# *Generalized Geminal Functional Theory*

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# Outline

- Background
- Anti-Symmetrized Geminal Products
- *Aufbau-Ansatz* for Generalized Anti-Symmetrized Geminal Products
- Four-Electron Applications
- Conclusions and Outlook

# Introduction

Time-independent Schrödinger Equation:

$$\mathbf{H}\Psi = E\Psi$$

The Hamiltonian operator:

$$\mathbf{H} : \mathcal{L}_2(X^N) \rightarrow \mathcal{L}_2(X^N)$$

$$\mathbf{H} = \sum \frac{1}{2m_i}\mathbf{p}_i^2 + \sum_{i>j} \frac{q_i q_j}{r_{ij}}$$

Momentum operator:

$$\mathbf{p}_i = -\mathcal{I} \cdot \hbar \cdot \begin{pmatrix} \frac{\partial}{\partial x_i} \\ \frac{\partial}{\partial y_i} \\ \frac{\partial}{\partial z_i} \end{pmatrix}$$

## Simplifying the Hamiltonian

$$
\begin{aligned}
E &= \int \psi(1,\ldots,n)\mathbf{H}\psi(1,\ldots,n)d1\cdots dn \\
&= \sum_i \int \psi(1,\ldots,n)\mathbf{h}_i\psi(1,\ldots,n)d1\cdots dn + \\
&\quad \sum_{i,j} \int \psi(1,\ldots,n)\frac{1}{r_{ij}}\psi(1,\ldots,n)d1\cdots dn \\
&= n\int \psi(1,\ldots,n)\mathbf{h}_1\psi(1,\ldots,n)d1\cdots dn + \\
&\quad \frac{n(n-1)}{2}\int \psi(1,\ldots,n)\frac{1}{r_{12}}\cdot\psi(1,\ldots,n)d1\cdots dn
\end{aligned}
$$

# Simplifying the Hamiltonian

$$D^{(m)} = \int \psi(1', \ldots, m', m+1, \ldots n) \cdot$$
$$\psi(1, \ldots, m, m+1, \ldots n)^* \cdot d(m+1) \cdots dn$$

$$\mathbf{K} = \frac{n}{2}(\mathbf{h}_1 + \mathbf{h}_2) + \frac{n(n-1)}{2}\frac{1}{r_{12}}$$
$$E = \mathrm{tr}\left(\mathbf{D}^{(2)}\mathbf{K}\right)$$

# Anti-Symmetrized Geminal Products

$$\psi_{AGP} = g^N = \mathbf{A}_N \prod_{i=1}^{N/2} g(2i-1, 2i)$$

$$\rho_2(\psi_{AGP}; 12, 1'2') = \sum b(ijkl) \cdot |\alpha_i(1)\alpha_j(2)| \cdot |\alpha_k(1')\alpha_l(2')|^*$$

where $\alpha_i$ are the natural spin-orbitals of $g$ and

- $\exists n : \{i,j\} = \{k,l\} = \{2n-1, 2n\} =: \sigma \Rightarrow b(\sigma\sigma) = 2c\lambda_\sigma a_{m-1}(\bar{\sigma})$
- $\sigma \neq \tau \Rightarrow b(\sigma\tau) = 2c\xi_\sigma \xi_\tau^* a_{m-1}(\bar{\sigma}\bar{\tau})$
- $\sigma \neq \tau, i \in \sigma, j \in \tau \Rightarrow b(ijij) = 2c\lambda_\sigma \lambda_\tau a_{m-2}(\bar{\sigma}\bar{\tau})$
- $\prod(1 + \lambda_\sigma t) = \sum a_m t^m; a_{m-1}(\bar{\sigma}) = \frac{\partial a_m}{\partial \lambda_\sigma}; a_{m-2}(\bar{\sigma}\bar{\tau}) = \frac{\partial^2 a_m}{\partial \lambda_\sigma \partial \lambda_\tau},$
  $c = 1/a_m$

# Anti-Symmetrized Geminal Products

Block diagonal form of $\rho_2$:

$$\rho_2(\psi_{AGP}) = \begin{pmatrix} \begin{array}{c|} b(\sigma\tau) \\ \hline \end{array} & & \\ & b(1313) & \\ & & \ddots \end{pmatrix} \equiv n\,|g\rangle\,\langle g| + \text{diag}$$

The 1-RDM of $\psi_{AGP}$:

$$(n-1)\hat{\rho}^{(1)} = \sum_{\substack{\sigma \\ i\in\sigma}} |i\rangle\,\langle i|\, c\lambda_\sigma a_{m-1}(\bar{\sigma}) + \sum_{\sigma>\tau} \sum_{\substack{i\in\sigma \\ j\in\tau}} (|i\rangle\,\langle i| + |j\rangle\,\langle j|)\, c\lambda_\sigma\lambda_\tau a_{m-2}(\bar{\sigma}\bar{\tau})$$

$$= \sum_{\substack{\sigma \\ i\in\sigma}} |i\rangle\,\langle i|\, c\lambda_\sigma (2m-1) a_{m-1}(\bar{\sigma})$$

## *Aufbau-Ansatz* for AGP

$$\Psi_{Aufbau} = \mathbf{A_n} \prod_{i=1}^{n/2} g_i(2i-1, 2i)$$

An iterative scheme may be derived:

$$\mathbf{A_{p+2}} g_i \psi_p = \frac{1}{(p+1)(p+2)} \left( 2 - 2 \sum_{i=3}^{p+2} [\mathbf{P_{1i}} + \mathbf{P_{2i}}] + \sum_{i \neq j > 2} \mathbf{P_{1i}} \mathbf{P_{2j}} \right) g_i \psi_p .$$

Six contributions to the 2-RDM follow:

$$D_{p+2}^{(2)} = F_1 + (F_2 + F_2^*) + (F_3 + F_3^*) + F_4 + (F_5 + F_5^*) + F_6$$

## *Aufbau-Ansatz* for AGP

$$F_1 = \mathbf{g}(\mathbf{12})\mathbf{g}(\mathbf{1'2'})\|\psi_{\mathbf{p}}\|^{\mathbf{2}}$$

$$F_6 = \binom{\mathbf{p}}{\mathbf{2}}\mathbf{D}_{\mathbf{p}}^{(\mathbf{2})}(\mathbf{12};\mathbf{1'2'})\|\mathbf{g}\|^{\mathbf{2}} +$$

$$2(p-2)\binom{p}{2}\int D_g^{(1)}(4;5)D_p^{(3)}(125;1'2'4)d3d4d5 +$$

$$\binom{p-2}{2}\binom{p}{2}\int g(34)g^*(56)D_p^{(4)}(1256;1'2'34)d3d4d5d6$$

## *Aufbau-Ansatz* for AGP

1. Release of $\xi_i$ only, i.e.,

$$g_j = \sum \xi_i^{(j)} \left|\alpha_{2i-1}\alpha_{2i}\right|$$

2. Releasing the ordering of the natural orbitals.

$$g_i = \sum \xi_j^{(i)} \left|\beta_{2j-1}^{(i)}\beta_{2j}^{(i)}\right|$$

$$\left\{\beta_j^{(i)}\right\}_j = \left\{\beta_l^{(k)}\right\}_l \forall i, k$$

3. Increasing the number of used geminals to $l$ geminals.

$$\Psi = \mathbf{A_n} \prod_{i=1}^{l} \Psi_{AGP}^{(m_i)}[g_i]\left(M_i + 1 \ldots M_{i+1}\right)$$

$$\sum_{1 \leq j < i} m_j = M_i, \sum_{i=1}^{l} m_i = n$$

# *Aufbau-Ansatz* for AGP

4. Enforce that no cross-contributions exist, i.e.,

$$\int g_i(1,2)g_j(2,3)g_k(3,4)d2d3 = 0 \Leftarrow i \neq j \text{ and } j \neq k$$

# Four Electron Applications

$E$ and $O$ are bilinear functionals:

$$E : A^2(V) \times A^2(V) \to \mathbb{R}$$

$$(x, y) \mapsto \left\langle x \wedge g \left| \hat{H} \right| y \wedge g \right\rangle = \left\langle x \left| \hat{H}'_g \right| y \right\rangle$$

$$\left\langle x \left| \hat{O}_g \right| y \right\rangle = \langle x \wedge g | y \wedge g \rangle$$

In previous formalism:

$$g^* \mapsto x, g \mapsto y$$

# Four Electron Applications

Optimization algorithm:

1. Start the calculation from the HF guess via $g_1 = |\phi_1 \phi_2|$ and $g_2 = |\phi_3 \phi_4|$.
2. Compute $\hat{H}'_{g_1}$ and the overlap matrix $\hat{O}_{g_1}$.
3. Solve the eigenvalue problem for $\hat{O}_{g_1}$ and transform $\hat{H}'_{g_1}$ by $\hat{O}_{g_1}^{-\frac{1}{2}}$.
4. Solve the eigenvalue problem for $\hat{O}_{g_1}^{-\frac{1}{2}} \hat{H}'_{g_1} \hat{O}_{g_1}^{-\frac{1}{2}}$ and set $g_2$ to the lowest eigenvalue-solution. That eigenvalue is the energy of $g_1 \wedge g_2$.
5. Repeat 2 through 4 for $g_2$.
6. Repeat 2 through 5 until convergence ($10^{-8}$ Hartree).

# Four Electron Applications

Problems of the algorithm:

- Inter-geminal dependencies ignored.
- Numerical instability in some cases due to transformation by $\hat{O}^{-\frac{1}{2}}$.
- Slow linear convergence.

# Four Electron Applications

| Species | $E_{UAGP}$ | $E_{HF}$ | EC | % EC UAGP | $\langle g_1 \vert g_2 \rangle$ |
|---|---|---|---|---|---|
| $Li^-$ | -7.44779627 | -7.41681880 | -0.03103634 | 99.81 | 0.983 |
| Be | -14.61732472 | -14.57233761 | -0.04507189 | 99.81 | 0.964 |
| $B^+$ | -24.29376828 | -24.23456235 | -0.05928717 | 99.86 | 0.689 |
| LiH[a] | -8.01467655 | -7.98368439 | -0.03109065 | 99.68 | 0.901 |
| $Li\cdots H$[b] | -7.93190893 | -7.93169893 | -0.00021699 | 96.77 | 0.687 |
| $BeH^+$[a] | -14.88453406 | -14.84960071 | -0.03524912 | 99.10 | 0.999 |
| $(Be\cdots H)^+$[b] | -14.77527156 | -14.77472034 | -0.00057408 | 96.02 | 0.867 |
| $He_2$ at eq.[a] | -5.77519072 | -5.71032168 | -0.06487425 | 99.99 | $3.14\cdot 10^{-6}$ |
| $He_2$ at $\infty$[b] | -5.77518966 | -5.71032095 | -0.06486871 | 100 | $3.83\cdot 10^{-13}$ |
| $HeH^-$[a] | -3.35749691 | -3.30402998 | -0.05347029 | 99.99 | $9.56\cdot 10^{-6}$ |
| $(He\cdots H)^-$[b] | -3.35745161 | -3.30398420 | -0.05346741 | 100 | $3.38\cdot 10^{-13}$ |
| linear $H_3^-$[a] | -1.63425811 | -1.57545074 | -0.06848456 | 85.87 | 0.056 |
| lin. $(H_2\cdots H)^-$[b] | -1.59624834 | -1.53310194 | -0.06314640[c] | n/a | $7.5\cdot 10^{-15}$ |

[a] CCSD geometry, [b] Distance was $10^9$ Bohr, [c]EC not based on FCI but on UAGP

## Conclusions and Outlook

- UAGP iterative scheme.
- UAGP renders quantitative recovery of electron correlation for 4 electron systems.
- UAGP does not simply collapse to AGP.
- Ground state may be approximated well by a function $g \wedge f$.
- BH with frozen core, for further testing.
- Partitioning of molecules into sets of strongly orthogonal 4-electron-functions.

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Born-Oppenheimer Approximation:

Nuclei are stationary.

Simplest anti-symmetric function:

$$|\chi_1 \cdots \chi_N| = \frac{1}{N!} \cdot \begin{vmatrix} \chi_1(\vec{x}_1) & \cdots & \chi_N(\vec{x}_1) \\ \vdots & \ddots & \vdots \\ \chi_1(\vec{x}_N) & \cdots & \chi_N(\vec{x}_N) \end{vmatrix} = \frac{1}{N!} \sum_{\sigma \in \Gamma} \operatorname{sgn} \sigma \prod_{i=1}^{N} \chi_i(\vec{x}_{\sigma_i})$$

Variation over all Slater determinants:

$$E_{HF} = \inf_{\{\chi_i\}} \int |\chi_1 \cdots \chi_N| \mathbf{H} |\chi_1 \cdots \chi_N| d1 \ldots dN$$

Tensor product of vector spaces $V$ and $W$ over the field $K$:

$$V \otimes W = V \times W / \{(kv, w) - (v, kw)\}$$

Tensor algebra:

$$T^0(V) = K \quad T^{m+1}(V) = V \otimes T^m(V) \quad T(V) = \bigoplus_{i=0}^{\infty} T^i(V)$$

Define alternation operator and symmetrizer:

$$\begin{aligned} \hat{A}_m &= \frac{1}{|\Gamma|} \sum_{\sigma \in \Gamma} \operatorname{sgn} \sigma \hat{P}_\sigma & \hat{S}_m &= \frac{1}{|\Gamma|} \sum_{\sigma \in \Gamma} \hat{P}_\sigma \\ \hat{A} &= \sum \hat{A}_m(V) & \hat{S} &= \sum \hat{S}_m(V) \end{aligned}$$

Multiplication on $A(V)$:

$$t \wedge t' = \hat{A}(t \otimes t')$$

Annihilation and creation operators:

$$\hat{a}_f^\dagger : A(V) \to A(V) :\Rightarrow t \in A^i(V) \mapsto \sqrt{i+1} \cdot f \wedge t \forall f \in V$$

$$\hat{a}_f : T(V) \to T(V)|A(V) :\Rightarrow t = v \otimes t' \mapsto \sqrt{i} \cdot f^*(v) t' \forall f \in V$$

Commutation relations between annihilation and creation operators:

$$\hat{a}_p^\dagger \hat{a}_q^\dagger = (\delta_{pq} - 1)\hat{a}_q^\dagger \hat{a}_p^\dagger \Leftrightarrow \{\hat{a}_p^\dagger, \hat{a}_q^\dagger\} = \delta_{pq}\hat{a}_q^\dagger \hat{a}_p^\dagger = 0$$

$$\hat{a}_p^\dagger \hat{a}_q = \delta_{pq} - \hat{a}_q \hat{a}_p^\dagger \Leftrightarrow \{\hat{a}_p^\dagger, \hat{a}_q\} = \delta_{pq}$$

$$\hat{a}_p \hat{a}_q = (\delta_{pq} - 1)\hat{a}_q \hat{a}_p \Leftrightarrow \{\hat{a}_p, \hat{a}_q\} = \delta_{pq}\hat{a}_q \hat{a}_p = 0$$

## Configuration interaction:

$$\hat{C}_0 = c_0$$

$$\hat{C}_1 = \sum_{a\in V, i\in V} c_i^a \cdot \hat{a}_a^\dagger \hat{a}_i$$

$$\hat{C}_2 = \sum_{a>b\in V, i>j\in V} c_{ab}^{ij} \cdot \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j$$

$$\vdots$$

$$\hat{C}_m = \sum_{\substack{a_1,\ldots,a_m\in V,\\ i_1,\ldots,i_m\in V}} c_{a_1,\ldots,a_m}^{i_1,\ldots,i_m} \cdot \hat{a}_{a_1}^\dagger \cdots \hat{a}_{a_m}^\dagger \hat{a}_{i_1} \cdots \hat{a}_{i_m}$$

$$|\Psi\rangle = \sum_{m=0}^{n} \hat{C}_m \, |\Phi_0\rangle$$

# Reduced Density Matrices

Let $\psi$ be a symmetric or antisymmetric $N$-particle function. Then,

$$D^p(\psi; s, s') = \int_X \psi(s,t)^* \psi(s',t) dt$$

is the (integration) kernel to the Reduced Density Operator(RDO) of order $p$, or Reduced Density Matrix (RDM). $s$ and $t$ are cumulative variables with $p$,$q$ variables, respectively, where $N = p + q$.

$$\operatorname{tr} \mathbf{D}^p = \langle \psi | \psi \rangle$$

$$\mathbf{D}^p = (\mathbf{D}^p)^*, \mathbf{D}^p \geq 0$$

## *norbs, nags, ...*

$$\mathbf{D}^p \alpha^p(1\dots p) = \lambda_\alpha^p \alpha^p(1\dots p)$$

$\alpha^1$ is called a natural orbital (*norb*).
$\alpha^2$ is called a natural geminal (*nag*). Representation of $\psi$ in terms of natural states:
Let $\alpha_i^p$, $\beta_i^q$ be eigenstates of $D^p, D^q$. Then,

$$\psi(s,t) = \sum c_i \alpha_i^p(s)\beta_i^q(t)$$

where $\lambda_i^p = \lambda_i^q = |c_i|^2$.
Let $N/p \in \mathbb{N}$ and $p$ odd. Then,

$$\psi = \sum_{\sigma=(\sigma_1,\dots,\sigma_{N/p})} \gamma_\sigma \prod c_{\sigma_i} \alpha_{\sigma_i}^p(ip+1,\dots,ip+p)$$

For $p=1$, a unitary transformation of $\alpha_i^p$ does not change the symmetry of $\psi$. **There is no such result for** $p=2$.

## $N$-Representability

Let $\rho$ be a density. Then,

$$\overline{\rho}(x) = \iint_{-\infty}^{+\infty} \rho(x, y, z) dydz$$

$$f(x) = 2\pi \int_{-\infty}^{x} \overline{\rho}(x') dx'$$

$$\phi_k(x, y, z) = \sqrt{\rho(x, y, z)} \mathrm{e}^{ikf(x)}$$

$$|\phi_k|^2 = \rho$$

The $\phi_k$ are orthonormal. **Any** $\rho$ is $N$-representable.

# $N$-Representability

In second quantization:

$$D^{(2)}_{ij,ab} = \Big( \langle \Psi | \, \hat{a}^\dagger_i \hat{a}^\dagger_j \Big) \cdot \left( \hat{a}_a \hat{a}_b \, | \Psi \rangle \right)$$

$$Q^{(2)}_{ij,ab} = \Big( \langle \Psi | \, \hat{a}^\dagger_i \hat{a}_j \Big) \cdot \left( \hat{a}^\dagger_a \hat{a}_b \, | \Psi \rangle \right) = \delta_{ja} D^{(1)}_{i,b} - D^{(2)}_{ia,jb}$$

$$\begin{cases} P^{(2)}_{ij,ab} = \left( \langle \Psi | \, \hat{a}_i \hat{a}_j \right) \cdot \Big( \hat{a}^\dagger_a \hat{a}^\dagger_b \, | \Psi \rangle \Big) \\ \qquad = \delta_{jb}\delta_{ia} - \delta_{ib}\delta_{ja} + \delta_{ja}\hat{D}^{(1)}_{i,b} - \delta_{ia}\hat{D}^{(1)}_{j,b} - \delta_{jb}\hat{D}^{(1)}_{i,a} + \delta_{ib}\hat{D}^{(1)}_{j,a} + \hat{D}^{(2)}_{ab,ij} \end{cases}$$

$$\hat{D}^{(2)} \geq 0, \;\; \hat{Q}^{(2)} \geq 0, \;\; \hat{P}^{(2)} \geq 0$$

## *Aufbau-Ansatz* for AGP

$$\Psi_{Aufbau} = \mathbf{A_n} \prod_{i=1}^{n/2} g_i(2i-1, 2i)$$

An iterative scheme may be derived:

$$\psi_{p+2} = \mathbf{A_{p+2}} g(1,2)\psi_p(3,\ldots,p+2)$$

$$\overline{\psi}_{p+2} = g(1,2)\psi_p(3,\ldots,p+2)$$

# *Aufbau-Ansatz* for AGP

$$\Psi_{Aufbau} = \mathbf{A_n} \prod_{i=1}^{n/2} g_i(2i-1, 2i)$$

An iterative scheme may be derived:

$$\mathbf{A_{p+2}} = \frac{1}{(p+1)(p+2)} \left( 1 - \sum_{i=2}^{p+2} \mathbf{P_{1i}} \right) \left( 1 - \sum_{j=3}^{p+2} \mathbf{P_{2j}} \right) \mathbf{A_p^{(2)}}$$

# *Aufbau-Ansatz* for AGP

$$\Psi_{Aufbau} = \mathbf{A_n} \prod_{i=1}^{n/2} g_i(2i-1, 2i)$$

An iterative scheme may be derived:

$$\mathbf{A_{p+2}} \overline{\psi}_{p+2} = \frac{1}{(p+1)(p+2)} \left( 1 - \sum_{i=2}^{p+2} \mathbf{P_{1i}} \right) \left( 1 - \sum_{j=3}^{p+2} \mathbf{P_{2j}} \right) \overline{\psi}_{p+2}$$

## *Aufbau-Ansatz* for AGP

$$D^{(2)}_{p+2} = F_1 + (F_2 + F_2^*) + (F_3 + F_3^*) + F_4 + (F_5 + F_5^*) + F_6$$

$$\mathbf{F_1} = \mathbf{g(12)g(1'2')}\|\psi_{\mathbf{p}}\|^{\mathbf{2}}$$

# *Aufbau-Ansatz* for AGP

$$D^{(2)}_{p+2} = F_1 + (F_2 + F_2^*) + (F_3 + F_3^*) + F_4 + (F_5 + F_5^*) + F_6$$

$$F_2 = -p \int g(12)g^*(1'3)D^{(1)}_p(3;2') - g(12)g^*(2'3)D^{(1)}_p(3;1')d3$$

## *Aufbau-Ansatz* for AGP

$$D_{p+2}^{(2)} = F_1 + (F_2 + F_2^*) + (F_3 + F_3^*) + F_4 + (F_5 + F_5^*) + F_6$$

$$F_3 = \binom{p}{2} \int g(12) g^*(34) D_p^{(2)}(34; 1'2') d3d4$$

# *Aufbau-Ansatz* for AGP

$$D^{(2)}_{p+2} = F_1 + (F_2 + F_2^*) + (F_3 + F_3^*) + F_4 + (F_5 + F_5^*) + F_6$$

$$\begin{aligned} F_4 = & 2\binom{p}{2} \int g(13)g^*(2'4)D^{(2)}_p(24;1'3) - g(23)g^*(2'4)D^{(2)}_p(14;1'3)d3d4 + \\ & 2\binom{p}{2} \int g(13)g^*(1'4)D^{(2)}_p(24;2'3) - g(23)g^*(1'4)D^{(2)}_p(14;2'3)d3d4 + \\ & p\left(D^{(1)}_g(1,1')D^{(1)}_p(2;2') + D^{(1)}_g(2,2')D^{(1)}_p(1;1')\right) - \\ & p\left(D^{(1)}_g(2,1')D^{(1)}_p(1;2') + D^{(1)}_g(1,2')D^{(1)}_p(2;1')\right) \end{aligned}$$

## *Aufbau-Ansatz* for AGP

$$D^{(2)}_{p+2} = F_1 + (F_2 + F_2^*) + (F_3 + F_3^*) + F_4 + (F_5 + F_5^*) + F_6$$

$$\begin{aligned} F_5 = & 2\binom{p}{2} \int D^{(1)}_g(1;4) D^{(2)}_p(24;1'2') - D^{(1)}_g(2;4) D^{(2)}_p(14;1'2') d4 \\ & - 6\binom{p}{3} \int g(13) g^*(45) D^{(3)}(245;1'2'3) d3d4d5 \\ & + 6\binom{p}{3} \int g(23) g^*(45) D^{(3)}(145;1'2'3) d3d4d5 \end{aligned}$$

## *Aufbau-Ansatz* for AGP

$$D^{(2)}_{p+2} = F_1 + (F_2 + F_2^*) + (F_3 + F_3^*) + F_4 + (F_5 + F_5^*) + F_6$$

$$F_6 = \binom{\mathbf{p}}{\mathbf{2}} \mathbf{D}^{(\mathbf{2})}_{\mathbf{p}}(\mathbf{12}; \mathbf{1}'\mathbf{2}') \|\mathbf{g}\|^{\mathbf{2}} +$$

$$2(p-2)\binom{p}{2} \int D^{(1)}_g(4;5) D^{(3)}_p(125; 1'2'4) d3d4d5 +$$

$$\binom{p-2}{2}\binom{p}{2} \int g(34) g^*(56) D^{(4)}_p(1256; 1'2'34) d3d4d5d6$$

## *Aufbau-Ansatz* for AGP

Since $g(34) = \sum_i \xi_i \alpha_i(3)\beta_i(4)$,

$$\int g(34)g(35)d3 = \sum_i |\xi_i|^2 \beta_i(4)\beta_i(5).$$

Also,

$$D^{(2)}(12;34) = \sum_i \int D^{(3)}(125;346)\beta_i(5)\beta_i(6)d5d6.$$

Due to $\sum_i |\xi_i|^2 = 1$ and $|\xi_i|^2 \leq 1/2$, we can conclude

$$\begin{aligned}\frac{1}{2}D_p^{(2)}(12;1'2') \geq \int g(34')^* g(3'4') D_p^{(3)}(123;1'2'3')d3d3'd4' \\ = \int g(34')^* g(3'4') \cdot \psi_p(1234\ldots p) \\ \cdot \psi_p(1'2'3'4\ldots p)^* d3'd4'd3\ldots dp.\end{aligned}$$

## *Aufbau-Ansatz* for AGP

Since $g(34) = \sum_i \xi_i \alpha_i(3)\beta_i(4)$,

$$\int g(34)g(35)d3 = \sum_i |\xi_i|^2 \beta_i(4)\beta_i(5).$$

Similarly,

$$\frac{1}{p} D_p^{(2)}(12;1'2') \geq \int g(34)^* g(3'4') D_p^{(4)}(1234;1'2'3'4')d3d4d3'd4'$$
$$= \int g(34)^* g(3'4') \cdot \psi_p(12345\ldots p)$$
$$\cdot \psi_p(1'2'3'4'5\ldots p)^* d3d4d3'd4'd5\ldots dp.$$

## *Aufbau-Ansatz* for AGP

In second quantization:

$$\hat{a}_\nu \hat{g}_i^\dagger = \hat{g}_i^\dagger \hat{a}_\nu + \hat{g}_i^{(\nu)\dagger}$$

$$\hat{g}_i^{(\nu)\dagger} = \sum_{j<\nu} g_{\nu j}^{(i)*} \hat{a}_j^\dagger - \sum_{j>\nu} g_{j\nu}^{(i)*} \hat{a}_j^\dagger$$

$$\hat{a}_\nu \prod \hat{g}_i^\dagger = \prod \hat{g}_i^\dagger \hat{a}_\nu + \sum \hat{g}_\nu^{(i)\dagger} \prod_{j\neq i} \hat{g}_j^\dagger$$

## *Aufbau-Ansatz* for AGP

In second quantization:

$$\hat{a}_\nu \hat{a}_\mu \prod \hat{g}_i^\dagger = \prod \hat{g}_i^\dagger \hat{a}_\nu \hat{a}_\mu +$$
$$\sum \hat{g}_i^{(\nu)\dagger} \prod_{j \neq i} \hat{g}_i^\dagger \hat{a}_\mu + \sum \hat{g}_i^{(\mu)\dagger} \prod_{j \neq i} \hat{g}_i^\dagger \hat{a}_\nu +$$
$$\sum g_{\nu\mu}^{(i)*} \prod_{j \neq i} \hat{g}_j^\dagger - \sum \hat{g}_i^{(\nu)\dagger} \hat{g}_j^{(\mu)\dagger} \prod_{k \notin \{i,j\}} \hat{g}_k^\dagger$$

# *Aufbau-Ansatz* for AGP

In second quantization:

$$\left\langle \bigwedge g_i \left| \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_k \hat{a}_l \right| \bigwedge g_i \right\rangle = \left\langle 1 \left| \left( \sum_i \left( \prod_{j \neq i} \hat{g}_j \right) g_{rs}^{(i)} \right) \left( \sum_i g_{kl}^{(i)*} \prod_{j \neq i} \hat{g}_j^\dagger \right) \right| 1 \right\rangle -$$
$$\left\langle 1 \left| \left( \sum_i \left( \prod_{j \neq i} \hat{g}_j \right) g_{rs}^{(i)} \right) \left( \sum_{i \neq j} \hat{g}_i^{(k)\dagger} \hat{g}_j^{(l)\dagger} \prod_{\kappa \notin \{i,j\}} \hat{g}_\kappa^\dagger \right) \right| 1 \right\rangle -$$
$$\left\langle 1 \left| \left( \sum_{i \neq j} \left( \prod_{\kappa \notin \{i,j\}} \hat{g}_\kappa \right) \hat{g}_j^{(s)} \hat{g}_i^{(r)} \right) \left( \sum_i g_{kl}^{(i)*} \prod_{j \neq i} \hat{g}_j^\dagger \right) \right| 1 \right\rangle +$$
$$\left\langle 1 \left| \left( \sum_{i \neq j} \left( \prod_{\kappa \notin \{i,j\}} \hat{g}_\kappa \right) \hat{g}_j^{(s)} \hat{g}_i^{(r)} \right) \left( \sum_{i \neq j} \hat{g}_i^{(k)\dagger} \hat{g}_j^{(l)\dagger} \prod_{\kappa \notin \{i,j\}} \hat{g}_\kappa^\dagger \right) \right| 1 \right\rangle$$

## *Aufbau-Ansatz* for AGP

1. Release of $\xi_i$ only, i.e.,

$$g_j = \sum \xi_i^{(j)} \left|\alpha_{2i-1}\alpha_{2i}\right|$$

2. Releasing the ordering of the natural orbitals.

$$g_i = \sum \xi_j^{(i)} \left|\beta_{2j-1}^{(i)}\beta_{2j}^{(i)}\right|$$

$$\left\{\beta_j^{(i)}\right\}_j = \left\{\beta_l^{(k)}\right\}_l \forall i, k$$

3. Increasing the number of used geminals to $l$ geminals.

$$\Psi = \mathbf{A_n} \prod_{i=1}^{l} \Psi_{AGP}^{(m_i)}[g_i]\left(M_i + 1 \ldots M_{i+1}\right)$$

$$\sum_{1\le j<i} m_j = M_i, \sum_{i=1}^{l} m_i = n$$

## *Aufbau-Ansatz* for AGP

4. Enforce P, Q conditions on the 2-RDM as well as

$$\int |\psi_{p+2}|^2 d1 \ldots dp+2 = \operatorname{tr} \hat{D}^{(2)}_{p+2} = 2\|g\|^2 \|\psi_p\|^2 - 2p \operatorname{tr}\left(\hat{D}^{(1)}_g \hat{D}^{(1)}_p\right) + \binom{p}{2} \left\langle g \left| \hat{D}^{(2)}_p \right| g \right\rangle$$

5. Enforce that no cross-contributions exist, i.e.,

$$\int g_i(1,2) g_j(2,3) g_k(3,4) d2d3 = 0 \Leftarrow i \neq j \text{ and } j \neq k$$