Introduction to \textit{ab-initio} methods and relation to nanomaterials research

George E. Froudakis
Associate Professor
Dept. of Chemistry
Uni. of Crete - Greece
Why we need theory and modeling?

- Explanation of experimental results
- Material testing *in silico*
- Designing novel materials
In past 30 years, computational power (driven by Moore’s Law) has increased by over 5 orders of magnitude.
Nano favors theory !!!
What is Quantum Chemistry?

- Quantum Mechanics applied to Atoms and Molecules
- Aim: Understanding of Electronic Structure
- Solution of the electronic Schrödinger equation
- Derived: Properties of Atoms and Molecules
Ab initio electronic structure theory
Hartree-Fock (HF)
Electron Correlation (MP2, CI, CC, etc.)

Goal: Insight into chemical phenomena.
## Part 1: Essential Concepts & Techniques

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Hamiltonian for a system with N-particles

\[ \hat{H}(r)\Psi(r) = E\Psi(r) \]

\[ \hat{H} = \hat{T} + \hat{V} \]

Sum of kinetic (T) and potential (V) energy

\[ \hat{T} = \sum_{i=1}^{N} \hat{T}_i = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_i^2 = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \]

Kinetic energy

\[ \nabla_i^2 = \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \]

Laplacian operator

\[ \hat{V} = \sum_{i=1}^{N} \sum_{j>1}^{N} V_{ij} = \sum_{i=1}^{N} \sum_{j>1}^{N} \frac{q_i q_j}{r_{ij}} \]

Potential energy
\[ \psi = \psi(R_1, R_2, \ldots, R_m, r_1, r_2, \ldots, r_n) \]

\[ H = T_n + T_e + V_{ee} + V_{nn} + V_{en} \]

\[ T_n = -\sum_{l=1}^{m} \frac{1}{2M_l} \nabla^2_R \]

\[ T_e = -\sum_{i=1}^{n} \frac{1}{2} \nabla^2_i \]

\[ V_{ee} = \sum_{i=1}^{n} \sum_{j<i} \frac{1}{|r_i - r_j|} \]

\[ V_{nn} = \sum_{l=1}^{m} \sum_{J<l} \frac{Z_l Z_J}{|R_l - \bar{R}_J|} \]

\[ V_{en} = -\sum_{i=1}^{n} \sum_{l=1}^{m} \frac{1}{|r_i - \bar{R}_l|} - \frac{1}{|r_j - \bar{R}_J|} \]
Born-Oppenheimer Approximation (1927)

• So far, the Hamiltonian contains the following terms:
\[ \hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn} \]

• Since nuclei are much heavier than electrons \((m_n/m_e=1836)\), their velocities are much smaller.
• To a good approximation (error <1/1000*), the Schrödinger equation can be separated into two parts:
  
  – One part describes the electronic wavefunction for a fixed nuclear geometry.
  – The second describes the nuclear wavefunction, where the electronic energy plays the role of a potential energy.
Born-Oppenheimer Approx. cont.

\[
H \psi = E \psi \\
H = H_e + T_n \\
\psi = \psi^e_i \psi^n_j \\
e : H_e \psi^e_i = E^e_i \psi^e_i \Rightarrow \\
n : (T_n + E^e_i) \psi^l_j
\]
Limitations of the Born-Oppenheimer approximation

• The BO approx. is usually very good, but breaks down when two (or more) electronic states are close in energy at particular nuclear geometries. In such situations, a “non-adiabatic” wavefunction - a product of nuclear and electronic wavefunctions - must be used.
Hartree-Fock Theory

Electron-electron interaction:

\[ V(r_1, r_i) = \frac{e^2}{4\pi\varepsilon_0} \left[ -\frac{Z}{r_1} + \sum_{i+1} \frac{1}{r_{1i}} \right] \]

\[ V(r_1) \approx \frac{e^2}{4\pi\varepsilon_0} \left[ -\frac{Z}{r_1} + \sum_{i+1} \frac{1}{r_{1i}} \right] \]

\[ V^{HF}(r_1) \approx \frac{e^2}{4\pi\varepsilon_0} \left[ -\frac{Z}{r_1} + \sum_{i+1} \frac{1}{r_{1i}} \right] \]
**Self-Consistent-Field**

Initial Guess for the orbitals

\[ V^{HF}(r_1) \]

Self consistency

\[-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x_1^2} + \frac{\partial^2 \psi}{\partial y_1^2} + \frac{\partial^2 \psi}{\partial z_1^2} \right) + V^{HF}(r_1)\psi = E\psi \]

**E^{HF}, \Psi^{HF} \Rightarrow new orbitals**
Restricted and Unrestricted Hartree-Fock

**Restricted Hartree-Fock (RHF)**
For even electron, closed-shell singlet states, electrons in a given MO with $\alpha$ and $\beta$ spin are constrained to have the same spatial dependence.

**Restricted Open-shell Hartree-Fock (ROHF)**
The spatial part of the doubly occupied orbitals are restricted to be the same.

**Unrestricted Hartree-fock (UHF)**
$\alpha$ and $\beta$ spinorbitals have different spatial parts.
Potential energy curves

Restricted HF does not ‘dissociate’ correctly

Figure 4.3 6-31G** potential energy curves for H₂.
Basis sets

\[ \psi(x, y, z) = \sum_{n} c_n \Phi_n(x, y, z) \]

- **Mathematical trick**: Instead of looking for an unknown functions (\(\psi\)) we are searching for coefficients (\(c\)).
- “**Atoms-in-Molecule**” approach: Atomic electron density is only weakly perturbed in formation of molecule
- Hydrogen-like functions centered at atoms in molecule
- Additional functions for specific purposes (polarization, correlation, bonding etc.)
Basis sets: STOs and GTOs

- Slater-Type Orbitals are H like
- Gaussian Type Orbitals
- $\alpha$: ‘exponent’
Basis sets: Why GTOs?

Situation in molecules:

- Use of atom-centered GTOs
- Products of two GTOs at centers A, B gives GTO at center E
- Hence: Ease of integration!
- Much faster than with STOs, despite increased number

Atomic centers A,B
Standard basis sets: Overview

- **STO-NG**: N GTO per STO

- **Split-valence 6-31+G(*) sets**: 
  SZ (core)/DZ(valence),
  +: diffuse functions
  *: polarization functions
  \(Z(\text{zeta})\): Number of contracted functions

- **(aug)-cc-(p)VXZ**: Correlation-consistent basis sets
Basis sets: Polarization functions

- Polarization of atomic density upon formation of chemical bond
- Molecular field breaks atomic symmetry!
- Use of higher angular-momentum functions
  E.g. p-functions for H, d-functions for C, etc.
- **Allows orbitals to change shape**
Complete Basis Set limit

\[ E_{HF} \]

HF-limit

CBS

# basis functions

- STO-3G
- 3-21G
- 6-31G
- 6-311G**
Configuration Interaction (CI)

- Principles:
  Based on HF (or MCSCF) wave function (orbitals)
  Linear expansion of many-particle wave function:

\[ \Psi_{CI} = c_0 \psi_0 + \sum_{ar}^c c^r_{a} \psi^r_{a} + \sum_{a<b}^{rs} c_{ab}^{rs} \psi^{rs}_{ab} + \sum_{a<b<c}^{rst} c_{abc}^{rst} \psi^{rst}_{abc} + \ldots \]

- \( c \): expansion coefficients (\( c_0 > 90\% \))
- \( \Psi \): Slater determinants, ground and excited
**CI: Excitation Level**

The Hamiltonian matrix in determinant basis

| Anregung | $|\Psi_0\rangle$ | $|S\rangle$ | $|D\rangle$ | $|T\rangle$ | $|Q\rangle$ |
|----------|------------------|-------------|-------------|-------------|-------------|
| $\langle \Psi_0 | \hat{H} | \Psi_0 \rangle$ | 0 | $\langle \Psi_0 | \hat{H} | D \rangle$ | 0 | 0 | ... |
| $\langle S | \hat{S} \rangle$ | $\langle S | \hat{H} | S \rangle$ | $\langle S | \hat{H} | D \rangle$ | $\langle S | \hat{H} | T \rangle$ | 0 | ... |
| $\langle D | \hat{S} \rangle$ | $\langle D | \hat{H} | D \rangle$ | $\langle D | \hat{H} | T \rangle$ | $\langle D | \hat{H} | Q \rangle$ | ... |
| $\langle T | \hat{S} \rangle$ | $\langle T | \hat{H} | T \rangle$ | $\langle T | \hat{H} | Q \rangle$ | ... |
| $\langle Q | \hat{S} \rangle$ | $\langle Q | \hat{H} | Q \rangle$ | ... |

- Double excitations couple directly to reference state
- All others couple indirectly (coupled linear equations)
- Strategy: Select important higher excitations!
Full-CI: the computational limitation

Full CI is the **most accurate** method for a define basis set but, it can be applied only to v. small molecules.

- Apply only a few type of excitations
  - CI-D
  - CI-SD
  - ...
- Apply all possible excitations inside a chosen window of energies around the gap
- Combination of both

CAS
Moller-Plesset Perturbation Theory

Electron correlation: \[ V = \sum_{i<j} \frac{1}{r_{ij}} - \sum_i v^{HF} \]

- Principles:
  
  **Idea:** Electron correlation is a perturbation
  
  \(<1\%\) of total energy

  Based on Rayleigh-Schrödinger PT

  Single-reference method!

  Size-consistent.
MPPT: Procedure

• Assume solution of zero-order problem (HF problem):
  \[ H_0 \Psi_0 = \sum_i f(i)\Psi_0 = E^{(0)}_0 \Psi_0 \]

• Definition of a perturbing potential:
  \[ V = \sum_{i<j} \frac{1}{r_{ij}} - \sum_i \nu^{HF} \]

• Total electronic Hamiltonian:
  \[ H = H_0 + V \]

• Apply Rayleigh-Schrödinger PT
  \[ E_i^{(2)} = \sum_{n \neq i} \left| \frac{\langle \Psi_i^{(0)} | \tilde{V} | \Psi_n^{(0)} \rangle}{E_i^{(0)} - E_n^{(0)}} \right|^2 \]
Density Functional Theory

**Hohenberg & Kohn* Theorem (1964):** The ground state properties of every system are function of its charge density \((\rho)\)

- **Total energy as functional of the electron density:**
  
  \[
  E[\rho] = T[\rho] + U[\rho] + E_{xc}[\rho]
  \]

  \[
  p(r) = \sum_{i} |\phi_i(r)|^2 \quad :\Phi= \text{occupied MOs}
  \]

  - T: Kinetic Energy
  - U: Coulomb interactions
  - xc: Exchange & correlation interactions

* Nobel price 1998
DFT: XC functionals

- **Local Density Approximation (LDA)**
  No gradient of electron density in $E_{xc}$
  Like a uniform electron gas!

- **Generalized Gradient Approximation (GGA)**
  Gradient corrected density

- **Hybrid Functionals**
  Becke (B) LYP, B3LYP functionals
  Contain a contribution of HF exchange interaction
Geometry optimization

Initial Geometry

Coordination system
Symmetry

$H\Psi = E\Psi \rightarrow E_e$

$\nabla E_e$

New Coordinates for lowering total energy

Convergence

YES

Structural & Electronic Properties

NO