UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO DI CHIMICA

An Efficient Computational Approach for the Calculation of the Vibrational Density of States

Fabio GABAS

Chiara AIETA

Michele CEOTTO

The vibrational density of states

The vibrational density of states of a chemical system is the number of vibrational states per unit of energy.

$$\rho_{vib}(E) = \frac{dN}{dE}$$

$$Q_{vib}(\beta) = \int \rho_{vib}(E) e^{-\beta E} \mathrm{d}E$$

How to calculate the vibrational density of states

Methods **Limitations**

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Inverse Laplace Transform	$N(E) = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{e^{\beta E}}{\beta 2^s \prod_{j=1}^{s} \sinh\left(\frac{1}{2}\beta\hbar\omega_j\right)} d\beta$	Limited in dimensionality and in energy range [1]

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$$\overline{\nu}_i = \nu_i + 2X_{ii} + \frac{1}{2}\sum_{j\neq i} X_{ij}$$

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Approximation: set of uncoupled harmonic oscillators of «effective» frequency

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Exact Count	$N(E) = \sum_{n_1=0,n_2=0,n_{F-1}=0}^{\infty} P_n(E_v)$	Affordable up to 4 atoms systems

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BSSR Algorithm[4]	$N(E) = \sum_{n_1=0,n_2=0,n_{F-1}=0}^{\infty} P_n(E_{sep})$	Approximation: uncoupled oscillators

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MultiWell

MultiWell is a program suite that calculates time dependent concentrations, reaction yields, vibrational distributions, and rate constants as functions of temperature and pressure for multi-well, multi-channel unimolecular reactions systems[5]

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Ann Arbor,
Department of Atmospheric,
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$$E = \sum_{i=1}^{nvib} \omega_i \left(v_i + \frac{1}{2} \right) + \sum_{i,j=1}^{nvib} X_{ij} \left(v_i + \frac{1}{2} \right) \left(v_j + \frac{1}{2} \right)$$

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$$\Delta N_{vib}(E)$$

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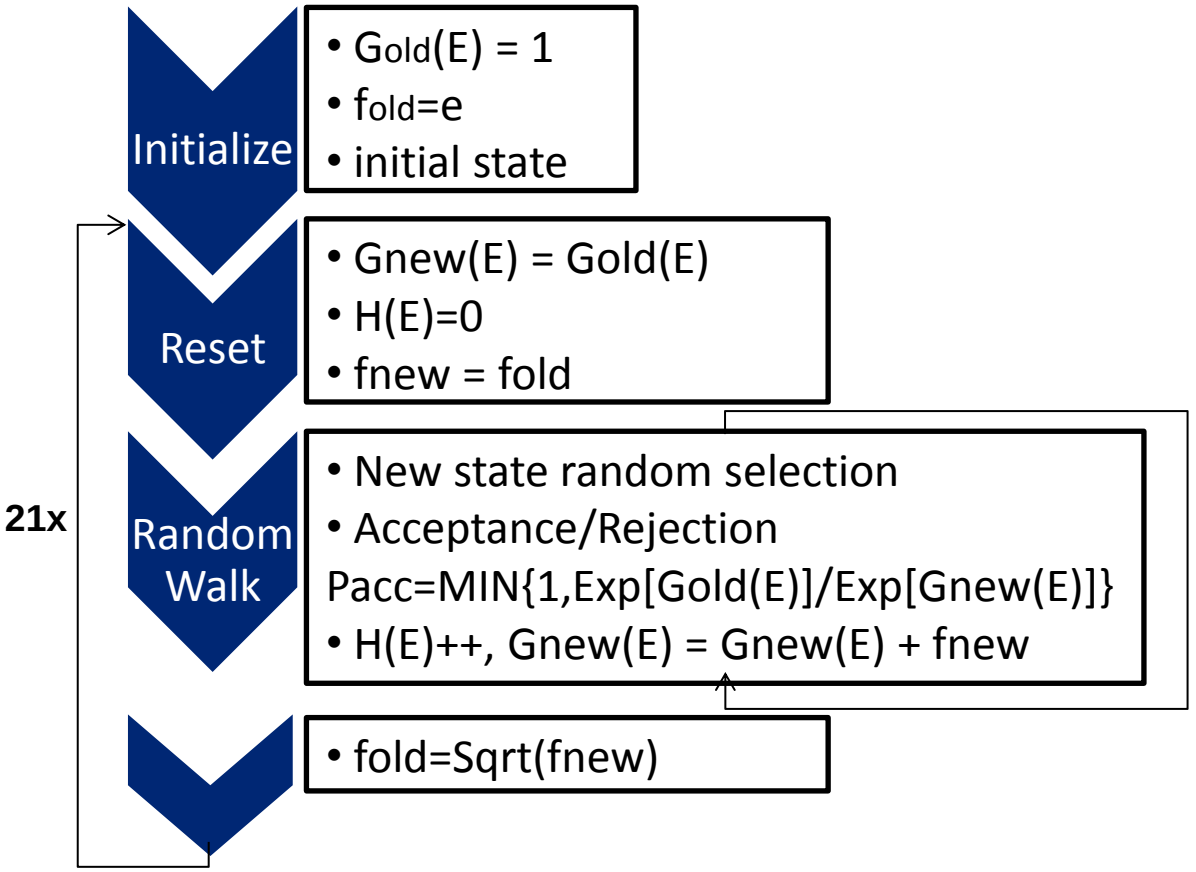
Wang Landau Monte Carlo in adensum

$$G(E) = \ln[\rho(E)] = \ln[\frac{dN(E)}{dE}]$$

The algorithm is based upon the observation that the histogram of visits H(E) will be flat when the probability of visiting each energy level for a random walk in the space of the quantum numbers is proportional to $1/\rho_{vib}(E)$ [6]



6) Wang, F.; Landau, D. P. Efficient, Multiple-range Random Walk Algorithm to Calculate the Density of States. Phys. Rev. Lett. 2001, 86, 2050–2053..

From adensum to paradensum: parallelization strategy

Limits of Adensum

- Serial code
- Not computationally fully optimized
- Limited in dimensionality

7) T. Vogel, Y. W. Li, T. Wust and P. Landau, PRL 110, 210603 (2013)

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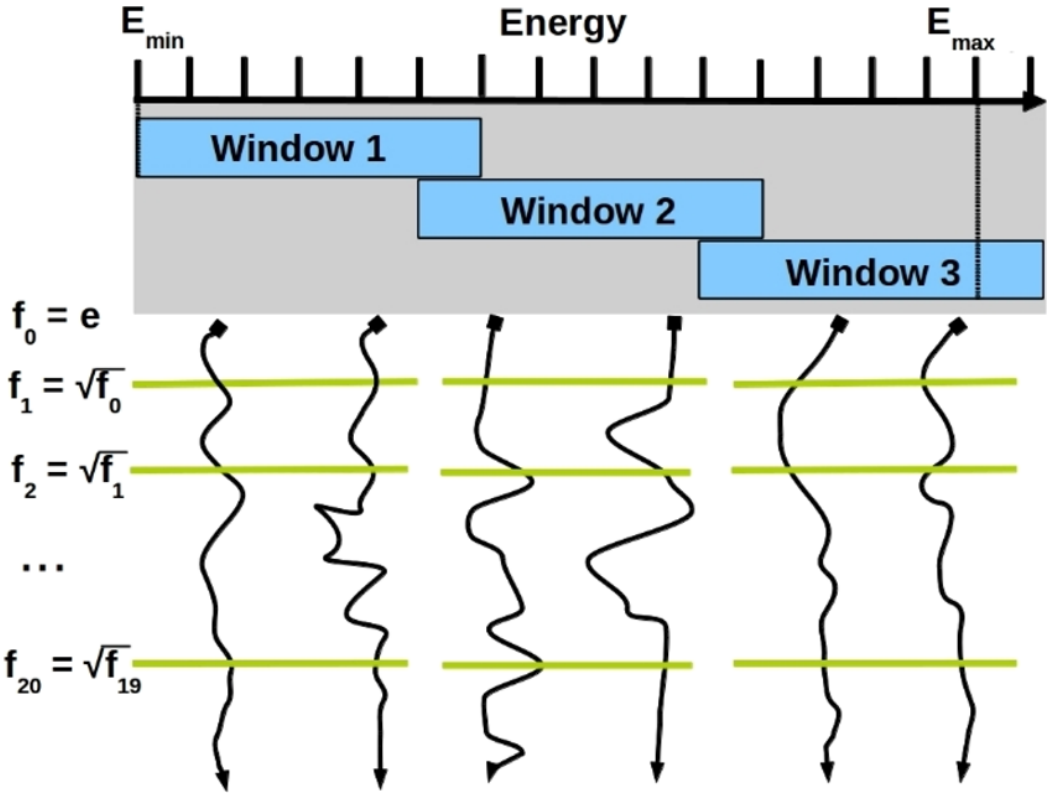
Parallelization Idea For the new Paradensum code

Having to search in a **smaller phase space** the alghorithm **converges faster**[7]



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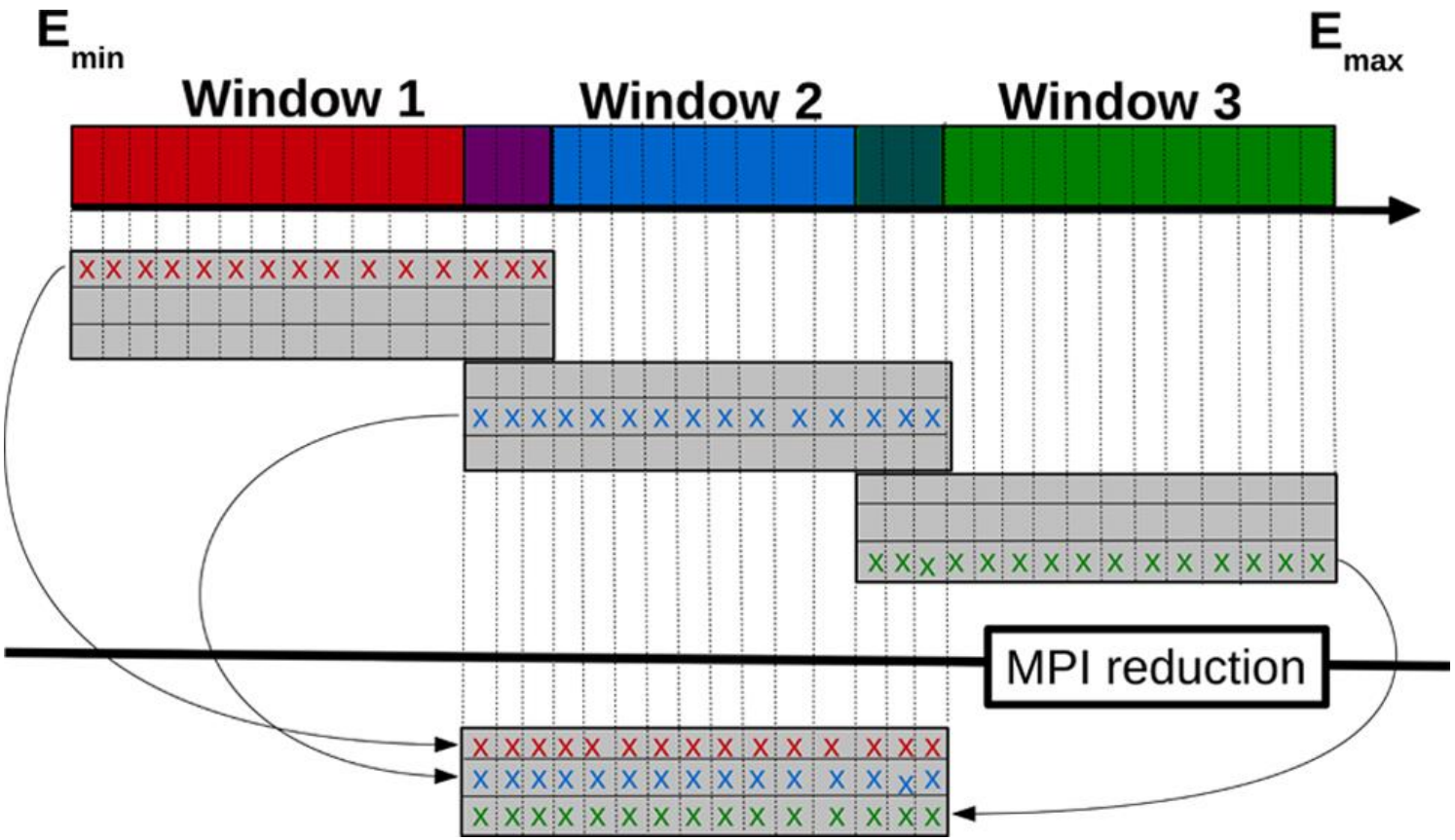
Parallel data subdivison and organization



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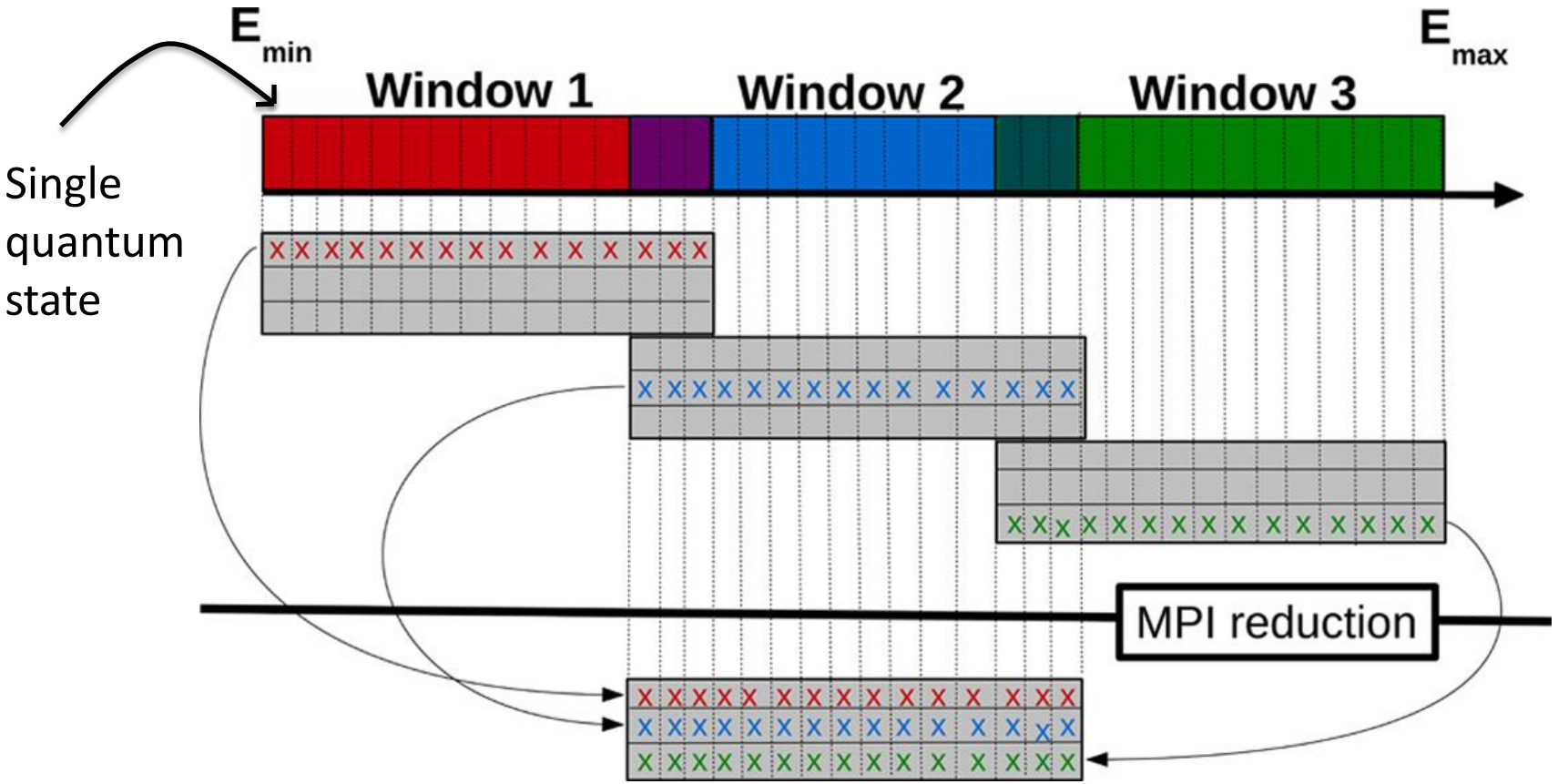

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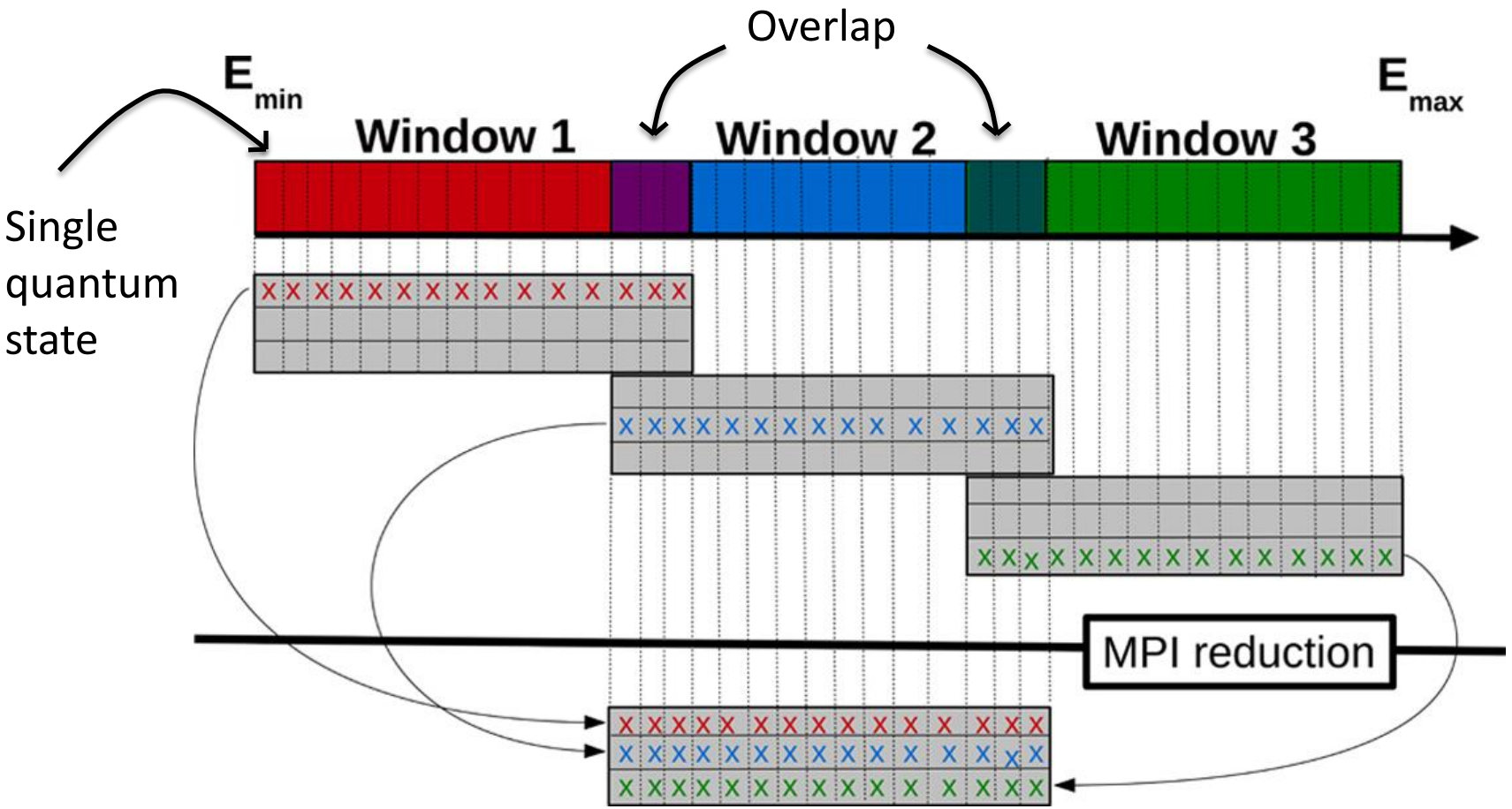


Paradensum new features

Parallelization

To overcome the limitations of the MultiWell adensum code, we modify the present algorithm structure and then implement it for parallel architectures by using the MPI

Flatness criterion

In the adensum code, f is updated after a fixed number of Monte Carlo sweeps. Instead, in paradensum the WL flatness criterion is applied and monitored separately for each window

Multiple averaging walkers

The code supports the

possibility to run multiple walkers for each energy window

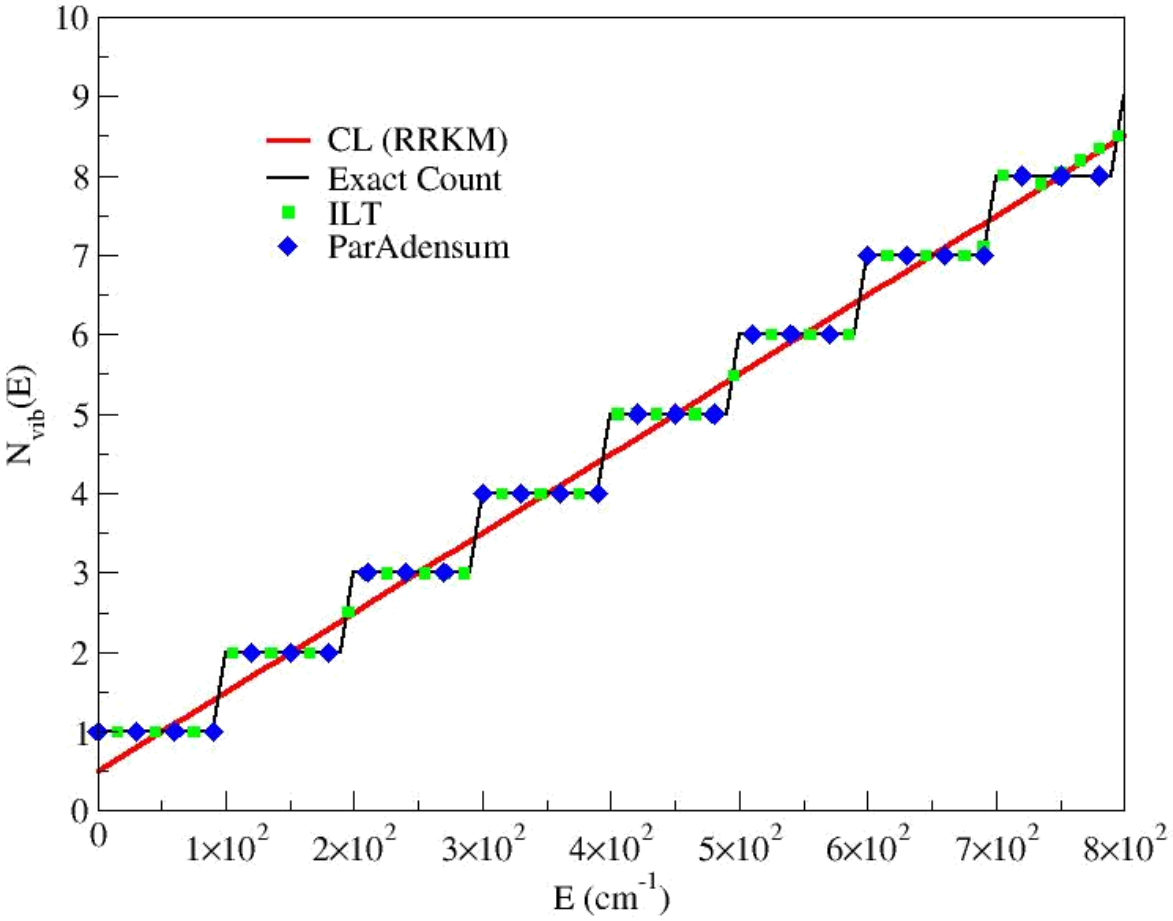
Results overview

Model Systems

Application to molecules

Timing and scalability

Model systems results: one dimensional HO



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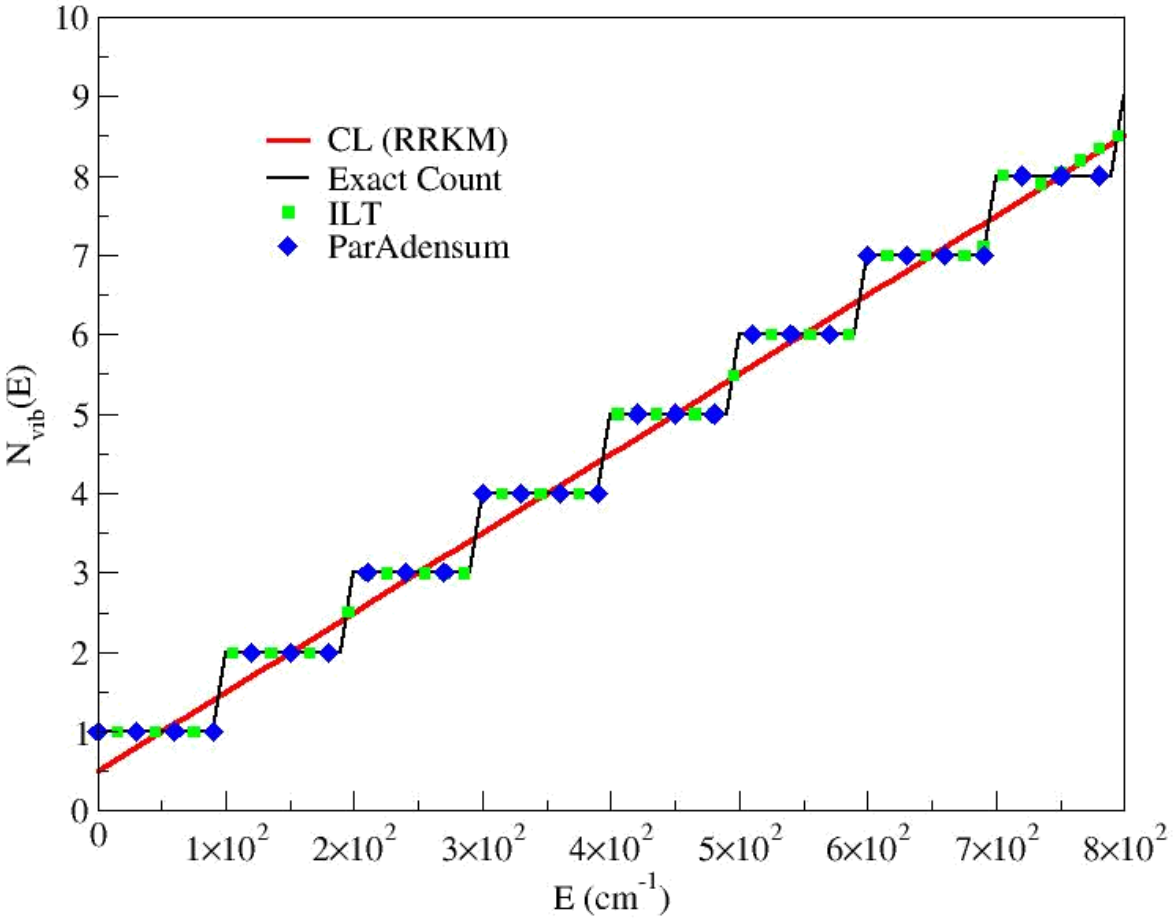

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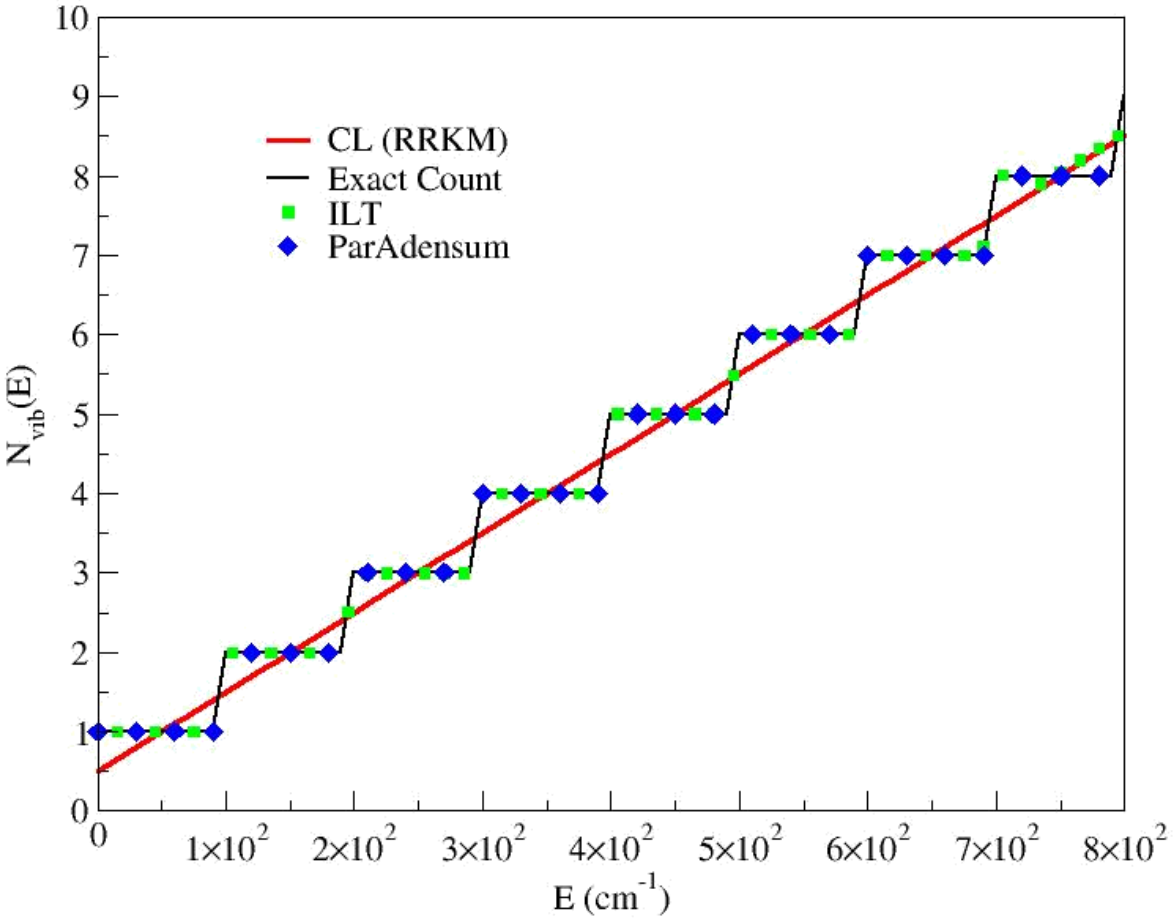

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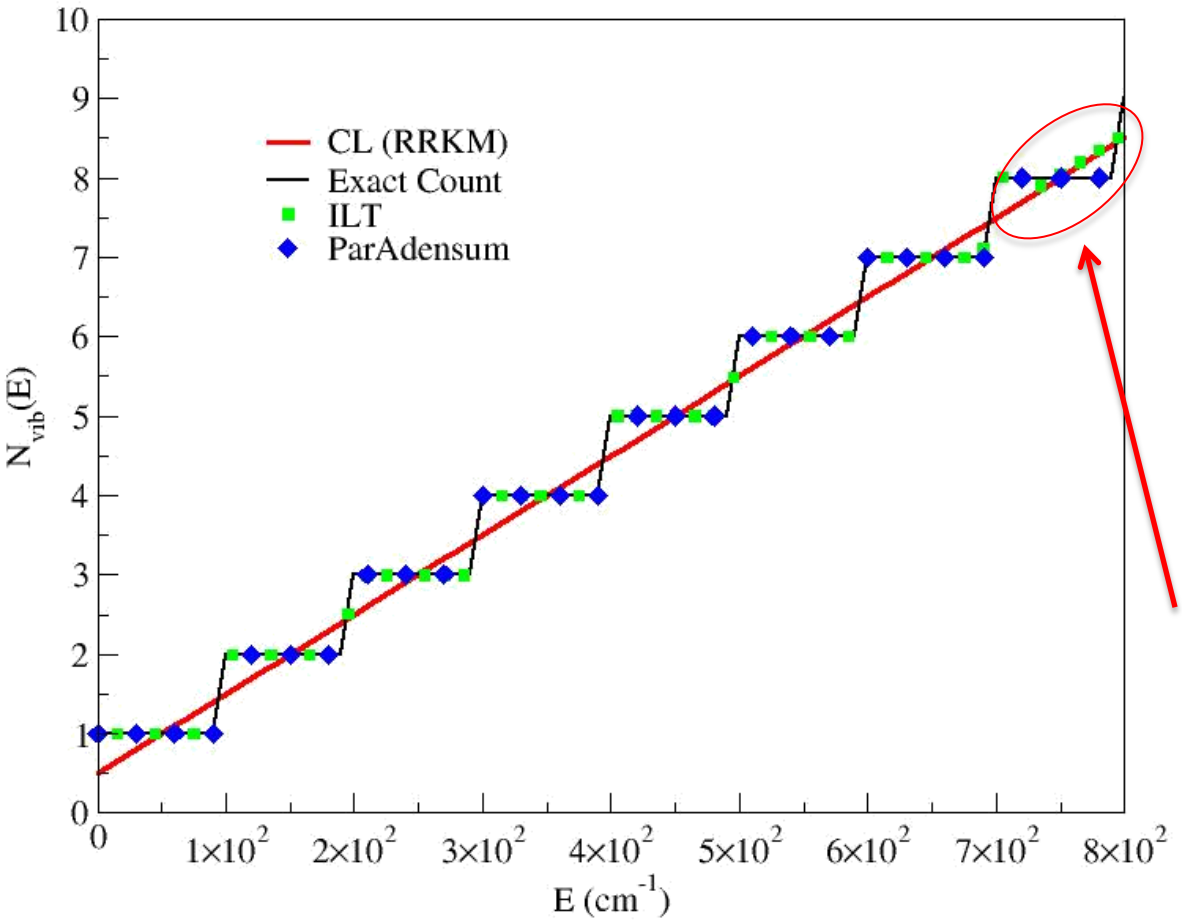

- Paradensum correctly reproduces the results provided by the exact counting of states
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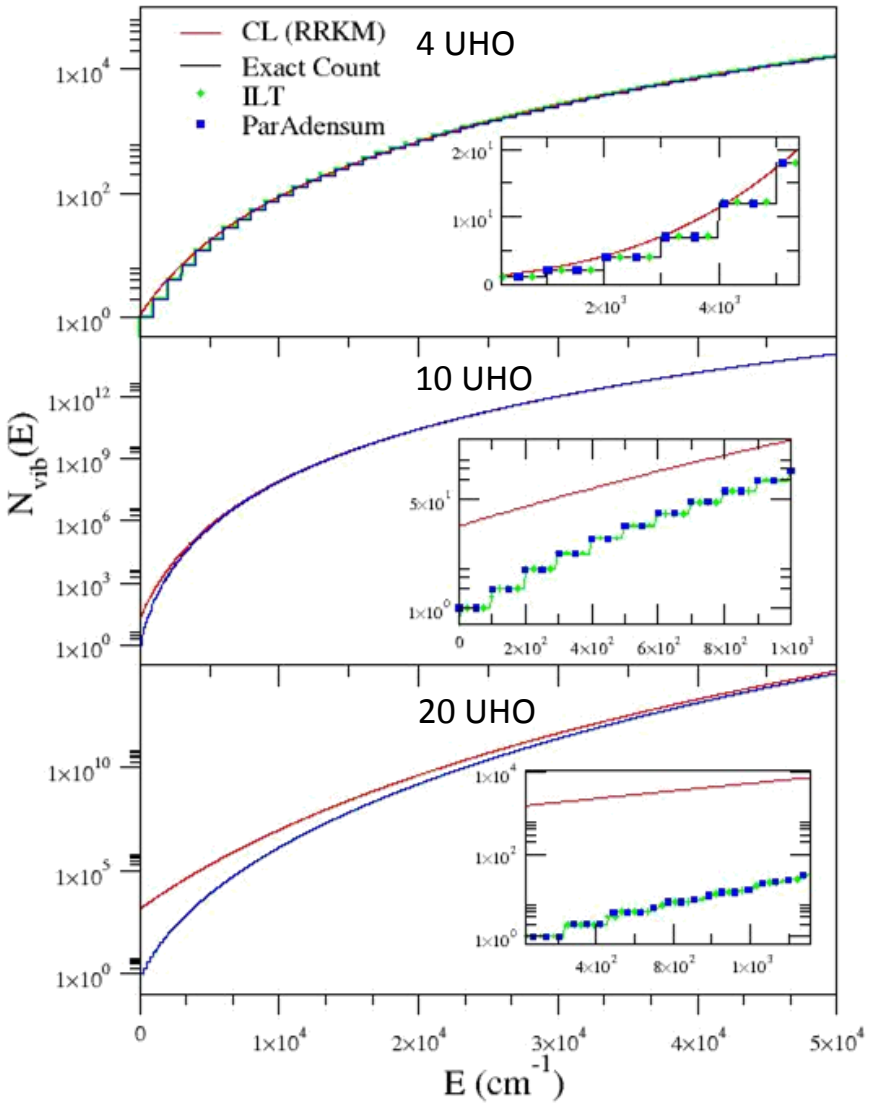
- The ILT can manage the exact counting up to an energy threshold. For higher energy, ILT results are on the top of the CL results

Model systems results: 4,10,20 UHO



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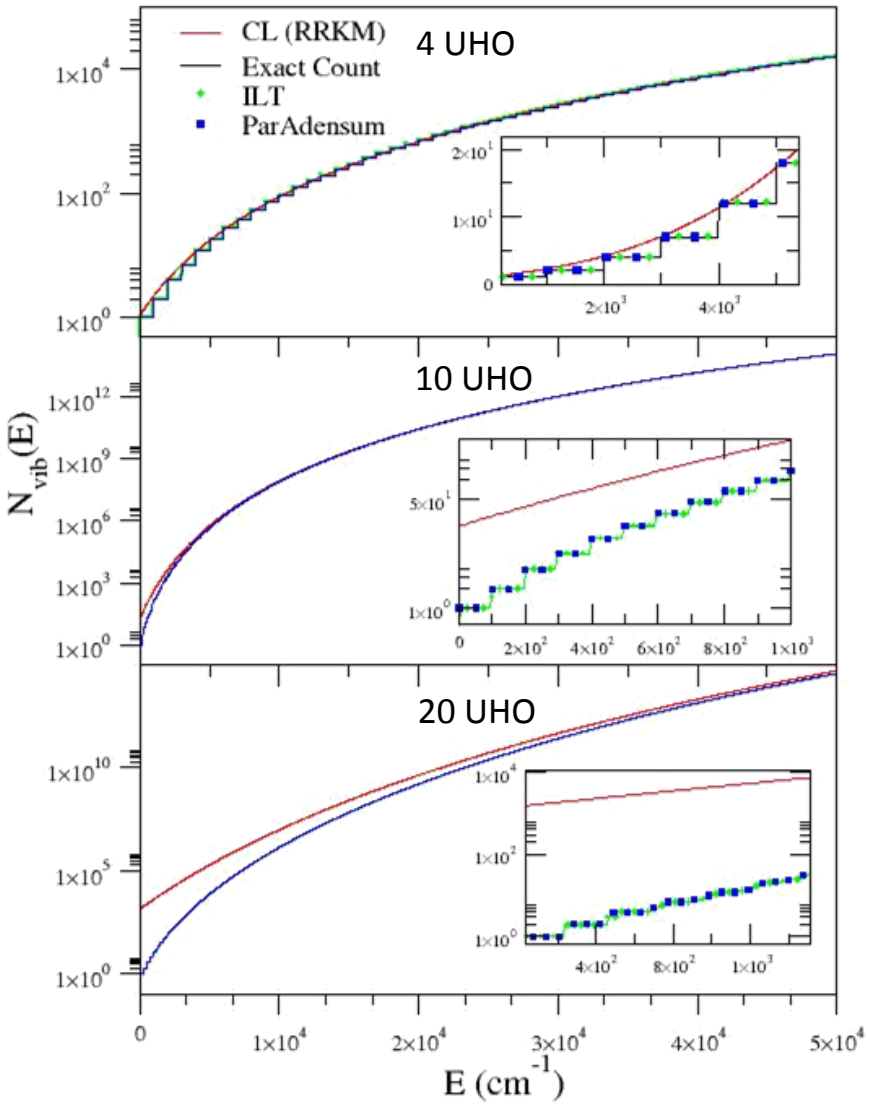

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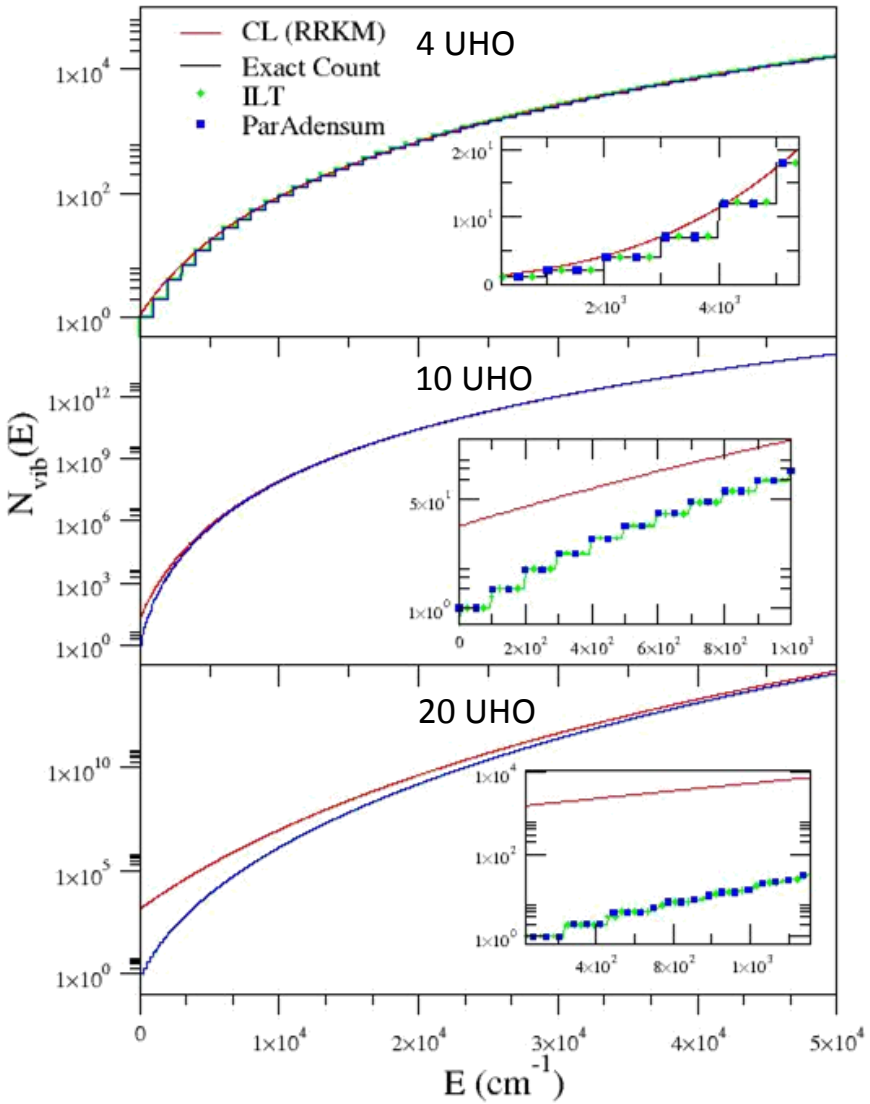

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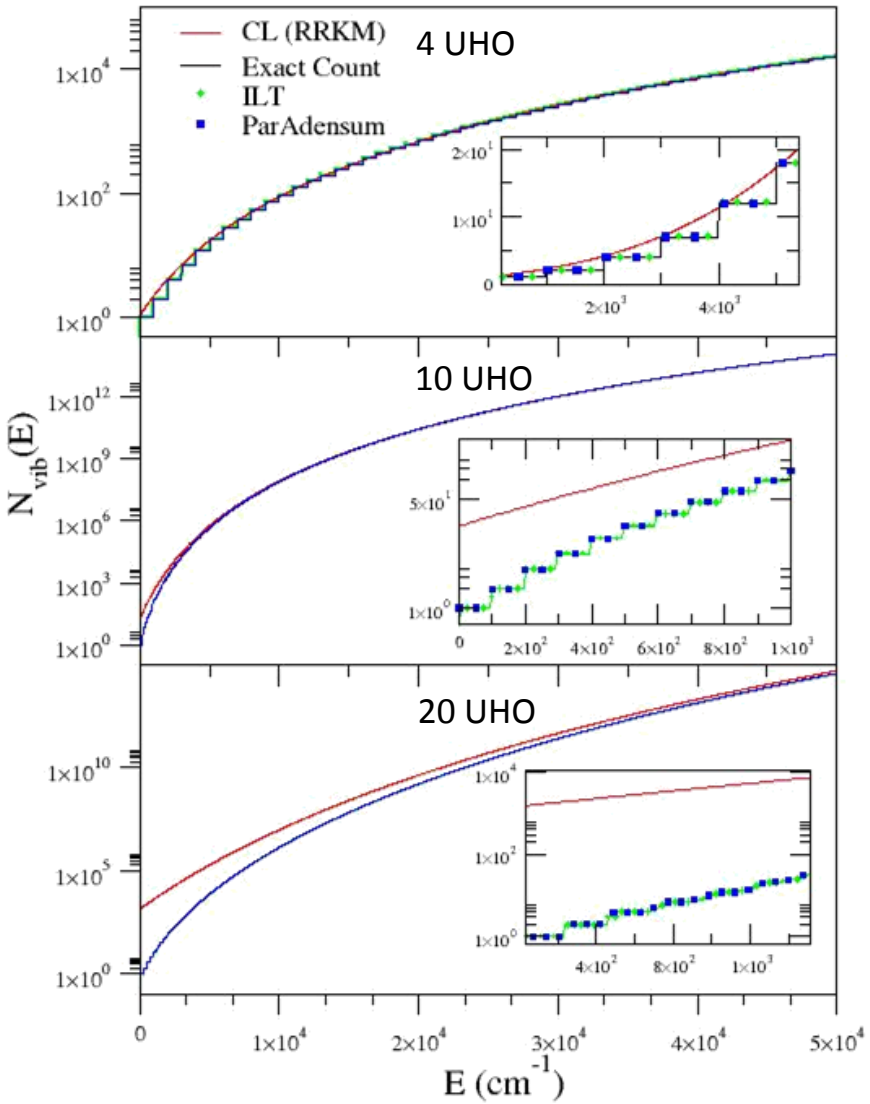

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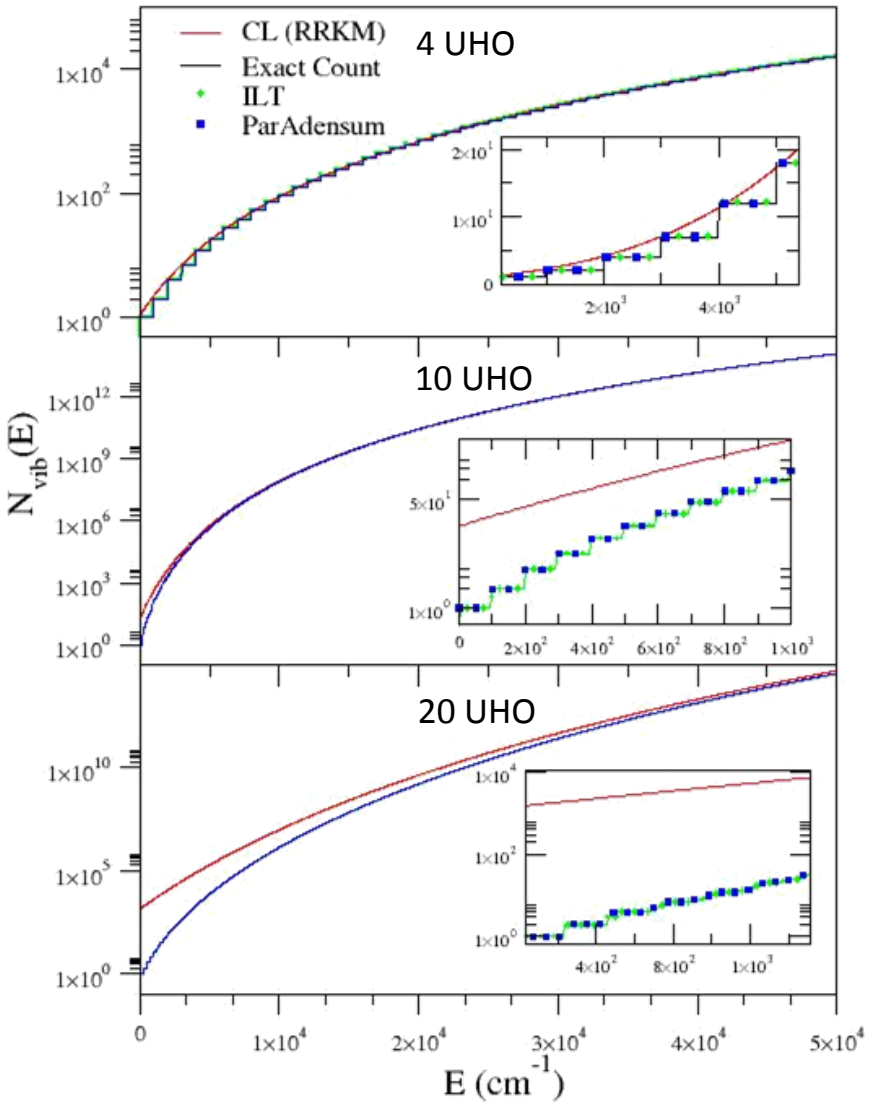

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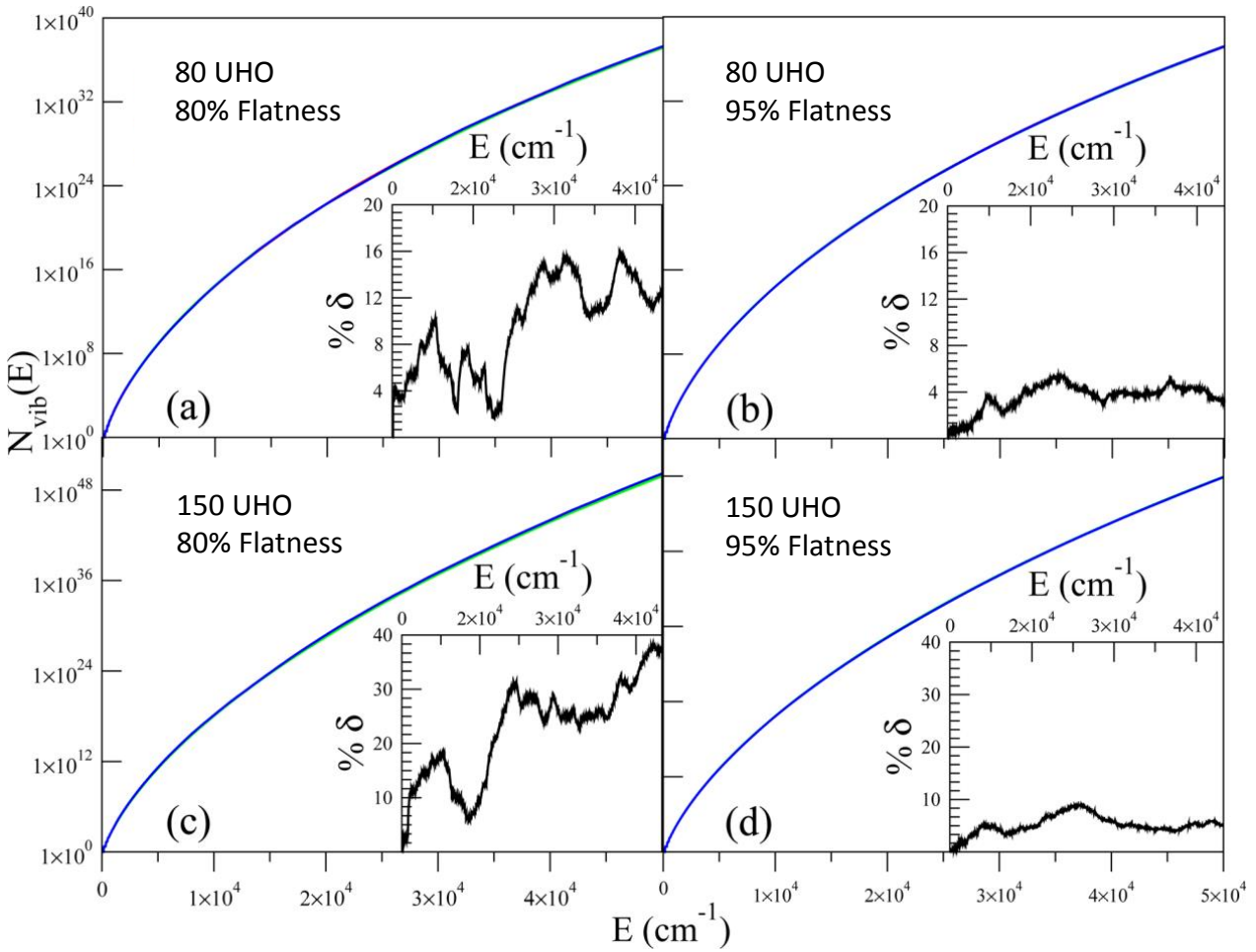
- Paradensum and ILT are in excellent agreement up to 20 dimensions

Model systems: 80 and 150 UHO

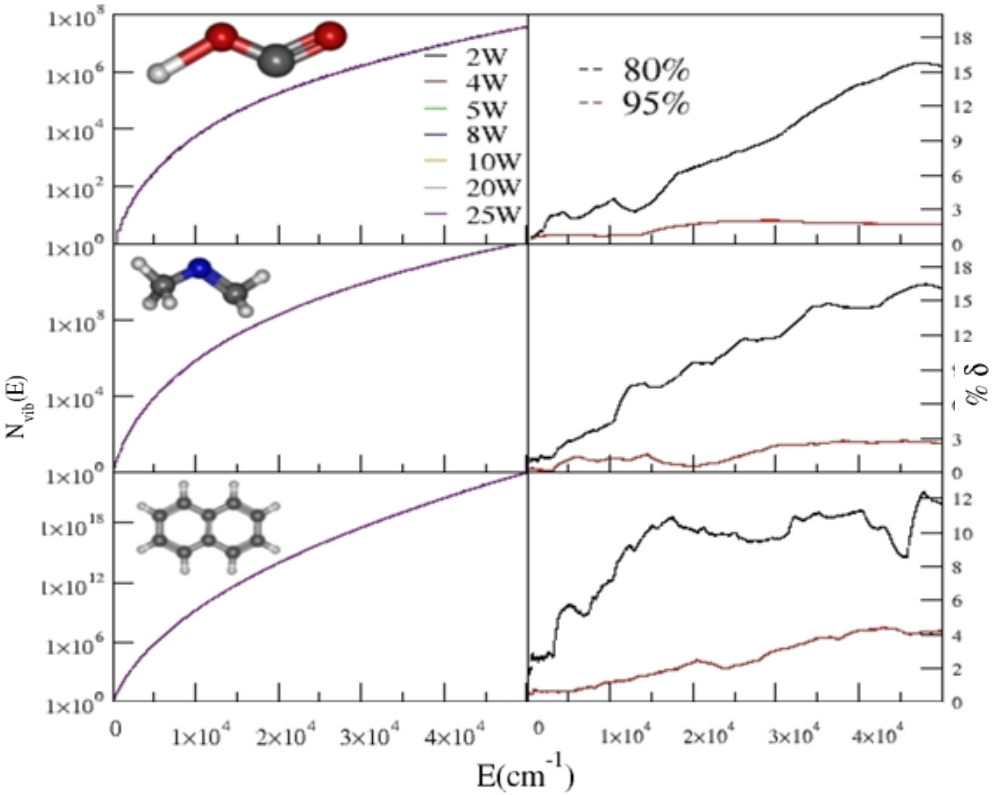


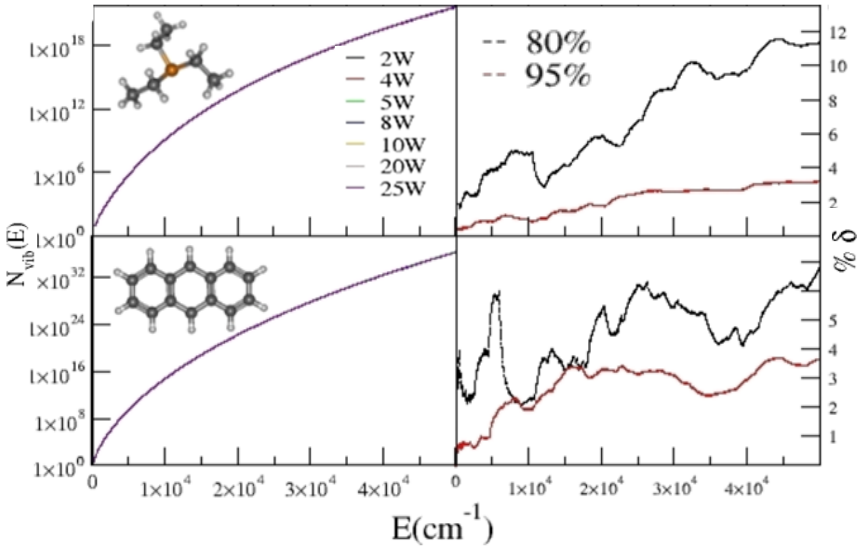
$$\%\boldsymbol{\delta} = 100 \cdot \frac{\sqrt{\sum_{i=1}^{W}(N_{vib,i}(E) - \overline{N_{vib,i}(E)})^2}}{\overline{N_{vib,i}(E)}}$$

$$\overline{N_{vib}(E)} = \frac{1}{W}\sum_{i=1}^{W} N_{vib,i}(E)$$

An increase in WL flatness criterion significantly reduces percentage deviations of the windowing and guarantees that the results are independent from the windowing choice

Application to molecules





Results for different numbers of windows are within 10% using a flatness criterion of 80%, and within 5%, for a 95% flatness choice.

Such a statistical interval of confidence proves the reliability of the parallelization strategy.

Timing and scalability

$$Speedup = \frac{T_{serial}}{T_{N\_processors}}$$

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$$Windowing\ Efficiency = \frac{Windowing\ Speedup}{N\_processors}$$

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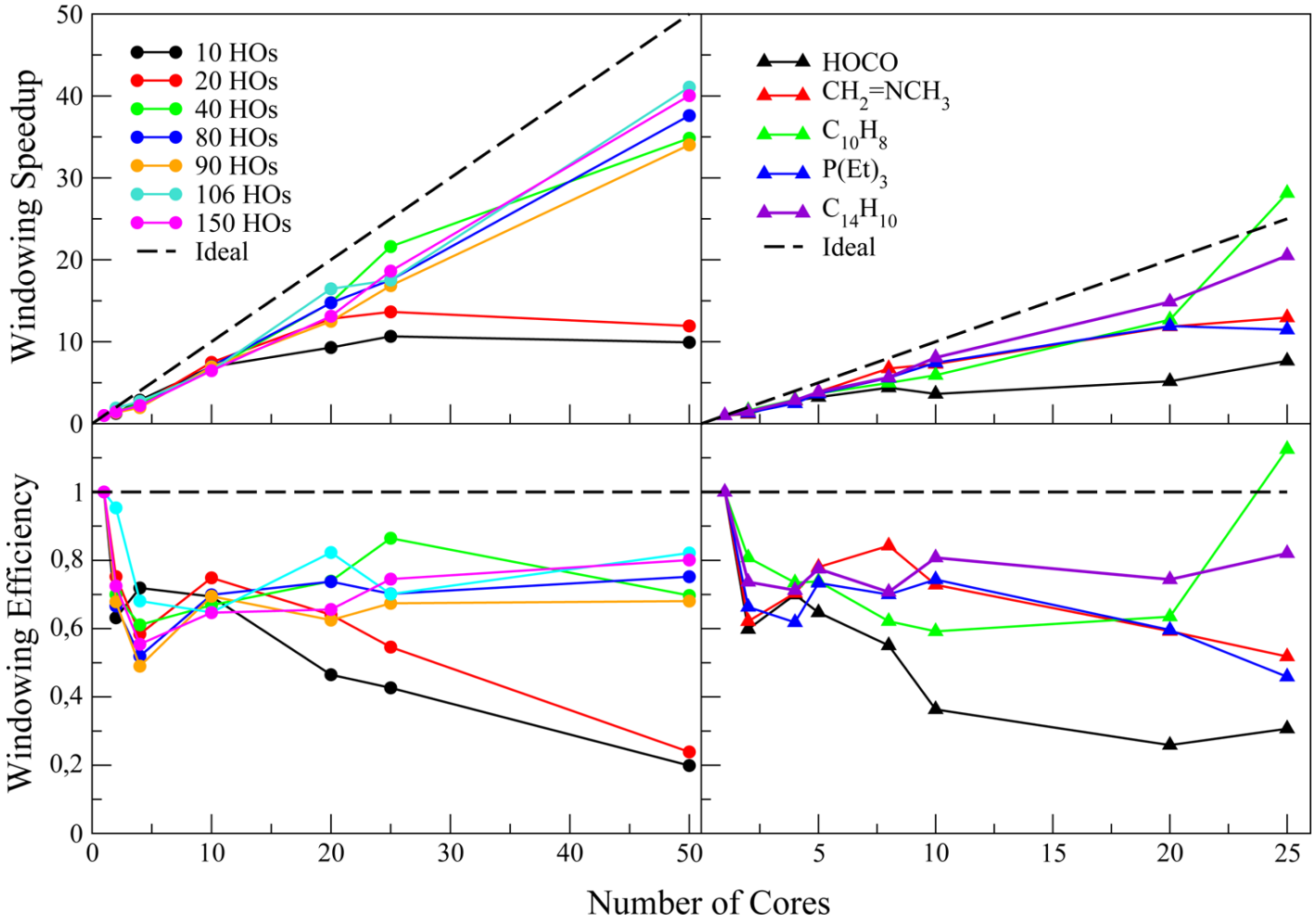

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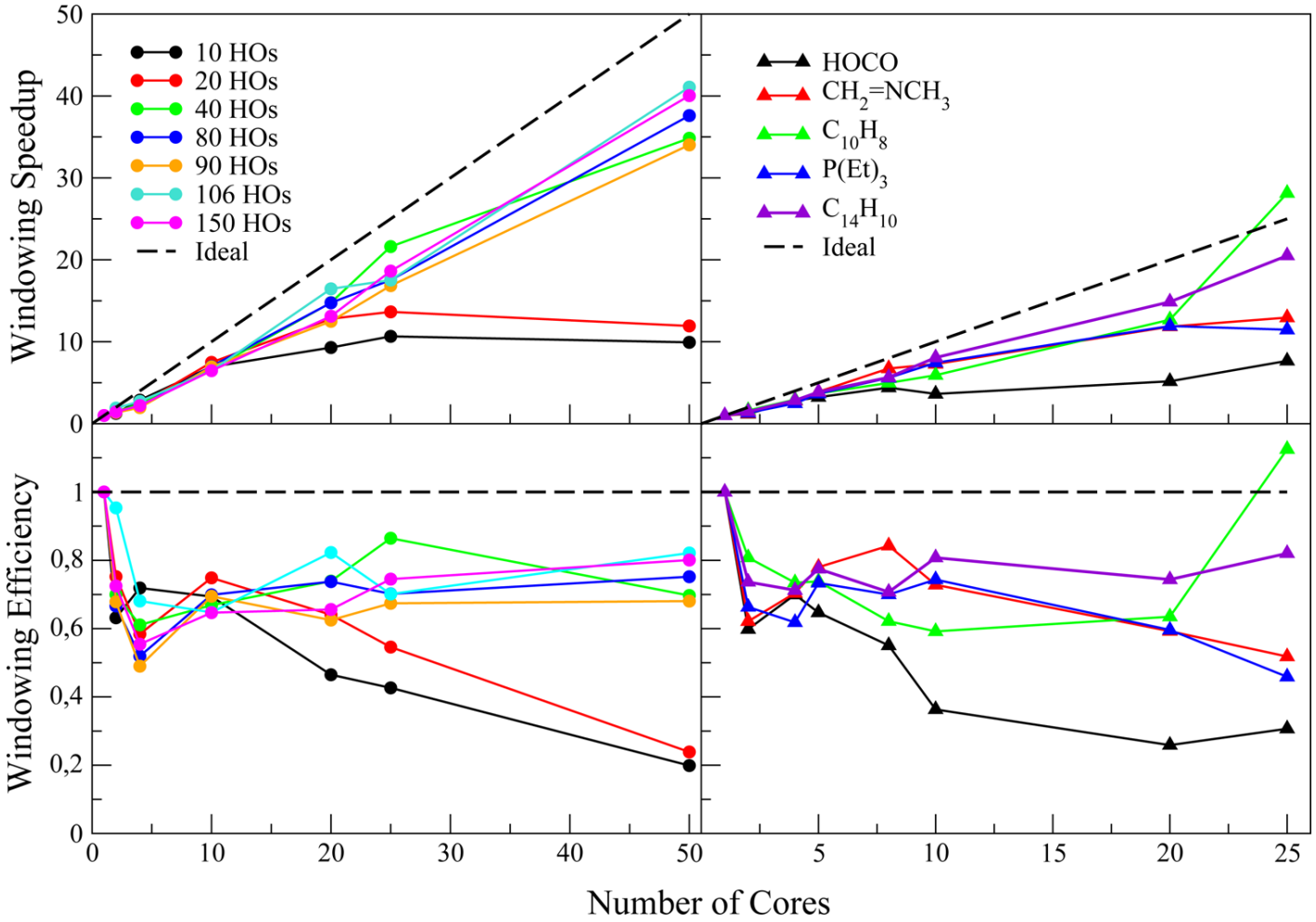

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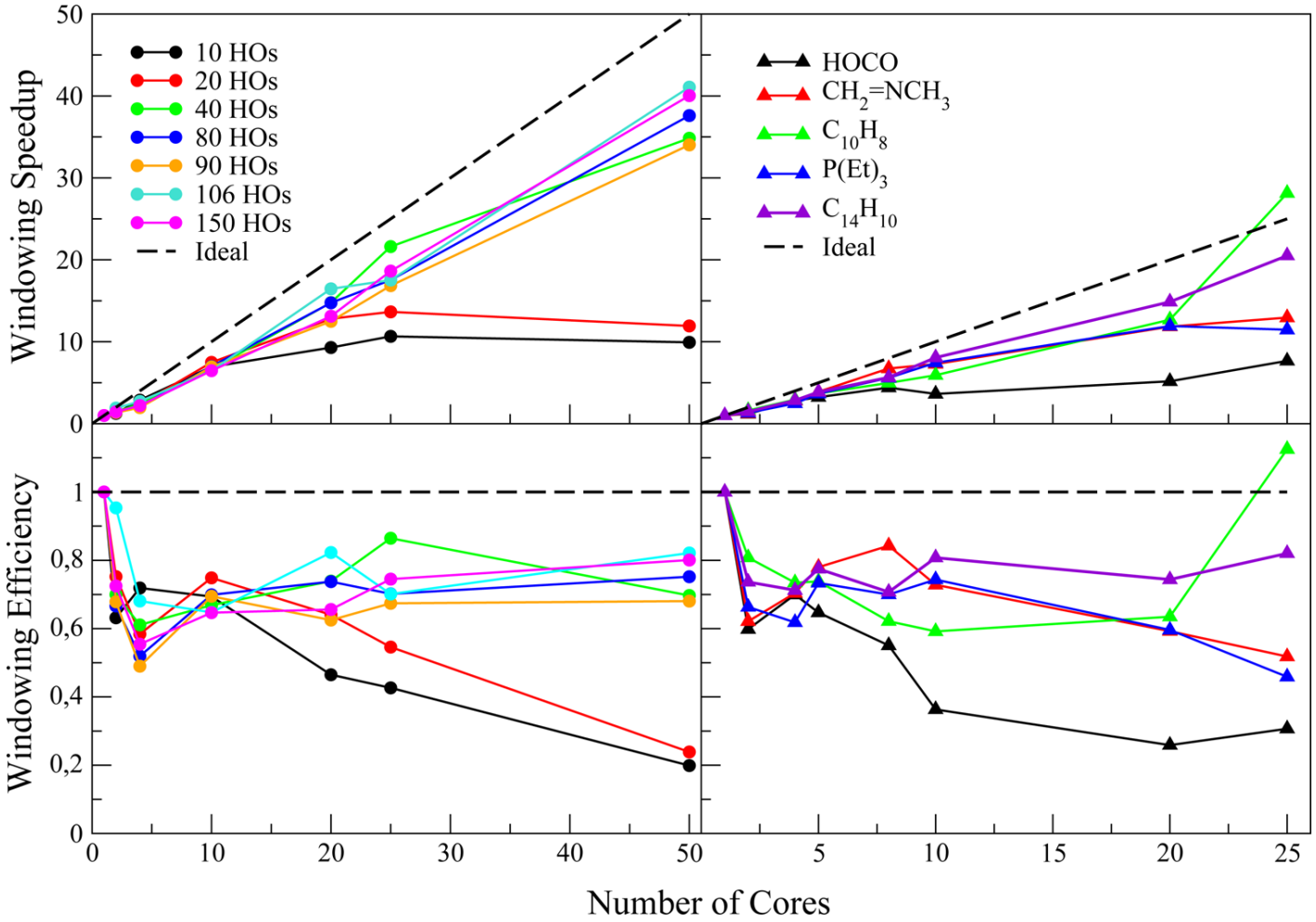

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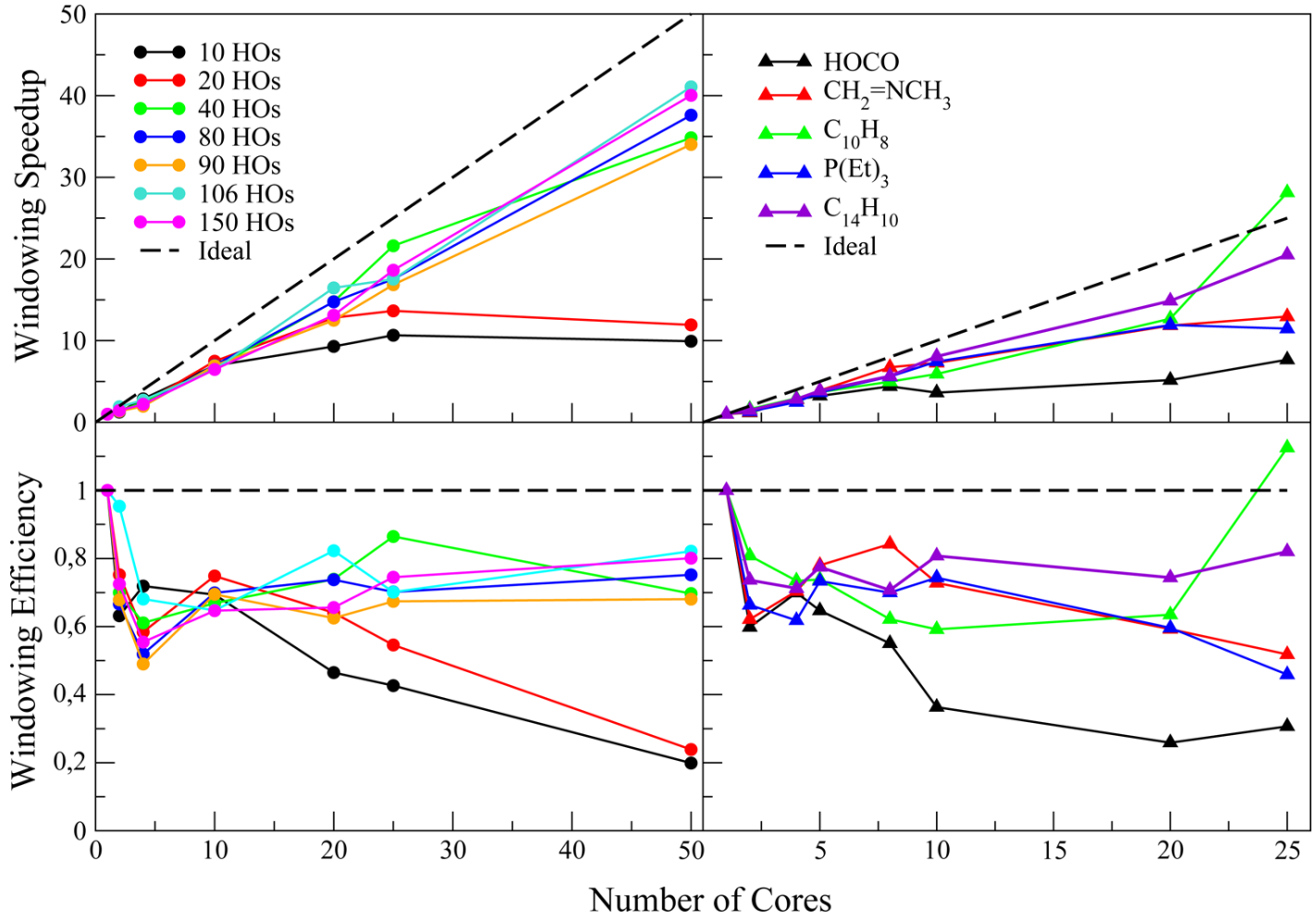

- Almost ideal speed up for UHO systems
- For small molecules it is not very efficient
- It becomes convenient as the number of degrees of freedom increases

Timing and scalability: a practical look

System	Original code execution time (s)	New code execution time (s)
HOCO	32	27
CH_2NCH_3	1352	140
$C_{10}H_8$	4611	611
$P(Et)_3$	8482	2973
$C_{14}H_{10}$	10303	2278
10 UHO	421	20
20 UHO	1235	19
40 UHO	3694	49
80 UHO	12885	226
90 UHO	16309	303
106 UHO	-	404
150 UHO	-	1387

Conclusion

Summary

Paradensum gives the possibility to calculate the fully coupled anharmonic density of states of high-dimensional systems

Paradensum gives the possibility to exploit parallel architectures

Future Developement

Testing the performance of multiwalkers

Parallelization of the Multiwell SCTST software that calculates the vibrational density of states for molecules in their transition state

Acknowledgement

Michele Ceotto, Aieta Chiara
And our research group

Cineca HPC Center

CINECA

Thank you for your kind attention