Approximate Methods in Quantum Chemistry
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Lecture No. 35
Basic Sets - I

Hello students! Welcome to this lecture. In the last few lectures we discussed the Hartree-Fock-Roothan scheme where we expressed orbitals as a linear combination of basis functions. In this lecture, we will discuss the form and properties of some of the popularly used basis functions.

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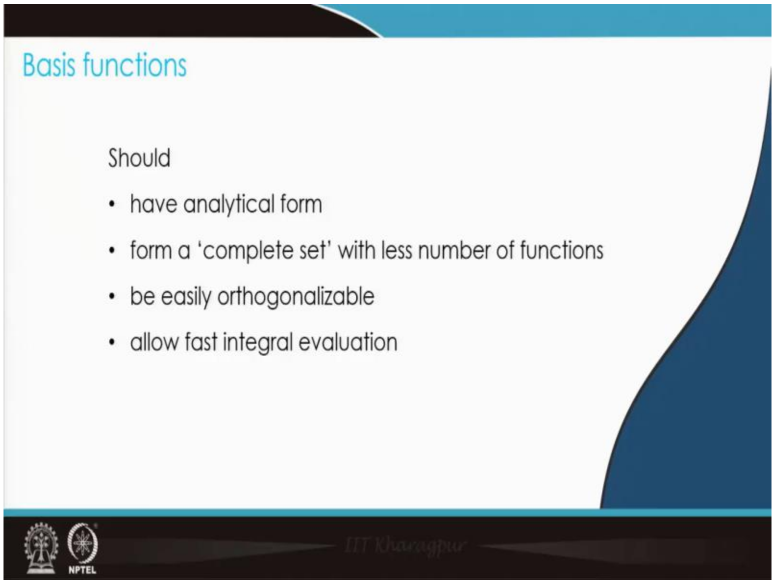

Basis functions

Should

- have analytical form
- form a 'complete set' with less number of functions
- be easily orthogonalizable
- allow fast integral evaluation

We would like to have a set of basis functions that have analytical form which not only gives us some physical insight but also helps in doing faster computation, for example in evaluating integrals. We would also like to have a basis set that works well even with less number of functions, since the number of functions influence the cost of the calculations. We also want functions that are easily orthogonalizable (without leading to numerical instabilities) and also those which allow fast integral evaluation, since we spend a lot of resources in evaluating large number of 2-electron integrals.

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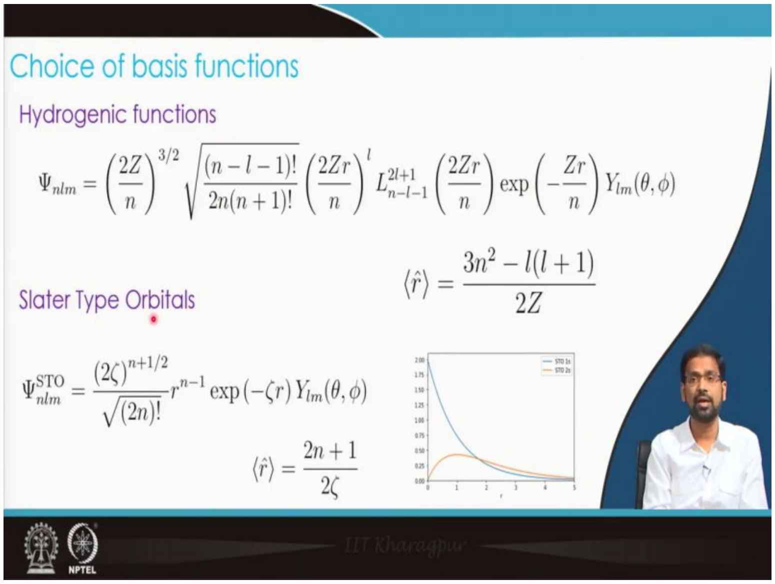

Choice of basis functions

Hydrogenic functions

$$\Psi_{nlm} = \left(\frac{2Z}{n}\right)^{3/2} \sqrt{\frac{(n-l-1)!}{2n(n+1)!}} \left(\frac{2Zr}{n}\right)^{l} L^{2l+1}_{n-l-1}\left(\frac{2Zr}{n}\right) \exp\left(-\frac{Zr}{n}\right) Y_{lm}(\theta,\phi)$$

$$\langle \hat{r} \rangle = \frac{3n^2 - l(l+1)}{2Z}$$

Slater Type Orbitals

$$\Psi^{\mathrm{STO}}_{nlm} = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}} r^{n-1} \exp\left(-\zeta r\right) Y_{lm}(\theta,\phi)$$

$$\langle \hat{r} \rangle = \frac{2n+1}{2\zeta}$$

Since quantum mechanics can offer an exact solution only for hydrogenic atoms, it is natural to design the basis functions for heavier atoms somewhat similar to those of the hydrogenic functions,

$$\Psi_{nlm} = \left(\frac{2Z}{n}\right)^{3/2} \sqrt{\frac{(n-l-1)!}{2n(n+1)!}} \left(\frac{2Zr}{n}\right)^{l} L^{2l+1}_{n-l-1}\left(\frac{2Zr}{n}\right) \exp\left(-\frac{Zr}{n}\right) Y_{lm}(\theta,\phi)$$

The hydrogenic functions have radial and angular parts. The angular part is given by spherical harmonics, while the radial part contains (apart from the normalization constant) an exponentially decaying function and some polynomial form given by the Laguerre polynomials. The latter provide the nodal structure to the radial function of the hydrogen atom. The expectation value of *r*, using the hydrogenic functions is given by

$$\langle \hat{r} \rangle = \frac{3n^2 - l(l+1)}{2Z}$$

which shows n^2 dependency, suggesting the highly diffused nature of the functions. To describe bonding with such functions would require a large number of functions in the basis set, thus raising the cost. The most popular alternative to the hydrogenic functions are the Slater type orbitals,

$$\Psi^{\mathrm{STO}}_{nlm} = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}} r^{n-1} \exp\left(-\zeta r\right) Y_{lm}(\theta,\phi)$$

Here, the angular part is still given by spherical harmonics. The exponential function now contains ζ, which refers to the orbital exponent that can be fitted to values that best represent the screening effects of other electrons that are closer to the nucleus. The most important difference from the hydrogenic functions is the replacement of Laguerre polynomials by the simple r^{n-1}. Instead of retaining the entire Laguerre polynomials and the nodal structures, the Slater type orbitals only considers the highest order term in the Laguerre polynomaial, i.e., r^{n-1}. This ensures the correct behaviour at large r while losing the nodal structure which leads to a more compact electron distribution, as can be seen from the expectation value of r $\langle \hat{r} \rangle = \dfrac{2n+1}{2\zeta}$

Slater type orbitals are fine for the calculations for atoms or diatomics. When the number of atom increases, it leads to more number of functions centred on different locations. This leads to the evaluation of more number of 4-centered 2-electron integrals. In such cases, the evaluation large number of integrals using the Slater type orbitals becomes extremely expensive. We, therefore, need an alternative.

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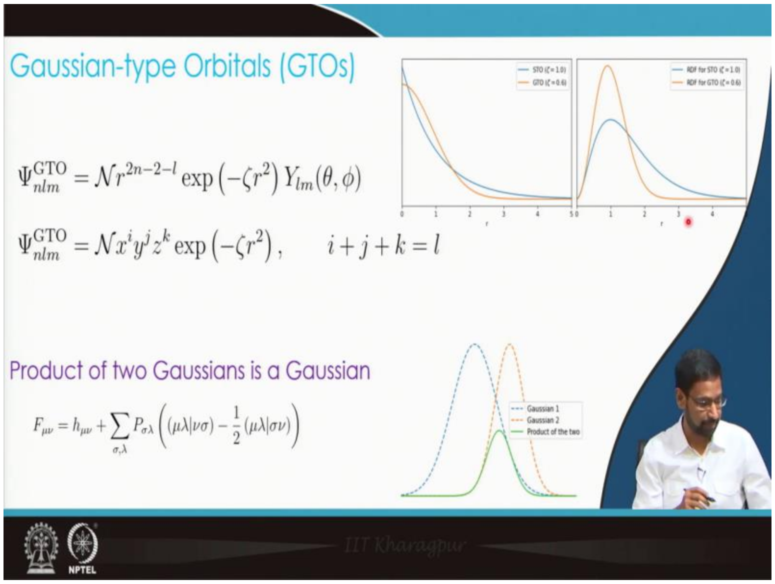

Gaussian-type Orbitals (GTOs)

$$\Psi_{nlm}^{\text{GTO}} = \mathcal{N} r^{2n-2-l} \exp\left(-\zeta r^2\right) Y_{lm}(\theta, \phi)$$

$$\Psi_{nlm}^{\text{GTO}} = \mathcal{N} x^i y^j z^k \exp\left(-\zeta r^2\right), \qquad i+j+k=l$$

Product of two Gaussians is a Gaussian

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma,\lambda} P_{\sigma\lambda}\left((\mu\lambda|\nu\sigma) - \frac{1}{2}(\mu\lambda|\sigma\nu)\right)$$

That search culminated in Pople's suggestion of using the so-called Gaussian type of functions as opposed to the Slater type of orbitals. A GTF has the form (in spherical-polar and Cartesian coordinates),

$$\Psi_{nlm}^{\text{GTO}} = \mathcal{N} r^{2n-2-l} \exp\left(-\zeta r^2\right) Y_{lm}(\theta, \phi)$$

Note the presence of $e^{-\zeta r^2}$ as opposed to an exponential function in the STO. The GTF contains the angular part and a radial polynomial r^{2n-2-l}. But the GTFs are popularly used in the Cartesian form.

$$\Psi_{nlm}^{\text{GTO}} = \mathcal{N} x^i y^j z^k \exp\left(-\zeta r^2\right), \qquad i+j+k=l$$

For an s-orbital basis function ($l = 0$), $i=j=k=0$. For a p-type function, i,j,k can have 1,0,0 or 0,1,0 or 0,0,1, representing a p_x, p_y, p_z, orbital. Similarly, for d-orbital there will 6 functions and for *f*-orbital there will be 10 functions. Using linear combination, the 6 (or 10) Cartesian functions are expressed as 5 (or 7) canonical d (or f) orbitals.

A key advantage of the GTFs over the STOs is the very useful property that the product of two Gaussians is a Gaussian. The width and location of the product Gaussian can be obtained from simple algebraic form of the width and location of the two Gaussians. This property significantly reduces the cost of integral evaluations, especially over those functions that are centered over different nuclei. But when we compare a Gaussian type of function to the realistic orbitals (for example, the Slater type orbitals in a hydrogen atom), we see that the cusp like feature is absent in the GTFs (at r = 0, see the above diagram in the slide). The radial distribution function of a GTF is quite different from that of a STO, especially at large r values.

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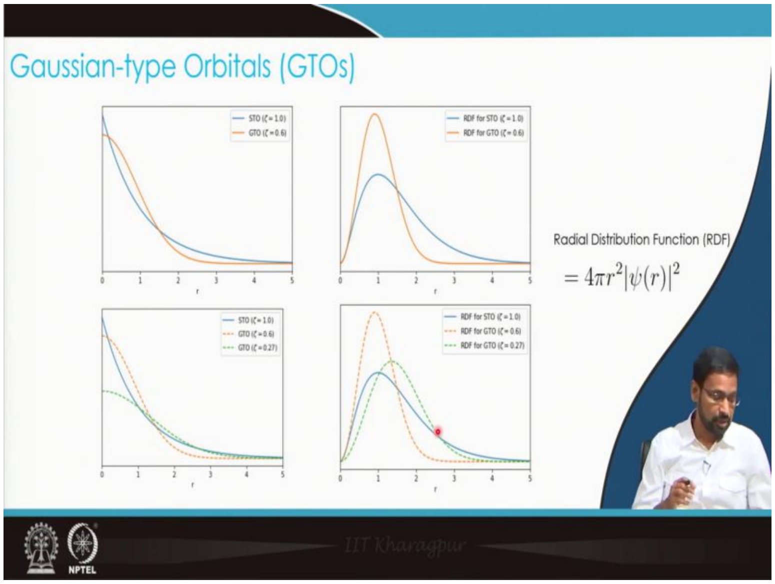

Gaussian-type Orbitals (GTOs)

Radial Distribution Function (RDF)

$$= 4\pi r^2 |\psi(r)|^2$$

Let us consider a STO with ζ = 1.0 and a GTF with ζ = 0.6. While the two functions compare reasonably well at small r (with obvious lack of cusp in the GTF), the similalrity is poor at at large *r*. Similar observation is also made when their radial distribution functions are compared, see the top two diagrams in the above slide. Next, let us compare the STO with a GTF with $\zeta = 0.27$. This GTF reproduces the large *r* behavior of the STO while significantly differing at small *r*. Same is observed in their radial distribution functions. While one GTF reproduces small *r* region of the STO the other one reproduces its large *r* behavior. Hence, it was proposed to use more than 1 GTFs to express a STO.

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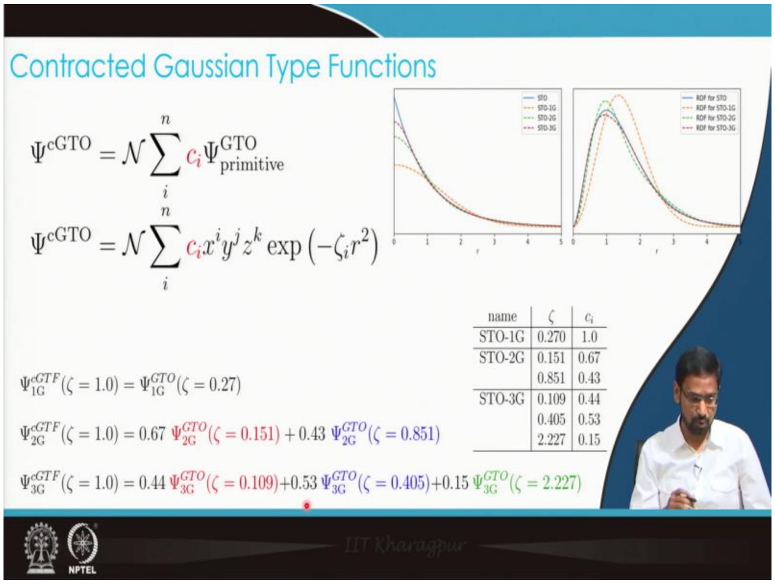

Contracted Gaussian Type Functions

$$\Psi^{\mathrm{cGTO}} = \mathcal{N}\sum_i^n c_i \Psi^{\mathrm{GTO}}_{\mathrm{primitive}}$$

$$\Psi^{\mathrm{cGTO}} = \mathcal{N}\sum_i^n c_i x^i y^j z^k \exp\left(-\zeta_i r^2\right)$$

name	ζ	c_i
STO-1G	0.270	1.0
STO-2G	0.151	0.67
	0.851	0.43
STO-3G	0.109	0.44
	0.405	0.53
	2.227	0.15

$\Psi^{cGTF}_{1\mathrm{G}}(\zeta = 1.0) = \Psi^{GTO}_{1\mathrm{G}}(\zeta = 0.27)$

$\Psi^{cGTF}_{2\mathrm{G}}(\zeta = 1.0) = 0.67\ \Psi^{GTO}_{2\mathrm{G}}(\zeta = 0.151) + 0.43\ \Psi^{GTO}_{2\mathrm{G}}(\zeta = 0.851)$

$\Psi^{cGTF}_{3\mathrm{G}}(\zeta = 1.0) = 0.44\ \Psi^{GTO}_{3\mathrm{G}}(\zeta = 0.109) + 0.53\ \Psi^{GTO}_{3\mathrm{G}}(\zeta = 0.405) + 0.15\ \Psi^{GTO}_{3\mathrm{G}}(\zeta = 2.227)$

This is achieved by the so-called contracted Gaussian type of functions, where one takes several *primitive* Gaussian type of functions (as a linear combination with coefficient c_is) and form a contracted GTO.

$$\Psi^{\mathrm{cGTO}} = \mathcal{N}\sum_i^n c_i \Psi^{\mathrm{GTO}}_{\mathrm{primitive}}$$

$$\Psi^{\mathrm{cGTO}} = \mathcal{N}\sum_i^n c_i x^i y^j z^k \exp\left(-\zeta_i r^2\right)$$

The coefficients are obtained by comparing the sum (the contracted GTO) to one Slater type of orbital corresponding to that electronic function. Following 3 contractions schemes show use of 1, 2, and 3 GTFs to reproduce a STO with $\zeta = 1.0$, i.e.,

$\Psi^{cGTF}_{1\mathrm{G}}(\zeta = 1.0) = \Psi^{GTO}_{1\mathrm{G}}(\zeta = 0.27)$

$\Psi^{cGTF}_{2\mathrm{G}}(\zeta = 1.0) = 0.67\ \Psi^{GTO}_{2\mathrm{G}}(\zeta = 0.151) + 0.43\ \Psi^{GTO}_{2\mathrm{G}}(\zeta = 0.851)$

$\Psi^{cGTF}_{3\mathrm{G}}(\zeta = 1.0) = 0.44\ \Psi^{GTO}_{3\mathrm{G}}(\zeta = 0.109) + 0.53\ \Psi^{GTO}_{3\mathrm{G}}(\zeta = 0.405) + 0.15\ \Psi^{GTO}_{3\mathrm{G}}(\zeta = 2.227)$

The comparison of these cGTFs with the STO are shown in the figures in the slide above. As can be seen, the STO is effectively reproduced by using 3 GTFs. Such a basis set is called STO-*n*G where n = 1, 2, 3 etc. In the STO-3G basis, we see a GTF with large exponent (fast decay) with small relative contribution (the coefficient) while a GTF with small exponent (slow decay) with a larger contribution. Such fine balancing between large/small exponent GTFs ensure a good match with the STO.

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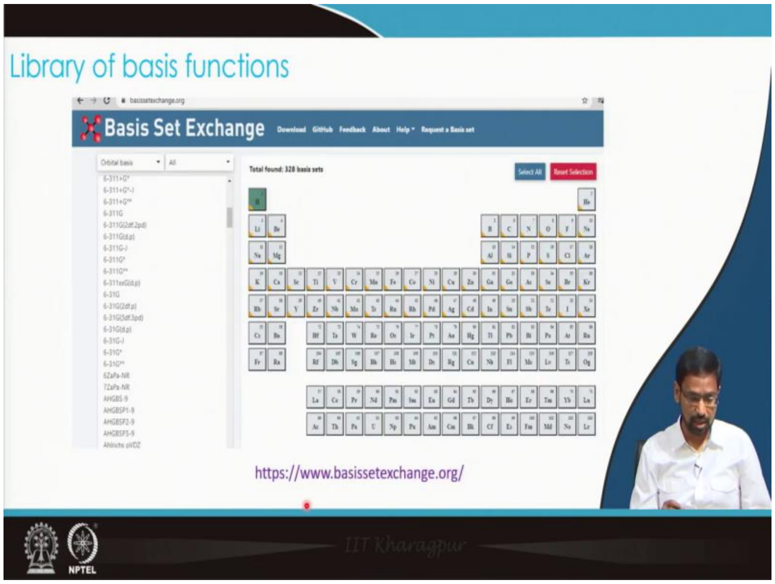

Library of basis functions

https://www.basissetexchange.org/

We can find these basis sets (the coefficients and the exponents) for different atoms from some standard library. One possible source is the website www.basissetexchange.org, where you have a clickable periodic table. You can select any element and you will see a list of available basis functions. We will discuss some of the the popular basis functions in our next lecture.

Thank you for your attention.