QMC Studies of the First Row Atoms

Lithium to Neon

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QMC in the Apuan Alps V

Introduction

- Motivation:
  - First row atoms are good benchmark set
  - Able to compute energies using all-electron calculations - no need for pseudopotentials
- Use VMC to compute ground-state energies of Li to Ne
- Obtain a well-optimised wavefunction for each atoms and calculate expectation values

Trial Wavefunction

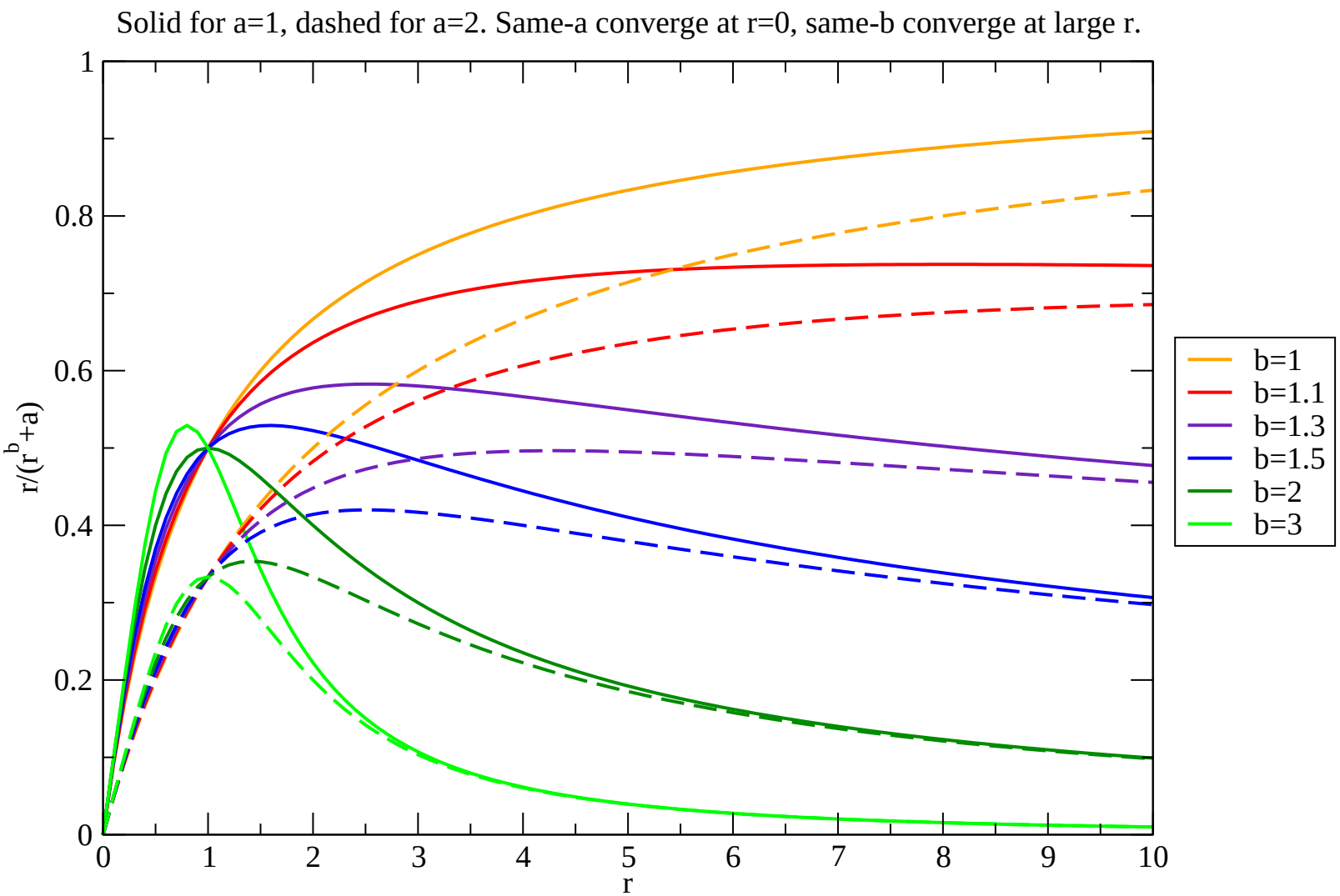
$$\Psi(\mathbf{R}) = e^{J(\mathbf{R})} \sum_{\text{CSFs}} \lambda_{\text{CSF}} \sum D_{\uparrow}(X_{\uparrow}(\mathbf{R}))D_{\downarrow}(X_{\downarrow}(\mathbf{R})) \qquad (1)$$

- Single determinant (SD) calcs use 1 CSF consisting of only the HF determinant
- Backflow:
  - $\mathbf{x}_i = \mathbf{r}_i + \mathbf{B}_i(\mathbf{R})$
  - López Ríos-Needs functional form
  - Two- and three-body terms - e-e, e-n and e-e-n
  - Expansion order: (e-e, e-n, 3-body e-e, 3-body e-n) = 9,9,4,4

Jastrow Factor

- Two- and three-body terms - e-e, e-n and e-e-n
- Originally used Drummond-Towler-Needs Jastrow form - polynomial in r
- Expansion order: (e-e, e-n, 3-body e-e, 3-body e-n) = 9,9,4,4
- Tested other basis functions: $\frac{r}{r+a}$, $\frac{r}{r^b+a}$, $\frac{1}{r+a}$
- Recalculated wavefunctions using $\frac{r}{r^b+a}$ basis
- Expansion order: (e-e, e-n, 3-body e-e, 3-body e-n) = 9,9,5,5
- Approximate values of parameters: $2 < a < 9$, $1.1 < b < 1.5$

Jastrow Basis Function



Optimisation

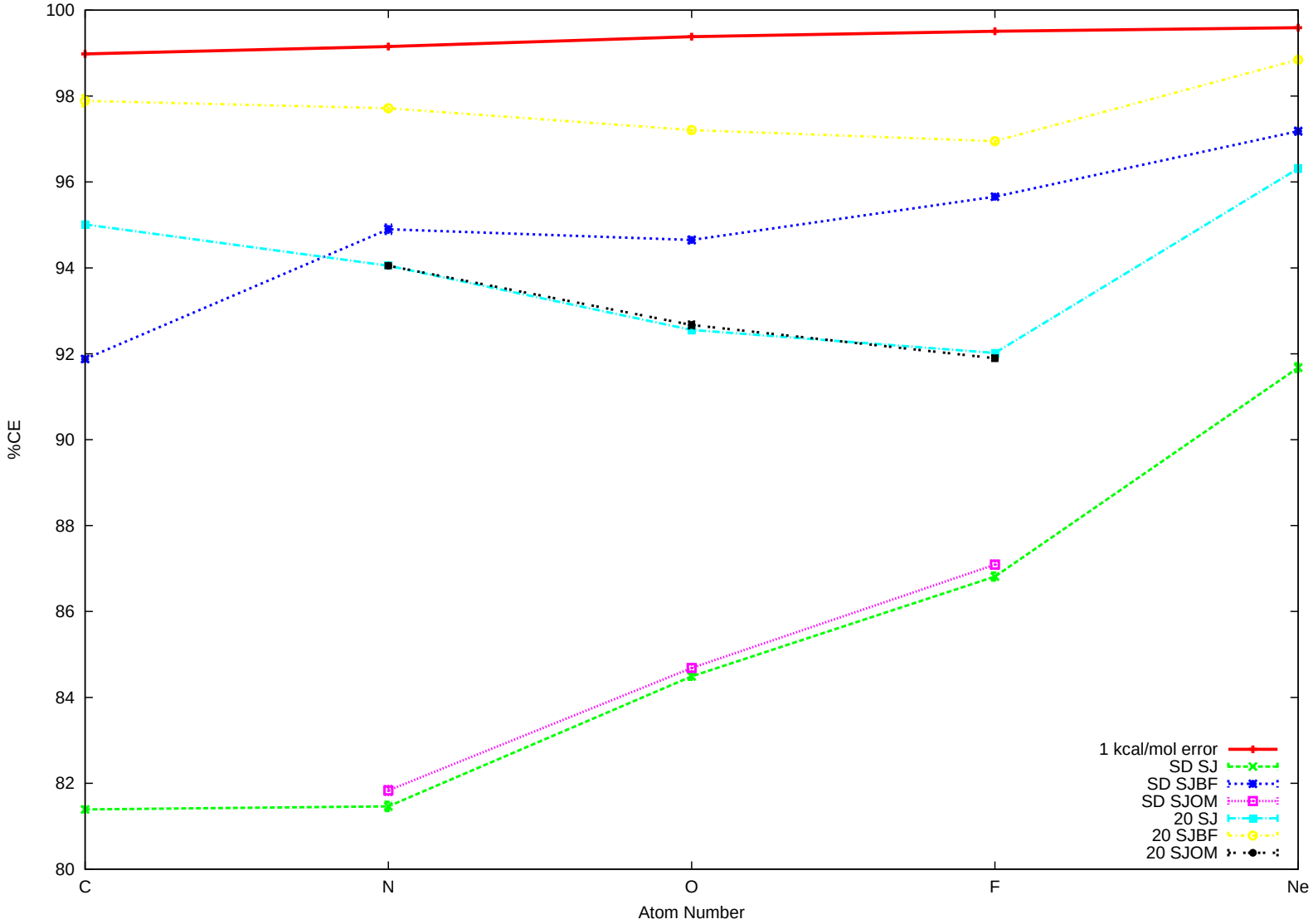
- Optimise SJ wavefunction, then add and optimise BF
- SD SJ wavefunction: 103 parameters, SD SJBF wavefunction: 241 parameters
- Optimising the orbitals after the Jastrow (SJOM) did not give any improvement
- For MCSF calcs, attempted to start with pre-optimised SD Jastrow factor - failed
- Spin dependencies in J and BF: do not distinguish between uu and dd e^- interactions, u-nucleus and d-nucleus interactions
- Energy minimisation and Mean Absolute Deviation (MAD) minimisation

$$MAD = \frac{\int |\Psi(\mathbf{R})|^2 |E_L(\mathbf{R}) - E_{med}| d\mathbf{R}}{\int |\Psi(\mathbf{R})|^2 d\mathbf{R}}. \quad (2)$$

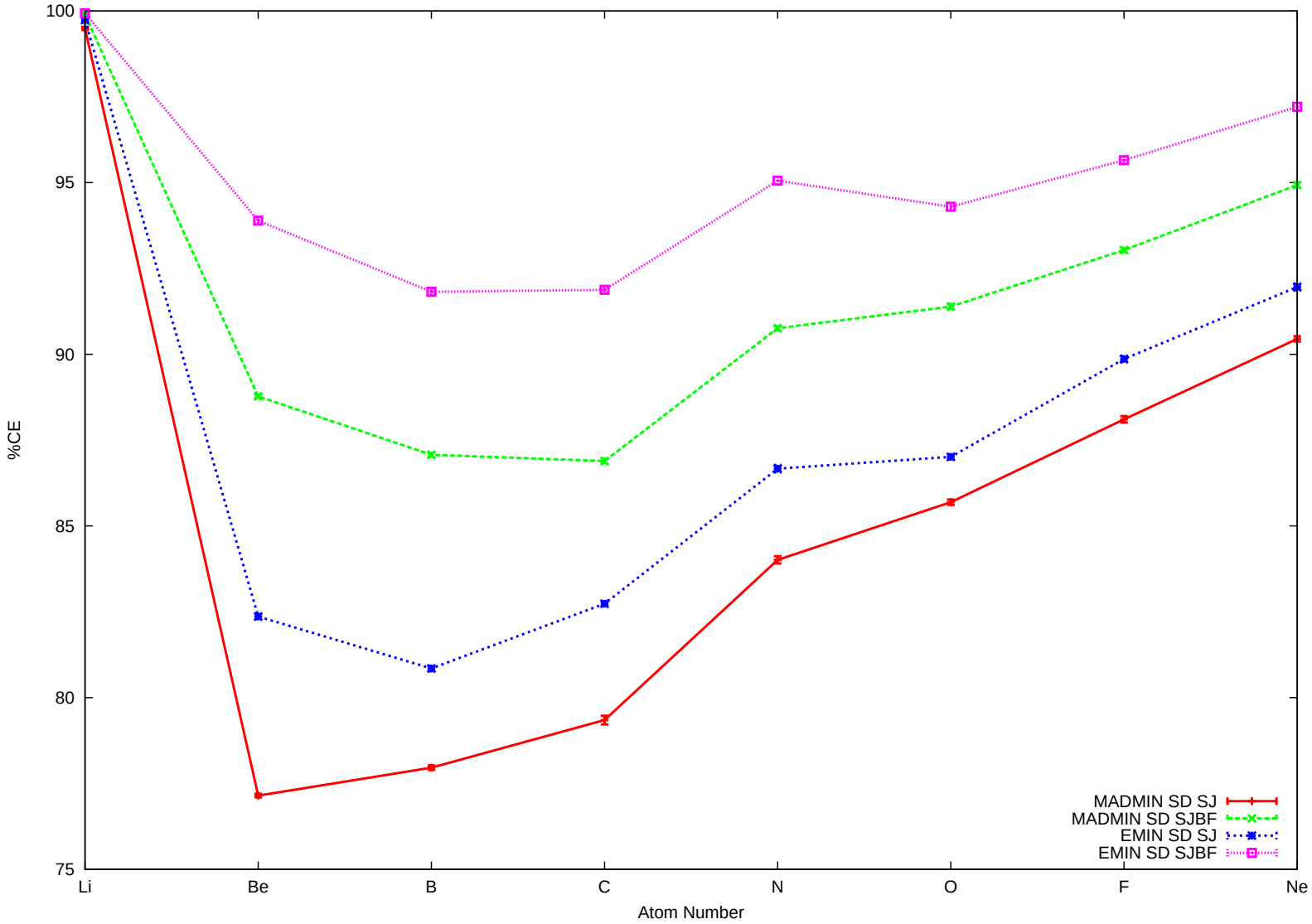
Optimisation Algorithm

1. Optimise Jastrow factor from scratch for $\sim$3 MADmin opt. cycles
2. Fix non-linear parameters (a, b in Jastrow) and optimise for $\sim$6 Emin opt. cycles
3. Add backflow and optimise from scratch for $\sim$3 MADmin opt. cycles with released non-linear parameters
4. Fix non-linear parameters (a, b in Jastrow and cutoffs in backflow) and optimise for $\sim$6 Emin opt.cycles

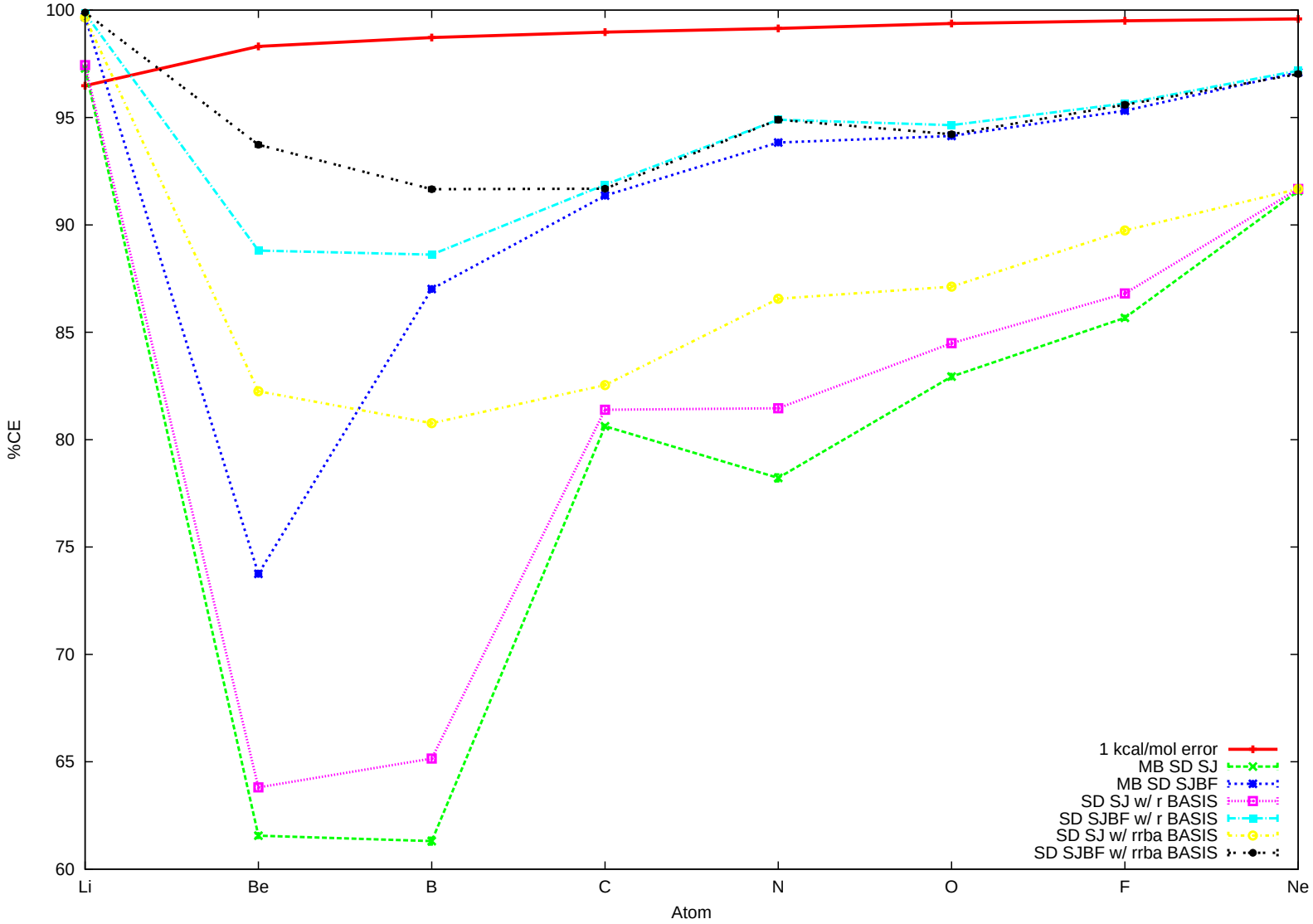
Optimisation Structures - Strengths and Weaknesses



%CE Gained using MADmin and Emin



MB's Es vs r Basis Es vs rrba Basis Es



Summary

- Best optimisation structure - madmin followed by emin with fixed non-linear parameters
- Better Jastrow basis - power of $\frac{r}{r^b+a}$

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- ...and boo yah George!

Future Work

- DMC calculations
- Atomic expectation values
  - Relativistic corrections
  - $\langle r_{ij}^n \rangle$ and $\langle r_{il}^n \rangle$ for $-2 \leq n \leq 4$
  - Charge density
- Ionisation energies, perhaps electron affinities?

References

- M.D. Brown et al, J. Chem. Phys., **126** 224110 (2007)
- S.J. Chakravorty et al, Phys. Rev. A, **47** 3649 (1993)
- C. Froese Fischer et al, Comput. Phys. Commun. **176** 559 (2007)

Thank you!

Thank you for your attention!