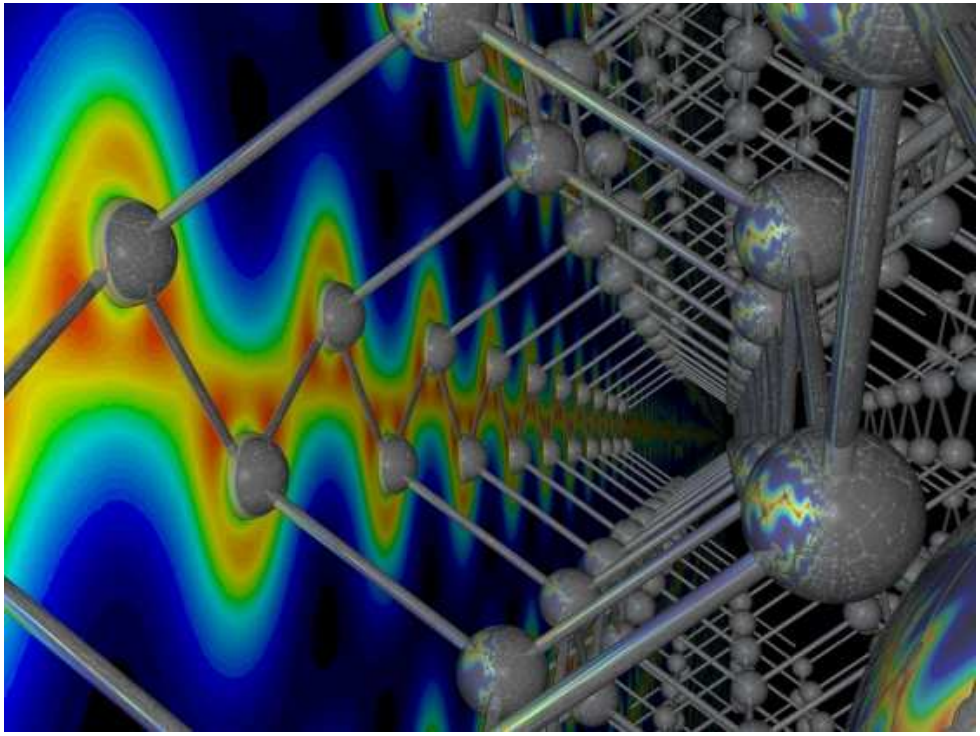
Localized orbitals and localized basis sets

STUDENT CHALLENGE



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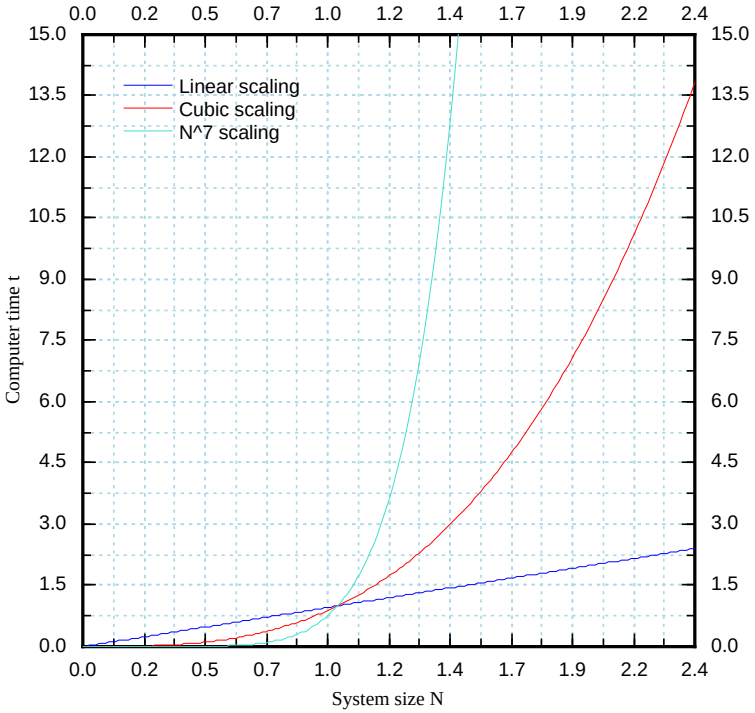
Linear scaling QMC



method	scaling
Hartree-Fock	$N^3 - N^4$
DFT	N^3
QMC	$N^3 - N^4$
CCSD(T)	N^7

Scaling improvement in QMC simply a matter of using localized orbitals and localized basis sets.

If an electron is far enough from the centre of a localized orbital, then we can assume it to be zero, thereby avoiding a great deal of unnecessary calculation.

Linear scaling QMC fallacy No. 1 - paper titles

Linear scaling quantum Monte Carlo calculations, Williamson et al. (2001).

Linear scaling quantum Monte Carlo technique with non-orthogonal localized orbitals, Alfè and Gillan (2004).

Linear scaling for the local energy in quantum Monte Carlo, Manten and Lüchow (2003).

- Memory requirement scales linearly.
- Time to do 1 MC move and calculate local energy once scales linearly.
- But need to do many MC moves - in fact an *increasing* number of them as the system size increases if you want to keep the error bar the same. Time taken to calculate the local energy to a given error bar thus scales as the square of the system size, so according to all previously established conventions, it should be called *quadratic scaling quantum Monte Carlo*.

Thus only Manten alludes to this in his choice of title.

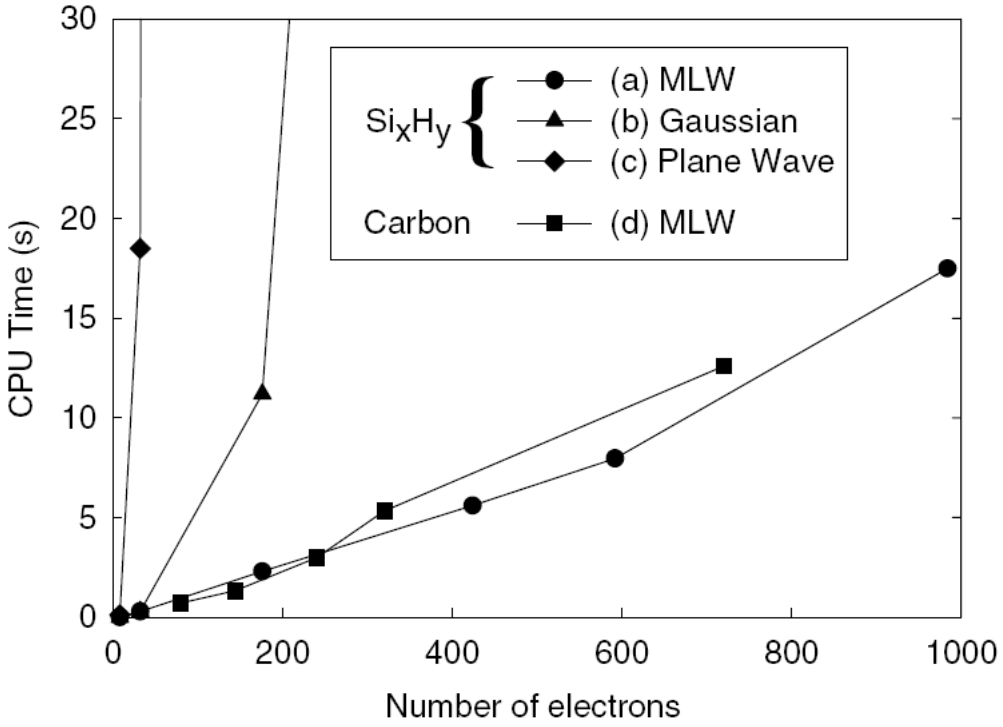
"I think you know the answer to that, Mike. Because it sounds cool."

A.J. Williamson, Leiden conference, 2004

Linear scaling QMC fallacy No. 2

The necessity of splines

Misleading figure from Williamson paper



Fails to mention that curves marked 'Gaussian' and 'Plane Wave' (which are basis sets) are produced with delocalized orbitals whereas his curve marked 'MLW' (Maximally Localized Wannier function - a kind of orbital) is done with localized orbitals in addition to his localized spline basis set.

In fact Gaussians have the potential to be just as effective a representation as splines in 'linear scaling QMC' calculations!

Localized orbitals with Gaussian basis sets

Good properties:

- Gaussian basis functions decay quickly
- We think we can build orbitals which are localized *without cutting them off* appreciably, unlike with plane-wave (and therefore blip) calcs.

Where to get localized orbitals expanded in Gaussians?

- CRYSTAL (Oh God..)

Options

- CRYSTAL2003 will calculate orthogonal Wannier functions.. we could use those directly.
- We could take CRYSTAL's regular delocalized orbitals and localize them according to a criterion of our own.

How to produce localized orbitals

• Calculate orthogonal extended Bloch orbitals in the usual way with your DFT program. Form appropriate linear combinations to produce orbitals localized according to some criterion.

$$\phi_m(\mathbf{r}) = \sum_{n=1}^{M} c_{mn}\psi_n(\mathbf{r}), \qquad m = 1, 2, \ldots, M$$

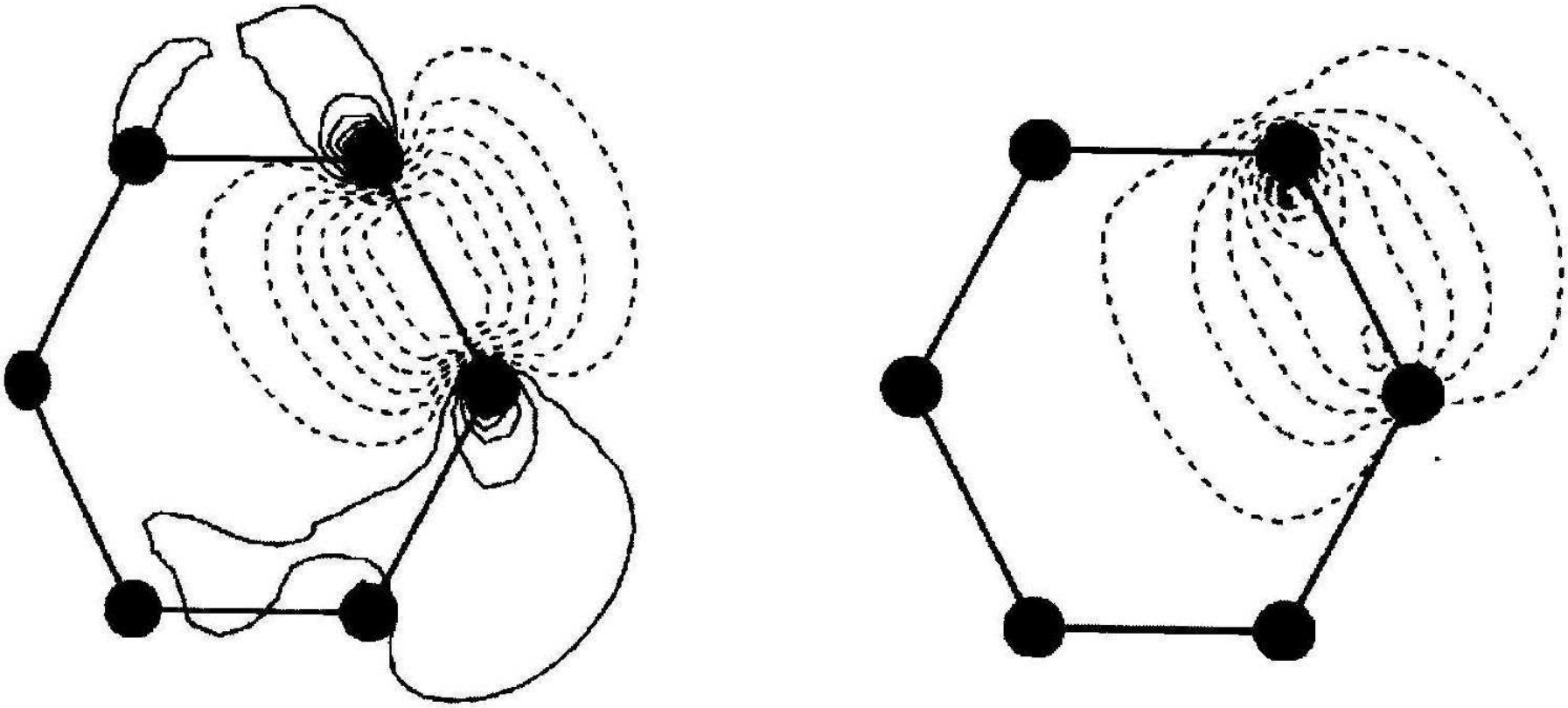
$$\det|\phi_m(\mathbf{r}_i)| = \det|c_{mn}| \cdot \det|\psi_n(\mathbf{r}_i)|$$

• Determinant unchanged apart from constant factor $\det|c_{mn}|$, therefore total energy unchanged in QMC.

• If the transformation matrix is unitary, then the resulting orbitals remain orthogonal. If it isn't, then they are nonorthogonal. Whichever - the above property of determinants is true. Therefore we can use nonorthogonal orbitals in QMC.

• Additional freedom gained by dispensing with orthogonality can be exploited to improve the localization of the orbitals.

Orthogonal vs. non-orthogonal



Comparison of orthogonal (left) and non-orthogonal (right) maximally localized orbitals for C-C σ bond in benzene C_6H_6. The non-orthogonal orbitals are more localized and more transferable since the extended wiggles in the orthogonal functions depend in detail upon the neighbouring atoms.

Alfè/Gillan localization

- Choose some region of arbitrary shape contained within the unit cell. Want to find the combination $\phi(\mathbf{r}) = \sum_{n=1}^{M} c_n \psi_n(\mathbf{r})$ such that $\phi(\mathbf{r})$ is maximally localized in this region.

- Can vary the c_n to maximize the *localization weight* P :

$$P = \frac{\int_{\text{region}} |\phi(\mathbf{r})|^2 \, d\mathbf{r}}{\int_{\text{cell}} |\phi(\mathbf{r})|^2 \, d\mathbf{r}} = \frac{\sum_{m,n} c_m^* A_{mn}^{\text{region}} c_n}{\sum_{m,n} c_M^* A_{mn}^{\text{cell}} c_n}$$

where

$$A_{mn}^{\Omega} = \int_{\Omega} \psi_m^* \psi_n \, d\mathbf{r}$$

Then P takes its maximum value when the c_n are the components of the eigenvector of the generalized eigenvalue equation

$$\sum_n A_{mn}^{\text{region}} c_n = \lambda_\alpha \sum_n A_{mn}^{\text{cell}} c_n$$

associated with largest eigenvalue λ_1, and this maximum P is equal to λ_1.

[*J. Phys.: Cond. Mat* **16**, L305 (2004)]

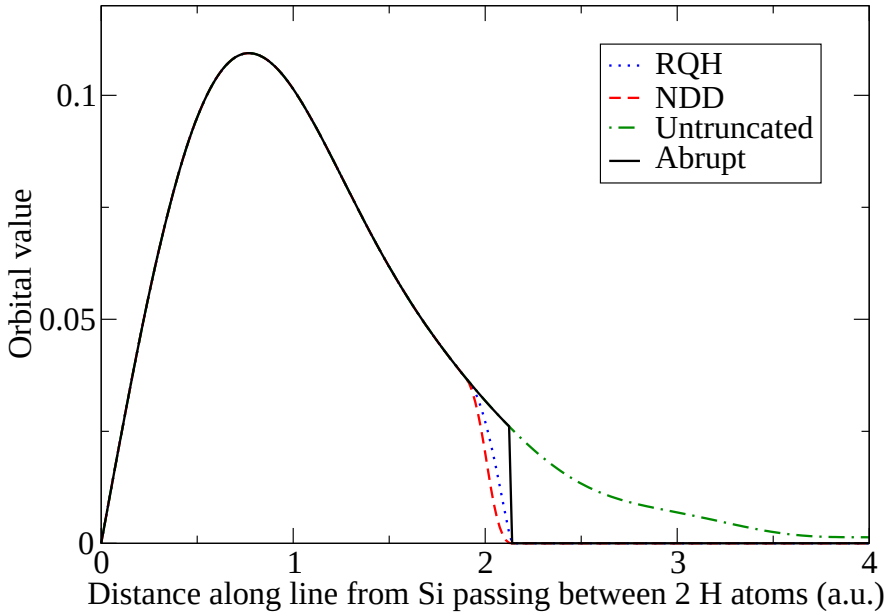
Reboredo-Williamson localization

Optimized nonorthogonal localized orbitals
for linear scaling QMC calculations

Phys. Rev. B **71**, *121105 (2005)*

Essentially the same thing as Alfè, though less clearly explained.

Cutting things off



- To get any benefit from localized orbitals, need to decide on *truncation radius* outside of which they are taken to be exactly zero. Then we don't need to do any work to calculate the orbital if electron is further away than this.

- Then need to decide how to cut off the orbital. Can cutoff abruptly, or can bring the orbital smoothly to zero over some truncation region by multiplying by an appropriate function. One might initially think the latter is more sensible.

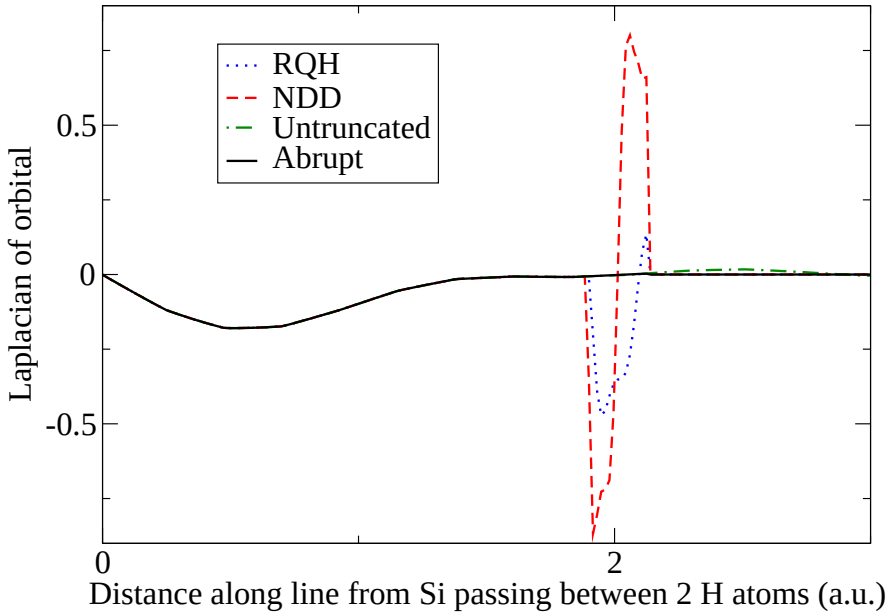
- Very nice analysis of this in Neil's Ph.D. thesis.

Neil cutoff results : VMC for silane

Truncation method	Total energy (a.u.)	KEI (a.u.)	FISQ (a.u.)
RQH	$-4.9550(7)$	$4.5159(7)$	$4.520(15)$
RQH2	$-4.9449(7)$	$4.5241(6)$	$4.521(7)$
RQH3	$-4.9026(7)$	$4.5639(7)$	$4.543(6)$
RQHNEW	$-5.0051(7)$	$4.4678(6)$	$4.455(6)$
NDD	$-4.8390(14)$	$4.6459(14)$	$4.65(2)$
RJN	$-4.9917(6)$	$4.4807(6)$	$4.492(13)$
Abrupt	$-5.9290(3)$	$3.4954(4)$	$3.275(3)$
Untruncated	$-5.9591(4)$	$3.3024(4)$	$3.300(3)$

Table 1: VMC kinetic energy and total energy with the different truncation schemes, the norm of the truncated functions being 94.87% of that of the original Wannier functions. No Jastrow factor is present. The kinetic energy calculated using density-functional theory (which, ideally, VMC should reproduce) is 3.30302 a.u. 100,000,000 configuration moves were carried out.

Laplacian of truncated orbitals in silane



Neil cutoff results : DMC for silane

Truncation method	Total energy (a.u.)	KEI (a.u.)	No. catastrophes
RQH	$-6.280(9)$	$3.317(15)$	2
RQH2	$-6.50(3)$	$3.00(6)$	15
RQH3	$-7.1(1)$	$2.2(1)$	28
RQHNEW	$-6.084(6)$	$3.597(13)$	3
NDD	$-6.301(6)$	$3.644(7)$	28
RJN	$-7.3(1)$	$1.9(1)$	12
Abrupt	$-6.276(1)$	$3.602(2)$	0
Untruncated	$-6.288(1)$	$3.401(2)$	0

Table 2: DMC results for SiH_4 calculated without a Jastrow factor, the norm of the truncated functions being 94.87% of that of the original Wannier functions. The time step was 0.02 a.u., the target population was 200 configurations and 220,000 statistics accumulation moves were carried out.

Neil cutoff conclusions

- "Abrupt truncation gives stable DMC simulations, low variances and energies similar to those of untruncated orbitals. However, it suffers from a theoretical drawback: the gradients and Laplacians of the orbitals contain Dirac delta functions, which are not sampled in QMC, thereby invalidating the variational principles usually satisfied by the VMC and DMC energies."

- "Various smooth truncation schemes have been tried, but none perform as well as abrupt truncation. All such schemes produce large, unphysical peaks in the local kinetic energy in the truncation region."

It is therefore recommended that localised orbitals be truncated abruptly.

- "If the truncation radii of the orbitals are sufficiently large, the bias due to abrupt truncation is much less than the statistical error. The bias in the kinetic energy is given approximately by the change in the sum of the orbital kinetic energies upon truncation, allowing an estimate to be made of this bias; the bias in the total energy is smaller than this."

Conclusions and challenge

- Present situation with cutting off localized orbitals is unsatisfactory.

Exercise for the student

- Is there a better way of cutting off orbitals expanded in blips/splines.

- Are localized orbitals expanded in Gaussian basis functions likely to offer any advantages? One can cut off a Gaussian at some radius when it has a very small value, incurring a negligible error, so it seems likely.

- If so, what is the best way to implement such a scheme? (localize within regions of basis set, rather than to regions of space?).

Discussion to be held on Friday!