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Introduction to basis sets

(1) Slater-type orbitals (STO) - historically based on atomic calculations. Hydrogen atom states:

$$\psi_{nlm}(\vec{r}) \sim (ar)^l L_{n-l-1}^{2l+1}(ar) e^{-\frac{a}{2}r} Y_{lm}(\hat{r}_A)$$

↑ generalized Laguerre polynomial

Motivation for STO:

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

↑  $\int \langle S_{\alpha} | S_{\alpha} \rangle = 1$       ↑ spherical STO

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

- Applications for diatomic molecules, 1960-1980, codes: ALCHEMY, ...
- Difficult to extend for polyatomics due to cumbersome 2-electron integrals  $[\chi\beta|\gamma\delta]$

(2) Gaussian-type orbitals (GTO)

$$g_{\alpha}^s(\vec{r}, \vec{R}_A, l, m, \xi_{\alpha}) = N_{\alpha}^s r_A^l e^{-\xi_{\alpha} r_A} Y_{lm}(\hat{r}_A) \dots$$

spherical primitive gaussian

$$g_{\alpha}^c(\vec{r}, \vec{R}_A, \xi_{\alpha}, m_x, m_y, m_z) = N_{\alpha}^c (x-A_x)^{m_x} (y-A_y)^{m_y} (z-A_z)^{m_z} e^{-\xi_{\alpha} (\vec{r}-\vec{R}_A)^2}$$

cartesian primitive Gaussian

$m_x + m_y + m_z = l$

- how are  $g_{\alpha}^s$  and  $g_{\alpha}^c$  linked?

Case  $l=0$  :

$$\left. \begin{aligned} g_{\alpha}^s &= N_{\alpha}^s e^{-\xi_{\alpha} (|\vec{r}-\vec{R}_A|)^2} \\ g_{\alpha}^c &= N_{\alpha}^c e^{-\xi_{\alpha} (\vec{r}-\vec{R}_A)^2} \end{aligned} \right\} \text{equal}$$

$\frac{1}{\sqrt{\pi}}$

case  $l=1$ :

$$g_{\alpha}^s = N_{\alpha}^s e^{-\xi_{\alpha}(\vec{r}-\vec{R}_{\alpha})^2} \underbrace{r_{\alpha}^l Y_{lm}(\hat{r}_{\alpha})}_{\substack{m=1: x_A + iy_A \\ m=0: z_A \\ m=-1: x_A - iy_A}}$$

$$g_{\alpha}^c = N_{\alpha}^c e^{-\xi_{\alpha}(\vec{r}-\vec{R}_{\alpha})^2} \begin{cases} (x-A_x) = X_A \\ (y-A_y) = Y_A \\ (z-A_z) = Z_A \end{cases}$$

case  $l=2$ :

$$g_{\alpha}^s = N_{\alpha}^s e^{-\xi_{\alpha}(\vec{r}-\vec{R}_{\alpha})^2} r_{\alpha}^2 Y_{2m}(\hat{r}_{\alpha}) \begin{cases} 5 \text{ components} \\ 2 \dots -2 \end{cases}$$

$$g_{\alpha}^c = N_{\alpha}^c e^{-\xi_{\alpha}(\vec{r}-\vec{R}_{\alpha})^2} \begin{matrix} m_x & m_y & m_z & \\ X_A & Y_A & Z_A & \\ & X_A^2 & Y_A^2 & \\ & Y_A Z_A & Z_A^2 & \\ & X_A Y_A & X_A Z_A & \\ & Y_A Z_A & & \end{matrix} \begin{cases} 6 \text{ components} \\ 1 \text{ is redundant} \end{cases}$$

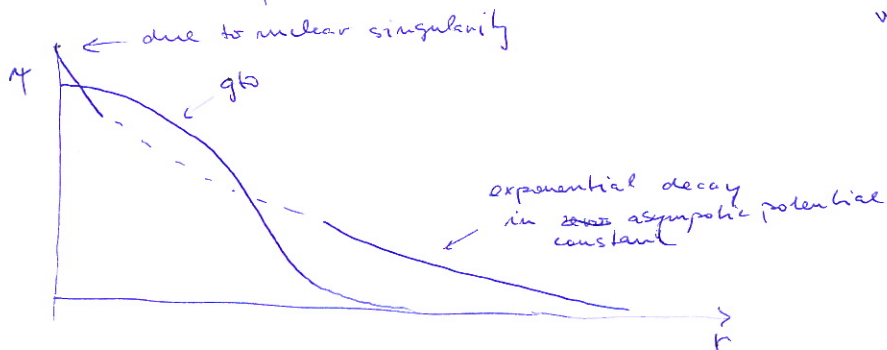
$m_x + m_y + m_z = 2$

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

etc

GTO is not that great basis!

Real wave function



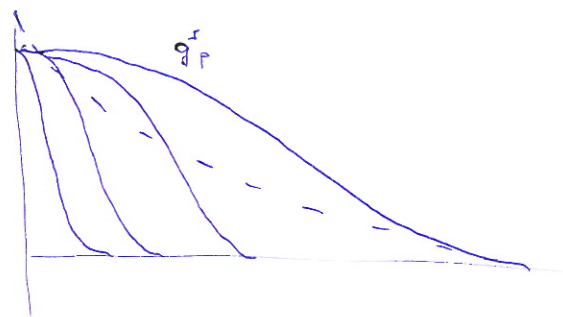
wrong behavior for  $r \rightarrow 0$   
 $r \rightarrow \infty$

Contracted Gaussian basis

$$g_{\alpha}(\vec{r}, \vec{R}_{\alpha}, \xi_{\alpha}, l, m, \xi_{\alpha}) = \sum_{p=1}^L c_p g_p^s(\vec{r}, \vec{R}_{\alpha}, l, m, \xi_p)$$

Optimization of  $g_{\alpha}$

- fit to STO (STO-3G)  
(STO-6G)
- fit to atomic energies



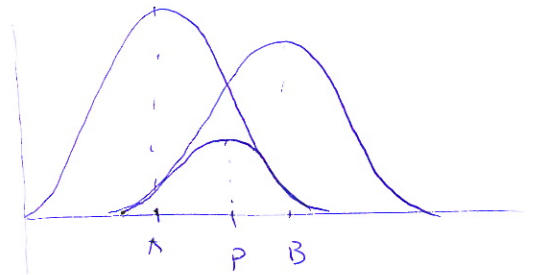
- minimum basis set - example of  $H_2$  - ~~one~~ one GTO on each atom
- double zeta + 1 s GTO, + 1 p GTO
- triple zeta + 1 s, + 1 p, + 1 d
- valence double zeta, valence triple zeta
- augmentation

Finally: Why people moved from STO to GTO?

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

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

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



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

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

