HIGH ORDER PATH INTEGRALS MADE EASY

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July 5, 2017

COSMO Computational Science and Modelling

École Polytechnique Fédérale de Lausanne

SCIENTIFIC TOOLS

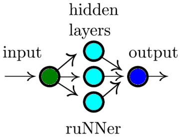


Figure : B3LYP energetics with a NN potential

128 molecules, T = 300 K, NVT ensemble

Behler *et al.*, PRL (2007), T. Morawietz *et al.* PNAS (2016)

SCIENTIFIC TOOLS

Figure : checkout: www.ipi-code.org

Ceriotti *et al.*, CPC (2014)

NUCLEAR QUANTUM EFFECTS

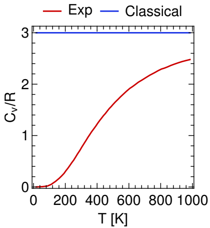


Figure : C_v

diamond

Raman, PIAS (1957)

NUCLEAR QUANTUM EFFECTS

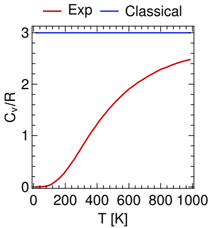


Figure : $\mathrm{C_v}$

diamond

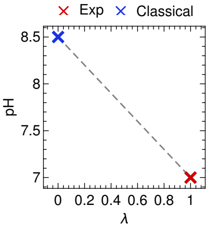
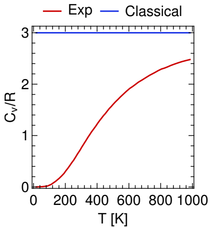


Figure : pH

water at 300 K

Ceriotti *et al.*, PNAS (2013)

NUCLEAR QUANTUM EFFECTS



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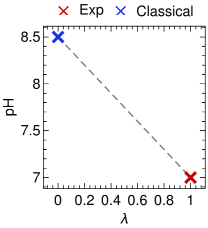

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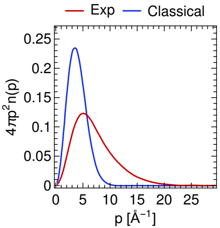

Figure : $\mathrm{n(p)}$

water at 300 K

Morrone *et al.*, PRL (2008)

$$H = \sum_{i=0}^{3N} \frac{p_i^2}{2m_i} + V(q_1, .., q_{3N})$$

$$Z = (2\pi\hbar)^{-3N} \int \mathtt{dpdq}\ \ e^{-\beta H}$$

ab initio SIMULATIONS

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billiard balls on
an *ab initio* surface

ab initio SIMULATIONS

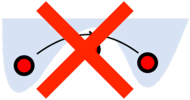

Figure : quantum tunnelling

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Figure : zero point energy

POSSIBLE SOLUTIONS?

$$\hat{H} = \sum_{i=0}^{3N} \frac{\hat{p}_i^2}{2m_i} + V(\hat{q}_1, .., \hat{q}_{3N})$$

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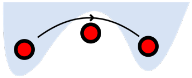

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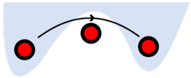

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how to compute it ?

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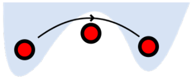

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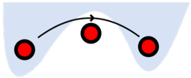

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Figure : zero point energy

how to compute it ?

schrödinger's equation ?

classical isomorphism of quantum statistics

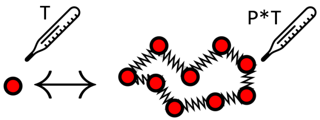


Figure : the isomorphism

Feynmann & Hibbs, McGraw Hill (1965)

PATH INTEGRAL MOLECULAR DYNAMICS

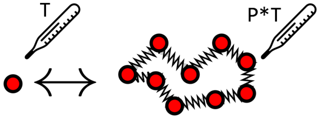


Figure : the isomorphism

$$\mathtt{tr}\left(e^{-\beta\hat{H}}\right) = \mathtt{tr}\left(e^{-\beta[\hat{T}+\hat{V}]}\right)$$
$$= \mathtt{tr}\left(\left[e^{-\beta\frac{\hat{V}}{2P}}e^{-\beta\frac{\hat{T}}{P}}e^{-\beta\frac{\hat{V}}{2P}}\right]^{P}\right) + \mathbb{O}\left(P^{-2}\right)$$
$$= (2\pi\hbar)^{-P}\int d\mathbb{p}\,d\mathbb{q}\;\; e^{-\beta_P H_P^{(2)}(\mathbb{p},\mathbb{q})} + \mathbb{O}\left(P^{-2}\right)$$

Feynmann & Hibbs, McGraw Hill (1965)

PATH INTEGRAL MOLECULAR DYNAMICS

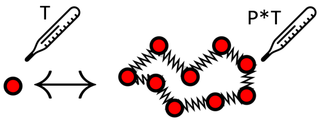


Figure : the isomorphism

$$
\begin{aligned}
\mathtt{tr}\left(e^{-\beta\hat{H}}\right) &= \mathtt{tr}\left(e^{-\beta[\hat{T}+\hat{V}]}\right) \\
&= \mathtt{tr}\left(\left[e^{-\beta\frac{\hat{V}}{2P}}e^{-\beta\frac{\hat{T}}{P}}e^{-\beta\frac{\hat{V}}{2P}}\right]^{P}\right) + \mathcal{O}\left(P^{-2}\right) \\
&= (2\pi\hbar)^{-P}\int d\mathbb{p}d\mathbb{q}\;\; e^{-\beta_P H_P^{(2)}(\mathbb{p},\mathbb{q})} + \mathcal{O}\left(P^{-2}\right)
\end{aligned}
$$

$$
\boxed{H_P^{(2)}(\mathbb{p},\mathbb{q}) = \sum_{i=0}^{P-1}\left(\frac{[p^{(i)}]^2}{2m} + V(q^{(i)}) + \frac{m\omega_P^2}{2}\left[q^{(i)} - q^{(i+1)}\right]^2\right)}
$$

Feynmann & Hibbs, McGraw Hill (1965)

PATH INTEGRAL MOLECULAR DYNAMICS

Figure : MD

Figure : PIMD

Chandler & Wolynes JCP (1981)

PATH INTEGRAL MOLECULAR DYNAMICS

$$\langle A \rangle = \frac{1}{P} \sum_{i=0}^{P-1} A(q^{(i)}) + \mathcal{O}\left(P^{-2}\right)$$

Figure : MD

Figure : PIMD

Chandler & Wolynes JCP (1981)

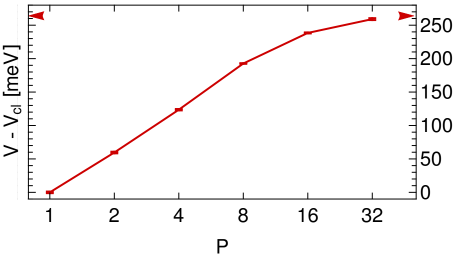


Figure : convergence of potential energy w.r.t P

Kapil *et al.* JCP (2016)

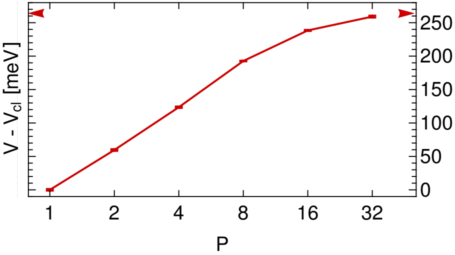
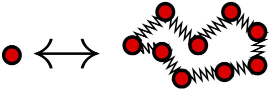


Figure : convergence of potential energy w.r.t P

x-axis = computational cost w.r.t. *ab inito* MD

Kapil *et al.* JCP (2016)

HIGH ORDER SPLITTINGS



$$\texttt{tr}\left(e^{-\beta\hat{H}}\right) = \texttt{tr}\left(\left[e^{-\beta\frac{\hat{V}}{2P}}e^{-\beta\frac{\hat{T}}{P}}e^{-\beta\frac{\hat{V}}{2P}}\right]^{P}\right) + \mathbb{O}\left(P^{-2}\right)$$

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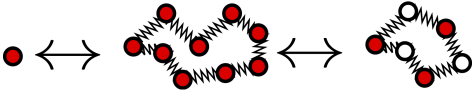
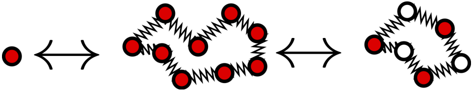


$$\mathtt{tr}\left(e^{-\beta\hat{H}}\right) = \mathtt{tr}\left(\left[e^{-\beta\frac{\hat{V}}{3P}}e^{-\beta\frac{\hat{T}}{P}}e^{-\beta\frac{4\hat{V}_o}{3P}}e^{-\beta\frac{\hat{T}}{P}}e^{-\beta\frac{\hat{V}}{3P}}\right]^{P/2}\right) + \mathbb{O}\left(P^{-4}\right)$$

Suzuki, PLA (1995)
Chin, PLA(1997)

HIGH ORDER SPLITTINGS



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$$\hat{V}_{\circ} = \hat{V} + \frac{1}{12P^2}\beta^2\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]$$

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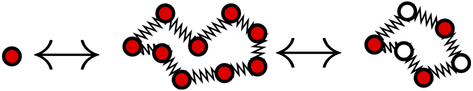

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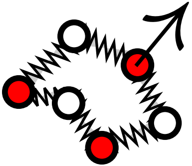
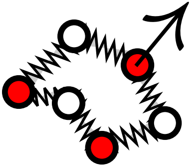


$$\tilde{V}(\vec{q}) = \frac{4}{3}V(\vec{q}) + \frac{m\beta^2}{9P^2}|\vec{f}|^2$$



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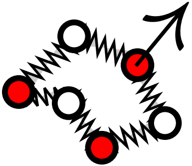

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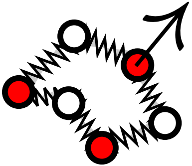
cost of computing the Hessian ☠



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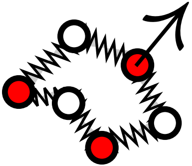
Kapil, JCP (2016)



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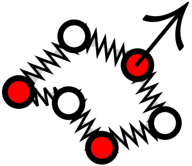

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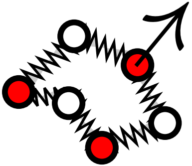

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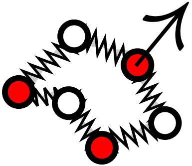

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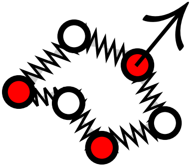
$$= \lim_{\epsilon\to 0}\frac{f_j(\vec{q}+\epsilon\vec{f}) - f_j(\vec{q})}{\epsilon}$$

Kapil, JCP (2016)



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cost of computing the Hessian ☠

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$1.5 \times$ additional cost

Kapil, JCP (2016)

MULTIPLE TIME SCALES

$$-\frac{d\tilde{V}(\vec{q})}{dq_j} = -\frac{4}{3}\frac{dV(\vec{q})}{dq_j} - \frac{2m\beta^2}{9P^2}\lim_{\epsilon\to 0}\frac{f_j(\vec{q}+\epsilon\vec{f}) - f_j(\vec{q})}{\epsilon}$$

Kapil, JCP (2016)
Kapil, JCP (2016)
Tuckerman, Berne JCP (1992)

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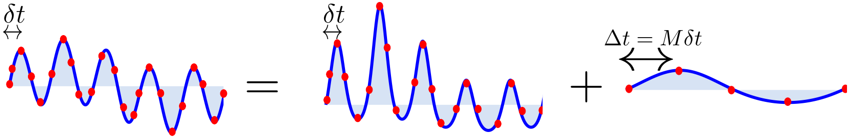

Kapil, JCP (2016)
Kapil, JCP (2016)
Tuckerman, Berne JCP (1992)

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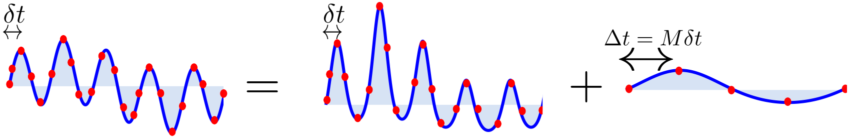


10% additional cost for $M = 4$

Kapil, JCP (2016)
Kapil, JCP (2016)
Tuckerman, Berne JCP (1992)

CONVERGENCE OF ENERGY

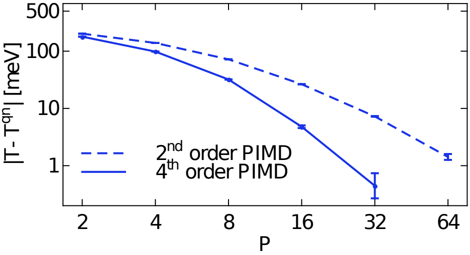


Figure : asymptotic convergence of kinetic energy for water at 300 K

Kapil, JCP (2016)

STABILITY OF THE FINITE DEVIATION

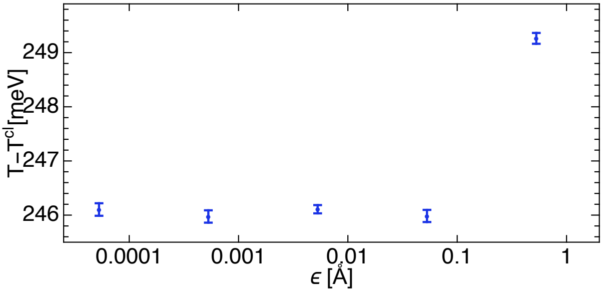
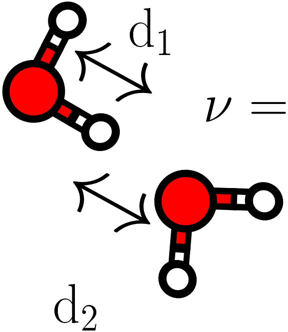


Figure : stability of the finite-difference scheme

Kapil, JCP (2016)

PROTON DELOCALIZATION

$$\langle A \rangle = \frac{2}{P} \sum_{i=0}^{\frac{P-1}{2}} A(q^{(2i)}) + \mathcal{O}\left(P^{-4}\right)$$



$$\nu = d_1 - d_2$$

Figure : proton delocalization in water

Kapil, arXiv (2016)

STRUCTURAL PROPERTIES

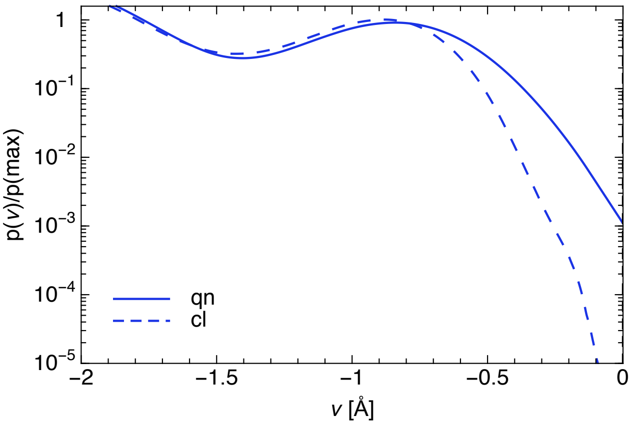


Figure : proton delocalization in water

Kapil, arXiv (2016)

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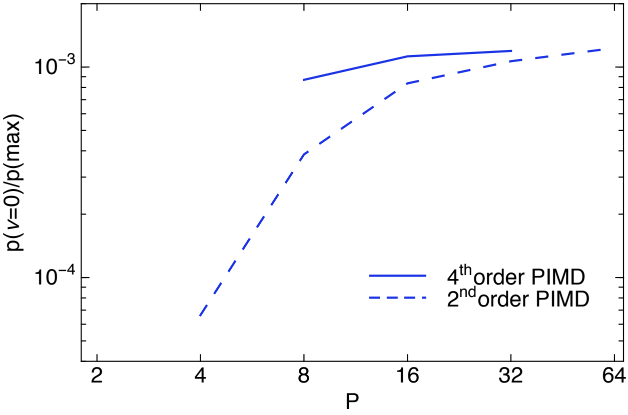

Figure : proton delocalization in water

Kapil, arXiv (2016)

OUTLOOKS

1. (Further) Speed up ? : MTS in real and imaginary time

Kapil *et al.*, JCP (2016), Marsalek *et al.*, JCP (2016)

OUTLOOKS

1. (Further) Speed up ? : MTS in real and imaginary time
2. Other ensembles: NPT, NST ?

Martyna *et al.*, JCP (1999), Raiteri *et al.* JPCM (2011)

OUTLOOKS

1. (Further) Speed up ? : MTS in real and imaginary time
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3. Other estimators: Cp, Cv, iso. frac. ratios ?

Yamamoto JCP (2005)

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4. A GLE thermostat : SC + GLE ?

Kapil *et al.* JCP (2016)

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Poltavsky *et al.* Chem. Sci., (2016)

OUTLOOKS

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5. Higher order corrections : SC + PPI ?
6. Enhanced Sampling : SC + MetaDynamics / REMD ?

Quhe *et al.* JCTC (2015)

THANK YOU

"Grazie mille"

Random Italian person, 2017

CURSE OF RE-WEIGHTED SAMPLING

High order terms can be treat as perturbations:

$$H_P^{(4)}(\vec{p},\vec{q}) = H_P^{(2)}(\vec{p},\vec{q}) + \Delta H_P(\vec{q})$$

The fourth order averages can be obtained by merely re-weighting:

$$\left\langle \hat{A} \right\rangle \approx \left\langle w(\vec{q}) \;\; A_P^{(2)}(\vec{q}(t))) \right\rangle_t$$

Ceriotti, Proc. R. Soc. A (2012)

CURSE OF RE-WEIGHTED SAMPLING

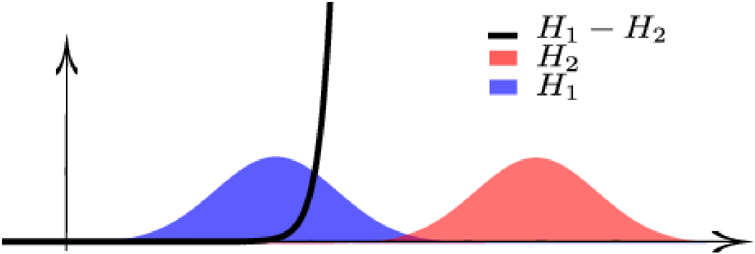

Figure : statistical weight of the difference Hamiltonian

$$\sigma^2(\beta_P \Delta H_P(\vec{q})) \approx N \frac{\hbar^6 \overline{\omega}^6 \beta^6}{216 P^4}; \quad \overline{\omega} = \left[(3N)^{-1} \sum_{i=0}^{3N-1} \omega_i^6 \right]^{\frac{1}{6}}$$

Ceriotti, Proc. R. Soc. A (2012)

CURSE OF RE-WEIGHTED SAMPLING

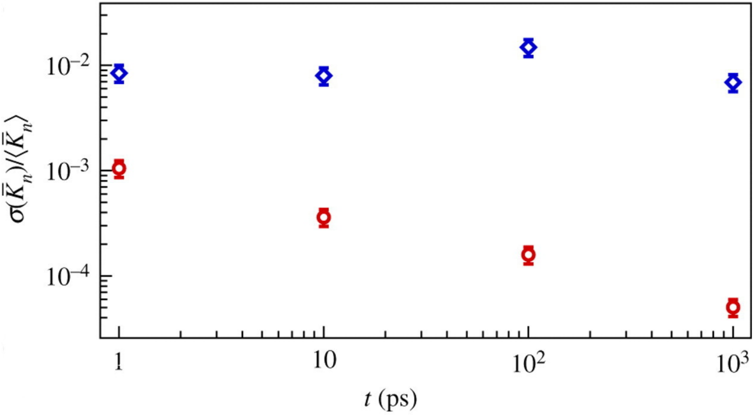

Figure : sampling efficiency as a function of simuation time