Introduction to Electronic Structure Theory

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What is Electronic Structure Theory

- Electronic structure theory (EST) describes the motion of electrons in atoms and molecules.
- The motion of electrons and nuclei of molecules can be separated into
  1. Electronic motion
  2. Vibrational motion of the nuclei
  3. Rotational motion of molecules
- In most electronic structure calculations, one is mainly interested in (1)
- In this brief introduction, (1) will be discussed, (2) is mentioned, and (3) is omitted.
Born-Oppenheimer Approximation

- Nuclei are much heavier than electrons
- The lightest nucleus \textit{i.e.}, the proton is 1836 times heavier than the electron.
- The heavy nuclei move much slower than the fast electrons
- The electronic motion can always adjust to the nuclear positions
- The electronic Schrödinger equation can be solved for given fixed positions of the nuclei
- The decoupling of electronic and nuclear motions is called \textbf{Born-Oppenheimer approximation} (BOA)
The decoupling of electronic and nuclear motions is called Born-Oppenheimer approximation (BOA).

BOA is the birth of molecular structure.

Calculating the electronic energy for a number of nuclear positions yields the potential energy surface of the molecule.

At the non-relativistic Schrödinger level, the Hamiltonian is:

\[
\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \frac{\hbar^2}{2M_A} \sum_A \nabla_A^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\varepsilon_0 r_{iA}} \\
+ \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R_{AB}} + \sum_{i>j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}
\]
Hamiltonian

\[ \hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \frac{\hbar^2}{2M_A} \sum_A \nabla_A^2 - \sum_{i,A} \frac{Z_Ae^2}{4\pi\epsilon_0 r_{iA}} \]

\[ + \sum_{A>B} \frac{Z_AZ_Be^2}{4\pi\epsilon_0 R_{AB}} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \]

where

- \( m_e \) is the electron mass,
- \( e \) is the charge of the electron,
- \( M_A \) is the mass of nucleus \( A \),
- \( Z_A \) is charge of nucleus \( A \),
- \( r_{iA} \) is the distance between electron \( i \) and nucleus \( A \),
- \( R_{AB} \) is internuclear distances,
- \( r_{ij} \) is interelectronic distances.
**Hamiltonian**

- In EST calculations, **atomic units** (a.u.) are used.
  - The electron mass $m_e = 1$
  - The charge of the electron $e = 1$
  - Dirac’s constant $\hbar = 1$
  - Coulomb’s constant $\frac{1}{4\pi\varepsilon_0} = 1$

\[
\hat{H} = -\sum_i \frac{1}{2} \nabla_i^2 - \sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_{i,A} \frac{Z_A}{r_{iA}} + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} + \sum_{i>j} \frac{1}{r_{ij}}
\]

- The 1st term is the kinetic energy of the electrons
- The 2nd term is the kinetic energy of the nuclei
- The 3rd term is the electron-nucleus Coulomb attraction
- The 4th term is the nucleus-nucleus Coulomb repulsion
- The 5th term is the electron-electron Coulomb repulsion
Hamiltonian

\[
\hat{H} = -\sum_i \frac{1}{2} \nabla_i^2 - \sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_{i,A} \frac{Z_A}{r_{iA}} + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} + \sum_{i>j} \frac{1}{r_{ij}}
\]

The Schrödinger equation reads

\[
\hat{H}\psi(r,R) = E\psi(r,R)
\]

The decoupling of electronic and nuclear motions (BOA) yields

\[
\psi(r,R) = \psi(r;R)\Phi(R)
\]

- \(\psi(r,R)\) is a function of electron and nuclear coordinates.
- \(\psi(r;R)\) is a function of electron coordinates for given parameters \(R\).
- \(\Phi(R)\) is a function of the nuclear coordinates.
Electronic and Nuclear Schrödinger Equations

The electronic Schrödinger equation in BOA

\[
\left( - \sum_i \frac{1}{2} \nabla_i^2 - \sum_{i,A} \frac{Z_A}{r_{iA}} + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} + \sum_{i>j} \frac{1}{r_{ij}} \right) \psi(r; R) = E_e(R) \psi(r; R)
\]

The nuclear Schrödinger equation in BOA

\[
\left( - \sum_A \frac{1}{2 M_A} \nabla_A^2 + E_e(R) \right) \Phi(R) = E_n \Phi(R)
\]
Computational Procedure

- The electronic Schrödinger equation is solved for given $R$.
- The nuclear positions are adjusted to obtain the lowest energy.
- The molecular structure with the lowest energy is called **equilibrium structure** or equilibrium geometry.
- The equilibrium structure is **THE molecular structure**.
- Check whether it is a minimum or a saddle point!
- For a minimum, the second derivative of the energy with respect to nuclear displacements should have a positive curvature in all dimensions.
- A first estimate of the nuclear motion (vibrational frequencies) of the molecule is the by-product.
Example of potential energy surfaces
Wave packages on potential energy surfaces

Chemical reactions and other events involving nuclear motion can be modeled as wave packets moving on the potential energy surface.
Computer Exercise

In the Computer exercise this afternoon you optimize the molecular structure of some small molecules.

- Optimize the molecular for your favourite small molecule
- Investigate how the molecular structure depends on the level
- Check whether you have found a minimum or a transition state
- Search for the transition state of a chemical reaction
- Simulate the vibrational spectrum
Electronic structure theory needs appropriate mathematical tools. A wave function $\psi(r)$ can be represented as a vector

$$|\psi\rangle = \sum_{i=1}^{n} a_i |\Phi_i\rangle$$

where $|\psi\rangle$ is a state vector, $a_i$ are expansion coefficients, and $|\Phi_i\rangle$ are fixed basis vectors of the Hilbert space.

$$|\psi\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix} \quad \langle\psi| = (a_1^* a_2^* \cdots a_n^*)$$
Dirac Notation

The scalar (inner) product is defined as

\[ \langle \Psi_a | \Psi_b \rangle = \sum_{i=1}^{n} a_i^* b_i = \langle a | b \rangle \]

\[ \langle \Psi_a | \Psi_b \rangle = \int_{-\infty}^{\infty} \psi_a^*(r) \psi_b(r) dr \]

An operator \( \hat{A} \) is characterized by its effect on the basis vectors

\[ \hat{A} | \psi_j \rangle = \sum_{i}^{n} | \psi_i \rangle A_{ij} \]

\[ A_{ij} = \langle i | \hat{A} | j \rangle = \int_{-\infty}^{\infty} \psi_i^*(r) \hat{A} \psi_j(r) dr \]
**Slater determinants**

The Slater determinant is a useful but clumsy notation

\[
\Psi = \frac{1}{N!} \left| \begin{array}{cccc}
\chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\
\chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N)
\end{array} \right|
\]

The equivalent Dirac notation is simpler and more practical

\[
\Psi = |\chi_1(x_1)\chi_2(x_2)\cdots\chi_N(x_N)\rangle
\]

The notation using occupation number \((n_i)\) vectors is

\[
\Psi = |n_1, n_2, \cdots n_N\rangle
\]

where \(n_i\) is 0 or 1. Appropriate mathematics is developed to simplify expressions involving occupation number vectors.
**Occupation number vectors**

- The abstract occupation number vectors can be used to represent Slater determinants.

- The main advantage is that an efficient algebra can be developed for them.

\[
|\psi\rangle = |k_1, k_2, \ldots, k_N\rangle \quad k_i = 1 \text{ for occupied orbital and } k_i = 0 \text{ for unoccupied orbital}
\]

Inner product:

\[
\langle k|m\rangle = \prod_{i=1}^{N} \delta_{k_i m_i}
\]

\[
|c\rangle = \sum_k c_k |k\rangle, \quad \langle c|d\rangle = \sum_k c_k^* d_k, \quad |k\rangle\langle k| = 1
\]
Second Quantization

The whole machinery of the second quantization is obtained from the algebra of the occupation number vectors.

Creation operator:

\[ a_P^\dagger |k_1, k_2, \ldots, 0_P, \ldots, k_N\rangle = \delta_{k_P, 0} \Gamma_P^k |k_1, k_2, \ldots, 1_P, \ldots, k_N\rangle \]

with \( \Gamma_P^k = \prod_{Q=1}^{P-1} (-1)^{k_Q} \)

Annihilation operator:

\[ a_P |k_1, k_2, \ldots, 1_P, \ldots, k_N\rangle = \delta_{k_P, 1} \Gamma_P^k |k_1, k_2, \ldots, 0_P, \ldots, k_N\rangle \]

Anticommutation relations:

\[ [a_P^\dagger, a_Q^\dagger]_+ = 0 \quad [a_P, a_Q]_+ = 0 \quad [a_P^\dagger, a_Q]_+ = \delta_{PQ} \]
Operators in Second Quantization

Hamiltonian and Energy ($E = \langle \hat{H} \rangle$):

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \sum_{pqrs} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q$$

One-electron interaction (e.g., dipole moment $\langle \hat{\mu} \rangle$ with $\hat{\mu} = \{ x, y, z \}$):

$$\hat{\mu} = \sum_{pq} \mu_{pq} a_p^\dagger a_q$$

Two-electron interaction (e.g., Coulomb and exchange energy $\langle \frac{1}{r_{12}} \rangle$):

$$\frac{1}{r_{12}} = \sum_{pqrs} (\frac{1}{r_{12}})_{pqrs} a_p^\dagger a_r^\dagger a_s a_q$$
The N-body Wave Function

The most simple ansatz for the N-body wave function is the Hartree Product

$$\Psi(x_1, x_2, \cdots, x_N) = \chi_1(x_1)\chi_2(x_2)\cdots\chi_N(x_N)$$

where $x_i$ are $4N$ coordinates, i.e., the three Cartesian coordinates plus the spin.

$\chi_i(x_i)$ are **spin orbitals**. $\chi_i(x_i) = \phi_i(r_i)|\alpha\rangle$ or $\chi_i(x_i) = \phi_i(r_i)|\beta\rangle$

$|\alpha\rangle$ and $|\beta\rangle$ denote spin up and spin down, respectively.

The Hartree product does not fulfill the antisymmetry condition of the electrons (fermions).
Accurate $N$-body Wave Functions

John C. Slater introduced determinants as $N$-body wave function.

The Slater determinants fulfil the antisymmetry condition of fermions. How can the wave function be improved?

The use of large one-particle basis sets makes it possible to approach the **basis-set limit**.

By writing the wave function as a linear combination of many Slater determinants improves the quality of the wave function.

By considering all possible Slater determinants in a given one-particle corresponds to the solution of the Schrödinger equation in that basis.
The Hartree-Fock Model

The Hartree-Fock or the **mean-field model** is obtained by assuming that the wave function consists of one single Slater determinant.

In the Hartree-Fock model, the electrons are assumed to move in the average field of all other electrons and nuclei.

The electronic motion is **uncorrelated**.
The Hartree-Fock Model

The equations of the Hartree-Fock model is obtained by expressing the energy as expectation value of the Hamiltonian for a one-Slater-determinant wave function

\[ E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle \]

Differentiating the energy expression with respect to linear parameters of the one-particle functions (orbitals) \( \phi_i \)

Ensuring that the orbitals are orthonormal \( \langle \phi_i | \phi_j \rangle = \delta_{ij} \)

The Hartree-Fock Lagrangian reads

\[ L(\phi_i) = E_{HF}(\phi_i) - \sum_{ij} \epsilon_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}) \]
The Fock Equation

The Hartree-Fock energy for closed-shell systems

\[ E_{HF} = 2 \sum_i h_{ii} + \sum_{ij} \left( 2g_{ijij} - g_{ijji} \right) \]

\[ h_{ij} = \int \phi_i^*(1) \hat{h}_1 \phi_j(1) dr_1 \]

\[ g_{ijkl} = \int \int \phi_i^*(1) \phi_k^*(2) r_{12}^{-1} \phi_j(1) \phi_l(2) dr_1 dr_2 \]

The molecular orbitals (MO), \( \phi_i \), are expanded in a set of non-orthonormal atomic orbitals (AO) \( \chi_\mu \)

\[ \phi_i = \sum_\mu \chi_\mu C_{\mu p} \]

Inserting it into the energy expression and differentiation with respect to \( C_{\mu p} \) yields the Fock equation
The Fock Equation

The Fock equation for non-orthonormal AOs reads

$$\sum_\nu F_{\mu\nu}^{AO} C_{\nu i} = \epsilon_i \sum_\nu S_{\mu\nu} C_{\nu i}$$

where the Fock matrix has been introduced

$$F_{\mu\nu}^{AO} = h_{\mu\nu} + \sum_i \left( 2g_{\mu\nu ii} - g_{\mu ii\nu} \right)$$

The AO Fock matrix can be calculated in the AO basis

$$F_{\mu\nu}^{AO} = h_{\mu\nu} + \sum_{\sigma\tau} D_{\sigma\tau}^{AO} \left( g_{\mu\nu\sigma\tau} - \frac{1}{2} g_{\mu\sigma\tau\nu} \right)$$
The Hartree-Fock Iterative Procedure

1. Guess $\mathbf{C}$
2. Calculate $\mathbf{D}^{AO} = \mathbf{C} \mathbf{D}^{MO} \mathbf{C}^T$
3. Calculate $\mathbf{F}^{AO}$
4. Diagonalize $\mathbf{F}^{AO} \mathbf{C} = \mathbf{S} \mathbf{C} \epsilon$
5. Determine an error vector e.g., $\mathbf{e} = \mathbf{FD}_{\text{S}} - \mathbf{SD}_{\text{F}}$
6. Check the convergence
7. Introduce damping using e.g., DIIS
8. Make a new guess for $\mathbf{C}$ and go to 2
9. End when converged
**Hellmann-Feynman Theorem**

Assume that the Hartree-Fock wave function \( \Psi \) is perturbed by an external perturbation \( V \):

The perturbed energy can be written as:

\[
E(\lambda) = \langle \Psi + \lambda \Delta \psi | \hat{H} + \lambda V | \Psi + \lambda \Delta \psi \rangle
\]

The first-order correction to the energy is obtained by differentiating \( E(\lambda) \) with respect to \( \lambda \)

\[
\frac{dE(\lambda)}{d\lambda} = 2 \text{Re} \langle \Delta \psi | \hat{H} + \lambda V | \Psi + \lambda \Delta \psi \rangle + \langle \Psi + \lambda \Delta \psi | V | \Psi + \lambda \Delta \psi \rangle
\]

\[
\left. \frac{dE(\lambda)}{d\lambda} \right|_{\lambda=0} = 2 \text{Re} \langle \Delta \psi | \hat{H} | \Psi \rangle + \langle \Psi | V | \Psi \rangle = 0
\]
Open-Shell Systems

For molecules with unpaired electrons or for general open-shell systems, different orbitals are used for describing the motion of the $\alpha$ (spin-up) and the $\beta$ (spin-down) electrons.

The unrestricted Hartree-Fock (UHF) model is a generalization of the restricted Hartree-Fock (RHF) model for closed-shell molecules.

The matrix sizes of the UHF are twice the size of the RHF ones.

UHF is not unproblematic as it might introduce spin contamination effects, convergence problems, negative gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO gap).

Correlation effects are often larger for open-shell systems than for the closed-shell ones.
Density Functional Theory

Hartree-Fock does not consider any electron correlation effects by definition

\[ E_{\text{Correlation}} = E_{\text{Exact non-relativistic}} - E_{\text{Hartree-Fock}} \]

Density functional theory (DFT) is the most simple model that consider electron correlation effects.

DFT is structurally quite similar to Hartree-Fock (HF)

The effective HF potential

\[ \hat{V}_{\text{eff}} = v_{\text{nuc}} + v_{\text{J}} + \hat{K} \]

The effective DFT potential

\[ \hat{V}_{\text{eff}} = v_{\text{nuc}} + v_{\text{J}} + v_{\text{xc}} \]
Density Functional Theory

DFT is formally exact. However $\nu_{xc}$ is not known.

The art of DFT is to find an accurate approximation to $\nu_{xc}$

DFT is based on the electron density, $\rho(r)$, which is the probability to find an electron in $dr$.

The electron density is related to the wave function

$$\rho(r_1) = n \int dr_2 \int dr_3 \cdots \int dr_n |\psi(r_1, r_2, \ldots, r_n)|^2$$

The density uniquely determines the Hamiltonian, because

- $\int \rho(r) dr = n$
- The cusps at the nuclei yield the nuclear positions
- The slope of the nuclear cusps yields the nuclear charge
Simple DFT approach:

- Take the exact $\rho(r)$
- Use $\rho(r)$ to obtain $\hat{H}$
- Construct and solve the Schrödinger equation
- The exact ground-state energy is obtained

The procedure can be formulated mathematically as

$$E_0 = E[\rho(r)]$$

which is an energy functional that is variational

$$E[\tilde{\rho}] \geq E[\rho]$$
Hohenberg-Kohn

The energy can be divided into something that explicitly depend on the electron density and the universal part (the rest)

$$E[\rho] = \int dr \rho(r)(v_{\text{nuc}} + v_{\text{electrostatic}}) + F_{\text{HK}}$$

The energy functional

$$E[\rho] = T[\rho] + J[\rho] + E_{\text{xc}}'[\rho] + \int dr \rho(r)v_{\text{nuc}}$$

The kinetic contribution is:

$$T[\rho] = T_s + T_c[\rho] \quad \text{with} \quad T_s = -\frac{1}{2} \sum_{i \in \text{occ}} \langle \psi_i | \nabla^2 | \psi_i \rangle$$

The Kohn-Sham energy is:

$$E_{\text{KS}} = T_s + J[\rho] + E_{\text{xc}}[\rho] + \int dr \rho(r)v_{\text{nuc}}$$
Kohn-Sham Equations

In

\[ E_{KS} = T_s + J[\rho] + E_{xc}[\rho] + \int dr \rho(r) v_{nuc} \]

everything is known except \( E_{xc}[\rho] \), which is small compared to the rest.

Different DFT functionals have their own approximation to \( E_{xc}[\rho] \)

Minimization of \( E_{KS} \) with respect to the orbitals yields the Kohn-Sham equations

\[
\left( -\frac{1}{2} \nabla_i^2 + v_{\text{nuc}} + v_J + v_{xc} \right) \psi_i = \epsilon_i \psi_i \quad \text{with} \quad v_{xc} = \frac{\delta E_{xc}[\rho]}{\delta \rho}
\]
Density functionals

LDA: \( v_{xc} \propto \rho(r)^{\frac{1}{3}} \)

GGA: \( v_{xc} = f(\rho, \vec{\nabla} \rho) \)

Hybrid \( v_{xc} = f(\rho, \vec{\nabla} \rho) + E_{HF,x} \)

Meta GGA \( v_{xc} = f(\rho, \vec{\nabla} \rho, \tau) \) where \( \tau = \sum_i \frac{1}{2} |\nabla \psi_i(r)|^2 \)

\[
E_{xc}^{B3LYP}[\rho] = (1-a)E_x^S[\rho] + aE_x^{HF} + bE_x^{B88}[\rho] + cE_c^{LYP} + (1-c)E_c^{VWN}[\rho]
\]

\[
a = 0.20 \quad b = 0.72 \quad c = 0.81
\]
Stairway to heaven

- The exact functional
- …
- Stairway to heaven
- Orbital dependent functionals
- Exact exchange functionals
- Parametrized functionals
- Meta GGA
- Hybrid functionals
- GGA functionals molecules
- LDA functionals formal
- Hartree-Fock Slater, the first
- Thomas Fermi
**Configuration Interaction**

**Configuration interaction** (CI) is the most simple *ab initio* method to consider electron correlation.

The wave function is expanded as a linear combination of Slater determinants (configurations).

\[ |\Psi_{CI}\rangle = \sum_l C_l |l\rangle \]

The expansion coefficients are determined by minimizing the CI energy, with the constraint that the states are orthonormal.

\[ E_{CI} = \langle \Psi_{CI} | \hat{H} | \Psi_{CI} \rangle \quad \text{with} \quad \langle \Psi_{CI} | \Psi_{CI} \rangle = 1 \]

\[ L_{CI} = E_{CI} - \epsilon (\langle \Psi_{CI} | \Psi_{CI} \rangle - 1) \]
**Configuration Interaction**

The CI wave function considers electron correlation

\[
|\psi_{CI}\rangle = C_{HF}|\psi_{HF}\rangle + C_{S}|\psi_{S}\rangle + C_{D}|\psi_{D}\rangle + C_{T}|\psi_{T}\rangle + \cdots + C_{N}|\psi_{N}\rangle
\]

The CI eigenvalue equation: \(\hat{H}\psi_{CI} = E_{CI}\psi_{CI}\)
**Configuration Interaction**

|\(\psi_S\) \rangle All configurations that are obtained by single excitations from the \(|\psi_{HF}\rangle\) reference.

|\(\psi_D\) \rangle All configurations that are obtained by double excitations from the \(|\psi_{HF}\rangle\) reference.

|\(\psi_T\) \rangle All configurations that are obtained by triple excitations from the \(|\psi_{HF}\rangle\) reference.

|\(\psi_N\) \rangle All configurations that are obtained by all \(N\) excitations from the \(|\psi_{HF}\rangle\) reference.

|\(\psi_{CI}\) \rangle including all terms up to \(|\psi_N\rangle\) is the **full configuration interaction** (FCI) or **exact diagonalization** wave function \(i.e.,\) it is the solution of the Schrödinger equation in the given basis set.
Excited Slater Determinants

\[ |\Psi\rangle = c_0 |\Psi_0\rangle + \sum c_i^a |\Psi_i^a\rangle + \sum c_{ij}^{ab} |\Psi_{ij}^{ab}\rangle + \sum c_{ijk}^{abc} |\Psi_{ijk}^{abc}\rangle + \ldots \]

Reference configuration | Single Excitations | Double Excitations | Triple Excitations
---|---|---|---
| | | ▼
| | | 1
| | ▼ | 1
| 1▼ | 1 | | ▼
| 1▼ | 1▼ | 1 | 1

The Slater determinants of the CI model are obtained by single (S), double (D), triple (T), \ldots alternations of the occupation of the Fock space.
Brillouin’s theorem says that single excited determinants do not directly couple with the Hartree-Fock reference.

The Hamiltonian matrix is banded because only Slater determinants which are connected via singles and double excitations yield non-vanishing matrix elements.
Configuration Interaction

CI is a straightforward method to consider electron correlation effects.

Truncated CI wave functions are not size-extensive \textit{i.e.}, the energy of two non-interacting fragments is not twice the energy of one of the fragments.

The only exception is the FCI wave function.

FCI calculations are computationally expensive. The largest FCI calculation as far as I know had 2500 billion ($2.5 \times 10^{12}$) Slater determinants.

FCI calculations are indispensable as benchmark, whereas truncated CI has lost its importance as production tool due to the size problem.
Most matrix element of the CI Hamiltonian vanish, because configurations whose occupation number vectors differ in more than two position pairs do not directly couple.

The reason is that the Hamiltonian contains only one- and two-body interaction terms.

The non-vanishing matrix elements of the CI Hamiltonian can be identified using second quantization.

The obtained expressions are called \textit{Slater-Condon rules}.
**One-electron Slater-Condon rules**

$|k\rangle$ is a occupation number vector containing the occupation of the orbitals for a given Slater determinant.

$k_P = 1$ for occupied orbitals

$k_P = 0$ for unoccupied orbitals

$f_{PQ}$ are the matrix elements of the one-electron operator $\hat{f}$

Identical bra and ket: $\langle k | \hat{f} | k \rangle = \sum_P k_P f_{PP}$

bra and ket differ in one pair: $\langle k | \hat{f} | l \rangle = \Gamma^k_i \Gamma^l_j f_{ij}$

bra and ket differ in two or more pairs: $\langle k | \hat{f} | l \rangle = 0$

with

$$\Gamma^k_P = \prod_{Q=1}^{P-1} (-1)^{k_Q}$$
Two-electron Slater-Condon rules

$g_{PQRS}$ are the matrix elements of the two-electron operator $\hat{g}$

Identical bra and ket
\[ \langle k | \hat{g} | k \rangle = \frac{1}{2} \sum_{PR} k_P k_R \left( g_{PPRR} - g_{PRRP} \right) \]

differ in one pair
\[ \langle k | \hat{g} | l \rangle = \Gamma^k_R \sum_R k_R \left( g_{IJRR} - g_{IRRJ} \right) \]

differ in two pairs
\[ \langle k | \hat{g} | l \rangle = \Gamma^k_I \Gamma^l_R \Gamma^l_J \left( g_{IKJL} - g_{ILJK} \right) \]

differ in more than two pairs
\[ \langle k | \hat{g} | l \rangle = 0 \]

with
\[ \Gamma^k_P = \prod_{Q=1}^{P-1} (-1)^{k_Q} \]
CAS and RAS Models

The Complete Active Space and Restricted Active Space

Define a chemically meaningful active space

CASSCF

Identify key orbitals

RASSCF

RAS1

RAS2

RAS3
Multireference Configuration Interaction

Multireference configuration interaction (MRCI) belong to the category of "As Full CI as possible" models.

RAS can be considered as a MRCI with orbital optimization.

The reference can also consist of a few selected important configurations with single and double replacements to the complementary space.
Multireference Perturbation Theory

The CASPT2 method is a multireference (MR) perturbation theory method with a CASSCF wave function as the reference.

MRPT should be formulated such that when $|\Phi_0\rangle \rightarrow |HF\rangle$ MRPT $\rightarrow$ Møller-Plesset PT. This is not trivial because the MR Fock operator is not unique.

In CASPT2, the spin-averaged first-order density matrix of the CAS function is used to define the Fock operator.

The open-shell and closed-shell configurations are then treated unequally, which is fixed with semi-empirical level shifts.

The NEVPT2 model avoids the problem by adding two-electron terms to $H_0$, but it yields orbital labelling dependent results.
**Multireference Perturbation Theory**

In the single reference case, $H_0$ is the sum of one-electron Fock operators, which is diagonal in canonical orbital basis.

The CAS reference is not an eigenfunction of the $n$-electron Fock operator, that is, $F_{\text{CAS}}$ is not a proper $H_0$. This is fixed by using projection operators

$$H_0 = PFP + QFQ$$

where $P$ projects to the CAS reference.

The Fock operator of the MR case is not diagonal. Unitary transformations in the individual spaces remove off-diagonal elements in each orbital block, but not between the inactive, active and secondary orbital blocks.
Multireference Perturbation Theory

The first-order wave function is obtained as in the single reference case as

$$ (H_0 - E_0) \psi_1 = (H_0 - H) \psi_0 $$

which has to be solved iteratively.

The first order wave function is expanded in the first-order interaction space

$$ \psi_1 = \sum_{pqrs} T_{qs}^r \hat{E}_{pq} \hat{E}_{rs} \psi_0 $$

where $\hat{E}_{pq}$ is the spin-averaged excitation operator that moves an electron from the $q$ orbital of the active or inactive spaces to an empty orbital $p$ of the secondary space.
**Multireference Perturbation Theory**

The configurations of $\Psi_1$ comprise those who have non-vanishing Hamiltonian matrix elements with $\Psi_0$.

This is called **internal contraction** that reduces significantly the number of $T_{qs}^{pr}$ amplitudes.

Internal contraction leads to complicated expressions involving higher-order density matrices and non-orthogonal configurations including linear dependencies.

CASPT2 is able to handle bond breaking, reactions, transition metals, and excited states.

CASPT2 yields pure spin states.
CASPT2 Problems

The internal contraction scheme leads to intruder states as for MR coupled-cluster, MRCI and other similar approaches.

CASPT2 is not a black box method. It requires experience and a deep understanding of the electronic structure of the investigated system to obtain reliable results.

All orbitals that should be in the active space cannot be included due to the huge computational costs.

The borderline between active and secondary orbitals is not obvious.

CASPT2 with the minimal reference based on chemical intuition often yield unreliable results.
**Coupled-Cluster Models**

The coupled-cluster ansatz for the wave function is

\[ \psi_{CC} = \exp(\hat{T})\phi_0 \quad \text{where} \quad \phi_0 = \Phi_{HF} \quad \text{in most cases} \]

\[ \exp(\hat{T}) = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots + \frac{\hat{T}^n}{n!} \]

The cluster operator \( \hat{T} \) consists of single \( \hat{T}_1 \), double \( \hat{T}_2 \), triple \( \hat{T}_3 \) replacement operators.

\[ \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_n \]

The maximum is \( n = \) number of electrons, which is identical to full CI.

When the series is cut at \( \hat{T}_2 \), it is the CCSD model and a cut at \( \hat{T}_3 \) yields the CCSDT model, etc.
**Coupled-Cluster Models**

The cluster operators $\hat{T}_k$ operating on the HF reference generates all Slater determinants for single (S), double (D), triple (T), ... replacements.

\[ \hat{T}_1 = \sum_{i}^{occ} \sum_{a}^{vir} t_i^a a_a^\dagger a_i \]

\[ \hat{T}_2 = \frac{1}{4} \sum_{ij}^{occ} \sum_{ab}^{vir} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_i a_j \]

$t_i^a$ and $t_{ij}^{ab}$ are the singles and doubles **amplitudes**, respectively

\[ \exp(\hat{T}) = \mathbb{1} + \left( \hat{T}_1 \right)_{\text{single}} + \left( \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \right)_{\text{double}} + \left( \hat{T}_3 + \hat{T}_2 \hat{T}_1 + \frac{1}{6} \hat{T}_1^3 \right)_{\text{triple}} \]
Coupled-Cluster Models

To keep the expressions as general as possible the coupled-cluster Schrödinger equation is multiplied from left by \( \exp(-\hat{T}) \)

\[
\hat{H}\ket{\psi} = E \ket{\psi} \\
\psi = \exp(\hat{T})\Phi_0 \\
\hat{H} \exp(\hat{T})\ket{\Phi_0} = E \exp(\hat{T})\ket{\Phi_0} \\
\exp(-\hat{T})\hat{H} \exp(\hat{T})\ket{\Phi_0} = E \exp(-\hat{T})\exp(\hat{T})\ket{\Phi_0} \\
\underbrace{\exp(-\hat{T})\hat{H} \exp(\hat{T})}_{\text{similarity transformed Hamiltonian}} \ket{\Phi_0} = E \ket{\Phi_0}
\]
The coupled cluster equations for the amplitudes are obtained by projecting the coupled-cluster Schrödinger equation against the excited Slater determinants

\[ \langle \mu \vert \exp(-\hat{T})\hat{H}\exp(\hat{T})\vert \Phi_0 \rangle = 0 \]

\( \langle \mu \vert \) are the Slater determinant that enter the coupled-cluster state with **connected amplitudes** \( \hat{T}_1, \hat{T}_2, \hat{T}_3, \cdots \)

\[ \langle \mu \vert = \langle \Phi_0 \vert \tau_{\mu}^\dagger; \quad \langle \mu \vert = \langle \Phi_i^a \vert, \langle \Phi_{ij}^{ab} \vert, \langle \Phi_{ijk}^{abc} \vert, \cdots \]

where \( \tau_{\mu} \) are second-quantization operators that creates all possible single, double, triple, ... replacements from the Hartree-Fock reference (\( \Phi_0 \))
**Coupled-cluster energy**

The coupled-cluster energy is obtained by projecting against the Hartree-Fock reference

\[ E = \langle \Phi_0 | \exp(-\hat{T})\hat{H}\exp(\hat{T})|\Phi_0 \rangle \]

The coupled-cluster energy can be expressed as

\[ E_{CC} = E_{HF} + \sum_{ia} f_{ia} t_{ia} + \frac{1}{4} \sum_{iajb} \langle ij||ab\rangle t_{ab}^{ij} + \frac{1}{2} \sum_{iajb} \langle ij||ab\rangle t_{i}^{a} t_{j}^{b} \]

\[ \langle pq||rs\rangle = \langle pq|rs\rangle - \langle pq|sr\rangle \]

\[ \langle pq|rs\rangle = \int \int \phi^{*}_{p}(1)\phi_{r}(1)r_{12}^{-1}\phi^{*}_{q}(2)\phi_{s}(2)dr_{1}dr_{2} \]

\( f_{ia} \) are elements of the Fock matrix in the MO basis
Approximate Coupled-Cluster SD and Related Methods

Coupled-cluster energy:

\[ E_{CC2} = \langle HF| \hat{\Phi}(\hat{T}_2 + \frac{1}{2} \hat{T}_1 \hat{T}_1)|HF\rangle , \quad \hat{H}^{(1)} = \hat{\Phi} = \hat{H} - \hat{F} \]

Second-order Møllet-Plesset perturbation theory

\[ E_{MP2} = \langle HF| \hat{\Phi}\hat{T}^{(1)}_2|HF\rangle = \sum_{aibj} t_{ij}^{ab} \langle HF| \hat{\Phi}|_{ij}^{ab} \rangle \]

Coupled-cluster equations:

\[ 0 = \langle_i^a | [\hat{H}, \hat{T}_2] + \hat{H}|HF\rangle , \]
\[ 0 = \langle_{ij}^{ab} | [\hat{F}, \hat{T}_2] + \hat{H}|HF\rangle , \]

Similarity-transformed Hamiltonian:

\[ \hat{H} = \exp(-\hat{T}_1) \hat{H} \exp(\hat{T}_1) \]
Approximate Coupled-Cluster and Related Methods

Jacobi matrix:

\[
A_{\mu_i \nu_j} = \left. \frac{d\Omega_{\mu_i}}{dt_{\nu_j}} \right|_{\epsilon=0} = \langle \mu_i | \exp(-\hat{T}) [\hat{H}, \hat{r}_{\nu_j}] \exp(\hat{T}) | \text{HF} \rangle ,
\]

Jacobi matrix for CC2:

\[
A^{\text{CC2}} = \begin{pmatrix}
\langle i | [(\hat{H} + [\hat{H}, \hat{T}_2]), \hat{r}_k^c] | \text{HF} \rangle & \langle i | [\hat{H}, \hat{r}_{kl}^{cd}] | \text{HF} \rangle \\
\langle i, j | [\hat{H}, \hat{r}_k^c] | \text{HF} \rangle & \langle i, j | [\hat{F}, \hat{r}_{kl}^{cd}] | \text{HF} \rangle
\end{pmatrix}.
\]

Jacobi matrix for CIS(D\(_\infty\)):

\[
A^{\text{CIS(D\(_\infty\))}} = \begin{pmatrix}
\langle i | [(\hat{H} + [\hat{H}, \hat{T}_2]), \hat{r}_k^c] | \text{HF} \rangle & \langle i | [\hat{H}, \hat{r}_{kl}^{cd}] | \text{HF} \rangle \\
\langle i, j | [\hat{H}, \hat{r}_k^c] | \text{HF} \rangle & \langle i, j | [\hat{F}, \hat{r}_{kl}^{cd}] | \text{HF} \rangle
\end{pmatrix}.
\]

Jacobi matrix for ADC(2):

\[
A^{\text{ADC(2)}} = \frac{1}{2} A^{\text{CIS(D\(_\infty\))}} + \frac{1}{2} \left( A^{\text{CIS(D\(_\infty\))}} \right)^\dagger.
\]
Approximate Coupled-Cluster and Related Methods

\[
\begin{pmatrix}
A_{\mu_1 \nu_1} & A_{\mu_1 \nu_2} \\
A_{\mu_2 \nu_1} & \delta_{\mu_2 \nu_2} \epsilon_{\nu_2}
\end{pmatrix}
\begin{pmatrix}
E_{\nu_1} \\
E_{\nu_2}
\end{pmatrix}
= \omega
\begin{pmatrix}
E_{\nu_1} \\
E_{\nu_2}
\end{pmatrix}
\]

\[
E_{\mu_2} = \frac{\sum_{\nu_1} A_{\mu_2 \nu_1} E_{\nu_1}}{\omega - \epsilon_{\mu_2}}
\]

\[
\sum_{\nu_1}
\left[
A_{\mu_1 \nu_1} + \sum_{\kappa_2} \frac{A_{\mu_1 \kappa_2} A_{\kappa_2 \nu_1}}{\omega - \epsilon_{\kappa_2}}
\right] E_{\nu_1}
= \sum_{\nu_1} A_{\mu_1 \nu_1}^{\text{eff}} (\omega) E_{\nu_1}
= \omega E_{\mu_1}
\]
Time-dependent density functional theory

TDDFT response equations:

\[
\begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}
\]

\[
(A + B)_{ia\sigma, jb\sigma'} = (\varepsilon_{a\sigma} - \varepsilon_{i\sigma}) \delta_{ij} \delta_{ab} \delta_{\sigma\sigma'} + 2(ia\sigma|jb\sigma')
\]

\[
+ 2f_{ia\sigma, jb\sigma'}^{xc} - c_x \delta_{\sigma\sigma'} [(ja\sigma|ib\sigma) + (ab\sigma|i j\sigma)]
\]

\[
(A - B)_{ia\sigma, jb\sigma'} = (\varepsilon_{a\sigma} - \varepsilon_{i\sigma}) \delta_{ij} \delta_{ab} \delta_{\sigma\sigma'}
\]

\[
+ c_x \delta_{\sigma\sigma'} [(ja\sigma|ib\sigma) - (ab\sigma|i j\sigma)]
\]
Van der Waals Interaction

The van der Waals (vdW) interaction originates from fluctuating dipoles due to the correlated motion of the electrons.

Hartree-Fock and the commonly used DFT functionals are not able to take vdW interaction into account.

Second-order Møller-Plesset perturbation theory (MP2) is the cheapest \textit{ab initio} method that include vdW interaction.

MP2 overestimate vdW interaction. The spin-component-scaled (SCS) MP2 yields often similar vdW energies as the computationally more expensive CCSD(T) method.

A simple semi-empirical patch to consider vdW interactions is Grimme’s D$_3$ method, which consider vdW interaction at molecular mechanics (MM) level.

B3LYP+D$_3$ is good and pragmatic level when optimizing the molecular structure of large molecules such as biomolecules.
Basis sets

Basis sets can be divided into the

- Gaussian-type (GTO) basis functions (in most quantum chemistry programs)
- Slater-type (STO) basis functions (in ADF), efficient for DFT
- Plane-wave basis sets, the favourite in the physics community (VASP)
- Numerical basis functions (GPAW uses grid and atom-centered basis functions)
- Fully numerical (Octopus)

GTOs are better than STOs in \textit{ab initio} correlation calculations, because GTOs have the \textbf{wrong asymptotic} form at the nuclei and at infinity. (Almlöf)
Classes of Gaussian-Type Basis Sets

• Cartesian basis sets $\chi_i(r) = x^l y^m z^n \exp(-\alpha_i r^2)$, (6d, 10f)

• Spherical basis sets $\chi_i(r) = r^l Y_{lm}^m(\theta, \varphi) \exp(-\alpha_i r^2)$, (5d, 7f)

• Even-tempered basis sets
  • Uncontracted primitive basis sets with constant ratio between the exponents $\alpha_{i-1}/\alpha_i = \alpha_i/\alpha_{i+1}$

• General contracted basis sets
  • All basis functions comprise all primitive basis functions

• Segmented contracted basis functions
  • As general contracted, but for small blocks of primitive basis functions

• Completeness-optimized uncontracted basis sets
  • Optimize the exponents to obtain as complete basis set as possible in a given range of exponents
Basis sets

Basis sets can be downloaded from https://bse.pnl.gov/bse/portal

A few personal principles concerning the choice of basis set.

- Use as large basis set as possible
- Use more than one basis set
- The series of Dunning basis sets is very useful when aiming at benchmarking.
- The Dunning basis sets are large, which put limitations on the size of the molecule and the level of theory.
- Diffuse basis functions might be needed when the molecule is not very large or when it is negatively charged
- Special basis sets might be need for some properties.
**Basis sets**

A few personal principles concerning the choice of basis set.

- The MOLCAS ANO basis sets should be used only in combination with MOLCAS and other programs that can take the advantage of general contracted basis sets.

- I prefer the Karlsruhe basis sets

- the def2-TZVP basis sets is usually enough for my purposes, def2-SVP in molecular structure optimization of large molecules.

- When diffuse basis functions are needed, the def2-TZVPD is much more cost efficient than Dunning’s aug- basis sets

- The Pople basis sets are not very accurate

- Use Stuttgart pseudopotentials instead of LANL2DZ ECPs
Direct Diagonalization

Large eigenvalue problems cannot be solved by constructing the matrix and diagonalizing it.

The largest matrix that fit into the memory of a modern computer is say 64 GB = $2 \cdot 10^9$ double precision words.

The size of the largest matrix is then less than $10^5$

The largest CI problem that has been solved consisted of $2.5 \cdot 10^{12}$ Slater determinants

The CI matrix has to be diagonalized using direct methods

Direct methods means that the linear transformation $H \ C = \sigma$ is performed without construction of $H$. 
**Davidson-Olsen diagonalization**

The Hamiltonian matrix can be written as

$$H = H_0 + H_1$$  \hspace{1cm} (1)

The eigenvector and the eigenvalue is analogously written as

$$C = C^{(0)} + C^{(1)} \quad \text{and} \quad E = E^{(0)} + E^{(1)}$$  \hspace{1cm} (2)

The approximate eigenvalue $E^{(0)}$ is obtained as

$$E^{(0)} = \frac{C^{(0)^T}HC^{(0)}}{C^{(0)^T}C^{(0)}}$$  \hspace{1cm} (3)

inserting Eq. (1) and Eq. (2) into $HC = EC$ and neglecting quadratic terms yields

$$(H_0 - E^{(0)})C^{(1)} = -(H - E^{(0)})C^{(0)} + E^{(1)}C^{(0)}$$  \hspace{1cm} (4)
The correction vector $C^{(1)}$ is the obtained as

$$C^{(1)} = -(H_0 - E^{(0)})^{-1}[(H - E^{(0)})C^{(0)} - E^{(1)}C^{(0)}]$$  \hspace{1cm} (5)

The energy correction $E^{(1)}$ is obtained by multiplying Eq. (5) from the left by $C^{(0)\top}$ and require orthonormality of the $C^{(0)}$ and $C^{(1)}$ vectors

$$E^{(1)} = \frac{C^{(0)\top}(H_0 - E^{(0)})^{-1}(H - E^{(0)})C^{(0)}}{C^{(0)\top}(H_0 - E^{(0)})^{-1}C^{(0)}}$$  \hspace{1cm} (6)

which can be inserted in Eq. (5)
The correction vector $C^{(1)}$ obtained using

$$C^{(1)} = -(H_0 - E^{(0)})^{-1} \times$$

$$\left[ (H - E^{(0)})C^{(0)} - \frac{C^{(0)^T}(H_0 - E^{(0)})^{-1}(H - E^{(0)})C^{(0)}}{C^{(0)^T}(H_0 - E^{(0)})^{-1}C^{(0)}} C^{(0)} \right]$$

(7)

is orthogonal against $C^{(0)}$ by construction regardless of how the partitioning of $H$ into $H_0 + H_1$ is done.

- The algorithm requires that the inverse $(H_0 - E^{(0)})^{-1}$ times a vector must be calculated.
- In the Davidson diagonalization algorithm $H_0$ is the diagonal of the $H$ matrix and the $E^{(1)}$ correction term is omitted.
The Davidson-Olsen formulation, which is correct to first order, has the following advantages as compared to the slightly simpler Davidson diagonalization procedure:

- The update vector $C^{(1)}$ is orthogonal against $C^{(0)}$.
- A better $H_0$ does not introduce any new formal problems, not even for the case $H_0 \rightarrow H$.
- Block diagonal $H_0$ or other more accurate approximations to $H$ can be used.
- An algorithm with only two vectors ($C^{(0)}$ and $C^{(1)}$) leads to convergence in only a few iterations.
- Very large CI problems can therefore be solved.
The zeroth-order Hamiltonian

The better $H_0$ the better is the convergence.

\[ H_0 = \begin{pmatrix} H_{\text{block}} & L^T \\ L & D \end{pmatrix} \]

The matrix times vector operation is the

\[ H_0 x = y \]

\[ \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \quad y = \begin{pmatrix} y_1 \\ y_2 \end{pmatrix} \]

\[ H_{\text{block}} x_1 + L^T x_2 = y_1 \]

\[ L x_1 + D x_2 = y_2 \]
The zeroth-order Hamiltonian

\[ x_2 = D^{-1} (y_2 - Lx_1) \]

\[ H_{block} x_1 + L^T D^{-1} (y_2 - Lx_1) = y_1 \]

\[ \left( H_{block} - L^T D^{-1} L \right) x_1 = y_1 - L^T D^{-1} y_2 \]

\[ x_1 = \left( H_{block} - L^T D^{-1} L \right)^{-1} \left( y_1 - L^T D^{-1} y_2 \right) \]

\[ x = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \quad y = \begin{pmatrix} y_1 \\ y_2 \end{pmatrix} \]
Direct Inversion of the Iterative Space

One of the most important developments in electronic structure calculations is the Direct Inversion of the Iterative Space (DIIS) method for damping the iterative procedure of the solution of the Fock and Kohn-Sham equations.

In the update of the new Fock matrix, the Fock matrices are considered

$$F_{n}^{AO} = \sum_{i}^{n} \omega_{i} F_{i}^{AO}$$

where $F_{i}^{AO}$ are the Fock matrices of the previous iterations and the DIIS weights $\omega_{i}$ are obtained by solving the DIIS equation.
Direct Inversion of the Iterative Space

The DIIS equation is obtained by constructing the DIIS Lagrangian

$$\mathcal{L} = \omega^\dagger B \omega - \lambda \left(1 - \sum_{i}^{m} \omega_i\right),$$

with

$$B_{ij} = \langle e_i | e_j \rangle.$$

constructed from the error vector

$$e_i = F_i^{AO} D_i S - S D_i F_i^{AO}$$

$D_i$ is the density matrix of iteration $i$ and $S$ the overlap matrix
Direct Inversion of the Iterative Space

The DIIS equation is a matrix equation of the size of the iteration space or of the $m$ last iterations.

\[
\begin{pmatrix}
    B_{11} & B_{12} & \cdots & B_{1m} & -1 \\
    B_{21} & B_{22} & \cdots & B_{2m} & -1 \\
    \vdots & \vdots & \ddots & \vdots & \vdots \\
    B_{m1} & B_{m2} & \cdots & B_{mm} & -1 \\
    -1 & -1 & \cdots & -1 & 0
\end{pmatrix}
\begin{pmatrix}
    \omega_1 \\
    \omega_2 \\
    \vdots \\
    \omega_m \\
    \lambda
\end{pmatrix}
= 
\begin{pmatrix}
    0 \\
    0 \\
    \vdots \\
    0 \\
    -1
\end{pmatrix}
\]

Solution of the DIIS equation yields $\omega_i$ which combined with $F_{k}^{AO}$, $k = 1, m$ yields the new extrapolated (damped) $F_{i}^{AO}$
The End

Now this is not the end.

It is not even the beginning of the end.

But it is, perhaps, the end of the beginning.

Sir Winston Churchill, Speech in November 1942
British politician (1874 - 1965)