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Orthogonalization of Fermion k-Body Operators and Representabilty

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Outline

- **The Representabilty Problem in Quantum Chemistry**
- **Orthogonalization of k-body Operators**

Section 1

The Representabilty Problem in Quantum Chemistry

Quantum Systems in Quantum Chemistry

- **Quantum chemistry**: *molecules* are usually modelled as finite-dimensional, non-relativistic, many-fermion quantum systems:
  - **Hilbert space**: Fermion Fock space $\mathcal{F} = \bigoplus_{k \geqslant 0} \bigwedge^k \mathfrak{h}$ with
    - *finite dimensional* 1-particle space $\mathfrak{h}$
    - creation- and annihilation operators $c^*, c : \mathfrak{h} \to \mathcal{B}(\mathcal{F})$
  - **Hamiltonian**: a *2-body observable*

$$\mathbb{H} = \mathbb{H}^* = \underbrace{\sum_{i,j} t_{ij} c_i^* c_j}_{\text{free part}} + \underbrace{\sum_{i,j,k,l} V_{ij;kl} c_i^* c_j^* c_l c_k}_{\text{interaction part}} \tag{1}$$

  - (normal) **States** $\varphi \in \mathcal{S}_0$ are represented by density matrices on $\mathcal{F}$, i.e. $\rho \in \mathcal{P} \doteq \mathcal{L}^1_+(\mathcal{F})$ of unit trace $\operatorname{tr} \rho = 1$.

Model Problem

Typical Problem: Compute the ground state energy

$$E_{gs} = \inf_{\varphi \in \mathcal{S}} \varphi(\mathbb{H}) = \inf_{\substack{\rho \in \mathcal{P} \\ \mathrm{tr}\{\rho\}=1}} \mathrm{tr}\{\rho \mathbb{H}\} \tag{2}$$

- **Observe**: density matrix ρ contains “too much” information – we only need the expectation values of 2-body observables A!
- **Idea**: Replace ρ by its *reduced 2-particle density matrix* (2-RDM)

Terminology I

Definition 1 (k-body operators)

A k**-body operator** is an element of

$$\mathcal{O}_k^{\mathbb{C}}(\mathcal{F}) \doteq \operatorname{span}_{\mathbb{C}}\{c^{\#}(f_1)\cdots c^{\#}(f_{2l}) \mid f_1, \ldots, f_s \in \mathfrak{h}, 0 \leqslant 2l \leqslant 2k\},$$

$\pi_k^{\mathbb{C}} : \mathcal{L}^2(\mathcal{F}) \to \mathcal{L}^2(\mathcal{F})$ denotes the *orthogonal projection* onto $\mathcal{O}_k^{\mathbb{C}}(\mathcal{F})$.

Note: Orthogonality is understood in the Hilbert-Schmidt geometry:

$$\langle a, b\rangle_{\mathcal{L}^2(\mathcal{F})} \doteq \operatorname{tr}\{a^* b\}$$

Terminology II

Definition 2 (k-body observables, k-RDMs)

Elements of $\mathcal{O}_k^{\mathbb{R}}(\mathcal{F}) \doteq \{A \in \mathcal{O}_k^{\mathbb{C}}(\mathcal{F}) \mid A^* = A\}$ are called **k-body observables**. The ($\mathbb{R}$-linear) orthogonal projection onto $\mathcal{O}_k^{\mathbb{R}}(\mathcal{F})$ is denoted by

$$\pi_k^{\mathbb{R}} : \mathcal{L}^2(\mathcal{F}) \to \mathcal{L}^2(\mathcal{F}).$$

For a density matrix ρ on $\mathcal{F}$, the image $\pi_k^{\mathbb{R}}(\rho)$ is called the **reduced k-particle density matrix** (k-RDM) of ρ.

Example 3

Let $\mathbb{H} \in \mathcal{O}_k^{\mathbb{R}}(\mathcal{F})$, then $\pi_k^{\mathbb{C}}(\mathbb{H}) = \pi_k^{\mathbb{R}}(\mathbb{H}) = \mathbb{H}$ and for any denity matrix ρ we have

$$\mathrm{tr}\{\rho\mathbb{H}\} = \langle \rho, \mathbb{H} \rangle_{\mathcal{L}^2(\mathcal{F})} = \langle \rho, \pi_k^{\mathbb{R}}(\mathbb{H}) \rangle_{\mathcal{L}^2(\mathcal{F})} = \langle \pi_k^{\mathbb{R}}(\rho), \mathbb{H} \rangle_{\mathcal{L}^2(\mathcal{F})} \tag{3}$$

Lesson:

- $\pi_k^{\mathbb{R}}(\rho)$ encodes precisely the expectation values of k-body observables in the state ρ.

Model Problem Revisited

Example 4

if ρ is a density matrix and $\mathbb{H} \in \mathcal{O}_2^{\mathbb{R}}(\mathcal{F})$, then

$$E_{gs} = \inf_{\substack{\rho \in \mathcal{L}_+^1(\mathcal{F}) \\ \mathrm{tr}\{\rho\}=1}} \mathrm{tr}\{\rho \mathbb{H}\} = \inf_{\substack{r \in \pi_2^{\mathbb{R}}(\mathcal{P}) \\ \mathrm{tr}\{r\}=1}} \langle r, \mathbb{H} \rangle_{\mathcal{L}^2(\mathcal{F})} \tag{4}$$

Conclusion:

- By replacing ρ with $\pi_k^{\mathbb{R}}(\rho)$, the dimension of the linear program (4) is reduced dramatically ($O(2^{2n})$ vs. $O(n^4)$)
- However, a *computationally efficient* characterization of $\pi_2^{\mathbb{R}}(\mathcal{P})$ is still unknown (**Representabilty Problem**)

Conclusion

A fundamental role for the representabilty problem plays the orthogonal projection

$$\pi_k^{\mathbb{R}} : \mathcal{L}^2(\mathcal{F}) \to \mathcal{L}^2(\mathcal{F}).$$

Section 2

Orthogonalization of k-body Operators

Goal & Naive Approach

Goal

Diagonalize $\pi_2^{\mathbb{R}}$, i.e. find an $\mathcal{L}^2$-orthonormal basis of $\mathcal{O}_2^{\mathbb{R}}(\mathcal{F})$

- **Naive approach**: Gram-Schmidt orthogonalization, i.e.
  1. Fix a *starting basis* $\mathfrak{B}_0 = \{b_1, \ldots, b_N\}$ of $\mathcal{O}_2^{\mathbb{R}}(\mathcal{F})$
  2. Iteratively compute

$$\tilde{b}_i \doteq b_i - \sum_{j=1}^{i-1} \frac{\langle b_i, \tilde{b}_j \rangle_{\mathcal{L}^2(\mathcal{F})}}{\langle \tilde{b}_j, \tilde{b}_j \rangle_{\mathcal{L}^2(\mathcal{F})}} \tilde{b}_j \tag{5}$$

  3. **Result**: $\mathfrak{B} \doteq \{\tilde{b}_1, \ldots, \tilde{b}_N\}$ is an orthogonal basis of $\mathcal{O}_2^{\mathbb{R}}(\mathcal{F})$

Drawbacks of Naive Approach

- **systematic**: obtained orthogonal basis $\mathfrak{B}$ depends on
  - the chosen starting basis $\mathfrak{B}_0$
  - the dimension n of the 1-particle Hilbert space $\mathfrak{h}$
- **computational**: dimensions of $\mathcal{F}$ and $\mathcal{O}_2^{\mathbb{R}}(\mathcal{F})$ grow very fast with n

Actual Approach

- **Step 1**: Fix $\mathbb{C}$-basis $\mathfrak{B}_0$ of (various subspaces of) $\mathcal{O}_k^{\mathbb{C}}(\mathcal{F})$
- **Step 2**: Orthogonalization:
  a) Determine Gram matrix with respect to $\mathfrak{B}_0$.
  b) Apply Gram-Schmidt orthogonalization in small dimensions n using computer algebra system
- **Step 3**: Review results
- **Step 4**: Guess general conjecture (and prove it!)

Summary of Results

Theorem 5 (Main Result)

To every ONB of $\mathfrak{h}$, there is an associated ONB $\mathfrak{B}$ of $\mathcal{L}^2(\mathfrak{F})$ such that

1. *$\mathfrak{B}$ restricts to an ONB $\mathfrak{B}_k^{\mathbb{C}}$ of $\mathcal{O}_k^{\mathbb{C}}(\mathfrak{F})$ for all $k \in \mathbb{N}_0$, i.e. $\mathfrak{B}$ is adapted to the linear flag*

$$0 \subsetneq \mathcal{O}_0^{\mathbb{C}}(\mathfrak{F}) \subsetneq \cdots \subsetneq \mathcal{O}_n^{\mathbb{C}}(\mathfrak{F}) \subsetneq \mathcal{L}^2(\mathfrak{F}). \tag{6}$$

2. *By taking the non-zero real- and imaginary parts of $\mathfrak{B}_k^{\mathbb{C}}$, we obtain an orthogonal basis $\mathfrak{B}_k^{\mathbb{R}}$ of $\mathcal{O}_k^{\mathbb{R}}(\mathfrak{F})$.*

That means: We have diagonalized $\pi_k^{\mathbb{K}}$ *simultaneously for all $k \in \mathbb{N}_0$*!

Step 1: Choice of Starting Basis $\mathfrak{B}_0$

Definition 6

Let $\varphi_1, \ldots, \varphi_n$ be an ONB of $\mathfrak{h}$ (an "orbital basis") and $\mathbb{N}_n \doteq \{1, \ldots, n\}$. To $I = \{i_1 < \cdots < i_l\} \subseteq \mathbb{N}_n$ define $\varphi_I \doteq \varphi_{i_1} \wedge \cdots \wedge \varphi_{i_l}$ and

$$c_I^* \doteq c_{i_1}^* \cdots c_{i_l}^* \qquad c_I \doteq (c_I^*)^* = c_{i_l} \cdots c_{i_1} \qquad n_I \doteq c_I^* c_I \tag{7}$$

- **Observe**: $\{c_I^* c_J \mid I, J \subseteq \mathbb{N}_n\}$ is a basis of $\mathcal{L}^2(\mathcal{F})$. However, it turns out that it's more convenient to choose

$$\mathfrak{B}_0 \doteq \{n_K c_I^* c_J \mid I, K, J \subseteq \mathbb{N}_n \text{ pairwise disjoint}\} \tag{8}$$

Step 2a: Compute the Gram Matrix Elements

Theorem 7 (Trace Formula)

Let $K, A, B \subseteq \mathbb{N}_n$ and $L, C, D \subseteq \mathbb{N}_n$ be mutually disjoint, respectively. Then

$$\langle n_K c_A^* c_B, n_L c_C^* c_D \rangle_{\mathcal{L}^2(\mathcal{F})} = \delta_{AC} \delta_{BD} 2^{n - |A \cup B \cup K \cup L|} \tag{9}$$

Proof.

1. For $I \subseteq \mathbb{N}_n$, the contributions $\langle \varphi_I, (n_K c_A^* c_B)^* n_L c_C^* c_D \varphi_I \rangle_{\mathcal{F}}$ can be computed elementary
2. Non-zero contributions are all equal to 1 and occur if and only if

$$A = C, B = D \text{ and } B \cup K \cup L \subseteq I \subseteq \mathbb{N}_n \setminus A$$

$\square$

Step 2b: Applying the Gram Schmidt Algorithm

Using a CAS (SymPy), we applied Gram-Schmidt algorithm in the following context:

- dimension $n = \dim \mathfrak{h} \leqslant 6$
- vector space = free $\mathbb{C}$-module over $\mathfrak{B}_0$
- inner product = *defined* by the trace formula (9)

Step 3: Review Results

Observation

The following elements are mutually orthogonal:

$$b_K \doteq \sum_{I \subseteq K} (-2)^{|I|} n_I, \quad K \subseteq \mathbb{N}_n \tag{10}$$

Step 4: General Theorem

Theorem 8

An orthogonal basis of $\mathcal{L}^2(\mathfrak{F})$ is given by

$$\mathfrak{B} \doteq \{ b_K c_I^* c_J | \, K, I, J \subseteq \mathbb{N}_n \text{ mutually disjoint} \} \tag{11}$$

Proof.

- Orthogonality of $\mathfrak{B}$ follows from the "magic formula"

$$\sum_{I \subseteq K} \sum_{J \subseteq L} (-2)^{|I|+|J|} 2^{-|I \cup J|} = \delta_{KL} \quad \forall K, L \text{ finite sets,} \tag{12}$$

  which is proved using the binomial formula $\sum_{Y \subseteq X} a^{|Y|} = (1+a)^{|X|}$.
- Rest follows for dimensional reasons: $|\mathfrak{B}| = 4^n = \dim_{\mathbb{C}} \mathcal{L}^2(\mathfrak{F})$.

$\square$

Orthogonalization of $\mathcal{O}_k^{\mathbb{C}}(\mathcal{F})$

Corollary 9

The basis $\mathfrak{B}$ restricts to the orthogonal basis $\mathfrak{B}_k^{\mathbb{C}}$ of $\mathcal{O}_k^{\mathbb{C}}(\mathcal{F})$, which is explicitly given by

$$\begin{aligned} \mathfrak{B}_k^{\mathbb{C}} &\doteq \mathfrak{B} \cap \mathcal{O}_k^{\mathbb{C}}(\mathcal{F}) \\ &= \left\{ b_K c_I^* c_J \;\middle|\; \begin{array}{c} K, I, J \subset \mathbb{N}_n \text{ pairwise disjoint,} \\ |I| + |J| + 2|K| = 2l \text{ with } 0 \leqslant l \leqslant k \end{array} \right\}. \end{aligned} \tag{13}$$

Proof.

- Orthogonality of $\mathcal{O}_k^{\mathbb{C}}(\mathcal{F})$ follows trivially,
- Rest follows from a dimensionality argument.

$\square$

Orthogonalization of $\mathcal{O}_k^{\mathbb{R}}(\mathcal{F})$

Corollary 10

An orthogonal basis $\mathfrak{B}_k^{\mathbb{R}}$ of $\mathcal{O}_k^{\mathbb{R}}(\mathcal{F})$ is given by the non-vanishing real- and imaginary parts of the elements of $\mathfrak{B}_k^{\mathbb{C}}$.

Thank you!