The Towler Institute

2013 Conference Programme

Quantum Monte Carlo in the Apuan Alps VIII

Vallico Sotto, Tuscany, Italy : 27th July - 3rd August 2013

www.vallico.net/tti/tti.html

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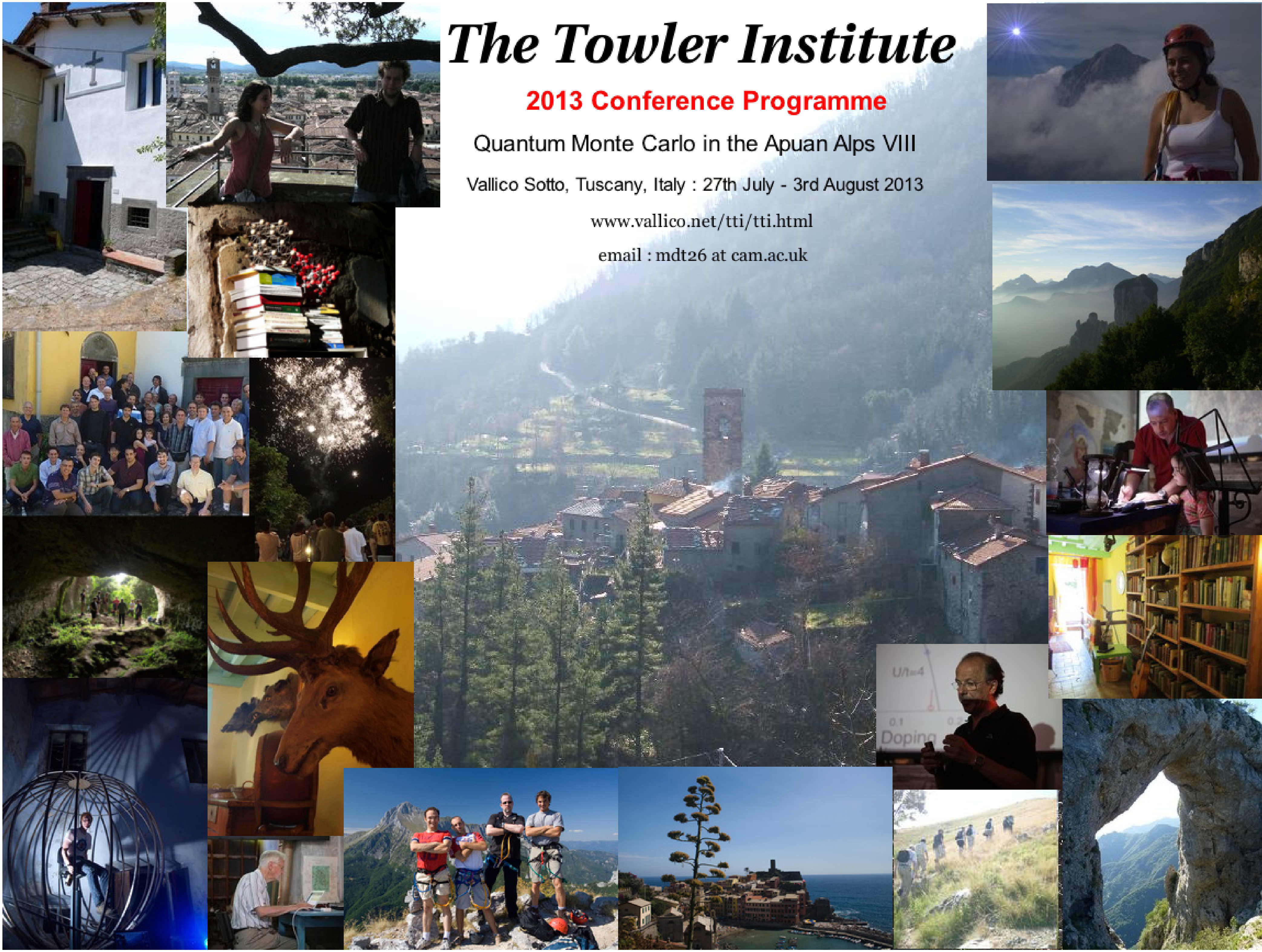
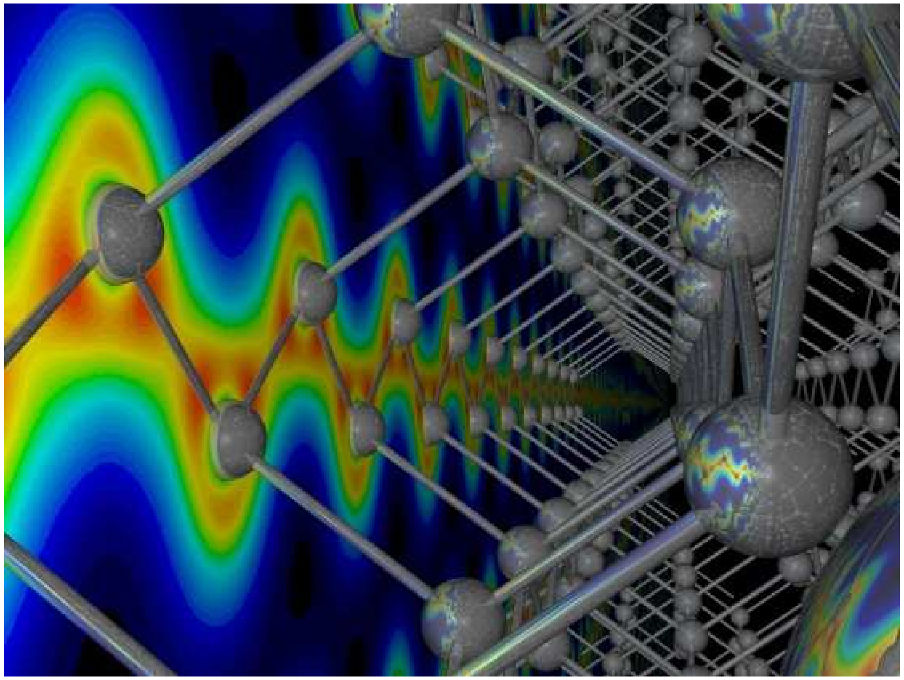


Some thoughts about QMC and molecular dynamics

Electronic Structure Discussion Group, November 2012



Mike Towler

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QMC web page: `www.tcm.phy.cam.ac.uk/∼mdt26/casino.html`

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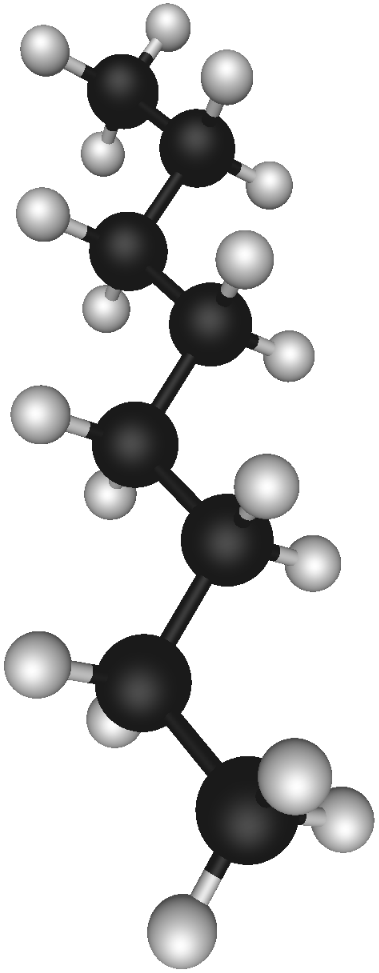
What am I going to talk about

Quantum Monte Carlo calculations normally done with *static nuclei*.

Hardly surprising since DMC is c. 1000 times more expensive than DFT, and in all fairness, even DFT calculations are too expensive to do *really* interesting things with fully *ab initio* molecular dynamics.

Nevertheless, real nuclei do move. Is there any scope whatever for this in DMC?



Implemented in CASINO:

- Grossman-Mitas molecular dynamics.
  What is this and is it of any use?

Selected other things in the literature

- Ceperley - DMC with quantum nuclei
- Coupled electron-ion Monte Carlo (CEIMC)
- Attaccalite and Sorella method

Did Mike have any ideas?

- Maybe. Maybe not.

Can QMC help with simpler models?

- Parametrized force fields? GAP potentials?, LOTF?

Time dependence: the time-dependent Schrödinger equation

Solve $i\hbar\frac{\partial}{\partial t}\Psi(x,t) = H\Psi(x,t)$ by separation of variables to give the following particular solutions (which have the counterintuitive property of predicting time-independent observables):

$$\Psi(x,t) = \phi_E(x)e^{-\frac{i}{\hbar}Et} \qquad |\Psi(x,t)|^2 = |\phi_E(x)|^2$$

Where has the time gone? It is restored to us by a general solution to the TDSE - an arbitrary superposition of the particular solutions:

$$\begin{aligned} \Psi(x,t) &= \sum_{n=1}^{\infty} a_n\phi_n(x)e^{-\frac{i}{\hbar}E_n t} && \text{(discrete spectrum)} \\ &= \int_0^{\infty} a(E)\phi_E(x)e^{-\frac{i}{\hbar}Et}\,\mathrm{d}E && \text{(continuous spectrum)} \end{aligned}$$

Quite generally, a *wave packet* - a superposition of states having different energies - is required in order to have a time-dependence in the probability density and in other observable quantities, such as the average position or momentum of a particle. Simplest example: a linear combination of just two particular solutions $\Psi(x,t) = a\phi_E(x)e^{-\frac{i}{\hbar}Et} + b\phi_{E'}(x)e^{-\frac{i}{\hbar}E't}$. The probability density is given by:

$$|\Psi(x,t)|^2 = |a|^2|\phi_E(x)|^2 + |b|^2|\Psi_{E'}(x)|^2 + 2\mathrm{Re}\left\{a^*b\phi_E^*(x)\phi_{E'}(x)\mathrm{e}^{-i\frac{(E'-E)t}{\hbar}}\right\}$$

All the time-dependence is contained in the interference term.

Time dependence: the approximations

TDSE generally expensive to solve directly (exponential scaling) - simplification required. Expand total Ψ in complete set of solutions of *time-independent* SE for all possible nuclear configurations R:

$$\Psi(\mathbf{r},\mathbf{R};t) = \sum_{l}^{\infty} \psi_l(\mathbf{r};\mathbf{R})\chi_l(\mathbf{R};t)$$

where nuclear wave functions χ are essentially 'time-dependent expansion coefficients'. Insert into *time-dependent* SE and manipulate - end up with set of coupled differential equations:

$$\left[-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + E_k(\mathbf{R}_I)\right]\chi_k + \sum_l C_{kl}\chi_l = i\hbar\frac{\partial}{\partial t}\chi_k$$

where the exact nonadiabatic coupling operator C_{kl} is:

$$C_{kl} = \int \psi_k^* \left[-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2\right]\psi_l \,\mathrm{d}\mathbf{r} + \frac{1}{M_I}\sum_I \left\{\int \psi_k^*[-i\hbar\nabla_I]\psi_l \,\mathrm{d}\mathbf{r}\right\}[-i\hbar\nabla_I]$$

Diagonal contribution C_{kk} depends only on single wave function ψ_k and thus represents correction to eigenvalue of electronic SE in this kth state. **Adiabatic approximation** considers only these diagonal terms, and for real wfns the green momentum term is zero, so we get complete decoupling:

$$\left[-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + E_k(\mathbf{R}_I) + C_{kk}(\mathbf{R}_I)\right]\chi_k = i\hbar\frac{\partial}{\partial t}\chi_k$$

Then can write $\Psi(\mathbf{r},\mathbf{R};t) \approx \psi_k(\mathbf{r};\mathbf{R})\chi_k(\mathbf{R};t)$ as direct product of electronic and nuclear wave functions. Neglecting diagonal coupling term gives the familiar **Born-Oppenheimer approximation**.

Time dependence: semi-classical molecular dynamics

To make the method *semi-classical*, we need to get rid of the nuclear wave function χ and replace it with classical point particles. **Bohm method**: write χ in polar form $A(\mathbf{R})\exp(iS(\mathbf{R})/\hbar)$, insert in the equation defining the BO approximation on previous slide, and separate real and imaginary parts. One part is a continuity equation which keeps the nuclear probability density normalized, the other is an equation which reduces to the Hamilton-Jacobi equation of classical mechanics if you delete the term involving $\hbar$ (er.. '*taking the classical limit*'). Transform this to Newtonian form and you have:

$$M_I\ddot{\mathbf{R}}_I(t) = -\nabla V_k^{BO}(\mathbf{R}_I(t))$$

Thus nuclei move according to *classical* mechanics in an effective potential V_k^{BO} which is given by the Born-Oppenheimer potential energy surface E_k obtained by solving simultaneously the *time-independent* electronic Schrödinger equation for the kth state at the nuclear configuration R.

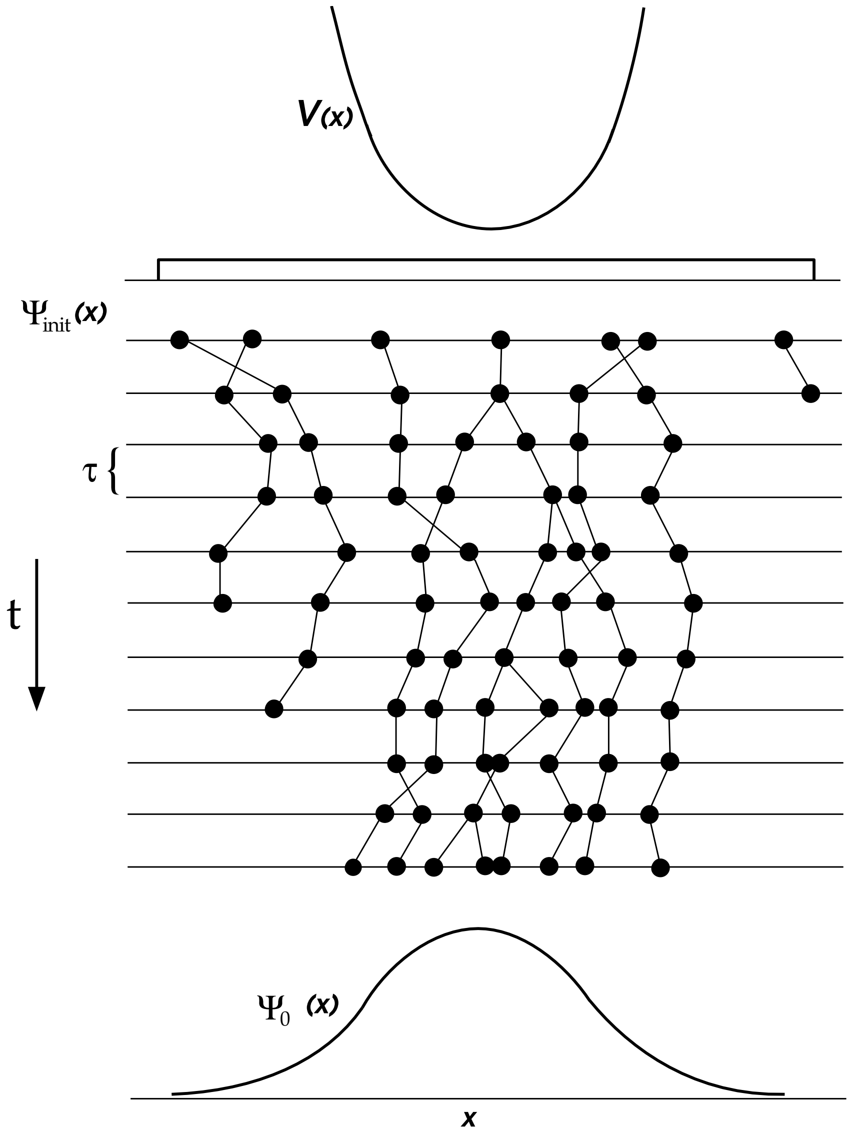
Alternative methods

AIMD	Nuclei	Electronic structure
Born-Oppenheimer	$M_I\ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\{\phi_i\}}\{\langle\Psi_0\|H_e\|\Psi_0\rangle\}$	$0 = -H_e\phi_i + \sum_j \Lambda_{ij}\phi_j$
Car-Parrinello	$M_I\ddot{\mathbf{R}}_I(t) = -\nabla_I\langle\Psi_0\|H_e\|\Psi_0\rangle$	$\mu\ddot{\phi}_i(t) = -H_e\phi_i + \sum_j \Lambda_{ij}\phi_j$
Ehrenfest	$M_I\ddot{\mathbf{R}}_I(t) = -\nabla_I\langle\Psi_0\|H_e\|\Psi_0\rangle$	$i\hbar\dot{\Psi}_0(t) = H_e\Psi_0$

Need to calculate forces!

CP and E propagate wave function dynamically and thus don't require explicit minimization of the total energy. Arguments about whether PC or BO is better are very boring.

What you need to know about QMC to understand this talk

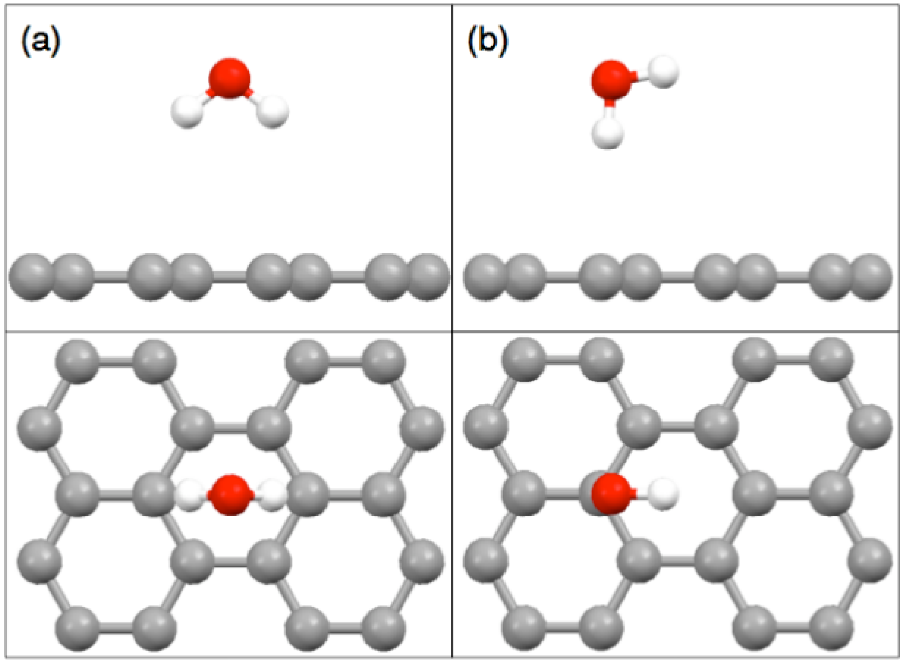


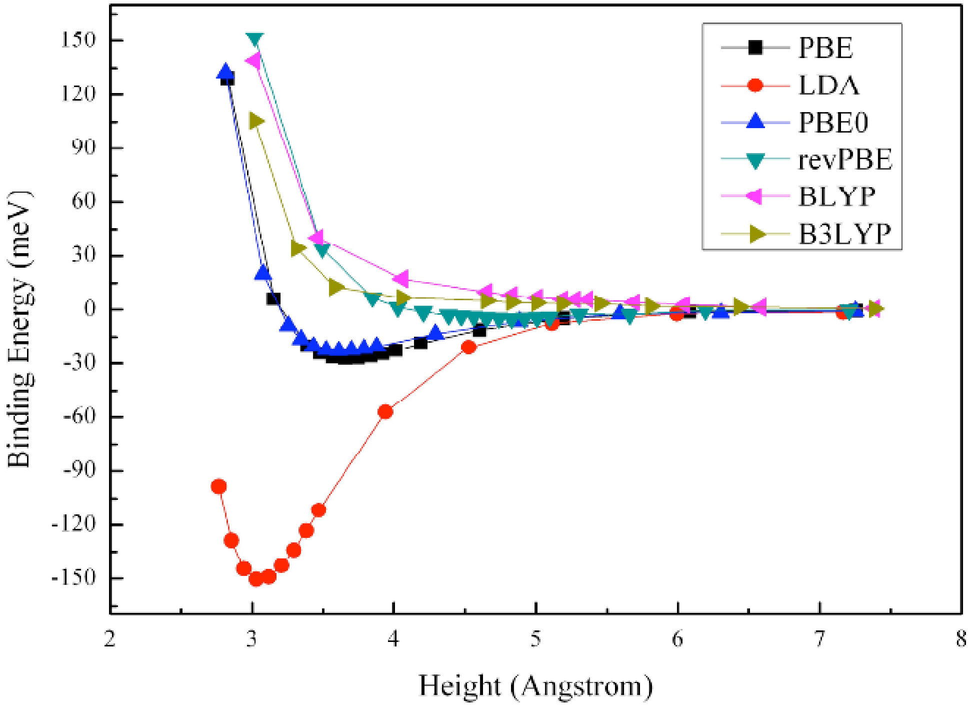
- *Diffusion Monte Carlo* (DMC): trial many-body wave function Φ_T can be made to evolve towards correct ground state wave function by 'evolving it in imaginary time'.
- DMC wave function Ψ represented by distribution in configuration space of an ensemble of copies of the system (each member of the ensemble is called a 'config' or a 'walker').
- The 'shape' of the DMC wave function is changed by deleting configs that move into high-energy regions, and by duplicating ones that move into low-energy regions, according to some magic algorithm. For technical reasons, nodal surface of Ψ constrained to be that of Φ_T (taken e.g. from DFT/HF calc) ⟶ '*fixed-node error*'.

There is no real-time dependence in the standard algorithm; the electrons move in the field of a fixed nuclear configuration generally taken from some optimized DFT calc (Born-Oppenheimer).

Why we need QMC

Water-graphene binding curve from DFT





Which functional shall I choose?

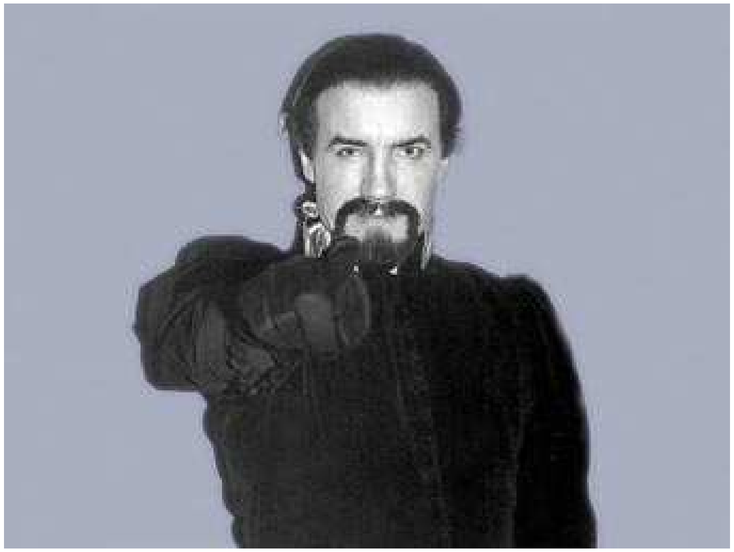
QMC is the only *highly-accurate practical method based on many-body correlated wave functions, the variational principle, and the many-electron Schrödinger equation that scales reasonably with system size (*N^2 *or* N^3*). It also scales perfectly on a parallel machine (demonstrated to 130000 cores - see MDT ESDG talk Jan 2012). It is the method of choice for tacking large quantum many-body problems.*

Grossman-Mitas molecular dynamics

Dario Alfè asked me to code this up in CASINO (to finish a project started by Norbert Nemec).

Jeff Grossman

Lubos Mitas



'*Efficient quantum Monte Carlo energies for molecular dynamics*', J.C. Grossman and L. Mitas, *Phys. Rev. Lett* **94**, 056403 (2005)

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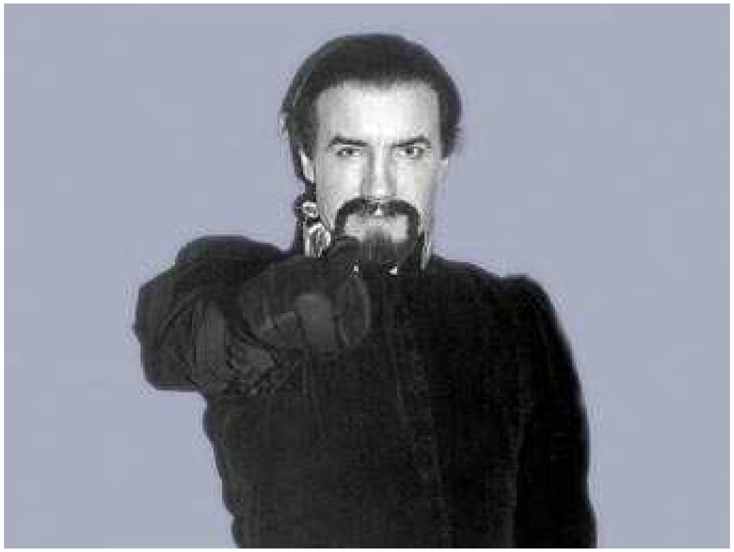

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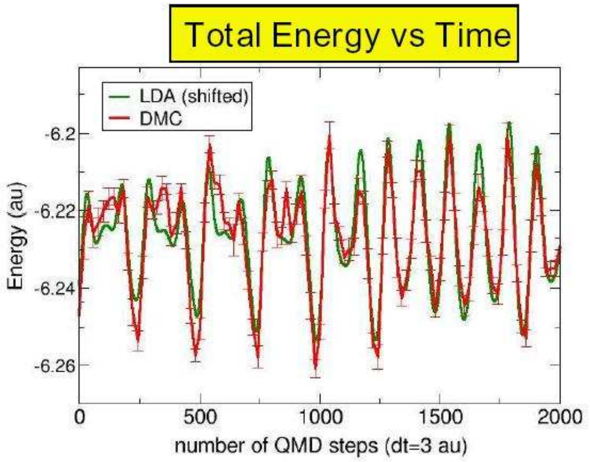
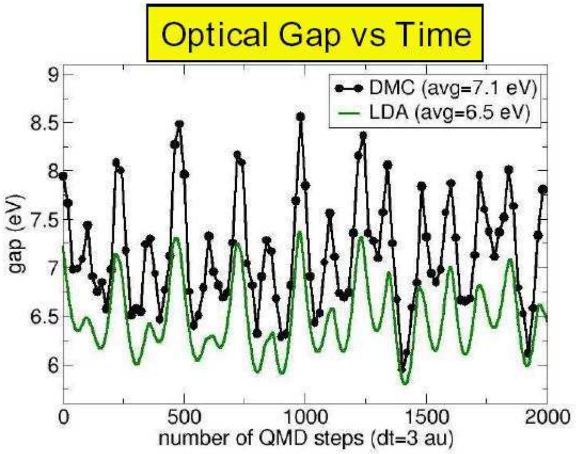




- Grossman-Mitas molecular dynamics (GM-MD) is a method to treat electrons within QMC 'on-the-fly' throughout a molecular dynamics simulation.
- The technique involves using a DFT code (the CASINO implementation uses PWSCF) to generate trial wave functions for each nuclear configuration along a DFT-MD Born-Oppenheimer trajectory, then doing separate DMC calculations at each point in order to get accurate energetics.
- Rather than doing a full DMC calculation for each trial function, each DMC run after the first is 'restarted' from the set of electron walkers stored in the file representing the previous nuclear configuration ('`config.out`') .
- On being read in each walker is 'reweighted' by the ratio of the square of the new and old wavefunctions and the best estimate of the DMC energy recomputed.
- As these walkers ought to be *almost* equilibrated for the slightly changed nuclear positions, it is suggested that very little, if any, DMC equilibration is required. Furthermore, only two or three DMC stats accumulation moves are performed for each MD step, apparently resulting in a huge speedup over doing repeated full DMC calculations.

How does the DMC-MD implementation work in CASINO?

Shell script `runqmcmd` used to automate DMC-MD using CASINO and the PWSCF DFT code (part of Quantum Espresso available for free at `www.quantum-espresso.org` - must use version 4.3+).

The script works by repeatedly calling CASINO run scripts `runpwscf` and `runqmc` which know how to run the two codes on any known machine. See instructions in `utils/runqmcmd/README`.

Setup the PWSCF input (‘`in.pwscf`’) and the CASINO input (‘`input`’ etc. but no wave function file) in the same directory. For the moment we assume you have an optimized Jastrow from somewhere (this will be automated later). Have the PWSCF setup as ‘**calculation = “md”**’, and ‘**nstep = 100**’ or whatever. The `runqmcmd` script will then run PWSCF once to generate 100 `xwfn.data` files, then it will run CASINO on each of the `xwfn.data`. The first will be a proper DMC run with full equilibration (using the values of **dmc_equil_nstep**, **dmc_stats_nstep** etc.). The second and subsequent steps (with slightly different nuclear positions) will be restarts from the previous converged `config.in` - each run will use new keywords **dmcmc_equil_nstep** and **dmcmd_stats_nstep** (with the number of blocks assumed to be 1. The latter values are used if new keyword **dmc_md** is set to T, and they should be very small).

It is recommended that you set **dmc_spacewarping** and **dmc_reweight_conf** to T in CASINO `input` when doing such calculations.

The calculation can be run through plane-wave `pwfn.data`, blip `bwfn.data` or binary blip `bwfn.data.b1` formats as specified in the `pw2casino.dat` file (see CASINO/PWSCF documentation).

```
runqmcmd --nproc=124680 --walltime=12hr --shmem
```

Though of course no one has ever used it apart from me. Sigh..

What question am I trying to answer?

Dario asked me to "*show that GM-MD was xxx times faster than standard sampling*".

This question is based on the claims in the original Grossman-Mitas paper that:

- '*This continuous evolution of the QMC electrons results in highly accurate total energies for the full dynamical trajectory at a fraction of the cost of conventional, discrete sampling.*'
- '[It provides]*an improved, significantly more accurate total energy for the full dynamical trajectory.*'
- '*This approach provides the same energies as conventional, discrete QMC sampling and gives error bars comparable to separate, much longer QMC calculations.*'

A casual reading of this might lead to the conclusion that we get effectively the same results as conventional DMC at each point along the trajectory. As we are only doing e.g. 3 DMC stats accumulation per step, we thus appear to be getting 'something for nothing'. What are we missing?

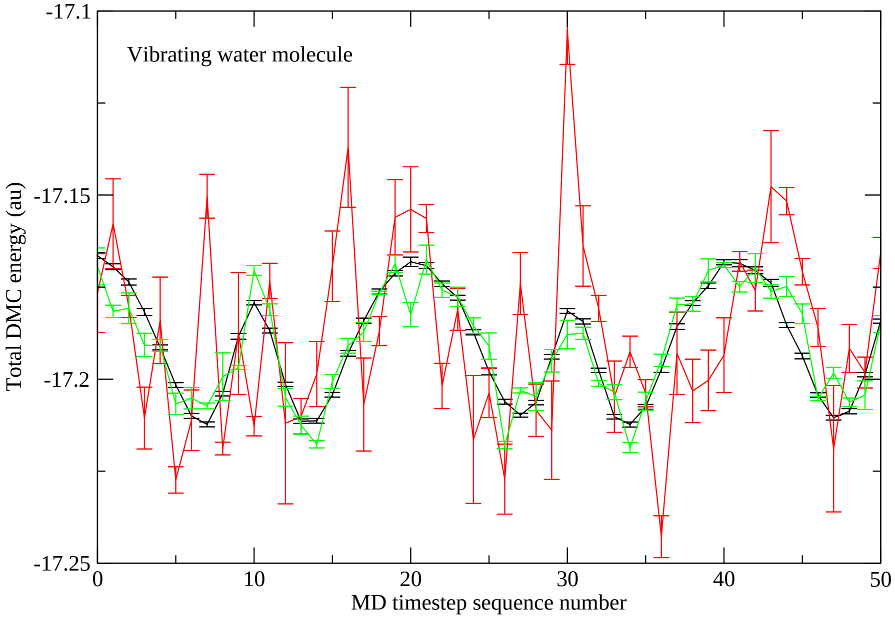
What are we missing?

(1) The point about GM-MD - and Lubos agrees with this - is that its true purpose is to calculate *thermodynamic averages* - an example being given in the paper of the heat of vaporization of H_2O. This is calculated as an average over the evolution path of the ions (at a given $T > 0$) and QMC and thermodynamic averages are done at the same time. Think of it as a method of Monte Carlo sampling a distribution in 3N-dimensional configuration space that is changing shape in time. Each nuclear configuration is sampled via far fewer (e.g. three moves times the number of walkers) electron configurations than usual. It is not intended that accurate energies for all nuclear configurations are calculated, only an accurate Monte-Carlo-sampled 'thermodynamic average' as the molecule (or whatever) vibrates or otherwise moves. This is not really made clear in the paper.

(2) If you want accurate answers and small error bars for the energies at each point along the MD trajectory then - done under normal conditions (number of DMC walkers etc.) - the method does not save you any time at all, apart from that spent doing DMC equilibration. It generally gives very noisy answers with huge error bars for the individual MD points - if you want proper DMC accuracy then you have to do the usual amount of statistical accumulation work.

(3) The only reason they are able to claim '*the same energies* [and error bars] *as conventional, discrete QMC sampling*' is because they use extremely large populations of walkers (this is difficult to scale to large systems). In the paper it is stated that '*we chose a number of walkers such that the statistical fluctuations in the GM-MD energies are one-tenth the size of the variation in the total energy as a function of the MD time* but it should be emphasized that this is considerably more than usual.

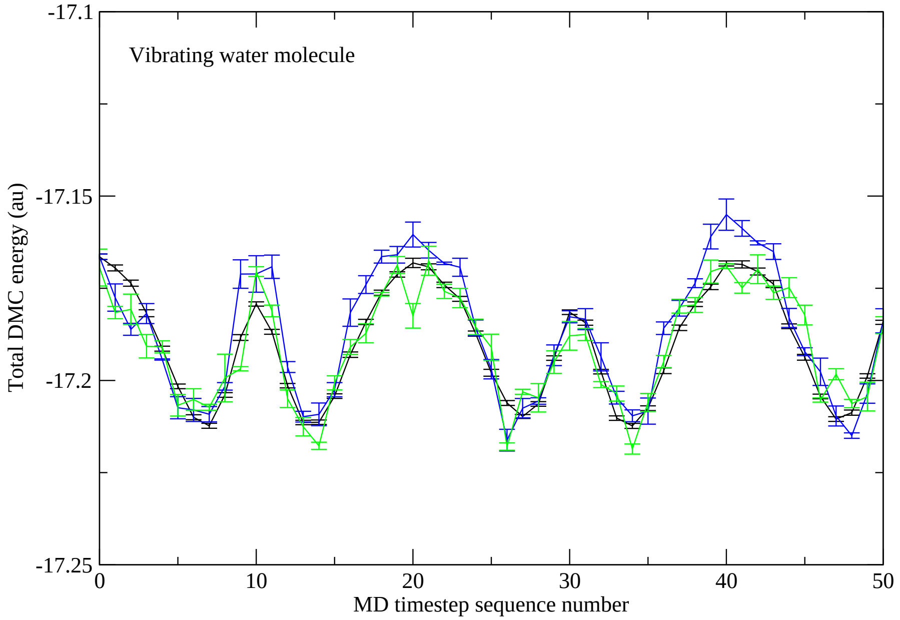
Some illustrative calculations (not GM-MD!)



Discrete DMC energies for vibrating water molecule. Black curve: converged DMC result with small error bar. Red curve: 1000 walkers (a 'typical' number), 1000 equil moves, 3 stats moves. Green curve: 14400 walkers, 1000 equil moves, 3 stats moves

- The red curve essentially does not follow the accurate curve. It can be made to do so by using a sufficiently large population of walkers - the green curve repeats the red calculations, but using 14400 walkers (14 times more) and the same number (3) of stats accumulation moves. This is effectively what GM do in order to claim '*the same energies as conventional discrete QMC sampling*' (though note the error bars in both the red and green curves are not accurate, there being insufficient data - only 3 moves worth - to calculate them properly).
- Because they do not mention the number of walkers used, it is possible to misconclude the nature of the speedup from their data e.g. if we normally do 3000 moves and now we're doing 3, we might think that a GM-MD calculation is 1000 times faster, but it's not because we're using 14 times more configs than usual.

Some GM-MD results



Discrete and GM-MD DMC energies for vibrating water molecule. Black curve: converged discrete DMC result with small error bar. Green curve: 14400 walkers, 1000 equil moves, 3 stats moves. Blue curve: 14400 walkers, no equil moves (each MD point restarted from previous), 3 stats moves.

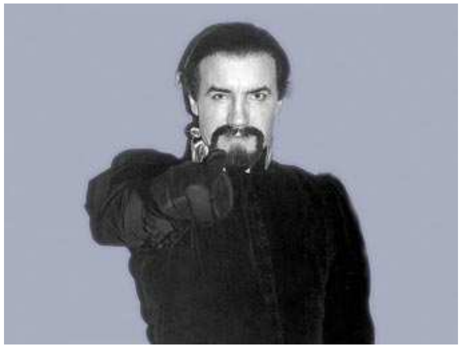
- A GM-MD restarted calculation is an *approximation* to the previous green curve (repeated above) (the approximation is done in order to save the time normally spent doing DMC equilibration).
- The new blue curve above is the GM-MD result with 14400 configs and 3 moves, but skipping the equilibration step for all MD steps after the first, and restarting from the equilbrated walkers from the previous step. Walker reweighting and spacewarping were both turned on.
- The GM-MD curve follows the green curve - where the equilibration is done explicitly - quite well (though its agreement with the full black curve is possibly not as good as that of the green curve, which is expected, as the reweighting is an additional approximation).
- Note that the approximation does not appear to 'get worse' over the course of MD time i.e. the error does not build-up.

Equilibration of walkers

Question: Can configs read at the restart be properly equilibrated for the new Ψ in so few moves?

- Can do 'extreme GM-MD' by just reweighting the configs when you read them in, recomputing the energy with the reweighted configs, and then not doing any DMC accumulation moves at all. The energies will be shifted compared to those of the original DFT calcs, but this is obtained almost in its entirety by the full DMC equilibration carried out at the initial nuclear configuration.
- Can reproduce demonstration calculation in GM paper this way. (where GM-MD total energies are shown tracking the discrete QMC energies for vibrating $\mathrm{Si}_x\mathrm{H}_y$ molecules). The DMC energy curve simply runs parallel to the DFT energies. DMC does not demonstrate any new physics besides a shift in the total energy. This shift is obtained by the initial equilibration, then it is simply translated on along the trajectory. Nothing gained. Why do DMC-MD at all in this case?
- One might suspect that this issue should be important when calculating a trajectory where DMC shows a feature in the energy landscape that is not present in DFT. The GM approach ought simply to 'iron out' these features because the distribution does not have enough time to equilibrate into the special quantum-correlations that cause the energy differences.
- In the end, if you want to get any meaningful DMC energies along a DFT trajectory, it is essential to do some re-equilibration for each MD step to allow the population to properly respond to the new nuclear configuration. If this re-equilibration is too short, any DMC-specific features will be smeared out in the DMC-energy curve.
- Note equilibration is an exponential process and the timescale is determined by physics rather than the initial distribution. The initial distribution largely determines the magnitude of the DMC energy error, not the rate at which it decays. Hence you would think that if you want to do a good job of equilibrating (significantly improve your distribution), *you always need to equilibrate for at least the time taken to diffuse across the longest physically relevant length scale*. TESTING REQUIRED.

GM-MD conclusions



- Rather than using 1000 times fewer stats accumulation moves than normal, and 10 times more configs than normal (say), would get same amount of statistical sampling using 100 times fewer stats accumulation moves with the usual number of configs. However, in the latter case have more propagation in imaginary time - expect wave function to adjust better to new nuclear configuration. So why not do this? Certainly it sounds more impressive to say 'you only need to do 2 moves' without mentioning larger number of configs required.
- Despite the fact that having a large number of walkers relative to the number of moves might facilitate parallelization, it remains the case that the total CPU time does not change when (number of walkers × number of DMC steps) is fixed.
- One might expect that it would be more efficient to sample widely differing nuclear configurations to get a thermodynamic average, rather than ones extremely close together as done in GM-MD.
- It would be nice to see - stated clearly and succinctly in a few lines, why we *expect* GM-MD to give us any speedup at all, even for thermodynamic averages.
- Problem: use of DFT forces! If LDA gives wrong structure then so does GM-MD. However DFT forces not intrinsic requirement; could use QMC forces in principle..

What to do next with this..? Hmmmm..

What have other people done?

Can just try direct '*DMC for electrons and nuclei*' by treating the nuclei in the same way as electrons [Ceperley and Alder, *PRB* **36**, 2092 (1987)]. However, no temperature effects and significant timescale separation problem, even for H.

- Proton is 1836 times more massive than the electron, it's diffusion with DMC (but not VMC, since the $1/m$ appears in the diffusion constant derived from the Green's function) is that much slower, and its root-mean-square displacement per step is hence 42 times smaller than that of the electron. Obviously much worse for higher Z nuclei!
- While the electronic distribution converges rapidly to its ground state, it is easy to find situations where the protonic distribution does not equilibrate in a reasonable amount of computer time. In principle the simulations for the electron-proton system several orders of magnitude longer than for a 1-component system, and this is not generally practical.

Obvious points

- Must thoroughly equilibrate initial ensemble by VMC so that for accurate trial functions the nuclear distribution will be close to the correct one.
- In crystal phases, the motion of the nuclei is severely limited in any case, so that the relevant equilibration time is much smaller (the inverse of the Debye temperature, in fact).
- Take care to use an accurate approximation to the nuclear wave function, if possible.

Can also use *restricted path-integral Monte Carlo* [Pierleoni, Ceperley, Bernu, Magro *PRL* **73**, 2145 (1994)] which uses the thermal density matrix to treat finite T electrons and nuclei. Very expensive, plus sampling problem at low temperature.

Coupled electron-ion Monte Carlo (CEIMC)

Born-Oppenheimer separation of time scales. Ground-state electrons, finite T nuclei. Samples the nuclear configuration space rather than trying to follow a dynamical trajectory.

- Metropolis Monte Carlo for the finite T nuclei. Generate Markov chain of nuclear configurations $\mathbf{R}$ according to the classical Boltzmann distribution $P(\mathbf{R}) = \exp[-\beta E_{BO}(\mathbf{R})]$. Propose move from $\mathbf{R}$ to $\mathbf{R}'$ and accept with probability

  $$A(\mathbf{R} \longrightarrow \mathbf{R}') = \min\left[1, \frac{T(\mathbf{R}' \longrightarrow \mathbf{R})e^{-\beta E_{BO}(\mathbf{R}')}}{T(\mathbf{R} \longrightarrow \mathbf{R}')e^{-\beta E_{BO}(\mathbf{R})}}\right]$$

  After a finite number of steps, the random walk will visit the states of the nuclear configuration space with a frequency proportional to their Boltzmann weight.
- Need to calculate full QMC energy E_{BO} for each nuclear configuration - expensive! Estimate of E_{BO} subject to noise - deal with this using *Penalty Method* - essentially requiring detailed balance to hold on average and not for any single energy configuration.
- Above requires evaluation of energy difference and the noise between two nuclear configurations (with all nuclei moved). Use *correlated sampling* to evaluate difference in 1 calculation rather than 2 separate ones.
- *Pre-reject* really stupid nuclear configurations using a classical potential model.
- Can apparently incorporate ‘quantum nuclei’ at little extra cost using a path-integral type thing.

See e.g. ‘*Computational methods in coupled electron-ion Monte Carlo simulations*’, C. Pierleoni and D.M. Ceperley, ChemPhysChem **6**, 1872 (2005) and Pierleoni 2005 ESDG talk (see ESDG web page).

Other approaches: Attaccalite and Sorella

CEIMC very expensive since reasonable acceptance probability requires statistical error bars on energy of order kT, and amplitude of nuclear moves has to be decreased with increasing system size.

Attaccalite and Sorella have made an interesting proposal for an AIMD using noisy QMC forces, with a method that does not contain any Metropolis rejection scheme (at the expense of the usual MD time discretization error).. Finite T MD simulation requires some external noise on the forces, but you get this for free with QMC!

- Use a generalized Langevin dynamics, i.e. you add two extra force terms - a frictional one $\gamma\mathbf{v}$ (proportional to the nuclear velocity) and a random one η to Newton's equation, in order to approximate the effects of neglected degrees of freedom. Thus : $\dot{\mathbf{v}} = F(\mathbf{R})/m - \gamma(\mathbf{R})\mathbf{v} + \eta(t)$
- From *fluctuation-dissipation theorem* the friction matrix γ is related to the temperature T by

$$\gamma(\mathbf{R}) = \frac{1}{2T}\alpha(\mathbf{R})$$

  where α is a symmetric correlation matrix giving statistical correlation between force components.
- Whatever – ignoring details the practical upshot is that for a given noise on the forces, and a desired temperature, you can set the friction tensor so that the dynamics produces nuclear configurations distributed according to the classical Boltzmann distribution.

See e.g. '*Stable liquid hydrogen at high pressure by a novel ab initio molecular dynamics calculation*', C. Attaccalite and S. Sorella, *PRL* **100**, 114501 (2008).

Can we compute forces with CASINO? To a limited extent, yes (Badinski *et al.*) but only with Gaussian basis set/pseudopotentials. Nobody has ever used them since they were implemented 5 years ago.. Foulkes group at Imperial claims amazing new method for DMC forces - awaiting details.

Some simple things that could be done with our CASINO code

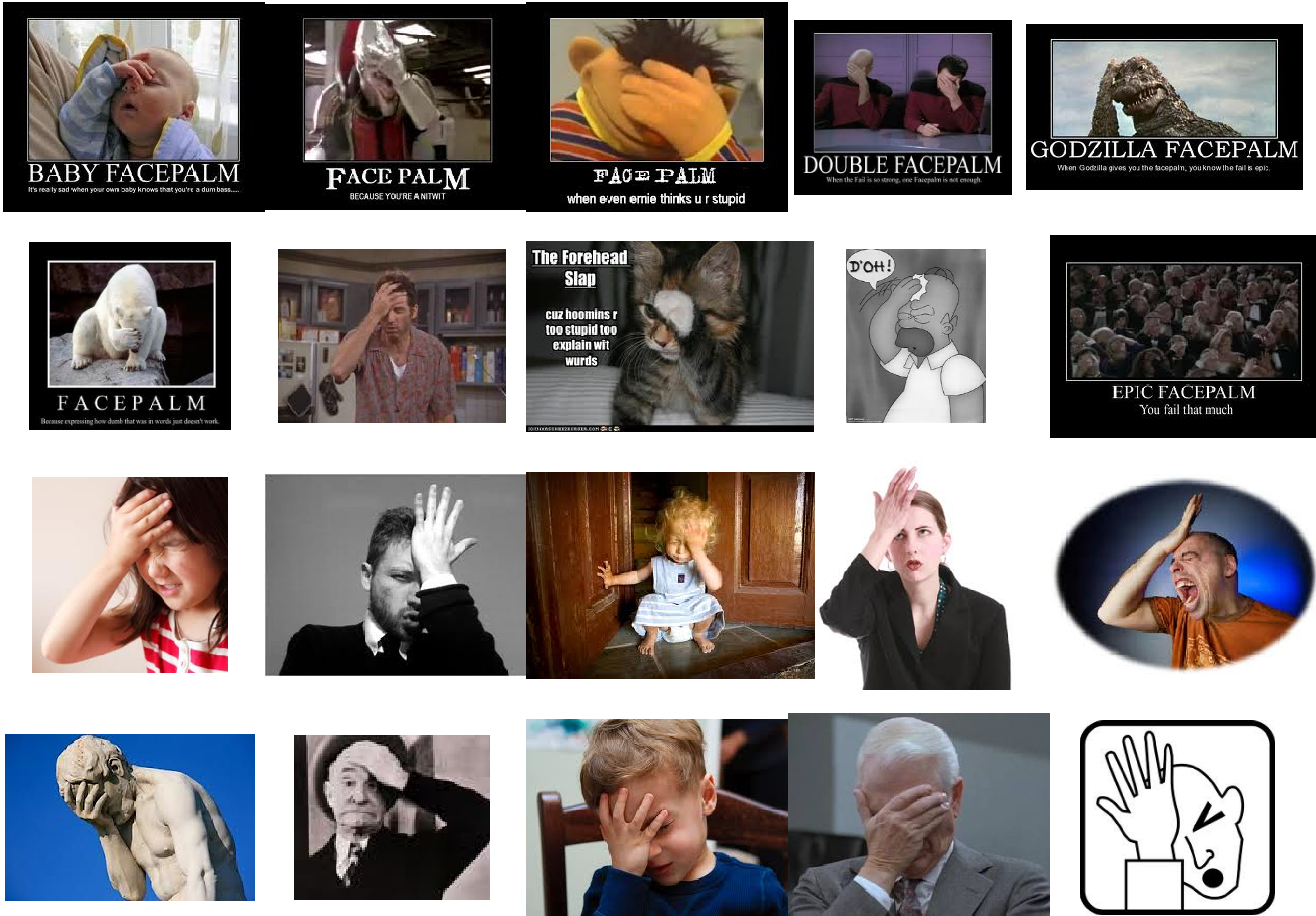
No reason we can't do DMC with light nuclei as quantum particles like in the Ceperley and Alder 1987 work mentioned earlier (computers are a bit faster these days!). Would be useful e.g. in hydrogen at high pressures - which is currently fashionable, see. e.g. RN/Chris Pickard work..

DMC calcs with quantum nuclei have been done more recently for hydrogen, see e.g. Natoli, Martin and Ceperley *PRL* **70**, 1952 (1993) and subsequent work (this would presumably be much easier now, and there is a greater knowledge of likely structures for high-pressure phases).

- Although DMC is a zero-temperature method, this would allow CASINO to e.g. calculate zero-point energies including anharmonicity (currently we have to get separate estimates from quasiharmonic DFT phonon calculations). Likely to be important to get this right.
- We would need to put some thought into representing the nuclear wave function. A good start (as Ceperley does) would be to use Gaussian orbitals centred on lattice sites with an optimizable width (no need to put them in a determinant, since they are effectively distinguishable), then stick some additional variational parameters describing nuclear-nuclear separations in the Jastrow (and possibly backflow) functions that form part of the standard Slater-Jastrow(-backflow) wave function used in CASINO.
- Apart from the extra wave function evaluation bits, need to include the masses in the relevant places in the DMC propagation routines, and a few more bits of administration. Relatively simple to code up!

Further though needs to be given to including temperature and to doing proper molecular dynamics trajectories to follow particular processes. It wouldn't be that difficult to code up something along the lines of CEIMC or Attacalite's work. Or is there something else we can do?

Let's use de Broglie-Bohm theory!



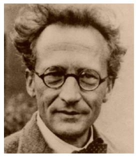
I'm not the only one! Some other de Broglie-Bohm theorists

(Admittedly all at my house..)

Classical atoms with *Newtonian* trajectories

Classical atoms are small and we cannot know their position with certainty, so we deal with a statistical ensemble in which only the *probability density* $\rho(\mathbf{x},t)$ is known.

- Probability must be conserved, i.e. $\int \rho d^3x = 1$ for each t. Therefore must satisfy continuity equation $\partial\rho/\partial t = -\nabla\cdot(\rho\mathbf{v})$ where $\mathbf{v}(\mathbf{x},t)$ is the velocity of the particle.
- Classical mechanics has various equivalent formulations. Choose the less well-known *Hamilton-Jacobi* version, where velocity $\mathbf{v}(\mathbf{x},t) = \frac{\nabla S(\mathbf{x},t)}{m}$ and $S(\mathbf{x},t)$ - related to the 'action' - is a solution of the Hamilton-Jacobi equation, $-\frac{\partial S}{\partial t} = \frac{(\nabla S)^2}{2m} + V$.
- Can write the two green *real* equations more elegantly as a single *complex* equation. To do this, introduce a complex function $\Psi = \sqrt{\rho}e^{\frac{iS}{\hbar}}$ where $\hbar$ is arbitrary constant giving dimensionless exponent. The two equations may then be rewritten as:



$$i\hbar\frac{\partial\Psi}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + V - Q\right)\Psi \qquad \text{with} \qquad Q = -\frac{\hbar^2}{2m}\frac{\nabla^2\sqrt{\rho}}{\sqrt{\rho}}.$$

This is the time-dependent Schrödinger equation (!) with an extra term Q. Note $|\psi(\mathbf{x},t)|^2$ has same interpretation as in QM: a probability density of particle positions. *So to recover classical mechanics from quantum mechanics we simply have to subtract out something that behaves exactly like a potential, thus implying that* **QM is just like classical statistical mechanics with a non-classical dynamics** *(due to an 'extra force' $-\nabla Q$ over and above the classical $-\nabla V$).*

First-order de Broglie-Bohm ('pilot-wave') theory

- Wave field evolution from Schrödinger equation $i\hbar\frac{\partial\Psi}{\partial t} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m_i}\nabla_i^2\Psi + V\Psi$. Evolving quantum system behaves like 'probability fluid' of density $|\Psi|^2 = \Psi\Psi^*$ with an associated time-dependent quantum *probability current* $\mathbf{j} = \frac{\hbar}{m}\mathrm{Im}(\Psi^*\nabla\Psi)$.
- Suspect particle trajectories follow streamlines of current: velocity $\mathbf{v} = \frac{\hbar}{m}\mathrm{Im}\nabla\ln\Psi$ (current/density). Using complex polar form $\Psi = |\Psi|\exp[iS/\hbar]$, the wave function *phase* $S(\mathbf{x}_1, \ldots, \mathbf{x}_N, t)$ is given by $S = \hbar\mathrm{Im}\ln\Psi$ (similar to velocity expression). Thus deduce trajectories $\mathbf{x}_i(t)$ given by *de Broglie guidance equation* for velocity:

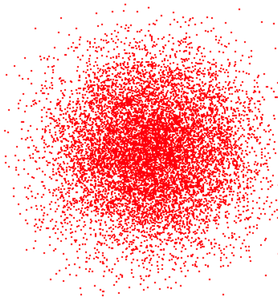
$$\mathbf{v}_i = \frac{d\mathbf{x}_i}{dt} = \frac{\nabla_i S}{m_i}$$

- Can write in 2nd-order '$F = ma$' form by taking t derivative: $m_i\ddot{\mathbf{x}}_i = -\nabla_i(V + Q)$, where $Q = -\sum_i \frac{\hbar^2}{2m_i}\frac{\nabla_i^2|\Psi|}{|\Psi|}$ (*quantum potential*). Extra 'quantum' force $-\nabla_i Q$ (big if large curvature in wave field). *Non-classical* dynamics since particles 'pushed along' by wave along trajectories perpendicular to surfaces of constant phase, as well as by classical force from other particles.
- Guidance equation *identical* to trajectory equation in Hamilton-Jacobi theory - a standard form of classical mechanics like Hamiltonian or Lagrangian dynamics. There S is indefinite integral of classical Lagrangian with respect to t (note the 'action' is the *definite* integral with fixed endpoints). Suggests immediately how to obtain the classical limit, i.e. when $Q = \nabla Q = 0$ the wave component of matter is passive and the particles follow classical trajectories (impossible in orthodox QM!). *This is what I did at the start when justifying semi-classical MD*.

Stochastic pilot-wave theories

To put DMC in deBB context, must first understand concept of *stochastic* pilot-wave theories. Additional random motion introduced in 1954 by Bohm and Vigier in context of why particles distributed as $|\Psi|^2$ (though no need - see MDT ESDG Feb 2010).

Imagine a deeper 'sub-quantum' level which imparts additional intrinsic randomness to particle motion (like in Brownian motion with pollen grains being hit by clouds of atoms). Velocity of individual particle is $\mathbf{v} = \frac{\nabla S}{m} + \xi(t)$ with $\xi(t)$ a chaotic contribution to the velocity fluctuating randomly with zero average. Usual $\frac{\nabla S}{m}$ trajectory produced by guiding equation thus *average* velocity not *actual* one.



- Assume - whatever its origin - stochastic process treatable as simple *diffusion*. With prob density P, diffusion constant D, there is diffusion current $\mathbf{j} = -D\nabla P$ and a conservation equation $\partial P/\partial t = -D\nabla^2 P$. Leads clearly to *uniform distribution* (change in P stops at zero density curvature, like ink drop spreading in water).
- If want *non-uniform* final distribution there must be another field giving rise to an *osmotic velocity*. **Example**: Einstein showed if add gravitational field in z-direction this velocity is $u = D\frac{mg}{kT}z$, the conservation equation becomes $\frac{\partial P}{\partial t} = -D\nabla\left[\frac{mg}{kT}zP + \nabla P\right]$. In equilibrium when $\frac{\partial P}{\partial t} = 0$ we have $\frac{\nabla P}{P} = \frac{mg}{kT}z + c$ or $P = A\exp(-\frac{mgz}{kT})$ - the Boltzmann factor. See also Attaccalite/Sorella!
- In stochastic pilot-wave theory require random diffusion process whose equilibrium state corresponds to prob density $P = |\Psi|^2 = \rho$ and mean current $\mathbf{j} = \rho\mathbf{v} = \rho(\frac{\nabla S}{m})$. Consistent possibility if $\Psi = \sqrt{\rho}\exp(\frac{iS}{\hbar})$ as this implies conservation equation $\frac{\partial\rho}{\partial t} + \nabla\cdot\mathbf{j} = 0$. Can be shown suitable osmotic velocity is $\mathbf{u} = \frac{D\nabla\rho}{\rho}$ - then follows there is an equilibrium state with $P = \rho$ in which the osmotic velocity is balanced by the diffusion current so the mean velocity is $\frac{\nabla S}{m}$.

DMC vs. stochastic pilot-wave theories

In the various theories at each timestep get change in particle position $\mathbf{dr}$ from some combination of guided velocity, random diffusion and a drift (osmotic) velocity. The χ in the diffusion part is a random variable with zero mean and unit variance. Atomic units are dispensed with ($\hbar$ and m are back).

Standard pilot wave $\quad d\mathbf{r} = \frac{\nabla S}{m}\mathrm{d}t$

Stochastic pilot wave $\quad d\mathbf{r} = \frac{\nabla S}{m}\mathrm{d}t + \chi\sqrt{\frac{\hbar}{m}}\mathrm{d}t + \frac{\hbar}{2m}\frac{\nabla|\Psi|^2}{|\Psi|^2}\mathrm{d}t$

DMC $\quad d\mathbf{r} = \chi\sqrt{\frac{\hbar}{m}}\mathrm{d}t + \frac{\hbar}{m}\frac{\nabla|\Phi_T|}{|\Phi_T|}\mathrm{d}t$

DMC2† $\quad d\mathbf{r} = \frac{\nabla S}{m}\mathrm{d}t + \chi\sqrt{\frac{\hbar}{m}}\mathrm{d}t + \frac{\hbar}{m}\frac{\nabla|\Phi_T|}{|\Phi_T|}\mathrm{d}t$

† If use complex Φ_T and retain imaginary part of complex drift vector $\nabla\Phi_T/\Phi_T$ (since for $\Psi = Re^{iS/\hbar}$ have $\frac{\hbar}{m}\frac{\nabla\Psi}{\Psi} = \frac{\hbar}{m}\nabla\ln\Psi = \frac{\hbar}{m}\frac{\nabla R}{R} + i\frac{\nabla S}{m}$). In this view, $\nabla S/m$ is that part of osmotic velocity accounting for target distribution changing shape in real time.

So methods have practically identical Langevin-type equations describing particle motion as result of drift and diffusion, and similar propagators K (one in real, one in imaginary time).

Notes

- In DMC complex Ψ hardly used: real arithmetic faster and real Ψ easier to map into probabilities.
- Where complex Ψ used one employs *fixed-phase approximation* instead of fixed-node i.e. say phase S is fixed and equal to phase of trial function Φ_T. DMC algorithm used to solve for modulus of Ψ.
- Note no-one ever does DMC for *time-dependent* wave functions - always stationary states.

Ideas

Question 1: Why does nobody do molecular dynamics using the first-order deBB theory i.e. calculate the trajectories directly from $m\mathbf{v} = \nabla S = \hbar \mathrm{Im}\frac{\nabla\Psi}{\Psi}$, instead of using its first time derivative $m\ddot{\mathbf{R}} = -\nabla V - \nabla Q$ or its classical limit.

- No need to calculate forces (in principle higher-order derivative than velocities)
- No integration step to get velocity from forces (what about T?)
- No need for BO approximation - full quantum effects without having to do path integrals.

Obviously because you need a proper wave function to take the gradient of, and because you presumably need to solve the time-dependent Schrödinger equation..?

Question 2: What's to stop you doing $\mathbf{v} = \frac{\nabla S}{m}$ directly in QMC?

- Need nuclear wave function, but not impossible - see earlier.
- No need to compute difficult forces? The $\frac{\nabla\Psi}{\Psi}$ is essentially the drift vector whose real part is already computed in order for DMC to work.

Question 3: If you insist on using the second order-form why does no-one just compute $-\nabla Q$ instead of doing path-integrals in order to get quantum trajectories?

Thought required!

Path integral vs. de Broglie-Bohm

Want to calculate *propagator* K (carries wave function Ψ from past into future).

- In *Feynman's path integral theory* the propagator is

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

Here propagator linking two spacetime points calculated by linearly superposing amplitudes $e^{iS/\hbar}$ (obtained by integrating **classical** Lagrangian $L_c(t) = \frac{1}{2}mv^2 - V$) associated with infinite number of **all possible paths** connecting the points. Get future wave function at $\mathbf{x}_1$ from $\Psi(\mathbf{x}_1, t_1) = \int K^F(\mathbf{x}_1, t_1; \mathbf{x}_0, t_0)\Psi(\mathbf{x}_0, t_0)\,\mathrm{d}x_0$.

- In the equivalent pilot-wave theory expression the propagator is

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

i.e. get same result as Feynman by integrating **quantum** Lagrangian $L_q(t) = \frac{1}{2}mv^2 - (V + Q)$ along precisely **one** path - the one the particle actually follows. Integral over K with different starting points not required since trajectories don't cross, i.e. $\Psi(\mathbf{x}_1, t_1) = K^{PW}(\mathbf{x}_1, t_1; \mathbf{x}_0, t_0)\Psi(\mathbf{x}_0, t_0)$

Not many people know this..

And other idea: why not propagate in complex time?

Repeat DMC imaginary time analysis with complex time $\tau = t + it'$*:*

Choose constant offset E_T in TDSE to be ground-state energy E_0 then, as $\tau \to \infty$, Ψ comes to look more like ground state ϕ_0 (as before). Difference is that exponentially-decaying bit now has t-dependent moving nodal surface. (Recall that a linear combination of stationary TDSE solutions with different energies, each with its own t-dependent phase factor, gives overall t-dependence in $|\Psi|^2$.)

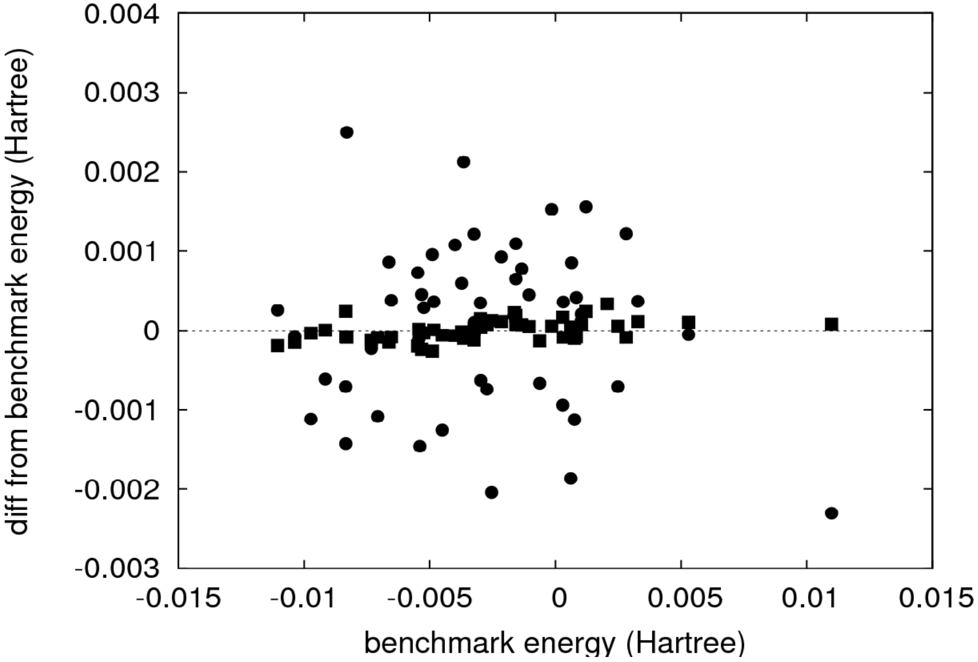
$$\Psi(\mathbf{x},\tau) = c_0\phi_0 + \sum_{n=1}^{\infty} c_n\phi_n(\mathbf{x})\mathrm{e}^{i(E_n-E_0)t}\mathrm{e}^{-(E_n-E_0)t'}$$

- With t-dependent complex Ψ nodal surfaces dissolve into nodal lines where surfaces of real and imaginary functions intersect. Fewer barriers to motion of configurations?
- Simulations will show us how particles guided by the wave field with rapidly-moving nodes quickly became distributed according to $|\Psi|^2$. Also see that nodal lines moving through particle distribution acted as 'particle mixers'; trajectories become 'more chaotic' with more nodes.
- Might think that while imaginary time propagation improves Ψ, real time propagation allows nodal surface to relax and Ψ to be optimized more efficiently. As excited-state contributions die away and distribution approaches stationary state, $\frac{\nabla S}{m}$ (and hence guided particle velocity) tends to zero (only diffusion and real part of drift velocity remain for computing statistical data and expectation values).

This is very nebulous - proper thought required!

Give-up: do classical potential models

- Is QMC of any use in developing classical force fields?
- Can it help with Gabor's GAP potentials (which use arbitrary QM data as 'evidence' when generating interatomic potentials)? (Albert BP, ESDG May 2012)
- Can it help with hybrid classical/quantum molecular dynamics methods like Gabor's Learn On The Fly (LOTF)? (GC, ESDG August 2003, Feb 2010)



Comparison of DMC total energies (filled squares) with accurate quantum chemistry benchmarks at CCSD(T) level for a sample of 50 geometries of the H_2O trimer drawn from an MD simulation of liquid water. Horizontal axis shows CCSD(T) energy, vertical axis shows deviation of DMC energy from CCSD(T) energy. Filled circles show the same comparison for DFT(PBE).