

Rust-based Electronic-structure Simulation Toolkit (REST)

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1 Restricted and Unrestricted Hartree-Fock

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

$$\mathbf{FC} = \mathbf{SC}\varepsilon \quad (1)$$

WARNING:

$$\sum_j F_{ij}^\alpha C_{jk}^\alpha = \varepsilon_k \sum_j S_{ij} C_{jk}^\alpha \quad (2)$$

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

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

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

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

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

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

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

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

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

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

Here, W_a^σ is the electron occupation number of the a th 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

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

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)

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

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

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

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:

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

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

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

where

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

and

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

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

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

which can be approximated by discrete numerical summations

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

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* $\omega_n(\mathbf{r})$ 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} ,

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

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

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

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

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

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:

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

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](https://doi.org/10.1016/0009-2614(96)00600-8)), which is a standard choice in many packages
 - 2) Laqua-Kusmann-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 ρ_{\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

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

Another way to evaluate density more efficiently is

$$\begin{aligned}
\rho_{\uparrow s} = \rho_{\uparrow}(\mathbf{r}_s) &= \sum_a^{occ} W_a^{\uparrow} |\phi_a^{\uparrow}(\mathbf{r}_s)|^2 \\
&= \sum_a W_a^{\uparrow} \sum_{ij} C_{ia}^{\uparrow} C_{ja}^{*\uparrow} \psi_i(\mathbf{r}_s) \psi_j^*(\mathbf{r}_s) \\
&= \sum_a \sum_i W_a^{\uparrow, \frac{1}{2}} C_{ia}^{\uparrow} \psi_i(\mathbf{r}_s) \sum_j W_a^{\uparrow, \frac{1}{2}} C_{ja}^{*\uparrow} \psi_j^*(\mathbf{r}_s)
\end{aligned} \tag{26}$$

Here, we define

$$\begin{aligned}
M_{as}^{\uparrow} &= \sum_i W_a^{\uparrow, \frac{1}{2}} C_{ia}^{\uparrow} \psi_i(\mathbf{r}_s) \\
&= \sum_i N_{ia}^{\uparrow} \psi_{is} \\
&= N^{\uparrow T} \cdot \Psi
\end{aligned} \tag{27}$$

Then

$$\begin{aligned}\rho_{\uparrow s} &= \sum_a \sum_i W_a^{\uparrow, \frac{1}{2}} C_{ia}^{\uparrow} \psi_i(\mathbf{r}_s) \sum_j W_a^{\uparrow, \frac{1}{2}} C_{ja}^{*\uparrow} \psi_j^*(\mathbf{r}_s) \\ &= \sum_a M_{as}^{\uparrow} * M_{as}^{\uparrow}\end{aligned}\quad (28)$$

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

$$\begin{aligned}g(a, A, l, m, n) &= (x - x_A)^l e^{-a(x-x_A)^2} (y - y_A)^m e^{-a(y-y_A)^2} (z - z_A)^n e^{-a(z-z_A)^2} \\ &= g(a, A, l) g(a, A, m) g(a, A, n) \\ G(a, A, l, m, n) &= G(a, A, l) G(a, A, m) G(a, A, n)\end{aligned}\quad (29)$$

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

$$N = N_l + N_m + N_n = \frac{1}{\sqrt{\int g^2 r^2 dr}} = \sqrt{\frac{2^{2l+3} (l+1)! (2a)^{l+1.5}}{(2l+2)! \sqrt{\pi}}}\quad (30)$$

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

$$G^s(a, A, l, m, n) = \sum_{lmn} T_{lmn} G(a, A, l, m, n)\quad (31)$$

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

For generalized gradient approximations (GGAs), we need

$$\begin{aligned}\sigma[0] &= \nabla \rho_\alpha \cdot \nabla \rho_\alpha \\ \sigma[1] &= \nabla \rho_\alpha \cdot \nabla \rho_\beta \\ \sigma[2] &= \nabla \rho_\beta \cdot \nabla \rho_\beta\end{aligned}\quad (32)$$

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

$$\begin{aligned}\nabla \rho_\alpha &= \frac{\partial \rho_\alpha}{\partial x} + \frac{\partial \rho_\alpha}{\partial y} + \frac{\partial \rho_\alpha}{\partial z} \\ &= \nabla_x \rho_\alpha + \nabla_y \rho_\alpha + \nabla_z \rho_\alpha\end{aligned}\quad (33)$$

where

$$\begin{aligned}\nabla_x \rho_\alpha &= \sum_{ij} D_{ij}^\alpha [(\nabla_x \psi_i) \psi_j + \psi_i (\nabla_x \psi_j^*)] \\ &= \sum_{ij} D_{ij}^\alpha [(\nabla_x \psi_i) \psi_j + \psi_i (\nabla_x \psi_j)] \Big|_{\psi \in \mathbb{R}} \\ &= 2 \sum_{ij} D_{ij}^\alpha (\nabla_x \psi_i) \psi_j \Big|_{\psi \in \mathbb{R}}\end{aligned}\quad (34)$$

Another way to evaluate the density derivitavative more efficiently:

$$\begin{aligned}\nabla_x \rho_\alpha &= 2 \sum_{ij} D_{ij}^\alpha (\nabla_x \psi_i) \psi_j \\ &= 2 \sum_{ij} \sum_a W_a^\alpha C_{ia}^\alpha C_{ja}^\alpha (\nabla_x \psi_i) \psi_j \\ &= 2 \sum_a W_a^\alpha \sum_i C_{ia}^\alpha (\nabla_x \psi_i) \sum_j C_{ja}^\alpha \psi_j \\ &= 2 \sum_a \sum_i \sqrt{W_a^\alpha} C_{ia}^\alpha (\nabla_x \psi_i) \sum_j \sqrt{W_a^\alpha} C_{ja}^\alpha \psi_j\end{aligned}\quad (35)$$

In consequence,

$$\sigma[0] = \nabla \rho_{\uparrow} \cdot \nabla \rho_{\uparrow} = \sum_{i=(x,y,z)} \nabla_i \rho_{\uparrow} \nabla_i \rho_{\uparrow} \quad (36)$$

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 .

$$\begin{aligned} \nabla_x \psi_i &= \sum_{lmn} \nabla_x G(a, A, l, m, n) \\ &= \sum_{lmn} N[\nabla_x g(a, A, l)] g(a, A, m) g(a, A, n) \\ &= \sum_{lmn} N g(a, A, m) g(a, A, n) [\nabla_x g(a, A, l)] \\ &= \sum_{lmn} N g(a, A, m) g(a, A, n) [l * g(a, A, l-1) - 2a * g(a, A, l+1)] \end{aligned} \quad (37)$$

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

$$\begin{aligned} \nabla_x g(a, A, l) &= \frac{\partial}{\partial x} (x - x_A)^l e^{-a(x-x_A)^2} \\ &= l(x - x_A)^{l-1} e^{-a(x-x_A)^2} + (x - x_A)^l e^{-a(x-x_A)^2} \frac{\partial}{\partial x} (-a(x - x_A)^2) \\ &= l * g(a, A, l-1) - 2a(x - x_A)^{l+1} e^{-a(x-x_A)^2} \\ &= l * g(a, A, l-1) - 2a * g(a, A, l+1) \\ &= [l(x - x_A)^{l-1} - 2a(x - x_A)^{l+1}] e^{-a(x-x_A)^2} \end{aligned} \quad (38)$$

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

$$\begin{aligned} v_{\rho} &= \frac{\partial \varepsilon_{xc}}{\partial \rho} \\ v_{\sigma_i} &= \frac{\partial \varepsilon_{xc}}{\partial \sigma_i} \end{aligned} \quad (39)$$

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

$$\begin{aligned} V_{xc,ij} &= \int d^3 \mathbf{r} \psi_i(\mathbf{r}) \hat{v}_{xc}(\mathbf{r}) \psi_j(\mathbf{r}) \\ &\quad \int d^3 \mathbf{r} [\psi_i(\mathbf{r}) \hat{v}_{\rho}(\mathbf{r}) \psi_j(\mathbf{r}) + 2\psi_i(\mathbf{r}) (\hat{v}_{\sigma_0}(\mathbf{r}) \nabla \rho(\mathbf{r})) \cdot \nabla \psi_j(\mathbf{r}) + 2\psi_j(\mathbf{r}) (\hat{v}_{\sigma_0}(\mathbf{r}) \nabla \rho(\mathbf{r})) \cdot \nabla \psi_i(\mathbf{r})] \end{aligned} \quad (40)$$

3.3 Others

$$V_{xc,ij} = \int d^3 \mathbf{r} \psi_i(\mathbf{r}) \hat{v}_{xc}(\mathbf{r}) \psi_j(\mathbf{r}) \quad (41)$$

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”

$$V_{xc,ij} = \sum_{at} \int d^3 \mathbf{r} p_{at}(\mathbf{r}) \psi_i(\mathbf{r}) \hat{v}_{xc}(\mathbf{r}) \psi_j(\mathbf{r}) \quad (42)$$

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

$$p_{at}(\mathbf{r}) = \frac{g_{at}(\mathbf{r})}{\sum_{at'} g_{at'}(\mathbf{r})} \quad (43)$$

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 $r(s)$ ($s = 1, \dots, N_r$) 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 $G_i(4, x)$

$$\begin{aligned} G_i(4, 0) &= G(0, 0, 4) + \frac{3}{8}(G(4, 0, 0) + G(0, 4, 0)) - \frac{3\sqrt{3}}{\sqrt{35}}(G(2, 0, 2) + G(0, 2, 2) - \frac{1}{4}G(2, 2, 0)) \\ G_i(4, 1) &= \sqrt{\frac{5}{7}}(G(1, 0, 3) + iG(0, 1, 3)) - \frac{3\sqrt{5}}{4\sqrt{7}}(G(3, 0, 1) + iG(0, 3, 1)) - \frac{3}{4\sqrt{7}}(G(1, 2, 1) + iG(2, 1, 1)) \\ G_i(4, -1) &= \sqrt{\frac{5}{7}}(G(1, 0, 3) - iG(0, 1, 3)) - \frac{3\sqrt{5}}{4\sqrt{7}}(G(3, 0, 1) - iG(0, 3, 1)) - \frac{3}{4\sqrt{7}}(G(1, 2, 1) - iG(2, 1, 1)) \\ G_i(4, 2) &= \frac{3\sqrt{3}}{2\sqrt{14}}(G(2, 0, 2) - G(0, 2, 2)) + \frac{3i}{\sqrt{14}}G(1, 1, 2) \\ &\quad - \frac{\sqrt{5}}{4\sqrt{2}}(G(4, 0, 0) - G(0, 4, 0)) - \frac{i\sqrt{5}}{2\sqrt{14}}(G(3, 1, 0) + G(1, 3, 0)) \\ G_i(4, -2) &= \frac{3\sqrt{3}}{2\sqrt{14}}(G(2, 0, 2) - G(0, 2, 2)) - \frac{3i}{\sqrt{14}}G(1, 1, 2) \\ &\quad - \frac{\sqrt{5}}{4\sqrt{2}}(G(4, 0, 0) - G(0, 4, 0)) + \frac{i\sqrt{5}}{2\sqrt{14}}(G(3, 1, 0) + G(1, 3, 0)) \\ G_i(4, 3) &= \frac{\sqrt{5}}{4}(G(3, 0, 1) - iG(0, 3, 1)) - \frac{3}{4}(G(1, 2, 1) - iG(2, 1, 1)) \\ G_i(4, -3) &= \frac{\sqrt{5}}{4}(G(3, 0, 1) + iG(0, 3, 1)) - \frac{3}{4}(G(1, 2, 1) + iG(2, 1, 1)) \\ G_i(4, 4) &= \frac{\sqrt{35}}{8\sqrt{2}}(G(4, 0, 0) + G(0, 4, 0)) - \frac{3\sqrt{3}}{4\sqrt{2}}G(2, 2, 0) + i\sqrt{\frac{5}{8}}(G(3, 1, 0) - G(1, 3, 0)) \\ G_i(4, -4) &= \frac{\sqrt{35}}{8\sqrt{2}}(G(4, 0, 0) + G(0, 4, 0)) - \frac{3\sqrt{3}}{4\sqrt{2}}G(2, 2, 0) - i\sqrt{\frac{5}{8}}(G(3, 1, 0) - G(1, 3, 0)) \end{aligned} \quad (44)$$

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

$$\begin{aligned}
G_r(4, 0) &= G_i(4, 0) \\
G_r(4, 1) &= \frac{1}{\sqrt{2}} (G_i(4, 1) + G_i(4, -1)) \\
&= \frac{2}{\sqrt{2}} \left(\sqrt{\frac{5}{7}} G(1, 0, 3) - \frac{3\sqrt{5}}{4\sqrt{7}} G(3, 0, 1) - \frac{3}{4\sqrt{7}} G(1, 2, 1) \right) \\
&= \sqrt{\frac{10}{7}} G(1, 0, 3) - \frac{3\sqrt{10}}{4\sqrt{7}} G(3, 0, 1) - \frac{3\sqrt{2}}{4\sqrt{7}} G(1, 2, 1) \\
G_r(4, -1) &= \frac{-i}{\sqrt{2}} (G_i(4, 1) - G_i(4, -1)) \\
&= \frac{2}{\sqrt{2}} \left(\sqrt{\frac{5}{7}} G(0, 1, 3) - \frac{3\sqrt{5}}{4\sqrt{7}} G(0, 3, 1) - \frac{3}{4\sqrt{7}} G(2, 1, 1) \right) \\
&= \sqrt{\frac{10}{7}} G(0, 1, 3) - \frac{3\sqrt{10}}{4\sqrt{7}} G(0, 3, 1) - \frac{3\sqrt{2}}{4\sqrt{7}} G(2, 1, 1) \\
G_r(4, 2) &= \frac{1}{\sqrt{2}} (G_i(4, 2) + G_i(4, -2)) \\
&= \frac{2}{\sqrt{2}} \left(\frac{3\sqrt{3}}{2\sqrt{14}} (G(2, 0, 2) - G(0, 2, 2)) - \frac{\sqrt{5}}{4\sqrt{2}} (G(4, 0, 0) - G(0, 4, 0)) \right) \\
&= \frac{3\sqrt{3}}{2\sqrt{7}} (G(2, 0, 2) - G(0, 2, 2)) - \frac{\sqrt{5}}{4} (G(4, 0, 0) - G(0, 4, 0)) \tag{45} \\
G_r(4, -2) &= \frac{-i}{\sqrt{2}} (G_i(4, 2) - G_i(4, -2)) \\
&= \frac{-2i}{\sqrt{2}} \left(\frac{3i}{\sqrt{14}} G(1, 1, 2) - \frac{i\sqrt{5}}{2\sqrt{14}} (G(3, 1, 0) + G(1, 3, 0)) \right) \\
&= \frac{3}{\sqrt{7}} G(1, 1, 2) - \frac{\sqrt{5}}{2\sqrt{7}} (G(3, 1, 0) + G(1, 3, 0)) \\
G_r(4, 3) &= \frac{1}{\sqrt{2}} (G_i(4, 3) + G_i(4, -3)) \\
&= \frac{2}{\sqrt{2}} \left(\frac{\sqrt{5}}{4} G(3, 0, 1) - \frac{3}{4} G(1, 2, 1) \right) \\
&= \frac{\sqrt{10}}{4} G(3, 0, 1) - \frac{3\sqrt{2}}{4} G(1, 2, 1) \\
G_r(4, -3) &= \frac{-i}{\sqrt{2}} (G_i(4, 3) - G_i(4, -3)) \\
&= \frac{-2i}{\sqrt{2}} \left(-\frac{i\sqrt{5}}{4} G(0, 3, 1) + \frac{3i}{4} G(2, 1, 1) \right) \\
&= -\frac{\sqrt{10}}{4} G(0, 3, 1) + \frac{3\sqrt{2}}{4} G(2, 1, 1)
\end{aligned}$$

$$\begin{aligned}
G_r(4, 4) &= \frac{1}{\sqrt{2}} (G_i(4, 4) + G_i(4, -4)) \\
&= \frac{2}{\sqrt{2}} \left(\frac{\sqrt{35}}{8\sqrt{2}} (G(4, 0, 0) + G(0, 4, 0)) - \frac{3\sqrt{3}}{4\sqrt{2}} G(2, 2, 0) \right) \\
&= \frac{\sqrt{35}}{8} (G(4, 0, 0) + G(0, 4, 0)) - \frac{3\sqrt{3}}{4} G(2, 2, 0) \\
G_r(4, -4) &= \frac{-i}{\sqrt{2}} (G_i(4, 4) - G_i(4, -4)) \\
&= \frac{-2i}{\sqrt{2}} \left(i\sqrt{\frac{5}{8}} (G(3, 1, 0) - G(1, 3, 0)) \right) \\
&= \frac{\sqrt{5}}{2} (G(3, 1, 0) - G(1, 3, 0))
\end{aligned} \tag{46}$$

4 The Fock exchange potential in reciprocal space

The Fock exchange potential is

$$V_x(\mathbf{r}, \mathbf{r}') = -e^2 \sum_{\mathbf{q}m} 2w_{\mathbf{q}} f_{\mathbf{q}m} \frac{\phi_{\mathbf{q}m}^*(\mathbf{r}') \phi_{\mathbf{q}m}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \quad (47)$$

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

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

$$\phi_{\mathbf{q}m}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} C_{\mathbf{q}m}(\mathbf{G}) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \quad (48)$$

Then the Fock exchange potential evolves

$$V_x(\mathbf{r}, \mathbf{r}') = -\frac{e^2}{\Omega} \sum_{\mathbf{q}m} \frac{2w_{\mathbf{q}} f_{\mathbf{q}m}}{|\mathbf{r} - \mathbf{r}'|} \sum_{\mathbf{G}\mathbf{G}'} C_{\mathbf{q}m}^*(\mathbf{G}') e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'} C_{\mathbf{q}m}(\mathbf{G}) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \quad (49)$$

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

$$\int d^3\mathbf{r} \frac{1}{|\mathbf{r}|} e^{-i\mathbf{q}\cdot\mathbf{r}} = \frac{4\pi}{|\mathbf{q}|^2} \quad (50)$$

And the reverse Fourier transform will be:

$$\frac{1}{|\mathbf{r}|} = \frac{1}{(2\pi)^3} \int d^3\mathbf{q} \frac{4\pi}{|\mathbf{q}|^2} e^{i\mathbf{q}\cdot\mathbf{r}} = \frac{1}{2\pi^2} \int d^3\mathbf{q} \frac{1}{|\mathbf{q}|^2} e^{i\mathbf{q}\cdot\mathbf{r}} \quad (51)$$

Insert this equation into the Fock exchange potential

$$\begin{aligned} V_x(\mathbf{r}, \mathbf{r}') &= -\frac{e^2}{2\pi^2\Omega} \sum_{\mathbf{q}m} 2w_{\mathbf{q}} f_{\mathbf{q}m} \int d^3\mathbf{k} \frac{1}{|\mathbf{k}|^2} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \\ &\quad \times \sum_{\mathbf{G}\mathbf{G}'} C_{\mathbf{q}m}^*(\mathbf{G}') e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'} C_{\mathbf{q}m}(\mathbf{G}) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \\ &= -\frac{e^2}{2\pi^2\Omega} \int d^3\mathbf{k} \sum_{\mathbf{G}\mathbf{G}'} \frac{1}{|\mathbf{k}|^2} \sum_{\mathbf{q}m} 2w_{\mathbf{q}} f_{\mathbf{q}m} \\ &\quad \times C_{\mathbf{q}m}^*(\mathbf{G}') e^{-i(\mathbf{k}+\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'} C_{\mathbf{q}m}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \end{aligned} \quad (52)$$

If we make a change

$$\begin{aligned} \mathbf{k}' &= \mathbf{k} + \mathbf{q} \\ \mathbf{k} &= \mathbf{q} - \mathbf{k}' \end{aligned} \quad (53)$$

Then

$$\begin{aligned} V_x(\mathbf{r}, \mathbf{r}') &= -\frac{e^2}{2\pi^2\Omega} \int d^3\mathbf{k}' \sum_{\mathbf{G}\mathbf{G}'} \frac{1}{|\mathbf{q} - \mathbf{k}'|^2} \sum_{\mathbf{q}m} 2w_{\mathbf{q}} f_{\mathbf{q}m} \\ &\quad \times C_{\mathbf{q}m}^*(\mathbf{G}') e^{-i(\mathbf{k}'+\mathbf{G}')\cdot\mathbf{r}'} C_{\mathbf{q}m}(\mathbf{G}) e^{i(\mathbf{k}'+\mathbf{G})\cdot\mathbf{r}} \\ &= \int d^3\mathbf{k} \sum_{\mathbf{G}\mathbf{G}'} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} e^{-i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}'} \\ &\quad \times -\frac{e^2}{2\pi^2\Omega} \sum_{\mathbf{q}m} 2w_{\mathbf{q}} f_{\mathbf{q}m} \frac{C_{\mathbf{q}m}^*(\mathbf{G}') C_{\mathbf{q}m}(\mathbf{G})}{|\mathbf{k} - \mathbf{q}|^2} \end{aligned} \quad (54)$$

?

5 Laplace transform of opposite-spin MP2

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

$$E_c^{PT2} = \frac{1}{N_q^3} \sum_{\mathbf{q}} \sum_{\delta \mathbf{k} \mathbf{k}'}^{occ.} \sum_{ab}^{vir.} \sum_{nm} \frac{\left| \sum_{\mu} L_{an}^{\mu}(\mathbf{k}, \mathbf{q}) R_{bm}^{\mu}(\mathbf{k}', \mathbf{q}') \right|^2}{\epsilon_{a\mathbf{k}} + \epsilon_{b\mathbf{k}'} - \epsilon_{n\mathbf{q}} - \epsilon_{m\mathbf{q}'}} \quad (55)$$

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

$$\begin{aligned} \frac{1}{\Delta_{a\mathbf{k}, b\mathbf{k}'}^{n\mathbf{q}, m\mathbf{q}'}} &= \int_0^{\infty} dt e^{-t \Delta_{a\mathbf{k}, b\mathbf{k}'}^{n\mathbf{q}, m\mathbf{q}'}} \\ &= \sum_q^{N_q} w_q e^{-t_q \Delta_{a\mathbf{k}, b\mathbf{k}'}^{n\mathbf{q}, m\mathbf{q}'}} \end{aligned} \quad (56)$$

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

$$\begin{aligned} E_c^{PT2} &= -\frac{1}{N_q^3} \sum_{\mathbf{q}} \sum_{\delta \mathbf{k} \mathbf{k}'}^{N_q} \sum_{ab}^{occ.} \sum_{nm}^{vir.} w_q \left| \sum_{\mu} L_{an}^{\mu}(\mathbf{k}, \mathbf{q}) R_{bm}^{\mu}(\mathbf{k}', \mathbf{q}') \right|^2 e^{-t_q \Delta_{a\mathbf{k}, b\mathbf{k}'}^{n\mathbf{q}, m\mathbf{q}'}} \\ &= -\frac{1}{N_q^3} \sum_{\mathbf{q}} \sum_{\delta \mathbf{k} \mathbf{k}'}^{N_q} \sum_{ab}^{occ.} \sum_{nm}^{vir.} \left| \sum_{\mu} w_q^{\frac{1}{4}} L_{an}^{\mu}(\mathbf{k}, \mathbf{q}) e^{-\frac{1}{2} t_q (\epsilon_{n\mathbf{q}} - \epsilon_{a\mathbf{k}})} w_q^{\frac{1}{4}} R_{bm}^{\mu}(\mathbf{k}', \mathbf{q}') e^{-\frac{1}{2} t_q (\epsilon_{m\mathbf{q}'} - \epsilon_{b\mathbf{k}'})} \right|^2 \\ &= -\frac{1}{N_q^3} \sum_{\mathbf{q}} \sum_{\delta \mathbf{k} \mathbf{k}'}^{N_q} \sum_{ab}^{occ.} \sum_{nm}^{vir.} \left| \sum_{\mu} \bar{L}_{an}^{\mu}(\mathbf{k}, \mathbf{q}) \bar{R}_{bm}^{\mu}(\mathbf{k}', \mathbf{q}') \right|^2 \\ &= -\frac{1}{N_q^3} \sum_{\mathbf{q}} \sum_{\delta \mathbf{k} \mathbf{k}'}^{N_q} \sum_{ab}^{occ.} \sum_{nm}^{vir.} \sum_{\mu\nu} \bar{L}_{an}^{\mu*}(\mathbf{k}, \mathbf{q}) \bar{L}_{an}^{\nu}(\mathbf{k}, \mathbf{q}) \bar{R}_{bm}^{\mu*}(\mathbf{k}', \mathbf{q}') \bar{R}_{bm}^{\nu}(\mathbf{k}', \mathbf{q}') \\ &= -\frac{1}{N_q^3} \sum_{\mathbf{q}} \sum_{\delta \mathbf{k} \mathbf{k}'}^{N_q} \sum_{q} \sum_{\mu\nu} \bar{L}_{an}^{\mu*}(\mathbf{k}, \mathbf{q}) \bar{L}_{an}^{\nu}(\mathbf{k}, \mathbf{q}) \sum_{bm} \bar{R}_{bm}^{\mu*}(\mathbf{k}', \mathbf{q}') \bar{R}_{bm}^{\nu}(\mathbf{k}', \mathbf{q}') \\ &= -\frac{1}{N_q^3} \sum_{\mathbf{q}} \sum_{\delta \mathbf{k} \mathbf{k}'}^{N_q} \sum_{\mu\nu} \bar{M}_{\mu\nu}(\mathbf{k}, \mathbf{q}) \bar{N}_{\mu\nu}(\mathbf{k}', \mathbf{q}') \end{aligned} \quad (57)$$

with

$$\begin{aligned} \bar{L}_{an}^{\mu}(\mathbf{k}, \mathbf{q}) &= w_q^{\frac{1}{4}} L_{an}^{\mu}(\mathbf{k}, \mathbf{q}) e^{-\frac{1}{2} t_q (\epsilon_{n\mathbf{q}} - \epsilon_{a\mathbf{k}})} \\ \bar{R}_{bm}^{\mu}(\mathbf{k}', \mathbf{q}') &= w_q^{\frac{1}{4}} R_{bm}^{\mu}(\mathbf{k}', \mathbf{q}') e^{-\frac{1}{2} t_q (\epsilon_{m\mathbf{q}'} - \epsilon_{b\mathbf{k}'})} \\ \bar{M}_{\mu\nu}(\mathbf{k}, \mathbf{q}) &= \sum_{an} \bar{L}_{an}^{\mu*}(\mathbf{k}, \mathbf{q}) \bar{L}_{an}^{\nu}(\mathbf{k}, \mathbf{q}) \\ &= \sum_{an} w^{\frac{1}{2}} e^{-t_q (\epsilon_{n\mathbf{q}} - \epsilon_{a\mathbf{k}})} L_{an}^{\mu*}(\mathbf{k}, \mathbf{q}) L_{an}^{\nu}(\mathbf{k}, \mathbf{q}) \\ \bar{N}_{\mu\nu}(\mathbf{k}', \mathbf{q}') &= \sum_{bm} \bar{R}_{bm}^{\mu*}(\mathbf{k}', \mathbf{q}') \bar{R}_{bm}^{\nu}(\mathbf{k}', \mathbf{q}') \\ &= \sum_{bm} w^{\frac{1}{2}} e^{-t_q (\epsilon_{m\mathbf{q}'} - \epsilon_{b\mathbf{k}'})} R_{bm}^{\mu*}(\mathbf{k}', \mathbf{q}') R_{bm}^{\nu}(\mathbf{k}', \mathbf{q}') \end{aligned} \quad (58)$$

6 Memory distribution for periodic-PT2