Final summary

(From HF to DFT)

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From HF to DFT

- Basic idea: FC=SCE
- Direct calculation of three-dimensional integration: **Unreasonable**
- Reduce 3-D integration to a sum of one-center integrations in spherical polar coordinates.

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\rho(\mathbf{r})r^2\sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi=\int\int_0^{\infty}\rho(\mathbf{r})r^2\mathrm{d}r\mathrm{d}\Omega$$

Becke's scheme

- Reweight the contribution according to position
- $\mu_{ij} = \frac{r_i - r_j}{R_{ij}}$, $f(\mu_{ij}) = \frac{3}{2}\mu_{ij} - \frac{1}{2}\mu_{ij}^3$, $p_{ij} = f(f(f(\mu_{ij})))$, $P_i(\mathbf{r}) = \prod_{j \neq i} p_{ij}$
- Normalize the weight by $W_i(\mathbf{r}) = \frac{P_i(\mathbf{r})}{\sum_j P_j(\mathbf{r})}$

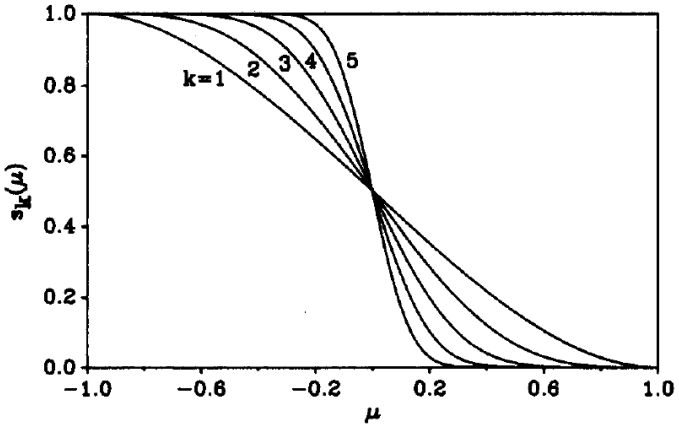
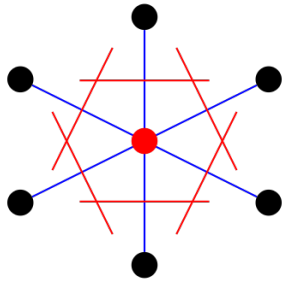


FIG. 1. Cutoff profiles $s_k(\mu)$ of Eq. (21) for $k = 1$ to 5.



[1] Becke, A. D. J. Chem. Phys. **1988**, 88, 2547

Numerical calculation

- The spherical surface part: sphere Lebedev rule
- The radial part: Chebyshev - Gauss Quadrature of the first case

$$\int_0^\infty \rho(\mathbf{r}) r^2 \mathrm{d}r \xrightarrow{r=\frac{1+x}{1-x}p} \int_{-1}^{1} \rho(x,\theta,\phi) \frac{(1+x)^2}{(1-x)^4} p^3 \mathrm{d}x$$

- Weight function: $\frac{1}{\sqrt{1-x^2}}$, x_i: $\cos\left(\frac{2i-1}{2n}\pi\right)$, weight: $\frac{\pi}{n}$
- In following calculation, n(chebyshev order)=40, p(expansion)=1, m(Lebedev order)=110.

Calculation of LDA (Xalpha)

- $V_x(\mathbf{r}) = -3\alpha[\frac{3}{4\pi}\rho(\mathbf{r})]^{1/3}$. Gaussian09's default number of α is 0.7.
- When trying to calculate the orbital energy of ammonia, SCF iteration fails to converge (although basis set used here is only STO-3G).

Iterations	Sum of orbital energy (plus background Coulomb repulsion)
1	-54.984166
2	-24.859824
3	-34.832507
4	-26.045267
5	-33.917869
6	-26.551132
7	-33.454861
8	-26.839427
9	-33.174086

Density mixing

- $\rho_{in}^{(i+1)} = \alpha \times \rho_{in}^{(i)} + (1-\alpha) \times \rho_{out}^{(i)},\ \alpha = 0.5$
- Self-consistent iteration reaches convergence after 8 hours.

Orbital	My result	Gaussian09
1	-13.60799	-13.60794
2	-0.68302	-0.68304
3	-0.31226	-0.31221
4	-0.31225	-0.31221
5	-0.02984	-0.02982
6	0.38949	0.38953
7	0.45905	0.45910
8	0.45908	0.45910

The necessity of smooth treatment

- Without smooth treatment, Xalpha/STO-3G calculation of H_2 converges slowly.
- n represents the Chebyshev order.

Orbital	smooth	n=40	n=100	n=250	n=500
1	-0.36135	-0.36368	-0.36391	-0.36091	-0.36061
2	0.58784	0.58785	0.58784	0.58784	0.58784

Acknowledgement

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