Way forward in quantum Monte Carlo: algorithms and applications

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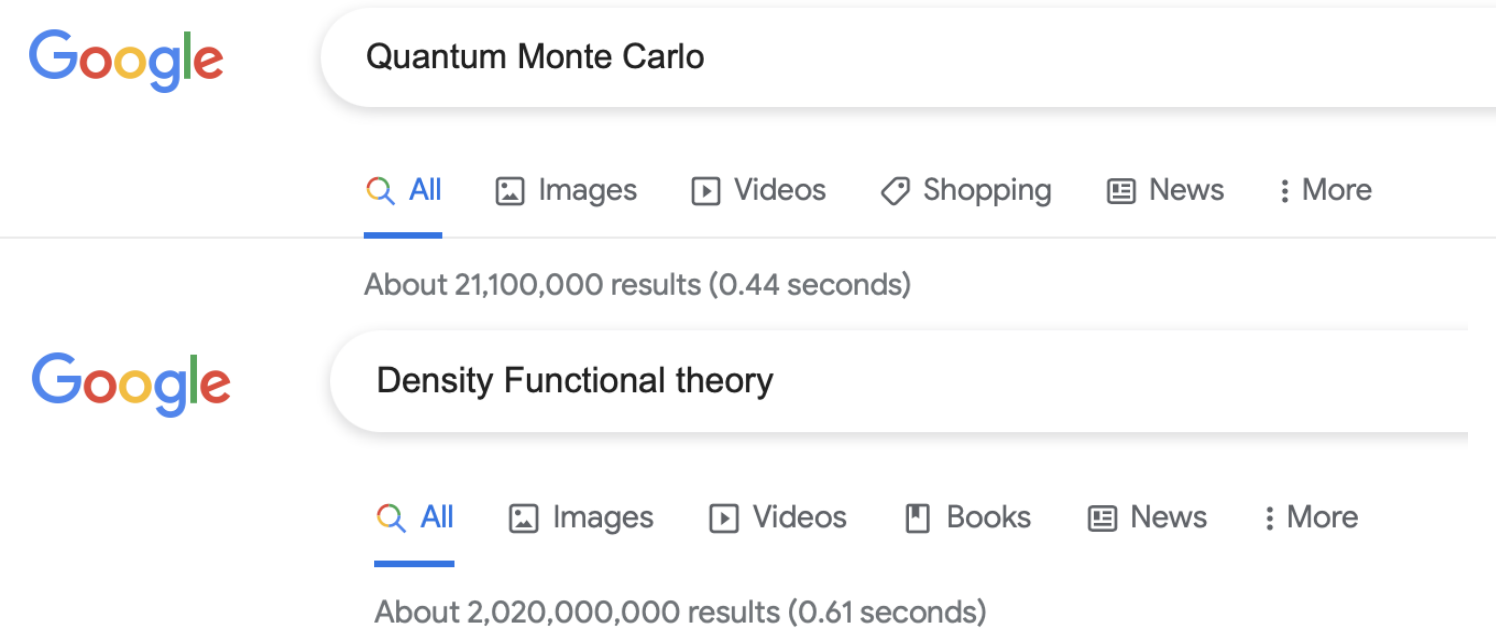
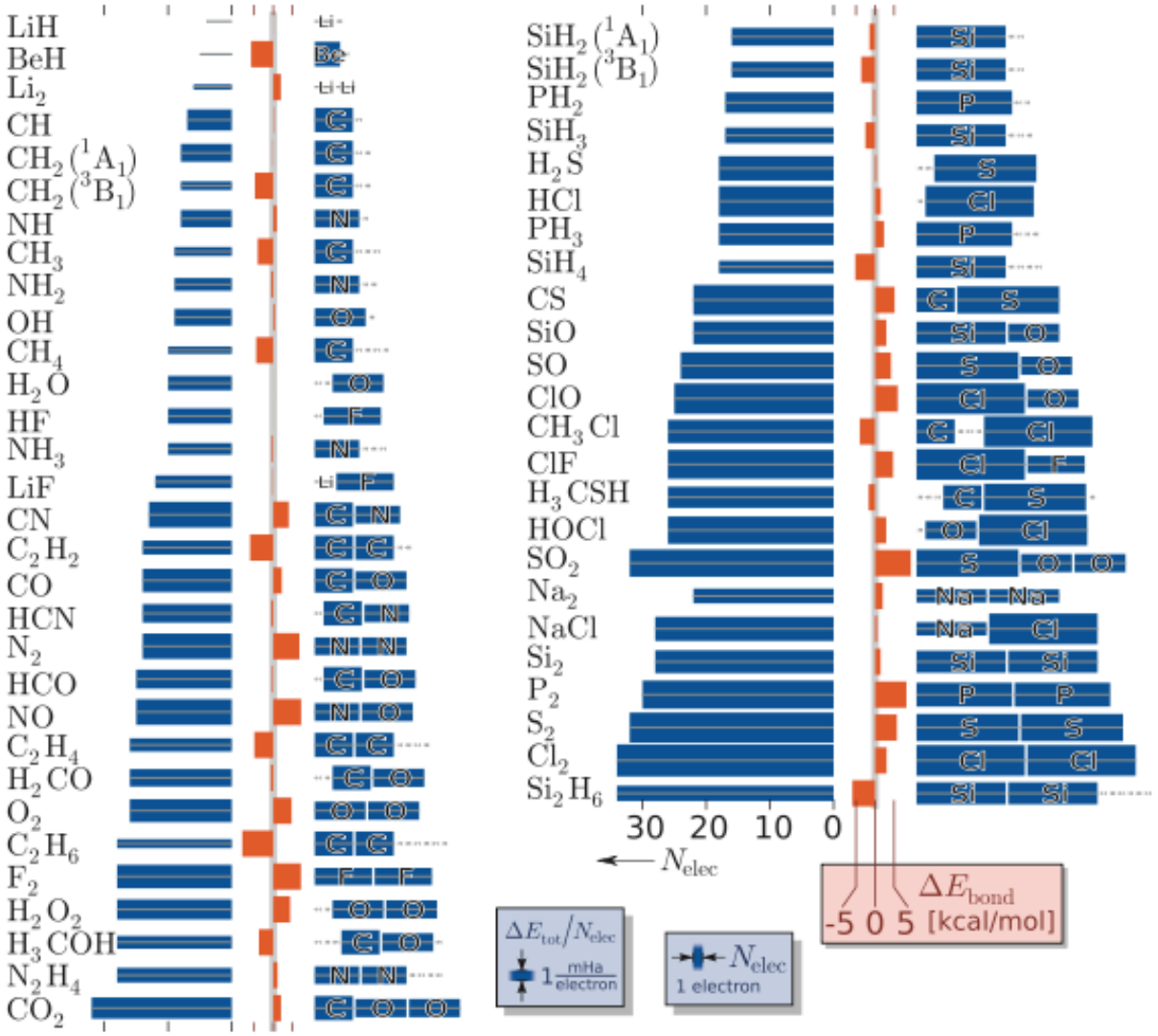


Do we aim to have more impact in the next future, e.g. 1/10 😇 of DFT?

The list

- Reaching chemical accuracy in large systems, multideterminants (too many?) , AGP, backflow not fully exploited yet.
- Use of Machine Learning technique to speedup calculation: predicting materials properties in silico
- Not only ground state but Excitations properties
- Dynamical correlations , e.g. Dynamical structure factor for direct comparison with experiments
- Finite temperature extension, a few methods that work so far, fixed node within path integral is still an unsolved problem, apparently complex (non polynomial).
- exploiting GPU acceleration for large system calculation

DFT nodal surface error in G2 set calculations



N. Nemec, *et al.* [J. Chem. Phys. 132, 034111 (2010)]

Calculation specifics (Nemec *et. al*)...

➔ Trial WFs (Nodal surfaces!) from DFT

➔ VMC optimization of JF

➔ DMC calculation (**nodal surface from DFT!**)

Using nodal surfaces from DFT (Fixed node approximation) MAD = **3.2 kcal/mol** (Not satisfactory!)

Chemical accuracies can't be achieved!

Slater Determinant limit!

Larger disagreement between DMC and CCSD(T)

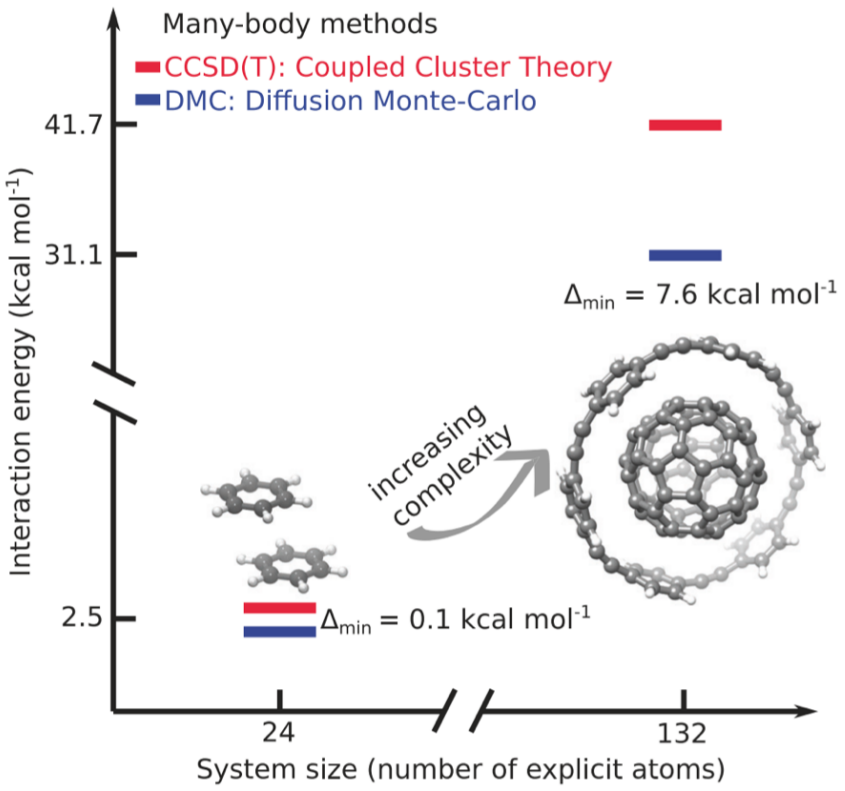


Table 1 Interaction energies in kcal mol^{-1} for best estimated CCSD(T) and FN-DMC, as well as their minimum differences (Δ_{min}) for dimers taken form the S66 compilaton, for the L7 supramolecular data set and the buckyball-ring complex (C_{60}@[6]CPPA). The indicated errors for CCSD(T) are extrapolated from the convergence of basis sets and local approximations in LNO-CCSD (T). The errors indicated in FN-DMC interaction energies account for the stochastic uncertainty of the estimation, and identifies a 95% confidence interval (i.e., ± 2σ).

Complex	No. of atoms	CCSD(T)	FN-DMC	Δ_{min} [a]
pyridine-pyridine PD	22	−3.70 ± 0.08	−3.51 ± 0.20	0.0
pyridine-pyridine TS	22	−3.48 ± 0.06	−3.44 ± 0.20	0.0
benzene-pyridine PD	23	−3.28 ± 0.07	−3.03 ± 0.16	0.0
benzene-pyridine TS	23	−3.24 ± 0.05	−3.08 ± 0.16	0.0
pyridine-uracil PD	23	−6.61 ± 0.09	−6.38 ± 0.18	0.0
benzene-benzene PD	24	−2.67 ± 0.07	−2.38 ± 0.12	*0.1*
benzene-benzene TS	24	−2.81 ± 0.06	−2.71 ± 0.12	0.0
uracil-uracil PD	24	−9.61 ± 0.10	−9.40 ± 0.16	0.0
benzene-uracil PD	24	−5.48 ± 0.11	−5.11 ± 0.18	*0.1*
GGG	48	−2.1 ± 0.2	−1.5 ± 0.6	0.0
CBH	112	−11.0 ± 0.2	−11.4 ± 0.8	0.0
GCGC	58	−13.6 ± 0.4	−12.4 ± 0.8	*0.1*
C3A	87	−16.5 ± 0.8	−15.0 ± 1.0	0.0
C2C2PD	72	−20.6 ± 0.6	−18.1 ± 0.8	**1.1**
PHE	87	−25.4 ± 0.2	−26.5 ± 1.3	0.0
C3GC	101	−28.7 ± 1.0	−24.2 ± 1.3	**2.2**
C_{60}@[6]CPPA	132	−41.7 ± 1.7	−31.1 ± 1.4	**7.6**

[a] Δ_{min} is 0.0 for statistically indistinguishable results. Thermodynamically consistent Δ_{min} is highlighted in italics and inconsistent Δ_{min} is highlighted in bold.

DMC with a single Slater determinant obtained from LDA (but tested also PBE0 in Supp. Info., as well as locality approximation versus T-move and DLA)

https://doi.org/10.1038/s41467-021-24119-3

Possible solution to reach Chemical accuracy

- Use several configurations → it works (semistochastic method Y. Yan .. C. Umrigar JCP 153, 124157, 2020) but difficult for large systems. Any comment?

- TurboRVB choice, exploit all correlation from single determinant /Pfaffian (see tomorrow)

- Backflow correlation → almost exact solution of Jellium electronic structure → CASINO implementation

No success so far, improved total energy but not energy differences

Machine Learning (ML) and Quantum Monte Carlo

There are two possible branches of applications of ML:

- Definition of systematically improvable Wf's (Carleo, Science 2017). Any comment?
- Definition of accurate ab-initio (not empirical!) force-field classical potential for BO-energy surface with QMC target chemical (TREX) accuracy

Second path perspective….

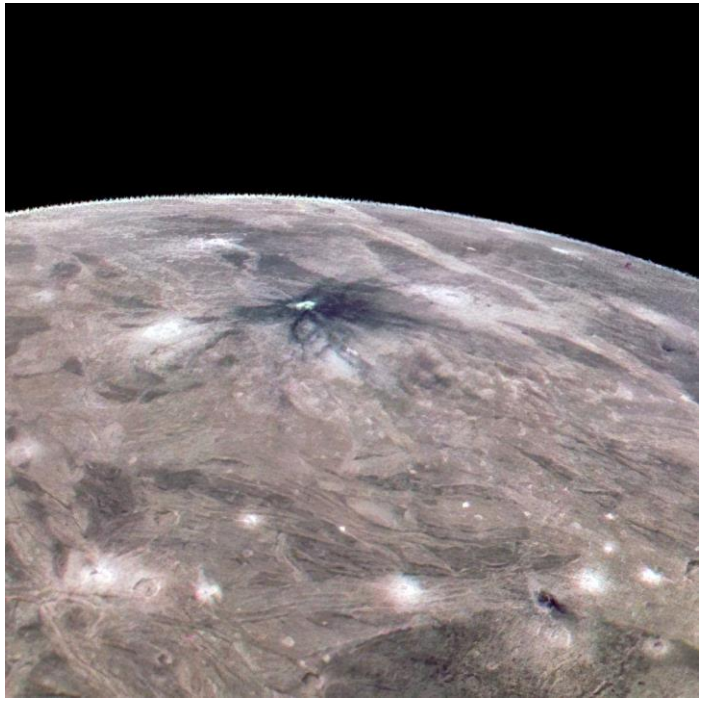
Would you go in a plane super high-tech build with a new material developed with a DFT based calculation using a new superaccurate functional? (Burke, 2000)

If ML+QMC will work the choice will be between a ML potential trained with QMC or DFT. Not only QMC fans will choose the best 😉

Perspectives in astrophysics and cosmology

When experiments cannot bbe done easily

Image of Jupiter from recent Juno mission (NASA)→



In the inner core of Jupiter pressures> 10^6 bar and T>2000K!!!

Dynamical correlation and excitations

In lattice models is quite popular to have access to dynamical correlations by means of projection of

$$\exp(iH\delta t)|\psi_{VMC}(\alpha(t)\rangle \simeq |\psi_{VMC}(\alpha(t)+\delta\alpha(t)\rangle$$

Access to dynamical VMC-approximated correlation functions, such as the dynamical structure factor S(q,ω)

Direct comparison with experiments, but so far no generalization to realistic calculation has been attempted. Worth to try…

Finite temperature calculations

Finite temperature extension of the fixed node is old (Ceperley …) but has been abandoned by the same author (CEICM).

At present we can deal with finite temperature nuclear effects within the BO approximation. But no way to estimate electronic entropy… This problem has no efficient solution (so far) not even in lattice models.

It is worth to think about that, as experiment are always finite T

Exploiting new advances in HPC (GPU et al.)

The lucky period for us is that QMC can exploit the superfast supercomputers and DFT can not, at least efficiently…

Though our community is rather small, we have now the chance to acquire more visibility and much more impact.

Let’s work on that….