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ICTP 40th Anniversary

SMR 1595 - 15

Joint DEMOCRITOS - ICTP School on
CONTINUUM QUANTUM MONTE CARLO METHODS
12 - 23 January 2004

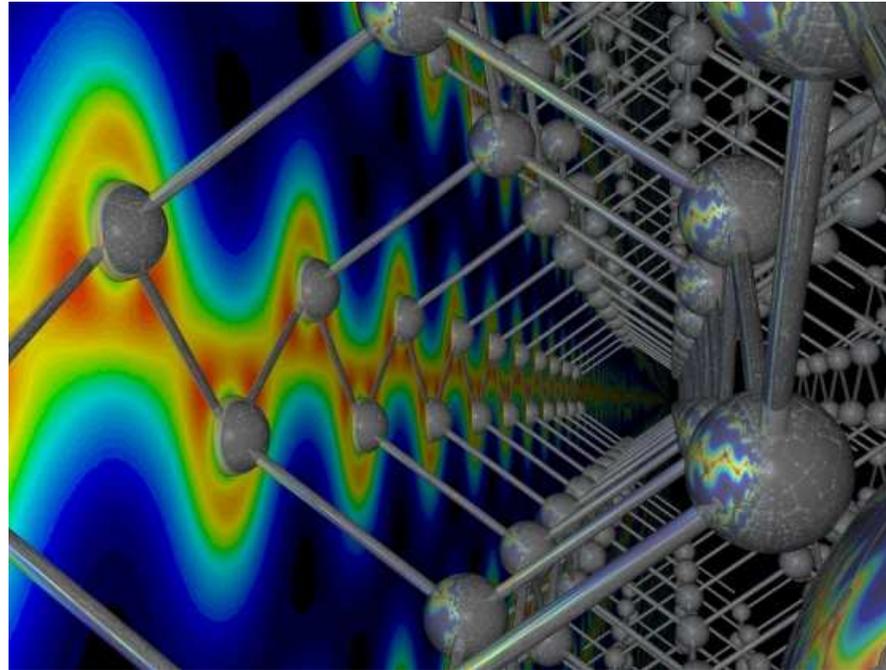
QUANTUM MONTE CARLO

Mike TOWLER
TCM Group, Cavendish Laboratory, Cambridge University
Cambridge CB3 0HE, U.K.

These are preliminary lecture notes, intended only for distribution to participants.

Quantum Monte Carlo

Practical QMC issues, solid-state applications and the CASINO program



Mike Towler

Theory of Condensed Matter Group
Cavendish Laboratory
University of Cambridge

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

Email: mdt26 at cam.ac.uk

Today's topics

- 09:00-09.55 : Practical QMC issues I
- 09:55-10:00 : Break
- 10:00-11:00 : Practical QMC issues II
- 11:00-11:30 : Break
- 11:30-12:30 : Solid state applications
- 12:30-15:00 : Lunch
- 15:00-18:00 : Computer lab : the CASINO program

Practical QMC issues

- Aims of the CASINO program
- Basic considerations and brief review
- Many electron wave functions
- Periodic boundary conditions and solid-state physics
- Wave function evaluation, representation of orbitals, and basis sets
- Cusp conditions, DMC stability, and heavy atoms
- Pseudopotentials
- Spin
- Jastrow factor and optimization strategies
- Considerations in evaluating the local energy
- Scaling with system size

CASINO

A general QMC electronic structure software package for finite and periodic systems

Generality

VMC/DMC for systems with 'arbitrary' system size (given enough computing power) and arbitrary geometry, including atoms; molecules; systems periodic in 1/2/3 dimensions (polymers, slabs, crystalline solids); various electron and electron-hole phases. Choice of basis sets (plane waves/Gaussians/blips/splines) or grids. Interfaces to wide-range of electronic structure codes for generating trial wave functions.

Portability

Strict Fortran90. Modern software design. Runs on 'any' parallel (MPI) and serial hardware. Automatic (but user customizable) compilation/setup.

Ease-of-use

Shell script automation. Full documentation (internal help system, comprehensive manual, on-line material including pseudopotential library). Wide range of examples included. Mailing list for discussions (`casino_users @ phy.cam.ac.uk`).

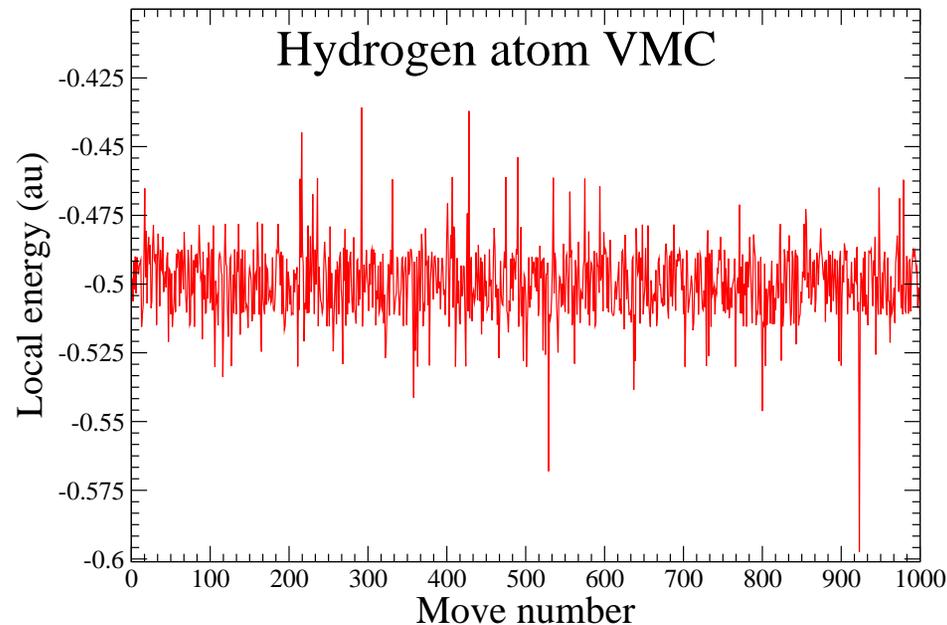
Speed

Use (hopefully) the most efficient algorithms optimized for speed, including new developments for improved scaling with system size.

VMC : review

$$E_{\text{VMC}} = \frac{\int \Psi \hat{H} \Psi d\mathbf{R}}{\int \Psi^2 d\mathbf{R}} = \frac{\int \Psi^2 \left(\frac{\hat{H}\Psi}{\Psi} \right) d\mathbf{R}}{\int \Psi^2 d\mathbf{R}}$$

- Generate points distributed according to Ψ^2 using a random walk and the Metropolis algorithm. Average local energies $\frac{\hat{H}\Psi}{\Psi}$ over the walk $\longrightarrow E_{\text{VMC}}$.



NOTE: VMC is not particularly useful as a technique in its own right. Its main purpose is to provide high-quality trial wave functions for DMC.

DMC : review

- Propagate Ψ in imaginary time to enhance ground state component.

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

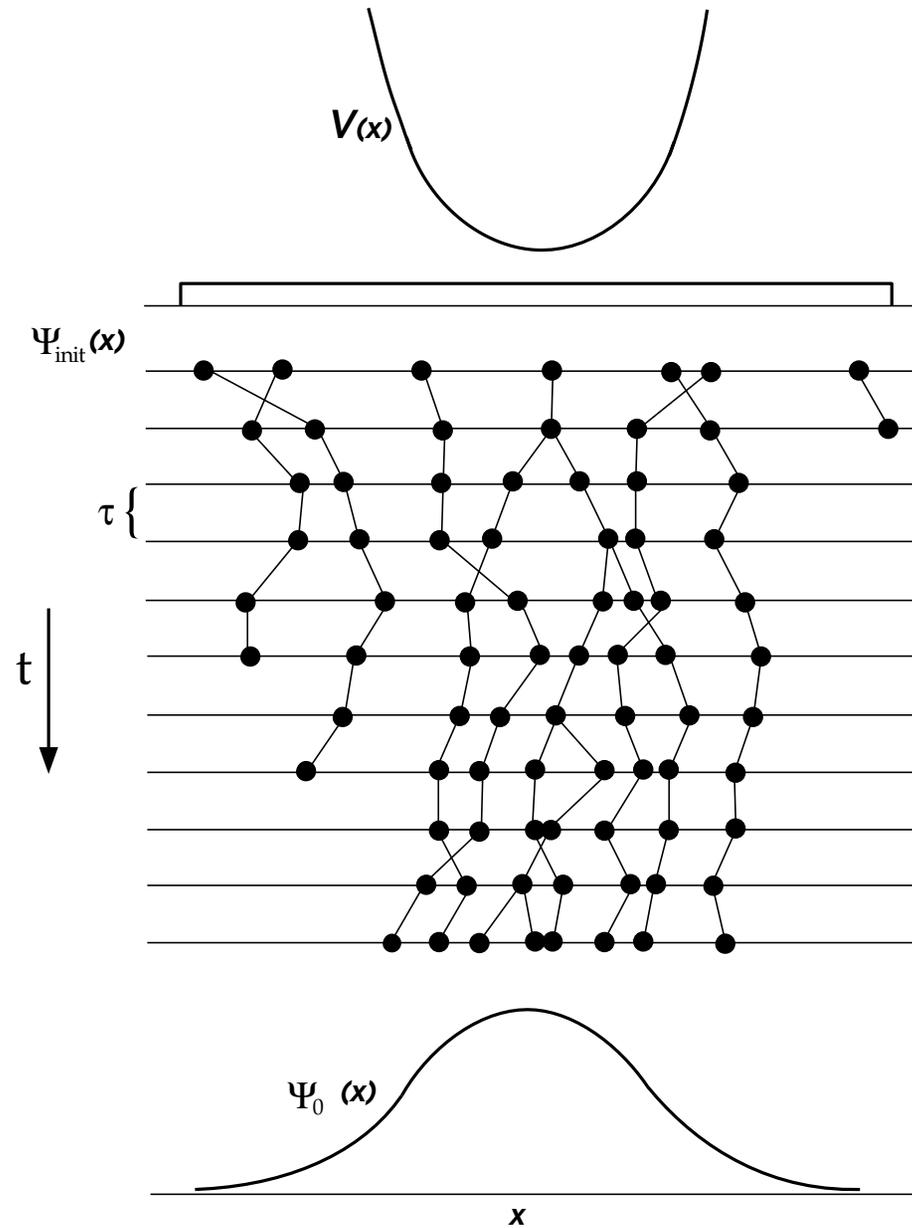
$$G(\mathbf{R}, \mathbf{R}', \delta\tau) = (2\pi\delta\tau)^{-\frac{3N}{2}} \exp\left(-\frac{|\mathbf{R} - \mathbf{R}'|^2}{2\delta\tau}\right) \\ \times \exp\left[-\delta\tau \left(\frac{V(\mathbf{R}) + V(\mathbf{R}')}{2} - E_T\right)\right]$$

- Impractical for fermions (ground state bosonic; huge fluctuations).
- Solution : use $f(\mathbf{R}, \tau) = \Psi(\mathbf{R}, \tau)\Phi_T(\mathbf{R})$ instead of $\Psi(\mathbf{R}, \tau)$.

$$G(\mathbf{R}', \mathbf{R}, \delta\tau) = (2\pi\delta\tau)^{-\frac{3N}{2}} \exp\left[-\left(\frac{\mathbf{R}' - \mathbf{R} - \delta\tau\mathbf{F}(\mathbf{R})}{2\delta\tau}\right)^2\right] \\ \times \exp\left[-\delta\tau \left(\frac{E_L(\mathbf{R}) + E_L(\mathbf{R}')}{2} - E_T\right)\right]$$

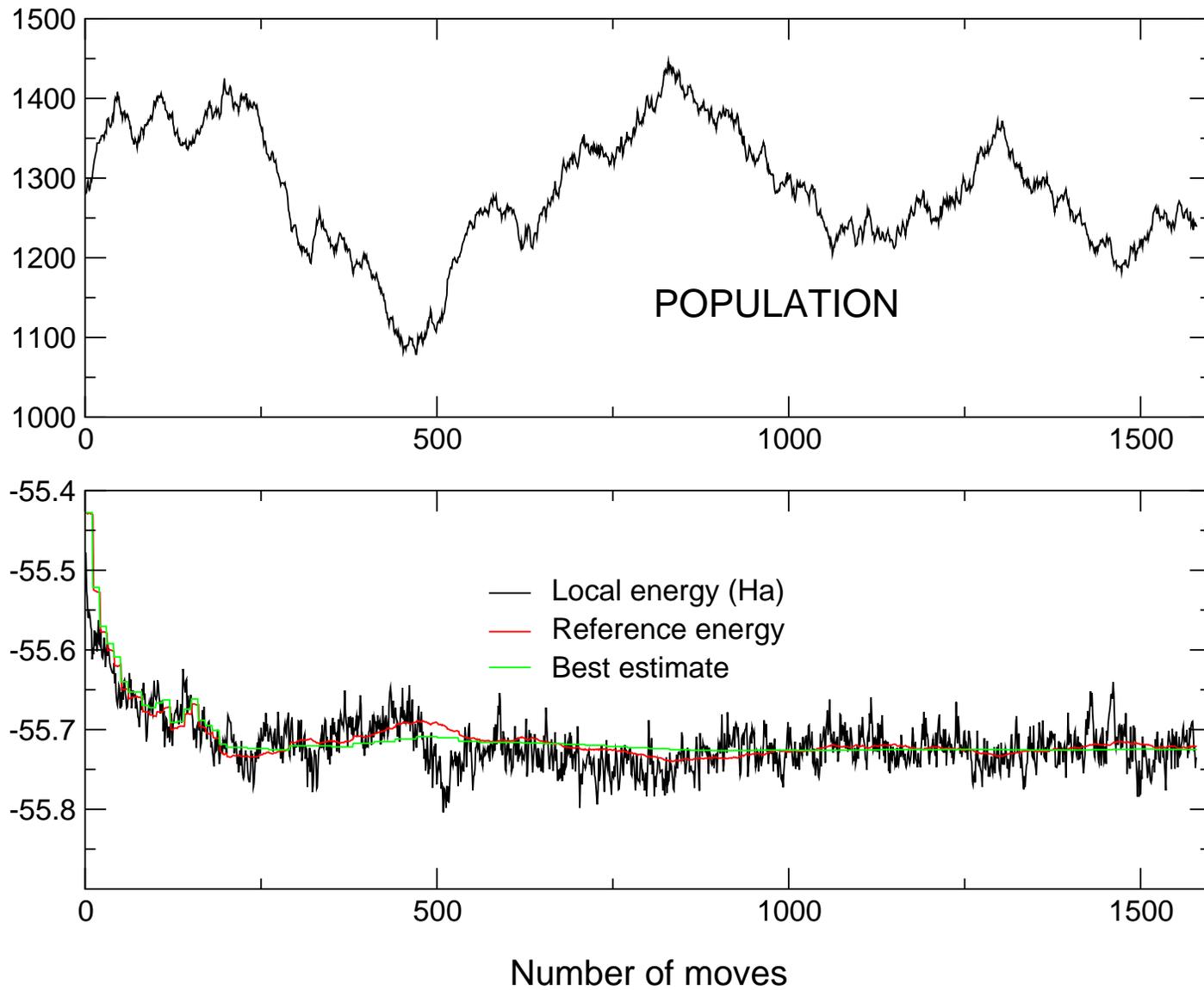
DMC

Single electron in a harmonic potential well



Results of DMC simulation with CASINO

Nickel oxide crystal



Many body wave functions in the solid-state

Can solve quantum-mechanical problems without reference to wave functions using e.g. Green's function/density matrices/density. These are simpler objects since depend on less variables. So why use wave functions?

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

- The equation satisfied by the wave function is quite simple!
- Not necessary to use serious uncontrolled approximations to get the total energy (e.g. exchange-correlation functionals..!).
- Not really 6×10^{23} variables. The secret for solids is just periodic boundary conditions (both for DFT and QMC). Feasible **now** to treat thousands of electrons per cell with QMC.

Walter Kohn: RMP **71**, 1253 (1999) " *..the many-electron wave function is not a legitimate scientific concept for more than about $N = 1000$ particles..*"

Overlap of approximate wave function with exact one tends exponentially to zero as N increases, unless use a number of parameters which increases exponentially with N . Not computable!

Not relevant to QMC (and surely applies to Kohn-Sham DFT as well?)!

Only need to get low-order correlation functions right to get accurate total energy even if overlap with exact wave function is low.

More about many-electron wave functions

- Slater-Jastrow function

$$\Psi(\mathbf{X}) = e^{J(\mathbf{X})} \sum_n c_n D_n(\mathbf{X})$$

where $\mathbf{X} = (\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$, $\mathbf{x}_i = \{\mathbf{r}_i, \sigma_i\}$, D is a determinant of orbitals, and $e^{J(\mathbf{X})}$ is a 'Jastrow factor' explicitly dependent on the mutual separation of pairs of electrons and their position with respect to the nuclear framework.

Points to note

- Sometimes useful to use more than one determinant.
- Nodal surface given entirely by determinant part (important for DMC).
- Best way to 'guess' appropriate orbitals for the determinant part is to use results from e.g. molecular orbital theory/band theory calculations.
- Calculating the orbitals is often the most expensive part of the calculation. Need to pay attention to representing them *efficiently*.
- Parameters in Jastrow factor obtained by optimization (variance minimization).

How to generate a trial wave function

Is the system finite or does it have periodic boundary conditions?

Use a 'molecular orbital theory' or 'band theory' method to generate suitable orbitals. A QMC code thus requires links to standard programs.

What method to use?

Hartree-Fock theory - best possible set of orbitals for a single determinant wave function in the case where the only correlation between particles is due to antisymmetry (parallel spins only).

Density functional theory - best possible set of orbitals for a single determinant (Kohn-Sham) wave function in a fictitious 'non-interacting' system with the same density as the true one. All the complicated many-body physics is transferred to the exchange-correlation functional which gives the 'interacting bit' of the total energy from this density.

Quantum chemistry correlated wave function methods - various multideterminant methods with acronyms (e.g. MCSCF, CASSCF, CIS, CISD, TD-DFT). Almost certainly overkill if you go too far down this road.

Exchange and correlation

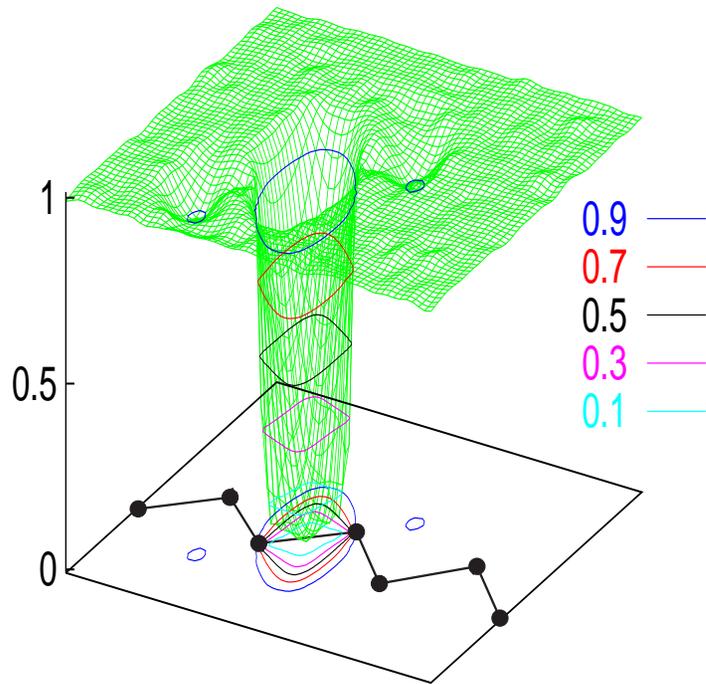
Pair-correlation function in silicon with Slater-Jastrow wave function

VMC

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

\mathbf{r} at bond center

\mathbf{r}' in (110) plane

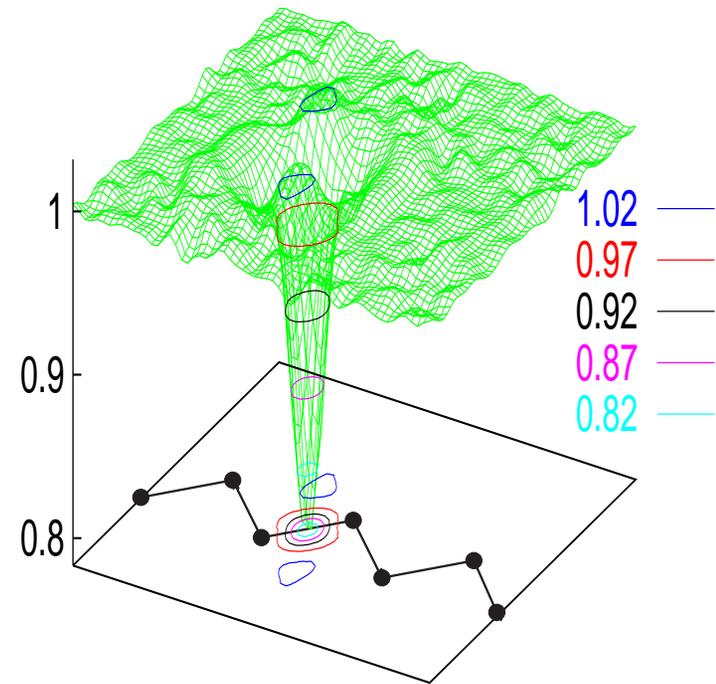


VMC

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

\mathbf{r} at bond center

\mathbf{r}' in (110) plane



What do we do with the wave function?

(1) Move the electrons

To implement the Metropolis algorithm, propose random electron moves accepted with probability :

$$a(\mathbf{r} \longrightarrow \mathbf{r}') = \min \left[1, \frac{\rho(\mathbf{r}')}{\rho(\mathbf{r})} \right] = \min \left[1, \frac{\Psi(\mathbf{X}')^2}{\Psi(\mathbf{X})^2} \right]$$

Slater matrix gives value of every orbital at current location of every electron. **Determinant of this matrix times the Jastrow factor** gives the value of the many-electron wave function at that point in configuration space. The **ratio of the squares of the old and new wave functions** after an electron hop appears in the Metropolis acceptance probability above.

NOTE: Not necessary to reevaluate entire determinant (scales as N^3) every time we move an electron. In fact we:

- propose move of an electron from point A to point B
- evaluate the value of every orbital at point B (i.e. we recalculate one column of the Slater matrix).
- new value of *ratio* given by a dot product of column of transpose of inverse Slater matrix with the regenerated column (scales as N). Update of inverse Slater matrix then scales as N^2 .

What do we do with the wave function?

(2) Need $\{x, y, z\}$ Cartesian first derivatives and the Laplacian of the orbitals at the new electron position to calculate energy and drift, e.g.

Kinetic energy

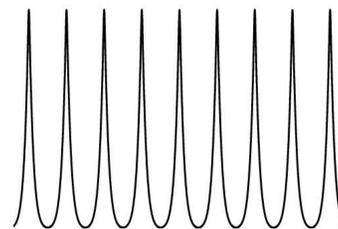
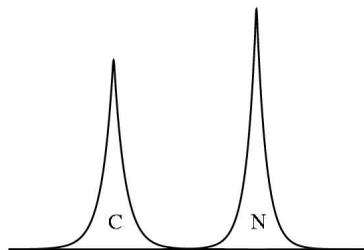
$$K = \sum_{i=1}^N K_i = \sum_{i=1}^N -\frac{1}{2} \frac{\nabla_i^2 \Psi}{\Psi}$$
$$\mathbf{F}_i = \frac{1}{\sqrt{2}} \nabla_i (\ln |\Psi|) = \frac{1}{\sqrt{2}} \frac{\nabla_i \Psi}{\Psi}$$
$$T_i = -\frac{1}{4} \nabla_i^2 (\ln |\Psi|) = -\frac{1}{4} \frac{\nabla_i^2 \Psi}{\Psi} + \frac{1}{4} \left(\frac{\nabla_i \Psi}{\Psi} \right)^2$$

K_i can then be expressed in terms of \mathbf{F}_i and T_i as $K_i = 2T_i - |\mathbf{F}_i|^2$.
Integrating shows that $\langle K_i \rangle = \langle |\mathbf{F}_i|^2 \rangle = \langle T_i \rangle$ - useful!

Drift vector

$$G^{\text{diffusion}}(\mathbf{R}', \mathbf{R}, \delta\tau) = (2\pi\delta\tau)^{-\frac{3N}{2}} \exp \left[- \left(\frac{\mathbf{R}' - \mathbf{R} - \delta\tau \frac{\nabla_{\mathbf{R}} \Psi}{\Psi}}{2\delta\tau} \right)^2 \right]$$

Representation of orbitals



Can represent orbitals and derivatives on a **grid**, or we can use an expansion in a **basis set** (which may consist of localized or delocalized functions).

Orbitals in periodic potential can be made to obey BLOCH'S THEOREM:

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \text{ or } \Psi(\mathbf{r} + \mathbf{t}) = \Psi(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{t}}$$

Delocalized basis (plane waves) : $\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} c_n^{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$.

Localized basis (e.g. atom-centred Gaussians $\{\chi\}$): form a *Bloch sum* by combining χ and its periodic images modulated by a phase factor:

$\Phi_{m\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{t}} \chi_m^{\mathbf{t}}(\mathbf{r} - \mathbf{r}_a - \mathbf{t}) e^{i\mathbf{k}\cdot\mathbf{t}}$ where $\chi_m^{\mathbf{t}}(\mathbf{r} - \mathbf{r}_a - \mathbf{t})$ is an atomic function (located at \mathbf{r}_a in the zero cell) translated into cell \mathbf{t} . Then :

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_m c_n^m \Phi_{m\mathbf{k}}(\mathbf{r})$$

In QMC, it is **hugely preferable to use localized functions** in the basis, since only a subset of them contribute to each orbital at a point. Gain a factor of N over plane waves in scaling with system size.

Math(s)

Given three *not-necessarily orthogonal* basis vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 , the component of an arbitrary vector \mathbf{d} along each basis vector is $\mathbf{d} \cdot \mathbf{b}_i$ where \mathbf{b}_i is a *reciprocal vector* to \mathbf{a}_i :

$$\mathbf{b}_1 = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \quad \mathbf{d} = \sum_i (\mathbf{d} \cdot \mathbf{b}_i) \mathbf{a}_i$$

Solid-state physics

If \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 are the primitive translation vectors of a real-space crystalline lattice, then the *reciprocal lattice* is then mapped out by the reciprocal lattice vectors \mathbf{G}_n defined by $\mathbf{G}_n = 2\pi(n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3)$ where \mathbf{n} represents an arbitrary triplet of integers n_1, n_2, n_3 .

The **reciprocal lattice** is a *Fourier space* for arbitrary functions that have the lattice periodicity

$$f(\mathbf{r}) = \sum_{\mathbf{n}} c_{\mathbf{n}} \exp(i\mathbf{G}_n \cdot \mathbf{r})$$

This is because all functions $\exp(i\mathbf{G}_n \cdot (\mathbf{r} + \mathbf{R}_m))$ are invariant under all possible lattice translations \mathbf{R}_m since $\exp(i\mathbf{G}_n \cdot \mathbf{R}_m) = 1$.

Arbitrary functions of position within the crystal

Consider a 1D reciprocal space. Make two sets of points :(1) the reciprocal lattice vectors \mathbf{G}_n , and (2) a set of \mathbf{k} points (all the points between $-\frac{1}{2}\mathbf{G}_1 = -\frac{\pi}{a}$ and $\frac{1}{2}\mathbf{G}_1 = \frac{\pi}{a}$ where a is real space primitive lattice constant).



- Waves $\exp(i\mathbf{G}_n \cdot \mathbf{r})$ are either constant ($\mathbf{G}_0 = 0$) or have a wavelength less than or equal to a ($\mathbf{G}_n \neq 0$). All are periodic in the primitive lattice.
- Waves $\exp(i\mathbf{k}_n \cdot \mathbf{r})$ are *not* periodic in the primitive lattice, and have a wavelength longer than a . Any \mathbf{k} not in the *first Brillouin zone* (i.e. not in the red cell) can be reduced into it since it is the sum of some \mathbf{G} and some \mathbf{k} between $-\frac{1}{2}\mathbf{G}_1$ and $\frac{1}{2}\mathbf{G}_1$.

Can therefore Fourier expand an arbitrary function of position within the solid which is not necessarily periodic in the real space lattice but obeys the boundary conditions at the surface :

$$g(\mathbf{r}) = \sum_{\mathbf{m}} \sum_{\mathbf{n}} c_{\mathbf{m},\mathbf{n}} e^{i(\mathbf{k}_n + \mathbf{G}_m) \cdot \mathbf{r}} = \sum_{\mathbf{n}} \left(\sum_{\mathbf{m}} c_{\mathbf{m},\mathbf{n}} e^{i\mathbf{G}_m \cdot \mathbf{r}} \right) e^{i\mathbf{k}_n \cdot \mathbf{r}} = \sum_{\mathbf{n}} u_{\mathbf{n}}(\mathbf{r}) e^{i\mathbf{k}_n \cdot \mathbf{r}}$$

where the red parts of the formula are cell-periodic functions.

Bloch functions

- The plane wave basis states $\exp(i(\mathbf{k}_n + \mathbf{G}_m))$ are not generally eigenfunctions ϕ of the Hamiltonian unless the potential is independent of position. We have seen that some linear combination of them must be:

$$\phi(\mathbf{r}) = \sum_{\mathbf{m}} \sum_{\mathbf{n}} c_{\mathbf{m},\mathbf{n}} e^{i(\mathbf{k}_n + \mathbf{G}_m) \cdot \mathbf{r}}$$

- Energy eigenvalues are found to depend on a specific vector \mathbf{k}_n . Can energy eigenfunctions be constructed from individual subsets of the set of terms appearing in this general expansion, each subset corresponding to a single value of \mathbf{k}_n ? Yes :

$$\phi_{\mathbf{n}}(\mathbf{r}) = \sum_{\mathbf{m}} \sum_{\mathbf{n}'} \delta_{\mathbf{n},\mathbf{n}'} c_{\mathbf{m},\mathbf{n}'} e^{i(\mathbf{k}'_{\mathbf{n}} + \mathbf{G}_m) \cdot \mathbf{r}} = e^{i\mathbf{k}_n \cdot \mathbf{r}} \sum_{\mathbf{m}} c_{\mathbf{n},\mathbf{m}} e^{i\mathbf{G}_m \cdot \mathbf{r}}$$

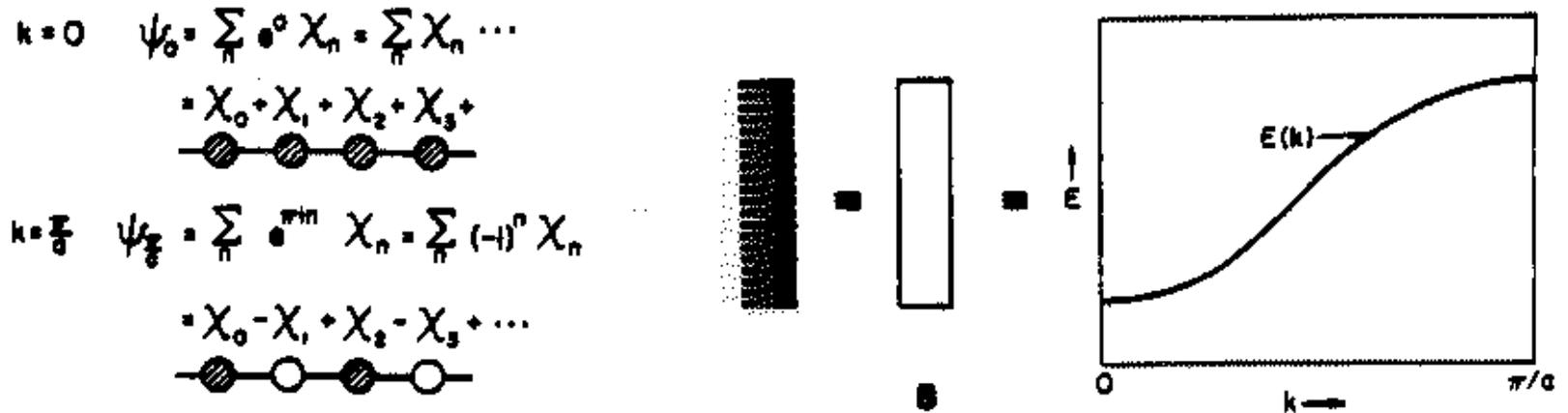
- Energy eigenfunctions for a periodic potential may be written in the form of **Bloch functions** :

$$\phi_{\mathbf{n}}(\mathbf{r}) = u_{\mathbf{n}}(\mathbf{r}) e^{i\mathbf{k}_n \cdot \mathbf{r}}$$

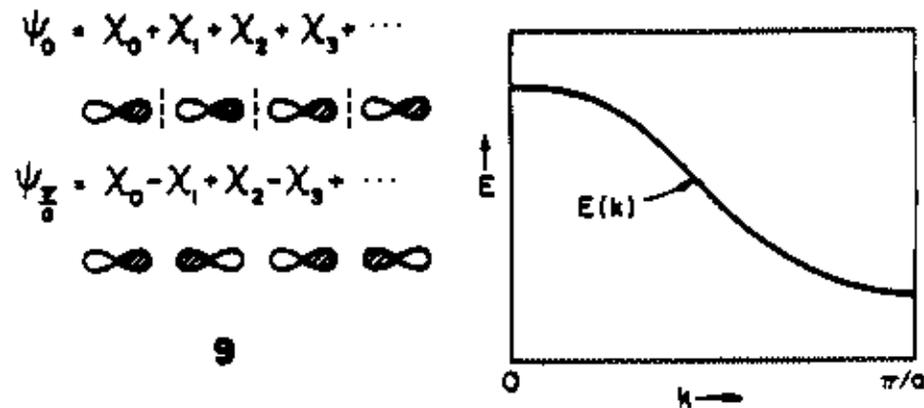
Any arbitrary function of position may be written as a linear combination of Bloch functions from different \mathbf{k} , and we will do so later in constructing *maximally localized Wannier orbitals* for 'linear scaling' QMC.

Band structure

s orbitals ($k = \frac{\pi}{a}$ most 'antibonding')



p orbitals ($k = 0$ most 'antibonding')

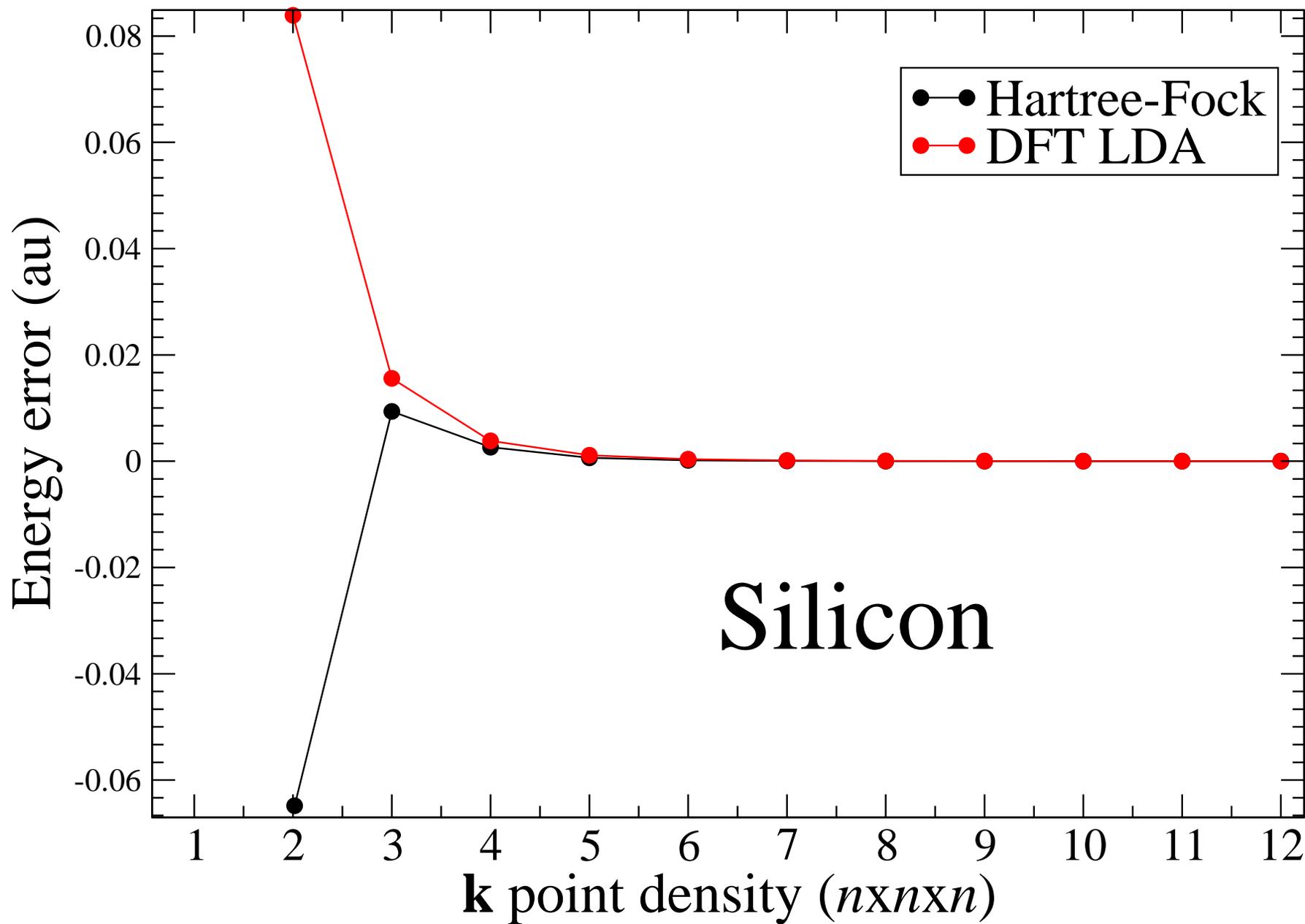


The topology of orbital interactions determines which way bands 'run'.

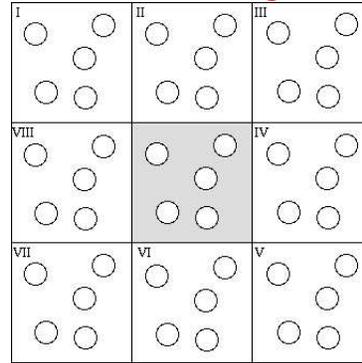
k point sampling

- Electronic states allowed only at set of \mathbf{k} points determined by boundary conditions on the bulk solid. Density of allowed \mathbf{k} points is proportional to the volume of the solid.
- Infinite number of electrons in the solid accounted for by an infinite number of \mathbf{k} points, and only a finite number of electronic states are occupied at each \mathbf{k} point.
- Don't need to calculate electronic states at infinite number of \mathbf{k} points, since the wave functions at \mathbf{k} points that are very close together will be almost identical. Represent *region* of \mathbf{k} space by single \mathbf{k} point. Then only finite number of objects need to be calculated in order to calculate the total energy of the solid.
- Calculation of properties requires *Brillouin zone integration* - done by straightforward sums over states using a special point scheme and modest number of \mathbf{k} points. Usual to use Monkhorst-Pack mesh (uniformly spaced \mathbf{k} -points with a possible offset of the origin).

Typical k point sampling errors



Many-body wave functions and periodic boundary conditions



- In band theory can reduce a problem into the real space primitive cell using \mathbf{k} points. In general with a many-body wave function we cannot.
- A primitive cell band theory calculation done on a $2 \times 2 \times 2$ \mathbf{k} -point grid defines a many-body wave function for a $2 \times 2 \times 2$ real-space supercell.
- How big does a cell need to be to represent the wave function properly? Needs to accommodate the exchange-correlation hole around each electron. Forces on particles in zero cell need to be approximately what they would be if the same cell was placed in genuine (aperiodic) bulk solid.
- For silicon, $2 \times 2 \times 2$ supercell might be sufficient (larger cells required for metals). Concept of 'plucking' useful to reduce errors in Brillouin zone integration in band theory calculation (subset of \mathbf{k} grid used in orbitals for supercell).

Many-body Bloch theorem

Invariance of \hat{H} under translation of *any* electron by simulation cell lattice vector :

$$\Psi_{\mathbf{k}_s}(\{\mathbf{r}_i\}) = u_{\mathbf{k}_s}(\{\mathbf{r}_i\}) \exp\left(i\mathbf{k}_s \cdot \sum_{i=1}^N \mathbf{r}_i\right)$$

Invariance of \hat{H} under translation of *all* electrons by primitive lattice vector.

$$\Psi_{\mathbf{k}_p}(\{\mathbf{r}_i\}) = w_{\mathbf{k}_p}(\{\mathbf{r}_i\}) \exp\left(i\mathbf{k}_p \cdot \frac{1}{N} \sum_{i=1}^N \mathbf{r}_i\right)$$

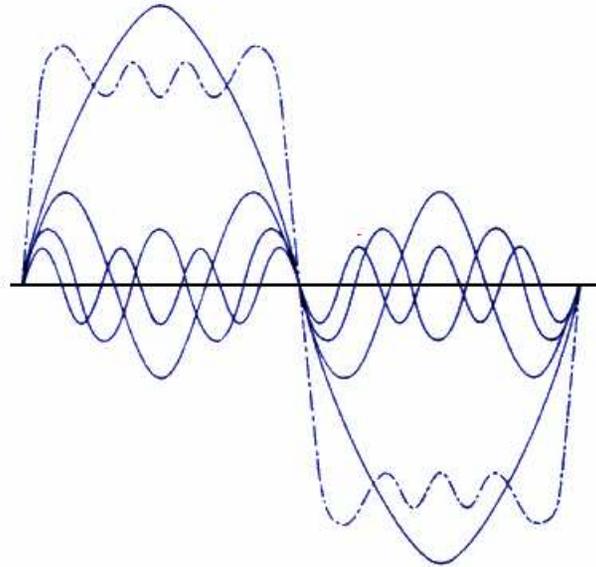
If simulation cell contains more than one primitive cell, the two wave vectors are distinct labels of the many-body wave function and both are required to specify the translational symmetry.

Other QMC considerations

- Bloch functions are normally complex, and need to make them real (with appropriate linear combinations) for use in FN-DMC.
- Minimize ‘independent particle finite size effects’ by choosing k_s appropriately. Still leaves ‘Coulomb finite size effects’ caused by the artificial periodicity in the many-electron Hamiltonian. Later.

Basis sets for orbitals : plane waves

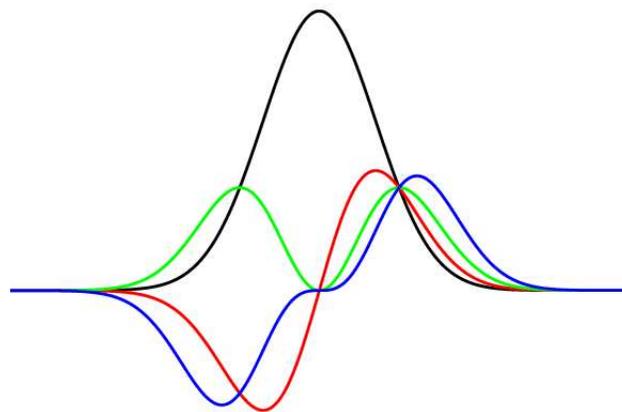
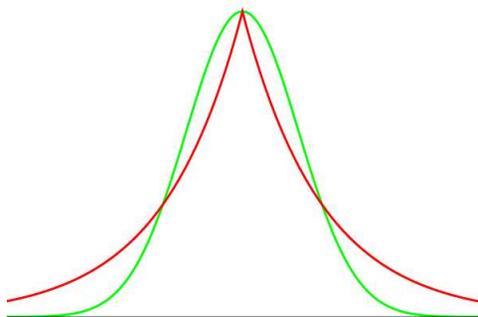
Use a Fourier expansion in plane waves, where the expansion coefficients are assumed to be zero for wave vectors \mathbf{G} whose kinetic energy $\frac{|\mathbf{G}|^2}{2}$ exceeds a cutoff.



GOOD : Orthonormal complete set. Universal. Systematic improvement by changing single cutoff parameter. DFT analytic gradients/forces accurate and cheap. Codes widely available.

BAD : Restricted detail in real space - need to use pseudopotentials. Must use periodic boundary conditions, even for molecules/surfaces etc. Non-local exchange difficult. FFTs not good for massively parallel computation. Delocalization \longrightarrow extra factor of N in scaling with system size in QMC.

Basis sets for orbitals : Gaussian functions



In quantum chemistry, long range behaviour and nuclear cusp originally suggested use of

Slater-type orbitals:

$$\chi^{STO} = r^{n-1} \exp(-\zeta r) Y_{lm}(\theta, \phi)$$

Not suitable for fast calc of multi-centre integrals so **Cartesian Gaussian functions** usually used instead:

$$\chi^{GTF} = \exp -\alpha r^2 x^l y^m z^n$$

SEPARABLE : $\chi^{GTF} = \chi_x \chi_y \chi_z$ with

$$\chi_x = \exp -\alpha(x - x_a)^2 (x - x_a)^l \text{ etc..}$$

Categorize into 'shells' with $L = l + m + n$:

s : 1 ($L = 0$)

p : x, y, z ($L = 1$)

d : $x^2, xy, xz, y^2, yz, z^2$ ($L=2$)

GOOD : Localized. Don't require pseudopotentials. Don't require periodic boundary conditions. Easier non-local exchange in one-electron codes (HF/hybrid DFT.. \rightarrow good for e.g. systems containing transition elements).

BAD : Not universal. Disobey electron-nuclear cusp conditions. Basis set superposition error. Physicists generally refuse to use them, chemists will use nothing else.

Tedious Acronyms for Gaussian basis sets

STO-2G, STO-3G, STO-6G, STO-3G*, 3-21G, 3-21++G, 3-21G*, 3-21GSP, 4-31G, 4-22GSP, 6-31G, 6-31G-Blaudeau, 6-31++G, 6-31G*, 6-31G**, 6-31G*-Blaudeau, 6-31+G*, 6-31++G**, 6-31G(3df,3pd), 6-311G, 6-311G*, 6-311G**, 6-311+G*, 6-311++G**, 6-311++G(2d,2p), 6-311G(2df,2pd), 6-311++G(3df,3pd), MINI (Huzinaga), MINI (Scaled), MIDI (Huzinaga), MIDI!, SV (Dunning-Hay), SVP+Diffuse (Dunning-Hay), DZ (Dunning), DZP (Dunning), DZP+Diffuse (Dunning), TZ (Dunning), Chipman DZP+Diffuse, cc-pVDZ, cc-PVTZ, cc-pVQZ, cc-pV5Z, cc-pV6Z, pV6Z, pV7Z, cc-pVDZ(seg-opt), cc-pVTZ(seg-opt), cc-PVQZ(seg-opt), cc-pCVDZ, cc-pCVTZ, cc-pCVQZ, cc-pCV5Z, aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, aug-cc-pV5Z, aug-cc-pV6Z, aug-pV7Z, aug-cc-pCVDZ, aug-cc-pCVTZ, aug-cc-pCVQZ, aug-cc-pCV5Z, d-aug-cc-pVDZ, d-aug-cc-pVTZ, d-aug-cc-pVQZ, d-aug-cc-pV5Z, d-aug-cc-pV6Z, Feller Misc. CVDZ, Feller Misc. cVTZ, Feller Misc. CVQZ, NASA Ames ANO, Roos Augmented Double Zeta ANO, Roos Augmented Triple Zeta ANO, WTBS, GAMESS V TZ, GAMESS PVTZ, Partridge Uncontr. 1, Partridge Uncontr. 2, Partridge Uncontr. 3, Ahlrichs VDZ, Ahlrichs, pVDZ, Ahlrichs VTZ, Ahlrichs TZV, Binning/Curtiss SV, Binning/Curtiss VTZ, Binning/Curtiss SVP, Binning-Curtiss VTZP, Mclean/Chandler VTZ, SV+Rydberg (Dunning-Hay), SVP+Rudberg (Dunning-Hay), SVP+Diffuse+Rydberg, DZ+Rydberg (Dunning), DZP+Rydberg (Dunning), DZ+Double Rydberg (Dunning-Hay), SV+Double Rydberg (Dunning-Hay), Wachters+f, Bauschlicher ANO, Sadlej pVTZ, Hay-Wadt MB(n+1)ECP, Hay-Wadt VDZ(n+1)ECP, LANL2DZ ECP, SBKJC VDZ ECP, CRENL ECP, CRENBS ECP, Stuttgart RLC ECP, Stuttgart RSC ECP, DZVP (DFT Orbital), DZVP2 (DFT Orbital), TZP (DFT Orbital), DeMon Coulomb Fitting, DGauss A1 DFT Coulomb Fitting, DGauss A1 DFT Exchange Fitting, DGauss A2 DFT Coulomb Fitting, DGauss A2 DFT Exchange Fitting, Ahlrichs Coulomb Fitting, cc-pVDZ-fit2-1, cc-pVTZ-fit2-1, cc-pVDZ_DK, cc-pVTZ_DK, cc-pVQZ_DK, cc-pV5Z_DK, cc-pVDZ(pt/sf/fw), cc-PVTZ(pt/sf/fw), cc-pVQZ(pt/sf/fw), cc-pV5Z(pt/sf/fw), cc-pVDZ(fi/sf/fw), cc-pVTZ(fi/sf/fw), cc-pVQZ(fi/sf/fw), cc-pV5Z(fi/sf/fw), cc-pVDZ(pt/sf/sc), cc-pVDZ(pt/sf/lc), cc-pVTZ(pt/sf/sc), cc-PVTZ(pt/sf/lc), ccp-PVQZ(pt/sf/sc), cc-pVQZ(pt/sf/lc), cc-PV5Z(pt/sf/sc), cc-PV5Z(pt/sf/lc), cc-pVDZ(fi/sf/sc), cc-PVDZ(fi/sf/lc), cc-PVTZ(fi/sf/sc), cc-PVTZ(fi/sf/lc), cc-PVQZ(fi/sf/sc), cc-PVQZ(fi/sf/lc), cc-PV5Z(fi/sf/sc), cc-pV5Z(fi/sf/lc), Pople-Style Diffuse, STO-3G* Polarization, 3-21G* Polarization, 6-31G* Polarization, 6-31G** Polarization, 6-311G* Polarization, 6-311G** Polarization, Pople (2d/2p) Polarization, Pople (3df,3pd) Polarization, HONDO7 Polarization, Huzinaga Polarization, Dunning-Hay Diffuse, aug-cc-pVDZ Diffuse, aug-cc-pVTZ Diffuse, aug-cc-pVQZ Diffuse, aug-cc-pV5Z Diffuse, aug-cc-pV6Z Diffuse, aug-pV7Z Diffuse, d-aug-cc-pVDZ Diffuse, d-aug-cc-pVTZ Diffuse, d-aug-cc-pVQZ Diffuse, d-aug-cc-pV5Z Diffuse, d-aug-cc-pV6Z Diffuse, DHMS Polarization, Dunning-Hay Rydberg, Dunning-Hay Double Rydberg, Binning-Curtiss (1d Polarization), Binning-Curtiss (df) Polarization, Ahlrichs Polarization, Glendenning Polarization, Blaudeau Polarization, Core/val. Functions (cc-pCVDZ), Core/val. Functions (cc-pCVTZ), Core/val. Functions (cc-pCVQZ), Core/val. Functions (cc-pCV5Z).

Contraction schemes

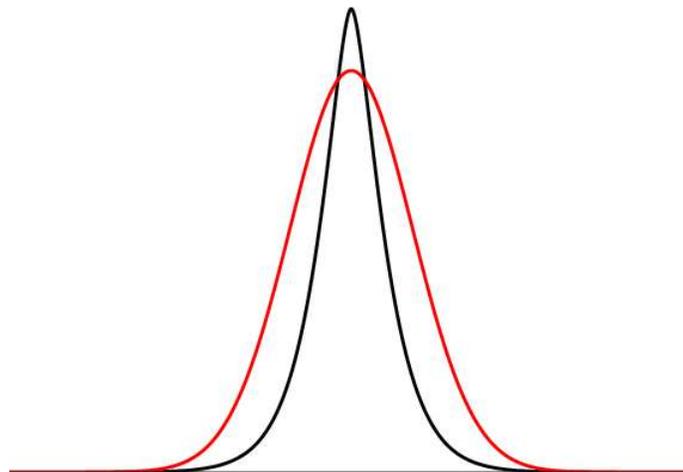
contraction m. 1 *(Tech.)* a linear combination of Gaussian primitives to be used as a basis function.

$$\chi_i^{CGTF}(r) = \sum_{j=1}^L c_j \chi_j^{GTF}(r)$$

$$\chi_j^{GTF}(r) = N_{lm}(\alpha) r^l Y_{lm}(\theta, \phi) \exp(-\alpha_j r^2)$$

- In HF etc. calculations, best results would be obtained if all coefficients in the Gaussian expansion were allowed to vary, but contractions give large increase in computational efficiency in HF etc. codes by reducing the number of orbital coefficients in the wave function.

α	c_j
3450660.8	0.000034
467601.94	0.000322
92314.514	0.0021
21992.520	0.0112
6082.9917	0.0475
1915.2715	0.157
676.43927	0.3524
263.00267	0.4238
106.89395	0.1593



Generic Gaussian basis set file

Oxygen basis with five shells

8 5

S 8 1.0

8020.0 0.00108

1338.0 0.00804

255.4 0.05324

69.22 0.1681

23.90 0.3581

9.264 0.3855

3.851 0.1468

1.212 0.0728

SP 4 1.0

49.43 -0.00883 0.00958

10.47 -0.0915 0.0696

3.235 -0.0402 0.2065

1.217 0.379 0.347

SP 1 1.0

0.4764 1.0 1.0

SP 1 1.0

0.1802 1.0 1.0

D 1 1.0 - polarization function

0.31 1.0

Web libraries

EMSL Molecular basis set library

www.emsl.pnl.gov/forms/basisform.html or www.cse.clrc.ac.uk/qcg/basis/

My basis set library (largely for solid-state calcs)

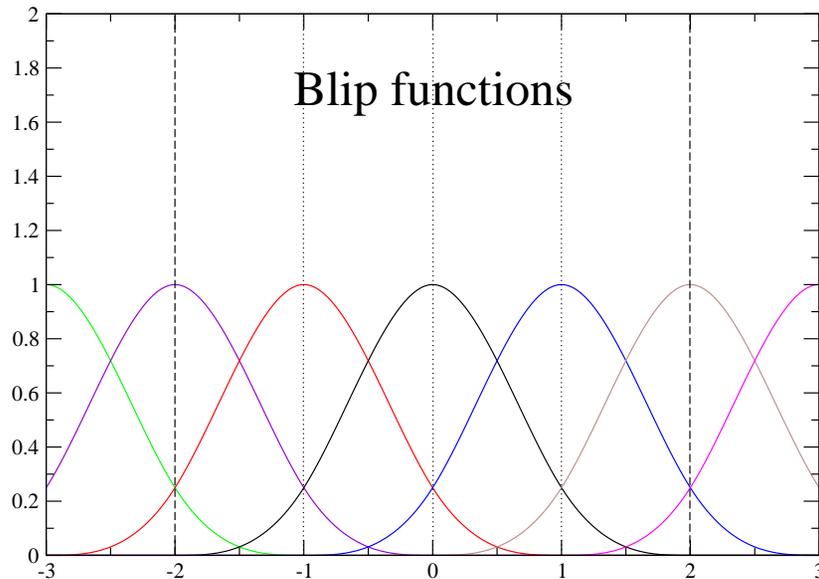
www.tcm.phy.cam.ac.uk/~mdt26/crystal.html

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uu _h	111 Uu _h	112 Uu _b	113 Uu _h	114 Uu _h	115 Uu _h	116 Uu _h	117 Uu _h	118 Uu _h
lanthanides			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
actinides			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Basis sets for orbitals : blip functions (splines)

Expansion in localized spline functions on a uniform grid

Grid spacing unity



$$\begin{aligned}\phi(x) &= 1 - \frac{3}{2}x^2 + \frac{3}{4}|x|^3 \quad 0 \leq |x| \leq 1 \\ &= \frac{1}{4}(2 - |x|)^3 \quad 1 < |x| \leq 2\end{aligned}$$

Grid spacing a

$$X_i = ia$$

$$\Theta(x - X_i) = \phi\left(\frac{(x - X_i)}{a}\right)$$

In 3 dimensions there are only 64 non-zero blips for each position \mathbf{r} . With plane waves the number of functions in e.g. silicon is around 100 per atom.

GOOD : Achieved from transformation of wave function expanded in plane waves with accompanying huge efficiency increase. Localized. Universal.

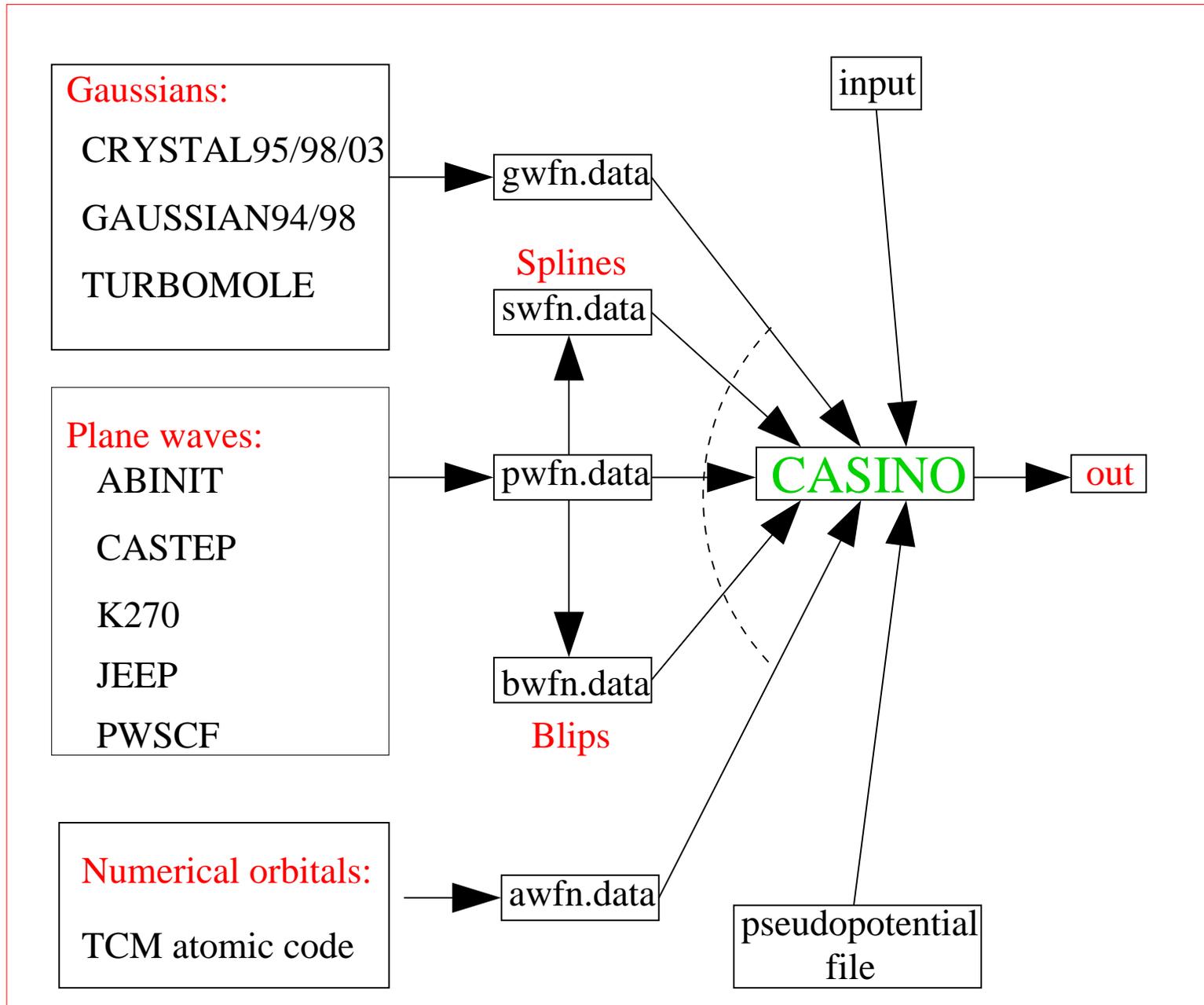
BAD : Somewhat greedy with memory and disk. Extra step required (blip transformation of plane wave data file).

No basis set : use a grid instead

Orbitals and their derivatives are represented numerically on a radial grid. Interpolate to get values at arbitrary position in space.

- Likely to be very expensive and inefficient for larger systems (though we have no direct experience with this).
- Implemented in CASINO for atoms only.

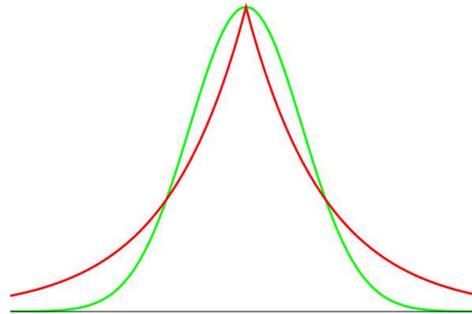
Interfaces to other programs



Cusp conditions

Cusp conditions prescribe the proper **derivative discontinuities** at the particle collision points, and ensure the divergence in the local potential is cancelled by an opposite divergence in the local kinetic energy.

- Electron-nuclear : e.g. H atom has **cusp** at origin : $\Psi(r) = \exp(-Zr)$



- Electron-electron : conditions on Slater-Jastrow $\Psi = D \exp(-u)$

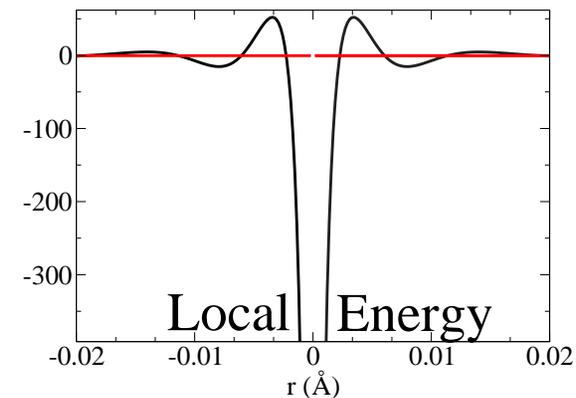
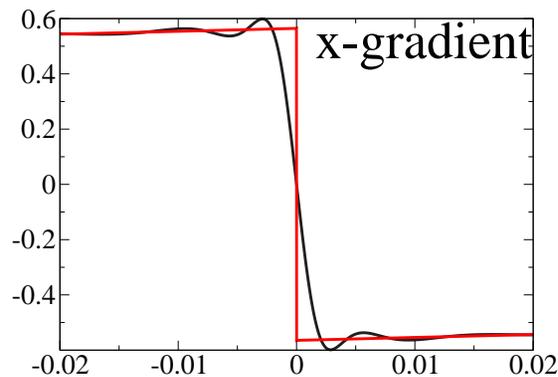
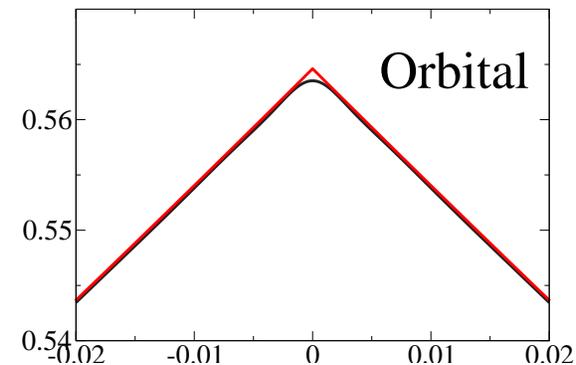
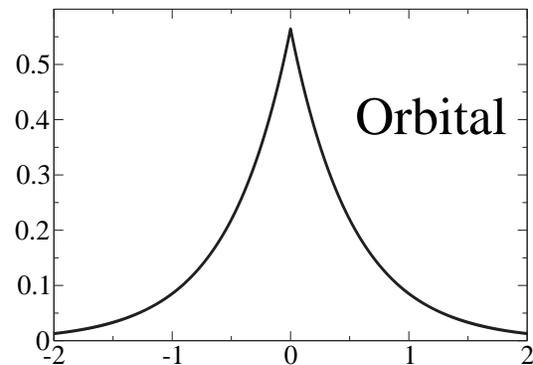
$$\left. \frac{\partial u}{\partial r} \right|_{r=0} = -\frac{1}{2} \quad \text{antiparallel spins}$$

$$\left. \frac{\partial u}{\partial r} \right|_{r=0} = -\frac{1}{4} \quad \text{parallel spins}$$

- Can therefore enforce electron-electron cusp conditions by imposing constraints on the Jastrow factor, but what about electron-nuclear?

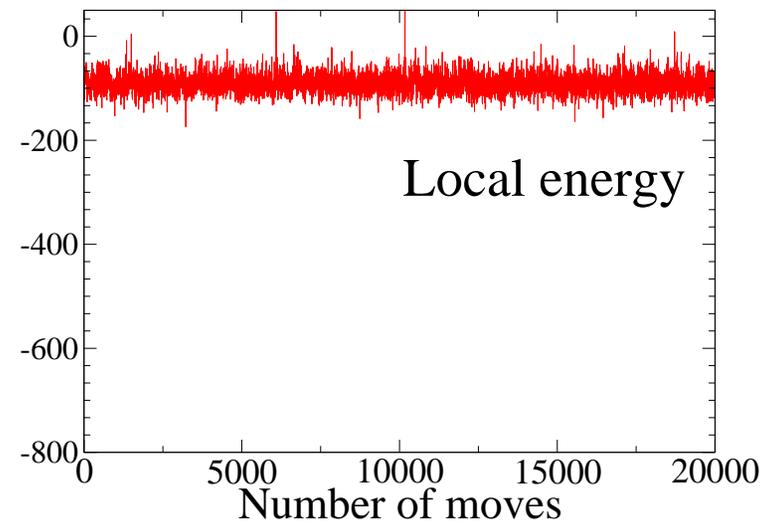
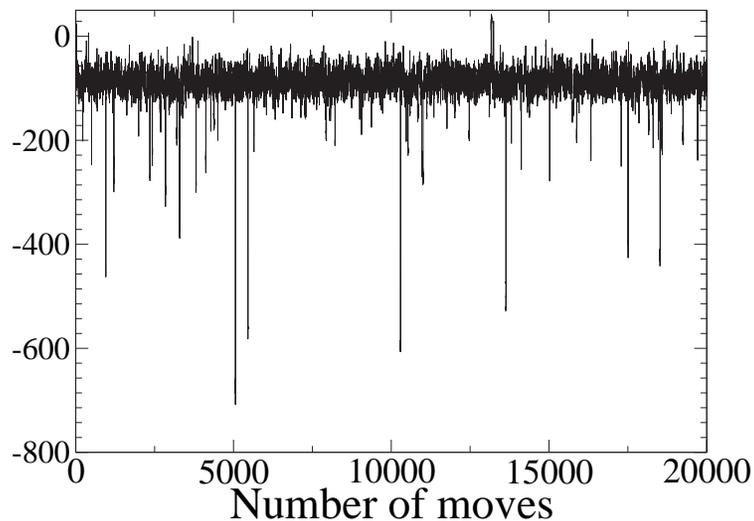
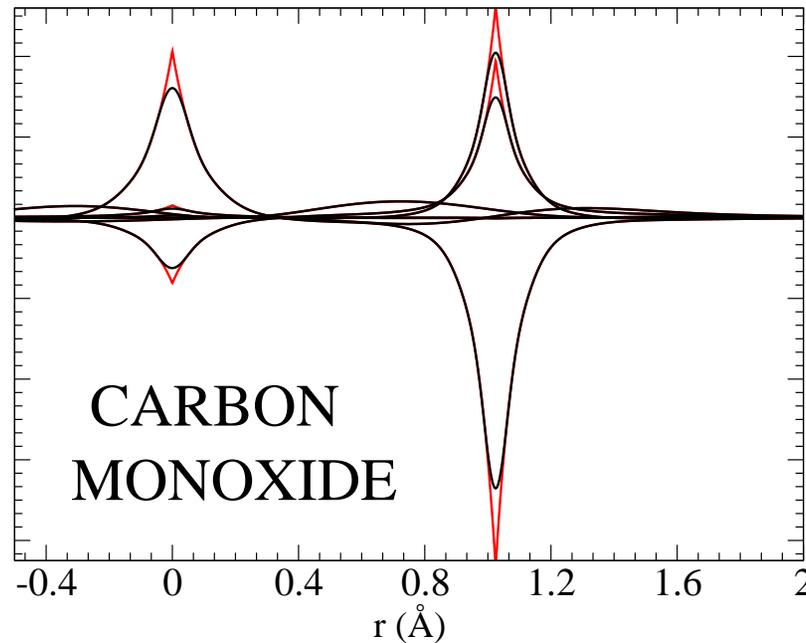
Cusp conditions for the orbitals

- Can imitate cusp by including very narrow Gaussians (i.e. with very high exponents) in the basis sets.
- Behaviour still incorrect in small region around nucleus. Can fix by chopping out part of the wave function in that region, and replacing with a polynomial that obeys suitable constraints (i.e. continuous first three derivatives at the join ; obey cusp condition ; choose $E_L(0)$ to minimize fluctuations in E_L inside cusp radius).



Cusp conditions for standard Gaussian basis sets

- Quantum chemists have developed libraries of standard Gaussian basis sets with perceived levels of accuracy. These often do not attempt to imitate the cusp (they are concerned with **integral properties**). How well do the polynomial cusp corrections work?



DMC stability

- Divergences of the local energy E_L (e.g. electron close to nucleus, or configuration close to nodal surface) can lead to instabilities in the DMC algorithm. Can cause configuration population explosions!
- Consider DMC branching factor (for configuration α at move m):

$$M_b(\alpha, m) = \exp \left[\left(-\frac{1}{2} \{ E_L(\mathbf{R}_{\alpha, m}) + E_L(\mathbf{R}'_{\alpha, m}) \} + E_T(m) \right) \tau \right]$$

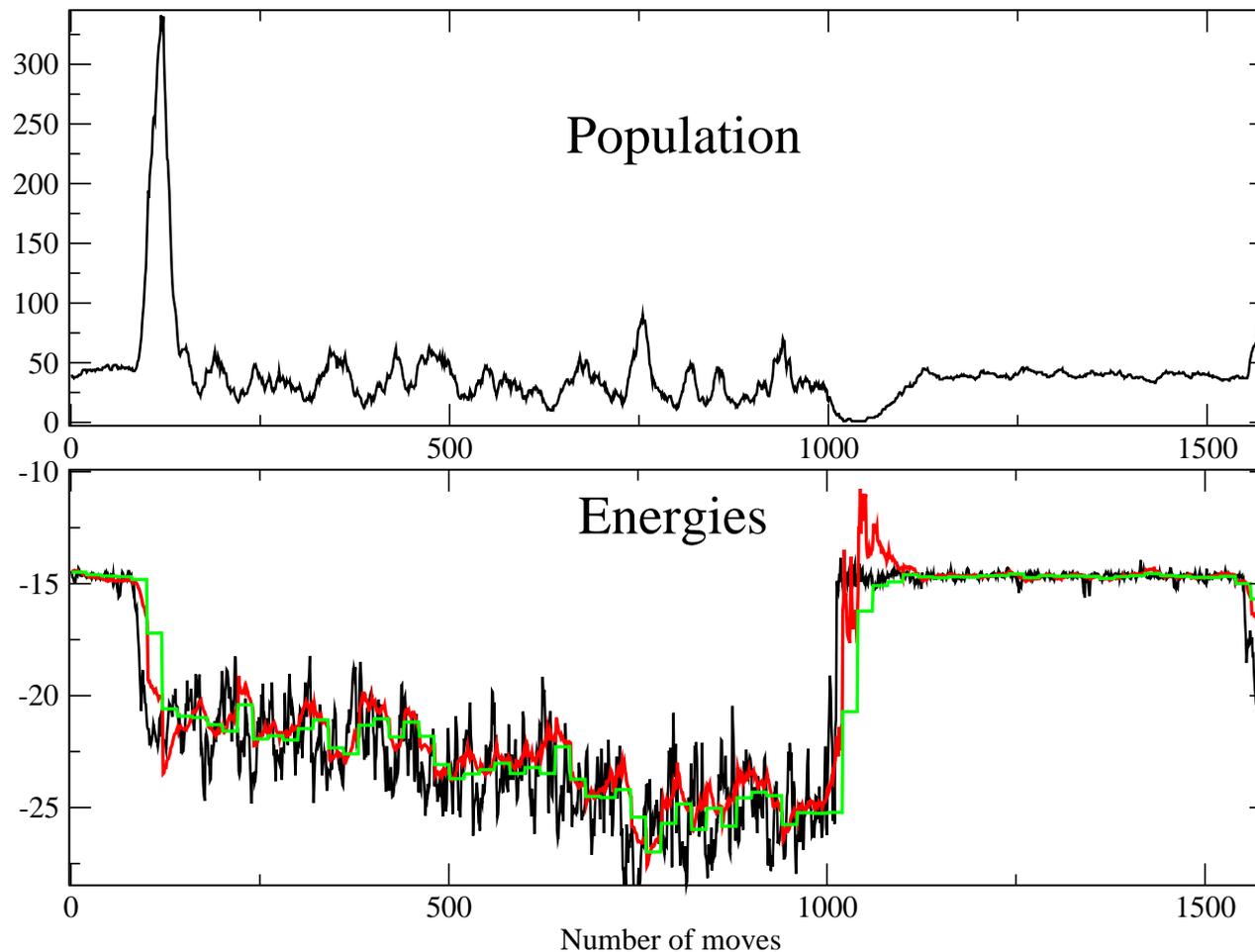
With unweighted DMC M copies of the configuration are made, where $M(\alpha, m) = \text{INT}\{\eta + M_b(\alpha, m)\}$ and η is random number from 0 to 1.

- Clearly if the average of $E_L(\mathbf{R})$ and $E_L(\mathbf{R}')$ is much less than E_T , the population of configurations will increase significantly. If much greater than E_T , the population will quickly decrease..
- Sometimes negative feedback from reference energy E_T will swing things back to normal ; sometimes a population containing low energy 'persistent electrons' is stabilized ; sometimes the fluctuation stops the calculation. Things get worse for bigger time steps and heavier nuclei..

Cusp corrections which minimize the fluctuations in E_L help prevent this!.

DMC catastrophes

As an example, here is a *persistent electron catastrophe* (increase DMC time step a lot to make it likely to see this. Combination of electron very close to nucleus with divergent local energy, with low probability of acceptance for moving away). Shift in E_T stabilizes it (and any copies). Fixed negative contribution to E_L until random fluctuation removes the persistent electron!



All-electron calculations for heavy atoms

QMC calculations scale quite badly with atomic number, and one rarely sees all-electron calculations for atoms with Z greater than around 6 (carbon). However, with the above cusp-correction scheme CASINO can be used to obtain DMC numbers relatively easily for heavy atoms. Here are some preliminary numbers for the noble gas atoms up to $Z = 54$ (using single determinant Slater-Jastrow wave functions, Gaussian basis set, time step around 0.002) :

atom	DMC total energy
neon ($Z = 10$)	-128.911312 ± 0.00043
argon ($Z = 18$)	-527.456985 ± 0.00090
krypton ($Z = 36$)	-2755.778517 ± 0.0037
xenon ($Z = 54$)	-7235.357378 ± 0.0033

Heaviest DMC all-electron calculations ever!

Pseudopotentials

The cost of all-electron QMC calculation increases *rapidly* with atomic number (somewhere between $Z^{5.5}$ and $Z^{6.5}$) (better with new algorithm?).

Why so much?

- Shorter length scale variations in the wave function near a nucleus of large Z require the use of a small time step. ('Acceleration schemes'?)
- Fluctuations in the local energy large near nucleus because KE and PE terms large there. (Fix up the cusp?)

What to do about it?

Most properties of interest depend on 'valence electrons' - so can use **pseudopotentials** to remove chemically inert core electrons (reduces effective Z). Errors inevitably introduced but gain in efficiency large enough to allow applications to heavy atoms.

I hate pseudopotentials!



What kind of pseudopotentials should we use?

Options

- Construct pseudos directly within QMC framework?
- Use pseudos from Hartree-Fock theory?
- Use pseudos from density functional theory?
- Watch out for standard pseudos which diverge at the nucleus.
- Should incorporate relativistic effects?
- Account for core-valence correlation using **core polarization potentials**.

Best option appears to be : **smooth non-divergent (D)HF pseudopotentials (with relativistic corrections) combined with core polarization potentials.**

Lock student in room for 5 years until :

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
Period																		
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Uu	Uub	Uuc	Uud	Uue	Uuf	Uug	Uuh	Uuo
lanthanides	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb				
actinides	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No				

Functional form of Jastrow factor in CASINO

$$\Psi = e^J \sum_n c_n D_n^\uparrow D_n^\downarrow \quad \text{with} \quad J = - \sum_{i>j,j} [u_0(r_{ij}) + S_1(r_{ij})] - \sum_i \sum_I S_2(r_{iI})$$

Non-linear r_{ij} term

$$u_0(r_{ij}) = \frac{A}{r_{ij}} \left[1 - \exp\left(-\frac{r_{ij}}{F}\right) \right] \exp\left(-\frac{r_{ij}^2}{L_0^2}\right),$$

Homogeneous r_{ij} term

$$S_1 = (r_{ij} - L')^2 r_{ij}^2 \sum_{l=0}^{l1} \alpha_l T_l(\bar{r}'_{ij}) + B' (r_{ij} - L')^2 \left(\frac{L'}{2} + r_{ij} \right)$$

r_i dependent term

$$S_2 = (r_i - L)^2 r_i^2 \sum_{l=0}^{l2} \beta_l T_l(\bar{r}_i) + B (r_i - L)^2 \left(\frac{L}{2} + r_i \right)$$

Red parameters need optimizing; green parameters are fixed (usually to sensible defaults); T_l are Chebyshev polynomials. Higher order terms ($S_3 - S_5$) are available but little used.

Variance minimization

So we have a bunch of parameters $\{\alpha_0\}$ that need optimizing to the optimum set $\{\alpha\}$. In CASINO these can be Jastrow parameters, determinant coefficients in a multideterminant wave function, or various specialized parameters in electron and electron-hole phases.

- In general can optimize variance or energy ; variance is usually preferred.

$$E_{\text{VMC}} = \frac{\int \Phi^2(\alpha) E_L(\alpha) d\mathbf{R}}{\int \Phi^2(\alpha) d\mathbf{R}}$$
$$\text{Var}(E) = \frac{\int \Phi^2(\alpha) [E_L(\alpha) - E_{\text{VMC}}(\alpha)]^2 d\mathbf{R}}{\int \Phi^2(\alpha) d\mathbf{R}}$$

approximated by

$$E_{\text{VMC}} \simeq \frac{1}{M} \sum_i^M E_L(\mathbf{R}_i; \alpha)$$
$$\text{Var}(E) \simeq \frac{1}{M} \sum_i^M [E_L(\mathbf{R}_i; \alpha) - E_{\text{VMC}}(\{\mathbf{R}_i\}; \alpha)]^2$$

We can't recalculate these every time we change the parameters so we must use another approach: *correlated sampling*.

Variance minimization

Rewrite energy and variance for correlated sampling

$$E_V = \frac{\int \Phi^2(\alpha_0) w(\alpha) E_L(\alpha) d\mathbf{R}}{\int \Phi^2(\alpha_0) w(\alpha) d\mathbf{R}}$$

$$\text{Var}(E) = \frac{\int \Phi^2(\alpha_0) w(\alpha) [E_L(\alpha) - E_V(\alpha)]^2 d\mathbf{R}}{\int \Phi^2(\alpha_0) w(\alpha) d\mathbf{R}}$$

$$w(\alpha) = \frac{\Phi^2(\alpha)}{\Phi^2(\alpha_0)} \quad \text{Weight}$$

Average over M configurations drawn from $\Phi^2(\alpha_0)$

$$E_V \simeq \frac{\sum_i^M w(\mathbf{R}_i; \alpha) E_L(\mathbf{R}_i; \alpha)}{\sum_i^M w(\mathbf{R}_i; \alpha)}$$

$$\text{Var}(E) \simeq \frac{\sum_i^M w(\mathbf{R}_i; \alpha) [E_L(\mathbf{R}_i; \alpha) - E_V(\{\mathbf{R}_i\}; \alpha)]^2}{\sum_i^M w(\mathbf{R}_i; \alpha)}$$

- Eigenstates of \hat{H} give zero variance for *any* set of configurations
- Eigenstates of \hat{H} give zero variance for *any* set of (positive) weights

Variance minimization

Procedure

1. *Configuration generation* : use the Metropolis algorithm to generate large number of configurations distributed according to an initial Ψ_T .
2. *Variance minimization* : vary the parameter set - calculating the variance using the equation with the weights in it - and find the parameter set for which the variance is minimized.
3. Return to step 1 if necessary and regenerate the configs using the partially optimized wave function.

Numerical instabilities can arise from the weights, particularly in large systems and when moving the nodes. To prevent this you can **limit their maximum value** or **set them to unity**. If the change in the parameters is relatively small, tests indicate that fixing them to unity is the best choice. This makes numerical optimization more stable in general, although it may require more config generation/variance minimization iterations.

In CASINO, all this is done automatically by the run script so one might type `'runvarmin -n 3 -v'` which would execute $n = 3$ of the above cycles followed by `(-v)` a final VMC run with configuration generation turned off to check the result of the final variance minimization.

Optimization strategies

Crucial point :

- How many parameters do you wish to optimize? (*As few as possible*).
- How many configurations do you use? (*As many as you can*)

Only possible to optimize a finite number of parameters. Progressively add more until decrease in energy from adding more parameters is comparable to the VMC error bar.

Other points :

- VMC run must be uncorrelated. Carry out a large number of VMC moves between writing out configurations. Minimize serial correlation by adjusting the VMC time step such that the move acceptance ratio is close to 50%.
- Turn off weighting in general (but beware pathological cases - remember with no weights we only affect the KE during the minimization).

Final checks :

- Does the VMC energy after each successive config generation/variance minimization iteration fall by a statistically significant amount?

Spin

Antisymmetric wave function for an N -electron system ($N = N_\uparrow + N_\downarrow$) in an $S_z = (N_\uparrow - N_\downarrow)/2$ state (non-relativistic; no external magnetic field) can be decomposed in terms of spin components:

$$\Psi(\mathbf{r}_1 s_1, \dots, \mathbf{r}_N s_N) = \sum_{i=1}^K F_i(\mathbf{r}_1, \dots, \mathbf{r}_N) \chi_i(s_1, \dots, s_N)$$

Permutation symmetry implies expectation value of spin-dependent operator with (Slater-Jastrow) wave function can be written as:

$$\Psi(\mathbf{R}) = e^{J(\mathbf{R})} \sum_i D_i^\uparrow(\mathbf{r}_1, \dots, \mathbf{r}_{N_\uparrow}) D_i^\downarrow(\mathbf{r}_{N_\uparrow+1}, \dots, \mathbf{r}_N)$$

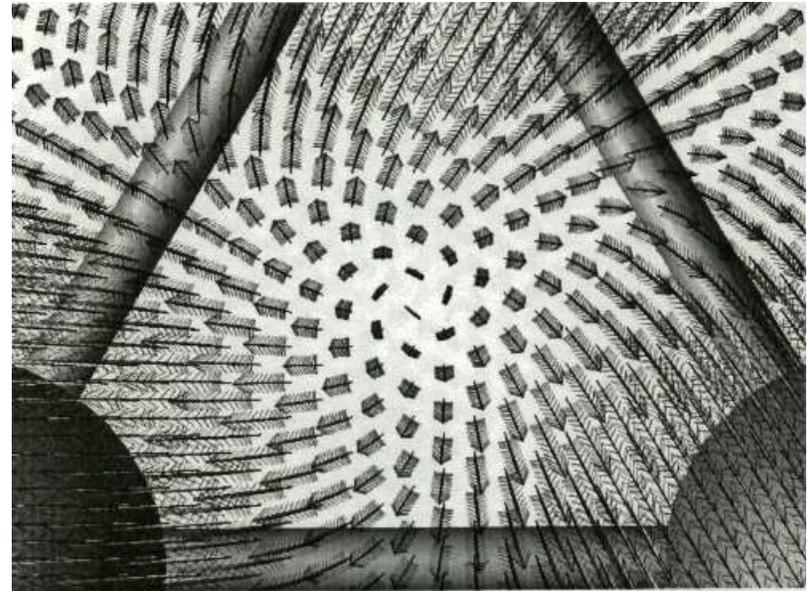
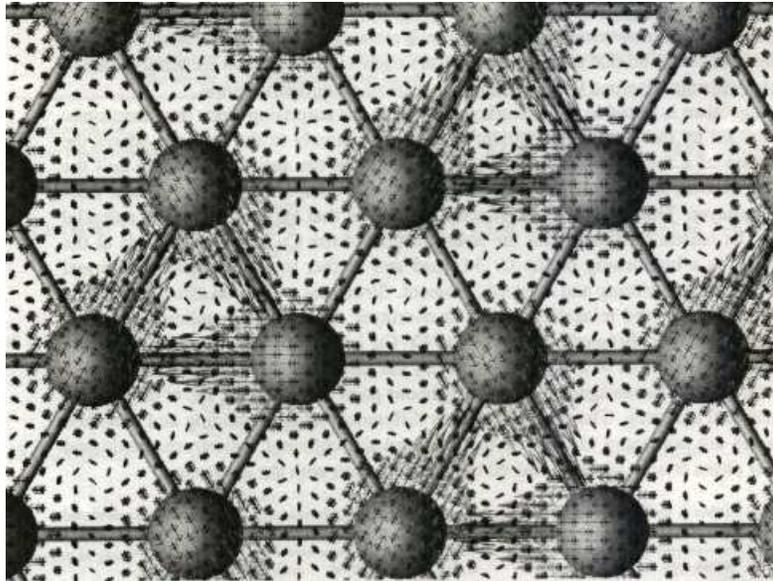
Is it an eigenstate of \hat{S}^2 as well as \hat{S}_z ? Determinant part can be constructed to be so (as in quantum chemistry). Jastrow not necessarily (not invariant under exchange of two antiparallel electrons). Options?

- Use totally symmetric Jastrow factor (increases energy and variance!)
- Wave function with asymmetric Jastrow satisfying cusp conditions (not generally eigenstate of \hat{S}^2 , but optimization reduces spin contamination).
- Can construct wave function that satisfies cusp conditions and is eigenstate of \hat{S}^2 (but increases scaling by N , since need to do explicit sum over spin components unless Jastrow is spin-independent).

Single determinants of one-electron spin orbitals

- **Restricted form** All spin orbitals are pure space-spin products of the form $\phi_n\alpha$ or $\phi_n\beta$ and are occupied singly or in pairs with a common orbital factor ϕ_n .
- **Unrestricted form** Spin orbitals no longer occupied in pairs but still pure space-spin products $\phi_n\alpha$ or $\bar{\phi}_n\beta$. However, now have different spatial factors ϕ_n and $\bar{\phi}_n$ for different spins.

What to do for non-collinear spin states?



- **General unrestricted form** No longer restrict to simple product form. Each spin orbital now a 2-component complex spinor orbital:
 $\Psi_1 = \phi_1^\alpha\alpha + \phi_1^\beta\beta$ and $\Psi_2 = \phi_2^\alpha\alpha + \phi_2^\beta\beta$. **Interesting QMC project!**

Total energy

Total energy = KE + electron-ion + electron-electron + ion-ion

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i\alpha} v_\alpha(\mathbf{r}_i, \mathbf{r}_\alpha) + \frac{1}{2} \sum_i \sum_{j \neq i} v(\mathbf{r}_i, \mathbf{r}_j) + \frac{1}{2} \sum_\alpha \sum_{\beta \neq \alpha} v(\mathbf{r}_\alpha, \mathbf{r}_\beta)$$

Electron-electron Coulomb interactions in periodic systems

Solve Poisson's equations subject to periodic boundary conditions:

$$v_E(\mathbf{r}, \mathbf{r}_j) = \sum_{\mathbf{R}} \frac{\operatorname{erfc}(\gamma^{\frac{1}{2}} |\mathbf{r} - (\mathbf{r}_j + \mathbf{R})|)}{|\mathbf{r} - (\mathbf{r}_j + \mathbf{R})|} - \frac{\pi}{\Omega \gamma}$$

3D Ewald formula

$$+ \frac{4\pi}{\Omega} \sum_{\mathbf{G} \neq 0} \frac{\exp(-G^2/4\gamma)}{G^2} \exp(i\mathbf{G} \cdot (\mathbf{r} - \mathbf{r}_j))$$

MANY-BODY BLOCH THEOREM

Ewald energy remains unchanged if single electron translated by a supercell lattice vector, or *all* electrons translated by a primitive cell lattice vector.

Coulomb finite size effects

How big does cell have to be before Ewald energy of zero cell in field of the rest of the crystal closely matches infinite supercell size limit?

Sources of error :

(1) 'Squeezing of XC hole' (minor effect, usually).

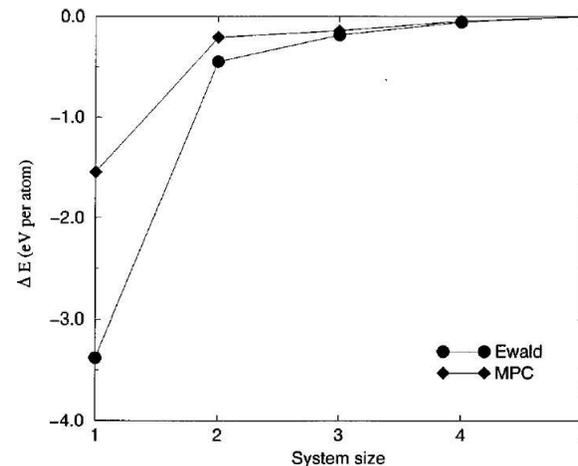
(2) Interaction with periodic array of XC holes, **OR EQUIVALENTLY**

Ewald interaction contains effective 'depolarization field' to cancel field due to surface charges. All supercells contain *same net dipole* due to random arrangement of electrons with respect to nuclei. Dipole and field interact.

Solution is to change many-body Hamiltonian so that interaction with XC hole is exactly $1/r$, without altering Hartree energy. Thus:

$$\hat{H}_{e-e}^{\text{exact}} = \sum_{i>j} f(\mathbf{r}_i - \mathbf{r}_j) + \sum_i \int_{\text{WS}} \rho(\mathbf{r}) [v_E(\mathbf{r}_i - \mathbf{r}) - f(\mathbf{r}_i - \mathbf{r})] d\mathbf{r}$$

**MODIFIED
PERIODIC
COULOMB (MPC)
INTERACTION**

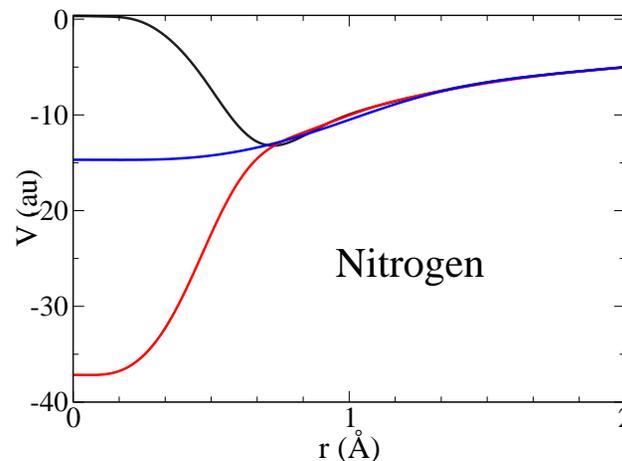


Electron-ion interactions

$$\hat{H}_{e-i} = \sum_{i=1}^N V_i^{\text{long}}(\mathbf{R}) + \sum_{i=1}^N V_i^{\text{short}}(\mathbf{R}) + \sum_{i=1}^N \frac{\hat{V}_{\text{nl},i}^{\text{short}} \Psi(\mathbf{R})}{\Psi(\mathbf{R})}$$

long-range local + short-range local + short-range non-local

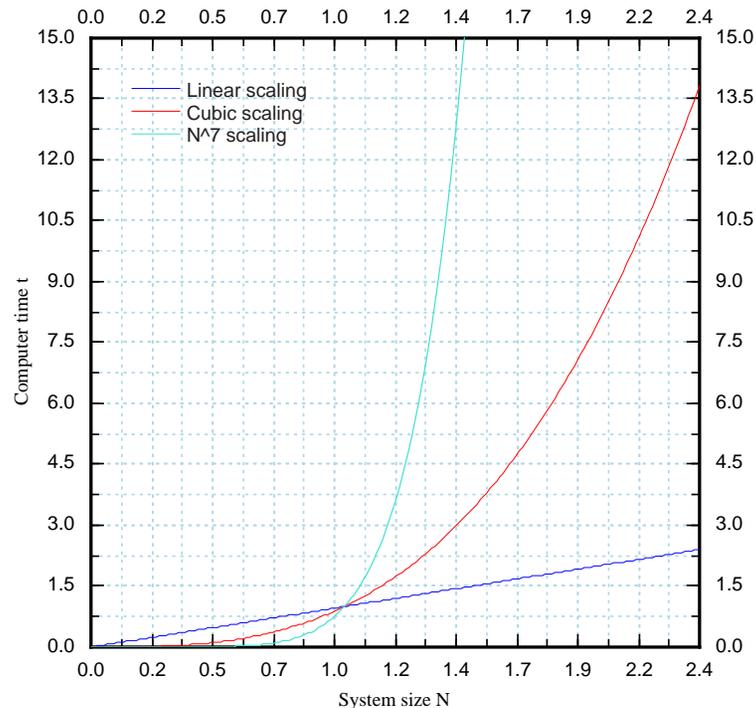
$$V_{\text{nl},i} = \sum_l V_{\text{nl},l}^{\text{ps}}(r_i) \frac{2l+1}{4\pi} \int P_l[\cos(\theta'_i)] \times \frac{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_{i-1}, \mathbf{r}'_i, \mathbf{r}_{i+1}, \dots, \mathbf{r}_N)}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_{i-1}, \mathbf{r}_i, \mathbf{r}_{i+1}, \dots, \mathbf{r}_N)} d\Omega_{\mathbf{r}'_i}$$



- Horrible non-local angular integration - takes a lot of time.
- Done *approximately* in DMC. Error should be small but not tested extensively ('LOCALITY APPROXIMATION').

Scaling with system size

Important consideration with all electronic structure methods : how does the computational cost increase as the size of the system N is increased?



method	scaling
Hartree-Fock	N^3
DFT	N^3
CCSD(T)	N^7

- Coupled cluster theory CCSD(T) probably most competitive quantum chemistry correlated wave function method, but the standard algorithm has disastrous scaling! (Recent developments could improve this).
- Great efforts made to write *linear-scaling* DFT codes over the last decade. Very difficult problem! Not completely solved.

So how does QMC scale with system size?

Moving all N electrons **once**, using delocalized basis (e.g. plane waves)

- Evaluating orbitals (N orbitals expanded in N basis functions at each of N electron positions): $\mathcal{O}(N^3)$ (RATE DETERMINING STEP)
- Evaluating electron-electron and electron-ion interactions and Jastrow factor : $\mathcal{O}(N^2)$
- Re-evaluating ratio of new to old Slater determinant (requires storing and updating the cofactors of the matrix) : $\epsilon \mathcal{O}(N^3)$

Moving all N electrons **once**, using localized basis (e.g. Gaussians/splines)

- Number of non-zero basis functions at random point independent of system size, therefore evaluating orbitals becomes $\mathcal{O}(N^2)$

$$\text{Standard algorithm : } C = AN^2 + \epsilon N^3$$

Current simulations :

ϵ is very small and currently $N \leq 2000$ electrons

$\implies \mathcal{O}(N^2)$ to move all electrons once

Can we do any better than this?

Use localized orbitals

- Non-singular linear transformations of the orbitals leave Slater determinants unchanged. So we can carry out such a transformation to a highly localized set of functions, truncate the functions so they are zero outside a certain radius and smoothly interpolate them to zero at a truncation radius.
- When an electron is moved, only a few functions must be evaluated; the others are zero as the electron is outside their truncation radii. The number of orbitals to be updated does not increase with system size.

$$\text{New algorithm : } C = AN + BN^2 + \epsilon N^3$$

ϵ is very small ; B is relatively small ; other tricks can improve the N^2 and N^3 terms $\implies \mathcal{O}(N)$ to move all electrons once \implies **linear scaling!**

This is the basis for the titles of the following papers :

Linear scaling quantum Monte Carlo, A.J. Williamson, R.Q. Hood, J.C. Grossman, Phys. Rev. Lett. **87**, 246406 (2001) (**CASINO**).

Linear-scaling for the local energy in quantum Monte Carlo, S. .Manten and A. Lüchow, J. Chem. Phys. **119** 1307 (2003).

However, we have forgotten something!

General linear scaling QMC is impossible!

Stochastic QMC \implies mean value \pm desired error bar from M statistically independent samples of local energy.

$$\text{Variance of mean energy : } \sigma_{\text{run}}^2 = \frac{\sigma^2}{M}$$

$$\text{Total computer time: } T_{\text{run}} = MT_{\text{sample}} = \frac{\sigma^2 T_{\text{sample}}}{\sigma_{\text{run}}^2} \text{ where}$$
$$T_{\text{sample}} \propto N + \epsilon N^2$$

Sample variance σ^2 proportional to number of electrons N (if assume energies of electrons uncorrelated), therefore multiply T_{run} by N to maintain desired error bar \implies **quadratic scaling!**

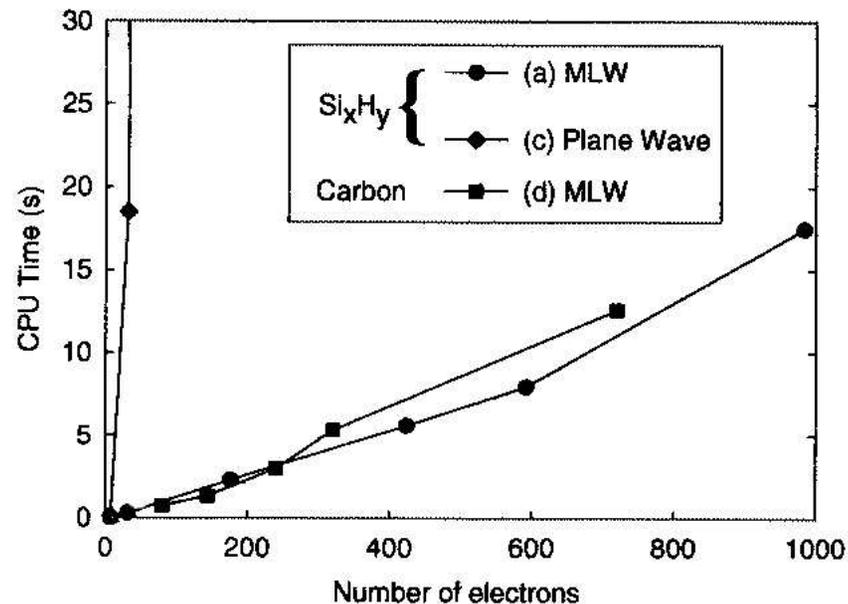
Properties of most interest: e.g. defect formation energies, energy barriers, excitation energies i.e. energy differences which become independent of system size when the system is large enough. To perform such a calculation we require a **statistical error bar which is independent of system size.**

NB : There are some properties (e.g. cohesive energies of solids) which can be derived from **total energies per atom**. In this case, the sample variance still increases linearly, but the error bar is decreased by a factor of N and thus the number of moves required *decreases* linearly. Hence the total cost is *independent of the size of the system* (even better than linear scaling!). However, such properties are of limited interest.

Linear scaling in CASINO

These algorithms have been implemented in CASINO.

- Form QMC wave functions with significant sparsity in the Slater determinant by using **maximally localized Wannier functions** instead of the delocalized Bloch orbitals that come out of standard band calculations. Use blip/spline basis.
- Currently trial wave functions must be generated with a plane-wave code. A utility is then used to perform a Wannier transformation to localized orbitals (still expanded in plane waves). A second utility is then used to reexpand the orbitals in splines. At the moment we are restricted to orthorhombic simulation cells and Γ -point only, but this will change.



Other terms

How do we get the improved scaling for the other terms?

Jastrow factor

- Truncate Jastrow at some distance which is independent of system size. Since correlations are essentially local, it is natural to truncate at the radius of the exchange-correlation hole. Doesn't affect final DMC answer since it leaves the nodal surface unchanged, but statistical noise may increase if truncate at too short a range.

Coulomb interactions

- More difficult. Cannot simply truncate Coulomb interaction, but can use the fact that the correlation is short-ranged to replace the long-range part by its Hartree contribution ('Modified Periodic Coulomb' or MPC interaction).

N^3 determinant update

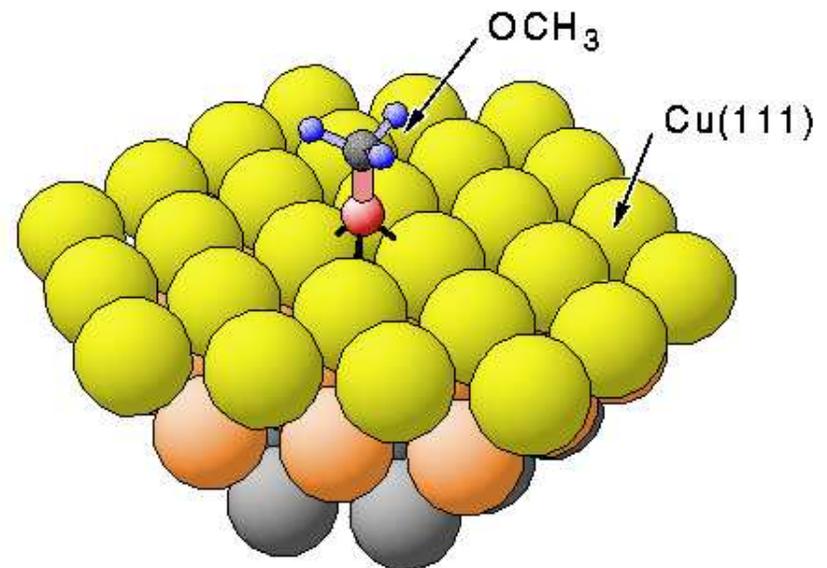
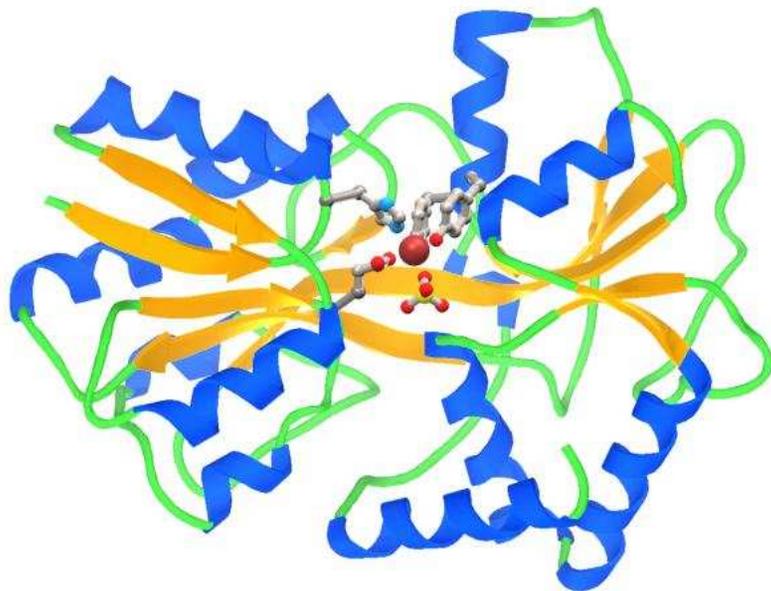
- In localized orbital representation, only subset of orbitals change when an electron is moved. Introduce new algorithm for performing the update procedure when the changes to the cofactor matrices are sparse (noting that nature of sparsity changes during the run.) The pre-factor is so small that in fact this term makes very little significant contribution to the overall cost of a calculation.

Interesting idea

A further useful thing one could do with this sort of technology would be :

A QMC EMBEDDING ALGORITHM

One could in some sense **embed** a QMC calculation within a cheaper DFT one. The idea is to use the higher accuracy of QMC where it most needed, such as around the active site of an enzyme, around a defect site in a solid, or in the neighbourhood of a molecule attached to a solid surface.



Likely to be easy with VMC and difficult with DMC.

Interesting current problems

- How to go beyond the fixed-node approximation?
- How to optimize orbitals efficiently?
- How to implement forces?
- How to increase efficiency/reduce the error bar (QMC always going to be expensive compared to standard band theory).
- Efficient finite temperature calculations.
- QMC/DFT embedding.
- How to implement non-collinear spins?

Coffee Break



Be back here at 11.30.