orbital relaxation pt.2

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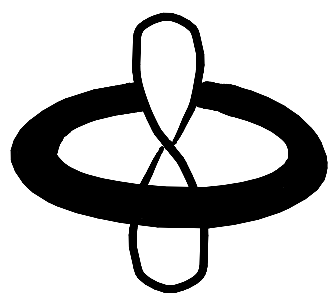
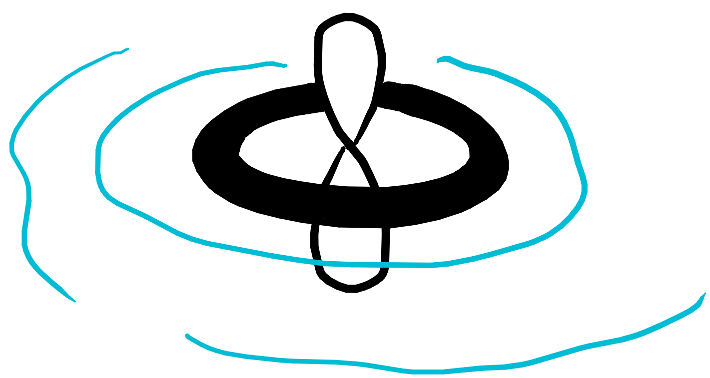
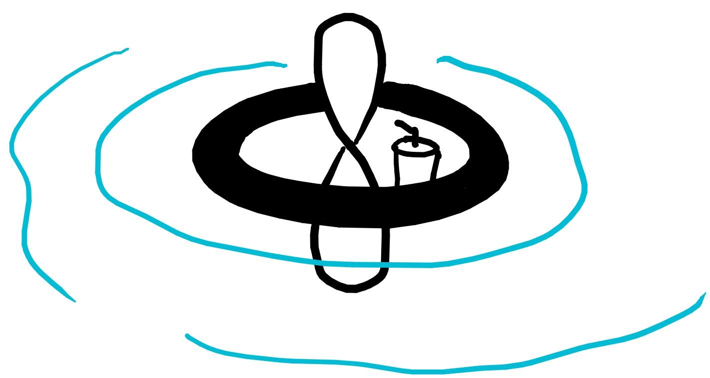


orbital relaxation pt.2



orbital relaxation pt.2



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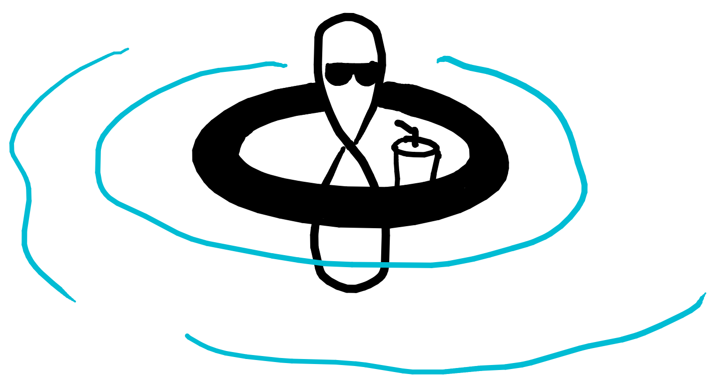

Newton-Raphson step:

Newton-Raphson step:

$$E(\mathbf{x})$$

Newton-Raphson step:

$$E(\mathbf{x}) \approx E(\mathbf{0})$$

Newton-Raphson step:

$$E(\mathbf{x}) \approx E(\mathbf{0}) + \mathbf{x}^{\dagger}\mathbf{w}$$

Newton-Raphson step:

$$E(\mathbf{x}) \approx E(\mathbf{0}) + \mathbf{x}^{\dagger}\mathbf{w} + \frac{1}{2}\mathbf{x}^{\dagger}\mathbf{A}\mathbf{x}$$

Newton-Raphson step:

$$E(\mathbf{x}) \approx E(\mathbf{0}) + \mathbf{x}^{+}\mathbf{w} + \frac{1}{2}\mathbf{x}^{+}A\mathbf{x}$$

$$\downarrow$$

$$\left.\frac{\partial E}{\partial \mathbf{x}^{+}}\right|_{0}$$

Newton-Raphson step:

$$E(\mathbf{x}) \approx E(0) + \mathbf{x}^{\dagger}\mathbf{w} + \frac{1}{2}\mathbf{x}^{\dagger}\mathbf{A}\mathbf{x}$$

$$\mathbf{w} \rightarrow \left.\frac{\partial E}{\partial \mathbf{x}^{\dagger}}\right|_{0} \qquad \mathbf{A} \rightarrow \left.\frac{\partial^2 E}{\partial \mathbf{x}^{\dagger}\partial \mathbf{x}}\right|_{0}$$

Newton-Raphson step:

$$E(\mathbf{x}) \approx E(0) + \mathbf{x}^{+}\mathbf{w} + \frac{1}{2}\mathbf{x}^{+}A\mathbf{x}$$

$$\mathbf{w} = \left.\frac{\partial E}{\partial \mathbf{x}^{+}}\right|_{0} \qquad A = \left.\frac{\partial^2 E}{\partial \mathbf{x}^{+}\partial \mathbf{x}}\right|_{0}$$

$$\frac{\partial E}{\partial \mathbf{x}^{+}}(\mathbf{x})$$

Newton-Raphson step:

$$E(\mathbf{x}) \approx E(\mathbf{0}) + \underbrace{\mathbf{x}^\dagger \mathbf{w}}_{\mathbf{w} = \left.\frac{\partial E}{\partial \mathbf{x}^\dagger}\right|_0} + \frac{1}{2}\underbrace{\mathbf{x}^\dagger \mathbf{A} \mathbf{x}}_{\mathbf{A} = \left.\frac{\partial^2 E}{\partial \mathbf{x}^\dagger \partial \mathbf{x}}\right|_0}$$

$$\frac{\partial E}{\partial \mathbf{x}^\dagger}(\mathbf{x}) \approx \mathbf{w} + \mathbf{A}\mathbf{x}$$

Newton-Raphson step:

$$E(\mathbf{x}) \approx E(\mathbf{0}) + \mathbf{x}^{\dagger} \underset{\substack{\downarrow \\ \left.\frac{\partial E}{\partial \mathbf{x}^{\dagger}}\right|_{0}}}{\mathbf{w}} + \frac{1}{2} \mathbf{x}^{\dagger} \underset{\substack{\downarrow \\ \left.\frac{\partial^{2} E}{\partial \mathbf{x}^{\dagger} \partial \mathbf{x}}\right|_{0}}}{A} \mathbf{x}$$

$$\frac{\partial E}{\partial \mathbf{x}^{\dagger}}(\mathbf{x}) \approx \mathbf{w} + A\mathbf{x} \stackrel{!}{=} 0$$

Newton-Raphson step:

$$E(\mathbf{x}) \approx E(\mathbf{0}) + \underbrace{\mathbf{x}^{+}\mathbf{w}}_{\left.\frac{\partial E}{\partial \mathbf{x}^{+}}\right|_0} + \underbrace{\tfrac{1}{2}\mathbf{x}^{+}A\mathbf{x}}_{\left.\frac{\partial^2 E}{\partial \mathbf{x}^{+}\partial \mathbf{x}}\right|_0}$$

$$\frac{\partial E}{\partial \mathbf{x}^{+}}(\mathbf{x}) \approx \mathbf{w} + A\mathbf{x} \overset{!}{=} 0$$

$$\Longrightarrow$$

Newton-Raphson step:

$$E(\mathbf{x}) \approx E(0) + \mathbf{x}^\dagger \underset{\substack{\big\downarrow \\ \left.\frac{\partial E}{\partial \mathbf{x}^\dagger}\right|_0}}{w} + \frac{1}{2}\mathbf{x}^\dagger \underset{\substack{\big\downarrow \\ \left.\frac{\partial^2 E}{\partial \mathbf{x}^\dagger \partial \mathbf{x}}\right|_0}}{A} \mathbf{x}$$

$$\frac{\partial E}{\partial \mathbf{x}^\dagger}(\mathbf{x}) \approx w + A\mathbf{x} \overset{!}{=} 0$$

$$\Longrightarrow \mathbf{x}$$

Newton-Raphson step:

$$E(\mathbf{x}) \approx E(\mathbf{0}) + \mathbf{x}^\dagger \underset{\substack{\downarrow \\ \left.\frac{\partial E}{\partial \mathbf{x}^\dagger}\right|_0}}{\mathbf{w}} + \frac{1}{2}\mathbf{x}^\dagger \underset{\substack{\downarrow \\ \left.\frac{\partial^2 E}{\partial \mathbf{x}^\dagger \partial \mathbf{x}}\right|_0}}{A} \mathbf{x}$$

$$\frac{\partial E}{\partial \mathbf{x}^\dagger}(\mathbf{x}) \approx \mathbf{w} + A\mathbf{x} \overset{!}{=} 0$$

$$\Longrightarrow \mathbf{x} = -A^{-1}\mathbf{w}$$

Orbital rotations:

Orbital rotations:

ψ'

Orbital rotations:

$$\psi' = \psi \mathbb{U}$$

Orbital rotations:

$$\boldsymbol{\psi}' = \boldsymbol{\psi}\mathbb{U} \qquad \mathbb{U} = \exp(\mathbb{X} - \mathbb{X}^{\dagger})$$

Orbital rotations:

$$\boldsymbol{\psi}' = \boldsymbol{\psi}\,\mathbb{U} \qquad \mathbb{U} = \exp(\mathbb{X} - \mathbb{X}^{+})$$

$a_p'^{+}$

Orbital rotations:

$$\psi' = \psi \mathbb{U} \qquad \mathbb{U} = \exp(\mathbb{X} - \mathbb{X}^{+})$$

$$a_p'^{+} = \sum_q a_q^{+} (\mathbb{U})_{qp}$$

Orbital rotations:

$$\psi' = \psi \mathbb{U} \qquad \mathbb{U} = \exp(\mathbb{X} - \mathbb{X}^\dagger)$$

$$a_p'^\dagger = \sum_q a_q^\dagger (\mathbb{U})_{qp}$$

$$= U a_p^\dagger U^\dagger$$

Orbital rotations:

$$\psi' = \psi \mathbb{U} \qquad \mathbb{U} = \exp(\mathbb{X} - \mathbb{X}^\dagger)$$

$$a_p'^\dagger = \sum_q a_q^\dagger (\mathbb{U})_{qp} \qquad U = \exp(X - X^\dagger)$$

$$= U a_p^\dagger U^\dagger$$

Orbital rotations:

$$\boldsymbol{\psi}' = \boldsymbol{\psi}\,\mathbb{U} \qquad \mathbb{U} = \exp(\mathbb{X} - \mathbb{X}^\dagger)$$

$$a'^{\dagger}_p = \sum_q a^\dagger_q (\mathbb{U})_{qp} \qquad U = \exp(X - X^\dagger)$$

$$= U a^\dagger_p U^\dagger \qquad X = x^i_a a^a_i$$

Orbital rotations:

$$\psi' = \psi \mathbb{U} \qquad \mathbb{U} = \exp(\mathbb{X} - \mathbb{X}^\dagger)$$

$$a_p'^\dagger = \sum_q a_q^\dagger (\mathbb{U})_{qp} \qquad U = \exp(X - X^\dagger)$$

$$= U a_p^\dagger U^\dagger \qquad X = x_a^i a_i^a$$

Note:

Orbital rotations:

$$\psi' = \psi \mathbb{U} \qquad \mathbb{U} = \exp(\mathbb{X} - \mathbb{X}^\dagger)$$

$$a_p'^\dagger = \sum_q a_q^\dagger (\mathbb{U})_{qp} \qquad U = \exp(X - X^\dagger)$$

$$= U a_p^\dagger U^\dagger \qquad X = x_a^i a_i^a$$

Note: $\qquad a_p'^\dagger a_q'^\dagger$

Orbital rotations:

$$\psi' = \psi \mathbb{U} \qquad \mathbb{U} = \exp(\mathbb{X} - \mathbb{X}^\dagger)$$

$$a_p'^\dagger = \sum_q a_q^\dagger (\mathbb{U})_{qp} \qquad U = \exp(X - X^\dagger)$$

$$= U a_p^\dagger U^\dagger \qquad X = x_a^i a_i^a$$

Note: $\quad a_p'^\dagger a_q'^\dagger = U a_p^\dagger U^\dagger U a_q^\dagger U^\dagger$

Orbital rotations:

$$\psi' = \psi\, \mathbb{U} \qquad\qquad \mathbb{U} = \exp(\mathbb{X} - \mathbb{X}^\dagger)$$

$$a'^\dagger_p = \sum_q a^\dagger_q\, (\mathbb{U})_{qp} \qquad\qquad U = \exp(X - X^\dagger)$$

$$= U a^\dagger_p U^\dagger \qquad\qquad X = x^i_a\, a^a_i$$

Note:

$$a'^\dagger_p\, a'^\dagger_q = U a^\dagger_p \cancelto{1}{U^\dagger U}\, a^\dagger_q\, U^\dagger$$

Orbital rotations:

$$\mathbb{\psi}' = \mathbb{\psi}\, \mathbb{U} \qquad \mathbb{U} = \exp(\mathbb{X} - \mathbb{X}^\dagger)$$

$$a'^\dagger_p = \sum_q a^\dagger_q (\mathbb{U})_{qp} \qquad U = \exp(X - X^\dagger)$$

$$= U a^\dagger_p U^\dagger \qquad X = x^i_a a^a_i$$

Note:

$$a'^\dagger_p a'^\dagger_q = U a^\dagger_p \cancel{U^\dagger U} a^\dagger_q U^\dagger$$

$$= U (a^\dagger_p a^\dagger_q) U^\dagger$$

$$\Phi'_{(p_1 \cdots p_n)}$$

$$\Phi'_{(p_1 \cdots p_n)} = a'^{\dagger}_{p_1} a'^{\dagger}_{p_2} \cdots a'^{\dagger}_{p_n} |vac\rangle$$

$$\Phi'_{(p_1 \cdots p_n)} = a'^{\dagger}_{p_1} a'^{\dagger}_{p_2} \cdots a'^{\dagger}_{p_n} |vac\rangle$$

$$= U a^{\dagger}_{p_1} a^{\dagger}_{p_2} \cdots a^{\dagger}_{p_n} U^{\dagger} |vac\rangle$$

$$\Phi'_{(p_1 \cdots p_n)} = a'^{\dagger}_{p_1} a'^{\dagger}_{p_2} \cdots a'^{\dagger}_{p_n} |vac\rangle$$

$$= U a^{\dagger}_{p_1} a^{\dagger}_{p_2} \cdots a^{\dagger}_{p_n} \underbrace{U^{\dagger} |vac\rangle}_{|vac\rangle}$$

$$\Phi'_{(p_1 \cdots p_n)} = a'^{\dagger}_{p_1} a'^{\dagger}_{p_2} \cdots a'^{\dagger}_{p_n} |vac\rangle$$

$$= U a^{\dagger}_{p_1} a^{\dagger}_{p_2} \cdots a^{\dagger}_{p_n} \underbrace{U^{\dagger} |vac\rangle}_{|vac\rangle}$$

$$= U \Phi_{(p_1 \cdots p_n)}$$

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$$= U \Phi_{(p_1 \cdots p_n)}$$

In general:

$$\Phi'_{(p_1 \cdots p_n)} = a'^{\dagger}_{p_1} a'^{\dagger}_{p_2} \cdots a'^{\dagger}_{p_n} |vac\rangle$$

$$= U a^{\dagger}_{p_1} a^{\dagger}_{p_2} \cdots a^{\dagger}_{p_n} \underbrace{U^{\dagger} |vac\rangle}_{|vac\rangle}$$

$$= U \, \Phi_{(p_1 \cdots p_n)}$$

In general: Ψ'

$$\Phi'_{(p_1 \cdots p_n)} = a'^{\dagger}_{p_1} a'^{\dagger}_{p_2} \cdots a'^{\dagger}_{p_n} |vac\rangle$$

$$= U a^{\dagger}_{p_1} a^{\dagger}_{p_2} \cdots a^{\dagger}_{p_n} \underbrace{U^{\dagger}|vac\rangle}_{|vac\rangle}$$

$$= U \Phi_{(p_1 \cdots p_n)}$$

In general: $\quad \Psi' = U \Psi$

$$\langle \Psi' | H | \Psi' \rangle$$

$$\langle \Psi' | H | \Psi' \rangle = \langle \Psi | U^{\dagger} H U | \Psi \rangle$$

$$\langle \Psi' | H | \Psi' \rangle = \langle \Psi | U^{\dagger} H U | \Psi \rangle$$

$$= \langle \Psi | \exp(X^{\dagger} - X) \, H \exp(X - X^{\dagger}) | \Psi \rangle$$

$$\langle \Psi' | H | \Psi' \rangle = \langle \Psi | U^\dagger H U | \Psi \rangle$$

$$= \underbrace{\langle \Psi | \exp(X^\dagger - X)\, H \exp(X - X^\dagger) | \Psi \rangle}_{E(X)}$$

$$\langle \Psi' | H | \Psi' \rangle = \langle \Psi | U^\dagger H U | \Psi \rangle$$

$$= \underbrace{\langle \Psi | \exp(X^\dagger - X)\, H \exp(X - X^\dagger) | \Psi \rangle}_{E(X)}$$

W_{ia}

$$\langle \Psi' | H | \Psi' \rangle = \langle \Psi | U^\dagger H U | \Psi \rangle$$

$$= \underbrace{\langle \Psi | \exp(X^\dagger - X)\, H \exp(X - X^\dagger) | \Psi \rangle}_{E(\mathbf{x})}$$

$$w_{ia} = \left. \frac{\partial E(\mathbf{x})}{\partial x_a^{i*}} \right|_0$$

$$\langle \Psi' | H | \Psi' \rangle = \langle \Psi | U^\dagger H U | \Psi \rangle$$

$$= \underbrace{\langle \Psi | \exp(X^\dagger - X)\, H \exp(X - X^\dagger) | \Psi \rangle}_{E(\mathbf{X})}$$

$$w_{ia} = \left. \frac{\partial E(\mathbf{X})}{\partial x_a^{i*}} \right|_0$$

$$= \langle \Psi | \left. \frac{\partial e^{X^\dagger - X}}{\partial x_a^{i*}} \right|_0 H \; + \; H \left. \frac{\partial e^{X - X^\dagger}}{\partial x_a^{i*}} \right|_0 | \Psi \rangle$$

$$\langle \Psi' | H | \Psi' \rangle = \langle \Psi | U^{\dagger} H U | \Psi \rangle$$

$$= \underbrace{\langle \Psi | \exp(X^{\dagger} - X)\, H \exp(X - X^{\dagger}) | \Psi \rangle}_{E(\mathbf{x})}$$

$$w_{ia} = \left. \frac{\partial E(\mathbf{x})}{\partial x_a^{i*}} \right|_0$$

$$= \langle \Psi | \left. \frac{\partial e^{X^{\dagger} - X}}{\partial x_a^{i*}} \right|_0 H + H \left. \frac{\partial e^{X - X^{\dagger}}}{\partial x_a^{i*}} \right|_0 | \Psi \rangle$$

$$= \langle \Psi | a_a^i H - H a_a^i | \Psi \rangle$$

Orb. gradient:

Orb. gradient: $w_{ia} = \langle \Psi | [a^i_a, H] | \Psi \rangle$

Orb. gradient: $w_{ia} = \langle \Psi | [a^i_a, H] | \Psi \rangle$

Orb. Hessian:

Orb. gradient: $w_{ia} = \langle \Psi | [a^i_a, H] | \Psi \rangle$

Orb. Hessian:

$A_{ia,jb}$

Orb. gradient: $w_{ia} = \langle \Psi | [a^i_a, H] | \Psi \rangle$

Orb. Hessian:

$$A_{ia,jb} = \left. \frac{\partial^2 E(\mathbf{x})}{\partial x^{i*}_a \, \partial x^j_b} \right|_0$$

Orb. gradient: $w_{ia} = \langle \Psi | [a_a^i, H] | \Psi \rangle$

Orb. Hessian:

$$A_{ia,jb} = \left. \frac{\partial^2 E(x)}{\partial x_a^{i*} \partial x_b^j} \right|_0$$

$$= \langle \Psi | [[a_a^i, H], a_j^b] | \Psi \rangle$$

Density matrices:

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E

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$$E = \langle \Psi | h_p^q a_q^p + \frac{1}{4} \bar{g}_{pq}^{rs} a_{rs}^{pq} | \Psi \rangle$$

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Density matrices:

$$E = \langle \Psi | h_p^q a_q^p + \frac{1}{4} \bar{g}_{pq}^{rs} a_{rs}^{pq} | \Psi \rangle$$

$$= h_p^q \underbrace{\langle \Psi | a_q^p | \Psi \rangle}_{\gamma_q^p} + \frac{1}{4} \bar{g}_{pq}^{rs} \langle \Psi | a_{rs}^{pq} | \Psi \rangle$$

Density matrices:

$$E = \langle \Psi | h_p^q a_q^p + \frac{1}{4} \bar{g}_{pq}^{rs} a_{rs}^{pq} | \Psi \rangle$$

$$= h_p^q \underbrace{\langle \Psi | a_q^p | \Psi \rangle}_{\gamma_q^p} + \frac{1}{4} \bar{g}_{pq}^{rs} \underbrace{\langle \Psi | a_{rs}^{pq} | \Psi \rangle}_{\gamma_{rs}^{pq}}$$

Density matrices:

$$E = \langle \Psi | h^q_p a^p_q + \tfrac{1}{4} \bar{g}^{rs}_{pq} a^{pq}_{rs} | \Psi \rangle$$

$$= h^q_p \underbrace{\langle \Psi | a^p_q | \Psi \rangle}_{\gamma^p_q} + \tfrac{1}{4} \bar{g}^{rs}_{pq} \underbrace{\langle \Psi | a^{pq}_{rs} | \Psi \rangle}_{\gamma^{pq}_{rs}}$$

To express orb. grad. in terms of d.m.s,

Density matrices:

$$E = \langle \Psi | h_p^q a_q^p + \tfrac{1}{4} \bar{g}_{pq}^{rs} a_{rs}^{pq} | \Psi \rangle$$

$$= h_p^q \underbrace{\langle \Psi | a_q^p | \Psi \rangle}_{\gamma_q^p} + \tfrac{1}{4} \bar{g}_{pq}^{rs} \underbrace{\langle \Psi | a_{rs}^{pq} | \Psi \rangle}_{\gamma_{rs}^{pq}}$$

To express orb. grad. in terms of d.m.s, evaluate $[a_a^i, a_q^p]$ and $[a_a^i, a_{rs}^{pq}]$

$$[a^i_a, a^p_q]$$

$$[a^i_a, a^p_q] = \delta^p_a a^i_q - \delta^i_q a^p_a$$

$$[a^i_a, a^p_q] = \delta^p_a a^i_q - \delta^i_q a^p_a$$

$$[a^i_a, a^{pq}_{rs}]$$

$$[a^i_a , a^p_q] = \delta^p_a \, a^i_q - \delta^i_q \, a^p_a$$

$$[a^i_a , a^{pq}_{rs}] = P^{(p/q)} \delta^p_a \, a^{iq}_{rs} - P_{(r/s)} \delta^i_r \, a^{pq}_{as}$$

$$[a^i_a, a^p_q] = \delta^p_a a^i_q - \delta^i_q a^p_a$$

$$[a^i_a, a^{pq}_{rs}] = P^{(p/q)} \delta^p_a a^{iq}_{rs} - P_{(r/s)} \delta^i_r a^{pq}_{as}$$

$\Longrightarrow$

$$[a_a^i, a_q^p] = \delta_a^p a_q^i - \delta_q^i a_a^p$$

$$[a_a^i, a_{rs}^{pq}] = P^{(p/q)} \delta_a^p a_{rs}^{iq} - P_{(r/s)} \delta_r^i a_{as}^{pq}$$

$\Longrightarrow \; w_{ia}$

$$[a^i_a, a^p_q] = \delta^p_a a^i_q - \delta^i_q a^p_a$$

$$[a^i_a, a^{pq}_{rs}] = P^{(p/q)} \delta^p_a a^{iq}_{rs} - P_{(r/s)} \delta^i_r a^{pq}_{as}$$

$$\Longrightarrow w_{ia} = \langle \Psi | h^q_p [a^i_a, a^p_q] + \frac{1}{4} \bar{g}^{rs}_{pq} [a^i_a, a^{pq}_{rs}] | \Psi \rangle$$

$$[a^i_a, a^p_q] = \delta^p_a a^i_q - \delta^i_q a^p_a$$

$$[a^i_a, a^{pq}_{rs}] = P^{(p/q)} \delta^p_a a^{iq}_{rs} - P_{(r/s)} \delta^i_r a^{pq}_{as}$$

$$\Longrightarrow w_{ia} = \langle \Psi | h^q_p [a^i_a, a^p_q] + \frac{1}{4} \bar{g}^{rs}_{pq} [a^i_a, a^{pq}_{rs}] | \Psi \rangle$$

$$= h^q_a \gamma^i_q - h^i_p \gamma^p_a$$

$$[a_a^i, a_q^p] = \delta_a^p a_q^i - \delta_q^i a_a^p$$

$$[a_a^i, a_{rs}^{pq}] = P^{(p/q)} \delta_a^p a_{rs}^{iq} - P_{(r/s)} \delta_r^i a_{as}^{pq}$$

$$\Longrightarrow w_{ia} = \langle \Psi | h_p^q [a_a^i, a_q^p] + \frac{1}{4} \bar{g}_{pq}^{rs} [a_a^i, a_{rs}^{pq}] | \Psi \rangle$$

$$= h_a^q \gamma_q^i - h_p^i \gamma_a^p + \frac{1}{2} \bar{g}_{aq}^{rs} \gamma_{rs}^{iq} - \frac{1}{2} \bar{g}_{pq}^{is} \gamma_{as}^{pq}$$

$$[a^i_a, a^p_q] = \delta^p_a a^i_q - \delta^i_q a^p_a$$

$$[a^i_a, a^{pq}_{rs}] = P^{(p/q)} \delta^p_a a^{iq}_{rs} - P_{(r/s)} \delta^i_r a^{pq}_{as}$$

$$\Longrightarrow w_{ia} = \langle \Psi | h^q_p [a^i_a, a^p_q] + \frac{1}{4} \bar{g}^{rs}_{pq} [a^i_a, a^{pq}_{rs}] | \Psi \rangle$$

$$= h^q_a \gamma^i_q - h^i_p \gamma^p_a + \frac{1}{2} \bar{g}^{rs}_{aq} \gamma^{iq}_{rs} - \frac{1}{2} \bar{g}^{is}_{pq} \gamma^{pq}_{as}$$

$$[a^i_a, a^p_q] = \delta^p_a \, a^i_q - \delta^i_q \, a^p_a$$

$$[a^i_a, a^{pq}_{rs}] = P^{(p/q)} \delta^p_a \, a^{iq}_{rs} - P_{(r/s)} \delta^i_r \, a^{pq}_{as}$$

$$\Longrightarrow \; w_{ia} = \langle \Psi | \, h^q_p [a^i_a, a^p_q] + \tfrac{1}{4} \bar{g}^{rs}_{pq} [a^i_a, a^{pq}_{rs}] \, | \Psi \rangle$$

$$= \underbrace{h^q_a \gamma^i_q - h^i_p \gamma^p_a + \tfrac{1}{2} \bar{g}^{rs}_{aq} \gamma^{iq}_{rs}}_{(F)^i_a} - \tfrac{1}{2} \bar{g}^{is}_{pq} \gamma^{pq}_{as}$$

$$[a^i_a, a^p_q] = \delta^p_a a^i_q - \delta^i_q a^p_a$$

$$[a^i_a, a^{pq}_{rs}] = P^{(p/q)} \delta^p_a a^{iq}_{rs} - P_{(r/s)} \delta^i_r a^{pq}_{as}$$

$$\Longrightarrow w_{ia} = \langle \Psi | h^q_p [a^i_a, a^p_q] + \frac{1}{4} \bar{g}^{rs}_{pq} [a^i_a, a^{pq}_{rs}] | \Psi \rangle$$

$$= \underbrace{h^q_a \gamma^i_q - h^i_p \gamma^p_a + \frac{1}{2} \bar{g}^{rs}_{aq}}_{(F)^i_a} \gamma^{iq}_{rs} - \frac{1}{2} \bar{g}^{is}_{pq} \gamma^{pq}_{as}$$

$$[a^i_a, a^p_q] = \delta^p_a a^i_q - \delta^i_q a^p_a$$

$$[a^i_a, a^{pq}_{rs}] = P^{(p/q)} \delta^p_a a^{iq}_{rs} - P_{(r/s)} \delta^i_r a^{pq}_{as}$$

$$\Longrightarrow w_{ia} = \langle \Psi | h^q_p [a^i_a, a^p_q] + \tfrac{1}{4} \bar{g}^{rs}_{pq} [a^i_a, a^{pq}_{rs}] | \Psi \rangle$$

$$= h^q_a \gamma^i_q - h^i_p \gamma^p_a + \tfrac{1}{2} \bar{g}^{rs}_{aq} \gamma^{iq}_{rs} - \tfrac{1}{2} \bar{g}^{is}_{pq} \gamma^{pq}_{as}$$

$$(F)^i_a \qquad (F^\dagger)^i_a$$

Orb Hessian

Orb Hessian

$$\left[[a_a^i, a_q^p], a_j^b\right]$$

$$\left[[a_a^i, a_{rs}^{pq}], a_j^b\right]$$

Orb Hessian

$$[[a^i_a, a^p_q], a^b_j] =$$

$$[[a^i_a, a^{pq}_{rs}], a^b_j] =$$

Orb Hessian

$$[[a_a^i, a_q^p], a_j^b] =$$

$$[[a_a^i, a_{rs}^{pq}], a_j^b] =$$

tedious.

Orb Hessian

$$[[a^i_a, a^p_q], a^b_j] =$$

tedious. Cheat!

$$[[a^i_a, a^{pq}_{rs}], a^b_j] =$$

Orb Hessian

$$[[a^i_a, a^p_q], a^b_j] =$$

$$[[a^i_a, a^{pq}_{rs}], a^b_j] =$$

tedious. Cheat!

$$A_{ia,jb}$$

Orb Hessian

$$[[a_a^i, a_q^p], a_j^b] =$$

$$[[a_a^i, a_{rs}^{pq}], a_j^b] =$$

tedious. Cheat!

$$A_{ia,jb} \approx \langle \Psi | [[a_a^i, H], a_j^b] | \Psi \rangle^{(0)}$$

Orb Hessian

$$[[a_a^i, a_q^p], a_j^b] =$$

$$[[a_a^i, a_{rs}^{pq}], a_j^b] =$$

tedious. Cheat!

$$A_{ia,jb} \approx \langle \Psi | [[a_a^i, H], a_j^b] | \Psi \rangle^{(0)}$$

$$= \langle \Phi | [[a_a^i, H_0], a_j^b] | \Phi \rangle$$

Orb Hessian

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$$= \frac{(\mathbb{F} - \mathbb{F}^\dagger)_i^a}{\varepsilon_a^i}$$

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5. If E not converged, return to 1.

the end.