

# Final Report of Introduction to Computational Physics

From HF to DFT

Name:	Yang Shen
Department:	CCME, PKU
ID:	1900011735
Date:	2021.12.19

# 1 Hartree-Fock: Obara-Saika scheme

The integrals involving Gaussian-type orbitals can be analytically computed, or at least the recurrence relation is accurate. First of all, the overlapping integrals are easy to calculate, and the details<sup>1</sup> are not mentioned here.

What's of great importance is the calculation of Coulomb potential integrals and two-electron integrals. The basic idea is to transform the complicated integrals into Gaussian-type integration, for example, by using the transform below.

$$\frac{1}{r_C} = \frac{1}{\pi} \int_{-\infty}^{\infty} \exp(-r_C^2 t^2) dt$$

So the Coulomb potential integration ( $\langle G | \frac{1}{r_C} | G \rangle$ ) can be written as a Gaussian-type integration. Two-electron integrals are slightly more complicated than Coulomb integrals, but similar scheme is adopted to treat them. For brevity, I will list the recurrence relation<sup>1</sup> used in HF calculation.

Here is the recurrence relation in calculation of Coulomb terms. I omit the deduction process of these relation, but if necessary, you can find them in Helgaker's book<sup>1</sup>. The terms  $i, j, k, l, m, n$  represent the orbital angular momentum (More precisely, it corresponds to the power of  $x, y, z$  of a specific orbital). What we want to do here is just reduce the problem to the most primary situation (All of them are equal to 0).

$$\begin{aligned} \Theta_{i+1,j,k,l,m,n}^N = & X_{PA} \Theta_{i,j,k,l,m,n}^N + \frac{1}{2p} (i \Theta_{i-1,j,k,l,m,n}^N + j \Theta_{i,j-1,k,l,m,n}^N) \\ & - X_{PC} \Theta_{i,j,k,l,m,n}^{N+1} - \frac{1}{2p} (i \Theta_{i-1,j,k,l,m,n}^{N+1} + j \Theta_{i,j-1,k,l,m,n}^{N+1}) \end{aligned} \quad (9.10.8)$$

Here is the recurrence relation in calculation of two-electron terms.

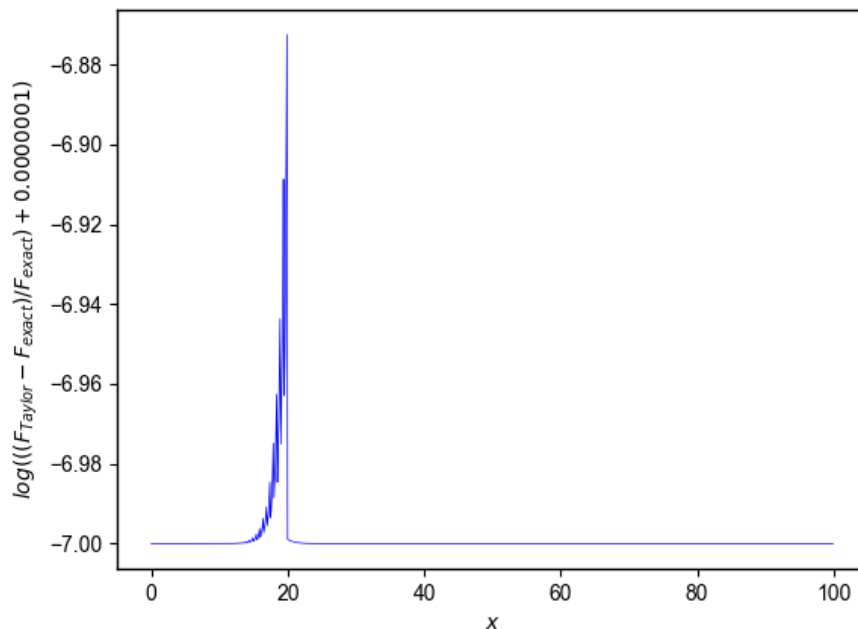
$$\begin{aligned} \Theta_{i,j,k+1,l}^N = & X_{QA} \Theta_{ijkl}^{N+1} + \frac{\alpha}{p} X_{PQ} \Theta_{ijkl}^{N+1} + \frac{i}{2p} (\Theta_{i-1,j,k,l}^N - \frac{\alpha}{q} \Theta_{i-1,j,k,l}^{N+1}) + \frac{j}{2p} (\Theta_{i,j-1,k,l}^N - \\ & \frac{\alpha}{p} \Theta_{i,j-1,k,l}^{N+1}) + \frac{k}{2(p+q)} \Theta_{i,j,k-1,l}^{N+1} + \frac{l}{2(p+q)} \Theta_{i,j,k,l-1}^{N+1} \end{aligned} \quad (9.10.24)$$

The final problem is how to calculate incomplete Gamma function.

$$F_n(x) = \int_0^1 \exp(-xt^2) t^{2n} dt$$

It seems more plausible to apply Laguerre-Gauss Quadrature, instead of calculating the integrals by Taylor expansion (when  $x$  is small) and expansion of upper limit to infinity (when  $x$  is large). I adopt the latter scheme, which is mentioned in Helgaker's book<sup>1</sup>. The necessary

order of Taylor expansion is approximately  $(2n+2x+25)$ , in order to get an accurate result. For the case  $n=0$ , I test the validity of this approximation, and the result is considerably satisfactory.



**Figure 1.** The validity of approximation when  $n=0$ . The order of Taylor expansion is  $(25+2x+2n)$ .

My result of HF/STO-3G calculation of ammonia coincides with Gaussian09 (**Table 1**).

**Table 1.** A comparison of HF/STO-3G calculation result of ammonia between my program and Gaussian09

Orbital	My result	Gaussian09
1	-15.30461	-15.30457
2	-1.08938	-1.08936
3	-0.57208	-0.52705
4	-0.57208	-0.57205
5	-0.35212	-0.35210
6	0.63810	0.63819
7	0.72955	0.72955
8	0.72955	0.72955

The result is considerably satisfactory.

## 2 Density functional theory: Becke's scheme

It's of great importance to calculate integrals involving electron density in a DFT program. However, recurrence relation and analytical result no longer pertain. To calculate the matrix of LDA Hamiltonian, we can hardly escape from numerical integration.

Obviously, directly using 3-dimensional cartesian coordinates is unreasonable. Given that electrons distribute mostly around the nuclei, calculating density integrals by multi-center integration sounds more plausible. Imagine there's an ammonia molecule. First, the nitrogen nucleus is chosen, and using it as a center, we calculate the integrals involving density in spherical polar coordinates. Then we repeat what we do to other nuclei. The multi-center integration is reduced to a sum of single-center integration. Of course, this operation will cause serious double counting problem.

However, what we need is merely reweighting. This means to divide space into different regions belonging to various atoms, just like what we do to divide space into several Wigner-Seitz primitive cells. Now, these polyhedra are called Voronoi polyhedra. In the simplest way, if a sampling point belongs to a polyhedron around a specific nucleus, the weight will be assigned to 1 in integration around this center. Otherwise, the weight will be 0 and this point will not be counted. Of course, this weight function is discontinuous and will lead to severe bugs. This coarse treatment is used to calculate the orbital energies of hydrogen as a demonstration of the necessity of smooth treatment. This result is provided at the end of this report and compared with result of smooth treatment. But now it's a good example to demonstrate what I want to do.

Becke<sup>2</sup> proposed a scheme of smooth treatment in his famous paper.

$$\mu_{i,j} = \frac{r_i - r_j}{R_{i,j}}, \quad r_i = |\mathbf{r} - \mathbf{R}_i|, \quad R_{i,j} = |\mathbf{R}_i - \mathbf{R}_j|$$

Obviously, the points in region  $\mu_{i,j} < 0$  contributes mostly to integration around nucleus i. The weight is decided by

$$p(\mu_{i,j}) = \frac{3}{2}\mu_{i,j} - \frac{1}{2}\mu_{i,j}^3, \quad f(\mu_{i,j}) = p(p(p(\mu_{i,j}))), \quad P_i(\mathbf{r}) = \prod_{j \neq i} f(\mu_{i,j}), \quad W_i(\mathbf{r}) = \frac{P_i(\mathbf{r})}{\sum_j P_j(\mathbf{r})}$$

Note that  $-1 < \mu_{i,j} < 1$ , so the first formula is reasonable. Becke utilized the iteration in second formula to sharpen weight distribution, and the scheme of three iterations is recommended. At last, normalization is necessary, and so comes the final expression of  $W_i(\mathbf{r})$ . This smooth treatment really helps to calculate density integrals accurately.

Now there is no problem hindering us from using spherical polar coordinates. The radial and spherical surface part of integrations can be considered separately. Here I use Sphere Lebedev rule to decide sampling points on the spherical surface, and Chebyshev-Gauss Quadrature of the first case is adopted to treat the radial integration.

$$\int_0^{2\pi} \int_0^\pi \int_0^\infty \rho(\mathbf{r}) r^2 \sin \theta dr d\theta d\phi \stackrel{r=\frac{1+x}{1-x}p}{=} \int \int_{-1}^1 \rho(x, \theta, \phi) \frac{(1+x)^2}{(1-x)^4} p^3 dx d\Omega$$

Although it's strange to find that  $p$  appears in the integration, but the value of  $p$  will not change the result of integration significantly. Noticing  $p$  is a parameter associated with expansion of sampling points, Becke recommend  $p$  to be the radii of atoms, but under most circumstance it doesn't matter, if  $p$  is chosen normally.

**Table 2.** Some testing result for accuracy of treatment mentioned above. The molecule studied here is ammonia, and I use orbitals calculated in HF/STO-3G to calculate the total number of electrons.

p(expansion)	n(chebyshev order)	m(lebedev order)	electrons
1	40	110	9.999786
1	70	110	9.999795
1	100	110	9.999795
0.5	40	110	9.999779
0.3	40	110	9.999820
0.1	40	110	9.999011
0.05	40	110	10.009613
0.5	40	4344	9.999994

And we find the result is considerably reliable, for we know that ammonia has 10 electrons. Although the result of 4344 Lebedev points is more satisfactory, the time consumed may be unbearable. For this reason, I adopt  $p = 1$ ,  $n = 40$ ,  $m = 110$  in following calculation.

In Xalpha (LDA), there's only exchange potential ( $V_x(\mathbf{r}) = -3\alpha(\frac{3\rho(\mathbf{r})}{4\pi})^{1/3}$ ), and correlation potential is ignored. This LDA functional is not adopted widely, but it's enough to demonstrate the validity of this algorithm, and changing to other complicated exchange-correlation potential is easy.

I plan to calculate the orbital energy of ammonia by Xalpha/STO-3G, but unfortunately, in SCF procedure, the sum of orbital energies oscillates. Time limited, I change the molecule

from ammonia to hydrogen. The result I calculated coincides with the result of Gaussian09. The orbital energies of 4334 Lebedev points scheme is almost as same as the result of 110 Lebedev points.

**Table 3.** Comparison of my result with Gaussian09

My result	Gaussian09
-0.36137	-0.36132
0.58782	0.58774

At the end of this report, I test the necessity of Becke's smooth treatment, and here is the result.

**Table 4.** The necessity of smooth treatment

Orbital	smooth	p=1(n,neglected)	p=0.5(n)	p=0.3(n)
1	-0.36135	-0.36368	-0.35604	-0.35743
2	0.58785	0.58785	0.58784	0.58783

The orbital energy of the bonding orbital differs significantly when  $p$  changes, while the energy of antibonding orbital keeps constant. The reason behind this phenomenon is simple: in the middle of two nuclei, electron density of antibonding orbital is low, so it's unaffected. You can also regard the phenomenon as a result of error cancellation. The same reason pertains to the situation of bonding orbitals.

### 3 Remaining problem

Although my DFT program is designed for more complicated situations, and I write this program in a general way (This means it has the ability to treat problems involving orbitals of higher angular momentum.), I have to give up applying it to calculate the property of ammonia, due to slow convergence. Maybe DIIS<sup>3</sup> algorithm is necessary, and I will have a try in the oncoming vacation. Another serious fault is about the algorithm efficiency. In a real DFT calculation, fitting the actual electron density distribution by a set of appropriate functions (for example, Gaussian functions) is necessary in accelerating the calculation of Coulomb matrix elements<sup>4</sup>. But in this project, accelerating algorithm is ignored.

## 4 Conclusion

In conclusion, I think the basic goal is achieved. The result of ammonia (HF/STO-3G) and hydrogen (Xalpha/STO-3G) coincides with the calculation of Gaussian09. According to the testing result, Becke's smooth treatment is of great necessity when treating the bonding orbital energy, but plays a minor role in calculation of antibonding orbitals.

## 5 Acknowledgement

Thanks for Prof.Chen and Yuhang Ai's gracious guidance.

## 6 Reference

- [1] Helgaker, T.; Jorgensen, P.; Olsen, J. 2000, Molecular Electronic-Structure Theory. John Wiley & Sons Ltd
- [2] Becke, A. D. *J. Chem. Phys.* **1988**, 88, 2547
- [3] Pulay, P. *Chem. Phys. Lett.* **1980**, 73, 393
- [4] Xu G. X.; Li, L. M.; Wang, D. M. *Quantum chemistry: basic principle and ab initio calculation method*. 2007, Science Press (in Chinese).