5th Homework Tutorial of Quantum Chemistry Programming - ver.01

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1 Members

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An old version refers https://github.com/Utenaq/2018QC-Project-Ab-initio-wavefunction-program .

2 compile and usage

2.1 compile

in the main directory or under `./src`, use `make` command; it needs g++ compiler.

2.2 usage

command	term	
`main -h`	get help info	
`main -d`	default test (eg. HeH+)	test file locates in `../test`
`main -f [file.gjf]`	normal calculation	a series test file are under `../test`

optional test file lies in `../test`[U+FF0C]including **H.gjf**, **He.gjf**, **H2.gjf**, **HeH.gjf**, **H4.gjf**, **CH4.gjf**.
use as `main -f ../test/H2.gjf`.

3 class and type

refer to class and type

4 handling of molecule integral

Radial gaussian and cartesian gaussian radial gaussian gives as:

$$g_{lmn}(\alpha, \mathbf{r}) = \Big(\sqrt{\frac{2}{\pi}}\frac{(4\alpha)^{n+1/2}}{(2n-1)!!}\Big) r^{n-1} e^{-\alpha r^2} Y_{lm}(\theta, \varphi)$$

but here we more often use the cartesian gaussian as:

$$g(A, \alpha, l, m, n) = N x_A^l y_A^m z_A^n e^{-\alpha r_A^2}$$

where by formula

$$\int_{-\infty}^{\infty} x^{2n} e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}}\frac{(2n-1)!!}{(2\alpha)^n}$$

we have

$$N = \big[\big(\frac{2\alpha}{\pi}\big)^{3/2}\frac{(4\alpha)^{l+m+n}}{(2l-1)!!(2m-1)!!(2n-1)!!}\big]^{1/2}$$

GTO product theorem

$$e^{-\alpha_1 r_A^2} e^{-\alpha_2 r_B^2} = \exp\big[-\frac{\alpha_1\alpha_2}{\alpha_1+\alpha_2}\big]\exp\big[-(\alpha_1+\alpha_2) r_P^2\big]$$

where

$$\mathbf{P} \stackrel{def}{=\!=} \frac{\alpha_1 \mathbf{A} + \alpha_2 \mathbf{B}}{\alpha_1 + \alpha_2}$$

so let $x_A^{l_1} x_B^{l_2}$ expand at x_P as:

$$\begin{aligned} x_A^{l_1} x_B^{l_2} &= (x_P - \overline{PA}_x)_A^{l_1}(x_P - \overline{PB}_x)_B^{l_2} \\ &= \sum_{i_1=0}^{l_1}\sum_{i_2=0}^{l_2}(-1)^{i_1+i_2} C_{l_1}^{i_1} C_{l_2}^{i_2} (\overline{PA}_x)^{l_1-i_1}(\overline{PB}_x)^{l_2-i_2} x_P^{i_1+i_2} \\ &= \sum_{l}^{l_1+l_2}(-1)^l f_l(l_1, l_2, \overline{PA}_x, \overline{PB}_x) x_P^l \end{aligned}$$

where

$$f_l(l_1, l_2, a, b) = \sum_{i_1=0}^{l_1}\sum_{i_2=0}^{l_2}\delta_{l,l_1+l_2} C_{l_1}^{i_1} C_{l_2}^{i_2} a^{l_1-i_1} b^{l_2-i_2}$$

and so on:

$$\begin{aligned} & g(A, \alpha_1, l_1, m_1, n_1) g(B, \alpha_2, l_2, m_2, n_2) \\ &= \sum_{l=0}^{l_1+l_2}\sum_{m=0}^{m_1+m_2}\sum_{n=0}^{n_1+n_2}(-1)^{l+m+n} f_l(l_1, l_2, \overline{PA}_x, \overline{PB}_x) f_m(m_1, m_2, \overline{PA}_y, \overline{PB}_y) \\ &\times f_n(n_1, n_2, \overline{PA}_z, \overline{PB}_z) x_P^l y_P^m z_P^n \exp\big[-\frac{\alpha_1\alpha_2}{\alpha_1+\alpha_2}\big]\exp\big[-(\alpha_1+\alpha_2) r_P^2\big] \end{aligned}$$

useful integral formula

1. $$\int_{-\infty}^{\infty} x^{2n} e^{-\alpha x^2} dx = (\frac{\pi}{\alpha})^{1/2} \frac{(2n-1)!!}{(2\alpha)^n}$$

2. $$\int_{-\infty}^{\infty} x^{2n+1} e^{-\alpha x^2} dx = 0$$

3. $$\int_{-\infty}^{\infty} e^{ixy} x^n e^{-\alpha x^2} dx = i^n (\frac{\pi}{\alpha})^{1/2} (\frac{1}{2\sqrt{\alpha}})^n H_n(\frac{y}{2\sqrt{\alpha}}) e^{-y^2/4\alpha}$$

   where H_n is Hermite polynomial:

   $$H_n(z) = (-1)^n e^{z^2} \frac{d^n}{dz^n} e^{-z^2} = n! \sum_{i=0}^{[n/2]} \frac{(-1)^i}{i!(n-2i)!} (2z)^{n-2i}$$

4. $$\frac{1}{r} = \frac{1}{2\pi^2} \int e^{i\mathbf{k}\cdot\mathbf{r}} \frac{1}{k^2} d\mathbf{k}$$

5. $$e^{-\sigma k^2} = 2\sigma k^2 \int_0^1 S^{-3} e^{-\sigma k^2/S^2} dS$$

6. defines

   $$F_n(t) = \int_0^1 u^{2n} e^{-tu^2} du$$

Radial integral formula (1s type) for n=1, l=m=0, or called 1s function, such integral is derived by **Boys** and **Shavitt**.

1. S integral

$$S = \int e^{-a(\mathbf{r}-\mathbf{A})^2 - b(\mathbf{r}-\mathbf{B})^2} = (\frac{\pi}{a+b})^{3/2} e^{-ab/(a+b)\cdot\overline{AB}^2}$$

2. T integral

$$T = \int e^{-a(\mathbf{r}-\mathbf{A})^2} (-) \frac{1}{2} \nabla^2 e^{-b(\mathbf{r}-\mathbf{B})^2} = (\frac{ab}{a+b})(3 - \frac{2ab}{a+b}) e^{-ab/(a+b)\cdot\overline{AB}^2}$$

3. V integral

$$V = \int e^{-a(\mathbf{r}-\mathbf{A})^2} \frac{1}{|\mathbf{r}-\mathbf{C}|} e^{-b(\mathbf{r}-\mathbf{B})^2} = (\frac{2\pi}{a+b}) F_0[(a+b)\overline{CP}^2] e^{-ab/(a+b)\cdot\overline{AB}^2}$$

4. ERI integral

$$\begin{aligned} I &= \int e^{-a(\mathbf{r_1}-\mathbf{A})^2 - b(\mathbf{r_1}-\mathbf{B})^2} \frac{1}{r_{12}} e^{-c(\mathbf{r_2}-\mathbf{C})^2 - c(\mathbf{r_2}-\mathbf{D})^2} \\ &= \frac{2\pi^{5/2}}{(a+b)(c+d)\sqrt{a+b+c+d}} F_0[\frac{(a+b)(c+d)}{a+b+c+d} \cdot \overline{PQ}^2] e^{-ab/(a+b)\cdot\overline{AB}^2 - cd/(c+d)\cdot\overline{CD}^2} \end{aligned}$$

Cartesian integral formula

- overlap integral (S integral)
  by GTO product theorem, we can easily get:

$$S = (\frac{\pi}{a+b})^{3/2} e^{-ab/(a+b)\cdot \overline{AB}^2} \tilde{S}_{l_1 l_2} \tilde{S}_{m_1 m_2} \tilde{S}_{n_1 n_2}$$

  where

$$\tilde{S}_{l_1 l_2} = \sum_{i=0}^{[\frac{l_1+l_2}{2}]} f_{2i}(l_1, l_2, \overline{PA}_x, \overline{PB}_x) \frac{(2i-1)!!}{2^i (a+b)^i}$$

- kinetic integral (T integral)
  note $g(A, a, l, m, n)$ as $\mid aAlmn\rangle$, it's easy to show that its derivatives have following properties:

$$\frac{\partial}{\partial x_A} \mid aAlmn\rangle = (l x_A^{-1} - 2a x_A) \mid aAlmn\rangle$$

$$\frac{\partial^2}{\partial x_A^2} \mid aAlmn\rangle = (l(l-1) x_A^{-2} - 2a(2l+1) + 4a^2 x_A^2) \mid aAlmn\rangle$$

  so that:

$$\begin{aligned} T = &\alpha_2 (2(l_2 + m_2 + n_2) + 3) S_{l_1 m_1 n_1; l_2 m_2 n_2} \\ &- 2\alpha_2^2 \big(S_{l_1 m_1 n_1; (l_2+2) m_2 n_2} + S_{l_1 m_1 n_1; l_2 (m_2+2) n_2} + S_{l_1 m_1 n_1; l_2 m_2 (n_2+2)} \big) \\ &- \frac{1}{2} \big(l_2 (l_2 - 1) S_{l_1 m_1 n_1; (l_2-2) m_2 n_2} + m_2 (m_2 - 1) S_{l_1 m_1 n_1; l_2 (m_2-2) n_2} \\ &+ n_2 (n_2 - 1) S_{l_1 m_1 n_1; l_2 m_2 (n_2-2)} \big) \end{aligned}$$

- nuclear Coulomb integral (V integral; without nucleus-nucleus Coulomb integral!)

$$\begin{aligned} V_{ABC} &= \int g(A, a, l_1, m_1, n_1) \frac{1}{r_C} g(B, b, l_2, m_2, n_2) d\tau \\ &= N_A N_B \frac{1}{2\pi} e^{-ab/(a+b)\cdot \overline{AB}^2} \sum_{lmn} f_l(l_1, l_2, \overline{PA}_x, \overline{PB}_x) f_m(m_1, m_2, \overline{PA}_y, \overline{PB}_y) f_n(n_1, n_2, \overline{PA}_z, \overline{PB}_z) \\ &\times \int e^{i\mathbf{k}\cdot \mathbf{r}_{cp}} \frac{1}{k^2} d\mathbf{k} \int e^{ik_x x} x^l e^{-(a+b)x^2} dx \int e^{ik_y y} y^m e^{-(a+b)y^2} dy \int e^{ik_y y} y^n e^{-(a+b)z^2} dz \end{aligned}$$

  we here omit the derivation, giving result directly as:

$$\begin{aligned} V_{ABC} = &\frac{2\pi}{a+b} e^{-ab/(a+b)\cdot \overline{AB}^2} \sum_{\nu}^{N} \sum_{I=0}^{l_1+l_2} \sum_{J=0}^{m_1+m_2} \sum_{K=0}^{n_1+n_2} G_{l_1 l_2}^{I}(A_x, B_x, C_x) \\ &\times G_{m_1 m_2}^{J}(A_y, B_y, C_y) G_{n_1 n_2}^{K}(A_z, B_z, C_z) F_\nu[(a+b)\overline{PC}^2] \delta_{\nu, I+J+K} \end{aligned}$$

where

$$G_{l_1 l_2}^{I}(A_x, B_x, C_x) = \sum_{i=0}^{l_1+l_2} \sum_{r=0}^{[i/2]} \sum_{u=0}^{[i/2]-r} (-1)^i f_i(l_1, l_2, \overline{PA}_x, \overline{PB}_x) \times \frac{(-1)^u i! (\overline{PC}_x)^{i-2r-2u}}{r! u! (i-2r-2u)!} (\frac{1}{4(a+b)})^{r+u} \delta_{I,i-2r-u}$$

- ERI integral

$$I = \frac{2\pi^2}{(a+b)(c+d)} (\frac{1}{a+b+c+d})^{1/2} e^{-ac/(a+b)\cdot\overline{AB}^2 - cd/(c+d)\cdot\overline{CD}^2} \times \sum_{\nu=0}^{N} F_\nu(\overline{PQ}^2/(4\gamma)) \sum_{I=0}^{l_1+l_2+l_3+l_4} \sum_{J=0}^{m_1+m_2+m_3+m_4} \sum_{K=0}^{n_1+n_2+n_3+n_4} D_{l_1 l_2 l_3 l_4}^{I}(A_x, B_x, C_x, D_x) \times D_{m_1 m_2 m_3 m_4}^{J}(A_y, B_y, C_y, D_y) D_{n_1 n_2 n_3 n_4}^{K}(A_z, B_z, C_z, D_z) \delta_{\nu, I+J+K}$$

where

$$\gamma = (a+b+c+d)/[4(a+b)(c+d)]$$

$$D_{l_1 l_2 l_3 l_4}^{I}(A_x, B_x, C_x, D_x) = \sum_{l=0}^{l_1+l_2} \sum_{l'=0}^{l_3+l_4} \sum_{u=0}^{[(l+l')/2]} \frac{(-1)^u (l+l')! \overline{PQ}_x^{l+l'-2u}}{u! (l+l'-2u)! \gamma^{l+l'-u}} \times H_{l_1 l_2}^{l}(\overline{PA}_x, \overline{PB}_x, a+b) (-1)^{l'} H_{l_3 l_4}^{l'}(\overline{QC}_x, \overline{QD}_x, c+d) \delta_{I, l+l'-u}$$

where

$$H_{l_1 l_2}^{l}(\overline{PA}_x, \overline{PB}_x, \beta) = \sum_{i=0}^{l_1+l_2} \sum_{r=0}^{[i/2]} \frac{i!}{r!(i-2r)!(4\beta)^{i-r}} f_i(l_1, l_2, \overline{PA}_x, \overline{PB}_x) \delta_{l, i-2r}$$

5 SCF procedure

procedure

1. read and construct basis set space.
2. calculate S, H, ERI inetgral matrix. Symmetric orthogonalize S to get transfrom matrix X and its inverse Y.
3. assume H as Fock matrix, solve the coefficents, then get initial density matrix P for guess.
4. from P, H, G matrix to claculate Fock matrix, by transform X to F'.
5. solve the eigenvalue problem of F', get its eigenvalues e and eigenvectors C', and by transform X to C.
6. determine the population of MOs, then calculate energy E, density matrix P.
7. if E and P is consistent with the last step, jump loop.

6 Symmetry(lack)

7 Test and result

test	result [au]	Gauss09 [au]	remark
H	-0.42244193	-0.4982329	not suit for open-shell
He	-2.85516043	-2.8551604	yes
H2	-1.11003090	-1.1100309	yes
HeH+	-2.89478689	-2.8947869	yes
H4	-1.80246920	-1.7251712	no
CH4	vibration	-39.9119255	no