Quantum Monte Carlo in a discrete space

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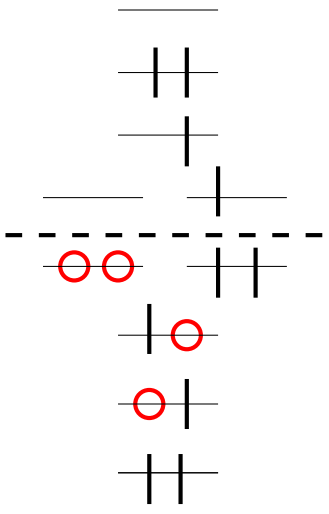
Slater Determinant Space



- N HF spin-orbitals are chosen out of $2M$ spin-orbitals $\{\phi_1, \phi_2, ..., \phi_{2M}\}$
- Orthogonal and antisymmetric
- Complete space of determinants is finite, but exponentially growing in N and M

Full Configuration Interaction

- Iterative diagonalisation of the sparse Hamiltonian in this space gives the "Full Configuration Interation" (FCI) solution.
- Matrix elements between determinants a simple combination of one- and two-electron Hamiltonian integrals.
- Variationally minimised energy Eigenvalue - total basis set correlation energy captured.

Monte Carlo

- Aim is to perform Monte Carlo simulation in the full space of determinants without *a priori* information.
- Due to the fundamental properties of the space, the Fermionic ground state is the lowest energy solution, so nodal surface should hopefully emerge naturally.
- This removes uncontrolled approximations, but introduces a basis-set dependence.
- "Exact", Size-consistent, Multireference and systematically improvable.

Movie shows the convergence of the algorithm.

Derivation of algorithm I

- Begin with imaginary-time TDSE

$$\frac{\partial \Psi}{\partial \tau} = -H\Psi \tag{1}$$

- Perform a long-time integration to project out ground state.

$$\Psi_0 = \lim_{\tau \to \infty} e^{-\tau(H-E_0)} D_{\mathbf{0}} \tag{2}$$

- Expressing wavefunction as linear combination of Slater Determinants ensures Fermionic solutions only.

$$\Psi(\tau) = \sum_{\mathbf{i}} C_{\mathbf{i}}(\tau) |D_{\mathbf{i}}\rangle \tag{3}$$

- Discretize amplitudes as a signed sum of walkers

$$C_{\mathbf{i}} \propto N_{\mathbf{i}} = \sum_{\alpha} s_\alpha \delta_{\mathbf{i},\mathbf{i}_\alpha} \tag{4}$$

Derivation of algorithm II

- Define K as $H - I\langle D_0|H|D_0\rangle$ to ensure positive diagonal elements and obtain:

$$-\frac{dC_i}{d\tau} = \sum_j (K_{ij} - S\delta_{ij})C_j$$
$$= (K_{ii} - S)C_i + \sum_{j\neq i} K_{ij}C_j$$

where S is an arbitrary energy "shift" which controls rate of population change. If we have

$$\sum_j K_{ij}C_j = SC_i \tag{5}$$

then we are at our eigenstate.

Spawing step

- Each iteration, for each particle, select coupled determinant $D_{\mathbf{j}}$ with normalised probability $p_{\mathrm{gen}}(\mathbf{j}|\mathbf{i})$ and attempt to spawn a child there with probability

$$p_s(\mathbf{j}|\mathbf{i}) = -\frac{\delta\tau|K_{\mathbf{ij}}|}{p_{\mathrm{gen}}(\mathbf{j}|\mathbf{i})} \tag{6}$$

- Positive $K_{\mathbf{ij}}$ connections will flip the sign of the spawned walker w.r.t the parent

Death step

- The particle attempts to die with probability

$$p_d(\mathbf{i}) = \delta\tau(K_{\mathbf{ii}} - S) \tag{7}$$

- If we desire to keep the total population of walkers constant, we can periodically (A iterations) adjust the S "shift" value to raise it if there has been a net decrease in walkers over the time period, or lower it if there has been a gain, according to

$$S(\tau) = S(\tau - A\delta\tau) - \frac{\zeta}{A\delta\tau} \ln \frac{N_w(\tau)}{N_w(\tau - A\delta\tau)} \tag{8}$$

Projected energy

We can calculate the energy in another way as the projection of $H|\Psi\rangle$ onto any wavefuntion with overlap with the ground state.

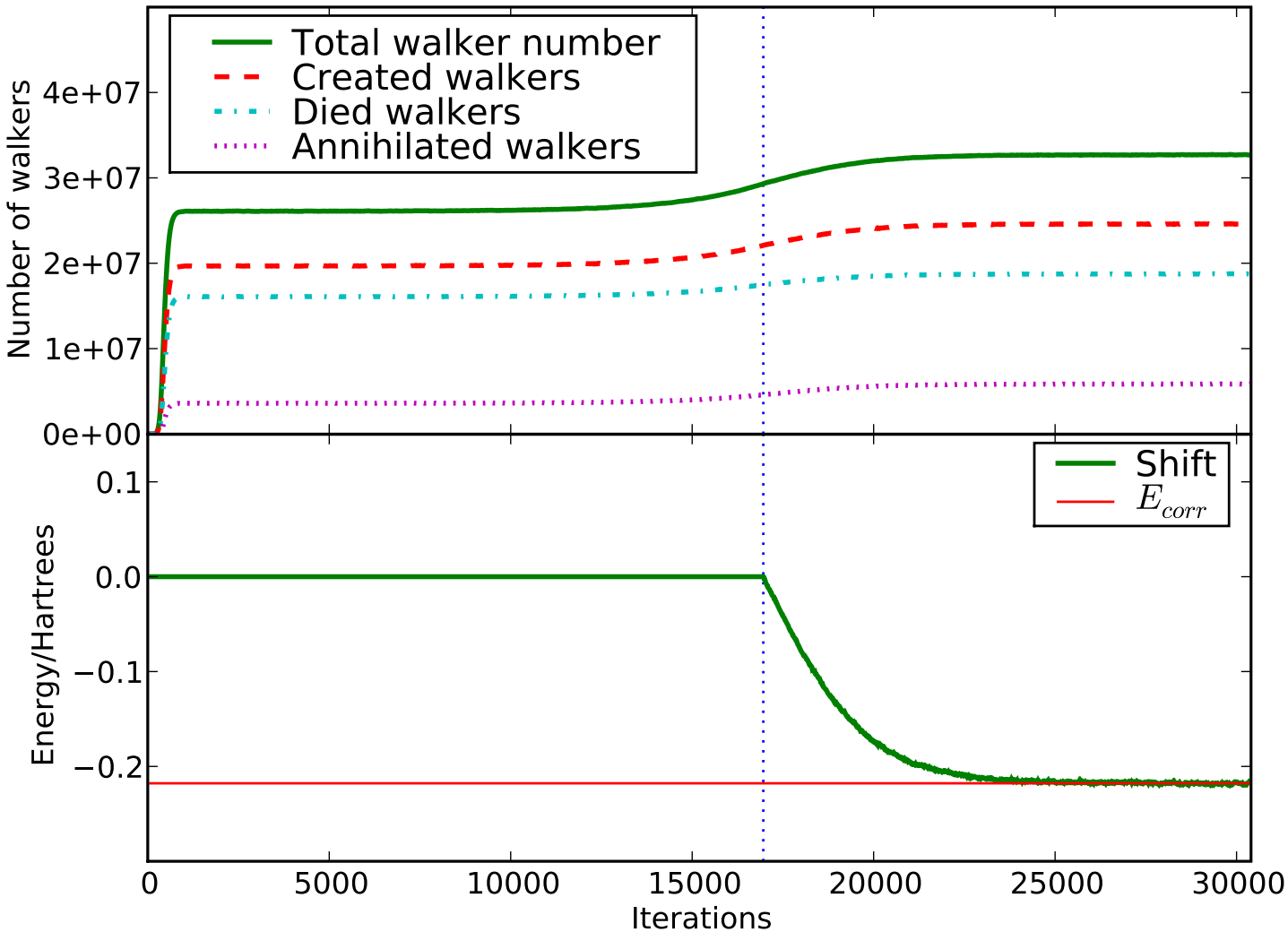
$$
\begin{aligned}
E(\tau) &= \frac{\langle D_{\mathbf{0}}|He^{-\tau H}|D_{\mathbf{0}}\rangle}{\langle D_{\mathbf{0}}|e^{-\tau H}|D_{\mathbf{0}}\rangle} \\
&= E_{\mathrm{HF}} + \sum_{\mathbf{j}\neq\mathbf{0}} \langle D_{\mathbf{j}}|H|D_{\mathbf{0}}\rangle \frac{C_{\mathbf{j}}(\tau)}{C_{\mathbf{0}}(\tau)} \\
&= E_{\mathrm{HF}} + \sum_{\mathbf{j}\neq\mathbf{0}} \langle D_{\mathbf{j}}|H|D_{\mathbf{0}}\rangle \frac{N_{\mathbf{j}}(\tau)}{N_{\mathbf{0}(}\tau)} \\
&= E_{\mathrm{HF}} + \sum_{\mathbf{j}\in\{\mathrm{Sings,\ Doubs}\}} \langle D_{\mathbf{j}}|H|D_{\mathbf{0}}\rangle \frac{N_{\mathbf{j}}(\tau)}{N_{\mathbf{0}}(\tau)}
\end{aligned}
$$

Walker Annihilation

- Walkers of opposite sign on the same determinant are annihilated after each iteration.
- This interaction between positive and negative walkers crucial in breaking symmetry between $\pm\Psi$ states.
- Without this, we observe the classic exponential decay of signal to noise ratio, seen in say nodal-release DMC, due to the dreaded 'sign problem'
- Walker annihilation has been studied previously in real spaces, but difficulty in achieving exact cancellation means this was not entirely successful.
- Annihilation effects give rise to a plateau in the particle growth - indicates critical sampling needed for sign-coherence of walkers and difficulty to converge energy of system

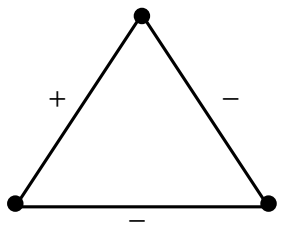
No annihilation vs. Annihilation movies.

Typical walker growth



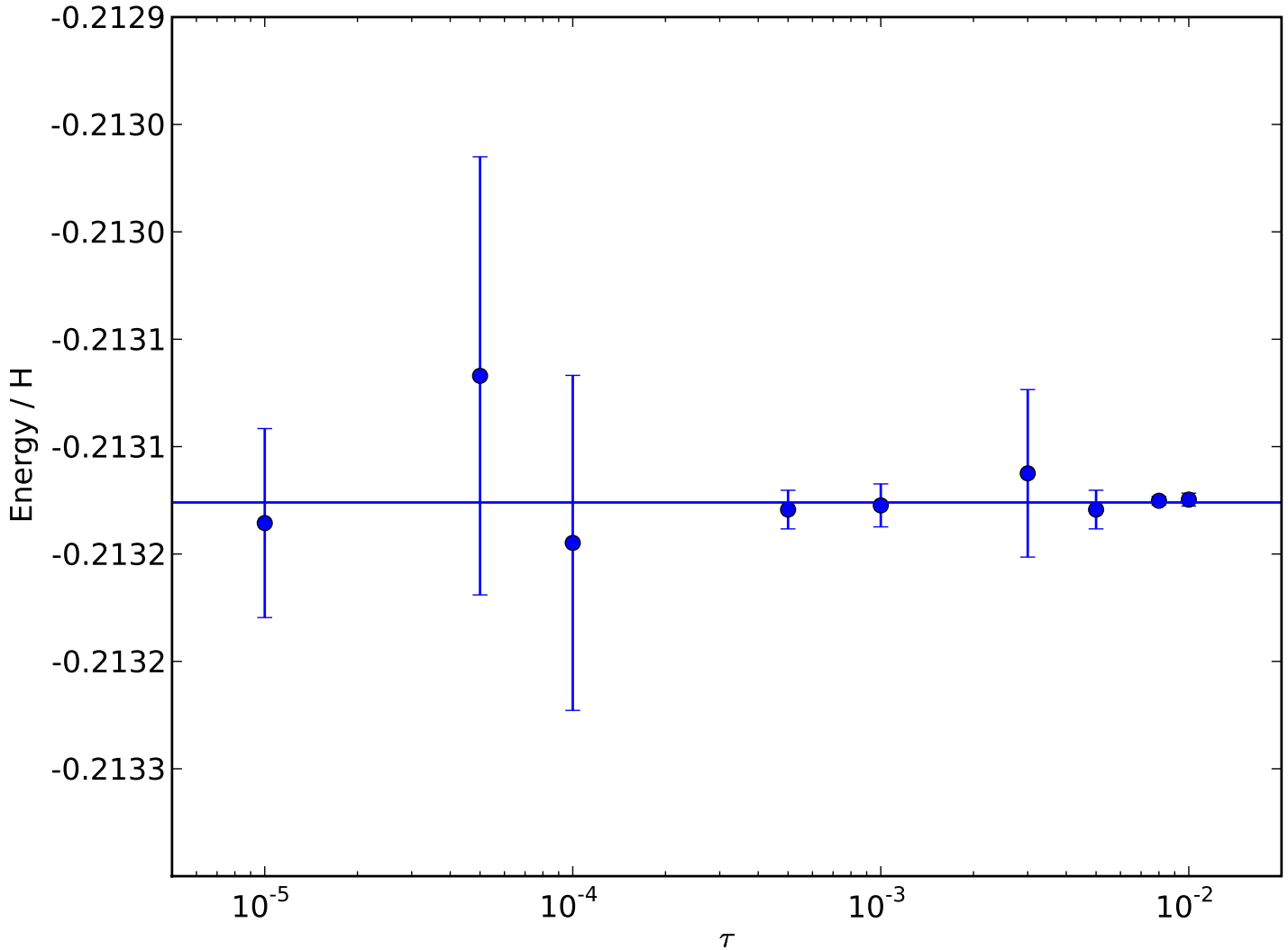
Sign-Coherence

- Whole space become sign-coherent over the course of the plateau - tested by looking at ACF
- Simplest space with sign-problem is a 3-cycle

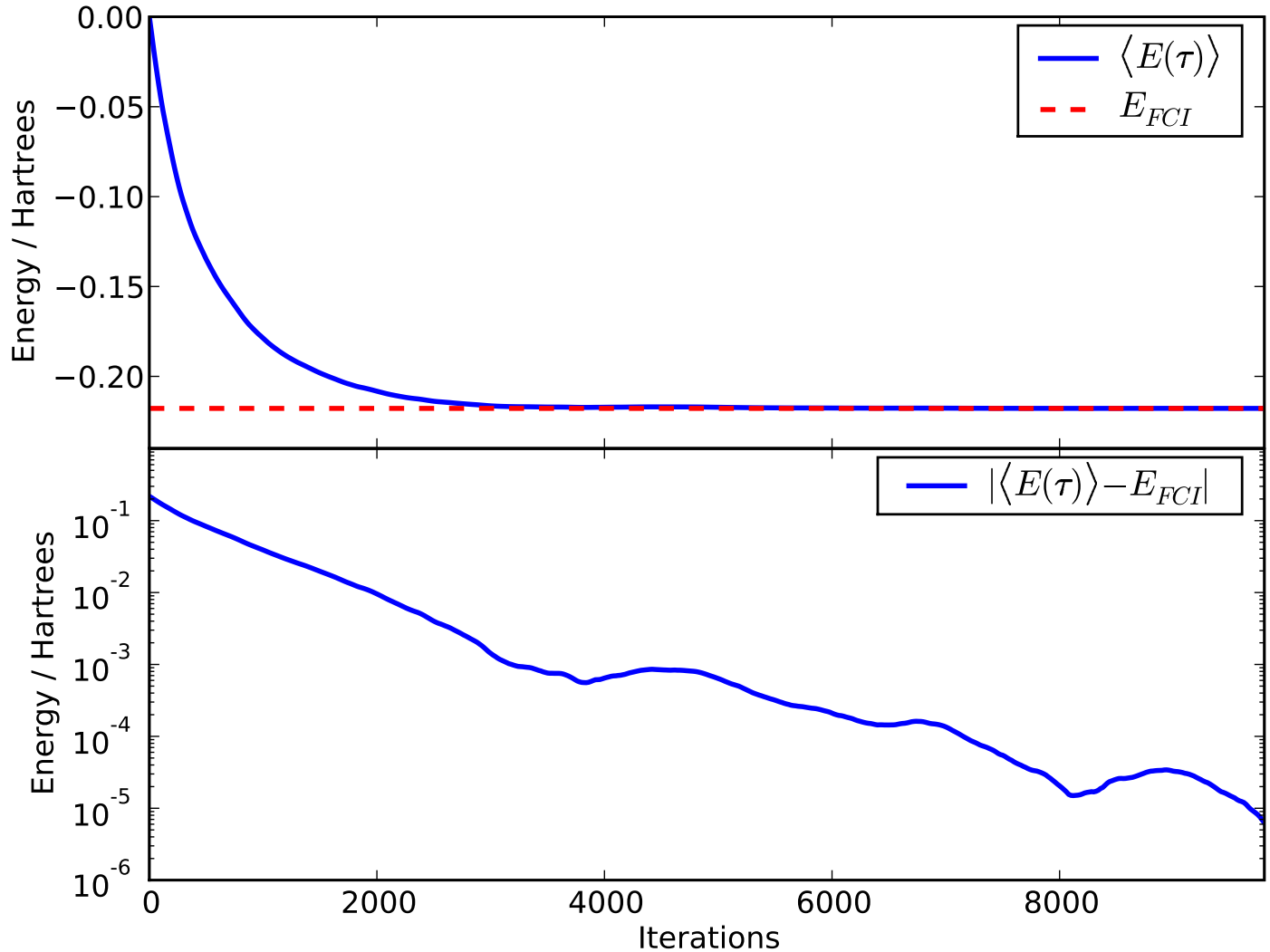


- Determinants which are weakly coupled (high energy or small matrix elements) to the rest of the space do not pose a problem.
- There is also no need to identify these determinants *a priori*

Timestep Errors



Convergence of energy for water molecule



New molecular energies

System	(N,M)	$N_{\mathrm{FCI}}/10^6$	$N_c/10^6$	f_c	E_{total}	$E_{\mathrm{CCSD(T)}}$
Be: cc-V5Z	(4,91)	2.11	0	0	-14.64638(2)	-14.64629
CN: cc-pVDZ	(9,26)	246	173	0.704	-92.4938(3)	-92.49164
HF: cc-pCVDZ	(10,23)	283	0.998	0.0035	-100.27098(3)	-100.27044
CH_4: cc-pVDZ	(8,33)	419	377	0.898	-40.38752(1)	-40.38974
CO: cc-pVDZ	(10,26)	1,080	777	0.719	-113.05644(4)	-113.05497
H_2O: cc-pCVDZ	(10,28)	2,410	47.4	0.0196	-76.28091(3)	-76.28028
O_2: cc-pVDZ	(12,26)	5,409	2,651	0.490	-149.9875(2)	-149.98562
NaH: cc-pCVDZ	(12,32)	205,300	63.8	0.00031	-162.6090(1)	-162.60901
Mg^{2+}: cc-pV5Z	(10,95)	420×10^6	139	3.3×10^{-7}	-198.8878(3)	-198.88779

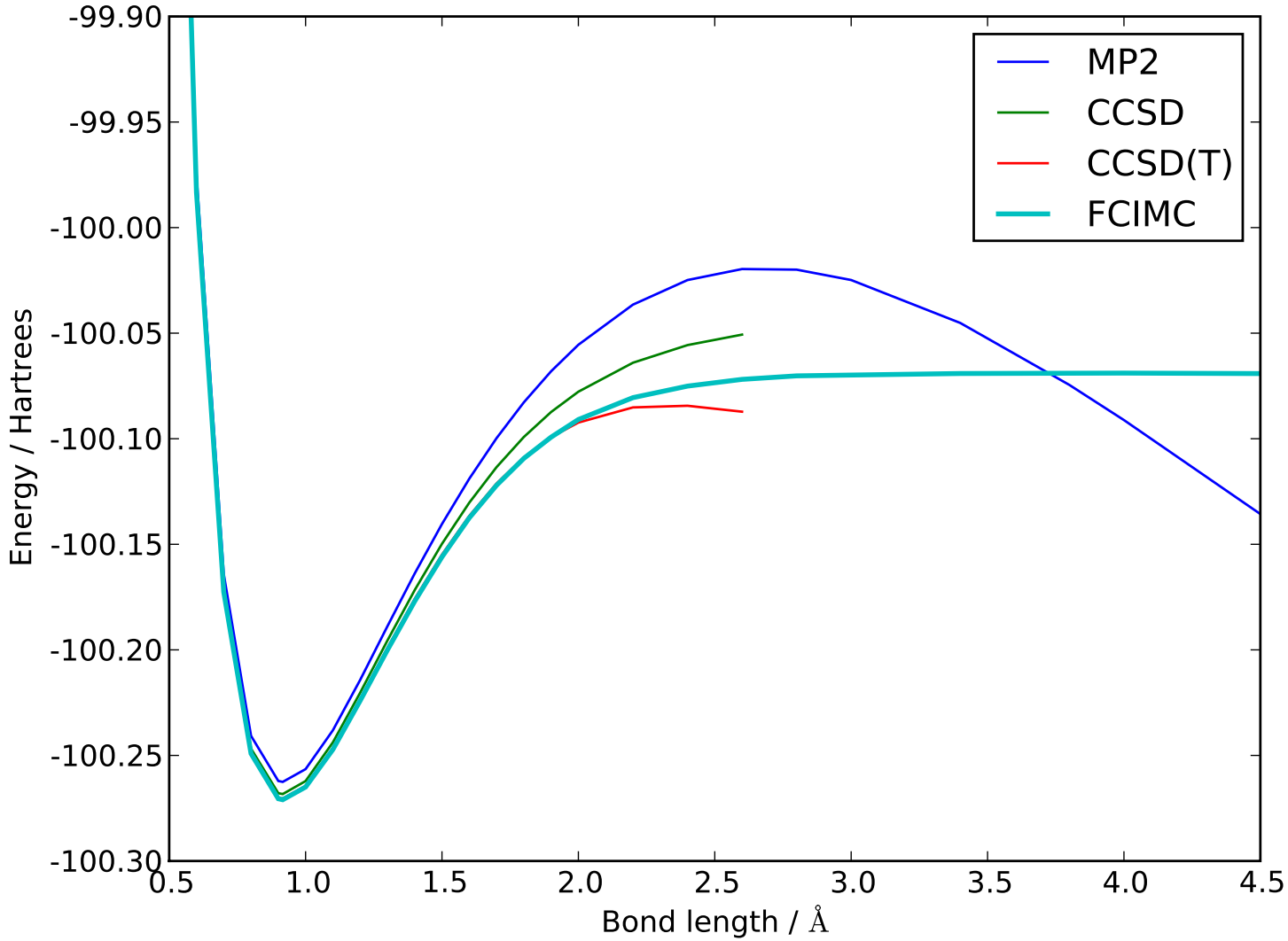
- It can be seen that in all cases, the number of walkers needed to achieve convergence is smaller than the full size of the space.

Neon Atom

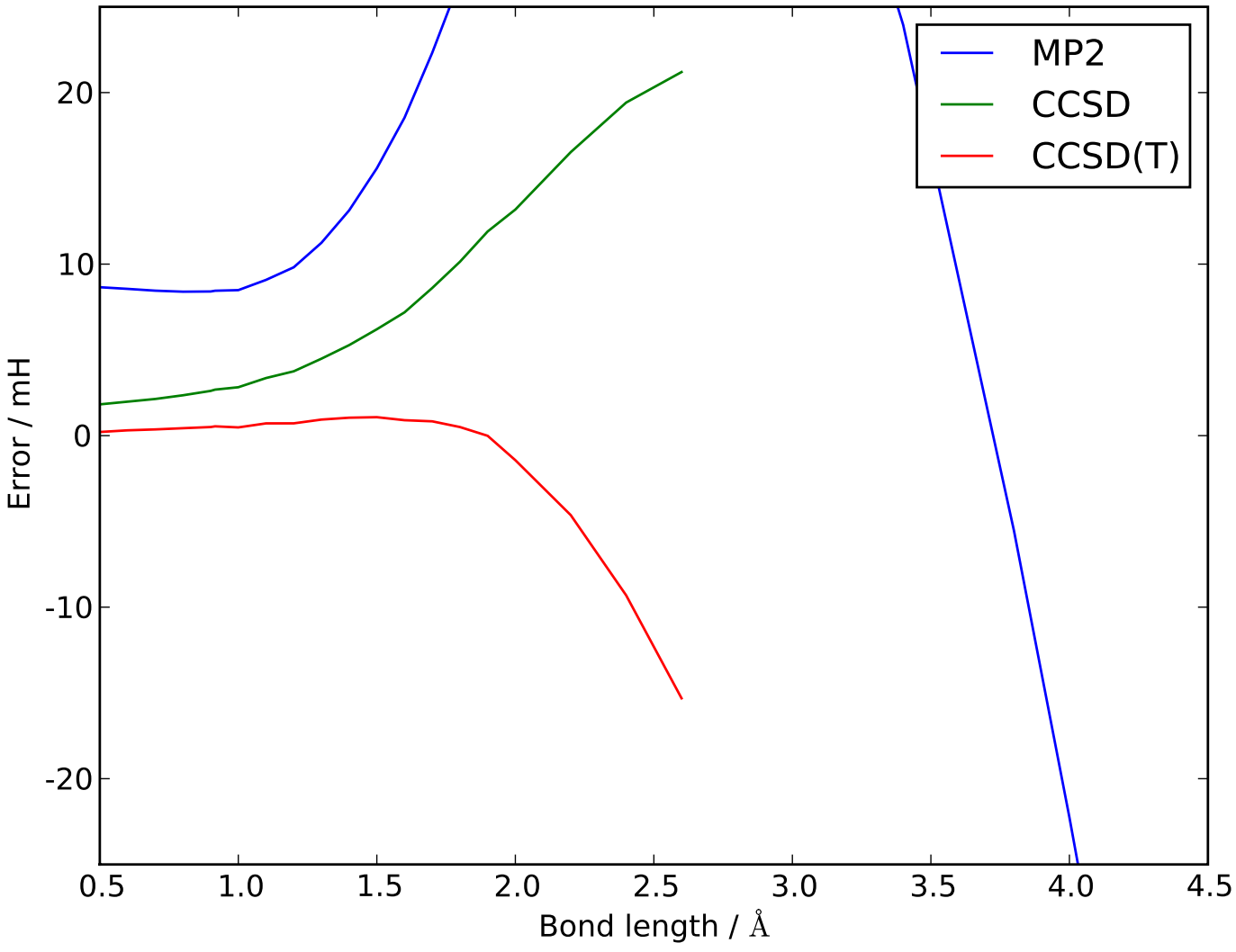
Basis Set	Orbitals	$N_{\mathrm{FCI}}/10^6$	$N_c/10^6$	$f_c/10^{-3}$	E_{corr}
VDZ	14	0.502	0	0	0.19211(4)
CVDZ	18	9.19	0	0	0.23365(3)
AVDZ	23	142	0.248	1.7	0.21510(3)
VTZ	30	2540	0.506	0.199	0.28341(9)
CVTZ	43	116,000	2.3	0.0198	0.33628(2)
AVTZ	46	235,000	338	1.43	0.2925(4)
VQZ	55	1.51×10^6	681	0.451	0.3347(10)
CVQZ	84	119×10^6	2200	0.0185	0.3691(1)
Extrap.					0.3930
Exact					0.3905

- The fact that f_c is relatively constant for a given basis set family indicates exponential scaling.

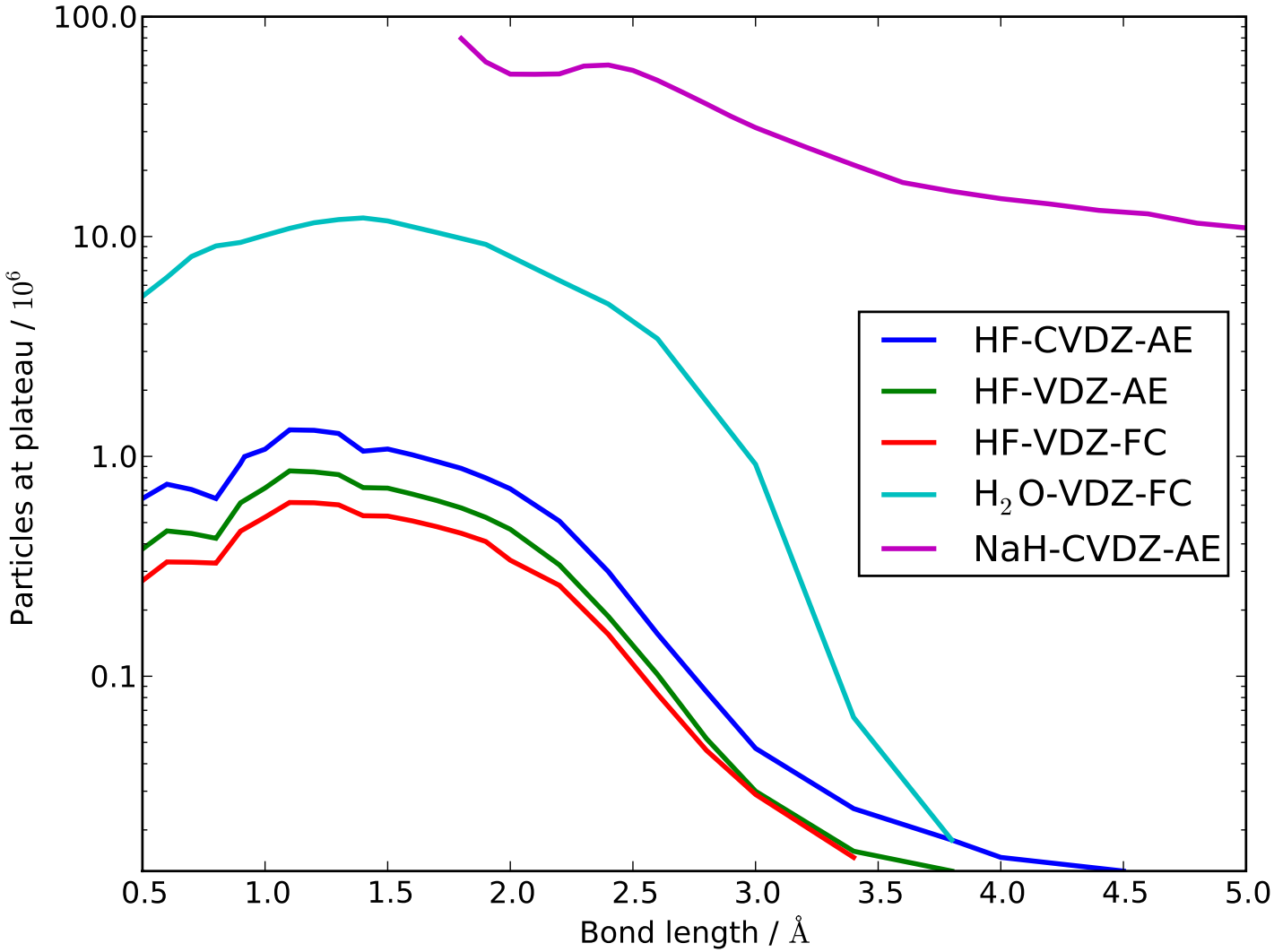
HF Binding Curve I



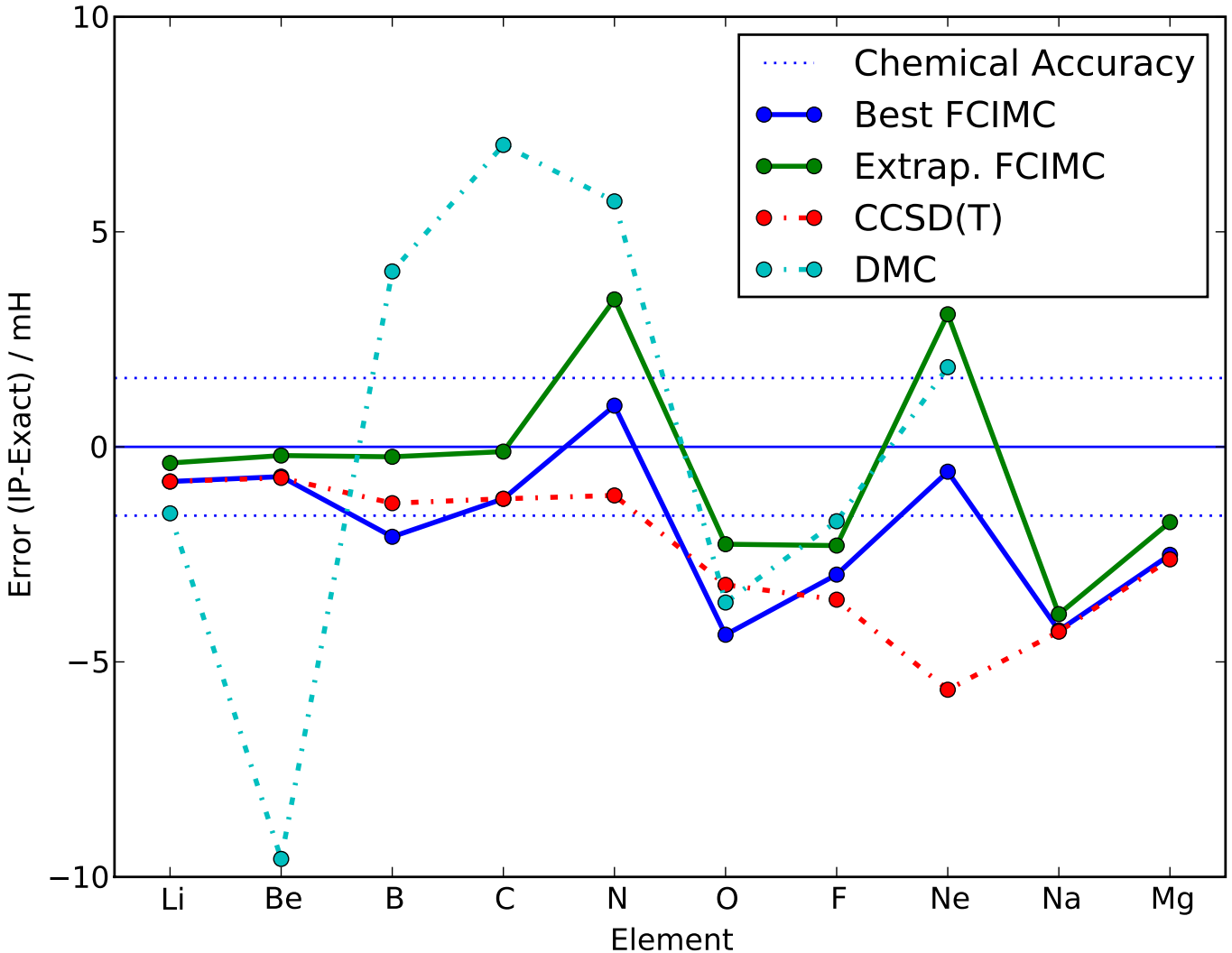
HF Binding Curve II



Binding Plateaus



Ionisation Potentials I



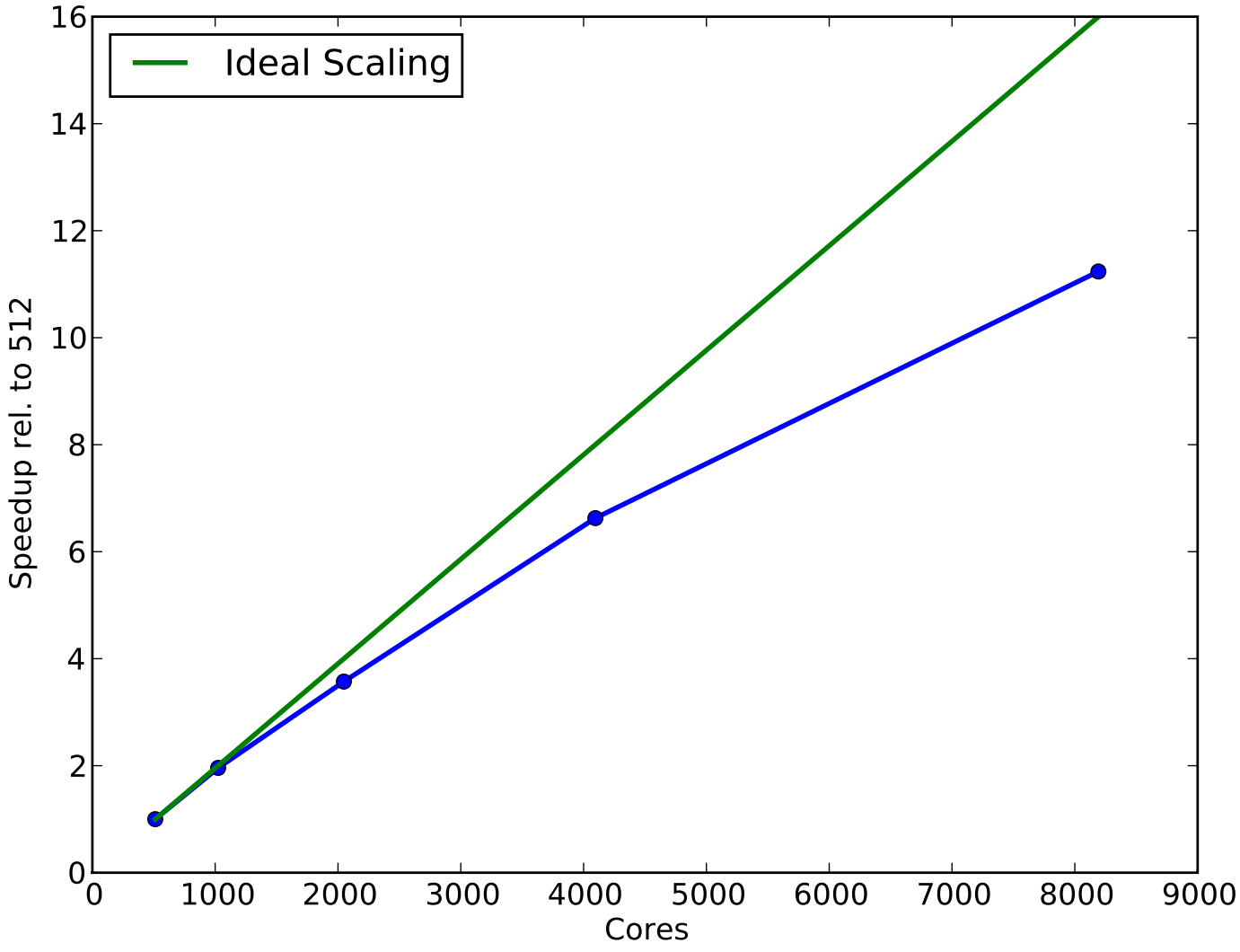
Ionisation Potentials II

	DMC	CCSD(T)	"Best" FCIMC	Extrap. FCIMC
A.M.Err (mH)	4.39	2.45	2.04	1.76
Max Err (mH)	9.58	5.65	4.369	3.428

- Results are work in progress
- If error > 0, cation is not as well described as neutral species and vice versa (same for DMC values)
- Generally, bottleneck is storage of N^4 integrals - simple computational problem
- Errors are simply due to basis set incompleteness, which are not optimized for this problem.
- Note the ease for the Na atom - space more than 10^{15} - also allowed calculation of K.

Materials Transactions, 47, 11 (2006), Yasuhara
JCP 124 224104 (2006), Drummond et al.
Theor. Chem. Acc. (1997), Takewaki

Current Code Scaling



Spin-coupled determinant pairs

- Swap alpha and beta electrons
- FCI amplitude equal up to a sign change
- Create objects which are (anti-)symmetric combination of open-shell determinants
- Space reduced by a factor tending to two
- Plateau height is also reduced by same factor
- Also spin-contamination in instantaneous energy value is reduced
- Partway towards working in a space of CSFs

Orbital basis rotations

- Energies invariant w.r.t. rotation of initial orbitals
- We can use this to hopefully find orbitals which are better suited to the algorithm and achieving sign-coherence of particles
- This will hopefully lower plateaus heights
- Various orbital localizations attempts, as well as Kohn-Sham orbitals and Bruckner orbitals.
- Some limited success with Edminsten-Reudenburg localization (Maximize $\langle ii|ii\rangle$ orbital self-repulsion), but still no consistent scheme.
- Ultimate aim is to reduce not just prefactor further, but also scaling!

Plane wave basis

- Interface to use VASP produced orbitals and integrals
- k-point expansion of energy for LiH similar to MP2 from 1x1x2 supercell
- Hoping to provide benchmark result for periodic systems
- LiH 2x2x2 supercell - 8 LiH pairs (16 electrons)
- Pseudopotential on Li 1s orbital and PAW method used

Truncated Level	Orbitals	Plateau height/10^6	$N_{\mathrm{CI}}/10^6$	f_c
CISDTQ	40	162	348	0.465
CISDTQ5	40	6,152	9,374	0.646
CISDTQ56	40	97,040	162,300	0.598
CISDTQ	51	499	1,151	0.433
CISDTQ	64	1,430	3,344	0.428

Approximate schemes

- Perturbative approximations for high energy virtuals
- CASSCF
- Other partitioning scheme for the space
- Dominant determinants as a nodal surface for DMC (Norbert and Priyanka)
- CCMC (Alex Thom)

Systems focus

- Application to more systems!
- Have recently found energy for C_2 cc-pVTZ basis set
- Binding curves with FCI accuracy for first row diatomics with extrapolation to complete basis set
- Multireference transistion metal dimers, Hubbard models ...

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