Density Fitting approximation to Coulomb part of Fock matrix.

Let us again consider the Coulomb part $J$ of the ee contribution to Fock matrix:

$$J_{\mu} = 2 \sum_{\sigma \tau} \langle \mu \sigma | \nu \tau \rangle D_{\sigma}^{\tau}$$

$$J_{\mu 0}^{\mathrm{VB}} = \frac{1}{N} \sum_{A} J_{\mu A}^{\mathrm{VB}} = \frac{2}{N} \sum_{\sigma \tau A, C, D} \langle \mu A \sigma C | \nu A + B \tau C + D \rangle D_{\sigma C}^{\tau C + D}$$

$$= \frac{2}{N} \sum_{\sigma \tau A, C, D} (\mu A \sigma A + B \dagger \sigma C \tau C + D) D_{\sigma 0}^{\tau D}$$

$$= \frac{2}{N} \sum_{\sigma \tau A, C, D} (\mu A \sigma A + B \dagger P)_{a} (J^{-1})_{P Q} (Q \dagger \sigma C \tau C + D)_{a} D_{\sigma 0}^{\tau D}$$

Here we have introduced a density fitting "resolution of the identity" (see document by Sherrill). The intermediate states are $g=0$, translationally symmetric, Bloch states of the fitting basis set, e.g:

$$\langle r | P \rangle = \frac{1}{\sqrt{N}} \sum_{A} f_{p}(r - A)$$

Using this kind of definition we can assemble, using $a(r_{12}) = \frac{\text{erfc}(r_{12}/a)}{r_{12}}$, the short-range part of the Coulomb potential:

$$J_{P Q} = \frac{1}{N} \sum_{A, B} \int dr_{1} dr_{2} f_{p}(r_{1} - A)a(r_{12})f_{q}(r_{2} - B)$$

$$= \frac{1}{N} \sum_{A} \sum_{B} \int dr_{1} dr_{2} f_{p}(r_{1})a(r_{12})f_{q}(r_{2} - (B - A))$$

$$= \sum_{B} \int dr_{1} dr_{2} f_{p}(r_{1})a(r_{12})f_{q}(r_{2} - B)$$

Similarly

$$\frac{1}{\sqrt{N}} \sum_{\sigma \tau A, C, D} (Q \dagger \sigma C \tau D + C) D_{\sigma 0}^{\tau D}$$

$$= \frac{1}{N} \sum_{\sigma \tau A, C, D} D_{\sigma 0}^{\tau D} \int dr_{1} dr_{2} f_{q}(r_{1} - A)a(r_{12})\varphi_{\sigma}(r_{2} - C)\varphi_{\tau}(r_{2} - (C + D))$$

$$= \frac{1}{N} \sum_{C} D_{\sigma 0}^{\tau D} \sum_{A, D} \int dr_{1} dr_{2} f_{q}(r_{1} - (A - C))a(r_{12})\varphi_{\sigma}(r_{2})\varphi_{\tau}(r_{2} D)$$

$$= D_{\sigma 0}^{\tau D} \sum_{A, D} \int dr_{1} dr_{2} f_{q}(r_{1} - A)a(r_{12})\varphi_{\sigma}(r_{2})\varphi_{\tau}(r_{2} D)$$

$$\equiv \sum_{\sigma \tau D} (Q \dagger \sigma 0 \tau D)_{a} D_{\sigma 0}^{\tau D}$$

and
\[
\frac{1}{\sqrt{N}} \sum_A \left( \mu AV_A + B | P \right)
= \frac{1}{N} \sum_A \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_\mu(\mathbf{r}_1 - \mathbf{A}) \varphi_\nu(\mathbf{r}_1 - (\mathbf{A} + \mathbf{B})) a(\mathbf{r}_2) f_\rho(\mathbf{r}_2 - \mathbf{C})
= \frac{1}{N} \sum_A \sum_C \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_\mu(\mathbf{r}_1) \varphi_\nu(\mathbf{r}_1 - \mathbf{B}) a(\mathbf{r}_2) f_\rho(\mathbf{r}_2 - (\mathbf{C} - \mathbf{A}))
= \sum_C \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_\mu(\mathbf{r}_1) \varphi_\nu(\mathbf{r}_1 - \mathbf{B}) a(\mathbf{r}_2) f_\rho(\mathbf{r}_2 - \mathbf{C})
\equiv \left( \mu 0 \nu B | P \right)
\]

The above integrals can all be assembled at the beginning of the calculation. The number of Bloch fit functions is equal to the number of AO fit functions associated with the unit cell. Such AO based fit functions are widely used in current electronic structure programs, and require about 3 times the number of basis functions as the molecular AO basis set. Because we know the density matrix is translationally symmetric and likewise the Fock matrix transforms as a \( g=0 \) quantity, the fit basis, expressed in Bloch functions only requires translationally invariant functions, and this can be quite small (depending on the size of the unit cell). The calculation of the integrals themselves may be expensive, but it has to be done only once, and requires limited amount of memory.

The final result is simple

\[
J_{\mu 0}^B = 2 \sum_{\sigma, \tau, A, C, D} \left( \mu 0 \nu B | P \right)_a (J_\rho^{-1})_{pq} (Q | \sigma 0 \tau D)_a D_{\sigma 0}^{\tau D}
\]

and this can be further simplified by diagonalizing the psoitive definite matrix \( J \), to obtain

\[
J_{\mu 0}^B = 2 \sum_{\sigma, \tau, B, D} \left( \mu 0 \nu B \right)_a \tilde{P} (\tilde{P} | \sigma 0 \tau D)_a D_{\sigma 0}^{\tau D}
\]

The intermediate quantities can be stored on disk.

There is an immediate analogy to how one would treat the long-range Coulomb part:

\[
J_{\mu 0}^B = 2 \sum_{\sigma, \tau, B, G \neq 0} \left( \mu 0 \nu B | G \right) e^{-|G|a^2} \frac{1}{|G|^2} (G | \sigma 0 \tau D)_a D_{\sigma 0}^{\tau D}
\]

The set of intermediate states are now the totally symmetric reciprocal lattice plane waves. The critical part is assembly of the intermediates. The use of these quantities in the \( J \)-engine in the iterative solution of the Hartree-Fock equations seems straightforward. For a given cell index \( B \), one can keep all quantities in memory, and assemble.