Correlated sampling without reweighting, computing properties with size-independent variances

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Some perspective on Quantum Monte Carlo (QMC)

Many problem in Quantum physics at zero temperature

The Schroedinger equation,

$$H\Phi = (-\sum_{i=1}^{N} \Delta_i + V(\mathbf{r_1}, \mathbf{r_2} \ldots \mathbf{r_N}))\Phi = E\Phi \quad (1)$$

- N number of particles.
- $\mathbf{r}_i$, 3 spatial coordinates of particle i.
- E lowest eigenvalue, the groundstate energy.
- $\Phi(\mathbf{r}_1 \ldots \mathbf{r}_N)$ the lowest eigen vector, the groundstate
- Φ antisymetric for electrons (fermions).

Stochastic technics in principle adapted for solving the Schroedinger equation :

Solving the many problem in Quantum Physics

$<=>$

Computing integrals in large dimensions.

Example : variational energy

Variational energy

$$E_V \equiv \langle \Psi | \hat{H} | \Psi \rangle$$

Average on a probability distribution

$$\langle \Psi | \hat{H} | \Psi \rangle = \int d\mathbf{R} \Psi^2(\mathbf{R}) \ \frac{H\Psi}{\Psi}(\mathbf{R})$$

$$= \left\langle \frac{H\Psi}{\Psi}(\mathbf{R}) \right\rangle_{\Psi^2} = \left\langle e(\mathbf{R}) \right\rangle_{\Psi^2}$$

$\mathbf{R}$: 3N coordinates of the N interacting particles

$$E_v = \frac{1}{N} \sum^{N} e(\mathbf{R}_k)$$

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In general

More generally

$$E_{\text{QMC}} = \left\langle e(\mathbf{R}) \right\rangle_{\Pi}$$

Depending on the QMC method, the nature of $\mathbf{R}$ might change :

- $3N$ particle coordinates (VMC,DMC..).
- Trajectories in the space of $3N$ particle coordinates (PDMC, PIMC, reptation...)

Accurate energies

No analytical integration

- Flexibility (choice of ψ in VMC).
- Weak limitation in system sizes.
- Possibility to improve “arbitrarily” the accuracy (“zero-variance zero-bias principle”, choice of ψ in VMC..).

In practice, reference methods for total energies on large systems (large N)

Quantites of physical interest

They are energy differences.

Exploiting accurate total energies

More tricky in QMC than in a deterministic method.

- Energy differences are usually very small.
- Statistical uncertainties.

Small statistical uncertainty on a total energy might be huge on a difference if energies are computed independently.

Why energy differences are usually small ?

Examples

- Binding energies, transition state energies. One, two particle gaps (electron affinities, ionization energies) . . .
- First order derivatives of the energy : Any observable (force, dipole, moment, densities...).
- Higher order derivatives : spectroscopic constants . . .

They are groundstate energies of similar systems

Paradigm : Calculation of an observable O

$$H_\lambda = H + \lambda O => \bar{O} = \frac{dE_\lambda}{d\lambda} \simeq \frac{E_\lambda - E_0}{\lambda} = \frac{\Delta_\lambda}{\lambda} \quad (2)$$

$$\Delta_\lambda = E_\lambda - E_0 \propto \lambda \text{ small}$$

Behavior as a function of the system size

$\lim_{N\to\infty} \Delta_\lambda(N) = K$ finite.

The perturbation λO depends usually on a few degrees of freedom.

Δ_λ has a locality property

In summary

Small λ and large N

$$\Delta_\lambda(N) \propto \lambda$$

Accuracy on Δ_λ in an independent energy calculation

$$\frac{\delta\Delta_\lambda}{\Delta_\lambda} \propto \frac{\delta E_0}{\lambda} \propto \frac{\sqrt{N}}{\lambda}$$

No locality property for the statistical uncertainty.

Comparison to total energy

$$\frac{\delta\Delta_\lambda}{\Delta_\lambda} \propto \frac{N^{\frac{3}{2}}}{\lambda}\frac{\delta E}{E}$$

Overview

1. Introduction
2. Correlated sampling with reweighting
   - The method
   - Statistical uncertainties
   - Numerical illustration
3. Correlated sampling with no reweighting
   - The method
   - Numerical illustration
4. Conclusion and perspectives

correlated sampling with reweighting

We have to compute the difference

$$E_\lambda - E_0 = \langle e_\lambda(\mathbf{R}) \rangle_{\pi_\lambda} - \langle e(\mathbf{R}) \rangle_\pi$$

Sampling the same distribution for the two energies

$$E_\lambda - E_0 = \frac{\left\langle e_\lambda \frac{\pi_\lambda}{\pi} \right\rangle_\pi}{\left\langle \frac{\pi_\lambda}{\pi} \right\rangle_\pi} - \langle e \rangle_\pi . \qquad (3)$$

weight w_λ

Different contexts

- Variational Monte Carlo $e_\lambda(\mathbf{R}) = \frac{H_\lambda \psi_\lambda}{\psi_\lambda}(\mathbf{R})$, $w_\lambda(\mathbf{R}) = \frac{\psi_\lambda^2}{\psi^2}(\mathbf{R})$
- Forward walking method inc ontext of DMC algorithms.
- ...

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General expression

Compact expression

$$\Delta_\lambda = E_\lambda - E_0 = \langle e_\lambda - e \rangle_\pi + \frac{\mathrm{cov}(e_\lambda, w_\lambda)}{\langle w_\lambda \rangle_\pi} \tag{4}$$

λ dependence

$$E_\lambda - E_0 = \lambda \frac{\partial E_\lambda}{d\lambda}|_{\lambda=0} + o(\lambda).$$

$$E'_\lambda = \langle e'_\lambda \rangle_\pi + \mathrm{cov}(e_\lambda, w'_\lambda)$$

Zero-Variance (ZV) estimator

Pulay correction

Finite statistical uncertainty on $E'_\lambda \Longrightarrow \frac{\delta\Delta_\lambda}{\Delta_\lambda} = K + o(\lambda)$

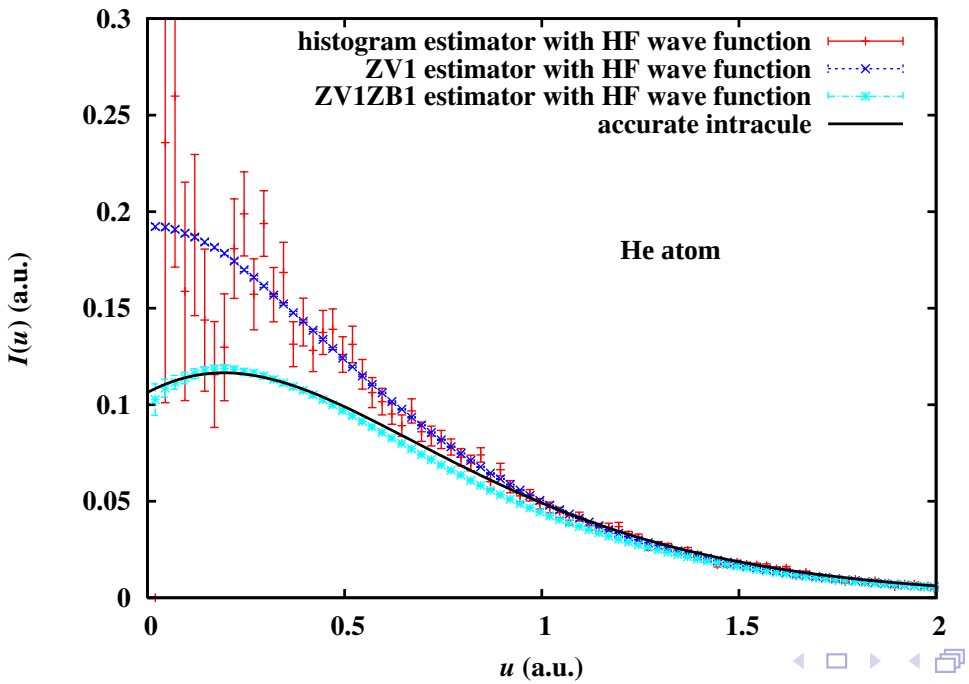
Pair correlation function

[J. Toulouse, R. Assaraf, C. J. Umrigar. J. Chem. Phys. **126** 244112 (2007)]

$O_u = \sum_{i<j} \delta(r_{ij} - u)$

Probability density to find a pair of electrons at distance u

ZV term : $\frac{dE_\lambda}{d\lambda} = \langle O_u + \frac{(H-e)\psi'}{\psi_0} \rangle_{\psi_0^2} = \langle O_u \rangle_{\psi_0^2}$



N-dependence

R. Assaraf, D. Domin, W. Lester.

Model of two separated (non interacting) subsystems

Particles coordinates $\mathbf{R}^l$ and $\mathbf{R}^u$. $H_\lambda = H^l_\lambda + H^u$

Variational Monte Carlo

- $\mathbf{R} = (\mathbf{R}^l, \mathbf{R}^u)$
- $\Psi_\lambda(\mathbf{R}) = \Psi_\lambda(\mathbf{R}^l, \mathbf{R}^u) = \Psi^l_\lambda(\mathbf{R}^l)\Psi^u(\mathbf{R}^u)$
- Local energy $e_\lambda(\mathbf{R}) = e^l_\lambda(\mathbf{R}^l) + e^u(\mathbf{R}^u)$

$$E_\lambda - E = \langle e^l_\lambda - e^l_0 \rangle + \frac{\mathrm{cov}(e_\lambda, w^l)}{\langle w^l \rangle} \qquad (5)$$

First term (ZV)

$\langle e_\lambda^l - e_0^l \rangle$ depends only on $\mathbf{R}^l$

$\Longrightarrow$ Locality property of its variance

Pulay term

$$\frac{\mathrm{cov}(e_\lambda, w^l)}{\langle w^l \rangle} = \frac{\mathrm{cov}(e^l_\lambda, w^l)}{\langle w^l \rangle} + \frac{\mathrm{cov}(e^u, w^l)}{\langle w^l \rangle} \tag{6}$$

Local

Non local

- The non local contribution is 0 (e^u and w^l independant)!
- Its variance on a finite sample $(e^u(\mathbf{R}^u_i), w^l(\mathbf{R}^l_i))_{i\in[1..M]}$:

$$\propto V(e^u) \propto N$$

.

$\Longrightarrow \delta\Delta_\lambda(N) \propto \sqrt{N}$ for large N.

Non locality property of the Pulay term.

Conclusion

$$\frac{\delta\Delta_\lambda}{\Delta_\lambda} \propto \sqrt{N} \tag{7}$$

Correlated sampling with reweighting solves the small λ difficulty but not the large N one

Illustration on H_n chains

Is the analysis for non interacting subsystems holds for interacting systems ?

- Hydrogen chains, metallic and insulating
- Calculation of the force on the first nucleus : derivative of the energy with respect to the position of the first nucleus
- Variational calculation
- ψ is a single determinant (Restricted Hartree Fock)

Metallic hydrogen chains

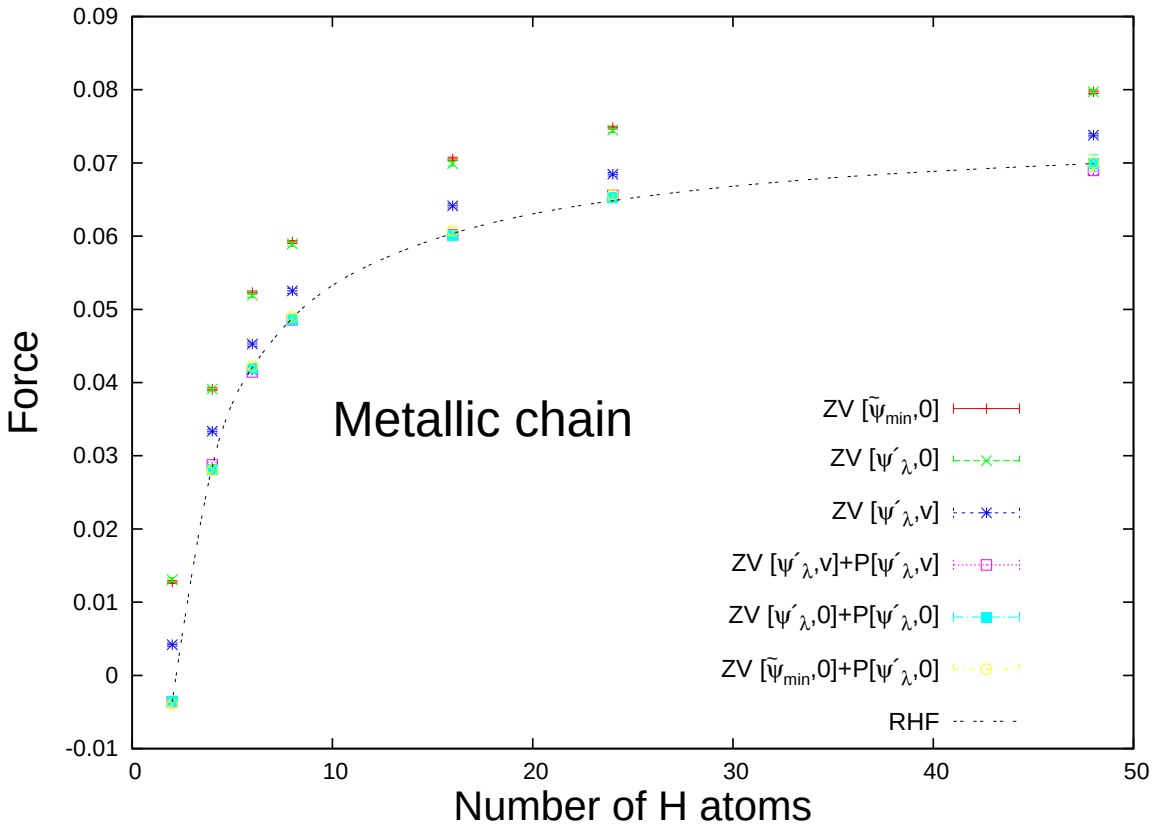


FIG.: Energy derivative, different estimators

Insulating hydrogen chains

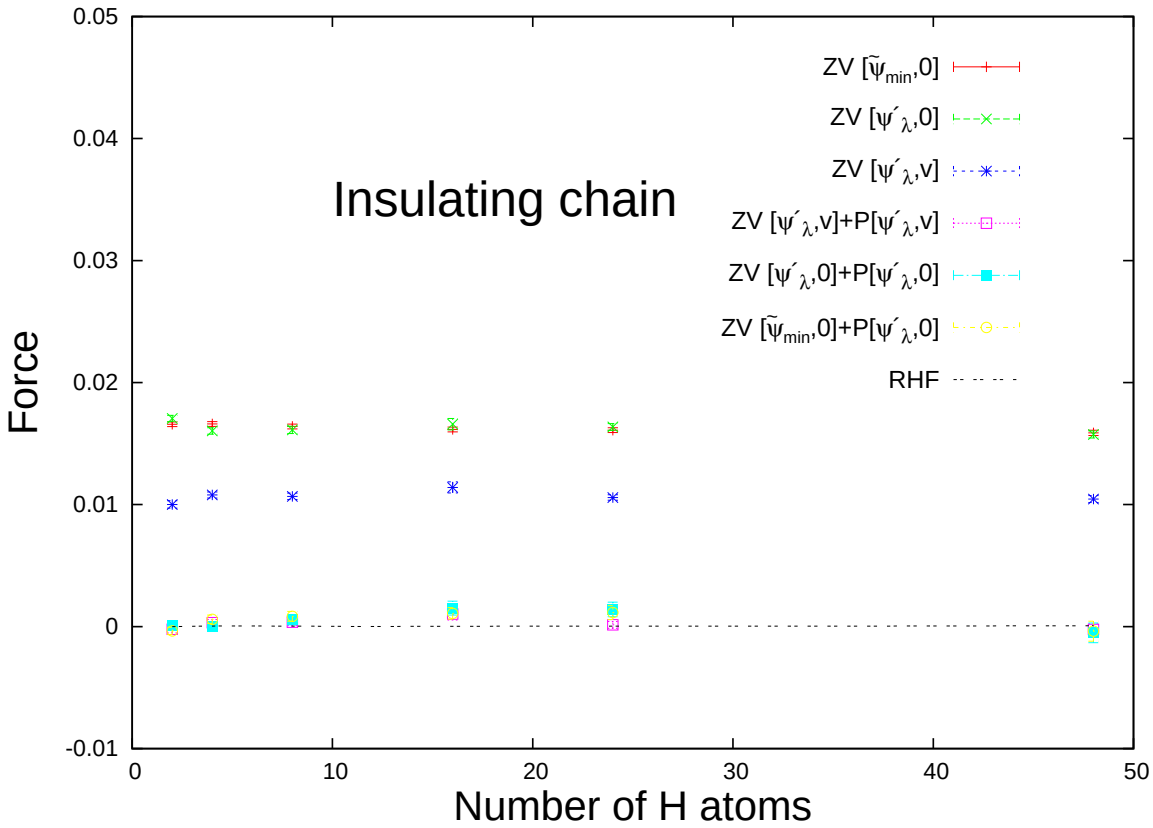


FIG.: Energy derivative, different estimators

Histogram of the ZV term, metallic chain

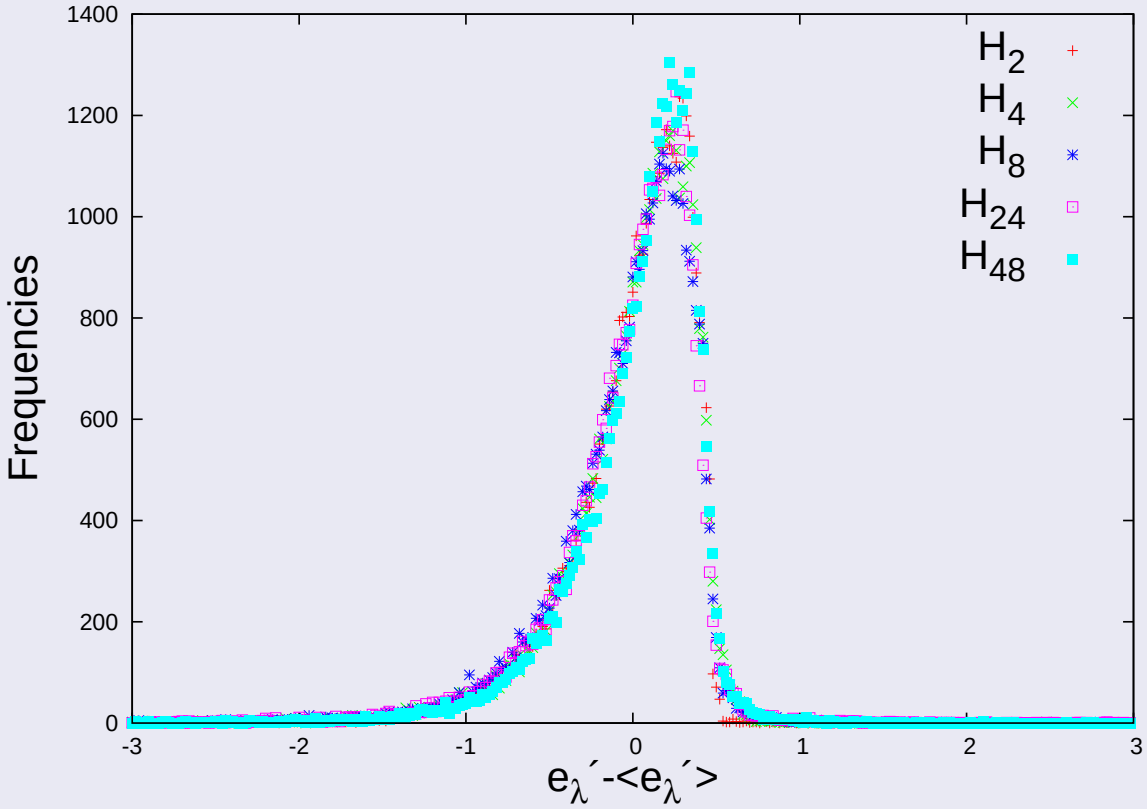


FIG.: Histogram of the energy derivative in the H_n chain

ZV contribution has the local property!!

Histogram of the local energy, metallic chain

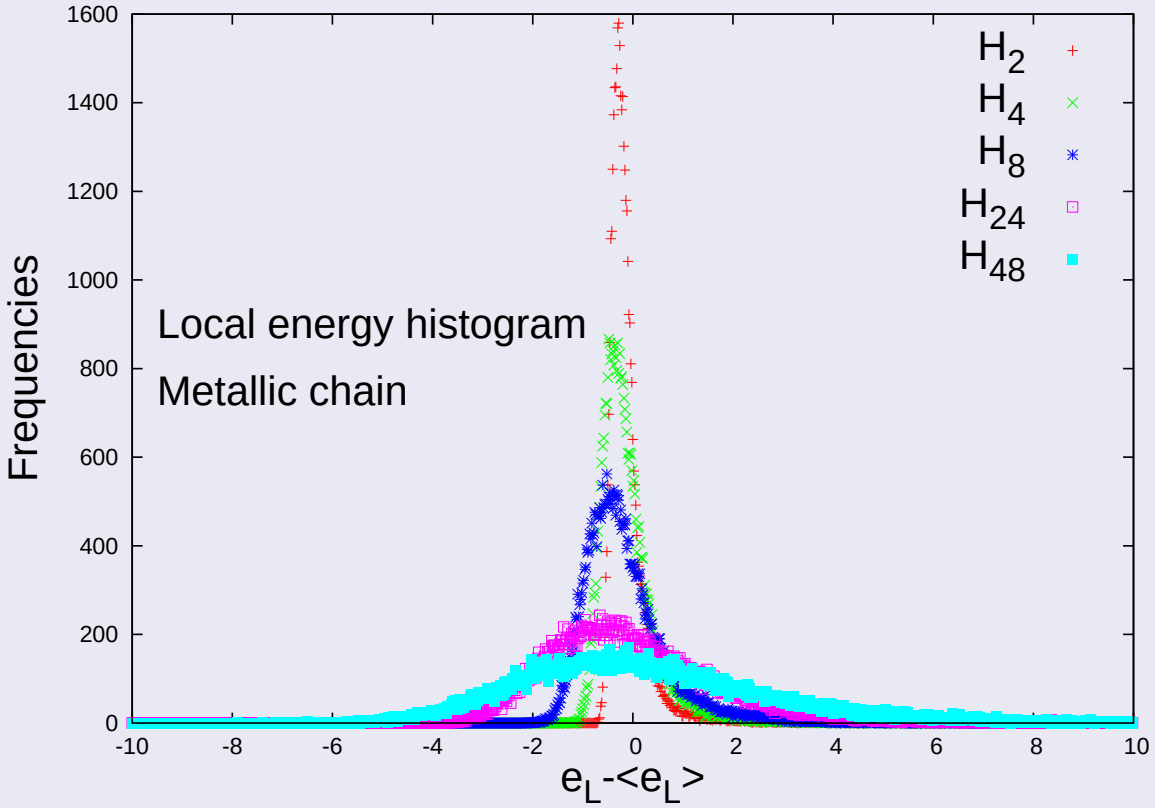


FIG.: Histogram of the local in the H_n chain

The local energy has not the local property

Statistical uncertainties

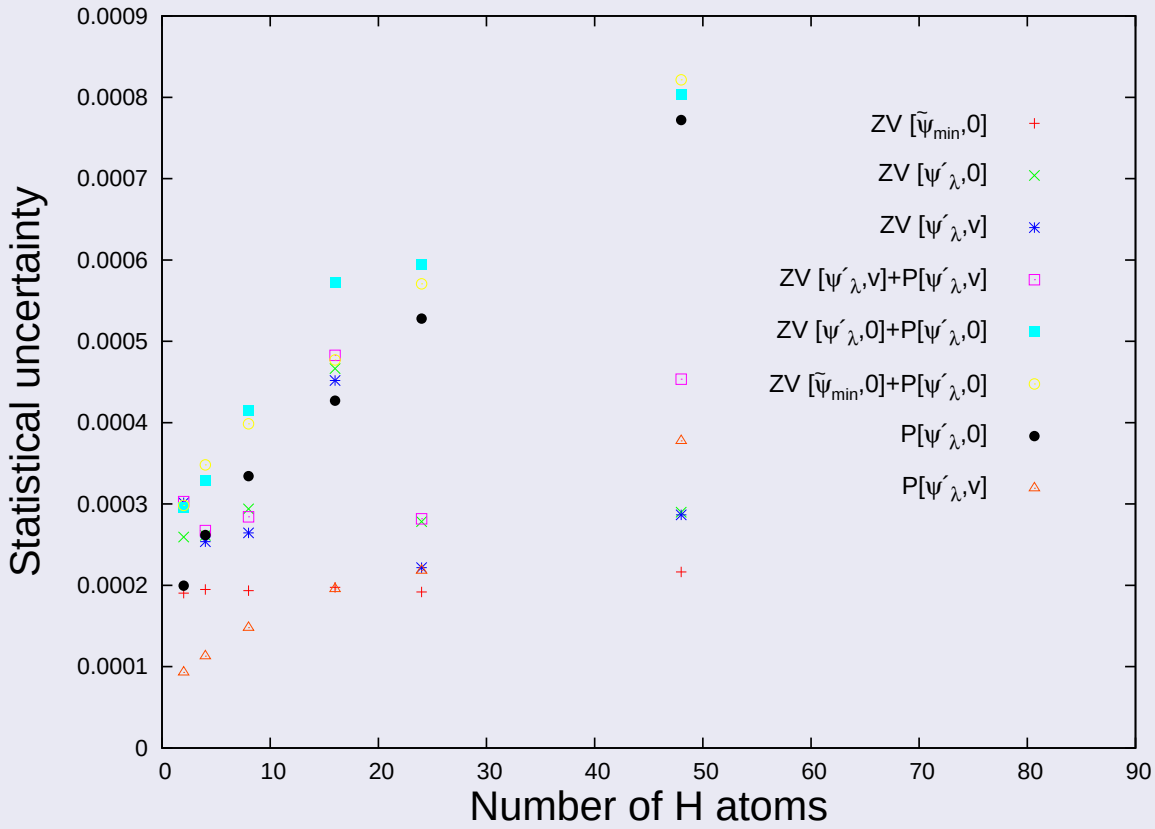


FIG.: Statistical uncertainties in the insulating H_n chain

Statistical uncertainties

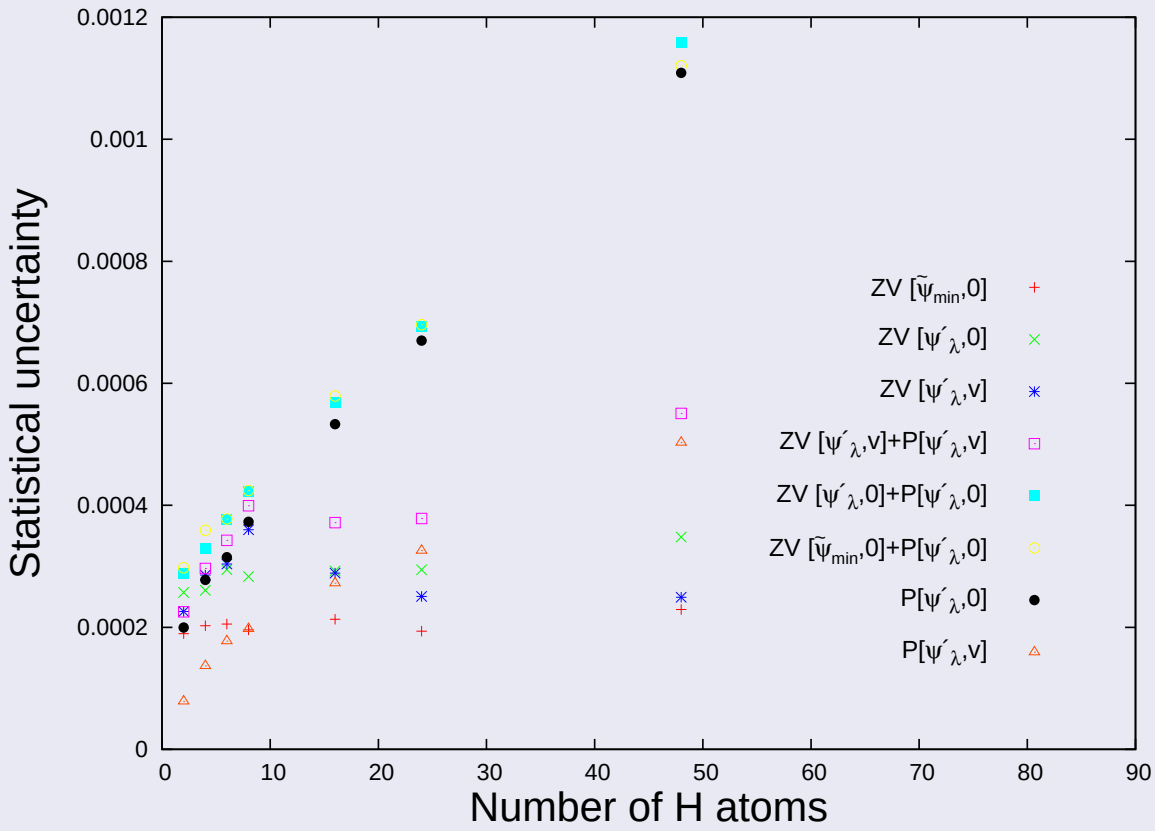


FIG.: Statistical uncertainties in the metallic H_n chain

The method

Assaraf, Caffarel, Kollias 2011

Basic idea

$$\langle e_\lambda(\mathbf{R})\rangle_{\pi_\lambda} - \langle e(\mathbf{R})\rangle_{\pi} = \langle e_\lambda(\mathbf{R}_\lambda) - e(\mathbf{R})\rangle_{\Pi(\mathbf{R},\mathbf{R}_\lambda)}$$

- Marginal distributions of $\Pi(\mathbf{R},\mathbf{R}_\lambda)$ must be $\pi(\mathbf{R}), \pi_\lambda(\mathbf{R}_\lambda)$.
- differences of the order of λ, $\langle(\mathbf{R}_\lambda) - \mathbf{R})^2\rangle = K\lambda^2$

How to build such a process

- Choosing close stochastic processe, L, L_λ having π and π_λ as stationary states.
- Stability versus chaos. Two trajectories with the different initial conditions and same pseudo random numbers meet exponentially fast.
- Insures that close processes will produce close trajectories.

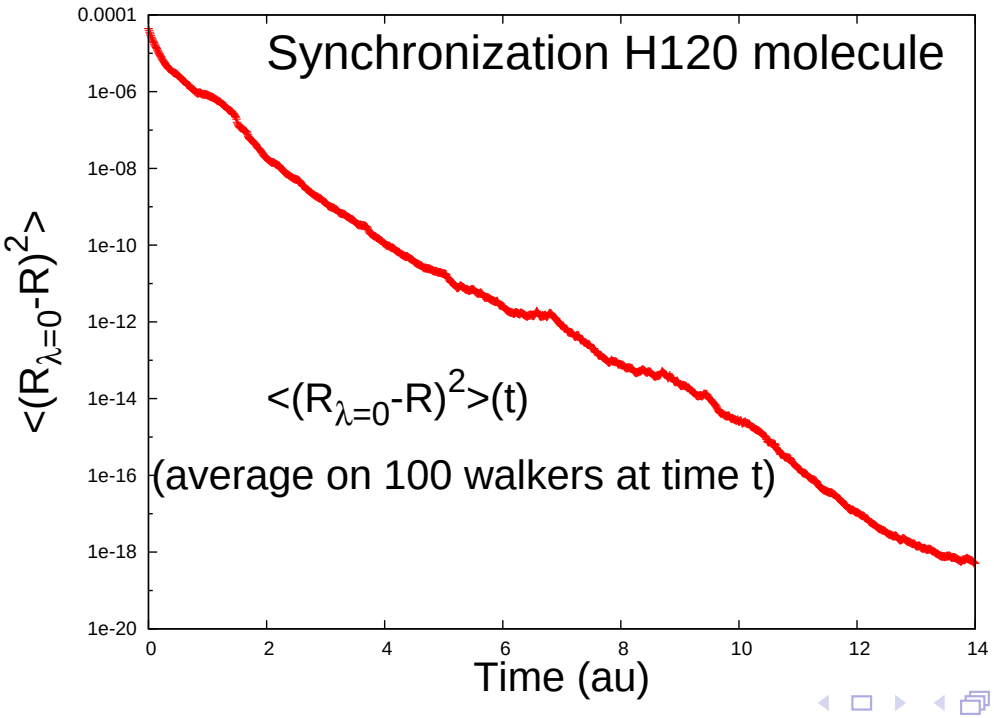
For example, with the overdamped Langevin process one would have

$$\mathbf{R}(t+dt) = \mathbf{R}(t) + \mathbf{b}\left[\mathbf{R}(t)\right] dt + \mathbf{dW} \quad (8)$$

$$\mathbf{R}_\lambda(t+dt) = \mathbf{R}_\lambda(t) + \mathbf{b}_\lambda\left[\mathbf{R}_\lambda(t)\right] dt + \mathbf{dW} \quad (9)$$

Stability of the process versus chaos

- Chain of 120 Hydrogens (120 electrons).
- Same process but different initial conditions.
- Perturbed system one atom displaced of $\lambda = 10^{-4} a.u$ (finite difference derivative).



Independance of the uncertainties on λ

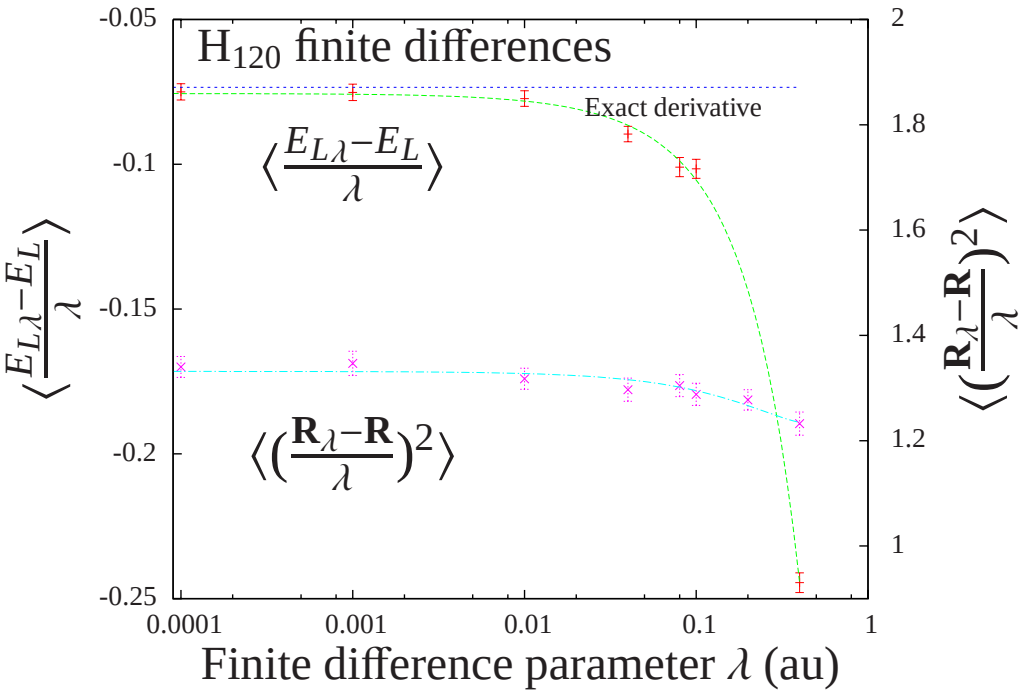


FIG.: Quadratic distances betwen the two processes

Locality of the algorithm

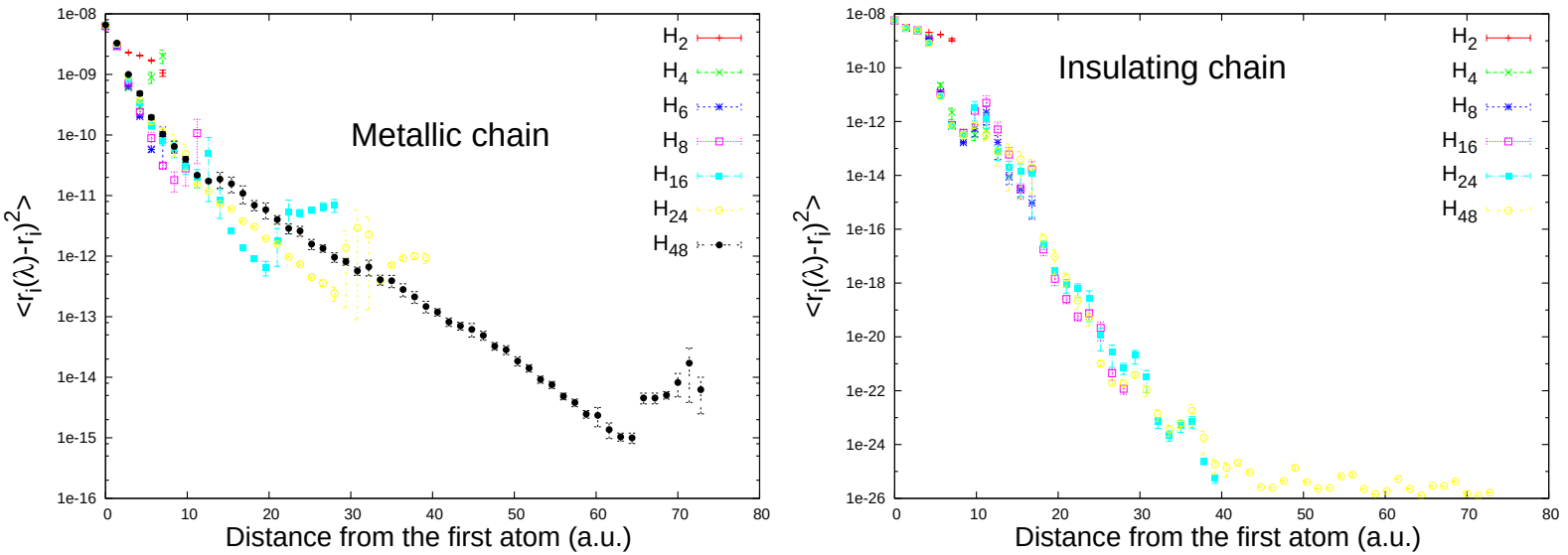


FIG.: Square average of the inter electron distance at a given distance from the first atom

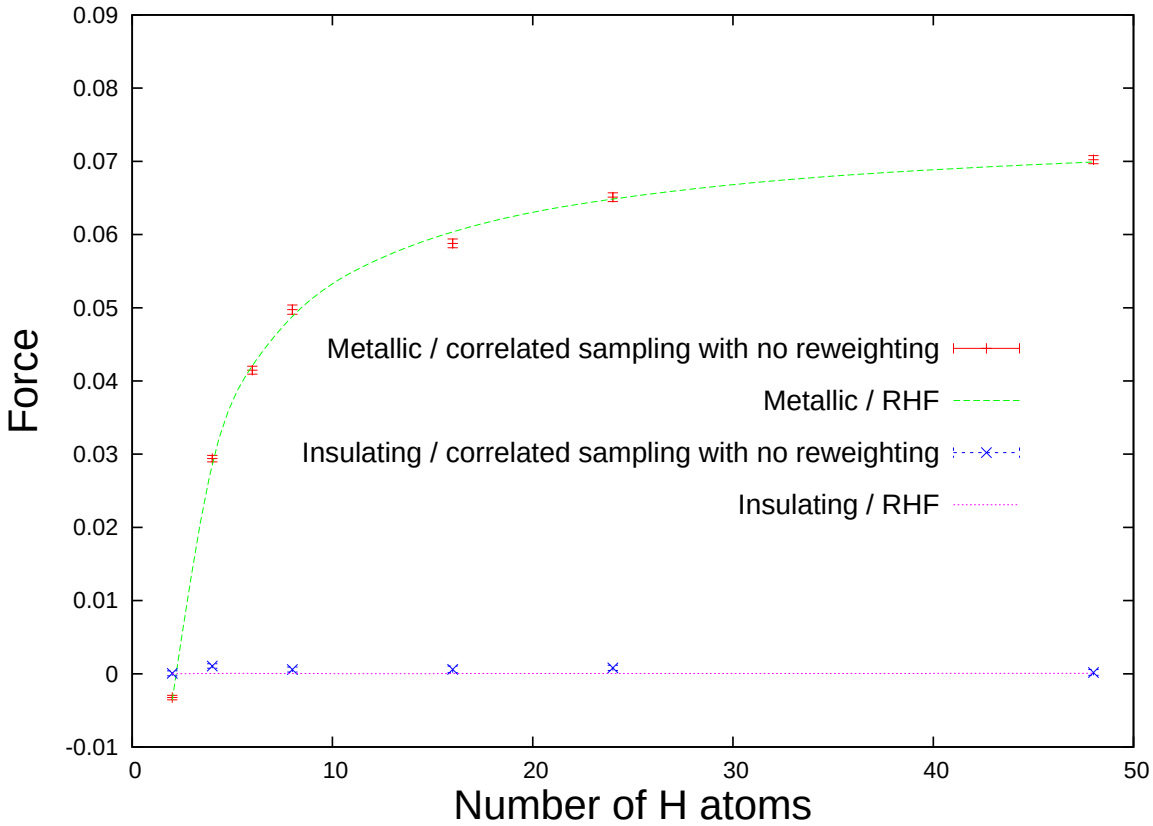


FIG.: Energy derivative with the correlated sampling with no reweighting

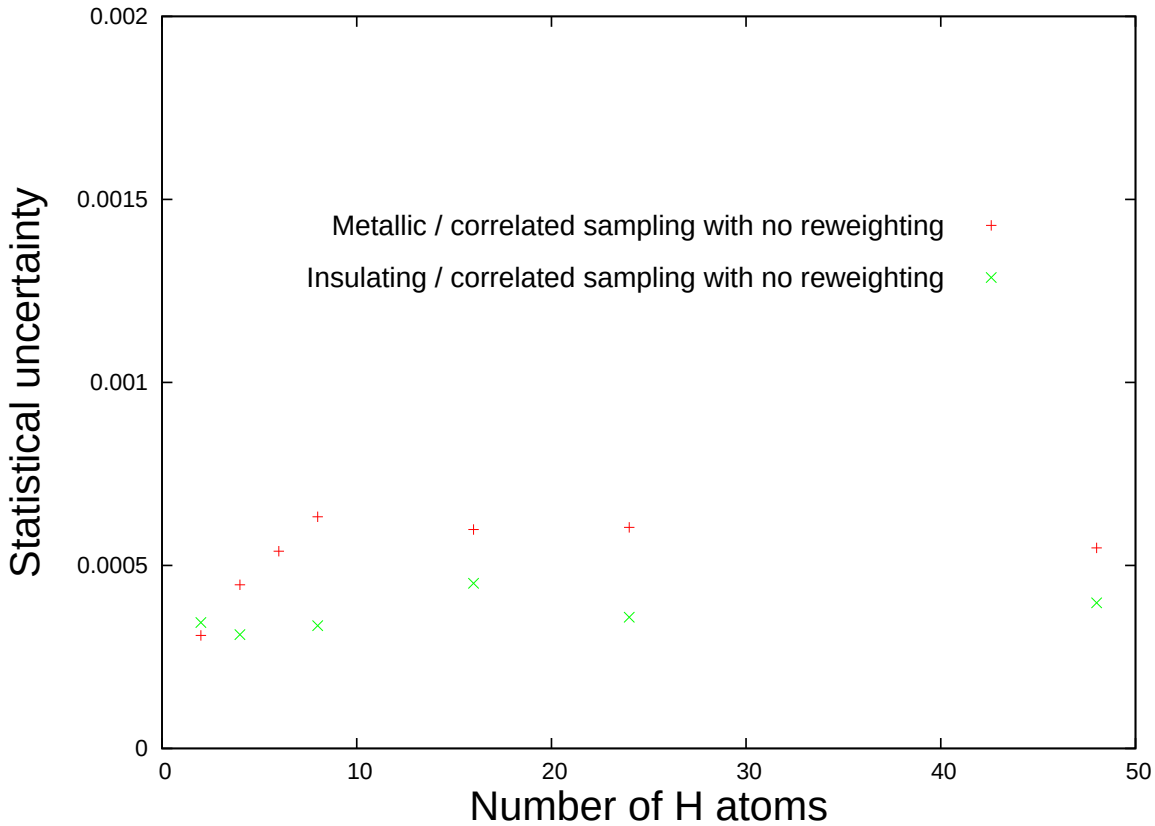


FIG.: Uncertainty as a function of N, metallic chains

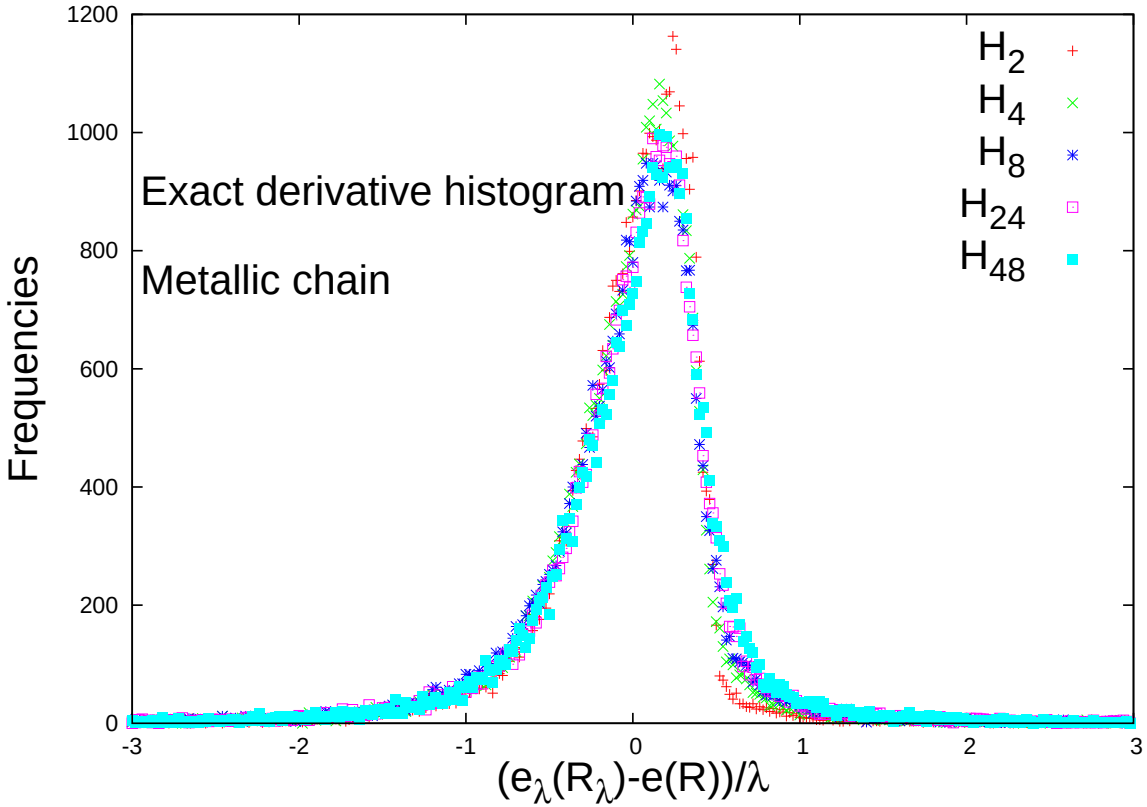


FIG.: Histogram of the correlated difference metallic chain

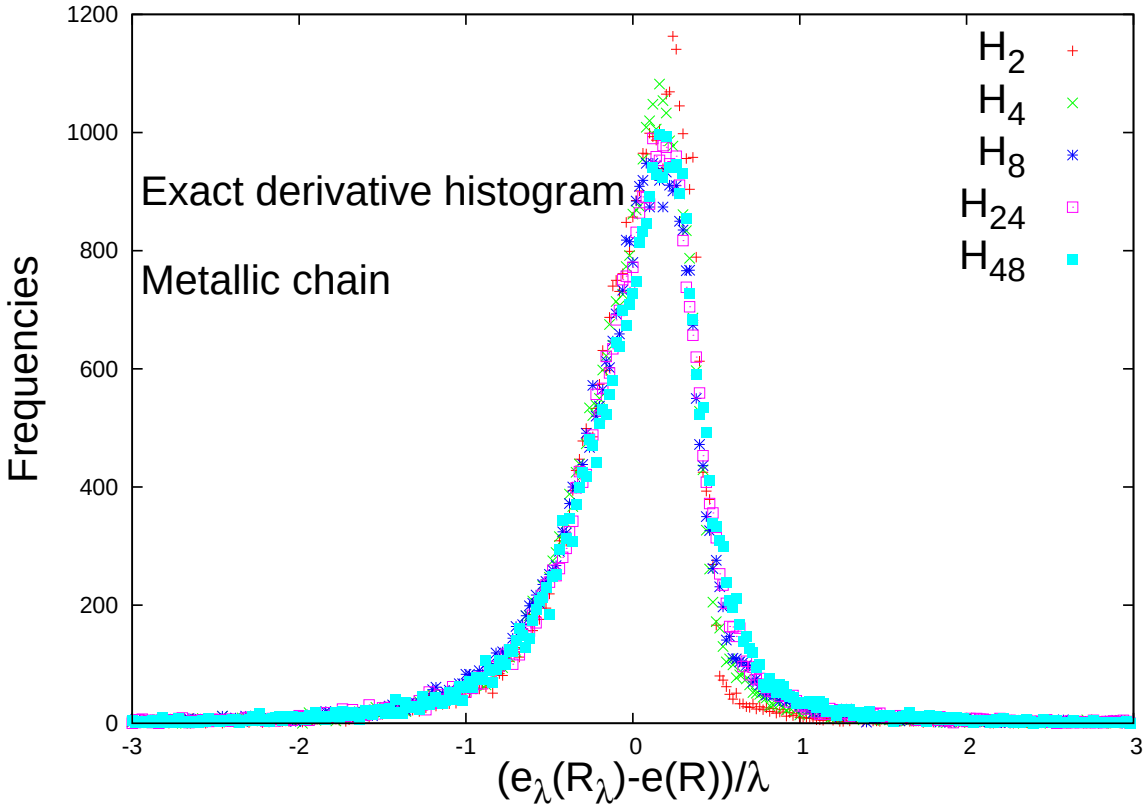


FIG.: Histogram of the correlated difference metallic chain

Reweighting introduces statistitical fluctuations difficult to control

- Solves the small perturbation problem (λ small).
- Sometimes large prefactors in the variance.
- Same large N behavior as independent energy calculations.

Correlated sampling with no reweighting

- Solves the small λ and large N undesirable behavior.
- Perspective to obtain small energy differences with comparable accuracy to the energy.
- Relies on some particular dynamics (stability with respect to the chaos).

Possible to build such stable dynamics

- At the core of perfect sampling (criteria of time convergence, see Fahy, Krauth...).
- Building such dynamics for general molecules is underway.
- Vast subject (numerically, mathematically). Collaborations are welcome...