Orbital Optimization

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1 Starting equation

The objective is to minimize the energy by optimizing the orbitals for given active space one- and two-body reduced density matrices η_k^l and η_{kl}^{nm}. The energy is given as

$$E = \sum_{kl} \eta_k^l \hat{h}_k^l + \frac{1}{2} \sum_{klmn} \eta_{kl}^{mn} g_{kl}^{mn} + \frac{1}{2} n_{occ} \sum_{kl\boldsymbol{a}} \eta_k^l \left(2 g_{\boldsymbol{a}k}^{\boldsymbol{a}l} - g_{\boldsymbol{a}k}^{l\boldsymbol{a}}\right) + c \tag{1}$$

with

η_k^l	One-body reduced density matrix
η_{kl}^{nm}	Two-body reduced density matrix
$\hat{h}_k^l = \langle \phi_k \vert \hat{h} \vert \phi_l \rangle$	One-body integrals
$g_{kl}^{mn} = \langle \phi_k \phi_l \vert g \vert \phi_m \phi_n \rangle$	Two-body integrals
k, l, m, n	Active space indicies
$\boldsymbol{a}, \boldsymbol{b}$	Core orbital indicies
x, y	All orbital indicies
n_{occ}	Maximum orbital occupation
	(1 for spin orbitals and 2 for spatial orbitals)

c is the core energy and remains constant during orbital refinement

$$c = n_{occ} \sum_{\boldsymbol{a}} \hat{h}_{\boldsymbol{a}}^{\boldsymbol{a}} + \frac{1}{2} n_{occ} \sum_{\boldsymbol{a},\boldsymbol{b}} \left(2 g_{\boldsymbol{a}\boldsymbol{b}}^{\boldsymbol{a}\boldsymbol{b}} - g_{\boldsymbol{a}\boldsymbol{b}}^{\boldsymbol{b}\boldsymbol{a}}\right) \tag{2}$$

The minimization is carried out via the corresponding Lagrangian, whereby the ortonormality of all orbitals is preserved via the Lagrange muliplier ϵ_{xy}

$$\mathcal{L} = \underbrace{\sum_{kl} \eta_k^l \hat{h}_k^l}_{\mathcal{L}_1} + \underbrace{\frac{1}{2} \sum_{klmn} \eta_{kl}^{mn} g_{kl}^{mn}}_{\mathcal{L}_2} + \underbrace{\frac{1}{2} n_{occ} \sum_{kl\boldsymbol{a}} \eta_k^l \left(2 g_{\boldsymbol{a}k}^{\boldsymbol{a}l} - g_{\boldsymbol{a}k}^{l\boldsymbol{a}}\right)}_{\mathcal{L}_3} - \underbrace{\sum_{xy} \epsilon_{xy} \left(\langle \phi_x \vert \phi_y \rangle - \delta_{xy}\right)}_{\mathcal{L}_4} \tag{3}$$

$$\frac{\partial \mathcal{L}}{\partial \phi_i} \stackrel{!}{=} 0 \tag{4}$$

We only refine active space orbitals i!

2 Derivation of the Lagrangian terms

$$\begin{aligned}
\frac{\partial \mathcal{L}_1}{\partial \phi_i} = \frac{\partial}{\partial \phi_i} \sum_{kl} \eta_k^l \hat{h}_k^l &= \sum_{kl} \eta_k^l \frac{\partial}{\partial \phi_i} \int \phi_k^* \hat{h} \phi_l dr \\
&= \sum_{kl} \eta_k^l \left(\delta_{ki} \hat{h} \phi_l + \phi_k^* \hat{h} \delta_{li} \right) \\
&= \sum_l \eta_i^l \hat{h} \phi_l + \sum_k \eta_k^i \hat{h} \phi_k^* \\
&= 2 \sum_k \eta_k^i \hat{h} \phi_k
\end{aligned} \tag{5}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}_2}{\partial \phi_i} &= \frac{\partial}{\partial \phi_i} \frac{1}{2} \sum_{klmn} \eta_{kl}^{mn} g_{kl}^{mn} \\
&= \frac{1}{2} \sum_{klmn} \eta_{kl}^{mn} \frac{\partial}{\partial \phi_i} \int \phi_k^*(r_1) \phi_l^*(r_2) \frac{1}{|r_1 - r_2|} \phi_m(r_1) \phi_n(r_2) dr_1 dr_2 \\
&= \frac{1}{2} \sum_{klmn} \eta_{kl}^{mn} \Bigg[\delta_{ki} \underbrace{\left(\int \phi_l^*(r_2) \frac{1}{|r_1 - r_2|} \phi_n(r_2) dr_2 \right)}_{g_l^n} \phi_m \\
&+ \delta_{li} \underbrace{\left(\int \phi_k^*(r_1) \frac{1}{|r_1 - r_2|} \phi_m(r_1) dr_1 \right)}_{g_k^m} \phi_n \\
&+ \delta_{mi} \underbrace{\left(\int \phi_l^*(r_2) \frac{1}{|r_1 - r_2|} \phi_n(r_2) dr_2 \right)}_{g_l^n} \phi_k^* \\
&+ \delta_{ni} \underbrace{\left(\int \phi_k^*(r_1) \frac{1}{|r_1 - r_2|} \phi_m(r_1) dr_1 \right)}_{g_k^m} \phi_l^* \Bigg] \\
&= \frac{1}{2} \sum_{klmn} \eta_{kl}^{mn} \left[\delta_{ki} g_l^n \phi_m + \delta_{li} g_k^m \phi_n + \delta_{mi} g_l^n \phi_k + \delta_{ni} g_k^m \phi_l \right] \\
&= \frac{1}{2} \sum_{ln} g_l^n \left(\sum_m \eta_{il}^{mn} \phi_m + \sum_k \eta_{kl}^{in} \phi_k \right) + \frac{1}{2} \sum_{km} g_k^m \left(\sum_n \eta_{ki}^{mn} \phi_n + \sum_l \eta_{kl}^{mi} \phi_l \right)
\end{aligned} \tag{6}$$

Renaming the sum indices and utilizing the integral symmetries for real orbitals $g_{kl}^{mn} = g_{lk}^{nm} = g_{mn}^{kl} = g_{nm}^{lk} = g_{ml}^{kn} = g_{nk}^{lm} = g_{kn}^{ml} = g_{lm}^{nk}$ results in

$$\frac{\partial \mathcal{L}_2}{\partial \phi_i} = 2 \sum_{lnk} g_l^n \eta_{kl}^{in} \phi_k \tag{7}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}_3}{\partial \phi_i} &= \frac{\partial}{\partial \phi_i} \frac{1}{2} n_{occ} \sum_{kl\boldsymbol{a}} \eta_k^l \left(2 g_{\boldsymbol{a}k}^{\boldsymbol{a}l} - g_{\boldsymbol{a}k}^{l\boldsymbol{a}}\right) \\
&= \frac{1}{2} n_{occ} \left(2 \sum_{kl\boldsymbol{a}} \eta_k^l \frac{\partial}{\partial \phi_i} g_{\boldsymbol{a}k}^{\boldsymbol{a}l} - \sum_{kl\boldsymbol{a}} \eta_k^l \frac{\partial}{\partial \phi_i} g_{\boldsymbol{a}k}^{l\boldsymbol{a}} \right)
\end{aligned} \tag{8}$$

$$\begin{aligned}
\sum_{kl\boldsymbol{a}} \eta_k^l \frac{\partial}{\partial \phi_i} g_{\boldsymbol{a}k}^{\boldsymbol{a}l} &= \sum_{kl\boldsymbol{a}} \eta_k^l \frac{\partial}{\partial \phi_i} \int \phi_{\boldsymbol{a}}^*(r_1) \phi_k^*(r_2) \frac{1}{|r_1 - r_2|} \phi_{\boldsymbol{a}}(r_1) \phi_l(r_2) dr_1 dr_2 \\
&= \text{...(Similar to Eq. 6)} \\
&= \sum_{kl\boldsymbol{a}} \eta_k^l \left[\delta_{\boldsymbol{a}i} g_k^l \phi_{\boldsymbol{a}} + \delta_{ki} g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_l + \delta_{\boldsymbol{a}i} g_k^l \phi_{\boldsymbol{a}} + \delta_{li} g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_k \right] \\
&= \sum_{kl\boldsymbol{a}} \eta_k^l \left[\delta_{ki} g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_l + \delta_{li} g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_k \right] \\
&= \sum_{l\boldsymbol{a}} \eta_i^l g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_l + \sum_{k\boldsymbol{a}} \eta_k^i g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_k \\
&= 2 \sum_{k\boldsymbol{a}} \eta_k^i g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_k \text{(Integral symmetries)}
\end{aligned} \tag{9}$$

$$\begin{aligned}
\sum_{kl\boldsymbol{a}} \eta_k^l \frac{\partial}{\partial \phi_i} g_{\boldsymbol{a}k}^{l\boldsymbol{a}} &= \sum_{kl\boldsymbol{a}} \eta_k^l \frac{\partial}{\partial \phi_i} \int \phi_{\boldsymbol{a}}^*(r_1) \phi_k^*(r_2) \frac{1}{|r_1 - r_2|} \phi_l(r_1) \phi_{\boldsymbol{a}}(r_2) dr_1 dr_2 \\
&= \text{...(Similar to Eq. 6)} \\
&= \sum_{kl\boldsymbol{a}} \eta_k^l \left[\delta_{\boldsymbol{a}i} g_k^{\boldsymbol{a}} \phi_l + \delta_{ki} g_{\boldsymbol{a}}^l \phi_{\boldsymbol{a}} + \delta_{li} g_k^{\boldsymbol{a}} \phi_{\boldsymbol{a}} + \delta_{\boldsymbol{a}i} g_{\boldsymbol{a}}^l \phi_k \right] \\
&= \sum_{kl\boldsymbol{a}} \eta_k^l \left[\delta_{ki} g_{\boldsymbol{a}}^l \phi_{\boldsymbol{a}} + \delta_{li} g_k^{\boldsymbol{a}} \phi_{\boldsymbol{a}} \right] \\
&= \sum_{l\boldsymbol{a}} \eta_i^l g_{\boldsymbol{a}}^l \phi_{\boldsymbol{a}} + \sum_{k\boldsymbol{a}} \eta_k^i g_k^{\boldsymbol{a}} \phi_{\boldsymbol{a}} \\
&= 2 \sum_{k\boldsymbol{a}} \eta_k^i g_k^{\boldsymbol{a}} \phi_{\boldsymbol{a}} \text{(Integral symmetries)}
\end{aligned} \tag{10}$$

$$
\begin{aligned}
\frac{\partial \mathcal{L}_3}{\partial \phi_i} &= \frac{1}{2} n_{occ} \left(2 \sum_{kl\boldsymbol{a}} \eta_k^l \frac{\partial}{\partial \phi_i} g_{\boldsymbol{a}k}^{\boldsymbol{a}l} - \sum_{kl\boldsymbol{a}} \eta_k^l \frac{\partial}{\partial \phi_i} g_{\boldsymbol{a}k}^{l\boldsymbol{a}} \right) \\
&= \frac{1}{2} n_{occ} \left(4 \sum_{k\boldsymbol{a}} \eta_k^i g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_k - 2 \sum_{k\boldsymbol{a}} \eta_k^i g_k^{\boldsymbol{a}} \phi_{\boldsymbol{a}} \right) \\
&= n_{occ} \sum_{k\boldsymbol{a}} \eta_k^i \left(2 g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_k - g_k^{\boldsymbol{a}} \phi_{\boldsymbol{a}} \right)
\end{aligned} \tag{11}
$$

$$
\begin{aligned}
\frac{\partial \mathcal{L}_4}{\partial \phi_i} &= \frac{\partial}{\partial \phi_i} \sum_{xy} \epsilon_{xy} \left(\langle \phi_x | \phi_y \rangle - \delta_{xy} \right) \\
&= \sum_{xy} \epsilon_{xy} \left(\frac{\partial}{\partial \phi_i} \int \phi_x^* \phi_y dr_1 - \delta_{xy} \right) \\
&= \sum_{xy} \epsilon_{xy} \left(\delta_{ix} \phi_y + \delta_{iy} \phi_x^* - 0 \right) \\
&= \sum_{y} \epsilon_{iy} \phi_y + \sum_{x} \epsilon_{xi} \phi_x \\
&= \sum_{x} \underbrace{\left(\epsilon_{ix} + \epsilon_{xi} \right)}_{2\epsilon_x^i} \phi_x
\end{aligned} \tag{12}
$$

3 Derivation of the orbital update equation

The fully derived Lagrangian for an orbital ϕ_i results as

$$
\frac{\partial \mathcal{L}}{\partial \phi_i} = 2 \left(\sum_k \eta_k^i \hat{h} \phi_k + \sum_{lnk} g_l^n \eta_{kl}^{in} \phi_k + \frac{1}{2} n_{occ} \sum_{k\boldsymbol{a}} \eta_k^i \left(2 g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_k - g_k^{\boldsymbol{a}} \phi_{\boldsymbol{a}} \right) - \sum_x \epsilon_x^i \phi_x \right) \tag{13}
$$

Dividing by 2 and using

$$
\sum_x \phi_x = \phi_i + \sum_{x \neq i} \phi_i
$$

results in

$$
\frac{\partial \mathcal{L}}{\partial \phi_i} = \eta_i^i \hat{h} \phi_i + \underbrace{\sum_{k \neq i} \phi_k^i \hat{h} \phi_i}_{=0 \text{ for NOs}} - \epsilon_i^i \phi_i - \sum_{x \neq i} \epsilon_x^i \phi_x + \sum_{lnk} g_l^n \eta_{kl}^{in} \phi_k + \frac{1}{2} n_{occ} \sum_{k\boldsymbol{a}} \eta_k^i \left(2 g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_k - g_k^{\boldsymbol{a}} \phi_{\boldsymbol{a}} \right) \tag{14}
$$

$$\frac{\partial \mathcal{L}}{\partial \phi_i} = \left(\eta_i^i \hat{h} - \epsilon_i^i\right)\phi_i - \sum_{x\neq i} \epsilon_x^i \phi_x + \sum_{lnk} g_l^n \eta_{kl}^{in} \phi_k + \frac{1}{2} n_{occ} \sum_{k\boldsymbol{a}} \eta_k^i \left(2 g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_k - g_k^{\boldsymbol{a}} \phi_{\boldsymbol{a}}\right) \tag{15}$$

Multiplication by $\frac{1}{\eta_i^i}$ yields

$$\frac{\partial \mathcal{L}}{\partial \phi_i} = \left(\hat{h} - \frac{\epsilon_i^i}{\eta_i^i}\right)\phi_i - \frac{1}{\eta_i^i} \sum_{x\neq i} \epsilon_x^i \phi_x + \frac{1}{\eta_i^i} \sum_{lnk} g_l^n \eta_{kl}^{in} \phi_k + \frac{1}{2\eta_i^i} n_{occ} \sum_{k\boldsymbol{a}} \eta_k^i \left(2 g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_k - g_k^{\boldsymbol{a}} \phi_{\boldsymbol{a}}\right) \tag{16}$$

Inserting $h = -\frac{\Delta}{2} + \hat{V}_{ne}$ finally results in

$$\left(\frac{\Delta}{2} + \frac{\epsilon_i^i}{\eta_i^i}\right)\phi_i = \hat{V}_{ne}\phi_i - \frac{1}{\eta_i^i} \sum_{x\neq i} \epsilon_x^i \phi_x + \frac{1}{\eta_i^i} \sum_{lnk} g_l^n \eta_{kl}^{in} \phi_k + \frac{1}{2\eta_i^i} n_{occ} \sum_{k\boldsymbol{a}} \eta_k^i \left(2 g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_k - g_k^{\boldsymbol{a}} \phi_{\boldsymbol{a}}\right) \tag{17}$$

and thus the final equation for the optimization of an orbital as

$$\phi_i = -2\hat{G}_{-\frac{\epsilon_i^i}{\eta_i^i}} \left(\hat{V}_{ne}\phi_i - \frac{1}{\eta_i^i} \sum_{x\neq i} \epsilon_x^i \phi_x + \frac{1}{\eta_i^i} \sum_{lnk} g_l^n \eta_{kl}^{in} \phi_k + \frac{1}{2\eta_i^i} n_{occ} \sum_{k\boldsymbol{a}} \eta_k^i \left(2 g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_k - g_k^{\boldsymbol{a}} \phi_{\boldsymbol{a}}\right)\right) \tag{18}$$

4 Derivation of Lagrangian multiplier

To determine the Lagrange multiplier ϵ_k^i from the sum $\sum_x \epsilon_x^i \phi_x$, $\langle\phi_z|$ is projected onto Eq. 13

$$\begin{aligned}\langle\phi_z|\frac{\partial \mathcal{L}}{\partial \phi_i}\rangle = 2\Bigg(&\underbrace{\sum_k \eta_k^i \langle\phi_z|\hat{h}|\phi_k\rangle}_{\text{NOs: } 2\eta_i^i h_z^i} + \sum_{lnk} \underbrace{\eta_{kl}^{in} \phi_z g_l^n \phi_k}_{\eta_{kl}^{in} g_{zl}^{kn}} \\ &+ \frac{1}{2} n_{occ} \sum_{k\boldsymbol{a}} \underbrace{\eta_k^i \left(2\phi_z g_{\boldsymbol{a}}^{\boldsymbol{a}} \phi_k - \phi_z g_k^{\boldsymbol{a}} \phi_{\boldsymbol{a}}\right)}_{\eta_k^i \left(2 g_{z\boldsymbol{a}}^{k\boldsymbol{a}} - g_{zk}^{\boldsymbol{a}\boldsymbol{a}}\right)} - \underbrace{\sum_x \epsilon_x^i \langle\phi_z|\phi_x\rangle}_{\epsilon_z^i}\Bigg)\end{aligned} \tag{19}$$

$$\epsilon_z^i = \eta_i^i h_z^i + \sum_{lnk} \eta_{kl}^{in} g_{zl}^{kn} + \frac{1}{2} n_{occ} \sum_{k\boldsymbol{a}} \eta_k^i \underbrace{\left(2 g_{z\boldsymbol{a}}^{k\boldsymbol{a}} - g_{zk}^{\boldsymbol{a}\boldsymbol{a}}\right)}_{2 g_{\boldsymbol{a}z}^{\boldsymbol{a}k} - g_{\boldsymbol{a}k}^{z\boldsymbol{a}}} \tag{20}$$