The conference's logo and entanglement
Internal matrices and applications

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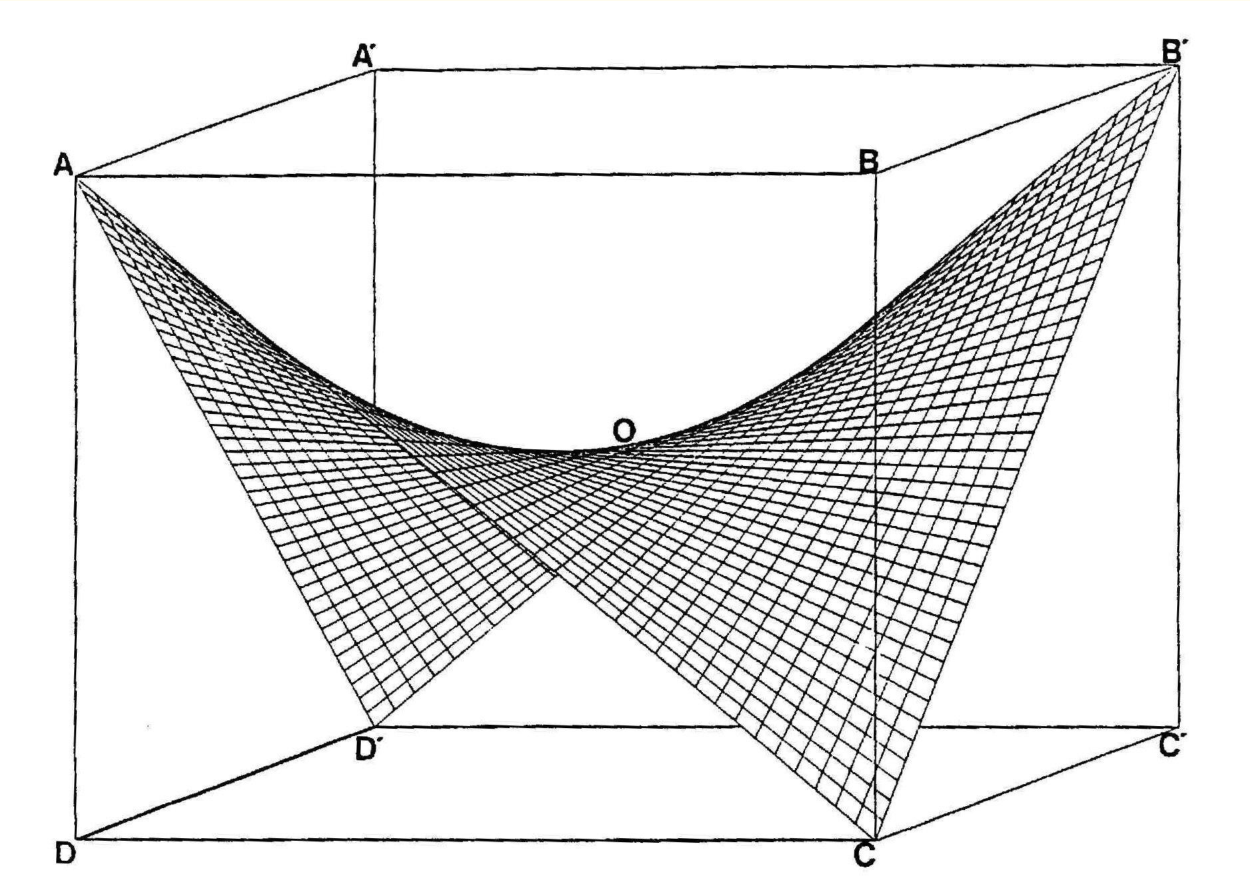
Logo



Questions which triggered the work behind the logo

- What is the subset of single determinantal functions in the space of all n -electron wave functions (Full CI space spanned by m orbitals)

$\Leftrightarrow$ Find necessary and sufficient conditions for a general electronic wave function, to be condensable into a single antisymmetrical product of orbitals

- More generally, what is the variational space explored by CASSCF methods of quantum chemistry in a fixed orbital basis set (HF is a particular case of CASSCF where the dimension of the active space is the number of electrons).

$\Leftrightarrow$ Find necessary and sufficient conditions for a general electronic wave function to be expressible with at most p linearly independant orbitals "active orbitals" ($n \leq p \leq m$).

Notation-1

- $\mathcal{H}$: Hilbert space of one-electron functions, spanned by a set of spin-orbitals $(\psi_i)_i$

- $\wedge^n \mathcal{H}$: Hilbert space of n-electron antisymmetric functions, spanned by the Slater determinantal functions $(\psi_{i_1} \wedge \psi_{i_2} \wedge \cdots \wedge \psi_{i_n})_{(i_1 < i_2 < \cdots < i_n)}$

- $\wedge \mathcal{H}$: Fermionic Fock space

$$\wedge \mathcal{H} := \bigoplus_{n \geq 0} \wedge^n \mathcal{H}$$

- $\wedge^{n_1} \mathcal{H} \otimes \cdots \otimes \wedge^{n_k} \mathcal{H}$: Hilbert space of partially antisymmetric functions for k distinguishable groups of electrons of respectively $n_1, \ldots, n_k$ electrons

Notation-2

- For any n-particle wave function, $\Phi := \sum_{I:=(i_1<\ldots<i_n)} c_I \, \psi_{i_1} \wedge \cdots \wedge \psi_{i_n}$,

- and any ordered sequence of length p, $K := (k_1 < \ldots < k_p) \in \mathcal{P}_{n,p}$, with $p \in \{0, \ldots, n\}$, $1 \leq k_j \leq n$,

- we set,

$$\cdots(\Phi)_K\cdots(\Phi)_{\bar{K}}\cdots := \rho_{K,\bar{K}} \sum_{I:=(i_1<\cdots<i_n)} c_I \, \cdots(\psi_{i_{k_1}} \wedge \cdots \wedge \psi_{i_{k_p}})\cdots(\psi_{i_{\bar{k}_1}} \wedge \cdots \wedge \psi_{i_{\bar{k}_{n-p}}})\cdots$$

- where $\bar{K} := (\bar{k}_1 < \ldots < \bar{k}_{n-p})$, complement of K in $(1 < 2 < \cdots < n)$, $\rho_{K,\bar{K}}$ is the sign of the permutation reordering the concatenated sequence $K//\bar{K}$ in increasing order; if the length, $|K|$, of K is 0 then, by convention, $(\Phi)_K := (\Phi)_\emptyset = 1$, and $\rho_{\emptyset,(1<\cdots<n)} = 1$; note that, $(\Phi)_{(1<\cdots<n)} = \Phi$.

Grassmann's exterior product:

$$\begin{aligned} \mathcal{X} : \wedge\mathcal{H} \otimes \wedge\mathcal{H} &\longmapsto \wedge\mathcal{H} \\ \Phi \otimes \Psi &\longrightarrow \mathcal{X}(\Phi \otimes \Psi) = \Phi \wedge \Psi \end{aligned}$$

The fermionic symmetry is built-in in this exterior algebra because of the following antisymmetry relation between exterior products of 1-particle functions:

$$\mathcal{X}(\phi \otimes \psi) = \phi \wedge \psi = -\psi \wedge \phi = -\mathcal{X}(\psi \otimes \phi)$$

which entirely determines the behavior of an n-fermion wave function under the symmetric group $\mathcal{S}_n$. That is to say, for an n-fermion single configuration:

$$\psi_1 \wedge \cdots \wedge \psi_n = (-1)^{|\sigma|} \psi_{\sigma(1)} \wedge \cdots \wedge \psi_{\sigma(n)}$$

Conjugate interior products:

$\forall\Theta \in \wedge^{n-p}\mathcal{H},\ \forall\Psi \in \wedge^{p}\mathcal{H},\ \forall\Phi \in \wedge^{n}\mathcal{H},$

- “left-interior product” $\langle\Theta|\Psi \hookleftarrow \Phi\rangle = \langle\Psi \wedge \Theta|\Phi\rangle$
- “right-interior product” $\langle\Theta|\Phi \hookrightarrow \Psi\rangle = \langle\Theta \wedge \Psi|\Phi\rangle$
- “anti-commutativity” $\Psi \hookleftarrow \Phi = (-1)^{p(n-p)}\ \Phi \hookrightarrow \Psi$
- explicit formula

$$\Psi \hookleftarrow \Phi = \sum_{K\in\mathcal{P}_{n,p}} \langle\Psi|\Phi_K\rangle \cdot \Phi_{\bar{K}}$$

- or for mono-configuration functions (Slater determinants)

$$(\psi_1\wedge\cdots\wedge\psi_p) \hookleftarrow (\phi_1\wedge\cdots\wedge\phi_n) = \sum_{K\in\mathcal{P}_{n,p}} \rho_{K,\bar{K}}\, det(\langle\psi_i|\phi_{k_j}\rangle)_{i,j\le p}\, \phi_{\bar{k}_1}\wedge\cdots\wedge\phi_{\bar{k}_{n-p}}$$

1-internal space of a wave function

Definition:

$$\mathcal{I}^1[\Psi] = \{\omega \in \mathcal{H}, \exists \Phi \in \wedge^{n-1}\mathcal{H}, \Phi \hookleftarrow \Psi = \omega\}$$

Example:

$$\begin{aligned}
\Psi_e \quad = \quad & \frac{1}{4}\{\phi_1^\alpha \wedge \phi_3^\alpha \wedge \phi_5^\alpha \wedge \phi_1^\beta \wedge \phi_3^\beta + \phi_1^\alpha \wedge \phi_3^\alpha \wedge \phi_6^\alpha \wedge \phi_1^\beta \wedge \phi_4^\beta + \\
& \phi_1^\alpha \wedge \phi_4^\alpha \wedge \phi_6^\alpha \wedge \phi_1^\beta \wedge \phi_3^\beta + \phi_1^\alpha \wedge \phi_4^\alpha \wedge \phi_5^\alpha \wedge \phi_1^\beta \wedge \phi_4^\beta + \\
& \phi_1^\alpha \wedge \phi_3^\alpha \wedge \phi_5^\alpha \wedge \phi_2^\beta \wedge \phi_3^\beta + \phi_1^\alpha \wedge \phi_3^\alpha \wedge \phi_6^\alpha \wedge \phi_2^\beta \wedge \phi_4^\beta + \\
& \phi_1^\alpha \wedge \phi_4^\alpha \wedge \phi_6^\alpha \wedge \phi_2^\beta \wedge \phi_3^\beta + \phi_1^\alpha \wedge \phi_4^\alpha \wedge \phi_5^\alpha \wedge \phi_2^\beta \wedge \phi_4^\beta + \\
& \phi_2^\alpha \wedge \phi_3^\alpha \wedge \phi_5^\alpha \wedge \phi_1^\beta \wedge \phi_3^\beta + \phi_2^\alpha \wedge \phi_3^\alpha \wedge \phi_6^\alpha \wedge \phi_1^\beta \wedge \phi_4^\beta + \\
& \phi_2^\alpha \wedge \phi_4^\alpha \wedge \phi_6^\alpha \wedge \phi_1^\beta \wedge \phi_3^\beta + \phi_2^\alpha \wedge \phi_4^\alpha \wedge \phi_5^\alpha \wedge \phi_1^\beta \wedge \phi_4^\beta + \\
& \phi_2^\alpha \wedge \phi_3^\alpha \wedge \phi_5^\alpha \wedge \phi_2^\beta \wedge \phi_3^\beta + \phi_2^\alpha \wedge \phi_3^\alpha \wedge \phi_6^\alpha \wedge \phi_2^\beta \wedge \phi_4^\beta + \\
& \phi_2^\alpha \wedge \phi_4^\alpha \wedge \phi_6^\alpha \wedge \phi_2^\beta \wedge \phi_3^\beta + \phi_2^\alpha \wedge \phi_4^\alpha \wedge \phi_5^\alpha \wedge \phi_2^\beta \wedge \phi_4^\beta\}
\end{aligned}$$

$$\mathcal{I}^1[\Psi_e] = \mathbb{C}(\psi_1^\alpha := \frac{1}{\sqrt{2}}(\phi_1^\alpha + \phi_2^\alpha), \psi_1^\beta := \frac{1}{\sqrt{2}}(\phi_1^\beta + \phi_2^\beta), \phi_3^\alpha, \phi_3^\beta, \phi_4^\alpha, \phi_4^\beta, \phi_5^\alpha, \phi_6^\alpha)$$

Applications

Application 1: compact expressions

- Smallest one-electron Hilbert-subspace allowing one to express Ψ:

$$\forall V \subseteq \mathcal{H}, \Psi \in \wedge^n V, \mathcal{I}^1[\Psi] \subseteq V$$

$$\Psi_e = \frac{1}{2}\psi_1^\alpha \wedge \psi_1^\beta \wedge (\phi_3^\alpha \wedge \phi_5^\alpha \wedge \phi_3^\beta + \phi_3^\alpha \wedge \phi_6^\alpha \wedge \phi_4^\beta + \phi_4^\alpha \wedge \phi_6^\alpha \wedge \phi_3^\beta + \phi_4^\alpha \wedge \phi_5^\alpha \wedge \phi_4^\beta).$$

Application 2: Characterization of variational spaces

- A UCASSCF calculation with p active spinorbitals (and no inactive occupied) consists in finding the stationary points of the energy functionnal $E(\Psi) = \frac{\langle\Psi|H\Psi\rangle}{\langle\Psi|\Psi\rangle}$ with the constraint that $dim\mathcal{I}^1[\Psi] \leq p$ i.e. within

$$\{ \quad \Psi \in \wedge^n \mathcal{H} \quad | \quad \forall \Phi_0, \ldots, \Phi_{p-n} \in \wedge^{n-1}\mathcal{H}, \quad (\Phi_0 \hookleftarrow \Psi) \wedge \cdots \wedge (\Phi_{p-n} \hookleftarrow \Psi) \wedge \Psi = 0 \quad \}.$$

The Complete Active Space Self-Consistent Field Method (CASSCF)

Example: Finite basis set of m spin-orbitals

$\forall H_0, \ldots, H_{p-n} \in \mathcal{P}_{m,n-1}, \ \forall G \in \mathcal{P}_{m,p+1}$

$$\sum_{\substack{(k_0<\cdots<k_{p-n})\subseteq G, \\ \{k_i\}\not\subseteq H_i}} \rho_{(k_0),H_0} \cdots \rho_{(k_{p-n}),H_{p-n}} \ \rho_{(k_0<\cdots<k_{p-n}),G\backslash(k_0<\cdots<k_{p-n})} \quad c_{(k_0)\cup H_0} \cdots c_{(k_{p-n})\cup H_{p-n}} \ c_{G\backslash(k_0<\cdots<k_{p-n})} = 0$$

- The case $p = n$ with no spin constraint is the UHF method first developed by Prof. Berthier (and not Pople as found in textbooks).

Variational spaces of traditional methods

$$\Phi = \quad \phi_1^\alpha \Lambda \phi_1^\beta + \beta \phi_1^\alpha \Lambda \phi_2^\beta + \gamma \phi_2^\alpha \Lambda \phi_1^\beta + \delta \phi_2^\alpha \Lambda \phi_2^\beta$$

The three, real, parameters β, γ, δ are considered as independent and varying on $]-\infty, +\infty[$ and an axis is associated with each parameter. In the 3-dimensional space obtained, UHF wave functions satisfy :

$$\beta\gamma = \delta ,$$

which is clearly the equation of a set of hyperbolae. Singlet wave functions satisfy : $\beta = \gamma$.

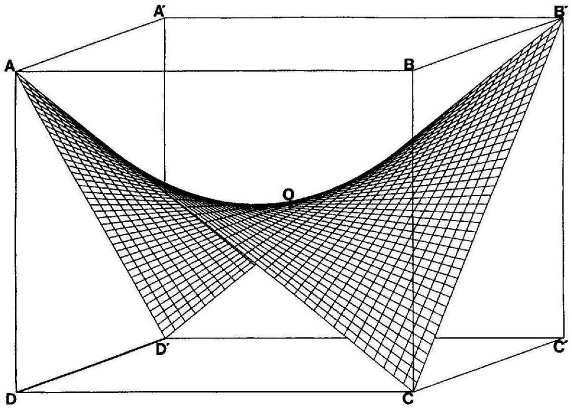


Fig. 1. 2 electrons, 2 orbitals, $S_z = 0$. Each point in the cube corresponds to a multi-configuration, the centre of the cube O being the configuration $\phi_1^\alpha \Lambda \phi_1^\beta$. The volume of the cube is the full unrestricted CI space, the hyperbolic surface $(AOB'CD')$ is the UHF space. The plane $(ADB'C')$ corresponds to the eigenfunctions of $\mathbf{S}^2$ with $S = 0$ (singlet plane). The intersection between the UHF surface and the singlet plane gives the RHF curve (AOB').

p-internal space of a wave function

Definition:

$$\mathcal{I}^p[\Psi] = \{\omega \in \wedge^p \mathcal{H}, \exists \Phi \in \wedge^{n-p}\mathcal{H}, \Phi \hookleftarrow \Psi = \omega\}$$

Example: $\Psi = \psi_1 \wedge \psi_2 \wedge \psi_3 \wedge \psi_4 + \psi_1 \wedge \psi_2 \wedge \psi_5 \wedge \psi_6$

$$\downarrow$$

$$dim \mathcal{I}^1[\Psi] = 6 \quad \Rightarrow \quad dim \wedge^2 \mathcal{I}^1[\Psi] = 15$$

$$BUT \left\{ \begin{array}{lll} \psi_3 \wedge \psi_5, \psi_3 \wedge \psi_6, \psi_4 \wedge \psi_5, \psi_4 \wedge \psi_6 & \Rightarrow & 0 \\ \psi_3 \wedge \psi_4, \psi_5 \wedge \psi_6 \quad \Rightarrow & \text{linear} & \text{dependencies} \end{array} \right\}$$

$$\downarrow$$

$$dim \mathcal{I}^2[\Psi] = 10$$

p-internal matrices and reduced density matrices

Internal operator $\hat{I}_\Psi : \bullet \hookleftarrow \Psi$

p-Internal matrix I^p_Ψ :

$$\Psi \in \wedge^n \mathcal{H}, \quad \Phi_K, \in \wedge^{n-p} \mathcal{H}, \quad \Phi_J, \in \wedge^p \mathcal{H}, \quad (I^p_\Psi)_{K,J} = \langle \Phi_K | \Phi_J \hookleftarrow \Psi \rangle$$

Recall that $\Phi_K \wedge \Phi_J = \rho_{K,J} \Phi_{K \cup J}$ so for $\Psi := \sum\limits_{I:=(i_1<\ldots<i_n)} c_I \, \Phi_I$,

$$(I^p_\Psi)_{K,J} = \rho_{J,K} c_{K \cup J}$$

Density operator $\hat{D}_\Psi : \Psi \hookrightarrow \bullet \hookleftarrow \Psi$

p-Reduced density matrix $D^p_\Psi : (D^p_\Psi)_{K,J} = \langle \Phi_K \hookleftarrow \Psi | \Phi_J \hookleftarrow \Psi \rangle$

$$(D^p_\Psi)_{K,J} = \left(I^{p^\dagger}_\Psi I^p_\Psi \right)_{K,J} = \sum_{H \in \mathcal{P}_{n-p}} \rho_{K,H} \rho_{J,H} \, c^*_{H \cup K} c_{H \cup J}$$

Strong orthogonality

Let Ψ_1 be the wave functions of an n_1 electron group and Ψ_2 that of an n_2 electron group. Ψ_1 and Ψ_2 are said strongly orthogonal if and only if: $\forall \tau_2, \ldots, \tau_{n_1}, \tau_2', \ldots, \tau_{n_2}'$

$$\int d\tau_1 \Psi_1(\tau_1, \tau_2, \ldots, \tau_{n_1}) \Psi_2(\tau_1, \tau_2', \ldots, \tau_{n_2}') = \langle \delta_{\tau_2} \wedge \ldots \wedge \delta_{\tau_{n_1}} \hookleftarrow \Psi_1 | \delta_{\tau_2'} \wedge \ldots \wedge \delta_{\tau_{n_2}'} \hookleftarrow \Psi_2 \rangle = 0.$$

Or by changing to a basis set representation $\{\phi_i\}_i$,

$$\langle \phi_{i_2} \wedge \ldots \wedge \phi_{i_{n_1}} \hookleftarrow \Psi_1 | \phi_{i_2'} \wedge \ldots \wedge \phi_{i_{n_2}'} \hookleftarrow \Psi_2 \rangle = 0 \qquad \forall i_2, \ldots, i_{n_1}, i_2', \ldots, i_{n_2}'.$$

Since, the $(n_1 - 1)$-particle functions, $\phi_{i_2} \wedge \ldots \wedge \phi_{i_{n_1}}$, span all of $\wedge^{(n_1-1)}\mathcal{H}$, and the $(n_2 - 1)$-particle functions, $\phi_{i_2'} \wedge \ldots \wedge \phi_{i_{n_2}'}$, span all of $\wedge^{(n_2-1)}\mathcal{H}$, the latter equation is equivalent to orthogonality between any pair of 1-internal functions, that is to say:

$$\mathcal{I}^1[\Psi_1] \perp \mathcal{I}^1[\Psi_2]$$

p-orthogonality

Definition:

Let Ψ_1 be the wave functions of an n_1 electron group and Ψ_2 that of an n_2 electron group. Ψ_1 and Ψ_2 are said p-orthogonal if and only if:

$$\mathcal{I}^p[\Psi_1] \perp \mathcal{I}^p[\Psi_2]$$

Proposition (graded orthogonality):

If two states represented by the wave functions Ψ_1 and Ψ_2 are p-orthogonal then they are *a fortiori* q-orthogonal for all q such that, $inf(n_1, n_2) \geq q \geq p$.

This justifies the term "strong orthogonality" used for one-orthogonality

p-orthogonality: Examples

Let $(\phi_i)_i$ be orthonormal spinorbitals.

Example 1: For integers, $n \geq p > 0$, the pairs,

$$\Psi_1 := \phi_1 \wedge \cdots \wedge \phi_{n-p} \wedge \phi_{n-p+1} \cdots \wedge \phi_n$$

and

$$\Psi_2 := \phi_1 \wedge \cdots \wedge \phi_{n-p} \wedge \phi_{n+1} \ldots \wedge \phi_{n+p},$$

are $(n-p+1)$-orthogonal but not $(n-p)$-orthogonal since for $\Phi_1 := \phi_{n-p+1} \wedge \ldots \wedge \phi_n$ and $\Phi_2 := \phi_{n+1} \wedge \ldots \wedge \phi_{n+p}$, $\langle \Phi_1 \hookleftarrow \Psi_1 | \Phi_2 \hookleftarrow \Psi_2 \rangle = \langle \phi_1 \wedge \ldots \wedge \phi_{n-p} | \phi_1 \wedge \ldots \wedge \phi_{n-p} \rangle = 1$ is non zero, although $(\Phi_i \hookleftarrow \Psi_i) \in \mathcal{I}^{n-p}[\Psi_i]$, for $i \in \{1, 2\}$, by definition.

Example 2:

$\Psi_1 := \phi_1 \wedge \phi_2 \wedge \phi_3 + \phi_4 \wedge \phi_5 \wedge \phi_6$ and $\Psi_2 := \phi_1 \wedge \phi_7 + \phi_2 \wedge \phi_8$ are 2-orthogonal (it is impossible to obtain Ψ_2 by annihilating a spinorbital in Ψ_1) but not 1-orthogonal since both ϕ_1 and ϕ_2 belongs to their one-internal space.

The Electronic Mean Field Configuration Interaction method

It consists in constructing successive, approximate, n-electron wave functions of the form:

$$\Psi = \Psi_1 \wedge \cdots \wedge \Psi_r \ ,$$

where $\Psi_i \in \wedge^{n_i}\mathcal{H}$, with $\sum_i n_i = n$, by means of a configuration interaction calculation in a basis set of group functions $\{\Psi_1^i \wedge \Psi_2^0 \wedge \cdots \wedge \Psi_r^0\}_i$ i.e., the wave functions of the first group functions are optimized in the mean field of the ground states of the other groups.

- The process can be iterated by switching to another group until self-consistence is achieved.

- Or/then a coarser partition of the n electron can be selected.

Geminal-SCF and p-orthogonality

Ground state energies in Hartree at "experimental" geometry (STO-3G calculations)

System	LiH	Be	Li_2	BeH_2	BH	Be_2
E^0_{FullCI}	-7.882392	-14.403655	-14.667340	-15.594861	-24.809945	-28.804345
$E^0_{geminal-SCF}$	-7.882372	-14.403655	-14.667114	-15.594715	-24.809938	-28.803212
with 2-orthogonality	-7.882368	-14.403654	-14.667090	-15.594703	-24.809920	-28.803080
with 1-orthogonality	-7.882203	-14.403630	-14.666584	-15.588630	-24.807908	-28.781789
E^0_{RHF}	-7.862002	-14.351880	-14.638725	-15.559405	-24.752780	-28.698990

Electric dipole moments

System	LiH	BH
D^z_{FullCI}	-4.6201	0.6138
D^z_{GSCF}	-4.6197	0.6138
with 2-orthogonality	-4.6189	0.6142
with 1-orthogonality	-4.6269	0.6861
D^z_{RHF}	-4.8578	0.9569

Conclusions: p-orthogonality

- Graded measure of indistinguishability in the sense that two sets of identical particles that are q-orthogonal can be seen as "more indistinguishable" than two sets that are p-orthogonal if $q > p$, because a larger subset of particles can possibly share (i.e. occupy) a substate, common (i.e. internal) to the quantum states of both sets.

- The graded structure of p-orthogonality constraints naturally leads one to consider a corresponding hierarchy of approximations for methods based on general antisymmetric product functions.

- The 2-orthogonality constraint is very weak for geminal product wave functions.

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