Ab-initio simulation of liquid water by quantum Monte Carlo

Sandro Sorella G. Mazzola & Y. Luo SISSA, IOM DEMOCRITOS, Trieste A. Zen, L. Guidoni U. of L'Aquila, L'Aquila

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Outline/Motivations

- → The correlated wave function for realistic systems: from Hubbard to Hydrogen and Water
- → Few examples on accuracy and achievements on small molecules $H_2 (H_2O)_2$
- → Large number of electrons/long simulations with QMC now possible.
- \rightarrow MD for realistic liquid
- \rightarrow example on Hydrogen at high pressures
- \rightarrow Can we do also liquid water?

Variational Gutzwiller ansatz

We assume that HTc superconductivity shows up in a correlated systems due to strong correlation. The paradigm wave function is the Gutzwiller partially projected BCS (Mean Field) wavefunction:

$$\left|\psi_{VMC}\right\rangle = \exp(-g\sum_{R}n_{R\uparrow}n_{R\downarrow})P_{N}\left|\mathrm{MF}\right\rangle$$

where $|MF\rangle$ is the ground state of the BCS hamiltonian

$$H = \sum_{k,\sigma} \left[-2(\cos k_x + \cos k_y) - \mu_{VMC} \right] c_{k,\sigma}^+ c_{k\sigma} + \sum_k \Delta(\cos k_x - \cos k_y) c_{k\uparrow}^+ c_{-k\downarrow}^+ + \text{h.c.}$$

$$P_N \left| BCS \right\rangle = \left| AGP \right\rangle = \left[\sum_k f_k c_{k\uparrow}^+ c_{-k\downarrow}^+ \right]^{N/2} \left| 0 \right\rangle$$

There are only 3 variational parameters for f_k .



In mean field (BCS) no way to have BCS>0 for U>0 Theorem Lieb '90

Qualitative **new** features appear if Jastrow and BCS optimized toghether: RVB insulator or supercond.

Generalization of the wave function to continuous

$$\left|\psi_{T}\right\rangle = J\left|MF\right\rangle$$

MF> may be a standard Slater determinant J is the so called Jastrow correlation term:

 $J = \exp \left| \sum_{i < i} g(\vec{r}_i, \vec{r}_j) \right| \quad \begin{array}{c} \text{g is a generic function} \\ \text{of two el. cooredinates} \end{array} \right|$

The peculiarity of our approach (TurboRVB) is to fully optimize |MF> and J in a localized basis of simple atomic orbitals (e.g. Gaussians 1s,2p...). Generalization to reality \rightarrow the Hamiltonian is:

$$H = -\sum_{i} \frac{\Delta_{i}}{2} - \sum_{ij} \frac{Z_{j}}{\left|\vec{r_{i}} - \vec{R}_{j}\right|} + \sum_{i < j} \frac{1}{\left|\vec{r_{i}} - \vec{r_{j}}\right|} + \frac{Z_{i}Z_{j}}{\left|\vec{R_{i}} - \vec{R}_{j}\right|}$$

 $\{R_i\}$ are atomic classical coordinates within the Born-Oppenheimer approximation

$$\langle \vec{r}_1, \vec{r}_2, \vec{r}_3 \cdots \vec{r}_N | J | SD \rangle = \exp\left[\sum_{i < j} g(\vec{r}_i, \vec{r}_j)\right] \times Det[\psi_i(\vec{r}_j)]$$

Given that, one can apply **Variational Monte Carlo** and compute all correlation functions by a statistical method

No further approximation required fully ab-initio (no U, no double counting)

But how to parametrize the function g?

The "Gutzwiller" for realistic systems

$$g(\vec{r}, \vec{r}') = u_{lr}(|\vec{r} - \vec{r}'|) + \sum_{a,b,i,j} \lambda_{i,j}^{a,b} \psi_i^a(\vec{r}) \psi_j^b(\vec{r}')$$

 $u_{lr}(r) = \frac{1}{2} \frac{r}{1+Br} \quad "a(b)" \text{ labels atom positions } R_a(R_b)$

The non-homogeneous part a=b is local like Gutzw. and useful to decrease # parameters (no 4-body $a\neq b$)

e.g.
$$\psi_k^a(\vec{r}) = \exp\left[-Z_k |\vec{r} - \vec{R}_a|^2\right]$$
, i.e. localized atomic orbitals, $\#\lambda_{kl}^{a,b} \propto \#$ atoms variational parameters (say~1000) determined by: $\min_{\lambda_{kl}^a}, SD \frac{\langle SD|JHJ|SD \rangle}{\langle SD|J^2|SD \rangle}$

Quantum Monte Carlo vs DFT, is it worth? In H₂ clear 0.05 0 Energy [Ha] -0.05 -0.1-Full CI VMC J-SD ansatz - this work DFT - PBE -0.15 DFT - HSE -0.2 2 3 5 4 r [bohr]

With a very small basis (2 gaussians/atom) one gets the essentially exact dispersion for H_2

The main question we want to address:

What happens when we apply large pressure to a hydrogen molecular liquid?

When the average distance between molecules is comparable with their bond length (\sim 1.4 a.u.) we have a transition to a system where the molecule is no longer defined (atomic). According to band theory, from an insulator 2el/unit (H₂) to an half-filled band 1el./unit (H) \rightarrow Metal, Wigner and Heterington prediction '35.

Example: DFT failure for hydrogen

PHYSICAL REVIEW B 88, 014115 (2013)

Fate of density functional theory in the study of high-pressure solid hydrogen

Sam Azadi and W. M. C. Foulkes

The Thomas Young Centre and the Department of Physics, Imperial College, Exhibition Road, London SW7 2AZ, United Kingdom (Received 5 April 2013; revised manuscript received 5 June 2013; published 31 July 2013; corrected 12 September 2013)



As we have learned by Car and Parrinello (1998) Phase Diagram of realistic systems → Ab-Initio Molecular dynamics with Born-Oppenheimer approx.

Evaluation of Forces are required within QMC

<u>Algorithmic differentiation helped much</u> and thanks also to Tapenade (automatic diff.): http://www-sop.inria.fr/tropics/tapenade.html

SS & Luca Capriotti, JCP 133, 234111(2010)

Cpu time referenced to simple VMC (only energy) for computing all 3M force components in water.



Use of pseudopotentials straightforward

Just to clarify a bit what we mean by AD

Just a black box "programming discipline" allowing to compute all derivatives of

$$e_L(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N, \vec{R}_1, \vec{R}_2, \cdots, \vec{R}_M)$$

With respect to all 3N electron coordinates And the 3M ionic coordinates at the same \sim cost of computing the local energy e_L And the same for the wave function.

Dynamics: 1. Efficient QMC forces



Check: Newtonian dynamics of a H₂molecule. Verlet integrator. Dynamics: 2. Generalized Langevin We have efficient but still noisy forces. We use Langevin dynamics in order to sample the canonical ensamble for the ions.

$$\dot{\boldsymbol{v}} = -\gamma \boldsymbol{v} + \boldsymbol{f}(\boldsymbol{R}) + \boldsymbol{\eta}(t)$$

$$\dot{\boldsymbol{R}} = \boldsymbol{v}$$

$$\langle \vec{\eta}_i(t) \vec{\eta}_j(t') \rangle = \delta(t - t') \bar{\alpha}(\vec{R})$$

$$\alpha(\boldsymbol{R}) = 2T\gamma(\boldsymbol{R})$$
Fluctuation - dissipation
$$\alpha = \alpha_0 I + \Delta_0 \alpha_{QMC}(\boldsymbol{R})$$

$$\boldsymbol{\psi}$$

$$\bar{\alpha}_{QMC}(\vec{R}) = \langle [\vec{f}_{\vec{R}_i} - \langle \vec{f}_{\vec{R}_i} \rangle] [\vec{f}_{\vec{R}_j} - \langle \vec{f}_{\vec{R}_j} \rangle] \rangle$$
Covariance matrix of the forces

Now the noise does not prevent the possibility of doing MD. Only renormalize the friction!

Dynamics: 2. Generalized Langevin

We have efficient but still noisy forces. We use Langevin dynamics in order to sample the canonical ensamble for the ions.



At large N the first order is evident from the g(r)



Liquid-liquid transition



Our quantum Monte Carlo phase diagram (♦) for the first time with N=256 Hydrogen, is now much different from DFT!!!!



We find that the molecular fluid is unexpectedly stable and the transition towards a fully atomic liquid occurs at much higher pressures.

Comparison small basis/good basis 54 atoms rs=1.44 T=1000K



increased accuracy \rightarrow more stable molecular !!!

Why is so different?

QMC vs DFT



How to distinguish a metal from insulator?

One can compute the density matrix:

$$D(r,r') = \sum_{i} \psi_i(r) \psi_i(r')$$

 $\psi_i(r)$ are the **optimized** molecular orbitals

Metal \rightarrow Fermi surface $\rightarrow |D(R,r)| \sim |R-r|^{-2}$ Insulator \rightarrow Gap $\rightarrow |D(R,r)| \sim \exp(-|R-r|/\xi)$

Thus
$$|DM| = \frac{1}{\# atoms} \sum_{R_a} \int dr^3 |D(R_a, r)|$$

Metal $|DM| \rightarrow \infty$

Insulator $|DM| \rightarrow$ Finite



And now few slides on liquid water

Why water liquid simulation?

It is fundamental in biological life, e.g. life with No water \rightarrow Non sense

Phase diagram of immense difficulties, low energy and competing (e.g. Hydrogen bond and vdW long range) scales and still many things to understand by computer simulations.

DFT problems, g(r) overstructured, eq. density large (20% off), supercooled liquid (melting at ~400K)

Reduction of number of parameters

In QMC optimization the number of parameters is proportional to the dimension of the basis. It is useful to reduce them by hybrid contraction

$$\varphi_{a,l,m,n}(r) = \sum_{lmn} c^a_{lmn} \psi^{GTO}_{lmn,a}(r)$$

This is not useful instead in chemistry as the molecular HF basis is used instead.

See A. Zen, Y. Luo, SS and L.Guidoni JCTC 2013

Water dimer test: NB in dynamics we are interested in relative forces, i.e. derivative of binding energy

Water dimer bond energy



Noise is useful!!!



Water dimer integration test: $\Delta_0 = 8a.u. 300K$



DFT has not the covariance of forces and is much less efficient (smaller time steps) than QMC



"E pur si muove (and yet it moves)" (Galileo Galilei)



Second order Langevin dynamics of 32 water molecules at 300K with Variational Monte Carlo G. Mazzola, A. Zen, Y. Luo, L. Guidoni, and S. Sorella in preparation (2014)

Some info on this simulation

2048 nodes on BG/Q, 30 days simulation: 24milion core hours

Time step = 1.54fs, Total time ~ 10ps

Each step MD→10 Optimization steps ~12000 Variational parameters ~100000 Sampling measurements/step Each sample after 1024 Metropolis step

A huge computation, impossible without HPC

A different phylosophy is to use DMC to correct DFT (Blyp-2) Alfe' et al JCP 2013.



FIG. 2. Oxygen-oxygen radial distribution function $g_{OO}(r)$ from simulations of liquid water (64 molecules in repeating cell) at T = 350 K performed with BLYP (dashed green curve) and BLYP-2 (solid red curve) approximations, compared with data from high-energy x-ray diffraction at 343 K⁴¹ (dotted blue curve). The BLYP and BLYP-2 simulations were performed at densities 0.778 and 1.049 g/cm³ respectively (see text)

But the quantum effects should play a role



i) Peak positions are not changed by quantumii) The radial distribution is substantially broaden

QMC water radial distribution function More than 4000 iterations~ 7ps

Neutron diffraction - Soper, Chem. Phys. 258,121 (2000) Neutron diffraction - Soper, ISRN Phys. Chem.,2013 (2013) X-ray diffraction - LB Skinner et al., JCP 138,074506 (2013) 32 waters VMC-based NVT MD simulation 32 waters DFT/BLYP-based NVT MD simulation



A. Zen, G. Mazzola,, Y. Luo, L. Guidoni, and S. Sorella in preparation (2014)

64 waters possible with 32764 nodes (>2 10^5 cores!!!)





DMC reduces much (and change sign) this value

Conclusions

Realistic simulation of liquids are now possible also within fully many-body wave function based approach. 256H (64 H_2O) are not so far from what is currently done within DFT ~500H (128 H_2O)

 \rightarrow Peak positions of the rdf are finally reproduced: no other ab-initio first principle simulation is able

 \rightarrow Accuracy of VMC probably not enough, and also quantum effects should play a role.

→Several applications are now possible, allowing to falsify or improve DFT predictions.
Liquid water is currently under investigation.

<u>TurboRVB Quantum Monte Carlo package</u>

main developers: Sandro Sorella Michele Casula Claudio Attaccalite A. Zen ____ Ye Luo G. Mazzola — E. Coccia

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