

Generalized Geminal Functional Theory

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Outline

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- *Aufbau-Ansatz* for Generalized Anti-Symmetrized Geminal Products
- Four-Electron Applications
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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

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

Simplifying the Hamiltonian

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

$$\mathbf{K} = \frac{n}{2}(\mathbf{h}_1 + \mathbf{h}_2) + \frac{n(n-1)}{2} \frac{1}{r_{12}}$$

$$E = \text{tr} \left(\mathbf{D}^{(2)} \mathbf{K} \right)$$

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 α_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 ρ_2 :

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

The 1-RDM of ψ_{AGP} :

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

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

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

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

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

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

Aufbau-Ansatz for AGP

1. Release of ξ_i only, i.e.,

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

2. Releasing the ordering of the natural orbitals.

$$g_i = \sum \xi_j^{(i)} |\beta_{2j-1}^{(i)} \beta_{2j}^{(i)}|$$
$$\left\{ \beta_j^{(i)} \right\}_j = \left\{ \beta_l^{(k)} \right\}_l \quad \forall i, k$$

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

$$\Psi = \mathbf{A}_n \prod_{i=1}^l \Psi_{AGP}^{(m_i)}[g_i] (M_i + 1 \dots M_{i+1})$$

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

Aufbau-Ansatz for AGP

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

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

Four Electron Applications

E and O are bilinear functionals:

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

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

$$\langle x \mid \hat{O}_g \mid y \rangle = \langle x \wedge g \mid y \wedge g \rangle$$

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	$\langle g_1 g_2 \rangle$
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...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...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 ∞ ^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...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 ...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:

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

Variation over all Slater determinants:

$$E_{HF} = \inf_{\{\chi_i\}} \int |\chi_1 \cdots \chi_N| \mathbf{H} |\chi_1 \cdots \chi_N| d\mathbf{1} \dots d\mathbf{N}$$

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:

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

Multiplication on $A(V)$:

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

Annihilation and creation operators:

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

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

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:

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

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

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

⋮

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

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

Reduced Density Matrices

Let ψ 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 $N = p + q$.

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

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

norbs, nags, ...

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

α^1 is called a natural orbital (*norb*).

α^2 is called a natural geminal (*nag*). Representation of ψ in terms of natural states:

Let α_i^p, β_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 α_i^p does not change the symmetry of ψ . **There is no such result for $p = 2$.**

N -Representability

Let ρ be a density. Then,

$$\bar{\rho}(x) = \int_{-\infty}^{+\infty} \int \rho(x, y, z) dy dz$$

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

$$\phi_k(x, y, z) = \sqrt{\rho(x, y, z)} \mathbf{e}^{ikf(x)}$$
$$|\phi_k|^2 = \rho$$

The ϕ_k are orthonormal. **Any** ρ is N -representable.

N -Representability

In second quantization:

$$D_{ij,ab}^{(2)} = \left(\langle \Psi | \hat{a}_i^\dagger \hat{a}_j^\dagger \right) \cdot (\hat{a}_a \hat{a}_b | \Psi \rangle)$$

$$Q_{ij,ab}^{(2)} = \left(\langle \Psi | \hat{a}_i^\dagger \hat{a}_j \right) \cdot (\hat{a}_a^\dagger \hat{a}_b | \Psi \rangle) = \delta_{ja} D_{i,b}^{(1)} - D_{ia,jb}^{(2)}$$

$$\left\{ \begin{aligned} P_{ij,ab}^{(2)} &= \left(\langle \Psi | \hat{a}_i \hat{a}_j \right) \cdot \left(\hat{a}_a^\dagger \hat{a}_b^\dagger | \Psi \rangle \right) \\ &= \delta_{jb} \delta_{ia} - \delta_{ib} \delta_{ja} + \delta_{ja} \hat{D}_{i,b}^{(1)} - \delta_{ia} \hat{D}_{j,b}^{(1)} - \delta_{jb} \hat{D}_{i,a}^{(1)} + \delta_{ib} \hat{D}_{j,a}^{(1)} + \hat{D}_{ab,ij}^{(2)} \end{aligned} \right.$$
$$\hat{D}^{(2)} \geq 0, \quad \hat{Q}^{(2)} \geq 0, \quad \hat{P}^{(2)} \geq 0$$

Aufbau-Ansatz for AGP

$$\bar{\Psi}_{Aufbau} = \mathbf{A}_n \prod_{i=1}^{n/2} g_i(2i-1, 2i)$$

An iterative scheme may be derived:

$$\psi_{p+2} = \mathbf{A}_{p+2} g(1, 2) \psi_p(3, \dots, p+2)$$

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

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:

$$\mathbf{A}_{p+2} \bar{\psi}_{p+2} = \frac{1}{(p+1)(p+2)} \left(1 - \sum_{i=2}^{p+2} \mathbf{P}_{1i} \right) \left(1 - \sum_{j=3}^{p+2} \mathbf{P}_{2j} \right) \bar{\psi}_{p+2}$$

Aufbau-Ansatz for AGP

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

$$\mathbf{F}_1 = \mathbf{g}(\mathbf{1}\mathbf{2})\mathbf{g}(\mathbf{1}'\mathbf{2}')\|\psi_{\mathbf{p}}\|^2$$

Aufbau-Ansatz for AGP

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

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

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

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

$$F_4 = 2 \binom{p}{2} \int g(13)g^*(2'4)D_p^{(2)}(24; 1'3) - g(23)g^*(2'4)D_p^{(2)}(14; 1'3)d3d4 +$$

$$2 \binom{p}{2} \int g(13)g^*(1'4)D_p^{(2)}(24; 2'3) - g(23)g^*(1'4)D_p^{(2)}(14; 2'3)d3d4 +$$

$$p \left(D_g^{(1)}(1, 1')D_p^{(1)}(2; 2') + D_g^{(1)}(2, 2')D_p^{(1)}(1; 1') \right) -$$

$$p \left(D_g^{(1)}(2, 1')D_p^{(1)}(1; 2') + D_g^{(1)}(1, 2')D_p^{(1)}(2; 1') \right)$$

Aufbau-Ansatz for AGP

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

$$\begin{aligned} F_5 = & 2 \binom{p}{2} \int D_g^{(1)}(1; 4) D_p^{(2)}(24; 1'2') - D_g^{(1)}(2; 4) D_p^{(2)}(14; 1'2') d4 \\ & - 6 \binom{p}{3} \int g(13) g^*(45) D^{(3)}(245; 1'2'3) d3 d4 d5 \\ & + 6 \binom{p}{3} \int g(23) g^*(45) D^{(3)}(145; 1'2'3) d3 d4 d5 \end{aligned}$$

Aufbau-Ansatz for AGP

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

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

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

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

Aufbau-Ansatz for AGP

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,

$$D^{(2)}(12; 34) = \sum_i \int D^{(3)}(125; 346) \beta_i(5) \beta_i(6) d5 d6.$$

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

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

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,

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

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:

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

Aufbau-Ansatz for AGP

In second quantization:

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

Aufbau-Ansatz for AGP

1. Release of ξ_i only, i.e.,

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

2. Releasing the ordering of the natural orbitals.

$$g_i = \sum \xi_j^{(i)} |\beta_{2j-1}^{(i)} \beta_{2j}^{(i)}|$$
$$\left\{ \beta_j^{(i)} \right\}_j = \left\{ \beta_l^{(k)} \right\}_l \quad \forall i, k$$

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

$$\Psi = \mathbf{A}_n \prod_{i=1}^l \Psi_{AGP}^{(m_i)}[g_i] (M_i + 1 \dots M_{i+1})$$

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

Aufbau-Ansatz for AGP

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

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

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

$$\int g_i(1, 2) g_j(2, 3) g_k(3, 4) d2 d3 = 0 \Leftrightarrow i \neq j \text{ and } j \neq k$$