Rust-based Electronic-structure Simulation Toolkit (REST)

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1 Restricted and Unrestricted Hartree-Fock

Refering to Szabo's book for Restricted and Unrestricted Hartree-Fock formulas

$$\boldsymbol{FC} = \boldsymbol{SC}\varepsilon \tag{1}$$

WARNNING:

$$\sum_j F^{\alpha}_{ij} C^{\alpha}_{jk} = \varepsilon_k \sum_j S_{ij} C^{\alpha}_{jk} \tag{2}$$

With the notation definition of four center integral $(ij|kl)$ of

$$(ij|kl) = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_i^*(1)\phi_j(1) r_{12}^{-1} \phi_k^*(2)\phi_l(2), \tag{3}$$

the close-shell expression of Fock matrix (Similar to Equations 3.148 and 3.154 on Pages 140 and 141) is

$$\begin{aligned} F_{ij} =& H^{core}_{ij} + \sum_{kl} D_{lk} \left[(ij|kl) - \frac{1}{2} (il|kj) \right] \\ =& H^{core}_{ij} + \sum_{kl} D_{kl} \left[(ij|kl) - \frac{1}{2} (ik|jl) \right] \Bigg|_{\mathbf{D}\in\mathbb{R}} \end{aligned} \tag{4}$$

The density matrix in the close shell is defined by (Equation 3.145 on Page 139)

$$\begin{aligned} D_{kl} =& 2 \sum_a^{N/2} C_{ka} C^*_{la} \\ =& 2 \sum_a^{N/2} C_{ka} C_{la} = D_{lk} \Bigg|_{\mathbf{D}\in\mathbb{R}} \end{aligned} \tag{5}$$

The unrestricted expression of Fock matrix (Similar to Equations 3.348 and 3.349 on Page 214) is defined by

$$\begin{aligned} F^{\sigma}_{ij} =& H^{core}_{ij} + \sum_{kl} \left[D^{Tot}_{lk} (ij|kl) - D^{\sigma}_{kl} (il|kj) \right] \\ =& H^{core}_{ij} + \sum_{kl} \left[D^{Tot}_{kl} (ij|kl) - D^{\sigma}_{kl} (ik|jl) \right] \Bigg|_{\mathbf{D}\in\mathbb{R}} \end{aligned} \tag{6}$$

The density matrix in the general cases (Similar to Equations 3.342-343 on Pages 213) is defined by

$$\begin{aligned} D^{\sigma}_{kl} =& \sum_a^{all} W^{\sigma}_a C^{\sigma}_{ka} C^{\sigma *}_{la} = \sum_a^{N_w} W^{\sigma}_a C^{\sigma}_{ka} C^{\sigma *}_{la} = \sum_a^{N_w} W^{\sigma}_a C^{\sigma}_{ka} C^{\sigma}_{la} \Bigg|_{\mathbf{C}\in\mathbb{R}} \\ \mathbf{D}^{\sigma} =& \mathbf{w}\mathbf{C}^{\sigma} \cdot \mathbf{C}^{\sigma H} = \mathbf{w}\mathbf{C}^{\sigma} \cdot \mathbf{C}^{\sigma T} \\ \mathbf{D}^{Tot} =& \sum_{\sigma} \mathbf{D}^{\sigma} = \mathbf{D}^{\alpha} + \mathbf{D}^{\beta} \end{aligned} \tag{7}$$

Here, W^{σ}_a is the electron occupation number of the ath orbital in the σ-spin channel. N_w is the number of orbitals that have non-zero electronic occupation.

For the coulomb term, the RI expression is:

$$\begin{aligned}
J_{ij}^{\sigma} &= \sum_{kl} D_{kl}^{\sigma} \left(ij|kl\right) \\
&= \sum_{kl} \sum_{\mu} D_{kl}^{\sigma} M_{ij}^{\mu} M_{kl}^{\mu} \\
&= \sum_{\mu} M_{ij}^{\mu} \left(\sum_{kl} D_{kl}^{\sigma} M_{kl}^{\mu} \right)
\end{aligned} \tag{8}$$

For the exchange term, the RI expression is

$$\begin{aligned}
K_{ij}^{\sigma} &= \sum_{kl} D_{kl}^{\sigma} \left(ik|jl\right) \\
&= \sum_{kl} \sum_{\mu} D_{kl}^{\sigma} M_{ik}^{\mu} M_{jl}^{\mu} \\
&= \sum_{a}^{all} W_{a}^{\sigma} \sum_{kl} \sum_{\mu} C_{ka}^{\sigma} C_{la}^{\sigma} M_{ik}^{\mu} M_{jl}^{\mu} \\
&= \sum_{\mu} \sum_{a}^{all} W_{a}^{\sigma} \left(\sum_{k} M_{ik}^{\mu} C_{ka} \right) \left(\sum_{l} M_{jl}^{\mu} C_{la} \right) \\
&= \sum_{\mu} \sum_{a}^{N_w} W_{a}^{\sigma} \left(\sum_{k} M_{ik}^{\mu} C_{ka}^{\sigma} \right) \left(\sum_{l} M_{jl}^{\mu} C_{la}^{\sigma} \right) \\
&= \sum_{a}^{N_w} W_{a}^{\sigma} \sum_{\mu} B_{ia}^{\mu\sigma} B_{ja}^{\mu\sigma} \\
&= \sum_{\mu} \sum_{a}^{N_w} W_{a}^{\sigma} B_{ia}^{\mu\sigma} B_{ja}^{\mu\sigma}
\end{aligned} \tag{9}$$

where N_w is the number of orbitals with non-zero electronic occupations.

The total energy of Restricted Hartree-Fock is defined by (Equation 3.184 on Page 150)

$$\begin{aligned}
E_0 &= \left\langle \Psi_0 \middle| \hat{H} \middle| \Psi_0 \right\rangle \\
&= \frac{1}{2} \sum_{i} \sum_{j} D_{ji} \left(H_{ij}^{core} + F_{ij} \right) \\
&= \frac{1}{2} \sum_{i} \sum_{j} D_{ij} \left(H_{ij}^{core} + F_{ij} \right) \Big|_{\mathbf{D}\in\mathbb{R}} \\
&= \frac{1}{2} \sum_{i} \sum_{j} D_{ij}^{*} \left(H_{ij}^{core} + F_{ij} \right) \Big|_{\mathbf{D}\in\mathbb{C}}
\end{aligned} \tag{10}$$

However, for Unrestricted Hartree-Fock method, the total energy expression is (Exercise 3.40 on Page 215)

$$\begin{aligned}
E_0 &= \frac{1}{2} \sum_{i} \sum_{j} \left[D_{ji}^{tot} H_{ij}^{core} + D_{ji}^{\alpha} F_{ij}^{\alpha} + D_{ji}^{\beta} F_{ij}^{\beta} \right] \\
&= \frac{1}{2} \sum_{i} \sum_{j} \left[D_{ij}^{tot} H_{ij}^{core} + D_{ij}^{\alpha} F_{ij}^{\alpha} + D_{ij}^{\beta} F_{ij}^{\beta} \right] \Big|_{\mathbf{D}\in\mathbb{R}} \\
&= \frac{1}{2} \sum_{i} \sum_{j} \left[D_{ij}^{tot*} H_{ij}^{core} + D_{ij}^{\alpha*} F_{ij}^{\alpha} + D_{ij}^{\beta*} F_{ij}^{\beta} \right] \Big|_{\mathbf{D}\in\mathbb{C}}
\end{aligned} \tag{11}$$

2 Numerical integration and DFT

V. Blum et al. Computer Physics Communications 180 (2009) 2175-2196

$$V_{xc,ij} = \int d^3\mathbf{r}\psi_i\mathbf{r}\hat{v}_{xc}(\mathbf{r})\psi_j(\mathbf{r}) \tag{12}$$

3 The Fock exchange potential in reciprocal space

The Fock exchange potential is

$$V_x(\boldsymbol{r},\boldsymbol{r}') = -e^2 \sum_{\boldsymbol{q}m} 2w_{\boldsymbol{q}} f_{\boldsymbol{q}m} \frac{\phi^*_{\boldsymbol{q}m}(\boldsymbol{r}')\phi_{\boldsymbol{q}m}(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|} \tag{13}$$

Here, $\boldsymbol{q}$ is the k point, and therefor $w_{\boldsymbol{q}}$ is the weight of the k-point $\boldsymbol{q}$. m is the band index, and therefore $f_{\boldsymbol{q}m}$ is the occupational number of the band m in the k-point $\boldsymbol{q}$.

To expand the orbital $\phi_{\boldsymbol{q}m}$ in plane wave, we have

$$\phi_{\boldsymbol{q}m}(\boldsymbol{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\boldsymbol{G}} C_{\boldsymbol{q}m}(\boldsymbol{G}) e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} \tag{14}$$

Then the Fock exchange potential evolves

$$V_x(\boldsymbol{r},\boldsymbol{r}') = -\frac{e^2}{\boldsymbol{\Omega}} \sum_{\boldsymbol{q}m} \frac{2w_{\boldsymbol{q}} f_{\boldsymbol{q}m}}{|\boldsymbol{r}-\boldsymbol{r}'|} \sum_{\boldsymbol{G}\boldsymbol{G}'} C^*_{\boldsymbol{q}m}(\boldsymbol{G}') e^{-i(\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}'} C_{\boldsymbol{q}m}(\boldsymbol{G}) e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} \tag{15}$$

Since, we can do the Fourier transform of the Coulomb operator as:

$$\int d^3\boldsymbol{r} \frac{1}{|\boldsymbol{r}|} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} = \frac{4\pi}{|\boldsymbol{q}|^2} \tag{16}$$

And the reverse Fourier transform will be:

$$\frac{1}{|\boldsymbol{r}|} = \frac{1}{(2\pi)^3} \int d^3\boldsymbol{q} \frac{4\pi}{|\boldsymbol{q}|^2} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} = \frac{1}{2\pi^2} \int d^3\boldsymbol{q} \frac{1}{|\boldsymbol{q}|^2} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \tag{17}$$

Insert this equation into the Fock exchange potential

$$\begin{aligned} V_x(\boldsymbol{r},\boldsymbol{r}') &= -\frac{e^2}{2\pi^2\boldsymbol{\Omega}} \sum_{\boldsymbol{q}m} 2w_{\boldsymbol{q}} f_{\boldsymbol{q}m} \int d^3\boldsymbol{k} \frac{1}{|\boldsymbol{k}|^2} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} \\ &\times \sum_{\boldsymbol{G}\boldsymbol{G}'} C^*_{\boldsymbol{q}m}(\boldsymbol{G}') e^{-i(\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}'} C_{\boldsymbol{q}m}(\boldsymbol{G}) e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} \\ &= -\frac{e^2}{2\pi^2\boldsymbol{\Omega}} \int d^3\boldsymbol{k} \sum_{\boldsymbol{G}\boldsymbol{G}'} \frac{1}{|\boldsymbol{k}|^2} \sum_{\boldsymbol{q}m} 2w_{\boldsymbol{q}} f_{\boldsymbol{q}m} \\ &\times C^*_{\boldsymbol{q}m}(\boldsymbol{G}') e^{-i(\boldsymbol{k}+\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}'} C_{\boldsymbol{q}m}(\boldsymbol{G}) e^{i(\boldsymbol{k}+\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} \end{aligned} \tag{18}$$

If we make a change

$$\begin{aligned} \boldsymbol{k}' &= \boldsymbol{k}+\boldsymbol{q} \\ \boldsymbol{k} &= \boldsymbol{q}-\boldsymbol{k}' \end{aligned} \tag{19}$$

Then

$$\begin{aligned} V_x(\boldsymbol{r},\boldsymbol{r}') &= -\frac{e^2}{2\pi^2\boldsymbol{\Omega}} \int d^3\boldsymbol{k}' \sum_{\boldsymbol{G}\boldsymbol{G}'} \frac{1}{|\boldsymbol{q}-\boldsymbol{k}'|^2} \sum_{\boldsymbol{q}m} 2w_{\boldsymbol{q}} f_{\boldsymbol{q}m} \\ &\times C^*_{\boldsymbol{q}m}(\boldsymbol{G}') e^{-i(\boldsymbol{k}'+\boldsymbol{G}')\cdot\boldsymbol{r}'} C_{\boldsymbol{q}m}(\boldsymbol{G}) e^{i(\boldsymbol{k}'+\boldsymbol{G})\cdot\boldsymbol{r}} \\ &= \int d^3\boldsymbol{k} \sum_{\boldsymbol{G}\boldsymbol{G}'} e^{i(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{r}} e^{-i(\boldsymbol{k}+\boldsymbol{G}')\cdot\boldsymbol{r}'} \\ &\times -\frac{e^2}{2\pi^2\boldsymbol{\Omega}} \sum_{\boldsymbol{q}m} 2w_{\boldsymbol{q}} f_{\boldsymbol{q}m} \frac{C^*_{\boldsymbol{q}m}(\boldsymbol{G}') C_{\boldsymbol{q}m}(\boldsymbol{G})}{|\boldsymbol{k}-\boldsymbol{q}|^2} \end{aligned} \tag{20}$$

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4 Laplace transform of opposite-spin MP2

The opposite-spin component of the second-order correlation energy (PT2) is written as

$$E_c^{PT2} = \frac{1}{N_{\boldsymbol{q}}^3} \sum_{\boldsymbol{\delta k k q'}} \sum_{ab}^{occ.} \sum_{nm}^{vir.} \frac{\left| \sum_\mu L_{an}^\mu(\boldsymbol{k}, \boldsymbol{q}) R_{bm}^\mu(\boldsymbol{k'}, \boldsymbol{q'}) \right|^2}{\epsilon_{a\boldsymbol{k}} + \epsilon_{b\boldsymbol{k'}} - \epsilon_{n\boldsymbol{q}} - \epsilon_{m\boldsymbol{q'}}} \tag{21}$$

For simplicity, we define $\Delta_{a\boldsymbol{k},b\boldsymbol{k'}}^{n\boldsymbol{q},m\boldsymbol{q'}} = \epsilon_{n\boldsymbol{q}} + \epsilon_{m\boldsymbol{q'}} - \epsilon_{a\boldsymbol{k}} - \epsilon_{b\boldsymbol{k'}}$. If we use the Laplace transformation

$$\begin{aligned} \frac{1}{\Delta_{a\boldsymbol{k},b\boldsymbol{k'}}^{n\boldsymbol{q},m\boldsymbol{q'}}} &= \int_0^\infty dt e^{-t\Delta_{a\boldsymbol{k},b\boldsymbol{k'}}^{n\boldsymbol{q},m\boldsymbol{q'}}} \\ &= \sum_q^{N_q} w_q e^{-t_q\Delta_{a\boldsymbol{k},b\boldsymbol{k'}}^{n\boldsymbol{q},m\boldsymbol{q'}}} \end{aligned} \tag{22}$$

to expand the opposite-spin PT2 correlation energy, we have

$$\begin{aligned} E_c^{PT2} &= -\frac{1}{N_{\boldsymbol{q}}^3} \sum_{\boldsymbol{\delta k k q'}} \sum_q^{N_q} \sum_{ab}^{occ.} \sum_{nm}^{vir.} w_q \left| \sum_\mu L_{an}^\mu(\boldsymbol{k}, \boldsymbol{q}) R_{bm}^\mu(\boldsymbol{k'}, \boldsymbol{q'}) \right|^2 e^{-t_q\Delta_{a\boldsymbol{k},b\boldsymbol{k'}}^{n\boldsymbol{q},m\boldsymbol{q'}}} \\ &= -\frac{1}{N_{\boldsymbol{q}}^3} \sum_{\boldsymbol{\delta k k q'}} \sum_q^{N_q} \sum_{ab}^{occ.} \sum_{nm}^{vir.} \left| \sum_\mu w_q^{\frac{1}{4}} L_{an}^\mu(\boldsymbol{k}, \boldsymbol{q}) e^{-\frac{1}{2}t_q(\epsilon_{n\boldsymbol{q}} - \epsilon_{a\boldsymbol{k}})} w_q^{\frac{1}{4}} R_{bm}^\mu(\boldsymbol{k'}, \boldsymbol{q'}) e^{-\frac{1}{2}t_q(\epsilon_{m\boldsymbol{q'}} - \epsilon_{b\boldsymbol{k'}})} \right|^2 \\ &= -\frac{1}{N_{\boldsymbol{q}}^3} \sum_{\boldsymbol{\delta k k q'}} \sum_q^{N_q} \sum_{ab}^{occ.} \sum_{nm}^{vir.} \left| \sum_\mu \bar{L}_{an}^\mu(\boldsymbol{k}, \boldsymbol{q}) \bar{R}_{bm}^\mu(\boldsymbol{k'}, \boldsymbol{q'}) \right|^2 \\ &= -\frac{1}{N_{\boldsymbol{q}}^3} \sum_{\boldsymbol{\delta k k q'}} \sum_q^{N_q} \sum_{ab}^{occ.} \sum_{nm}^{vir.} \sum_{\mu v} \bar{L}_{an}^{\mu *}(\boldsymbol{k}, \boldsymbol{q}) \bar{L}_{an}^{v}(\boldsymbol{k}, \boldsymbol{q}) \bar{R}_{bm}^{\mu *}(\boldsymbol{k'}, \boldsymbol{q'}) \bar{R}_{bm}^{v}(\boldsymbol{k'}, \boldsymbol{q'}) \\ &= -\frac{1}{N_{\boldsymbol{q}}^3} \sum_{\boldsymbol{\delta k k q'}} \sum_q^{N_q} \sum_{\mu v} \sum_{an} \bar{L}_{an}^{\mu *}(\boldsymbol{k}, \boldsymbol{q}) \bar{L}_{an}^{v}(\boldsymbol{k}, \boldsymbol{q}) \sum_{bm} \bar{R}_{bm}^{\mu *}(\boldsymbol{k'}, \boldsymbol{q'}) \bar{R}_{bm}^{v}(\boldsymbol{k'}, \boldsymbol{q'}) \\ &= -\frac{1}{N_{\boldsymbol{q}}^3} \sum_{\boldsymbol{\delta k k q'}} \sum_q^{N_q} \sum_{\mu v} \bar{M}_{\mu v}(\boldsymbol{k}, \boldsymbol{q}) \bar{N}_{\mu v}(\boldsymbol{k'}, \boldsymbol{q'}) \end{aligned} \tag{23}$$

with

$$\begin{aligned} \bar{L}_{an}^\mu(\boldsymbol{k}, \boldsymbol{q}) &= w_q^{\frac{1}{4}} L_{an}^\mu(\boldsymbol{k}, \boldsymbol{q}) e^{-\frac{1}{2}t_q(\epsilon_{n\boldsymbol{q}} - \epsilon_{a\boldsymbol{k}})} \\ \bar{R}_{bm}^\mu(\boldsymbol{k'}, \boldsymbol{q'}) &= w_q^{\frac{1}{4}} R_{bm}^\mu(\boldsymbol{k'}, \boldsymbol{q'}) e^{-\frac{1}{2}t_q(\epsilon_{m\boldsymbol{q'}} - \epsilon_{b\boldsymbol{k'}})} \\ \bar{M}_{\mu v}(\boldsymbol{k}, \boldsymbol{q}) &= \sum_{an} \bar{L}_{an}^{\mu *}(\boldsymbol{k}, \boldsymbol{q}) \bar{L}_{an}^{v}(\boldsymbol{k}, \boldsymbol{q}) \\ &= \sum_{an} w^{\frac{1}{2}} e^{-t_q(\epsilon_{n\boldsymbol{q}} - \epsilon_{a\boldsymbol{k}})} L_{an}^{\mu *}(\boldsymbol{k}, \boldsymbol{q}) L_{an}^{v}(\boldsymbol{k}, \boldsymbol{q}) \\ \bar{N}_{\mu v}(\boldsymbol{k'}, \boldsymbol{q'}) &= \sum_{bm} \bar{R}_{bm}^{\mu *}(\boldsymbol{k'}, \boldsymbol{q'}) \bar{R}_{bm}^{v}(\boldsymbol{k'}, \boldsymbol{q'}) \\ &= \sum_{bm} w^{\frac{1}{2}} e^{-t_q(\epsilon_{m\boldsymbol{q'}} - \epsilon_{b\boldsymbol{k'}})} R_{bm}^{\mu *}(\boldsymbol{k'}, \boldsymbol{q'}) R_{bm}^{v}(\boldsymbol{k'}, \boldsymbol{q'}) \end{aligned} \tag{24}$$

5 Memory distribution for periodic-PT2