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A Review on Basis Sets in Quantum Chemistry

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Abstract

Basis sets play a central role in quantum chemical calculations by providing mathematical functions to approximate molecular orbitals. The accuracy of methods such as Hartree–Fock (HF) and Density Functional Theory (DFT) strongly depends on the choice of basis set. This review summarizes the theoretical foundation, classification, commonly used basis sets, and recent developments, highlighting their importance in achieving reliable computational results while balancing computational cost.

1 Introduction

A basis set is a mathematical representation of a system's orbitals used in modeling or approximation theoretical calculations. It is a collection of fundamental functional building pieces that can be added to or stacked to provide the characteristics we require [1]. In mathematics, "stacking" refers to the addition of items, possibly after each is multiplied by a constant:

$$\psi = a_1\phi_1 + a_2\phi_2 + \ldots + a_k\phi_k$$

where k is the size of the basis set, $\phi 1$, $\phi 2$, . . . ,ϕk are the basis functions and $a1$, $a2$, . . . ,ak are the normalization constants. Slater Type Orbitals (STOs), or orbital computing utilizing basis sets, were initially used by John C. Slater [2]. As shown in Table 1, the solution of the Schrödinger equation for the hydrogen atom and other one-electron ions yields atomic orbitals that are the product of a spherical harmonic and a radial function that depends on the electron's distance from the nucleus [3].

Table 1 Radial and angular wavefunctions of orbitals. Here, *z* is the effective nuclear charge for that orbital of the atom, *r* is the radius in atomic units.

No.	Orbital	Radial wavefunction	Angular wavefunction
1	1s	$2 \times z^{3/2} \times e^{-\rho/2}$	$1 \times (\pi/4)^{1/2}$
2	2s	$(\sqrt{2}/2) \times (2-\rho) \times z^{3/2} \times e^{-\rho/2}$	$1 \times (\pi/4)^{1/2}$
3	2p	$(\sqrt{6}/2) \times \rho \times z^{3/2} \times e^{-\rho/2}$	$\sqrt{3} \times (x/r) \times (\pi/4)^{1/2}$
4	3s	$\left(\sqrt{3}/9 \times \left(6-6\rho+\rho^2\right) \times z^{3/2} \times e^{-\rho/2}\right)$	$1 \times (\pi/4)^{1/2}$
5	3p	$\left(\sqrt{6}/9 \times \rho\,(4-\rho) \times z^{3/2} \times e^{-\rho/2}\right)$	$\sqrt{3} \times (x/r) \times (\pi/4)^{1/2}$

Quantum chemistry aims to solve the Schrödinger equation for molecular systems. Since exact solutions are not feasible for multi-electron systems, approximations are required. One such approximation involves expressing molecular orbitals as linear combinations of basis functions, typically cantered on atoms (Linear Combination of Atomic Orbitals, LCAO). The choice of basis set significantly affects the accuracy of calculated properties such as energies, geometries, dipole moments, and spectroscopic parameters. Therefore, understanding basis sets is crucial for reliable computational modelling [4].

2. Theoretical Background

In the LCAO approach, a molecular orbital ψ is expressed as:

$$\psi = \sum_i c_i \phi_i$$

where ϕ_i are basis functions and c_i are coefficients determined variationally.

The basis sets are primarily classified by the type of function used and their size or level of complexity. There are two main types of basis functions are used. These are Slater-Type Orbitals (STOs) and is given by

$$\phi(r) \propto e^{-\zeta r}$$

The STOs resemble hydrogen-like orbitals but are computationally expensive [5]. The second is Gaussian-Type Orbitals (GTO) and is represented as

$$\phi(r) \propto e^{-\alpha r^2}$$

These are computationally efficient and widely used despite their less accurate radial behaviour [6].

3. Classification of Basis Sets

Basis sets are further categorized based on how many functions they use to describe each orbital. These are:

3.1 Minimal Basis Sets

Minimal basis sets use the smallest number of functions required to represent each atomic orbital. STO-3G basis set is one of the example of a minimal basis set. These types of basis sets have low computational cost but they have poor accuracy [2].

3.2 Split-Valence Basis Sets

These basis sets use multiple functions for valence orbitals to improve flexibility. The examples are 3-21G, 6-31G. Here double-zeta (DZ) and triple-zeta (TZ) basis sets increase accuracy of computation [2].

3.3 Polarized Basis Sets

Polarization functions allow orbitals to distort in the presence of bonding or external fields. These are represented as 6-31G(d), 6-31G(d,p), 6-311G(d,p) etc. These basis sets improve description of chemical bonding and reactivity [2].

3.4 Diffuse Basis Sets

Diffuse functions are important for systems with loosely bound electrons. These basis sets are denoted as 6-31+G, 6-31++G(d,p) etc. These basis sets are useful for anions, excited states, and weak interactions [2].

3.5 Correlation-Consistent Basis Sets

Developed to systematically converge electron correlation energy. The cc-pVDZ, cc-pVTZ, cc-pVQZ etc. are some examples of such types of basis sets and are widely used in post-HF methods [2].

3.6 Pople Basis Sets

The Pople basis sets are very popular and widely used in DFT and HF calculations. The examples are 6-31G, 6-311G etc. These basis sets are easy to use but less systematic compared to modern sets [2].

3.7 Def2 Basis Sets

Def2 Basis Sets are modern basis sets with improved efficiency and accuracy. The basis sets like def2-SVP, def2-TZVP etc. are the examples of such type of basis sets. These are compatible with effective core potentials (ECPs) [2].

4. Effective Core Potentials (ECPs)

ECPs replace inner core electrons with an effective potential, reducing computational cost. These are useful for heavy atoms and LANL2DZ, Stuttgart-Dresden ECPs are the examples of this type of basis sets [7].

5. Basis Set Superposition Error (BSSE)

BSSE arises when basis functions from one fragment artificially stabilize another fragment in a complex. These are corrected using the counterpoise method and are important in weakly bound systems (e.g., van der Waals complexes).

6. Basis Set Convergence

Increasing basis set size improves accuracy but increases computational cost. A balance is required:

- Minimal → qualitative results
- Double-zeta → moderate accuracy
- Triple-zeta and higher → high accuracy

7. Recent Developments in Basis Sets

Recent advancements in basis sets include explicitly correlated methods (F12) for faster convergence, adaptive and numerical basis sets, machine learning-assisted basis set optimization and development of property-optimized basis sets.

8. Applications

Basis sets have various application and are essential in molecular structure optimization, spectroscopic property prediction, reaction mechanism studies, drug design and materials science and nonlinear optical (NLO) property calculations.

9. Conclusion

Basis sets are fundamental to quantum chemical calculations, influencing both accuracy and efficiency. While minimal basis sets offer computational speed, larger and more flexible basis sets provide better accuracy. Modern developments aim to achieve near-complete basis set accuracy with reduced computational cost, making them indispensable tools in computational chemistry.

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