Ab-initio simulation of liquid water by quantum Monte Carlo

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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.
MD for realistic liquid
example on Hydrogen at high pressures
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:

$$|\psi_{VMC}\rangle = \exp(-g \sum_R n_{R\uparrow} n_{R\downarrow}) P_N |\text{MF}\rangle$$

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

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

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

There are only 3 variational parameters for $f_k$. 
Important to optimize Jastrow and BCS together.

Hubbard Model: \[ H = -t \sum_{\langle ij \rangle, \sigma} c_{i\sigma}^+ c_{j\sigma} + U \sum_i n_i^\uparrow n_i^\downarrow \]

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 together: RVB insulator or supercond.
Generalization of the wave function to continuous coordinates:

$$|\psi_T\rangle = J |MF\rangle$$

|MF⟩ may be a standard Slater determinant

J is the so called Jastrow correlation term:

$$J = \exp\left[\sum_{i<j} g(\vec{r}_i, \vec{r}_j)\right]$$

g is a generic function of two el. coordinates

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:

$$H = -\sum_i \frac{\Delta_i}{2} - \sum_{ij} \frac{Z_j}{|\vec{r}_i - \vec{R}_j|} + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{Z_i Z_j}{|\vec{R}_i - \vec{R}_j|}$$

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

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

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

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

\[ u_{lr}(r) = \frac{1}{2} \frac{r}{1 + Br} \]

"a(b)" 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. \( \psi_k^a(\vec{r}) = \exp[-Z_k |\vec{r} - \vec{R}_a|^2] \), 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 $\text{H}_2$ clear.

With a very small basis (2 gaussians/atom) one gets the essentially exact dispersion for $\text{H}_2$. 

![Energy vs Distance Graph](image)

- Full CI
- VMC J-SD ansatz - this work
- DFT - PBE
- DFT - HSE
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 (\(\sim 1.4 \text{ a.u.}\)) we have a transition to a system where the molecule is no longer defined (atomic). According to band theory, from an insulator 2el/unit (H\(_2\)) to an half-filled band 1el/unit (H) \(\rightarrow\) Metal, Wigner and Heterington prediction ‘35.
Example: DFT failure for hydrogen

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

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

Evaluation of Forces are required within QMC

Algorithmic differentiation helped much

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 ~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 \( \text{H}_2 \) molecule. Verlet integrator.
Dynamics: 2. Generalized Langevin

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

\[
\dot{\mathbf{v}} = -\gamma \mathbf{v} + \mathbf{f}(\mathbf{R}) + \eta(t) \\
\dot{\mathbf{R}} = \mathbf{v}
\]

\[
\langle \tilde{\eta}_i(t) \tilde{\eta}_j(t') \rangle = \delta(t - t') \tilde{\alpha}(\tilde{\mathbf{R}})
\]

\[
\tilde{\alpha}(\mathbf{R}) = 2T \gamma(\mathbf{R})
\]

\[
\alpha = \alpha_0 I + \Delta_0 \alpha_{QMC}(\mathbf{R})
\]

\[
\tilde{\alpha}_{QMC}(\mathbf{R}) = \langle [\tilde{f}_{\mathbf{R}_i} - \langle \tilde{f}_{\mathbf{R}_i} \rangle] [\tilde{f}_{\mathbf{R}_j} - \langle \tilde{f}_{\mathbf{R}_j} \rangle] \rangle
\]

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 ensemble for the ions.

\[ \dot{v} = -\gamma v + f(R) + \eta(t) \]

\[ \dot{R} = v \]

\[ \alpha(R) = 2T\gamma(R) \]
At large $N$ the first order is evident from the $g(r)$

$T = 600 \text{ K}$
Liquid-liquid transition

\[ T = 2300 \text{ K} \]
We find that the molecular fluid is unexpectedly stable and the transition towards a fully atomic liquid occurs at much higher pressures.

Our quantum Monte Carlo phase diagram (◊) for the first time with N=256 Hydrogen, is now much different from DFT!!!
Comparison small basis/good basis 54 atoms \( r_s = 1.44 \) \( T = 1000 \text{K} \)

increased accuracy \( \rightarrow \) more stable molecular !!!
Why is so different? QMC vs DFT

PES for a single molecule inside the bulk (54H)
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\[ |DM| = \frac{1}{\# \text{atoms}} \sum_{R_a} \int dr^3 |D(R_a, r)| \]

Metal \( |DM| \rightarrow \infty \)  Insulator \( |DM| \rightarrow \text{Finite} \)
There is some interesting crossover at $T=2400\text{K}$.

But we do not have enough large size for the MIT.
And now few slides on liquid water

Why water liquid simulation?

It is fundamental in biological life, e.g. life with No water → 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

$$\varphi_{a,l,m,n}(r) = \sum_{lmn} c_{lmn}^{a} \psi_{lmn,a}^{GTO}(r)$$

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
Noise is useful!!!

- Choice of $\bar{\gamma}$
  - Great freedom
  - properly damping fast modes
  - large time step
  - reducing the correlation time

- Our choice estimated by QMC contains info of Hessian

$$\bar{\alpha} = \alpha_0 I + \Delta_0 \alpha_{\text{QMC}}$$

$$\alpha_{\text{QMC}} = \text{cov}(f')$$
Water dimer integration test: $\Delta_0 = 8\text{a.u. } 300K$

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

Y. Luo, A. Zen and S. Sorella submitted to JCP
“E pur si muove (and yet it moves)” (Galileo Galilei)

Second order Langevin dynamics of 32 water molecules at 300K with Variational Monte Carlo
Some info on this simulation

2048 nodes on BG/Q, 30 days simulation:
24million 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 philosophy 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 K$^{41}$ (dotted blue curve). The BLYP and BLYP-2 simulations were performed at densities 0.778 and 1.049 g/cm$^3$, respectively (see text).
But the quantum effects should play a role

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

from J. A. Morrone and R. Car PRL, 2008
QMC water radial distribution function

32 waters VMC-based NVT MD simulation
32 waters DFT/BLYP-based NVT MD simulation

More than 4000 iterations ~ 7ps

Remaining differences:
Ionic quantum effects?
More accuracy?
Size effects?

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

First peak in \(g_{OO}(r)\)

Convergence \(r_{MAX}\)

**Neutron diffraction**

**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
64 waters DFT/BLYP-based NVT MD simulation
The pressure problem: At the right density the average pressure is 0.47Gpa $>> 1\text{ atm}(=10^{-5}\text{ Gpa})$.

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$_2$O) are not so far from what is currently done within DFT ~500H (128 H$_2$O)

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

→ 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.
• **TurboRVB Quantum Monte Carlo package**

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