MAX-PLANCK-GESELLSCHAFT

FHI-aims

The ab initio materials simulation package

Tutorial Series:
Ab initio molecular dynamics

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mpsd

Addressing nuclear degrees of freedom

Schrödinger Equation

$$\hat{H}\Psi = E\Psi$$

$$i\hbar\frac{\partial\Psi(t)}{\partial t} = \hat{H}\Psi(t)$$

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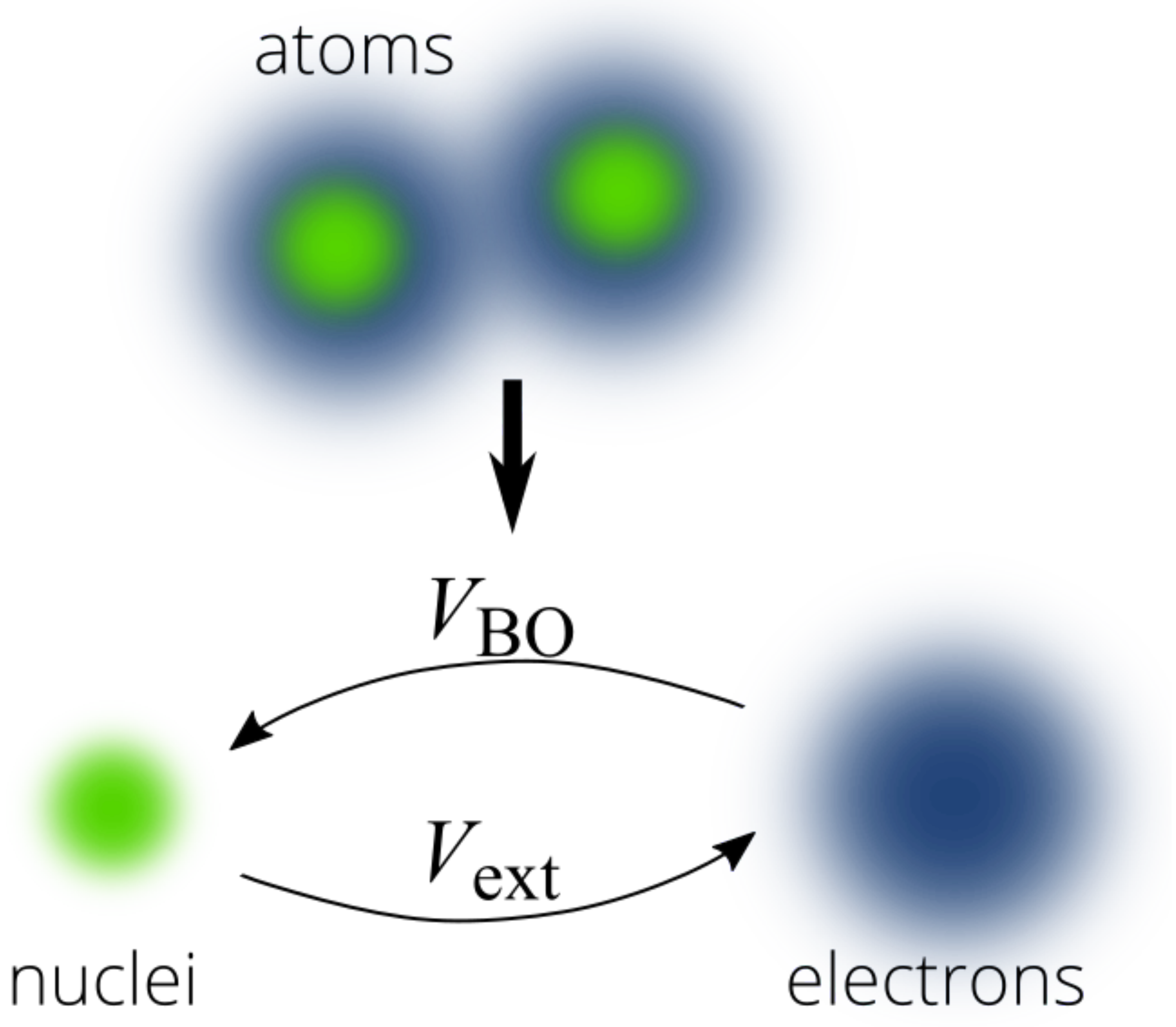

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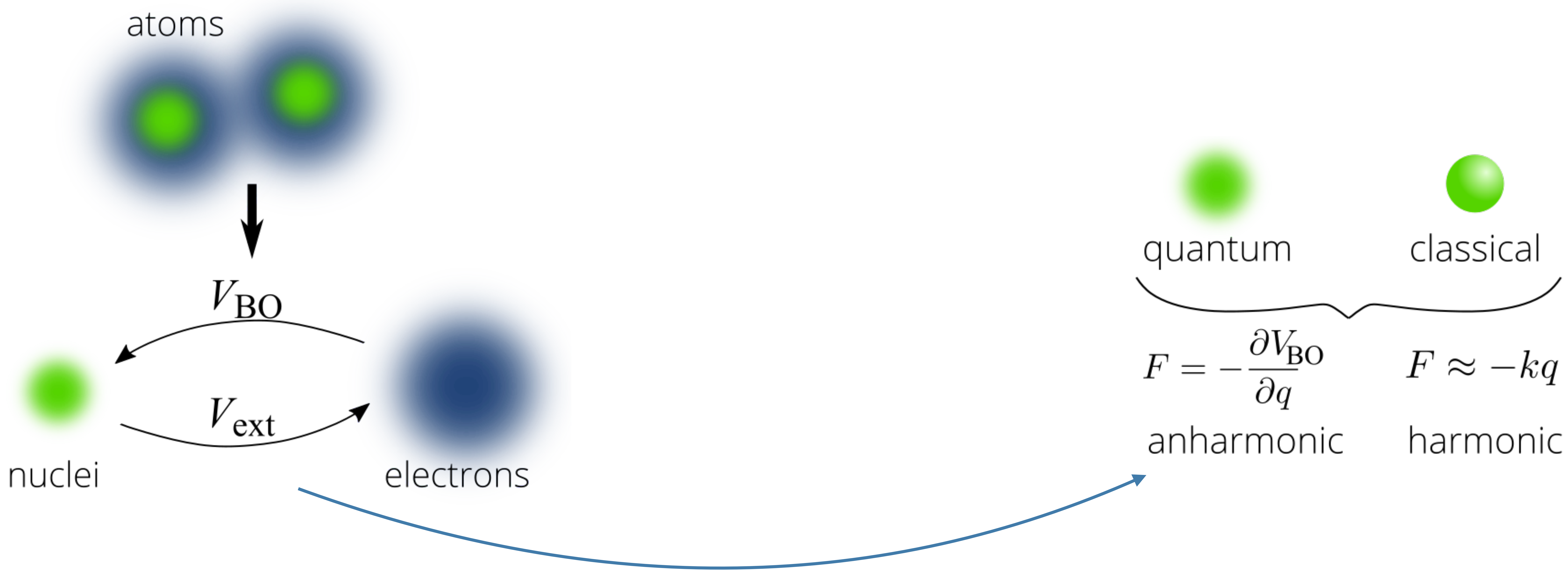

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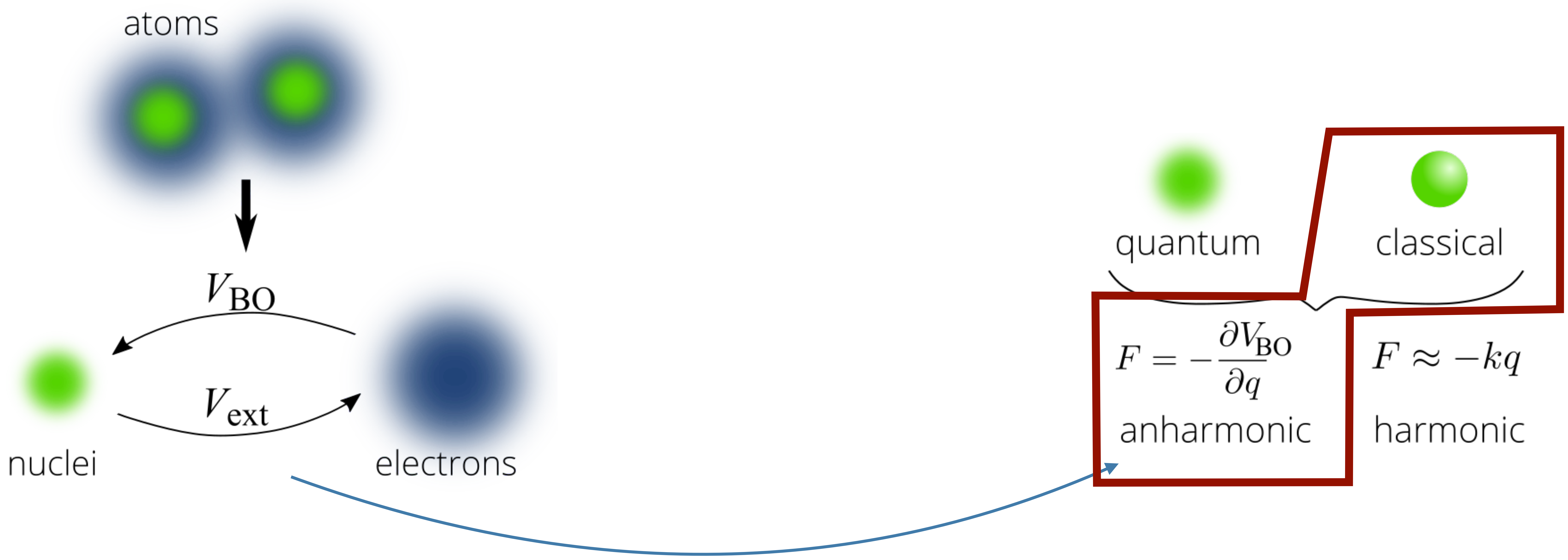

atoms

V_{BO}

V_{ext}

nuclei

electrons

$$\underbrace{\text{quantum} \qquad \text{classical}}$$

$F = -\dfrac{\partial V_{\mathrm{BO}}}{\partial q}$

anharmonic

$F \approx -kq$

harmonic

Nuclear Hamiltonian (classical) and the canonical ensemble

$$H(\mathbf{p}, \mathbf{q}) = \sum_{I=1}^{N} \frac{p_I^2}{2M_I} + V_{BO}(q_1, \ldots, q_N)$$

- Probability in the canonical ensemble (*N*, *V*, *T* fixed) given by

$$\mathscr{P}(p, q) = \frac{e^{-\beta H(p,q)}}{Z} \qquad \beta = 1/k_B T \qquad Z = \int dp \int dq e^{-\beta H(p,q)}$$

Probabilities and averages

- In classical mechanics, positions and momenta are ***not*** correlated

$$\mathscr{P}(p,q) = \mathscr{P}(p)\mathscr{P}(q) = \frac{e^{-\beta p^2/2M}}{\int dp e^{-\beta p^2/2M}} \frac{e^{-\beta V(q)}}{\int dq e^{-\beta V(q)}}$$

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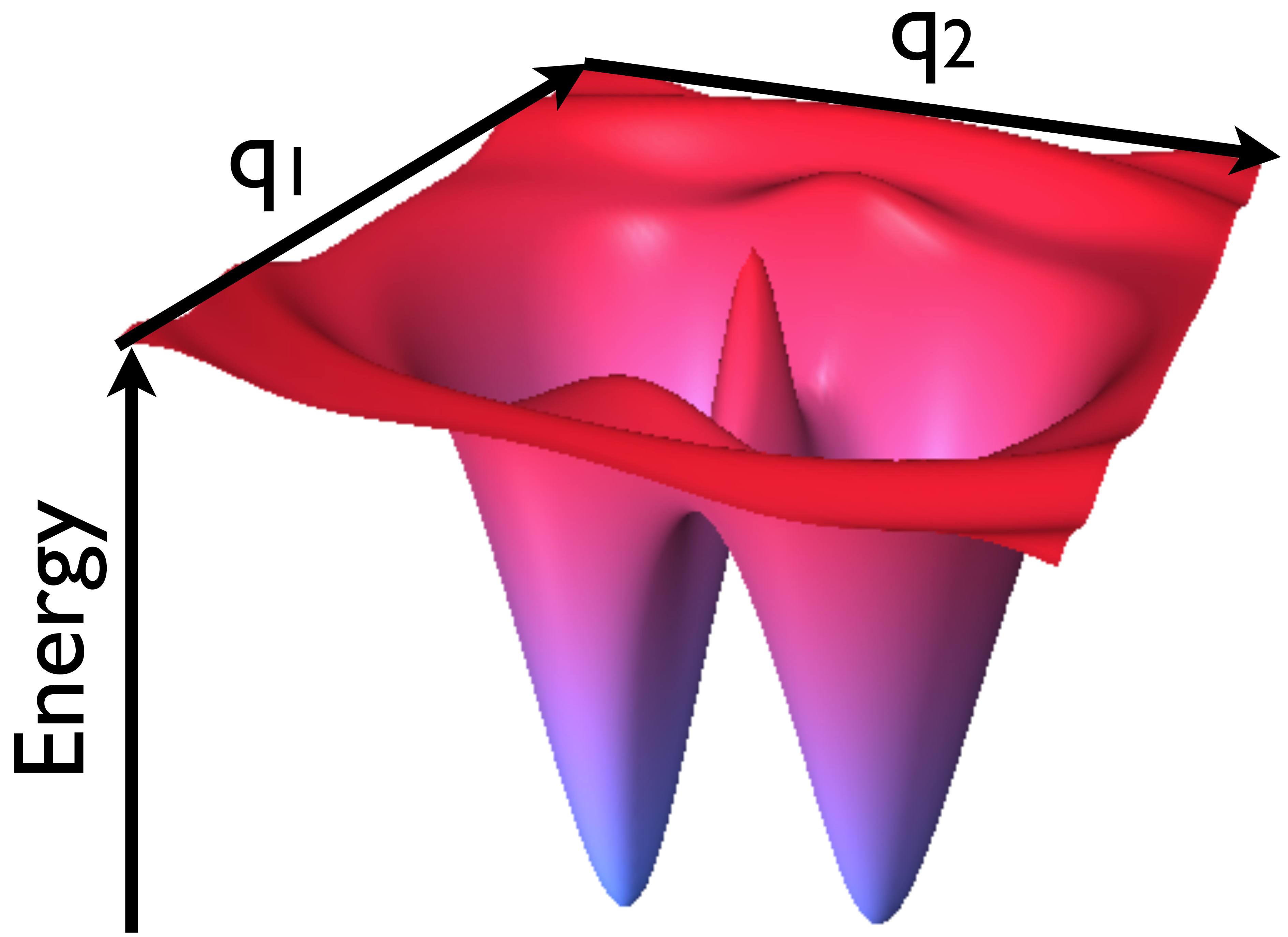
- The blue term is easy to calculate, while the red term tends to be very difficult. Important because:

$$\langle A(q) \rangle = \int dp dq \mathscr{P}(p,q) A(q) = \int dq A(q) \mathscr{P}(q)$$

$$\langle A(q_0) B(q_t) \rangle = \int dp dq \mathscr{P}(p,q) A(q_0) B(q_t) = \int dq \mathscr{P}(q) A(q_0) B(q_t)$$

Static and equilibrium properties at finite *T*

$$\langle A(q) \rangle = \int dp\,dq\,\mathscr{P}(p,q)A(q) = \int dq\,A(q)\mathscr{P}(q)$$



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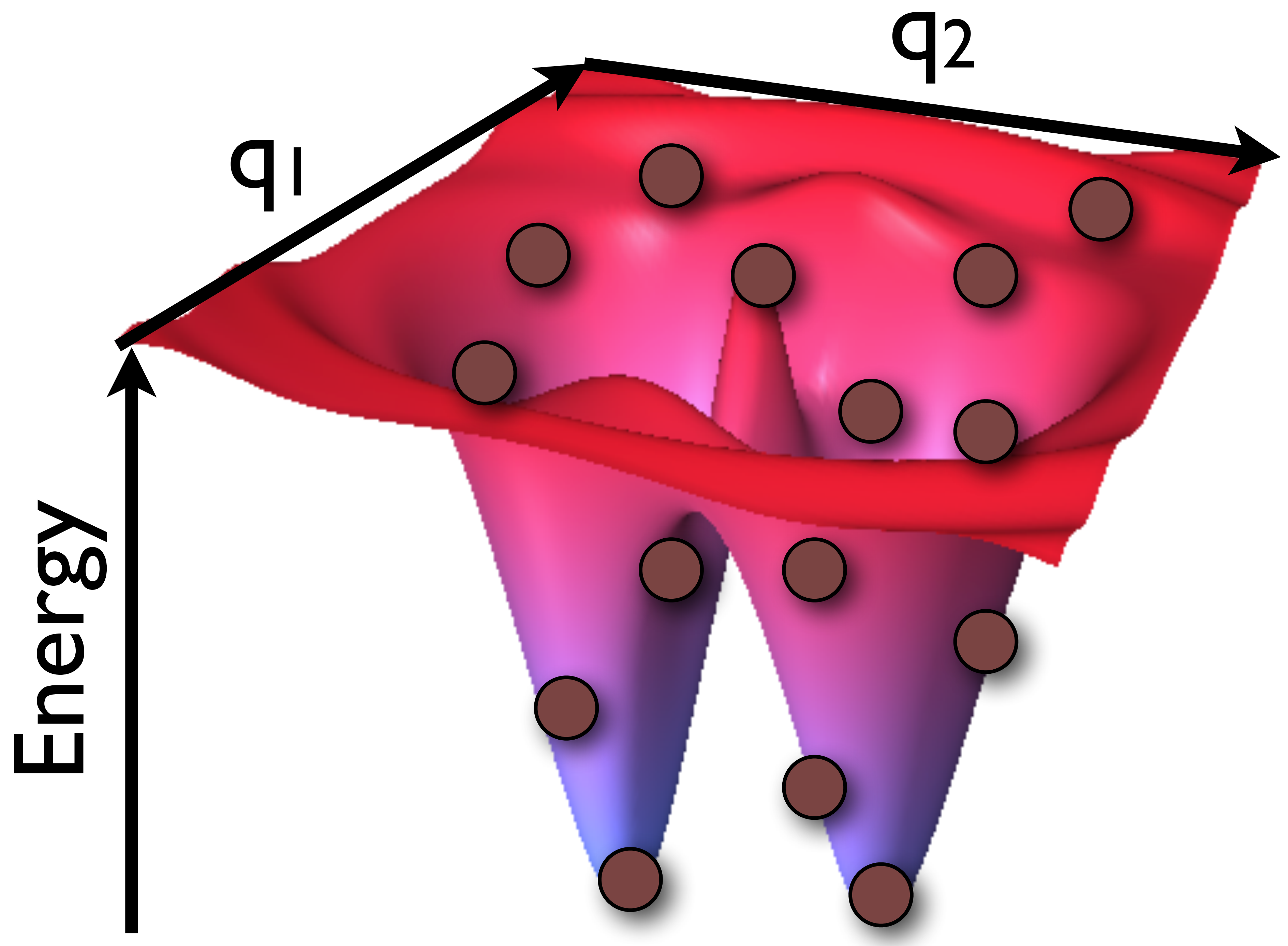

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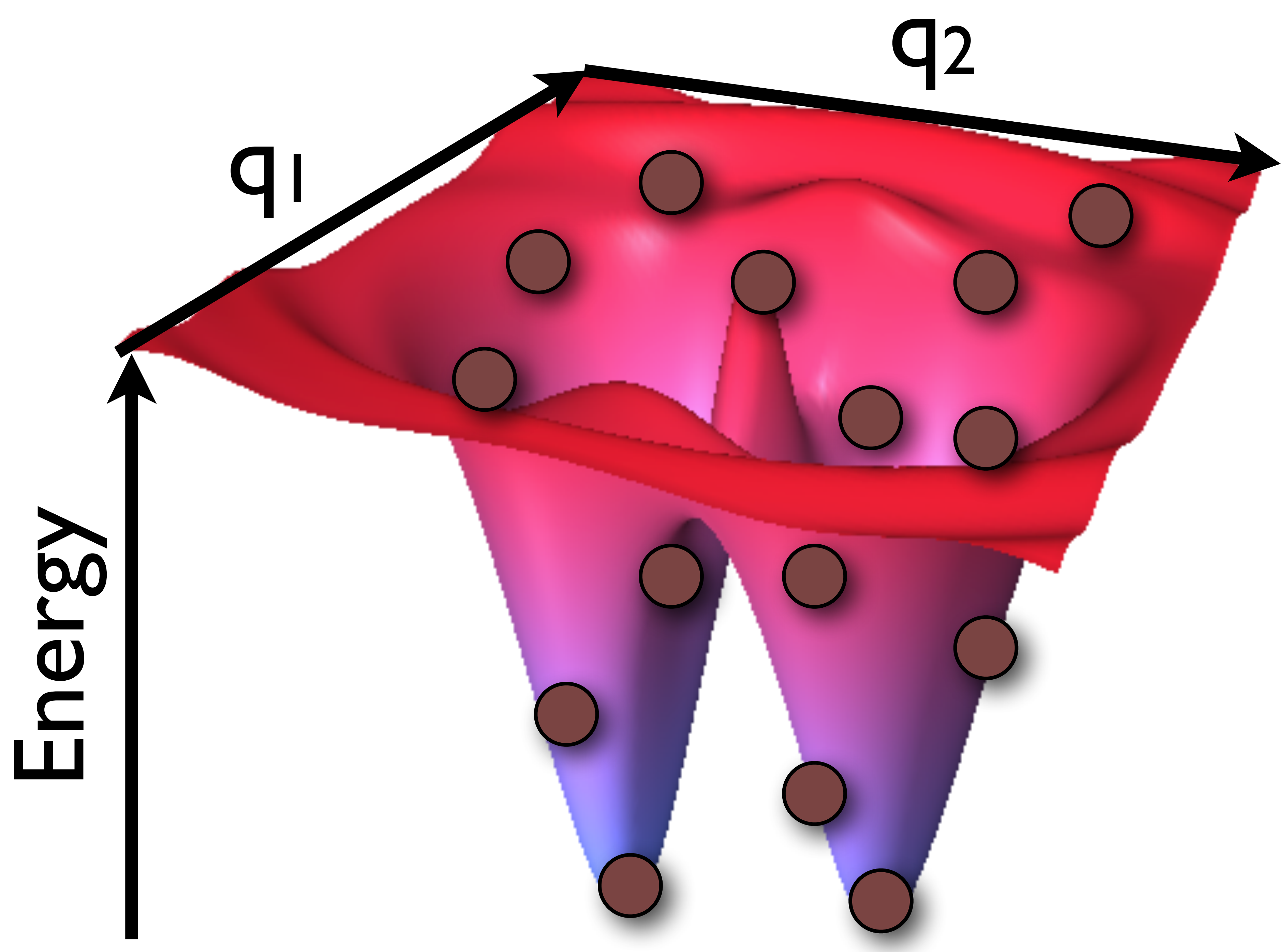
- Calculating such integrals on a grid scales as G^{3N} (G grid points, N atoms)
- Instead, it is better to perform some sort of importance sampling



Static and equilibrium properties at finite *T*

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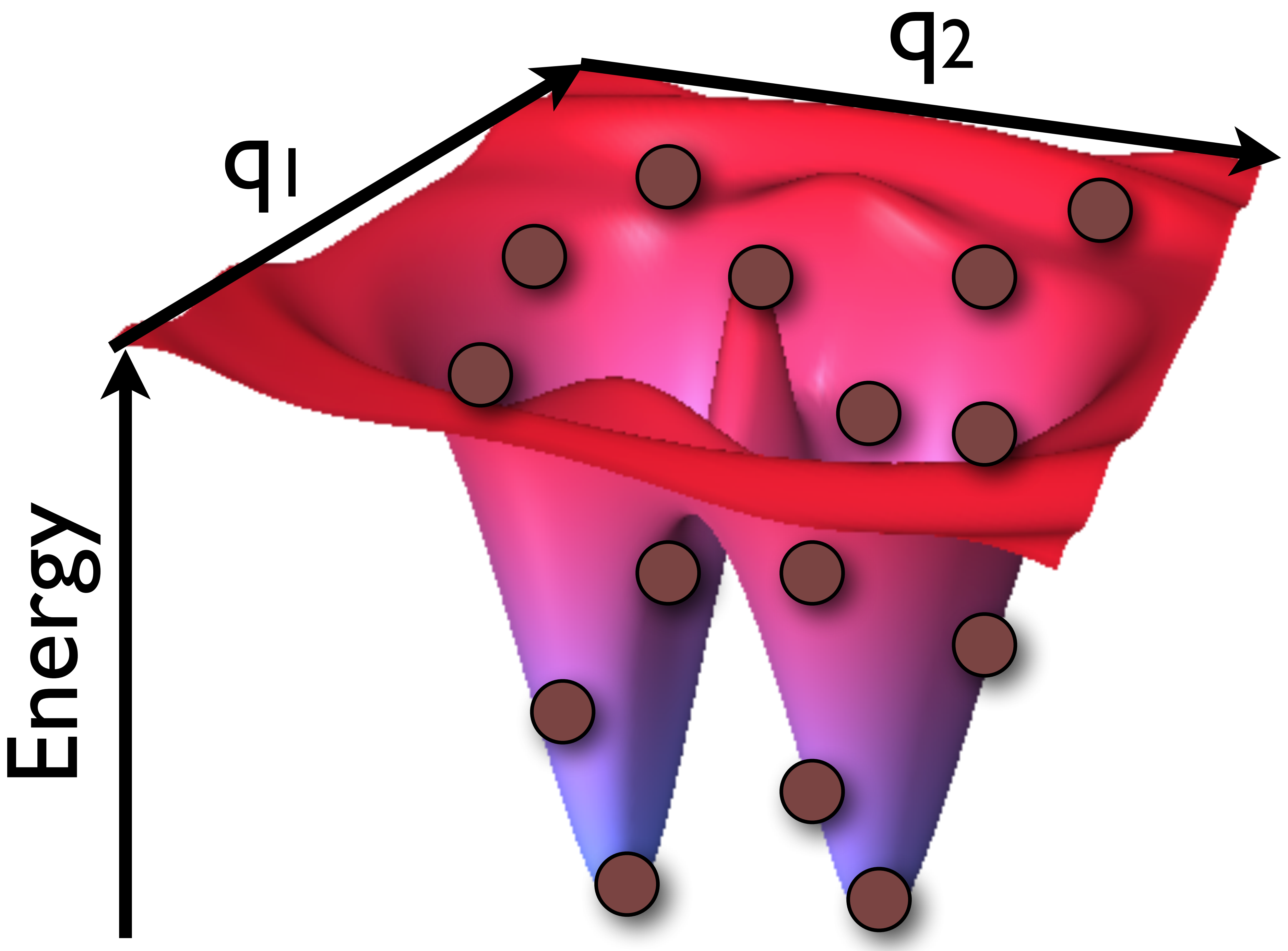
- Calculating such integrals on a grid scales as G^{3N} (G grid points, N atoms)
- Instead, it is better to perform some sort of importance sampling
- Generate many configurations q_s according to $\mathscr{P}(q)$ and calculate

$$\langle A(q)\rangle \approx \frac{1}{M}\sum_{s=1}^{M} A(q_s)$$



The Hamiltonian time evolution

$$H(\mathbf{p}, \mathbf{q}) = \sum_I \frac{p_I}{2M} + V_{BO}(q_1, \ldots, q_N)$$

$$\dot{q}_I = \frac{\partial H}{\partial p_I} = \frac{p_I}{M_I} \qquad \dot{p}_I = -\frac{\partial H}{\partial q_I} = -\nabla_I V(q)$$

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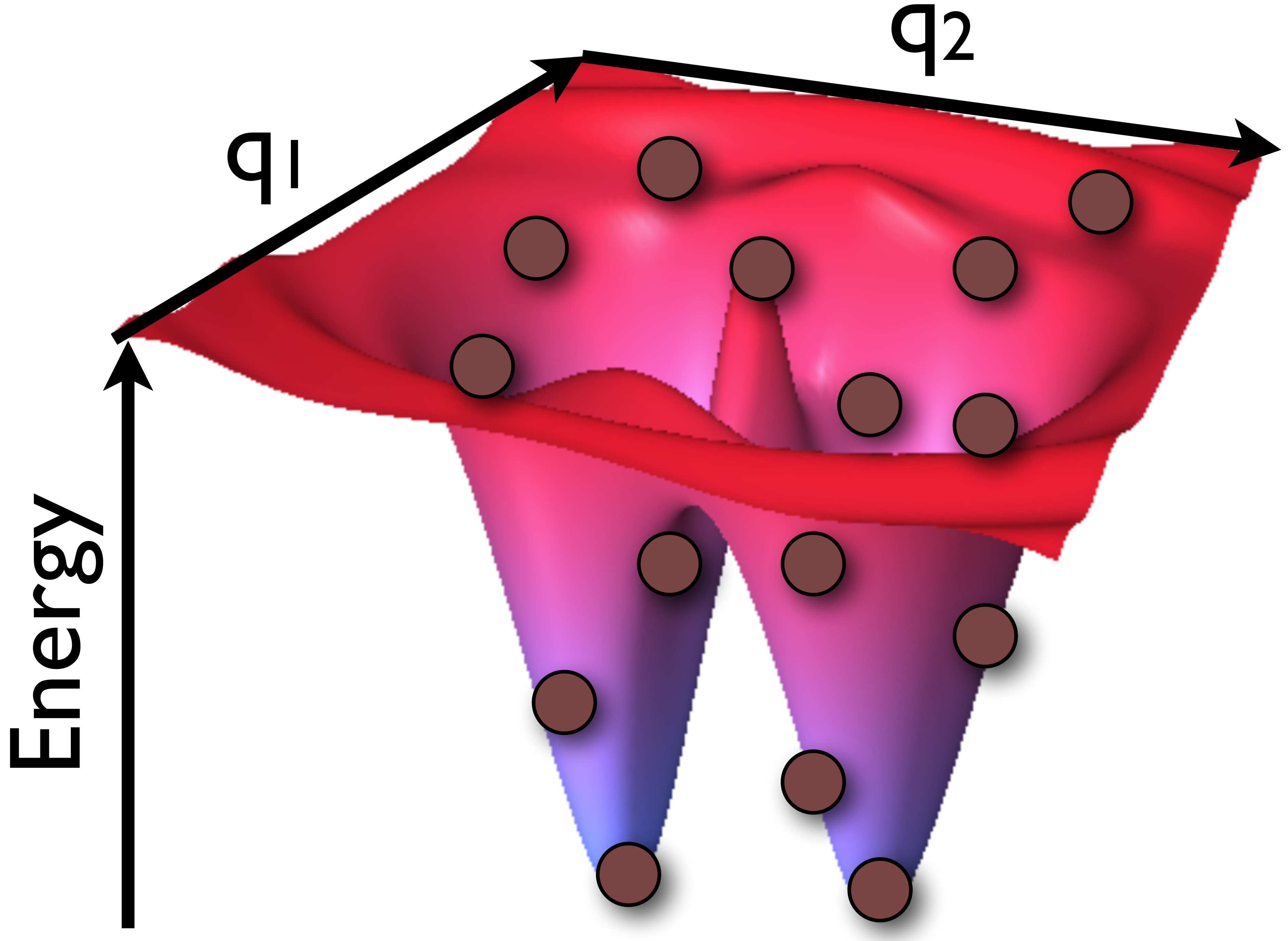
- Configurations created by this time evolution are consistent with and conserve $\mathscr{P}(p, q)$

$$\frac{d\mathscr{P}(p, q)}{dt} \propto e^{-\beta H} \frac{dH}{dt} = 0 \qquad \mathscr{P}(p_0, q_0) = \mathscr{P}(p_t, q_t)$$

Static and equilibrium properties at finite *T*

- Ergodic hypothesis: ensemble average equal to time average

$$\langle A(q)\rangle = \int dp\,dq\,\mathscr{P}(p,q)A(q) = \mathbf{lim}_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau} A[q(t)]dt$$



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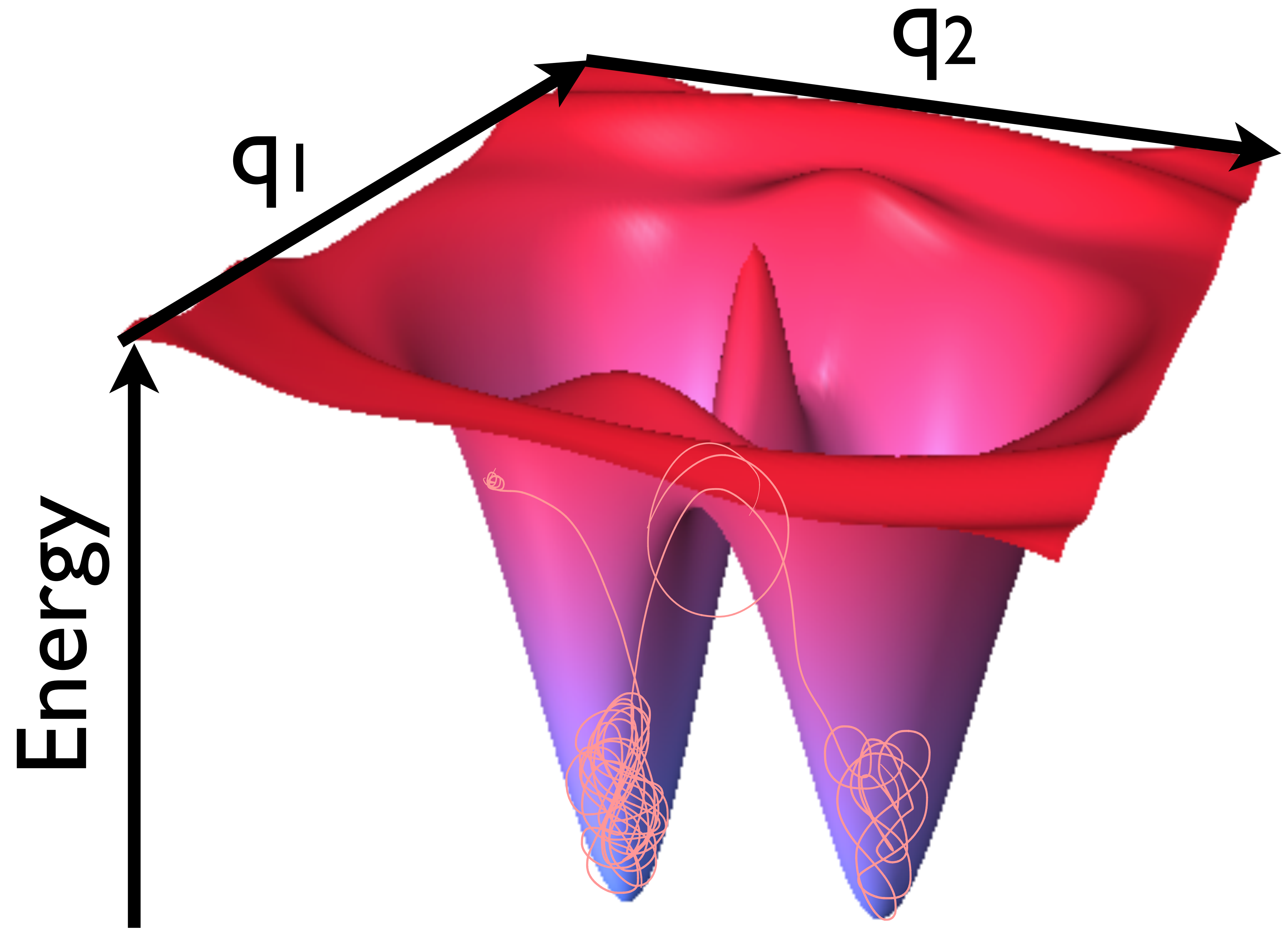

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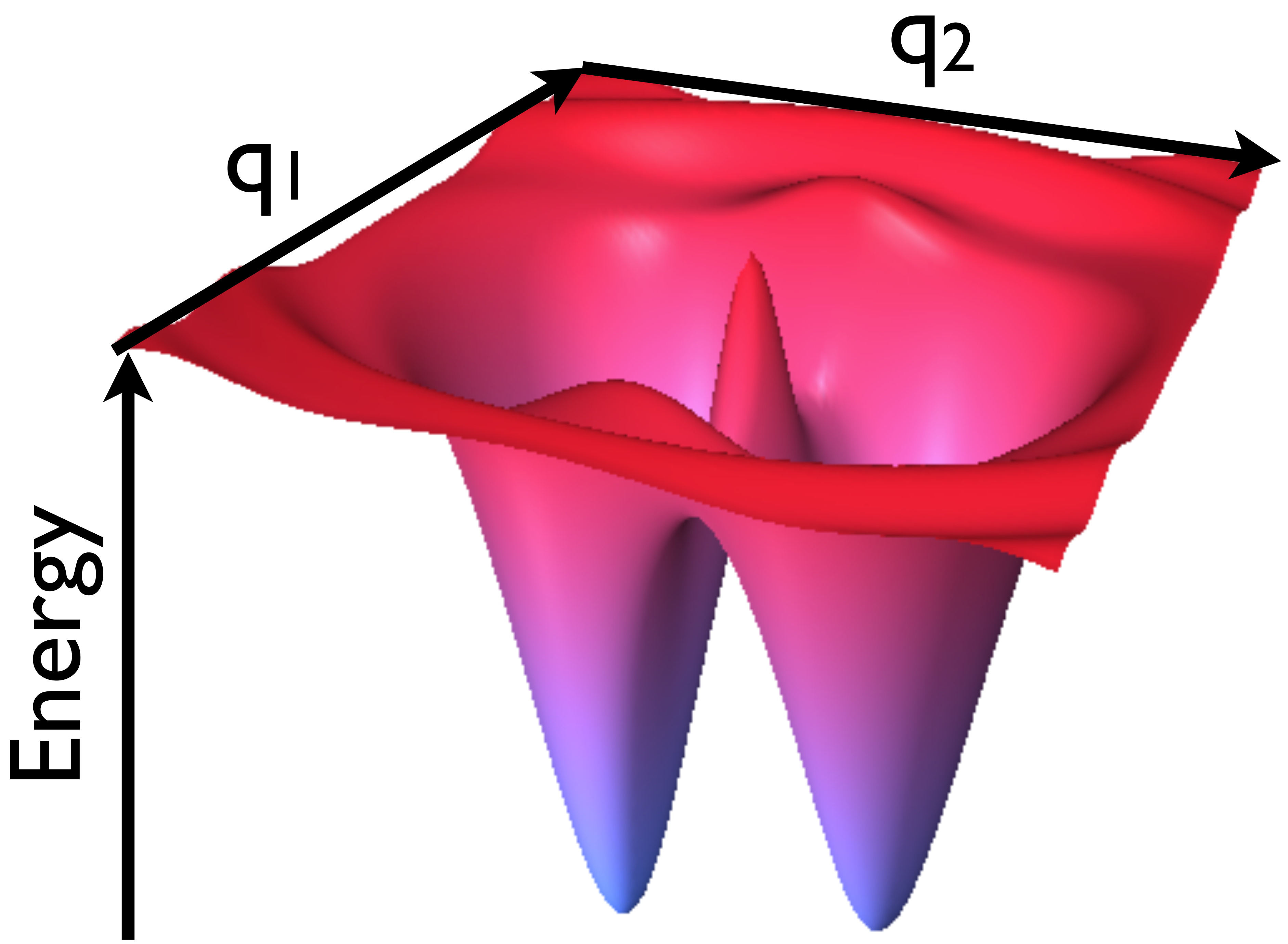
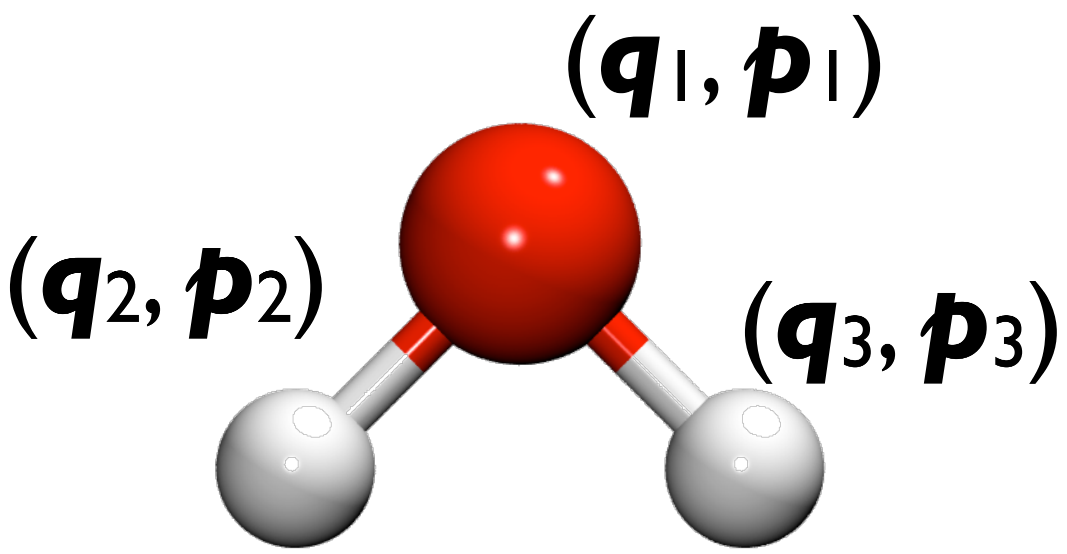
Can be calculated through “molecular dynamics”



How to get (classical) trajectories?

Molecular dynamics



1. Assign initial $\boldsymbol{q}$ (position) and $\boldsymbol{p}$ (momenta)

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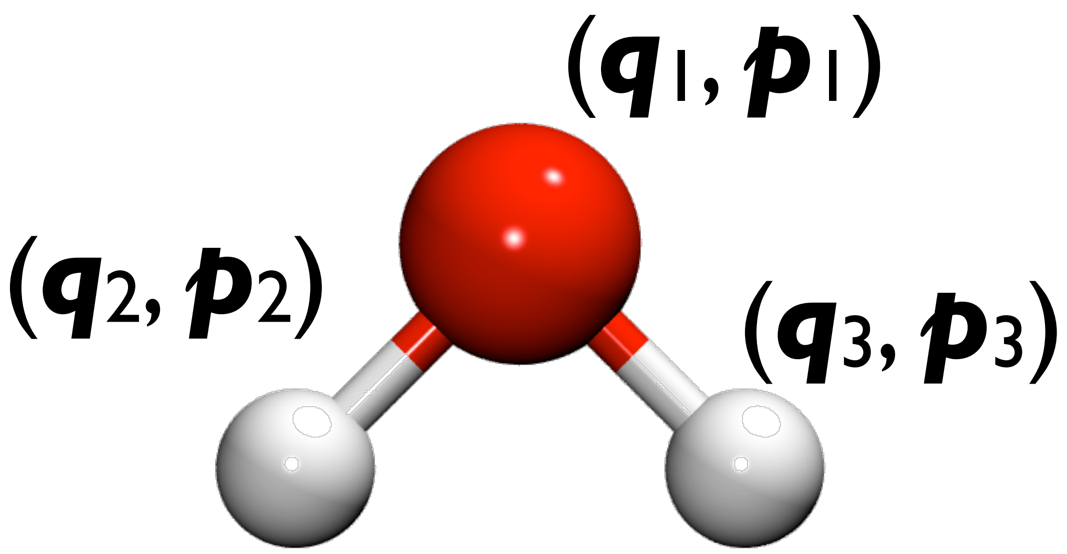

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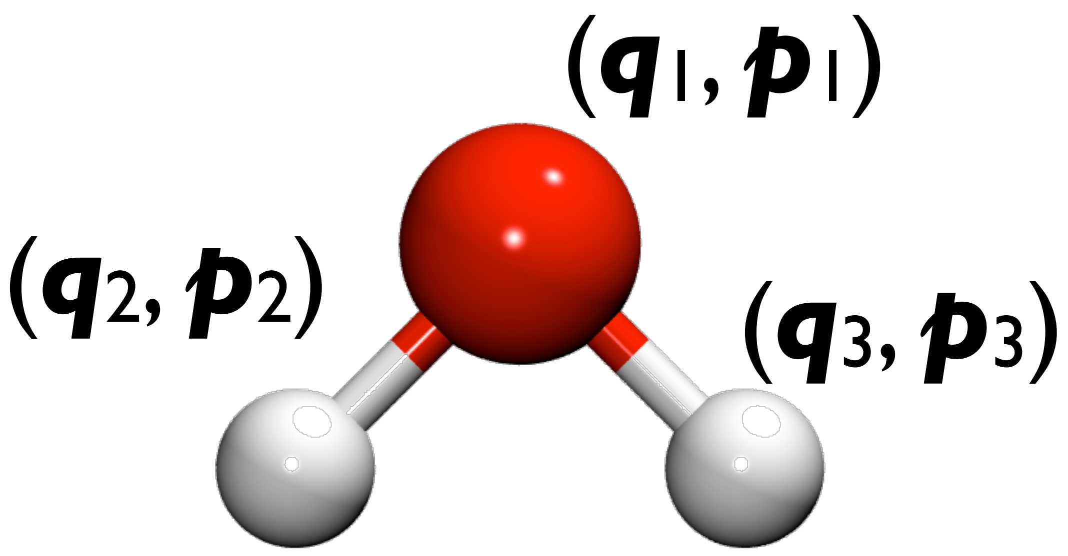

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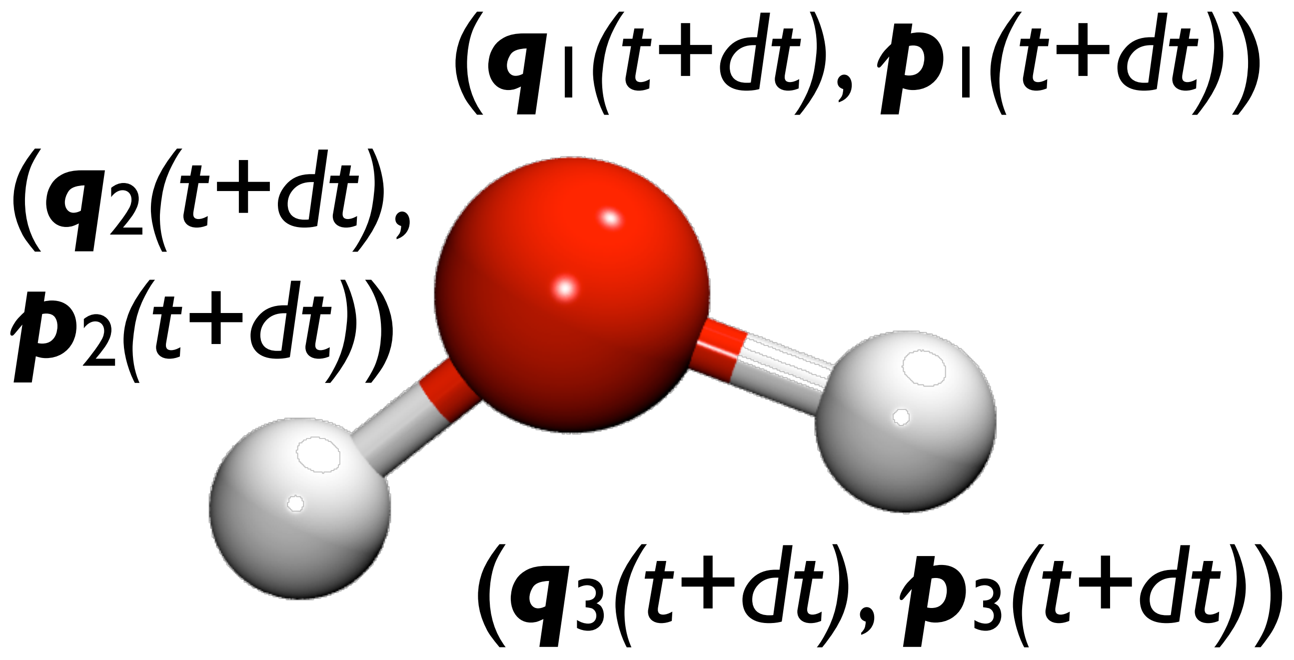

3. Assign new position and momenta

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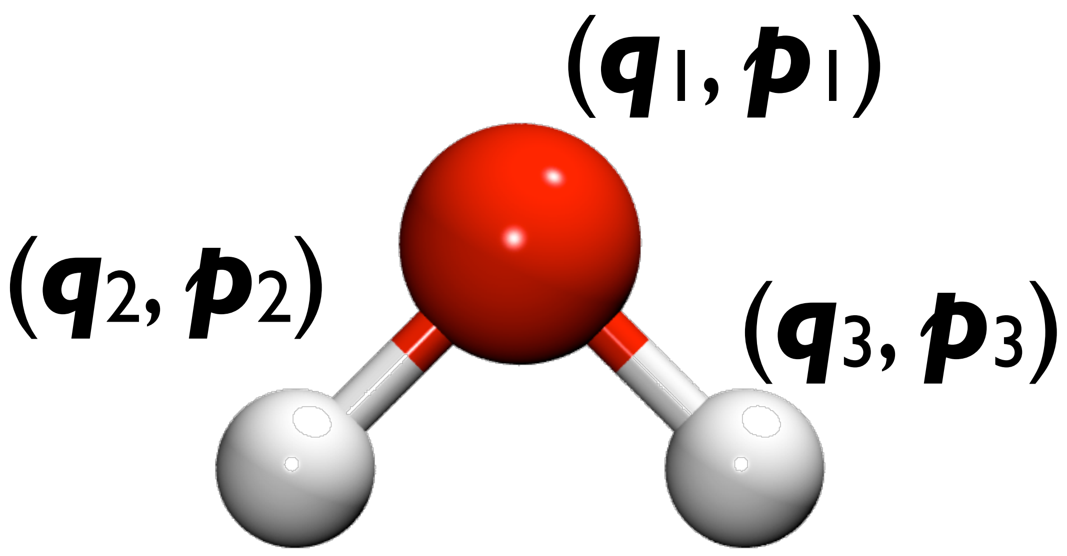

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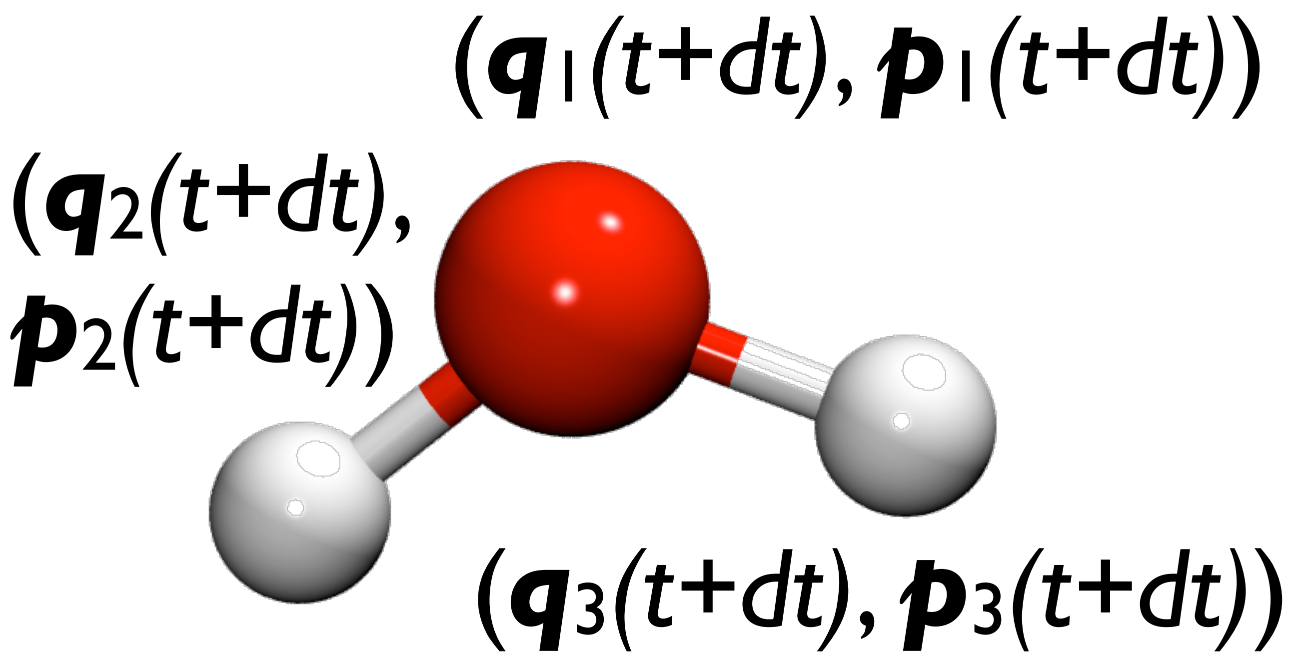

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Integrating the equations of motion

- Taylor expansion of q

$$q(t+\Delta t) = q(t) + \Delta t \dot{q}(t) + \frac{1}{2}\ddot{q}(t)\Delta t^2 + \mathcal{O}(\Delta t^3)$$

Integrating the equations of motion

- Taylor expansion of *q*

$$\begin{array}{l}
q(t+\Delta t) = q(t) + \Delta t\dot{q}(t) + \frac{1}{2}\ddot{q}(t)\Delta t^2 + \mathcal{O}(\Delta t^3) \\
q(t-\Delta t) = q(t) - \Delta t\dot{q}(t) + \frac{1}{2}\ddot{q}(t)\Delta t^2 - \mathcal{O}(\Delta t^3) \\
+ \\
\hline
q(t+\Delta t) + q(t-\Delta t) = 2q(t) + \ddot{q}(t)\Delta t^2 + \mathcal{O}(\Delta t^4)
\end{array}$$

$$\ddot{q}(t) \longrightarrow -\frac{\nabla V(q(t))}{M} = \frac{F(t)}{M}$$

Integrating the equations of motion

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$$q(t+\Delta t) + q(t-\Delta t) = 2q(t) + \ddot{q}(t)\Delta t^2 + \mathcal{O}(\Delta t^4)$$

$$-\frac{\nabla V(q(t))}{M} = \frac{F(t)}{M}$$

- "Velocity Verlet"

$$\dot{q}(t+\Delta t) = \dot{q}(t) + \frac{F(t)}{M}\Delta t$$

"Verlet" is time reversible and symplectic

Symmetric splitting of velocity Verlet

- Implemented in most codes (including FHI-aims)

One Step

$$\dot{q}(t+\frac{\Delta t}{2}) = \dot{q}(t) + \frac{F(t)}{M}\frac{\Delta t}{2}$$

$$q(t+\Delta t) = q(t) + \dot{q}(t+\frac{\Delta t}{2})\Delta t$$

Evaluate $F(t+\Delta t)$ **from** $q(t+\Delta t)$

$$\dot{q}(t+\Delta t) = \dot{q}(t+\frac{\Delta t}{2}) + \frac{F(t+\Delta t)}{M}\frac{\Delta t}{2}$$

Compute any instantaneous properties at step Δt

The *ab initio* forces

“Evaluate $F(t+\Delta t)$ from $q(t+\Delta t)$”

$$F(q) = -\nabla_q[\mathbf{min}_\rho E[\rho]]$$

- Calculating these forces tends *not to be trivial* within an electronic structure architecture

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- In FHI-aims we have (at least!):

$$F = \underset{\substack{\nearrow\\\text{Hellman-Feynman}}}{F^{HF}} + \underset{\substack{\nearrow\\\text{Pulay}\\\text{(incl. GGA, mGGA,}\\\text{and relativity)}}}{F^{P}} + \underset{\substack{\uparrow\\\text{Non self-consistent}\\\text{Hartree pot.}}}{F^{NSC}} + \underset{\substack{\nwarrow\\\text{Hartree pot.}\\\text{multipole expansion}}}{F^{mp}}$$

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Hellman-Feynman

Pulay
(incl. GGA, mGGA,
and relativity)

Non self-consistent
Hartree pot.

Hartree pot.
multipole expansion

$$+F^{vdW} + F^{exx} + \dots$$

The Hellman-Feynman and Pulay forces

- The Harris functional

$$E[\rho] = \sum_i f_i \varepsilon_i - \frac{1}{2}\int \rho(\mathbf{r})\nu_H d\mathbf{r} - \int \rho(\mathbf{r})\nu_{xc} d\mathbf{r} + E_{xc}[\rho] + E_{NN}$$

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$$\frac{1}{2}\sum_{IJ}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

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$$\rightarrow \boxed{\frac{1}{2}\sum_{IJ}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}}$$

- The forces

$$F = -\frac{\delta E[\rho(r;R),\boxed{R}]}{\delta R} \quad \equiv q$$

- Hellman-Feynman forces

$$\underline{\epsilon_i = \langle \psi_i | \hat{h}_{KS} | \psi_i \rangle}$$

$$F^{HF} = -\frac{\partial E_{NN}}{\partial R_I} - \int \rho_{KS}(\mathbf{r})\frac{\partial \nu_{ext}}{\partial R_I} d\mathbf{r}$$

The Hellman-Feynman and Pulay forces

- Pulay forces come from

$$\sum_i f_i \delta\varepsilon_i = \sum_i f_i \langle \psi_i | \delta\hat{h}_{KS} | \psi_i \rangle + \boxed{\sum_i f_i \langle \delta\psi_i | \hat{h}_{KS} | \psi_i \rangle + \sum_i f_i \langle \psi_i | \hat{h}_{KS} | \delta\psi_i \rangle}$$

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- By using $\psi_i = \sum_\mu c_{\mu i}\varphi_\mu$ and $\sum_\mu c_{i\mu}h_{\mu\nu} = \epsilon_i \sum_\mu c_{i\mu}s_{\mu\nu}$, plus imposing $\delta\langle\psi_i|\psi_i\rangle = \delta(\sum_{\mu\nu} s_{\mu\nu}c^*_{i\mu}c_{i\nu}) = 0$

$$F_c^P = -2\mathbf{Re}\left[\sum_{i\mu\nu} f_i c^*_{i\mu} c_{i\nu} \langle \frac{\partial\varphi_\mu}{\partial R} | \hat{h}_{KS} - \epsilon_i | \varphi_\nu \rangle \right]$$

- “Beyond LDA” functionals and relativistic corrections add further terms to the Pulay forces. *See Blum et al., CPC (2009)*

Hartree potential non-self-consistent force correction

- Still not the whole story. The energy functional at a given m SCF step is actually

$$E^{(m)}[\rho] = \sum_i f_i^{(m)} \varepsilon_i^{(m)} - \frac{1}{2}\int \rho^{(m-1)}(\mathbf{r})\nu_H^{(m-1)} d\mathbf{r} - \int \rho^{(m-1)}(\mathbf{r})\nu_{xc}^{(m-1)} d\mathbf{r} + E_{xc}[\rho^{(m-1)}] + E_{NN}$$

Mixed density at step *m*-1

- After some math we get

$$F^{NSC} = \int (\rho^{(m-1)}(\mathbf{r}) - \rho_{KS}^{(m)}(\mathbf{r})) \frac{\delta \nu_H^{(m-1)}}{\delta R_I} d\mathbf{r} + \int (\rho^{(m-1)}(\mathbf{r}) - \rho_{KS}^{(m)}(\mathbf{r})) \frac{\delta \nu_{xc}^{(m-1)}}{\delta R_I} d\mathbf{r}$$

Unmixed density at step *m*

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Unmixed density at step *m*

Implemented in 2021 by Herzain Rivera & Mariana Rossi

Need of accurate self-consistency

- Hamiltonian dynamics (microcanonical ensemble): Energy should be conserved!
- How close to self consistency do we need to be?

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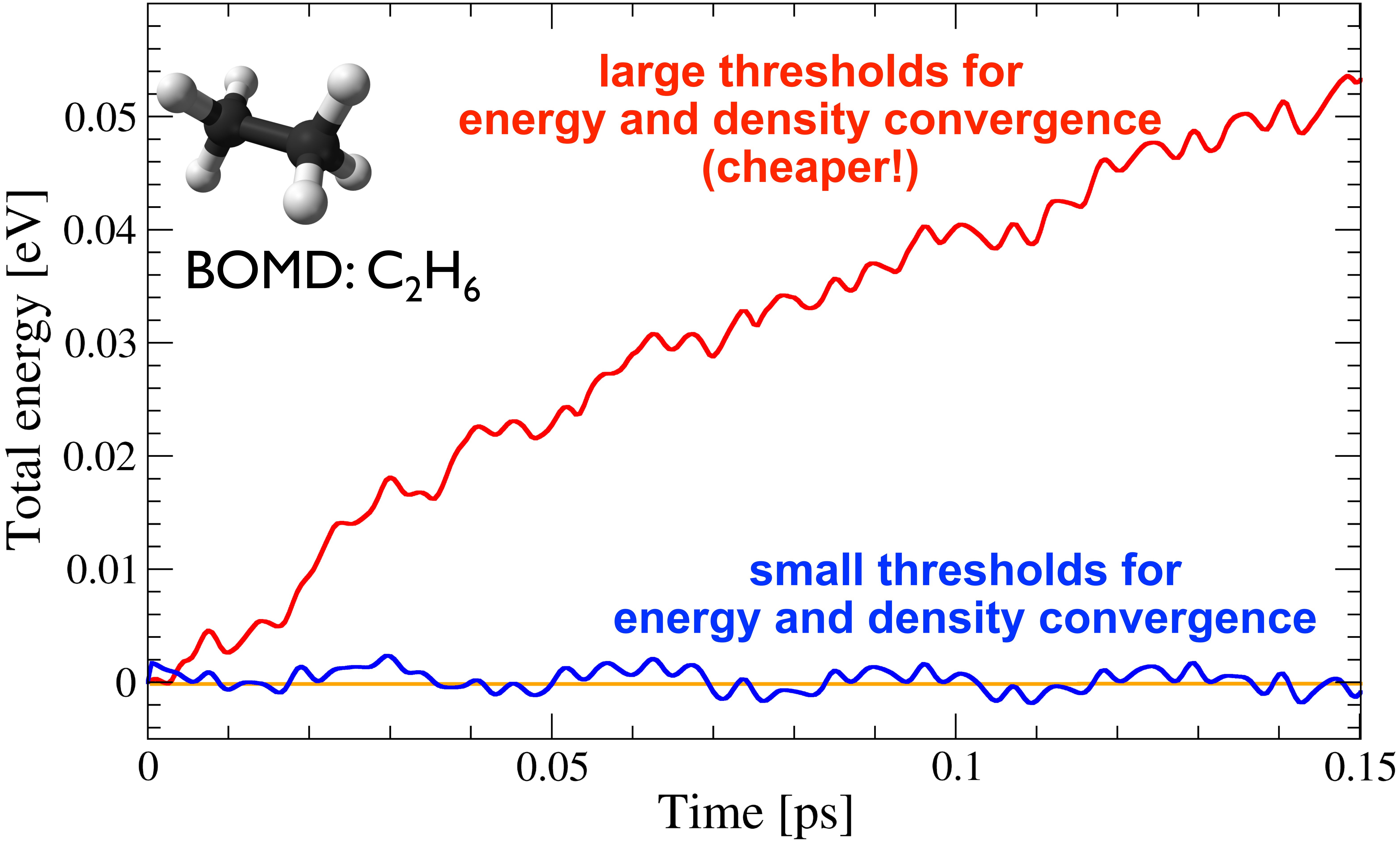
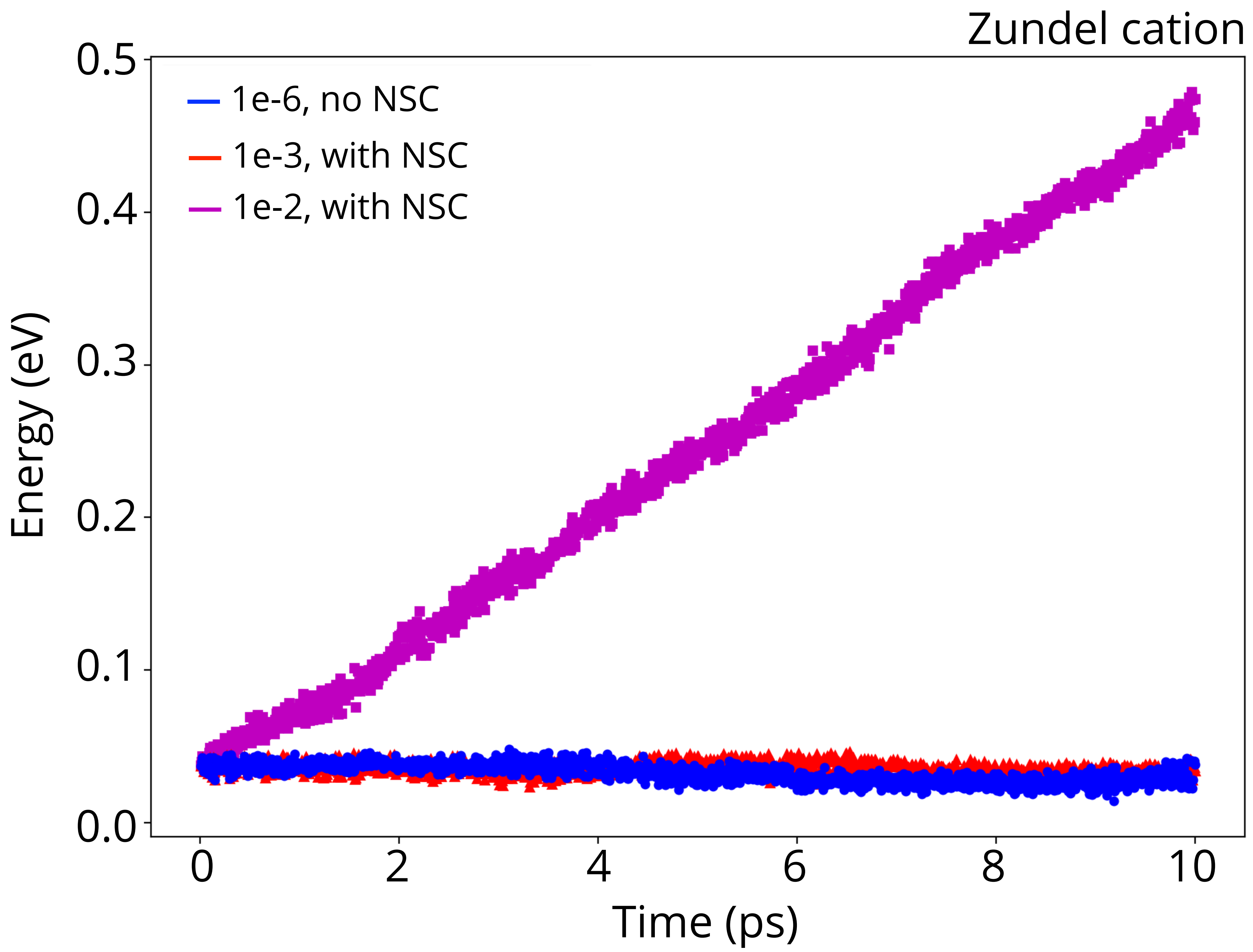


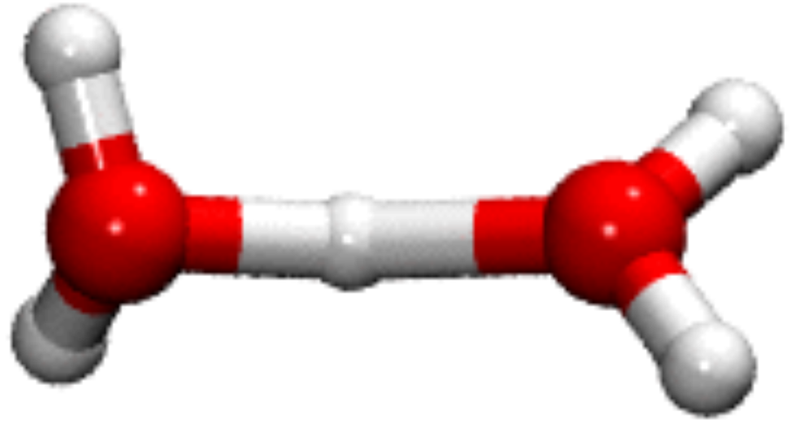
Hartree potential non-self-consistent force correction

- Impact of non-self-consistent force correction term from Hartree potential



Time step and the accuracy of integration

$\Delta t = 3\text{fs}$



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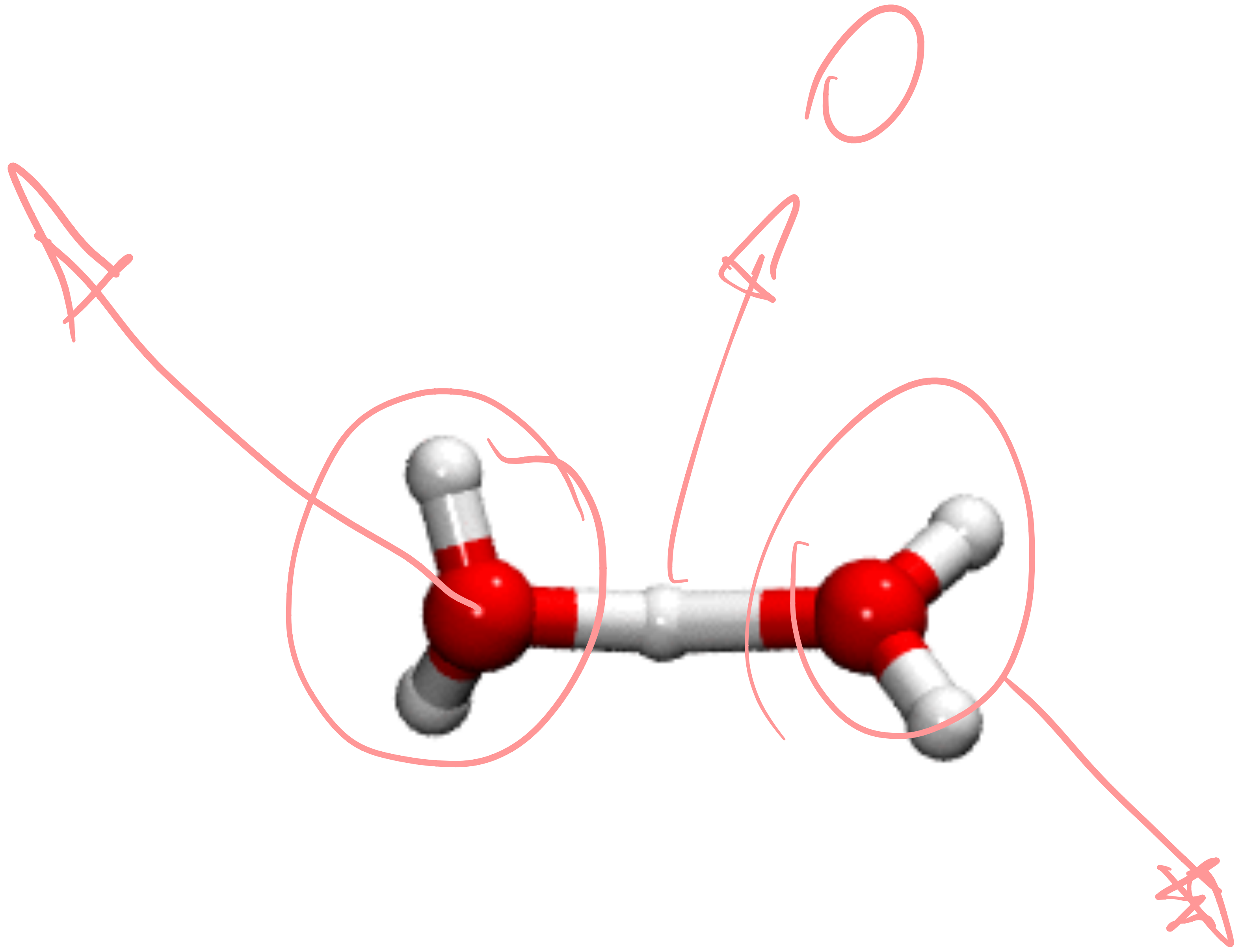

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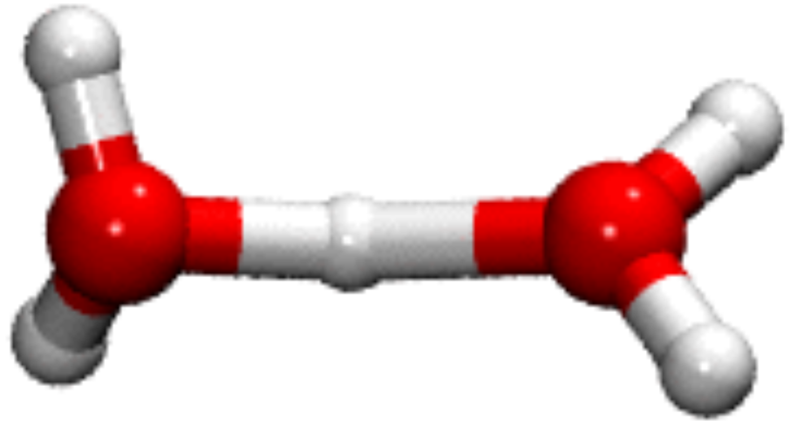

- What is a good time step?
  - Depends on the highest vibrational frequency (thus mass) of your system ($\omega \approx \sqrt{k/M}$)
  - Typically, choose a time step corresponding to ~$1/(10\omega_{max})$ (femtosecond time scale)

A bit about Car-Parrinello MD

R. Car and M. Parrinello, Phys. Rev. Lett. ***55****, 2471-2474 (1985)*

- Extended Lagrangian: add (fictitious) degrees of freedom for the electrons in the Lagrangian and solve coupled equations of motion

$$\mathcal{L} = \frac{1}{2}\left[\sum_I M_I \dot{\mathbf{R}}_I^2 + \mu \sum_i \int d\mathbf{r} |\dot{\phi}_i(\mathbf{r},t)|^2\right] - V(\phi,\phi^*;\mathbf{R}) + \underset{ij}{\sum} 2\lambda_{ij}\left[\int d\mathbf{r}\,\phi_i^*(\mathbf{r},t)\phi_j(\mathbf{r},t) - \delta_{ij}\right]$$

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Fictitious electron mass

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Fictitious electron mass

Kohn-Sham orbitals

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I V(\phi, \phi^*; \mathbf{R})$$

$$\mu \ddot{\phi}_i = -\frac{1}{2}\frac{\delta V(\phi, \phi^*; \mathbf{R})}{\delta \phi_i^*} + \sum_j \phi_j \lambda_{ji}$$

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R. Car and M. Parrinello, Phys. Rev. Lett. ***55****, 2471-2474 (1985)*

- Extended Lagrangian: add (fictitious) degrees of freedom for the electrons in the Lagrangian and solve coupled equations of motion

Lagrange multipliers

$$\mathcal{L} = \frac{1}{2}\left[\sum_I M_I \dot{\mathbf{R}}_I^2 + \mu \sum_i \int d\mathbf{r} |\dot{\phi}_i(\mathbf{r},t)|^2\right] - V(\phi, \phi^*, \mathbf{R}) + 2\lambda_{ij}\left[\int d\mathbf{r}\phi_i^*(\mathbf{r},t)\phi_j(\mathbf{r},t) - \delta_{ij}\right]$$

Fictitious electron mass

Kohn-Sham orbitals

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I V(\phi, \phi^*; \mathbf{R}) \qquad \mu\ddot{\phi}_i = -\frac{1}{2}\frac{\delta V(\phi, \phi^*; \mathbf{R})}{\delta \phi_i^*} + \sum_j \phi_j \lambda_{ji}$$

- Adiabatic separation: fictitious mass of the electrons need to be very small ⇒ smaller time step

- Electrons “follow” nuclei - *avoids* self consistency calculation at every step

Other Acceleration Techniques

J. Kolafa JCC 25, 335 (2004);T. Kühne, et al. PRL 98, 066401 (2007); Steneteg et al., PRB 82, 075110 (2010); Niklasson JCTC 16 (2020)

- Idea: Use a very good guess for the wave function of the "next step". Ensuring time-reversibility is key for stability of propagation.

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- Naïve (and frequently used): Use converged electronic density from previous step
- More involved:
  - Extrapolate electronic density (or flavors of the density matrix) based on information of previous time steps
  - Formulate types of extended Lagrangian formalisms with auxiliary variables (density, wave functions) that move in a harmonic potential around the self-consistent solution

$$\phi_i = \sum_j c_{ij} \underbrace{\varphi_j}_{\textit{Basis Sets}} \qquad \boldsymbol{\phi} = \mathbf{C}\boldsymbol{\varphi} \qquad \underbrace{\mathbf{P}}_{\textit{Density Matrix}} = \mathbf{C}^T\mathbf{C}$$

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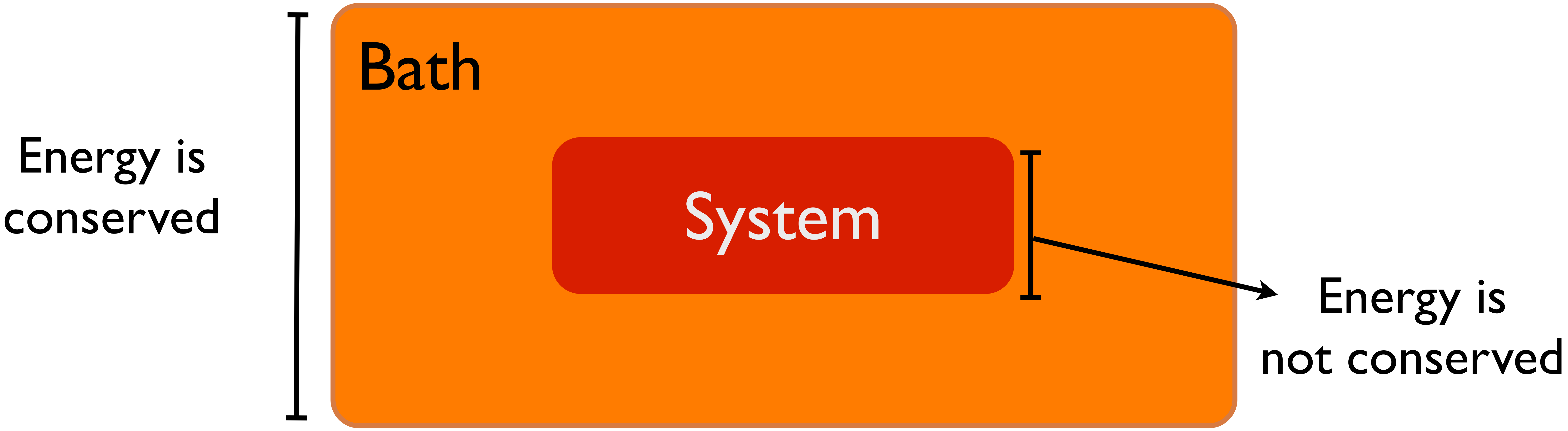
- Some of these techniques have been implemented in FHI-aims with limited success. Ongoing efforts!

Temperature control: the canonical ensemble

- The idea: couple the system to a thermostat (heat bath)
- Interesting because:
  - Experiments are usually done at constant temperature
  - Better modeling of conformational changes



Bath

System

Energy is conserved

Energy is not conserved

Nosé-Hoover thermostat

S. Nosé, *J. Chem. Phys.* **81**, 511 (1984) & W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).

Extended Hamiltonian (or Lagrangian):

$$\mathcal{H}_{NH} = \sum_I \frac{\mathbf{p}_I^2}{2M_I} + V(\mathbf{R}) + \frac{p_\eta^2}{2Q} + 3Nk_BT\eta$$

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Extended Hamiltonian (or Lagrangian):

$$\mathcal{H}_{NH} = \underset{\text{Original system}}{\boxed{\sum_I \frac{\mathbf{p}_I^2}{2M_I} + V(\mathbf{R})}} + \underset{\text{Fictitious Oscillator}}{\boxed{\frac{p_\eta^2}{2Q} + 3Nk_BT\eta}}$$

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Original system

Fictitious Oscillator

- Momenta are damped by fictitious oscillator: $\dot{\mathbf{p}}_I = \mathbf{F}_I - \frac{p_\eta}{Q}\mathbf{p}_I$

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- Momenta are damped by fictitious oscillator: $\dot{\mathbf{p}}_I = \mathbf{F}_I - \frac{p_\eta}{Q}\mathbf{p}_I$
- Ergodicity problems - system may be stuck in a region of phase space
  - Possible solution: Nosé-Hoover chains
    Attach another fictitious oscillator to the first, and another to the second, and another to the third, ... (chain of fictitious oscillators)

Martyna, Klein, Tuckerman, *J. Chem. Phys.* **97**, 2635 (1992)

How to model a thermostat: first ideas

- Temperature rescaling: Berendsen “thermostat”
  - Rescale velocities by a factor containing the ratio of target and instant temperature
  - Does not sample the canonical ensemble (wrong temperature distribution)
  - “Flying ice-cube” effect: rotations and translations acquire high E_{kin} and vibrations are frozen

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- Simple stochastic idea: Andersen thermostat
  - At each n^{th} time-step, replace velocity of a random particle by one drawn from a Maxwell-Boltzmann distribution at target temperature
  - Not very efficient, no conserved quantity
  - Very sensitive on *n*

H. C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980)

Stochastic Velocity Rescaling

G. Bussi, D. Donadio, and M. Parrinello, *J. Chem. Phys.* **126**, 014101 (2007).

Combine concepts from velocity rescaling (fast!) with concepts from stochastic thermostats (accurate!)

Target temperature follows a stochastic differential equation:

$$\frac{dT}{\bar{T}} = \left[1 - \frac{T(t)}{\bar{T}}\right] \frac{dt}{\tau} - 2\sqrt{\frac{T(t)}{3\bar{T}N\tau}}\xi(t)$$

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Temperature rescaling

White noise

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- Very successful thermostat, weakly dependent on relaxation time τ
- Pseudo-Hamiltonian is conserved

Bussi, Parrinello, *Phys. Rev. E* **75**, 056707 (2007)

Langevin (stochastic) thermostat

S. A. Adelman and J. D. Doll, *J. Chem. Phys.* **64**, 2375 (1976).

Model dynamics via the Langevin equation:

$$M_I \ddot{\mathbf{R}}_I = \mathbf{F}_I - \gamma_I \dot{\mathbf{R}}_I + \xi(t)$$

$$\langle \xi(t) \xi(0) \rangle = 2 k_B T \gamma \delta(t)$$

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Original system

Friction and White Noise

$$\langle \xi(t)\xi(0)\rangle = 2k_BT\gamma\delta(t)$$

- Sensitive on γ
  - For systems spanning a wide range of frequencies, how to achieve the “best” critical damping?
- Disturbs dynamics considerably

Colored noise thermostats

M. Ceriotti, G. Bussi, M. Parrinello, *JCTC* **2010**, 6, 1170-1180 (**http://gle4md.org/index.html**)

Extremely flexible class of thermostats based on the
Generalized Langevin Equation (GLE)

- Markovian (no memory) process in high dimensions

$$\begin{pmatrix} \dot{p} \\ \dot{\mathbf{s}} \end{pmatrix} = \begin{pmatrix} -V'(R) \\ 0 \end{pmatrix} - \mathbf{A}_p \begin{pmatrix} p \\ \mathbf{s} \end{pmatrix} + \mathbf{B}_p \left(\boldsymbol{\xi} \right)$$

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- Non-Markovian process for the system (integrating out ***s***):

$$\dot{p} = F - \int_{-\infty}^{t} d\tau K(t-\tau)p(\tau) + \zeta(t)$$

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Memory Kernel

Colored Noise

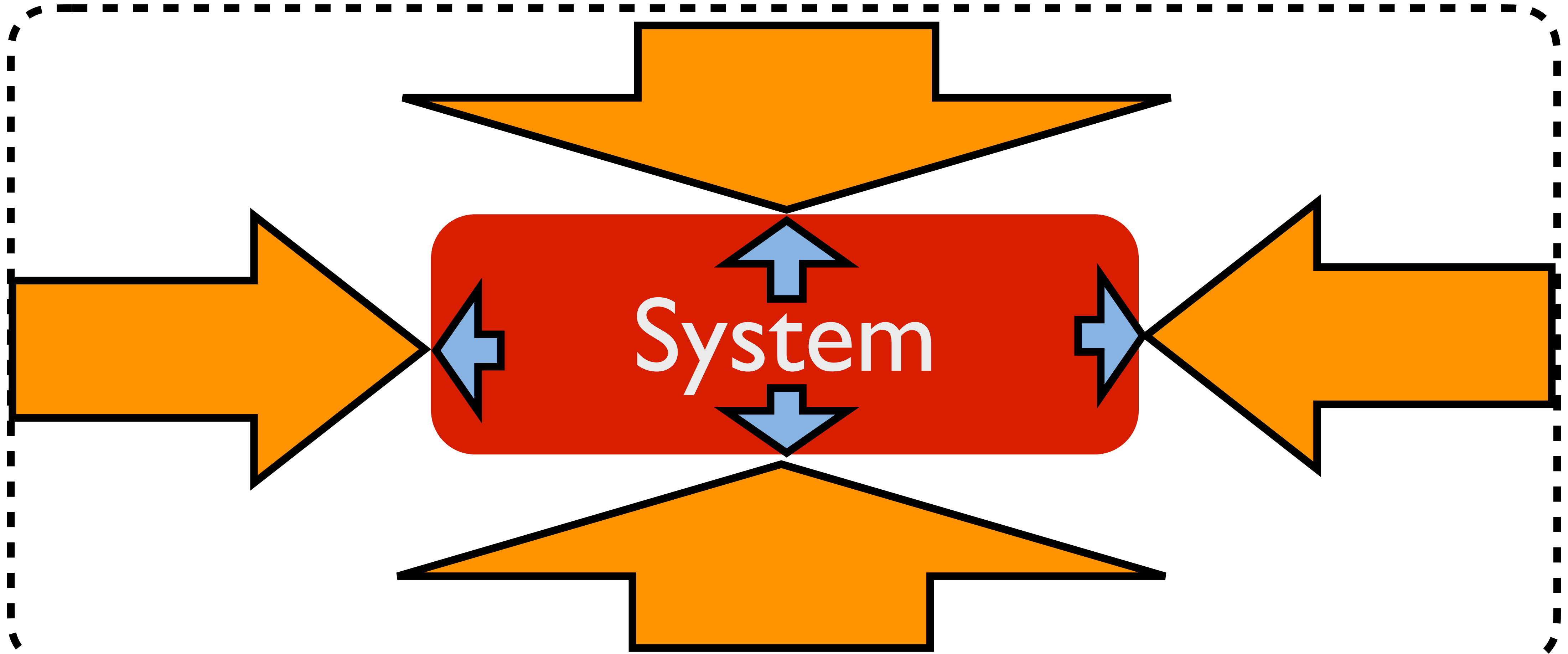
Fluctuation Dissipation: $H(t) = \langle\zeta(t)\zeta(0)\rangle = k_B T K(t)$

Pressure control: Isobaric-isothermic ensemble

- Definition of instantaneous pressure:

$$P_{\alpha\beta}^{(\mathrm{int})} = -\frac{1}{\det(\boldsymbol{h})}\sum_{\gamma=1}^{3}\boxed{\frac{\partial E[\{\psi\},\mathbf{R}]}{\partial h_{\alpha\gamma}}}\,h_{\beta\gamma} + P_{\alpha\beta}^{\mathrm{T}}$$

Stress Tensor



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Parinello and Rahman, J. Appl. Phys 52, 7182 (1981);
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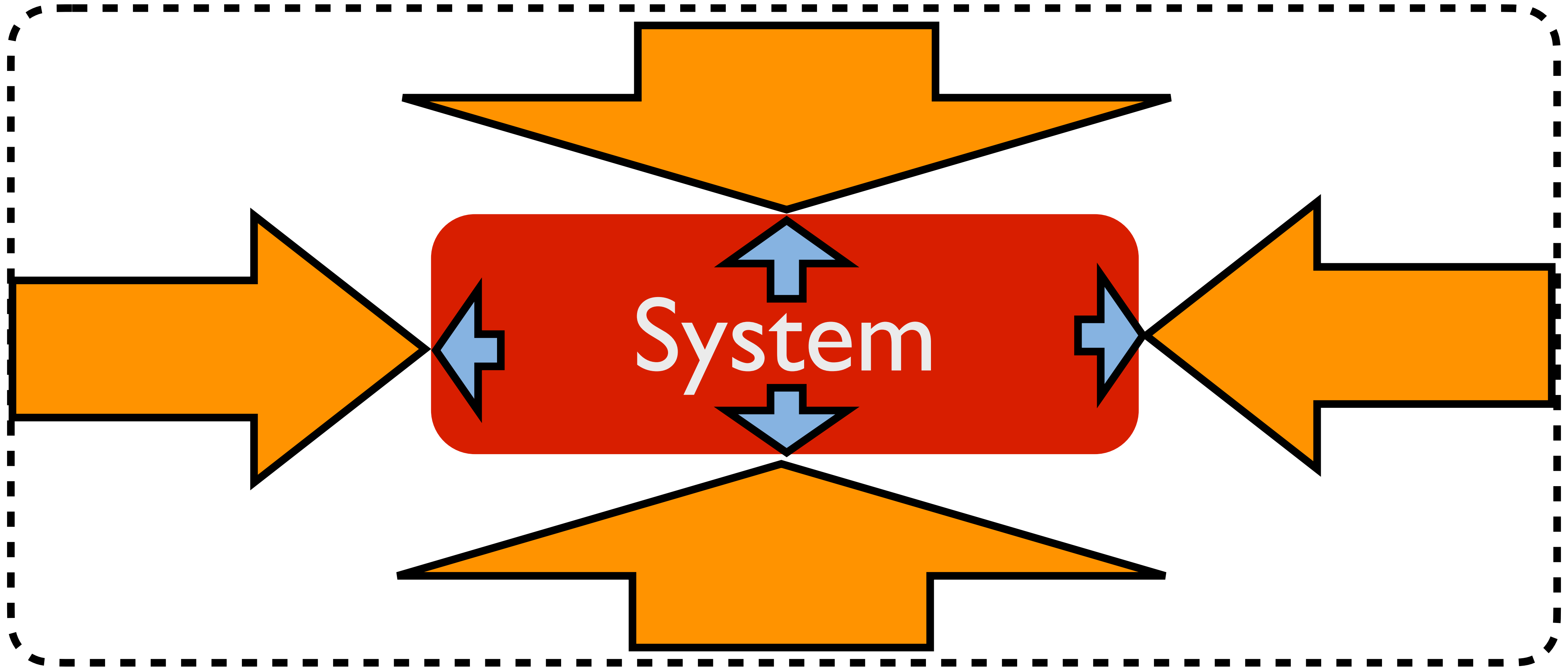

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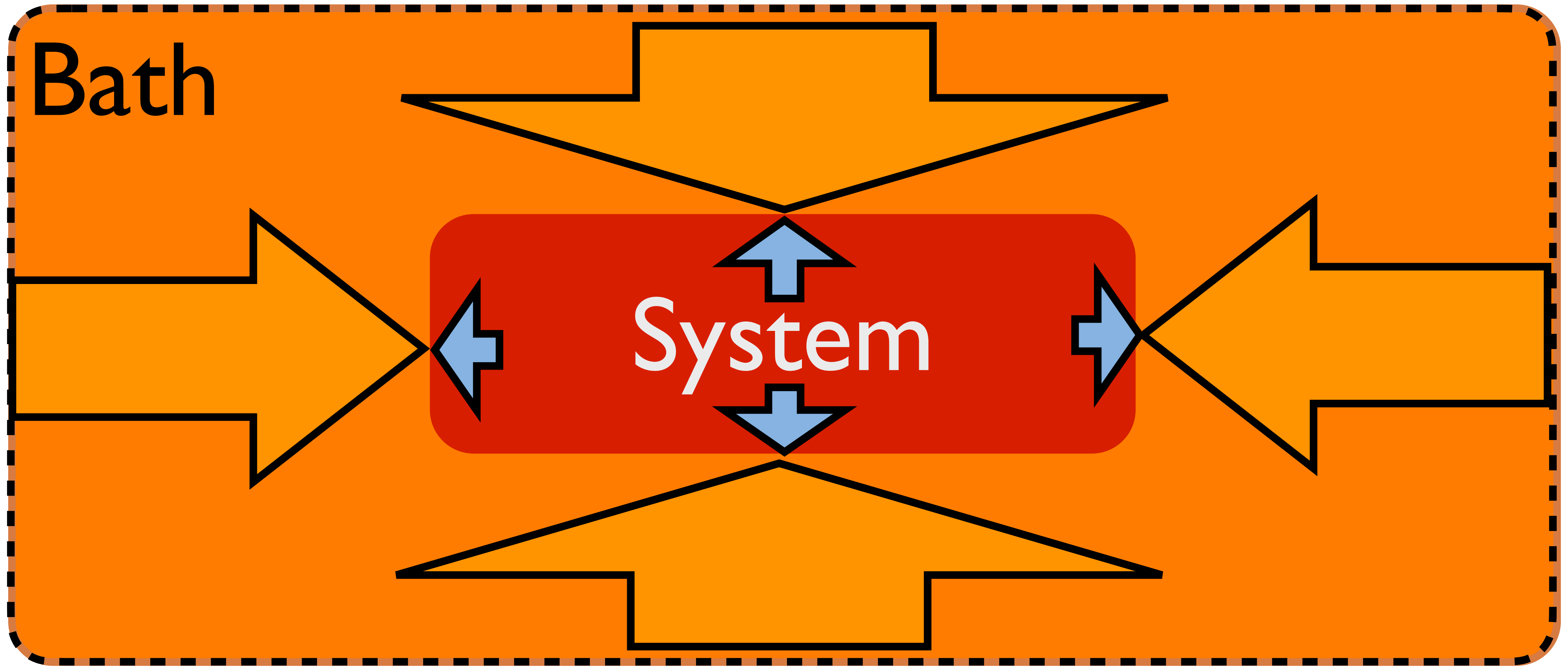
- Use thermostat together with a barostat to control pressure and temperature



The i-PI wrapper code: sockets interface

- The i-PI code is a python interface for the calculation of (path integral *ab initio*) molecular dynamics
- i-PI communicates with the electronic structure codes through internet (or UNIX) sockets, making it extremely flexible
- Interfaced to many electronic structure codes (check our webpage!)

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http://ipi-code.org/

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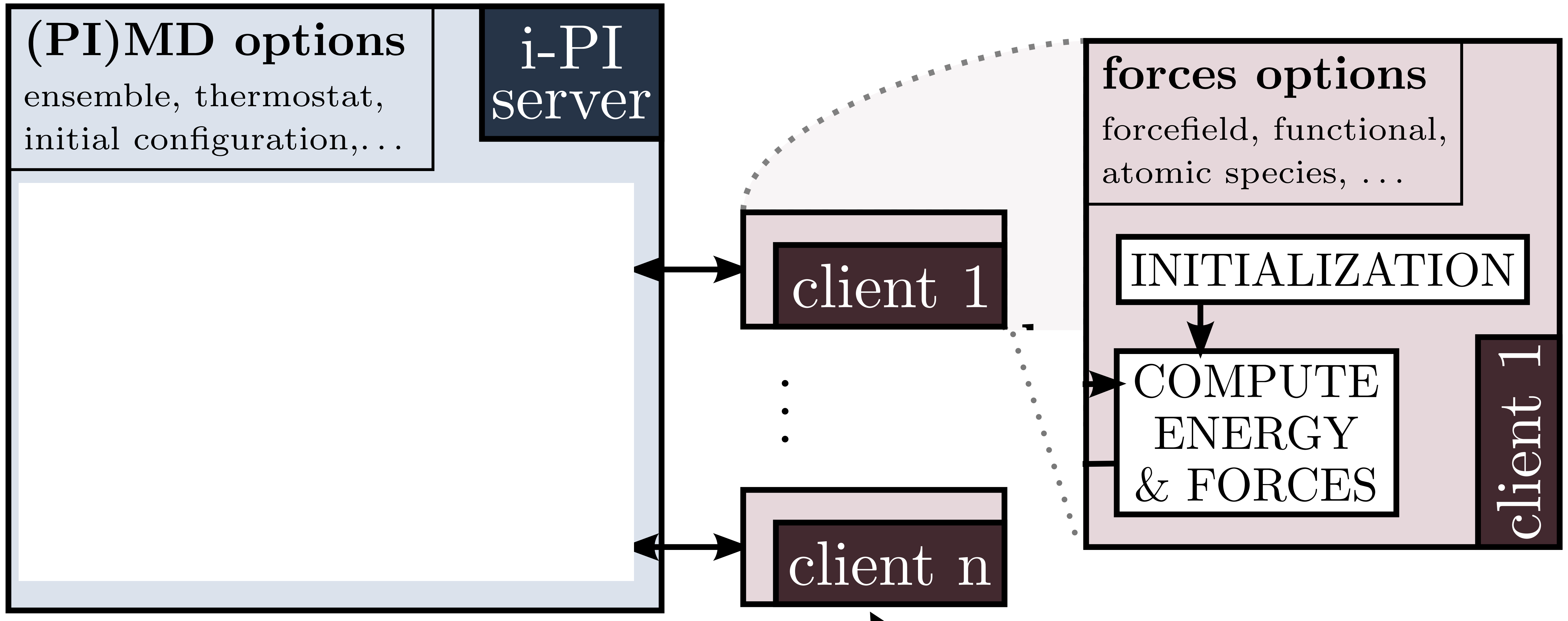

Can be several different codes too

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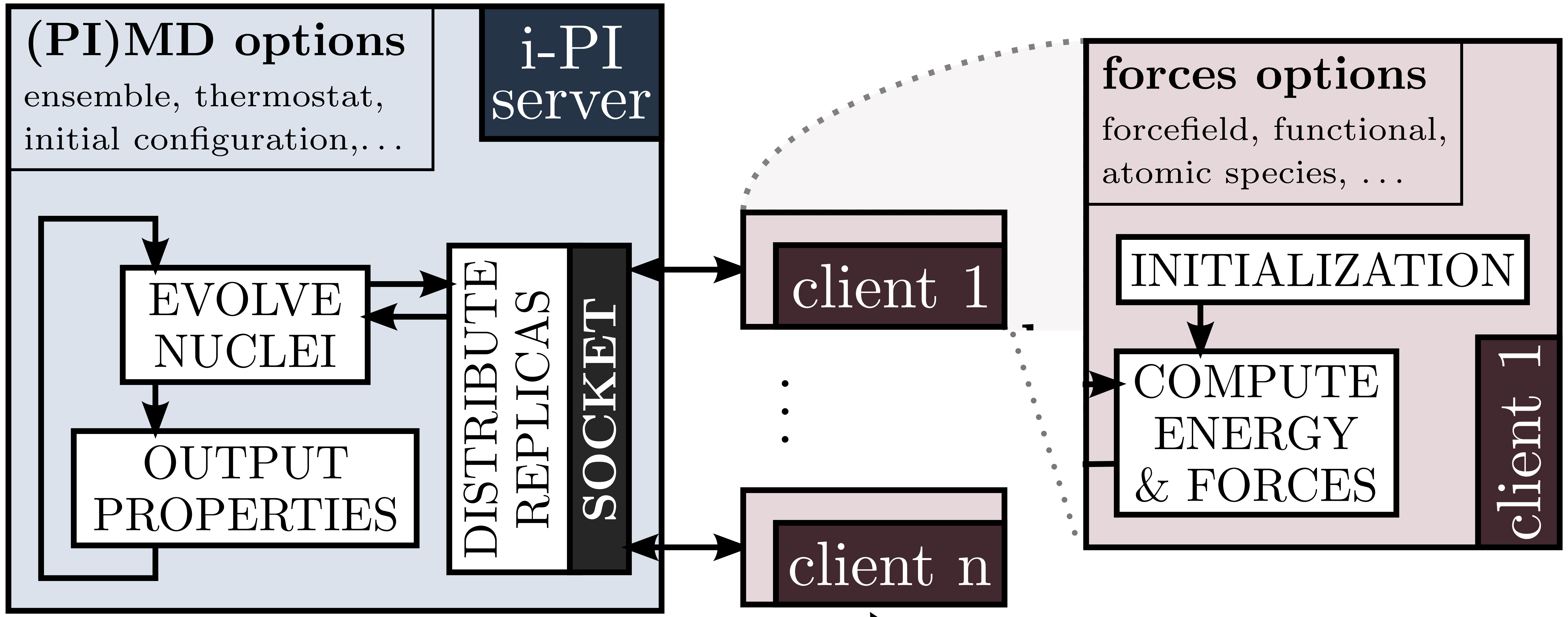

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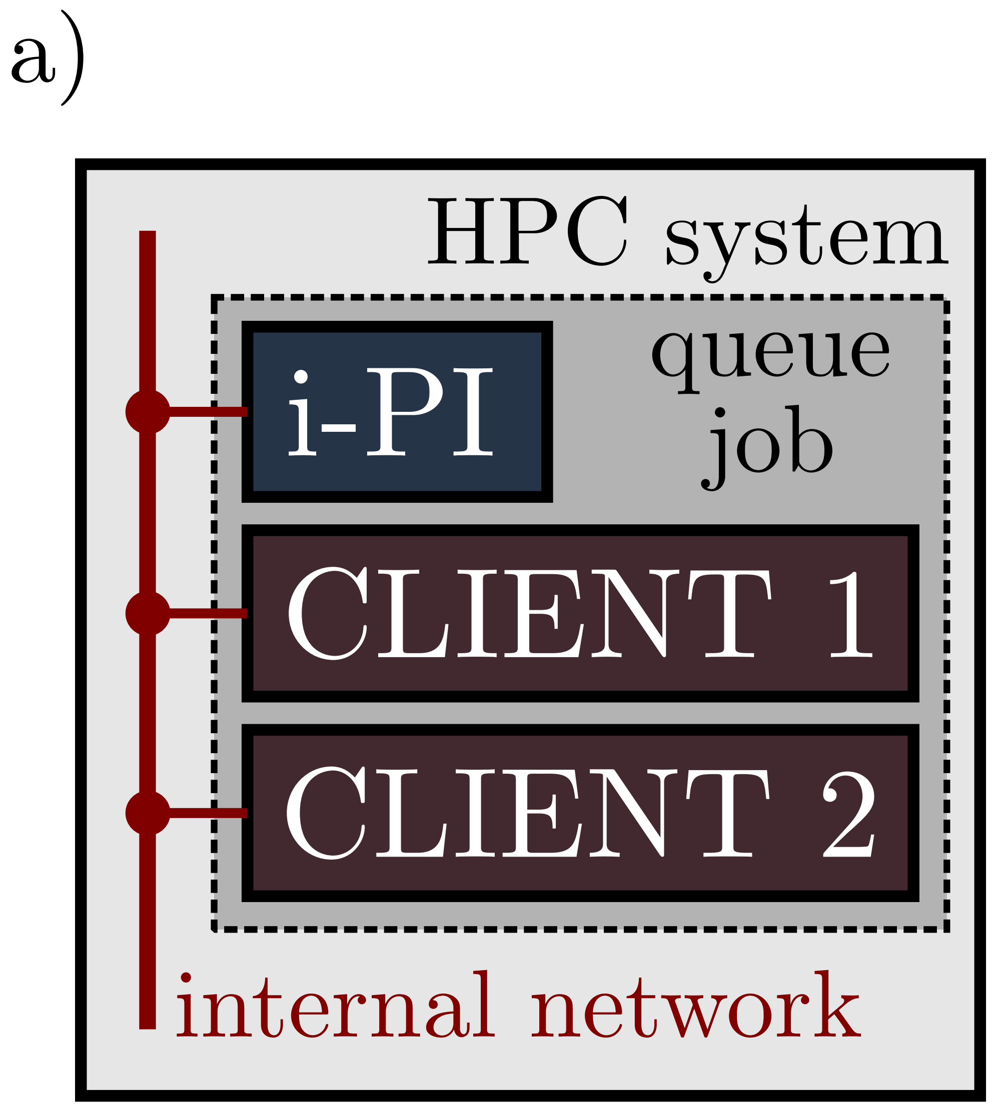
Communication in HPC systems

- The point of using sockets is to enable remote execution — server must talk to client
- In HPC systems it might not be trivial



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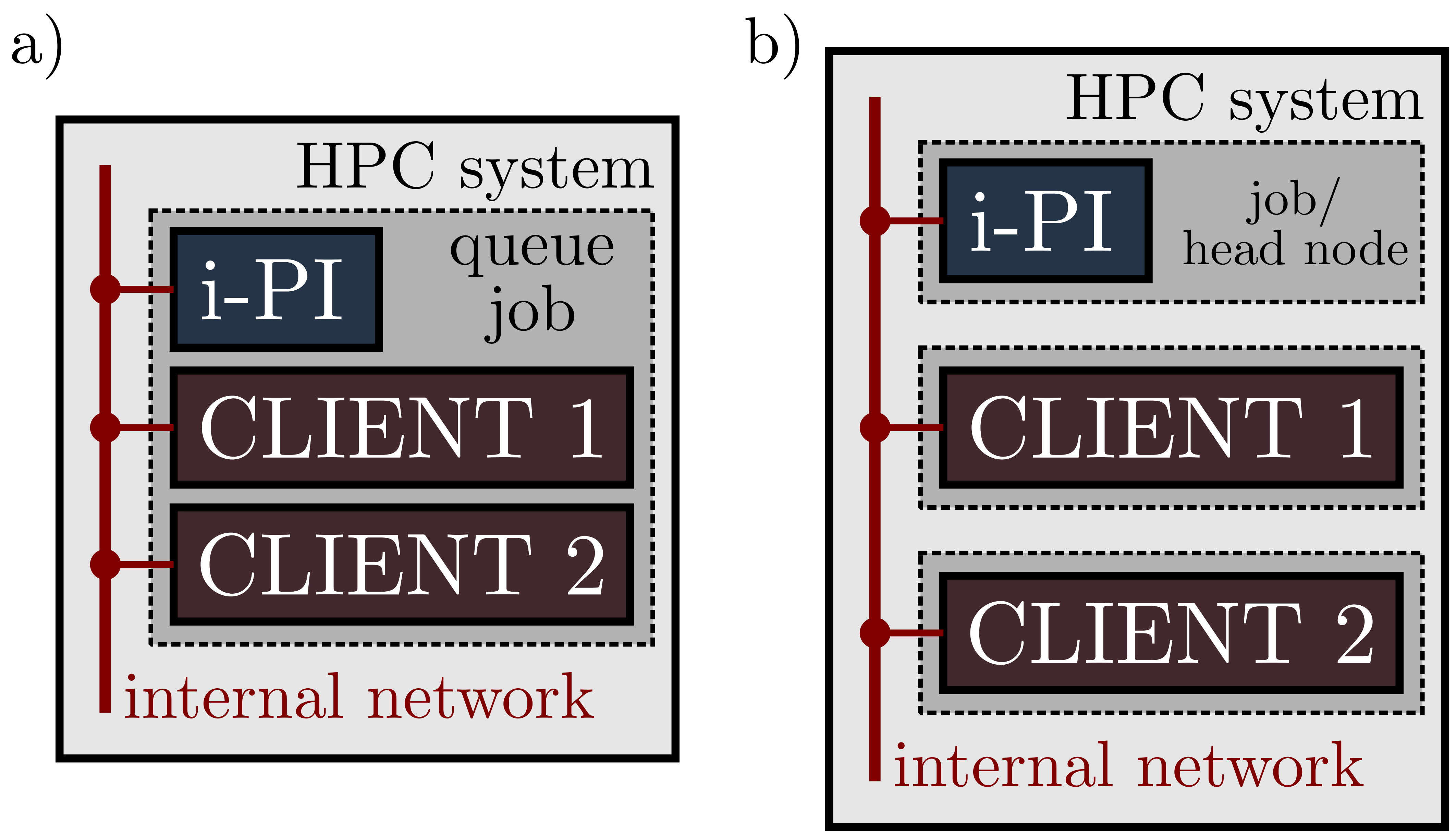

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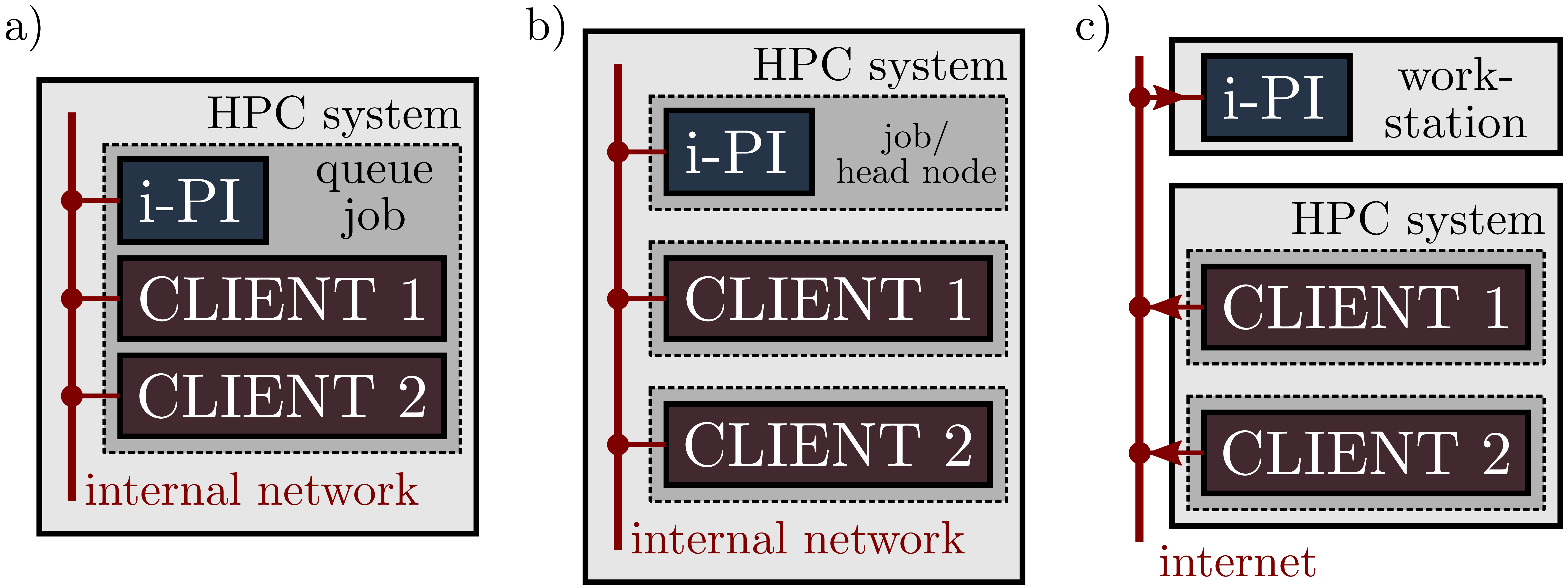
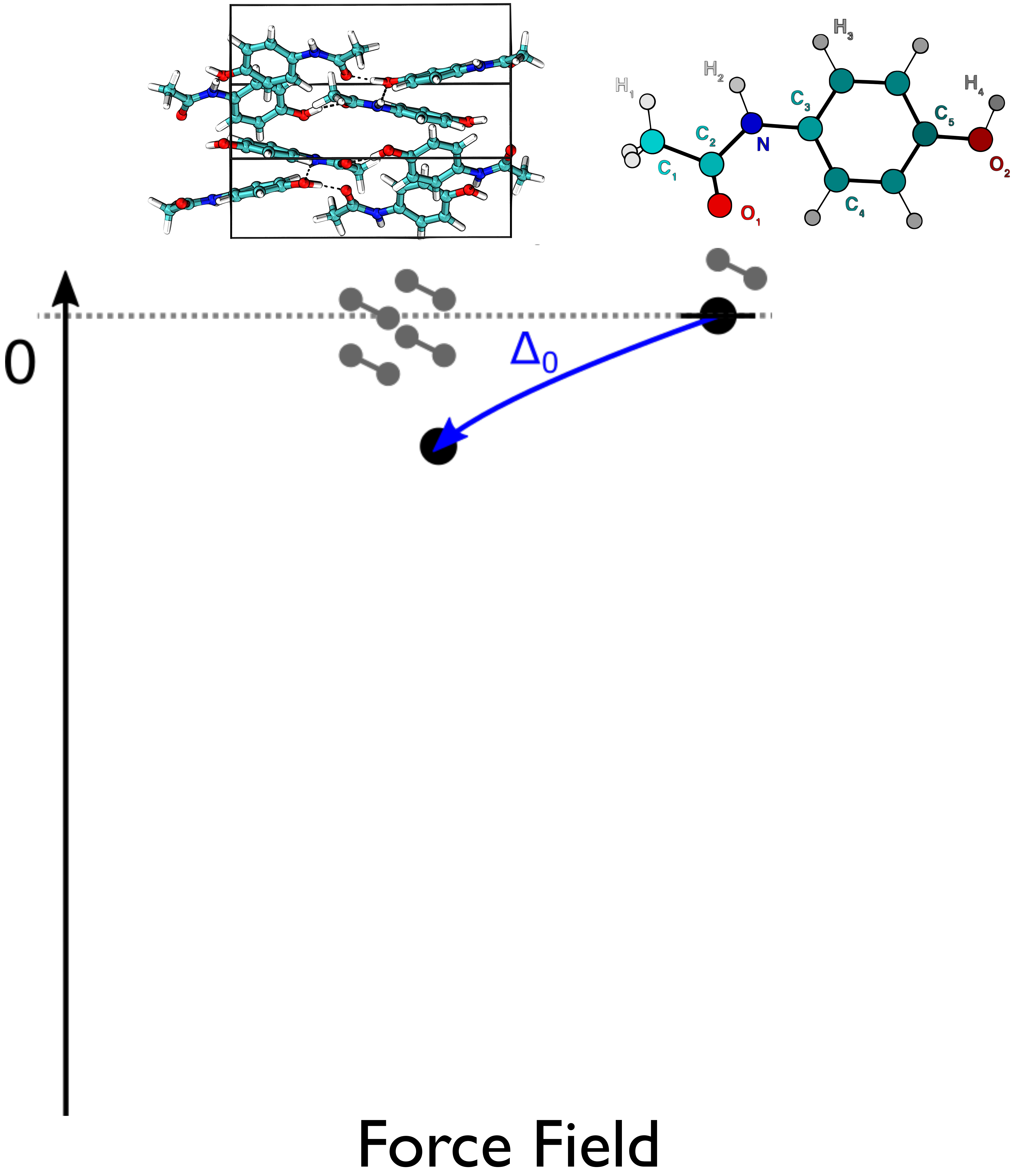


Molecular Crystals: Free Energy Differences

$\Delta = E_{cryst}/N\text{-}E_{mol}$

Rossi, Gasparotto, Ceriotti, PRL ***117***, *115702 (2016)*



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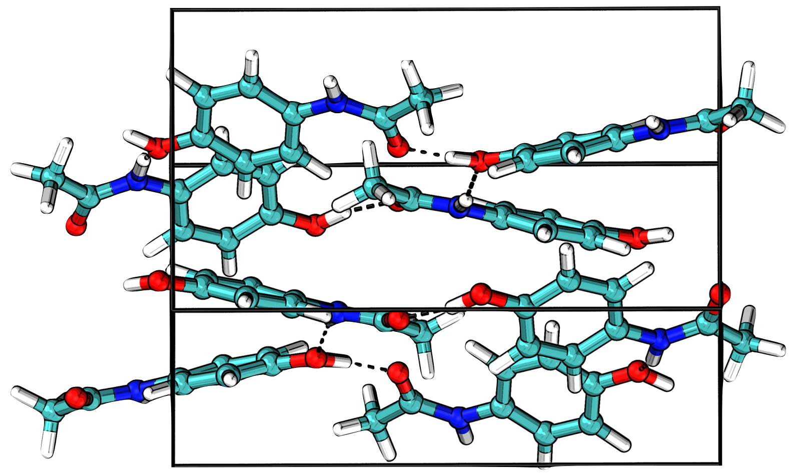

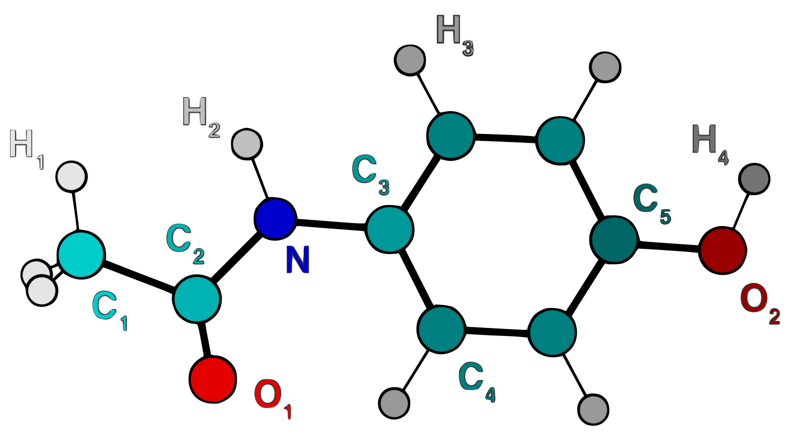

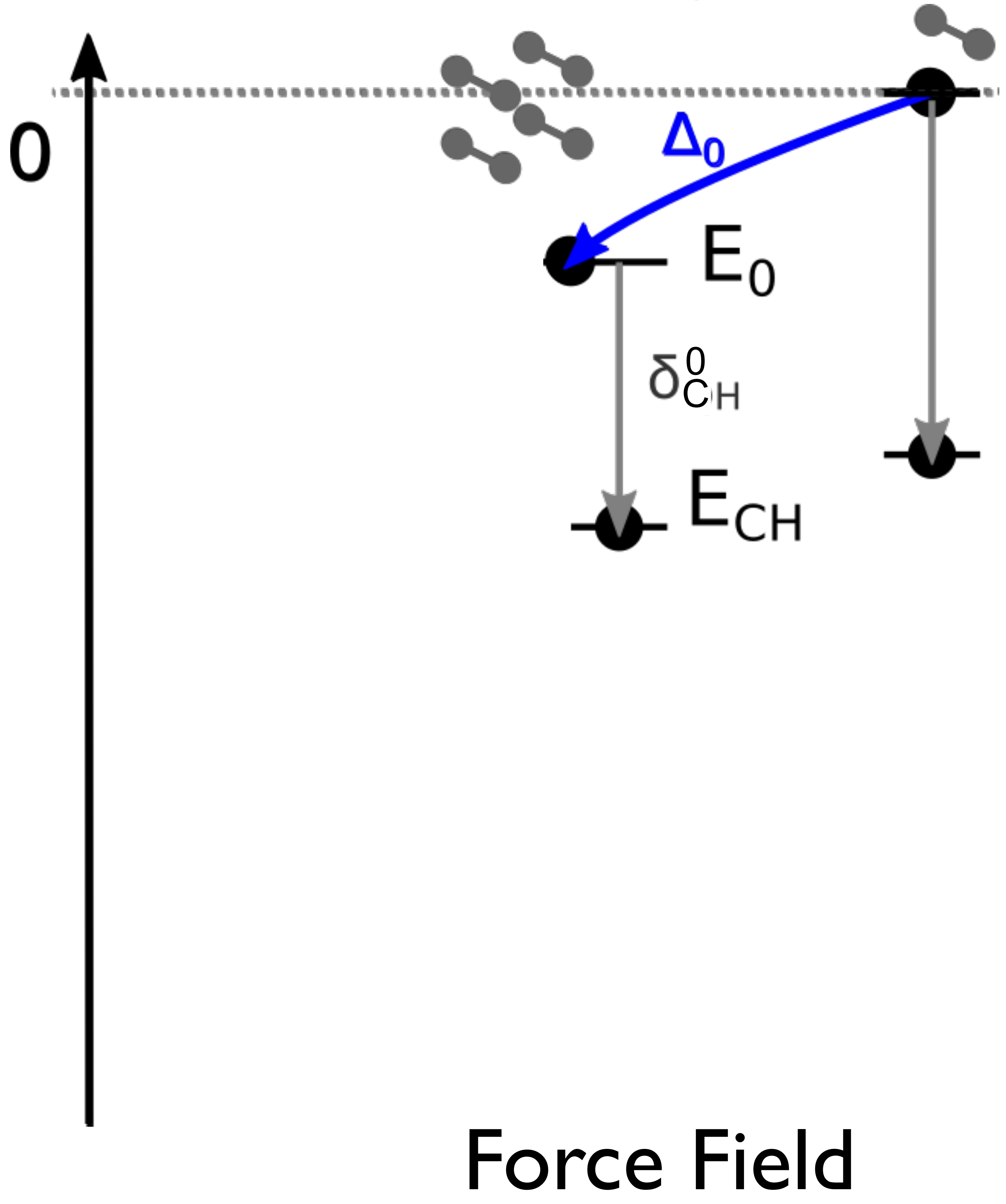

$$\delta^0_{CH} = -k_B T \sum_i \ln\left[k_B T/(\hbar\omega_i)\right] - E_0$$

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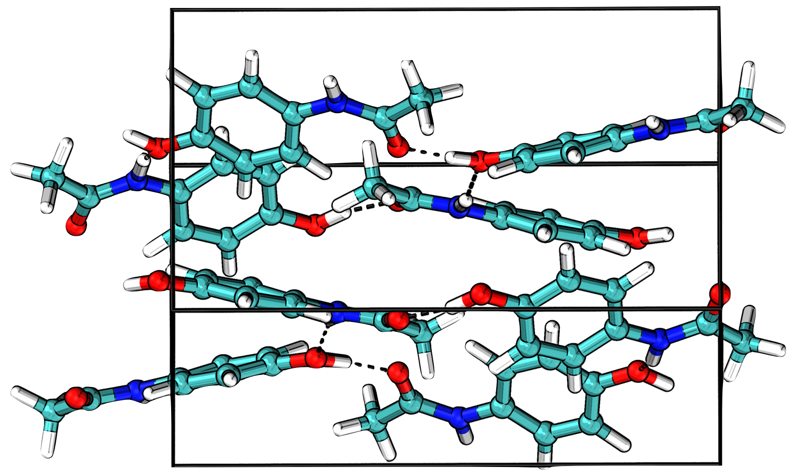

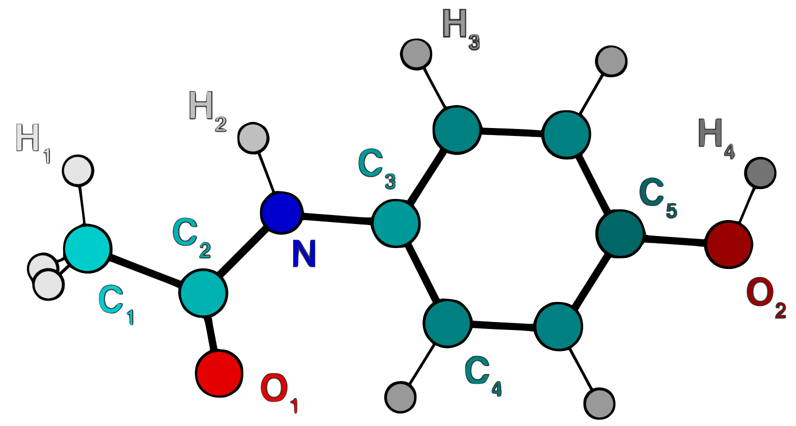

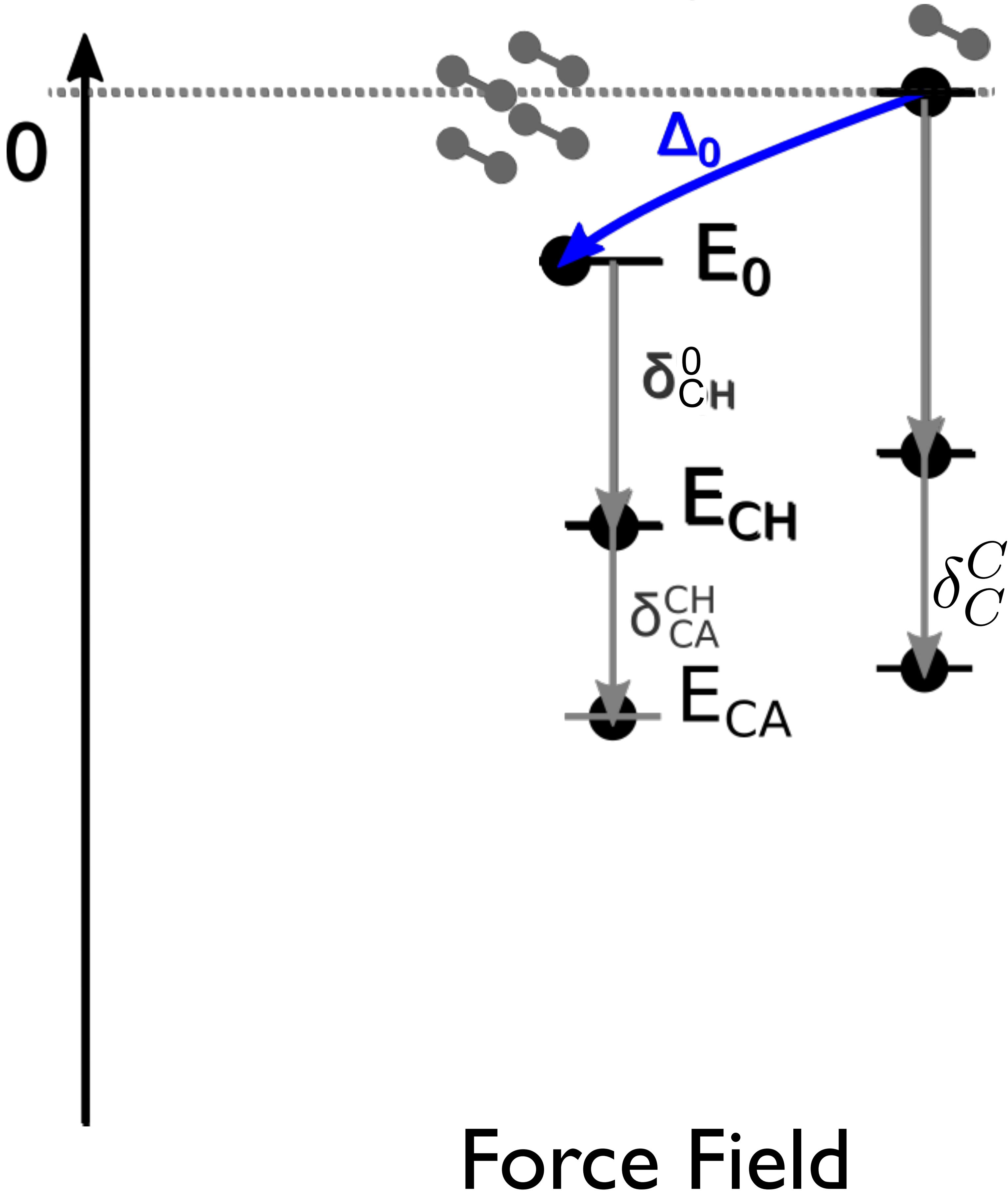

$$V(\lambda) = \lambda V_{FF} + (1-\lambda) V_{Debye}$$

$$\delta^{CH}_{CA} = \int_0^1 \left\langle \frac{\partial V(\lambda)}{\partial \lambda} \right\rangle_\lambda d\lambda = \int_0^1 \langle V_{FF} - V_{Debye} \rangle_\lambda d\lambda$$

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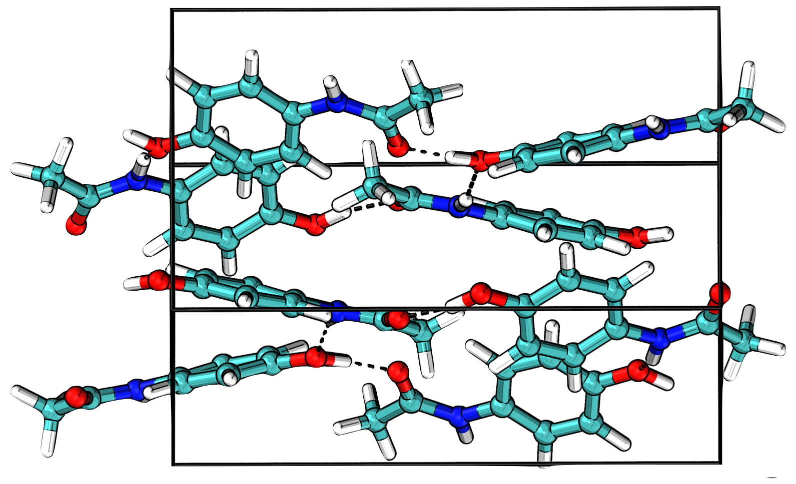

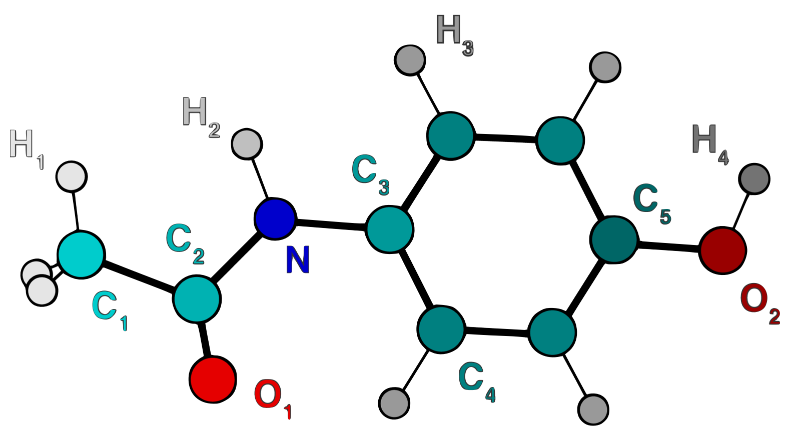

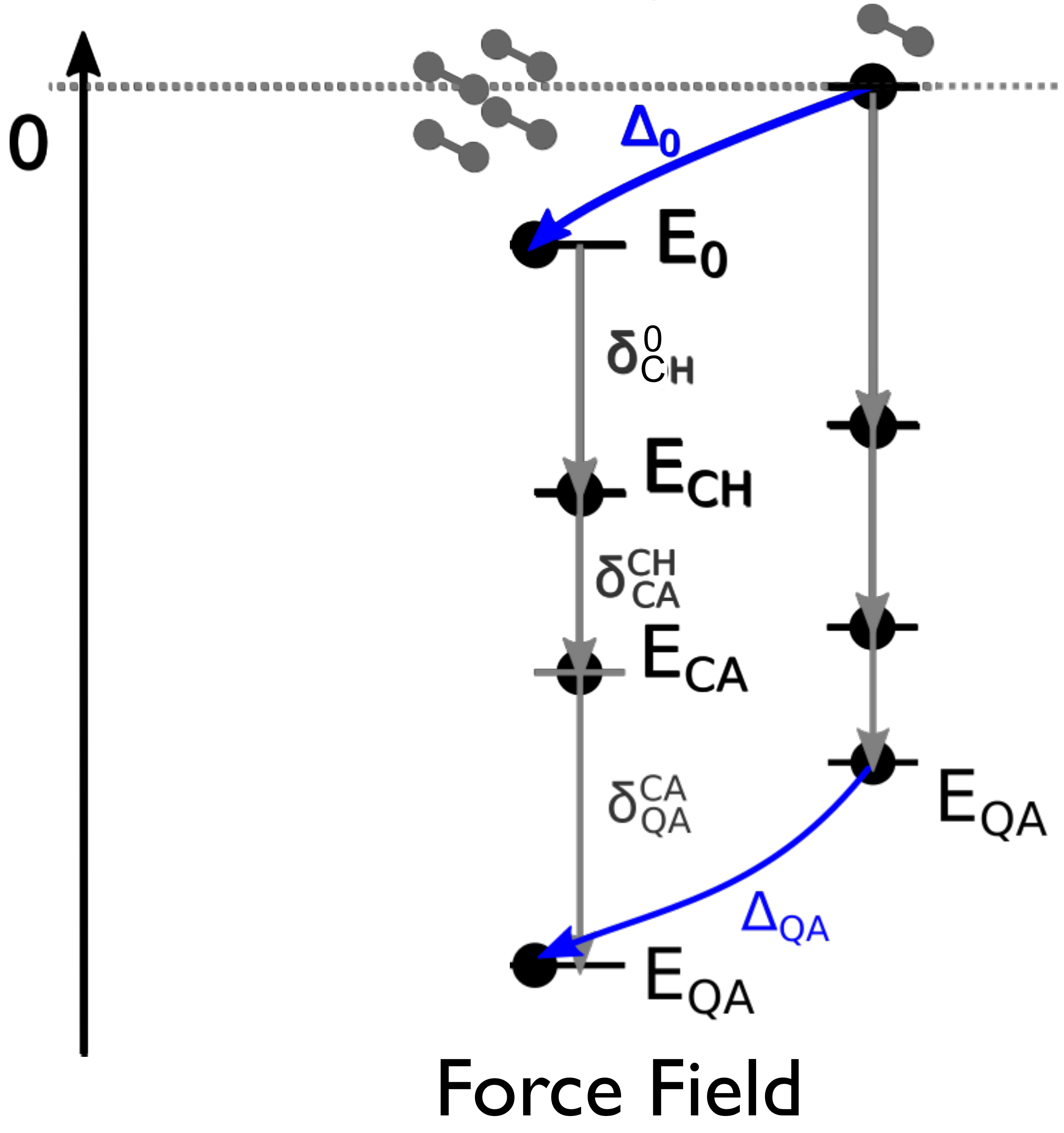

$$\delta^{CA}_{QA} = -\int_{m_0}^{\infty} \frac{\langle K(\mu)\rangle_\mu - 3k_BT/2}{\mu} d\mu$$

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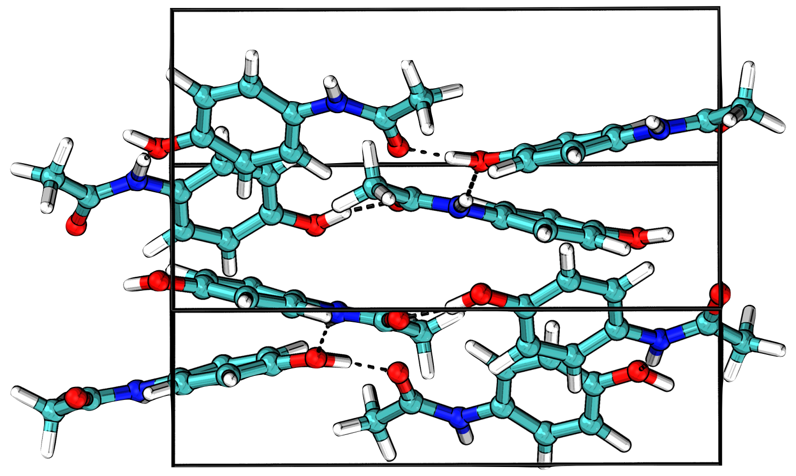

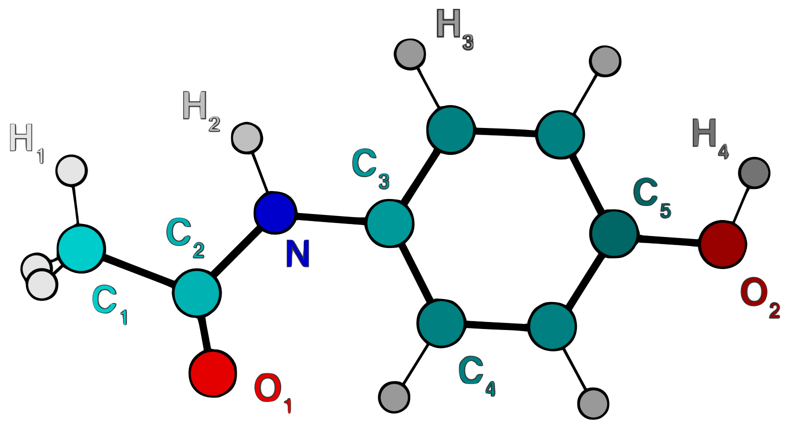

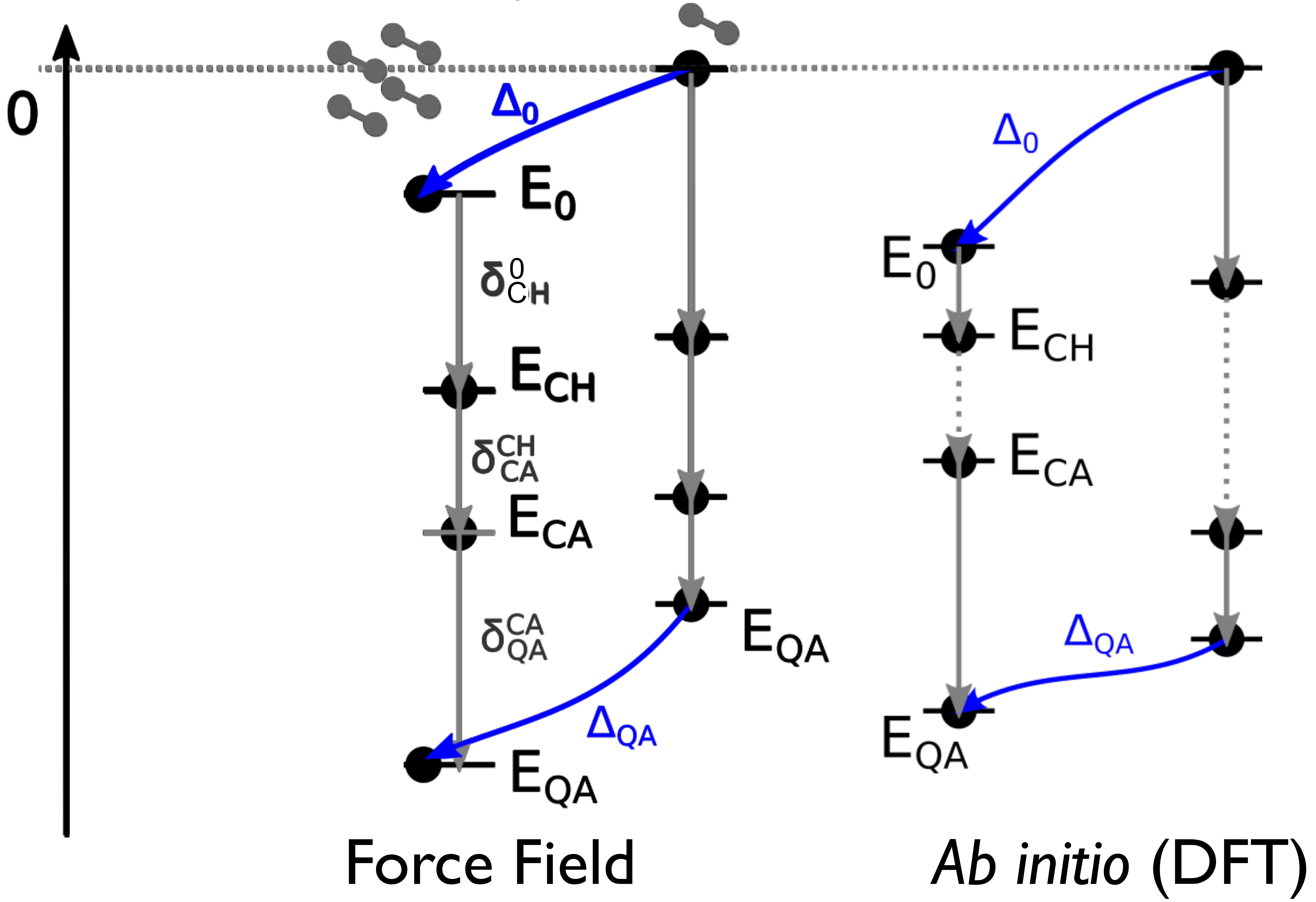

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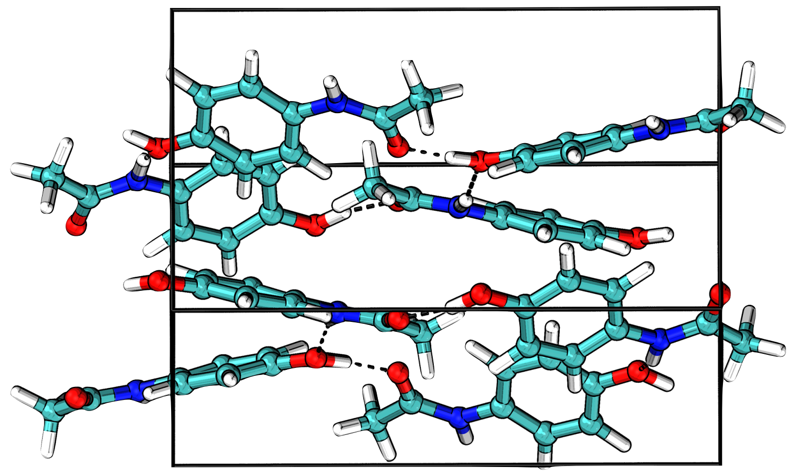

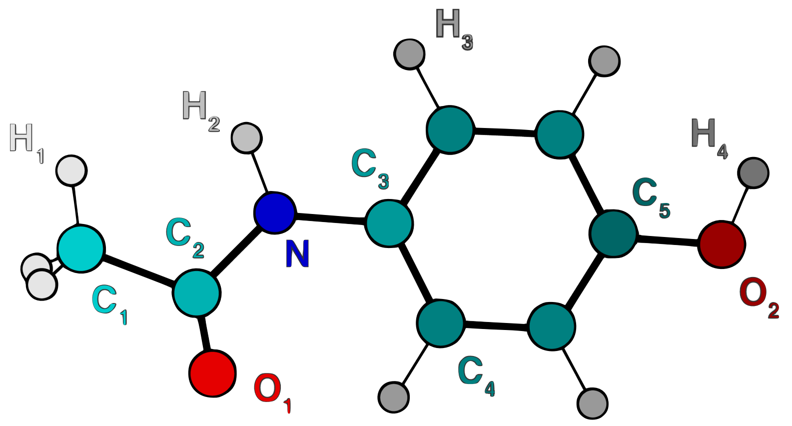

$$V(\lambda) = \lambda V_{DFT} + (1-\lambda)V_{FF}$$

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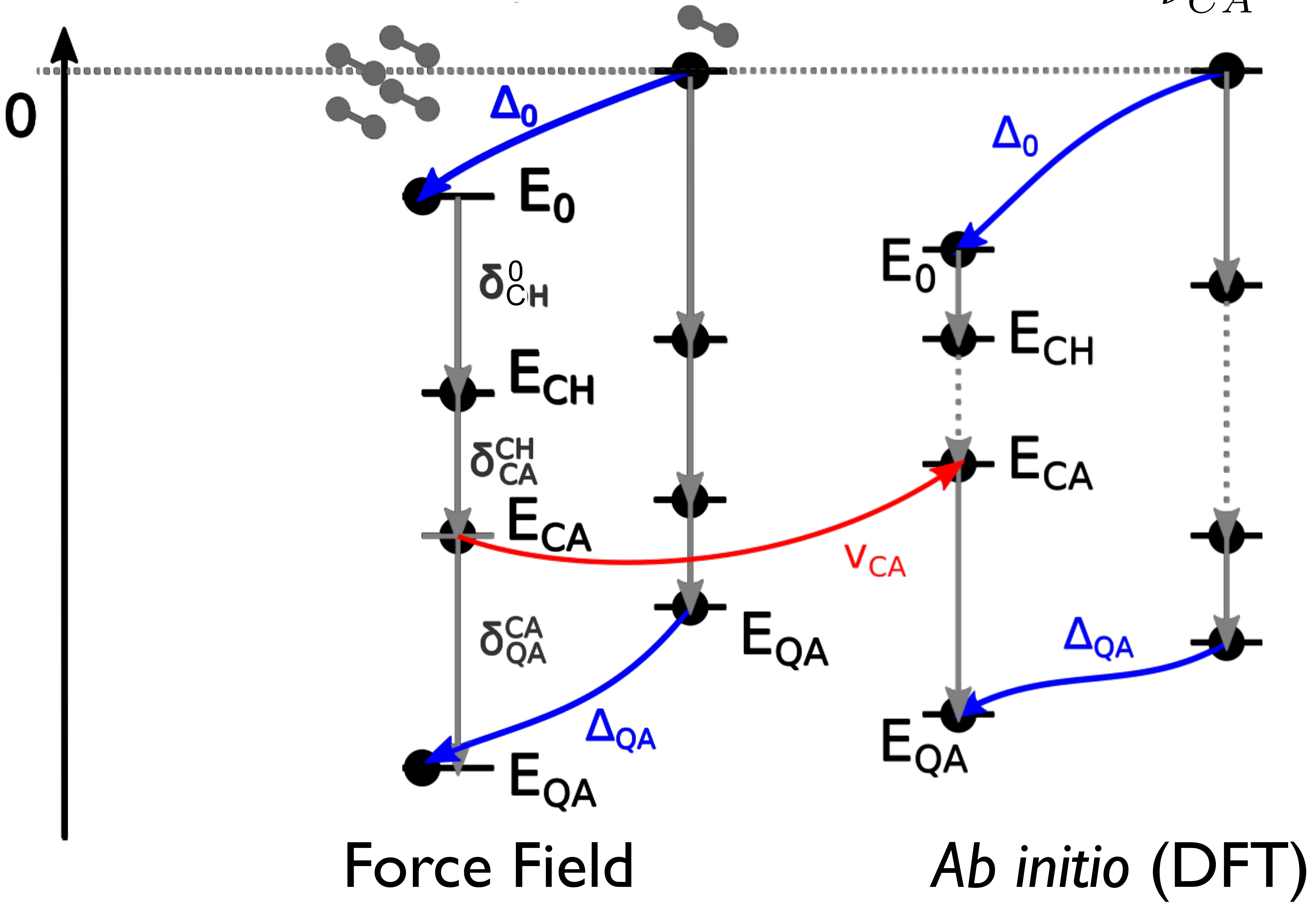

The Fully Quantum Free Energy Differences

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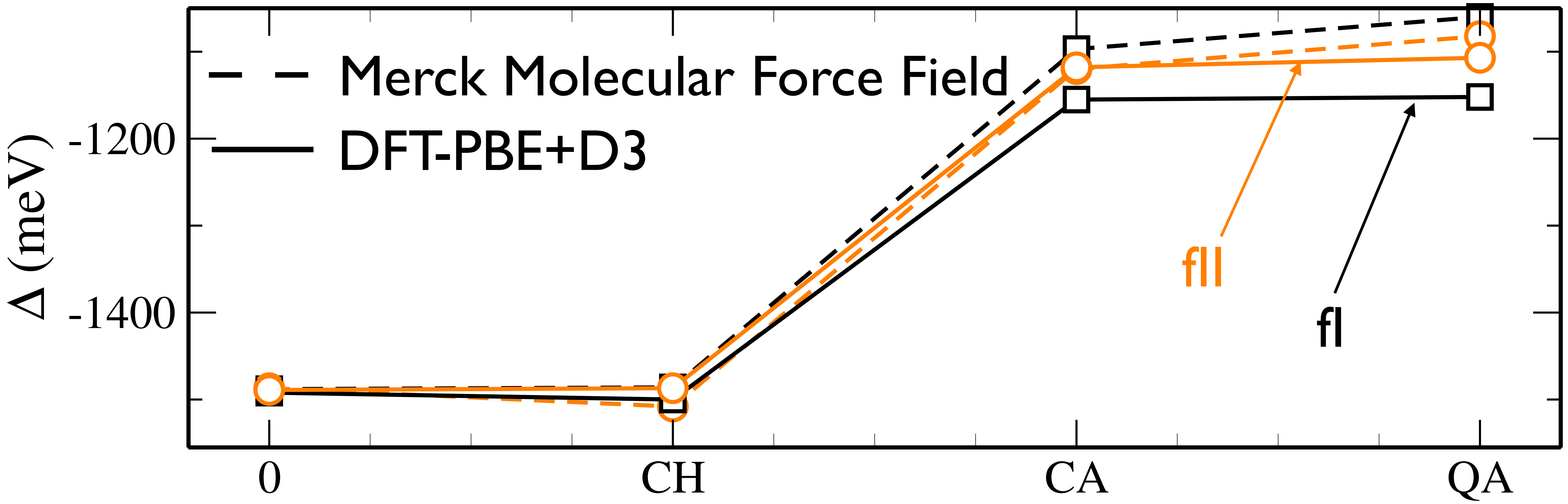
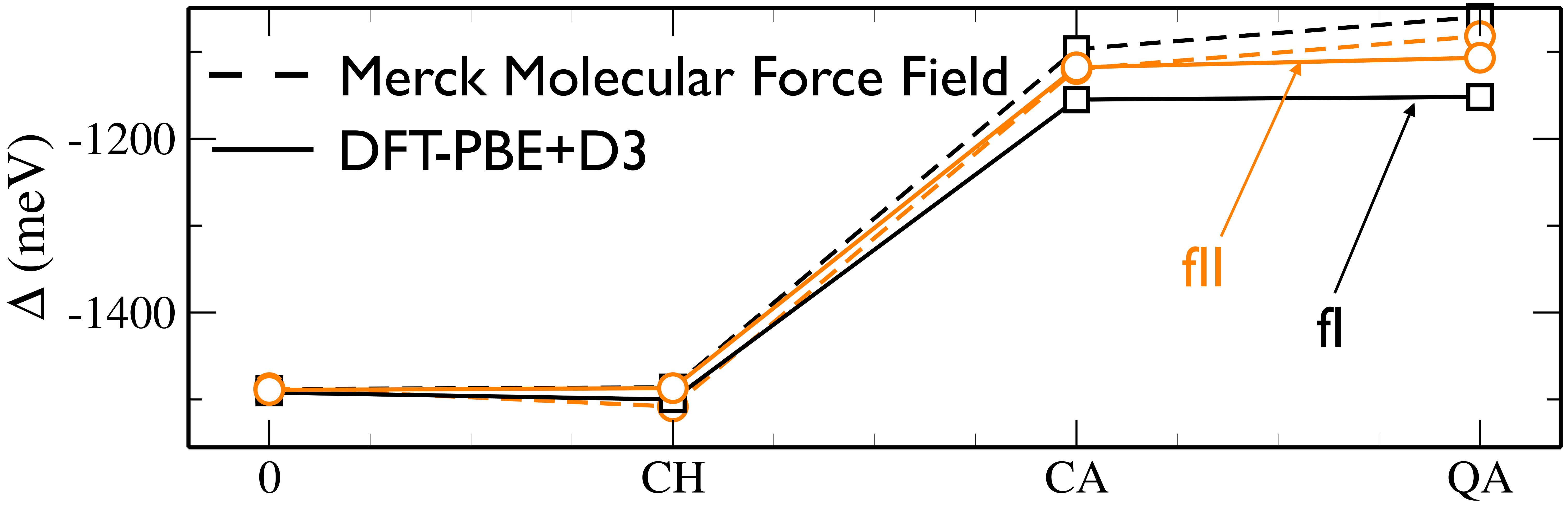


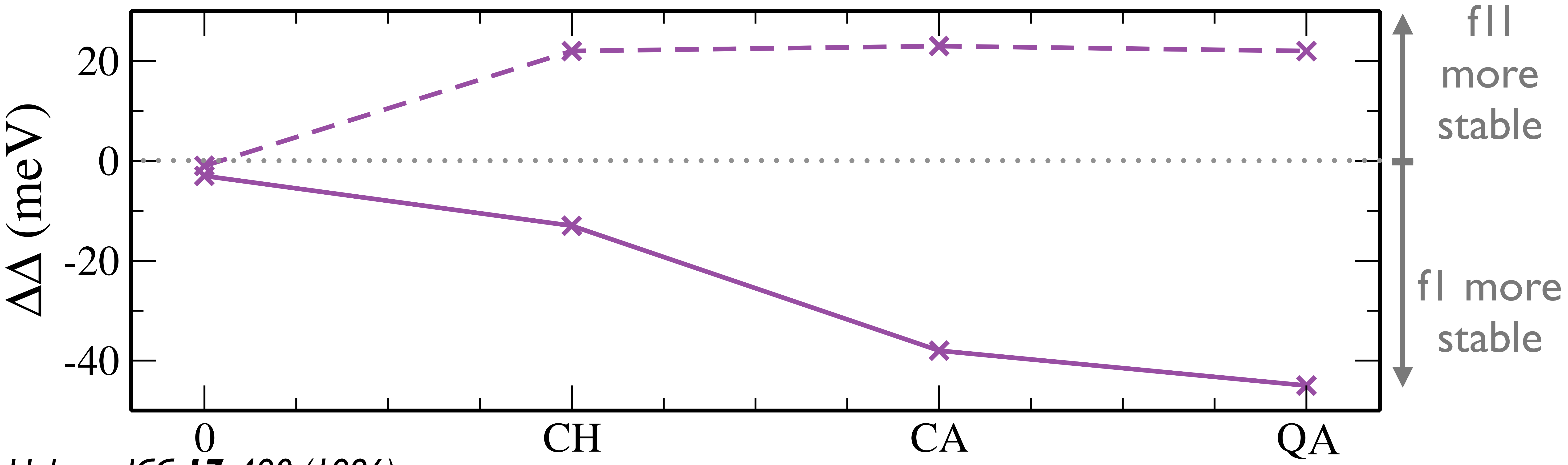
MMFF: *Halgren, JCC* ***17****, 490 (1996)*
D3: *Grimme, et al. JCP* ***132****, 154104 (2010)*

The Fully Quantum Free Energy Differences

$\Delta = (E_{cryst}/N) - E_{mol}$



$\Delta\Delta = \Delta fI - \Delta fII$



MMFF: *Halgren, JCC* ***17****, 490 (1996)*

D3: *Grimme, et al. JCP* ***132****, 154104 (2010)*

References for AIMD and PIMD (books)

Understanding Molecular Simulation: From Algorithms to Applications
D. Frenkel and B. Smith

Statistical Mechanics: Theory and Molecular Simulation
M. Tuckerman

Ab initio molecular dynamics: Theory and Implementation
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Thank you!