1 Summary: Derivation of Z-Vector Equation

1.1 Notation and Convention

MP2 Lagrangian:

$$\mathcal{L}_{\mathrm{MP2}} = E_{\mathrm{HF}} + E_{\mathrm{H}} + \frac{1}{2}\sum_{ai}\left(z_{ai}f_{ai} + z_{ai}^{*}f_{ai}^{*}\right) \tag{1}$$

in which E_{H} is the Hylleraas functional:

$$\begin{aligned} E_{\mathrm{H}} = &\sum_{ij} h_{ij}\gamma_{ij}^{\mathrm{H}} + \sum_{ab} h_{ab}\gamma_{ab}^{\mathrm{H}} + \sum_{ijab}\langle ab||ij\rangle(\Gamma^{\mathrm{H}})_{ij}^{ab} + \sum_{ijab}\langle ij||ab\rangle(\Gamma^{\mathrm{H}})_{ab}^{ij} \\ &+ \sum_{ijkl}\langle ij||kl\rangle(\Gamma^{\mathrm{H}})_{kl}^{ij} + \sum_{ijab}\langle ai||bj\rangle(\Gamma^{\mathrm{H}})_{bj}^{ai} \end{aligned} \tag{2}$$

Unrelaxed reduced density matrices (RDMs):

$$\gamma_{pq} = \gamma_{pq}^{\mathrm{HF}} + \gamma_{pq}^{\mathrm{H}} \tag{3}$$

$$\Gamma_{rs}^{pq} = (\Gamma^{\mathrm{HF}})_{rs}^{pq} + (\Gamma^{\mathrm{H}})_{rs}^{pq} \tag{4}$$

$$\gamma_{ij}^{\mathrm{H}} = \frac{1}{2}\sum_{kab}(T_{jk}^{ab})^{*}T_{ki}^{ab} \qquad \gamma_{ij}^{\mathrm{HF}} = \delta_{ij} \tag{5}$$

$$\gamma_{ab}^{\mathrm{H}} = -\frac{1}{2}\sum_{ijc}(T_{ij}^{ac})^{*}T_{ij}^{cb} \tag{6}$$

$$(\Gamma^{\mathrm{H}})_{ij}^{ab} = \frac{1}{4}(T_{ij}^{ab})^{*} \tag{7}$$

$$(\Gamma^{\mathrm{H}})_{ab}^{ij} = \frac{1}{4}T_{ij}^{ab} \tag{8}$$

$$(\Gamma^{\mathrm{H}})_{kl}^{ij} = \frac{1}{2}\sum_{mab}(T_{km}^{ab})^{*}T_{mi}^{ab}\delta_{jl} = \gamma_{ik}^{\mathrm{H}}\delta_{jl} \qquad (\Gamma^{\mathrm{HF}})_{kl}^{ij} = \frac{1}{2}\delta_{ik}\delta_{jl} \tag{9}$$

$$(\Gamma^{\mathrm{H}})_{bj}^{ai} = -\frac{1}{2}\sum_{klc}(T_{kl}^{ac})^{*}T_{kl}^{cb}\delta_{ij} = \gamma_{ab}^{\mathrm{H}}\delta_{ij} \tag{10}$$

The MP2 amplitudes and its symmetry:

$$T_{ij}^{ab} = -T_{ij}^{ba} = -T_{ji}^{ab} = T_{ji}^{ba} = \frac{\langle ab||ij\rangle}{\Delta_{ab}^{ij}} \tag{11}$$

Constraint on orbital rotation for the Lagrangian (i.e. z-vector equation):

$$\frac{\partial\mathcal{L}_{\mathrm{MP2}}}{\partial\kappa_{bj}} = \frac{\partial E_{\mathrm{H}}}{\partial\kappa_{bj}} + \frac{1}{2}\sum_{ai}\left(z_{ai}\frac{\partial f_{ai}}{\partial\kappa_{bj}} + z_{ai}^{*}\frac{\partial f_{ai}^{*}}{\partial\kappa_{bj}}\right) = 0 \tag{12}$$

$$\frac{\partial\mathcal{L}_{\mathrm{MP2}}}{\partial\kappa_{bj}^{*}} = \frac{\partial E_{\mathrm{H}}}{\partial\kappa_{bj}^{*}} + \frac{1}{2}\sum_{ai}\left(z_{ai}\frac{\partial f_{ai}}{\partial\kappa_{bj}^{*}} + z_{ai}^{*}\frac{\partial f_{ai}^{*}}{\partial\kappa_{bj}^{*}}\right) = 0 \tag{13}$$

The LHS of z-vector equation contains z-vector terms, and the RHS is the derivative of the Hylleraas functional.
In this derivation, the following index convention is used:

- p, q, r, s, x, y: general space
- i, j, k, l, m, n: internal space
- a, b, c, d, e, f: virtual space

*All the derivatives are taken at zero-point of the external perturbation, i.e. $\lambda = 0$, and canonical orbitals are used throughout.

1.2 Intermediate Derivatives

Here's a summary of intermediate derivatives which are used repeatedly in further derivation.

$$\frac{\partial h_{pq}}{\partial \kappa_{rs}} = h_{sq}\delta_{pr} - h_{pr}\delta_{sq} \tag{14}$$

$$\frac{\partial h_{pq}}{\partial \kappa^*_{rs}} = -\frac{\partial h_{pq}}{\partial \kappa_{sr}} = -h_{rq}\delta_{ps} + h_{ps}\delta_{rq} \tag{15}$$

$$\frac{\partial \langle pq||rs\rangle}{\partial \kappa_{xy}} = \langle yq||rs\rangle\delta_{px} + \langle py||rs\rangle\delta_{qx} - \langle pq||xs\rangle\delta_{ry} - \langle pq||rx\rangle\delta_{sy} \tag{16}$$

$$\frac{\partial \langle pq||rs\rangle}{\partial \kappa^*_{xy}} = -\frac{\partial \langle pq||rs\rangle}{\partial \kappa_{yx}} = -\langle xq||rs\rangle\delta_{py} - \langle px||rs\rangle\delta_{qy} + \langle pq||ys\rangle\delta_{rx} + \langle pq||ry\rangle\delta_{sx} \tag{17}$$

1.3 LHS

The LHS of Z-Vector equation:

$$\frac{\partial f_{ai}}{\partial \kappa_{bj}} =(\varepsilon_i - \varepsilon_a)\delta_{ij}\delta_{ab} - \langle aj||ib\rangle \tag{18}$$

$$\frac{\partial f^*_{ai}}{\partial \kappa_{bj}} =- \langle ij||ab\rangle \tag{19}$$

$$\frac{\partial f_{ai}}{\partial \kappa^*_{bj}} =- \langle ab||ij\rangle \tag{20}$$

$$\frac{\partial f^*_{ai}}{\partial \kappa^*_{bj}} =(\varepsilon_i - \varepsilon_a)\delta_{ij}\delta_{ab} - \langle ib||aj\rangle \tag{21}$$

$$\begin{aligned}
\text{LHS} =& \frac{1}{2}\sum_{ai}\left(z_{ai}\frac{\partial f_{ai}}{\partial \kappa_{bj}} + z^*_{ai}\frac{\partial f^*_{ai}}{\partial \kappa_{bj}}\right) \\
=& \frac{1}{2}\sum_{ai} z_{ai}\Big((\varepsilon_i - \varepsilon_a)\delta_{ij}\delta_{ab} - \langle aj||ib\rangle\Big) - \frac{1}{2}\sum_{ai} z^*_{ai}\langle ij||ab\rangle \\
=& \frac{1}{2}z_{bj}\left(\varepsilon_j - \varepsilon_b\right) - \frac{1}{2}\sum_{ai}\Big(z_{ai}\langle aj||ib\rangle + z^*_{ai}\langle ij||ab\rangle\Big)
\end{aligned} \tag{22}$$

1.4 RHS

The RHS of Z-Vector equation comes from the Hylleraas response to orbital rotation.

$$\frac{\partial E_{\mathrm{H}}}{\partial \kappa_{em}} = \sum_{ij} \frac{\partial (h_{ij}\gamma^{\mathrm{H}}_{ij})}{\partial \kappa_{em}} + \sum_{ab} \frac{\partial (h_{ab}\gamma^{\mathrm{H}}_{ab})}{\partial \kappa_{em}} + \sum_{ijab} \frac{\partial (\langle ab||ij\rangle (\Gamma^{\mathrm{H}})^{ab}_{ij})}{\partial \kappa_{em}} + \sum_{ijab} \frac{\partial (\langle ij||ab\rangle (\Gamma^{\mathrm{H}})^{ij}_{ab})}{\partial \kappa_{em}}$$
$$+ \sum_{ijkl} \frac{\partial (\langle ij||kl\rangle (\Gamma^{\mathrm{H}})^{ij}_{kl})}{\partial \kappa_{em}} + \sum_{ijab} \frac{\partial (\langle ai||bj\rangle (\Gamma^{\mathrm{H}})^{ai}_{bj})}{\partial \kappa_{em}} \tag{23}$$

As the one- and two-body unrelaxed RDMs only depends on MP2 amplitudes, which are treated indepently from the orbital rotation parameter $\boldsymbol{\kappa}$, hence only the derivatives of electron integrals against $\boldsymbol{\kappa}$ are concerned.

$\gamma^{\mathbf{H}}_{ij}$ Part

$$\sum_{ij} \frac{\partial h_{ij}}{\partial \kappa_{em}} \gamma^{\mathrm{H}}_{ij} = -\sum_{i} h_{ie}\gamma^{\mathrm{H}}_{im} \tag{24}$$

$\gamma^{\mathbf{H}}_{ab}$ Part

$$\sum_{ab} \frac{\partial h_{ab}}{\partial \kappa_{em}} \gamma^{\mathrm{H}}_{ab} = \sum_{a} h_{ma}\gamma^{\mathrm{H}}_{ea} \tag{25}$$

$(\Gamma^{\mathbf{H}})^{ab}_{ij}$ Part

$$\sum_{ijab} \frac{\partial \langle ab||ij\rangle}{\partial \kappa_{em}} \left(\Gamma^{\mathrm{H}}\right)^{ab}_{ij} = 2\sum_{ija} \langle am||ji\rangle (\Gamma^{\mathrm{H}})^{ea}_{ij} - 2\sum_{iab} \langle ab||ei\rangle (\Gamma^{\mathrm{H}})^{ab}_{mi} \tag{26}$$

$(\Gamma^{\mathbf{H}})^{ij}_{ab}$ Part

$$\sum_{ijab} \frac{\partial \langle ij||ab\rangle}{\partial \kappa_{em}} \left(\Gamma^{\mathrm{H}}\right)^{ij}_{ab} = 0 \tag{27}$$

$(\Gamma^{\mathbf{H}})^{ij}_{kl}$ Part

$$\sum_{ijkl} \frac{\partial \langle ij||kl\rangle}{\partial \kappa_{em}} \left(\Gamma^{\mathrm{H}}\right)^{ij}_{kl} = -\sum_{ijk} \langle ij||ek\rangle (\Gamma^{\mathrm{H}})^{ij}_{mk} - \sum_{ijk} \langle ij||ek\rangle (\Gamma^{\mathrm{H}})^{ji}_{km} \tag{28}$$

$(\Gamma^{\mathbf{H}})^{ai}_{bj}$ Part

$$\sum_{ijab} \frac{\partial \langle ai||bj\rangle}{\partial \kappa_{em}} \left(\Gamma^{\mathrm{H}}\right)^{ai}_{bj} = \sum_{ijb} \langle mi||bj\rangle (\Gamma^{\mathrm{H}})^{ei}_{bj} - \sum_{iab} \langle ai||be\rangle (\Gamma^{\mathrm{H}})^{ai}_{bm} \tag{29}$$

Overall

Summing over the constituent parts:

$$
\begin{aligned}
&-\sum_i h_{ie}\gamma^{\mathrm{H}}_{im} + \sum_a h_{ma}\gamma^{\mathrm{H}}_{ea} + 2\sum_{ija}\langle am||ji\rangle(\Gamma^{\mathrm{H}})^{ea}_{ij} - 2\sum_{iab}\langle ab||ei\rangle(\Gamma^{\mathrm{H}})^{ab}_{mi} \\
&-\sum_{ijk}\langle ij||ek\rangle(\Gamma^{\mathrm{H}})^{ij}_{mk} - \sum_{ijk}\langle ij||ek\rangle(\Gamma^{\mathrm{H}})^{ji}_{km} + \sum_{ijb}\langle mi||bj\rangle(\Gamma^{\mathrm{H}})^{ei}_{bj} - \sum_{iab}\langle ai||be\rangle(\Gamma^{\mathrm{H}})^{ai}_{bm} \\
=&-\sum_i h_{ie}\gamma^{\mathrm{H}}_{im} + \sum_a h_{ma}\gamma^{\mathrm{H}}_{ea} + \frac{1}{2}\sum_{ija}\langle am||ji\rangle(T^{ea}_{ij})^* - \frac{1}{2}\sum_{iab}\langle ab||ei\rangle(T^{ab}_{mi})^* \\
&-\sum_{ijk}\langle ij||ek\rangle\gamma^{\mathrm{H}}_{im}\delta_{jk} - \sum_{ijk}\langle ij||ek\rangle\gamma^{\mathrm{H}}_{jk}\delta_{im} + \sum_{ijb}\langle mi||aj\rangle\gamma^{\mathrm{H}}_{ea}\delta_{ij} - \sum_{iab}\langle ai||be\rangle\gamma^{\mathrm{H}}_{ab}\delta_{im} \\
=&-\sum_i f_{ie}\gamma^{\mathrm{H}}_{im} + \sum_a f_{ma}\gamma^{\mathrm{H}}_{ea} + \frac{1}{2}\sum_{ija}\langle am||ji\rangle(T^{ea}_{ij})^* - \frac{1}{2}\sum_{iab}\langle ab||ei\rangle(T^{ab}_{mi})^* \\
&-\sum_{jk}\langle mj||ek\rangle\gamma^{\mathrm{H}}_{jk} - \sum_{ab}\langle am||be\rangle\gamma^{\mathrm{H}}_{ab} \\
=&\frac{1}{2}\sum_{ija}\langle ma||ij\rangle(T^{ea}_{ij})^* - \frac{1}{2}\sum_{iab}\langle ab||ei\rangle(T^{ab}_{mi})^* - \sum_{jk}\langle mj||ek\rangle\gamma^{\mathrm{H}}_{jk} - \sum_{ab}\langle am||be\rangle\gamma^{\mathrm{H}}_{ab} \\
=&-X_{em}
\end{aligned} \tag{30}
$$

as defined in Gauss 1993 papar [J. Chem. Phys. 99, 3629 (1993)], and this makes the RHS of the z-vector equation. We should address these terms as the orbital gradient.

Therefore, the z-vector equation reads:

$$
\frac{1}{2}z_{em}(\varepsilon_e - \varepsilon_m) + \frac{1}{2}\sum_{ai}(z_{ai}\langle am||ie\rangle + z^*_{ai}\langle im||ae\rangle) = -X_{em} \tag{31}
$$

with X_{em} defined as above.