Nuclear Quantum Effects in Two-temperature Hydrogen via Orbital-free DFT Path Integral MD

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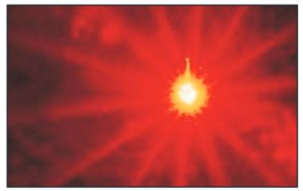

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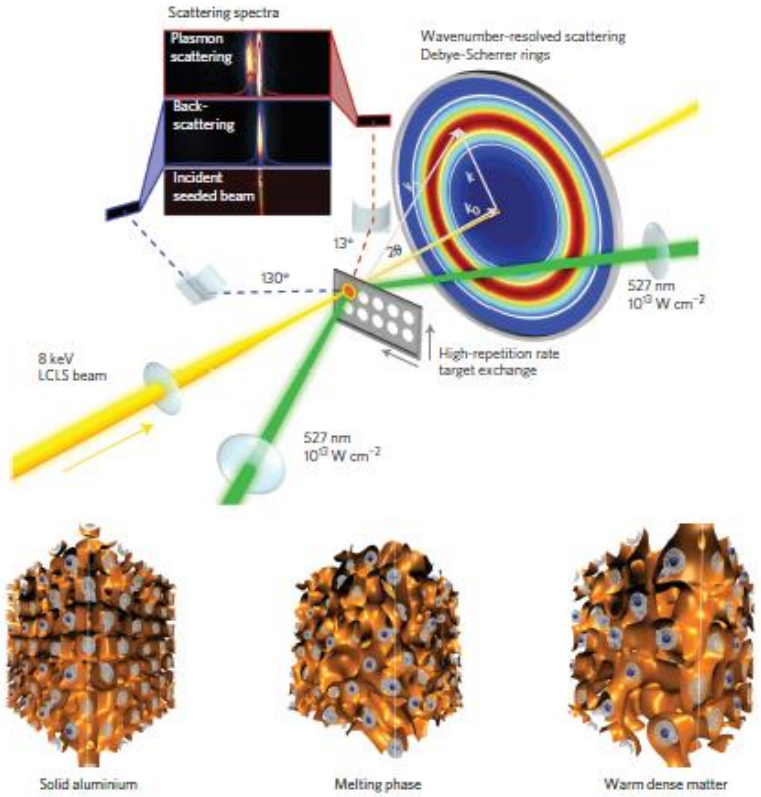
Publications, preprints, & software at http://www.qtp.ufl.edu/ofdft

NERSC National Energy Research Scientific Computing Center

HiPerGator RESEARCH COMPUTING

UF

General motivation – extreme chemistry & physics



Upper: Schematic of MEC instrument at LCLS; 50 fs monoenergetic X-ray beam hits Al target.

Lower: Ab Initio MD simulations show that ions (blue) eventually leave lattice positions, conduction electrons (orange isosurfaces) are highly delocalized, core electrons (grey) remain localized

Fletcher et al., Nature Photonics 9, 274 (2015)

Warm Dense Matter "WDM"

• Challenging region *between* normal condensed matter and plasmas:

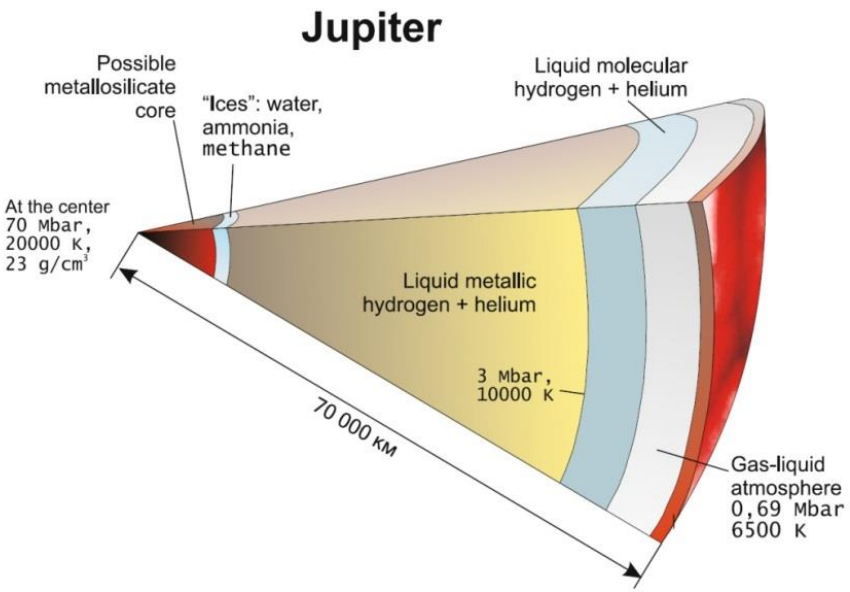
T < 100eV (≈1,100,000 K)

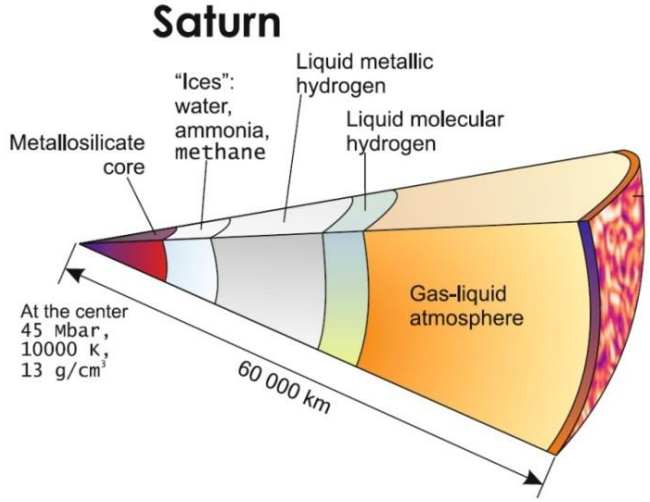
***P* from 0 thousands of GPa.**

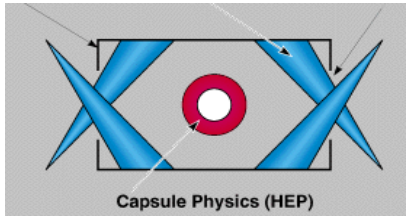
• Inertial confinement fusion pathway; giant planet & exo-planet interiors; shock compression experiments

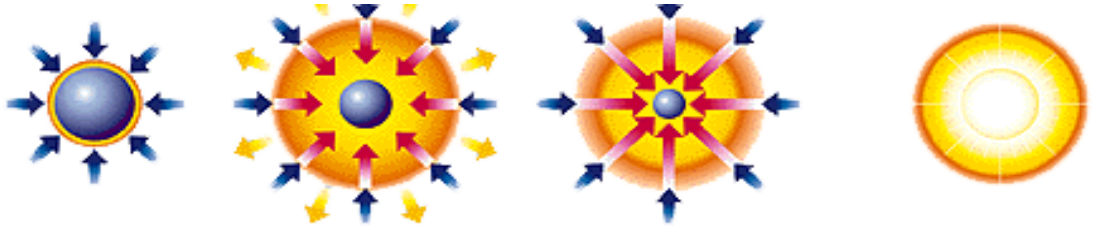
Warm Dense Matter Panel, High Energy Density Laboratory Plasma ReNew Workshop; Nov. 2009

Hydrogen is important for modeling giant planetary interiors and ICF experiments



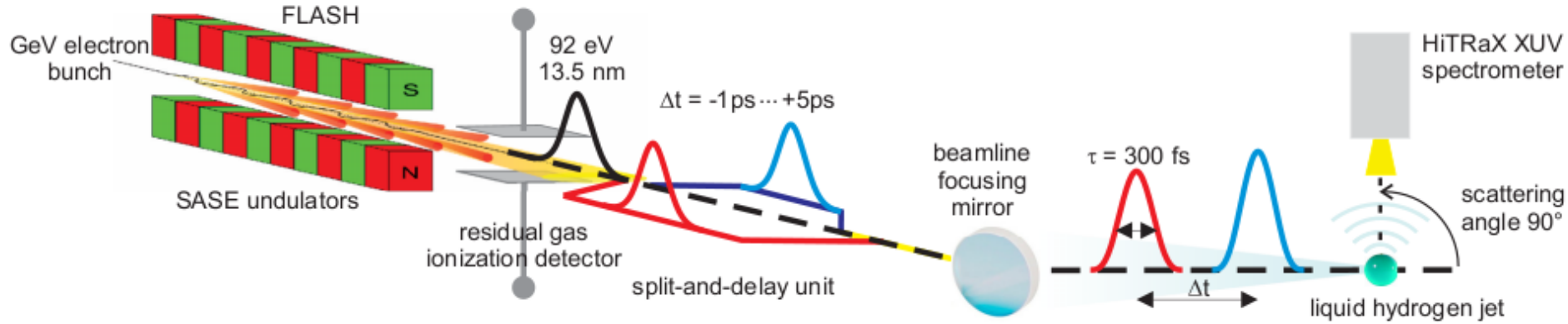


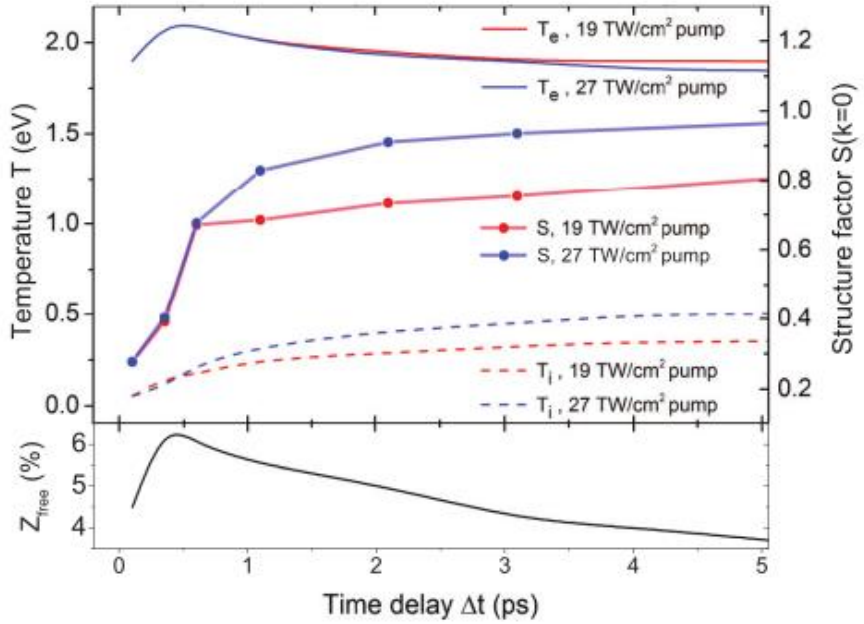




Adapted from Fig. 7.9 "Extreme States of Matter", V.E. Fortov

Two-temperature warm dense hydrogen - experiment



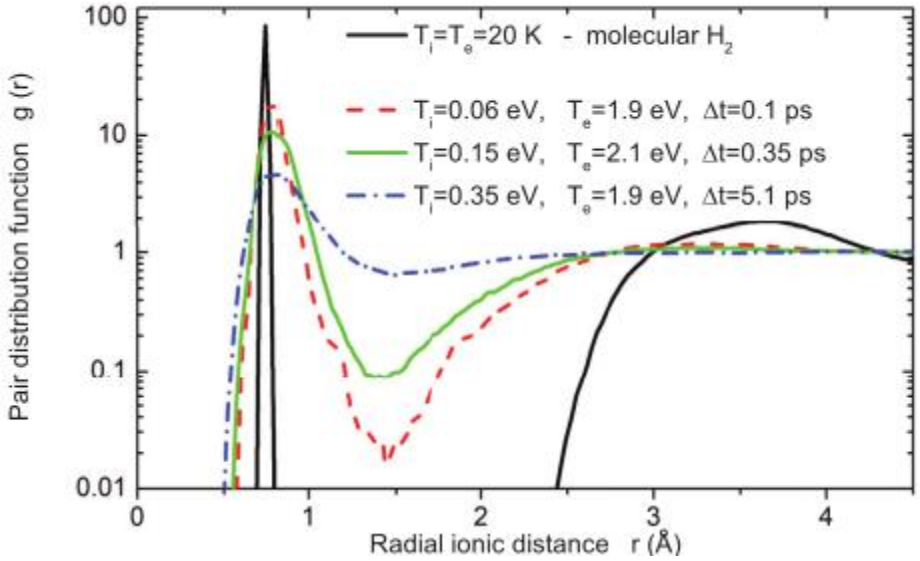


Ultrafast heating in cryogenic hydrogen by free electron laser x-ray burst.

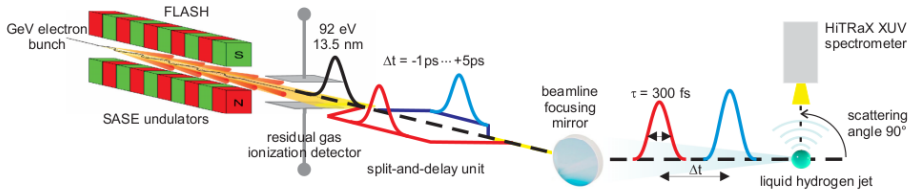
Electron temperature T_e and ion temperature T_i clearly are distinct for long times relative to electron timescales

Zastrau et al, PRL 112, 105002 (2014); Phys. Rev. E 90, 013104 (2014)

Two-temperature warm dense hydrogen - experiment



The electron-ion equilibration dynamics was validated by two-temperature DFT MD calculations.



Zastrau et al, PRL 112, 105002 (2014); Phys. Rev. E 90, 013104 (2014)

Ingredients for accurate, fast ab initio MD (AIMD)

- **Accurate, computationally efficient exchange-correlation (XC) free energy functional**

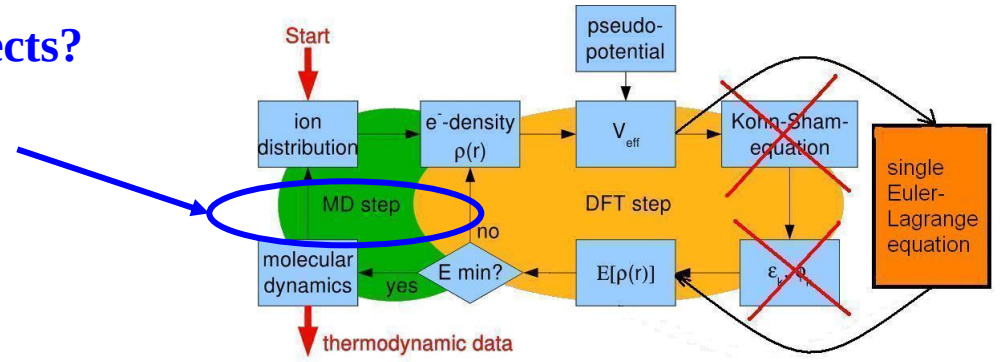
- **Orbital-free DFT for linear scaling ⇒ orbital-free non-interacting KE and non-interacting entropy**

$$\mathrm{F}[n] = T_s[n] + \mathrm{S}_s[n] + E_H[n] + F_{xc}[n] + E_{ext}[n]$$

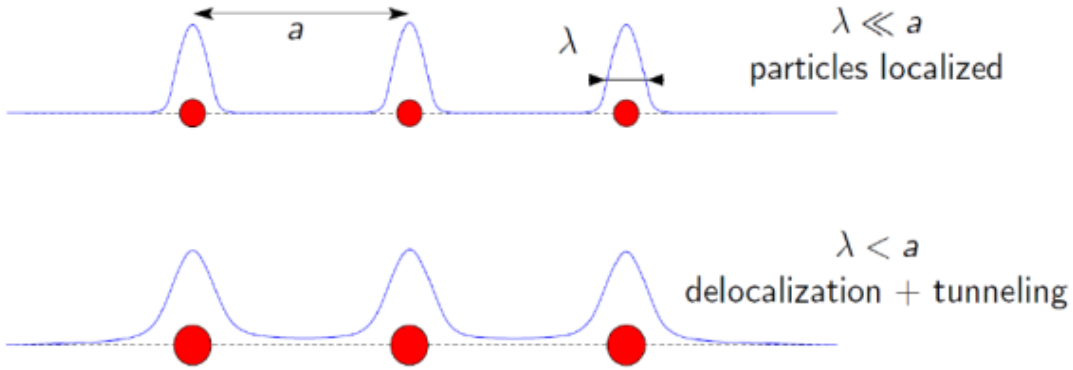
Modified (single orbital) Kohn-Sham equation $\dfrac{\delta \mathrm{F}[n]}{\delta n} = \mu$

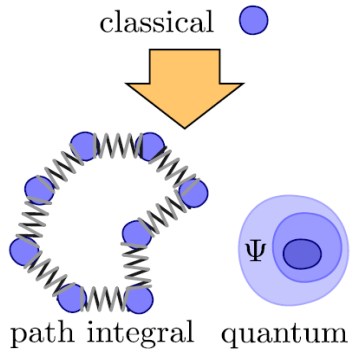
Never use the K-S orbitals explicitly.

What about nuclear quantum effects?
Which AIMD, BO-MD or PIMD?



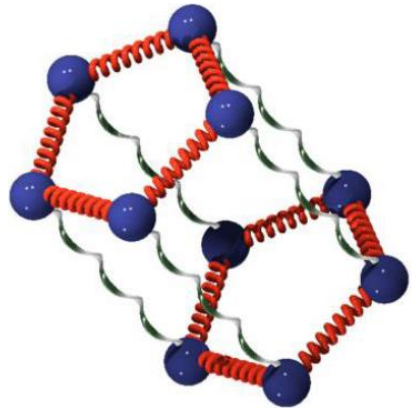
Nuclear quantum effects & path integral molecular dynamics





N-particle quantum system → **N-polymer classical system, each polymer has P beads**

Density functional theory



***Ab initio* path-integral molecular dynamics (i-PI code)**

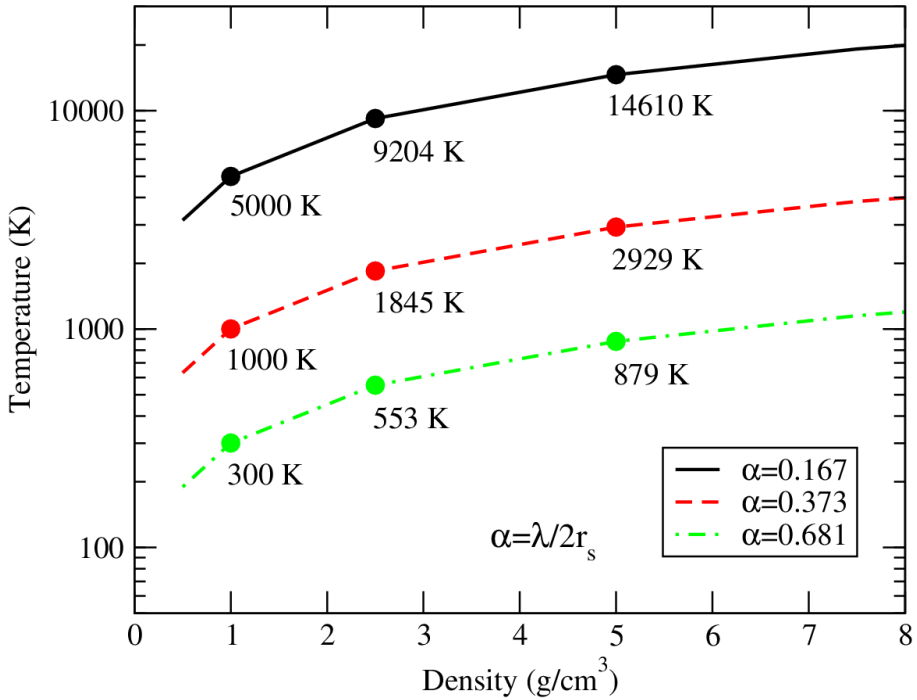
Z. Phys. B 95, 143 (1994)

PIMD with orbital-free DFT or "PI-OFMD"

- ***LKTF noninteracting free energy functional [Phys. Rev. B 98, 041111 (2018), Phys. Rev. B 101, 075116 (2020)]***
- ***KSDT finite-T XC functional [Phys. Rev. Lett. 112, 076403 (2014)]***
- ***Modified PROFESS code***

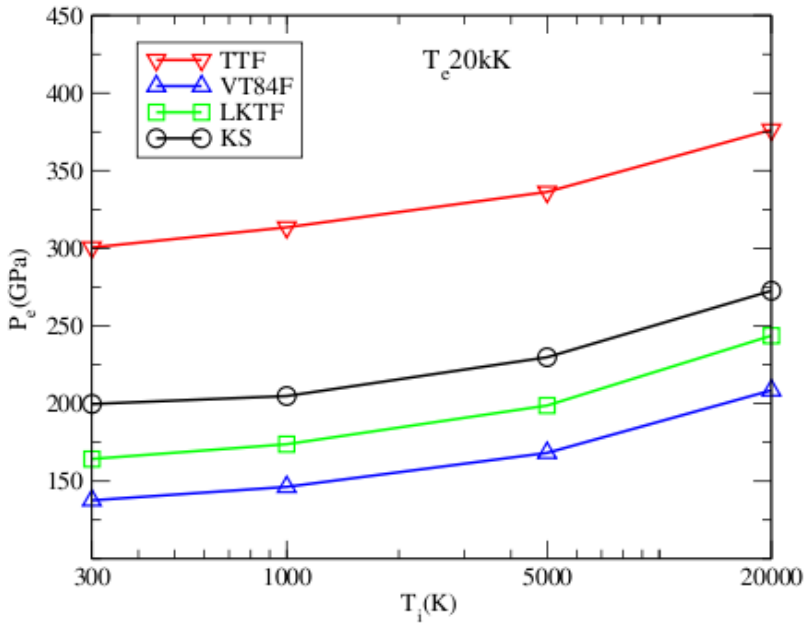
$$\alpha = \frac{\lambda}{2r_s}$$

α is the ratio of the ionic thermal de Broglie wavelength to the mean distance between ions.



State points of density and ion temperature used.

Functional comparison; PI-OFMD vs CEIMC comparison



OFMD vs KSMD; ρ = 1 g/cm^3 ,
T_e = 20 kK ≈ 1.7 eV

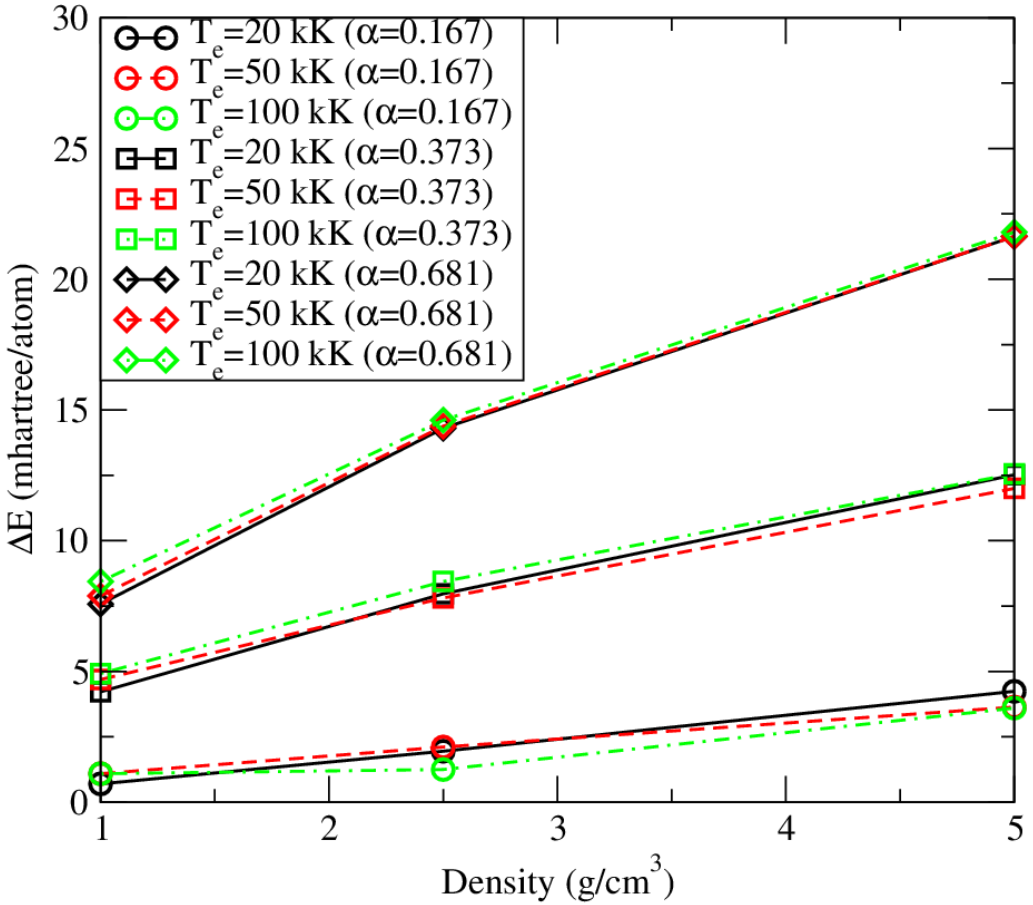
- ***Different OFKE functionals have significant impact; TF is useless, LKTF improves significantly on VT84F.***

TABLE I. Quantum nuclear corrections to the energy and pressure of hydrogen from CEIMC and PI-OFMD calculations at an equilibrium temperature $T_e = T_i = 2000$ K. Corrections are defined as $\Delta E = (E - E_{\text{classical}})/N$ and $\Delta P = P - P_{\text{classical}}$, respectively. The ratio of the pressure corrections to the pressure obtained classically $\Delta P/P$ is presented. Statistical errors are reported in parentheses as the uncertainty on the last digit.

	r_s	α	ΔE (mhartree/atom)	ΔP (GPa)	$\Delta P/P$ (%)
CEIMC[a]	1.05	0.350	4.0(7)	7(3)	0.4
	1.10	0.334	3.8(3)	9(1)	0.7
	1.25	0.294	2.8(5)	5(1)	1.0
PI-OFMD	1.05	0.350	7.0(7)	27.7(4)	1.9
	1.10	0.334	6.3(7)	23.6(3)	2.2
	1.25	0.294	4.1(6)	11.1(2)	2.5

- ***NQE corrections from PI-OFMD are substantially larger than those from CEIMC for both the energy and pressure.***

NQEs and electronic temperature



NQE corrections to the energy per H atom as function of density at constant α

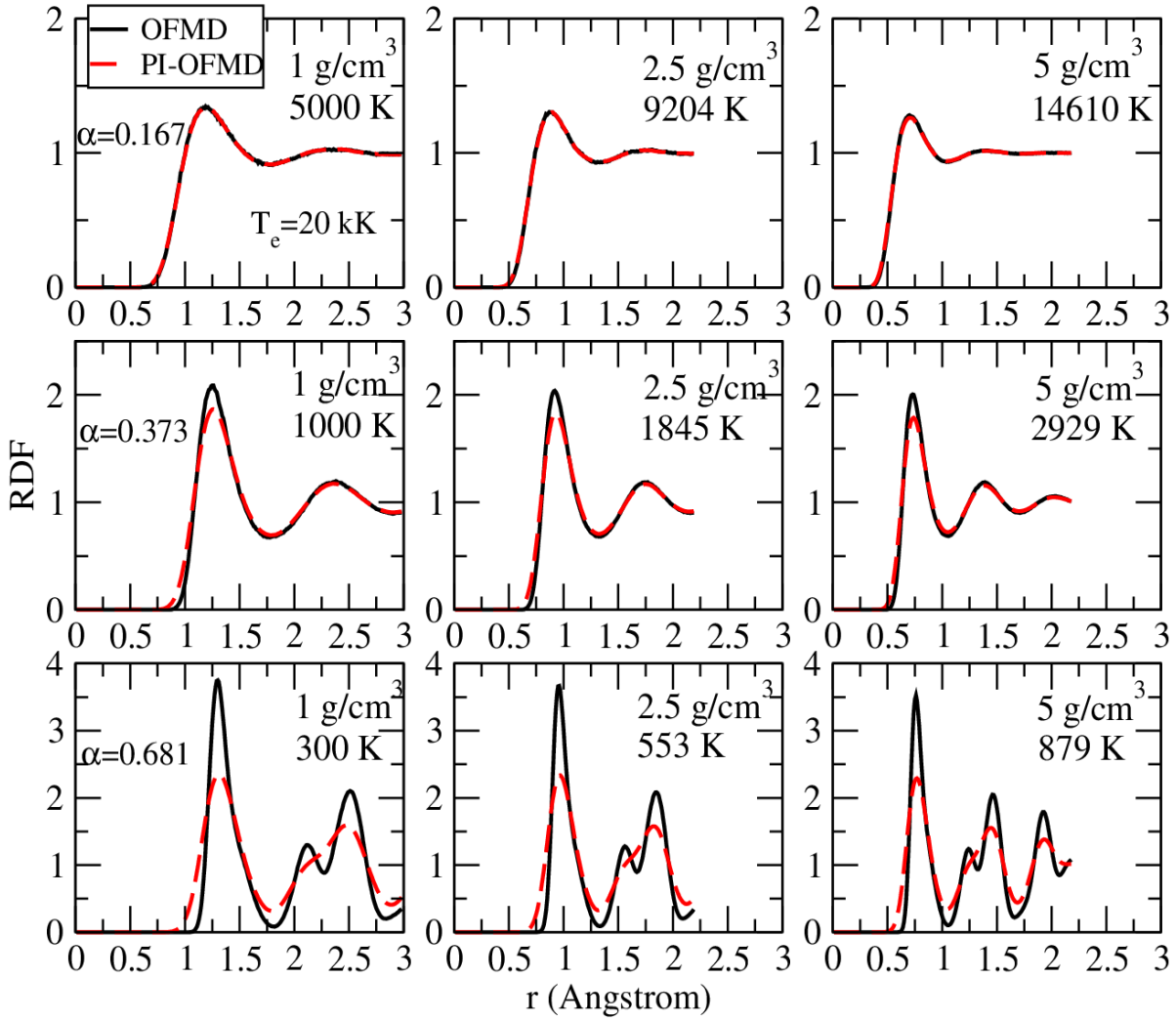
- ***Differing T_e has almost no impact on NQE corrections to the energy.***

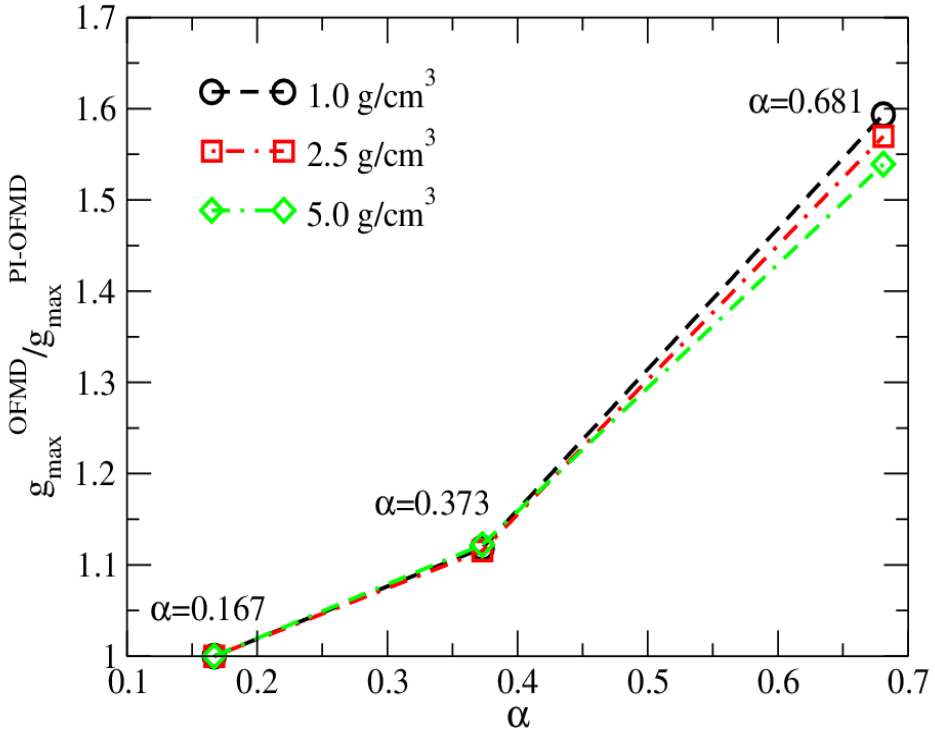
NQE corrections to pressures

TABLE II. Summary of the pressures contributed by electrons and ions and total pressure of two-temperature hydrogen with differing densities and electronic and ion temperatures from OFMD and PI-OFMD calculations. P_e, P_i, and P are the electronic pressure, ionic pressure, and total pressure calculated from quantum simulations, while $P_e^{\text{classical}}$, $P_i^{\text{classical}}$, and $P^{\text{classical}}$ are their classical simulation counterparts. Dependence upon the dimensionless size parameter α also is given.

T_e kK	α	ρ g/cm^3	T_i K	$P_e^{\text{classical}}$ GPa	P_e GPa	$\Delta P_e/P_e$ %	$P_i^{\text{classical}}$ GPa	P_i GPa	$\Delta P_i/P_i$ %	$P^{\text{classical}}$ GPa	P GPa	$\Delta P/P$ %
20	0.167	1.0	5000	198.99	199.15	0.08	40.68	40.43	-0.60	239.67	239.58	-0.04
20	0.167	2.5	9204	1815.79	1819.70	0.21	194.40	200.18	2.97	2010.20	2019.88	0.48
20	0.167	5.0	14610	7389.67	7408.13	0.25	589.51	626.58	6.29	7979.17	8034.71	0.70
20	0.373	1.0	1000	174.56	178.68	2.36	8.31	12.15	46.21	182.86	190.83	4.36
20	0.373	2.5	1845	1725.10	1740.63	0.90	38.77	56.40	45.47	1763.87	1797.03	1.88
20	0.373	5.0	2929	7151.90	7196.04	0.62	117.03	174.99	49.53	7268.92	7371.03	1.40
20	0.681	1.0	300	164.42	172.17	4.71	2.46	9.08	269.10	166.88	181.25	8.61
20	0.681	2.5	553	1689.21	1717.70	1.69	11.46	42.49	270.77	1700.67	1760.19	3.50
20	0.681	5.0	879	7060.90	7135.82	1.06	36.30	129.85	257.71	7097.19	7265.67	2.37
50	0.167	1.0	5000	258.40	259.23	0.32	41.51	42.52	2.43	299.91	301.75	0.61
50	0.167	2.5	9204	1921.09	1924.74	0.19	184.84	188.11	1.77	2105.93	2112.84	0.33
50	0.167	5.0	14610	7557.53	7572.51	0.20	598.92	618.34	3.24	8156.45	8190.84	0.42
50	0.373	1.0	1000	235.36	239.65	1.82	8.06	12.33	52.98	243.42	251.98	3.52
50	0.373	2.5	1845	1836.57	1851.04	0.79	38.59	55.28	43.25	1875.16	1906.33	1.66
50	0.373	5.0	2929	7322.82	7362.95	0.55	119.67	172.68	44.30	7442.49	7535.63	1.25
50	0.681	1.0	300	226.57	233.68	3.14	2.42	9.26	282.64	229.00	242.94	6.09
50	0.681	2.5	553	1801.53	1829.30	1.54	11.22	42.39	277.81	1812.76	1871.69	3.25
50	0.681	5.0	879	7230.73	7304.81	1.02	36.56	130.00	255.58	7267.29	7434.81	2.31
100	0.167	1.0	5000	466.02	466.47	0.10	41.08	41.89	1.97	507.10	508.36	0.25
100	0.167	2.5	9204	2248.03	2248.48	0.02	189.55	187.94	-0.85	2437.58	2436.41	-0.05
100	0.167	5.0	14610	8027.68	8041.09	0.17	593.45	618.83	4.28	8621.13	8659.92	0.45
100	0.373	1.0	1000	448.47	451.61	0.70	8.41	12.66	50.54	456.88	464.27	1.62
100	0.373	2.5	1845	2166.42	2181.17	0.68	37.46	55.76	48.85	2203.88	2236.93	1.50
100	0.373	5.0	2929	7797.50	7839.59	0.54	118.42	175.35	48.07	7915.92	8014.94	1.25
100	0.681	1.0	300	441.51	447.02	1.25	2.41	9.76	304.98	443.92	456.78	2.90
100	0.681	2.5	553	2135.69	2160.99	1.18	11.20	42.68	281.07	2146.89	2203.67	2.64
100	0.681	5.0	879	7708.87	7781.02	0.94	36.15	130.24	260.28	7745.02	7911.26	2.15

Radial distribution functions





When the ratio of the ionic thermal de Broglie wavelength to the mean distance between them is larger than about 0.30, the ionic radial distribution function is affected perceptibly by NQEs.

Preprint -

Two-temperature warm dense hydrogen simulation with quantum protons driven by orbital-free density functional theory electronic forces

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(Dated: 23 Dec. 2019)

Nuclear quantum effects (NQEs) on structure and thermodynamic properties of two-temperature warm dense hydrogen are investigated using path integral molecular dynamics simulations driven by orbital-free density functional calculations. State-of-the-art non-interacting free energy and exchange-correlation functionals are used for including explicit temperature dependence. The results show that when the ratio of the thermal de Broglie wavelength of ions to the mean distance between them is larger than about 0.30, the ionic radial distribution function is meaningfully affected by inclusion of NQEs. Moreover, NQEs induce a substantial increase in both the ionic and electronic pressures. This confirms that NQEs should not be neglected when high-accuracy equation of state data for hydrogen are required. The differing electron temperature in the warm dense hydrogen has slight effects on the ionic radial distribution function and equation of state in the range of densities considered in this study. In addition, compared to the thermostatted ring-polymer molecular dynamics, the primitive path integral molecular dynamics algorithm is demonstrated to yield overestimated electronic pressures, a consequence of the different ionic description.

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Phys. Rev. B (submitted)

Summary

1. ***Nuclear quantum effects (NQEs) play important roles in structure and thermodynamic properties of warm dense hydrogen.***
2. ***When the ratio of the ionic thermal de Broglie wavelength to their mean distance separation is larger than about 0.30, the ionic radial distribution function is meaningfully affected by NQEs.***
3. ***NQEs induce a substantial increase in the ionic pressure and some non-trivial increases in electronic pressures. Thus NQEs should not be neglected when high-accuracy equation of state data for hydrogen are required.***
4. ***Differing electron and ionic temperatures has only small effects on the ionic radial distribution function and equation of state in the range of densities considered.***