Argonne
NATIONAL LABORATORY

SELECTED CI TRIAL WAVEFUNCTION WITH QUANTUM PACKAGE AND QMCPACK

ANOUAR BENALI

COMPUTATIONAL SCIENCE DIVISON

ARGONNE NATIONAL LABORATORY

9700 S. CASS AVE. LEMONT IL, USA

QMCPACK

Quantum Package

ACKNOWLEDGEMENTS

MOTIVATION FOR MSD

- Standard single-determinant Diffusion Monte Carlo shows good results for molecules and solids but is not exact. Accuracy: a few kcal/mol or ~0.1eV

- Sources of bias:
  - Pseudopotential approximation
  - Locality error
  - Lack of Spin-Orbit (High Z)
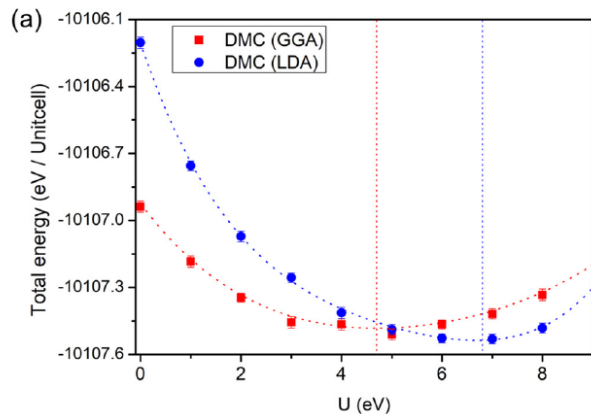 - …

  Controllable

  - Nodal surface

  Fixed node (FN) Approximation (unknown in solids)

- DMC is **variational,** and gives an upper bound to the exact energy. (If nodal surface is exact, DMC is exact)

Question: How to systematically improve the nodal surface?

Argonne
NATIONAL LABORATORY

COMMON METHOD TO REDUCE FN ERROR

Strategy: Scan through various nodal surfaces

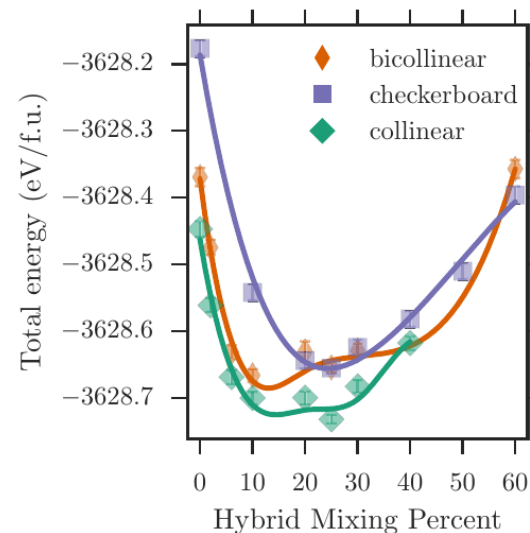-Varying the Hubbard value of U in LDA/GGA+U in NiO solid

FIG. 9. DMC optimization of the exchange-correlation functional for the DFT calculations. The exchange-correlation function depends on w as $E_{xc}^{w}[n] = w E_{x}^{HF}[n] + (1-w)E_{x}^{PBE}[n] + E_{c}^{PBE}[n]$. Lines are a cubic spline interpolation as a guide to the eye.

Not systematic, expensive and no guarantee finding the global minimum

Left Panel: *Shin et al.* Phys. Rev. Mat, 1, 073603 (2017)
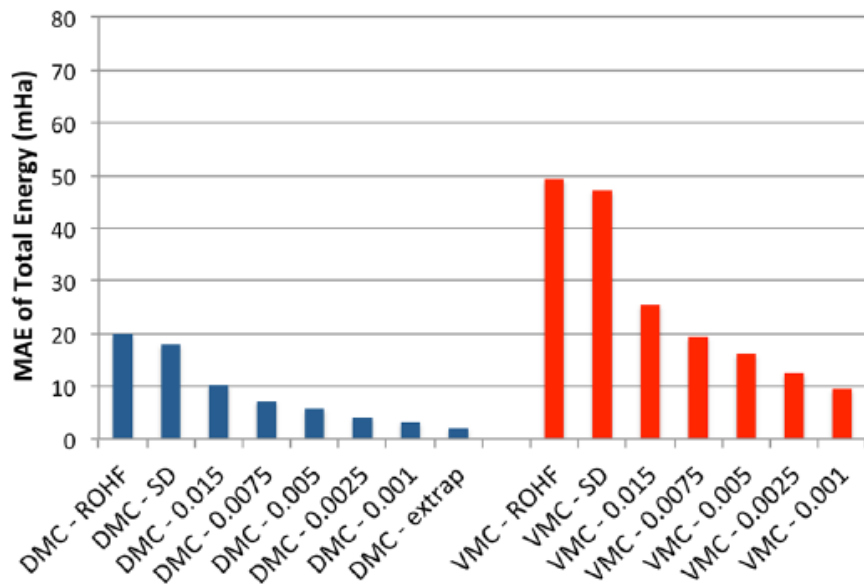Right Panel: *Busemeyer et al.* Phys. Rev B. 94, 035108 (2016) – (FeSe)

USING MULTIDETERMINANTS

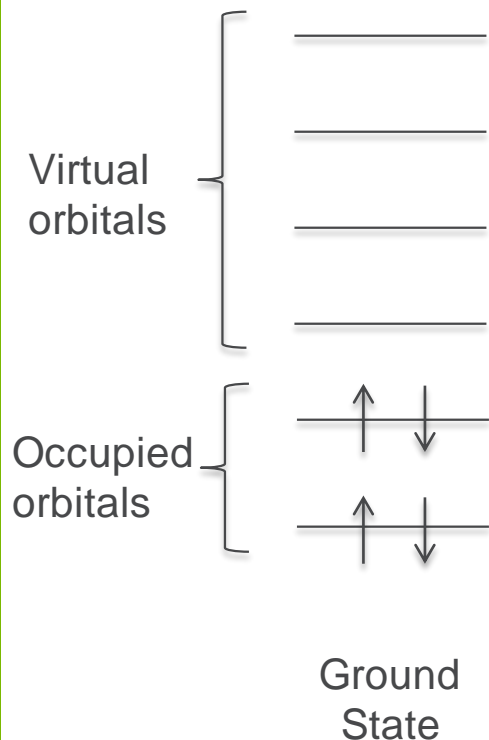Strategy: Increase the complexity of the trial wavefunction using a multideterminant expansion

$$\Psi_T(\vec{r}) = e^{J(\vec{r})} \sum_k c_k \sum_q d_{k,q} D_{k,q\uparrow}(\vec{r}^{\uparrow}) D_{k,q\downarrow}(\vec{r}^{\downarrow})$$
Multi-Slater Determinant Jastrow

G1 test set

Morales et al. J. Chem. Theory Comput. 8, 2181−2188, (2012)

CONFIGURATION OF INTERACTION

Virtual orbitals

Occupied orbitals
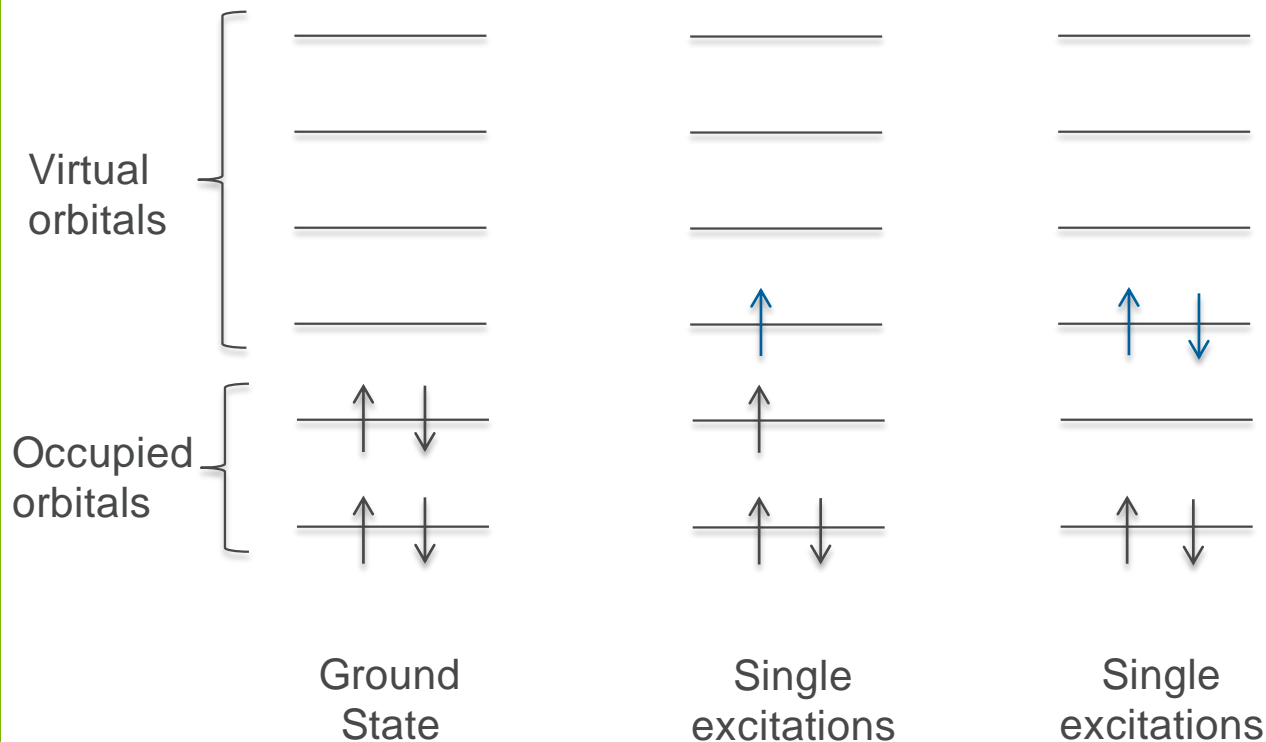
Ground State
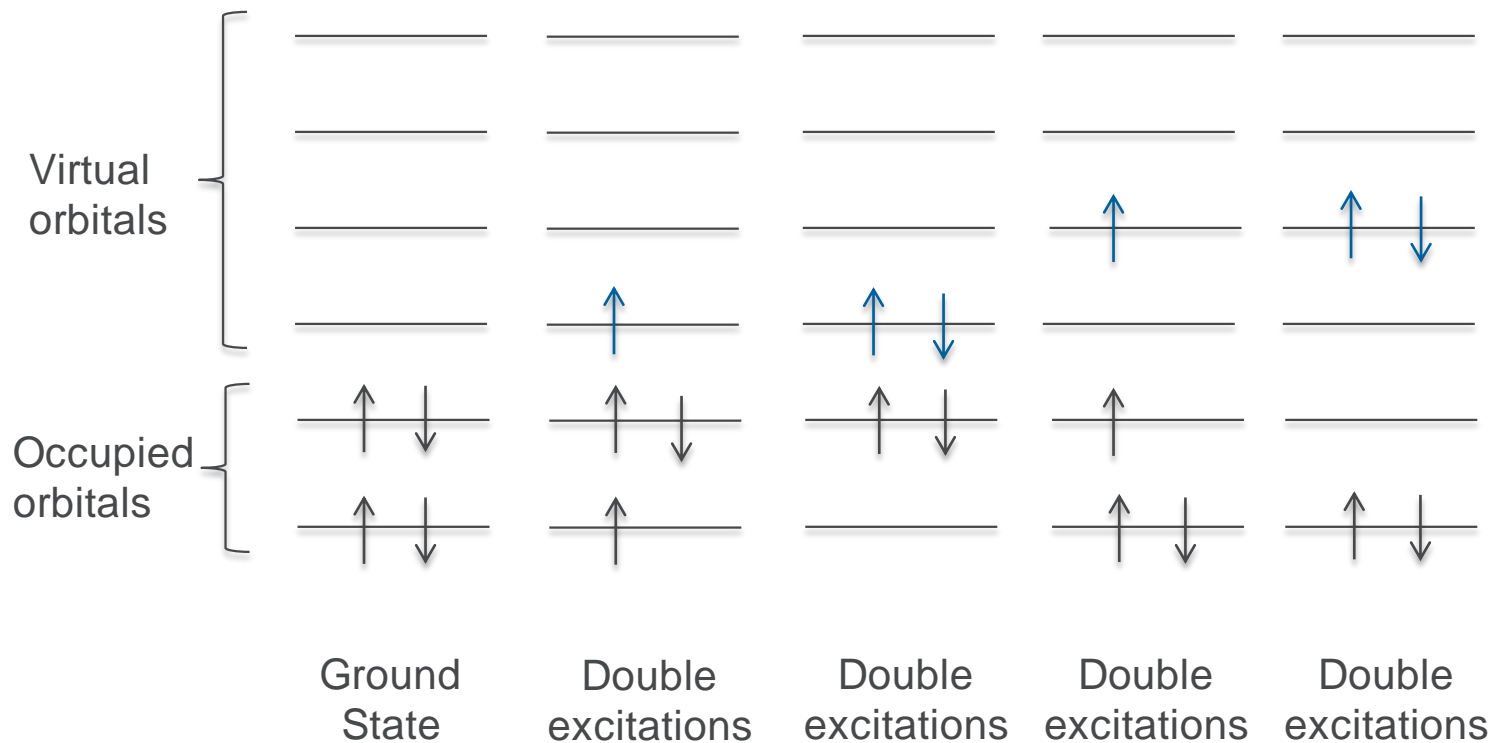
Uses a variational wave function that is a linear combination of configuration state functions (CSFs) built from spin orbitals

$$\Psi = \sum_{I=0} c_I \Phi_I^{SO} = c_0 \Phi_0^{SO} + c_1 \Phi_1^{SO} + \dots$$

Argonne
NATIONAL LABORATORY

CONFIGURATION OF INTERACTION

Virtual orbitals

Occupied orbitals

Ground State

Single excitations

Single excitations

CONFIGURATION OF INTERACTION

CONFIGURATION OF INTERACTION

Virtual orbitals

Occupied orbitals

| Ground State | Triple excitations | Triple excitations | Triple excitations | Triple excitations |
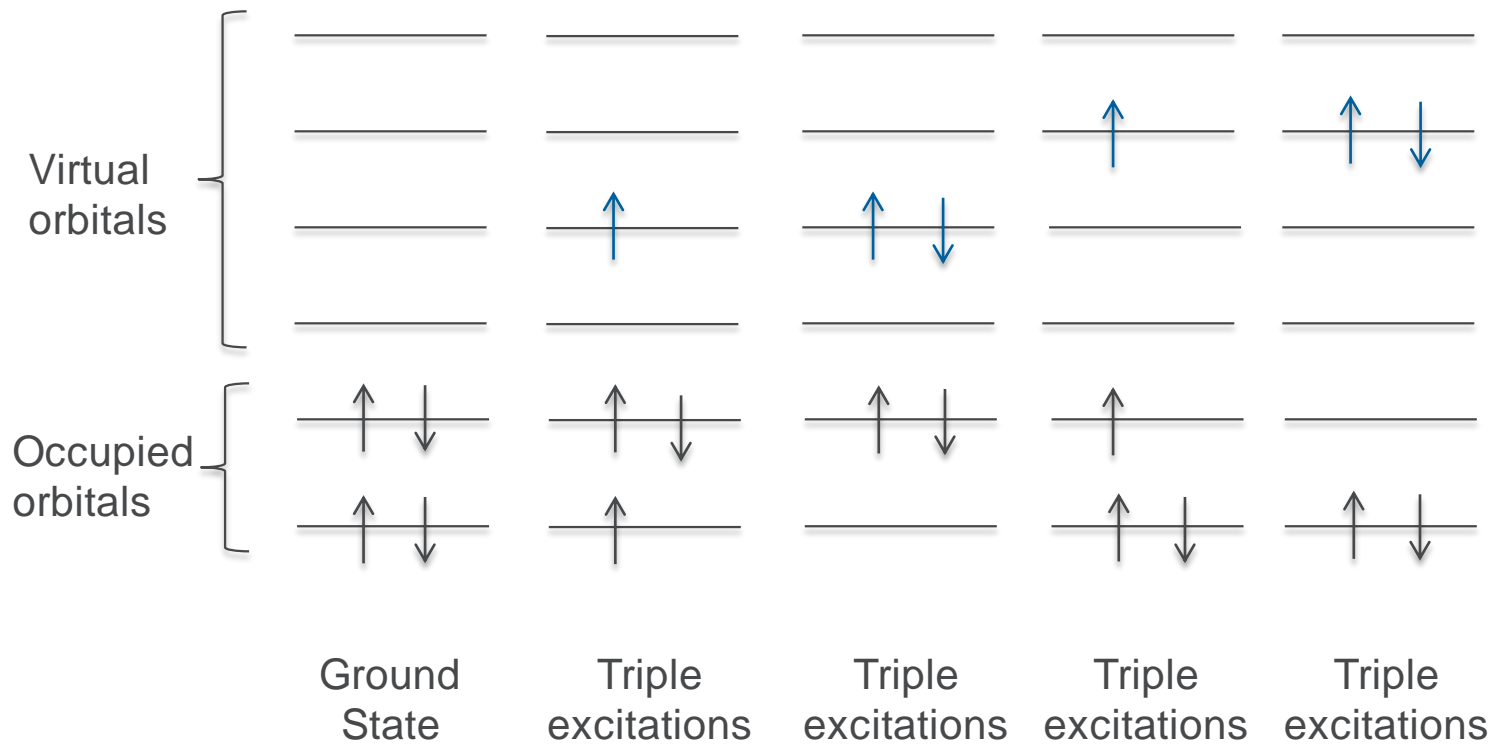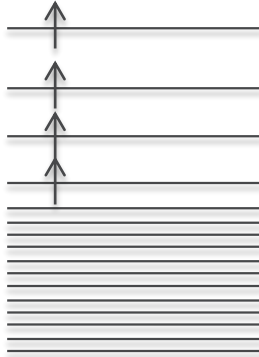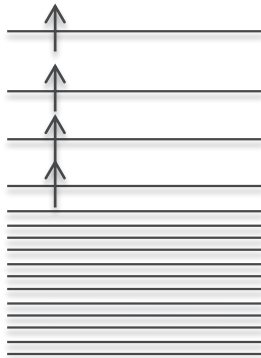
And so on…

And so on…

$$N_{FCI} = \binom{N_{\mathrm{MO}}}{N_\uparrow} \binom{N_{\mathrm{MO}}}{N_\downarrow}$$

Not all the determinants have the same weight and their contributions to the energy become less and less important as the order of excitations increases

Argonne
NATIONAL LABORATORY

And so on…

$$N_{FCI} = \begin{pmatrix} N_{\mathrm{MO}} \\ N_\uparrow \end{pmatrix} \begin{pmatrix} N_{\mathrm{MO}} \\ N_\downarrow \end{pmatrix}$$

Not all the determinants have the same weight and their contributions to the energy become less and less important as the order of excitations increases

Wouldn't it be great to just select the
determinants with the largest contributions??!!

Argonne
NATIONAL LABORATORY

Iterative perturbation calculations of ground and excited state energies from multiconfigurational wavefunctions

B. Huron

Departement de Physique Stellaire, Observatoire de Meudon, 92 France

J. P. Malrieu

Laboratoire de Chimie Quantique, 13 rue P. et M. Curie, Paris 75, France

P. Rancurel

Departement de Radioastronomie Spatiale, Observatoire de Meudon, 92 France

(Received 30 July 1971)

A method is proposed to calculate the effect of configuration interaction by a Rayleigh–Schrödinger perturbation expansion when starting from a multiconfigurational wavefunction. It is shown that a careless choice of H_0 may lead to absurd transition energies between two states, at the first orders of the perturbation, even when the perturbation converges for both states. A barycentric definition of H_0 is proposed, which ensures the cancellation of common diagrams in the calculated transition energies. A practical iterative procedure is defined which allows a progressive improvement of the unperturbed wavefunction ψ^0; the CI matrix restricted to a subspace S of strongly interacting determinants is diagonalized. The desired eigenvector ψ^0 of this matrix is perturbed by the determinants which do not belong to S. The most important determinants in ψ^1 are added to S, etc. The energy thus obtained after the second-order correction is compared with the ordinary perturbation series where ψ^0 is a single determinant. For the ground state, this procedure includes, besides the whole second-order correction, the most important terms of the third and fourth orders. The question of orthogonality of excited states is discussed. This technique, hereafter called CIPSI, has been tested on the ground and several excited states of H_2, Ne, and MgO, showing both a rapid convergence of the calculated transition energy and the importance of correlation effects on transition energy.

J. Chem. Phys. 58, 5745 (1973); http://dx.doi.org/10.1063/1.167919
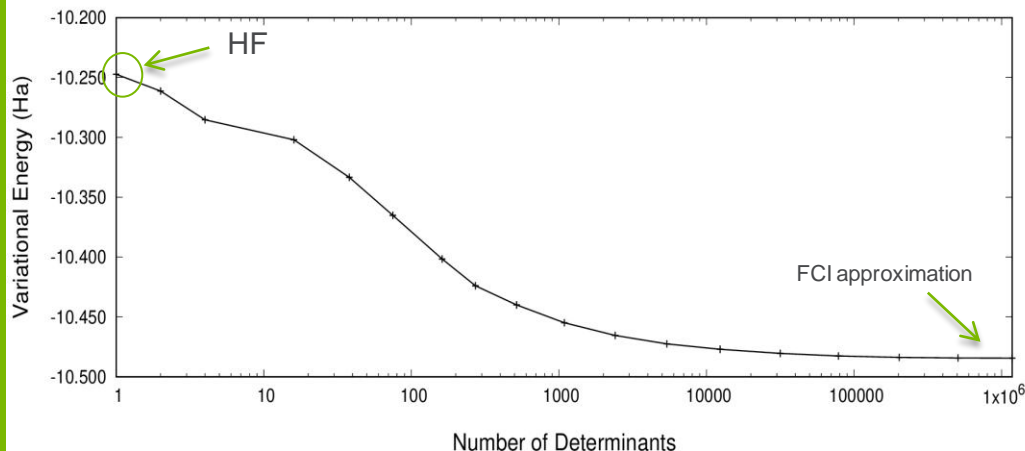
CIPSI CONVERGENCE

- Convergence at 0.1 mHa with 1.2M determinants

1. Define a reference wave function:

$$|\Psi\rangle = \sum_{i \in D} c_i |i\rangle \qquad E_{va} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

2. Generate external Determinants

   All single and double excitations

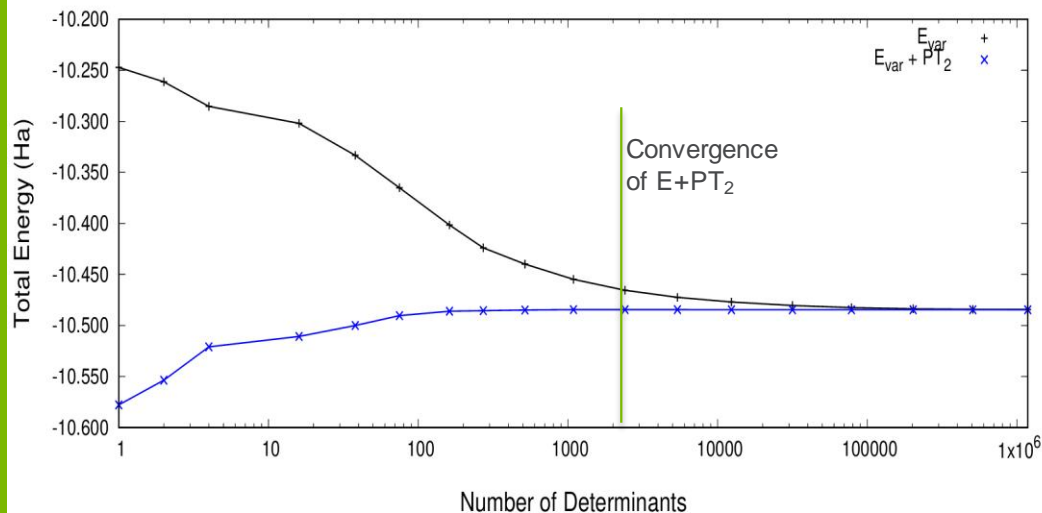3. Second order perturbative contribution of each determinant $|\alpha\rangle$

$$\Delta E = \frac{\langle \Psi | \hat{H} | \alpha \rangle \langle \alpha | \hat{H} | \Psi \rangle}{E_{va} - \langle \alpha | \hat{H} | \alpha \rangle}$$

4. Select $|\alpha\rangle$'s with largest ΔE_α and add them to Determinant space (D)

5. Diagonalize $\hat{H}$ in D then update $|\Psi\rangle$ and E_{var}

6. Iterate until reaching convergence.

- Selected CI (CIPSI) systematically reduces the energy
- Selecting all determinants leads rigorously to the FCI energy

Argonne
NATIONAL LABORATORY

TRUNCATING THE NUMBER OF DETERMINANTS

Total Energy (Ha) vs Number of Determinants

Legend: E_{var} +, $E_{var} + PT_2$ ×

Convergence of E+PT$_2$

- f(E+PT$_2$) converges within 0.1 mHa with ~2100 determinants

3. Second order perturbative contribution of each determinant $|\alpha\rangle$

$$\Delta E = \frac{\langle \Psi | \hat{H} | \alpha \rangle \langle \alpha | \hat{H} | \Psi \rangle^r}{E_{va} - \langle \alpha | \hat{H} | \alpha \rangle}$$

4. Select $|\alpha\rangle$'s with largest ΔE_α and add them to Determinant space (D)

5. Diagonalize $\hat{H}$ in D then update $|\Psi\rangle$ and E_{var}
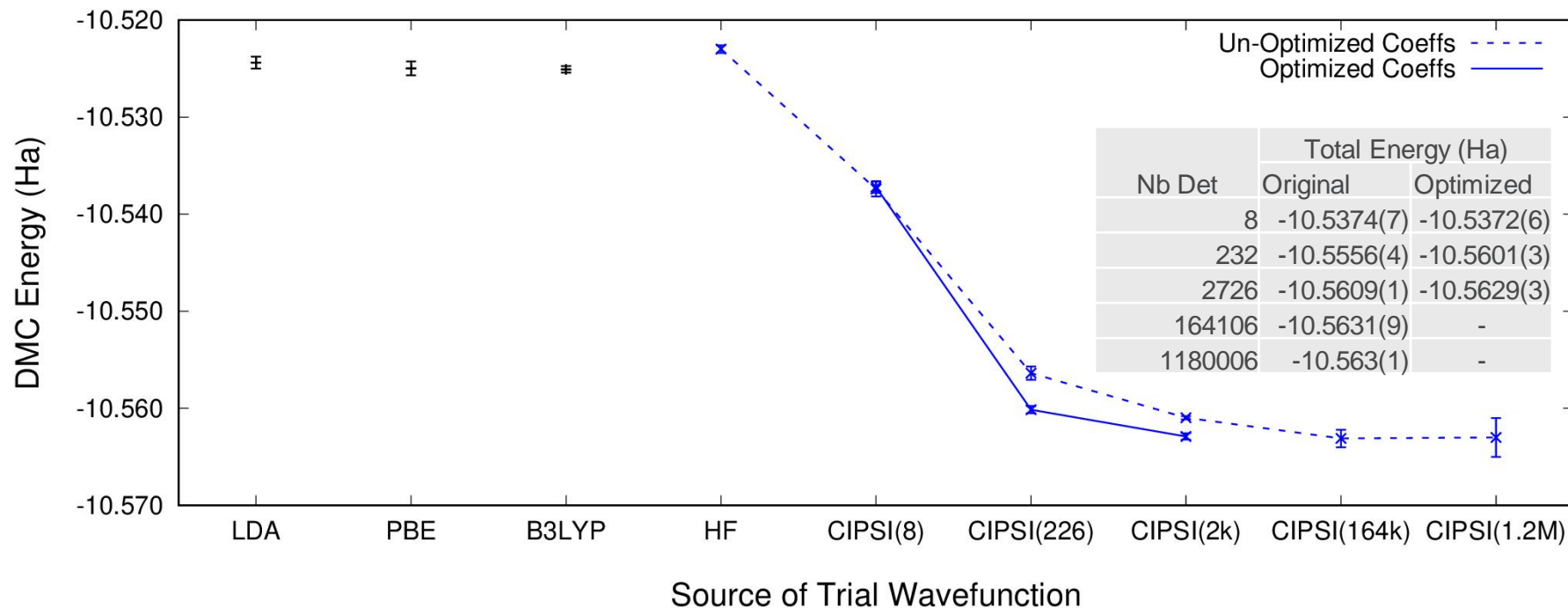
6. Iterate until reaching convergence.

At anytime

$$E_{PT} = \sum_\alpha \Delta E_\alpha^2$$

estimates the distance to the exact FCI solution

f(E+PT$_2$) converges faster reducing significantly the number of determinant

Argonne
NATIONAL LABORATORY

DMC Total energy (BFD-vDz)

|	Total Energy (Ha)	
Nb Det	Original	Optimized
8	-10.5374(7)	-10.5372(6)
232	-10.5556(4)	-10.5601(3)
2726	-10.5609(1)	-10.5629(3)
164106	-10.5631(9)	-
1180006	-10.563(1)	-

- DMC energy is **systematically** reduced with CIPSI wavefunctions.
  Number of determinants needs to be reduced to be useful in general.
  Only 232 VMC optimized determinant coefficients are sufficient to converge within 3mHa
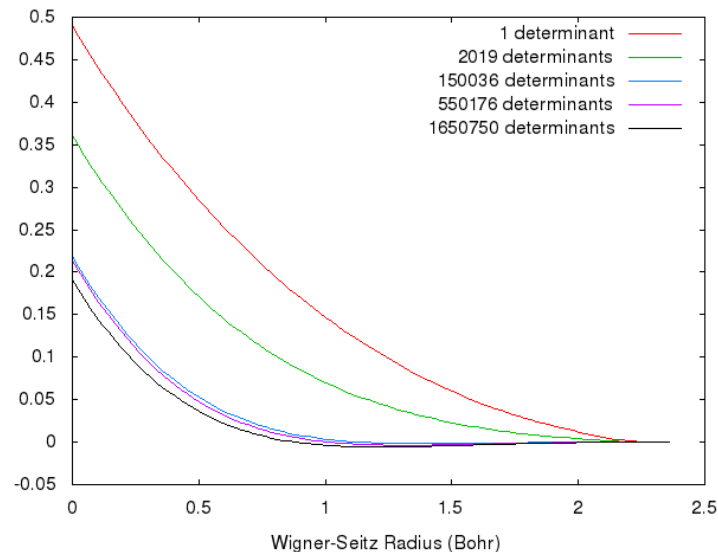
MULTI-DETERMINANT

- Multideterminants improve electron-electron cusp (affects nodal surface). 2 body-Jastrow improves electron-electron cusp without changing the nodal surface (affects variance).

$$J2 = \sum_i^e \sum_{j>i}^e u_{ab}(|r_i - r_j|)$$
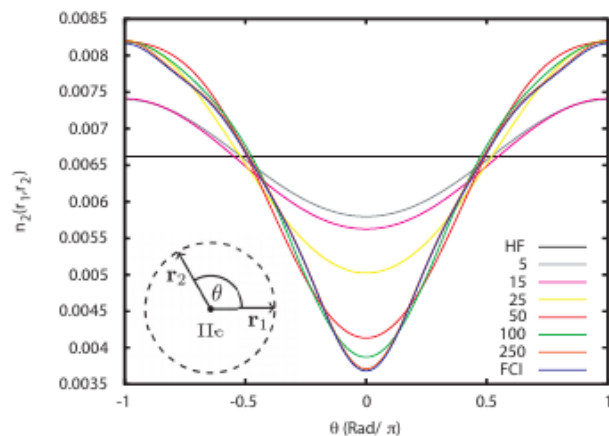
J2 dn

High Energy determinants only to correct for the Cusp. 2-Body Jastrows in QMC already do some of that work.

HANDS ON!

H2O

QUANTUM PACKAGE

Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs

Yann Garniron,[1] Thomas Applencourt,[2] Kevin Gasperich,[2,3] Anouar Benali,[2] Anthony Ferté,[4] Julien Paquier,[4] Barthélémy Pradines,[4,5] Roland Assaraf,[4] Peter Reinhardt,[4] Julien Toulouse,[4] Pierrette Barbaresco,[6] Nicolas Renon,[6] Grégoire David,[7] Jean-Paul Malrieu,[1] Mickaël Véril,[1] Michel Caffarel,[1] Pierre-François Loos,[1, a)] Emmanuel Giner,[4, b)] and Anthony Scemama[1, c)]

[1] *Laboratoire de Chimie et Physique Quantiques (UMR 5626), Université de Toulouse, CNRS, UPS, France*
[2] *Computational Science Division, Argonne National Laboratory, Argonne, IL 60439, United States*
[3] *Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, United States*
[4] *Laboratoire de Chimie Théorique, Sorbonne Université, CNRS, Paris, France*
[5] *Institut des Sciences du Calcul et des Données, Sorbonne Université, F-75005 Paris, France*
[6] *CALMIP, Université de Toulouse, CNRS, INPT, INSA, UPS, UMS 3667, France*
[7] *Aix-Marseille Univ, CNRS, ICR, Marseille, France*

Quantum chemistry is a discipline which relies heavily on very expensive numerical computations. The scaling of correlated wave function methods lies, in their standard implementation, between $\mathcal{O}(N^5)$ and $\mathcal{O}(e^N)$, where N is proportional to the system size. Therefore, performing accurate calculations on chemically meaningful systems requires i) approximations that can lower the computational scaling, and ii) efficient implementations that take advantage of modern massively parallel architectures. QUANTUM

https://github.com/QuantumPackage/qp2

Argonne
NATIONAL LABORATORY

All data available in: **/qmcpack_workshop_2019/day2_CIPSI**

INPUT FILE

H2O.xyz

```
3

H          0.00000000      0.75720000     -0.46920000
H          0.00000000     -0.75720000     -0.46920000
O          0.00000000      0.00000000      0.11730000
```

```
> source $HOME/apps/qp2/quantum_package.rc
> qp_create_ezfio  -b "O:cc-pcvtz | H:cc-pvtz" H2O.xyz
```

Argonne ▲
NATIONAL LABORATORY

QP_RUN

> qp_run -h

* cis
* cisd
* diagonalize_h
* fci
* fcidump
* four_idx_transform
* install
* ks_scf
* molden
* print_ci_vectors
* print_e_conv
* print_ecmd_pbe_ontop
* print_h0j
* print_pgm
* print_rsdft_variational_energy
* print_wf
* pt2
* qmc_create_wf
* qmc_e_curve
* qp_ao_ijkl_r3_ints
* qp_cipsi_rsh

* qp_convert_qmcpack_to_ezfio.py
* reorder_dets
* rs_ks_scf
* save_for_qmcpack
* save_natorb
* save_one_e_dm
* save_ortho_mos
* scf
* sort_by_fock_energies
* swap_mos
* target_pt2_qmc
* truncate_wf_spin
* truncate_wf_spin_no_H
* two_body_dm.main
* uninstall
* write_2_body_dm_fci_dump
* write_effective_rsdft_hamiltonian
* write_erf_and_regular_ints
* write_integrals_erf
* write_rsdft_h_read_ints

Argonne
NATIONAL LABORATORY

HARTREE FOCK

> qp_run scf H2O.ezfio | tee H2O-scf.out

-76.05731727176526 Ha

NATURAL ORBITALS

> echo "50000" > H2O.ezfio/determinants/n_det_max
> qp_run fci H2O.ezfio | tee H2O-fci0.out

```
Summary at N_det =        63603
----------------------------------

# ============  ===========================
            State      1
# ============  ===========================
# E            -76.37451832
# PT2          -0.01477441     0.00002951
#
# E+PT2        -76.38929273     0.00002951
# ============  ===========================
```
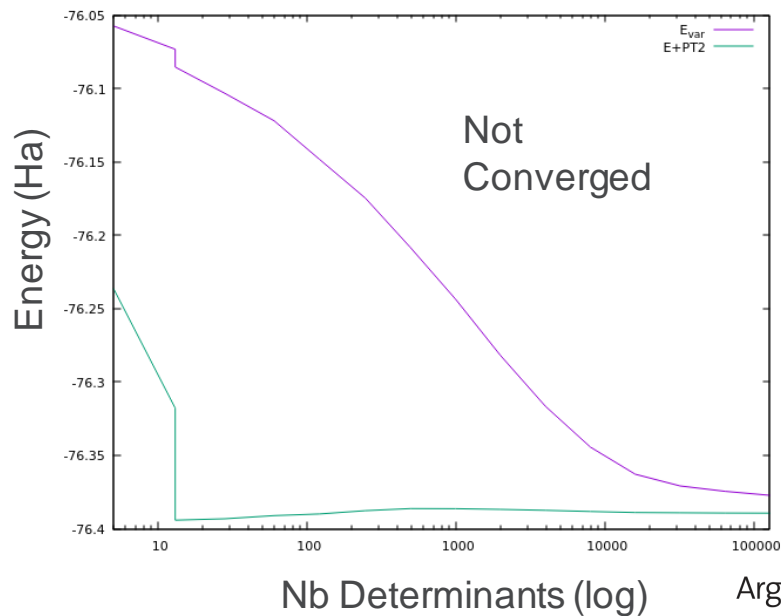
```
> qp_run save_natorb H2O.ezfio
```

SELECTED CI

```
> echo "100000" > H2O.ezfio/determinants/n_det_max
> qp_run fci H2O.ezfio | tee H2O-fci.out
> qp_run print_e_conv H2O.ezfio
```

```
Summary at N_det =      127246
---------------------------------

# ============  =============================
             State    1
# ============  =============================
# E            -76.37725295
# PT2          -0.01213658     0.00002141
#
# E+PT2        -76.38938953     0.00002141
```
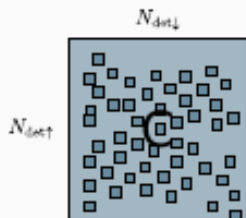
PRUNING THE DETERMINANTS FOR QMC

Usual truncation

$$\Psi(R) = \sum_k c_k \mathcal{D}_k = \sum_i \sum_j C_{ij} D_{i\uparrow}(R_\uparrow) D_{j\downarrow}(R_\downarrow)$$

Used truncation

- Based on the $|c_k|$ (or CSF coefficients)
- Removes mostly same-spin doubles in CISD $\Longrightarrow$ some gain is observed.
- Makes the matrix **C** more sparse
- For CASSCF or FCI : Needs a severe truncation to remove $D_\uparrow$ or $D_\downarrow$: the whole column must be zero
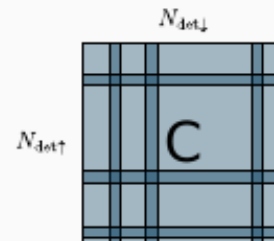
- Contribution of $D_\uparrow$ and $D_\downarrow$ to the norm of Ψ

$$\mathcal{N} = \sum_{i=1}^{N_{\text{det}\uparrow}} \sum_{j=1}^{N_{\text{det}\downarrow}} C_{ij}^2 = \sum_{i=1}^{N_{\text{det}\uparrow}} \mathcal{N}_i^\uparrow = \sum_{j=1}^{N_{\text{det}\downarrow}} \mathcal{N}_j^\downarrow$$

- Remove $D_{i\uparrow}$ when $\mathcal{N}_i^\uparrow = \sum_{j=1}^{N_{\text{det}\downarrow}} C_{ij}^2 < \epsilon$

Argonne
NATIONAL LABORATORY

PRUNING THE DETERMINANTS FOR QMC

Used truncation

Converged FCI/cc-pVTZ FN-DMC energy with $\epsilon = 10^{-5}$: 7.1× the cost of a single-determinant

- Contribution of $D_\uparrow$ and $D_\downarrow$ to the norm of Ψ
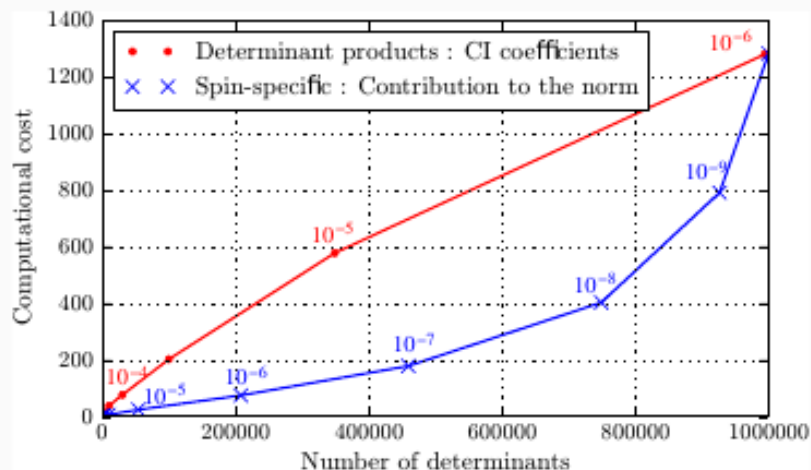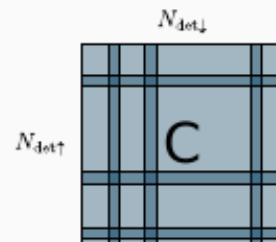
$$\mathcal{N} = \sum_{i=1}^{N_{\text{det}\uparrow}} \sum_{j=1}^{N_{\text{det}\downarrow}} C_{ij}^2 = \sum_{i=1}^{N_{\text{det}\uparrow}} \mathcal{N}_i^\uparrow = \sum_{j=1}^{N_{\text{det}\downarrow}} \mathcal{N}_j^\downarrow$$

- Remove $D_{i\uparrow}$ when $\mathcal{N}_i^\uparrow = \sum_{j=1}^{N_{\text{det}\downarrow}} C_{ij}^2 < \epsilon$

```
> for i in 4 5 6 8; do
>   mkdir Truncate$i
>   cp -r H2O.ezfio Truncate$i/
>   echo "1.0e-0$i" > Truncate$i/H2O.ezfio/qmcpack/ci_threshold
>   cd Truncate$i
>   qp_run truncate_wf_spin H2O.ezfio | tee H2O-Tr$i.out
>   qp_run pt2 H2O.ezfio | tee H2O-Tr$i-pt2.out
>   cd ../;
> done
```

Summary at N_det =	2602		Summary at N_det =	18863		Summary at N_det =	44694		Summary at N_det =	98113	
# E	-76.22508762		# E	-76.31730026		# E	-76.35988257		# E	-76.37632447	
# PT2	-0.16030042	0.00006342	# PT2	-0.06866748	0.00012203	# PT2	-0.02732998	0.00005145	# PT2	-0.01302276	0.00002173
# E+PT2	-76.38538804	0.00006342	# E+PT2	-76.38596775	0.00012203	# E+PT2	-76.38721256	0.00005145	# E+PT2	-76.38934723	0.00002173

SAVE FOR QMCPACK

```
> qp_run save_for_qmcpack H2O.ezfio > H2O-Tr4
> convert4qmc –QP H2O-Tr4 –production -addCusp
```

Argonne
NATIONAL LABORATORY

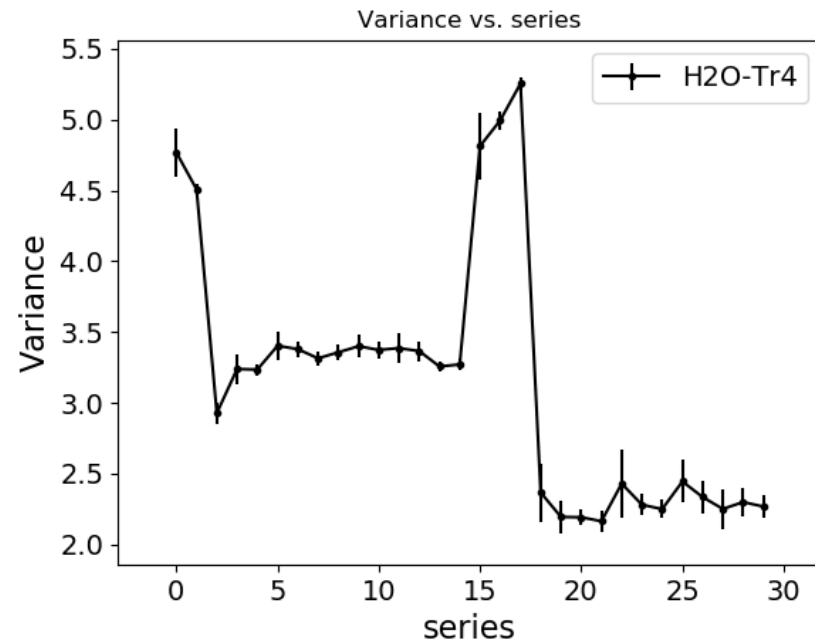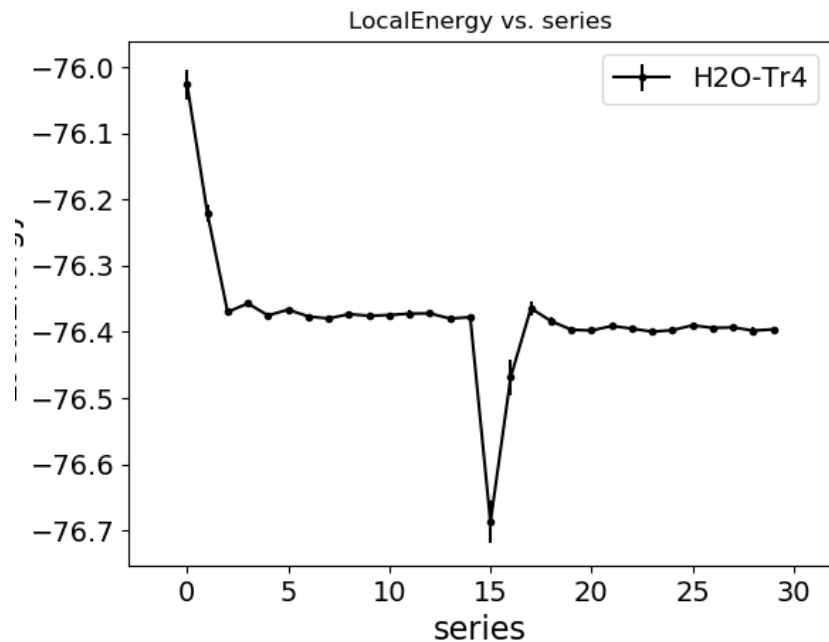# TRIAL WAVEFUNCTION

```xml
<?xml version="1.0"?>
<qmcsystem>
 <wavefunction name="psi0" target="e">
  <determinantset type="MolecularOrbital" name="LCAOBSet" source="ion0" transform="yes" cuspCorrection="yes" href="../H2O-Tr4.orbs.h5">
   <sposet basisset="LCAOBSet" name="spo-up" size="71" cuspInfo="../CuspCorrection/spo-up.cuspInfo.xml">
    <occupation mode="ground"/>
    <coefficient size="71" spindataset="0"/>
   </sposet>
   <sposet basisset="LCAOBSet" name="spo-dn" size="71" cuspInfo="../CuspCorrection/spo-dn.cuspInfo.xml">
    <occupation mode="ground"/>
    <coefficient size="71" spindataset="0"/>
   </sposet>
   <multideterminant optimize="no" spo_up="spo-up" spo_dn="spo-dn">
    <detlist size="2602" type="DETS" nca="0" ncb="0" nea="5" neb="5" nstates="71" cutoff="1e-20" href="../H2O-Tr4.orbs.h5"/>
   </multideterminant>
  </determinantset>
```
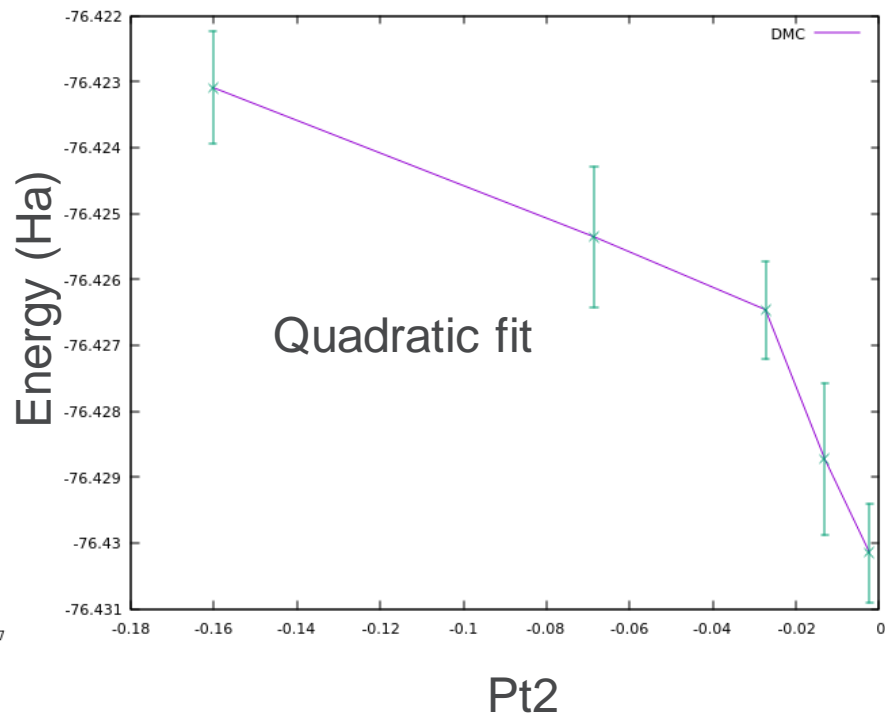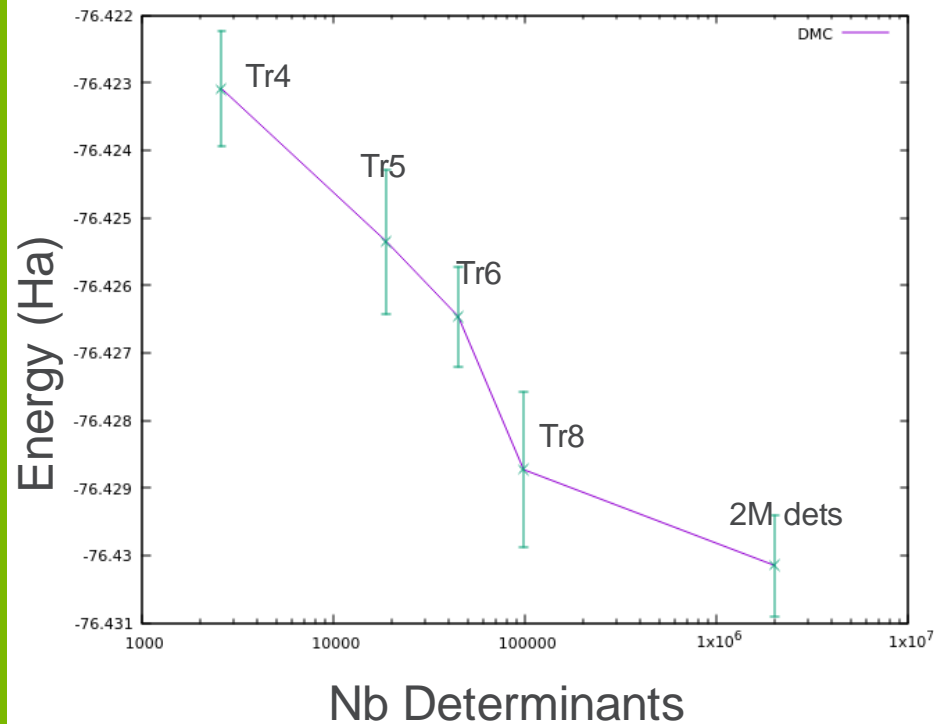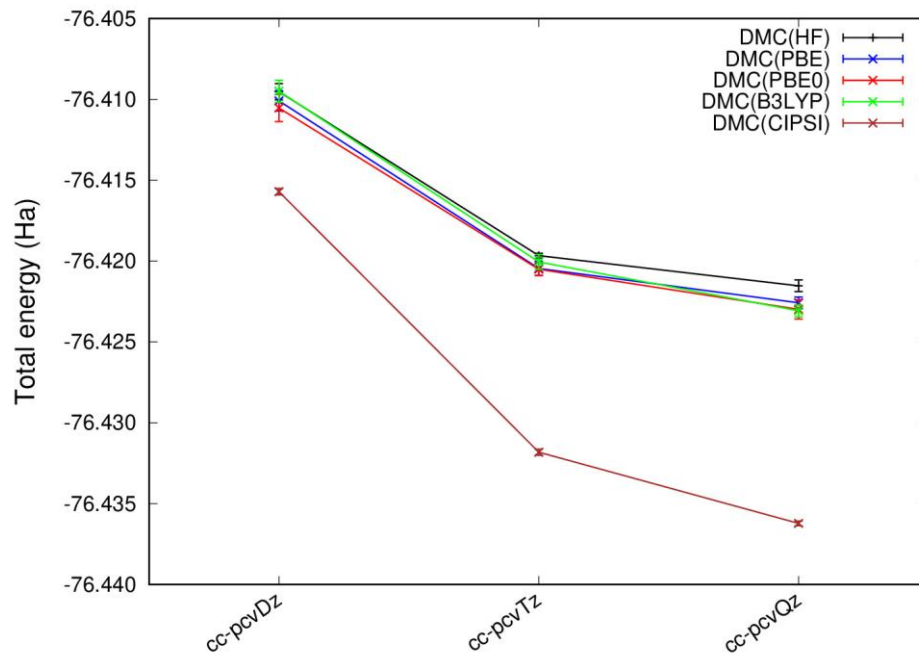
TRIAL WAVEFUNCTION

<**multideterminant** optimize="no" spo_up="spo-up" spo_dn="spo-dn">
  <**detlist** size="2602" type="DETS" nca="0" ncb="0" nea="5" neb="5" nstates="71" cutoff="1e-20">
   <**ci** id="CIcoeff_0" coeff="0.977146" qc_coeff="0.977146"
alpha="11111000000000000000000000000000000000000000000000000000000000000000000"
beta="11111000000000000000000000000000000000000000000000000000000000000000000"**/>**
   <**ci** id="CIcoeff_1" coeff="-0.0477192" qc_coeff="-0.0477192"
alpha="11110000001000000000000000000000000000000000000000000000000000000000000"
beta="11110000001000000000000000000000000000000000000000000000000000000000000"**/>**
   <**ci** id="CIcoeff_2" coeff="-0.030325" qc_coeff="-0.030325"
alpha="11101000010000000000000000000000000000000000000000000000000000000000000"
beta="11101000010000000000000000000000000000000000000000000000000000000000000"**/>**
   <**ci** id="CIcoeff_3" coeff="-0.0262995" qc_coeff="-0.0262995"
alpha="11011001000000000000000000000000000000000000000000000000000000000000000"
beta="11011001000000000000000000000000000000000000000000000000000000000000000"**/>**
   <**ci** id="CIcoeff_4" coeff="-0.0261026" qc_coeff="-0.0261026"
alpha="11110000001000000000000000000000000000000000000000000000000000000000000"
beta="11101000010000000000000000000000000000000000000000000000000000000000000"**/>**
   <**ci** id="CIcoeff_5" coeff="-0.0261026" qc_coeff="-0.0261026"
alpha="11101000010000000000000000000000000000000000000000000000000000000000000"
beta="11110000001000000000000000000000000000000000000000000000000000000000000"**/>**

JASTROW OPTIMIZATION

LocalEnergy vs. series

Variance vs. series
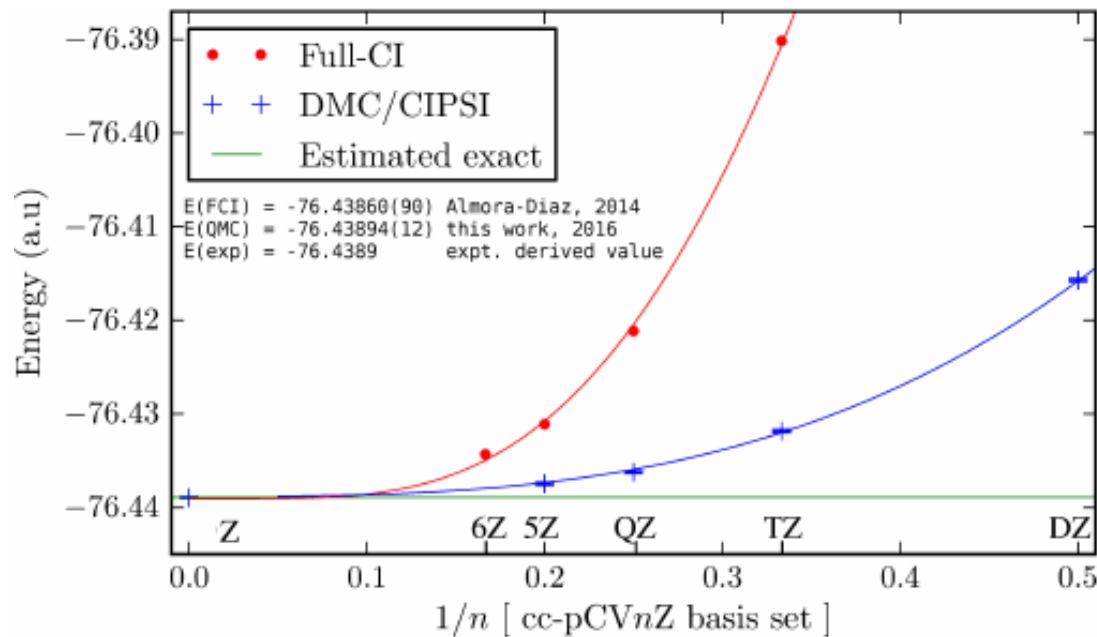
Extrapolating the DMC energy

Case of H$_2$O

- CIPSI nodal surface is significantly better than SD-Trial Wavefunction.

WATER MOLECULE (GROUND STATE)

Basis set	FCI size	# dets used in DMC	E_0^{var}	FCI, Almora-Díaz[27]	Deviation
cc-pCVDZ	$\sim 10^{10}$	172 256	-76.282136	-76.282865	0.0007
cc-pCVTZ	$\sim 2.10^{14}$	640 426	-76.388287	-76.390158	0.0018
cc-pCVQZ	$\sim 2.10^{17}$	666 927	-76.419324	-76.421148	0.0018
cc-pCV5Z	$\sim 7.10^{19}$	1 423 377	-76.428550	-76.431105	0.0025

Summary

- It is possible to systematically improve the nodal surface for Molecules using selected CI

- Method is costly but modern implementation allows to generate a trial wavefunction for molecules (to about 350 orbitals) and solids (using Density Fitting to about 900 orbitals).

- Research is in progress to reduce the determinant space and allow more compact trial wavefunctions.

QUESTION?!

Multi-determinant Range Separated DFT

$$\frac{1}{r} = \hat{w}_{ee}^{lr} + \hat{w}_{ee}^{sr}$$

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\mathrm{d}t$$

$\hat{V}_{ee}$ Ca be decomp o int a ion ran an a sho ran compo

We can use an error function null on x=0 and equals 1 when $x \to \infty$

We can rewrite in function of a parameter μ (inverse to the cutoff radius)

$$\hat{w}_{ee}^{lr,\mu}(r) = \frac{\mathrm{erf}(\mu r)}{r} \qquad \hat{w}_{ee}^{sr,\mu}(r) = \frac{1}{r} - \hat{w}_{ee}^{lr,\mu}(r) = \frac{1 - \mathrm{erf}(\mu r)}{r}$$

Within DFT formalism:

$$E_0 = \left\langle \Psi^{lr,\mu} \left| \hat{T}_e + \hat{W}_{ee}^{lr,\mu} + \hat{V}_{ne} \right| \Psi^{lr,\mu} \right\rangle + \bar{E}_{\mathrm{Hxc}}^{sr,\mu}\left[n_{\Psi^{lr,\mu}} \right]$$

sCI: recovers static correlation

DFT (LDA or PBE)

36

APPLICATIONS TO WATER

Benali et al. in preparation

37