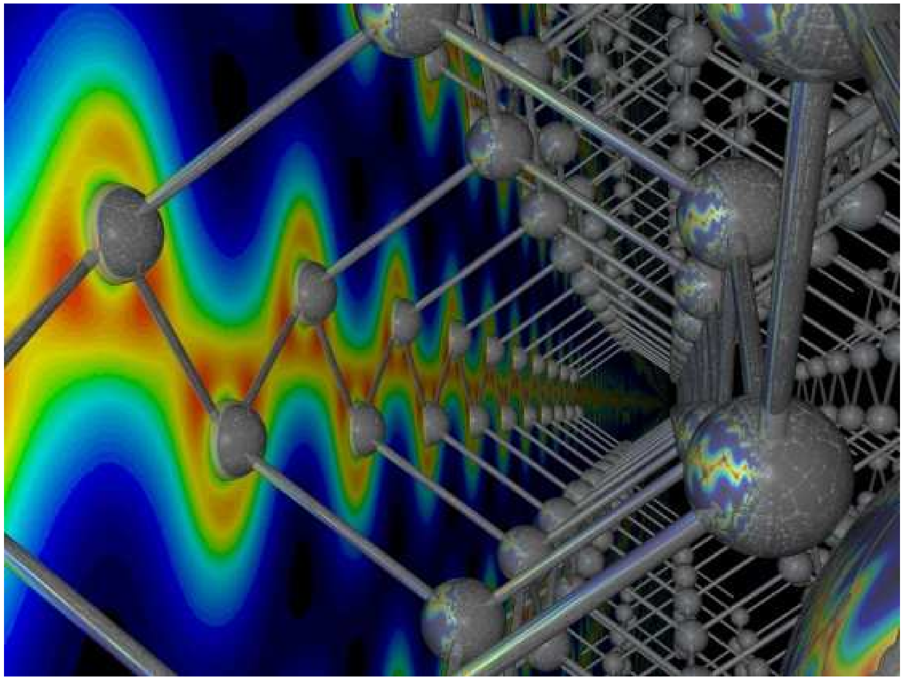
Quantum Monte Carlo: accuracy, generality, and scalability in the electron correlation problem

Scuola Normale, Pisa, April 2014



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What is quantum Monte Carlo?

QMC is, essentially, '*accurate calculation of the properties of assemblies of interacting quantum particles using* **random sampling** *of the full many-body Schrödinger wave function..*' For my purposes, it is applied to 'continuum fermion' cases i.e. realistic atoms, molecules, and crystalline solids just as in regular quantum chemistry.

Why use wave functions? We work directly with the many-body wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$ rather than the density $\rho(\mathbf{x})$ since we can write down exactly the equation that Ψ obeys (a very helpful thing to do when requiring *accuracy*. . .):

$$\boxed{\hat{H}\Psi = E\Psi}$$

- *Variational Monte Carlo* (VMC) - a cheaper less accurate technique which directly computes expectation values such as the one below using standard Monte Carlo numerical integration. May also involve optimization of Ψ by direct variation of any parameters upon which it depends. Limited by flexibility of parameterization..

$$E_{\mathrm{VMC}} = \frac{\int \Psi \hat{H} \Psi \, \mathrm{d}\mathbf{x}}{\int \Psi^2 \, \mathrm{d}\mathbf{x}}$$

- *Diffusion Monte Carlo* (DMC) - a more sophisticated, accurate (and expensive) method which - in principle - projects out the exact ground state wave function from a given 'starting guess' and then computes expectation values as above.

Good things about DMC

- 'Chemical accuracy' (1 kcal/mol or 0.04 eV) and beyond readily achievable. Can feed results of standard DFT/HF/etc.. calculations into a QMC code and greatly 'improve' the answer. Provides *reliable benchmarking* comparable to CCSD(T).
- Required computer time scales as N^3 with system size (improvable to N^2 with some extra complication). Very favourable compared to standard correlated wave function methods (up to N^7 for similar accuracy).
- QMC algorithm intrinsically parallel. With certain caveats speed of calculation increases linearly with number of processors (tested in practice to more than half a million cores). Can therefore fully exploit top-of-the-range supercomputers and other modern hardware including - in principle - GPUs. Most standard methods cannot exploit more than a few thousand processors..
- 'Natural' description of electron correlation. Uses arbitrarily complex many-electron Ψ with no need for analytic integrability. No BSSE or size consistency problems. Not overly dependent on basis set quality - Ψ not represented by basis set.
- Can calculate ground states, excited states, chemical reaction barriers and other properties within single unified methodological framework to high accuracy, based solely on the variational principle. Works for finite or periodic systems.

QMC is essentially the only highly accurate method whose cost can be made to scale reasonably with system size without significantly degrading the quality of the answer.

Why use QMC when we can use DFT?

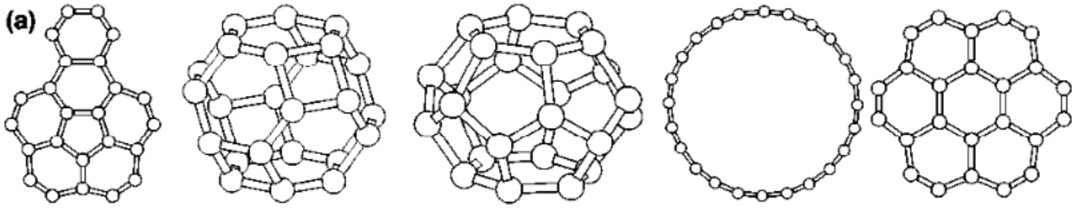
"Ψ is a high-dimensional object, dependent on $3N$ electron Cartesian coordinates, N electron spin coordinates, and $3N_n$ nuclear coordinates. For a molecule such as benzene, with 12 nuclei and 42 electrons, this object exists in $162 - 6 = 156$-dimensional Cartesian space! The determinant has $42! = 1.4 \times 10^{51}$ terms! We can't even make a picture of it. If we were to store it as a numerical object, with a resolution of 0.1 au out to 10 au, we would need 10^{312} numbers to store, at single precision (4 bytes/number), at 2 Gbytes/cm^2 (counting electrical connections access), we would need more than 10^{293} km^2 of surface to store that information. The Earth has a surface area of less than 10^9 km^2. The promised knowledge hidden in the Schrödinger equation is not quite easily accessible! We must make do with much much less. How much less can we do with?" [**from an online DFT course**]

DFT texts always begin by saying it is better to use the density - which depends on 3 variables - instead of Ψ - which depends on $3N$ variables - and thus we use DFT. Fine - who has 10^{284} planets after all? - but (a) in QMC we don't represent Ψ everywhere in configuration space - we just sample it, and (b) unfortunately the *equation* satisfied by the density is simply not known:

$$\boxed{E[\rho] = T[\rho] + \int V_{ext}(\mathbf{x})\rho(\mathbf{x})\,\mathrm{d}x + V_H[\rho] + ??E_{xc}[\rho]??}$$

Exchange-correlation functionals are *serious uncontrolled approximations*..

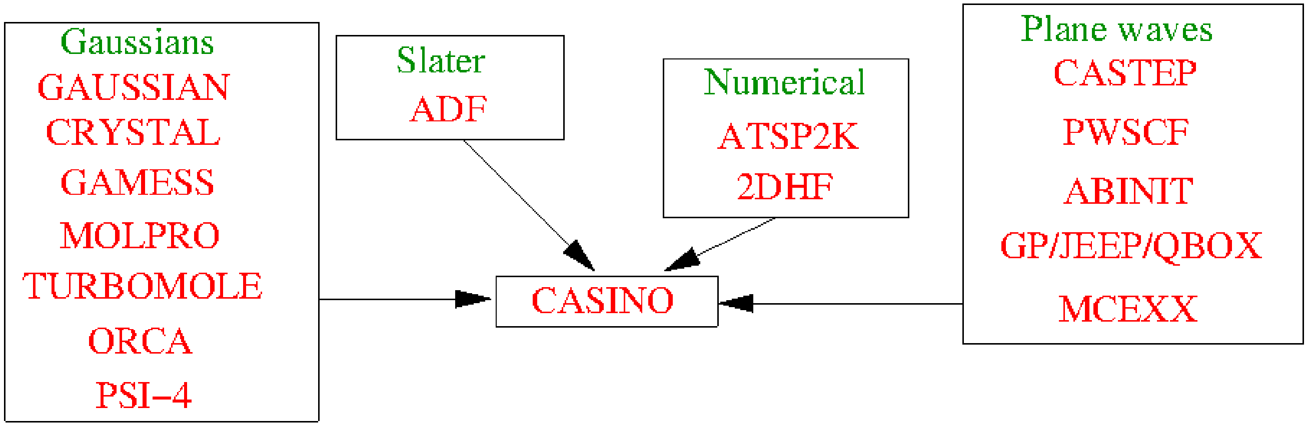
- There are large classes of problem for which DFT gives qualitatively the wrong answer (weak interactions, strongly-correlated systems, energy differences between different types of system, etc.)
- Huge dependence on XC functional. Answers not *reliable* i.e. even for functionals which give better results *on average*, there is no guarantee it gives better answers for any single system.
- Many DFT users are unaware of this, and consider their results to be the 'quantum' answer. Until recently - particularly in periodic systems - no benchmark method available to check accuracy.



Why use QMC instead of proper quantum chemistry methods?

- Usually takes serious computational effort to be accurate *enough* (e.g. the 'gold standard' CCSD(T) extrapolated to complete basis limit).
- *In principle* can solve the Schrödinger equation as accurately as you like - just do full CI with a complete basis set. This is not the point. The key point is *scaling of computer time with system size* - in the modern age N^7 will not do - as such calculations quickly become impossible. We need to scale at most as a low-order polynomial to do most problems of technological interest. QMC can do this.
- In general, you can do higher-order quantum chemistry techniques for atoms and molecules but not for *periodic* systems such as crystalline solids.
- QMC is not restricted to the regular paradigm of expanding the many-electron wave function in a basis set of differently occupied many-electron determinants constructed from orbitals expanded in analytically integrable Gaussian basis sets. If a mathematical expansion requires millions or billions of terms to converge, this is normally taken to mean that the basis set is very poor. Why should the quantum chemistry case be any different?
- Note that real wave functions have a cusp (gradient discontinuity) as an electron passes through a nuclear position - this is impossible to represent with a set of Gaussian functions all with zero gradient at the nucleus.
- Difficult to efficiently exploit many processors on large computers with QC methods.

What's wrong with QMC?



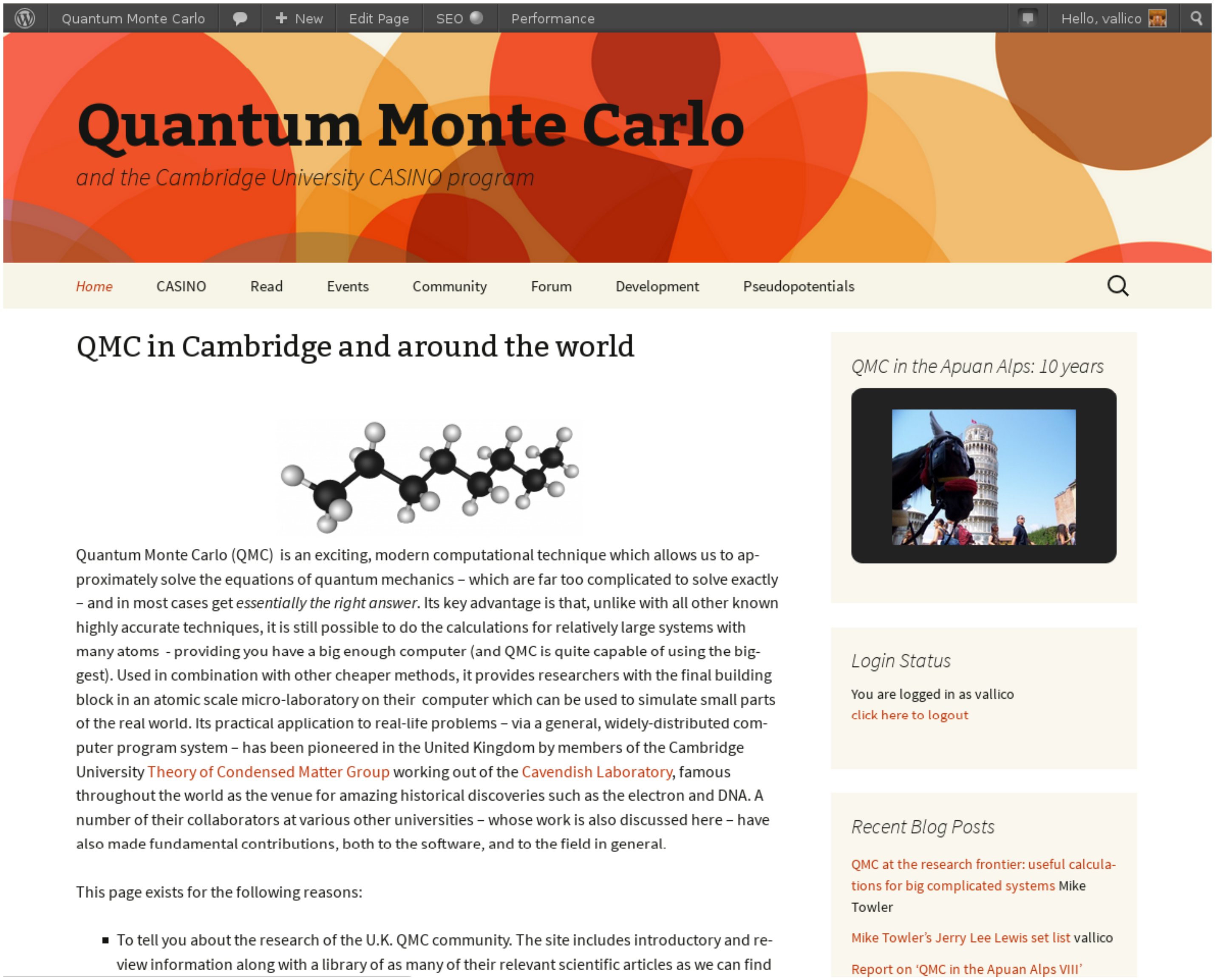
- Need to do a preparatory calculation with someone else's HF/DFT code, and your QMC software must have an explicit interface to that code. Often people find that their HF/DFT code of choice is not supported, so they give up before they start.
- DMC is computationally expensive. Even though the scaling with system size is good, there is a large pre-factor.. (c. 1000× slower than DFT).
- Difficult to compute forces and hence dynamics. Usually zero temperature.
- You will have no friends (both in the sense of being lonely - because to a first approximation no-one else does it - and also because everybody hates a smartarse..)

QMC is not being advocated as a *replacement* for any of these other techniques - which are all very useful in the spheres where they work; it should be considered as the *final building block* in our atomic scale micro-laboratory of multiple techniques that we use to simulate small parts of the real world.

CASINO: the Cambridge quantum Monte Carlo software

M.D.Towler, N.D. Drummond, P. López Ríos, and R.J. Needs

Full details, discussion forum, and immediate download at `http://vallico.net/casinoqmc/`



Quantum Monte Carlo

and the Cambridge University CASINO program

QMC in Cambridge and around the world

Quantum Monte Carlo (QMC) is an exciting, modern computational technique which allows us to approximately solve the equations of quantum mechanics – which are far too complicated to solve exactly – and in most cases get *essentially the right answer*. Its key advantage is that, unlike with all other known highly accurate techniques, it is still possible to do the calculations for relatively large systems with many atoms - providing you have a big enough computer (and QMC is quite capable of using the biggest). Used in combination with other cheaper methods, it provides researchers with the final building block in an atomic scale micro-laboratory on their computer which can be used to simulate small parts of the real world. Its practical application to real-life problems – via a general, widely-distributed computer program system – has been pioneered in the United Kingdom by members of the Cambridge University Theory of Condensed Matter Group working out of the Cavendish Laboratory, famous throughout the world as the venue for amazing historical discoveries such as the electron and DNA. A number of their collaborators at various other universities – whose work is also discussed here – have also made fundamental contributions, both to the software, and to the field in general.

This page exists for the following reasons:

- To tell you about the research of the U.K. QMC community. The site includes introductory and review information along with a library of as many of their relevant scientific articles as we can find

QMC in the Apuan Alps: 10 years

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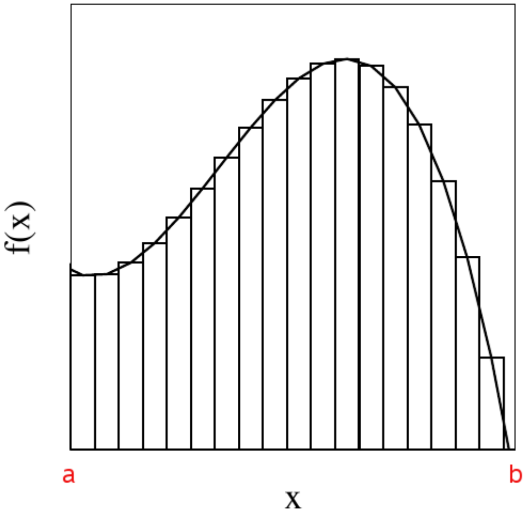
So how does QMC work? Some technical details..

Monte Carlo integration

Alternative to traditional fixed-grid quadrature methods for evaluation of integrals, the main difference being that the sampling points are chosen *at random*.



- $I = \int_a^b f(x)\,dx = (b-a)\bar{f}$ with $\bar{f}$ mean value of $f(x)$.
- Unbiased estimate of $\bar{f}$ is $\langle f \rangle = \frac{1}{M}\sum_{i=1}^{M} f(x_i)$ with the x_i randomly selected from the interval $a \leq x_i \leq b$.
- Statistical uncertainty in $\langle f \rangle$ is given by $\sigma = \frac{\sigma_{\text{sample}}}{\sqrt{M}}$ with $\sigma_{\text{sample}} = \sqrt{\langle f^2 \rangle - \langle f \rangle^2}$. If M large enough, estimate of the mean $\bar{f}$ is *normally* distributed ('Central Limit Theorem').

- For Monte Carlo integration, error decreases as the square root of the number of sampling points (i.e. as $\frac{1}{\sqrt{M}}$) *irrespective of the dimensionality* d *of the integral.*
- For a standard grid method such as the trapezoidal rule the error decreases as $\mathcal{O}(M^{-\frac{2}{d}})$. Monte Carlo wins in more than four dimensions.
- To make the estimate of a 100-dimensional integral ten times more accurate requires 100 times more work with Monte Carlo integration. With the trapezium rule it would require 10^{50} times more work!
- For N particle system we must do $3N$-dimensional integrals. For high-dimensional numerical integration there is effectively *no alternative* to Monte Carlo methods.

How to sample things from probability distributions

In previous example, implicitly selected random points from *uniform probability distribution* (i.e. from anywhere in interval with equal probability). Not sensible for integral like $\int_{-\infty}^{+\infty} \mathrm{e}^{-x^2}\,\mathrm{d}x$ - few if any points would lie in region where integrand is finite. Thus required to sample points from *non-uniform probability distributions*.

Properties of probability distributions

- $p(x)$ = probability density; $p(x)dx$ = probability to be in interval $(x, x+\mathrm{d}x)$.
- $p(x)$ must be positive and normalized to unity: $\int p(x)dx = 1$
- Average values $\langle f(x)\rangle = \int p(x)f(x)\mathrm{d}x$ with $\sigma^2 = \int p(x)f(x)^2\mathrm{d}x - \langle f(x)\rangle^2$.

To do Monte Carlo integration with a non-uniform distribution, generate set of M points x_i distributed according to desired $p(x)$. This can be done using a *random walk* moved according to the *Metropolis algorithm*. Then $\langle f(x)\rangle \simeq \frac{1}{M}\sum_i f(x_i)$ with $\sigma^2 \simeq \frac{1}{M}\sum_i f(x_i)^2 - \left(\frac{1}{M}\sum_i f(x_i)\right)^2$.

What is best $p(x)$ to use? The one that minimizes the variance: $p_{best}(x) = \frac{|f(x)|}{\int |f(x')|\,\mathrm{d}x'}$. Thus concentrate sampling points in regions where absolute value of integrand large - *importance sampling*. Don't in general know normalization though..

How does Metropolis work? Random walk moving from $\mathbf{r}$ to $\mathbf{r}'$ with prob $T(\mathbf{r} \longrightarrow \mathbf{r}')$ (e.g. Gaussian). Accept move with probability: $a(\mathbf{r} \longrightarrow \mathbf{r}') = \min\left[1, \frac{T(\mathbf{r}' \longrightarrow \mathbf{r})p(\mathbf{r}')}{T(\mathbf{r} \longrightarrow \mathbf{r}')p(\mathbf{r})}\right]$ i.e. occasionally reject moves to regions of lower probability. *Equilibration* required.

Many-electron wave functions

- Hartree product: $\Psi_{\mathcal{H}} = \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\ldots\psi_N(\mathbf{x}_N)$
- Single determinant:

$$\Psi_{\mathcal{D}} = \frac{1}{\sqrt{N_e}}\begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_1(\mathbf{x}_2) & \ldots & \psi_1(\mathbf{x}_{N_e}) \\ \psi_2(\mathbf{x}_1) & \psi_2(\mathbf{x}_2) & & \\ \vdots & & \ddots & \\ \psi_{N_e}(\mathbf{x}_1) & & & \psi_{N_e}(\mathbf{x}_{N_e}) \end{vmatrix}$$

- Single determinant Slater-Jastrow function: $\Psi_{\mathcal{DJ}} = \Psi_{\mathcal{D}}\Psi_{\mathcal{J}}$
- Multi-determinant Slater-Jastrow function: $\Psi_{n\mathcal{DJ}} = (\sum_i^n c_i\Psi_{\mathcal{D}_i})\Psi_{\mathcal{J}}$
- Multi- or single determinant Slater-Jastrow function with *backflow*

Jastrow factor $\Psi_{\mathcal{J}} = \exp\left(\mathcal{J}\right)$ is optimizable functional form for pair correlation, e.g.:

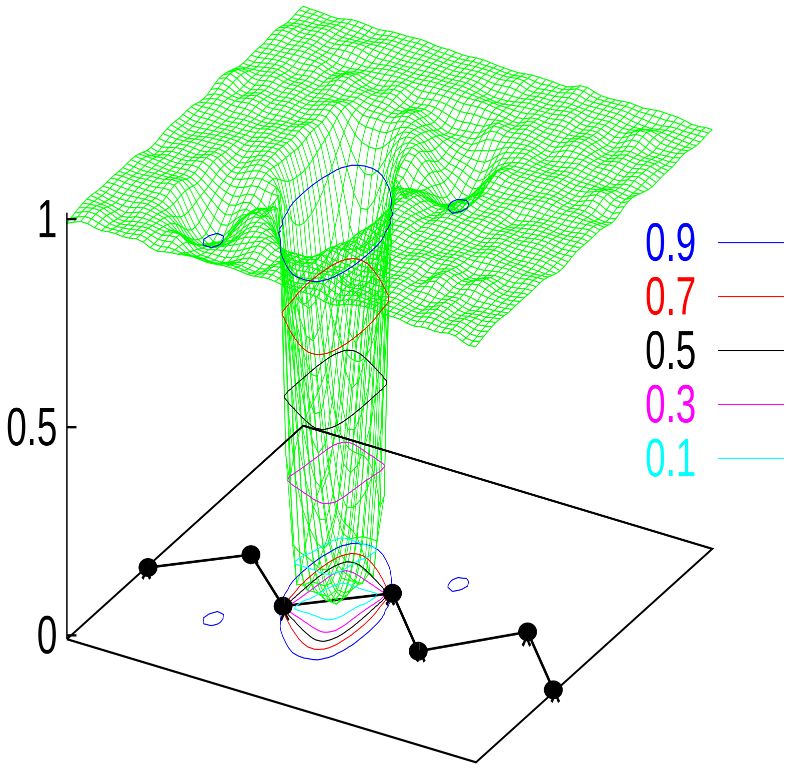
$$\mathcal{J} = \sum_{i\neq j}^{N_e}\left[-U_0(r_{ij}) - U(r_{ij}) + \sum_n^{N_n} S^n(\mathbf{r}_i, \mathbf{r}_j, r_{ij})\right] \text{ and } U_0(r_{ij}) = \frac{A}{r_{ij}}\left(1 - \exp\left(-\frac{r_{ij}}{F}\right)\right)$$

with U power series expansion in e-e separation and S^n set of atom-centred functions giving additional variational freedom in description of pair correlation near nuclei.

Backflow: replace coords $\mathbf{x}_i$ in $\Psi_{\mathcal{D}}$ with *collective coords* $\mathbf{r}_i(\{\mathbf{x}_j\})$ given by $\mathbf{r}_i = \mathbf{x}_i + \xi_i(\{\mathbf{x}_j\})$ with ξ_i configuration-dependent *backflow displacement* of particle i.

Pair correlation function

Silicon with Slater-Jastrow wave function

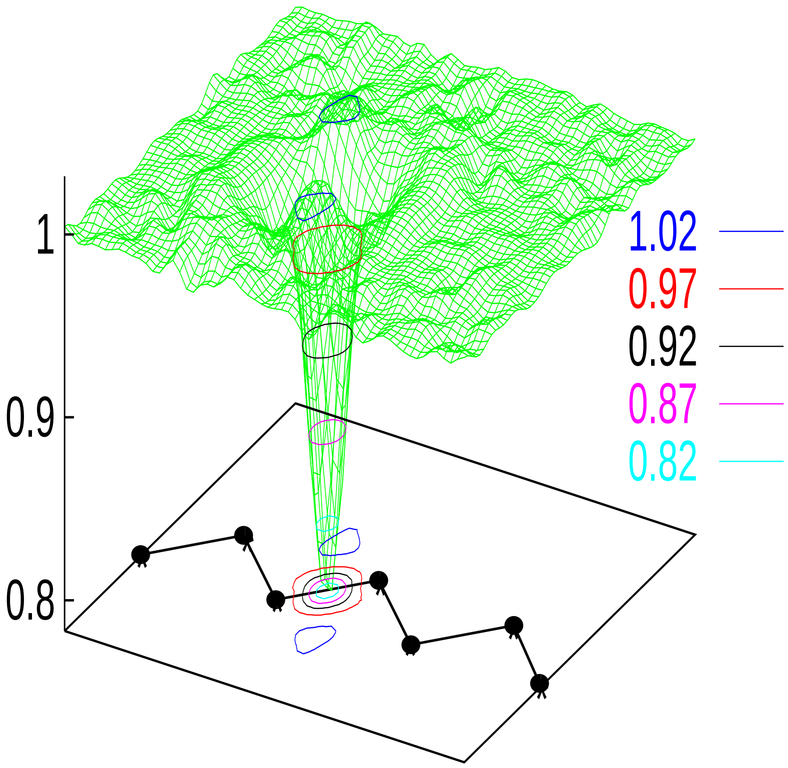


VMC

$\bar{g}_{\uparrow\uparrow}(\mathbf{r},\mathbf{r}';[n])$

$\mathbf{r}$ at bond center

$\mathbf{r}'$ in (110) plane



VMC

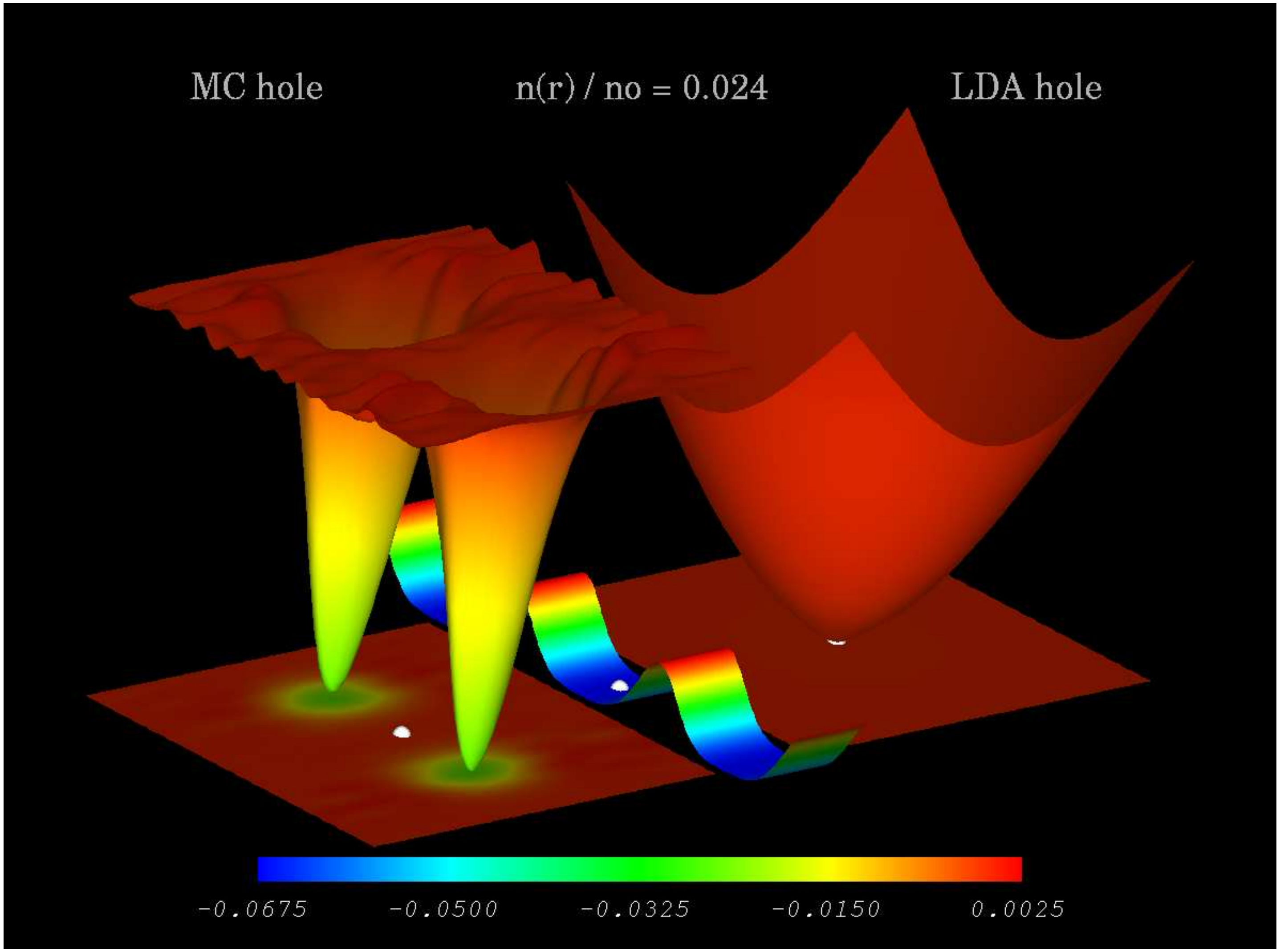
$\bar{g}_{\uparrow\downarrow}(\mathbf{r},\mathbf{r}';[n])$

$\mathbf{r}$ at bond center

$\mathbf{r}'$ in (110) plane

Exchange-correlation hole

Inhomogeneous electron gas

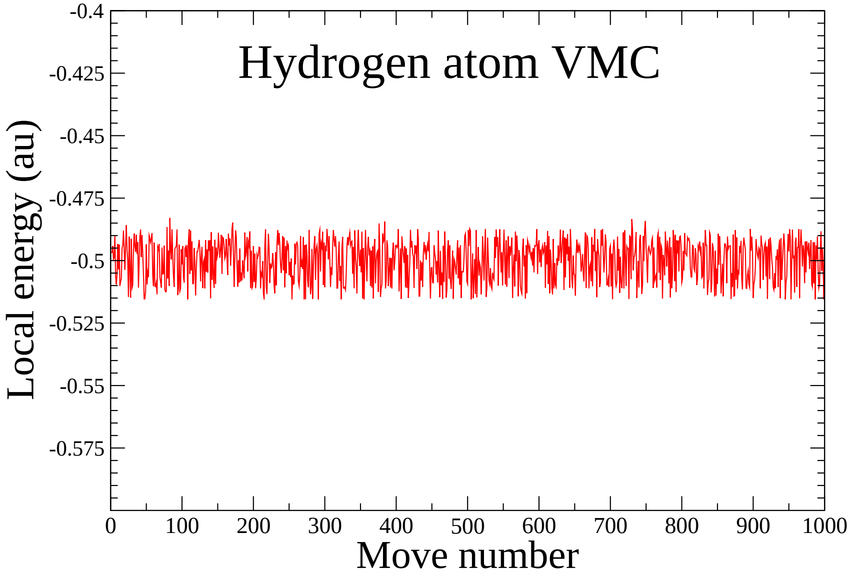


Variational Monte Carlo

Stochastic integration method for evaluating expectation values for fixed trial many-body wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \equiv \Psi(\mathbf{x})$:

$$E_{\mathrm{VMC}} = \frac{\int \Psi \hat{H} \Psi \, \mathrm{d}\mathbf{x}}{\int \Psi^2 \, \mathrm{d}\mathbf{x}} = \frac{\int \Psi^2 \left(\frac{\hat{H}\Psi}{\Psi}\right) \mathrm{d}\mathbf{x}}{\int \Psi^2 \, \mathrm{d}\mathbf{x}} \left(\equiv \int p(x) f(x) \, \mathrm{d}x \right)$$

where $f(x) = \frac{\hat{H}\Psi}{\Psi} \equiv E_{\mathrm{L}} =$ ‘local energy’ and $p(x) = \Psi^2 / \int \Psi^2 \, \mathrm{d}\mathbf{x}$.



- Generate M points distributed as Ψ^2 and average local energies $E_{\mathrm{VMC}} \simeq \frac{1}{M} \sum_i E_{\mathrm{L}}(\mathbf{x}_i)$.
- Optimal probability density $p(x) = |f(x)| / \int |f(x')| \, \mathrm{d}x' = |\Psi \hat{H} \Psi| / \int \Psi \hat{H} \Psi \, \mathrm{d}\mathbf{x}$ but this tends to $|\Psi|^2 / \int \Psi^2 \, \mathrm{d}\mathbf{x}$ as Ψ tends to exact wave function when $\hat{H}\Psi = E\Psi$.
- As Ψ tends to exact wave function, fluctuations in E_{L} tend to zero (the ‘*zero variance principle*’).

Effectively still a *basis set method* - you get out what you put in.

Wave function optimization

Trial wave functions contain parameters (Jastrow, backflow, det coeffs etc.) that must be *optimized* in VMC so Ψ has optimal functional form. Need *objective function* to minimize with respect to parameter set $\{\alpha\}$ - generally choose *energy* or *variance*:

$$E_{\rm V} = \frac{\int \Psi^2(\alpha) E_{\rm L}(\alpha)\,{\rm d}\mathbf{x}}{\int \Psi^2(\alpha)\,{\rm d}\mathbf{x}} \quad \text{or} \quad {\rm var}(E) = \frac{\int \Psi^2(\alpha)[E_{\rm L}(\alpha) - E_{\rm V}(\alpha)]^2\,{\rm d}\mathbf{x}}{\int \Psi^2(\alpha)\,{\rm d}\mathbf{x}}$$

Until recently more usual to minimize variance, because:

- It has a known lower bound of zero.
- It can be applied to excited states.
- Efficient algorithms known for minimizing objective functions expressible as sum of squares (for many years energy minimization was considered to be a difficult numerical problem).
- Varmin-optimized trial-functions exhibits greater numerical stability than energy minimized ones in DMC (there is a smaller tendency for population explosions).

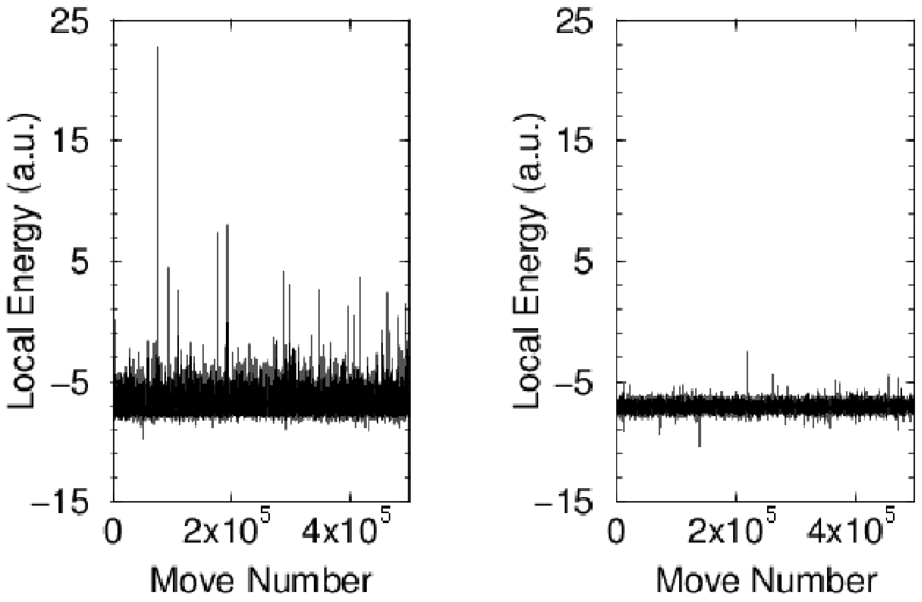
Still default choice if want DMC energies with Slater-Jastrow trial function.

Now also common to minimize energy, because:

- Efficient, numerically-stable algorithms for doing so have been discovered.
- Since trial wave functions cannot represent eigenstate exactly, the energy and variance minima don't coincide. Energy minimization should therefore produce lower VMC energies (and consequently better DMC wave functions - see later).
- Better at optimizing parameters that change *nodal surface* - significance will become clear shortly.
- Resulting wave functions give better forces (and some other properties).

Results of a VMC simulation

No Jastrow



Optimized Jastrow

- Answer given as $E_{\mathrm{VMC}} \pm \sigma$, where σ is some statistical error bar.
- Better Ψ give lower energy (variational principle) and smaller error bar.
- Statistical analysis required to eliminate serial correlation and get correct error bar.

Example results: cohesive energies

Method	Si	Ge	C	BN
DFT/LDA	5.28	4.59	8.61	15.07
VMC	4.48±0.01	3.80±0.02	7.36±0.01	12.85±0.03
Exp.	4.62	3.85	7.37	12.9

Not bad but not brilliant either..

VMC is not enough

VMC results are OK (might recover $75-85\%$ of correlation energy) - not really good enough to be worth the effort. Results highly dependent on trial wave function and basis set quality. Problem is one of **complexity** *- not clear how to make arbitrarily accurate wave functions this way.*

However, there is class of methods - collectively called *projector Monte Carlo* - which in principle solve quantum problems exactly. Idea is to project out ground state by repeated iteration of a projection operator $\hat{P}$, i.e., $\lim_{i\longrightarrow\infty}\hat{P}^i|\Psi_T\rangle \approx |\Psi_0\rangle$. After many iterations excited state $|\Psi_i\rangle$ contribution filtered out and ground state recovered.

Such methods depend upon guessed properties of many-body Ψ only in computational efficiency, if at all. *Diffusion Monte Carlo* (DMC) is one such method.

Characteristics of diffusion Monte Carlo

- Systematically improves Ψ through magic process: *stochastic propagation in imaginary time*.
- Extremely weakly dependent on basis set quality.
- Scales as N^3 or better with system size.
- Taken to limit, comparable in accuracy with benchmark quantum chemistry correlated methods.

The main use of VMC in practical calculations is to prepare the input for a diffusion Monte Carlo simulation.

Propagators: motivation

Let's say we wish to integrate the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial\Psi(\mathbf{x},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{x},t) + V(\mathbf{x},t)\Psi(\mathbf{x},t) = \hat{H}\Psi(\mathbf{x},t)$$

where $\mathbf{x} = \{\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N\}$. Usually use atomic units: $\hbar = 1, m = 1$.

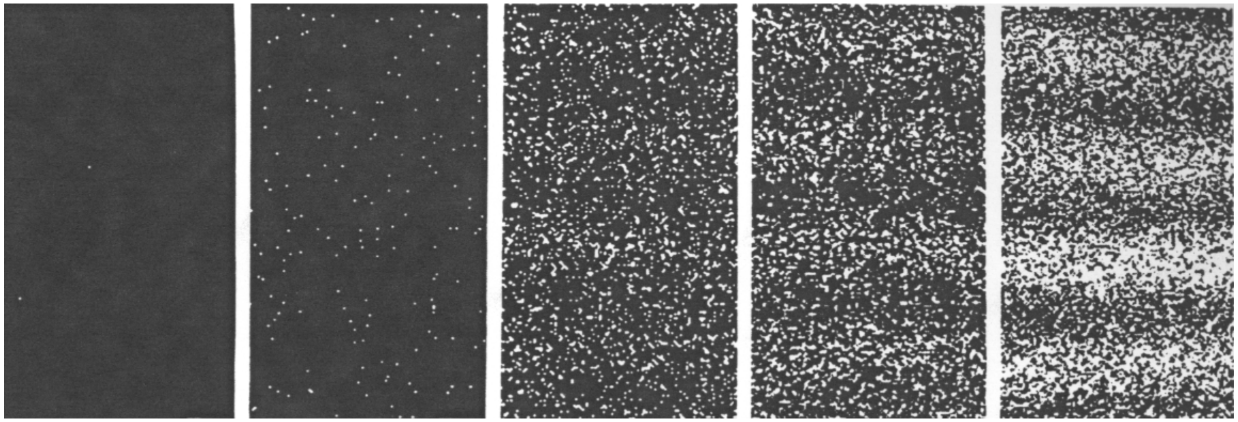
- Inverse of this differential equation is an integral equation involving the *propagator*:

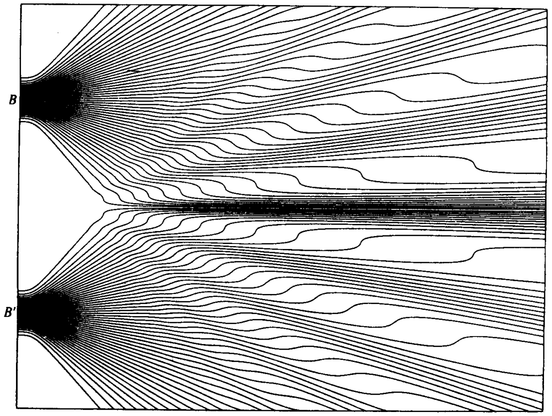
$$\Psi(\mathbf{x},t) = \int K(\mathbf{x},t;\mathbf{x}',t')\Psi(\mathbf{x}',t')\,\mathrm{d}x'$$

  The propagator is the *probability amplitude for a particle to travel from one place to another in a given time*. It is a *Green's function* for the Schrödinger equation.

- Ordinarily one might use the *Feynman path-integral* formulation of quantum mechanics to calculate the propagator. For given start and end points, overall amplitude given by summing contributions of infinite number of all possible *histories* which include those points. Amplitude contributed by a particular history proportional to $e^{iS_{cl}/\hbar}$ where S_{cl} is classical *action* of that history i.e. time integral of classical Lagrangian $T - V$ along corresponding phase space path of system.

Pilot wave theory





Otherwise known as *de Broglie-Bohm theory* or *Bohmian mechanics*, this is an interpretation of QM where particles exist and have *trajectories* (most people believe not possible!). Invented in **1927** by de Broglie, but unfairly overruled by *logical positivists* of Copenhagen school (Bohr, Heisenberg, etc.).

- Particles *guided* by wave along streamlines of probability flow, following trajectory $\mathbf{v} = \nabla S/m$ where S is *phase* of Schrödinger wave function written in polar form $\Psi(x,t) = R(x,t)e^{iS(x,t)/\hbar}$.
- Whole thing follows from a single semantic change in the meaning of a word: $|\Psi|^2$ is *probability of* ***being*** *at* x rather than *probability of being* ***found there in a suitable measurement***. Under this assumption, measurement problem and all quantum 'paradoxes' simply disappear.

Quantum trajectory method

Pilot-wave theory not just interpretation: mathematical formulation of QM useful to compute propagator! Substitute Ψ polar form in Schrödinger equation. Separate real and imaginary parts. Get equations of *quantum hydrodynamics* - a 'quantum trajectory method' (analogy with fluid mechanics):

$\frac{\partial \rho}{\partial t} = -\rho \nabla \cdot \mathbf{v}$ (continuity equation, where $\rho = R^2$) and $\frac{\partial S}{\partial t} = L(t) = \frac{1}{2}mv^2 - (V+Q)$ (the quantum Hamilton-Jacobi equation - an equation for the phase involving the *quantum potential* Q).

Wave function synthesis along quantum trajectory

$$\boxed{\Psi = R(x,t)\mathrm{e}^{\frac{iS(\mathbf{x},t)}{\hbar}}}$$

Propagation of the amplitude

Along trajectory $\mathbf{x}(t)$ from $(\mathbf{x}_0, t_0)$ to $(\mathbf{x}_1, t_1)$ rate of change of density $\frac{\partial \rho}{\partial t} = -\rho\nabla\cdot\mathbf{v}$. Amplitude $R = \rho^{\frac{1}{2}}$ so $\frac{\partial R}{\partial t} = -\frac{R}{2}\nabla\cdot\mathbf{v}$. Integrate to get new R in terms of value at t_0.

$$\frac{\mathrm{d}R}{R} = -\frac{1}{2}\nabla\cdot\mathbf{v}\ \mathrm{d}t \xrightarrow{\text{integrate}} \ln R + c = -\frac{1}{2}\int_{t_0}^{t_1}\nabla\cdot\mathbf{v}\ \mathrm{d}t \xrightarrow{\text{exponentiate}} A\exp(\ln R) = \exp\left[-\frac{1}{2}\int_{t_0}^{t_1}\nabla\cdot\mathbf{v}\ \mathrm{d}t\right]$$

$$R(\mathbf{x}_1, t_1) = \exp\left[-\frac{1}{2}\int_{t_0}^{t_1}(\nabla\cdot\mathbf{v})_{\mathbf{x}(t)}\ \mathrm{d}t\right] R(\mathbf{x}_0, t_0)$$

To propagate R we integrate the *divergence of the velocity field* along the trajectory.

Propagation of the exponential of the phase

Quantum H-J eqn is $\frac{\partial S}{\partial t} = L(t) = \frac{1}{2}mv^2 - (V+Q)$. From $S(t_1) = S(t_0) + \int_{t_0}^{t_1}\frac{\partial S}{\partial t}\ \mathrm{d}t \xrightarrow{\times\frac{i}{\hbar}\ \text{and exponentiate}}$

$$\mathrm{e}^{\frac{iS(\mathbf{x}_1,t_1)}{\hbar}} = \exp\left[\frac{i}{\hbar}\int_{t_0}^{t_1}L(t)\ \mathrm{d}t\right]\mathrm{e}^{\frac{iS(\mathbf{x}_0,t_0)}{\hbar}}$$

To propagate $e^{\frac{iS(\mathbf{x},t)}{\hbar}}$ we integrate the *quantum Lagrangian* along the trajectory.

Wave function synthesis along quantum trajectory

We multiply the expressions for the R propagator and the $e^{\frac{iS(\mathbf{x},t)}{\hbar}}$ propagator to obtain an expression for updating the full wave function along the trajectory:

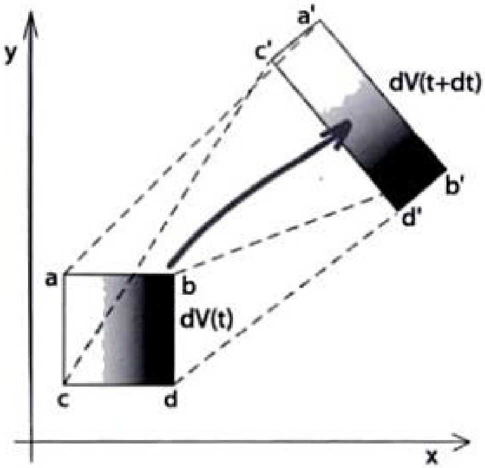
$$\boxed{\Psi(\mathbf{x}_1,t_1) = \exp\left[-\frac{1}{2}\int_{t_0}^{t_1}(\nabla\cdot\mathbf{v})_{\mathbf{x}(t)}\,\mathrm{d}t\right]\exp\left[\frac{i}{\hbar}\int_{t_0}^{t_1}L(t)\,\mathrm{d}t\right]\Psi(\mathbf{x}_0,t_0)}$$

Hydrodynamical wave function propagator (HWFP) $K^Q(\mathbf{x}_1,t_1;\mathbf{x}_0,t_0)$

What does $\nabla\cdot\mathbf{v}$ mean here?

At time t have volume element $\mathrm{d}V(t)$. Element corners defined by trajectory positions $\{a,b,c,d\}$. Increment time by $\mathrm{d}t$ and equations of motion shift corners to $\{a',b',c',d'\}$ and volume element changes to $\mathrm{d}V(t{+}\mathrm{d}t)$. Ratio of new to old volumes is the *Jacobian*: $\mathrm{d}V(t{+}\mathrm{d}t) = J(t+\mathrm{d}t,t)\mathrm{d}V(t)$. Can be shown Jacobian is:

$$J(t_1,t_0) = \exp\left[\int_{t_0}^{t_1}\nabla\cdot\mathbf{v}\;\mathrm{d}t\right].$$



- Implies if velocity field has positive divergence (velocity vectors 'point away from each other') then Jacobian increasing and local volume element *expanding* along flow. So velocity divergence locally measures rate of change of geometric quantity.
- Note the R-propagator $\exp\left[-\frac{1}{2}\int_{t_0}^{t_1}\nabla\cdot\mathbf{v}\;\mathrm{d}t\right]$ is thus just $J(t)^{-\frac{1}{2}}$.

An interesting comparison

Quantum trajectories and Feynman path integrals

- In the expression $\Psi(\mathbf{x}_1,t_1) = K^Q(\mathbf{x}_1,t_1;\mathbf{x}_0,t_0)\Psi(\mathbf{x}_0,t_0)$ that propagates the wave function along the quantum trajectory, the propagator K^Q may - expressing the R-propagator in terms of the Jacobian - be written as

$$K^Q(\mathbf{x}_1,t_1;\mathbf{x}_0,t_0) = \frac{1}{J(t)^{\frac{1}{2}}}\exp\left[\frac{i}{\hbar}\int_{t_0}^{t_1} L(t)\;\mathrm{d}t\right].$$

- In *Feynman's path integral formulation of quantum mechanics* the equivalent propagator may be written as

$$K^F(\mathbf{x}_1,t_1;\mathbf{x}_0,t_0) = N\sum_{\text{all paths}}\exp\left[\frac{i}{\hbar}\int_{t_0}^{t_1} L_{cl}(t)\;\mathrm{d}t\right].$$

Here propagator linking two spacetime points calculated by linearly superposing amplitudes $e^{iS/\hbar}$ (obtained by integrating **classical** Lagrangian $L_{cl}(t) = \frac{1}{2}mv^2 - V$) associated with infinite number of **all possible paths** connecting the points.

In pilot-wave approach, achieve same effect by integrating the **quantum** *Lagrangian* $L(t) = \frac{1}{2}mv^2 - (V+Q)$*along precisely* **one** *path. Bet you didn't know that..*

Quantum trajectories and quantum Monte Carlo

What connection, if any, is there between quantum trajectory methods and state-of-the-art techniques like **quantum Monte Carlo** *that accurately solve the time-independent Schrödinger equation sampling the full many-electron* Ψ*?*

Diffusion Monte Carlo

The most highly-evolved QMC variant with broad scope is *diffusion Monte Carlo* (DMC). It is probably the most accurate method known for solving the many-electron Schrödinger equation that also scales reasonably with the number of particles. It remains tractable (and highly accurate) for large system sizes; simulations of periodic systems with over 2000 electrons per cell have been reported.

It propagates an arbitrary starting wave function using a (Green's function) propagator just like the ones we have been discussing. The main difference is that the propagation occurs in *imaginary time* τ as opposed to real time t. This has the effect of 'improving' the wave function i.e. making it look more like the ground state as imaginary time passes (see later).

$$\Psi(\mathbf{x}, \tau + \delta\tau) = \int K(\mathbf{x}, \mathbf{x}', \delta\tau)\Psi(\mathbf{x}', \tau)\, d\mathbf{x}'$$

Evolving wave function represented by distribution in space and time of randomly-diffusing electron positions over an ensemble of copies of the system. From pilot-wave perspective, this is something like calculating expectation values by 'sampling trajectories' (from ensemble of different launch points).

Further reading

Quantum Monte Carlo simulations of solids, W.M.C. Foulkes, L. Mitas, R.J. Needs and G. Rajagopal, *Rev. Mod. Phys.* **73**, 33 (2001).
The quantum Monte Carlo method, M.D. Towler, *Phys. Stat. Solidi* **243**, 2573 (2006).

Why do we propagate Ψ in imaginary time in DMC?

Consider Schrödinger equation (in a.u.) with constant offset E_T to zero of potential:

$$-\frac{\partial\Psi(\mathbf{x},t)}{i\partial t} = \left(\hat{H} - E_T\right)\Psi(\mathbf{x},t).$$

For eigenstate, general solution is clearly

$$\phi(\mathbf{x},t) = \phi(\mathbf{x},0)\mathrm{e}^{-i(\hat{H}-E_T)t}.$$

Then expand an *arbitrary* (‘guessed’) $\Psi(\mathbf{x},t)$ in complete set of eigenfunctions of $\hat{H}$.

$$\Psi(\mathbf{x},t) = \sum_{n=0}^{\infty} c_n\phi_n(\mathbf{x})\mathrm{e}^{-i(E_n-E_T)t}$$

Substitute it with *imaginary time* $\tau = it$. Oscillatory behaviour becomes exponential.

$$\Psi(\mathbf{x},\tau) = \sum_{n=0}^{\infty} c_n\phi_n(\mathbf{x})\mathrm{e}^{-(E_n-E_T)\tau}$$

Get imaginary time independence by choosing constant E_T to be ground state eigenvalue E_0. As $\tau \to \infty$, Ψ comes to look more and more like the ground state ϕ_0.

$$\Psi(\mathbf{x},\tau) = c_0\phi_0 + \sum_{n=1}^{\infty} c_n\phi_n(\mathbf{x})\mathrm{e}^{-(E_n-E_0)\tau}$$

How do we propagate Ψ in imaginary time in DMC?

- We use a Green's function propagator $K(\mathbf{x},\mathbf{x}',\delta\tau)$:

$$\Psi(\mathbf{x},\tau+\delta\tau)=\int K(\mathbf{x},\mathbf{x}',\delta\tau)\Psi(\mathbf{x}',\tau)\,d\mathbf{x}'$$

- How do we find an expression for the propagator K? Consider imaginary-time Schrödinger equation in two parts:

$$\begin{aligned}\frac{\partial\Psi}{\partial\tau} &= \frac{1}{2}\nabla^2_{\mathbf{x}}\Psi \quad \text{(diffusion equation)}\\ \frac{\partial\Psi}{\partial\tau} &= -V\Psi \quad \text{(rate equation)}\end{aligned}$$

- Propagator for diffusion equation well-known: it is a $3N$-dimensional Gaussian with variance $\delta\tau$ in each dimension. Propagator for rate equation known - gives so-called 'branching factor' which can be interpreted as a position-dependent *weight* or *stochastic survival probability* for a member of an ensemble.

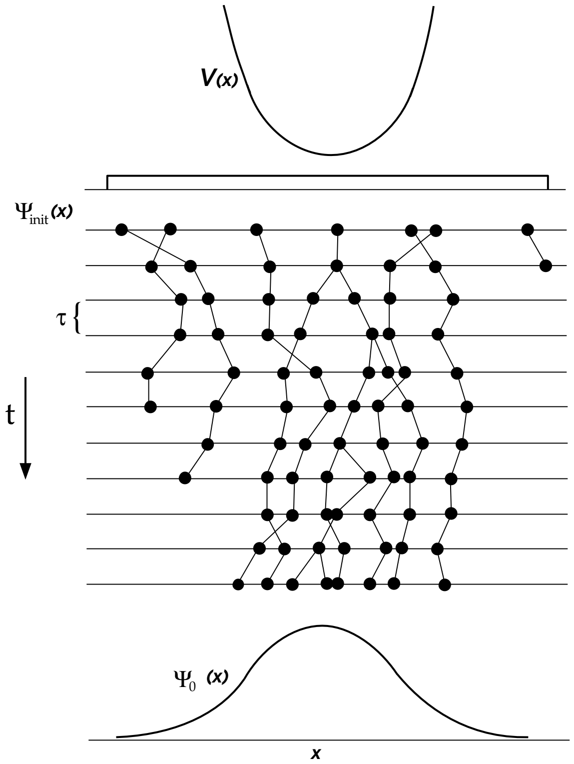
$$K(\mathbf{x},\mathbf{x}',\delta\tau)=\frac{1}{(2\pi\delta\tau)^{\frac{3N}{2}}}\exp\left(-\frac{|\mathbf{x}-\mathbf{x}'|^2}{2\delta\tau}\right)\times\exp\left[-\delta\tau\left(\frac{V(\mathbf{x})+V(\mathbf{x}')-2E_T}{2}\right)\right]$$

Multiplying the two together to get the propagator for the imaginary-time Schrödinger equation is an *approximation* valid in the limit of small $\delta\tau$.

A Diffusion Monte Carlo simulation

- Interpret Ψ as a *probability density*, then diffusion equation $\frac{\partial\Psi}{\partial\tau} = \frac{1}{2}\nabla^2_{\mathbf{x}}\Psi$ represents movement of N diffusing particles. Turning this around, can represent $\Psi(\mathbf{x},\tau)$ by *ensemble* of such sets of particles. Member of ensemble called a ‘configuration’.
- Interpret propagator $K(\mathbf{x},\mathbf{x}',\delta\tau)$ as probability of configuration moving from $\mathbf{x}'$ to $\mathbf{x}$ in a time $\delta\tau$. Branching factor determines population of configurations: in regions of high V configurations will be killed off; in low V regions configurations will multiply. It is this that ‘changes the shape of the wave function’ as it evolves.
- Propagate distribution in imaginary time, and after sufficiently long time excited states will have decayed away to leave the ground-state Ψ. Can then continue propagation and accumulate averages of observables.

Guess that the ground-state wave function for a single electron in a harmonic potential well is a constant over some range (stupid!). Start with seven copies of the system over which ensemble the electrons are distributed according to this constant probability distribution. Propagate the particle distribution in imaginary time according to the prescription above, and watch the electrons become distributed according to the proper Gaussian shape of the exact ground-state wave function. The change in shape is produced by the branching factor occasionally eliminating configurations in high V regions and duplicating ones in low V regions..

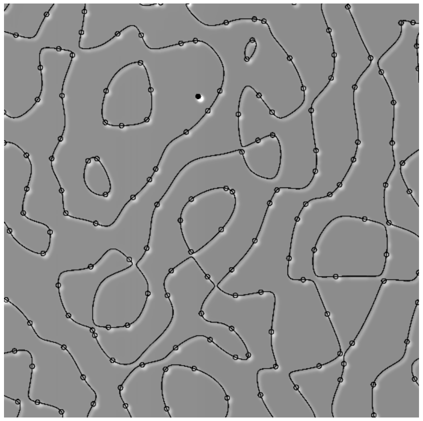


Importance sampling and the fixed-node approximation in DMC

The basic DMC algorithm sounds nice but *doesn't work* in practice. This is because:

- Ψ can only be a probability distribution if of one sign everywhere (e.g. H atom, boson system). For multi-particle fermion systems it necessarily has positive and negative bits. Obvious ways of getting round this (e.g. separate probabilities for different signs) fail on account of signal-to-noise problems ('*fermion sign problem*').
- Branching factor $\exp\left[-\frac{\delta\tau}{2}\left(V(\mathbf{x})+V(\mathbf{x}')-2E_{\rm T}\right)\right]$ contains potential V varying from $-\infty$ to $+\infty$. Sampling of points e.g. near nucleus leads to massive fluctuations in branching factor and significant numerical instabilities.

Fix problem by introducing *importance sampling* via a guessed trial function Φ_T (from a HF or DFT calculation, say). Require propagation to produce distribution $f(\mathbf{x},\tau)=\Psi(\mathbf{x},\tau)\Phi_T(\mathbf{x})$ - forced to be of one sign by demanding fixed Φ_T and variable Ψ functions have same *nodal surface* i.e. same zeroes ('*fixed-node approximation*').



New 'imaginary time Schrödinger equation' (Fokker-Planck)

$$-\frac{\partial f(\mathbf{x},\tau)}{\partial\tau} = -\frac{1}{2}\nabla_{\mathbf{x}}^2 f(\mathbf{x},\tau) + \nabla_{\mathbf{x}}\cdot\left[\mathbf{F}(\mathbf{x})f(\mathbf{x},\tau)\right] - \left(E_{\rm L}(\mathbf{x})-E_{\rm T}\right)f(\mathbf{x},\tau)$$

$\mathbf{F}(\mathbf{x}) \equiv \frac{\nabla_{\mathbf{x}}\Phi_T}{\Phi_T}$ 'drift vector' $\qquad$ $E_L = \frac{\hat{H}\Psi}{\Psi}$ 'local energy'

$$f(\mathbf{x},\tau+\delta\tau) = \int K(\mathbf{x}',\mathbf{x},\delta\tau)\,f(\mathbf{x},\tau)\,d\mathbf{x}'$$

Problem solved - more or less

Final propagator consists of diffusion, drift and branching processes:

$$K(\mathbf{x}',\mathbf{x},\delta\tau) = \frac{1}{(2\pi\delta\tau)^{\frac{3N}{2}}} \exp\left[-\frac{(\mathbf{x}'-\mathbf{x}-\delta\tau\mathbf{F}(\mathbf{x}))^2}{2\delta\tau}\right] \exp\left[-\frac{\delta\tau}{2}\left(E_{\mathrm{L}}(\mathbf{x})+E_{\mathrm{L}}(\mathbf{x}')-2E_{\mathrm{T}}\right)\right]$$

To be compared with the original propagator without importance sampling:

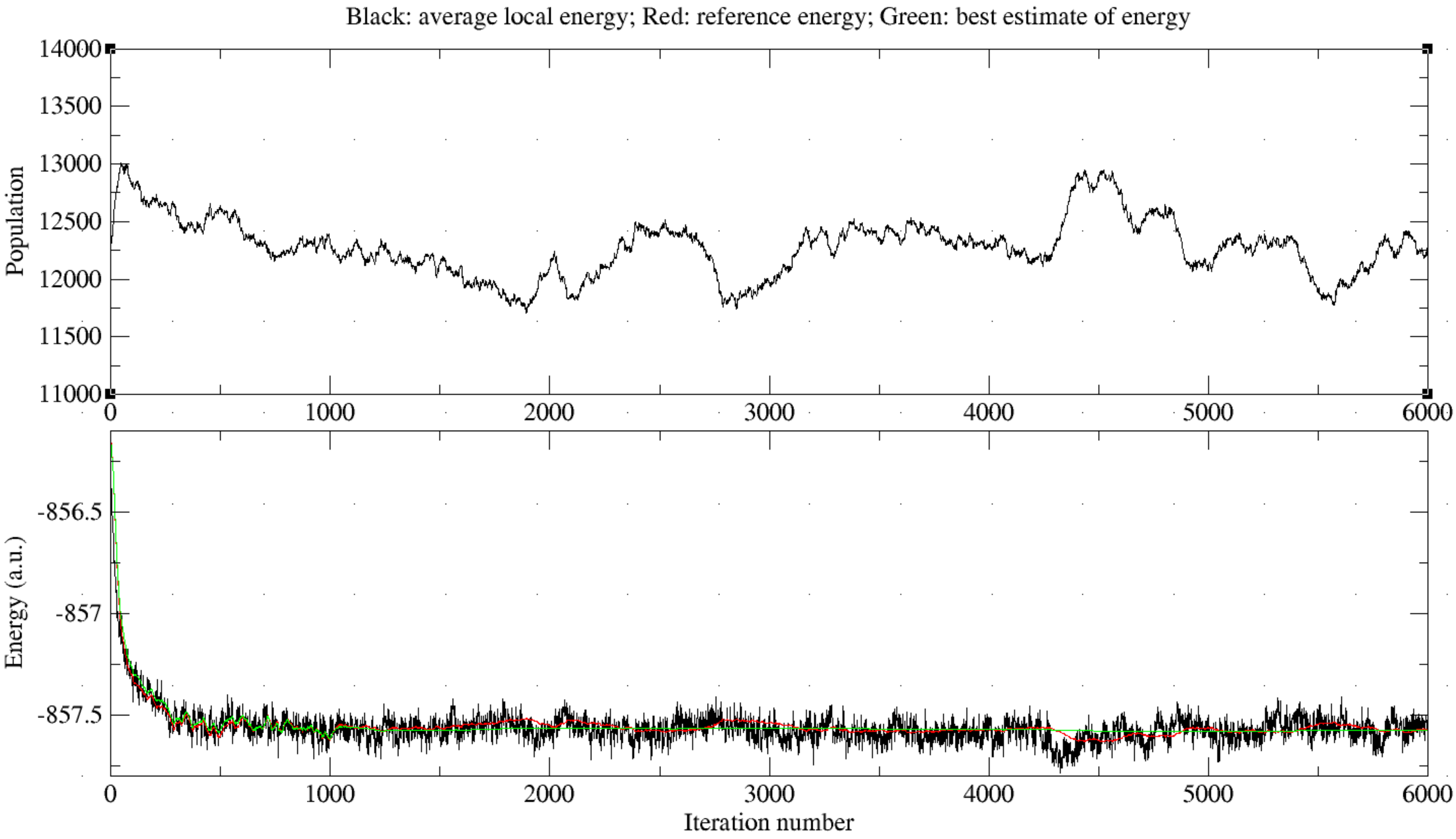
$$K(\mathbf{x},\mathbf{x}',\delta\tau) = \frac{1}{(2\pi\delta\tau)^{\frac{3N}{2}}} \exp\left(-\frac{(\mathbf{x}-\mathbf{x}')^2}{2\delta\tau}\right) \exp\left[-\frac{\delta\tau}{2}\left(V(\mathbf{x})+V(\mathbf{x}')-2E_T\right)\right]$$

- Mixed distribution $f=\Psi\Phi_T$ of one sign everywhere so no more sign problem (at cost of reducing flexibility by fixing the nodes).
- Branching term now contains local energy $E_L=\hat{H}\Psi/\Psi$ which fluctuates much less than the potential V (for an eigenstate, E_L is constant everywhere in configuration space). No more numerical instability in the branching.
- Importance sampling from drift term $\mathbf{F}(\mathbf{x})=\nabla\Phi_T/\Phi_T$ enhancing density of configs where Φ_T is large i.e. there is a *drift* or *osmotic velocity* directed towards large Φ_T on top of the random diffusion - like electric field on Brownian motion.

Fixed-node approximation most serious error in DMC, but still recover 95-100% of the total energy error made in a Hartree-Fock calculation (the ‘correlation energy’) for typical systems.

Results of DMC simulation

sI methane clathrate (178 atoms per cell)



DMC cohesive energies

Method	Si	Ge	C	BN	NiO
DFT/LDA	5.28	4.59	8.61	15.07	10.96
VMC	4.48±0.01	3.80±0.02	7.36±0.01	12.85±0.03	8.57±0.01
DMC	4.63±0.02	3.85±0.02	7.35±0.01		9.44±0.01
Exp.	4.62	3.85	7.37	12.9	9.45

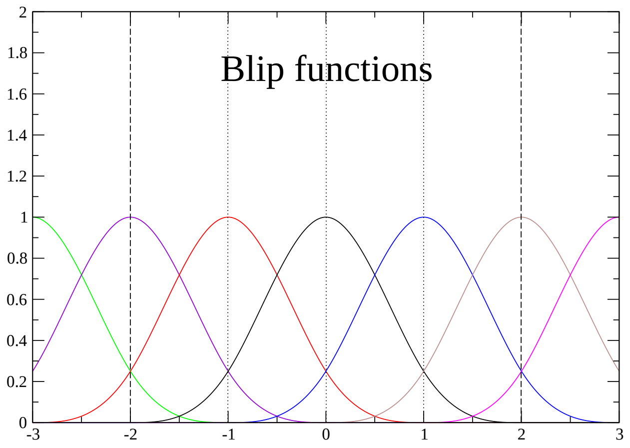
Units: eV per atom Si/Ge/C and eV per 2 atoms BN/NiO

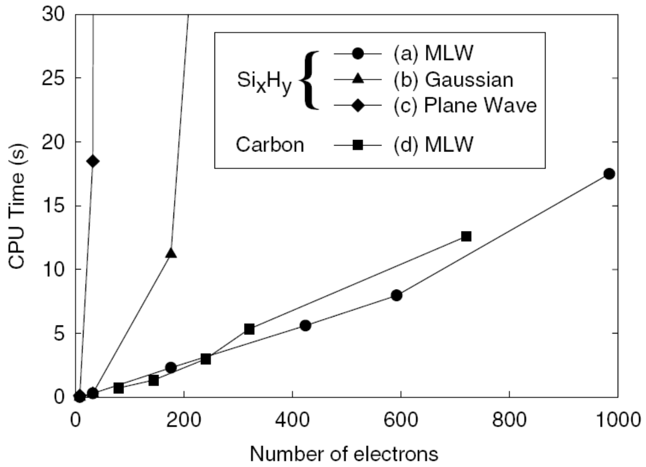
DMC is a big improvement!

Scaling with system size

How does the computational cost of DMC increase with the number of electrons?

- The rate limiting step is the *evaluation of the orbitals* in the Slater matrix (whose determinant - assuming no Jastrow - is value of wave function at a point in configuration space).
- **Moving all N electrons once** using a delocalized basis set (e.g. plane-waves) is $\mathcal{O}(N^3)$ (from N orbitals expanded in N basis functions at each of N electron positions).
- Improve to $\mathcal{O}(N^2)$ using a *localized basis set* (Gaussians, blip functions) since number of non-zero basis functions at a point does not increase with system size
- Improve to $\mathcal{O}(N)$ using *localized orbitals* as linear combinations of originals: $\phi_m(\mathbf{r}) = \sum_{n=1}^{M} c_{mn}\psi_n(\mathbf{r})$. Doesn't change energy since $\det|\phi_m(\mathbf{r}_i)| = \det|c_{mn}| \cdot \det|\psi_n(\mathbf{r}_i)|$ i.e. determinant unchanged apart from constant $\det|c_{mn}|$. *Unitary* transformation matrices give *orthogonal* orbitals; *non-unitary* transformations give *non-orthogonal ones*; the latter tend to be more localized and therefore preferred.
- **Moving all electrons enough times to get desired error bar** adds extra factor of N to scaling, as increasing system size increases sample variance, and must run calculation for longer to bring error bar down. Overall $\mathcal{O}(N^2)$ scaling - compares favourably with $\mathcal{O}(N^7)$ for e.g. CCSD(T).



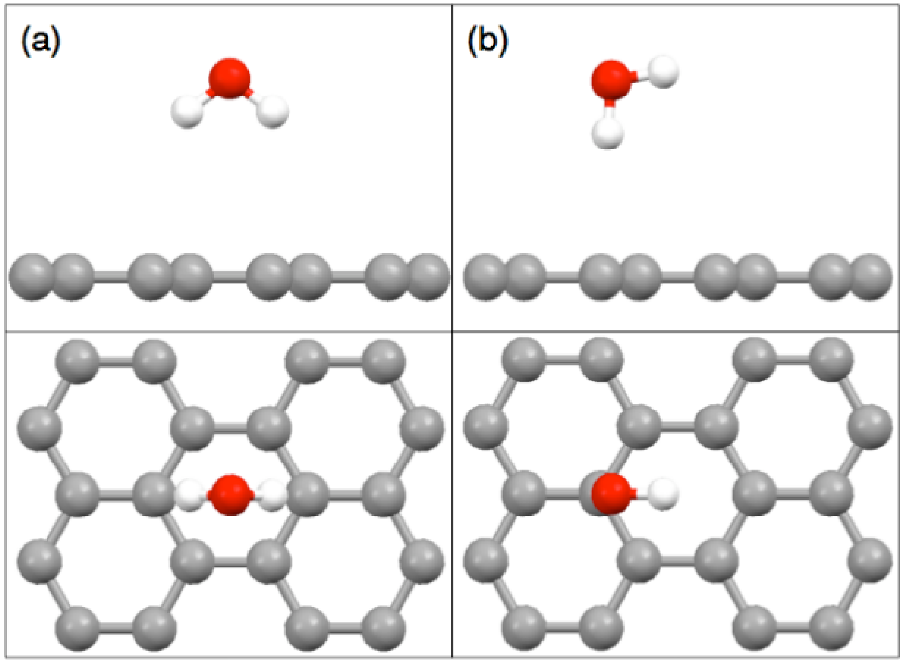


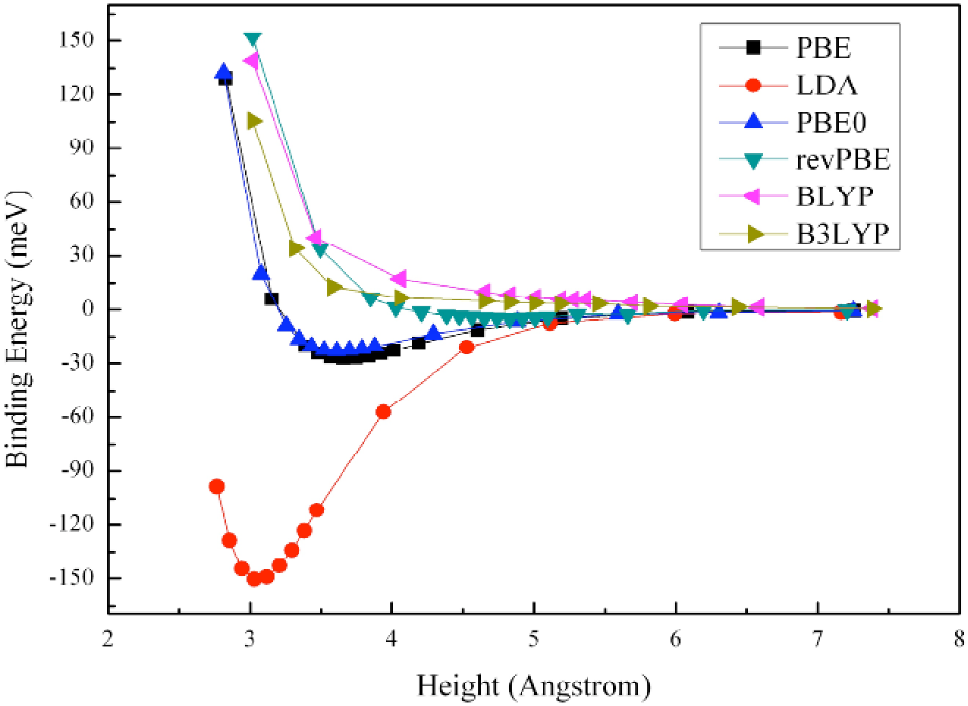
Some applications of DMC..

Weak interactions

Simple question: does a water molecule stick to a graphene surface or not?

Water interacts with materials via van der Waals dispersion and hydrogen bonding - both weak interactions which DFT has a problem with. You can basically get any answer you like depending on which exchange-correlation functional you select.



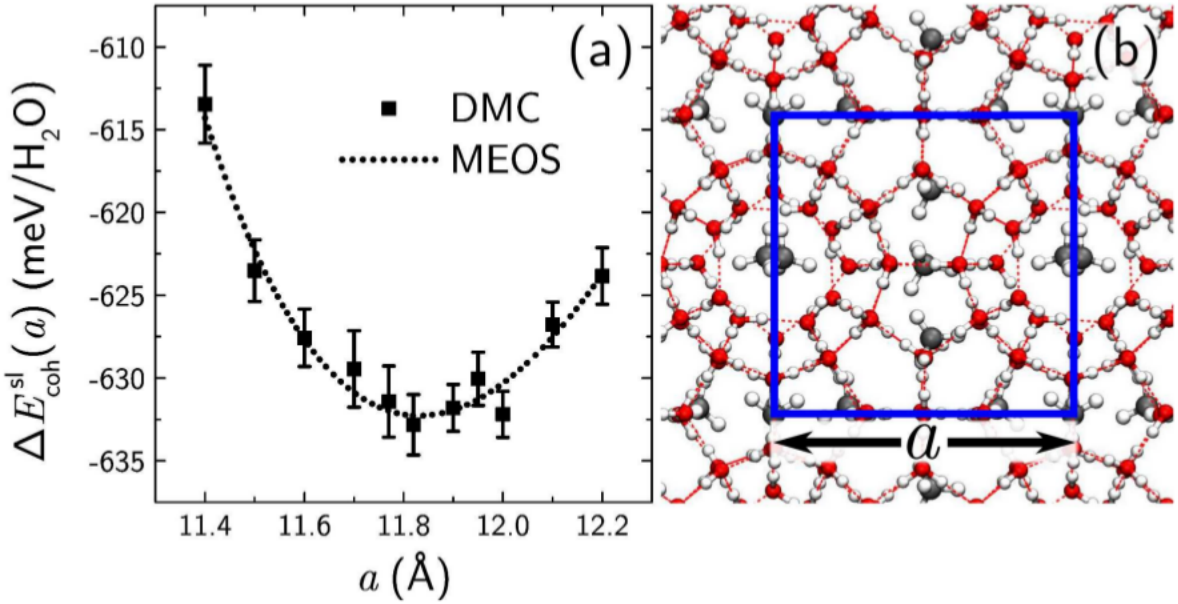


Which functional shall I choose? No real answer to this without comparing with a DMC benchmark..

The fashion nowadays would be to bring in one of the new functionals that supposedly incorporate empirical ‘van der Waals corrections’. Do these work? Again - very difficult to say without comparison with DMC benchmarks. Let’s try this with a complex material of current industrial interest..

Gas hydrates

Gas hydrates pose problems to the energy industry (their formation blocks gas lines) and they are a potential untapped energy resource (abundance of naturally occurring methane hydrate exceeding conventional gas reserves by at least an order of mangitude). Difficult for DFT since held together by hydrogen bonds and van der Waals. Our recent paper provides high-quality DMC reference data.

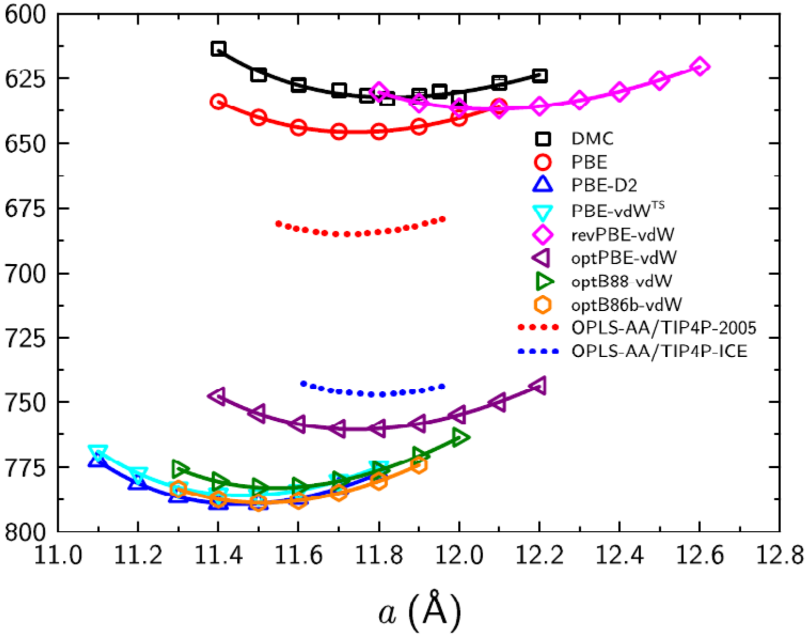


[Cox, Towler, Michaelides, Alfè, `arXiv:1402.6874` (2014)]

- Clathrate structures of gas hydrates are like ice (extended hydrogen bonded network of water molecules) but contain *cavities* - dodecahedrons and 14-sided tetrakaidecahedrons(!) in the sI structure considered here - that gas molecules like methane can occupy. Complex crystals with 178-atom simulation cells.
- I used CASINO to calculate (1) the lattice constant (11.83±0.02 Å, cf. exp. 11.821±0.001 Å), and (2) the cohesive energy for complete dissociation of the filled hydrate (into 46 water molecules and 8 methanes). In order to understand better the behaviour of DFT, we decompose this into two contributions by also calculating: (3) the cohesive energy of the empty hydrate (into 46 water molecules), and (4) the binding energy of methane to the empty hydrate..

My collaborator Stephen Cox did some DFT calculations as well.. How do they do?

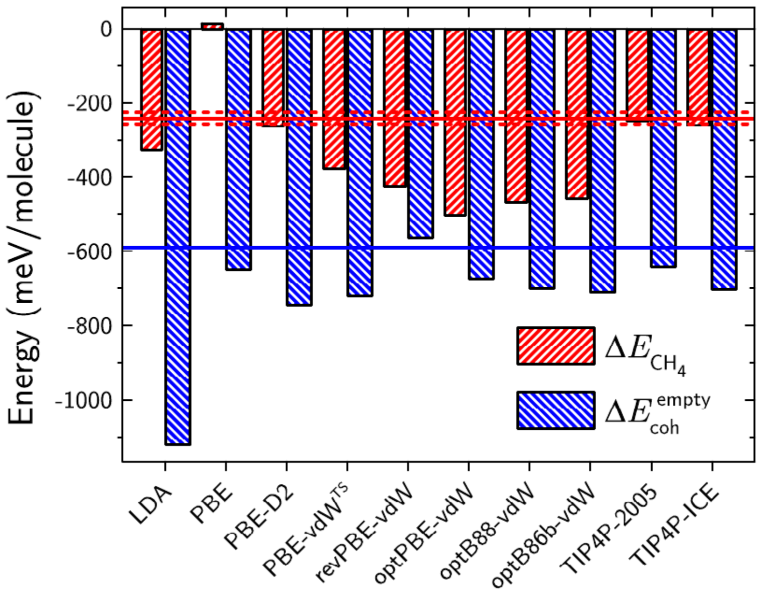
DFT vdW corrections don't work for gas hydrates



Variation of full cohesive energy with lattice constant

- With exception of PBE-D2, the vdW-corrected functionals all *overcorrect*: methane binding energies too strong by 83-130 meV/H_2O. Similar analyses can be made for the other functionals.
- All results assume H_2O/CH_4 vapour phases as reference state. More important to gas hydrate phase equilibria is relative energy of hydrate to CH_4 gas and either liquid water or ice. For case of ice I_h DMC predicts endothermic dissociation costing 155±34 meV/CH_4.
- Experimental dissociation enthalpy 188±3 meV/CH_4. DMC value reasonable - though total ΔEs not enthalpies; expect difference due to neglect of T, P and also from non-stoichiometry (methane occupancy 96% in this study - configurational entropy effects?). Alternative analysis of experimental data sets using Clapeyron equation exists suggesting dissociation enthalpy 157±6 meV/CH_4.
- PBE disastrous: predicts sI methane hydrate will explode.
- Best functional for agreement with DMC in this case is PBE-D2, closely followed by er.. LDA and PBE-vdW.

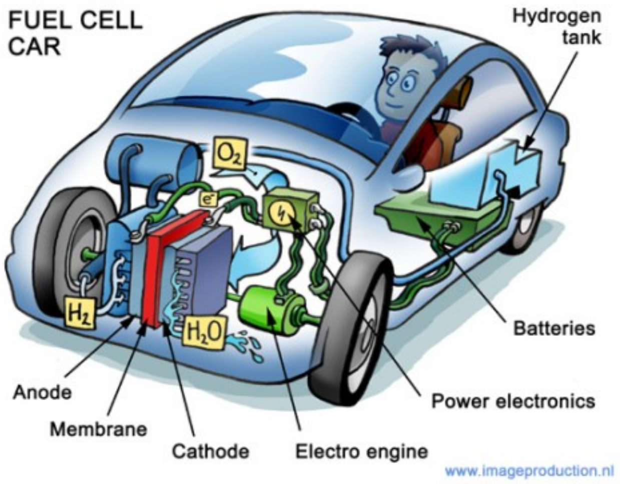
- All DFT functionals overbind the filled hydrate, most of them significantly. Only PBE gets more or less the right cohesive energy and lattice constant - even though it doesn't account for vdW interaction at all (note that correcting for it totally stuffs up the answer!)..
- If no vDW how come PBE *overbinds* at all then? VdW is an attractive force isn't it?
- Answer (see below): Lack of vDW in PBE means there is *no binding at all* between the methane and the water, but this is compensated for by an overbinding of the hydrogen-bonded water framework.
- Although overbinding of water framework is small per molecule, water and methane exist in a ratio of 23:4 in the stoichiometric hydrate - so small errors in describing water-water interactions are much amplified compared to apparently larger errors in the methane binding energy.



Binding energy of methane to the empty hydrate (red) and formation energy of empty hydrate (blue). Horizontal lines are DMC.

Hydrogen storage

Desirable to replace petrol as a fuel with portable form of hydrogen (since plenty of it, high energy density, and used efficiently by fuel cells). Use materials-based H storage - trade some of high energy/mass performance to improve low energy/volume performance.



- Requires very particular material with desorption enthalpy ΔH^0 in precise 20 kJ/mol range (to allow recharging under moderate pressure and desorption under moderate temp). Difficult to achieve since chemical bounds normally too strong and hydrogen bonds usually too weak..
- *Metal hydrides* (where the metal is e.g. Li, Na, Mg, Al) good candidates: high H content, thermodynamically stable relative to physisorption materials.
- However most metal hydrides bind with H very strongly - high T required to release it ($\longrightarrow$ low equilibrium vapour pressure). Can improve this by using alloys which consists of 'strong' hydride and 'weak' one e.g. $LiNH_2$, $LiBH_4$ and $NaBH_4$. These are able to form weaker bonds, thereby requiring less energy input to release stored hydrogen. Also: using *nanoscale* particles could help: surface energy then additional lever to adjust ΔH^0.

Basic questions

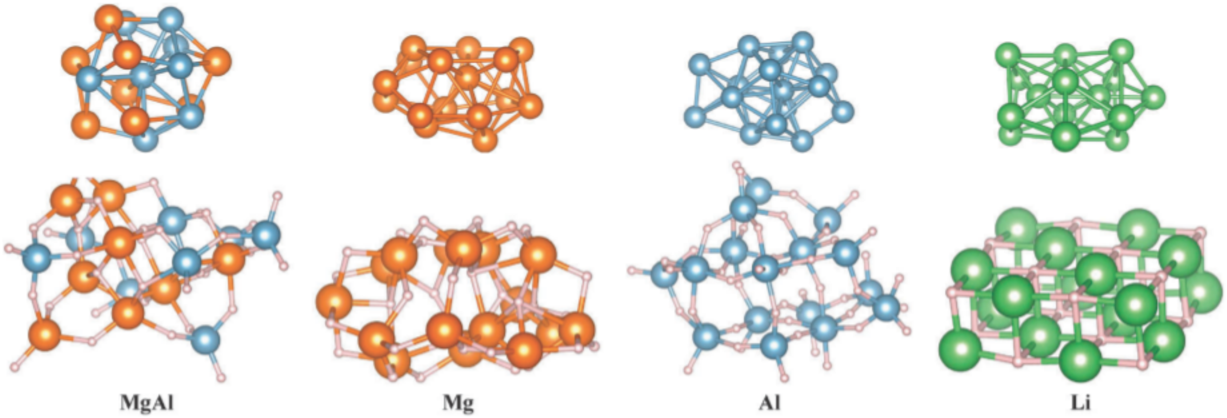
(1) To what extent can we use size and composition to control ΔH^0 in metal hydrides?
(2) How much can we rely on DFT in such cases?

'*Tuning metal hydride thermodynamics via size + composition: Li-H, Mg-H, Al-H, and Mg-Al-H nanoclusters for H storage*' Wagner *et al.* (2012)

Hydrogen storage

Wagner *et al.* used DMC to compute change in energy in the reaction $(MH_m)_n \longrightarrow M_n + \frac{mn}{2}H_2$ for M = Li, Mg, Al, and two alloys of MgAl. Motivation: MgH_2 is too stable, but AlH_3 is too unstable - attempt to 'interpolate between them'.

DMC shows that mixed Mg-Al nanoclusters are predicted to have intermediate stability, and that their size composition can be tuned to obtain H_2 desorption thermodynamics within the desired range for onboard H storage.



Calculations

- Generate minimum energy structures of metal hydride and pure metal clusters with number of metal atoms up to 20 (c. 1 nm regime, where most atoms reside at the surface). They use something like Pickard/Needs random structure searching.
- Evaluate hydrogen desorption energies ΔE with both DFT and DMC (good approximation to enthalpy ΔH^0 since standard pressure v. small compared to internal energy in these nanostructures).
- Do some test calculations with CCSD(T) extrapolated to complete basis set limit for the small clusters where this is feasible to check it agrees with DMC (it does).
- Calculate zero-point energy in the usual way when comparing to experimental numbers.

Hydrogen storage

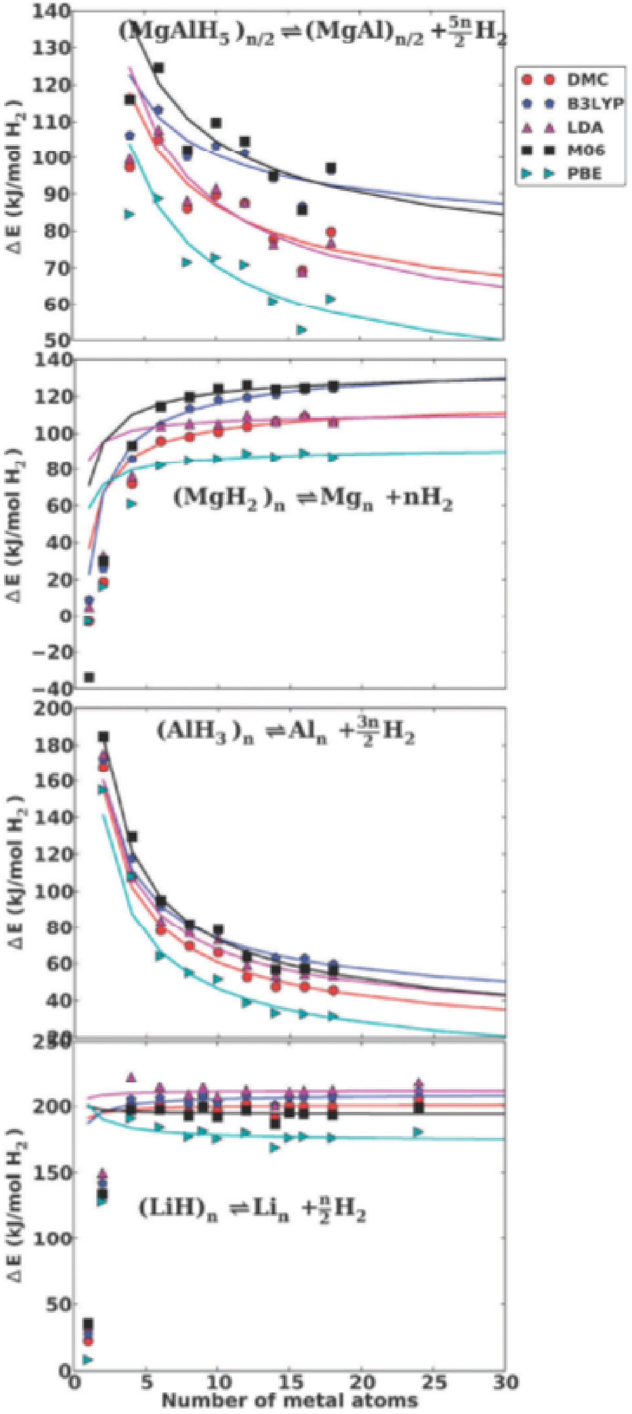
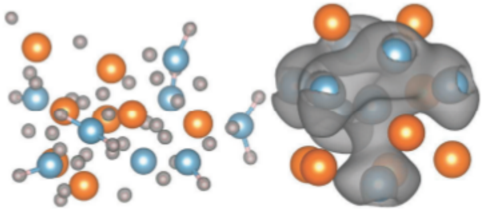
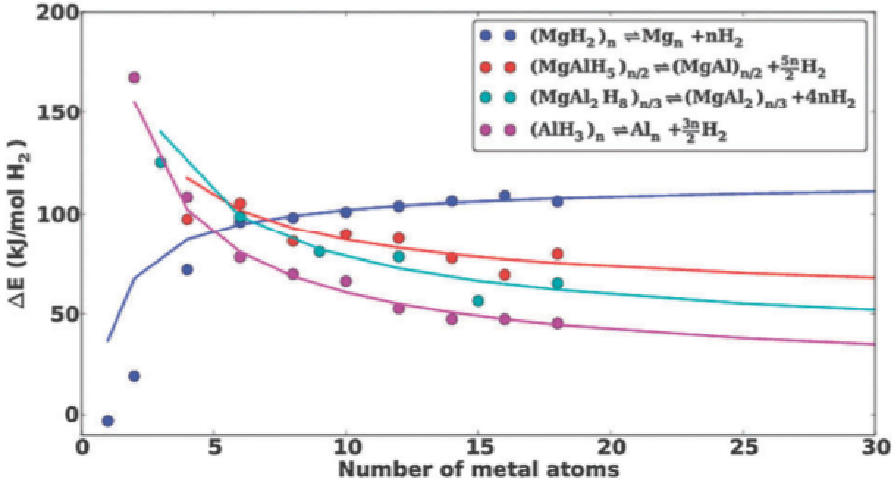


Fig. 3 The trends of the reaction energy for various methods, alon with fits to $\Delta E(n) = \alpha/n^{2/3} + \beta$ (solid lines). The stochastic errors c the DMC data are smaller than the symbol sizes. The CCSD(T) result are indistinguishable from the DMC results on these scales.

- DFT results all over the place: functional-dependent spread of 30-40 kJ/mol. Not good enough to predict what kind of alloy/cluster will have a ΔH in some 20kJ/mol range.
- Generally, hydride nanoparticles are ionic (H acts as charge acceptor) but pure metal clusters increase metallic character with size. DFT not capable of reliably calculating difference between such qualititatively different electronic states.

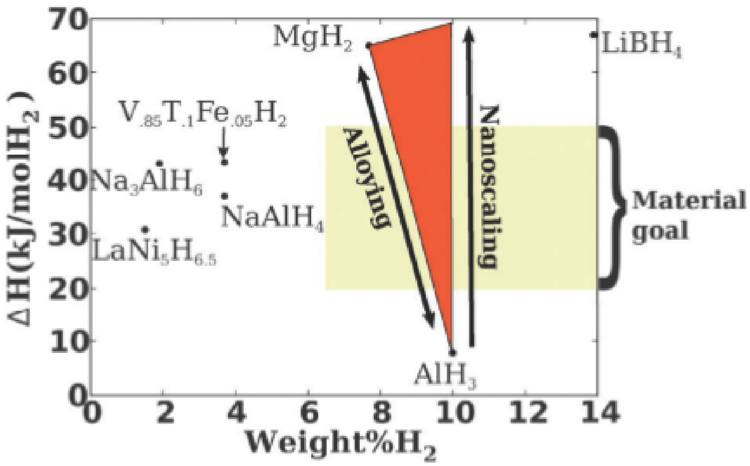


- 'More sophisticated' functionals (M06, B3LYP) no better than LDA and PBE.
- Idea of 'interpolation' really does work:



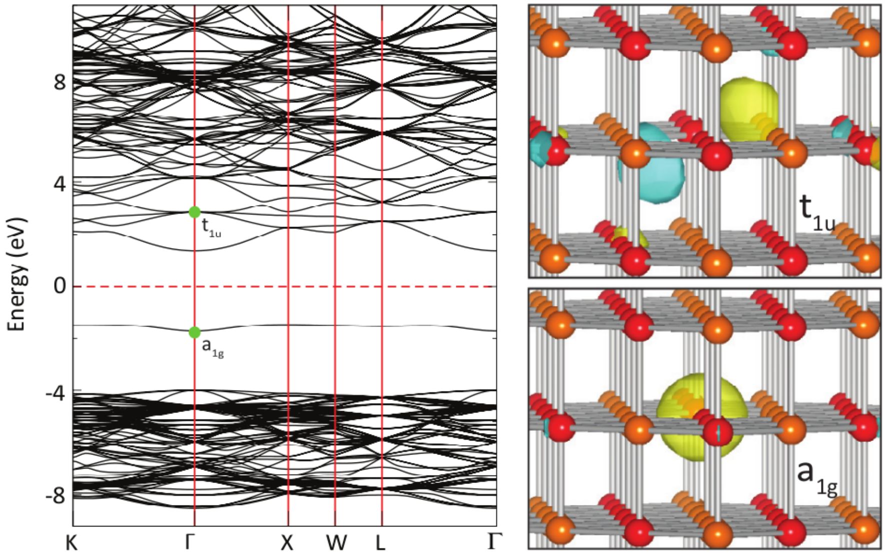
Hydrogen storage: conclusions

- High-accuracy DMC scaling curves for the hydrogen desorption energy of several different intermetallic alloys were computed as a function of nanoparticle size. Strong size dependence in the scaling of ΔE as the nanoparticle size becomes close to 1 nm. Specific predictions for nanoparticle sizes with ΔE in the correct range were made (see paper). Occurs for MgAl and Al clusters only, not Mg or Li.
- Similar predictions with DFT depend hugely on the chosen functional, and are simply not reliable.
- The computational cost of the several hundred required DMC calculations was not prohibitive (about the same as the relaxation of the atomic coordinates in DFT). Future calculations should therefore use DMC energetics to correct the DFT ones.
- Alloying can significantly alter the size range in which the nanoparticles have the desired desorption energies. The alloys are generally *stabilized* by nanoscale effects.
- So here we have a suggestion for a tunable hydrogen storage system that uses alloys of Mg and Al. Either the alloy composition or particle size can be tuned to optimize the ease of making and storing the nanoparticles, while the other variable can be tuned to obtain the correct desorption energy. Kinetics at the nanoscale will likely be much improved over the bulk systems.



Defect energetics

'*Point-defect optical transitions and thermal ionization energies from quantum Monte Carlo methods: application to the F-center defect in MgO*, Ertekin, Wagner, Grossman, *Phys. Rev. B* **87**, 155210 (2013).



DFT-PBE band structure for 64-atom MgO cell containing single oxygen vacancy. Introduces localized midgap defect level of symmetry a_{1g}

- Application of QMC to F-center defect (oxygen vacancy) in MgO: defect formation energies, thermal ionization levels, optical ionization energies.
- Experimental properties ambiguous. Different charge states apparently have near-identical optical absorption energies. GW and now DMC disagree. Time for reassessment of experiment?
- DFT band gap severely underestimated - problem for midgap defect states, defect energetics, defect-induced optical adsorption/emission energies!
- DMC treatment of pure MgO: calculate ground state E_0, Γ-point optically excited state $E_{\Gamma\rightarrow\Gamma}$, and the positively and negatively charged states E_+ and E_-. Then ionization potential $IP = E_0 - E_+$, electron affinity $EA = E_- - E_0$, quasiparticle gap $QP = EA - IP$, optical gap $E_{\Gamma\rightarrow\Gamma} - E_0$. Good agreement with experiment where possible to compare; DFT not.

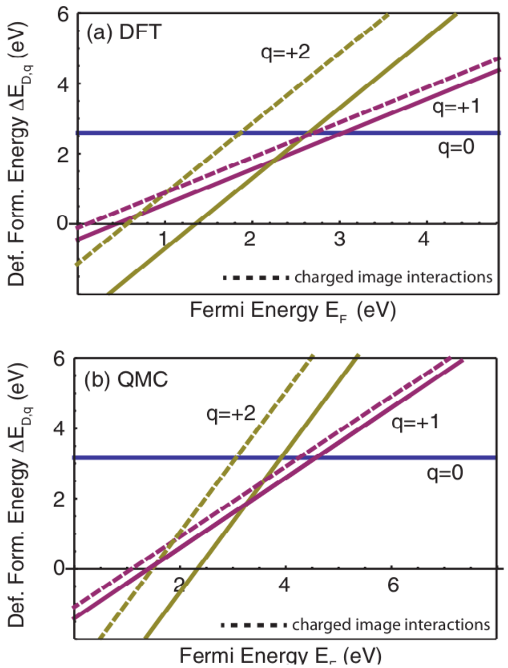
Compute defect formation energies:

$$\boxed{\Delta E_{D,q} = (E_{D,q} - E_{\rm perf}) - \textstyle\sum_i n_i \mu_i + q(E_V + E_F)}$$

Here $E_{D,q}$ is the (computed) total energy of the supercell containing a defect D in the charge state q, and $E_{\rm perf}$ is the (computed) total energy of the perfect supercell. The n_i is the number of atoms of species i added to create the defect (can be negative). The μ_i are the set of chemical potentials to represent different environmental conditions. E_V is energy of valence band maximum (ionization potential in DMC), and E_F is the Fermi energy referenced to E_V so that $0 \leq E_F \leq E_g$ where E_g is the band gap.

Charged defects introduce electrostatic image interactions between neighbouring supercells which manifest as finite size errors. These can be estimated using an extrapolation approach. For simplicity the authors use the DFT extrapolation; even though expensive this can also be done in QMC in principle, and probably should be since differences in electron localization and screening in the two approaches should lead to different answers..

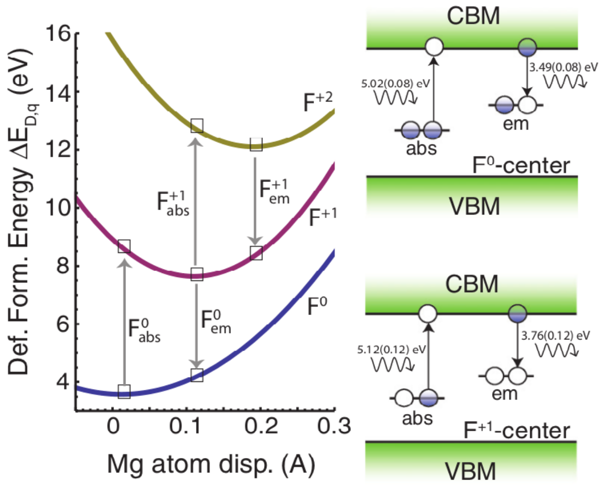
Defect energetics



- *Thermal ionization energies* correspond to the Fermi energies at which the energetically most-favoured charge state of the defect changes.
- Creation of an F^0 centre results in formation of filled midgap defect level. Very little lattice relaxation on removal of O.
- When electron is removed to form F^{+1} centre, there is large lattice relaxation - positive Mg ions move outward away from and negative O ions move inward towards, the positively charged vacancy in conjunction with a 0.55 eV drop in energy (DFT). Further ionization to form F^{+2} centre gives further lattice relaxation and energy recovery of 1.18 eV.
- Defect formation energies and thermal ionization energies plotted on left as function of Fermi energy. Note domain of Fermi energy (length of x-axis) determined by the band gap of the method in question (which is much better for DMC).
- DMC modifies somewhat the absolute values of the defect formation energies (by 0.5eV for F^0), but maintains thermal ionization levels near midgap. DMC shows that DFT underestimates formation energies in the case of occupied midgap levels.

- QMC description of optical ionization energies (which correspond to vertical Franck-Condon transitions).
- Optical transition occurs when photon absorbed or emitted by defect - takes place essentially instantaneously at fixed atomic coordinates. Therefore compute these transition using the relaxed coords of the *initial state*. Implies difference between absorption and emission.
- DMC absorption energies in excellent agreement with experiment and GW calculations. DMC emission energies agree with GW, but disagree with experiment. GW authors suggest experimental people have misinterpreted their results (something to do with electrons in the defect level recombine with holes in the valence band). Our QMC people agree with this.

Application of QMC to point defects still relatively new field, but lots of fascinating possibilities!



	F^0_{abs}	F^0_{em}	F^{+1}_{abs}	F^{+1}_{em}
QMC	5.0(1)	3.8(1)	5.1(1)	3.5(1)
GW[8]	4.95	3.6	4.92	3.4
Exp	5.00	3.1-3.2	4.95	2.3-2.4

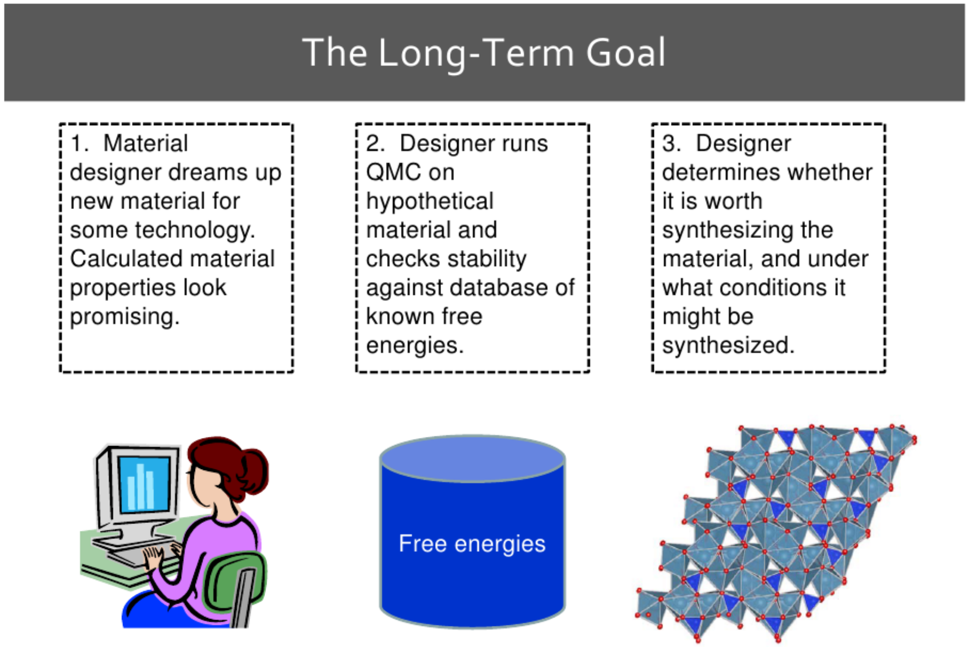
Databases/high-througput QMC

Various efforts are ongoing to create standard benchmarks and databases of DMC results for large numbers of material with different types of binding.

Requires development of consistent, automated procedures to achieve high throughput. See, for example:

‘*Quantum Monte Carlo applied to solids*’, Shulenburger, Mattsson,
Phys. Rev. B **88**, 245117 (2013)

‘*Quantum Monte Carlo for materials design*, Mueller,
`http://vallico.net/talk_archive/mueller_tti2013.pdf`



The Long-Term Goal

1. Material designer dreams up new material for some technology. Calculated material properties look promising.

2. Designer runs QMC on hypothetical material and checks stability against database of known free energies.

3. Designer determines whether it is worth synthesizing the material, and under what conditions it might be synthesized.

“By 2016-ish, we should be able to calculate QMC energies for every known inorganic material on a single supercomputer in about a week (roughly).” [Tim Mueller, Vallico Sotto, August 2013]

Strongly correlated materials

From Wikipedia, the free encyclopedia

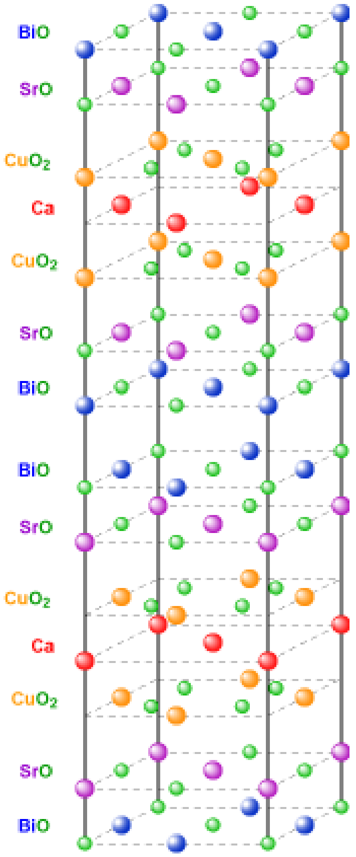
"Strongly correlated materials are a wide class of electronic materials that show unusual (often technologically useful) electronic and magnetic properties, such as metal-insulator transitions or half-metallicity. The essential feature that defines these materials is that the behavior of their electrons cannot be described effectively in terms of non-interacting entities.Theoretical models of the electronic structure of strongly correlated materials must include electronic correlation to be accurate.

Many transition metal oxides belong into this class which may be subdivided according to their behavior, e.g. high-T$_c$, spintronic materials, Mott insulators, spin Peierls materials, heavy fermion materials, quasi-low-dimensional materials, etc. The single most intensively studied effect is probably high-temperature superconductivity in doped cuprates, e.g. $La_{2-x}Sr_xCuO_4$. Other ordering or magnetic phenomena and temperature-induced phase transitions in many transition-metal oxides are also gathered under the term 'strongly correlated materials'.

Typically, strongly correlated materials have *incompletely filled d- or f-electron shells* with narrow energy bands. One can no longer consider any electron in the material as being in a 'sea' of the averaged motion of the others (also known as mean field theory). Each single electron has a complex influence on its neighbors.

The term strong correlation refers to behavior of electrons in solids that is not well-described (often not even in a qualitatively correct manner) by simple one-electron theories such as the local-density approximation (LDA) of density-functional theory or Hartree-Fock theory. For instance, the seemingly simple material NiO has a partially filled $3d$-band (the Ni atom has 8 of 10 possible $3d$-electrons) and therefore would be expected to be a good conductor. However, strong Coulomb repulsion (a correlation effect) between d-electrons makes NiO instead a wide-band gap insulator. Thus, strongly correlated materials have electronic structures that are neither simply free-electron-like nor completely ionic, but a mixture of both.

Extensions to the LDA (LDA+U, GGA, SIC, GW, etc.) as well as simplified models Hamiltonians (e.g. Hubbard-like models) have been proposed and developed in order to describe phenomena that are due to strong electron correlation. Among them, Dynamical Mean Field Theory successfully captures the main features of correlated materials. Schemes that use both LDA and DMFT explain many experimental results in the field of correlated electrons."

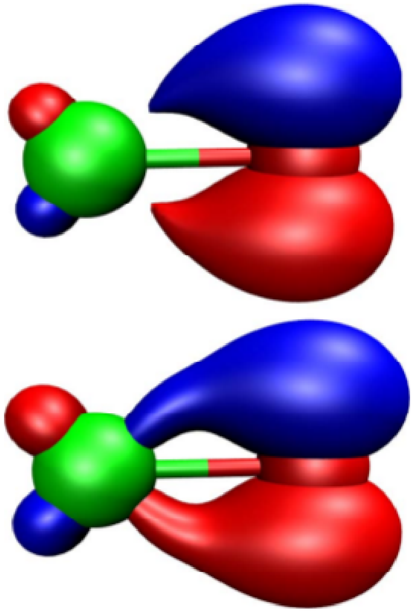


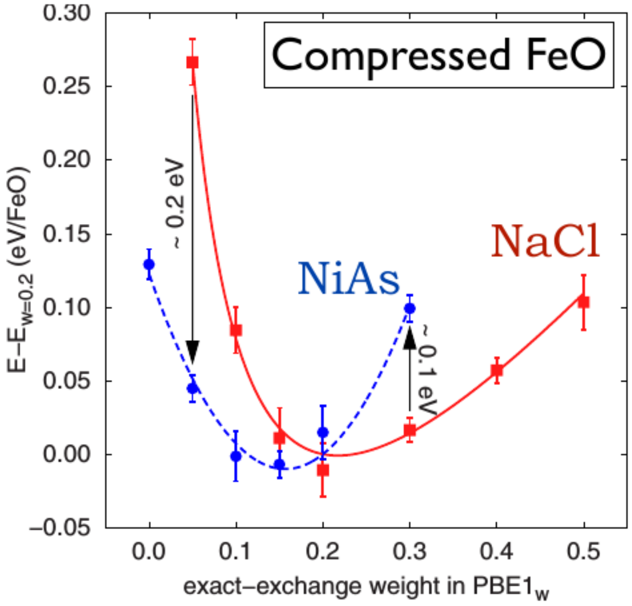
The perovskite structure of BSCCO, a high-temperature superconductor and a strongly correlated material

NB: must understand what the above means when translated to our language - not the same thing. In general 'strongly correlated electron physicists' misunderstand what we do. QMC actually very promising approach to accurately computing everything required with no parameters - a fact not generally appreciated..

Optimizing the nodal surface in strongly-correlated system

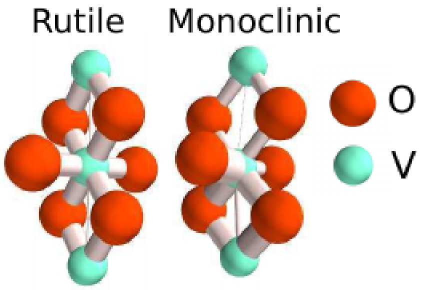
Because these materials are quite complex, need to pay more attention to getting the nodal surface right. An excellent practical way to do this - exploiting the variational nature of the DMC method - is to treat the percentage of HF exchange in a hybrid DFT functional such as B3LYP as a variable parameter (effectively varying the amount of *d*-*p* hybridization). (Could also optimize orbitals directly; this is more difficult but not impossible. Multireference trial functions could also be useful in some circumstances.). This is, not usually thought to be necessary for 'normal' compounds without transition elements where the nodal surface is usually 'good enough'.





Above left is an isosurface of the *d*-*p* hybridization orbital for the TiO molecule, calculated in Hartree-Fock (above) and DFT-B3LYP (below). Oxygen atom in red on the right. Titanium in green on the left. UHF solution overionizes the *p* orbital and causes large fixed-node errors. See Wagner, *J. Phys.: Cond. Mat.* **19**, 343201 (2007). Above right is graph showing variation in DMC energy as the nodal surface is varied with the exchange weight for two structures (NiAs and NaCl) of FeO.

Mechanism of vanadium dioxide (VO_2) metal-insulator transition



VO_2 undergoes metal-insulator transition at T=340 K, with accompanying decrease in conductivity of more than 4 orders of magnitude and change in structure from rutile (high T, V at centre of O octahedra, equidistant V) to monoclinic (low T, zigzag of V dimers).

Zheng and Wagner, arXiv:1310.1066 (Oct 2013)

Long-standing debate for 50 years whether transition is primarily caused by structural change that doubles the unit cell (Peierls distortion) or by 'strong correlation effects' that drive the system to become insulating.

Predictions of traditional theoretical methods

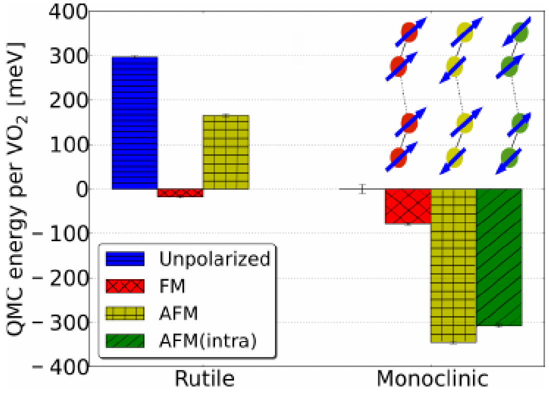
- DFT(LDA), DFT(GGA): monoclinic VO_2 metallic (wrong)
- DFT(hybrid functional): rutile metallic, monoclinic insulating (yes!); rutile lower in energy (wrong).
- DFT+U: monoclinic VO_2 insulating (yes!); rutile VO_2 insulating (wrong); incorrect magnetic GS for monoclinic VO_2 (wrong); depends on parameter; no total energy.
- cluster DMFT: correct gaps, but depends on parameters; no total energy.
- GW: correct gap; does not address magnetic properties; no total energy.

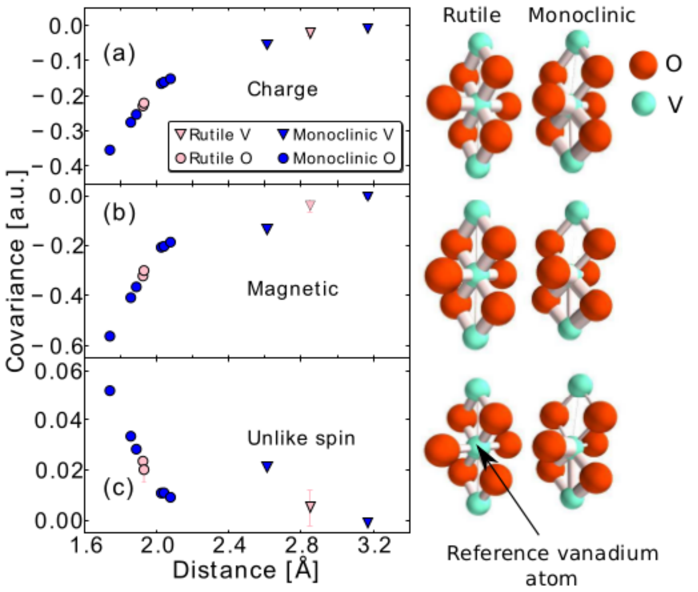
Predictions of DMC

Zheng and Wagner's DMC calculations (using PBE, PBE0, UHF trial wave functions from CRYSTAL09): correct low energy monoclinic structure for VO_2; correct energy gap and characterization of magnetic states for both phases, all in agreement with experiment (yes!)

What is the mechanism of the transition in VO_2 in DMC?

Structural distortion changes orbital hybridization and results in strong charge localization within V dimers - rearranges crystalline orbitals near Fermi surface, leading to strong magneto-structural coupling. In particular, get strong intra-dimer antiferromagnetic coupling in monoclinic VO_2 which drives system to a state made of spin-singlet dimers.





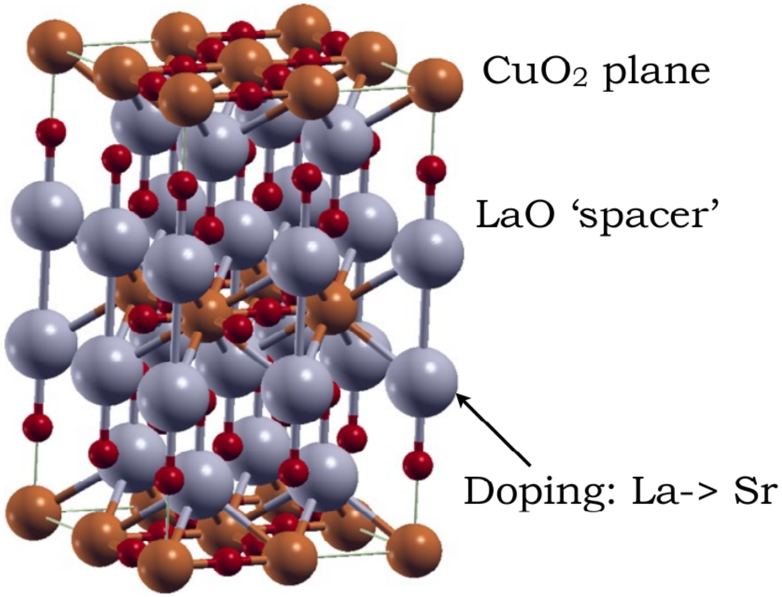
Clever bit: Calculate atomic charges $\langle n_i \rangle$, spins $\langle n_i^{\uparrow} \rangle$ and $\langle n_i^{\downarrow} \rangle$, and magnetic moments $\langle n_i^{\uparrow} - n_i^{\downarrow} \rangle$ (by counting electrons of a given spin in Voronoi polyhedra around each nucleus). Calculate fluctuations such as $\langle n_i^{\uparrow} - \langle n_i^{\uparrow} \rangle \rangle^2$ (zero in the atomic limit; large for metallic systems), and spatial correlations through covariances such as $\langle O_i O_j \rangle - \langle O_i \rangle \langle O_j \rangle$. (Can also associate such quantities with U and hopping t).

Intersite charge, magnetic moment, and unlike-spin covariance plotted on left. All decay with distance. Because of change in interatomic distances in monoclinic structure, intra-dimer V-V covariance 2× that of rutile, inter-dimer V-V almost zero (dramatic decrease in charge mobility $\longrightarrow$ insulator!). Magneto-structural coupling associated with substantial enhancement of intra-dimer charge fluctuations at expense of inter-dimer charge fluctuations. Monoclinic VO_2 forms weakly coupled spin-singlet V-V dimers rather than long-range AFM order (confirmed by intersite magnetic covariance).

MIT in VO_2 more complex than Peierls distortion (which just opens gap near Fermi surface). Strong correlations resulting in different magnetic couplings in rutile/monoclinic phases important. Both mechanisms will drive structural distortion, but amount of energy reduction due to intra-dimer singlet formation of same order as Peierls distortion with no magnetic ordering. Electron correlations provide crucial role in lowering E and opening large gap.

DMC provides high accuracy with no parameters.. can solve 50-year old problems. Good!

High-T$_c$ cuprates with DMC



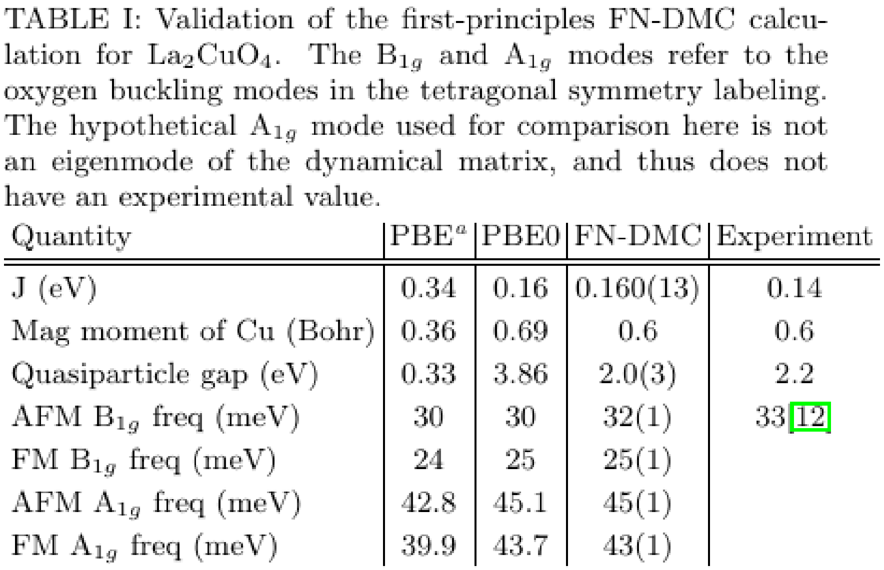


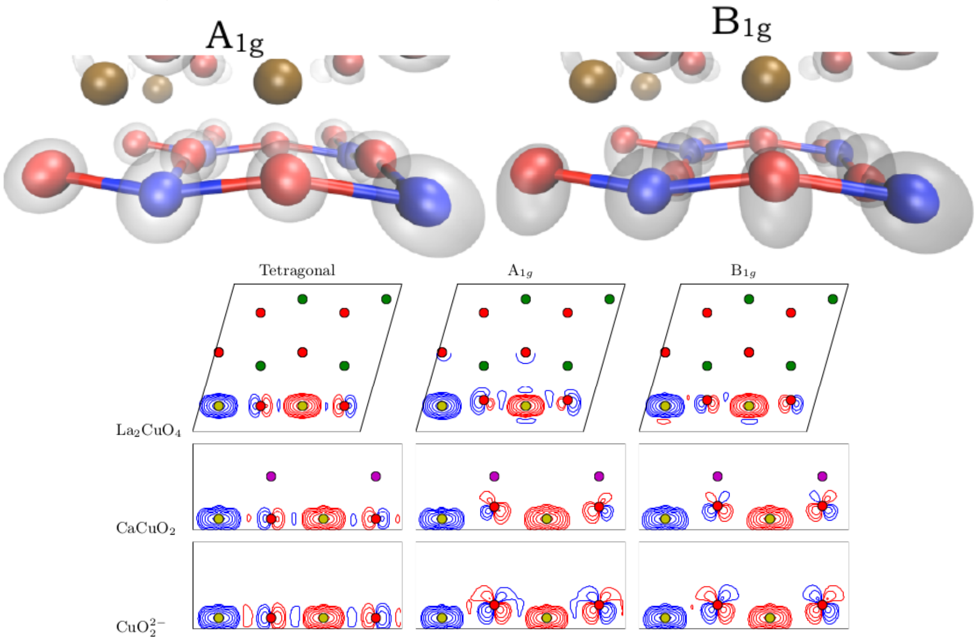
TABLE I: Validation of the first-principles FN-DMC calculation for La_2CuO_4. The B_{1g} and A_{1g} modes refer to the oxygen buckling modes in the tetragonal symmetry labeling. The hypothetical A_{1g} mode used for comparison here is not an eigenmode of the dynamical matrix, and thus does not have an experimental value.

Quantity	PBE^a	PBE0	FN-DMC	Experiment
J (eV)	0.34	0.16	0.160(13)	0.14
Mag moment of Cu (Bohr)	0.36	0.69	0.6	0.6
Quasiparticle gap (eV)	0.33	3.86	2.0(3)	2.2
AFM B_{1g} freq (meV)	30	30	32(1)	33[12]
FM B_{1g} freq (meV)	24	25	25(1)	
AFM A_{1g} freq (meV)	42.8	45.1	45(1)	
FM A_{1g} freq (meV)	39.9	43.7	43(1)	

Proper understanding of these materials still lacking after decades of research; clear that spin, charge, and lattice degrees of freedom are active in the phase space near the superconducting state, but precise roles still controversial. Difficult to probe experimentally and theoretically.

Wagner and Abbamonte did DMC calculations of undoped La_2CuO_4, $CaCuO_4$, and a hypothetical unsupported CuO_2^{2-} plane. Very accurate results *with no parameters* for all basic properties: spin coupling J, correlated gap, Cu magnetic moment, and s-wave A_{1g} and d-wave B_{1g} phonon frequencies.

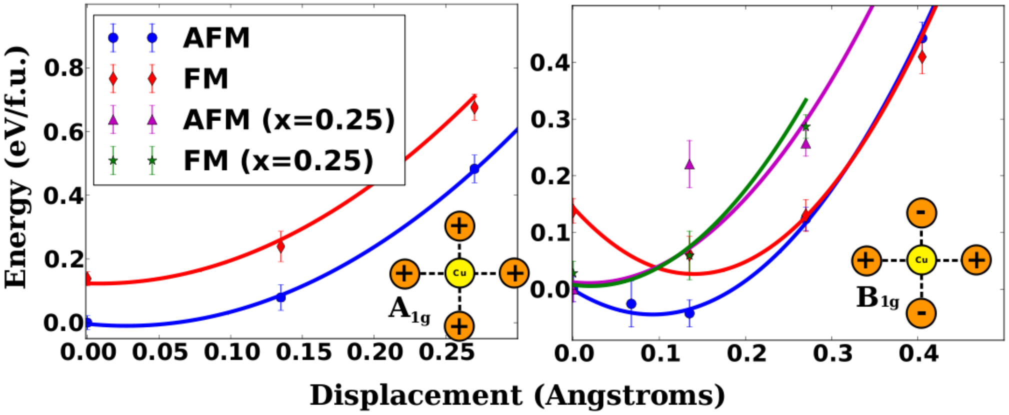
arXiv:1402.4680 (2014)

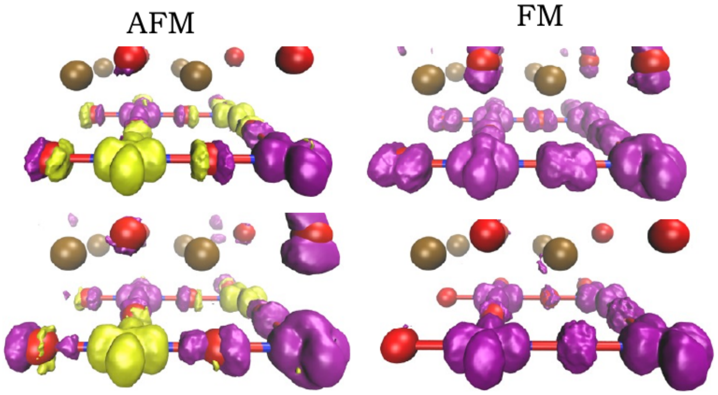


Superconductivity in cuprates with QMC

Experimentally B_{1g} mode shifts and broadens on entering the superconducting state, while A_{1g} does not. Wagner-Abbamonte DMC showed modes differ through interaction with interlayer - comparing La_2CuO_4 (apical O), $CaCuO_4$ (no apical O), and the pure CuO_2^{2-} plane (no interlayer at all). In A_{1g} mode interlayer prevents magneto-elastic coupling, mainly by shifting phonon frequency up. Plot bottom right of previous slide shows Cu-O bonding/superexchange clearly affected by interlayer once phonon mode is activated. Thus DMC results show magneto-elastic coupling highly dependent on supposedly inert plane layers - may help explain why different cuprates have very different T_c:

Doping





Some lattice degrees of freedom depend strongly on the magnetic state!

However - spin lattice coupling removed with 25% doping.

This is because hole introduced by doping sits on *oxygen* (which mediates the AFM ‘superexchange’ interaction). Upper valence band mainly O states for later 3d oxides (Ni, Cu, etc.).

[See my previous ESDG talks and various papers on manganites, $KCuF_3$, Li-doped NiO, La_2CuO_4 etc.. This ancient one from 16 years ago is v. interesting: `www.tcm.phy.cam.ac.uk/∼mdt26/tmo/scm_talk.html`. Glad someone has finally done what I suggested! I’ve been far too lazy..]

“*Despite all these years, the mechanism of high-Tc superconductivity is still highly controversial, mostly due to the lack of exact theoretical computations on such strongly interacting electron systems*” [Wikipedia, ‘High-temperature superconductivity’, 2014] Is that really all they need? Cool..

Quantum Monte Carlo in 2014

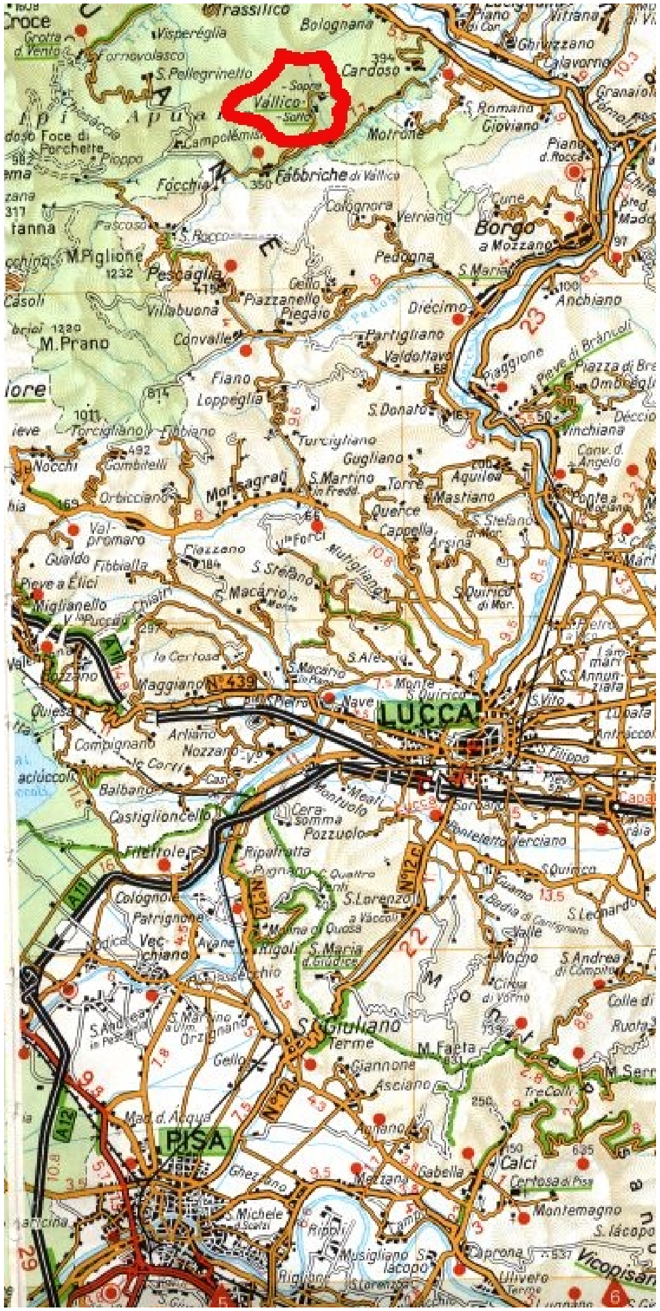
- Quantum Monte Carlo is in robust health, with groups from all over the world engaged in pushing the boundaries of what can be done with this technique.
- Computers are now fast enough that the application of QMC to proper, genuine scientific and technical problems is becoming routine.
- For many of these problems, QMC is the *only* known method which can normally be relied on to get the answer right without an unreasonable amount of computing effort.
- Much work remains to be done - in code development as much as in running applications. Get in touch if you're interested..

Engage with the QMC community:

http://vallico.net/casinoqmc/

http://vallico.net/casino-forum/

Or just come and visit..



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