Schrödinger Equation

Time-Independent Form:

\[ \hat{H}|\Psi\rangle = E|\Psi\rangle \]

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

Variational Theorem:

\[ E = \langle \Psi | \hat{H} | \Psi \rangle \leq \langle \Phi | \hat{H} | \Phi \rangle \]

“The ground state energy of any approximate wavefunction is always an upper bound to the exact ground state energy”

The exact wavefunction can be approximated by finding a solution that minimizes energy
The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

— Paul Dirac, 1929
Simplifying Approximations

\[ \hat{H} = \sum_{i}^{N_e} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{i}^{N_n} \sum_{j}^{N_e} \frac{e^2 Z_i}{|\vec{r}_j - \vec{R}_i|} + \sum_{i<j}^{N_n} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \sum_{i<j}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \]

- **Electronic kinetic energy**
- **Nuclear-electronic attraction**
- **Nuclear-nuclear repulsion**
- **Electron-electron repulsion**

**Trivial to calculate**

**No known solution**

(Many-body problem)

**Born-Oppenheimer Approximation:**

The motion of nuclei is slow relative to the motion of electrons, so we can treat them as stationary

- No nuclear kinetic energy term in Hamiltonian
- Nuclear-electronic attraction term depends only on position of electrons
- Nuclear-nuclear repulsion term becomes a constant
Linear Combination of Atomic Orbitals (LCAO):

• Molecular orbitals are expressed in terms of hydrogen-like atomic orbitals (known exactly)
• Bonding interactions correspond to constructive interference
• Antibonding interactions correspond to destructive interference

Hydrogen 1s orbital

$H_2 \sigma$-bonding orbital

$H_2 \sigma$-antibonding orbital
Linear Combination of Atomic Orbitals (LCAO):

- Molecular orbitals are expressed in terms of hydrogen-like atomic orbitals (known exactly)
- Bonding interactions correspond to constructive interference
- Antibonding interactions correspond to destructive interference

Probability densities:

1s orbitals

σ-orbitals
Simplifying Approximations

\[ \hat{H} = \sum_{i}^{N_e} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{i}^{N_n} \sum_{j}^{N_e} \frac{e^2 Z_i}{|\vec{r}_j - \vec{R}_i|} + \sum_{i<j}^{N_n} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \sum_{i<j}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \]

- Electronic kinetic energy
- Nuclear-electronic attraction
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Hartree-Fock:

- Assume that the wavefunction can be expressed as the product of one-electron wavefunctions (orbitals)
- Electrons interact with electric field from average position of other electrons
- *Antisymmetrized* to satisfy Pauli exclusion principal (permutation of electrons changes sign)
- Variational principle used to find minimum-energy electronic state
\[ \hat{H} = \sum_{i}^{N_e} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{i}^{N_n} \sum_{j}^{N_e} \frac{e^2 Z_i}{|\vec{r}_j - \vec{R}_i|} + \sum_{i<j}^{N_n} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \sum_{i<j}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \]

electronic kinetic energy
nuclear-electronic attraction
nuclear-nuclear repulsion
electron-electron repulsion

Hartree-Fock:

He atom cannot be solved exactly
Simplifying Approximations

\[ \hat{H} = \sum_{i}^{N_e} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{i}^{N_n} \sum_{j}^{N_e} \frac{e^2 Z_i}{|\vec{r}_j - \vec{R}_i|} + \sum_{i<j}^{N_n} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \sum_{i<j}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \]

- electronic kinetic energy
- nuclear-electronic attraction
- nuclear-nuclear repulsion
- electron-electron repulsion

Hartree-Fock:

Self-consistent field (SCF): electronic charge distribution must be consistent with its own electrostatic field.

Provides a method for determining orbital coefficients

average field of other electrons
Gaussian Basis Sets

Overlap integral cannot be evaluated analytically for Slater type orbitals!

Solution: use Gaussian type orbitals as an approximation
Gaussian Basis Sets

Overlap integral cannot be evaluated analytically for Slater type orbitals!

Solution: use Gaussian type orbitals as an approximation

Summing over multiple Gaussian functions improves accuracy

\[ \Phi(r) = e^{-\alpha_0 r} \]

\[ \Phi(r) = \sum_i c_i e^{-\alpha_i r^2} \]
Gaussian Basis Sets

Some terminology:

**Basis functions** are the fundamental components that form molecular orbitals (where an electron can possibly be)

Individual Gaussian functions are called Gaussian **primitives**

**Contraction** is the process of grouping primitives to form basis functions

The number of contractions per orbital is referred to as **zeta** (double zeta, triple, etc.)

\[ \Phi(r) = \sum_i c_i e^{-\alpha_i r^2} \]
Gaussian Basis Sets

Pople style basis sets

STO-3G

“Minimal basis set” (single zeta)
Slater type basis functions each approximated by 3 Gaussian primitives
Gaussian Basis Sets

Pople style basis sets

6-31G

6 primitives per core electron
3 primitives for first valence basis function
1 primitive for second valence basis function
Gaussian Basis Sets

Pople style basis sets

6-311G

6 primitives per core electron
3 primitives for first valence basis function
1 primitive for second valence basis function
1 primitive for third valence basis function
Polarization Functions

Limitation of LCAO: molecular orbitals cannot be described using only occupied atomic orbitals
Solution: add additional basis functions of higher angular momentum (polarization functions)

(The true space of possible electronic configurations has infinite dimension)
Describing negatively charged molecules becomes difficult using only neutral hydrogen-like atomic orbitals.

Add extra basis functions with larger radius (simulate shielding effect).
Pople style basis sets

6-31+G(d,p)

- 6 primitives per core electron
- 3 primitives for first valence basis function
- 1 primitive for second valence basis function
- diffuse function on heavy atoms (Li and beyond)
- d polarization on heavy atoms, p polarization on light atoms (H, He)
Pople style basis sets

6-311++G(2d,2p)

6 primitives per core electron
3 primitives for first valence basis function
1 primitive for second valence basis function
1 primitive for third valence basis function
  + diffuse function on heavy atoms
  + diffuse function on light atoms
2 d polarization functions on heavy atoms
2 p polarization functions on light atoms
### Choice of Basis Set

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**LanL2DZ:** Ignores core electrons, replaces them with a potential (often used for metals)
Choice of Basis Set

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- Converge energy quickly
- “Well balanced” with polarization functions built in
- Matching auxiliary basis sets speed up integral evaluation
- def2-TZVP usually “good enough” for organic molecules
## Choice of Basis Set

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- More highly contracted than def2
- Good for correlated methods (post-HF)
- Good choice for anions, excited states, long-range interactions using augmented version (diffuse functions)
Choice of Basis Set

Using larger basis sets, the energy tends toward the *Hartree-Fock Limit* (complete basis set limit)
How can we recover the correlation energy?
Correlated Methods

Wavefunction Theory

Configuration interaction (full CI, CIS, CISD, etc.)

MP2 (perturbation theory)

Coupled cluster theory (CCSD, CCSD(T))

CASSCF, RASSCF, QCI, composite methods, etc.

Density Functional Theory
Hohenberg-Kohn Theorem I

“For a nondegenerate ground state of a many-electron system, the properties of the system are uniquely determined by the electron density.”

Hohenberg-Kohn Theorem II

“The functional that delivers the ground-state energy of the system gives the lowest energy if and only if the input density is the true ground-state density.”
Density Functional Theory

\[ E = F[\rho(r)] \]

“The universal density functional”

\[ E[\rho(r)] = T + V_{ne} + E_{ee} + E_{xc} \]

Electronic energy determined by:
- kinetic energy
- nuclear attraction
- electronic repulsion
- exchange and correlation

Electron interacting with itself
Express the electron density in an *orbital basis set*

Orbitals consist of *fictitious, noninteracting* electrons

Density for noninteracting system can be solved *exactly*

Hartree-Fock: *Approximate* solution to *real* problem
Kohn-Sham: *Exact* solution to *hypothetical* problem
Exchange-Correlation Functional

Local Density Approximation: XC energy as a functional of local electron density, integrate over all space

$$E_{xc}^{LDA}[\rho(r)] = \int \rho(r) \epsilon_{xc}(\rho(r)) dr$$

Generalized Gradient Approximation: XC energy as a functional of electron density and gradient

$$E_{xc}^{GGA}[\rho(r)] = E_{xc}^{LDA}[\rho(r)] + \Delta E[\nabla \rho(r)]$$

*Meta-GGA*: Use higher order gradients
Observation:

For Hartree-Fock, we didn’t know the correlation energy, but we knew the exchange energy exactly.

Divide XC functional into X and C functionals

\[ E_{xc}[\rho(r)] = E_x[\rho(r)] + E_c[\rho(r)] \]

Use exchange energy from HF to obtain a more accurate approximation

\[ E_x[\rho(r)] = aE_x[\rho(r)] + (1 - a)E_x^{HF} \]
Some Examples

Increasing Cost
Increasing Accuracy

Hybrid-meta-GGA: M06, M06-2x, TPSS0
Hybrid-GGA: B3LYP, PBE0, B3P86
Meta-GGA: M06-L, TPSS
GGA: PBE, BP86, B97
LDA

Which functional should I use?
Check benchmarks
Do the experiment!
Some Examples

Increasing Cost
Increasing Accuracy

Hybrid-meta-GGA: M06, M06-2x, TPSS0

Hybrid-GGA: B3LYP, PBE0, B3P86

Meta-GGA: M06-L, TPSS

GGA: PBE, BP86, B97

LDA

Can we improve accuracy even more?
Range-Separated Hybrids

Key Concept:

Don’t use a fixed mixture of Hartree-Fock and DFT exchange, vary exchange with distance.
Range-Separated Hybrids

Examples:

CAM-B3LYP, ω-B97X-D, ω-B97M-V

Good for noncovalent/long-range interactions
Double Hybrids

Key Concept:

Mixing in some Hartree-Fock improved exchange energy

Can we use the same strategy to improve correlation energy?

*Remember: Hartree-Fock is not correlated*

Use MP2 to improve correlation energy

\[
E_{xc}[\rho(r)] = a_x E_x[\rho(r)] + a_c E_c[\rho(r)] + (1 - a_x)E_x^{HF} + (1 - a_c)E_c^{MP2}
\]

Examples:

B2-PLYP, mPW2-PLYP, B2K-PLYP, DSD-PBEP86
Geometry Optimization

Find geometry where gradient is 0 (stationary point)

\[- \frac{\partial E}{\partial x} = \text{Force} \]

\[\nabla E = \left( \frac{\partial E}{\partial x_1}, \ldots, \frac{\partial E}{\partial x_n} \right) = \text{Gradient} \]

Eigenvalues of \( \mathbf{H} \) determine concavity (minimum vs. saddlepoint)

\[
\mathbf{H} = \begin{pmatrix}
\frac{\partial^2 E}{\partial x_1 \partial x_1} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_1 \partial x_n} \\
\frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2 \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_2 \partial x_n} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial^2 E}{\partial x_n \partial x_1} & \frac{\partial^2 E}{\partial x_n \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_n \partial x_n}
\end{pmatrix} = \text{Hessian}
Your calculations are only as good as your geometries!

- Consider conformational effects when building a structure
  - When in doubt, run the calculation for each conformer
  - Always do an optimization and frequency calculation

-3 kcal/mol
We usually aren’t interested only in gas-phase properties

Explicit solvation: Add solvent molecules
(expensive/inconvenient, but sometimes necessary)

Implicit solvation: Create a polarizable surface around molecule corresponding to solvent dielectric and polarizability
Important Topics Not Covered

Spin contamination

Basis set superposition error

Semiempirical/Composite DFT Methods

Dispersion corrections (D3(0), D3(BJ), D4)

Relativistic Corrections (ZORA, Douglas-Kroll-Hess)

Excited state calculations (TD-DFT)

Optimization algorithms (RFO, quasi-Newton, etc.)