

# One-step treatment of spin-orbit coupling and electron correlation in large active spaces.

New applications for the SHCI algorithm

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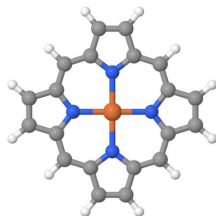
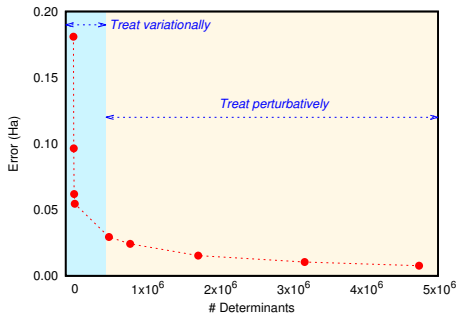
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## SHCI

An algorithm that allows us to do **cheap** and **near exact large active space** calculations.



Fe(Porphyrin)

Active space (32e,29o) Fe 3d, C 2p<sub>z</sub>, N 2p<sub>z</sub>  
 The Hilbert space is  $> 10^{14}$  determinants

## Selected CI + Perturbation theory

[Huron JCP (1973)]

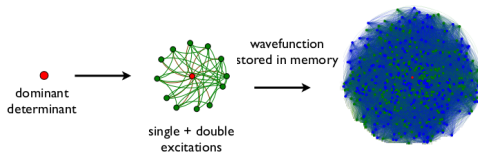
- 1) Variational stage: calculate  $E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$  in a space of important det.

→ How to quickly select the “important” determinants?

- 2) Perturbational stage: calculate  $E_2 = \langle \Psi_0 | \hat{V} \frac{1}{\hat{H} - E_0} \hat{V} | \Psi_0 \rangle$

→ How to avoid the memory bottleneck?

→ Iteratively find important det. by connections to a current space.



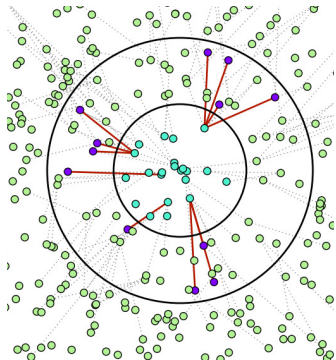
At iteration  $\mu$ , we know  $|\Psi_0^\mu\rangle$ , and  $c_i^\mu$ . The variational space  $\mathcal{V}^\mu$  is augmented by the determinants in:

$$\mathcal{C}^\mu(\epsilon_1) = \{ |D_a\rangle \mid \mathbf{f}^\mu(|D_a\rangle) > \epsilon_1 \}$$

SHCI does that with a simple criterion  $\mathbf{f}^\mu$  that allows an **easy, and fast implementation**:

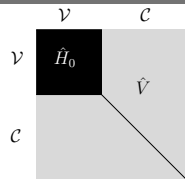
$$\mathbf{f}^\mu(|D_a\rangle) = \max_{D_i \in \mathcal{V}^\mu} |H_{ai} c_i^\mu|$$

$\hat{H}$  is diagonalized in  $\mathcal{V}^\mu + \mathcal{C}^\mu$  to get  $|\Psi_0^{\mu+1}\rangle$  and  $c_i^{\mu+1}$ .



$$E_2 = \langle \Psi_0 | \hat{V} \frac{1}{\hat{H}_0 - E_0} \hat{V} | \Psi_0 \rangle = \sum_{D_a \in \mathcal{C}} \frac{1}{E_a - E_0} \left( \sum_{D_i \in \mathcal{V}} H_{ai} c_i \right)^2$$

$\Psi_1$



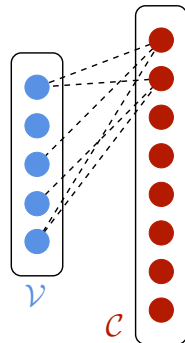
### 1) Deterministic evaluation (involves a truncation)

$$E_2^D = \sum_{D_a \in \mathcal{C}(\epsilon_2)} \frac{1}{E_a - E_0} \left( \sum_{D_i \in \mathcal{V}}^{(\epsilon_2)} H_{ai} c_i \right)^2$$

### 2) Stochastic estimate (unbiased)

$$E_2^S = \langle \Psi_0 | \hat{V} \frac{1}{\hat{H}_0 - E_0} \hat{V} | \Psi_0 \rangle$$

where about  $\approx 10^2$  dets of  $|\Psi_0\rangle$  are sampled



### 3) Semistochastic implementation (low stochastic error)

$$E_2 = E_2^D[\epsilon_2^{\text{large}}] + \left( E_2^S[\epsilon_2^{\text{small}}] - E_2^S[\epsilon_2^{\text{large}}] \right)$$

→ too memory intensive!

$$e^2 v^2 N_V \approx 12^2 50^2 10^7 = 10^{12}$$

SHCI = vHCI (optimal active space det) + Semistochastic PT

→ One-parameter ( $\epsilon_1$ ) method that allows efficient large active space calculations with perturbative corrections.

## Ground state energies

[Holmes,Tubman,Umrigar, JCTC (2016)]

[Sharma *et al.* JCTC (2017)]

- First row dimers (**14e,108o**)

- Cr<sub>2</sub> (**12e,190o**)

- Mn(Salen) (**28e,22o**)

- Acenes (singlet fission)

## Excited states

[Holmes,Umrigar,Sharma (2017)]

## Self-consistent field feature

[Smith,**BM**,Holmes,Sharma JCTC (2017) **Editor's Choice for 2017**]

## Spin-orbit coupling

[**BM**,Sharma JCTC (2017)]

## Dynamical correlation

[**BM**,Smith,Sharma (in prep.)]

## **Spin-Orbit Coupling**

**Relativistic effects** are important to capture phosphorescence, magnetic spectroscopy, hyperfine constant, g-tensors, ZFS,...

In heavy atoms, it is also comparable to electron correlation.

H																	He				
Li	Be															B	C	N	O	F	Ne
Na	Mg															Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg											

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

**Issue**  $\langle N_{\alpha} N_{\beta} | \mathbf{H}^{\text{relat.}} | N'_{\alpha} N'_{\beta} \rangle \neq 0$

→ The size of the Hilbert space of the problem sharply increases

→ The SOC is often treated perturbatively after an SOC-free SCF calculation.

$$\left( \frac{n/2}{e/2} \right)^2 \rightarrow \binom{n}{e}$$

→ SHCI is used with an SOC Hamiltonian to treat relativistic effects with large active spaces in a one-step procedure on an equal footing with correlation

HCI retains its ability to effectively discard large parts of low importance in the increased-size Hilbert space.



In practice, the most accurate procedures to treat relativistic effects in molecular systems use the four-component **Dirac-Coulomb-Breit (DCB)** Hamiltonian.

## 1) Dirac Hamiltonian (with a nuclei-electron potential $\mathbf{V}$ )

This is a **one-body non-interacting** Hamiltonian:

$$\mathbf{H}^{\text{Dirac}} = \begin{pmatrix} \mathbf{V} + mc^2 & \mathbf{c} \boldsymbol{\sigma} \cdot \mathbf{p} \\ \mathbf{c} \boldsymbol{\sigma} \cdot \mathbf{p} & \mathbf{V} - mc^2 \end{pmatrix} \quad \boldsymbol{\sigma} = \left\{ \begin{pmatrix} \mathbf{0}_2 & \boldsymbol{\sigma}_x \\ \boldsymbol{\sigma}_x & \mathbf{0}_2 \end{pmatrix}, \dots \right\}$$

$4 \times 4$   
block  
structure

$\boldsymbol{\sigma}_x$  are Pauli matrices

## 2) Two-body interaction (adding the **two-body interaction**)

This contains the instantaneous interaction + terms that account for **retardation**:

$$\mathbf{V}^{\text{Coulomb-Breit}} = \sum_{ij} \underbrace{\left( \frac{1}{r_{ij}} \right)}_{\text{Coulomb}} - \underbrace{\left( \frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}} \right)}_{\text{Gaunt}} + \underbrace{\left( \frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{2r_{ij}} - \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})}{2r_{ij}^3} \right)}_{\text{Gauge}}$$

Breit

Given the  $4 \times 4$  structure of those Hamiltonians, the equation  $\mathbf{H}\Psi = E\Psi$  have **four-component solutions**, i.e. they yield four **coupled** eigenvalue problems:

$$\begin{pmatrix} \mathbf{V} + mc^2 & 0 & c \mathbf{p}_z & c (\mathbf{p}_x - i\mathbf{p}_y) \\ 0 & \mathbf{V} + mc^2 & c (\mathbf{p}_x + i\mathbf{p}_y) & -c \mathbf{p}_z \\ c \mathbf{p}_z & c (\mathbf{p}_x - i\mathbf{p}_y) & \mathbf{V} - mc^2 & 0 \\ c (\mathbf{p}_x + i\mathbf{p}_y) & -c \mathbf{p}_z & 0 & \mathbf{V} - mc^2 \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} = E \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix}$$

$c \boldsymbol{\sigma} \cdot \mathbf{p}$

“Large” and “Small” components

$\Psi$  is a bispinor (a complex vector of four components)

$\Psi^L$  and  $\Psi^S$  are spinors (complex vector of two components)

$\Psi_1, \dots, \Psi_4$  are wavefunctions (one-component)

$$\Psi = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} = \begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix}$$

$$\Psi^S = \frac{c \boldsymbol{\sigma} \cdot \mathbf{p}}{E - V + mc^2} \Psi^L \underset{E-V \sim mc^2}{\sim} \underset{p \sim mv}{\sim} \frac{\sigma v}{2c} \Psi^L \ll \Psi^L$$

An alternative is to use **two-component Hamiltonians** which are capable of delivering quantitative accuracy for realistic relativistic problems.

**Foldy-Wouthuysen (FW):** find the **unitary  $U$  which decouples  $\psi^L$  and  $\psi^S$**

**1) An FW is done on the one-body Dirac Hamiltonian** (block-diagonalized):

$$\begin{pmatrix} \mathbf{H}^{2c} & \mathbf{0} \\ \mathbf{0} & \mathbf{H} \end{pmatrix} \begin{pmatrix} \psi^{2c} \\ \psi \end{pmatrix} = E \begin{pmatrix} \psi^{2c} \\ \psi \end{pmatrix}$$

**2) The FW transformation is then applied to the two-body interaction**

Two-body two-component Hamiltonian: 
$$\mathbf{H}^{2c} = \underbrace{\mathbf{H}^{\text{Schrödinger}} + \mathbf{H}^{\text{spin-free(SF)}}}_{\mathbf{H}^{\text{scalar-relativistic(SR)}}} + \mathbf{H}^{\text{SOC}}$$

**State-of-the-art**

Two-step process with QDPT:

1) obtain the eigenstates  $|\psi_1\rangle, |\psi_2\rangle, \dots, |\psi_n\rangle$  of  $\mathbf{H}^{\text{SR}}$

2) let them interact by diagonalizing  $\langle \psi_i | \mathbf{H}^{\text{SR}} + \mathbf{H}^{\text{SOC}} | \psi_j \rangle$

The **BP Hamiltonian** is obtained through an **approximate analytic FW** transformation performed on the four-component **one-body Dirac Hamiltonian**. Its two-body terms are obtained from transforming the Coulomb and Breit terms.

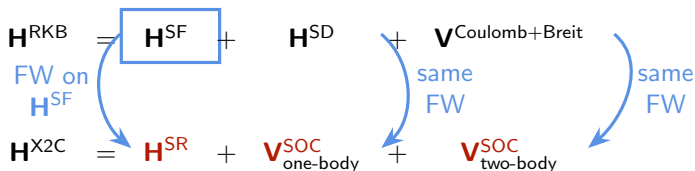
$$\begin{array}{lcl}
 \mathbf{H}^{\text{DCB}} & = & \boxed{\mathbf{H}^{\text{Dirac}}} + \mathbf{V}^{\text{Coulomb+Breit}} \\
 \text{FW on } \mathbf{H}^{\text{Dirac}} & \searrow & \\
 \mathbf{H}^{\text{BP}} & = & \mathbf{H}^{\text{SR}} + \mathbf{V}_{\text{one-body}}^{\text{SOC}} + \mathbf{V}_{\text{two-body}}^{\text{SOC}}
 \end{array}$$

same FW

The **X2C Hamiltonian** starts from the **restricted kinetic balance** i.e. from the four-component **modified one-body Dirac equation**:

$$\mathbf{H}^{\text{SF}} + \mathbf{H}^{\text{SD}} \leftarrow \begin{pmatrix} \mathbf{V} & \mathbf{T} \\ \mathbf{T} & \mathbf{W} - \mathbf{T} \end{pmatrix} \begin{pmatrix} \Psi^{\text{L}} \\ \Psi^{\ell} \end{pmatrix} = \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & \frac{\alpha^2}{4} \mathbf{T} \end{pmatrix} \begin{pmatrix} \Psi^{\text{L}} \\ \Psi^{\ell} \end{pmatrix} E$$

The FW transformation is performed **exactly algebraically**.



The RKB replaces  $\Psi^{\text{S}}$  with the “pseudo-large component”  $\Psi^{\ell} = \frac{2c}{\sigma \cdot \mathbf{p}} \Psi^{\text{S}}$ , effectively insuring that  $\Psi^{\text{L}}$  and  $\Psi^{\ell}$  can be expanded with a common basis set.

**Non-Relativistic**

1-component, 2-body

$$\Psi$$

**Dirac**

4-component, 1-body

**Dirac-Coulomb-Breit**

4-component, 2-body

$$\Psi = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix}$$

**Breit-Pauli & X2C**

2-component, 2-body

$$\Psi = \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix}$$

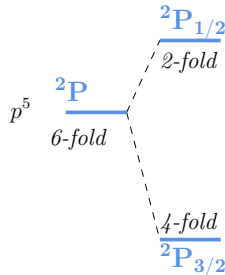
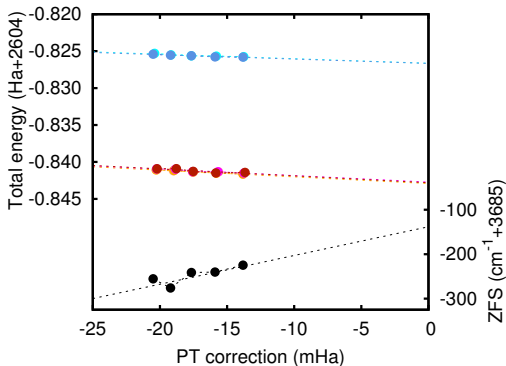
## Halogens

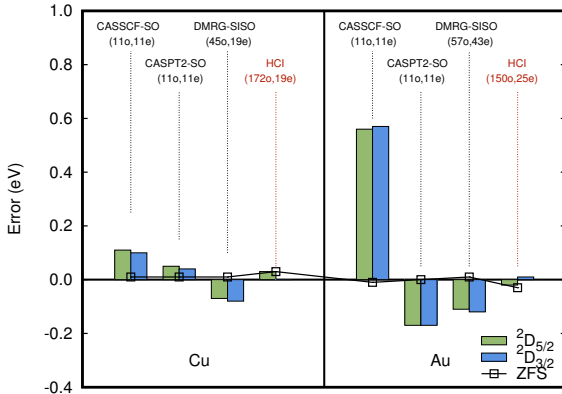
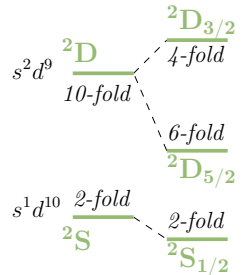
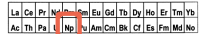
	(7e,4o)	$\approx(7e,100o)$	$\approx(17e,100o)$	Ref.
F	405	399		398
Cl	827	806	866	876
Br	3428	3403	3454	3649
I	7021	7277	7487	7755

H																	He																												
Li	Be									B	C	N	O	F	Ne																														
Na	Mg									Al	Si	P	S	Cl	Ar																														
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																												
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																												
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																												
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg																																			
<table><tr><td>La</td><td>Ce</td><td>Pr</td><td>Nd</td><td>Pm</td><td>Sm</td><td>Eu</td><td>Gd</td><td>Tb</td><td>Dy</td><td>Ho</td><td>Er</td><td>Tm</td><td>Yb</td></tr><tr><td>Ac</td><td>Th</td><td>Pa</td><td>U</td><td>Np</td><td>Pu</td><td>Am</td><td>Cm</td><td>Bk</td><td>Cf</td><td>Es</td><td>Fm</td><td>Md</td><td>No</td></tr></table>																		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb																																
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No																																

For I (17e,121o), the Hilbert space is  $10^{24}$

→ Results are converged to better than 1%

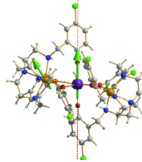


[illegible]

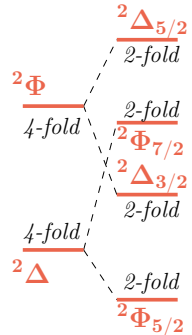
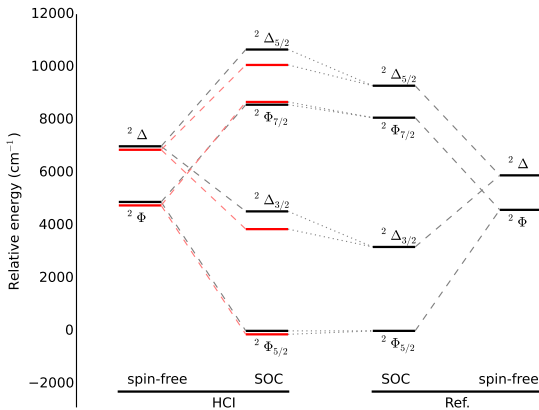
→ Au (25e,150o):  $10^{30}$ ,  
converged results with  $10^7$



- SOC splitting is larger than the crystal field

[illegible]

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No



### - **Dynamical correlation**

The addition of out-of-active space dynamical correlation can be necessary for some systems.

We are working on interfacing SHCI with the recently-introduced MRLCC.

### - **Spin-orbit coupling**

Four-component DCB Hamiltonian exactly, Quantitative calculations for realistic systems, Ab-initio parameters for model spin-Hamiltonian (analytical response theory).

### - **Non-linear wavefunction ansatz**

We are investigating the use of non-linear wavefunctions in SHCI.

### - **Machine learning**

The use of gaussian process techniques could allow us to grow the variational space even more intelligently.

<https://sanshar.github.io/Dice/>

Sandeep Sharma, James E. T. Smith, Adam A. Holmes, Bastien Mussard

Dice is interfaced with PySCF, a widely-used *ab initio* computational chemistry program implemented in Python and available with pip

## Welcome to Dice's documentation!



*Dice* implements the semistochastic heat bath configuration interaction (SHCI) algorithm for *ab initio* Hamiltonian of a quantum chemical system. Unlike full configuration interaction (FCI), SHCI can be used to treat active spaces containing 30–100 orbitals. SHCI is able to accomplish this by taking advantage of the fact that although the full Hilbert space may be enormous, only a small fraction of the determinants in the space have appreciable coefficients. Compared to other methods in its class SHCI is often not only orders of magnitude faster, it also does not suffer from a serious memory bottleneck that plagues such methods. The resulting algorithm as implemented in *Dice* allows us to treat difficult benchmark systems such as the Chromium dimer and Mn–Salen (a challenging bioinorganic cluster) at a cost that is often an order of magnitude faster than either density matrix renormalization group (DMRG) or full configuration interaction quantum Monte Carlo (FCIQMC). Thus if you are interested in performing multireference calculations with active space containing several tens to hundreds of orbitals, SHCI might be an ideal choice for you.

Contents:

- [Overview](#)
  - [Algorithm](#)

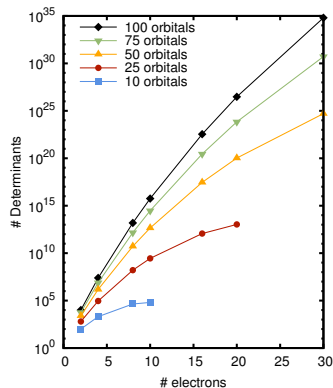
## **Appendix**

The wavefunction is written with **determinants**:

$$|\Psi_{\text{FCI}}\rangle = \sum_{\mathbf{D}_i \in \text{all}} c_i |D_i\rangle \quad \text{all orbitals} \quad \binom{N_{\text{orb}}}{N_{\text{elec}}}$$

In **multireference methods**, one chooses a subset of orbitals and a subset of electrons, defining an **active space** which is treated exactly:

$$|\Psi_{\text{CAS}}\rangle = \sum_{\mathbf{D}_n \in \text{active}} c_n |D_n\rangle \quad \begin{array}{|c|c|c|} \hline \text{Core} & \text{Active} & \text{Virtual} \\ \hline \end{array} \quad \binom{N_{\text{orb}}}{N_{\text{elec}}}$$



For larger, more challenging systems, it is impossible to perform exact calculations for reasonable active spaces, and approximate methods are devised.

→ The size of the tractable active space is a crucial parameter.

## ★ About the SHCI criterion

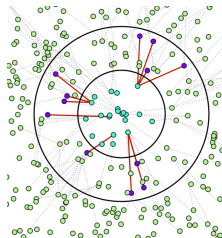
A determinant is chosen based on its **contribution to the first-order correction to the wavefunction**:

$$|\Psi_1\rangle = \sum_{D_a \in \mathcal{C}} \frac{\sum_{D_i \in \mathcal{V}^\mu} H_{ai} c_i^\mu}{E_0 - E_a} |D_a\rangle$$

One possible choice for  $\mathbf{f}^\mu$  is:  $\mathbf{f}^\mu(|D_a\rangle) = \frac{\sum_{D_i \in \mathcal{V}^\mu} H_{ai} c_i^\mu}{E_0 - E_a}$

- the numerator is dominated by  $\max_{D_i \in \mathcal{V}^\mu} |H_{ai} c_i^\mu|$
- the denominator  $E_0 - E_a$  is fairly constant

That is why SHCI uses:  $\mathbf{f}^\mu(|D_a\rangle) = \max_{D_i \in \mathcal{V}^\mu} |H_{ai} c_i^\mu|$



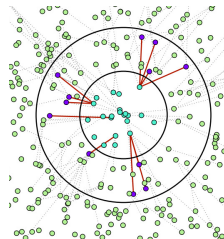
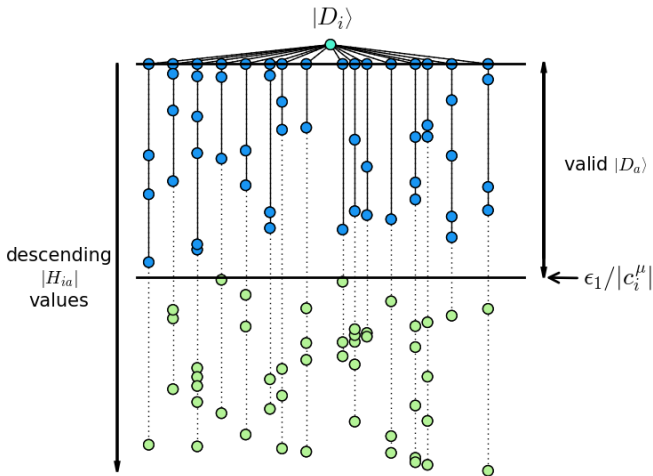
→ The two criteria will pick the same determinants

## ★ About the SHCI criterion

→  $H_{ai} = \langle D_a | \hat{H} | D_i \rangle$  depends only on the orbitals that change between  $D_a$  and  $D_i$

$$H_{ia} = \left\langle \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \left| \hat{H} \right| \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \right\rangle = \left\langle \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \left| \hat{H} \right| \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \right\rangle = H_{jb}$$

r  
p

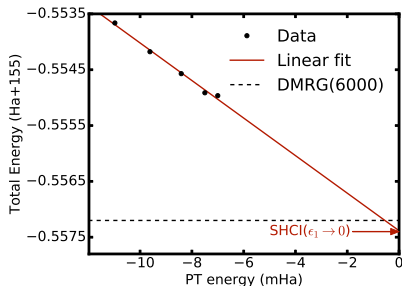


## Butadiene



with (22e,82o) (all electrons except 1s)

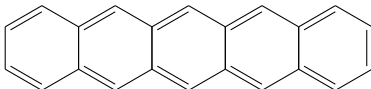
$\epsilon_1$	$N_{\text{var}}$	vHCl	SHCl
$3 \cdot 10^{-5}$	$1 \cdot 10^7$	-0.5411	-0.5534(1)
$2 \cdot 10^{-5}$	$2 \cdot 10^7$	-0.5441	-0.5540(1)
$1 \cdot 10^{-5}$	$6 \cdot 10^7$	-0.5481	-0.5550(1)
SHCl( $\epsilon_1 \rightarrow 0$ )		-0.5574(8)	
CCSD(T)		-0.5550	
CCSDT		-0.5560	
DMRG(M=6000)		-0.5572	



→ The extrapolation procedure is automated in our implementation.



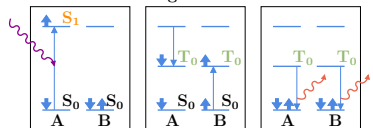
## Pentacene



with (22e,22o) ( $\pi$  and  $\pi^*$  orbitals)

	$E_{\text{SHCI}}$ (Ha+841)	$E_{\text{ex}}$ (kcal/mol)	$E_{\text{ref}}$ (kcal/mol)
Singlet Geometry			
$^1A_{\text{g}}$	-0.6174(6)	28.5	27.0
$^3B_{2\text{u}}$	-0.5720(8)		
Triplet Geometry			
$^1A_{\text{g}}$	-0.6050(7)	18.6	19.8
$^3B_{2\text{u}}$	-0.5751(9)		

## Singlet Fission



Two coupled molecules split an incoming excitation

The two states become more multireference as the chain length increases, and multireference methods are needed to obtain an accurate gap.