

Real-time response from imaginary-time simulation

Hacking quantum statistics with path-integral Monte Carlo

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Background

Quantum mechanical simulation in the imaginary time is tempting. One of the biggest challenges in electronic structure theory, the many-body correlation, can be treated accurately using stochastic methods, the quantum Monte Carlo (QMC). The imaginary-time is also associated with quantum statistics at the finite temperature, the exact thermal equilibrium. Robust and controllable QMC methods are increasingly popular and capable to simulate real-life experimental conditions – except the real-time response functions. Numerical inversion from imaginary-time to the real domain is painfully ill-posed and can only be done approximately using techniques such as Maximum Entropy method.

Linear response

Following Ref. 1, a weak time-dependent perturbation, such as a laser field $h(t) = \theta(t - t')QF(t)$, is incident to a quantum system at time t' . It induces a linear shift in property $P(t)$

$$\delta P(t) = \frac{i}{\hbar} \int_{-\infty}^t dt' \langle [h(t'), P(t)] \rangle = \int_{-\infty}^t dt' \chi^R(t, t') F(t'),$$

where

$$\chi^R(t, t') = \langle TP(t)Q(t') \rangle = C^R(t) \equiv \chi^R(t_1)$$

is the retarded generalized susceptibility. That is, the linear response is readily obtained from a real-time quantum **correlation function** C between the two operators. Frequency-dependent response is simply the Fourier transform

$$\chi^R(\omega) = \mathcal{F}\chi^R(t_1).$$

The spectral representation gives rise to Kramers–Kronig relation

$$\chi(\omega) = \int_0^\infty \frac{d\omega'}{2\pi} A(\omega') \left[\frac{1}{\omega - \omega' - i\eta} + \frac{1}{\omega + \omega' + i\eta} \right],$$

where η is a positive infinitesimal and A is the spectral function given by

$$A(\omega) = i[\chi^R(\omega) - \chi^A(\omega)] = 2\text{Im}[\chi^R(\omega)].$$

The susceptibility χ is complex: the real part is related to dispersion and the imaginary part to absorption/emission, *i.e.*, allowed transitions. Higher-order terms, *nonlinear response*, is obtained similarly but it produces more involved formulas [2-3].

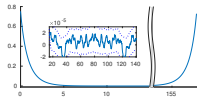
Analytic continuation

The quantum correlation can be analytically continued to imaginary time: $t \rightarrow it \equiv \tau$. The correlation function is defined in terms of imaginary arguments [4]:

$$C(\tau) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{e^{-\tau\omega}}{1 \pm e^{-\beta\hbar\omega}} A(\omega)$$

$$C(i\omega_n) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{1}{i\omega_n - \omega} A(\omega),$$

where $\omega_n = 2n\pi/\beta$ are the bosonic Matsubara frequencies and $A(\omega)$ is the associated spectral function.



Unfortunately, the inversion – obtaining $A(\omega)$ from $C(\tau)$ or $C(i\omega_n)$ – is an ill-posed challenge. In numerical implementations, there are usually multiple spectra for each estimate of C . **Maximum Entropy** is an approach that picks the most probable solution based on *a priori* knowledge [4].

Path-integral Monte Carlo

The imaginary-time correlation function $C(\tau)$ is very straightforward to compute in path-integral Monte Carlo (PIMC) [5]. In PIMC, thermal many-body density matrix corresponds to a finite trajectory in imaginary-time $\beta = 1/kT$:

$$\rho(R, R'; \beta) = \langle R | e^{-\beta \hat{H}} | R' \rangle$$

where $\hat{H}$ is the many-body Hamiltonian with exact Coulomb interactions. One can sample it accurately in real space R by using discrete time-slicing $\Delta\tau = \beta/M$, where the Trotter number M is a large integer. The PIMC walker is a closed ring-polymer, where the imaginary-time correlation function is very easily estimated by correlating the measurements at each time-slice:

$$\langle C(\tau) \rangle = \langle TP(0)Q(\tau) \rangle$$

$$\langle C(m\Delta\tau) \rangle = Z^{-1} \int dR_1 \dots dR_M \rho(R_0, R_1) \dots \rho(R_M, R_0) P(0)Q(m)$$

where $m = 0, 1, \dots, M - 1$. Symmetry properties and averaging can be used for further optimization.

The Markovian walker contains ring-polymers for each particle (including the nuclei) that are equilibrated and sampled using Metropolis Monte Carlo.



Electric field interaction

Accurate quantum mechanical simulation of electric field interaction – multipole polarizability – is a well-motivated challenge. The polarizability is arguably the most important electronic response property: directly related to, *e.g.*, optical dispersion, spectroscopy and even van der Waals forces.

Interaction to the classical time-dependent vector field $F(t)$ can be expanded in electric multipoles

$$h(t) = -\theta(t - t') [\mu \cdot F(t) + \Omega : \nabla F(t) + \dots],$$

where the dots denote inner products of vectors and tensors with same ranks. From the first term we can extract, *e.g.*, the dipole polarizability, which is the dipole moment induced by dipole radiation, *i.e.*

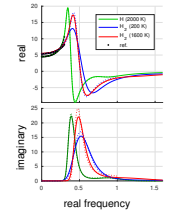
$$\alpha_1(\omega) = \chi_1^R(\omega) = -\frac{i}{\hbar} \mathcal{F}\theta(t - t') \langle [\mu(t), \mu(t')] \rangle,$$

where 1 refers to dipole, 2 to quadrupole, etc.

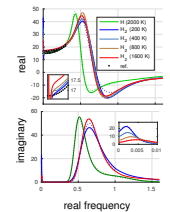
Dynamic polarizability

PIMC simultaneously samples electronic and rovibrational degrees of freedom, isotope effects and recoil effects; a unique interface to total nonadiabatic response properties at finite temperature.

Only electronic **dipole** transitions are allowed for nonpolar species, such as H and H₂. Real and imaginary parts of the electric field response match the reference data [6] at low frequencies. There are no notable thermal effects, except for a small centrifugal distortion of H₂. The level of detail is limited in the resonant region [1].



The **quadrupole** transition is rotationally active, because H₂ has a nonzero quadrupole moment. The rotation is coupled to the temperature such that the orientational effect decays as the higher rotational ensemble is occupied. [1] The effect has been studied more extensively in the static limit [2-3,7], and it also manifests in polarizabilities of higher order.



van der Waals coefficients

Long-range interaction between species is associated with the imaginary-domain polarizability. Dispersion interaction between spherically symmetric systems A and B can be written as

$$V_{\text{vdw}}(r) = -C_6/r^6 - C_8/r^8 - C_{10}/r^{10},$$

where the van der Waals coefficients are obtained from the Matsubara data using the simplified Casimir–Polder formulas:

$$C_6^{AB} = \frac{3}{4} \int_0^\infty d\omega \alpha_1^A(i\omega) \alpha_1^B(i\omega)$$

$$C_8^{AB} = \frac{35}{32} \int_0^\infty d\omega (\alpha_1^A(i\omega) \alpha_2^B(i\omega) + \alpha_2^A(i\omega) \alpha_1^B(i\omega))$$

$$C_{10}^{AB} = \frac{11}{16} \int_0^\infty d\omega (\alpha_1^A(i\omega) \alpha_3^B(i\omega) + \alpha_3^A(i\omega) \alpha_1^B(i\omega))$$

$$+ \frac{35}{16} \int_0^\infty d\omega \alpha_2^A(i\omega) \alpha_2^B(i\omega)$$

If some of the polarizabilities have thermal dependencies, they are also present in dispersion coefficients. This can have important consequences in realistic finite temperature simulations employing van der Waals parameters.

Below: Exemplary results from Ref. [1] for pairs of atoms and molecules in 300 K, using $\Delta\tau = 0.02$, and 0 K reference values [6].

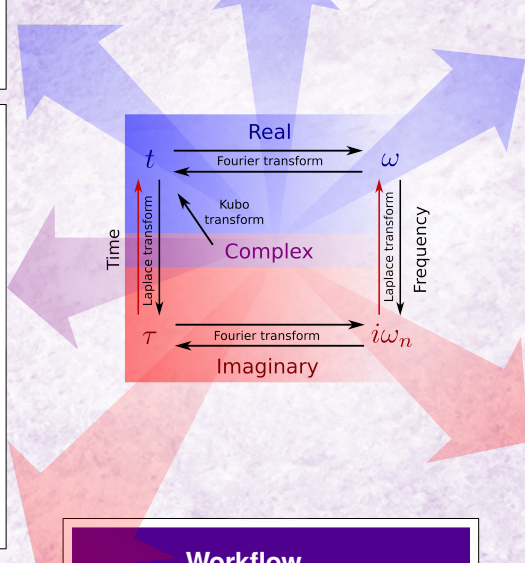
	C_6	C_8	C_{10}
H–H	6.50(4)	124.7(4)	3300(9)
ref.	6.4990267	124.39908	3285.8284
H ₂ –H ₂	12.04(12)	219(2)	4870(20)
ref.	12.058168		
H ₂ –Ps	45.2(4)	401(4)	13270(70)

Acknowledgements

We are grateful for the support from Jenny and Antti Wihuri foundation and TUT Graduate school, and the computational resources of CSC and TCSC.

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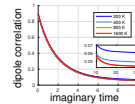


Workflow

Step 1

$$C(\tau) = \langle \mu(-\tau) \mu \rangle$$

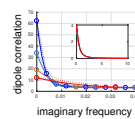
Correlation function from PIMC. Stochastic accuracy of the estimate can be improved indefinitely.



Step 2

$$C(i\omega) = \int_0^\beta d\tau e^{i\omega\tau} C(\tau)$$

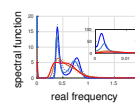
Matsubara data from Fourier transform. Can be used to compute van der Waals coefficients.



Step 3

$$C(i\omega_n) = \int_{-\infty}^{\infty} d\omega \frac{A(\omega)}{i\omega_n - \omega}$$

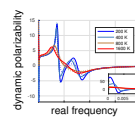
Spectral function from MaxEnt inversion. Can be improved by using better *a priori* default model.



Step 4

$$\alpha(\omega) = \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} A(\omega') \left(\frac{1}{\omega - \omega' - i\eta} + \frac{1}{\omega + \omega' + i\eta} \right)$$

Complex polarizability from an integral transform gives the optical response.



Figures from Ref. 1 show the total dipole polarizabilities of HD⁺, which is rotationally active.