Quantum Thermal Bath for *ab initio* MD simulations

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QTB for *ab initio* MD simulations:
Co-workers

- Method & Algorithms
  - M. HAYOUN
    - LSI, CEA-DRF, Ecole Polytechnique
  - F. BRIEUC
    - CentraleSupélec Dr.
- Implementation in ABINIT (2015)
  - G. GENESTE
    - CEA - DAM
  - M. TORRENT
    - CEA - DAM

Outline

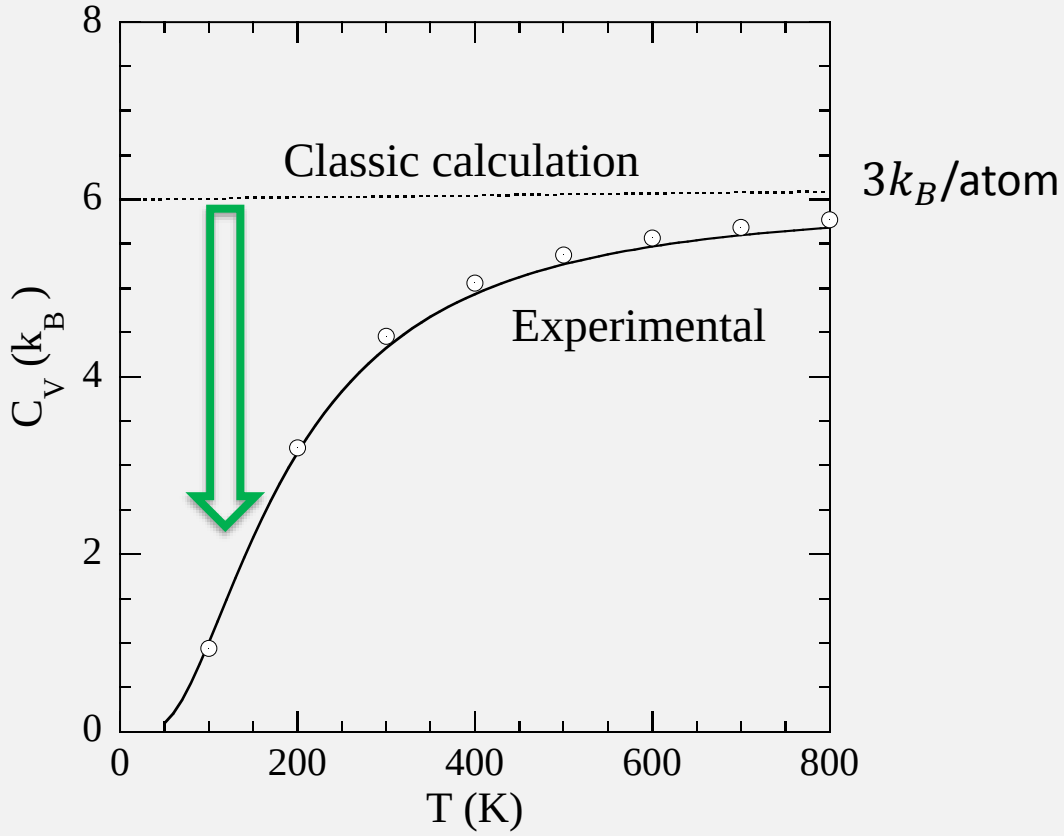
1. Introduction
2. Simulation of nuclear quantum effects
   a. Path Integral Molecular Dynamics (PIMD)
   b. Quantum Thermal Bath Molecular Dynamics (QTB-MD)
   c. Combining QTB and PIMD
3. Conclusion

What are Nucelar Quantum Effects ?

1. Introduction

1. Introduction

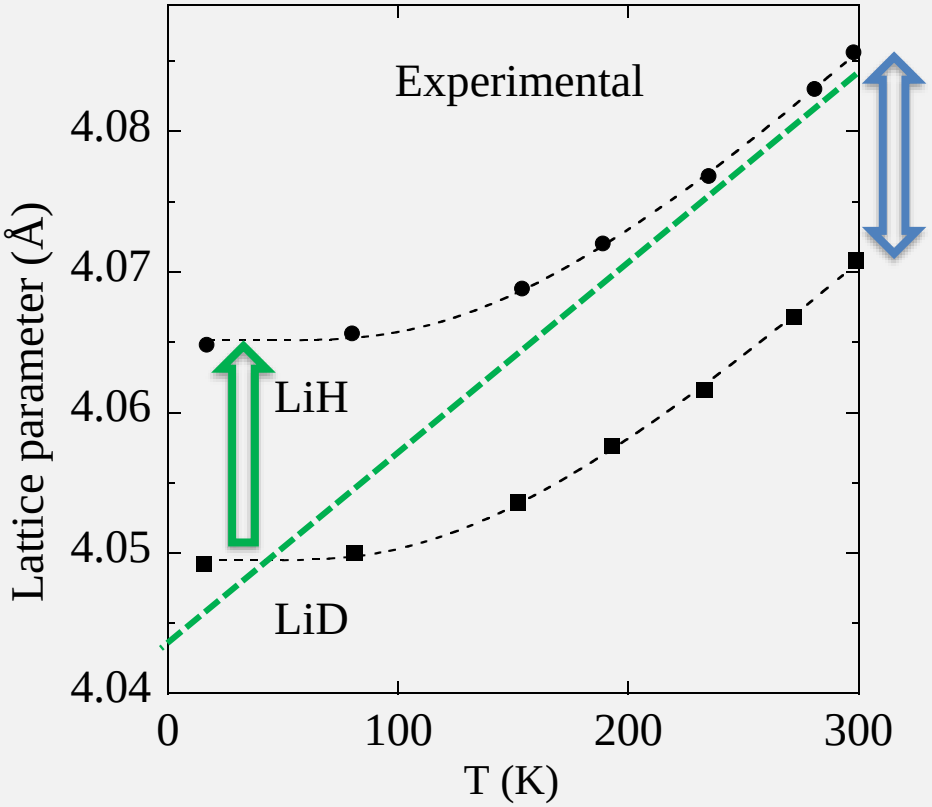
- Heat capacity of MgO crystal



Nuclear quantum effect : decrease of the heat capacity for $T < \theta_{Debye}$

1. Introduction

- Lattice parameter of crystals at low T

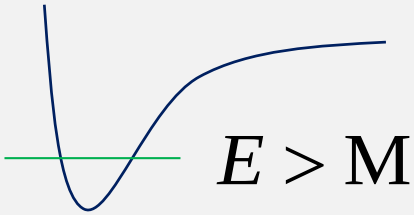


Lattice parameter derived from ab initio calculations (relaxation at 0K) should usually be lower than the experimental one
(~ - 0.02Å)

1st nuclear quantum effect: Freezing of the lattice parameter at low T

2nd nuclear quantum effect: Isotopic shift in the lattice parameter

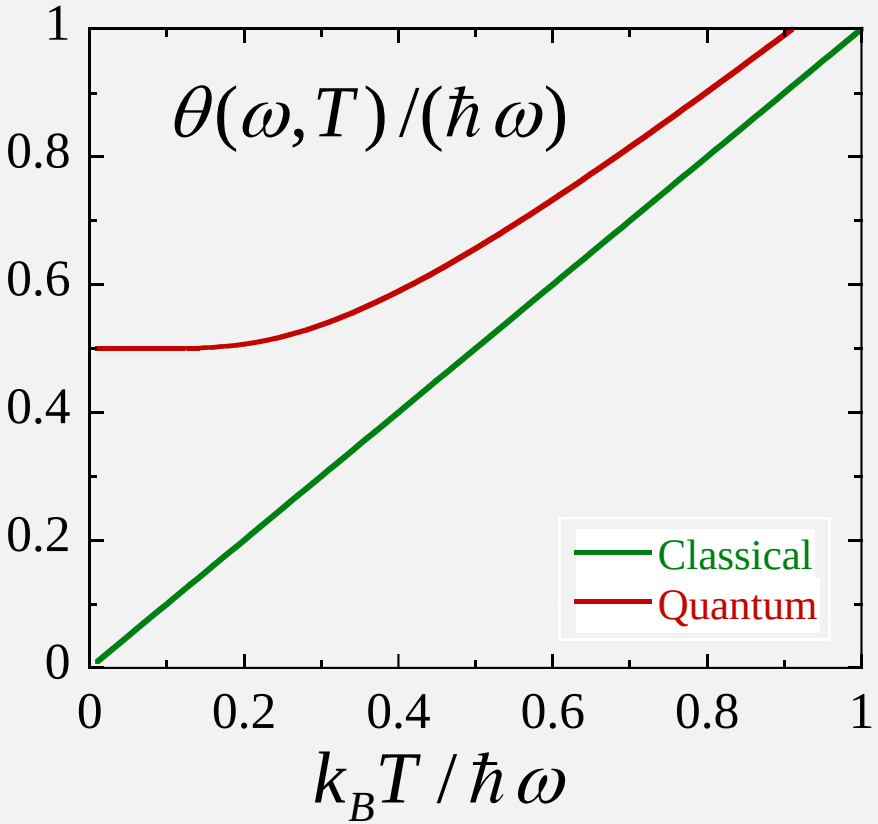
Quantum effects at low temperatures



$$E > \mathrm{Min}(V)$$

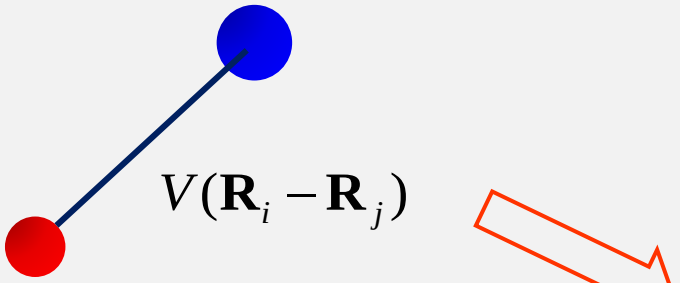
- « Zero-point energy »
  - even at 0K, position and momentum fluctuations ≠ 0
- Energie of a vibration mode
  - in harmonic approximation

$$\theta(\omega,T) = \hbar\omega\left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right]$$

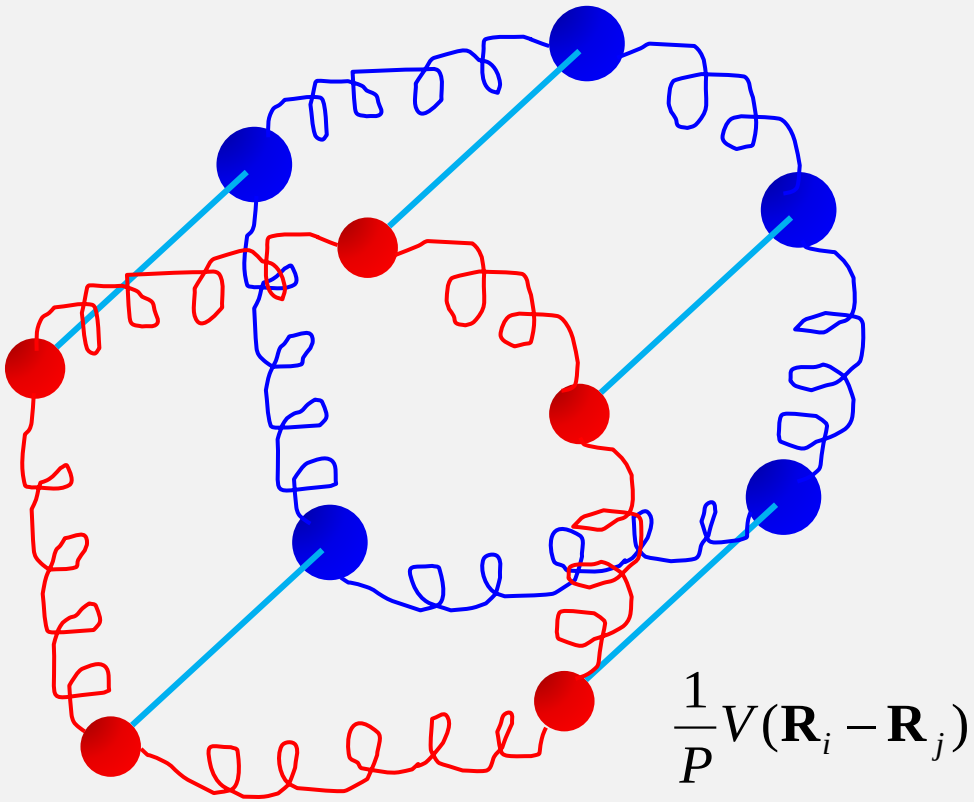


2. Simulation of nuclear quantum effects

2.a. PIMD: Path Integral Molecular Dynamics



Quantum particles



« quantum » spring with zero length

$$P\frac{m_i}{2\beta^2\hbar^2}(\mathbf{R}_{i,s} - \mathbf{R}_{i,s+1})^2$$

$$s = 1, 2, \cdots, P$$

Classical ring-polymer

PIMD

- N×P equations of motion

$$m_i \ddot{\mathbf{r}}_{i,s} = -\frac{1}{P}\nabla_{\mathbf{r}_i} V(\mathbf{r}_{1,s},\ldots,\mathbf{r}_{N,s}) - \frac{P m_i}{\beta^2\hbar^2}(2\mathbf{r}_{i,s} - \mathbf{r}_{i,s+1} - \mathbf{r}_{i,s-1})$$

- Potential energy estimator

$$\sum_{s=1}^{P} \frac{1}{P} V(\mathbf{r}_{1,s},\ldots,\mathbf{r}_{N,s})$$

- Kinetic energy estimator

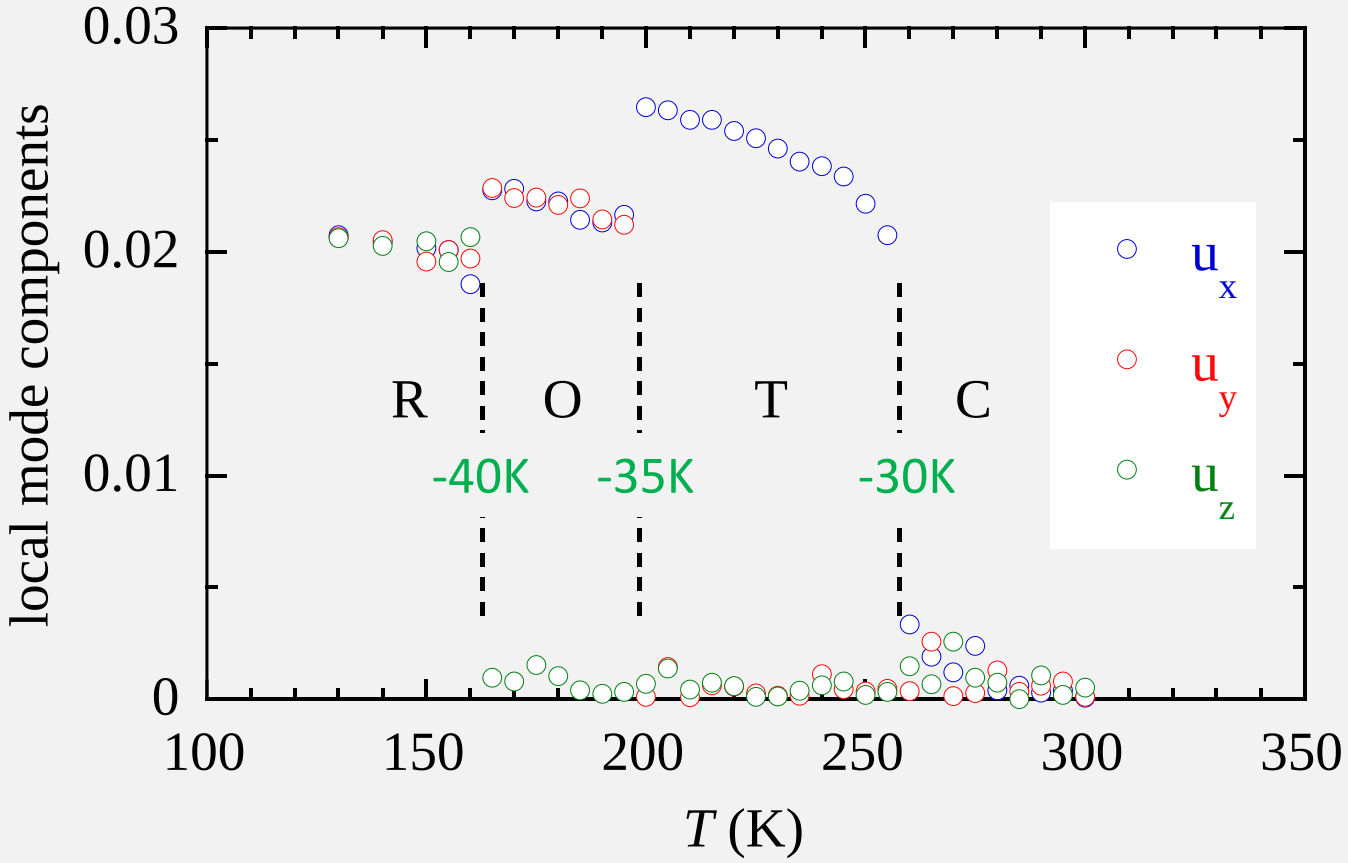
$$\sum_{i=1}^{N}\sum_{s=1}^{P} \frac{1}{2} m_i \dot{\mathbf{r}}_{i,s}^2 - \sum_{i=1}^{N}\sum_{s=1}^{P} \frac{1}{2} \frac{P m_i}{\beta^2\hbar^2}(\mathbf{r}_{i,s} - \mathbf{r}_{i,s+1})^2$$

Application of PIMD to $BaTiO_3$

- P = 16

G. Geneste et al. Phys. Rev. B 87, 014113 (2013)

Effective Hamiltonien description : Polar mode



Nuclear quantum effect : négative shift of the transition temperature

PIMD: Conclusion

- Advantage
  - Provides exact results at the convergence (P)
- Disadvantages
  - computationally demanding when the number of beads increases, in particular at low temperature (PxT ~ 10000)
  - Imaginary time
    - CMD, RPMD, …

PIMD is implemented in ABINIT by G. Geneste and M. Torrent in 2011

Available with a Langevin thermostat (imgmov=9) or with Nose-Hoover chains (imgmov=13)

2.b. Quantum thermal Bath method

Dammak et al. Phys. Rev. Lett. 103 (2009) 190601

- « Langevin-like equation »

$$\frac{\mathrm{d}\, p_{ix}}{\mathrm{d}\, t} = -\frac{\partial V}{\partial x_i} + R_{ix}(t) - \gamma\, p_{ix}$$

  - Colored random force R_{ix}

$$\left\langle R_{ix}(t) R_{ix}(t+\tau) \right\rangle = \int_{-\infty}^{+\infty} I_R(\omega, T) \exp(-i\omega\tau) \frac{d\omega}{2\pi}$$

  - Power spectral density from quantum fluctuation–dissipation theorem

$$I_R(\omega) = 2m\gamma\,\theta(\omega, T) \qquad \theta = \hbar\omega\left[\tfrac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right]$$

Callen and Welton, Phys. Rev. 83, 34 (1951)

Quantum thermal Bath method

- Random force generation with respect to $I_R(\omega)$
  - Numerical technique designed to generate Gaussian random function

Maradudin, Ann. Phys. 203, 255 (1990)

    - For n δt MD steps
    - Frequency step: 1/(n δt)
    - Generation of

$$R_{ix}(\omega_j) = \sqrt{\frac{n\,\delta t\, I_R(\omega_j)}{2}}(a_j + i\,b_j)$$

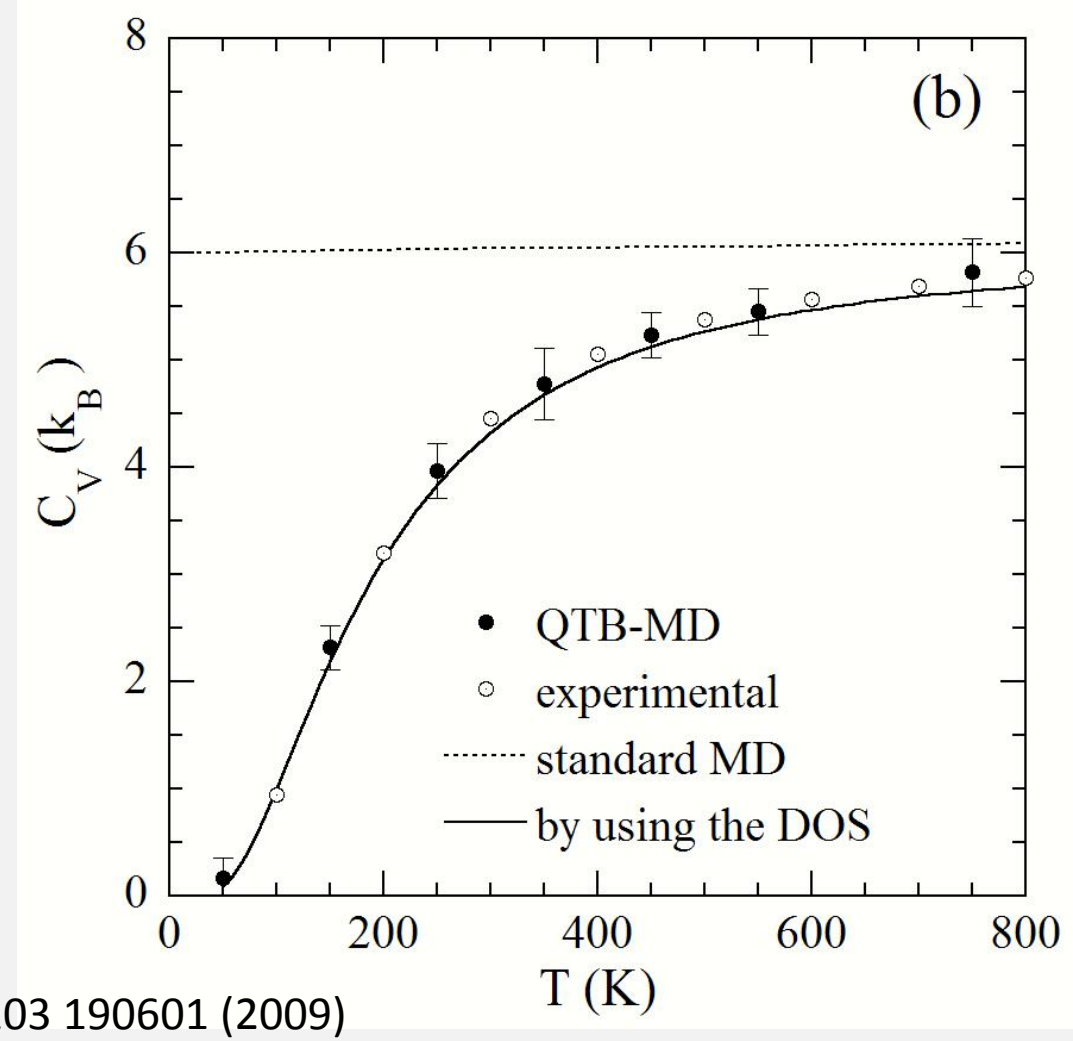
    - **Inverse Fourier Transform**

$$R_{ix}(t_j) = \mathrm{FT}(R(\omega_j))$$

Algorithm of generation given in Phys. Rev. B 84 (2011) 224301

Application of the QTB method

- MgO heat capacity

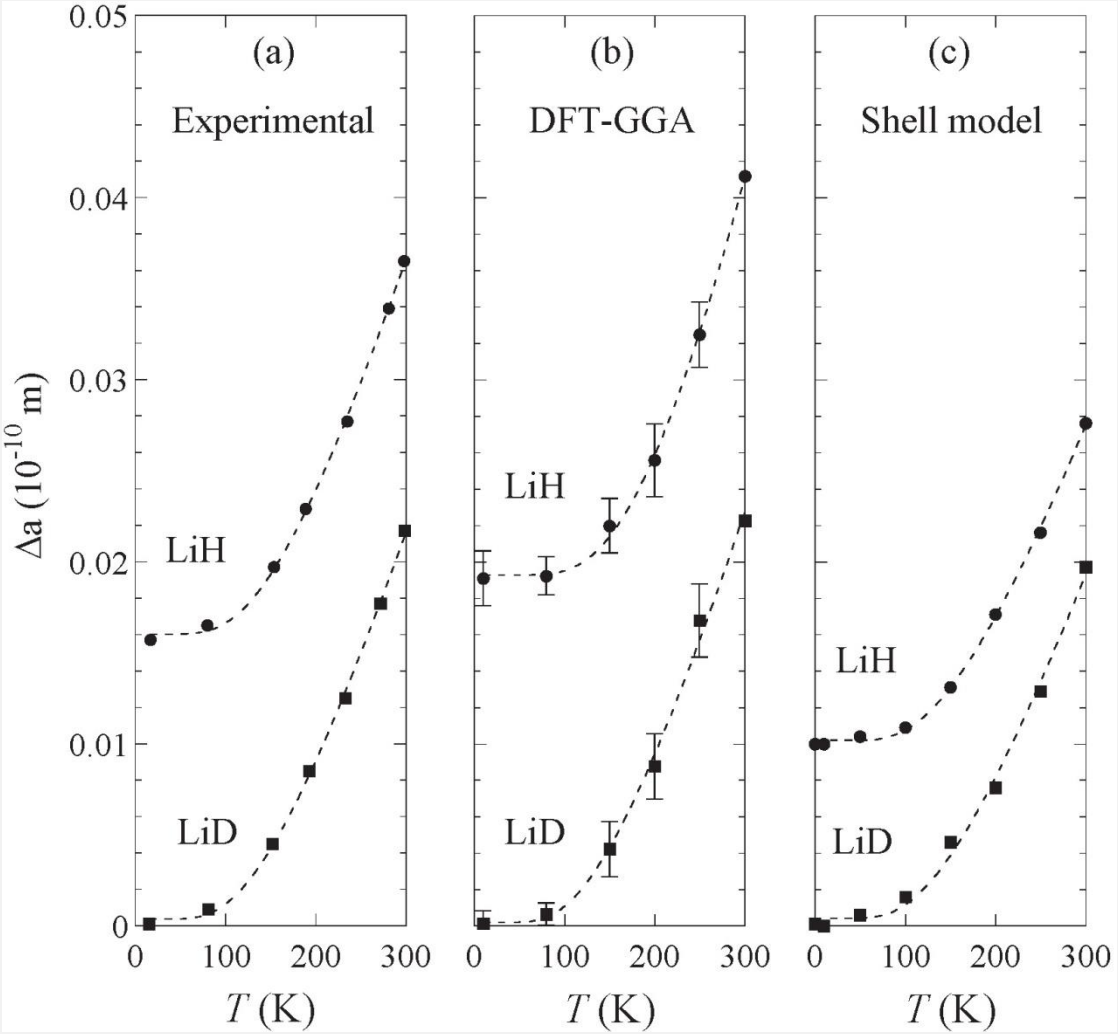


Phys. Rev. Lett. 103 190601 (2009)

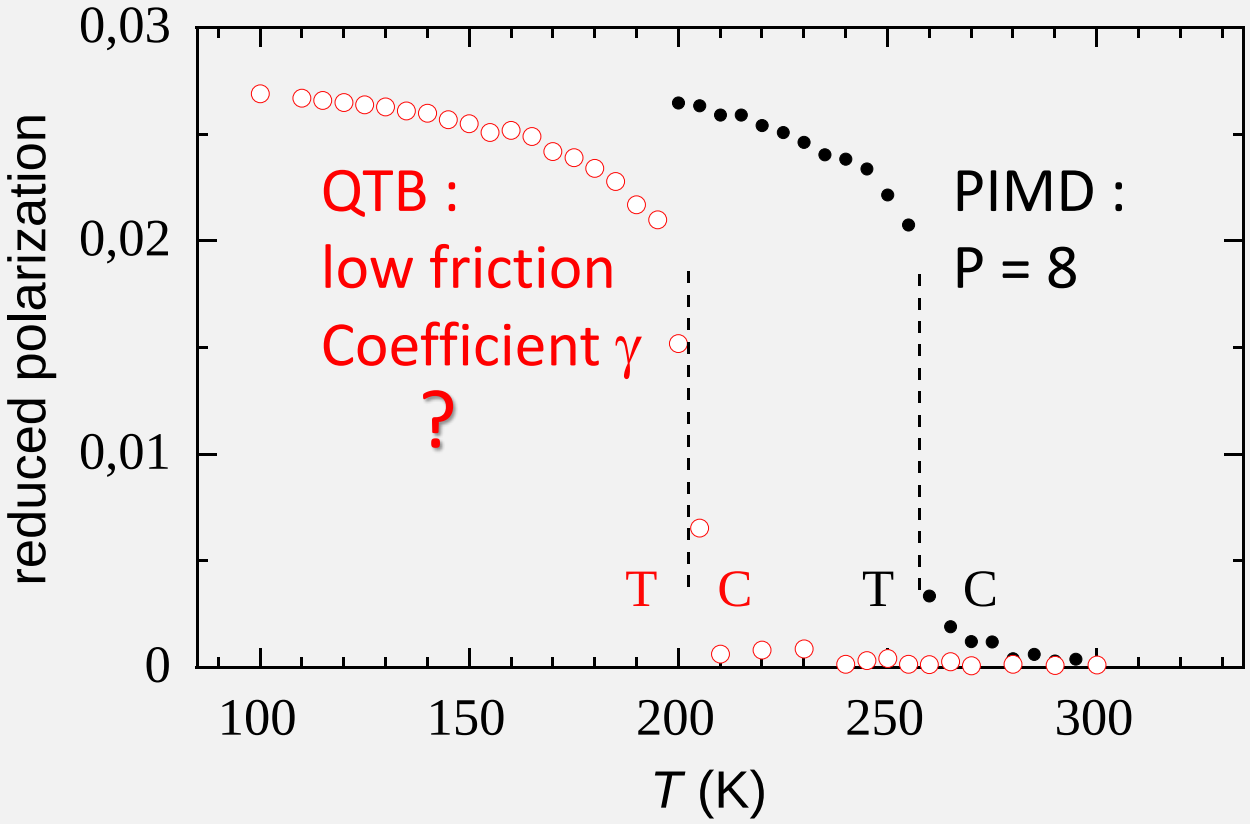
Application of the QTB method

- Isotope effect in LiH and LiD

J. Phys.: Condens. Matter 14 (2012) 435402



Application of QTB-MD to $BaTiO_3$

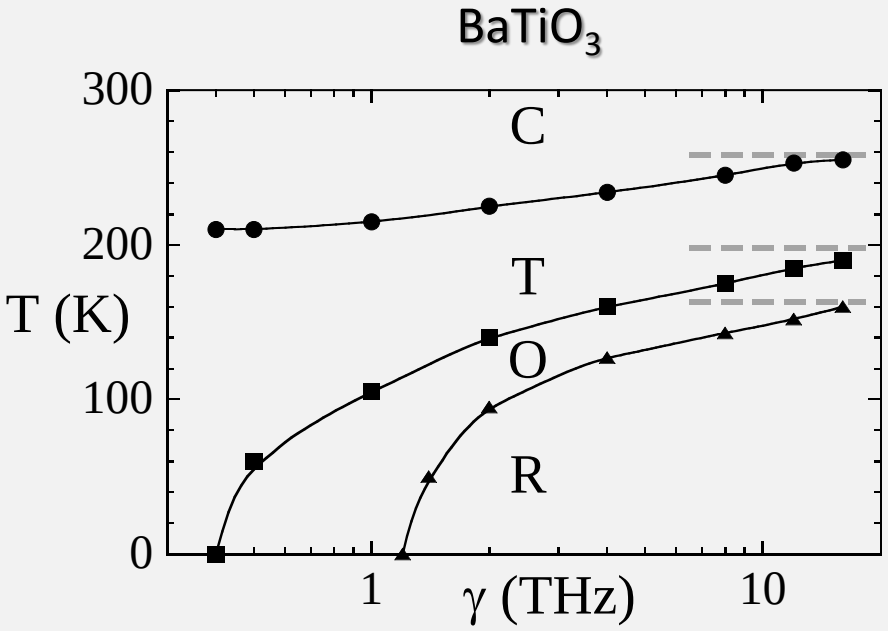


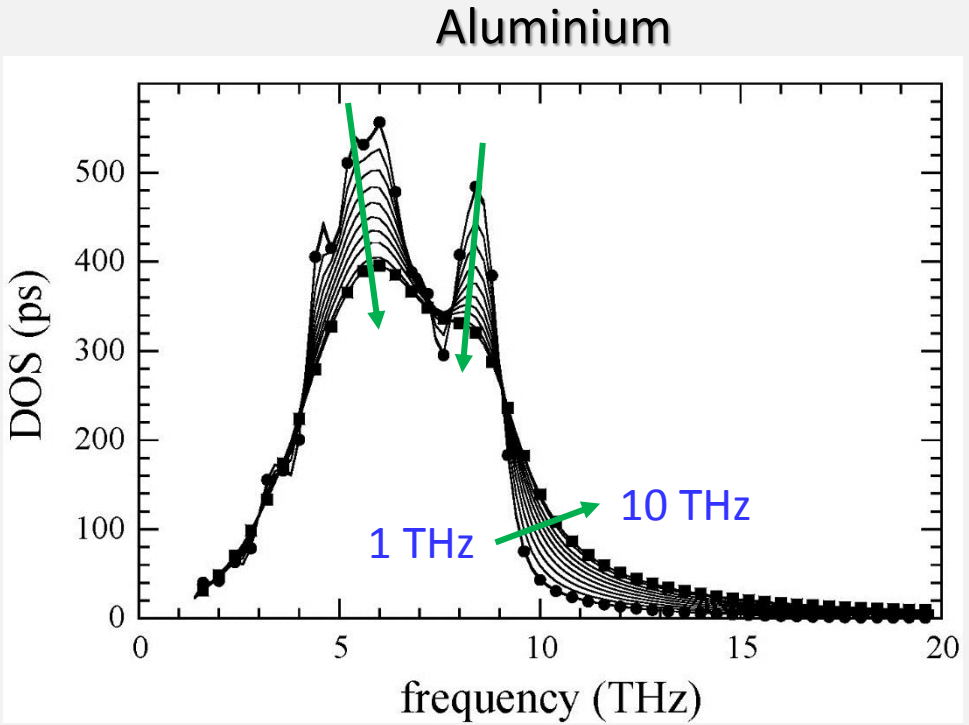
Problem of zero-point energy leakage (ZPEL) in highly anharmonic systems

ZPE ($\hbar\omega/2$) of the high-frequency modes is transferred to the low-frequency ones.

Solving the ZPEL problem in QTB-MD

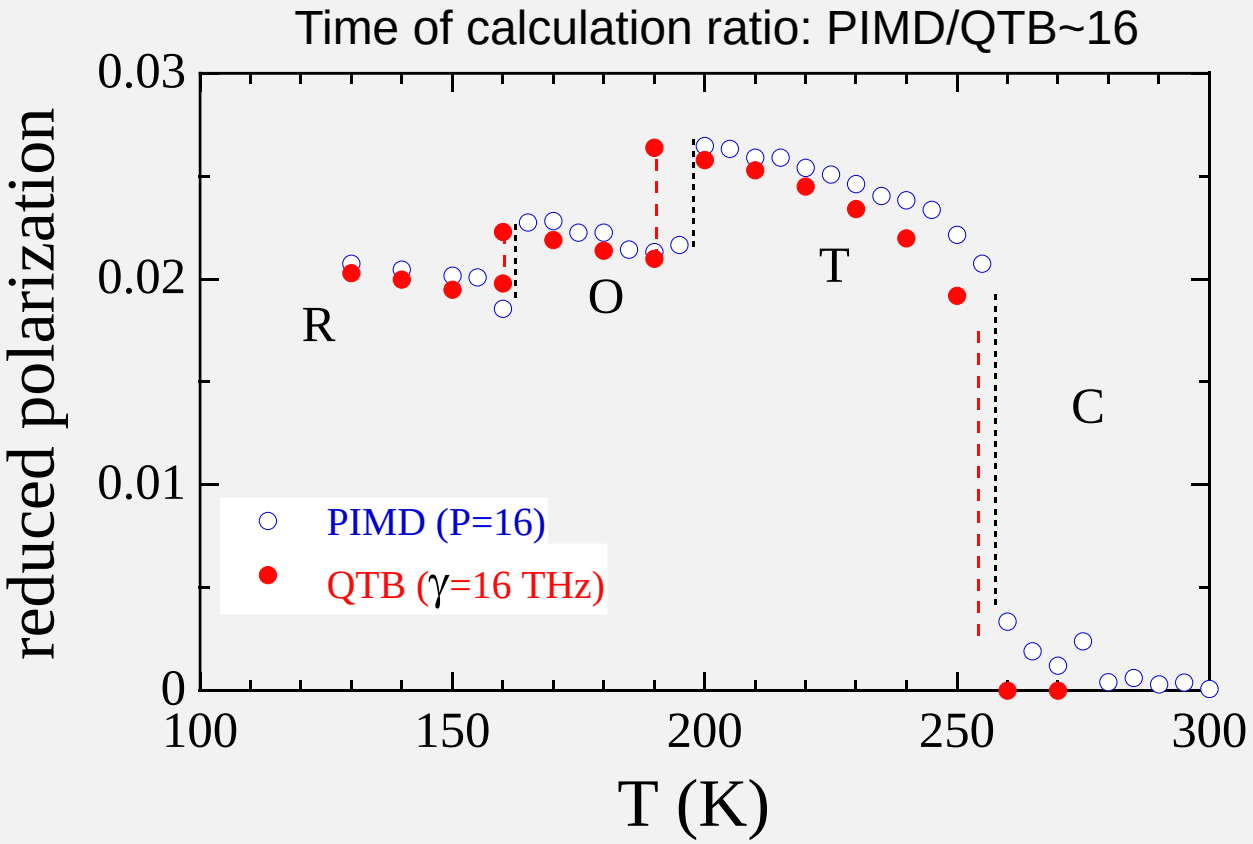
- Influence of the friction coefficient





Brieuc et al., J. Chem. Theory Comput. 12 (2016) 5688

Solving the ZPEL problem in QTB-MD



Brieuc et al., J. Chem. Theory Comput. 12 (2016) 5688

QTB-MD: Conclusion

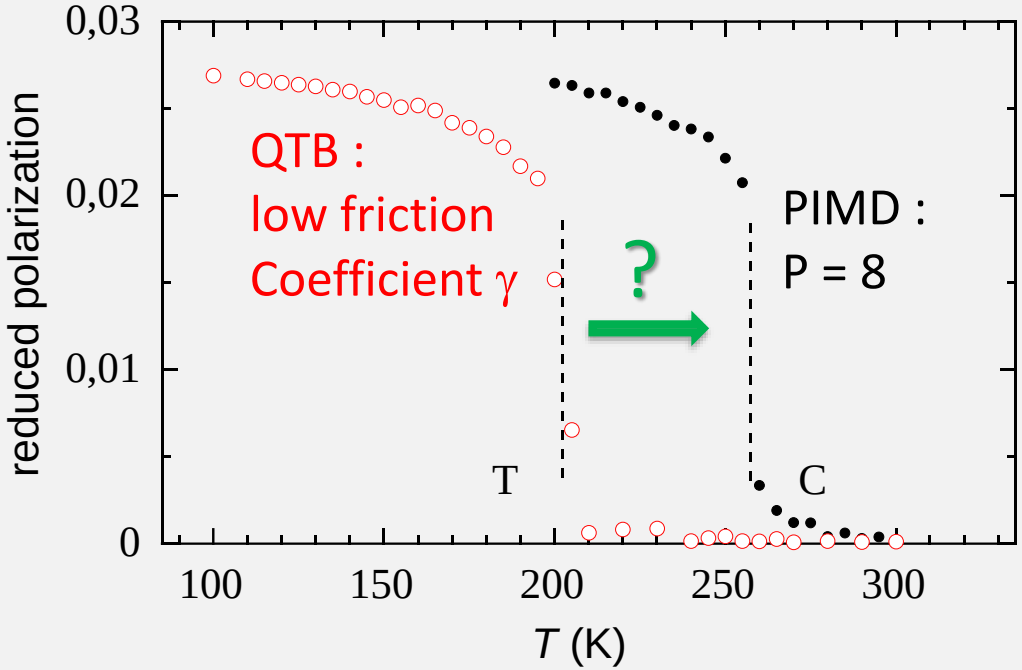
- Disadvantage
  - Approximated method
  - ZPEL for strongly anharmonic systems
    - overdamping is required to avoid ZPEL
- Advantages
  - Computationally similar to standard MD
  - Provides time correlation functions
  - Provides quantum effects at 0K !

Implemented in ABINIT (8.0.8)
Available with (imgmov=10)
Requires piqtb_force file

QTB force generation code is available but not yet included.

2.c. Combining QTB and PIMD

QTB versus PIMD

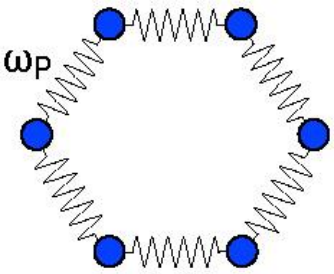


- The aim:
  - improve the PIMD convergence
  - a small number of replicas allows the correction of the failures of the QTB-MD (ZPEL)

Combining QTB and PIMD

Brieuc et al., J. Chem. Theory Comput. 12 (2016) 1351

- QTB random forces are applied on normal modes of the ring polymer



$$\omega_k^2 = \frac{\omega^2}{P} + 4\omega_P^2 \sin^2\left(\frac{k\pi}{P}\right)$$

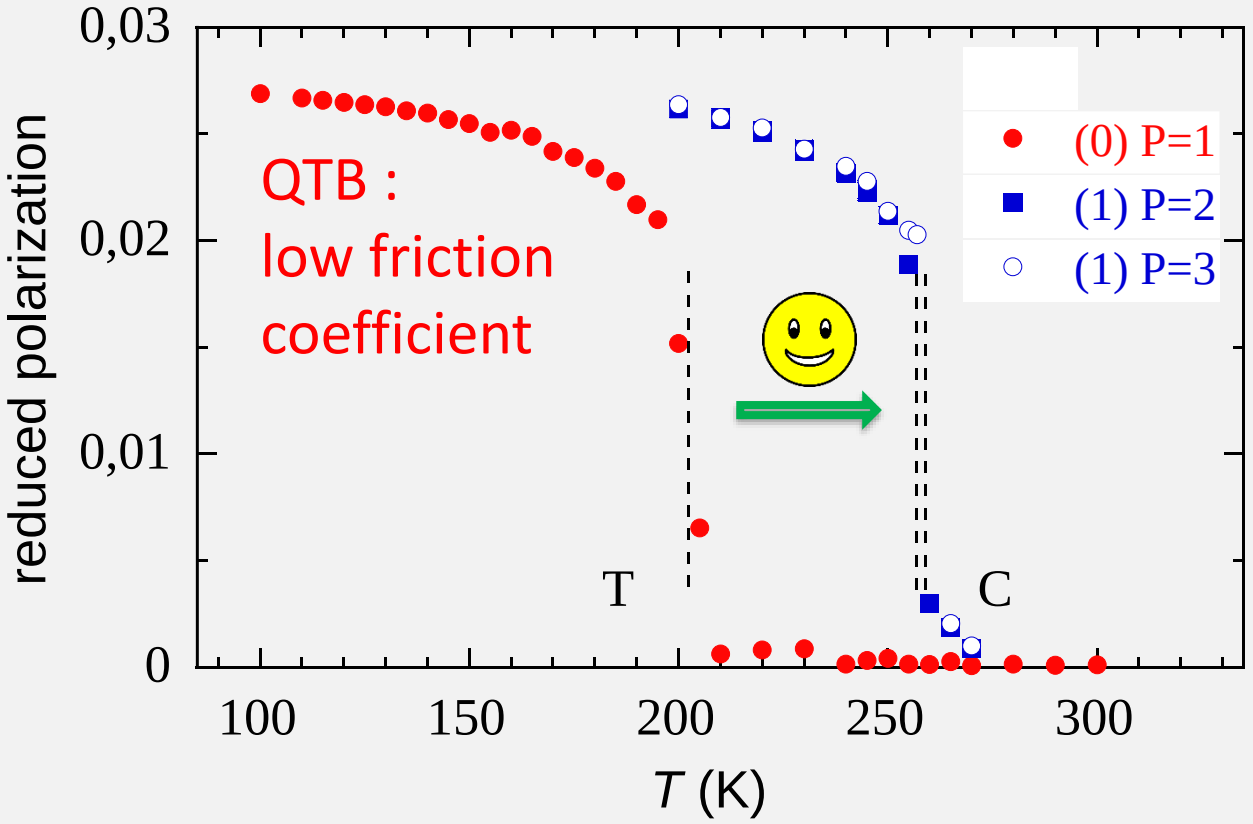
$$I_R(\omega_k, T) = 2m\gamma\kappa_P(\omega_k, T)$$

- Modification of the power spectral density of the random force

$$\frac{1}{P}\sum_{k=0}^{P-1}\frac{\kappa_P(\omega_k, T)}{m\omega_k^2} = \frac{\theta(\omega, T)}{m\omega^2}$$

QTB-PIMD applied to $BaTiO_3$

- Tetragonal-Cubic transition



PIMD requires P > 8

3. Conclusion

Conclusion

- Nuclear quantum effects can be included using ABINIT (from 8.0.8)
  - PIMD: exact method but very time consuming
  - QTB: alternative method
    avoid ZPEL by tuning the coefficient of friction.
  - QTB-PIMD: for strongly anharmonic systems

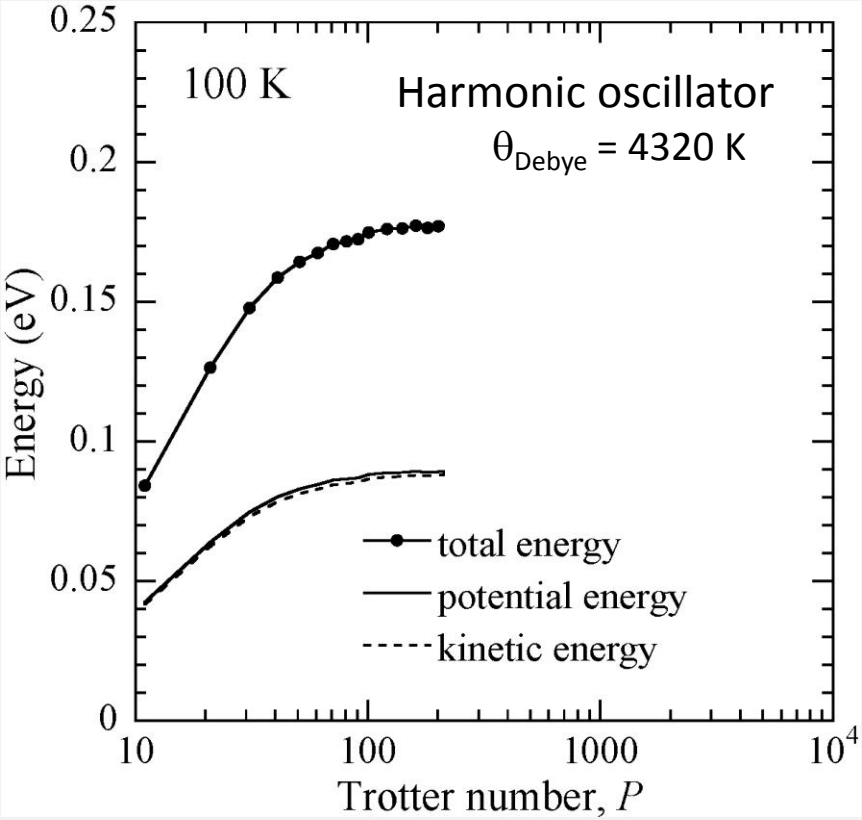
Implemented in ABINIT (8.0.8)
Available with (imgmov=10)
Requires piqtb_force file

QTB force generation code is available but not yet included.

Appendix

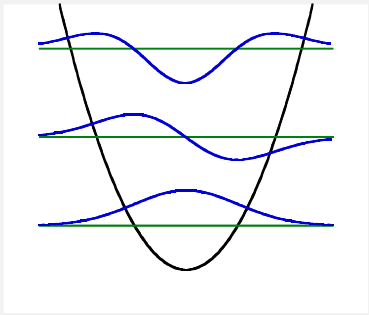
Application of PIMD to H. O.

- Convergence:
  - P x T = 10000



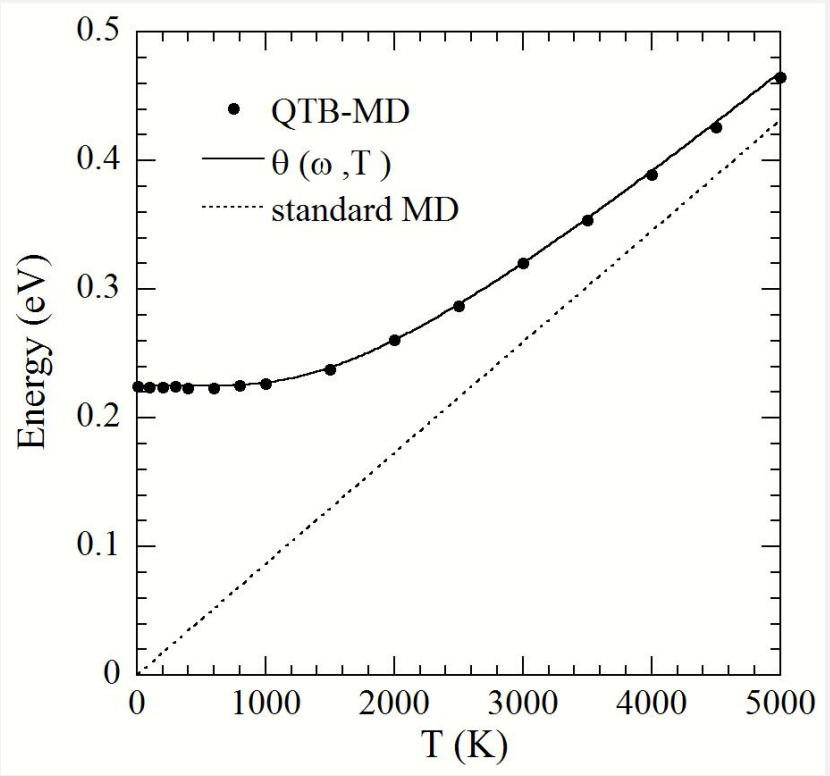
Application of the QTB method

- Case of an « harmonic » molecule H-D
  - $\nu = 1{,}09 \times 10^{14}$ Hz



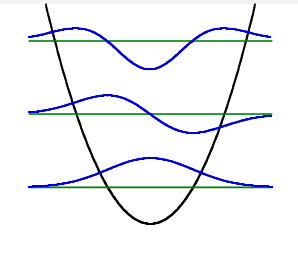
$$E_n = (n + \tfrac{1}{2})\,\hbar\omega$$

$$\sum E_n \frac{e^{-\beta E_n}}{Z} = \theta(\omega, T)$$



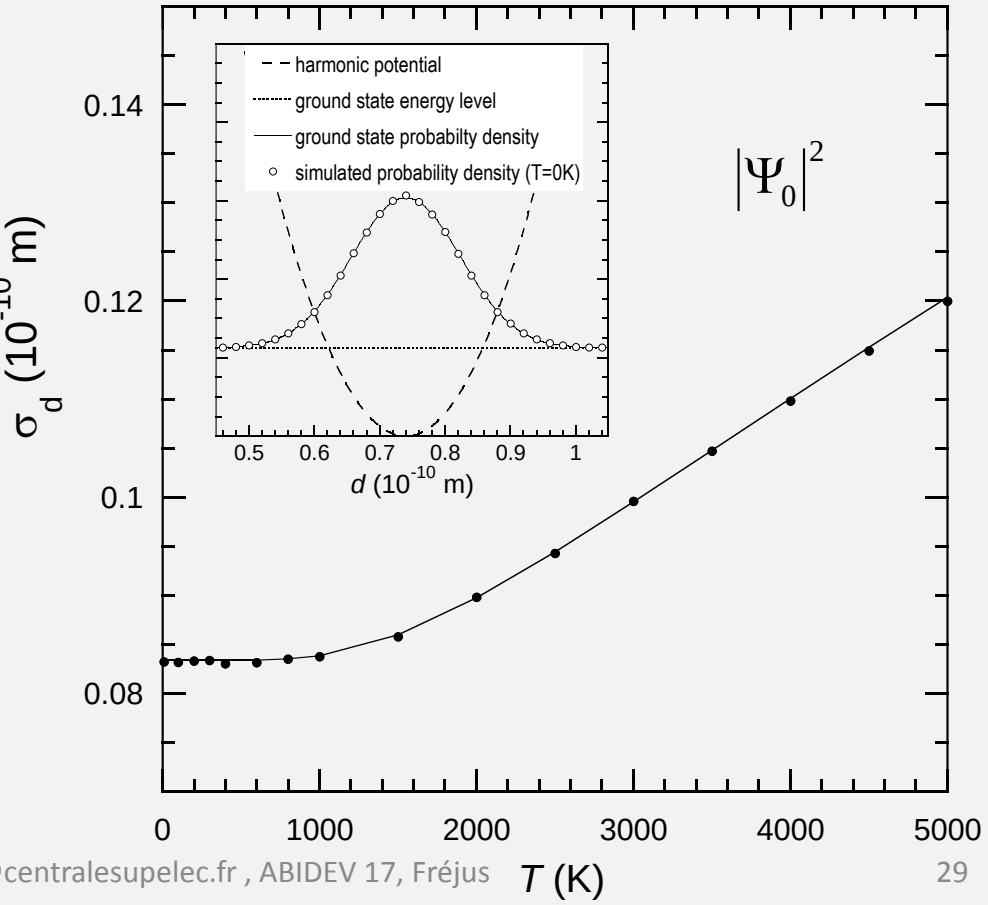
Application of the QTB method

- Fluctuation of position for a harmonic oscillator
  - H-D molecule



$$\sigma_x^2(n) = (n+\tfrac{1}{2})\,\sigma_x^2(0)$$

$$\sqrt{\sum \sigma_x^2(n)\frac{e^{-\beta E_n}}{Z}}$$



Combining QTB and PIMD

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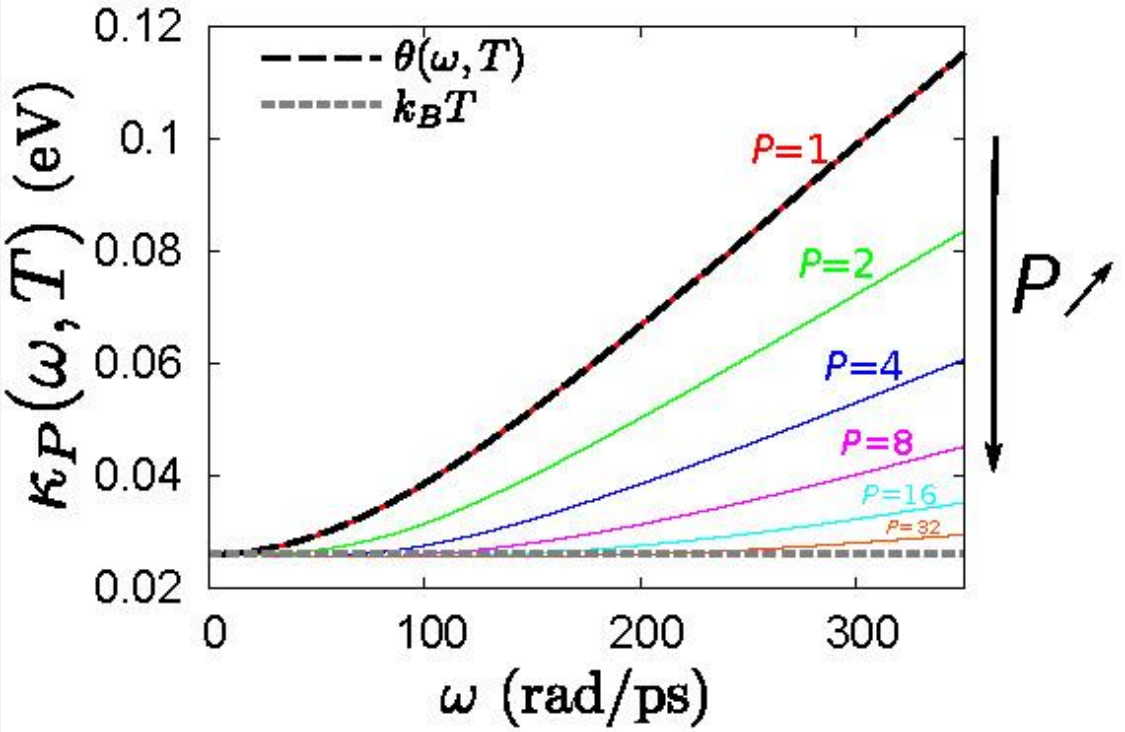

QTB-PIMD applied to $BaTiO_3$

- Convergence @ 240 K