Electronic Density Response of Warm Dense Hydrogen: *Ab initio* Path Integral Monte Carlo Simulations

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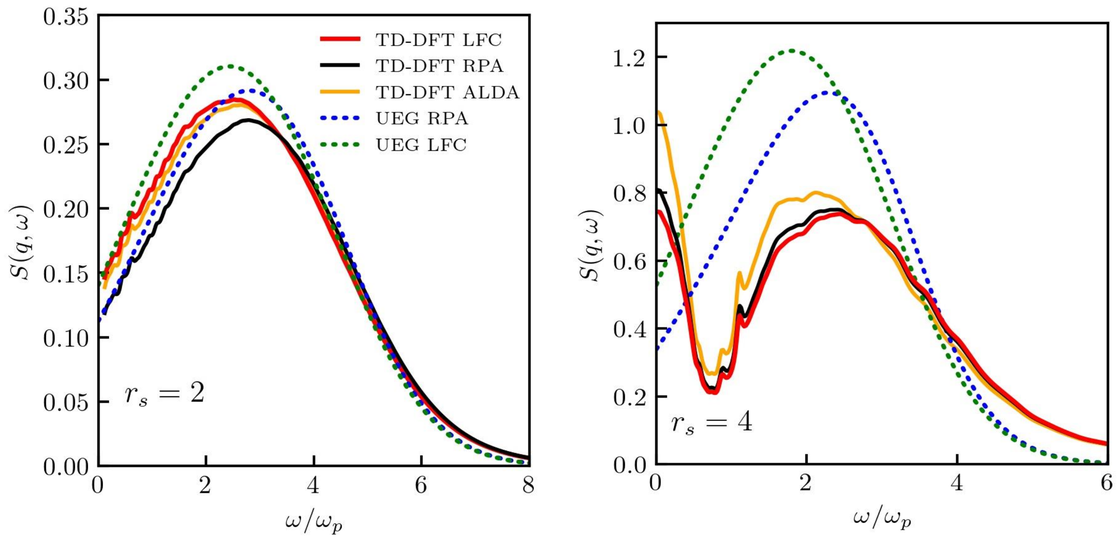
Motivation and Outline

Hydrogen is one of the most abundant elements in the universe. However, its theoretical description is yet not sufficiently developed to accurately describe its behavior in the warm dense matter (WDM) regime. In this work we employ *ab initio* Path-Integral Monte-Carlo (PIMC) simulations for ion-snapshots from DFT-simulations in order to solve the electronic structure problem. The properties extracted from these simulations are exact up to a statistical error. We then extract the static local field correction G(q,0) for Warm Dense Hydrogen in order to compute the dynamic structure factor for TD-DFT with the exact XC-effects included.

Pre-Print:

S(q,ω) using PIMC and TD-DFT (Θ = 1)



Snapshot PIMC

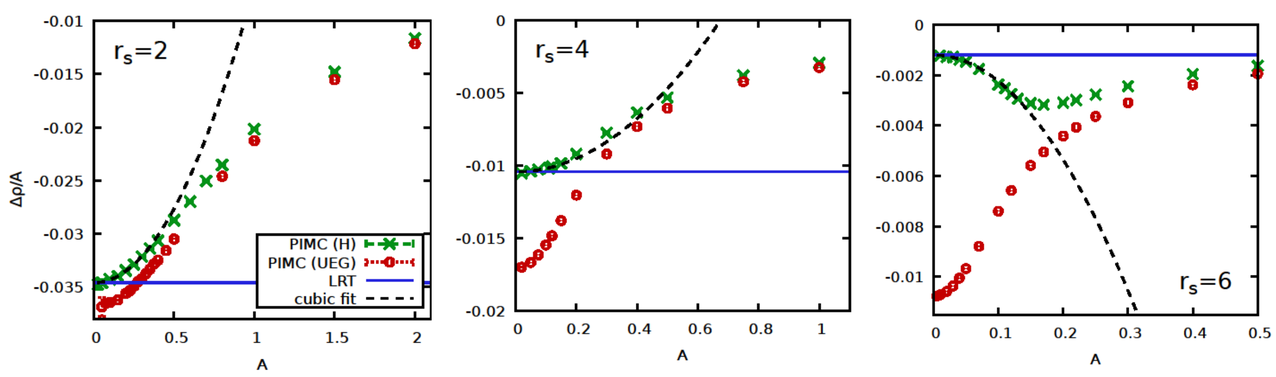
- We ran DFT-MD simulations in order to sample the ionic position of warm dense hydrogen
- By extracting the ionic position snapshots from DFT and loading them into PIMC we sample the electronic partition function connected to the following Hamiltonian

$$\hat{H} = -\frac{1}{2}\sum_{l=1}^{N}\nabla_l^2 + \hat{W}_{\mathrm{ee}} + \hat{V}_{\mathrm{ei}} + 2A\sum_{l=1}^{N}\cos\left(\mathbf{q}\cdot\hat{\mathbf{r}}_l\right)$$

- Since the ions in the WDM regime have low mobility and behave like point-like particles, due to their large mass and high temperature, we neglect the sampling of the ion paths
- The perturbation term allows us to extract the density response of the electronic system including the electron-ion interaction

$$\langle\hat{\rho}_{\mathbf{k}}\rangle_{q,A} = \frac{1}{V}\left\langle\sum_{l=1}^{N}e^{-i\mathbf{k}\cdot\hat{\mathbf{r}}_l}\right\rangle_{q,A}$$

q = 2π (0,0,2)^T /L, Θ = 1, N = 14



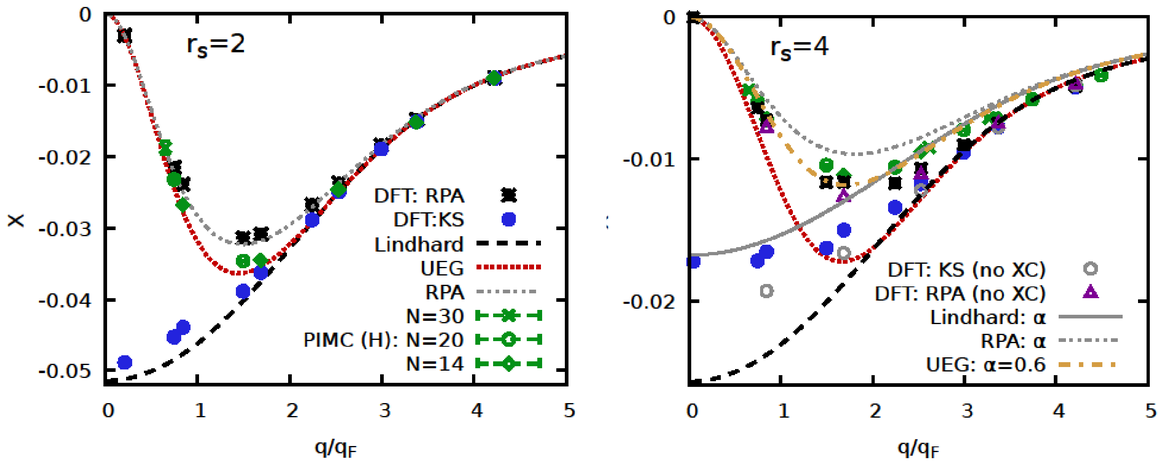
- The above figures show the density induced by the perturbation term as a function of perturbation strength
- Linear response theory already fails at weak perturbation strengths of A < 0.2
- Significant differences between the UEG result and hydrogen snapshots in the induced density are visible

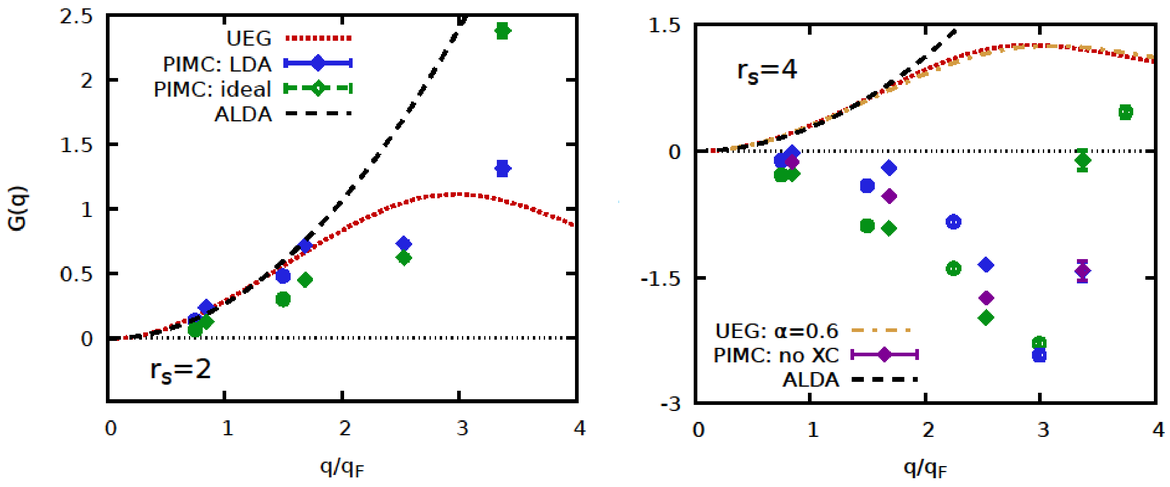
Extracting the density response

- We can access the density response function by fitting the above results to the polynomial expression

$$\Delta\rho(\mathbf{q},A) = \chi(\mathbf{q})A + \chi^{\mathrm{cubic}}(\mathbf{q})A^3$$

- The results on the right depict the comparison between snapshot PIMC results (green), DFT RPA (black), the noninteracting system (blue), Lindhard density response and RPA
- For r_s=4: by introducing an ionization degree α = N_{free} / N, one can get a qualitative agreement between the UEG results and our PIMC simulations
- α = 0.6 is in good agreement with [2] of α = 0.54





Hydrogen exchange-correlation Kernel

- The local field correction (LFC) for any χ_0 is defined by

$$\chi(\mathbf{q},\omega) = \frac{\chi_0(\mathbf{q},\omega)}{1 - \frac{4\pi}{q^2}\left[1 - G(\mathbf{q},\omega)\right]\chi_0(\mathbf{q},\omega)}$$

- The LFC is connected to the XC-Kernel formalism by the identity

$$G(\mathbf{q},\omega) = -\frac{q^2}{4\pi}K_{\mathrm{xc}}(\mathbf{q},\omega)$$

- In PIMC we are only able to sample the LFC in the static limit G(**q**)=G(**q**,0)
- With the usage of the fluctuation-dissipation theorem one can now calculate the dynamic structure factor including exact XC-effects

[1] T. Dornheim, J. Vorberger, S. Groth, N. Hoffmann, Zh.A. Moldabekov, and M. Bonitz, "The static local field correction of the warm dense electron gas: An ab initio path integral Monte Carlo study and machine learning representation," J. Chem. Phys 151, 194104 (2019)
[2] B Militzer, DM Ceperley, Path integral monte Carlo simulation of the low-density hydrogen plasma.Phys. Rev. E63, 066404 (2001).
[3] T Dornheim, J Vorberger, M Bonitz, Nonlinear electronic density response in warm dense matter.Phys. Rev. Lett.125, 085001 (2020)

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