

QMC Studies of the First Row Atoms and Ions

Continued...

Priyanka Seth, Pablo López Ríos and Richard Needs

Theory of Condensed Matter, University of Cambridge
ps479@cam.ac.uk

30th July 2010
QMC in the Apuan Alps VI

- Motivation:
 - Learning to achieve chemical accuracy for small systems
→ first-row atoms are a good benchmark set
 - All-electron approach → avoid pseudopotential approximation
 - Could help in making pseudopotentials
- Plan:
 - Optimise wave functions for Li to Ne, Li^+ to Ne^+
 - Ground-state energies of each atom and ion
 - First ionisation energies for the atoms
 - Charge densities

Trial Wave Function

$$\Psi(\mathbf{R}) = e^{J(\mathbf{R})} \sum_{\text{CSFs}} \lambda_{\text{CSF}} \sum_{\text{dets}} D_{\uparrow}(X_{\uparrow}(\mathbf{R})) D_{\downarrow}(X_{\downarrow}(\mathbf{R}))$$

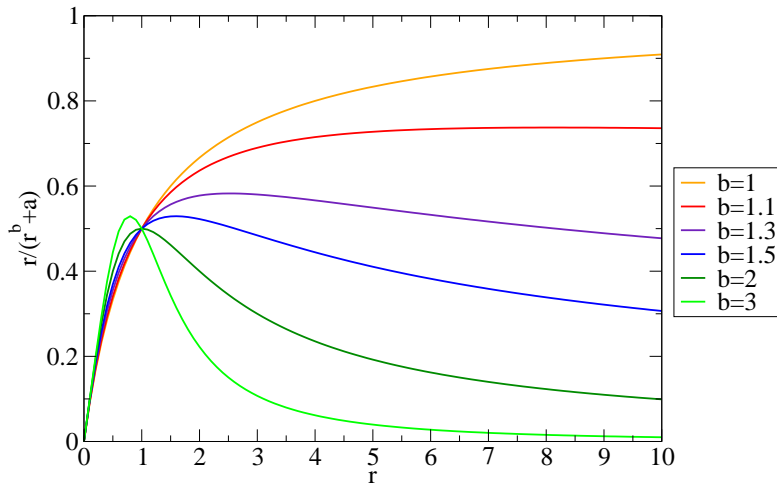
- Orbitals generated using MCHF package ATSP2K, defined numerically on a grid
- Split Slater determinants into up-spin and down-spin parts
- Group determinants into CSFs according to symmetry
- Initially study SD, 20 CSF, 50 CSF and 100 CSF (latter only for O, F, Ne) wave functions

Jastrow Factor

- e-e, e-n and e-e-n Jastrow terms
- Originally used Drummond-Towler-Needs (2004) Jastrow form - polynomial in r
- Tested other basis functions: $\frac{r}{r+a}$, $\frac{r}{r^{b+a}}$, $\frac{1}{r+a}$
- Recalculated wave functions using $\frac{r}{r^{b+a}}$ basis
- Range of parameter values: $2 < a < 9$, $1.1 < b < 1.5$
- Expansion order: (e-e, e-n, e-e-n) = 9,9,5

Jastrow Basis Function

The $r/(r^b+a)$ function with $a=1$



- $\mathbf{x}_i = \mathbf{r}_i + \mathbf{B}_i(\mathbf{R})$
- López Ríos et al. (2006) functional form - polynomial expansion in r
- e-e, e-n and e-e-n backflow terms
- Expansion order: (e-e, e-n, e-e-n) = 9,9,4

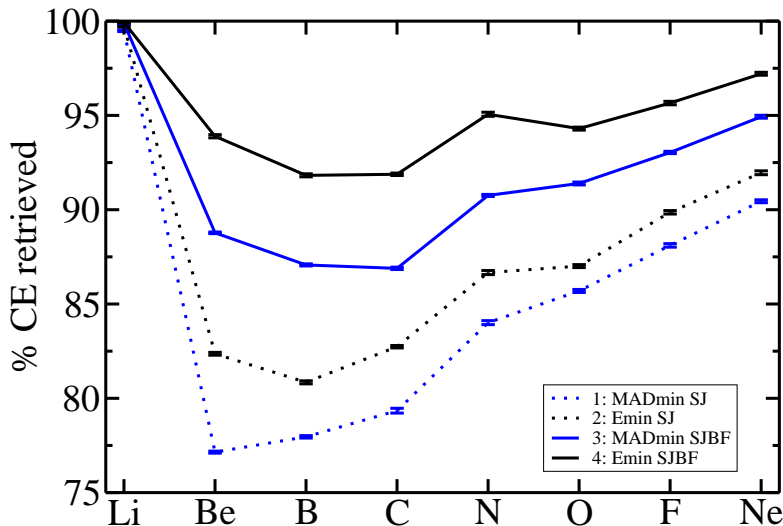
- Mean Absolute Deviation minimisation (MADmin) and Energy minimisation (Emin)
- Unsuccessful strategies:
 - Orbital optimisation
 - Using a pre-optimised SD Jastrow factor with MCSF expansion
 - Spin dependencies in J and BF: distinguishing between u-u and d-d e^- interactions, u-nucleus and d-nucleus interactions
 - Optimising only CSF coefficients for one cycle upon convergence
 - Varmin, Emin for non-linear parameters

The best optimisation algorithm

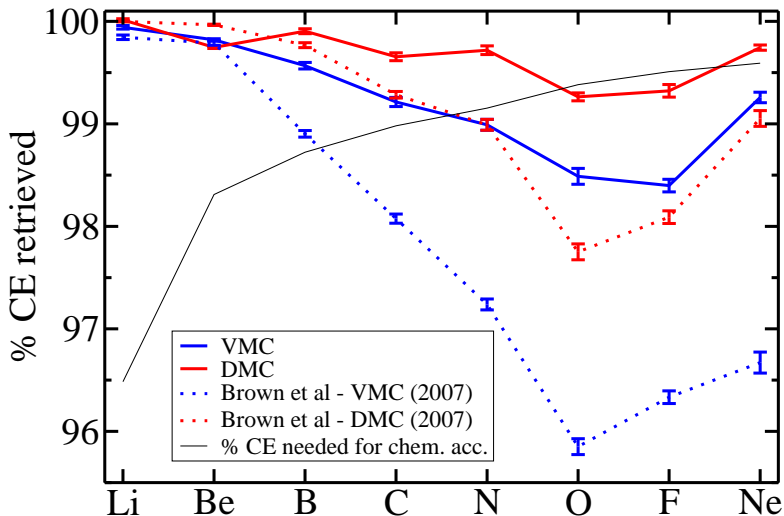
- 1 Optimise Jastrow factor from scratch for ~ 3 MADmin cycles
- 2 Fix non-linear parameters and optimise for ~ 6 Emin cycles
- 3 Add backflow and optimise from scratch for ~ 3 MADmin cycles with released non-linear parameters
- 4 Fix non-linear parameters and optimise for ~ 6 Emin cycles

%CE Gained using MADmin and Emin at VMC level

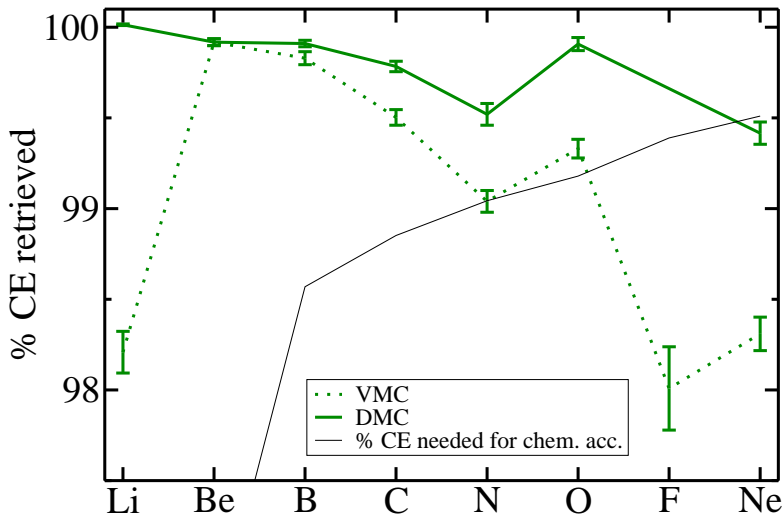
Stages of Optimisation for SD wavefunctions



Atomic ground-state energies



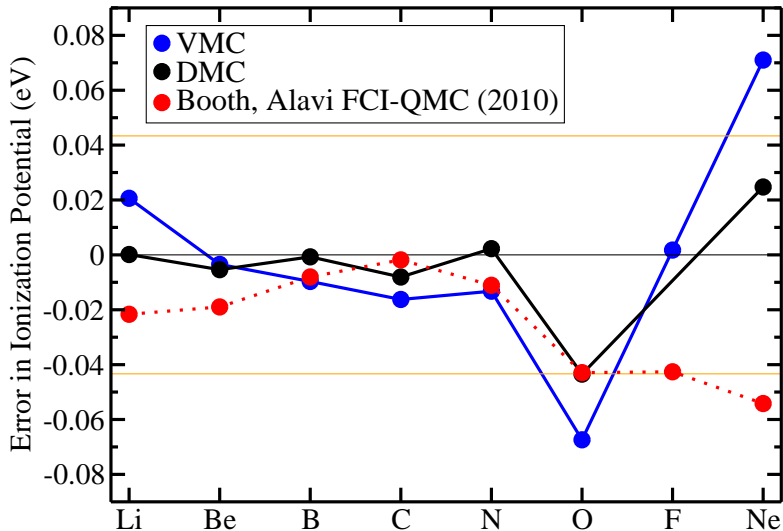
Ionic ground-state energies



Ionization Potentials

- HF
 - Calculate energy of atom and ion separately, take difference
 - Orbital relaxation included, still no correlation
 - IE underestimated
- QMC
 - Includes correlation effects and orbital relaxation
 - As ion has one less electron, expect energy to be more accurate for ion than for atom (except for Ne)
 - Normally underestimate IE

Ionization Potentials



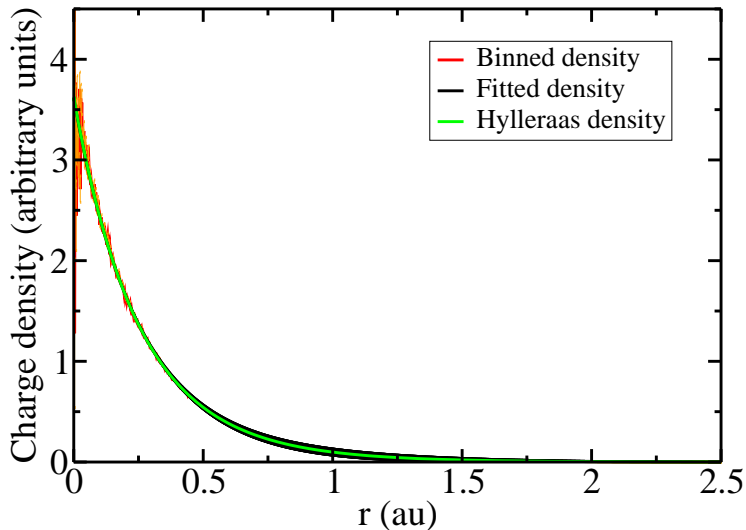
- Accumulation in radial bins
- Non-linear least squares fitting to exponential of Padé polynomial:

$$\rho(r) = \exp\left(-\frac{a_0 + 2Zr + a_2r^2 + \dots + a_nr^n}{1 + b_2r^2 + \dots + b_{n-1}r^{n-1}}\right)$$

- Satisfies cusp condition at origin - log derivative approaches $-2Z$
- Correct large- r behaviour

Binning and Fitting the Charge Density

Total charge density for He atom



Summary

- Best optimisation structure - MADmin followed by Emin with fixed non-linear parameters
- Better Jastrow basis - power of $\frac{r}{r^b+a}$
- Energies are within chemical accuracy for Li-N for atoms and ions at VMC level
- Over 99% of CE retrieved for all atoms and ions studied
- DMC IPs within chemical accuracy
- Functional form to fit charge densities

- R.J. Needs et al, J. Phys.:Condensed Matter, **22** 023201 (2010)
- M.D. Brown et al, J. Chem. Phys., **126** 224110 (2007)
- C. Froese Fischer et al, Comput. Phys. Commun. **176** 559 (2007)
- S.J. Chakravorty et al, Phys. Rev. A, **47** 3649 (1993)
- E.R. Davidson et al, Phys. Rev. A, **44** 7071 (1991)
- M. Puchalski et al, Phys. Rev. A, **73** 022503 (2006)
- G. H. Booth and A. Alavi, J. Chem. Phys., **132** 174104 (2010)

Acknowledgements

Pablo López Ríos
Richard Needs
QMC group

HPCS
Cambridge Commonwealth Trust

Thank you!

VMC and DMC calculations

- 50 CSFs (=171-2018 determinants) for Li, Be, B, C, N, Ne and their ions
- 100 CSFs (=3386-4613 determinants) for O, F and their ions

VMC:

- 10,000,000 steps
- Large decorrelation period - 25 steps

DMC:

- 100,000 steps
- 2048 walkers
- Timestep ranging from 0.00375 for Li to 0.00070 for Ne