Anharmonic spectral features via trajectory-based quantum dynamics: A perturbative analysis of the interplay between dynamics and sampling

Federica Troni – 04.12.2024

Goal

ref: https://doi.org/10.1063/5.0056824

Study of the ability of different trajectory-based methods to describe **anharmonic spectral features** (i.e. peaks in **momentum auto-correlation spectrum** of potential)

Study simple prototype models obtained by adding **anharmonic perturbations** to a **harmonic reference potential**

$$\boxed{V(q) = \frac{1}{2} m\omega_0^2 q^2}$$

Methods

1. RPMD, CMD, Matsubara dynamics
2. LSC-IVR– different approximations to sample Wigner distribution
3. Quantum Thermal Bath (QTB), ad-QTB (adaptive version)

To compute

$$C_{pp}(t) = \Re[\overline{C}_{pp}(t)] = \int \mathrm{d}q\mathrm{d}p\, \boxed{\rho_{\mathrm{W}}(q,p)}\, p e^{i\mathscr{L}_{\mathrm{Q}}t} p$$

$$\rho_{\mathrm{W}}(q,p) = \frac{1}{2\pi\hbar\mathcal{Z}} \int \mathrm{d}\Delta\, e^{\frac{ip\Delta}{\hbar}} \left\langle q - \frac{\Delta}{2} \middle| e^{-\beta\hat{H}} \middle| q + \frac{\Delta}{2} \right\rangle$$

Path Integral-Based Methods

RPMD
Ring Polymer Molecular Dynamics

CMD
Centroid Molecular Dynamics

Matsubara dynamics

directly provide approximations to the Kubo-transformed ATCF

$$K_{pp}(\omega) = \frac{\boxed{C_{pp}(\omega)}}{\beta\Theta(\omega, \beta)}$$

LSC-IVR

Linearized Semi-Classical Initial Value Representation

$$\rho_{\mathrm{W}}(q,p) = \left\langle q \middle| \frac{e^{-\beta\hat{H}}}{\mathcal{Z}} \middle| q \right\rangle \times \frac{\int \mathrm{d}\Delta e^{i\frac{p\Delta}{\hbar}} \left\langle q - \frac{\Delta}{2} \middle| e^{-\beta\hat{H}} \middle| q + \frac{\Delta}{2} \right\rangle}{2\pi\hbar \left\langle q \middle| e^{-\beta\hat{H}} \middle| q \right\rangle}$$
$$= \rho_{\mathrm{W}}^{m}(q) \times \rho_{\mathrm{W}}^{c}(p|q).$$

3 different approximations to sample the conditional Wigner distribution:

1. Equilibrium harmonic approximation (IVR0) $V(\hat{q}) \approx V(q_0) + \frac{1}{2}m\Omega_0^2(\hat{q}-q_0)^2$
2. Local harmonic approximation (LHA) $\Omega^2(q) = \frac{1}{m}\frac{\mathrm{d}^2 V}{\mathrm{d}q^2}$
3. Edgeworth conditional momentum approximation (ECMA) (allows $\rho_W < 0$)

QTB

Quantum thermal bath

Acts a frequency-dependent thermostat to thermalize the vibration modes of the system with an average energy $\Theta(\omega, \beta)$ → accounting for **zero-point contributions**

$$\boxed{\frac{dp}{dt} = -\frac{\partial V}{\partial q} - \gamma p + F(t)} \longrightarrow C_{FF}(\omega) = 2m\gamma_r(\omega)\Theta(\omega, \beta)$$

Cons - suffers from **zero-point energy (ZPE) leakage.** Injected at high frequencies tends to unphysically flow toward low frequencies.

Solution - adaptive QTB (adQTB): adjust the random force amplitude $\gamma_r(\omega)$ on the fly:

- to compensate for ZPE leakage in a systematic way
- to restore the fluctuation–dissipation theorem

Overtones

$$V(q) = \frac{1}{2} m\omega_0^2 q^2 + \frac{\lambda}{3} q^3$$

harmonic + small anharmonic contribution (overtone) at angular frequency $2\omega_0$

Observable

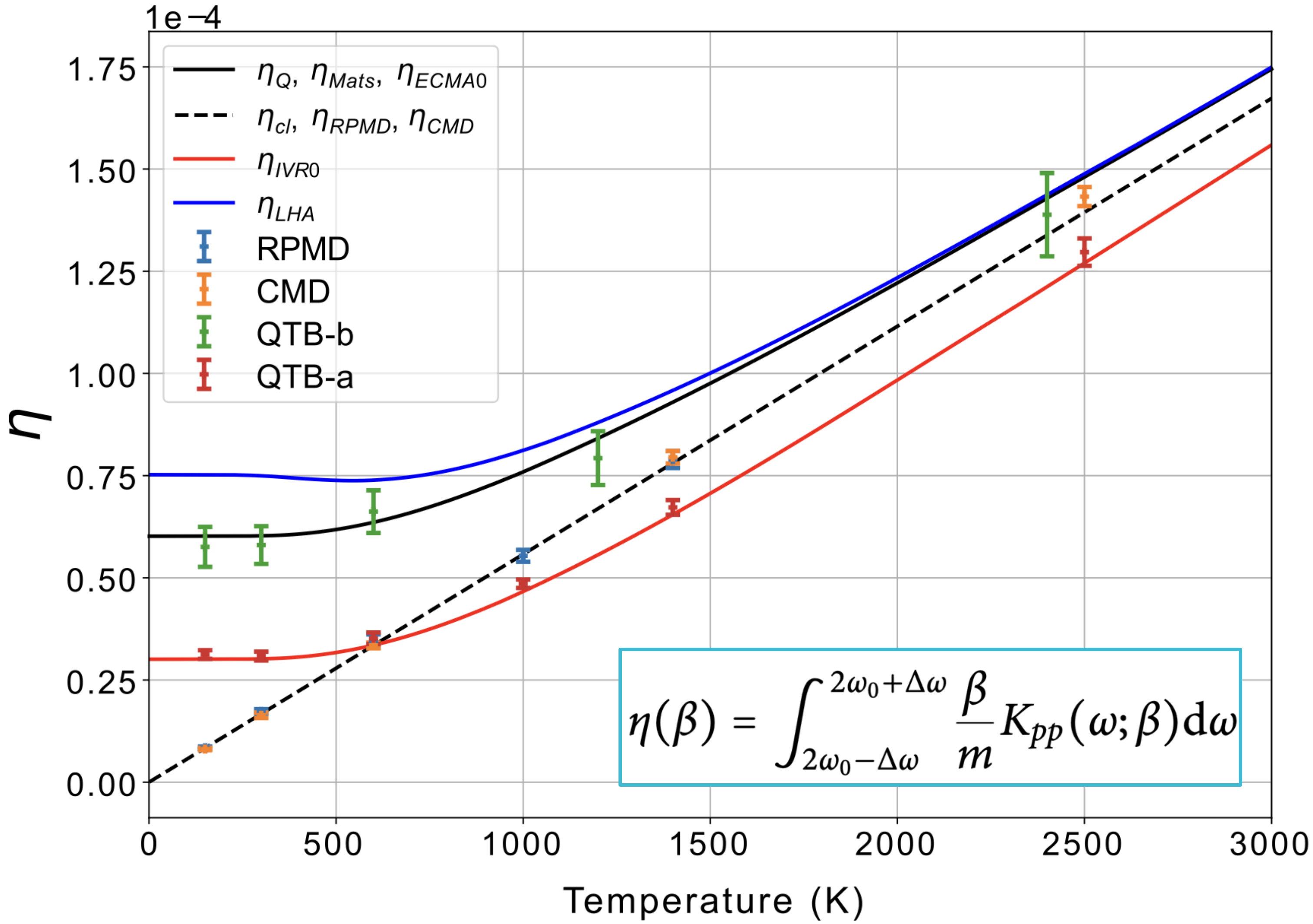
$$\eta(\beta) = \int_{2\omega_0-\Delta\omega}^{2\omega_0+\Delta\omega} \frac{\beta}{m} K_{pp}(\omega;\beta)\mathrm{d}\omega$$

Integral of vibrational density of state (VDOS) of a quantum system

Transformed momentum autocorrelation function

measures the fraction of the system **vibration energy** that is contained in the overtone

Investigating overtones



Combination bands

$$\boxed{V(q_1, q_2) = \frac{1}{2} m_1 \omega_1 q_1^2 + \frac{1}{2} m_2 \omega_2 q_2^2 + \lambda q_1 q_2^2}$$

Overtone at $2\omega_2$

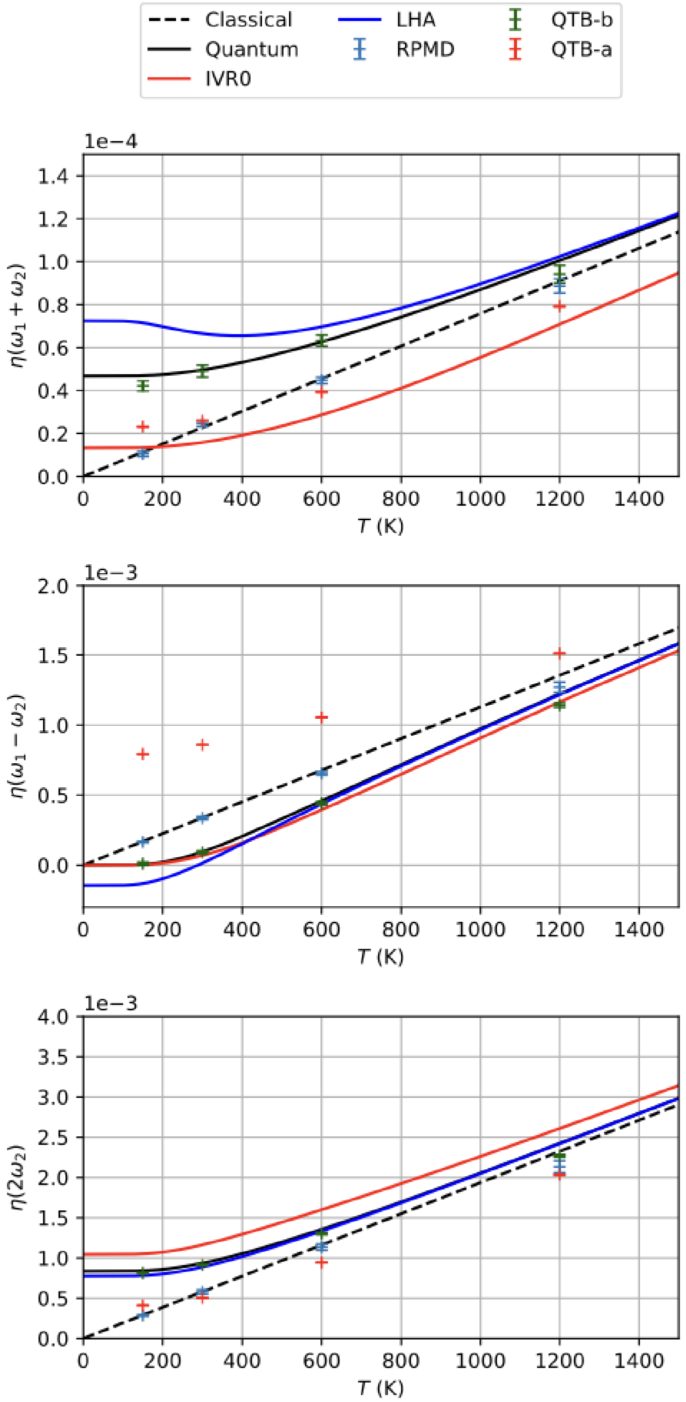
2 combination bands:

- $\omega_1 + \omega_2$
- $\omega_1 - \omega_2$

Same observable as before, but now I compute it around 3 different peaks

$$\eta(2\omega_2), \eta(\omega_1 + \omega_2), \eta(\omega_1 - \omega_2)$$

Investigating combination bands



Fermi resonances

Special case: $\omega_1 \approx 2\omega_2$ → perturbative approach used for combination bands breaks down

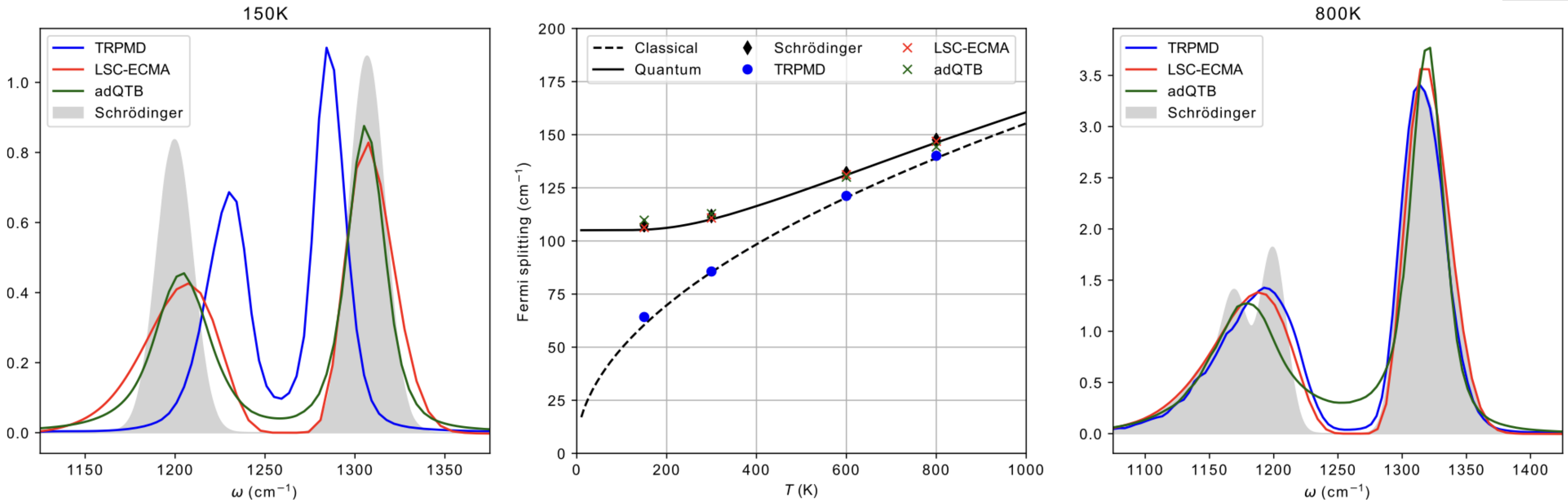
interaction between $\boldsymbol{2\omega_2}$**- overtone &** $\boldsymbol{\omega_1}$**- mode** causes the high-frequency peak in the vibration spectrum to **split**

$$\boxed{\begin{aligned} V(x,y,z) = \frac{1}{2}m_1\omega_1^2x^2 + \frac{1}{2}m_2\omega_2^2y^2 + \frac{1}{2}m_2\omega_2^2z^2 \\ + \frac{1}{2}\chi_{12}x(y^2+z^2)\sqrt{m_1}m_2, \end{aligned}}$$

3D model for gas-phase CO_2

x = symmetric stretching coordinate
y, z = degenerate bending modes
m_1, m_2 = reduced masses
$\omega_1 = 1261\ cm^{-1}$
$\omega_2 = 634\ cm^{-1}$
$\chi_{12} = 1.479 \cdot 10^{-7}$ a.u.

Investigating Fermi resonances



Conclusions

Comparison of Methods:

- **LSC-IVR**: Performs well when combined with ECMA, capturing quantum effects in anharmonic spectra with minimal error
- **Path Integral-Based Methods**: fail to describe anharmonic features like overtones and combination bands
- **adQTB**: computationally efficient & accurate alternative for simulating anharmonic spectral features, particularly for overtones and Fermi resonances

Conclusions

General results:

- adQTB as a **promising tool** for studying vibrational spectra in condensed matter and molecular systems
- Inaccuracy of many trajectory-based quantum dynamics methods arises more from **inadequate sampling of initial conditions** (Wigner distribution) than from the lack of quantum coherence in dynamics