Summer Lesson 3 (2017)

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Introduction to basis sets

(1) Slater-type orbitals (STO)

- historically based on atomic calculations. Hydrogen atom states:

$$\psi_{n\ell m}(\vec{r}) \propto (ar)^{\ell} L^{2\ell+1}_{n-\ell-1}(ar)\, e^{-\frac{a}{2}r}\, Y_{\ell m}(\hat{r}_A)$$

$L^{2\ell+1}_{n-\ell-1}$ ... generalized Laguerre polynomial

Motivation for STO:

$$S_\alpha(\vec{r}, \vec{R}_A, \ell, m, \xi_\alpha) = N_\alpha\, r_A^{\ell}\, e^{-\xi_\alpha |\vec{r}-\vec{R}_A|}\, Y_{\ell m}(\hat{r})$$

$Y_{\ell m}(\hat{r})$ ... spherical STO

$r_A = |\vec{r} - \vec{R}_A|$

$\oint \langle S_\alpha | S_\alpha \rangle = 1$

- Applications for diatomic molecules, 1960 – 1980, codes ALCHEMY, ...
- Difficult to extend for polyatomics due to cumbersome 2-electron integrals [xp1pr5]

(2) Gaussian-type orbitals (GTO)

$$g^s_\alpha(\vec{r}, \vec{R}_A, \ell, m, \xi_\alpha) = N^s_\alpha\, r_A^{\ell}\, e^{-\xi_\alpha r_A^2}\, Y_{\ell m}(\hat{r}_A)$$ ... spherical primitive gaussian

$$g^c_\alpha(\vec{r}, \vec{R}_A, \xi_\alpha, n_x, n_y, n_z) = N^c_\alpha (x-A_x)^{n_x}(y-A_y)^{n_y}(z-A_z)^{n_z}\, e^{-\xi_\alpha (\vec{r}-\vec{R}_A)^2}$$ ... cartesian primitive Gaussian

$n_x + n_y + n_z = \ell$

- how are g^s_α and g^c_α linked?

Case $\ell = 0$:

$$g^s_\alpha = N^s_\alpha\, e^{-\xi_\alpha (\vec{r}-\vec{R}_A)^2} \cdot \frac{1}{\sqrt{4\pi}}$$

$$g^c_\alpha = N^c_\alpha\, e^{-\xi_\alpha (\vec{r}-\vec{R}_A)^2}$$

} equal

case $l=1$:

$$g_\alpha^s = N_\alpha^s \; e^{-\xi_\alpha (\vec{r}-\vec{R}_A)^2} \; r_A Y_{1m}(\hat{r}_A)$$

$m=1$: $x_A + i y_A$

$m=0$: z_A

$m=-1$: $x_A - i y_A$

$$g_\alpha^c = N_\alpha \; e^{-\xi_\alpha (\vec{r}-\vec{R}_A)^2}$$

$(x - A_x) = X_A$

$(y - A_y) = y_A$

$(z - A_z) = z_A$

case $l=2$:

$$g_\alpha^s = N_\alpha^s \; e^{-\xi_\alpha (\vec{r}-\vec{R}_A)^2} \; r_A^2 Y_{2m}(\hat{r}_A)$$

5 components

$2 \dots -2$

$$g_\alpha^c = N_\alpha^c \; e^{-\xi_\alpha (\vec{r}-R_A)^2}$$

$x_A^{m_x} y_A^{m_y} z_A^{m_z}$, $m_x + m_y + m_z = 2$

x_A^2, y_A^2, z_A^2, $x_A y_A$, $x_A z_A$, $y_A z_A$

6 components

1 is redundant

case $l=3$: 7 spherical vs. 10 cartesian

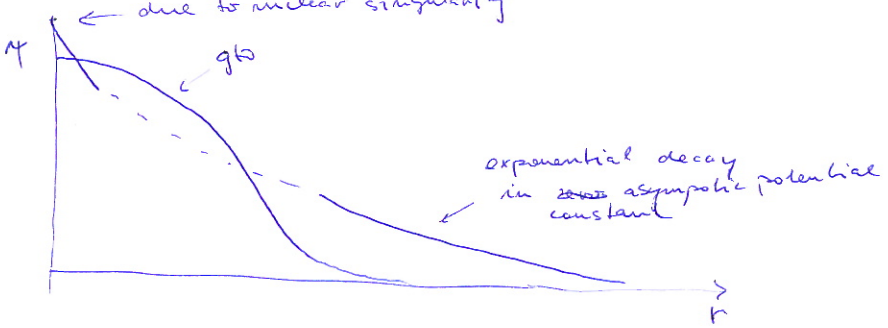
etc

GTO is not that great basis !

Real wave function

← due to nuclear singularity

wrong behavior for $r \to 0$, $r \to \infty$

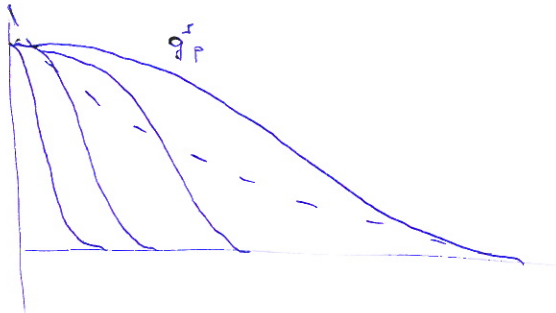


Contracted Gaussian basis

$$g_\alpha(\vec{r}, \vec{R}_A, \underbrace{l, m, \xi_\alpha}_{n_x+n_y+n_z}) = \sum_{p=1}^{L} d_{p\alpha} \, g_p^s(\vec{r}, \vec{R}_A, l, m, \xi_p)$$

Optimization of $g_{p\alpha}$

- fit to STO (STO-3G), (STO$_6$-6G)
- fit to atomic energies



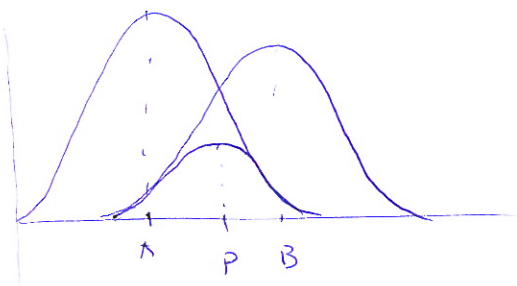
- minimum basis set – example of H_2 – one GTO on each atom
- double zeta + 1 s GTO, + 1 p GTO
- triple zeta + 1 s, + 1 p, + 1 d
- valence double zeta, valence triple zeta
- augmentation

Finally: Why people moved from STO to GTO?

- Because the 2-electron integrals are managable in analytic manner!

Example: $[S_\alpha S_\beta | S_\gamma S_\delta] \sim \int d^3r\, d^3r' \frac{e^{-\alpha(\vec{r}-\vec{A})^2} e^{-\beta(\vec{r}-\vec{B})^2} e^{-\gamma(\vec{r}'-\vec{C})^2} e^{-\delta(\vec{r}'-\vec{D})^2}}{|\vec{r}-\vec{r}'|}$

In 1-dimension $e^{-\alpha(x-A)^2} e^{-\beta(x-B)^2} = e^{-(\alpha+\beta)(x-P)^2} \cdot e^{-\frac{\alpha\beta}{\alpha+\beta}(A-B)^2}$



Integral needs to be made separable in x, y, z

$$\frac{1}{|\vec{r}-\vec{r}'|} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} ds\, e^{-(\vec{r}-\vec{r}')^2 s^2}$$