# Lecture 5 - Basis Sets



- Basis sets: Expansion of real solutions.
- Gaussian basis sets.
- Contracted and primitive Gaussians.
- Angular dependence of basis functions.

# Orbital Expansion Into a Basis Set



- A discrete representation of a wave function is needed.
- The usual approach: expand the unknown function $\psi(\vec{r})$ in a series of basis functions $b_i(\vec{r})$

$$\psi(\vec{r}) = \sum_i c_i b_i(\vec{r}) \, .$$

- Vector of expansion coefficients $[c_i]$ constitutes a discrete representation of the function $\psi(\vec{r})$.
- Proper choice of the basis set $b_i(\vec{r})$ is crucial.

# Common Basis Sets

- equidistant grid has a long history in the numerical analysis.
  - + Many well established algorithms exist and resulting equations are very simple.
  - + needed integrals are trivial to compute due to orthogonality.
  - - dense grid necessary.
- Slater orbitals.
  - + This basis set converges very fast, particularly for light atoms.
  - - sensitive to *basis set superposition error*, Basis Set Supperposition Error (BSSE) because of difusiness
  - - needed integrals usually cannot be evaluated analytically when this basis set is used and require time-consuming numerical integration.
- Gaussian functions $\exp(-\alpha r^2)$
  - + Many integrals can be evaluated analytically.
  - - Some BSSE problem.

# Contracted Gaussians.



- Core orbitals require many primitives to reproduce the sharp tip close to nuclei.
- Core orbitals rarely change in molecules
- Solution: fix the expansion coefficients and reduce the number of coefficients by factor $X$.

$$\varphi_j(\vec{r}) = \sum_{p=1}^{KX} c_{pj} G_p(\vec{r}) \quad \rightarrow \quad \varphi_j(\vec{r}) = \sum_{p=1}^{K} c'_{pj} \sum_{r=1}^{X} G_{pr}(\vec{r})$$

- Works well in most cases: energies, chemistry, properties dependent on valence structure.
- Removes flexibility: Breaks when small perturbations to core orbitals are investigated.
- Valence orbitals very seldom contracted.

# Angular Dependence of Basis Functions



- Need for angular dependence evident in atoms (*s*, *p*, *d* shells).
- In molecules, chemical bonds introduce additional angular dependence.
- Cartesian vs Spherical harmonics.

$$\{1\}G(r), \{x, y, z\}G(r) \dots$$

Cartesian: $\{x^2, y^2, xz, yz, z^2, xy\}G(r)$
Spherical $\{x^2, y^2, xz, yz, 3z^2 - 1\}G(r)$.

# Classes of Gaussian Basis Sets.



- Minimal basis set.
- Double-zeta, triple zeta: add extra radial flexibility to the basis set.
- "Polarized" basis sets: better bond description.
- Diffuse (augmented) basis sets: better description of polarized or excited states.

# Exercise



- Prove the Gaussian Product Rule: given a Gaussian function $G_\alpha(x) = \exp(-\alpha x^2)$, prove that their product is another Gaussian, centered at some new center $X_{12}$, with some exponent $\gamma$ and with a prefactor $a$:

$$G_\alpha(x - X_1)G_\beta(x - X_2) = aG_\gamma(x - X_{12})$$

  Determine $X_{12}$, $\gamma$ and $a$.

- Use it to compute overlap between two one dimensional Gaussian functions (this is needed to construct the overlap matrix).

$$S_{pq} = \int_{-\infty}^{\infty} \left(\frac{2\alpha_p}{\pi}\right)^{1/4} e^{-\alpha_p|x-x_p|^2} \left(\frac{2\alpha_q}{\pi}\right)^{1/4} e^{-\alpha_q|x-x_q|^2} \, \mathrm{d}x$$