

High-Pressure Phases of Hydrogen

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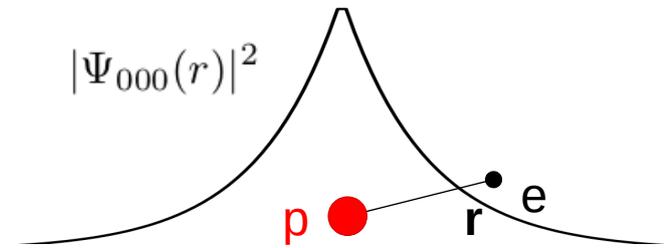
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- Introduction – Motivation
- Coupled Electron-Ion Monte Carlo:
 - Computation methods
 - Results

Hydrogen: From a single atom to many...molecules...

Hydrogen atom H

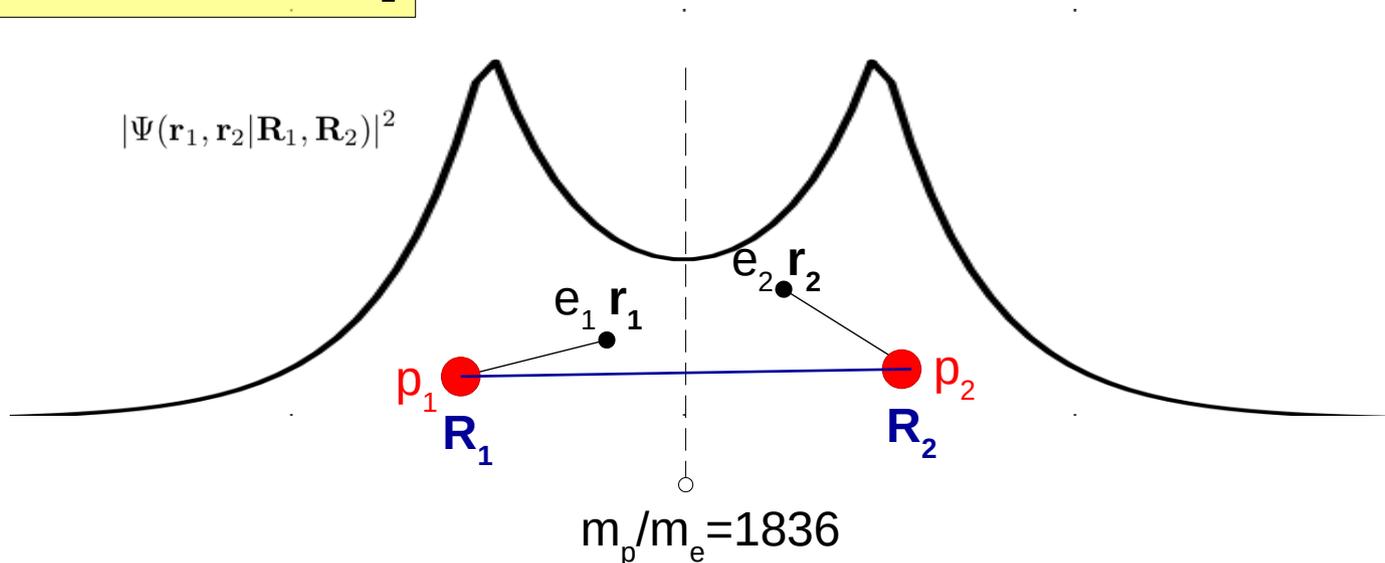
$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{r} \right] \Psi_{nlm}(\mathbf{r}) = E_n \Psi_{nlm}(\mathbf{r}) \quad E_n \simeq -\frac{13.6\text{eV}}{n^2}$$



N atoms:

$$H = -\frac{\hbar^2}{2m_p} \sum_I \nabla_I^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I < J} \frac{e^2}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i, I} \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_I|}$$

Hydrogen molecule H₂



Electronic excitations:

~ 11eV

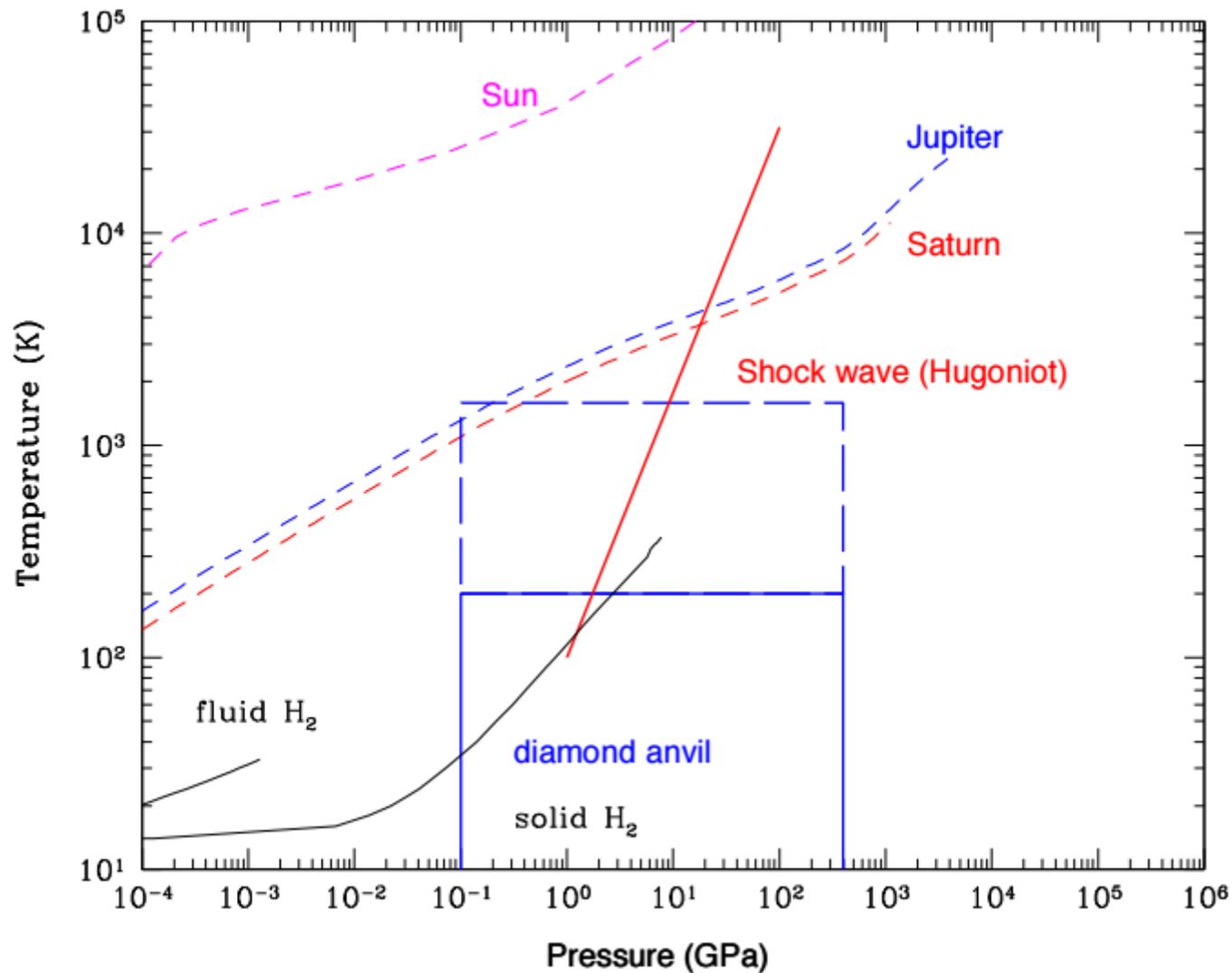
Vibrational:

~ 0.5eV ~ 6000K

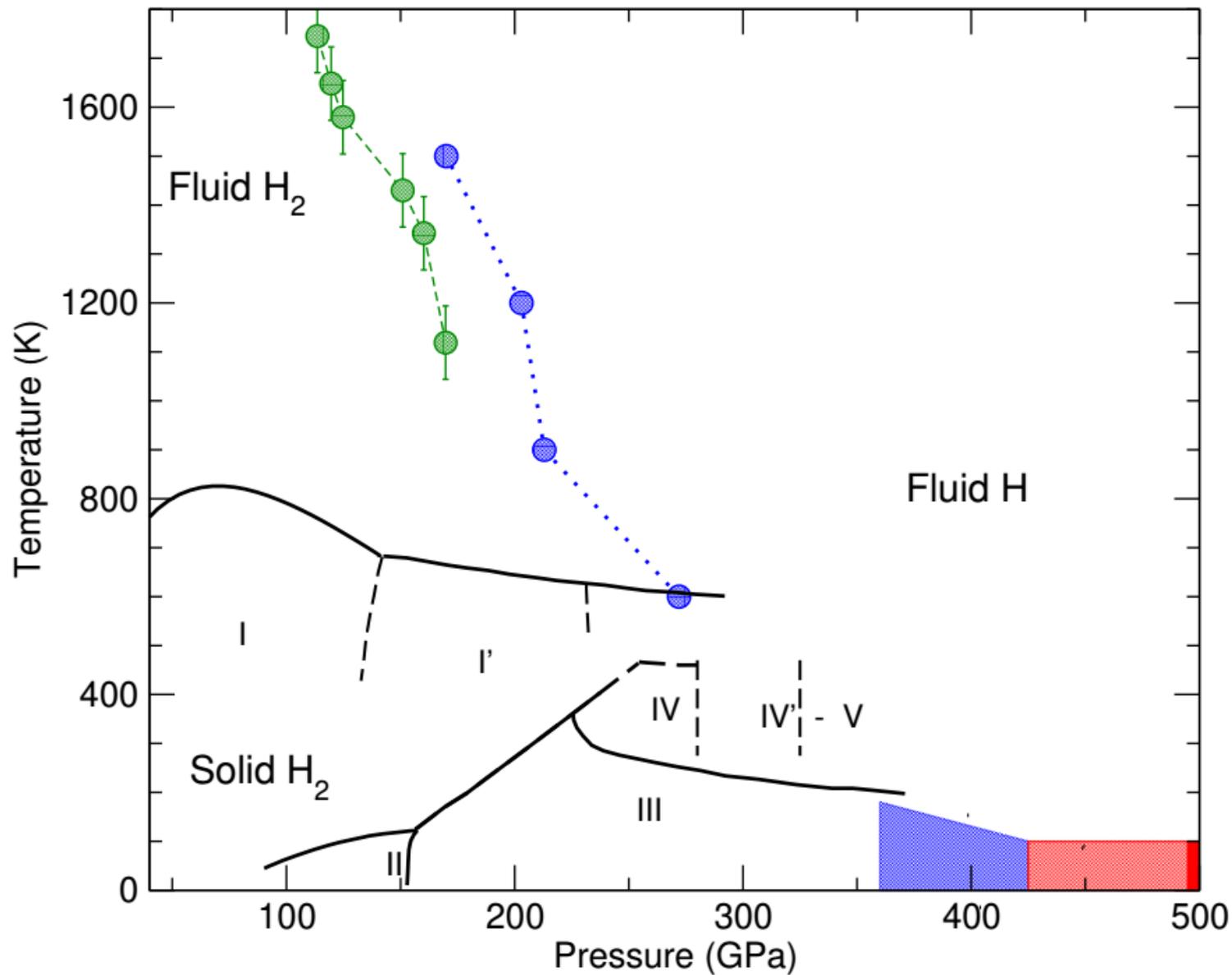
Rotational:

~ 0.017eV ~ 200K

Temperature-Pressure region (I)



Solid hydrogen: static compression



Born-Oppenheimer approximation

- Non-relativistic Hamiltonian for ions and electrons

$$\begin{aligned}
 H &= - \sum_n \frac{\hbar^2 \nabla_n^2}{2M} - \sum_i \frac{\hbar^2 \nabla_i^2}{2m} + \sum_{n < m} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{n,i} \frac{Ze^2}{|\mathbf{r}_i - \mathbf{R}_n|} + \sum_{n < m} \frac{Z^2 e^2}{|\mathbf{R}_n - \mathbf{R}_m|} \\
 &= - \sum_n \frac{\hbar^2 \nabla_n^2}{2M} + H_e(\mathbf{R})
 \end{aligned}$$

- Born-Oppenheimer approximation ($T \ll T_F$):
electronic ground state for fixed ion positions

$$H_e(\mathbf{R})\Psi(\mathbf{r}) = E_0(\mathbf{R})\Psi(\mathbf{r})$$

- Density matrix/ distribution of ions

quantum protons

classical protons

$$\rho(\mathbf{R}) = \langle \mathbf{R} | e^{-H/T} | \mathbf{R} \rangle \simeq \left\langle \mathbf{R} \left| \exp \left\{ - \frac{- \sum_n \frac{\hbar^2 \nabla_n^2}{2M} + E_0(\mathbf{R})}{T} \right\} \right| \mathbf{R} \right\rangle \sim e^{-E_0(\mathbf{R})/T}$$



Sampling quantum protons in the Born-Oppenheimer approximation (BO): Coupled-Electron-Ion Monte Carlo

BO Hamiltonian $H = T_n + V(\mathbf{R})$ $T_n = -\frac{\hbar^2}{2m_p} \sum_I \nabla_I^2$

- Sample thermal distribution $\rho(\mathbf{R}) \sim \langle \mathbf{R} | e^{-\beta H} | \mathbf{R} \rangle$ $\beta = 1/T$

➡ via Path-Integral Monte Carlo methods

- Needed precise BO energies $V(\mathbf{R}) = E_0(\mathbf{R}) \equiv \langle \Psi_0(\mathbf{R}) | H_e(\mathbf{R}) | \Psi_0(\mathbf{R}) \rangle$

➡ via Variational and Projector Monte Carlo

controlled by variational principle $E_0 \leq E_T \equiv \frac{\langle \Psi_T | H_e | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle}$

- Systematic bias
- Fixed-node error
 - Finite size effects

- MC sampling of noisy actions/energies $V(\mathbf{R}) = E_0(\mathbf{R}) \pm \sigma$

➡ Penalty method

Path-Integral Monte Carlo methods

- Based on Trotter's theorem:

$$e^{-\beta H} = \left(e^{-\beta H/M} \right)^M = \lim_{M \rightarrow \infty} \left(e^{-\beta T_N/M} e^{-\beta V/M} \right)^M$$

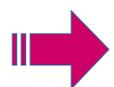
using $\langle \mathbf{R} | e^{-\beta V/M} | \mathbf{R}' \rangle = \delta(\mathbf{R} - \mathbf{R}') e^{-\beta V(\mathbf{R})/M}$

$$\langle \mathbf{R} | e^{-\beta T_n/M} | \mathbf{R}' \rangle = \sum_{\mathbf{P}} \langle \mathbf{R} | \mathbf{P} \rangle e^{-\frac{(\beta/M)\mathbf{P}^2}{2m_p}} \langle \mathbf{P} | \mathbf{R}' \rangle = \left(\frac{2\pi\hbar^2\beta/M}{m_p} \right)^{-3N/2} e^{-\frac{m_p(\mathbf{R}-\mathbf{R}')^2}{2\hbar^2\beta/M}}$$

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

$$= \lim_{M \rightarrow \infty} \left(\frac{2\pi\hbar^2\beta/M}{m_p} \right)^{-3MN/2} \prod_{m=1}^{M-1} \int d\mathbf{R}^m e^{-\sum_{m=0}^{M-1} \left[\frac{m_p(\mathbf{R}^{m+1} - \mathbf{R}^m)^2}{2\hbar^2\beta/M} + (\beta/M)V(\mathbf{R}^m) \right]}$$

$$\mathbf{R}^0 \equiv \mathbf{R} \quad \mathbf{R}^M \equiv \mathbf{R}'$$



Sample by classical (Markov-chain) Monte Carlo (with M finite!)
perform numerical extrapolation to infinite M

- quantum statistics:

$$\rho_{B/F}(\mathbf{R}', \mathbf{R}; \beta) = \frac{1}{N!} \sum_P (\pm)^{|P|} \rho(P\mathbf{R}', \mathbf{R}; \beta)$$

$$P\mathbf{R} \equiv (\mathbf{r}_{P(1)}, \mathbf{r}_{P(1)}, \dots, \mathbf{r}_{P(N)})$$

Proton antisymmetry frequently neglected at not too high proton density

However: intra-molecule exchange possible, import for phases at low temperatures!

- Nuclear spin determines boson/fermion sign
- ortho/para H₂
- Adiabatic phase needs to be included in BO (usually not done)

How to get “good” BO-energies?

Variational principle:
$$E_0(\mathbf{R}) \leq \frac{\int d\mathbf{r} \Psi_T(\mathbf{r}) H_e(\mathbf{R}) \Psi_T(\mathbf{r})}{\int d\mathbf{r} \Psi_T^2(\mathbf{r})}$$

- Upper bound for the BO energy for any trial wave function $\Psi_T(\mathbf{r})$ of same symmetry and boundary conditions
- Depends on nuclear (protons/ions) positions \mathbf{R} is only parametrically (laplacian in H_e does not act on \mathbf{R})

$$\Psi_T(\mathbf{r}) \equiv \Psi_T(\mathbf{r}|\mathbf{R})$$

What to use as “trial wavefunction”?

- Single Slater determinant $\Psi_T(\mathbf{r}) = \det_{ni} \varphi_n(\mathbf{r}_i)$

optimize orbitals to find lowest energy \Rightarrow Hartree-Fock (no correlations!)

Idea: use orbitals from DFT to include correlations ?.....??

- (Pair-)Correlated wave functions (“Jastrow” wfn) $\Psi_T(\mathbf{r}) = \det_{ni} \varphi_n(\mathbf{r}_i) e^{-U(\mathbf{r})}$
 $U(\mathbf{r})$: symmetric, pairwise correlation factor

$$U(\mathbf{r}) = \sum_{i < j} u_{ee}(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{iI} u_{ep}(|\mathbf{r}_i - \mathbf{R}_I|)$$

\Rightarrow How to calculate now the integrals? How to determine orbitals, u_{ee}, u_{ep}, \dots ?

Variational Monte Carlo Stochastic optimization

- Rewrite energy expectation value

$$E_T = \frac{\int d\mathbf{r} |\Psi_T(\mathbf{r})|^2 E_L(\mathbf{r})}{\int d\mathbf{r} |\Psi_T(\mathbf{r})|^2} = \int d\mathbf{r} p(\mathbf{r}) E_L(\mathbf{r})$$

remember $\mathbf{r} \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$

“local energy” $E_L(\mathbf{r}) \equiv \frac{\langle \mathbf{r} | H | \Psi_T \rangle}{\langle \mathbf{r} | \Psi_T \rangle} = \frac{H \Psi_T(\mathbf{r})}{\Psi_T(\mathbf{r})}$

Sample probability distribution
by **classical** (Markov chain) **Monte Carlo**

$$p(\mathbf{r}) \sim |\Psi_T(\mathbf{r})|^2$$

for any (given) wave function, e.g. $\Psi_T(\mathbf{r}) = \det_{ni} \varphi_n(\mathbf{r}_i) e^{-U(\mathbf{r})}$

Unbiased estimate for E_T but intrinsically affected by **stochastic** (random) noise

$$E_T = \mathbb{E}_{\mathbf{r} \sim \Psi_T^2} [E_L(\mathbf{r})]$$

$$\sim \sqrt{\sigma_T^2 / N_{MC}}$$

- Improving (lowering) the bound: parametrize wave function $\Psi(\mathbf{r}|\alpha)$ $\alpha = (\alpha_1, \alpha_2, \dots)$
(many) parameters

optimize trial energy with respect to parameters using gradient descent

$$\alpha \leftarrow \alpha - \epsilon \partial_\alpha E_T(\alpha) \quad \partial_\alpha E_T(\alpha) = 2 \mathbb{E}_{\mathbf{r} \sim \Psi_T^2} [\{E_L(\mathbf{r}|\alpha) - E_T(\alpha)\} \partial_\alpha \log \Psi_T(\mathbf{r}|\alpha)]$$

“Learning” rate

Unbiased despite stochastic evaluation of gradient!

Robust optimization possible for a dozen million parameters!

Stochastic improvement of wfn/energies: Projector (Diffusion) Monte Carlo

- Project trial wave function in 'imaginary' time $\Psi_t(\mathbf{r}) \sim \langle \mathbf{r} | e^{-tH} | \Psi_T \rangle$
always lowers energies:

$$E_t = \frac{\langle \Psi_t | H | \Psi_t \rangle}{\langle \Psi_t | \Psi_t \rangle} \leq E_T \equiv \frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle}$$

Exponential convergences to exact ground state energy $\mathcal{E}_0 = \lim_{t \rightarrow \infty} E_t$

- How to project in imaginary time? \Rightarrow see Path-Integral Monte Carlo

$$\Psi_t(\mathbf{r}) = \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_M \langle \mathbf{r} | e^{-tH/M} | \mathbf{r}_1 \rangle \langle \mathbf{r}_1 | e^{-tH/M} | \mathbf{r}_2 \rangle \langle \mathbf{r}_2 | \cdots e^{-tH/M} | \mathbf{r}_M \rangle \Psi_T(\mathbf{r}_M)$$

- Different names for different numerical implementations:
Ground state path integral, PIGS, Reptation Monte Carlo,

- Diffusion Monte Carlo (DMC):

construction random walk to sample distribution corresponding to infinite projection time

Introduce importance sample based on mixed distribution: $f_t(\mathbf{r}) = \Psi_t(\mathbf{r})\Psi_T(\mathbf{r})$

DMC algorithm samples $\pi(\mathbf{r}) = \Psi_0(\mathbf{r})\Psi_T(\mathbf{r}) = \lim_{t \rightarrow \infty} f_t(\mathbf{r})$

converges to exact (unbiased) ground state energies

observables are in general biased

$$\mathcal{E}_0 = \lim_{t \rightarrow \infty} \frac{\langle \Psi_T | H | \Psi_t \rangle}{\langle \Psi_T | \Psi_t \rangle} = \mathbb{E}_{\mathbf{r} \sim f_\infty} E_L(\mathbf{r})$$

Fermion sign problem Fixed-node approximation

- Bosons: symmetric ground states
- Fermions: antisymmetric ground states

$$\Psi_{B/F}(\dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots) = \pm \Psi_{B/F}(\dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots)$$

- Theorem: ground state of any (reasonable) H is bosonic
- How does the sign affect imaginary time projection?

$$e^{-tH} = |\Psi_B\rangle\langle\Psi_B|e^{-tE_B} + |\Psi_F\rangle\langle\Psi_F|e^{-tE_F} + \dots \quad E_B \leq E_F \sim N$$

$$\begin{aligned} \Psi_t(\mathbf{R}) &= \langle \mathbf{R} | e^{-tH} | \Psi_T \rangle = \langle \mathbf{R} | \Psi_B \rangle \langle \Psi_B | \Psi_T \rangle e^{-tE_B} + \langle \mathbf{R} | \Psi_F \rangle \langle \Psi_F | \Psi_T \rangle e^{-tE_F} + \dots \\ &\sim \Psi_B(\mathbf{R}) \int d\mathbf{R}' \underbrace{\Psi_B^*(\mathbf{R}')}_{=0} \Psi_T(\mathbf{R}') + \Psi_F(\mathbf{R}) e^{-t(E_F - E_B)} \underbrace{\int d\mathbf{R}' \Psi_F^*(\mathbf{R}') \Psi_T(\mathbf{R}')}_{\#} + \dots \end{aligned}$$

(Monte Carlo stochastic error)

Stochastic uncertainty needed to project on fermion ground state:

$$|\epsilon| \ll \# e^{-tN\#}$$

- Fixed-node solution: sample only restricted space with $\mathbf{R}^+ : \Psi_F(\mathbf{R}^+) \geq 0$
 - Fixed node approximation use: $\Psi_T(\mathbf{R}^+) \geq 0$ $H\Psi_F(\mathbf{R}^+) = E_F\Psi_F(\mathbf{R}^+)$
- Fixed-node ground state $\Psi_F(\mathbf{R}) = \Psi_T(\mathbf{R})e^{-U(\mathbf{R})}$ “best” real U: upper bound energies

Thermodynamic limit extrapolation: Energies

S. Chiesa, D.M. Ceperley, R.M. Martin, and M. H., Phys. Rev. Lett. **97**, 076404 (2006)

physicists: extrapolate always bigger systems with PBC...

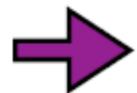
$$E(L), E(2L), E(4L), \dots, \Rightarrow E(\infty) \quad L: \text{size of system}$$

or:

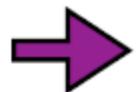
$$E(L) = \sum_k \frac{k^2}{2m} n_k^L + \sum_k v(k) [S^L(k) - 1]$$



$$\frac{E(\infty)}{V} = \int \frac{d^D k}{(2\pi)^D} \frac{k^2}{2m} n_k^\infty + \int \frac{d^D k}{(2\pi)^D} v(k) [S^\infty(k) - 1]$$



finite size errors are integration errors



singularities/non-analytic points dominate size errors

Electronic Finite Size Effects

- Simulations can be only done with small systems $N \lesssim 10^3$ $L \sim N^{-1/3}$
- What are the physical length scales involved?
 - Kinetic energy: estimate via non-interacting electrons, Fermi wave length

$$n_{\mathbf{k}}^0 = \theta(k_F - k) \quad \lambda_F/L \simeq 2.03N^{-1/3}$$

Play with boundary conditions to improve kinetic energy convergence,
use general (twisted) boundary conditions

$$\Psi(\dots, \mathbf{r}_i + L, \dots) = e^{i\theta} \Psi(\dots, \mathbf{r}_i, \dots)$$

Average over calculations with differenced twists

$$\lim_{N_\theta \rightarrow \infty} \frac{1}{N_\theta} \sum_{\theta} f(\mathbf{k} + \theta) = \frac{V}{(2\pi)^3} \int d^3q f(q) \quad (\text{TABC})$$

Efficiently corrects for single body observables (kinetic energy, Fermi surface...)

- Potential energy: screening length (plasmon)

$$\mathcal{V}_N \equiv V_N/N = \frac{1}{2V} \sum_{\mathbf{k} \neq 0} v_k [S_N(k) - 1] \quad S_N(k) \simeq S_\infty(k)$$

$$\mathcal{V}_\infty - \mathcal{V}_N = \left[\int \frac{d\mathbf{k}}{(2\pi)^3} - \frac{1}{V} \sum_{\mathbf{k} \neq 0} \right] \frac{v_k}{2} [S_\infty(k) - 1] \quad v_M \sim N^{-1/3}$$

MC with Noisy actions/energies: Penalty method

- Partition function of classical protons: $Z = \int d\mathbf{R} e^{-\beta E_{\mathbf{R}}}$

Problem: BO energies $E_{\mathbf{R}} \equiv E_0(\mathbf{R})$ are only known up to a stochastic error

We have $\epsilon = E_{\mathbf{R}} \pm r$ the error r is normal distributed

$$g(\epsilon | E_{\mathbf{R}} \sigma_{\mathbf{R}}^2) \sim e^{-(\epsilon - E)^2 / 2\sigma^2}$$

We can still calculate the partition function exactly

$$Z = \int d\mathbf{R} e^{-\beta E_{\mathbf{R}}} = \int d\epsilon \int d\mathbf{R} e^{-\beta\epsilon - \beta^2\sigma_{\mathbf{R}}^2/2} g(\epsilon | E_{\mathbf{R}} \sigma_{\mathbf{R}}^2)$$

=> stochastic error doesn't prevent unbiased Monte Carlo calculations!

- Penalty method: extend Metropolis algorithm to noisy (normal distributed) energy differences, detailed balance is satisfied on average, transition matrix given by

$$\tilde{T}(\mathbf{R} \rightarrow \mathbf{R}'; \Delta\epsilon) = g(\Delta\epsilon | E_{\mathbf{R}'} - E_{\mathbf{R}}, \sigma^2) \min \left[1, e^{-\beta\Delta\epsilon - \beta^2\sigma^2/2} \right]$$

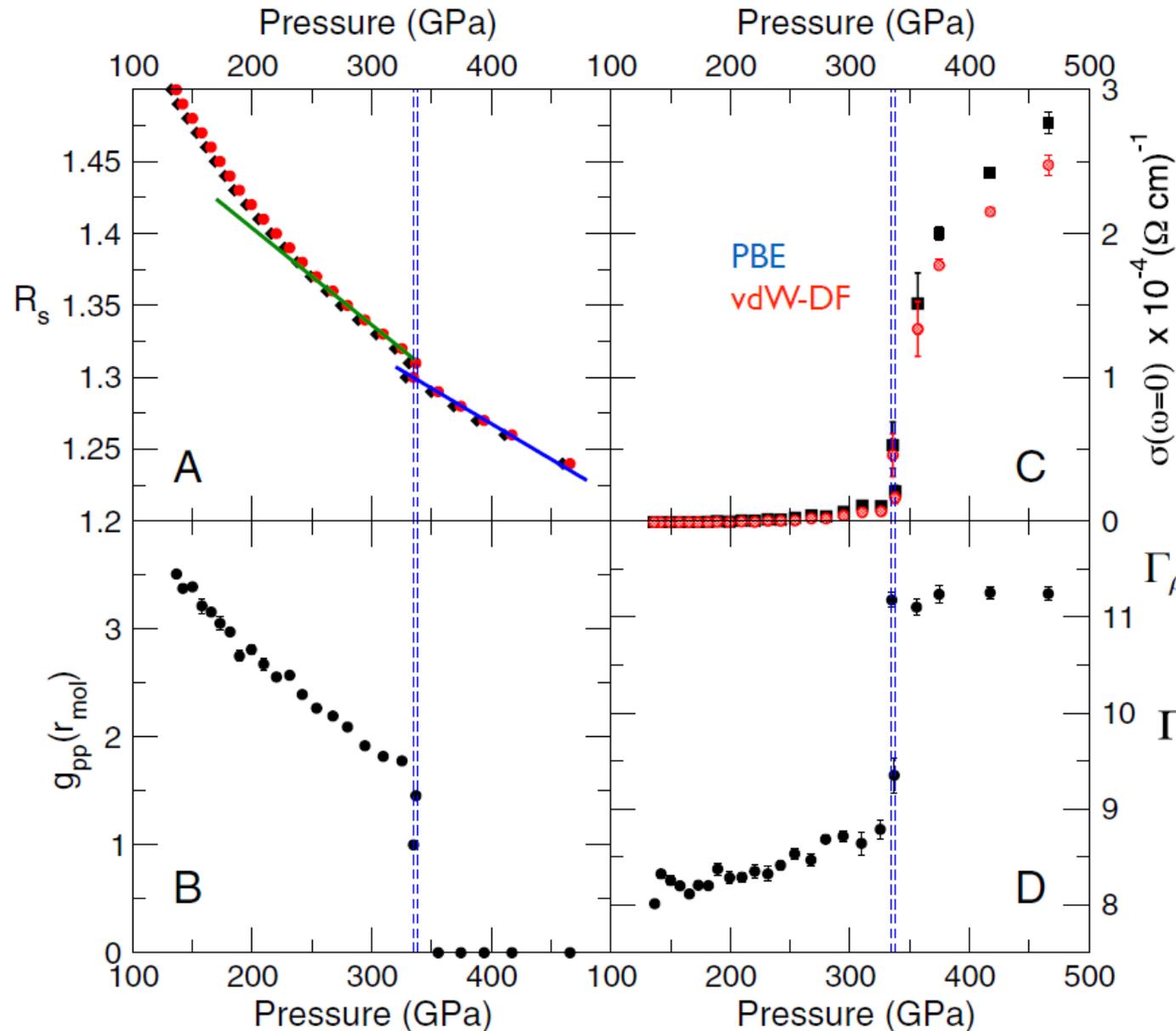
Putting all pieces together: Coupled Electron-Ion Monte Carlo (CEIMC)

- Classical or quantum nuclei at finite temperature
- Born-Oppenheimer energies from VMC
 - Wave functions: orbitals from DFT (why?) dressed by backflow coordinates
two and three body Jastrow correlations,
analytical expressions + global optimizations of few parameters
- Full exploration of phase diagrams is computationally very expensive
 - Reweighting of trajectories by DMC/Reptation MC BO energies
 - No structural optimization so far (geometry of simulation cell from DFT)
 - Benchmark of DFT functional by QMC energies
 - Machine learning effective potentials learned from QMC energies/forces

Molecular liquid to atomic liquid transition (LLPT)

CEIMC: T=600K classical

Pierleoni, Morales, Rillo, Holzmann, Ceperley PNAS 113, 4953 (2016)



- absence of hysteresis allows to detect the transition pressure directly
- Electrical conductivity from Kubo-Greenwood with DFT on nuclear configurations from CEIMC

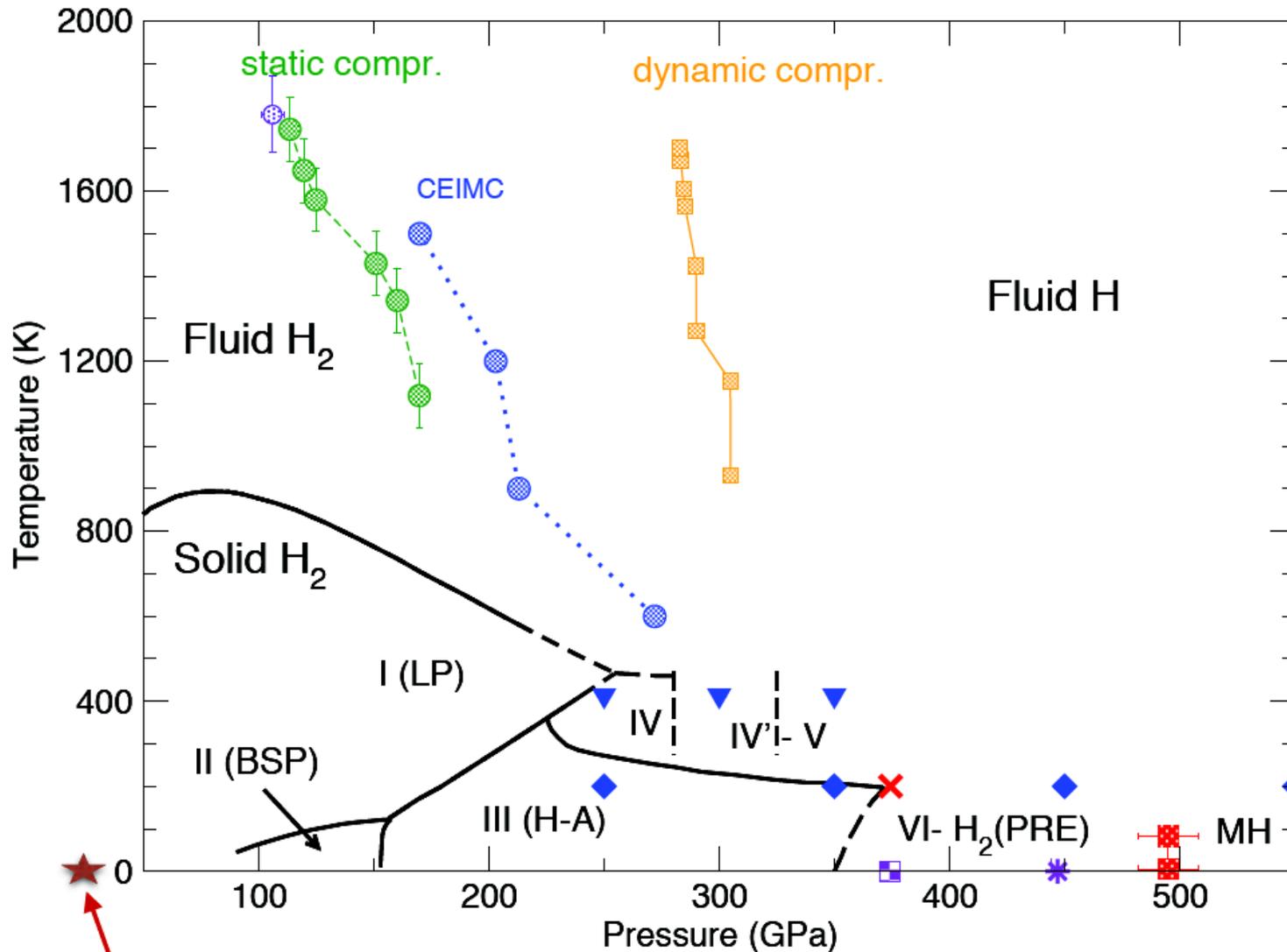
$$\Gamma_\rho = \frac{1}{N} \int_V \frac{d\mathbf{r}d\mathbf{r}'}{V} \left| \rho^{(1)}(\mathbf{r}, \mathbf{r}') \right|,$$

Γ_ρ ← electron localization function

$\rho^{(1)}(\mathbf{r}, \mathbf{r}')$ ← single electron density matrix

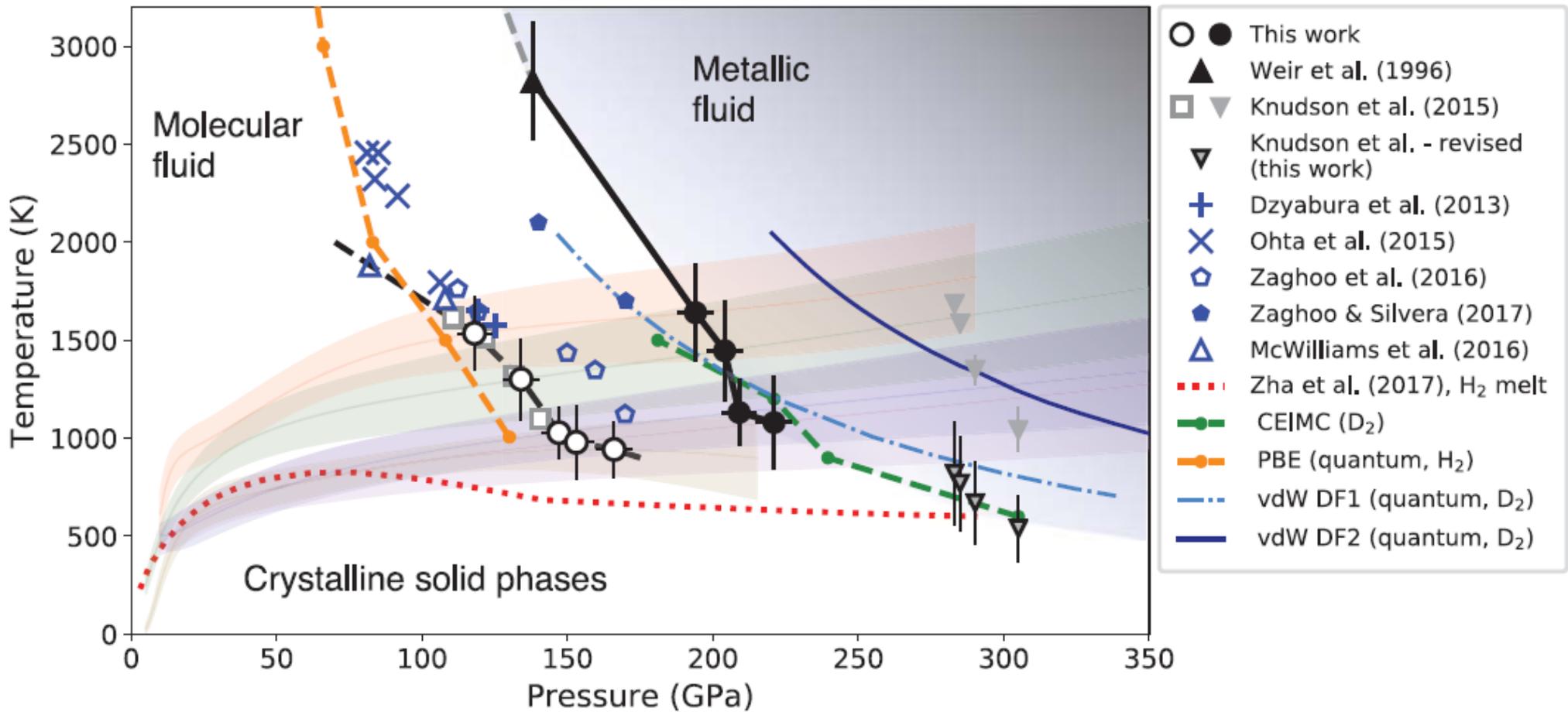
Molecular liquid to atomic liquid transition (LLPT)

Hydrogen phase diagram



Wigner-Huntington IMT

Comparison with experiment (NIF)



Celliers et al., Science 261, 677 (2018)

How to study electronic excitations?

- Fundamental electronic gap (ideal structure):

$$\tilde{\Delta} = E_0(N_n + 1) + E_0(N_n - 1) - 2E_0(N_n)$$

Size effects given by
dielectric constant $\tilde{\Delta}_\infty - \tilde{\Delta}_N \sim \frac{1}{\epsilon N^{1/3}}$

- Including nuclear quantum/thermal motion

$$\Delta = F(N_n + 1) + F(N_n - 1) - 2F(N_n)$$

within BO $Z(N_n \pm 1) = Z(N_n) \langle e^{-\beta[E_{\mathbf{R}}(N_n \pm 1) - E_{\mathbf{R}}(N_n)]} \rangle$
 $\geq e^{-\beta \langle E_{\mathbf{R}}(N_n \pm 1) - E_{\mathbf{R}}(N_n) \rangle}$

$$\Delta = \langle E_{\mathbf{R}}(N_n + 1) + E_{\mathbf{R}}(N_n - 1) - 2E_{\mathbf{R}}(N_n) \rangle \equiv \langle \tilde{\Delta}_{\mathbf{R}} \rangle$$

“quantum average” of gaps over sampled configurations
(different from semiclassical gaps!)

Fundamental (charged) and neutral gap In solid H₂ (phase I - HCP)

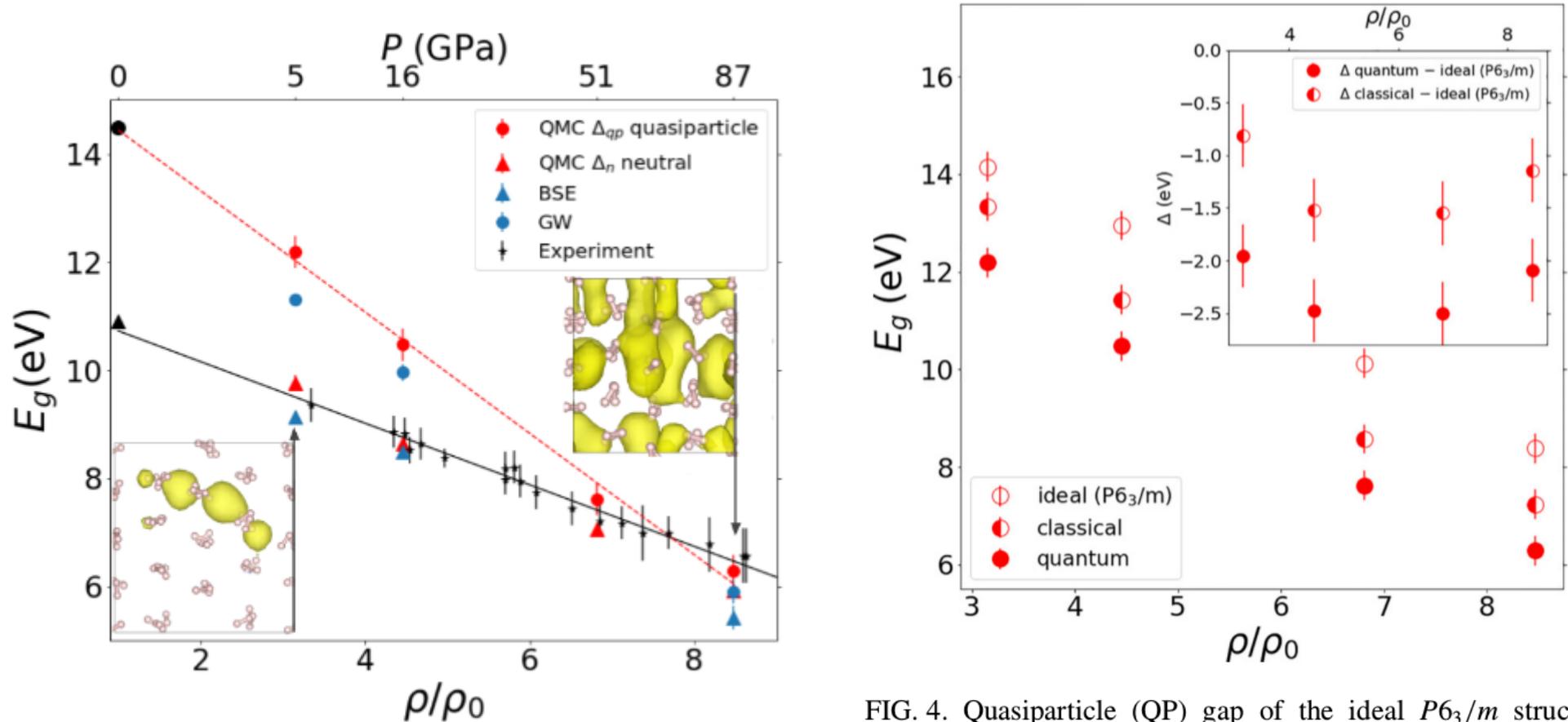


FIG. 4. Quasiparticle (QP) gap of the ideal $P6_3/m$ structure (open circles), QP gap with classical protons at room temperature (half circle), and QP gap with quantum protons at room temperature (solid circle). Inset: The reduction of the quasiparticle gap due to temperature and quantum nuclear effects (solid circles) and with only temperature effects (half-filled circles).

Electronic momentum distribution and fundamental gap at the LLPT

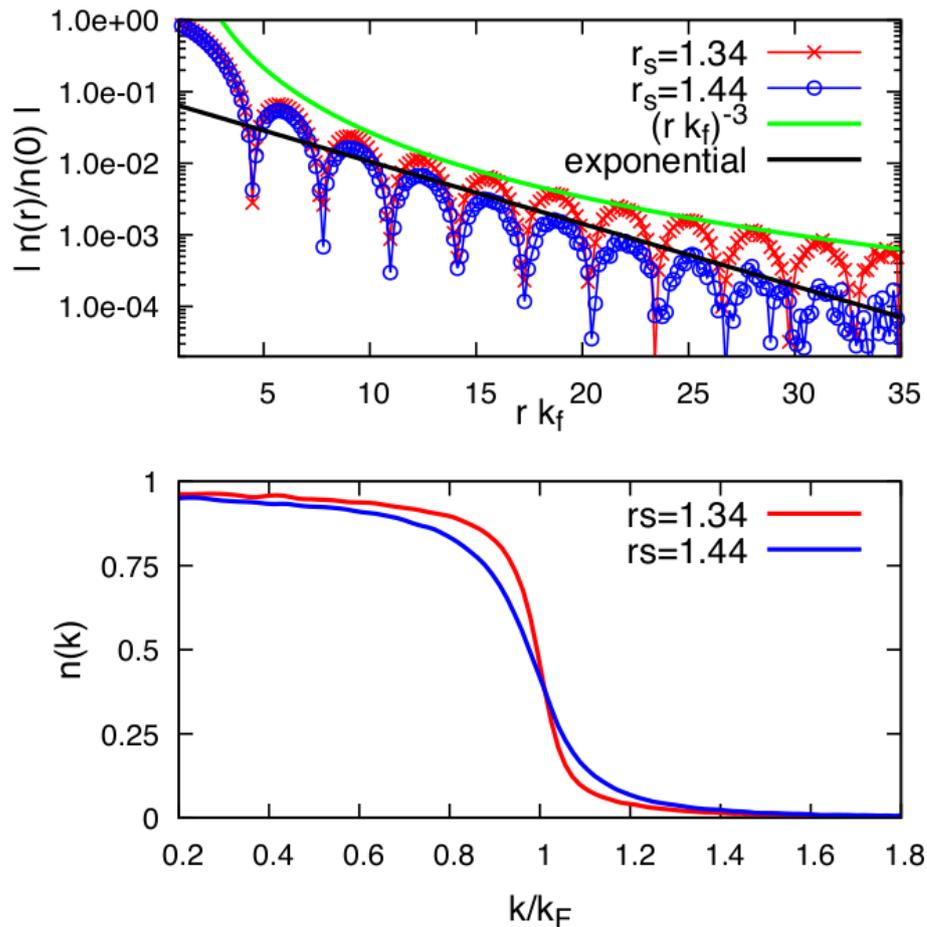


FIG. 30. Electronic momentum distribution of hydrogen at two densities across the LLPT at $T = 1200$ K, computed using Slater-Jastrow backflow trial wavefunction with configurations from CEIMC. In the molecular phase (blue) the single-electron density matrix, $n(r)$, decreases exponentially with r , while in the dissociate phase (red) it decreases as r^{-3} because the electrons are delocalized.

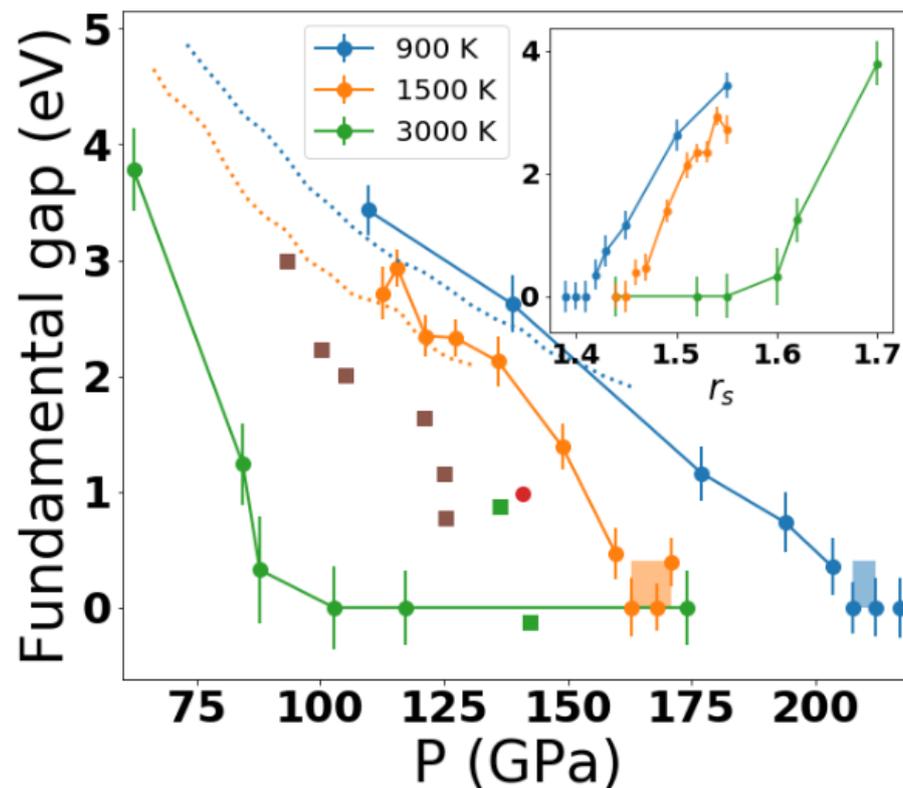
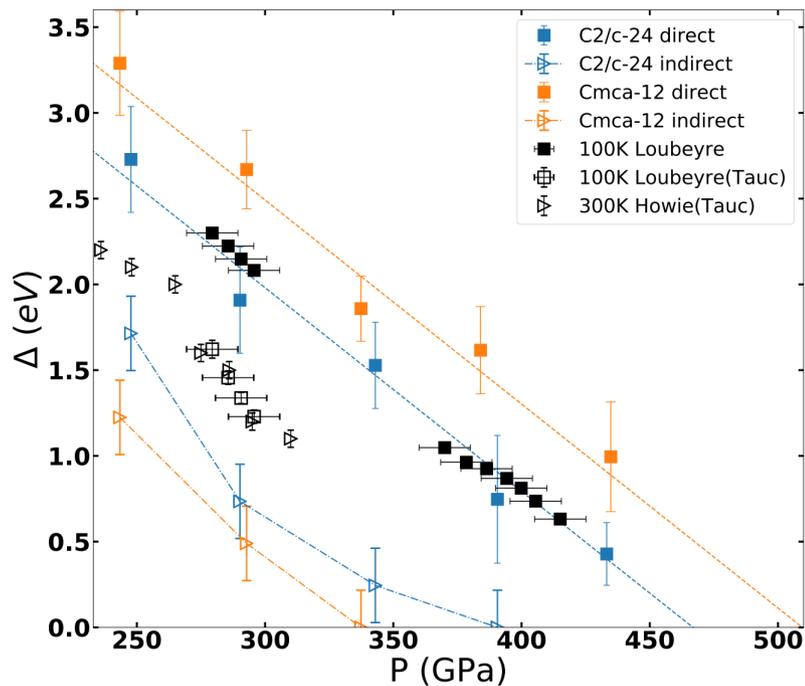


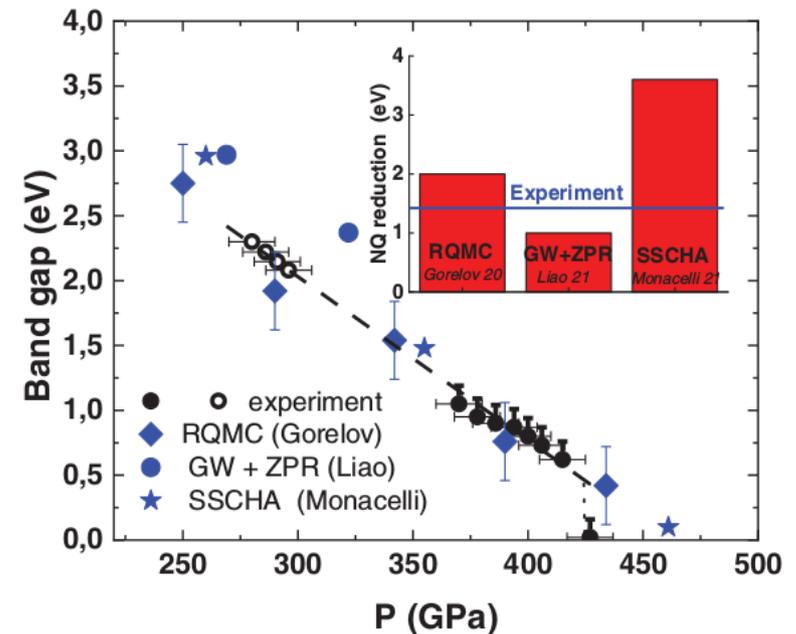
FIG. 31. The fundamental energy gap of liquid hydrogen along the isotherms: $T = 900$ K, 1500 K and 3000 K, as a function of pressure. Inset: the same gap as a function of r_s , a measure of density, Eq. (1). The lines connect the gap data only up to the molecular-atomic transition region. The colored rectangles show the coexistence region of the LLPT according to Ref. ²⁰⁹. The dotted lines are the gaps reported by P.M. Cellier *et al.* ²³⁴. The brown and green squares are the results of W.J. Nellis *et al.* for temperatures of 2000 K... 3000 K ⁶⁸⁶ reanalyzed in Ref. ⁶⁸⁷. The red dot is the gap reported by R.S. McWilliams *et al.* at 2400 K ⁶⁸⁸. Adapted from Ref. ⁵¹⁰.

High pressure hydrogen: Insulator-metal transition

- Characterize insulator:
spectral (optical) properties, gaps,...



V. Gorelov, M. Holzmann, D. Ceperley,
C. Pierleoni, PRL 124, 116401 (2020)



P. Loubeyre, F. Occelli, P. Dumas,
PRL 129, 035501 (2022)

→ Exploring phase diagram:



Machine learned effective proton-proton potential

H. Niu, Y. Yang, S. Jensen, M. H., C. Pierleoni, D.M. Ceperley, Phys. Rev. Lett. 130, 076102 (2023)

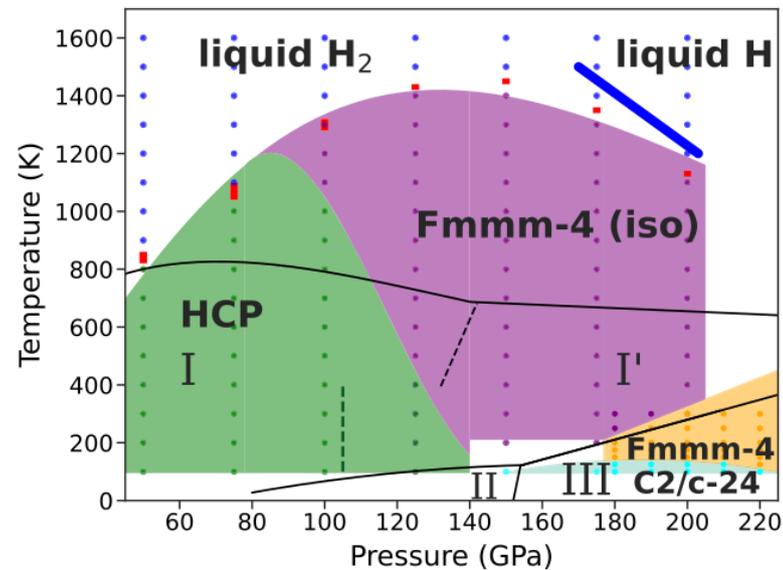
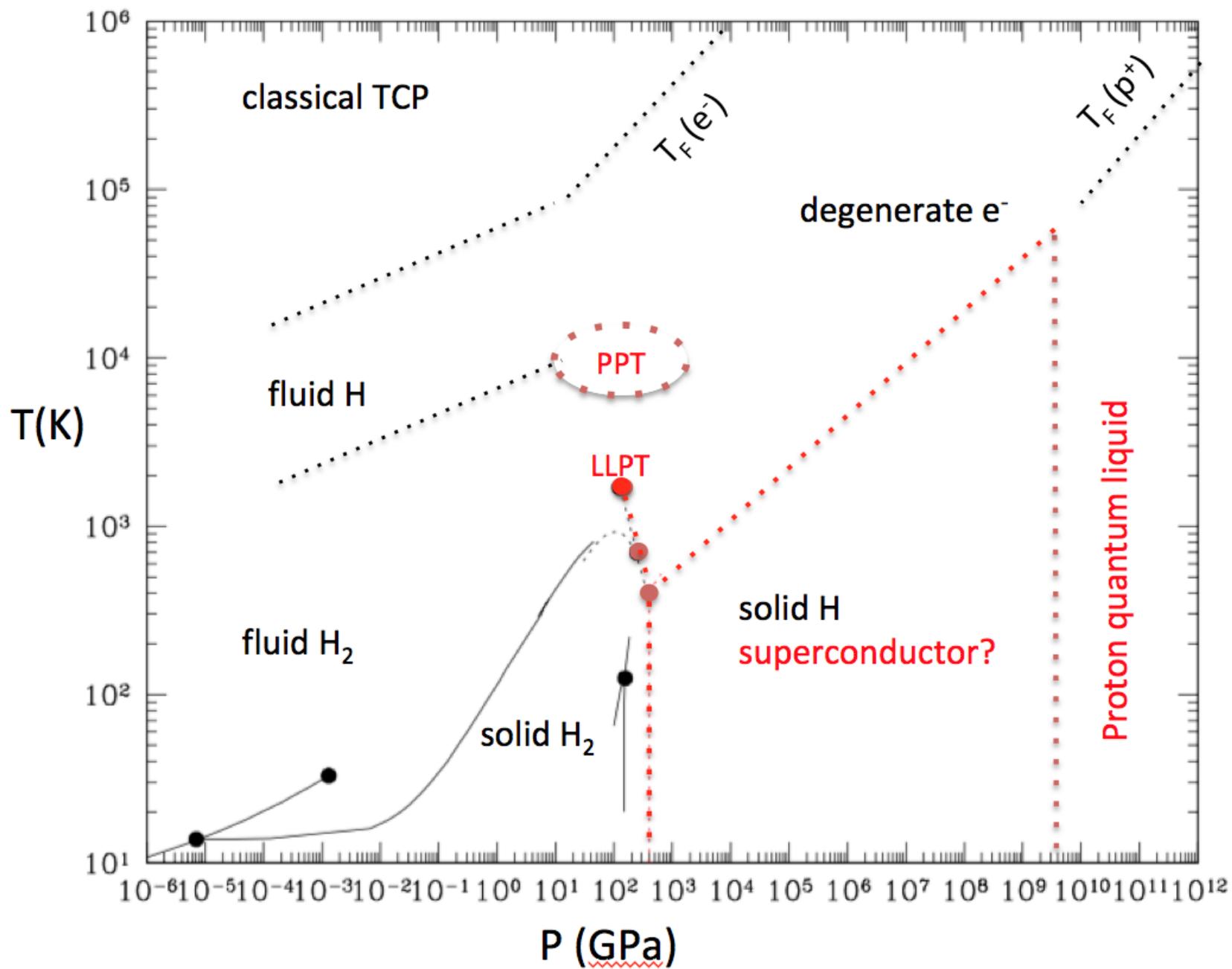


FIG. 1. Phase diagram of dense hydrogen. The dots indicate the (P, T) values where we ran PIMD simulations using a DMC-trained DPMD interatomic potential. Colors indicate the identified phase: dark blue (liquid), green (HCP), purple ($Fmmm-4$ isotropic), orange ($Fmmm-4$ oriented), and cyan ($C2/c-24$). The vertical green dashed line at 105 GPa indicates a crossover within HCP to an in-plane orientation. The thick blue line is the estimate of the transition from liquid H_2 to liquid H from Ref. [10]. Red bars are estimates of the melting temperature from two-phase coexistence simulation. The black lines are experimental estimates of phase boundaries, solid lines for the melting, dashed line for I-I' transition [39].

Temperature-Pressure region (II)

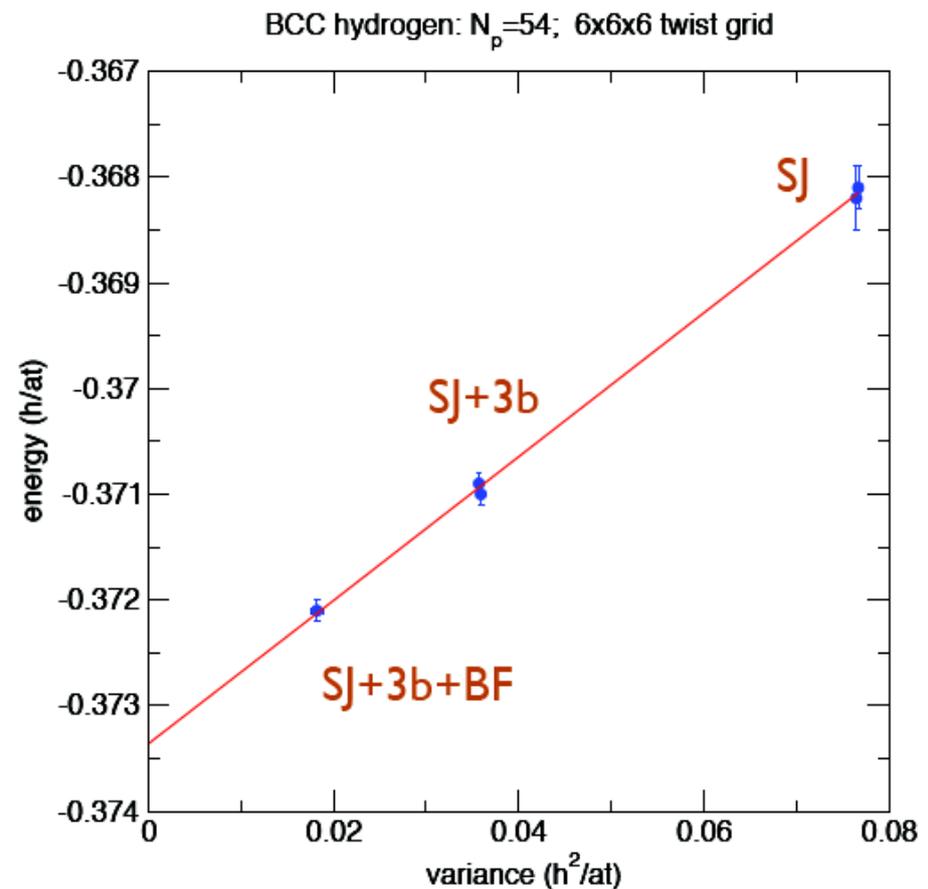
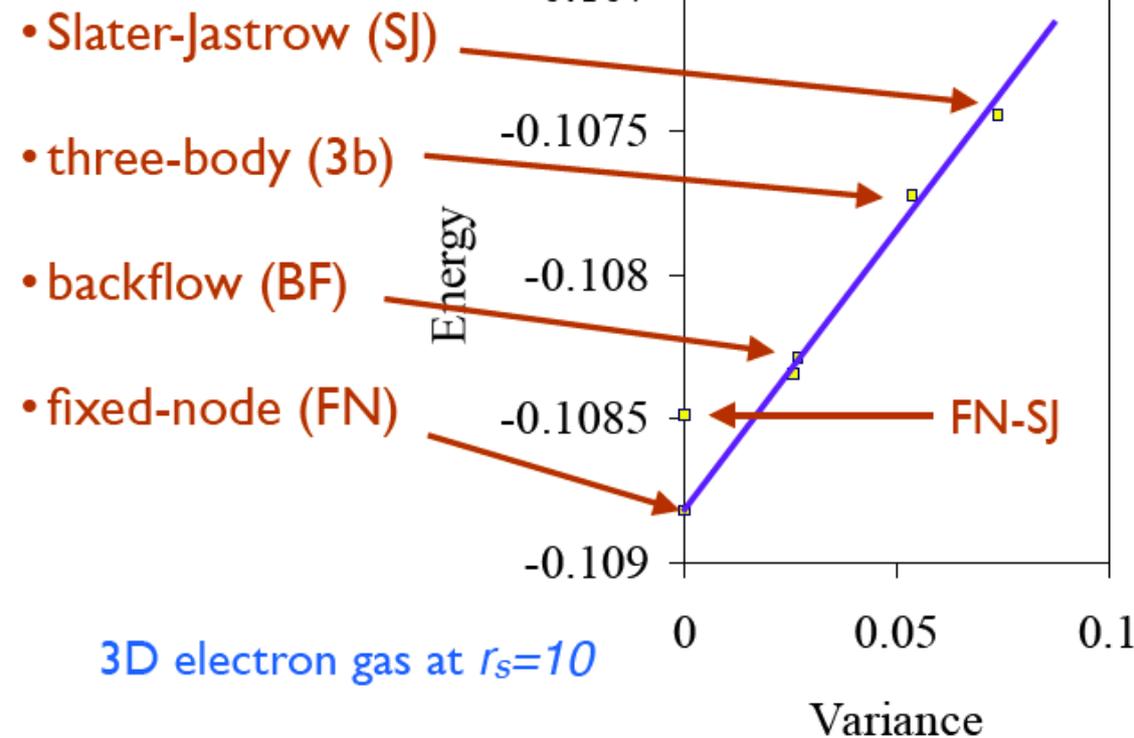


$\Psi_T(r|R)$ depends explicitly on some *free parameters to be optimized* using the variational principle: the lower the energy and the variance the better the quality of the solution.

The variational principle provides an *internal consistency check* when comparing various trial functions.

Imaginary time projection automatically optimizes but requires an approximation for fermions: the *fixed node approximation* but the method remain *variational*

$$\lim_{t \rightarrow \infty} e^{-t\hat{H}} |\Psi_T\rangle \propto |\Phi_0\rangle$$

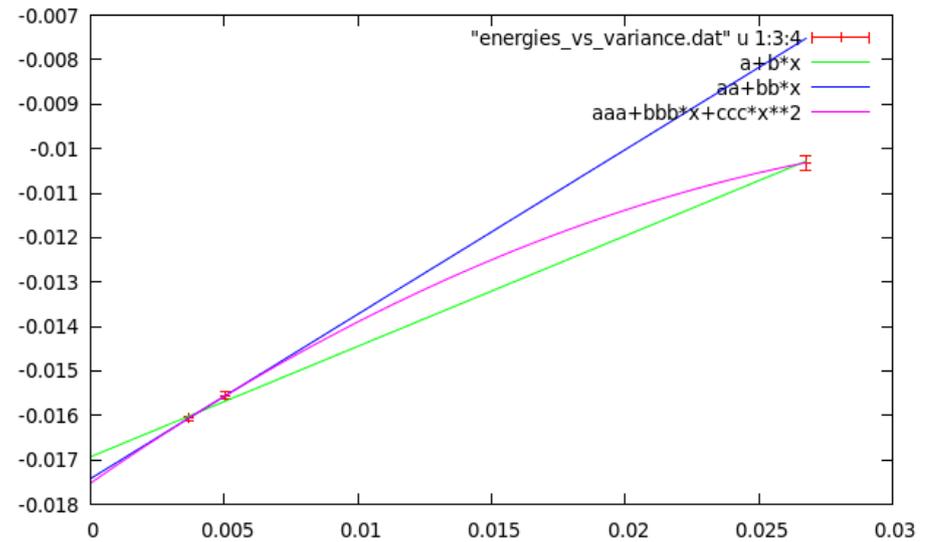


Variance extrapolation: HEG, N=14, comparison with FCIQMC

- $r_s=2$: $E_0 = -0.0174(1)$ Ry

FCIQMC: $E_0 = -0.01745(6)$ Ry

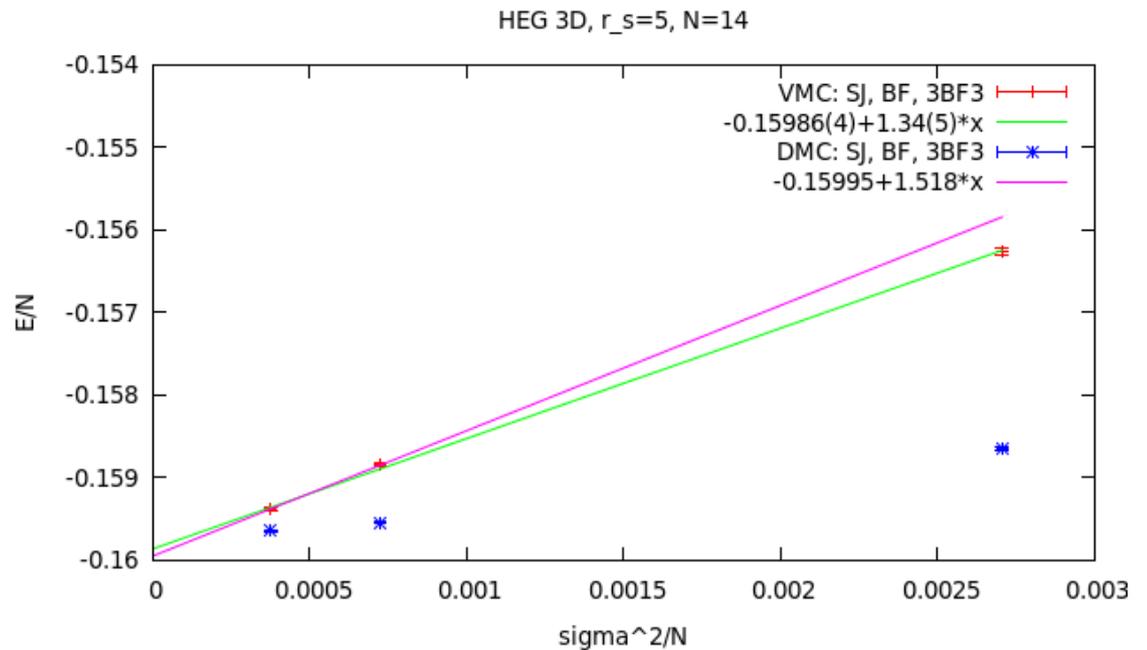
Shepherd, Booth, Alavi, J. Chem. Phys. 136, 244101 (2012)



- $R_s=5$: $E_0 = -0.1599(1)$ Ry

FCIQMC: $E_0 = -0.16005(4)$ Ry

Luo, Alavi, arXiv 1712.07524 (2017)



Orbital bias

atomic **molecular**

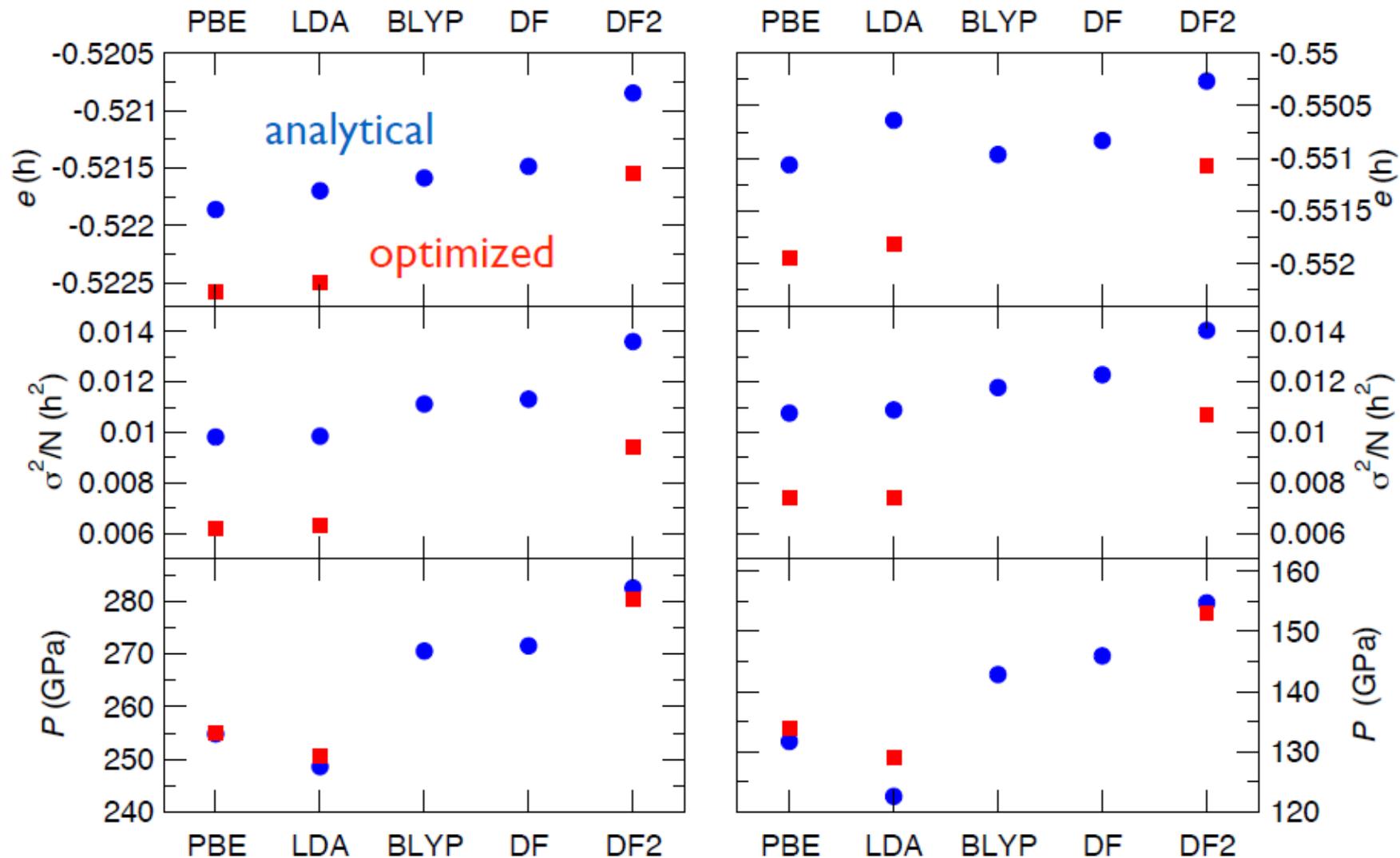
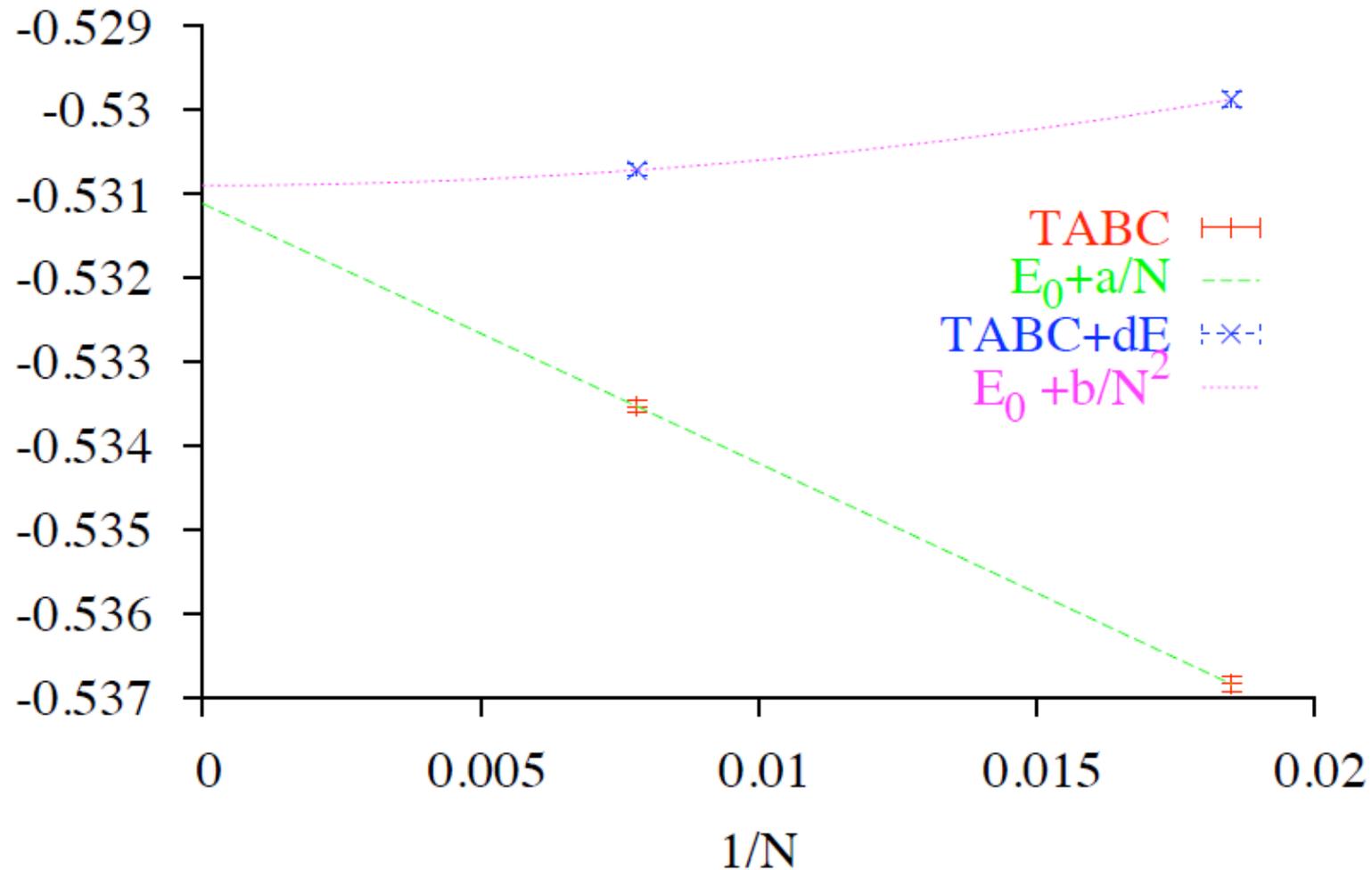


FIG. 6. (color online) Single nuclear configuration energy (upper panels), variance (middle panels) and pressure (lower panels) from various kind of orbitals as indicated on the abscissa. The left panels refers to a typical atomic configuration ($r_s = 1.34$) while the right panels correspond to a typical molecular configuration ($r_s = 1.49$). For PBE, LDA and vdW-DF2 we show both the SJ results with the analytical form of the trial function (blue circles) and the results when the correlation and backflow terms are optimized (red squares), while for BLYP and vdW-DF only results for the analytical form are reported (blue circles). Statistical error bars are smaller than the symbols.

Finite size effects

Energy vs $1/N$, $r_s=1.44$ $T=1200\text{K}$, $E_0=-0.531(1)$

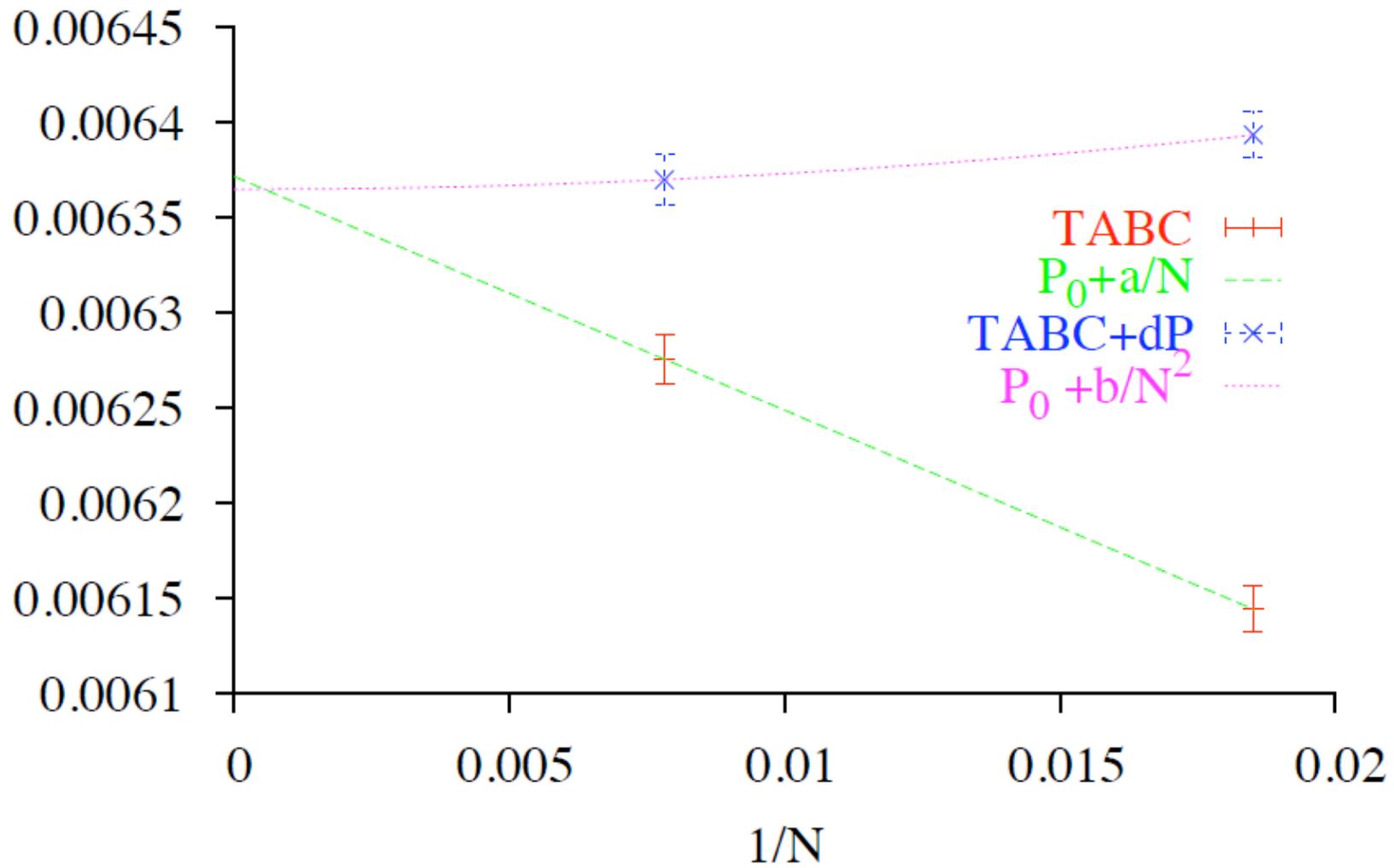


M.H. R.Clay, M.Morales, N.Tubman, D.Ceperley, C.Pierleoni, PRB 94, 035126 (2016)

$$\Delta e = [e(128) - e(54)] \sim 3.5 \text{ mH/at}$$

$$\Delta e^\infty = [e(\infty) - e(54)] \sim 6 \text{ mH/at}$$

Pressure vs $1/N$, $r_s=1.44$ $T=1200K$, $P_0=0.00636(5)$



$$\Delta p = [p(128) - p(54)] / p(54) \sim 2\%$$

$$\Delta p^\infty = [p(\infty) - p(54)] \sim 3.5\%$$