Some Density Fitting Techniques for Molecular and Periodic Systems, and Application to Exchange Operators

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Contents

In this note, we provide a succinct review on the density fitting techniques, from molecular systems to periodic systems.

1 Density Fitting for Approximating Two-electron Integrals

We firstly follow the discussion in the note [She10]. The two-electron integrals $(pq|rs)$ is used to denote the following double integration

$$(pq|rs) = \int \mathrm{d}\boldsymbol{r_1} \int \mathrm{d}\boldsymbol{r_2}\ \phi_p^*(\boldsymbol{r_1})\phi_q(\boldsymbol{r_1})\frac{1}{r_{12}}\phi_r^*(\boldsymbol{r_2})\phi_s(\boldsymbol{r_2}). \tag{1}$$

This can also be viewed as the repulsion between the two electron densities $\rho_{pq} := \phi_p^*\phi_q$ and $\rho_{rs} := \phi_r^*\phi_s$.

The idea is to approximate the densities using an auxiliary basis set $\{\chi_P\}_P$ as

$$\rho_{pq}(\boldsymbol{r}) \approx \overline{\rho}_{pq}(\boldsymbol{r}) := \sum_P d_{pq}^P \chi_P(\boldsymbol{r}). \tag{2}$$

A common functional to minimize is

$$\Delta_{pq} := \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 \frac{[(\rho_{pq}-\overline{\rho}_{pq})(\boldsymbol{r}_1)][(\rho_{pq}-\overline{\rho}_{pq})(\boldsymbol{r}_2)]}{r_{12}} = (\rho_{pq}-\overline{\rho}_{pq}|\rho_{pq}-\overline{\rho}_{pq}), \tag{3}$$

where the inner product is induced by the operator $\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}$. By the linearity of inner products, Δ_{pq} can be written as

$$(\rho_{pq}|\rho_{pq}) - 2\Re(\rho_{pq}|\overline{\rho}_{pq}) + (\overline{\rho}_{pq}|\overline{\rho}_{pq}). \tag{4}$$

Plug in the coefficients, we have

$$\Delta_{pq} = (\rho_{pq}|\rho_{pq}) - \sum_P d_{pq}^P (\chi_P|\rho_{pq}) - \sum_P (d_{pq}^P)^* (\rho_{pq}|\chi_P) + \sum_{PQ} (d_{pq}^P)^* (d_{pq}^Q)(\chi_Q|\chi_P). \tag{5}$$

Take the derivative with respect to $(d_{pq}^P)^*$ and set that as zero, we know

$$(\rho_{pq}|\chi_P) = \sum_Q d_{pq}^Q (\chi_Q|\chi_P), \tag{6}$$

indicating the right coefficients should be

$$d_{pq}^Q = \sum_P [J^{-1}]_{PQ} (\rho_{pq}|\chi_P), \tag{7}$$

where the matrix J is constructed as $J_{PQ} := (\chi_Q|\chi_P)$.

Remark 1. *Minimizing the functional Δ_{pq} guarantees that*

$$(\chi_P|\rho_{pq} - \overline{\rho}_{pq}) = 0. \tag{8}$$

This can be intuitively understood as Δ_{pq} minimizes the residual by projecting the original density to the space spanned by the auxiliary basis set.

Since we already know the optimal representation of the coefficients under the functional Δ_{pq}, the ERI $(pq|rs)$ can thus be approximated as

$$(pq|rs) \approx (\sum_P d_{pq}^P \chi_P|\rho_{rs}) = \sum_P d_{pq}^P (\chi_P|\rho_{rs}) = \sum_{PQ} [J^{-1}]_{QP} (\rho_{pq}|\chi_Q)(\chi_P|\rho_{rs}). \tag{9}$$

Note that we do not need to expand ρ_{rs} due to the reason in Remark 1.

Equation 9 can be factorized as

$$\sum_{PQ} (\rho_{pq}|\chi_Q)(\sum_R [J^{-1/2}]_{QR}[J^{-1/2}]_{RP})(\chi_P|\rho_{rs}) =: \sum_R (b_{pq}^R)^* b_{rs}^R, \tag{10}$$

where $b_{rs}^R = \sum_P [J^{-1/2}]_{RP} (\chi_P|\rho_{rs})$.

As an application, we may take a look at the MP2. The MP2 correlation enery is written as

$$E_{\text{corr}}^{\text{MP2}} := \sum_{iajb} (ia|jb) \frac{2(ia|jb) - (ib|ja)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \tag{11}$$

and the consuming part is the evaluation of $(ia|jb) = \sum_{iajb} C_\mu^i C_\nu^a C_\rho^j C_\sigma^b (\mu\nu|\rho\sigma)$ where C is molecular coefficients after SCF, i, j are representing occupied bands and a, b are representing virtual bands. It is clear that to evaluate $(ia|jb)$ requires $\mathcal{O}(N_{\text{occ}} N_{\text{AO}}^4)$ operations. Under the density fitting framework, $(ia|jb)$ is

$$(ia|jb) \approx \sum_R (b_{ia}^R)^* b_{jb}^R, \tag{12}$$

which takes $\mathcal{O}(N_{\text{occ}}^2 N_{\text{vir}}^2 N_{\text{aux}})$ operations and would provide considerable speedup.

2 Concentric Atomic Density Fitting

CADF(Concentric Atomic Density Fitting) is to construct the densities using only auxiliary functions that centered at the same atom as the composite function μ and ν [HSV17]. Now we use a subscript to note some

orbital is assigned to a specific atom. For example, μ_a is an atomic orbital assigned to atom a, and the same also applies for the auxiliary functions. Now the fitting equation 6 is changed into

$$(Y_{ab}|\mu_a\nu_b) = \sum_{X\in(ab)} C^{X_{ab}}_{\mu_a\nu_b}(Y_{ab}|X_{ab}), \tag{13}$$

where the density $\mu_a\nu_b$ is only approximated by those auxiliary functions assigned to atoms a and b. The two electron ERI can thus be simply written as

$$(\mu_a\nu_b|\lambda_c\sigma_d) \approx \sum_{X\in(ab),Y\in(cd)} (C^{X_{ab}}_{\mu_a\nu_b})^* C^{Y_{cd}}_{\lambda_c\sigma_d}(X_{ab}|Y_{cd}). \tag{14}$$

Unrigorously, we may write $\mu_a\nu_b = \sum_{X\in(ab)} C^{X_{ab}}_{\mu_a\nu_b} X_{ab} + r_{\mu_a\nu_b}$ where $r_{\mu_a\nu_b}$ is representing the residual. Then the density-fitted error is

$$(\mu_a\nu_b|\lambda_c\sigma_d) - \sum_{X\in(ab),Y\in(cd)} (C^{X_{ab}}_{\mu_a\nu_b})^* C^{Y_{cd}}_{\lambda_c\sigma_d}(X_{ab}|Y_{cd}) = (\mu_a\nu_b|r_{\lambda_c\sigma_d}) + (r_{\mu_a\nu_b}|\lambda_c\sigma_d) + (r_{\mu_a\nu_b}|r_{\lambda_c\sigma_d}). \tag{15}$$

In the mean time, if we only approximate the ERI on one side,

$$(\mu_a\nu_b|\lambda_c\sigma_d) = \sum_{X\in(ab)} (C^{X_{ab}}_{\mu_a\nu_b})^* (X_{ab}|\lambda_c\sigma_d) + (r_{\mu_a\nu_b}|\lambda_c\sigma_d). \tag{16}$$

Thus the error terms $(\mu_a\nu_b|r_{\lambda_c\sigma_d})$ and $(r_{\mu_a\nu_b}|\lambda_c\sigma_d)$ can be canceled out by

$$(\mu_a\nu_b|\lambda_c\sigma_d) \approx \sum_{X\in(ab)} (C^{X_{ab}}_{\mu_a\nu_b})^* (X_{ab}|\lambda_c\sigma_d) + \sum_{Y\in(cd)} C^{Y_{cd}}_{\lambda_c\sigma_d}(\mu_a\nu_b|Y_{cd}) - \sum_{X\in(ab),Y\in(cd)} (C^{X_{ab}}_{\mu_a\nu_b})^* C^{Y_{cd}}_{\lambda_c\sigma_d}(X_{ab}|Y_{cd}). \tag{17}$$

Equation 17 has the problem of making $(\mu_a\nu_b|\lambda_c\sigma_d)$ losing the semi-positive definiteness. A way of treating this is introduced in [HSV14].

3 Pair Atomic Resolution of the Identity

Now we use the notation from [MEHG14]. The goal here is to build the exchange operator efficiently via density fitting. For an RI quantity, we denote it as

$$|\widetilde{\mu\nu}\rangle = \sum_Q C^{\mu\nu}_Q |Q\rangle . \tag{18}$$

The Fock exchange can be built as

$$\begin{aligned} K_{\mu\nu} &= \sum_{\lambda\sigma}(\mu\lambda|\nu\sigma)P_{\lambda\sigma} = \sum_{\lambda\sigma}\left[(\widetilde{\mu\lambda}|\nu\sigma) + (\mu\lambda|\widetilde{\nu\sigma}) - (\widetilde{\mu\lambda}|\widetilde{\nu\sigma})\right] P_{\lambda\sigma} \\ &= \sum_{\lambda\sigma}\left[(\widetilde{\mu\lambda}|\nu\sigma) - \frac{1}{2}(\widetilde{\mu\lambda}|\widetilde{\nu\sigma})\right] P_{\lambda\sigma} + \sum_{\lambda\sigma}\left[(\widetilde{\nu\lambda}|\mu\sigma) - \frac{1}{2}(\widetilde{\nu\lambda}|\widetilde{\mu\sigma})\right] P_{\lambda\sigma} \\ &=: L_{\mu\nu} + L_{\nu\mu}, \end{aligned} \tag{19}$$

Thus we only need to construct L. Expand the coefficients for the density fitting out in L, we have

$$L_{\mu\nu} = \sum_{\lambda\sigma}\left[\sum_Q C^{\mu\lambda}_Q(\nu\sigma|Q) - \frac{1}{2}\sum_{QR} C^{\mu\lambda}_Q C^{\nu\sigma}_R (R|Q)\right] P_{\lambda\sigma} = \sum_{\lambda\sigma,Q} C^{\mu\lambda}_Q \left[(\nu\sigma|Q) - \frac{1}{2}\sum_R C^{\nu\sigma}_R (R|Q)\right] P_{\lambda\sigma}. \tag{20}$$

The cost of the contraction above is $\mathcal{O}(N^3_{AO} N_{aux})$.

One may use the fact that $P_{\lambda\sigma} = \sum_i M_i^\lambda M_i^\sigma$ (assuming real orbitals), thus

$$L_{\mu\nu} = \sum_{i,Q} \left[C_Q^{\mu\lambda} M_i^\lambda\right] \left[\sum_\sigma M_i^\sigma \left((\nu\sigma|Q) - \frac{1}{2}\sum_R C_R^{\nu\sigma}(R|Q)\right)\right] =: \sum_{i,Q} D_i^{\mu Q} H_i^{\nu Q}. \tag{21}$$

The contraction above uses $\mathcal{O}(N_{AO}^2 N_{occ} N_{aux})$ operations.

We would expect that $N_{occ} < N_{AO}$ thus the new contraction above would be cheaper than that in Equation 20.

Remark 2. *As mentioned in [MEHG14], there could be sparsity in the tensor $D_i^{\mu Q}$ but it is not convenient to utilize.*

4 Periodic Gaussian Density Fitting

Consider an AO basis $\{\phi_\mu^{\boldsymbol{m}}\}$ where $\phi_\mu^{\boldsymbol{m}}(\boldsymbol{r}) = \phi_\mu^{\boldsymbol{0}}(\boldsymbol{r} - \boldsymbol{m})$, we have

$$\phi_\mu^{\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{m}} e^{\imath \boldsymbol{k}\cdot\boldsymbol{m}} \phi_\mu^{\boldsymbol{m}}(\boldsymbol{r}). \tag{22}$$

For $\rho_{\mu\nu}^{\boldsymbol{k_1 k_2}} := (\phi_\mu^{\boldsymbol{k_1}})^* \phi_\nu^{\boldsymbol{k_2}}$, the ERIs are defined as

$$(\rho_{\mu\nu}^{\boldsymbol{k_1 k_2}}|\rho_{\lambda\sigma}^{\boldsymbol{k_3 k_4}}) := \int_\Omega \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}_3} \mathrm{d}\boldsymbol{r_2}\ \rho_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{r_1}) \frac{1}{r_{12}} \rho_{\lambda\sigma}^{\boldsymbol{k_3 k_4}}(\boldsymbol{r_2}), \tag{23}$$

where Ω is the unit cell.

Remark 3. *It is clear that $\rho_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{r} + \boldsymbol{m}) = e^{\imath(\boldsymbol{k_2} - \boldsymbol{k_1})\cdot\boldsymbol{m}} \rho_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{r})$. It is reasonable to require*

$$\int_\Omega \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}_3} \mathrm{d}\boldsymbol{r_2}\ \rho_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{r_1}) \frac{1}{r_{12}} \rho_{\lambda\sigma}^{\boldsymbol{k_3 k_4}}(\boldsymbol{r_2}) = \int_{\Omega+\boldsymbol{m}} \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}_3} \mathrm{d}\boldsymbol{r_2}\ \rho_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{r_1}) \frac{1}{r_{12}} \rho_{\lambda\sigma}^{\boldsymbol{k_3 k_4}}(\boldsymbol{r_2}) \tag{24}$$

since for an infinitely large crystal the unit cell is not "unique". Meanwhile,

$$\begin{aligned} &\int_{\Omega+\boldsymbol{m}} \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}_3} \mathrm{d}\boldsymbol{r_2}\ \rho_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{r_1}) \frac{1}{r_{12}} \rho_{\lambda\sigma}^{\boldsymbol{k_3 k_4}}(\boldsymbol{r_2}) \\ &= \int_\Omega \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}_3} \mathrm{d}\boldsymbol{r_2}\ \rho_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{r_1} - \boldsymbol{m}) \frac{1}{r_{12}} \rho_{\lambda\sigma}^{\boldsymbol{k_3 k_4}}(\boldsymbol{r_2} - \boldsymbol{m}) = e^{\imath(\boldsymbol{k_2} - \boldsymbol{k_1} + \boldsymbol{k_4} - \boldsymbol{k_3})\cdot\boldsymbol{m}} (\rho_{\mu\nu}^{\boldsymbol{k_1 k_2}}|\rho_{\lambda\sigma}^{\boldsymbol{k_3 k_4}}). \end{aligned} \tag{25}$$

Which means that we should require that

$$e^{\imath(\boldsymbol{k_2} - \boldsymbol{k_1} + \boldsymbol{k_4} - \boldsymbol{k_3})\cdot\boldsymbol{m}} = 1. \tag{26}$$

This automatically holds if we do not do any twisted average.

To reduce computational complexity, the density $\rho_{\mu\nu}^{\boldsymbol{k_1 k_2}}$ is approximated by

$$\rho_{\mu\nu}^{\boldsymbol{k_1 k_2}} \approx \sum_Q d_{Q\mu\nu}^{\boldsymbol{k_1 k_2}} \chi_Q^{\boldsymbol{k_{12}}} \tag{27}$$

where $\boldsymbol{k_{12}} = \boldsymbol{k_2} - \boldsymbol{k_1}$.

Remark 4. *There is only one $\boldsymbol{k}$ index on χ since $\rho_{\mu\nu}^{\boldsymbol{k_1 k_2}}$ behaves periodic except the phase factor depending on $\boldsymbol{k}_{12}$.*

Minimizing the residual under $(\cdot|\cdot)$ induced by some operator $w(r_{12})$ would lead to some linear system for $d_{Q\mu\nu}^{\boldsymbol{k_1 k_2}}$ as

$$\sum_Q J_{PQ}^{\boldsymbol{k}_{12}} d_{Q\mu\nu}^{\boldsymbol{k1 k_2}} = V_{P\mu\nu}^{\boldsymbol{k_1 k_2}}, \tag{28}$$

where $J_{PQ}^{\boldsymbol{k}} := (\chi_P^{\boldsymbol{k}}|w|\chi_Q^{\boldsymbol{k}})$ and $V_{P\mu\nu}^{\boldsymbol{k_1 k_2}} := (\chi_P^{\boldsymbol{k}_{12}}|w|\rho_{\mu\nu}^{\boldsymbol{k_1 k_2}})$.

5 The Three Center Integral

The most expensive step here is to compute $V_{P_{\mu\nu}}^{\boldsymbol{k_1 k_2}}$. One can deal with it in either the reciprocal space,

$$\begin{aligned}
V_{P_{\mu\nu}}^{\boldsymbol{k_1 k_2}} &= (\chi_P^{\boldsymbol{k_{12}}}|w|P_{\mu\nu}^{\boldsymbol{k_1 k_2}}) = \int_\Omega \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{r_2}\ (\chi_P^{\boldsymbol{k_{12}}})^*(\boldsymbol{r}_1) w(r_{12}) \rho_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{r}_2) \\
&= \int_\Omega \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{r_2}\ (e^{\imath \boldsymbol{k_{12}}\cdot\boldsymbol{r}_1} \sum_{\boldsymbol{G_1}} \tilde{\chi}_P^{\boldsymbol{k_{12}}}(\boldsymbol{G_1}) e^{\imath \boldsymbol{G_1}\cdot\boldsymbol{r}_1})^* w(r_{12}) e^{\imath \boldsymbol{k_{12}}\cdot\boldsymbol{r}_2} \sum_{\boldsymbol{G}_2} \tilde{\rho}_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{G}_2) e^{\imath \boldsymbol{G}_2\cdot\boldsymbol{r}_2} \\
&= \sum_{\boldsymbol{G_1 G_2}} \tilde{\chi}_P^{\boldsymbol{k_{12}}}(\boldsymbol{G_1}) \tilde{\rho}_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{G}_2) \int_\Omega \mathrm{d}\boldsymbol{r}_1 \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{r}_2 e^{-\imath \boldsymbol{G_1}\cdot\boldsymbol{r}_1} e^{\imath \boldsymbol{G}_2\cdot\boldsymbol{r}_2} e^{\imath \boldsymbol{k_{12}}\cdot(\boldsymbol{r}_2-\boldsymbol{r}_1)} w(r_{12}) \\
&= \sum_{\boldsymbol{G_1 G_2}} \tilde{\chi}_P^{\boldsymbol{k_{12}}}(\boldsymbol{G_1}) \tilde{\rho}_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{G}_2) \int_\Omega \mathrm{d}\boldsymbol{r}_1 e^{-\imath(\boldsymbol{G_1}-\boldsymbol{G_2})\cdot\boldsymbol{r}_1} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{r}_2 e^{\imath(\boldsymbol{G}_2+\boldsymbol{k_{12}})\cdot(\boldsymbol{r}_2-\boldsymbol{r}_1)} w(r_{12}) \\
&= \sum_{\boldsymbol{G}} \tilde{\chi}_P^{\boldsymbol{k_{12}}}(-\boldsymbol{G}) \tilde{\rho}_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{G}) \tilde{w}(\boldsymbol{G}+\boldsymbol{k_{12}}).
\end{aligned} \tag{29}$$

or the real space:

$$\begin{aligned}
&V_{P_{\mu\nu}}^{\boldsymbol{k_1 k_2}} = (\chi_P^{\boldsymbol{k_{12}}}|w|P_{\mu\nu}^{\boldsymbol{k_1 k_2}}) = \int_\Omega \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{r_2}\ (\chi_P^{\boldsymbol{k_{12}}})^*(\boldsymbol{r}_1) w(r_{12}) \rho_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{r}_2) \\
&= \int_\Omega \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{r_2}\ (\sum_{\boldsymbol{m}} e^{\imath \boldsymbol{k_{12}}\cdot\boldsymbol{m}} \chi_P^{\boldsymbol{m}})^*(\boldsymbol{r}_1) w(r_{12}) \sum_{\boldsymbol{m_1 m_2}} e^{-\imath \boldsymbol{k_1}\cdot\boldsymbol{m_1}} e^{\imath \boldsymbol{k_2}\cdot\boldsymbol{m_2}} \mu_{\boldsymbol{m_1}}^*(\boldsymbol{r_2}) \nu_{\boldsymbol{m_2}}(\boldsymbol{r_2}) \\
&= \sum_{\boldsymbol{m},\boldsymbol{m_1},\boldsymbol{m_2}} \int_{\Omega-\boldsymbol{m}} \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{r_2}\ e^{-\imath \boldsymbol{k_{12}}\cdot\boldsymbol{m}} (\chi_P^{\boldsymbol{m}})^*(\boldsymbol{r}_1+\boldsymbol{m}) w(|\boldsymbol{r_2}-\boldsymbol{r_1}-\boldsymbol{m}|) e^{-\imath \boldsymbol{k_1}\cdot\boldsymbol{m_1}} e^{\imath \boldsymbol{k_2}\cdot\boldsymbol{m_2}} \mu_{\boldsymbol{m_1}}^*(\boldsymbol{r_2}) \nu_{\boldsymbol{m_2}}(\boldsymbol{r_2}) \\
&= \sum_{\boldsymbol{m},\boldsymbol{m_1},\boldsymbol{m_2}} \int_{\Omega-\boldsymbol{m}} \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{r_2}\ e^{-\imath \boldsymbol{k_{12}}\cdot\boldsymbol{m}} (\chi_P^{\boldsymbol{m}})^*(\boldsymbol{r}_1+\boldsymbol{m}) w(r_{12}) e^{-\imath \boldsymbol{k_1}\cdot\boldsymbol{m_1}} e^{\imath \boldsymbol{k_2}\cdot\boldsymbol{m_2}} \mu_{\boldsymbol{m_1}}^*(\boldsymbol{r_2}+\boldsymbol{m}) \nu_{\boldsymbol{m_2}}(\boldsymbol{r_2}+\boldsymbol{m}) \\
&= \sum_{\boldsymbol{m},\boldsymbol{m_1},\boldsymbol{m_2}} \int_{\Omega-\boldsymbol{m}} \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{r_2}\ e^{-\imath \boldsymbol{k_{12}}\cdot\boldsymbol{m}} (\chi_P^{\boldsymbol{0}})^*(\boldsymbol{r}_1) w(r_{12}) e^{-\imath \boldsymbol{k_1}\cdot\boldsymbol{m_1}} e^{\imath \boldsymbol{k_2}\cdot\boldsymbol{m_2}} \mu_{\boldsymbol{m_1}-\boldsymbol{m}}^*(\boldsymbol{r_2}) \nu_{\boldsymbol{m_2}-\boldsymbol{m}}(\boldsymbol{r_2}) \\
&= \sum_{\boldsymbol{m},\boldsymbol{m_1},\boldsymbol{m_2}} \int_{\Omega-\boldsymbol{m}} \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{r_2}\ (\chi_P^{\boldsymbol{0}})^*(\boldsymbol{r}_1) w(r_{12}) e^{-\imath \boldsymbol{k_1}\cdot(\boldsymbol{m_1}-\boldsymbol{m})} e^{\imath \boldsymbol{k_2}\cdot(\boldsymbol{m_2}-\boldsymbol{m})} \mu_{\boldsymbol{m_1}-\boldsymbol{m}}^*(\boldsymbol{r_2}) \nu_{\boldsymbol{m_2}-\boldsymbol{m}}(\boldsymbol{r_2}) \\
&= \sum_{\boldsymbol{m},\boldsymbol{m_1},\boldsymbol{m_2}} \int_{\Omega-\boldsymbol{m}} \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{r_2}\ (\chi_P^{\boldsymbol{0}})^*(\boldsymbol{r}_1) w(r_{12}) e^{-\imath \boldsymbol{k_1}\cdot\boldsymbol{m_1}} e^{\imath \boldsymbol{k_2}\cdot\boldsymbol{m_2}} \mu_{\boldsymbol{m_1}}^*(\boldsymbol{r_2}) \nu_{\boldsymbol{m_2}}(\boldsymbol{r_2}) \\
&= \sum_{\boldsymbol{m_1},\boldsymbol{m_2}} e^{-\imath \boldsymbol{k_1}\cdot(\boldsymbol{m_1})} e^{\imath \boldsymbol{k_2}\cdot(\boldsymbol{m_2})} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{r_1} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{r_2}\ (\chi_P^{\boldsymbol{0}})^*(\boldsymbol{r}_1) w(r_{12}) \mu_{\boldsymbol{m_1}}^*(\boldsymbol{r_2}) \nu_{\boldsymbol{m_2}}(\boldsymbol{r_2}).
\end{aligned} \tag{30}$$

Note that till now we have not made any assumption on $w(r_{12})$. Let us firstly use $w(r_{12}) = \frac{1}{|\boldsymbol{r_1}-\boldsymbol{r_2}|}$ to see what is actually going on. For the reciprocal space,

$$\begin{aligned}
&\sum_{\boldsymbol{G}} \tilde{\chi}_P^{\boldsymbol{k_{12}}}(-\boldsymbol{G}) \tilde{\rho}_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{G}) \tilde{w}(\boldsymbol{G}+\boldsymbol{k_{12}}) = \sum_{\boldsymbol{G}} \tilde{\chi}_P^{\boldsymbol{k_{12}}}(-\boldsymbol{G}) \tilde{\rho}_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{G}) \frac{4\pi}{|\boldsymbol{G}+\boldsymbol{k_{12}}|^2} \delta_{\boldsymbol{G}+\boldsymbol{k_{12}}\neq 0} \\
&\sim \sum_{\boldsymbol{G}\neq\boldsymbol{0} \text{ for } \boldsymbol{k_{12}}=\boldsymbol{0}} \tilde{\chi}_P^{\boldsymbol{k_{12}}}(-\boldsymbol{G}) \tilde{\rho}_{\mu\nu}^{\boldsymbol{k_1 k_2}}(\boldsymbol{G}) \frac{4\pi}{|\boldsymbol{G}+\boldsymbol{k_{12}}|^2},
\end{aligned} \tag{31}$$

due to the fact that

$$\frac{1}{|\boldsymbol{r}|} \longleftrightarrow \frac{4\pi}{|\boldsymbol{G}|^2}. \tag{32}$$

Note this Fourier transformation is not exact since there is an artificial part of truncating the $\boldsymbol{G}=0$ part.

6 Gaussian Density Fitting by Range Separation

This section mainly reviews [YB21]. The Coulomb operator $1/r_{12}$ can be splited as $1/r_{12} = w^{\mathrm{SR}}(r_{12};\omega) + w^{\mathrm{LR}}(r_{12};\omega) = \frac{\mathrm{erfc}(\omega r_{12})}{r_{12}} + \frac{\mathrm{erf}(\omega r_{12})}{r_{12}}$, where the SR and LR stand for "Short Range" and "Long Range", respectively. The purpose of this split is to deal with the short range part in the real space while manage the long range part in the reciprocal space.

The long range part. The Fourier transform of the function $\mathrm{erf}(\omega r_{12})/r_{12}$ is $\frac{4\pi}{|\boldsymbol{k}|^2}\exp(-\frac{|\boldsymbol{k}|^2}{4\omega^2})$. So we would write

$$(V_{P\mu\nu}^{\boldsymbol{k_1}\boldsymbol{k_2}})_{\omega}^{\mathrm{LR}} = 4\pi \sum_{\boldsymbol{G}} \frac{\exp(-|\boldsymbol{G}+\boldsymbol{k_{12}}|^2/4\omega^2)}{|\boldsymbol{G}+\boldsymbol{k_{12}}|^2} \tilde{\chi}_P^{\boldsymbol{k_{12}}}(-\boldsymbol{G})\tilde{\rho}_{\mu\nu}^{\boldsymbol{k_1}\boldsymbol{k_2}}(\boldsymbol{G}). \tag{33}$$

The terms of $\boldsymbol{G}=\boldsymbol{0}$ and $\boldsymbol{k_1}=\boldsymbol{k_2}$ terms can be taken out of the summation and corrected afterwards by a constant led by an auxiliary function.

The short range part. The short range part can then be written as

$$\sum_{\boldsymbol{m_1}\boldsymbol{m_2}} e^{-\imath\boldsymbol{k_1}\cdot\boldsymbol{m_1}} e^{\imath\boldsymbol{k_2}\cdot\boldsymbol{m_2}} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \mathrm{d}\boldsymbol{r_1}\mathrm{d}\boldsymbol{r_2} (\chi_P^{\boldsymbol{0}})^*(\boldsymbol{r_1}) \frac{\mathrm{erfc}(\omega r_{12})}{r_{12}} \mu_{\boldsymbol{m_1}}^*(\boldsymbol{r_2})\nu_{\boldsymbol{m_2}}(\boldsymbol{r_2}). \tag{34}$$

Note that the Fourier transformation of $\frac{\mathrm{erfc}(\omega r_{12})}{r_{12}}$ is $\frac{4\pi}{|\boldsymbol{k}|^2}(1-e^{-|\boldsymbol{k}|^2/(4\omega^2)})$, meaning it has a finite limit being $\frac{\pi}{\omega^2}$ as $\boldsymbol{k}$ goes to $\boldsymbol{0}$. Because we prepare to deal with the $\boldsymbol{G}=0$ components in the long range part later on (by adding a constant corresponding to the operator $1/r_{12}$), we will also want to remove the $\boldsymbol{G}=\boldsymbol{0}$ part for the short range part, i.e.

$$-\frac{\pi}{\omega^2}\left(\int_{\Omega}\mathrm{d}\boldsymbol{r}\chi_{\boldsymbol{P}}^{\boldsymbol{k_{12}}}(\boldsymbol{r})\right)\left(\int_{\Omega}\mathrm{d}\boldsymbol{r}\rho_{\mu\nu}^{\boldsymbol{k_1}\boldsymbol{k_2}}(\boldsymbol{r})\right). \tag{35}$$

Remark 5. *For diffuse orbitals, one can use FFT since it only has low frequencies in the reciprocal space. For compact orbitals, one can use AFT since it has high frequencies but can be easily captured by a small number of sampled points in the real space.*

Remark 6. *The range separation idea itself is providing speed-ups for HF exchange evaluation, as the short range part (high frequency) is dealt in real space while long range part is done in reciprocal space.*

Remark 7. *This RSGDF procedure can be readily used for speeding up the HF exchange energy calculation, since*

$$K_{\mu\nu}^{\boldsymbol{k}} = \frac{1}{N_k}\sum_{\boldsymbol{k'},\lambda,\sigma} D_{\lambda\sigma}^{\boldsymbol{k'}}(\mu_{\boldsymbol{k}}\lambda_{\boldsymbol{k'}}|\sigma_{\boldsymbol{k'}}\nu_{\boldsymbol{k}}). \tag{36}$$

However, it does not change the convergence rate (to TDL, which depends on the choice of exact exchange divergence (exxdiv).

7 Concentric Atomic Density Fitting for Periodic Systems

Now we discuss how to use CADF for the exchange operators in the periodic systems, where aside of clever algorithm ideas and numerical treatments, it is basically applying PARI to the ERIs appeared in the periodic exchange operator. For consistency with the reference [WLV20], we turn to use their notation. The exchange operator K in the real space can be written as

$$K_{\mu(\boldsymbol{0}),\nu(\boldsymbol{R})} = \sum_{\boldsymbol{G},\boldsymbol{L}}\sum_{\rho,\sigma}\left(\mu(\boldsymbol{0})\rho(\boldsymbol{G})|\frac{1}{r_{12}}|\sigma(\boldsymbol{G}+\boldsymbol{L})\nu(\boldsymbol{R})\right) D_{\rho(\boldsymbol{0}),\sigma(\boldsymbol{L})}. \tag{37}$$

Use the fact that

$$(\mu\nu|\rho\sigma) \approx \sum_{X\in(\mu,\nu)} C_{\mu,\nu}^{X_{\mu,\nu}}(X_{\mu,\nu}|\rho\sigma) + \sum_{Y\in(\rho,\sigma)} C_{\rho,\sigma}^{Y_{\rho,\sigma}}(\mu\nu|Y_{\rho,\sigma}) - \sum_{X\in(\mu,\nu),Y\in(\rho,\sigma)} C_{\mu,\nu}^{X_{\mu,\nu}}(X_{\mu,\nu}|Y_{\rho,\sigma})C_{\rho,\sigma}^{Y_{\rho,\sigma}}, \tag{38}$$

we know

$$K_{\mu(\mathbf{0}),\nu(\boldsymbol{R})} \approx \sum_{\boldsymbol{G},\boldsymbol{L},\rho,\sigma} [\sum_{X} C^{X_{\mu(\mathbf{0}),\rho(\boldsymbol{G})}}_{\mu(\mathbf{0}),\rho(\boldsymbol{G})} (X_{\mu(\mathbf{0}),\rho(\boldsymbol{G})}|\sigma(\boldsymbol{G}+\boldsymbol{L})\nu(\boldsymbol{R})) + \sum_{Y} (\mu(\mathbf{0})\rho(\boldsymbol{G})|Y_{\sigma(\boldsymbol{G}+\boldsymbol{L}),\nu(\boldsymbol{R})} C^{Y_{\sigma(\boldsymbol{G}+\boldsymbol{L}),\nu(\boldsymbol{R})}}_{\sigma(\boldsymbol{G}+\boldsymbol{L}),\nu(\boldsymbol{R})}) - \sum_{X,Y} C^{X}_{\mu(\mathbf{0}),\rho(\boldsymbol{G})} (X_{\mu(\mathbf{0}),\rho(\boldsymbol{G})}|Y_{\sigma(\boldsymbol{G}+\boldsymbol{L}),\nu(\boldsymbol{R})}) C^{Y}_{\sigma(\boldsymbol{G}+\boldsymbol{L}),\nu(\boldsymbol{R})}] D_{\rho(\mathbf{0}),\sigma(\boldsymbol{L})}. \tag{39}$$

The first two terms in the expression above could be the same if a sufficiently large lattice summation domain is guaranteed. The summation range of $\boldsymbol{G}$ and $\boldsymbol{R}$ is determined by one-electron wavefunction overlaps, while $\boldsymbol{L}$ is determined by the decaying rate of the density.

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