Hydrogen note

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1 Atomic orbitals

Basis set is the starting point of quantum chemistry calculation. In general, atomic orbitals are preferred by chemists, and plane wave orbitals are preferred by physicists. Because atomic orbitals, such as GTOs and STOs, are good for molecules. And physicist cares about solid more than molecules.

In hydrogen problem, PBC atomic orbital maybe a good starting point.

1.1 Gaussian type orbitals

We use Gaussian type orbitals (GTOs) as basis functions. The basis we used here, as well as in PYSCF, is a little bit different from CP2K. Take gth-dzvp as an example.

```
1              H  DZVP–GTH
2                     2
3                     1   0   0   4   2
4                         8.3744350009    −0.0283380461    0.0000000000
5                         1.8058681460    −0.1333810052    0.0000000000
6                         0.4852528328    −0.3995676063    0.0000000000
7                         0.1658236932    −0.5531027541    1.0000000000
8                     2   1   1   1   1
9                         0.7270000000     1.0000000000
```

We explain the file-format using in the example.

Line 1 are the name of the element and basis set.

Line 2 specifies the number of sets this basis set contains (here 2).

Line 3 specifies the composition of the first set.

The first number specifies the principal quantum number (here: 1).

The second number specifies the minimal angular quantum number l_{min} (here: 0).

The third number specifies the maximal angular quantum number l_{max} (here: 0).

The fourth number specifies the number of exponents N (here: 4).

The following numbers specify the number of contracted basis functions for each angular momentum value n_l (here only $l = 0$).

The fifth number specifies the number of contractions for $l = 0$ (here: 2).

Line 4-7 specify the coefficients of the first set. Each line consists of an exponent α_j, followed by contraction coefficients c_{ij}.

Line 8 specifies the composition of the second set.

Line 9 specifies the coefficients of the second set.

We use the same contracted GTOs with PYSCF.

$$\varphi_i(\mathbf{r}) = N_{\mathbf{m}} x^{m_x} y^{m_y} z^{m_z} \sum_{j=1}^{N} N_j c_{ij} \exp\left(-\alpha_j \cdot r^2\right) \tag{1}$$

Where $N_{\mathbf{m}}$ and N_j are normalization factors. So the five bases of hydrogen in the example are as follows,

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$\varphi_1(\mathbf{r}) = \left(\frac{2}{\pi}\right)^{\frac{3}{4}} \left[0.028 \cdot (8.374)^{\frac{3}{4}} \cdot e^{-8.374r^2} + 0.133 \cdot (1.806)^{\frac{3}{4}} \cdot e^{-1.806r^2} + 0.400 \cdot (0.485)^{\frac{3}{4}} \cdot e^{-0.485r^2} + 0.553 \cdot (0.166)^{\frac{3}{4}} \cdot e^{-0.166r^2}\right]$

$\varphi_2(\mathbf{r}) = \left(\frac{2}{\pi}\right)^{\frac{3}{4}} 1.000 \cdot (0.166)^{\frac{3}{4}} \cdot e^{-0.166r^2}$

$\varphi_3(\mathbf{r}) = 1.000 \cdot x e^{-0.727r^2}$

$\varphi_4(\mathbf{r}) = 1.000 \cdot y e^{-0.727r^2}$

$\varphi_5(\mathbf{r}) = 1.000 \cdot z e^{-0.727r^2}$

Normalization factors may be different from PYSCF. To be verified.

1.2 PBC orbitals

Crystalline orbitals Gaussian basis function ϕ is a lattice sum over local contracted Gaussians φ

$$\phi_{\mathbf{k},i}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \varphi_i(\mathbf{r} - \mathbf{T}) \tag{2}$$

where $\mathbf{k}$ is a vector in the first Brillouin zone and $\mathbf{T}$ is a lattice translational vector. It should be noted that this $\phi_{\mathbf{k},i}(\mathbf{r})$ is not a periodic function, so PBC here maybe a misleading word, TBC is more accurate. According to Bloch's theorem, we have

$$\phi_{\mathbf{k},i}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k},i}(\mathbf{r}) \tag{3}$$

where $u_{\mathbf{k},i}(\mathbf{r})$ is fully periodic with respect to all lattice translations. Therefore, we can exactly expand the crystalline AOs in a set of auxiliary plane-waves

$$\phi_{\mathbf{k},i}(\mathbf{r}) = \sum_{\mathbf{G}} \phi_{\mathbf{k},i}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \tag{4}$$

$$\phi_{\mathbf{k},i}(\mathbf{G}) = \frac{1}{\Omega} \int_{\Omega} d\mathbf{r}\ \phi_{\mathbf{k},i}(\mathbf{r}) e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \tag{5}$$

In practice, we can get PBC orbitals both from eq.(2) and eq.(4). The summations in these two equations are done in a cutoff range. To compare the computational complexity of eq.(2) and eq.(4), we have to specify the fourier coefficients by using eq.(5).

$$
\begin{aligned}
\phi_{\mathbf{k},i}(\mathbf{G}) &= \frac{1}{\Omega} \int_{\Omega} d\mathbf{r}\ \phi_{\mathbf{k},i}(\mathbf{r}) e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \\
&= \frac{1}{\Omega} \int_{\Omega} d\mathbf{r}\ \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \varphi_i(\mathbf{r} - \mathbf{T}) e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \\
&= \frac{1}{\Omega} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \int_{\Omega} d\mathbf{r}\ \varphi_i(\mathbf{r} - \mathbf{T}) e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \\
&= \frac{1}{\Omega} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \int_{\Omega-\mathbf{T}} d\mathbf{r}'\ \varphi_i(\mathbf{r}') e^{-i(\mathbf{k}+\mathbf{G})\cdot(\mathbf{r}'+\mathbf{T})} \\
&= \frac{1}{\Omega} \sum_{\mathbf{T}} \int_{\Omega-\mathbf{T}} d\mathbf{r}'\ \varphi_i(\mathbf{r}') e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}'} \\
&= \frac{1}{\Omega} \int d\mathbf{r}'\ \varphi_i(\mathbf{r}') e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}'}
\end{aligned}
$$

For GTOs, the fourier coefficients can be performed analytically

$$\phi_{\mathbf{k},i}(\mathbf{G}) = \frac{1}{\Omega} \int d\mathbf{r}\ \varphi_i(\mathbf{r}) e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \tag{6}$$

Take a simple s orbital $\varphi(\mathbf{r}) = e^{-\alpha r^2}$ as an example. Using eq.(2), we can get PBC orbitals

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} e^{-\alpha(\mathbf{r}-\mathbf{T})^2} \tag{7}$$

On the other hand, the fourier coefficients from eq.(6) is

$$\phi_{\mathbf{k}}(\mathbf{G}) = \frac{1}{\Omega} \left(\frac{\pi}{\alpha}\right)^{\frac{3}{2}} \exp\left[-\frac{(\mathbf{k}+\mathbf{G})^2}{4\alpha}\right]$$

Using eq.(4), we can get PBC orbitals

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega} \left(\frac{\pi}{\alpha}\right)^{\frac{3}{2}} \sum_{\mathbf{G}} \exp\left[-\frac{(\mathbf{k}+\mathbf{G})^2}{4\alpha}\right] e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \tag{8}$$

Compare these two equations eq.(7) and eq.(8), **we have this conclusion**: For large α, whose atomic orbital is sharp, directly summation eq.(2) has a faster convergence speed, and for small α, which has gradual atomic orbital, eq.(4) has a faster convergence speed.

2 PBC Hartree Fock

In this part, we will introduce Hartree Fock method on these PBC orbitals. Here we use index μ, ν, σ, ρ to specify atoms, p, q, r, s to specify atomic orbitals of each atom, i, j, k, l to specify coefficients of each atomic orbital, m, n to specify molecular orbital. Then the p th PBC contracted GTO of μ th atom can be described as

$$\phi_{\mathbf{k},p}(\mathbf{r}-\mathbf{R}_\mu) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \varphi_p(\mathbf{r}-\mathbf{R}_\mu-\mathbf{T}) \tag{9}$$

or

$$\phi_{\mathbf{k},p}(\mathbf{r}-\mathbf{R}_\mu) = \sum_{\mathbf{G}} \phi_{\mathbf{k},p}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot(\mathbf{r}-\mathbf{R}_\mu)} \tag{10}$$

where

$$\phi_{\mathbf{k},p}(\mathbf{G}) = \frac{1}{\Omega} \int d\mathbf{r} \; \varphi_p(\mathbf{r}) e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \tag{11}$$

In this part, we will show overlap, kinetic energy and local potential integrals both in real space and reciprocal space. To simplify the index, we will use the following abbreviations. The atoms indexs are incorporated into the orbitals indexs.

$$\phi_{\mathbf{k},p}(\mathbf{r}-\mathbf{R}_\mu) \rightarrow \phi_{\mathbf{k}p}(\mathbf{r})$$

2.1 Integtals

Here are some commonly used tricks in this part. Assume $\varphi(x)$ is a 1D atomic orbital, the 1D PBC atomic orbital is

$$\phi_{kp}(x) = \sum_{n=-\infty}^{+\infty} e^{inkT} \varphi_p(x-nT)$$

or

$$\phi_{kp}(x) = \sum_{n=-\infty}^{+\infty} \phi_{k,p}(nG) e^{i(k+nG)x}$$

General 1D integral of periodic operator $A(x)$ is given by

$$A_{pq}(k) = \int_0^T dx \; \phi_{kp}^*(x) A(x) \phi_{kq}(x)$$

In real space, the integral in a unit cell turns into infinite 1D integrals, which always have analytical expressions for GTOs

$$A_{pq}(k) = \int_0^T dx \left[\sum_m e^{-imkT} \varphi_p(x - mT) \right] A(x) \left[\sum_n e^{inkT} \varphi_q(x - nT) \right]$$

$$= \sum_{m,n} e^{-i(m-n)kT} \int_{-mT}^{(-m+1)T} dx' \ \varphi_p(x') A(x' + mT) \varphi_q[x' + (m-n)T]$$

$$= \sum_{m,m-n} e^{-i(m-n)kT} \int_{-mT}^{(-m+1)T} dx' \ \varphi_p(x') A(x') \varphi_q[x' + (m-n)T]$$

$$= \sum_{n'} e^{-in'kT} \int_{-\infty}^{\infty} dx' \ \varphi_p(x') A(x') \varphi_q(x' + n'T)$$

General 1D integral in reciprocal space is given by

$$A_{pq}(k) = \int_0^T dx \left[\sum_m \phi_{kp}^*(mG) e^{-i(k+mG)x} \right] A(x) \left[\sum_n \phi_{kq}(nG) e^{i(k+nG)x} \right]$$

$$= \sum_{m,n} \phi_{kp}^*(mG) \phi_{kq}(nG) \int_0^T dx \ A(x) e^{i(n-m)Gx}$$

The integrals in a unit cell sometimes have results like $\delta_{m,n}$. Of course there is a third way to get the integral result: we can always do numerical integration on a mesh in the unit cell, and sometimes it is worthy on account of FFT.

2.1.1 Overlap

The **overlap** matrix element[1] is given by

$$S_{pq}(\mathbf{k}) = \int_\Omega d\mathbf{r} \ \phi_{\mathbf{k}p}^*(\mathbf{r}) \phi_{\mathbf{k}q}(\mathbf{r}) \tag{12}$$

For PBC s-orbital GTOs,

$$\phi_{\mathbf{k}p}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \sum_i c_{pi} \left(\frac{2\alpha_i}{\pi} \right)^{\frac{3}{4}} e^{-\alpha_i(\mathbf{r}-\mathbf{T})^2}$$

The result of real-space integration is

$$S_{\mu p, \nu q}(\mathbf{k}) = \sum_{ij\mathbf{T}} S_{\mu pi, \nu qj, \mathbf{T}}(\mathbf{k}) \tag{13}$$

where

$$S_{\mu pi, \nu qj, \mathbf{T}}(\mathbf{k}) = c_{pi} c_{qj} \left(\frac{2\sqrt{\alpha_i \alpha_j}}{\alpha_i + \alpha_j} \right)^{\frac{3}{2}} e^{-i\mathbf{k}\cdot\mathbf{T}} e^{-\alpha_{ij}(\mathbf{R}_\mu - \mathbf{R}_\nu + \mathbf{T})^2} \tag{14}$$

$$\alpha_{ij} = \frac{\alpha_i \alpha_j}{\alpha_i + \alpha_j}$$

The **overlap** integral of reciprocal-space integration is

$$S_{\mu p, \nu q}(\mathbf{k}) = \Omega \sum_{\mathbf{G}} \phi_{\mathbf{k}p}(\mathbf{G}) \phi_{\mathbf{k}q}(\mathbf{G}) e^{i(\mathbf{G}+\mathbf{k})\cdot(\mathbf{R}_\mu - \mathbf{R}_\nu)} \tag{15}$$

2.1.2 Kinetic

The **kinetic** matrix element is given by

$$T_{pq}(\mathbf{k}) = -\frac{1}{2} \int_\Omega d\mathbf{r} \ \phi_{\mathbf{k}p}^*(\mathbf{r}) \nabla_{\mathbf{r}}^2 \phi_{\mathbf{k}q}(\mathbf{r}) \tag{16}$$

The result of real-space integration is

$$T_{\mu p, \nu q}(\mathbf{k}) = \sum_{ij\mathbf{T}} S_{\mu pi, \nu qj, \mathbf{T}}(\mathbf{k}) \alpha_{ij} \left[3 - 2\alpha_{ij}(\mathbf{R}_\mu - \mathbf{R}_\nu + \mathbf{T})^2 \right] \tag{17}$$

The **kinetic** integral of reciprocal-space integration is

$$T_{\mu p, \nu q}(\mathbf{k}) = \frac{\Omega}{2} \sum_{\mathbf{G}} \phi_{\mathbf{k}p}(\mathbf{G}) \phi_{\mathbf{k}q}(\mathbf{G}) e^{i(\mathbf{G}+\mathbf{k})\cdot(\mathbf{R}_\mu - \mathbf{R}_\nu)} \cdot (\mathbf{G} + \mathbf{k})^2 \tag{18}$$

2.1.3 Potential

The **local potential** matrix element[1] is given by

$$V_{pq}^L(\mathbf{k}) = \int_\Omega d\mathbf{r}\; \phi_{\mathbf{k}p}^*(\mathbf{r})v^L(\mathbf{r})\phi_{\mathbf{k}q}(\mathbf{r}) \tag{19}$$

The local potential is

$$v^L(\mathbf{r}) = \sum_\sigma V(\mathbf{r} - \mathbf{R}_\sigma) = -\sum_{\sigma\mathbf{T}} \frac{1}{|\mathbf{r} - \mathbf{R}_\sigma - \mathbf{T}|}$$

The two-gaussian integral has analytical result

$$V_{\mu p,\nu q}^L(\mathbf{k}) = -2\sum_\sigma \sum_{ij\mathbf{T}\mathbf{T}'} S_{\mu pi,\nu qj,\mathbf{T}} \sqrt{\frac{\alpha_i + \alpha_j}{\pi}} F_0\left[(\alpha_i + \alpha_j)(\mathbf{R}_{\sigma,\mathbf{T}'} - \mathbf{R}_{\mu i,\nu j,\mathbf{T}})^2\right] \tag{20}$$

where

$$F_0[x] = \frac{\sqrt{\pi}\,erf(\sqrt{x})}{2\sqrt{x}} \quad \& \quad F_0[0] = 1 \tag{21}$$

and some shorthand symbols

$$\mathbf{R}_{\sigma,\mathbf{T}} = \mathbf{R}_\sigma - \mathbf{T}$$

$$\mathbf{R}_{\mu i,\nu j,\mathbf{T}} = \frac{\alpha_i\mathbf{R}_\mu + \alpha_j\mathbf{R}_{\nu,\mathbf{T}}}{\alpha_i + \alpha_j}$$

but this summation eq.(20) is divergent. We should add a uniform negative charge density background to offset the positive charge without influencing the movement of electrons, or remove the $\mathbf{k} = 0$ term from the Fourier expansion. The Fourier expansion of Coulomb potential is

$$v(\mathbf{r}) = -\sum_\mathbf{T} \frac{1}{|\mathbf{r} - \mathbf{T}|} = -\sum_\mathbf{G} V(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}} \tag{22}$$

where

$$V(\mathbf{G}) = \frac{4\pi}{\Omega}\frac{1}{G^2} \tag{23}$$

so eq.(20) turns into

$$V_{\mu p,\nu q}^L(\mathbf{k}) = -\sum_\sigma \sum_{\mathbf{G}\neq 0} \sum_{ij\mathbf{T}} V(\mathbf{G})S_{\mu pi,\nu qj,\mathbf{T}} \exp\left[-i\mathbf{G}\cdot(\mathbf{R}_\sigma - \mathbf{R}_{\mu i,\nu j,\mathbf{T}})\right]\exp\left[-\frac{G^2}{4(\alpha_i + \alpha_j)}\right] \tag{24}$$

(caution: something is still wrong with eq.(24).) In practice, obtaining $V(\mathbf{r})$ from FFT and do numerical integration in a unit cell is a more economic way.

$$v^L(\mathbf{r}) = \sum_\sigma v(\mathbf{r} - \mathbf{R}_\sigma) = -\sum_{\sigma\mathbf{G}} V(\mathbf{G})e^{i\mathbf{G}\cdot(\mathbf{r}-\mathbf{R}_\sigma)} = -\sum_\mathbf{G} \left(\sum_\sigma e^{-i\mathbf{G}\cdot\mathbf{R}_\sigma}\right)V(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}}$$

The structure factor

$$S(\mathbf{G}) = \sum_\sigma e^{-i\mathbf{G}\cdot\mathbf{R}_\sigma} \tag{25}$$

so the local potential becomes

$$v^L(\mathbf{r}) = -\sum_\mathbf{G} S(\mathbf{G})V(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}} \tag{26}$$

In order to get local potential on the uniform grid in a unit cell, we need do FFT on reciprocal lattice $\mathbf{G}$. Take the 1D case as an example. The 1D uniform grid in a unit cell L is

$$0, \frac{L}{n}, \frac{2L}{n}, \dots, \frac{(N-1)L}{n}$$

The 1D reciprocal lattice is

$$0, \frac{2\pi}{L}, \frac{4\pi}{L}, \dots, \frac{2(n-1)\pi}{L}$$

The 1D inverse DFT is defined as

$$a_m = \text{iFFT}(A_k) = \frac{1}{n} \sum_{k=0}^{n-1} A_k \exp\left\{2\pi i \frac{mk}{n}\right\} \tag{27}$$

So the 1D local potential is

$$v^l\left(m\frac{L}{n}\right) = -n \cdot \frac{1}{n} \sum_{k=0}^{n-1} V(G_k) \exp\left\{i \cdot k\frac{2\pi}{L} \cdot m\frac{L}{n}\right\} = -n \cdot \text{iFFT}\left[V(G_k)\right] \ \text{ for } m = 0, 1, \ldots, n-1 \tag{28}$$

where the mapping of G_k to G is

$$G_k = \begin{cases} k\frac{2\pi}{L}, & if \ 0 \le k < n/2 \\ (k-n)\frac{2\pi}{L}, & if \ n/2 \le k < n \end{cases} \tag{29}$$

The **local potential** integral of reciprocal-space integration is

$$V_{\mu p,\nu q}^L(\mathbf{k}) = -\Omega \sum_{\mathbf{G_1 G_2}} \phi_{\mathbf{k}p}(\mathbf{G_1})\phi_{\mathbf{k}q}(\mathbf{G_2})e^{i(\mathbf{G_1}+\mathbf{k})\cdot\mathbf{R}_\mu} e^{-i(\mathbf{G_2}+\mathbf{k})\cdot\mathbf{R}_\nu} S(\mathbf{G_1}-\mathbf{G_2})V(\mathbf{G_1}-\mathbf{G_2}) \tag{30}$$

2.1.4 Hartree and Exchange

The **Hartree** and **Exchange** term matrix element[1] is given by

$$J_{pq}(\mathbf{k}) = \int_\Omega d\mathbf{r} \ \phi_{\mathbf{k}p}^*(\mathbf{r}) \int d\mathbf{r}' \ \rho(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_{\mathbf{k}q}(\mathbf{r}) \tag{31}$$

$$K_{pq}(\mathbf{k}) = \int_\Omega d\mathbf{r} \int d\mathbf{r}' \ \phi_{\mathbf{k}p}^*(\mathbf{r})\frac{\rho(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_{\mathbf{k}q}(\mathbf{r}') \tag{32}$$

where the electron density $\rho(\mathbf{r},\mathbf{r}')$ is an average of all k-points in the Brillouin zone

$$\rho(\mathbf{r},\mathbf{r}') = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_{m}^{occ} \psi_{\mathbf{k}m}(\mathbf{r})\psi_{\mathbf{k}m}^*(\mathbf{r}')$$

$$= \frac{1}{N_k} \sum_{\mathbf{k}} \sum_{rs} P_{rs}(\mathbf{k})\phi_{\mathbf{k}r}(\mathbf{r})\phi_{\mathbf{k}s}^*(\mathbf{r}') \tag{33}$$

and the one electron density is

$$\rho(\mathbf{r}) = \rho(\mathbf{r},\mathbf{r}) = \frac{1}{N_k} \sum_{\mathbf{k}} \sum_{rs} P_{rs}(\mathbf{k})\rho_{r\mathbf{k},s\mathbf{k}}(\mathbf{r}) \tag{34}$$

the density matrix is given by

$$P_{rs}(\mathbf{k}) = 2\sum_{m}^{occ} C_{rm}(\mathbf{k})C_{sm}^*(\mathbf{k}) \tag{35}$$

the coefficients C_{rm} are molecular orbital coefficients

$$\psi_{\mathbf{k}m}(\mathbf{r}) = \sum_r C_{rm}(\mathbf{k})\phi_{\mathbf{k}r}(\mathbf{r}) \tag{36}$$

in practical code the Hartree matrix eq.(31) is given by

$$J_{pq}(\mathbf{k}) = \int_\Omega d\mathbf{r} \ \phi_{\mathbf{k}p}^*(\mathbf{r})v_H(\mathbf{r})\phi_{\mathbf{k}q}(\mathbf{r}) \tag{37}$$

in terms of Hartree potential

$$v_H(\mathbf{r}) = \int d\mathbf{r}' \ \rho(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{4\pi}{\Omega} \sum_{\mathbf{G}\neq 0} \frac{\rho(\mathbf{G})}{G^2}e^{i\mathbf{G}\cdot\mathbf{r}} \tag{38}$$

where

$$\rho(\mathbf{G}) = \int_\Omega d\mathbf{r} \; \rho(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}}$$

$$= \frac{1}{N_k} \sum_{\mathbf{k}} \sum_{rs} P_{rs}(\mathbf{k}) \int_\Omega d\mathbf{r} \; \phi_{\mathbf{k}r}(\mathbf{r}) \phi^*_{\mathbf{k}s}(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}}$$

$$= \frac{1}{N_k} \sum_{\mathbf{k}} \sum_{rs} P_{rs}(\mathbf{k}) \rho_{r\mathbf{k},s\mathbf{k}}(\mathbf{G}) \tag{39}$$

the exchange matrix is given by

$$K_{pq}(\mathbf{k}) = \frac{1}{N_k} \sum_{\mathbf{k}'} \sum_{rs} P_{rs}(\mathbf{k}') \int_\Omega d\mathbf{r} \; \phi^*_{\mathbf{k}p}(\mathbf{r}) v^X_{q\mathbf{k},s\mathbf{k}'}(\mathbf{r}) \phi_{\mathbf{k}'r}(\mathbf{r}) \tag{40}$$

in terms of exchange potential

$$v^X_{q\mathbf{k},s\mathbf{k}'}(\mathbf{r}) = \int d\mathbf{r}' \; \frac{\phi_{\mathbf{k}q}(\mathbf{r}') \phi^*_{\mathbf{k}'s}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$= \int d\mathbf{r}' \; \frac{\rho_{q\mathbf{k},s\mathbf{k}'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$= \frac{4\pi}{\Omega} \sum_{\mathbf{G}}{}' \frac{\rho_{q\mathbf{k},s\mathbf{k}'}(\mathbf{G})}{|\mathbf{k}-\mathbf{k}'+\mathbf{G}|^2} e^{i(\mathbf{k}-\mathbf{k}'+\mathbf{G})\cdot\mathbf{r}} \tag{41}$$

where

$$\rho_{q\mathbf{k},s\mathbf{k}'}(\mathbf{r}) = \phi_{\mathbf{k}q}(\mathbf{r})\phi^*_{\mathbf{k}'s}(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{q\mathbf{k},s\mathbf{k}'}(\mathbf{G}) e^{i(\mathbf{k}-\mathbf{k}'+\mathbf{G})\cdot\mathbf{r}} \tag{42}$$

$$\rho_{q\mathbf{k},s\mathbf{k}'}(\mathbf{G}) = \int_\Omega d\mathbf{r} \; \rho_{q\mathbf{k},s\mathbf{k}'}(\mathbf{r}) e^{-i(\mathbf{k}-\mathbf{k}'+\mathbf{G})\cdot\mathbf{r}} \tag{43}$$

$$= \sum_{\mathbf{T}} e^{i\mathbf{k}'\cdot\mathbf{T}} \int d\mathbf{r} \; \varphi_q(\mathbf{r}) \varphi^*_s(\mathbf{r}-\mathbf{T}) e^{-i(\mathbf{G}+\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}} \tag{44}$$

$$= \left(\frac{2\sqrt{\alpha_s \alpha_q}}{\alpha_s + \alpha_q}\right)^{\frac{3}{2}} e^{-\frac{G^2}{4(\alpha_s+\alpha_q)}} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} e^{-\alpha_{sq}|\mathbf{R}_s-\mathbf{R}_q-\mathbf{T}|^2} e^{-\frac{i\mathbf{G}}{\alpha_s+\alpha_q}\cdot[\alpha_s\mathbf{R}_s+\alpha_q(\mathbf{R}_q+\mathbf{T})]} \tag{45}$$

So we can get the expression of Hartree and exchange matrix

$$J_{pq}(\mathbf{k}) = \frac{4\pi}{\Omega} \frac{1}{N_k} \sum_{\mathbf{k}'} \sum_{rs} P_{rs}(\mathbf{k}') \sum_{\mathbf{G}\neq 0} \frac{\rho_{r\mathbf{k}',s\mathbf{k}'}(\mathbf{G})\rho_{q\mathbf{k},p\mathbf{k}}(-\mathbf{G})}{G^2} \tag{46}$$

$$K_{pq}(\mathbf{k}) = \frac{4\pi}{\Omega} \frac{1}{N_k} \sum_{\mathbf{k}'} \sum_{rs} P_{rs}(\mathbf{k}') \sum_{\mathbf{G}}{}' \frac{\rho_{q\mathbf{k},s\mathbf{k}'}(\mathbf{G})\rho_{r\mathbf{k}',p\mathbf{k}}(-\mathbf{G})}{|\mathbf{k}-\mathbf{k}'+\mathbf{G}|^2} \tag{47}$$

If we just need the HF result on a **single k-point**, the Hartree and exchange matrix turn out to be quite easy.

$$J_{pq}(\mathbf{k}) = \frac{4\pi}{\Omega} \sum_{rs} P_{rs}(\mathbf{k}) \sum_{\mathbf{G}\neq 0} \frac{\rho_{rs}(\mathbf{G})\rho_{qp}(-\mathbf{G})}{G^2} \tag{48}$$

$$K_{pq}(\mathbf{k}) = \frac{4\pi}{\Omega} \sum_{rs} P_{rs}(\mathbf{k}) \sum_{\mathbf{G}\neq 0} \frac{\rho_{qs}(\mathbf{G})\rho_{rp}(-\mathbf{G})}{G^2} \tag{49}$$

define the four-center two-electron repulsion integrals

$$(pr|sq)_{\mathbf{k}} = \sum_{\mathbf{G}\neq 0} \frac{\rho_{rs}(\mathbf{G})\rho_{qp}(-\mathbf{G})}{G^2} \tag{50}$$

Then

$$J_{pq}(\mathbf{k}) = \frac{4\pi}{\Omega} \sum_{rs} P_{rs}(\mathbf{k})(pr|sq)_{\mathbf{k}} \tag{51}$$

$$K_{pq}(\mathbf{k}) = \frac{4\pi}{\Omega} \sum_{rs} P_{rs}(\mathbf{k})(pq|sr)_{\mathbf{k}} \tag{52}$$

2.1.5 Range Separation

In the previous part, we have used a lot of fourier transform while getting Coulomb repulsion. Range separation[2, 3] is a method to get the long-range and short-range part of Coulomb repulsion separately. It is commonly used in the calculation of nuclear-nuclear repulsion (Ewald sum), electron Coulomb repulsion and exchange and so on. We can use error function[3] or gaussian function[4] to separate the Coulomb potential. Here we take the error function as an example. The long-range and short-range part is separated by error function (erf) and complementary error function (erfc).

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \tag{53}$$

$$\text{erfc}(x) = 1 - \text{erf}(x) \tag{54}$$

the Coulomb potential could be devided into two parts

$$\frac{1}{r} = \frac{\text{erf}(r)}{r} + \frac{\text{erfc}(r)}{r} \tag{55}$$

and the Coulomb potential of PBC system

$$v(\mathbf{r}) = -\sum_{\mathbf{T}} \frac{1}{|\mathbf{r} - \mathbf{T}|} = -\sum_{\mathbf{T}} \frac{\text{erf}(\omega|\mathbf{r} - \mathbf{T}|)}{|\mathbf{r} - \mathbf{T}|} - \sum_{\mathbf{T}} \frac{\text{erfc}(\omega|\mathbf{r} - \mathbf{T}|)}{|\mathbf{r} - \mathbf{T}|}$$

$$= -\frac{4\pi}{\Omega} \sum_{\mathbf{G}} \frac{\exp\left(-\frac{G^2}{4\omega}\right)}{G^2} e^{i\mathbf{G}\cdot\mathbf{r}} - \sum_{\mathbf{T}} \frac{\text{erfc}(\omega|\mathbf{r} - \mathbf{T}|)}{|\mathbf{r} - \mathbf{T}|} \tag{56}$$

The first term is a summation of all reciprocal lattice vector, the second term is a summation on real space. Both parts converge faster than before. We can also use this trick on getting electron repulsion integrals (ERIs). Take the **single k-point** case as an example

$$(pr|sq)_{\mathbf{k}} = \frac{4\pi}{\Omega} \sum_{\mathbf{G}\neq 0} \frac{\exp(-\frac{G^2}{4\omega})}{G^2} \rho_{rs}(\mathbf{G})\rho_{qp}(-\mathbf{G})$$

$$+ \sum_{\mathbf{T}} \iint_{\Omega} d\mathbf{r}d\mathbf{r}' \frac{\text{erfc}(\omega|\mathbf{r} - \mathbf{r}' + \mathbf{T}|)}{|\mathbf{r} - \mathbf{r}' + \mathbf{T}|} \rho_{qp}(\mathbf{r})\rho_{rs}(\mathbf{r}') \tag{57}$$

The first term is the long-range (LR) term. Less $\mathbf{G}$ is required to converge the integrals due to the factor $\exp(-\frac{G^2}{4\omega})$. The second term is the short-range (SR) term. The short-range Coulomb potential $\frac{\text{erfc}(\omega r)}{r}$ has the inverse fourier transform form

$$\frac{\text{erfc}(\omega r)}{r} = \frac{1}{(2\pi)^3} \int d\mathbf{k} \frac{4\pi}{k^2} \left[1 - e^{-\frac{k^2}{4\omega^2}}\right] e^{i\mathbf{k}\cdot\mathbf{r}} \tag{58}$$

So the short-range (SR) term

$$(pr|sq)_{\mathbf{k}}^{SR} = \sum_{\mathbf{T}} \iint_{\Omega} d\mathbf{r}d\mathbf{r}' \frac{\text{erfc}(\omega|\mathbf{r} - \mathbf{r}' + \mathbf{T}|)}{|\mathbf{r} - \mathbf{r}' + \mathbf{T}|} \rho_{qp}(\mathbf{r})\rho_{rs}(\mathbf{r}')$$

$$= \frac{1}{(2\pi)^3} \sum_{\mathbf{T},\mathbf{T}_1,\mathbf{T}_2} e^{i\mathbf{k}\cdot(\mathbf{T}_1+\mathbf{T}_2)} \iiint d\mathbf{r}d\mathbf{r}'d\mathbf{k}_1\ \varphi_p^*(\mathbf{r})\varphi_q(\mathbf{r}-\mathbf{T}_1)\varphi_s^*(\mathbf{r}')\varphi_r(\mathbf{r}'-\mathbf{T}_2)\frac{4\pi}{k_1^2}\left[1 - e^{-\frac{k_1^2}{4\omega^2}}\right]e^{i\mathbf{k}_1\cdot(\mathbf{r}-\mathbf{r}'+\mathbf{T})}$$

$$= \frac{4}{\pi^2}\left[\frac{(\alpha_p\alpha_q\alpha_s\alpha_r)^{\frac{1}{2}}}{(\alpha_p+\alpha_q)(\alpha_r+\alpha_s)}\right]^{\frac{3}{2}} \sum_{\mathbf{T},\mathbf{T}_1,\mathbf{T}_2} e^{i\mathbf{k}\cdot(\mathbf{T}_1+\mathbf{T}_2)} \int d\mathbf{k}_1 \frac{1}{k_1^2}\left[1 - e^{-\frac{k_1^2}{4\omega^2}}\right]e^{-\frac{\alpha_p+\alpha_q+\alpha_r+\alpha_s}{4(\alpha_p+\alpha_q)(\alpha_r+\alpha_s)}k_1^2}e^{i\mathbf{k}_1\cdot(\mathbf{R}_{p,q\mathbf{T}_1}-\mathbf{R}_{s,r\mathbf{T}_2}+\mathbf{T})}$$

$$= \frac{16}{\sqrt{\pi}}\left[\frac{(\alpha_p\alpha_q\alpha_s\alpha_r)^{\frac{1}{2}}}{(\alpha_p+\alpha_q)(\alpha_r+\alpha_s)}\right]^{\frac{3}{2}} \sum_{\mathbf{T},\mathbf{T}_1,\mathbf{T}_2} e^{i\mathbf{k}\cdot(\mathbf{T}_1+\mathbf{T}_2)}$$

$$\left[\sqrt{\gamma_{pqrs}}F_0(\gamma_{pqrs}|\mathbf{R}_{p,q\mathbf{T}_1}-\mathbf{R}_{s,r\mathbf{T}_2}+\mathbf{T}|^2) - \sqrt{\frac{\gamma_{pqrs}\omega^2}{\gamma_{pqrs}+\omega^2}}F_0(\frac{\gamma_{pqrs}\omega^2}{\gamma_{pqrs}+\omega^2}|\mathbf{R}_{p,q\mathbf{T}_1}-\mathbf{R}_{s,r\mathbf{T}_2}+\mathbf{T}|^2)\right] \tag{59}$$

where $F_0(x)$ follows eq.(21), and γ_{pqrs} is

$$\gamma_{pqrs} = \frac{(\alpha_p+\alpha_q)(\alpha_r+\alpha_s)}{\alpha_p+\alpha_q+\alpha_r+\alpha_s} \tag{60}$$

2.1.6 Density Fitting

Density fitting (DF) or resolution of identity (RI) approximation is a method to approximate the four-index ERIs by two- and three-index tensors.

2.2 Solution of generalised eigenvalue problem

Core Hamiltonian matrix element without interaction

$$\mathbf{H}(\mathbf{k}) = \mathbf{T}(\mathbf{k}) + \mathbf{V}^L(\mathbf{k}) \tag{61}$$

Fock operator

$$\mathbf{F}(\mathbf{k}) = \mathbf{H}(\mathbf{k}) + \mathbf{J}(\mathbf{k}) - \frac{1}{2}\mathbf{K}(\mathbf{k}) \tag{62}$$

Roothaan equation

$$\mathbf{F}(\mathbf{k})\mathbf{C}(\mathbf{k}) = \epsilon(\mathbf{k})\mathbf{S}(\mathbf{k})\mathbf{C}(\mathbf{k}) \tag{63}$$

This is a generalised eigenvalue problem since these bases are not orthogonal to each other. To change the bases, solve the eigenvalue equation of $\mathbf{S}$

$$\mathbf{SU} = \mathbf{Us}$$

Then the unitary matrix $\mathbf{U}$ can diagonalise $\mathbf{S}$

$$\mathbf{U}^\dagger\mathbf{SU} = \mathbf{s}$$

Define matrix $\mathbf{V}$

$$\mathbf{V} \equiv \mathbf{Us}^{-1/2} \tag{64}$$

Then we have

$$\mathbf{V}^\dagger\mathbf{SV} = \mathbf{s}^{-1/2}\mathbf{U}^\dagger\mathbf{SUs}^{-1/2} = \mathbf{I}$$

Then the eigenvalue equation $\mathbf{HC} = \mathbf{SCE}$ turns into

$$\mathbf{V}^\dagger\mathbf{HVV}^{-1}\mathbf{C} = \mathbf{V}^\dagger\mathbf{SVV}^{-1}\mathbf{CE} = \mathbf{V}^{-1}\mathbf{CE}$$

define

$$\mathbf{H}' \equiv \mathbf{V}^\dagger\mathbf{HV} \tag{65}$$

$$\mathbf{C}' \equiv \mathbf{V}^{-1}\mathbf{C} \tag{66}$$

We can rewrite the eigenvalue equation as

$$\mathbf{H}'\mathbf{C}' = \mathbf{C}'\mathbf{E} \tag{67}$$

Solve this eigenvalue problem then we can get the eigenvalues $\mathbf{E}$ and the eigenstate $\mathbf{C}'$ Then the eigenstate of the generalised eigenvalue problem is

$$\mathbf{C} = \mathbf{VC}' \tag{68}$$

The elements in matrix $\mathbf{C}$ are coefficients transform the atomic orbitals to molecular orbitals. The shape of $\mathbf{C}(\mathbf{k})$ is (n_{ao}, n_{mo}). In hydrogen problem, assuming N hydrogen atoms per unit cell, the HF determinant includes the $N_k N$ orbitals with the lowest eigenvalues out of all k-points. We can get the density matrix

$$P_{rs}(\mathbf{k}) = 2\sum_m^{occ} C_{rm}(\mathbf{k})C_{sm}^*(\mathbf{k}) \tag{69}$$

The energy is

$$E(\mathbf{k}) = \frac{1}{2}\sum_{pq}\left[F_{pq}(\mathbf{k}) + H_{pq}(\mathbf{k})\right]P_{qp}(\mathbf{k}) \tag{70}$$

Note that the nuclear-nuclear repulsion, which is computed using the Ewald expression, is excluded from this energy. The molecular orbitals are

$$\psi_{\mathbf{k}m}(\mathbf{r}) = \sum_r C_{rm}(\mathbf{k})\phi_{\mathbf{k}r}(\mathbf{r}) \tag{71}$$

References

[1] James McClain, Qiming Sun, Garnet Kin-Lic Chan, and Timothy C. Berkelbach. Gaussian-based coupled-cluster theory for the ground-state and band structure of solids. *Journal of Chemical Theory and Computation*, 13(3):1209–1218, 2017. PMID: 28218843.

[2] Qiming Sun. Exact exchange matrix of periodic hartree-fock theory for all-electron simulations, 2020.

[3] Hong-Zhou Ye and Timothy C. Berkelbach. Fast periodic Gaussian density fitting by range separation. *The Journal of Chemical Physics*, 154(13), 04 2021. 131104.

[4] Tomomi Shimazaki and Takahito Nakajima. Gaussian-based range-separation approach on hartree–fock exchange interaction and second-order perturbation theory. *Chemical Physics Letters*, 647:132–138, 2016.

Appendix

Fourier Transform of Coulomb Potential

Consider the Yukawa potential (reference)

$$V_\lambda(\mathbf{r}) = \frac{e^{-\lambda r}}{r} \tag{72}$$

The fourier transform of Yukawa potential is

$$
\begin{aligned}
\mathcal{F}[V_\lambda(r)] &= \int \frac{e^{-\lambda r}}{r} e^{-i\mathbf{k}\cdot\mathbf{r}} d^3 r \\
&= \int_0^{2\pi} d\phi \int_0^\pi d\theta \int_0^\infty dr \frac{e^{-\lambda r}}{r} e^{-ikr cos\theta} r^2 sin\theta \\
&= 2\pi \int_{-1}^1 du \int_0^\infty dr\ re^{-\lambda r} e^{-ikru} \\
&= 2\pi \int_0^\infty dr\ re^{-\lambda r} \frac{1}{-ikr} \left[e^{-ikru} \right]_{-1}^1 \\
&= \frac{2\pi}{ik} \int_0^\infty dr\ e^{-\lambda r} \left[e^{ikr} - e^{-ikr} \right] \\
&= \frac{2\pi}{ik} \int_0^\infty dr\ \left[e^{(ik-\lambda)r} - e^{-(ik+\lambda)r} \right] \\
&= \frac{2\pi}{ik} \left[\frac{e^{(ik-\lambda)r}}{ik-\lambda} + \frac{e^{-(ik+\lambda)r}}{ik+\lambda} \right]_0^\infty \\
&= \frac{2\pi}{ik} \left[\frac{-(ik+\lambda)e^{(ik-\lambda)r} - (ik-\lambda)e^{-(ik+\lambda)r}}{k^2+\lambda^2} \right]_0^\infty \\
&= \frac{2\pi}{ik} \left[\frac{-ike^{(ik-\lambda)r} - \lambda e^{(ik-\lambda)r} - ike^{-(ik+\lambda)r} + \lambda e^{-(ik+\lambda)r}}{k^2+\lambda^2} \right]_0^\infty \\
&= \frac{2\pi}{ik} \left[\frac{ik+\lambda+ik-\lambda}{k^2+\lambda^2} \right] \\
&= \frac{4\pi}{k^2+\lambda^2}
\end{aligned}
\tag{73}
$$

When $\lambda = 0$,

$$\mathcal{F}[V(\mathbf{r})] = \frac{4\pi}{k^2} \tag{74}$$

In the same way, for the short-range Coulomb potential

$$V^{SR}(\mathbf{r}) = \frac{\text{erfc}(\omega r)}{r} \tag{75}$$

The fourier transform is

$$
\begin{aligned}
\mathcal{F}[V^{SR}(\mathbf{r})] &= \int \frac{\mathrm{erfc}(\omega r)}{r} e^{-i\mathbf{k}\cdot\mathbf{r}} d^3 r \\
&= \frac{2\pi}{ik} \int_0^\infty dr\ \mathrm{erfc}(\omega r) \left[e^{ikr} - e^{-ikr} \right] \\
&= \frac{4\pi}{k} \int_0^\infty dr\ \mathrm{erfc}(\omega r) \sin(kr) \\
&= \frac{4\pi}{k^2} \left[1 - e^{-\frac{k^2}{4\omega^2}} \right]
\end{aligned}
\tag{76}
$$

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