

Ab Initio

The term "Ab Initio" means "from the beginning". This name is given to computations which are derived directly from theoretical principles, with no inclusion of experimental data. Most of the time this is referring to an approximate quantum mechanical calculation. The approximations made are usually mathematical approximations, such as using a simpler functional form for a function or getting an approximate solution to a differential equation.

The most common type of ab initio calculation is called a Hartree Fock calculation (abbreviated HF), in which the primary approximation is called the central field approximation. This means that the Coulombic electron-electron repulsion is not specifically taken into account. However, its net effect is included in the calculation. This is a variational calculation, meaning that the approximate energies calculated are all equal to or greater than the exact energy. The energies calculated are usually in units called Hartrees ($1 \text{ H} = 27.2114 \text{ eV}$). ***Because of the central field approximation, the energies from HF calculations are always greater than the exact energy and tend to a limiting value called the Hartree Fock limit.***

The second approximation in HF calculations is that the wave function must be described by some functional form, which is only known exactly for a few one electron systems. The functions used most often are linear combinations of Slater type orbitals $\exp(-ax)$ or Gaussian type orbitals $\exp(-ax^2)$, abbreviated STO and GTO. The wave function is formed from linear combinations of atomic orbitals or more often from linear combinations of basis functions. Because of this approximation, most HF calculations give a computed energy greater than the Hartree Fock limit. The exact set of basis functions used is often specified by an abbreviation, such as STO-3G or 6-311++g**.

A number of types of calculations begin with a HF calculation then correct for the explicit electron-electron repulsion, referred to as correlation. Some of these methods are Moller-Plesset perturbation theory (MP n , where n is the order of correction), the Configuration Interaction (CI) etc.

An alternative ab initio method is Density Functional Theory (DFT), in which the total energy is expressed in terms of the total electron density, rather than the wavefunction. In this type of calculation, there is an approximate Hamiltonian and an approximate expression for the total electron density.

The good side of ab initio methods is that they eventually converge to the exact solution, once all of the approximations are made sufficiently small in magnitude. However, this convergence is not monotonic. Sometimes, the smallest calculation gives the best result for a given property.

The bad side of ab initio methods is that they are expensive. These methods often take enormous amounts of computer cpu time, memory and disk space. The HF method scales as N^4 , where N is the number of basis functions, so a calculation twice as big takes 16 times as long to complete. Correlated calculations often scale much worse than this. In practice, extremely accurate solutions are only obtainable when the molecule contains half a dozen electrons or less.

In general, ab initio calculations give very good qualitative results and can give increasingly accurate quantitative results as the molecules in question become small.

The first step in computational chemistry is the calculation of the molecular orbitals (MOs) for a given molecule. If we can calculate the MOs for a molecule, then we can know lots of things about the molecule, including its:

- energy
- electron density
- electrostatic potential
- transition state
- frequency

BASIS SET APPROXIMATION

A molecular-orbital theory calculation is a mathematical expression of an electron in a molecule. Although there are many types of molecular-orbital functions, in this lab we will only look at the Slater Type Orbitals (STOs) and the Gaussian Type Orbitals (GTOs).

Although there is not a major difference in these two methods when calculating small molecules, major discrepancies arise for larger molecules of 30 or more atoms. STOs require more calculating, which takes tremendous amounts of time, however their calculations have been found to be more accurate than GTOs. On the other hand, GTOs, although less accurate, are much faster to calculate than STOs. This forced scientists to compromise time or accuracy.

Eventually, scientists realized that by adding several GTOs, they were able to mimic the STOs accuracy. In fact, as the number of GTOs used increased, the better they were able to model the STO equation.

When using GTOs to model STOs, the new equations are given a new name. They are identified as STO-kG equations where k is a constant that represents the number of GTOs used. For instance, two common equations are the STO-3G and the STO-6G in which 3 and 6 GTOs are used respectively.

BASIS SETS

- In quantum chemistry, the “basis set” usually refers to the set of (nonorthogonal) one-particle functions used to build molecular orbitals.
- Sometimes, theorists might also refer to N-electron basis sets, which is something else entirely — sets of Slater determinants.

Basis Sets in Quantum Chemistry

- LCAO-MO approximation: MO's built from AO's
- An “orbital” is a one-electron function

- AO's represented by atom-centered Gaussians in most quantum chemistry programs
- Some older programs used "Slater functions" (STO's)

SLATER TYPE ORBITAL

$$\Phi_{abc}^{\text{STO}}(x, y, z) = N x^a y^b z^c e^{-\zeta r}$$

- N is a normalization constant
- a, b, c control angular momentum, $L = a + b + c$
- ζ (zeta) controls the width of the orbital (Large ζ gives tight function, small ζ gives diffuse function)
- These are H-atom-like functions, at least for 1s; however, they lack radial nodes and are not pure spherical harmonics.
- but they possess correct short-range and long-range behavior

GAUSSIAN TYPE ORBITAL

$$\Phi_{abc}^{\text{GTO}}(x, y, z) = N x^a y^b z^c e^{-\zeta r^2}$$

- Again, a, b, c control angular momentum, $L = a + b + c$
- Again, ζ controls width of orbital
- No longer H-atom-like, even for 1s
- Much easier to compute (Gaussian product theorem)
- Almost universally used by quantum chemists

CONTRACTED GAUSSIAN-TYPE ORBITALS (CGTO'S)

- STO's are more accurate, but it takes longer to compute integrals using them.
- So we use a linear combination of enough GTO's to mimic an STO
- A combination of GTO's used to mimic an STO is called an STO-nG even though it is made of contracted GTO's

$$\Phi_{abc}^{\text{CGTO}}(x, y, z) = N \sum c_i x^a y^b z^c e^{-\zeta_i r^2}$$

A basis set of Contracted Gaussian-Type Orbitals (CGTO's) needs to specify the exponents (ζ 's) and the contraction coefficients (c 's).

TYPES OF BASIS SETS

- 1) **Minimal basis set:** One basis function (STO, GTO, or CGTO) for each atomic orbital in the atom
- 2) **Double-zeta basis set:** Two basis functions for each AO. It allows treatment of spatially different bonds at the same atom.
- 3) **Triple-zeta basis sets:** Three basis functions for each AO

and etc.

Having different-sized functions allows the orbital to get bigger or smaller when other atoms approach it

SPLIT VALENCE

- A "split-valence" basis uses only one basis function for each core AO, and a larger basis for the valence AO's .
- In Split-valence basis set each valence orbital are modeled by two or more basis functions that have different exponents

Examples

- H atom, minimal basis: One 1s AO, one (STO, GTO, or CGTO) basis function
- C atom, minimal basis: 1s, 2s, 2px, 2py, 2pz AO's (5), so 5 basis functions
- C atom, double-zeta basis: Two basis functions per AO, so 10 basis functions
- C atom, split-valence double-zeta basis: 9 basis functions

Note: Application of double zeta basis functions

- C-H σ -bond: H 1s orbital and C 2pz.
- C-N π -bond: C and N 2px (and 2py) AOs.
- π -bond is more diffuse: optimal ζ for px (py) is smaller than for more localized pz.

Double Zeta describe charge distribution in both parts of the molecule: optimized AO coefficient (in MO expansion) of 'tighter' inner pz function on carbon will be larger in the C-H bond. More diffuse outer px and py functions will have larger AO coefficients in the π -bond.

POLARIZATION FUNCTIONS

- As other atoms approach, an atom's orbitals might want to shift to one side or the other (polarization).
- An s orbital can polarize in one direction if it's mixed with a p orbital.
 - p orbitals can polarize if mixed with d orbitals
 - In general, to polarize a basis function with angular momentum l , mix it with basis functions of angular momentum $l + 1$
 - This gives "polarized double-zeta", or "double-zeta plus polarization" basis sets, etc

Counting Polarization Functions

- We know there should be 5 d functions (usually chosen as dx^2-y^2 , dz^2 , dxy , dxz , and dyz); these are called "pure angular momentum" functions
- Computers would prefer to work with 6 d functions (dx^2 , dy^2 , dz^2 , dxy , dxz , and dyz); these are called "6 Cartesian d functions"

- $dx^2 + dy^2 + dz^2$ looks like an s orbital
- Similar answers are obtained using 5 or 6 d functions
- For f functions, it's 7 versus 10 f functions
- Some basis sets were developed using 5d's [cc-pVXZ, newer Pople basis sets like 6-311G(3df)], & some using 6 d's [older Pople basis sets like 6-31G(d)]; results don't change much, but it is more consistent to use the same number of polarization functions as the basis set designer

DIFFUSE FUNCTIONS

- Diffuse functions have small ζ exponents; this means the electron is held far away from the nucleus
- Necessary for anions, Rydberg states, very electronegative atoms (fluorine) with a lot of electron density
- Necessary for accurate polarizabilities or binding energies of van der Waals complexes (bound by dispersion)
- It is very bad to do computations on anions without using diffuse functions; results could change completely.

POPLE BASIS SETS

Developed by the late Nobel Laureate, **John Pople**, and popularized by the Gaussian set of programs

- **STO-3G is a minimal basis set in which each AO is represented by 3 Gaussians (3G), chosen to mimic the behavior of a STO**
- **Pople's split-valence double-zeta basis set is called 6-31G; the core orbital is a CGTO made of 6 Gaussians, and the valence is described by two orbitals — one CGTO made of 3 Gaussians, and one single Gaussian.**
- **6-31G* [or 6-31G(d)] is 6-31G with added d polarization functions on non-hydrogen atoms; 6-31G** [or 6-31G(d,p)] is 6-31G* plus p polarization functions for hydrogen**
- **6-311G is a split-valence triple-zeta basis; it adds one GTO to 6-31G**

- **6-31+G is 6-31G plus diffuse s and p functions for non- hydrogen atoms; 6-31++G has diffuse functions for hydrogen also**
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DUNNING'S CORRELATION-CONSISTENT BASIS SETS

- Thom Dunning pointed out that basis sets optimized at the Hartree-Fock level might not be ideal for correlated computations
- The “correlation consistent” basis sets are optimized using correlated wave functions
- cc-pVXZ means a Dunning correlation-consistent, polarized valence, X-zeta basis; X=D,T,Q,5,6,7
- Functions are added in shells. cc-pVDZ for C atom consists of 3s2p1d. cc-pVTZ would be 4s3p2d1f. cc-pVQZ would be 5s4p3d2f1g.
- The Dunning basis sets are designed to converge smoothly toward the complete (infinite) basis set limit
- A prefix “aug” means one set of diffuse functions is added for every angular momentum present in the basis; aug-cc-pVDZ for C atom has diffuse s,p,d

HARTREE-FOCK LIMIT

Hartree-Fock limit is the energy that is obtained after variation based Optimization method SCF. On using HF method and compute the energy (by SCF), one reaches a stable point in energy after 'many' iterations of SCF which will be *always higher* than the exact energy.

This energy is the upper bound of Ground state energy of the molecule as all the electronic correlations are not taken into account. Hartree-Fock just considers some electron correlations.

This is a prime reason why the HF theory is less accurate. It gives very approximate results. Higher theories include MP2, DFT and coupled cluster methods.

POST HARTREE – FOCK METHODS

- In computational chemistry, post-Hartree–Fock methods are the set of methods developed to improve on the Hartree–Fock (HF), or self-consistent field (SCF) method.
- They add electron correlation which is a more accurate way of including the repulsions between electrons than in the Hartree–Fock method where repulsions are only averaged.

ELECTRONIC CORRELATIONS

- The correlation energy is sensitive to changes in the number of electron pairs
 - The correlation energy is always negative
 - There are two components to the correlation energy:
 - Dynamic correlation is the energy associated with the electrons as they try to avoid one another.
 - This is important in bond breaking processes.
 - Static correlation arises from deficiencies in the single determinant wavefunction and is important in systems with stretched bonds and low-lying excited states.
 - Computing the correlation energy is the single most important problem in quantum chemistry
- There are two broad categories of such approaches: those based on perturbation theory and those based on the variation principle.
- We study one method from each discipline, Namely :
 - I. Configuration Interaction (CI) (from variational method)
 - II. Moller Plesset Perturbation theory (from perturbational methods)

CONFIGURATION INTERACTION (CI)

Configuration interaction (CI) methods are one of the conceptually simplest methods for solving the many-body Hamiltonian. Although theoretically elegant, in principle exact, and relatively simple to implement, in practice full CI can be applied to only the smallest of systems

The basis for CI methods is the simple observation that an *exact* many-body wavefunction, Ψ , may be written as a linear combination of Slater determinants, D_k

$$\Psi = \sum_{k=0}^{\infty} c_k D_k ,$$

where the D_k fully span the Hilbert space of the wavefunction. The determinants can be any complete set of N -electron antisymmetric functions but are typically constructed from Hartree-Fock orbitals such that D_0 is the ground-state Hartree-Fock determinant

Configuration simply describes the linear combination of Slater determinants used for the wave function. In terms of a specification of orbital occupation (for instance, (1s)2(2s)2(2p)1...), interaction means the mixing (interaction) of different electronic configurations (states). Due to the long CPU time and large memory required for CI calculations, the method is limited to relatively small systems.

In contrast to the Hartree–Fock method, in order to account for electron correlation, CI uses a variational wave function that is a linear combination of configuration state functions (CSFs) built from spin orbitals (denoted by the superscript SO),

The scientific problem in adapting the CI method into a practical one is to obtain the best wavefunction, and hence lowest CI energy, with the shortest expansion length. A typical approach would be to truncate the expansion after only double or quadruple excitations from the reference determinant, where an excitation consists of replacing a ground state occupied orbital by an unoccupied one. These levels of truncation are the CI singles-doubles (CISD) and CI

singles-doubles-triples-quadruples (CISDTQ) methods. A formidable number of terms are still left in the expansion. Accurate applications of the methods are consequently limited due to their computational cost.

When performed within a finite reference space, an additional problem with the method becomes apparent: the methods lack "size-extensivity" and do not perform equally well in systems of differing size. As the size of system increases, the proportion of the electronic correlation energy contained within a fixed reference space (such as all single and double excitations) decreases. The lack of size-extensivity results in a non-cancellation of errors when systems of different sizes are compared, resulting in difficulties when interaction or bonding energies are required.

- A method is size-consistent if it yields M times the energy of a single monomer when applied to M non-interacting monomers.
- HF and Full-CI theories are size consistent, but truncated (shortened) CI approaches are not.

Note :

Truncated CI methods limit the types of excitations that can occur:

CIS adds only single excitations (same as HF)

CID adds only double excitations

CISD adds single and double excitations

CISDT adds single, double and triple excitations

Note :

A method that is not size-consistent yields poor dissociation energies, treats large systems poorly because the correlation energy per monomer tends to zero as the number of monomers increases.

MØLLER-PLESSET PERTURBATION THEORY

➤ In Møller-Plesset Perturbation Theory the Hamiltonian is divided into two parts:

$$\hat{H} = \hat{H}_0 + \lambda V$$

- The perturbation λV , is assumed to be small
- The wave function and energy are then expanded as a power series in λ (which is later set to unity)

$$\Psi_\lambda = \Psi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 + \dots$$

$$E_\lambda = E_0 + \lambda E_1 + \lambda^2 E_2 + \dots$$

Ψ_0 and E_0 are the HF wavefunction and energy

- MPn is obtained by truncating the expansion at order λ^n
- The MP1 energy is the same as the HF energy
- The MP2 calculations typically recovers 80-90% of the correlation energy
- The MPn energy is size-consistent
- Second order Møller-Plesset perturbation theory (MP2) is one of the simplest and most useful levels of theory beyond the Hartree-Fock approximation.
- Second (MP2) third (MP3) and fourth (MP4) order Møller-Plesset calculations are standard levels used in calculating small systems and are implemented in many computational chemistry codes. Higher level MP calculations, generally only MP5, are possible in some codes. However, they are rarely used because of their cost.