Multideterminant atomic wave functions for Quantum Monte Carlo

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TTI July 2005

We want to obtain accurate total energies for light atoms, from QMC.

Why?

- Atoms are a basic building block of condensed matter
- Very accurate experimental estimates of E_{tot} are available for light atoms
- *ab initio* results accurate enough for comparison are available for H and He (and arguably Li and Be)
- DMC using $\Psi_T = e^J D_\uparrow D_\downarrow$ results in large fixed node errors
- Look at improvements possible by a many determinant trial function

$$\Psi_T = e^J \sum_j D_{j,\uparrow} D_{j,\downarrow}$$

Accurate experimental estimates of total energy

- Spectroscopy gives accurate ionisation energies:

$$\begin{array}{lcl} \text{Ne} & \rightarrow & \text{Ne}^{+} \\ \text{Ne}^{+} & \rightarrow & \text{Ne}^{2+} \\ & \vdots & \\ \text{Ne}^{8+} & \rightarrow & \text{Ne}^{9+} \end{array}$$

ab initio energy for Ne^{9+} is available exactly.

Summing differences in total energies for different ions, and one electron energy gives an estimate of total energy.

We requires the total energy for:

- No relativity or $\mathbf{L}.\mathbf{S}$ coupling
- Fixed nucleus
- Point charge nucleus

So correct experimental ionisation energies for these effects.

(See Davidson *et al.* PRA **47** 3649 (1993).)

How much correlation is there?

Comparing the experimental estimate for total energies, and exact numerical Hartree-Fock energies:

Total energies

Atom	$-E_{HF}$	$-E_{Exp}$
He	2.861680	2.90372
Li	7.432727	7.47806
Be	14.573023	14.66736
B	24.529061	24.65391
C	37.688619	37.8450
N	54.400934	54.5892
O	74.809398	75.0673
F	99.409349	99.7339
Ne	128.547098	128.9376

For example, $E_c \sim 0.1 - 0.5\ au$ is typical.

$\longrightarrow$ Correlation is significant, and needs to be described well.

Geminal wavefunctions

Variational method with ansatz:

$$\Psi(\mathbf{R}) = \hat{\mathcal{A}}\left[\sum_k w_k \exp\left(-\sum_i \sum_j a_{ij,k} r_{ij}^2\right)\right]$$

$\hat{\mathcal{A}}$ is an antisymmetrisation operator.

- Vary $\{w_k, a_{ij,k}\}$ to minimise the total energy.
- Includes correlation explicitly but is very expensive.
- Accurate results for Be are possible - Komasa *et al.* obtain 100.0% of the correlation energy with 12000 parameters.

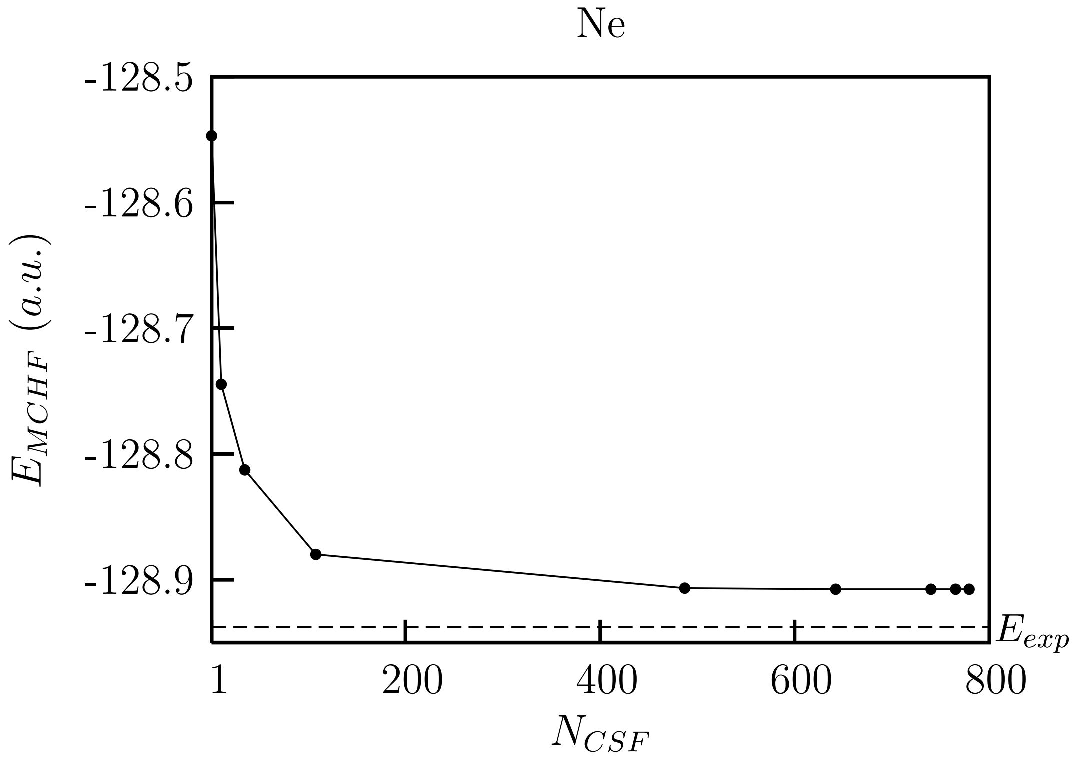
Numerical MCHF

Variational method with ansatz:

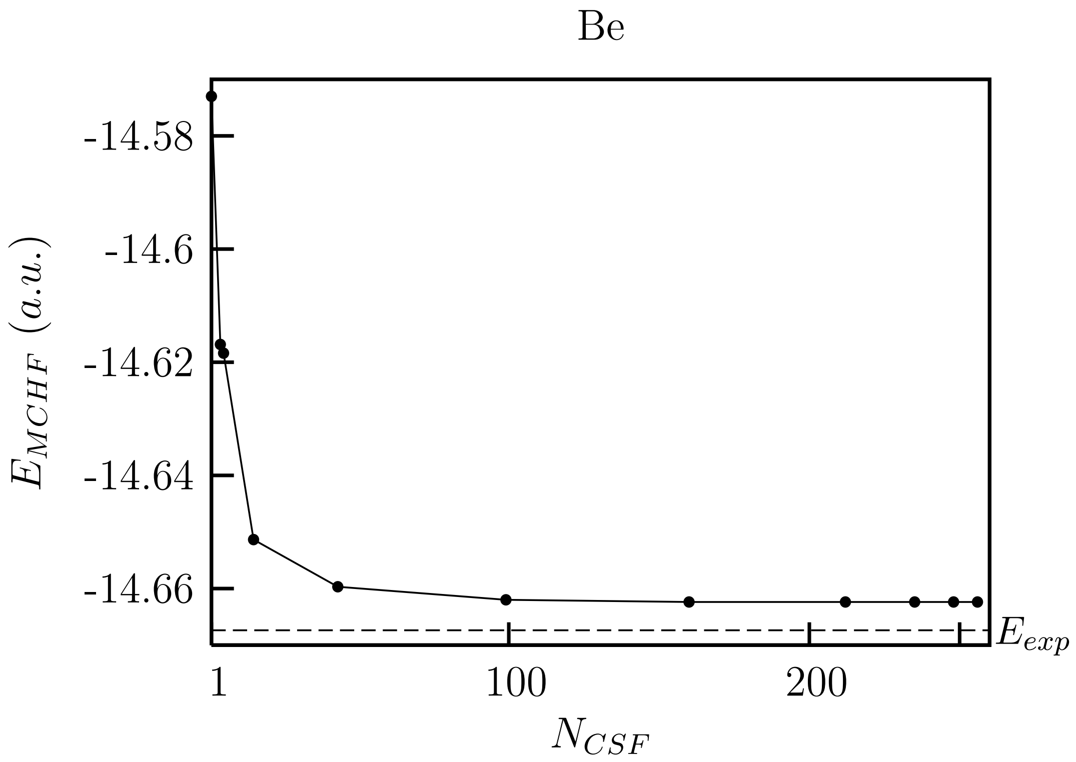
$$\Psi(\mathbf{R}) = w_1|1s^2.2s^2\rangle + w_2|1s^2.2s^1.2p^1\rangle + w_3|1s^2.2s^2.2p^2\rangle + ..$$

- $|\ldots\rangle$ are Configuration State Functions (CSF), specified by occupancy of subshells of the atom, and the angular momentum of the atom
- $|\ldots\rangle$ are calculated self-consistently for a given $\{w_j\}$.
- $\{w_j\}$ are varied to minimise the total energy.
- A set of CSF is specified by excitations from an initial state
- For a complete set of CSF, we would obtain the exact many-body energy

Convergence is slow:



- Slow convergence due inadequate description of electron-electron cusp
- First few CSFs in expansion provide significant correlation energy, even for a closed shell atom.
- Experimental accuracy not possible.



● Dynamic correlation - multiconfiguration expansion does not describe the electron-electron cusp well $\longrightarrow$ long tail in the convergence is due to this

● Static correlation - multiconfiguration expansion does describe correlation due to mixing of configuration states close in energy.

eg for Be, $\left|1s^2.2s^2\right\rangle$ and $\left|1s^2.2p^2\right\rangle$ CSFs have similar energies, so including both improves energy

Diffusion Monte Carlo

Typical results using $\Psi_T = e^J D_\uparrow D_\downarrow$ from HF with a Gaussian basis give:

	Total energy	Correlation energy
Atom	$-E^*_{DMC}$	$E_c(\%)^\dagger$
He	$2.903719(2)$	100.0
Li	$7.4779(2)$	99.6
Be	$14.6563(4)$	88.3
B	$24.6390(5)$	88.0
C	$37.8283(5)$	89.3
N	$54.5768(6)$	93.4
O	$75.0494(6)$	93.0
F	$99.7165(5)$	94.6
Ne	$128.922(2)$	96.0

$*$ Langfelder *et al.* 1997, $\dagger$ $\%$ of E_c obtained by comparison with experimental estimates

Can we improve on this using

$$\Psi_T = e^J \sum_j D_{j,\uparrow} D_{j,\downarrow}$$

?

5 Seperate steps

1 - Perform a numerical MCHF calculation

2 - Decide which of the CSF to use, using some criteria

3 - Transform the CSF expansion into a sum of Slater determinants

4 - Variance minimisation via VMC to obtain a Jastrow-Slater trial function for DMC

5 - Perform DMC to get the fixed node energy.

By varying the weights of each CSF in step 4 the nodal surface is changed to minimise the variance of the local energy, so the final DMC calculation is performed using an optimised nodal surface.

1) Numerical MCHF calculation

Use code ATSP2K (G.I. Tachiev and C. Froese Fischer)

- Uses symmetry to break problem into a set of coupled self-consistent 1-dimensional differential equations, which are solved numerically.

- Provides the w_j (the weight of each CSF) and the radial part of the single particle orbitals $R_{nl}(r)$, one for each subshell.

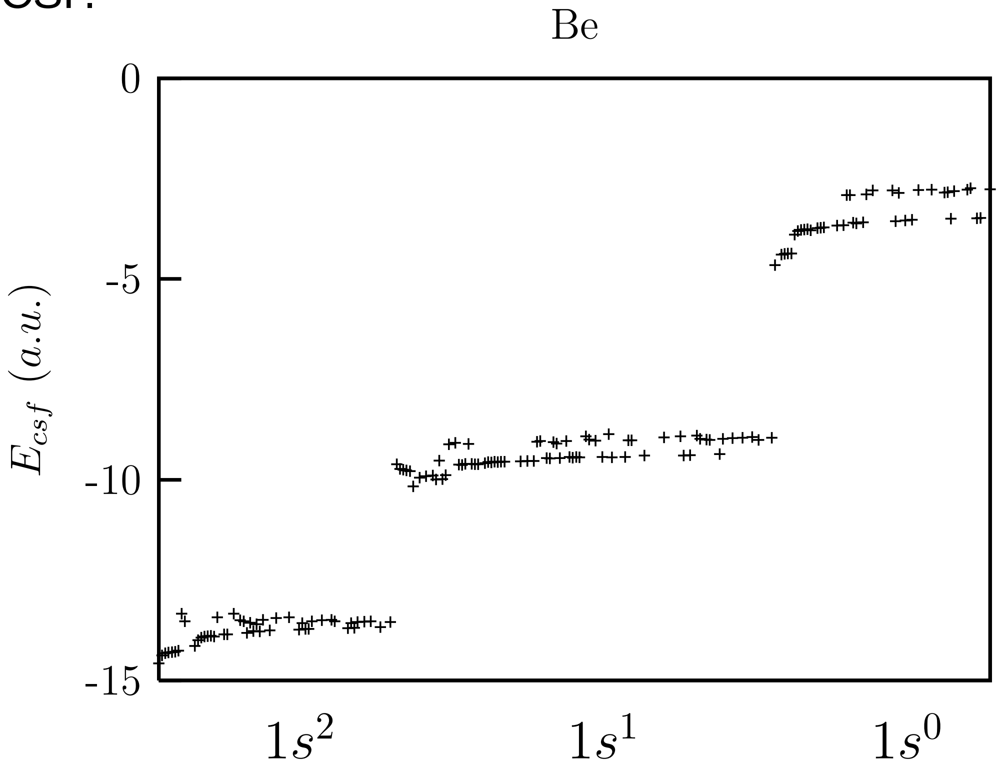
- Does not provide CSF expanded as Slater determinants.

Specify our CSF expansion in terms of types of excitations.

Be - include all CSF obtained by exciting 1 or 2 electrons from $1s^2.2s^2$ (^1S) to anything up to and including the $n = 7, l = 4$ subshell.
Provides 256 CSF.

2) Choose CSF to use in QMC

- Choose by weight of CSF. Take a w_{tol} and choose states where $w_j > w_{tol}$
- Choose CSF where MCHF carried out with this CSF only, E_{CSF}, is close to the HF ground state CSF.



A frozen core may be the best decription of static correlation, even if core excitations have significant w_j.

3) Convert CSF into a sum of Slater determinants

What are the configuration state functions?

● Spherically symmetric, so each CSF is an eigenstate of the total angular momentum operators, $\hat{L}$,$\hat{L}_z$,$\hat{S}$ and $\hat{S}_z$:

$$\begin{aligned}
\hat{L}^2|\mathbf{X};LM_LSM_S\rangle &= L(L+1)|\mathbf{X};LM_LSM_S\rangle \\
\hat{L}_z|\mathbf{X};LM_LSM_S\rangle &= M_L|\mathbf{X};LM_LSM_S\rangle \\
\hat{S}^2|\mathbf{X};LM_LSM_S\rangle &= S(S+1)|\mathbf{X};LM_LSM_S\rangle \\
\hat{S}_z|\mathbf{X};LM_LSM_S\rangle &= M_S|\mathbf{X};LM_LSM_S\rangle
\end{aligned}$$

● For each angular momentum state, specified by LM_LSM_S, and each configuration (for example $1s^2.2s^2$) there is a unique CSF.

● They are antisymmetric functions of the set of combined spatial/spin variables $\mathbf{X}$.

● A CSF is a finite sum of determinants constructed from single particle orbitals $\phi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\hat{\mathbf{r}})$.

Combine two different eigenfunctions of angular momenta $l_1 m_1 s_1 m_{s_1}$ and $l_2 m_2 s_2 m_{s_2}$ to give and eigenfunction of angular momenta $LM_L SM_S$

Take a linear combination:

$$|(\mathbf{x}_1, \mathbf{x}_2) l_1 l_2 s_1 s_2 LM_L SM_S\rangle' = \sum_{m_{l_1} m_{l_2}} \sum_{m_{s_1} m_{s_2}} \langle l_1 l_2 m_{l_1} m_{l_2} | LM_L\rangle \langle s_1 s_2 m_{s_1} m_{s_2} | SM_S\rangle \times$$
$$|(\mathbf{x_1}) l_1 m_{l_1} s_1 m_{s_1}\rangle |(\mathbf{x_2}) l_2 m_{l_2} s_2 m_{s_2}\rangle$$

Coefficients are the Clebsh-Gordon coefficients.

• $|(\mathbf{x}_1, \mathbf{x}_2) l_1 l_2 s_1 s_2 LM_L SM_S\rangle'$ is an eigenstate of $LM_L SM_S$, but also depends on the starting states.

• $|(\mathbf{x}_1, \mathbf{x}_2) l_1 l_2 s_1 s_2 LM_L SM_S\rangle'$ is not anti-symmetric on interchange of co-ordinates.

To obtain an anti-symmetric function we construct a linear combination of these terms that is anti-symmetric:

$$|(\mathbf{x}_1,\mathbf{x}_2)LM_LSM_S\alpha\rangle = \sum_{l_1l_2s_1s_2} f(l_1l_2s_1s_2\alpha)|(\mathbf{x}_1,\mathbf{x}_2)l_1l_2s_1s_2LM_LSM_S\rangle'$$

$f(l_1l_2s_1s_2)$ are the ‘coefficients of fractional parentage’. The extra index α appears since distinct linear combinations may sometimes be found that are lineary independant and antisymmetric.

- $|(\mathbf{x}_1,\mathbf{x}_2)LM_LSM_S\alpha\rangle$ is the CSF of combined system.
- This expression is the same if $|(\mathbf{x_1})l_1m_{l_1}s_1m_{s_1}\rangle$ is a CSF of more than 1-electron.

So we can couple 2CSFs together to get all the CSF's that they can combine to give.

Consider $B\ 1s^2.2p^3$.

First consider subshell p.

$\{|2p^1\rangle\}$, $\{|2p^1\rangle\} \rightarrow \{|2p^2\rangle\}$

$\{|2p^1\rangle\}$, $\{|2p^2\rangle\} \rightarrow \{|2p^3\rangle\}$

then subshell s

$\{|1s^1\rangle\}$, $\{|1s^1\rangle\} \rightarrow \{|1s^2\rangle\}$

then couple subshells s and p together

$\{|1s^2\rangle\}$, $\{|2p^3\rangle\} \rightarrow \{|1s^2.2p^3\rangle\}$

This gives us a selection of CSF for the full atom, and we pick of the LM_LSM_S we require.

Example: 2 electron in a p-subshell

For 2 electrons in a p-subshell, the ^1D ($S = 0, L = 2$) CSF with $M_L = 0$,$M_S = 0$ is given by

$$|2p^2\rangle = R_{1d}.R_{1d}.\tfrac{1}{2\sqrt{3}}\left(|Y_{1-1}Y_{11}\chi_\uparrow\chi_\downarrow| + 2|Y_{10}Y_{10}\chi_\uparrow\chi_\downarrow| + |Y_{11}Y_{1-1}\chi_\uparrow\chi_\downarrow|\right)$$

this sum of 3 determinants is 1 of 15 possible CSF that two p electrons may be in:

1 ^1S CSFs

3 ^3P CSFs

5 ^1D CSFs

Two final points:

- Remove terms resulting from permutation of electrons of opposite spin, and renormalise to get a sum of products of $\uparrow$ and $\downarrow$ determinants.
- Take linear combination of $M_L = \pm L$ to get a real CSF

This is applied to every CSF in the multi-configuration expansion to generate a multi-determinant expansion for use in QMC.

Summary

- MCHF calculation for Be ${}^1S$ ($M_L = 0, M_S = 0$)
- Choose CSFs with large w_j
- MCHF calculation with this subset of CSF
- Convert result to real multi-determinant expansion for QMC
- Introduce a Jastrow factor
- Optimise Jastrow and $\{w_j\}$ parameters
- Perform DMC calculation

Be ^1S

Consider 4 different cases, each for different w_{tol}:

N_{CSF}	N_{Det}	Config.
1	1	$1s^2.2s^2$
2	4	$1s^2.2s^2$
		$1s^2.2p^2$
4	13	$1s^2.2s^2$
		$1s^2.2p^2$
		$1s^2.2p^1.3p^1$
8	23	$1s^2.2s^2$
		$1s^2.2s^1.3s^1$
		$1s^2.2s^1.4s^1$
		$1s^2.2p^2$
		$1s^2.2p^1.3p^1$
		$1s^2.3s^2$
		$1s^2.3p^2$
		$1s^2.3d^2$

Resulting total energies are

N_{CSF}	N_{Det}	E_{MCHF}	E_{VMC}	E_{DMC}
1	1	-14.573023	$-14.6264(9)$	$-14.6564(5)$
2	4	-14.616845	$-14.6621(6)$	$-14.66720(3)$
4	13	-14.616977	$-14.6604(7)$	$-14.66721(4)$
8	23	-14.618906	$-14.6647(6)$	$-14.66727(3)$
256	2869	-14.662379	$-$	$-$

E_{DMC} improves with increasing N_{Det}, and for $N_{Det} \geq 4$ results agree well with experimental results.

For $N_{Det} = 23$ we recover 97.2% and 99.9% of the correlation energy for VMC and DMC respectively.

For Be to go beyond a modest MCHF energy, we need $N_{Det} \geq 4$ in DMC.

Conclusions

- Multi-determinant trial functions for DMC can be constructed from numerical MC-SCF atomic calculations
- Accuracy increases with number of Configurations included, if we exclude core excitations
- How does it do for the rest of the first row atoms?
- We can answer the question ‘What is a useful number of determinants to use in atomic DMC?’