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:

$$\sum_j F_{ij}^\alpha C_{jk}^\alpha = \varepsilon_k \sum_j S_{ij} C_{jk}^\alpha \tag{2}$$

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

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

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

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

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

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

Here, W_a^σ 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:

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

For the exchange term, the RI expression is

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

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)

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

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

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

2 Restricted and Unrestricted Kohn-Sham

Similar to the Hartree-Fock approximation, the Kohn-Sham approximation has the close-shell expression of Fock matrix

$$
\begin{aligned}
F_{ij}^{KS} =& H_{ij}^{core} + \sum_{kl} D_{lk} \left[(ij|kl) - \frac{\alpha}{2} (il|kj) \right] + \int d^3\mathbf{r} \psi_i(\mathbf{r}) v_{xc}(\rho, \mathbf{r}) \psi_j(\mathbf{r}) \\
=& H_{ij}^{core} + \sum_{kl} D_{kl} \left[(ij|kl) - \frac{\alpha}{2} (ik|jl) \right] \Bigg|_{\mathbf{D}\in\mathbb{R}} + V_{xc,ij}
\end{aligned}
\tag{12}
$$

where α is the mixing factor of exact exchange. For (semi-)local DFAs, like LDA, GGAs and meta-GGAs, $\alpha = 0$ $V_{xc,ij} = \int d^3\mathbf{r} \psi_i(\mathbf{r}) v_{xc}(\rho, \mathbf{r}) \psi_j(\mathbf{r})$ has no analytic expression, which should be integrated numerically:

$$
\begin{aligned}
V_{xc,ij} =& \int d^3\mathbf{r} \psi_i(\mathbf{r}) \hat{v}_{xc}(\mathbf{r}) \psi_j(\mathbf{r}) \\
=& \sum_{at} \int d^3 p_{at}(\mathbf{r}) \psi_i(\mathbf{r}) \hat{v}_{xc}(\mathbf{r}) \psi_j(\mathbf{r}) \\
=& \sum_{at,s,t} w(\mathbf{r}) \psi_i(\mathbf{r}) \hat{v}_{xc}(\mathbf{r}) \psi_j(\mathbf{r})
\end{aligned}
\tag{13}
$$

where $\mathbf{r} = \mathbf{r}(at, s, t)$ and $w(\mathbf{r}) = p_{at}(\mathbf{r}) \cdot w_{rad}(s) \cdot w_{ang}(t)$. The only problem remained is to determine the atom-centered radial and angular grid points and their weights.

The total energy of Restricted Kohn-Sham is defined as

$$
\begin{aligned}
E_0 =& \left\langle \Psi_0 \left| \hat{H}_{noxc} \right| \Psi_0 \right\rangle + E_{xc} \\
=& \frac{1}{2} \sum_i \sum_j D_{ji} \left(H_{ij}^{core} + F_{ij} - V_{xc,ij} \right) + E_{xc} \\
=& \frac{1}{2} \sum_i \sum_j D_{ij} \left(H_{ij}^{core} + F_{ij} \right) - V_{xc} + E_{xc} \Bigg|_{\mathbf{D}\in\mathbb{R}} \\
=& \frac{1}{2} \sum_i \sum_j D_{ij}^* \left(H_{ij}^{core} + F_{ij} \right) - V_{xc} + E_{xc} \Bigg|_{\mathbf{D}\in\mathbb{C}}
\end{aligned}
\tag{14}
$$

where

$$
V_{xc} = \frac{1}{2} \sum_i \sum_j D_{ij} * V_{xc,ij}
\tag{15}
$$

and

$$
\begin{aligned}
E_{xc} =& \int d^3\mathbf{r} \rho(\mathbf{r}) \varepsilon_{xc}(\mathbf{r}) \\
=& \sum_{at,s,t} w(\mathbf{r}) \omega(\mathbf{r}) \rho(\mathbf{r}) \varepsilon_{xc}(\mathbf{r})
\end{aligned}
\tag{16}
$$

3 Numerical integration and DFT

3.1 Basic knowledge of numerical integration for molecules

Generally speaking, the three-dimensional molecular integrals have the form of

$$
I = \int d^3\mathbf{r} F(\mathbf{r})
\tag{17}
$$

4

which can be approximated by discrete numerical summations

$$I = \sum_i A_i F(\mathbf{r}_i) \tag{18}$$

where the $\mathbf{r}_i$ and A_i are discrete integration points and their respective integration weights.

In quantum chemistry, the orbitals no matter occupied or virtual features a cusp at atomic nuclei. In consequence, a better way for this multi-center integration problem is to partition the molecular space into discrete regions according to each atom, namely cellular approaches. In Becke's original proposal [see A. D. Becke J. Chem. Phys. 88 (4), 15], the cellular approach was established according to a partition function $p_{at}(\mathbf{r})$, which was called *relative weight function $\omega_n(\boldsymbol{r})$* in the original paper. This partition function was assigned to each nucleus at in the system for all $\mathbf{r}$ and is normalized at every $\mathbf{r}$,

$$\sum_{at} p_{at}(\mathbf{r}) = 1. \tag{19}$$

Then any arbitrary molecular function $F(\mathbf{r})$ can be decomposed into single-center components $F_n(\mathbf{r})$

$$F(\mathbf{r}) = \sum_{at} p_{at}(\mathbf{r}) F(\mathbf{r}) = \sum_{at} F_{at}(\mathbf{r}). \tag{20}$$

With this partition, the integration I therefore reduces to a sum of single-center integrations I_{at} over each of the nuclei in the system

$$\begin{aligned} I &= \int d^3\mathbf{r} F(\mathbf{r}) = \sum_{at} \int d^3 p_{at}(\mathbf{r}) F(\mathbf{r}) \\ &= \sum_{at} \int d^3 F_{at}(\mathbf{r}) = \sum_{at} I_{at} \end{aligned} \tag{21}$$

The remaining problem is to design a well-behaved partition function $p_{at}(\mathbf{r})$, such that each atomic sub-integration I_{at} can be carried out using standard single-center numerical techniques in spherical polar coordinates:

$$I_{at} = \int_0^\infty dr \int_0^{2\pi} d\theta \int_0^\pi d\phi F_{at}(r, \theta, \phi) r^2 \sin(\theta), \tag{22}$$

This 3D integration can be carried out by treating each of (r, θ, ϕ) independently. The standard choice of the grids for the angular part, i.e. $(\theta \in [0, 2\pi), \phi \in [0, \pi])$ with a fixed r is Lebedev's quadratures. In the original paper, Becke chose the Gauss-Chebyshev quadrature of the second kind for the radial integration (for $r \in [0, +\infty)$).

The current version of REST makes use of the exiting library "numgrid" to prepare the numerical integration grids. However, "numgrid" provides only a very limiting options to generate the grids:

- Partition function p_{at}: only Becke's original algorithm

- Radial grid: 1) Lindh-Malmqvist-Gagliardi; 2) Krack-Köster

- Angular grid: Lebedev

To Do List:

- Partition function p_{at}:
  1) Stratmann-Scuseria-Frisch (`https://doi.org/10.1016/0009-2614(96)00600-8`), which is a standard choice in many packages
  2) Laqua-Kussmann-Ochsenfeld (`https://doi.org/10.1063/1.5049435`).

- Radial grids: MultiExp (`https://doi.org/10.1002/jcc.10211`).

- Pruned grids for SG-0, SG-1, SG-2, and SG-3 standard grids. (refer to the code in PySCF)

3.2 Density integration

In general, the exchange-correlation energy E_{xc} of semi-local density functional approximations and the corresponding exchange-correlation potential V_{xc} depends on density ρ, density gradient $\nabla\rho$ and kinetic density τ. Therefore, we should prepare the tabulated values of these quantities for the numerical integration of E_{xc} and V_{xc}.

The spin density $\rho_\uparrow$ in the atomic-orbital representation is shown:

$$
\begin{aligned}
\rho_\uparrow(\mathbf{r}) &= \sum_a^{occ} W_a^\uparrow |\phi_a^\uparrow(\mathbf{r})|^2 \\
&= \sum_a W_a^\uparrow \sum_{ij} C_{ia}^\uparrow C_{ja}^{*\uparrow} \psi_i(\mathbf{r})\psi_j^*(\mathbf{r}) \\
&= \sum_{ij} \psi_i(\mathbf{r})\psi_j^*(\mathbf{r}) \sum_a W_a^\uparrow C_{ia}^\uparrow C_{ja}^{*\uparrow} \\
&= \sum_{ij} \psi_i(\mathbf{r})\psi_j^*(\mathbf{r}) D_{ij}^\uparrow
\end{aligned}
\tag{23}
$$

In consequence, the tabulated density $P_{\uparrow,s}$ is:

$$
\begin{aligned}
P_{\uparrow s} &= \sum_{ij} \psi_{is} D_{ij}^\uparrow \psi_{js}^* \\
&= \sum_{ij} \psi_{is} W_{js} \\
W &= D \cdot \psi^*
\end{aligned}
\tag{24}
$$

where the index s is associated with the tabulated grids. The corresponding numerical integration for the total electron number is

$$
\begin{aligned}
\int d\mathbf{r}^3 \rho_\uparrow(\mathbf{r}) &= \int d\mathbf{r}^3 \sum_{ij} \psi_i(\mathbf{r})\psi_j^*(\mathbf{r}) D_{ij}^\uparrow \\
&= \sum_s w_s \sum_{ij} \psi_i(\mathbf{r}_s)\psi_j^*(\mathbf{r}_s) D_{ij}^\uparrow
\end{aligned}
\tag{25}
$$

The atomic-orbital basis function ψ_i is a normalized GTO. At first, we consider a normalized Cartesian GTO $\psi_i = G(a, A, l, m, n) = N * g(a, A, l, m, n)$. Here the normalized GTO $G(a, A, l, m, n)$ and the unnormalized one $g(a, A, l, m, n)$ are defined as

$$
\begin{aligned}
g(a, A, l, m, n) &= (x - x_A)^l e^{-a(x-x_A)^2} (y - y_A)^m e^{-a(y-y_A)^2} (z - z_A)^n e^{-a(z-z_A)^2} \\
&= g(a, A, l)g(a, A, m)g(a, A, n) \\
G(a, A, l, m, n) &= G(a, A, l)G(a, A, m)G(a, A, n)
\end{aligned}
\tag{26}
$$

where $g(a, A, l) = (x - x_A)^l e^{-a(x-x_A)^2}$, $G(a, A, l) = N_l g(a, A, l)$, and the normalization factor N is

$$
N = N_l + N_m + N_n = \frac{1}{\sqrt{\int g^2 r^2 dr}} = \sqrt{\frac{2^{2l+3}(l+1)!(2a)^{l+1.5}}{(2l+2)!\sqrt{\pi}}}
\tag{27}
$$

In consequence, a spheric GTO can be expressed as a linear combination of a set of normalized Cartesian GTOs

$$
G^s(a, A, l, m, n) = \sum_{lmn} T_{lmn} G(a, A, l, m, n)
\tag{28}
$$

WARNING: at present, the transition matrix T is implemented for only s,p,d.

For generalized gradient approximations (GGAs), we need

$$\sigma[0] = \nabla\rho_\alpha \cdot \nabla\rho_\alpha$$
$$\sigma[1] = \nabla\rho_\alpha \cdot \nabla\rho_\beta \qquad (29)$$
$$\sigma[2] = \nabla\rho_\beta \cdot \nabla\rho_\beta$$

The key quantity is the density derivative $\nabla\rho_\alpha$

$$\nabla\rho_\alpha = \frac{\partial\rho_\alpha}{\partial x} + \frac{\partial\rho_\alpha}{\partial y} + \frac{\partial\rho_\alpha}{\partial z}$$
$$= \nabla_x\rho_\alpha + \nabla_y\rho_\alpha + \nabla_z\rho_\alpha \qquad (30)$$

where

$$\nabla_x\rho_\alpha = \sum_{ij} D_{ij}^\alpha \left[(\nabla_x\psi_i)\psi_j + \psi_i(\nabla_x\psi_j^*)\right]$$

$$= \sum_{ij} D_{ij}^\alpha \left[(\nabla_x\psi_i)\psi_j + \psi_i(\nabla_x\psi_j)\right]\Bigg|_{\psi\in\mathbb{R}} \qquad (31)$$

$$= 2\sum_{ij} D_{ij}^\alpha (\nabla_x\psi_i)\psi_j \Bigg|_{\psi\in\mathbb{R}}$$

In consequence,

$$\sigma[0] = \nabla\rho_\uparrow \cdot \nabla\rho_\uparrow = \sum_{i=(x,y,z)} \nabla_i\rho_\uparrow \nabla_i\rho_\uparrow \qquad (32)$$

Apparently, $\{\nabla_x\psi_i, \nabla_y\psi_i, \nabla_z\psi_i\}$ are the new variables that should be prepared for the evaluation of σ.

$$\nabla_x\psi_i = \sum_{lmn} \nabla_x G(a, A, l, m, n)$$
$$= \sum_{lmn} N[\nabla_x g(a, A, l)]g(a, A, m)g(a, A, n)$$
$$= \sum_{lmn} N g(a, A, m)g(a, A, n)[\nabla_x g(a, A, l)] \qquad (33)$$
$$= \sum_{lmn} N g(a, A, m)g(a, A, n)[l * g(a, A, l-1) - 2a * g(a, A, l+1)]$$

The last equation in the above formation is a simplification of the following derivations

$$\nabla_x g(a, A, l) = \frac{\partial}{\partial x}(x - x_A)^l e^{-a(x-x_A)^2}$$
$$= l(x - x_A)^{l-1} e^{-a(x-x_A)^2} + (x - x_A)^l e^{-a(x-x_A)^2} \frac{\partial}{\partial x}(-a(x - x_A)^2)$$
$$= l * g(a, A, l-1) - 2a(x - x_A)^{l+1} e^{-a(x-x_A)^2} \qquad (34)$$
$$= l * g(a, A, l-1) - 2a * g(a, A, l+1)$$
$$= \left[l(x - x_A)^{l-1} - 2a(x - x_A)^{l+1}\right] e^{-a(x-x_A)^2}$$

For GGAs, we put the variables $\{\rho, \sigma_i \text{ with } i = (\uparrow\uparrow, \uparrow\downarrow, \downarrow\downarrow)\}$ into libxc and obtain

$$v_\rho = \frac{\partial\varepsilon_{xc}}{\partial\rho}$$
$$v_{\sigma_i} = \frac{\partial\varepsilon_{xc}}{\partial\sigma_i} \qquad (35)$$

For close-shell case (spin-channel $= 1$)

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

$$\int d^3\mathbf{r}\left[\psi_i(\mathbf{r})\hat{v}_\rho(\mathbf{r})\psi_j(\mathbf{r}) + 2\psi_i(\mathbf{r})(\hat{v}_{\sigma_0}(\mathbf{r})\nabla\rho(\mathbf{r}))\cdot\nabla\psi_j(\mathbf{r}) + 2\psi_j(\mathbf{r})(\hat{v}_{\sigma_0}(\mathbf{r})\nabla\rho(\mathbf{r}))\cdot\nabla\psi_i(\mathbf{r})\right]$$

$$(36)$$

3.3 Others

$$V_{xc,ij} = \int d^3\mathbf{r}\psi_i\mathbf{r}\hat{v}_{xc}(\mathbf{r})\psi_j(\mathbf{r}) \tag{37}$$

Following the reference of V. Blum et al. Computer Physics Communications 180 (2009) 2175-2196. (Page 9, starting from Eq. 15), the integration can be formally divided into localized atom-centered pieces by a "partition of unity"

$$V_{xc,ij} = \sum_{at} \int d^3 p_{at}(\mathbf{r})\psi_i\mathbf{r}\hat{v}_{xc}(\mathbf{r})\psi_j(\mathbf{r}) \tag{38}$$

where $p_{at}(\mathbf{r})$ is the atom-centered partition function, which is defined by

$$p_{at}(\mathbf{r}) = \frac{g_{at}(\mathbf{r})}{\sum_{at'} g_{at'}(\mathbf{r})} \tag{39}$$

The normalizing sum over at' in the denominator runs over all atoms in the system, and g_{at} *is a strongly peaked function about its originating atom.*

Under this formula, each single-atom integrand is integrated on its own grid of N_r spherical integration shells $r(s)$ ($s = 1, \ldots, N_r$) with the corresponding weight of $w_{rad}(s)$. Meanwhile the angular integration points Ω_t with tabulated integration weights $w_{ang}(t)$ are distributed so as to integrate angular momentum functions up to a certain order exactly (often called Lebedev grids).

Here is the transformation for l=4 and spherical harmonic GTOs $G_i(4, x)$

$$G_i(4,0) = G(0,0,4) + \frac{3}{8}(G(4,0,0) + G(0,4,0)) - \frac{3\sqrt{3}}{\sqrt{35}}(G(2,0,2) + G(0,2,2) - \frac{1}{4}G(2,2,0))$$

$$G_i(4,1) = \sqrt{\frac{5}{7}}(G(1,0,3) + iG(0,1,3)) - \frac{3\sqrt{5}}{4\sqrt{7}}(G(3,0,1) + iG(0,3,1)) - \frac{3}{4\sqrt{7}}(G(1,2,1) + iG(2,1,1))$$

$$G_i(4,-1) = \sqrt{\frac{5}{7}}(G(1,0,3) - iG(0,1,3)) - \frac{3\sqrt{5}}{4\sqrt{7}}(G(3,0,1) - iG(0,3,1)) - \frac{3}{4\sqrt{7}}(G(1,2,1) - iG(2,1,1))$$

$$G_i(4,2) = \frac{3\sqrt{3}}{2\sqrt{14}}(G(2,0,2) - G(0,2,2)) + \frac{3i}{\sqrt{14}}G(1,1,2)$$
$$- \frac{\sqrt{5}}{4\sqrt{2}}(G(4,0,0) - G(0,4,0)) - \frac{i\sqrt{5}}{2\sqrt{14}}(G(3,1,0) + G(1,3,0))$$

$$G_i(4,-2) = \frac{3\sqrt{3}}{2\sqrt{14}}(G(2,0,2) - G(0,2,2)) - \frac{3i}{\sqrt{14}}G(1,1,2)$$
$$- \frac{\sqrt{5}}{4\sqrt{2}}(G(4,0,0) - G(0,4,0)) + \frac{i\sqrt{5}}{2\sqrt{14}}(G(3,1,0) + G(1,3,0))$$

$$G_i(4,3) = \frac{\sqrt{5}}{4}(G(3,0,1) - iG(0,3,1)) - \frac{3}{4}(G(1,2,1) - iG(2,1,1))$$

$$G_i(4,-3) = \frac{\sqrt{5}}{4}(G(3,0,1) + iG(0,3,1)) - \frac{3}{4}(G(1,2,1) + iG(2,1,1))$$

$$G_i(4,4) = \frac{\sqrt{35}}{8\sqrt{2}}(G(4,0,0) + G(0,4,0)) - \frac{3\sqrt{3}}{4\sqrt{2}}G(2,2,0) + i\sqrt{\frac{5}{8}}(G(3,1,0) - G(1,3,0))$$

$$G_i(4,-4) = \frac{\sqrt{35}}{8\sqrt{2}}(G(4,0,0) + G(0,4,0)) - \frac{3\sqrt{3}}{4\sqrt{2}}G(2,2,0) - i\sqrt{\frac{5}{8}}(G(3,1,0) - G(1,3,0))$$

$$(40)$$

The real spheric GTOs $G_r(4, x)$ are than defined as

$$
\begin{aligned}
G_r(4,0) =& G_i(4,0) \\
G_r(4,1) =& \frac{1}{\sqrt{2}} \left(G_i(4,1) + G_i(4,-1) \right) \\
=& \frac{2}{\sqrt{2}} \left(\sqrt{\frac{5}{7}} G(1,0,3) - \frac{3\sqrt{5}}{4\sqrt{7}} G(3,0,1) - \frac{3}{4\sqrt{7}} G(1,2,1) \right) \\
=& \sqrt{\frac{10}{7}} G(1,0,3) - \frac{3\sqrt{10}}{4\sqrt{7}} G(3,0,1) - \frac{3\sqrt{2}}{4\sqrt{7}} G(1,2,1) \\
G_r(4,-1) =& \frac{-i}{\sqrt{2}} \left(G_i(4,1) - G_i(4,-1) \right) \\
=& \frac{2}{\sqrt{2}} \left(\sqrt{\frac{5}{7}} G(0,1,3) - \frac{3\sqrt{5}}{4\sqrt{7}} G(0,3,1) - \frac{3}{4\sqrt{7}} G(2,1,1) \right) \\
=& \sqrt{\frac{10}{7}} G(0,1,3) - \frac{3\sqrt{10}}{4\sqrt{7}} G(0,3,1) - \frac{3\sqrt{2}}{4\sqrt{7}} G(2,1,1) \\
G_r(4,2) =& \frac{1}{\sqrt{2}} \left(G_i(4,2) + G_i(4,-2) \right) \\
=& \frac{2}{\sqrt{2}} \left(\frac{3\sqrt{3}}{2\sqrt{14}} (G(2,0,2) - G(0,2,2)) - \frac{\sqrt{5}}{4\sqrt{2}} (G(4,0,0) - G(0,4,0)) \right) \\
=& \frac{3\sqrt{3}}{2\sqrt{7}} (G(2,0,2) - G(0,2,2)) - \frac{\sqrt{5}}{4} (G(4,0,0) - G(0,4,0)) \qquad (41) \\
G_r(4,-2) =& \frac{-i}{\sqrt{2}} \left(G_i(4,2) - G_i(4,-2) \right) \\
=& \frac{-2i}{\sqrt{2}} \left(\frac{3i}{\sqrt{14}} G(1,1,2) - \frac{i\sqrt{5}}{2\sqrt{14}} (G(3,1,0) + G(1,3,0)) \right) \\
=& \frac{3}{\sqrt{7}} G(1,1,2) - \frac{\sqrt{5}}{2\sqrt{7}} (G(3,1,0) + G(1,3,0)) \\
G_r(4,3) =& \frac{1}{\sqrt{2}} \left(G_i(4,3) + G_i(4,-3) \right) \\
=& \frac{2}{\sqrt{2}} \left(\frac{\sqrt{5}}{4} G(3,0,1) - \frac{3}{4} G(1,2,1) \right) \\
=& \frac{\sqrt{10}}{4} G(3,0,1) - \frac{3\sqrt{2}}{4} G(1,2,1) \\
G_r(4,-3) =& \frac{-i}{\sqrt{2}} \left(G_i(4,3) - G_i(4,-3) \right) \\
=& \frac{-2i}{\sqrt{2}} \left(-\frac{i\sqrt{5}}{4} G(0,3,1) + \frac{3i}{4} G(2,1,1) \right) \\
=& -\frac{\sqrt{10}}{4} G(0,3,1) + \frac{3\sqrt{2}}{4} G(2,1,1)
\end{aligned}
$$

$$
\begin{aligned}
G_r(4,4) =& \frac{1}{\sqrt{2}}\left(G_i(4,4) + G_i(4,-4)\right) \\
=& \frac{2}{\sqrt{2}}\left(\frac{\sqrt{35}}{8\sqrt{2}}(G(4,0,0) + G(0,4,0)) - \frac{3\sqrt{3}}{4\sqrt{2}}G(2,2,0)\right) \\
=& \frac{\sqrt{35}}{8}(G(4,0,0) + G(0,4,0)) - \frac{3\sqrt{3}}{4}G(2,2,0) \\
G_r(4,-4) =& \frac{-i}{\sqrt{2}}\left(G_i(4,4) - G_i(4,-4)\right) \\
=& \frac{-2i}{\sqrt{2}}\left(i\sqrt{\frac{5}{8}}(G(3,1,0) - G(1,3,0))\right) \\
=& \frac{\sqrt{5}}{2}(G(3,1,0) - G(1,3,0))
\end{aligned}
\tag{42}
$$

4 The Fock exchange potential in reciprocal space

The Fock exchange potential is

$$V_x(\boldsymbol{r}, \boldsymbol{r}') = -e^2 \sum_{\boldsymbol{q}m} 2w_{\boldsymbol{q}} f_{\boldsymbol{q}m} \frac{\phi_{\boldsymbol{q}m}^*(\boldsymbol{r}')\phi_{\boldsymbol{q}m}(\boldsymbol{r})}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{43}$$

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

$$\phi_{\boldsymbol{q}m}(\boldsymbol{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\boldsymbol{G}} C_{\boldsymbol{q}m}(\boldsymbol{G}) e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} \tag{44}$$

Then the Fock exchange potential evolves

$$V_x(\boldsymbol{r}, \boldsymbol{r}') = -\frac{e^2}{\Omega} \sum_{\boldsymbol{q}m} \frac{2w_{\boldsymbol{q}} f_{\boldsymbol{q}m}}{|\boldsymbol{r} - \boldsymbol{r}'|} \sum_{\boldsymbol{G}\boldsymbol{G}'} C_{\boldsymbol{q}m}^*(\boldsymbol{G}') e^{-i(\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}'} C_{\boldsymbol{q}m}(\boldsymbol{G}) e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} \tag{45}$$

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

$$\int d^3\boldsymbol{r} \frac{1}{|\boldsymbol{r}|} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} = \frac{4\pi}{|\boldsymbol{q}|^2} \tag{46}$$

And the reverse Fourier transform will be:

$$\frac{1}{|\boldsymbol{r}|} = \frac{1}{(2\pi)^3} \int d^3\boldsymbol{q} \frac{4\pi}{|\boldsymbol{q}|^2} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} = \frac{1}{2\pi^2} \int d^3\boldsymbol{q} \frac{1}{|\boldsymbol{q}|^2} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \tag{47}$$

Insert this equation into the Fock exchange potential

$$
\begin{aligned}
V_x(\boldsymbol{r}, \boldsymbol{r}') &= -\frac{e^2}{2\pi^2\Omega} \sum_{\boldsymbol{q}m} 2w_{\boldsymbol{q}} f_{\boldsymbol{q}m} \int d^3\boldsymbol{k} \frac{1}{|\boldsymbol{k}|^2} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} \\
&\quad \times \sum_{\boldsymbol{G}\boldsymbol{G}'} C_{\boldsymbol{q}m}^*(\boldsymbol{G}') e^{-i(\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}'} C_{\boldsymbol{q}m}(\boldsymbol{G}) e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} \\
&= -\frac{e^2}{2\pi^2\Omega} \int d^3\boldsymbol{k} \sum_{\boldsymbol{G}\boldsymbol{G}'} \frac{1}{|\boldsymbol{k}|^2} \sum_{\boldsymbol{q}m} 2w_{\boldsymbol{q}} f_{\boldsymbol{q}m} \\
&\quad \times C_{\boldsymbol{q}m}^*(\boldsymbol{G}') e^{-i(\boldsymbol{k}+\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}'} C_{\boldsymbol{q}m}(\boldsymbol{G}) e^{i(\boldsymbol{k}+\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}
\end{aligned}
\tag{48}
$$

If we make a change

$$
\begin{aligned}
\boldsymbol{k}' &= \boldsymbol{k} + \boldsymbol{q} \\
\boldsymbol{k} &= \boldsymbol{q} - \boldsymbol{k}'
\end{aligned}
\tag{49}
$$

Then

$$
\begin{aligned}
V_x(\boldsymbol{r}, \boldsymbol{r}') &= -\frac{e^2}{2\pi^2\Omega} \int d^3\boldsymbol{k}' \sum_{\boldsymbol{G}\boldsymbol{G}'} \frac{1}{|\boldsymbol{q}-\boldsymbol{k}'|^2} \sum_{\boldsymbol{q}m} 2w_{\boldsymbol{q}} f_{\boldsymbol{q}m} \\
&\quad \times C_{\boldsymbol{q}m}^*(\boldsymbol{G}') e^{-i(\boldsymbol{k}'+\boldsymbol{G}')\cdot\boldsymbol{r}'} C_{\boldsymbol{q}m}(\boldsymbol{G}) e^{i(\boldsymbol{k}'+\boldsymbol{G})\cdot\boldsymbol{r}} \\
&= \int d^3\boldsymbol{k} \sum_{\boldsymbol{G}\boldsymbol{G}'} e^{i(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{r}} e^{-i(\boldsymbol{k}+\boldsymbol{G}')\cdot\boldsymbol{r}'} \\
&\quad \times -\frac{e^2}{2\pi^2\Omega} \sum_{\boldsymbol{q}m} 2w_{\boldsymbol{q}} f_{\boldsymbol{q}m} \frac{C_{\boldsymbol{q}m}^*(\boldsymbol{G}') C_{\boldsymbol{q}m}(\boldsymbol{G})}{|\boldsymbol{k}-\boldsymbol{q}|^2}
\end{aligned}
\tag{50}
$$

?

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5 Laplace transform of opposite-spin MP2

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

$$E_c^{PT2} = \frac{1}{N_q^3} \sum_{\delta \boldsymbol{k} \boldsymbol{k} \boldsymbol{q}'} \sum_{ab}^{occ.} \sum_{nm}^{vir.} \frac{\left| \sum_\mu L_{an}^\mu(\boldsymbol{k}, \boldsymbol{q}) R_{bm}^\mu(\boldsymbol{k}', \boldsymbol{q}') \right|^2}{\epsilon_{a\boldsymbol{k}} + \epsilon_{b\boldsymbol{k}'} - \epsilon_{n\boldsymbol{q}} - \epsilon_{m\boldsymbol{q}'}} \tag{51}$$

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

$$
\begin{aligned}
\frac{1}{\Delta_{a\boldsymbol{k},b\boldsymbol{k}'}^{n\boldsymbol{q},m\boldsymbol{q}'}} &= \int_0^\infty dt e^{-t \Delta_{a\boldsymbol{k},b\boldsymbol{k}'}^{n\boldsymbol{q},m\boldsymbol{q}'}} \\
&= \sum_q^{N_q} w_q e^{-t_q \Delta_{a\boldsymbol{k},b\boldsymbol{k}'}^{n\boldsymbol{q},m\boldsymbol{q}'}}
\end{aligned}
\tag{52}
$$

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

$$
\begin{aligned}
E_c^{PT2} &= -\frac{1}{N_q^3} \sum_{\delta \boldsymbol{k} \boldsymbol{k} \boldsymbol{q}'} \sum_q^{N_q} \sum_{ab}^{occ.} \sum_{nm}^{vir.} w_q \left| \sum_\mu L_{an}^\mu(\boldsymbol{k}, \boldsymbol{q}) R_{bm}^\mu(\boldsymbol{k}', \boldsymbol{q}') \right|^2 e^{-t_q \Delta_{a\boldsymbol{k},b\boldsymbol{k}'}^{n\boldsymbol{q},m\boldsymbol{q}'}} \\
&= -\frac{1}{N_q^3} \sum_{\delta \boldsymbol{k} \boldsymbol{k} \boldsymbol{q}'} \sum_q^{N_q} \sum_{ab}^{occ.} \sum_{nm}^{vir.} \left| \sum_\mu w_q^{\frac{1}{4}} L_{an}^\mu(\boldsymbol{k}, \boldsymbol{q}) e^{-\frac{1}{2} t_q (\epsilon_{n\boldsymbol{q}} - \epsilon_{a\boldsymbol{k}})} w_q^{\frac{1}{4}} R_{bm}^\mu(\boldsymbol{k}', \boldsymbol{q}') e^{-\frac{1}{2} t_q (\epsilon_{m\boldsymbol{q}'} - \epsilon_{b\boldsymbol{k}'})} \right|^2 \\
&= -\frac{1}{N_q^3} \sum_{\delta \boldsymbol{k} \boldsymbol{k} \boldsymbol{q}'} \sum_q^{N_q} \sum_{ab}^{occ.} \sum_{nm}^{vir.} \left| \sum_\mu \bar{L}_{an}^\mu(\boldsymbol{k}, \boldsymbol{q}) \bar{R}_{bm}^\mu(\boldsymbol{k}', \boldsymbol{q}') \right|^2 \\
&= -\frac{1}{N_q^3} \sum_{\delta \boldsymbol{k} \boldsymbol{k} \boldsymbol{q}'} \sum_q^{N_q} \sum_{ab}^{occ.} \sum_{nm}^{vir.} \sum_{\mu v} \bar{L}_{an}^{\mu*}(\boldsymbol{k}, \boldsymbol{q}) \bar{L}_{an}^v(\boldsymbol{k}, \boldsymbol{q}) \bar{R}_{bm}^{\mu*}(\boldsymbol{k}', \boldsymbol{q}') \bar{R}_{bm}^v(\boldsymbol{k}', \boldsymbol{q}') \\
&= -\frac{1}{N_q^3} \sum_{\delta \boldsymbol{k} \boldsymbol{k} \boldsymbol{q}'} \sum_q^{N_q} \sum_{\mu v} \sum_{an} \bar{L}_{an}^{\mu*}(\boldsymbol{k}, \boldsymbol{q}) \bar{L}_{an}^v(\boldsymbol{k}, \boldsymbol{q}) \sum_{bm} \bar{R}_{bm}^{\mu*}(\boldsymbol{k}', \boldsymbol{q}') \bar{R}_{bm}^v(\boldsymbol{k}', \boldsymbol{q}') \\
&= -\frac{1}{N_q^3} \sum_{\delta \boldsymbol{k} \boldsymbol{k} \boldsymbol{q}'} \sum_q^{N_q} \sum_{\mu v} \bar{M}_{\mu v}(\boldsymbol{k}, \boldsymbol{q}) \bar{N}_{\mu v}(\boldsymbol{k}', \boldsymbol{q}')
\end{aligned}
\tag{53}
$$

with

$$
\begin{aligned}
\bar{L}_{an}^\mu(\boldsymbol{k}, \boldsymbol{q}) &= w_q^{\frac{1}{4}} L_{an}^\mu(\boldsymbol{k}, \boldsymbol{q}) e^{-\frac{1}{2} t_q (\epsilon_{n\boldsymbol{q}} - \epsilon_{a\boldsymbol{k}})} \\
\bar{R}_{bm}^\mu(\boldsymbol{k}', \boldsymbol{q}') &= w_q^{\frac{1}{4}} R_{bm}^\mu(\boldsymbol{k}', \boldsymbol{q}') e^{-\frac{1}{2} t_q (\epsilon_{m\boldsymbol{q}'} - \epsilon_{b\boldsymbol{k}'})} \\
\bar{M}_{\mu v}(\boldsymbol{k}, \boldsymbol{q}) &= \sum_{an} \bar{L}_{an}^{\mu*}(\boldsymbol{k}, \boldsymbol{q}) \bar{L}_{an}^v(\boldsymbol{k}, \boldsymbol{q}) \\
&= \sum_{an} w^{\frac{1}{2}} e^{-t_q (\epsilon_{n\boldsymbol{q}} - \epsilon_{a\boldsymbol{k}})} L_{an}^{\mu*}(\boldsymbol{k}, \boldsymbol{q}) L_{an}^v(\boldsymbol{k}, \boldsymbol{q}) \\
\bar{N}_{\mu v}(\boldsymbol{k}', \boldsymbol{q}') &= \sum_{bm} \bar{R}_{bm}^{\mu*}(\boldsymbol{k}', \boldsymbol{q}') \bar{R}_{bm}^v(\boldsymbol{k}', \boldsymbol{q}') \\
&= \sum_{bm} w^{\frac{1}{2}} e^{-t_q (\epsilon_{m\boldsymbol{q}'} - \epsilon_{b\boldsymbol{k}'})} R_{bm}^{\mu*}(\boldsymbol{k}', \boldsymbol{q}') R_{bm}^v(\boldsymbol{k}', \boldsymbol{q}')
\end{aligned}
\tag{54}
$$

6 Memory distribution for periodic-PT2