Pair-Decoupling Nuclear Degrees of Freedom in Molecular Dynamics Simulations

Michele Gandolfi

CEOTTO GROUP

VISTA talk

Università degli Studi di Milano,
Department of Chemistry

February 21st 2024

Pair-Decoupling Nuclear Degrees of Freedom in Molecular Dynamics Simulations (OR When a Vibrating Molecule Is a Divisible Set of Vibrating Fragments)

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Correlated and Uncorrelated Dynamics (PhD in a pub!) [1]

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Correlated

Uncorrelated

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Correlated and Uncorrelated Dynamics (atoms in molecules!)

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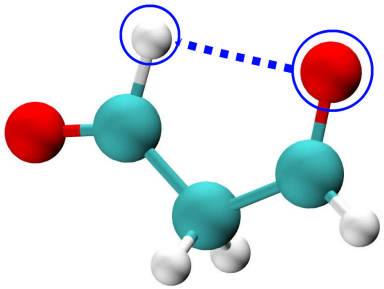
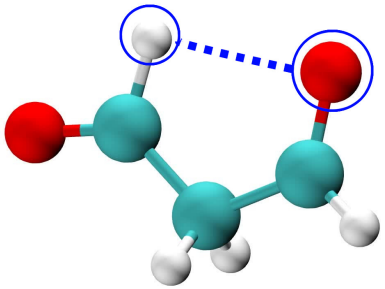


Uncorrelated



Atoms perceive each other in a complicated network of pairwise *simulataneous* interactions

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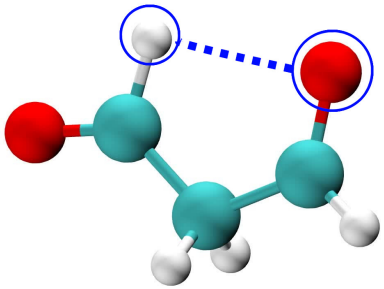

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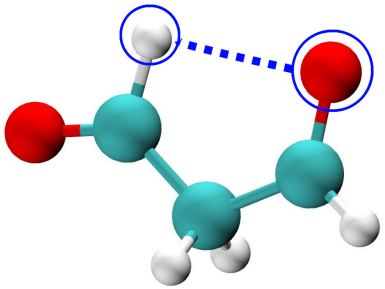

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- What happens if we impose decorrelation?

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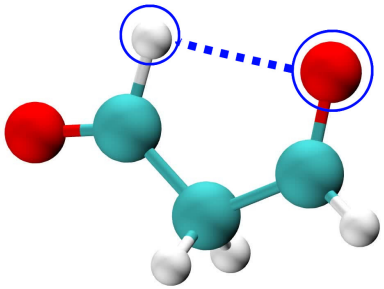

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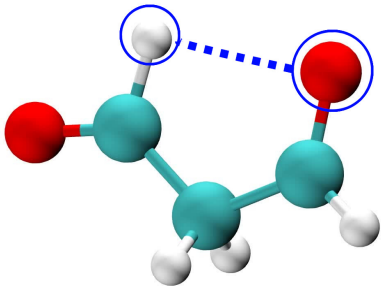

Atoms perceive each other in a complicated network of pairwise *simulataneous* interactions

- What happens if we impose decorrelation?
- When can we say a molecule is composed of dynamically independent groups?

Symplectic Structure and Liouville Theorem

Classical systems are deterministic

$$\frac{\partial \mathsf{z}(t)}{\partial \mathsf{z}(t')} = \begin{pmatrix} \frac{\partial q(t)}{\partial q(t')} & \frac{\partial q(t)}{\partial p(t')} \\ \frac{\partial p(t)}{\partial q(t')} & \frac{\partial p(t)}{\partial p(t')} \end{pmatrix} \qquad \mathsf{z}(t) = (q(t), p(t))$$

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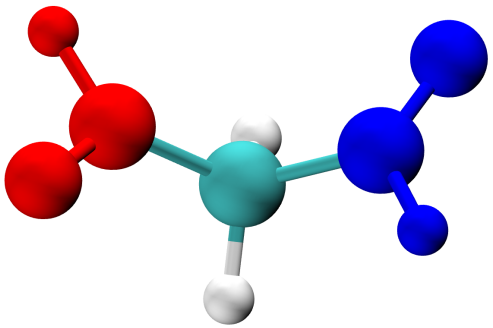
$$\begin{pmatrix} \frac{\partial \tilde{q}(t)}{\partial \tilde{q}(t')} & \cdots & \cdots \\ \vdots & \ddots & \vdots \\ \cdots & \cdots & \frac{\partial \tilde{q}(t)}{\partial \tilde{q}(t')} \end{pmatrix}$$



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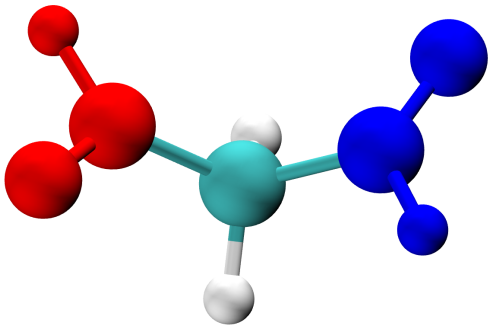

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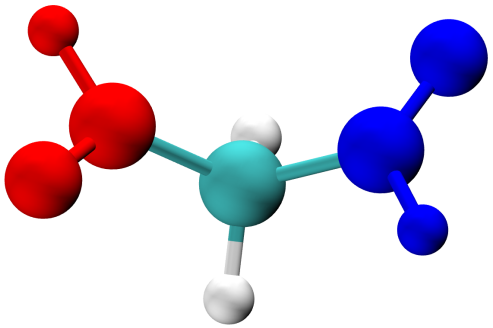

Is the linear Symplectic structure preserved?

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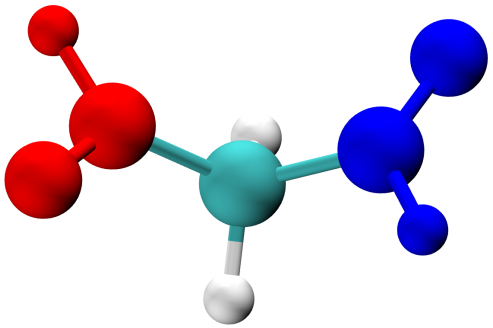

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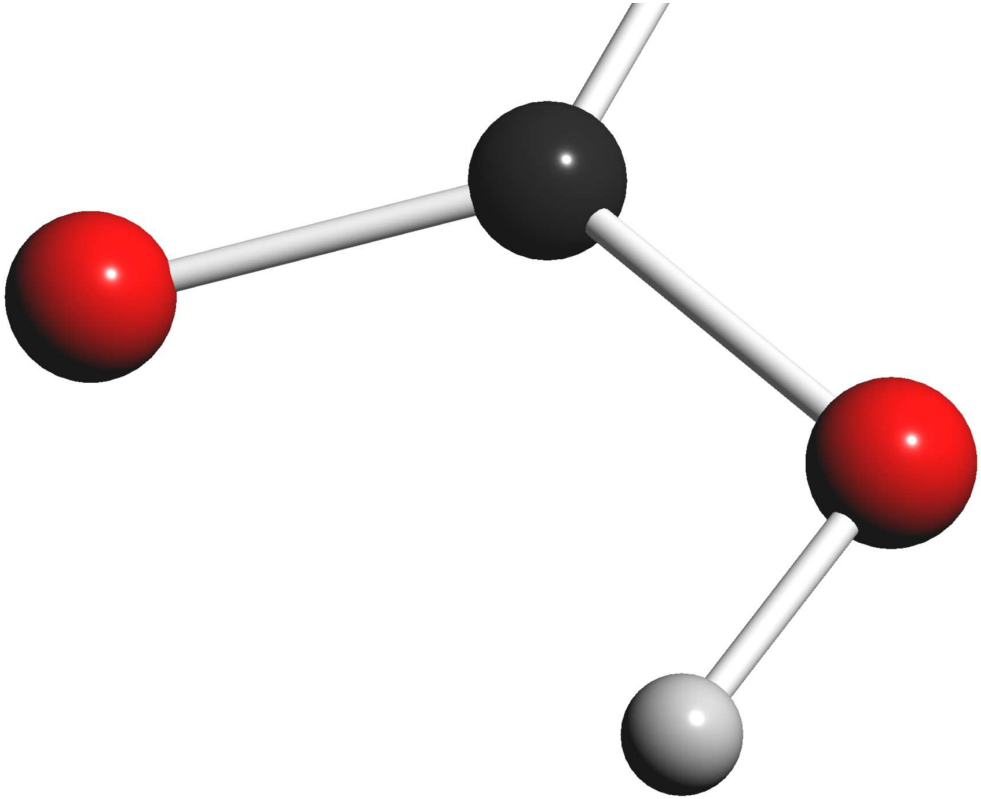
Is Liouville's theorem satisfied?

$$\det \frac{\partial \tilde{\mathsf{z}}(t)}{\partial \tilde{\mathsf{z}}(t')} \approx 1 \quad \forall \quad t, t'$$

The Pair-Decoupled System



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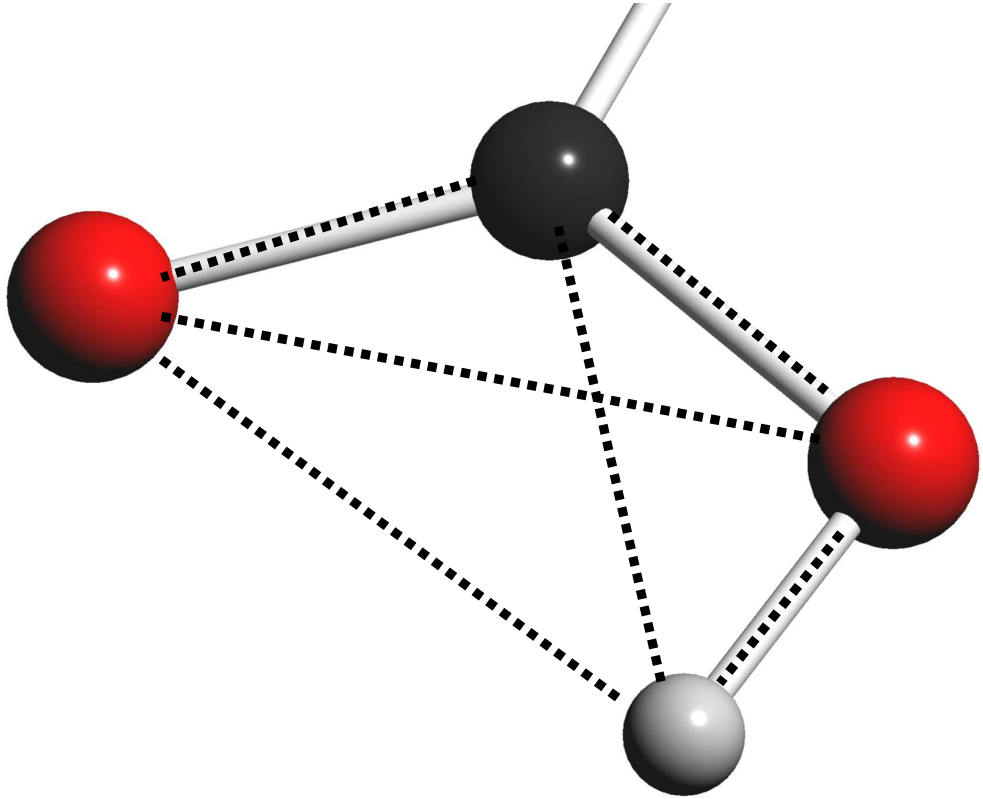

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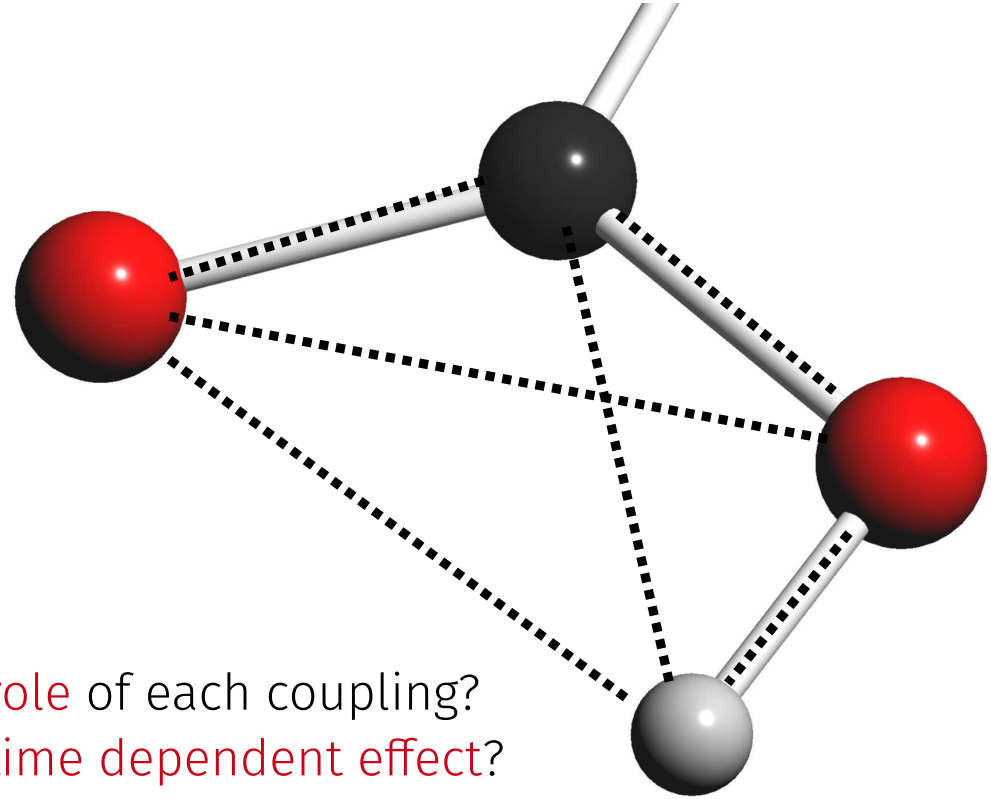
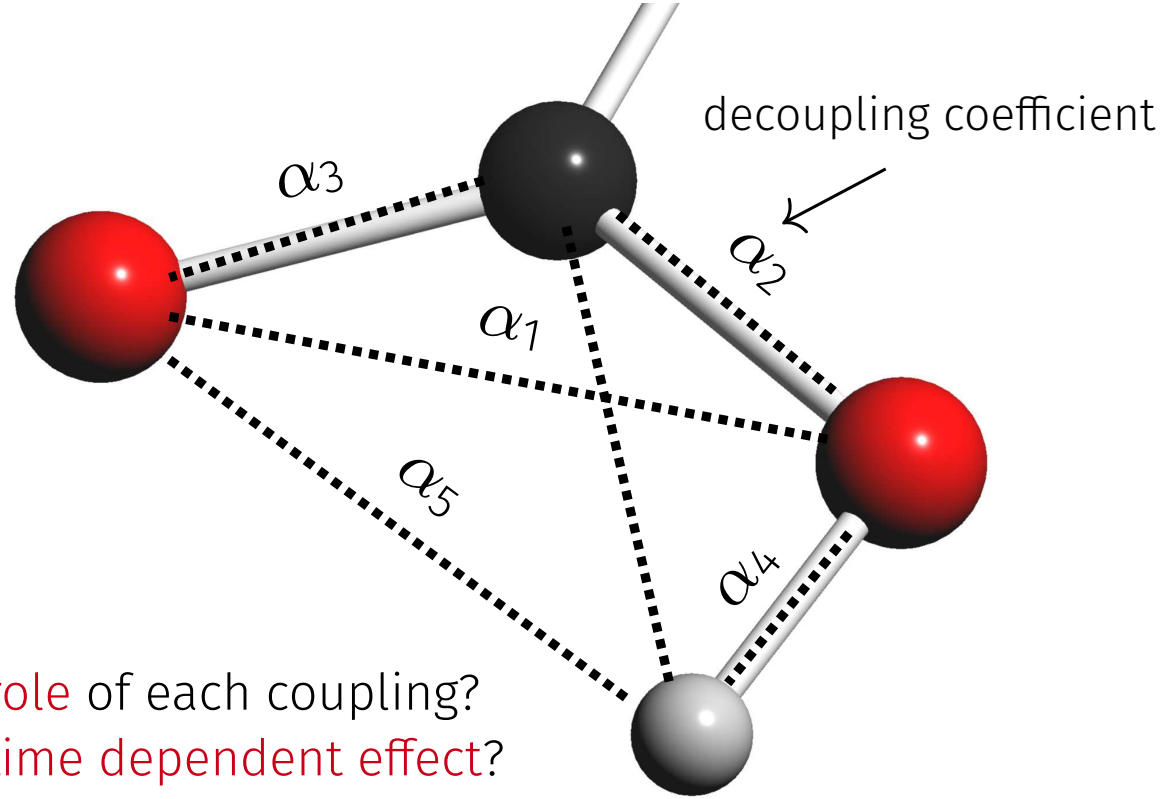


- what is the role of each coupling?
- what is the time dependent effect?

The Pair-Decoupled System



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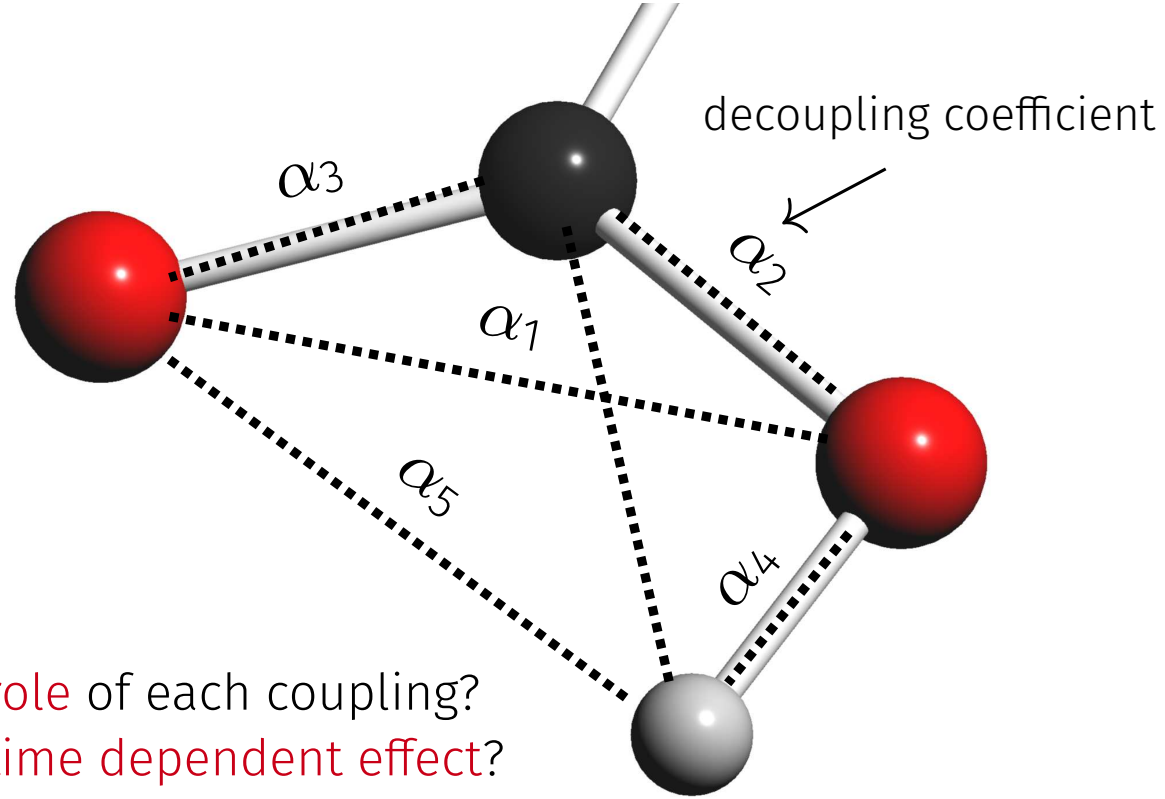

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design numerical experiments with atom-pair decouplings

Define the pair-decoupled Hamiltonian

$$H(\mathbf{q}, \mathbf{p}; \alpha_1; \alpha_2; \ldots; \alpha_n) = \tilde{H}(\tilde{\mathbf{q}}, \tilde{\mathbf{p}})$$

Molecular Dynamics of Pair-Decoupled System [2]

Evolve pair-decoupled system with Hamiltonian $\tilde{H} = K(\tilde{p}) + \tilde{V}(\tilde{q})$

$$\begin{cases} \dot{\tilde{q}} = \quad \nabla_{\tilde{p}} K \\ \dot{\tilde{p}} = -\nabla_{\tilde{q}} \tilde{V} \end{cases}$$

[2] M. Gandolfi, M. Ceotto, *J. Chem. Theory Comput.* (2023)

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Practical implementation of the pair-decoupling idea:

$$-\nabla_{\tilde{q}} \tilde{V} = \tilde{\mathbf{F}} = \int^{\tau} \tilde{\mathbf{V}}''(\tilde{\mathbf{q}}(t)) \cdot \dot{\tilde{\mathbf{q}}}(t) dt$$

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$$\tilde{\mathbf{V}}'' = \begin{pmatrix} V''_{11} & \cdots & \alpha V''_{1n} \\ \vdots & \ddots & \vdots \\ \alpha V''_{1n} & \cdots & V''_{nn} \end{pmatrix}$$

$$0 \leq \alpha_{ij} \leq 1$$

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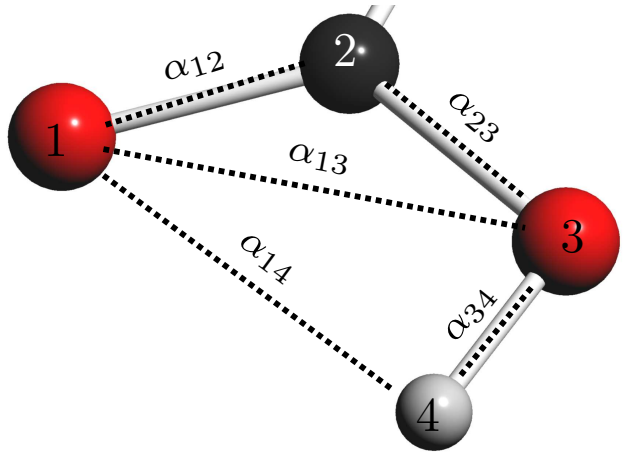

$$\tilde{\mathbf{V}}'' = \begin{pmatrix} V''_{11} & \alpha_{12} V''_{12} & \alpha_{13} V''_{13} & \alpha_{14} V''_{14} \\ \alpha_{12} V''_{12} & V''_{22} & \alpha_{23} V''_{23} & \alpha_{24} V''_{24} \\ \alpha_{13} V''_{13} & \alpha_{23} V''_{23} & V''_{33} & \alpha_{34} V''_{34} \\ \alpha_{14} V''_{14} & \alpha_{24} V''_{12} & \alpha_{34} V''_{34} & V''_{44} \end{pmatrix}$$

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Time Evolution: Explicit Symplectic Integrators [3]

$$\mathsf{z}(\tau) = e^{-\tau\{H,\cdot\}}\mathsf{z}(0) \quad \text{where} \quad \mathsf{z}(t) = (\mathsf{p}(t), \mathsf{q}(t))$$

[3] A.J. Dragt, et al. *Annu. Rev. Nucl. Part.* (1988); H. Yoshida, *Phys. Lett.* (1990); S.A. Chin, *Am. J. Phys.* (2020);

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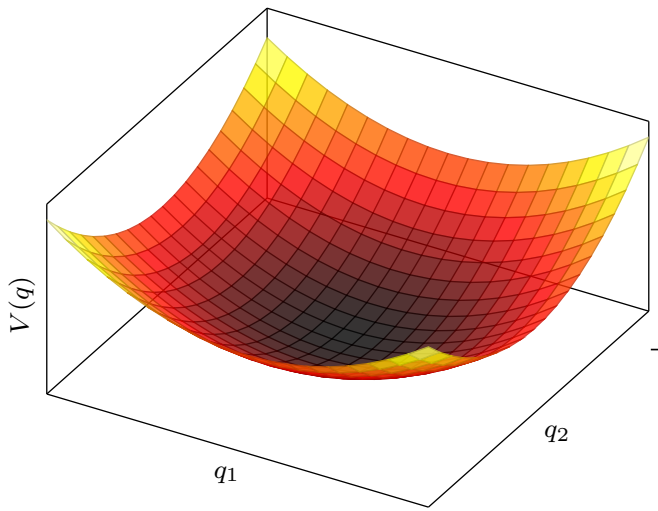
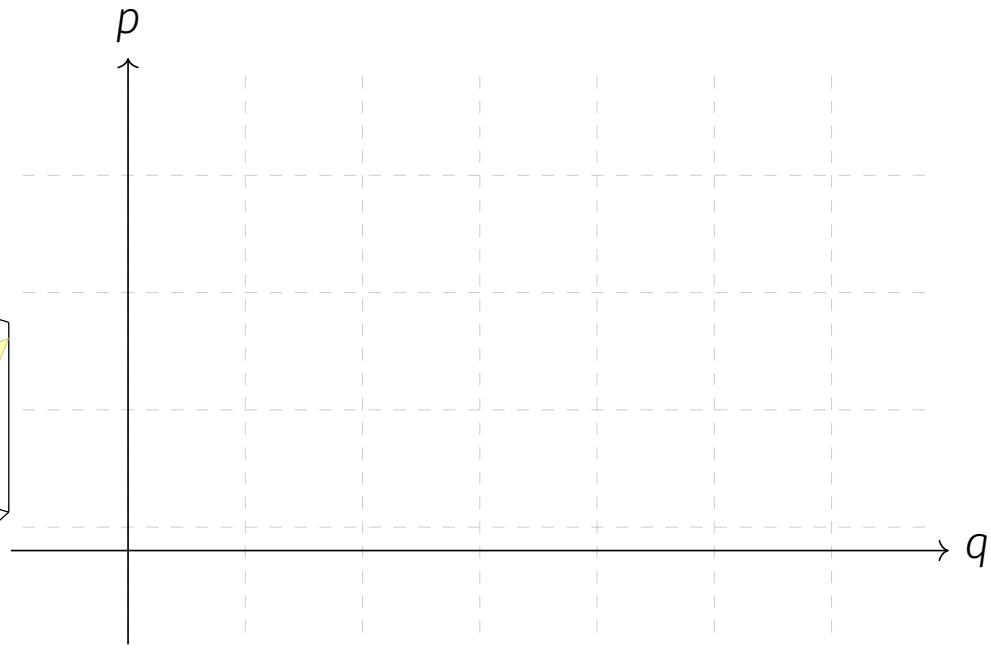
The time evolution operator is approximated by a map

$$e^{-\tau\{H,\cdot\}} \approx e^{-\tau b_k\{V,\cdot\}} e^{-\tau a_k\{K,\cdot\}} \dots e^{-\tau b_1\{V,\cdot\}} e^{-\tau a_1\{K,\cdot\}}$$





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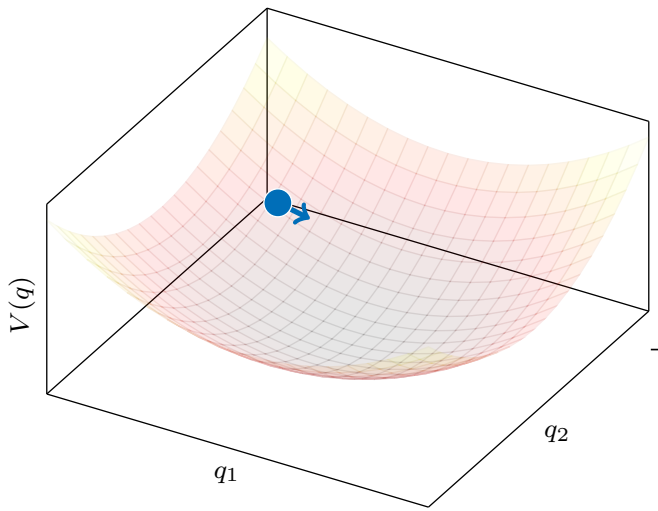

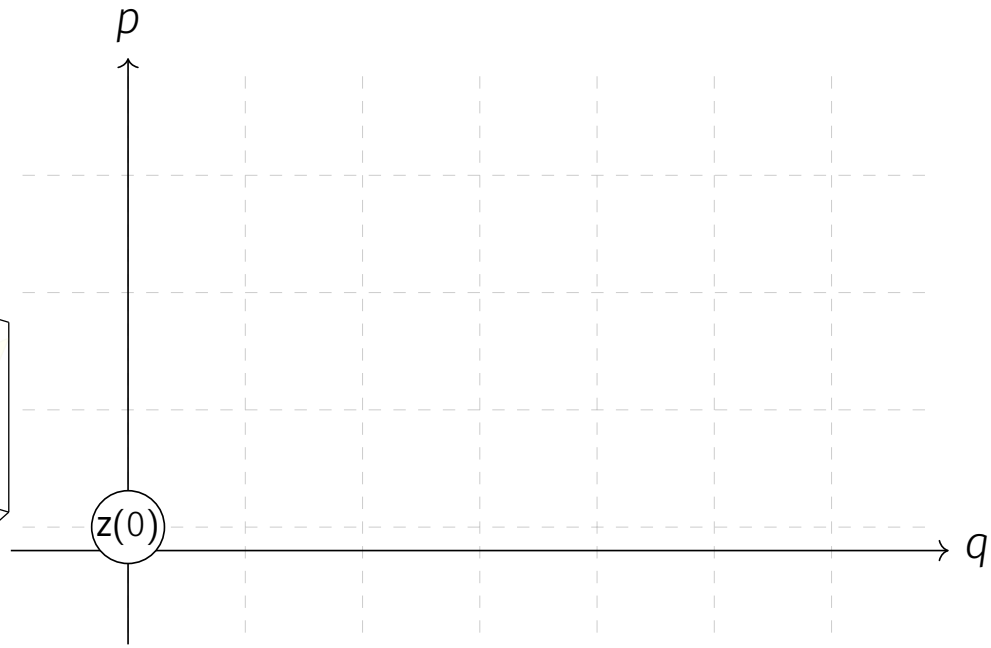

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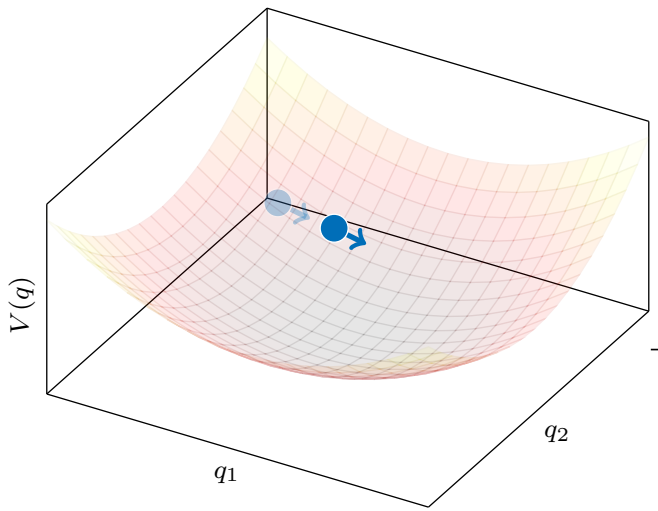

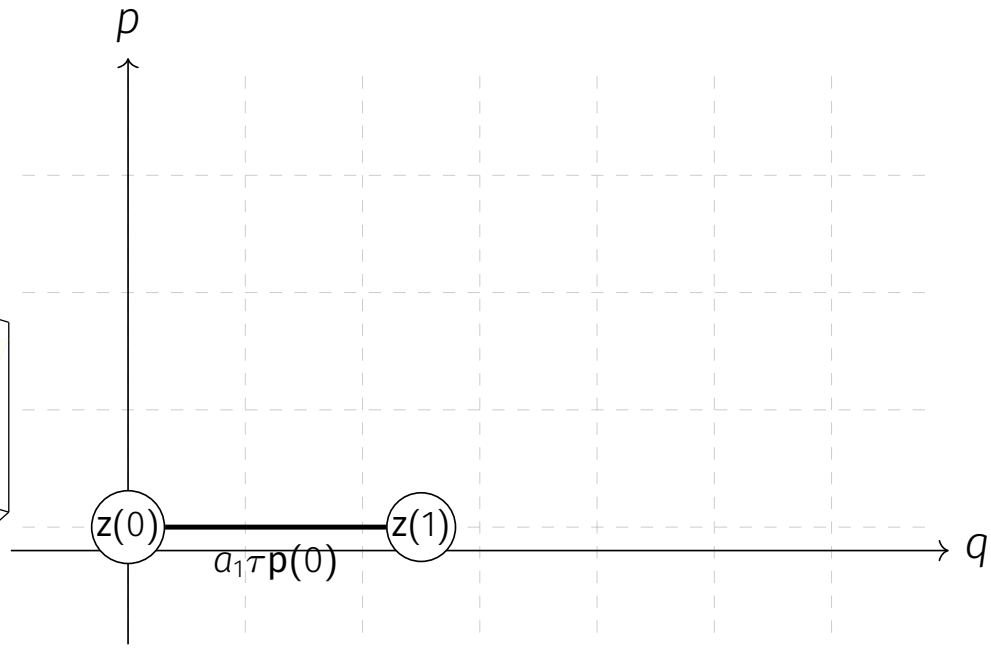

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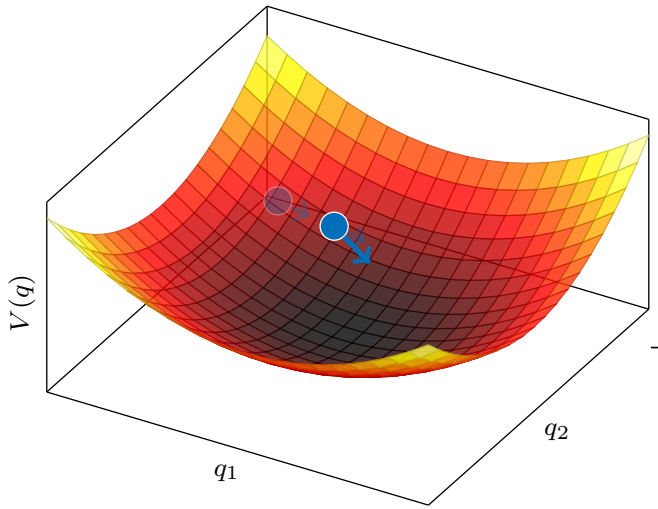

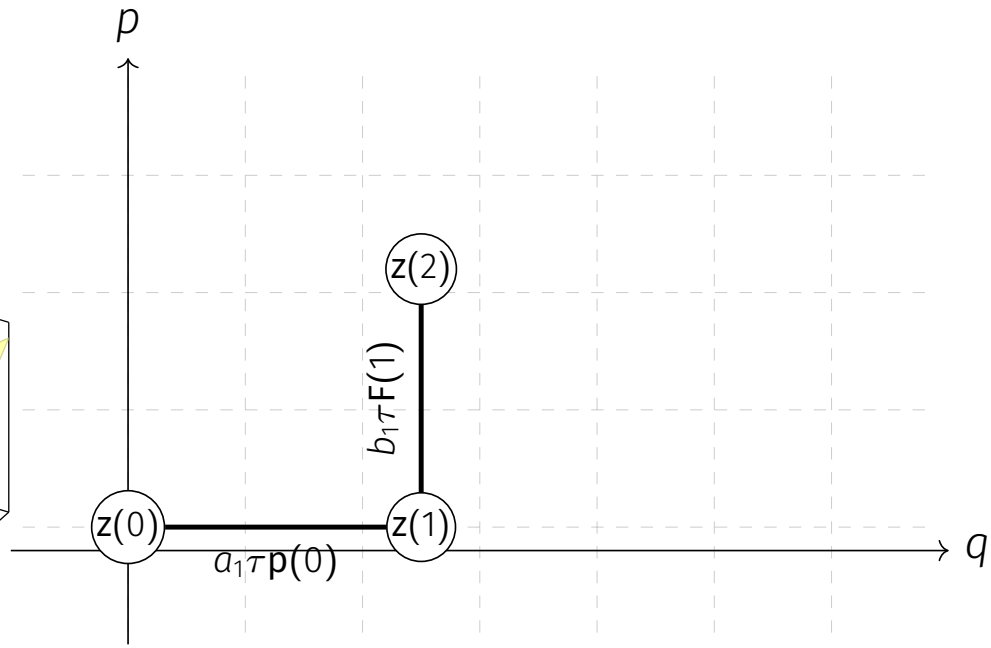

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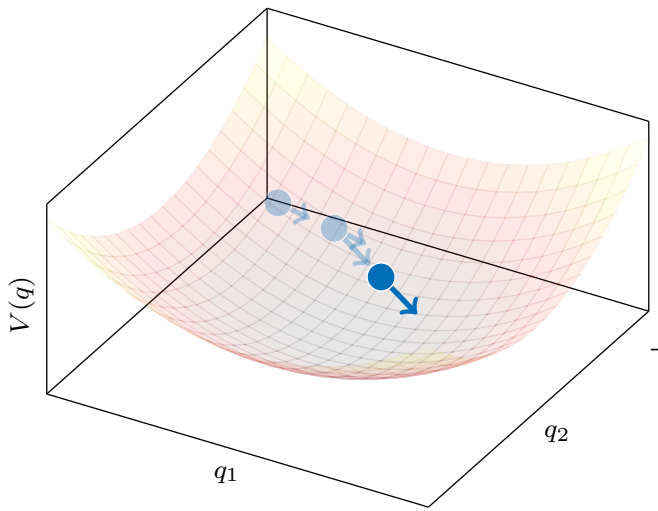
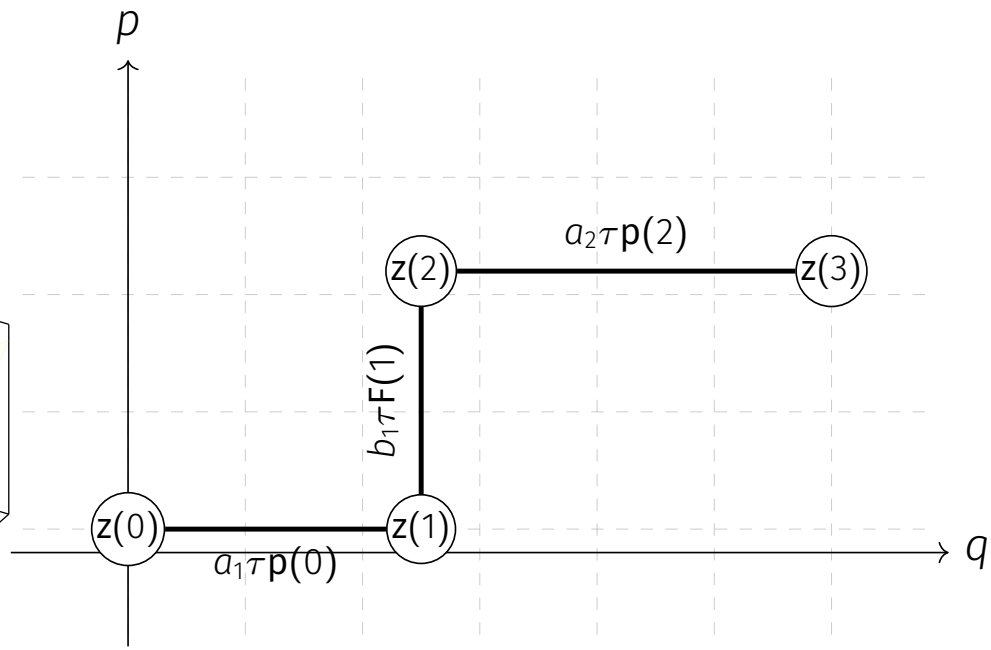
$$\mathsf{z}(\tau) = e^{-\tau\{H,\cdot\}}\mathsf{z}(0) \quad \text{where} \quad \mathsf{z}(t) = (\mathsf{p}(t), \mathsf{q}(t))$$

The time evolution operator is approximated by a map

$$e^{-\tau\{H,\cdot\}} \approx e^{-\tau b_k\{V,\cdot\}} e^{-\tau a_k\{K,\cdot\}} \dots e^{-\tau b_1\{V,\cdot\}} e^{-\tau a_1\{K,\cdot\}}$$

$$\mathsf{z}(1) = e^{-\tau a_1\{K,\cdot\}}\mathsf{z}(0)$$
$$\mathsf{z}(2) = e^{-\tau b_1\{V,\cdot\}}\mathsf{z}(1)$$
$$\mathsf{z}(3) = e^{-\tau a_2\{K,\cdot\}}\mathsf{z}(2)$$





[3] A.J. Dragt, et al. *Annu. Rev. Nucl. Part.* (1988); H. Yoshida, *Phys. Lett.* (1990); S.A. Chin, *Am. J. Phys.* (2020);

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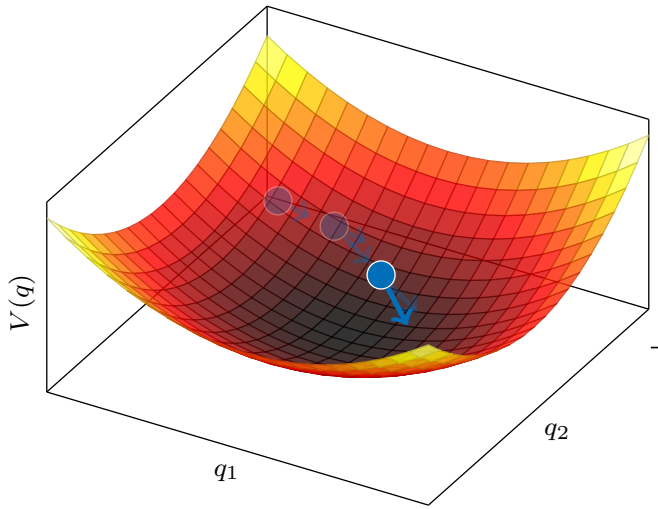
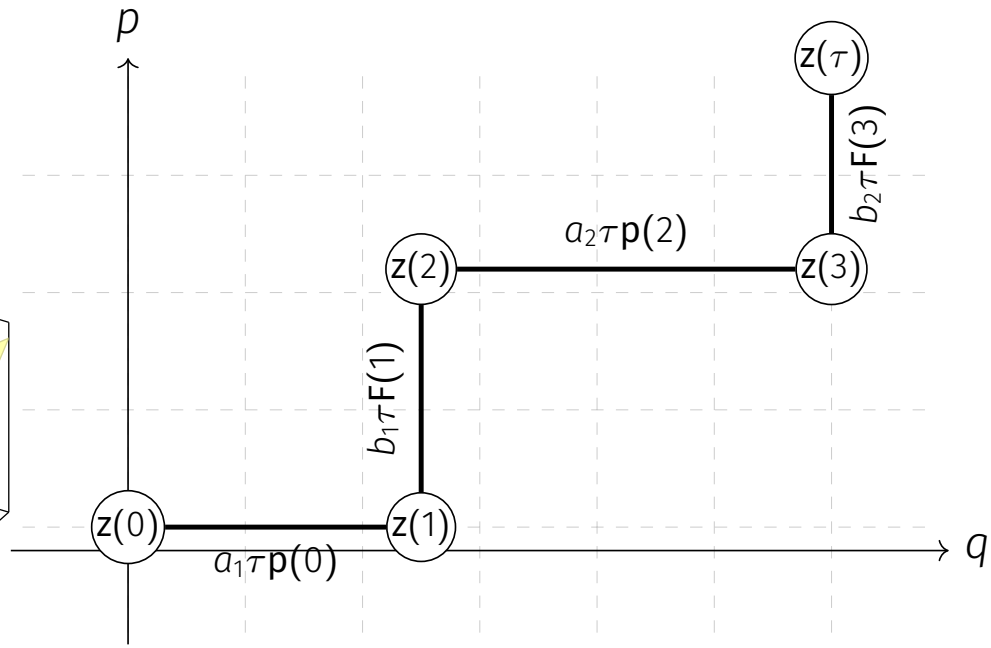
$$\mathsf{z}(3) = e^{-\tau a_2\{K,\cdot\}}\mathsf{z}(2)$$
$$\mathsf{z}(\tau) = e^{-\tau b_2\{V,\cdot\}}\mathsf{z}(3)$$





[3] A.J. Dragt, et al. *Annu. Rev. Nucl. Part.* (1988); H. Yoshida, *Phys. Lett.* (1990); S.A. Chin, *Am. J. Phys.* (2020);

Time Evolution: Explicit Symplectic Integrators [3]

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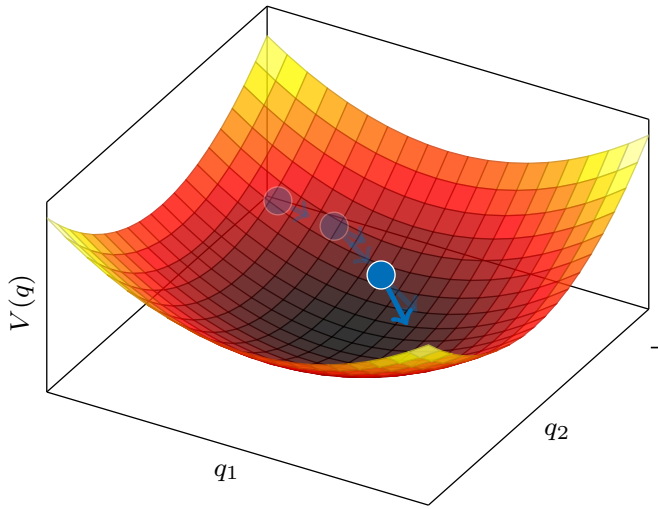
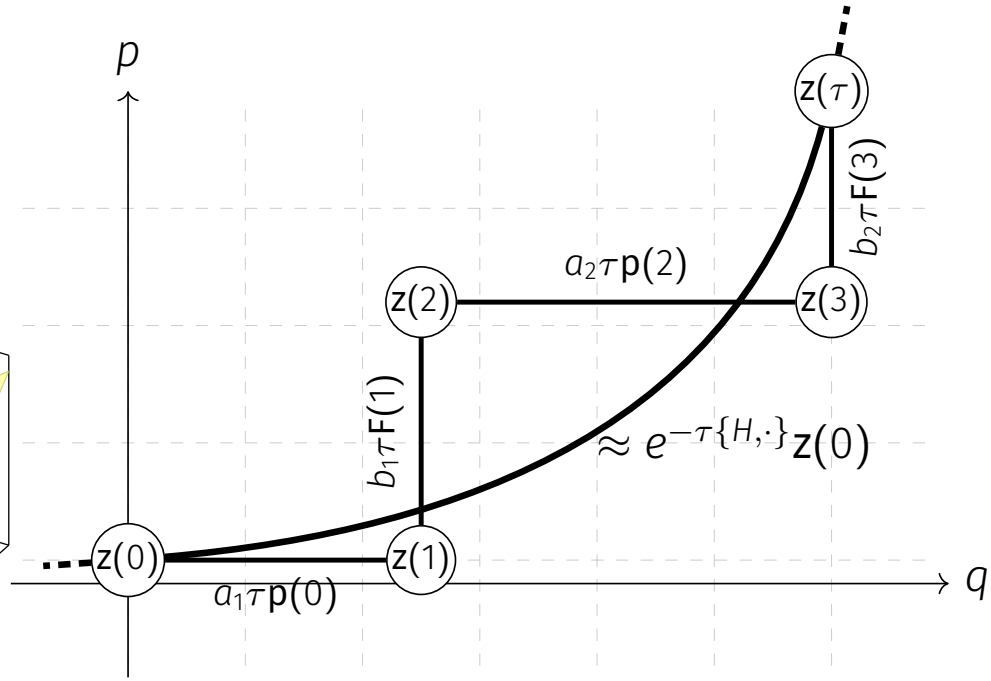
The time evolution operator is approximated by a map

$$e^{-\tau\{H,\cdot\}} \approx e^{-\tau b_k\{V,\cdot\}} e^{-\tau a_k\{K,\cdot\}} \dots e^{-\tau b_1\{V,\cdot\}} e^{-\tau a_1\{K,\cdot\}}$$

$$\begin{aligned}
\mathsf{z}(1) &= e^{-\tau a_1\{K,\cdot\}}\mathsf{z}(0) \\
\mathsf{z}(2) &= e^{-\tau b_1\{V,\cdot\}}\mathsf{z}(1) \\
\mathsf{z}(3) &= e^{-\tau a_2\{K,\cdot\}}\mathsf{z}(2) \\
\mathsf{z}(\tau) &= e^{-\tau b_2\{V,\cdot\}}\mathsf{z}(3)
\end{aligned}$$





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$$\mathsf{z}(1) = e^{-\tau a_1\{K,\cdot\}}\mathsf{z}(0)$$
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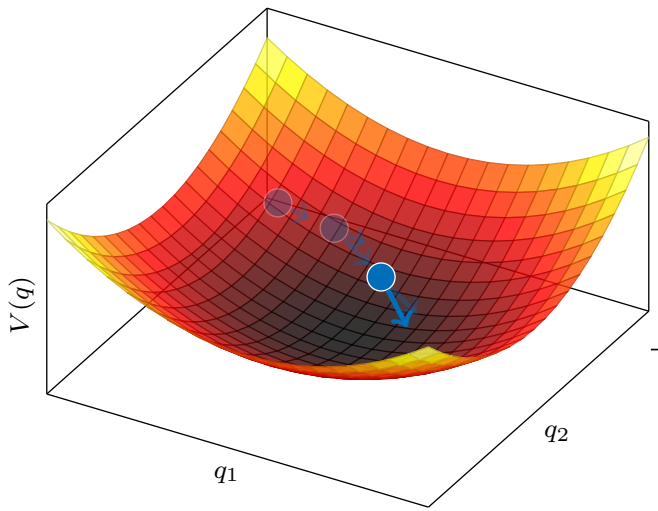
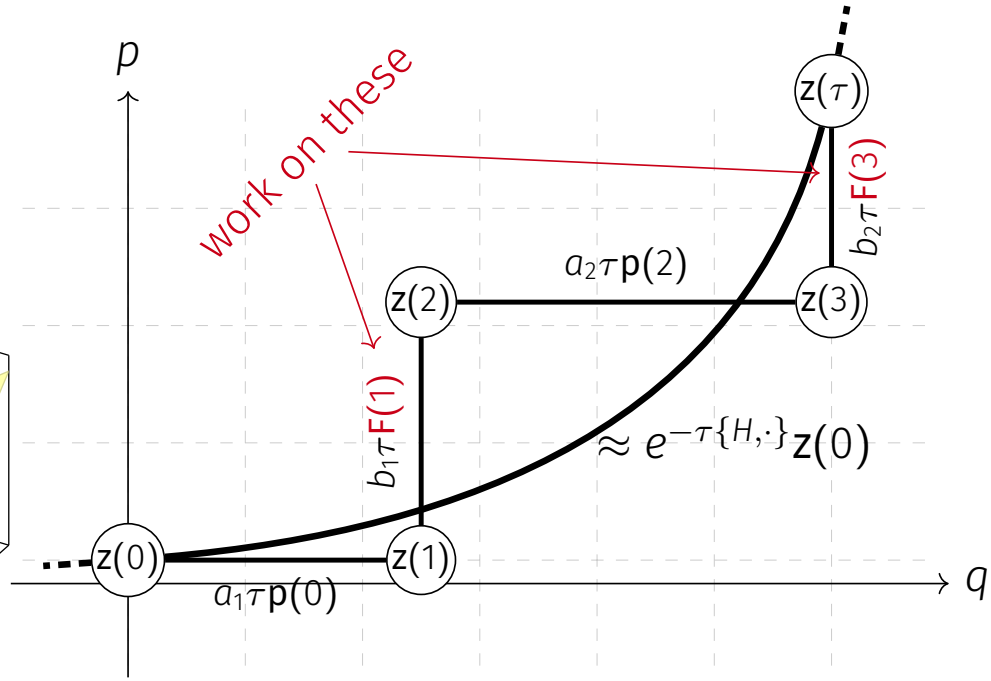
$$\mathsf{z}(\tau) = e^{-\tau b_2\{V,\cdot\}}\mathsf{z}(3)$$





[3] A.J. Dragt, et al. *Annu. Rev. Nucl. Part.* (1988); H. Yoshida, *Phys. Lett.* (1990); S.A. Chin, *Am. J. Phys.* (2020);

Time Evolution: Integrated Force [2]

Update the force by time integration of the Hessian

$$\tilde{\mathsf{F}}(\tau) - \tilde{\mathsf{F}}(0) = \int_0^\tau \frac{d\tilde{\mathsf{F}}(t)}{dt}\, dt$$

[2] M. Gandolfi, M. Ceotto, *J. Chem. Theory Comput.* (2023)

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$$\tilde{\mathbf{F}}(\tau) - \tilde{\mathbf{F}}(0) = \int_0^\tau \frac{d\tilde{\mathbf{F}}(t)}{dt}\, dt = -\int_0^\tau \tilde{\mathbf{V}}''(t) \cdot \dot{\tilde{\mathbf{q}}}(t)\, dt$$

[2] M. Gandolfi, M. Ceotto, *J. Chem. Theory Comput.* (2023)

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The time evolution operator is approximated by a map

$$e^{-\tau\left\{\tilde{H},\cdot\right\}} \approx e^{-\tau b_k\left\{\tilde{V},\cdot\right\}} e^{-\tau a_k\{K,\cdot\}} \ldots e^{-\tau b_1\left\{\tilde{V},\cdot\right\}} e^{-\tau a_1\{K,\cdot\}}$$

[2] M. Gandolfi, M. Ceotto, *J. Chem. Theory Comput.* (2023)

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Update the force by time integration of the Hessian

$$\tilde{\mathsf{F}}(\tau) - \tilde{\mathsf{F}}(0) \quad = \quad \int_0^\tau \frac{d\tilde{\mathsf{F}}(t)}{dt}\, dt \approx -\sum_{j=1}^{k} \left[\tilde{\mathsf{V}}'' \left(q(\Sigma_i^j a_i \tau) \right) \cdot \dot{q}(\Sigma_i^j a_i \tau) c_j \tau \right]$$

The time evolution operator is approximated by a map

$$e^{-\tau \left\{ \tilde{H}, \cdot \right\}} \approx e^{-\tau b_k \left\{ \tilde{v}, \cdot \right\}} e^{-\tau a_k \{K, \cdot\}} \ldots e^{-\tau b_1 \left\{ \tilde{v}, \cdot \right\}} e^{-\tau a_1 \{K, \cdot\}}$$

[2] M. Gandolfi, M. Ceotto, *J. Chem. Theory Comput.* (2023)

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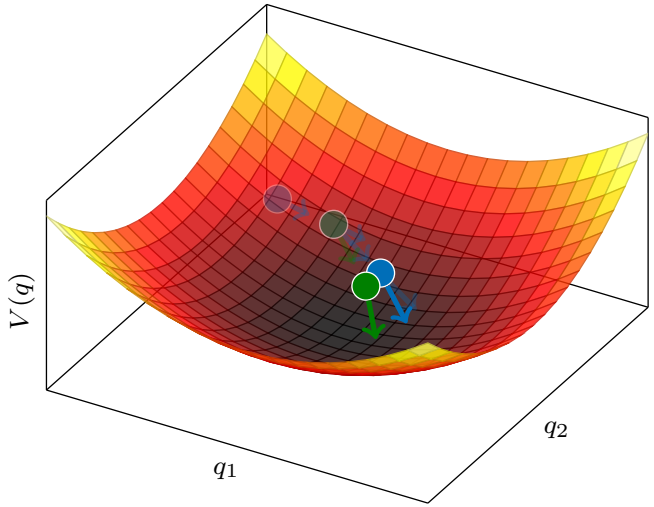
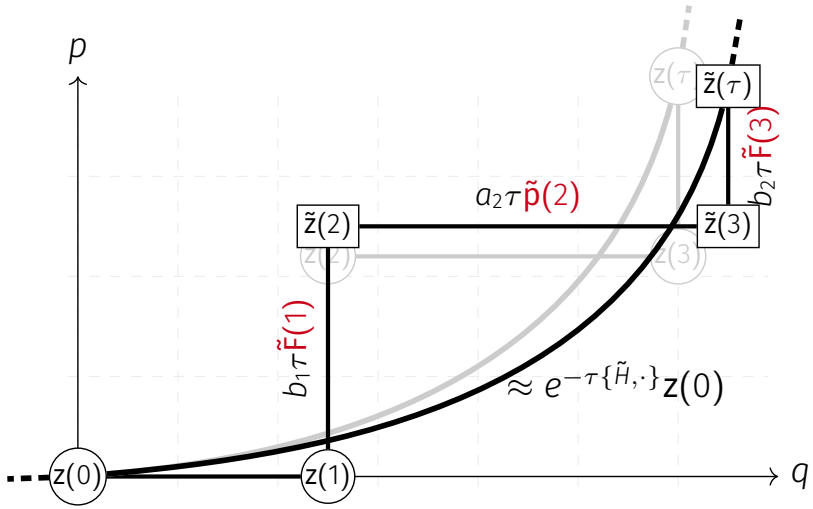




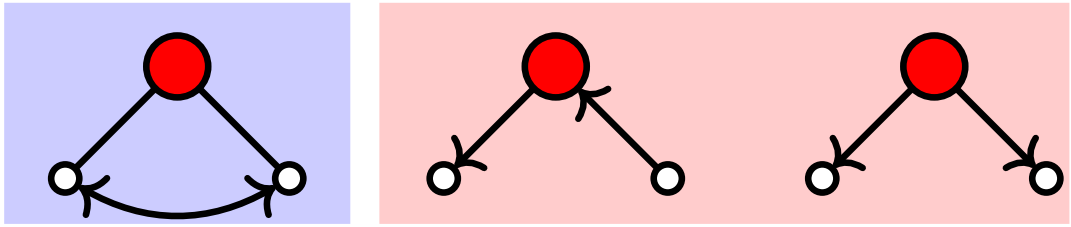
[2] M. Gandolfi, M. Ceotto, *J. Chem. Theory Comput.* (2023)

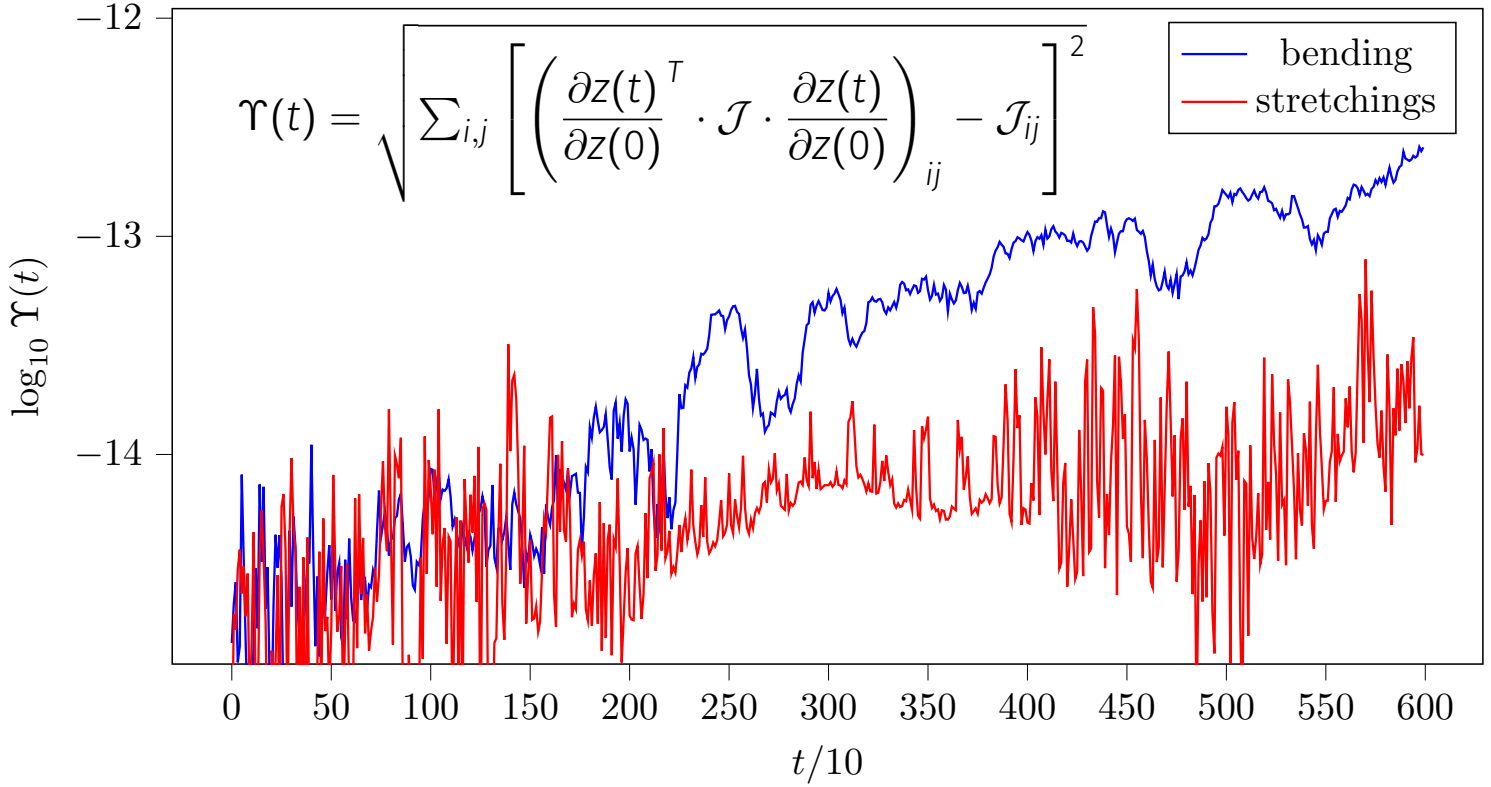
Time Evolution: Solution [2]

coeff.	$k=1$	$k=2$	$k=3$	$k=4$
a_k	$1/2$	$1/2$	0	0
b_k	0	1	0	0
c_k	$1/2$	$1/2$	0	0
a_k	$\frac{(2^{1/3}+2^{-1/3}+2)}{6}$	$\frac{-(2^{1/3}+2^{-1/3}-1)}{6}$	$\frac{-(2^{1/3}+2^{-1/3}-1)}{6}$	$\frac{(2^{1/3}+2^{-1/3}+2)}{6}$
b_k	0	$\frac{(2^{4/3}+2^{2/3}+4)}{6}$	$\frac{-(2^{7/3}+2^{5/3}+2)}{6}$	$\frac{(2^{4/3}+2^{2/3}+4)}{6}$
c_k	$\frac{(2^{1/3}+2^{-1/3}+2)}{6}$	$\frac{-(2^{1/3}+2^{-1/3}-1)}{6}$	$\frac{-(2^{1/3}+2^{-1/3}-1)}{6}$	$\frac{(2^{1/3}+2^{-1/3}+2)}{6}$
a_k	$\sqrt{3}/6+1/2$	$-\sqrt{3}/3$	$\sqrt{3}/3$	$-\sqrt{3}/6+1/2$
b_k	0	$-\sqrt{3}/6+1/4$	$1/2$	$\sqrt{3}/6+1/4$
c_k	$5/26$	$8\sqrt{3}/39+4/13$	$-8\sqrt{3}/39+4/13$	$5/26$
a_k	$\sqrt{3}/6+1/2$	$-\sqrt{3}/3$	$\sqrt{3}/3$	$-\sqrt{3}/6+1/2$
b_k	0	$-\sqrt{3}/6+1/4$	$1/2$	$\sqrt{3}/6+1/4$
c_k	$5\sqrt{3}/48$	$\sqrt{3}/8+1/2$	$-\sqrt{3}/8+1/2$	$-5\sqrt{3}/48$
a_k	$\sqrt{3}/6+1/2$	$-\sqrt{3}/3$	$\sqrt{3}/3$	$-\sqrt{3}/6+1/2$
b_k	0	$-\sqrt{3}/6+1/4$	$1/2$	$\sqrt{3}/6+1/4$
c_k	$1/4$	$\sqrt{3}/6+1/4$	$-\sqrt{3}/6+1/4$	$1/4$
a_k	$\sqrt{3}/6+1/2$	$-\sqrt{3}/3$	$\sqrt{3}/3$	$-\sqrt{3}/6+1/2$
b_k	0	$-\sqrt{3}/6+1/4$	$1/2$	$\sqrt{3}/6+1/4$
c_k	$\sqrt{3}/6$	$1/2$	$1/2$	$-\sqrt{3}/6$

[2] M. Gandolfi, M. Ceotto, *J. Chem. Theory Comput.* (2023)

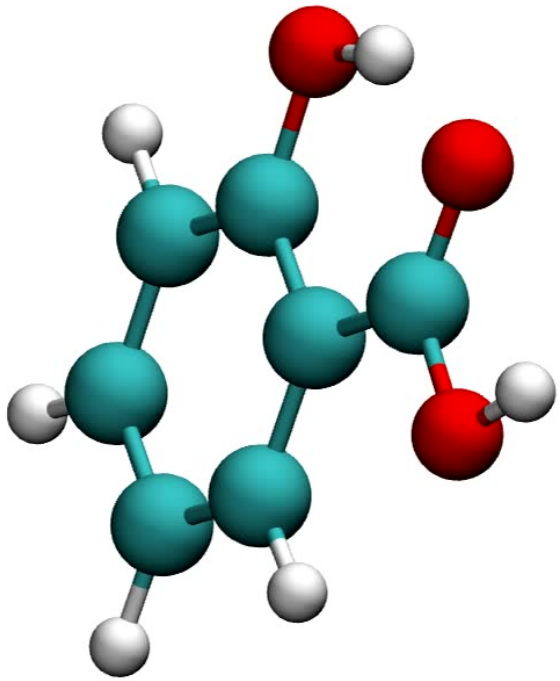
Symplectic structure conservation H_2O normal modes [2]





[2] M. Gandolfi, M. Ceotto, *J. Chem. Theory Comput.* (2023)

Pair-Decouple Movie: Salicylic Acid ($\alpha = 1$) [2] [4]

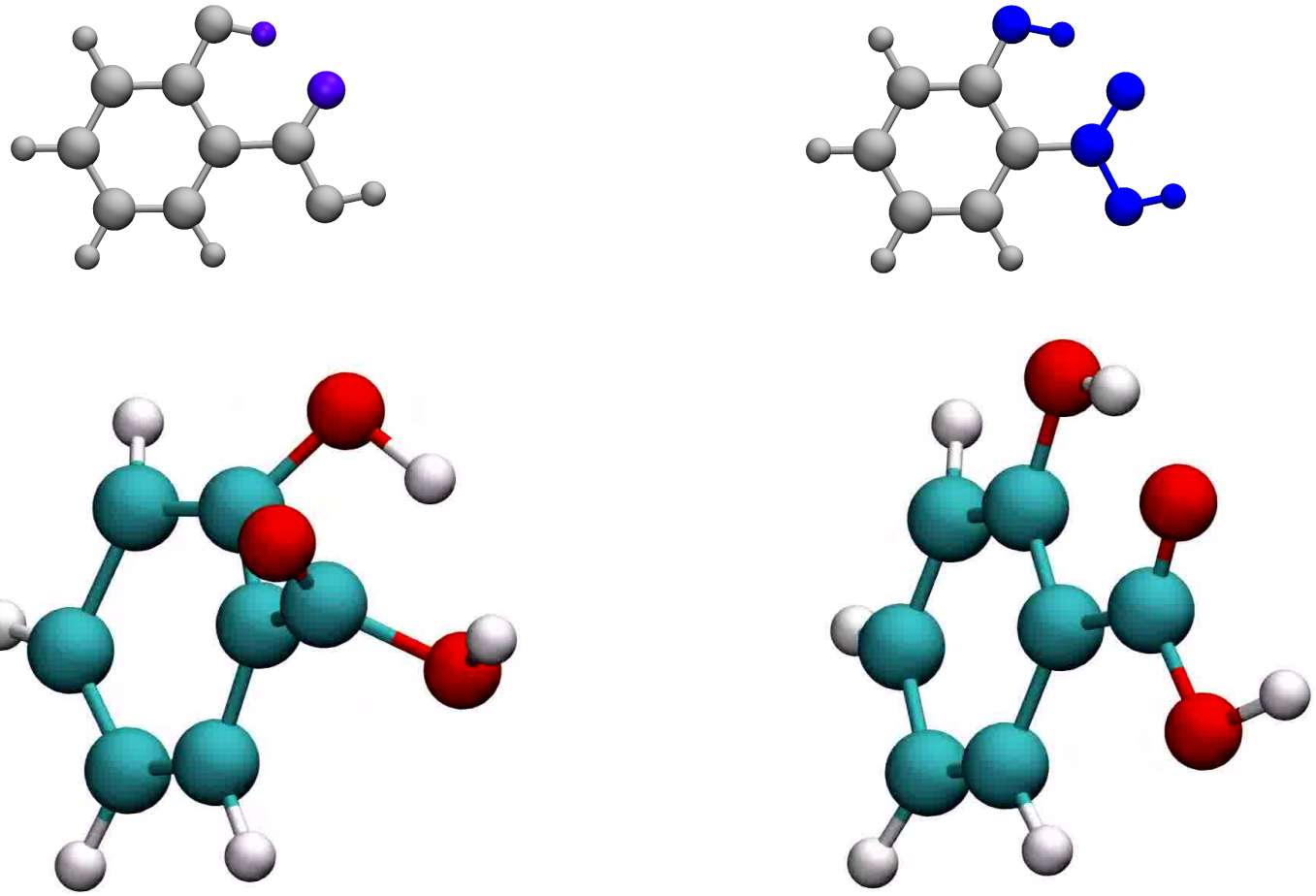


Salycilic Acid vibrates on a plane

[2] M. Gandolfi, M. Ceotto, *J. Chem. Theory Comput.* (2023)

[4] S. Chmiela, et al., *Nat. Comm.* (2018)

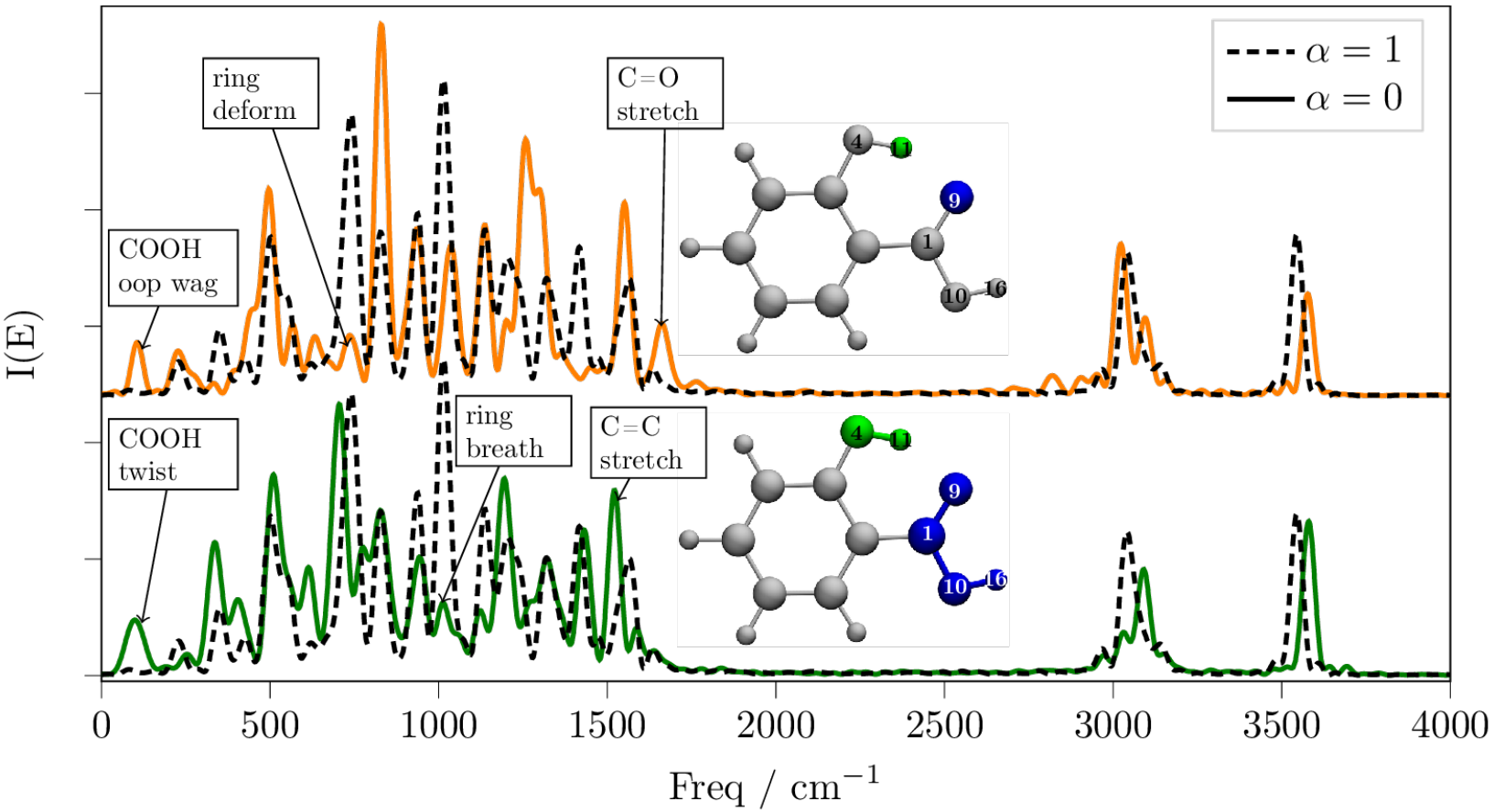
Pair-Decouple Movie: Salicylic Acid ($\alpha = 0$) [2] [4]



[2] M. Gandolfi, M. Ceotto, *J. Chem. Theory Comput.* (2023)

[4] S. Chmiela, et al., *Nat. Comm.* (2018)

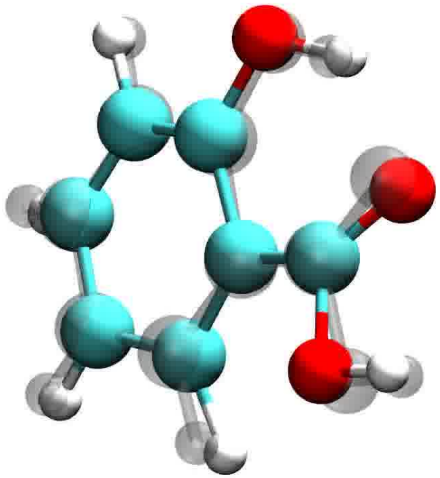
Pair-Decouple Spectroscopy: Salicylic Acid [2]

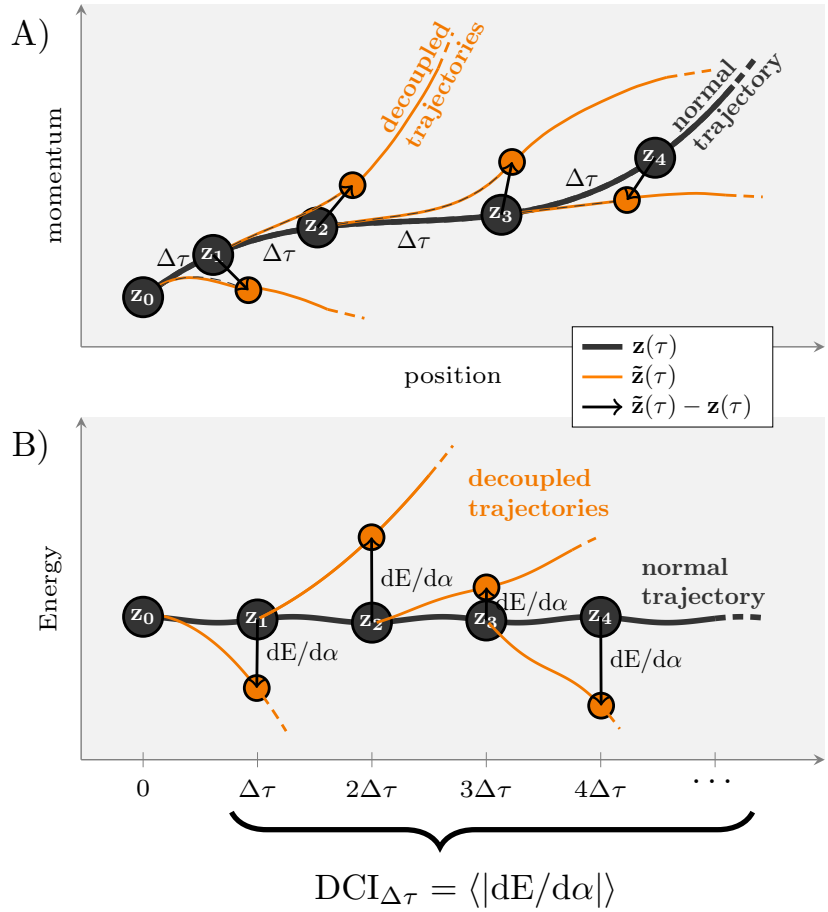


[2] M. Gandolfi, M. Ceotto, *J. Chem. Theory Comput.* (2023)

The Pair-Decoupled Trajectory

α makes the pair-decoupled trajectory drift from the non decoupled one:





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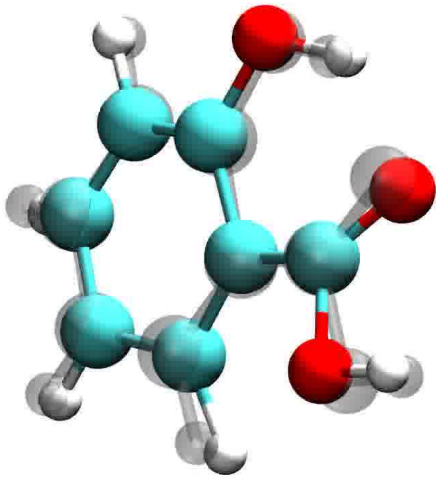
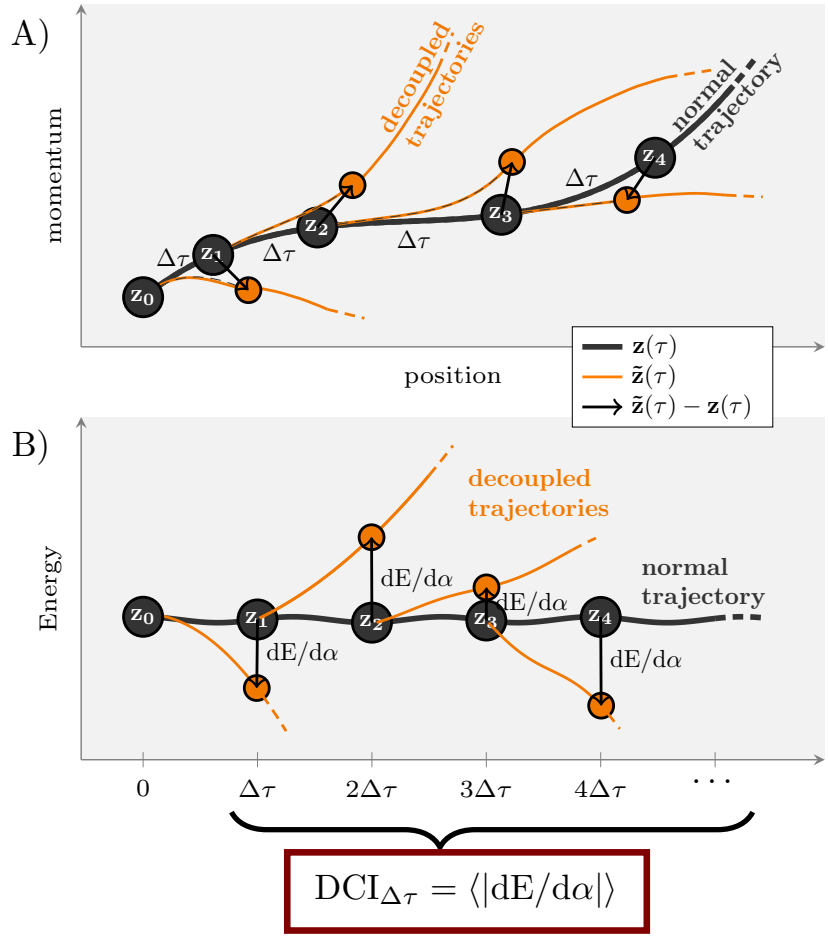
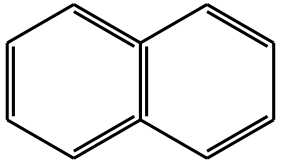


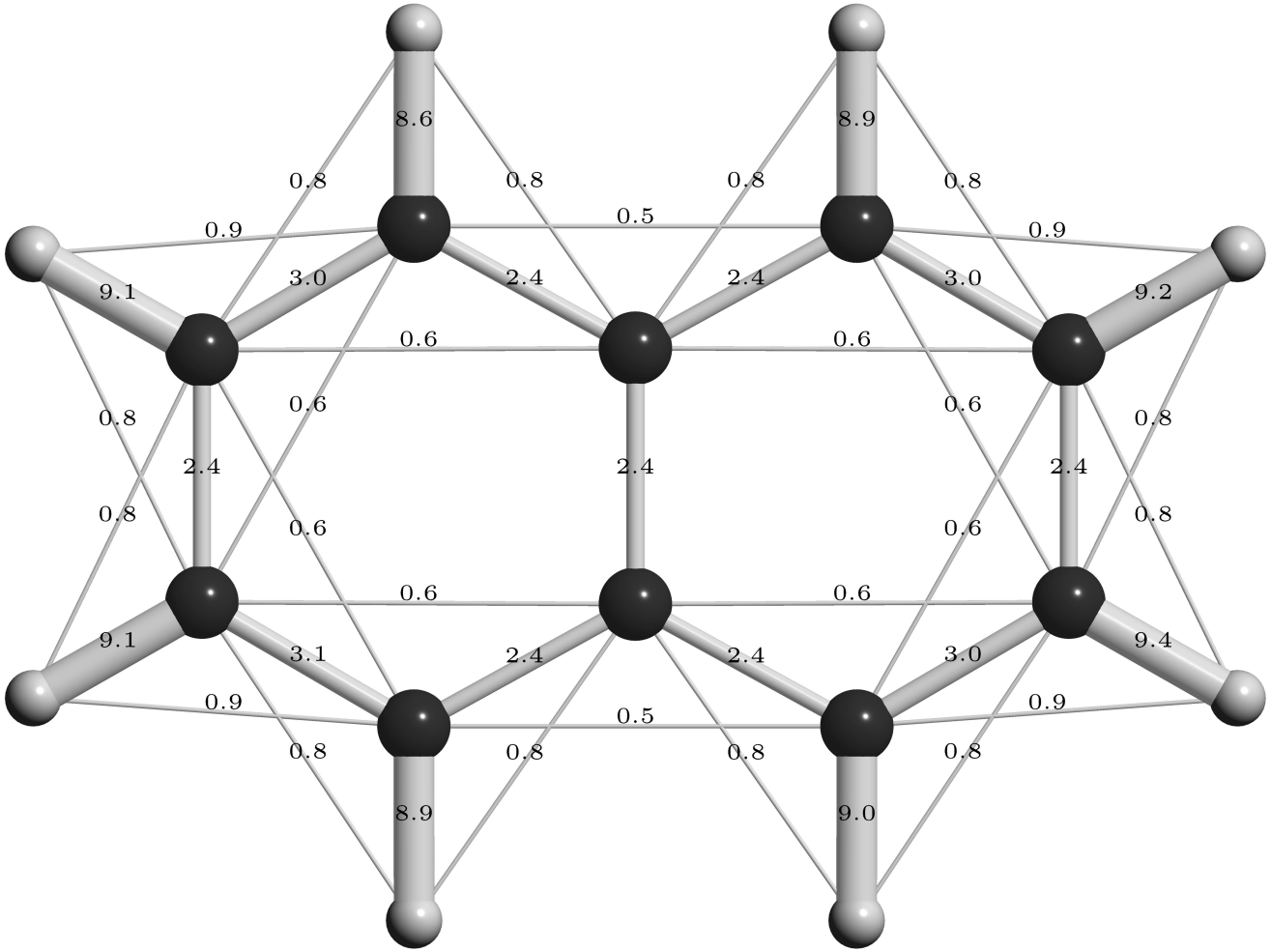


Molecular Blocks DCI Part I

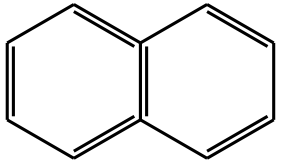


$\alpha = 1$

threshold $=$ 0.5 μHartree

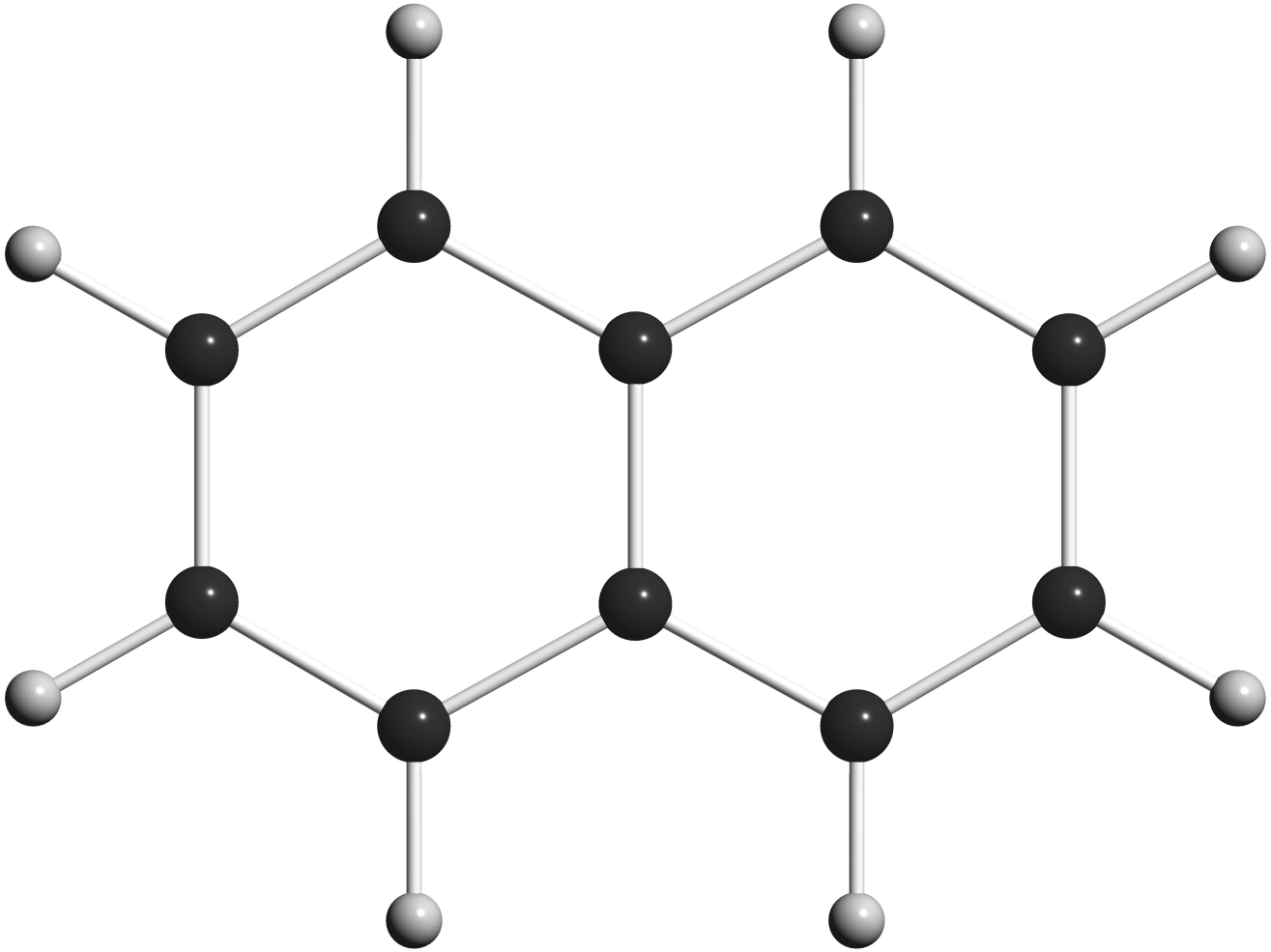


Molecular Blocks DCI Part I

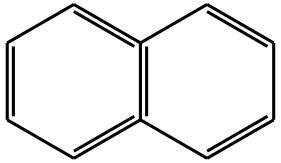


$\alpha = 1$

threshold $= 1.0 - 2.3\ \mu$Hartree

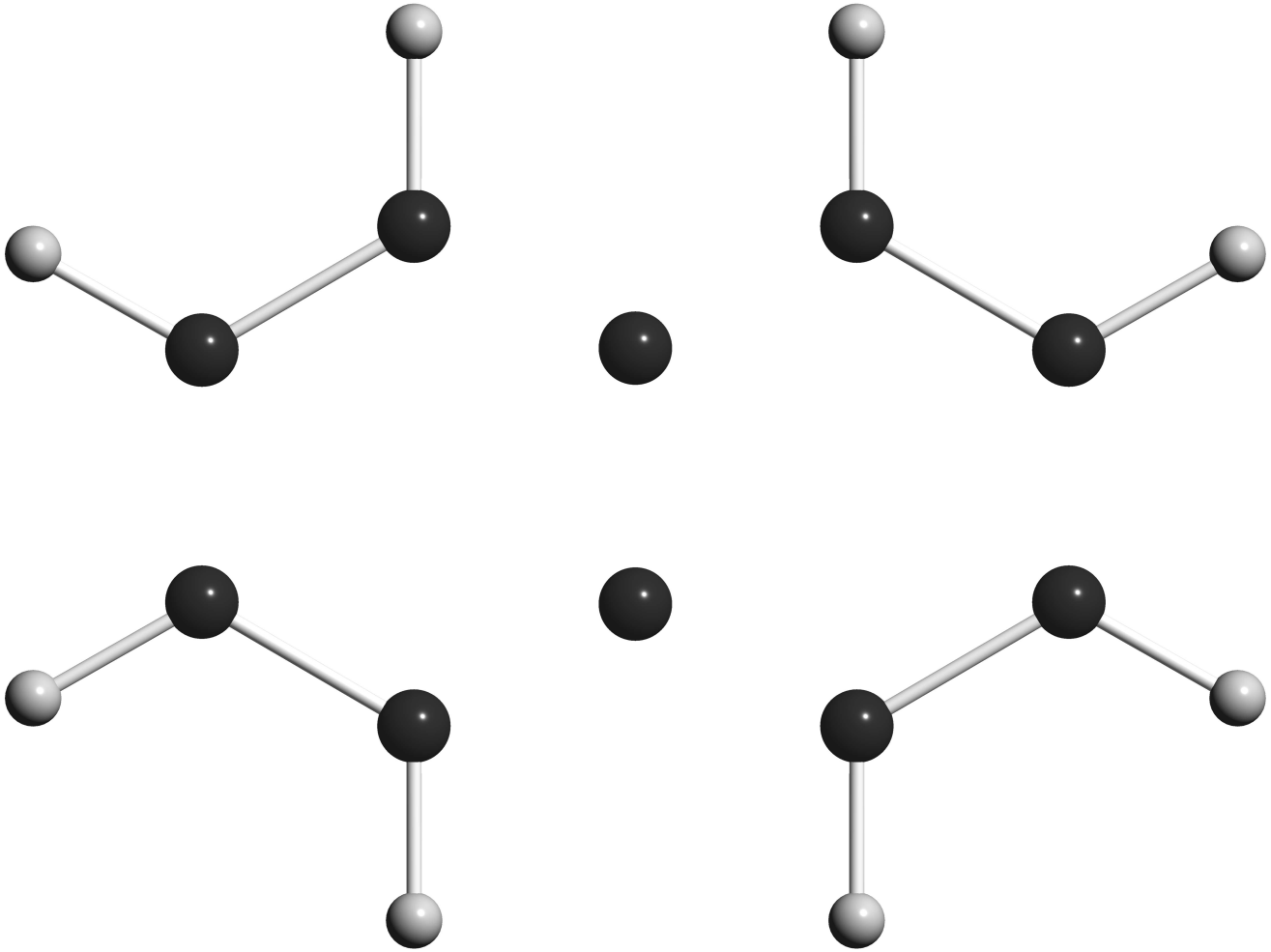


Molecular Blocks DCI Part I

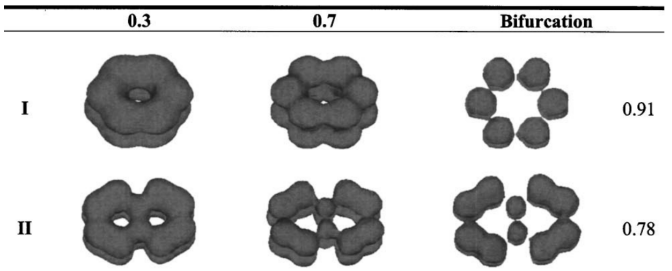


$\alpha = 1$

threshold $= 2.5 - 2.9\ \mu$Hartree



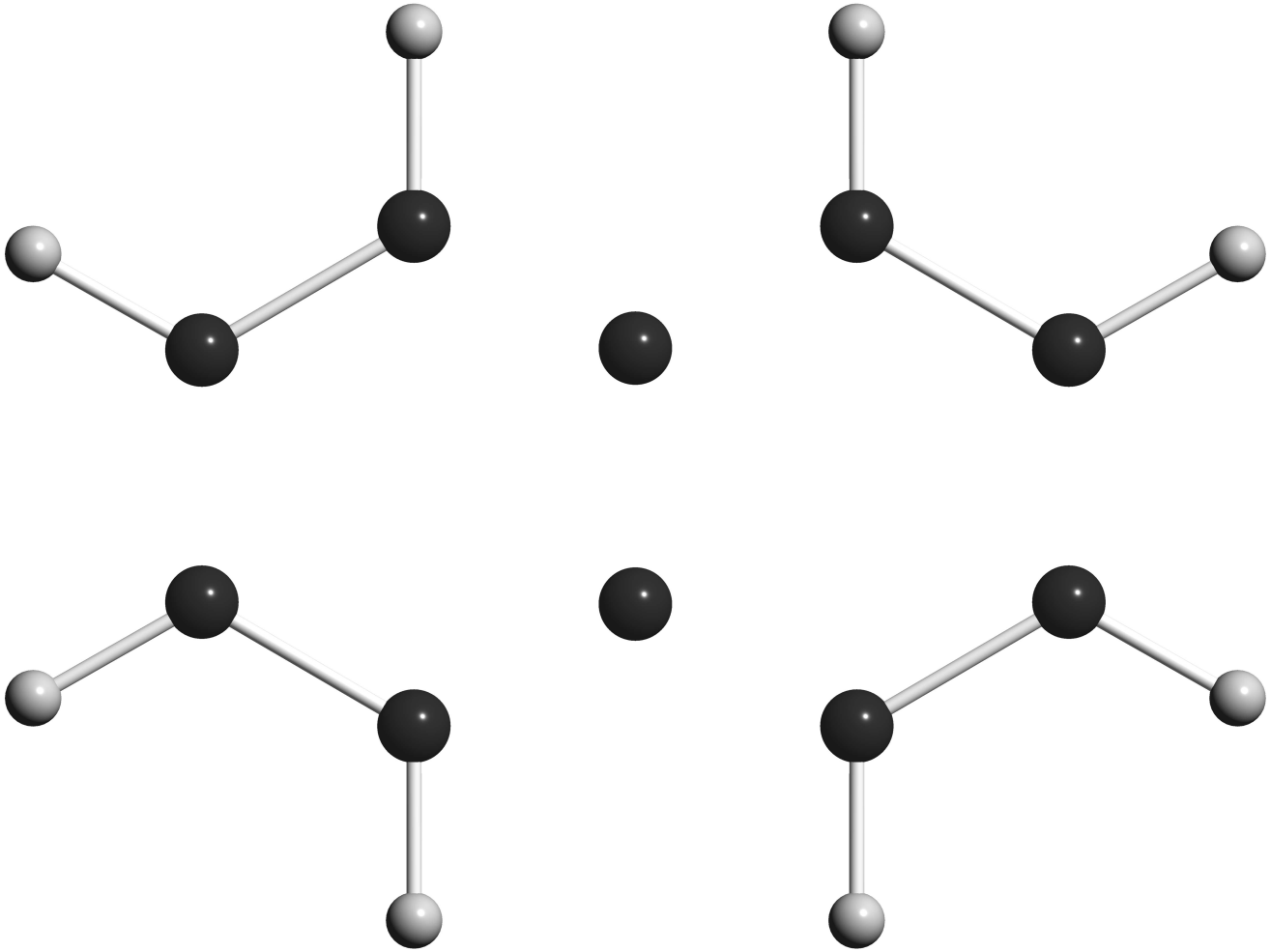
Molecular Blocks DCI Part I



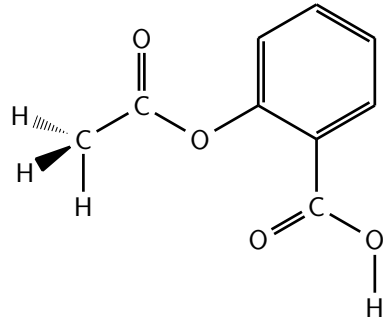
Picture from J.C. Santos, et al., *J. Chem. Phys.* (2004)

$\alpha = 1$

threshold $= 2.5 - 2.9\ \mu$Hartree

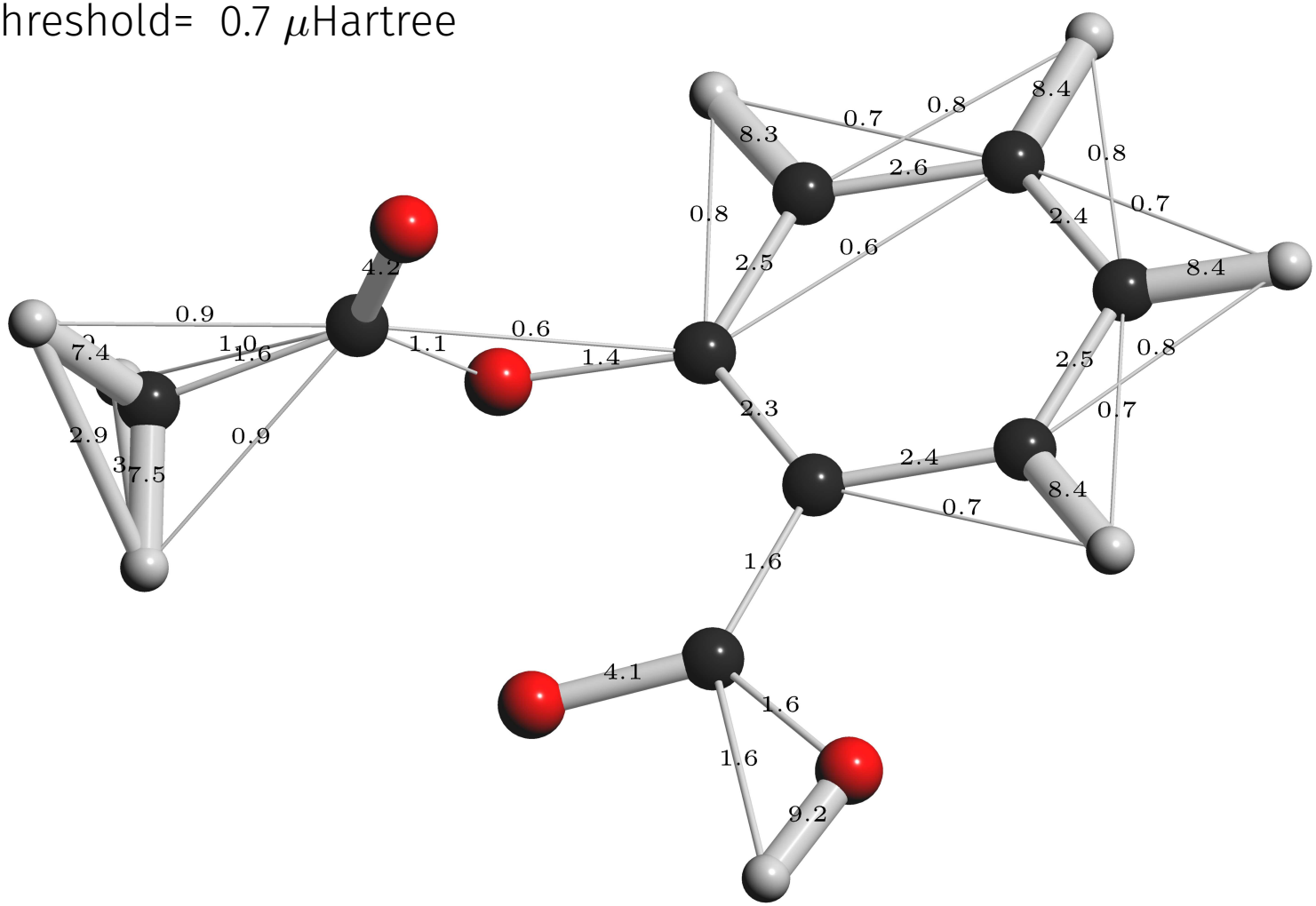


Molecular Blocks DCI Part II

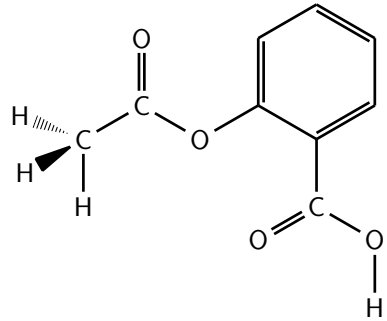


$\alpha = 1$

threshold= 0.7 μHartree

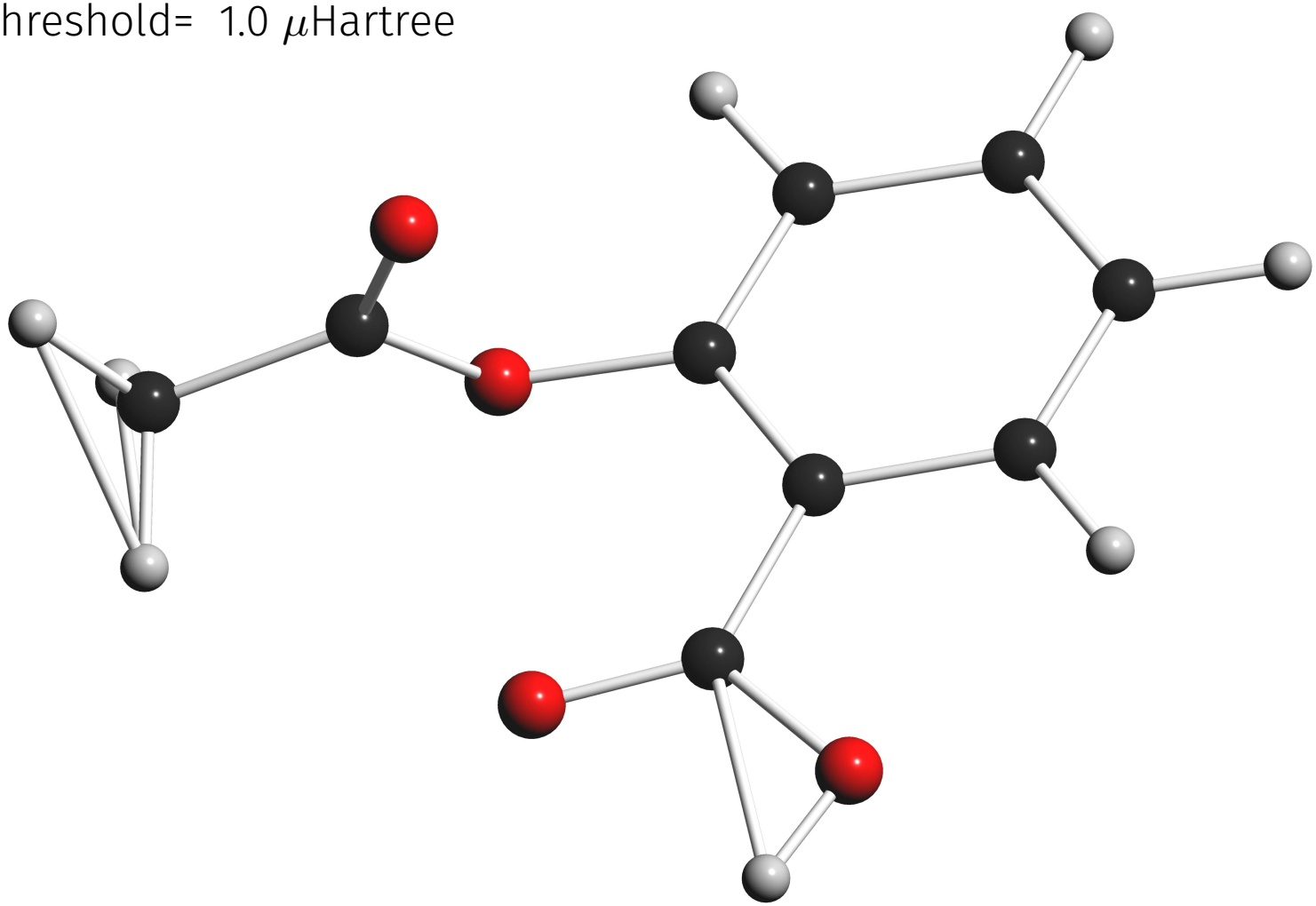


Molecular Blocks DCI Part II

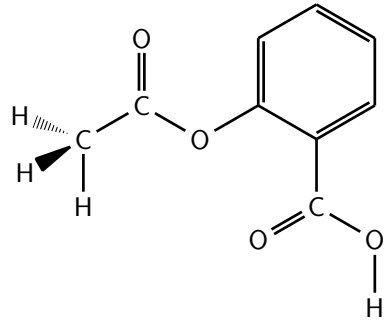


$\alpha = 1$

threshold= 1.0 μHartree

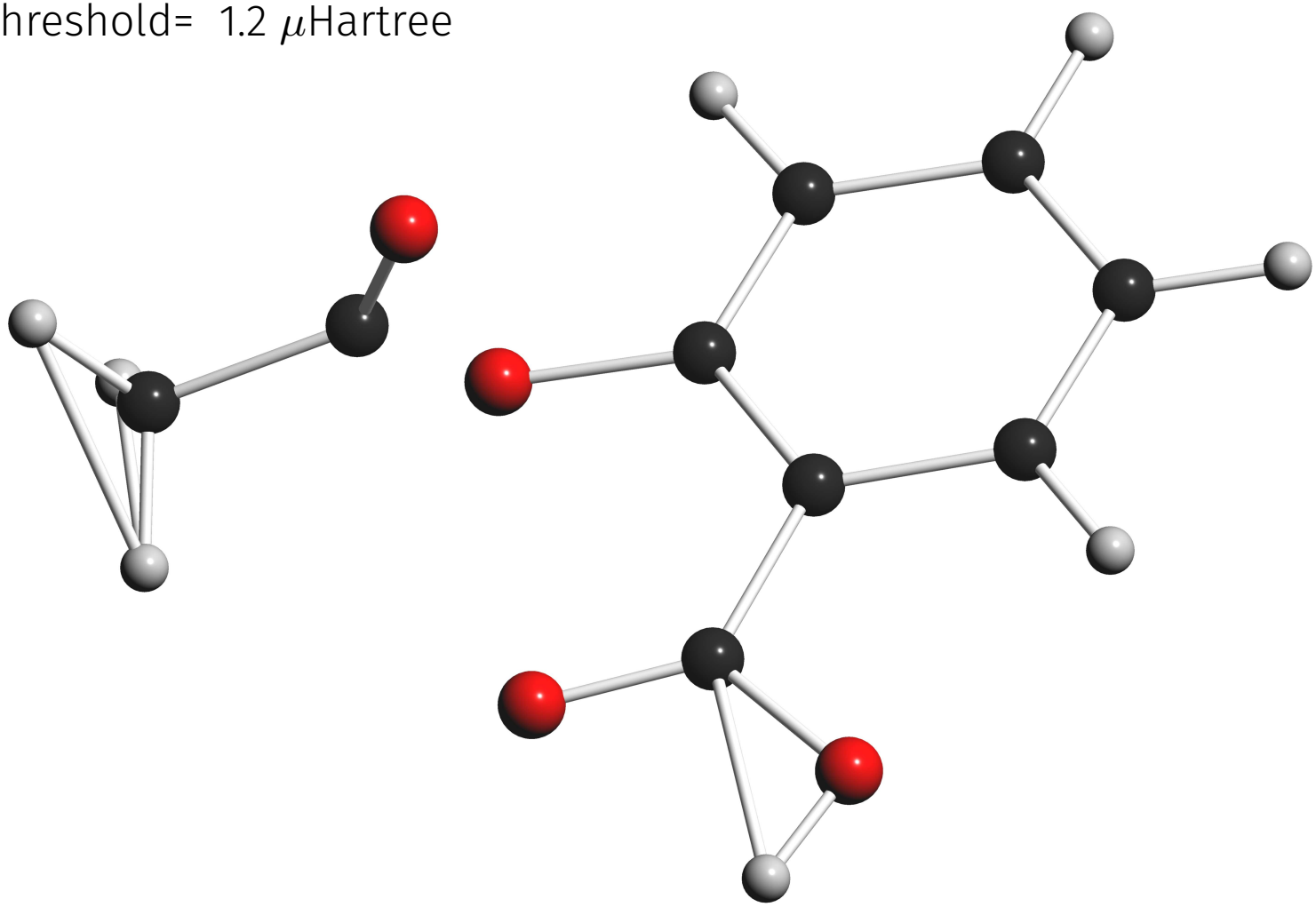


Molecular Blocks DCI Part II

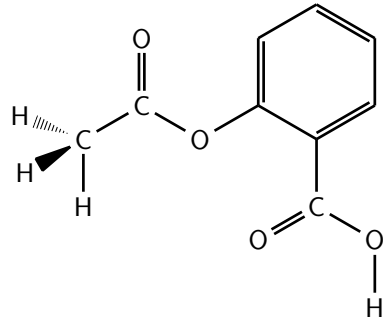


$\alpha = 1$

threshold= 1.2 μHartree

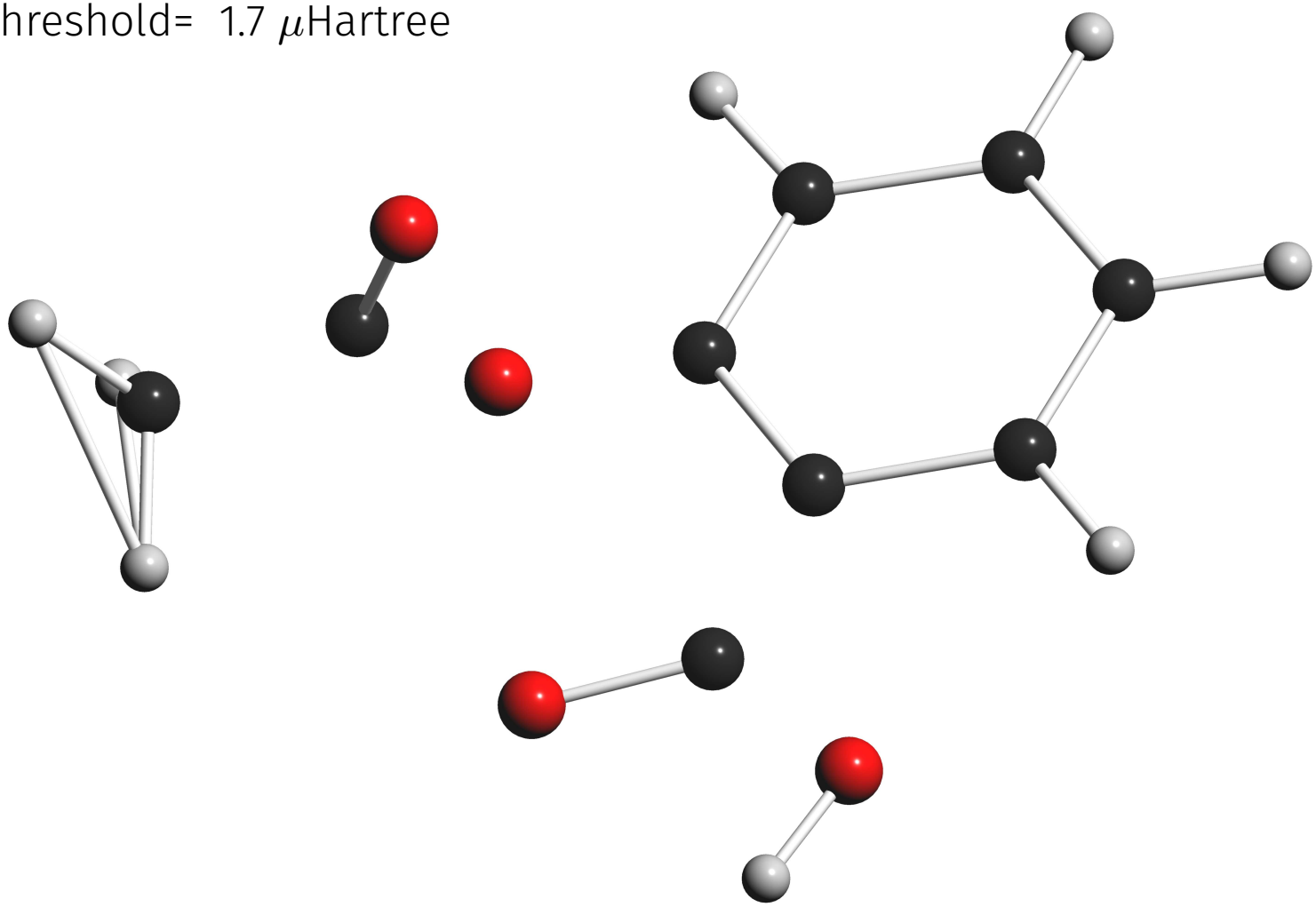


Molecular Blocks DCI Part II

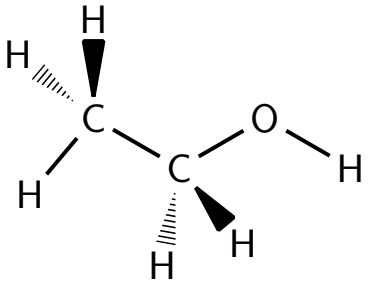


$\alpha = 1$

threshold= 1.7 μHartree

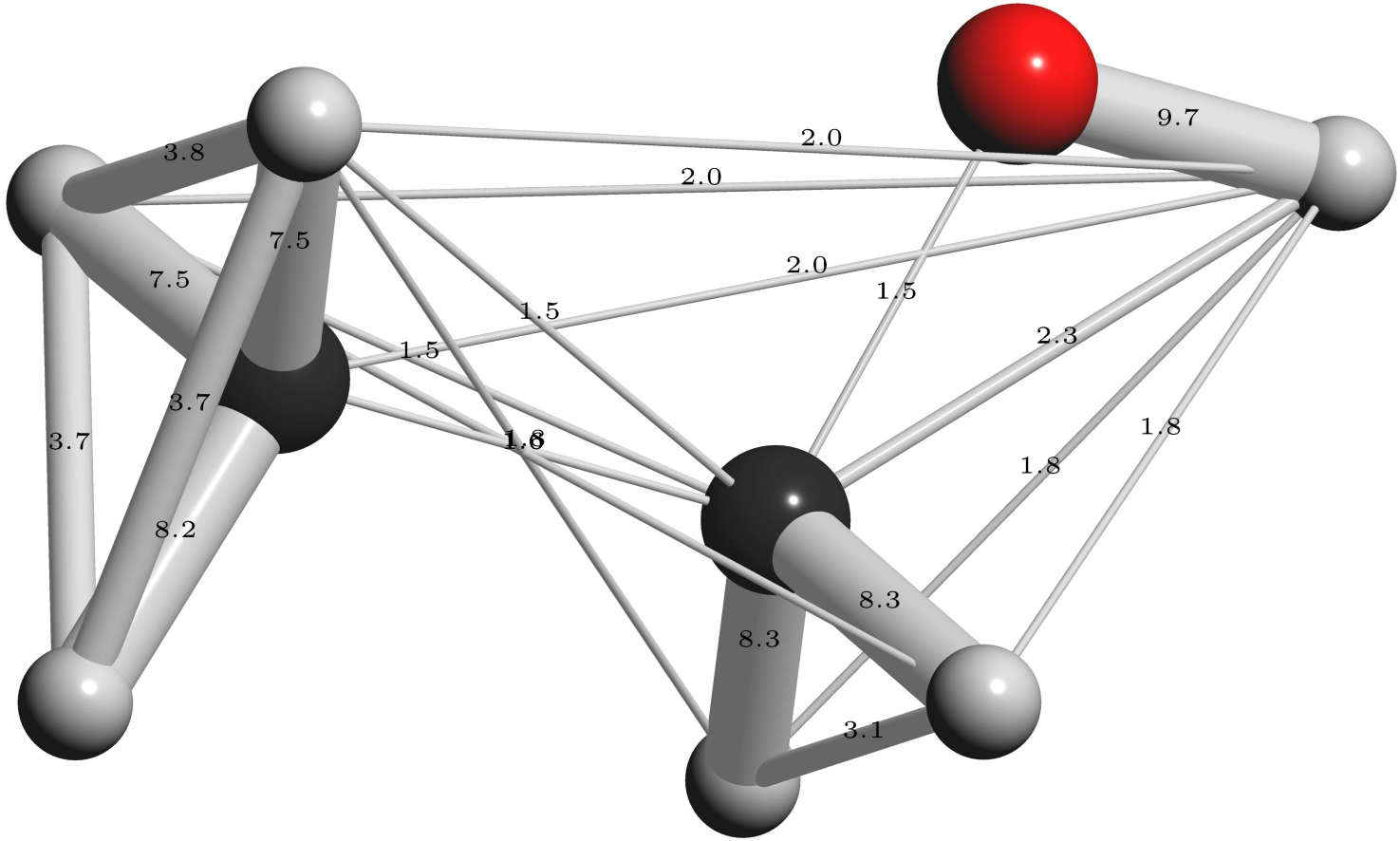


Molecular Blocks DCI Part III

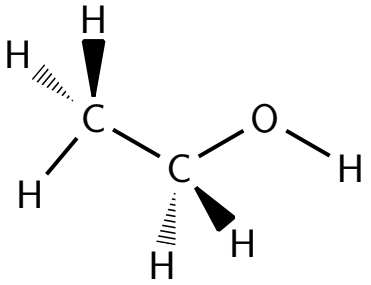


$\alpha = 1$

threshold= 1.45 μHartree

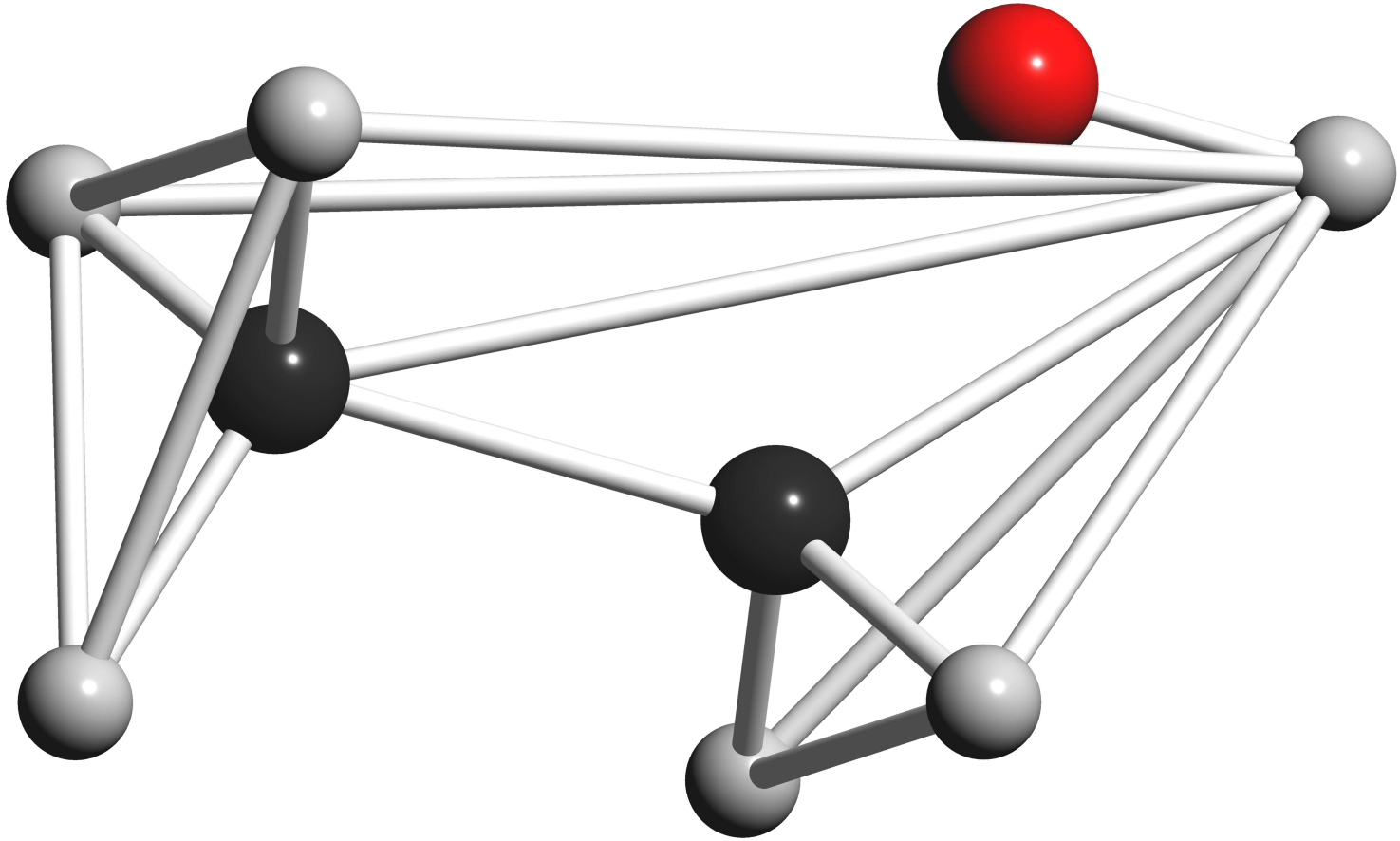


Molecular Blocks DCI Part III

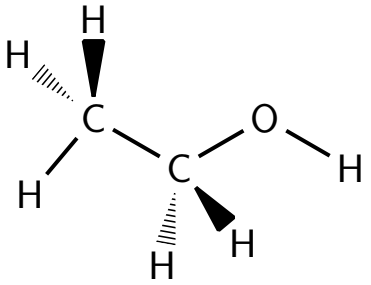


$\alpha = 1$

threshold= 1.7 μHartree

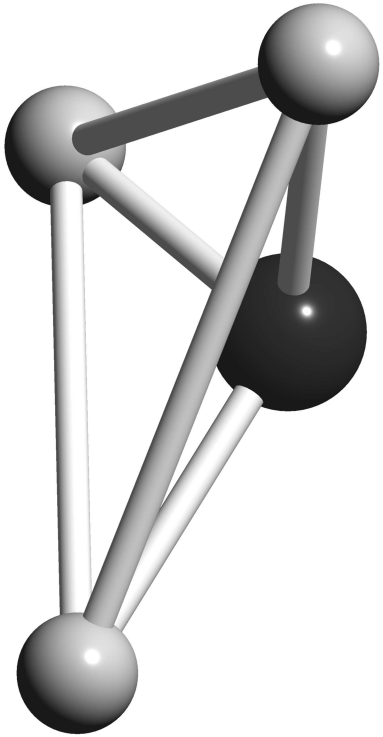


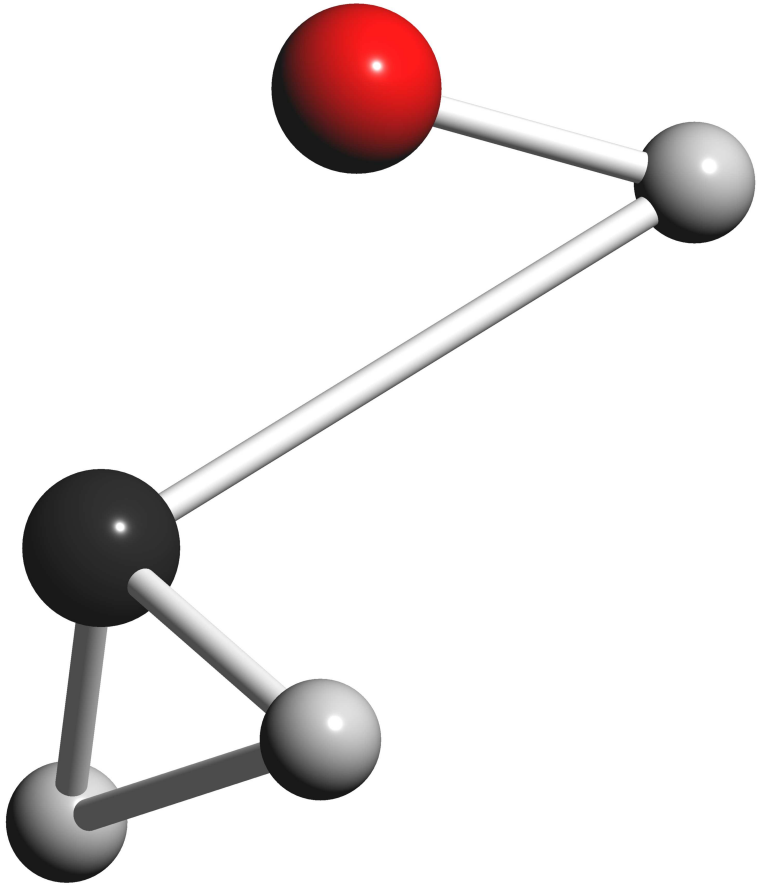
Molecular Blocks DCI Part III



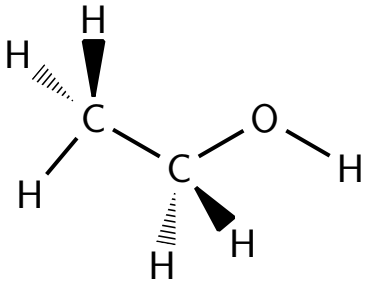
$\alpha = 1$

threshold= 2.2 μHartree



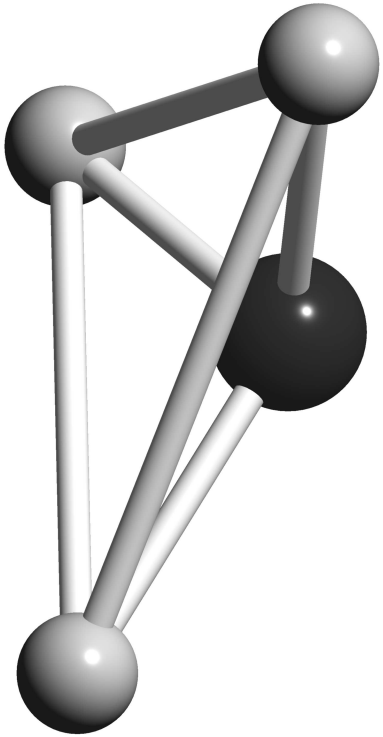


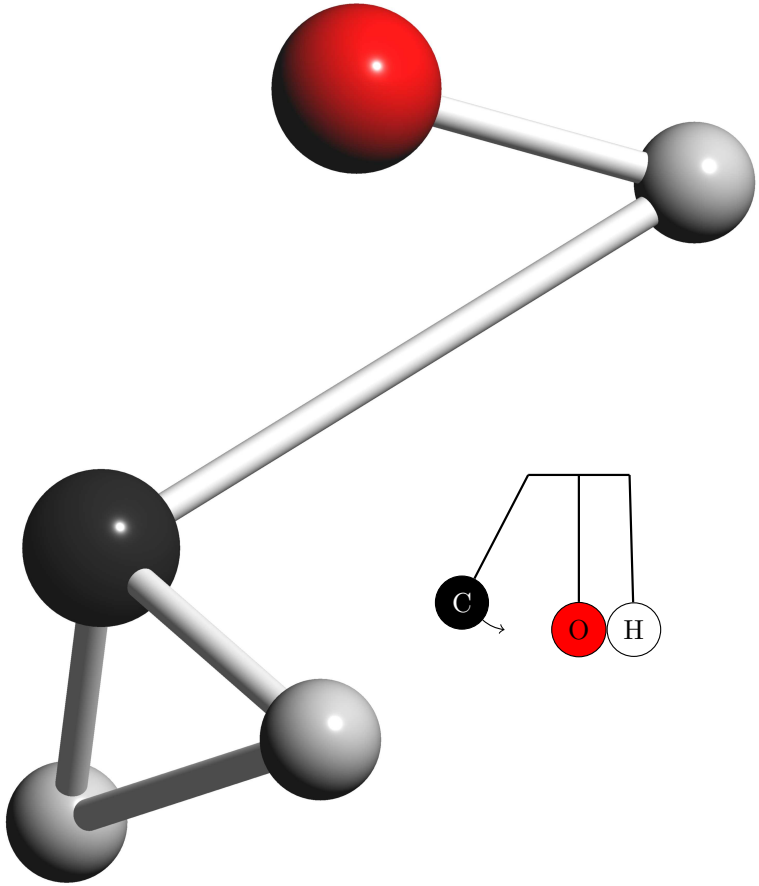
Molecular Blocks DCI Part III



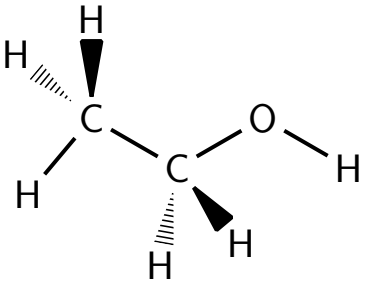
$\alpha = 1$

threshold= 2.2 μHartree





Molecular Blocks DCI Part III



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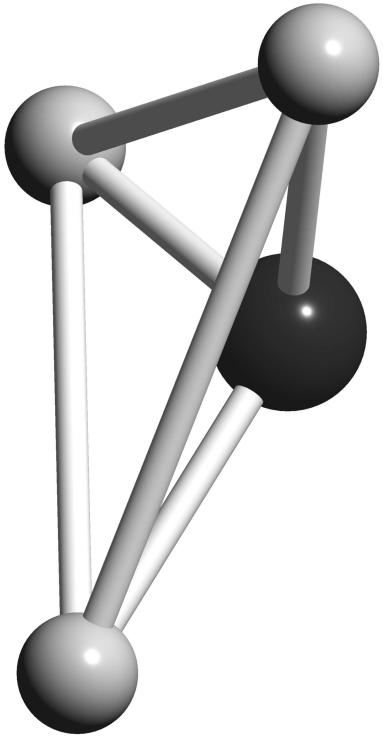

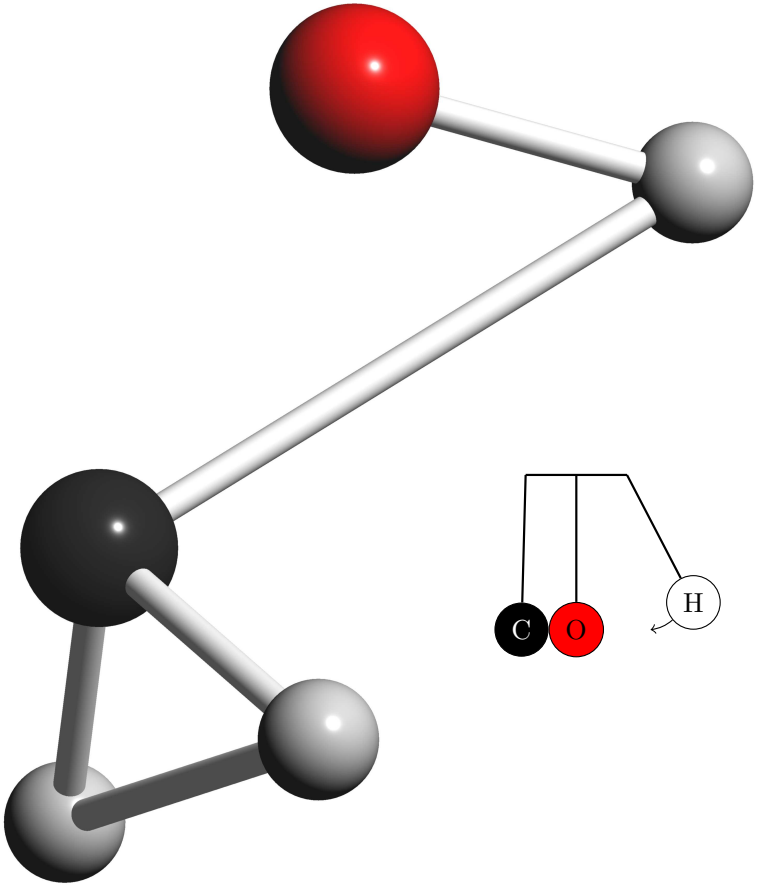

Final Remarks

- We describe a rigourous criterion to establish when a system is divisible, based on its dynamics, and algorithms to compute it effectively; [5] [6]

[5] M. Gandolfi, A. Rognoni, C. Aieta, R. Conte, M. Ceotto, *J. Chem. Phys* (2020)

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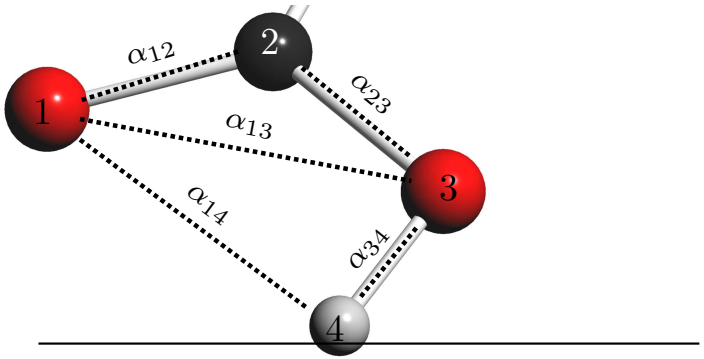

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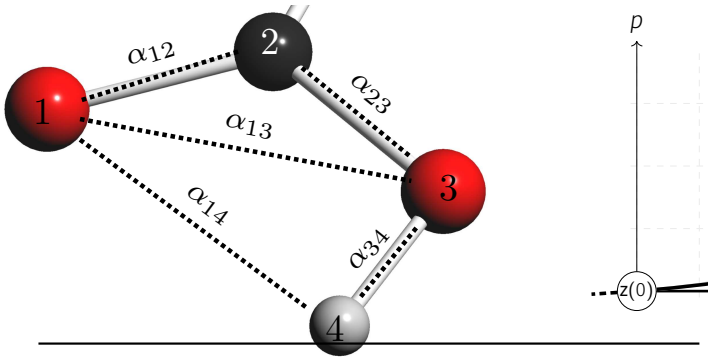

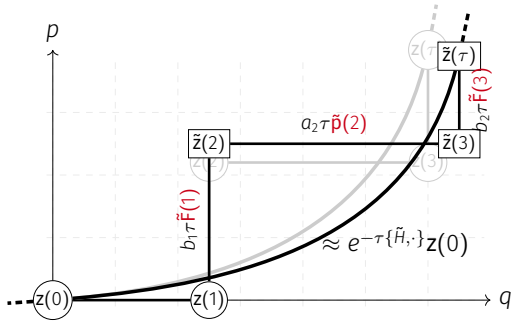

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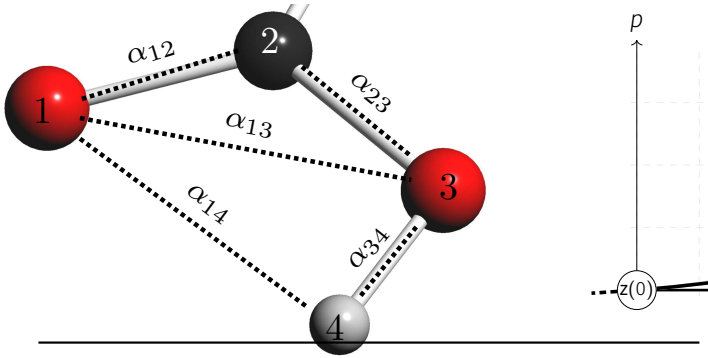
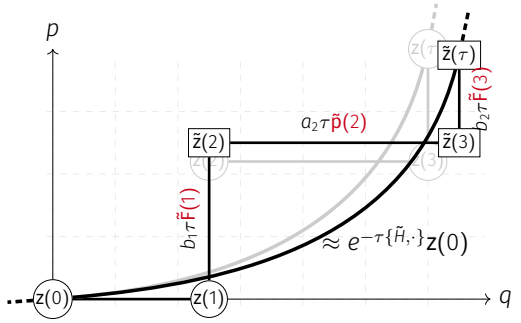
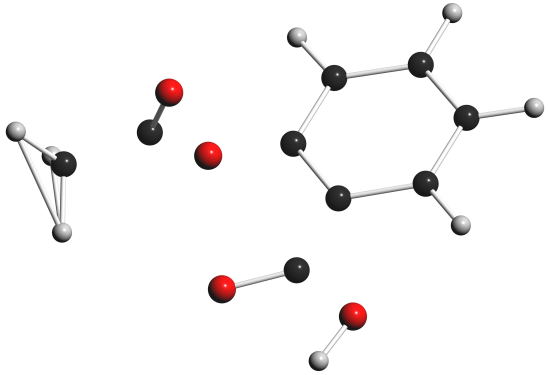
- We provide an integration rule to do numerical experiments;
- The DCI molecular descriptor gives a quantitative measure of the average coupling and allows the identification of building blocks.







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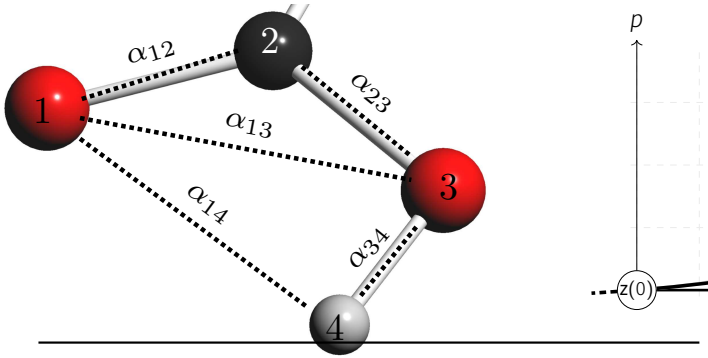
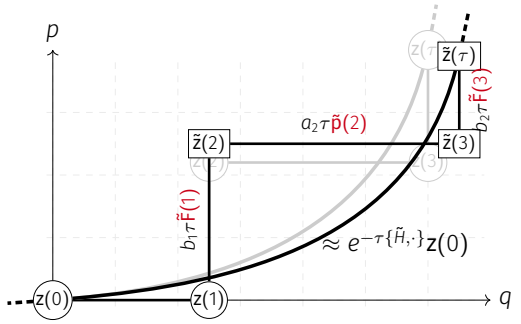
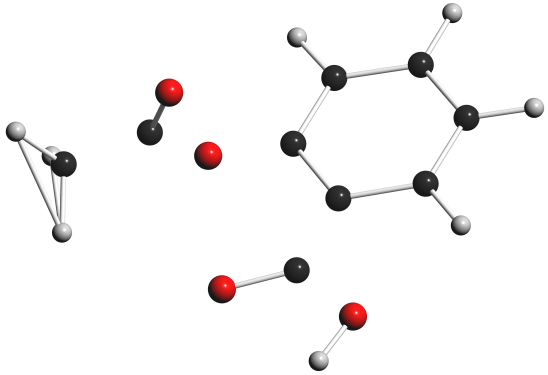
- We provide an integration rule to do numerical experiments;
- The DCI molecular descriptor gives a quantitative measure of the average coupling and allows the identification of building blocks. Is the functional group picture consistent with divisibility criteria?







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