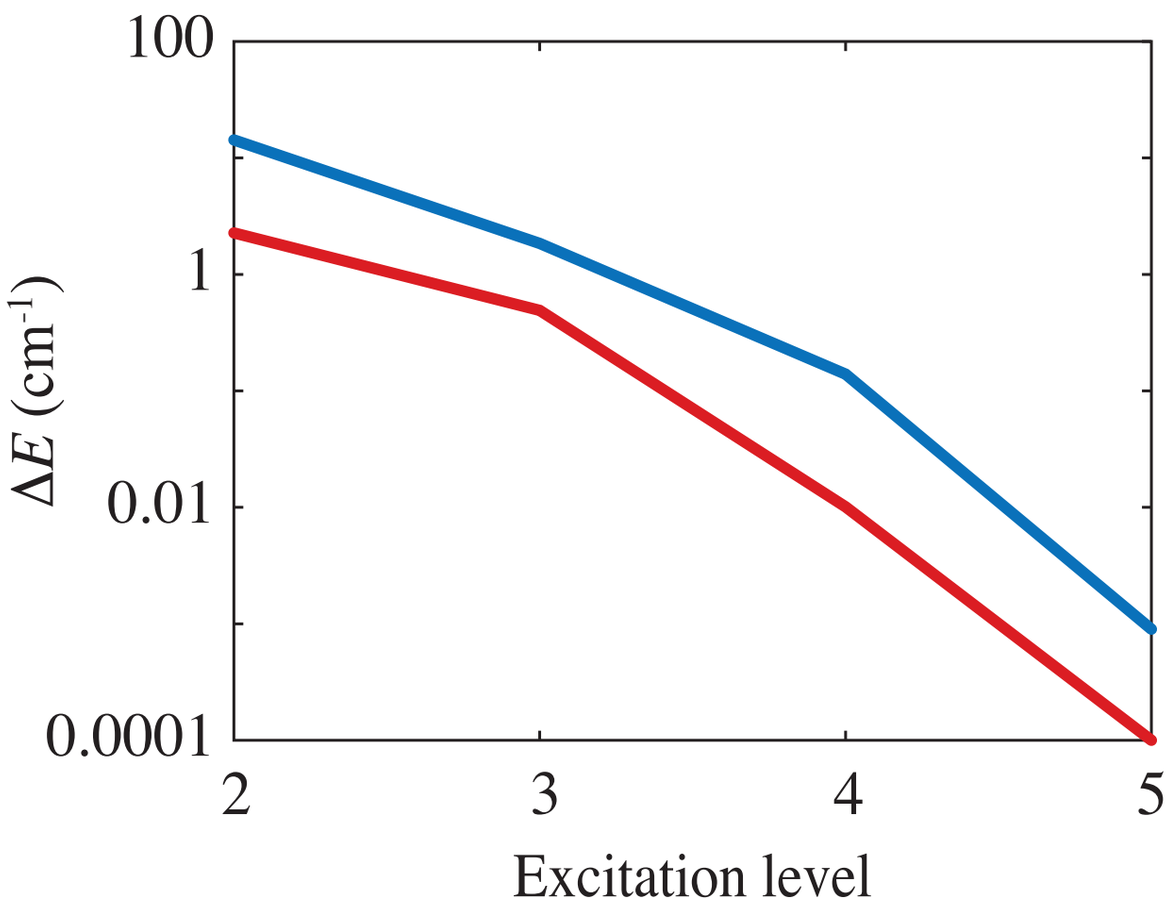


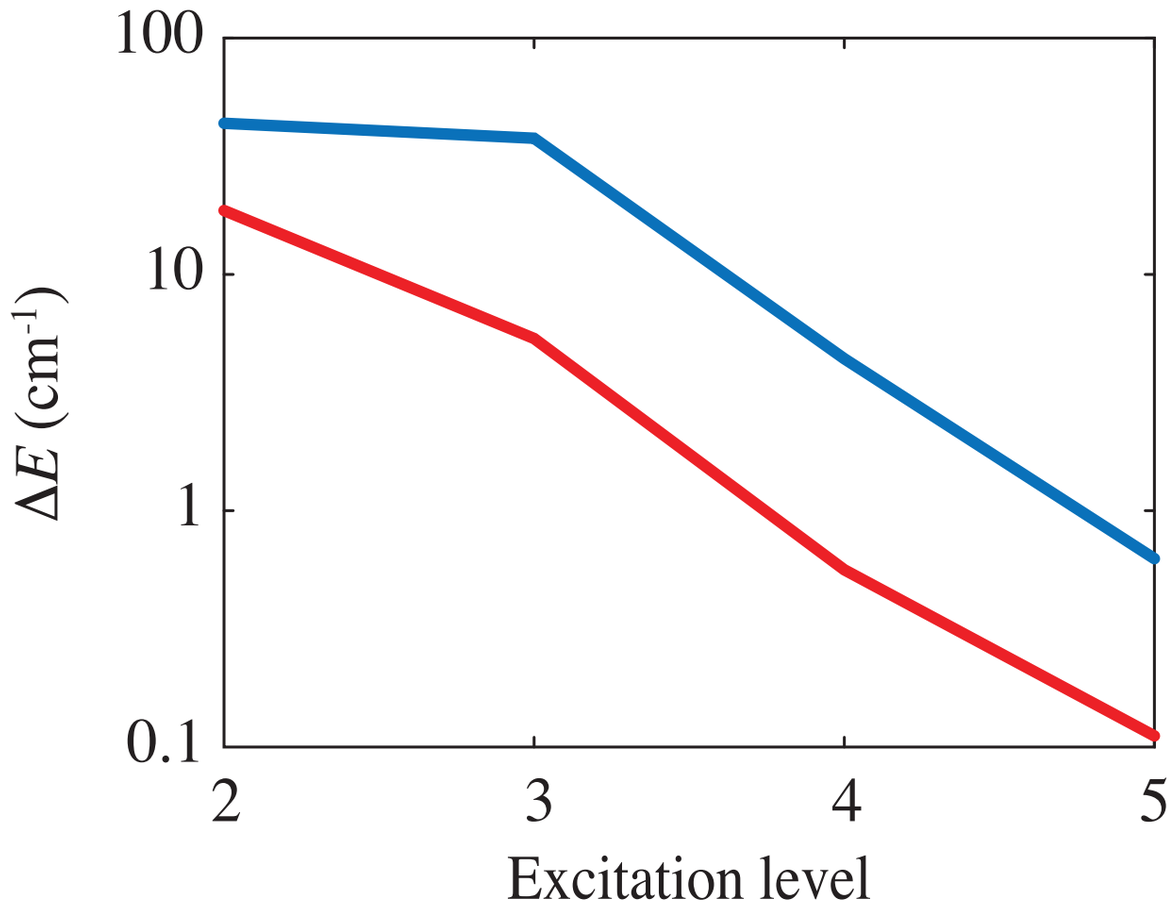
Ethylene 3M potential



VCI

VCC





The challenge of implementing VCC:
One of 39 pages of equations for VCC[3] with H3

$$
\begin{array}{lll}
- & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & c_{m_0m_1m_2} \cdot t^{m_0m_1} \cdot i_{m_1m_2} \cdot t^{m_2}_{m_0} & M^3O^3N^3 \\
+ & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & {}^{\{m_2\}}\big[c_{m_1m_2m_3}, t^{m_2}_{m_3}\big]_{\{m_1\}} \cdot t^{m_0m_1} \cdot i_{m_1m_2} & M^3O^2N^3 \\
+ & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & {}_{\{m_1\}}\big[c_{m_0m_1m_3}, i_{m_1m_3}\big]_{\{m_0\}} \cdot t^{m_0m_1} \cdot t^{m_2}_{m_0} & M^3ON^3 \\
- & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & {}_{\{m_1\}}\big[{}_{\{m_1\}}\big[c_{m_1m_3m_4}, i_{m_1m_3}\big]_{\{m_4\}}, t^{m_2}_{m_4}\big]^{\{m_2\}} \cdot t^{m_0m_1} & M^3N^3 \\
- & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & \big[c_{m_1m_2m_3}, i_{m_3}\big]_{\{m_1m_2\}} \cdot t^{m_0m_1} \cdot {}^{m_2}t_{m_1} & M^3O^2N^3 \\
+ & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & {}_{\{m_2\}}\big[c_{m_1m_2m_3}, i_{m_2m_3}\big]_{\{m_1\}} \cdot t^{m_0m_1} \cdot t^{m_2}_{m_1} & M^3ON^3 \\
- & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & \big[c_{m_1m_3m_4}, i_{m_3m_4}\big]_{\{m_1\}} \cdot t^{m_0m_1} \cdot t^{m_2}_{m_1} & M^3ON^3 \\
+ & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & c_{m_0m_1m_2} \cdot u^{m_0} \cdot t^{m_1m_2} \cdot t_{m_1m_2} & M^3O^3N^3 \\
- & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & {}_{\{m_2\}}\big[c_{m_0m_2m_3}, t_{m_2m_3}\big]_{\{m_0\}} \cdot u^{m_0} \cdot t^{m_1m_2} & M^3ON^3 \\
+\frac{1}{6}[[[H_3,T_2],T_2],T_2] & & & \\
+ & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & \big[c_{m_0m_1m_3}, t^{m_2}_{m_3}\big]^{\{m_2\}}_{\{m_0m_1\}} \cdot t^{m_0}_{m_1} \cdot t^{m_1}_{m_0} & M^3O^2N^3 \\
- & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & c_{m_0m_1m_2} \cdot t^{m_0}_{m_1} \cdot t^{m_1}_{m_2} \cdot t^{m_2}_{m_0} & M^3O^3N^3 \\
+ & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & {}^{\{m_2\}}\big[c_{m_1m_2m_3}, t^{m_2}_{m_3}\big]_{\{m_1\}} \cdot t^{m_0}_{m_1} \cdot t^{m_1}_{m_2} & M^3O^2N^3 \\
- & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & {}^{\{m_1\}}\big[{}^{\{m_1\}}\big[c_{m_1m_3m_4}, t^{m_1}_{m_3}\big]_{\{m_4\}}, t^{m_2}_{m_4}\big]^{\{m_2\}} \cdot t^{m_0}_{m_1} & M^3ON^3 \\
+ & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & \big[\big[\big[c_{m_3m_4m_5}, t^{m_0}_{m_3}\big]^{\{m_0\}}_{\{m_4m_5\}}, t^{m_1}_{m_4}\big]^{\{m_0\}\{m_1\}}_{\{m_5\}}, t^{m_2}_{m_5}\big]^{\{m_0\}\{m_1\}\{m_2\}} & M^3N^3 \\
+ & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & \big[c_{m_0m_1m_3}, t^{m_2}_{m_3}\big]^{\{m_2\}}_{\{m_0m_1\}} \cdot t^{m_0m_1} \cdot t_{m_0m_1} & M^3O^2N^3 \\
- & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & c_{m_0m_1m_2} \cdot t^{m_0m_1} \cdot t_{m_1m_2} \cdot t^{m_2}_{m_0} & M^3O^3N^3 \\
+ & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & {}^{\{m_2\}}\big[c_{m_1m_2m_3}, t^{m_2}_{m_3}\big]_{\{m_1\}} \cdot t^{m_0m_1} \cdot t_{m_1m_2} & M^3O^2N^3 \\
+ & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & {}_{\{m_1\}}\big[c_{m_0m_1m_3}, t_{m_1m_3}\big]_{\{m_0\}} \cdot t^{m_0m_1} \cdot t^{m_2}_{m_0} & M^3ON^3 \\
- & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & {}_{\{m_1\}}\big[{}_{\{m_1\}}\big[c_{m_1m_3m_4}, t_{m_1m_3}\big]_{\{m_4\}}, t^{m_2}_{m_4}\big]^{\{m_2\}} \cdot t^{m_0m_1} & M^3N^3 \\
+ & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & {}_{\{m_2\}}\big[c_{m_1m_2m_3}, t_{m_2m_3}\big]_{\{m_1\}} \cdot t^{m_0m_1} \cdot t^{m_2}_{m_1} & M^3ON^3 \\
- & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & \big[c_{m_1m_3m_4}, t_{m_3m_4}\big]_{\{m_1\}} \cdot t^{m_0m_1} \cdot t^{m_2}_{m_1} & M^3ON^3 \\
+[[H_3,T_2],T_3] & & & \\
- & \mathcal{D}^{m_0'm_1'm_2'}_{m_0m_1m_2} & {}_{\{m_1\}}\big[c_{m_0m_1m_3}, t^{m_1m_2}_{m_3}\big]^{\{m_2\}}_{\{m_0\}} \cdot {}^{m_0}t_{m_1} & M^3O^2N^3
\end{array}
$$

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.

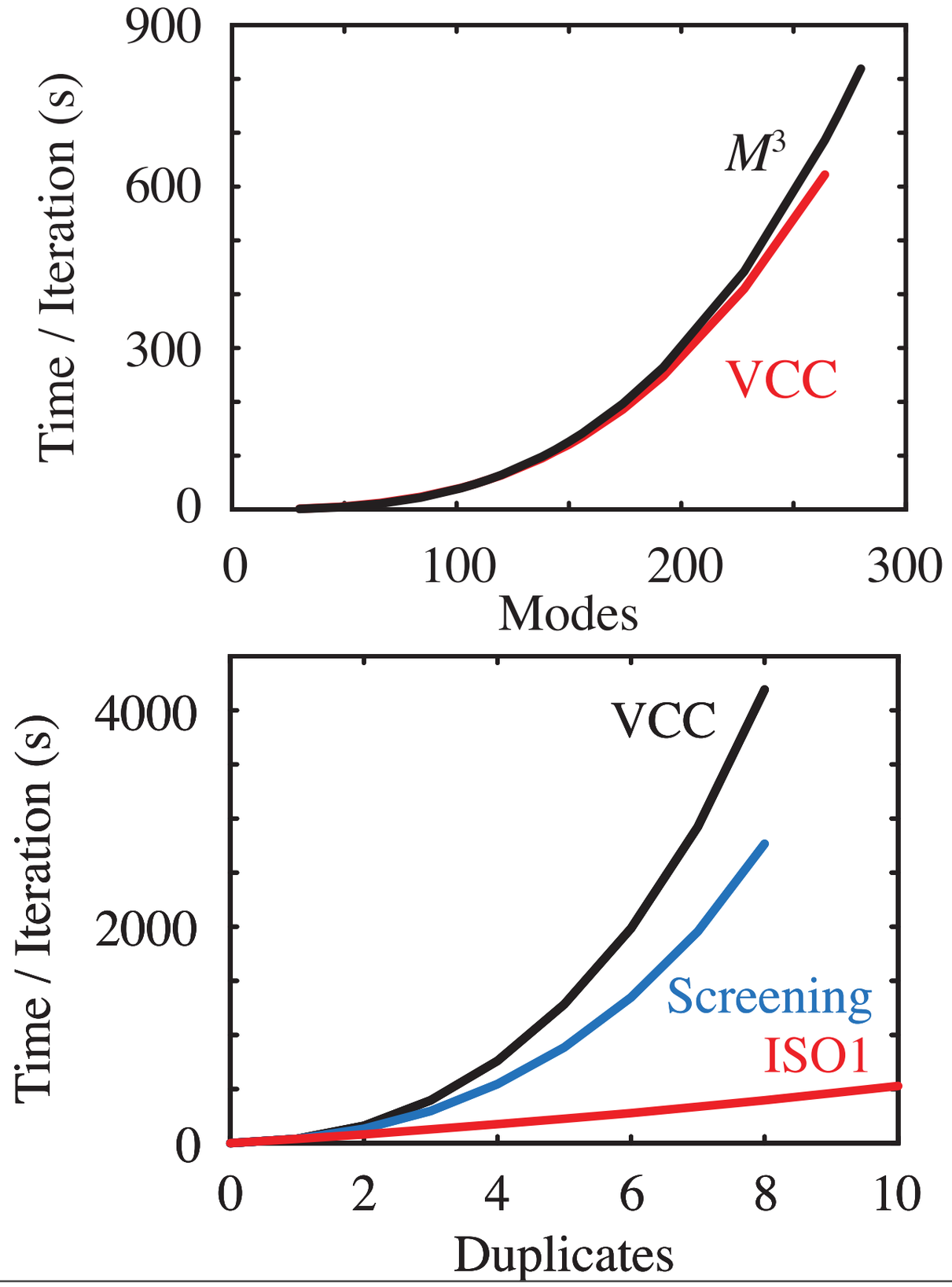
3. Process the resulting lists of terms and intermediates

Computational scaling: VCI and VCC similar scaling

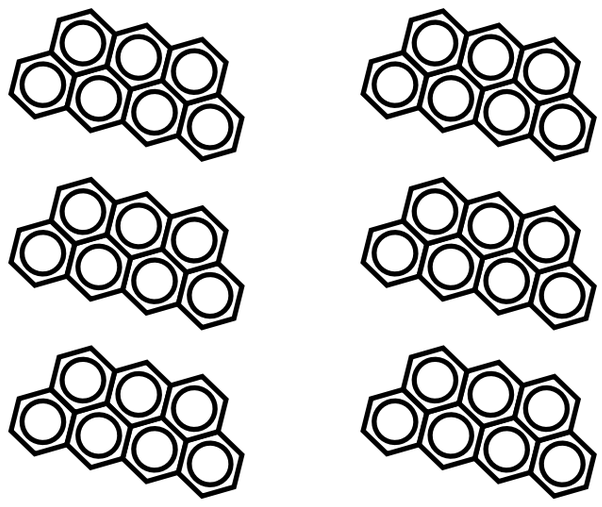
	VCC[2]	VCC[3]	VCC[4]	VCC[5]	VCC[6]
H2	M^3	M^4	M^5	M^6	M^7
H3	M^3	M^4	M^5	M^6	M^7
H4	M^4	M^5	M^6	M^7	M^8
H5	M^5	M^6	M^6	M^7	M^8

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

VCC scaling illustrations



VCC[2]s
2M PES
PAHs



Non-interacting fragments

VCC cost reductions

- Now: General and “fast” - difficult to develop but now we have a general framework.
- Shown only a glimse of the theory and details
- Further avenues to explore
  - ➡ Parrallelization is in progress
  - ➡ Exploit sparsity
  - ➡ Define other models and reduction tricks

Additional Members:VCC[2pt3]

Full 2M, approximate 3M

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

$$\begin{aligned} F^{(0)} &= H_1 + F_2 + F_3 \\ U_2^{(1)} &= H_2 - F_2 \\ U_3^{(2)} &= H_3 - F_3 \end{aligned}$$

Tildes: T1 similarity transf.

JCP,2009

Additional Members:VCC[2pt3]

Full 2M, approximate 3M

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

$$\begin{aligned} F^{(0)} &= H_1 + F_2 + F_3 \\ U_2^{(1)} &= H_2 - F_2 \\ U_3^{(2)} &= H_3 - F_3 \end{aligned}$$

Tildes: T1 similarity transf.

3M equations

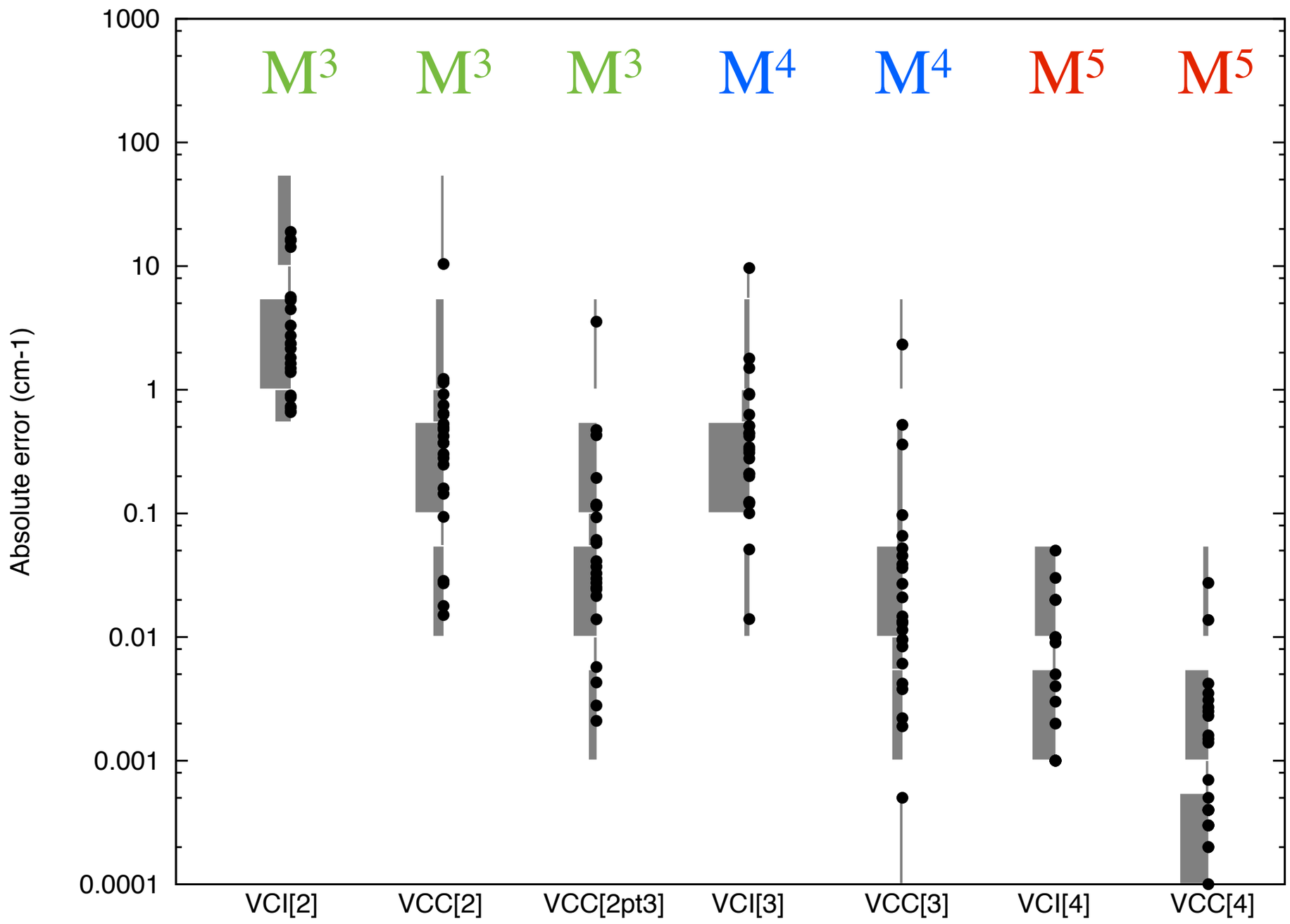
$$\begin{aligned} e_{\mu_3} = \langle \mu_3 | & [F, T_3]^{(2)} + \tilde{U}_3^{(2)} + [\tilde{U}_2^{(1)}, T_2]^{(2)} + [\tilde{U}_3^{(2)}, T_2]^{(3)} + [\tilde{U}_2^{(1)}, T_3]^{(3)} + [\tilde{U}_3^{(2)}, T_3]^{(4)} \\ & + \frac{1}{2}[[\tilde{U}_2^{(1)}, T_2], T_2]^{(3)} + \frac{1}{2}[[\tilde{U}_3^{(2)},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

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

JCP,2009

VCC[2pt3]

Benchmarks: H_2CO, $SOCl_2$, HFCO, CCl_2O



Another newcomer: VCC[3pt4]
NB: Poster Alberto Zoccante

The new hierarchy

VCC[2]
VCC[2pt3]
VCC[3]
VCC[3pt4]
VCC[4]
...

Deviation from VCC[4].

VCC[3pt4] M^4	VCI[4] M^5
3.8	12.0
-1.5	31.9
0.2	1.9
0.2	1.7
0.1	2.3

Ethylene-oxide. 3M PES.
5 fundamentals of B1 symmetry.

Spectra and states

- Challenge: The number of states increases wildly with the number of degrees of freedom.
- Calculating all the states explicitely becomes impossible
- The stable determination of specific states in dense regions is problematic.
- Can we work around this?

Excited state Calcs.: Response Theory

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

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

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

Linear response function (exact)

general operators

$$\langle\langle X, Y\rangle\rangle^{\gamma}_{\omega_Y} = \sum_k \left[\frac{\langle 0|X|k\rangle\langle k|Y|0\rangle}{\omega_Y + i\gamma - \omega_k} - \frac{\langle 0|Y|k\rangle\langle k|X|0\rangle}{\omega_Y + i\gamma + \omega_k} \right]$$

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 quadratic response function: Two-photon spectra

From response functions to spectra

Linear response function (exact)

$$\langle\langle X,Y\rangle\rangle^{\gamma}_{\omega_Y} = \sum_k \left[\frac{\langle 0|X|k\rangle\langle k|Y|0\rangle}{\omega_Y + i\gamma - \omega_k} - \frac{\langle 0|Y|k\rangle\langle k|X|0\rangle}{\omega_Y + i\gamma + \omega_k} \right]$$

$$\Psi_{exact}(t) \rightarrow \langle\langle X,Y\rangle\rangle^{\text{exact}}_{\omega_y} \rightarrow \text{spectra}$$

$$\Psi_{\text{approx}}(t) \rightarrow \langle\langle X,Y\rangle\rangle^{\text{approx}}_{\omega_y} \rightarrow \text{approx. spectra}$$

1. Let $\gamma \rightarrow 0$. Note that there are poles at $\omega_y \rightarrow \omega_k$

Poles and residues determines excitation energies and transition probabilities

Leads to response eigenvalue equations - that is what was used before

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

2. Consider a finite γ:

A Lorentzian broadened spectrum occur

$$Im\{\langle\langle Y,Y\rangle\rangle^{\gamma}_{\omega_y}\} = \sum_{k\neq 0} |\langle\Psi_o|Y|\Psi_k\rangle|^2 \left(\frac{\gamma}{(\omega_y-\omega_k)^2+\gamma^2} - \frac{\gamma}{(\omega_y+\omega_k)^2+\gamma^2}\right)$$

Idea now: use directly damped response functions to determine absorption spectra

Linear response functions determine the absorption spectrum defined as

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

VCI wave function -> VCI response function -> VCI spectrum
VCC wave function -> VCC response function -> VCC spectrum

VCI & VCC response functions have been derived and implemented in our group.

VCI relatively simple.
VCC significantly more complicated structure. General VCC algorithm provides framework for implementing the additional vector and matrix contractions.

How solved in practice? Lanczos iteration

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

Contribution to response functions for VCI / VCC

Asymmetric matrix Lanzcos iteration on response A matrix:

$$\boldsymbol{q}_1 = \boldsymbol{v} \qquad \boldsymbol{p}_1 = \boldsymbol{u}$$

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

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

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

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

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

NB Focus is not on Lanzcos as eigensolver, but on accurate calculation of matrix functions. Note start guess.

The moments of the spectra converges with increasing Lanczos iterations

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

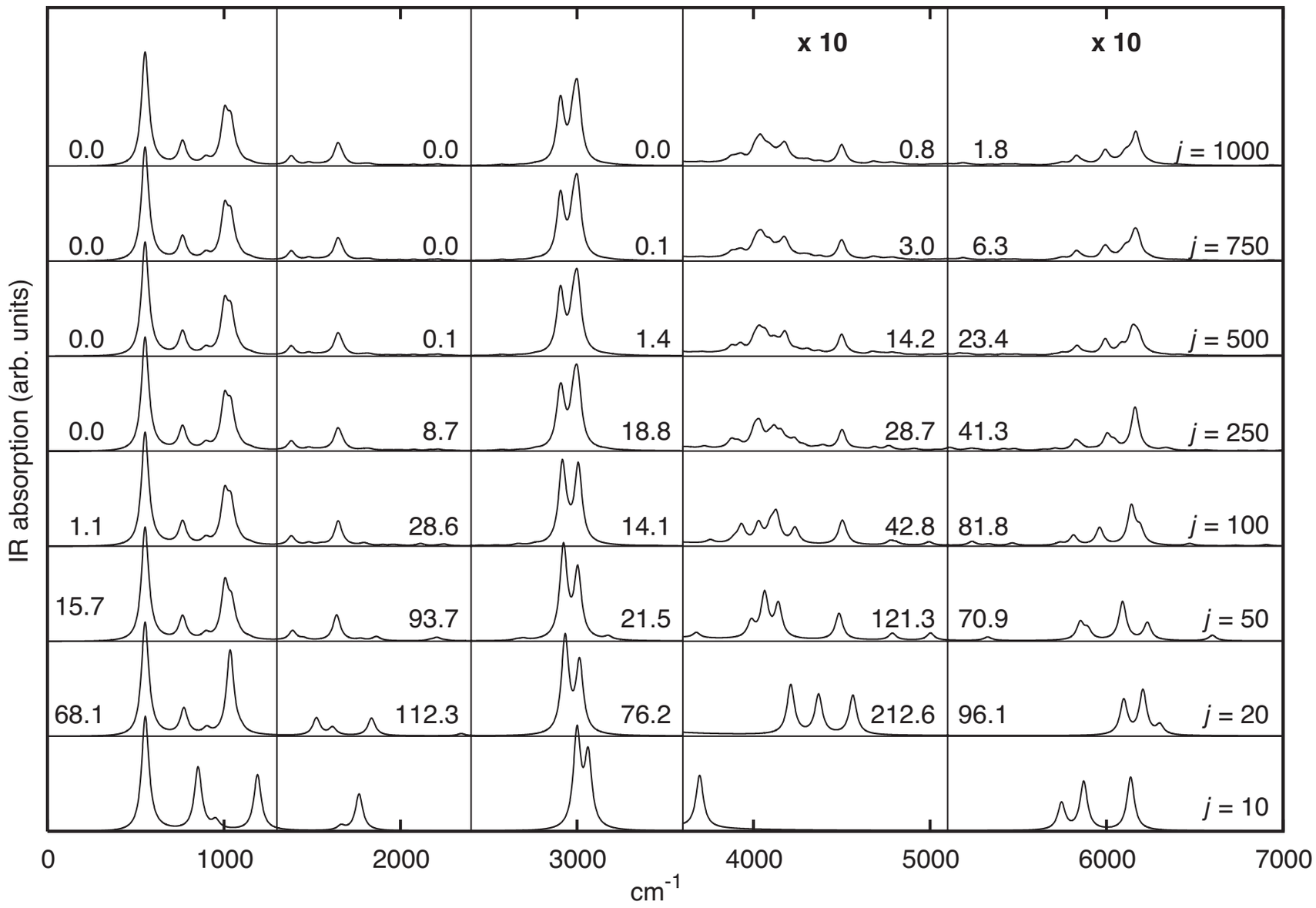
"Exact" spectrum

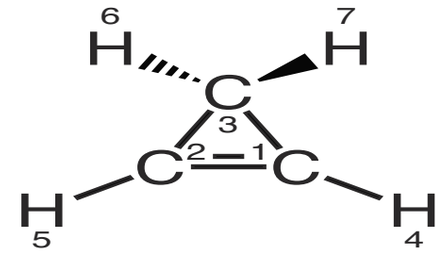
$$[\sigma_X^{(j)}(\omega)]_n = \int_0^\infty \sigma_X^{(j)}(\omega)\omega^n d\omega$$

The Lanzcos spectrum truncated at j-th step.

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

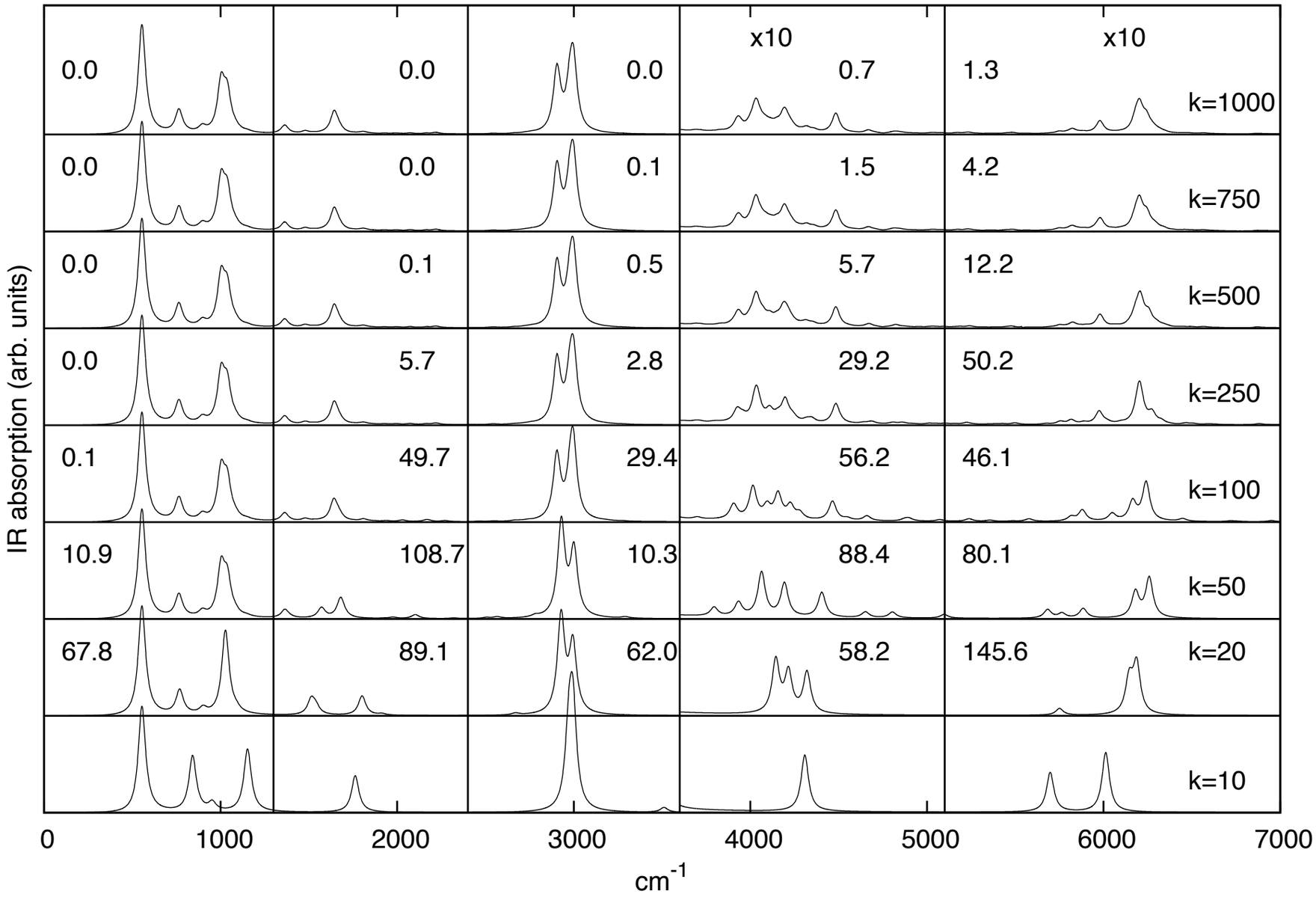
Convergence of spectra with Lanzcos iterations:Cyclopropene

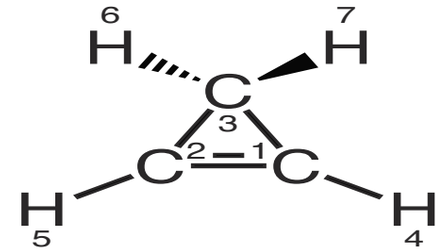




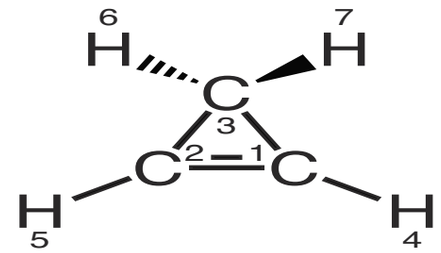
VCI[4]

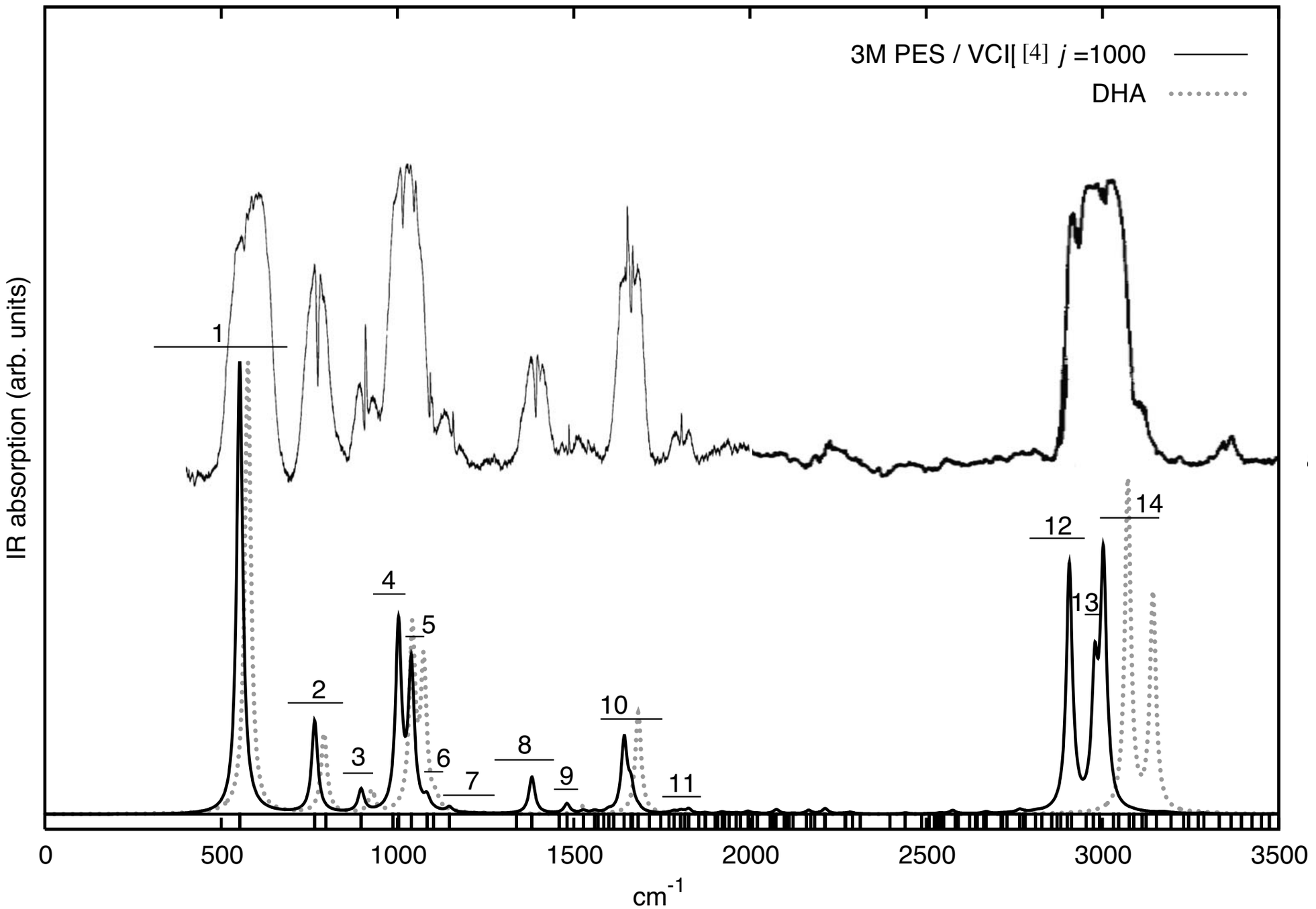
Convergence of spectra with Lanzcos iterations:Cyclopropene





VCC[3]

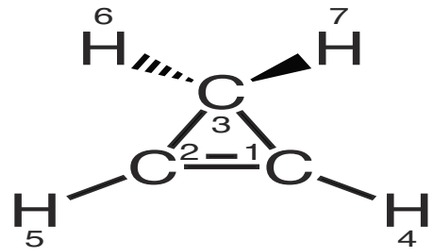


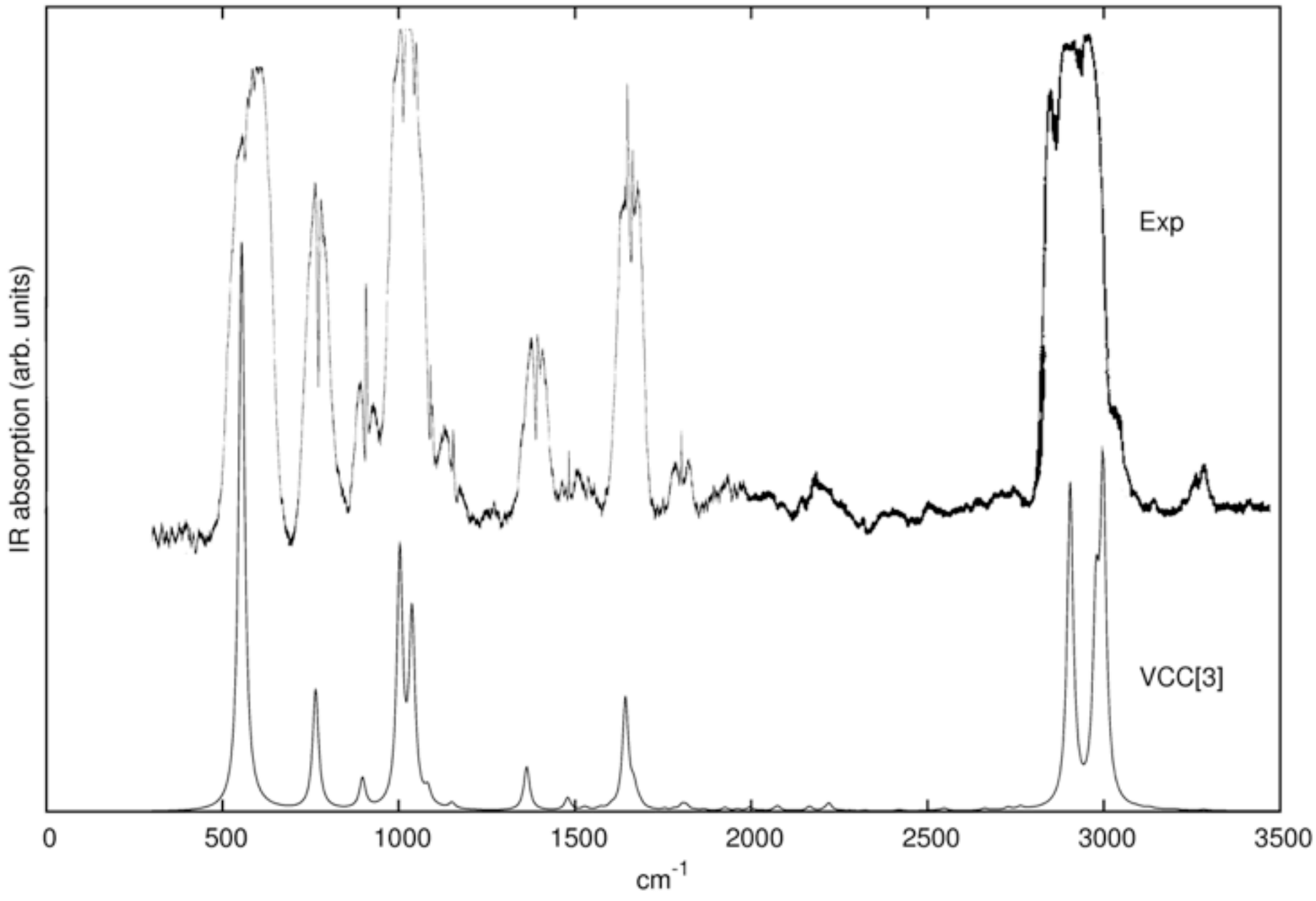


Exp.

Calc.

PES: 3M, CCSD(T)/cc-pVTZ



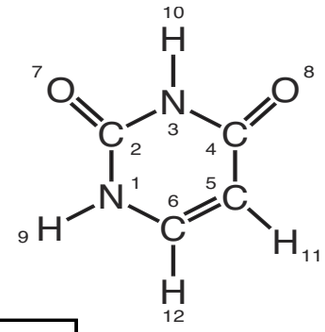


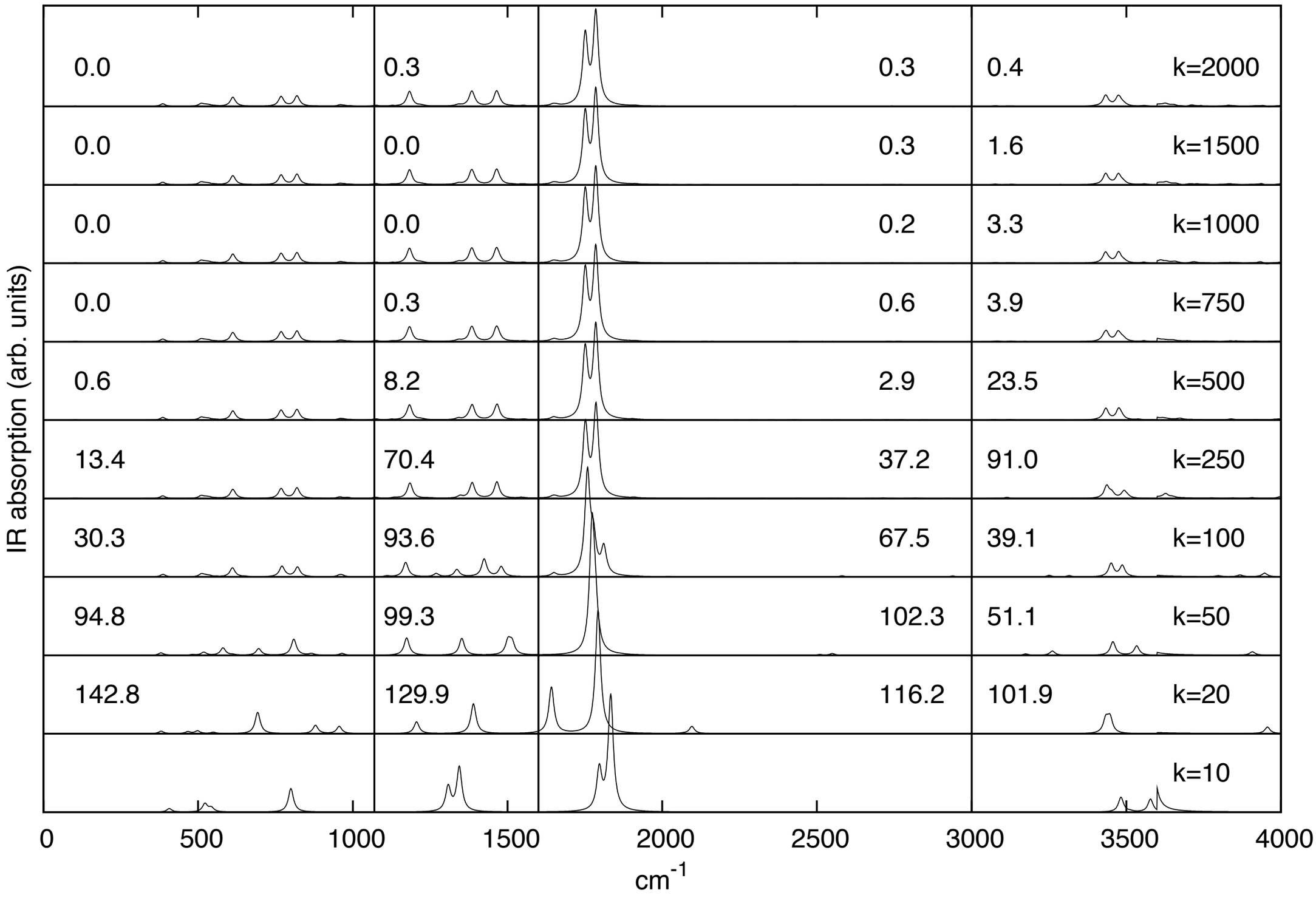
Exp.

Calc.

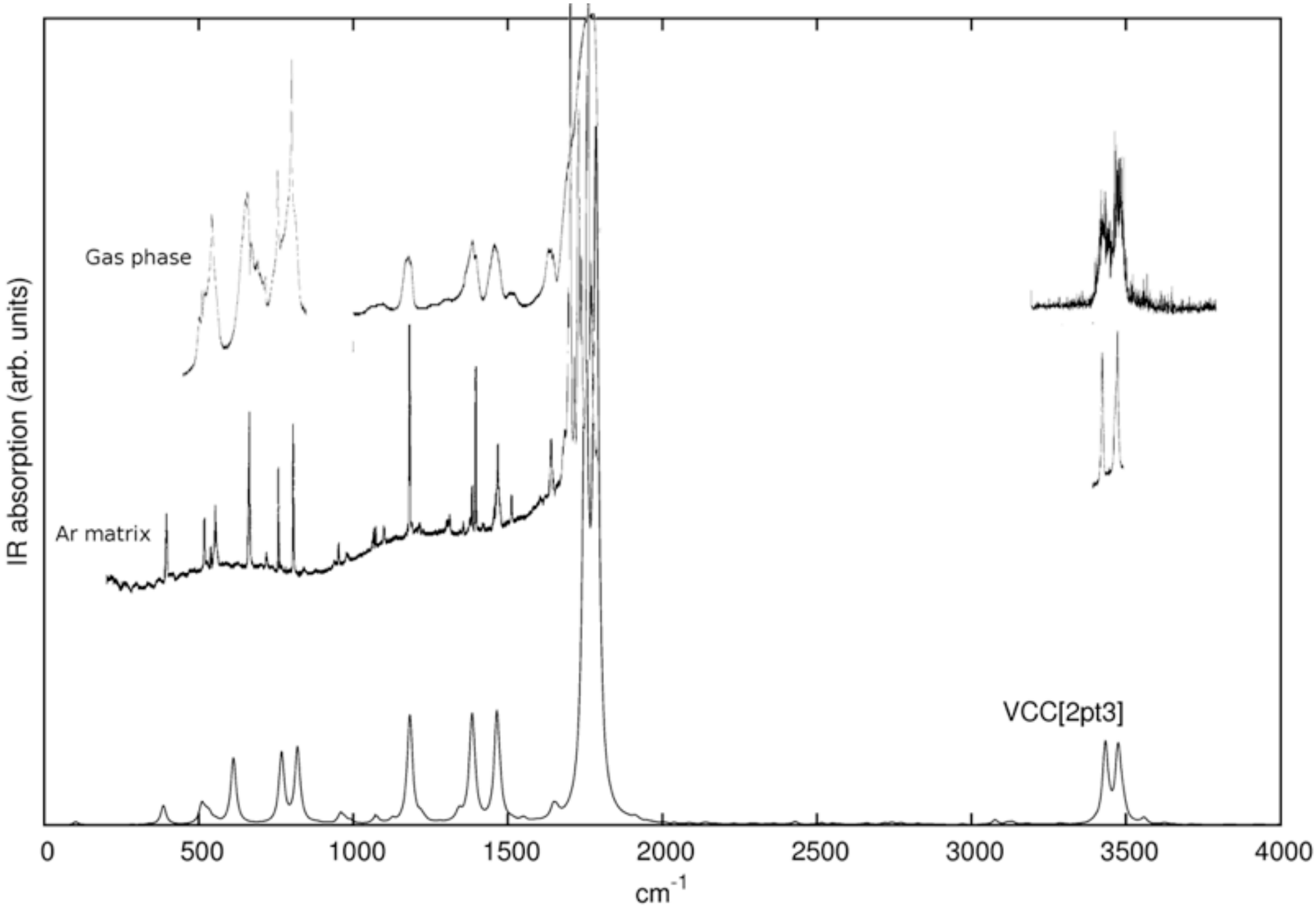
PES: 3M, CCSD(T)/cc-pVTZ

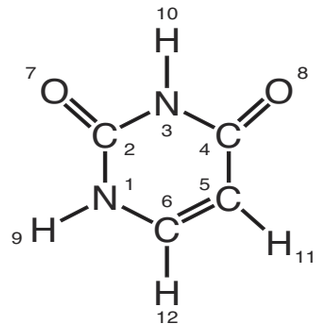
Convergence of spectra with Lanzcos iterations: Uracil VCC[2pt3]





Uracil





PES:
ADGA, 2M
RI-MP2/TZVPP

Seidler et al. JCP 2010 + to be published

Summary

VCC the accurate choice at given excitation level

→ theoretically attractive (size-extensivity)

→ 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: Lanzcos-powered damped response functions.

Automatic PES construction.

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

“Release” expected 2010

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- The Danish National Research Foundation:
  Center for Oxygen Microscopy and Imaging (COMI).
- Danish Center for Scientific Computing.

Thankyou for your attention

Summary: PES

ADGA: Adaptive Density Guided Approach
→ Black box & Adaptive
→ Reduced cost & Scaling

We are addressing the scaling of the construction of the PES through a combination of:

→ ADGA: Adaptive Density Guided Approach
→ Derivative information
→ Multi-level approaches
→ automatic a priori neglect of mode combinations

Other different CCs

Usual quantum chemistry CC, fermions

CC for bosons

Other exponential/non-linear parameterizations for anharmonic vibrations:

R.F. Bishop et al. (1D)
M.Durga-Prasad et al. Banik et al.

Starts from Harmonic Oscillator step up/down ops
SQ algebra different, Gaussian reference

Our VCC: a natural CC for distinguishable d.o.f. (VSCF or not)

Wave Function approaches

MCTDH: Multi-configurational Time-dependent Hartree

Meyer, Cederbaum, Manthe

VSCF: Vibrational Self Consistent Field

VCI: Vibrational Configuration Interaction

Bowman and co-workers (1979), Rauthut..... many other .....

VMP: Møller-Plesset perturbation theory

Gerber and co-workers (1996) OC (2003), general order and coupling

Quasi-degenerate perturbation theory, Configuration selection, Yagi, Hirata, Hirao

VCC: Vibrational coupled cluster theory

OC(2004), Seidler and OC (2007-...)

Second quantization & Response theory

How solved in practice? Lanczos iteration

Asymmetric matrix Lanzcos iteration:

$$\boldsymbol{AQ = QT}$$

$$\boldsymbol{A^T P = P T^T}$$

$$\boldsymbol{P^T Q = 1}$$

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

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

NB Focus is not on Lanzcos as eigensolver, but as a vehicle for accurate calculation of matrix functions.