Introduction to Quantum Chemical Methods

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„All science begins by wondering why the things are as they are“

„Science starts by being curious“

Aristotle
(384 BC - 322 BC)

Linus Pauling
(1901-1994)
How Theoretical Chemistry almost didn’t Start

„Any attempt to use mathematical methods for the investigation of chemical questions must be considered as completely irrational and is strongly opposing the spirit of chemistry. If mathematics will ever occupy a prominent place in chemistry - an absurd idea that fortunately is completely unrealistic - this would lead to a rapid and irreversible decay of this scientific discipline“

Isidore Marie Auguste François Xavier Comte (1798-1857)

Comte, IMAFX Cours der philosophie positive, Schleicher, Paris, 1838, p- 28-29
... but then

Erwin Schrödinger

\[ \left\{ -\frac{1}{2} \nabla^2 + V(r) \right\} \psi(r) = E\psi(r) \]

Wave Mechanics (1926)

Werner Heisenberg

\[ \left\{ T + V \right\} C = EC \]

Matrix Mechanics (1926)

Paul A.M. Dirac

\[
\begin{pmatrix}
V(r) & c\sigma \mathbf{p} \\
c\sigma \mathbf{p} & V(r) - 2c
\end{pmatrix}
\begin{pmatrix}
\psi_L(r) \\
\psi_L(r)
\end{pmatrix} = E
\begin{pmatrix}
\psi_L(r) \\
\psi_L(r)
\end{pmatrix}
\]

Relativistic Quantum Mechanics (1928)
... and shortly after

The fundamental laws necessary for the mathematical treatment of large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that applications of these laws leads to equations that are too complex to be solved “

„... hence it would be desirable to develop practical approximation schemes for the application of quantum mechanics“

.. up to

We can calculate everything!
(1975)

Enrico Clementi
(born 1931)
Why Quantum Chemistry?

• In order to predict quantities that can not be measured (example: short lived intermediates that never accumulate enough for experimental studies)

• In order to interpret the outcome of experiments (example: complex NMR or EPR spectra)

• In order to obtain insight in the regularities of data (example: understand the key factors that contribute to reactivity trends in a series of related molecules)

• In order to predict the outcome of future experiments (example: Design of materials - how do I have to change the molecule in order to optimize a given property)

• ... many other reasons why the synergy between theory and experiment is greatly enhancing the efficiency and the depths of the scientific analysis
Fundamental Interactions in Molecules

Just 2 Laws:

1. Coulomb’s Law

\[
E = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{|\mathbf{r}_1 - \mathbf{r}_2|}
\]

2. Kinetic Energy

\[
E = \frac{1}{2} m v^2 = \frac{p^2}{2m}
\]

\[
E = T_e + T_N + V_{eN} + V_{NN} + V_{ee}
\]
**From Classical to Quantum Mechanics**

★ In classical mechanics **Newton’s equations** are solved that contain the positions \( \mathbf{r} \) and momenta \( \mathbf{p} \) (recall \( \mathbf{p} = m \mathbf{v} \)) as unknown variables. The solutions are \( \mathbf{r}(t) \) and \( \mathbf{p}(t) \) (the „trajectory“ of the particles).

★ In quantum mechanics the **uncertainty principle** forbids us to know \( \mathbf{r}(t) \) and \( \mathbf{p}(t) \) simultaneously. Instead we are aiming for the „wavefunction“ that provides us with the probability of finding the particles at given points in space with given velocities (a more detailed definition follows).

★ In order to calculate the wavefunction, a special form of the equations of motion are used - the **Hamiltonian formalism** that is most readily transferred from classical to quantum mechanics.

★ The „**Hamiltonian**“ of the system corresponds to the total energy. Thus, it is the sum of all terms that contribute to the total energy

\[
\hat{H}(\mathbf{r}, \mathbf{R}) = T_e + T_N + V_{eN} + V_{ee} + V_{NN}
\]

\[
T_e = \sum_{i} p_i^2 / 2m_{e_i} \quad V_{ee} = \frac{e_0^2}{4\pi\varepsilon_0} \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}
\]

\[
T_N = \sum_A p_A^2 / 2m_A \quad V_{NN} = \frac{e_0^2}{4\pi\varepsilon_0} \sum_{A<B} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}
\]

\[
V_{eN} = -\frac{e_0^2}{4\pi\varepsilon_0} \sum_{A,i} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|}
\]

**Note**: \( i,j \) sum over electrons, \( A,B \) sum over nuclei, \( Z_A,M_A\) - Charge and Mass of Nucleus ,\( A' \)
The Schrödinger Equation

★ In order to go to quantum mechanics we move over to **atomic units** in which

\[
\hbar = 4\pi \varepsilon_0 = e_0 = m_e = 1 \quad c = 137.06
\]

★ And replace the **momentum** by its quantum mechanical analogue:

\[
p_i \rightarrow -i \nabla_i \quad \mathbf{\nabla} = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \quad \hat{i} = \text{imaginary unit} \quad \hat{i}^2 = -1
\]

★ We finally need to introduce the **spin of each electron** $\sigma_i$ that can only assume the two values $\alpha$ and $\beta$. The three space and one spin variable for each electron are collected in the vector $\mathbf{x}$.

★ **Schrödinger’s equation** for the many particle wavefunction $\Psi(x_1,\ldots,x_N,R_1,\ldots,R_M,t)$

\[
\equiv \Psi(x,R,t) \text{ is:}
\]

\[
\hat{i} \frac{\partial}{\partial t} \Psi(x,R,t) = \hat{H}(x,R,t)\Psi(x,R,t)
\]

★ But if the Hamiltonian does not depend on time (which is assumed henceforth), we obtain the **time-independent Schrödinger eigenvalue equation**

\[
\hat{H}(x,R)\Psi(x,R) = E\Psi(x,R) \quad E = \text{Total Energy}
\]
The Born-Oppenheimer Approximation

★ As a final step, we need the **Born-Oppenheimer approximation** which amounts to the neglect of the kinetic energy of the nuclei.

\[ \hat{H}(\mathbf{r}, \mathbf{R}) \rightarrow \hat{H}_{BO}(\mathbf{r}, \mathbf{R}) = T_e + V_{eN} + V_{ee} + V_{NN} \]

★ **Justification (heuristic):** Nuclei are much heavier and move much slower than electrons. hence, electrons adjust themselves immediately to any nuclear configuration.

★ **Consequence 1:** The concepts of chemical structures and potential energy surfaces (Energy as function of nuclear coordinates) emerges!

★ **Consequence 2:** The Schrödinger equation separates into two equations. One of the electrons for any given arrangement of the nuclei and one for the nuclei on a given potential energy surface!

\[ \hat{H}_{BO} \Psi(x \mid \mathbf{R}) = E(\mathbf{R})\Psi(x \mid \mathbf{R}) \]

\[ \left\{ \hat{T}_N + E(\mathbf{R}) \right\} \Theta(\mathbf{R}) = \mathcal{E} \Theta(\mathbf{R}) \]

The total wavefunction would be the product of the electronic wavefunction and the nuclear wavefunction but here we are mainly concerned with the electronic part.
Is the Born-Oppenheimer Approximation Good?

The BO Hamiltonian - despite its (apparent) simplicity - is a great achievement: it describes 99% of all chemistry correctly. Exceptions are:

★ The BO Hamiltonian does not contain terms that describe the interactions of nuclei and electrons with external electric and magnetic fields
★ The BO Hamiltonian misses many small terms that are associated with the electron and nuclear spins
★ The BO Hamiltonian does assume a point like nucleus
★ The BO Hamiltonian breaks down in situations where the separation of nuclear and electronic movements is no longer well separated. For example in Jahn-Teller systems.
★ The Born-Oppenheimer Hamiltonian needs to be partly replaced or supplemented with relativistic terms if heavy elements are involved.

Only for the description of more advanced spectroscopies, such as EPR spectroscopy, do we need to proceed beyond the Born-Oppenheimer approximation.
The Many Particle Wavefunction

**Born-Interpretation:**

\[ \left| \Psi(x \mid R) \right|^2 = \Psi^*(r_1 \sigma_1, \ldots, r_N \sigma_N \mid R)\Psi(r_1 \sigma_1, \ldots, r_N \sigma_N \mid R) \]

Given the nuclear configuration \( R \), the square of \( \Psi \) gives the **conditional probability** for finding electron 1 at \( r_1 \) with spin \( \sigma_1 \), electron 2 at \( r_2 \) with spin \( \sigma_2 \), ...

**Pauli-Principle:**

\[ \Psi(x_1, \ldots, x_i, \ldots, x_j, \ldots, x_N \mid R) = -\Psi(x_1, \ldots, x_j, \ldots, x_i, \ldots, x_N \mid R) \]

**Antisymmetry** with respect to particle interchanges (electrons are Fermions)

**How do I picture the many electron wavefunction?**

**You don’t**

- Nobody can intuitively picture a function of 4N variables.
- Insight has to come from elsewhere

**Important NOTE: NO ORBITALS YET! Orbitals are not fundamental objects**
The Total Energy

What is the total energy $E(R)$?
The energy that is required to separate the molecule into noninteracting protons and electrons.

Is this observable?
In principle: YES
in practice: NO

What is its relevance?
In chemistry and spectroscopy we measure energy differences! This will be elaborated below

How large is it?
Quite typically, for a transition metal complex, it is, say, 10,000-100,000 eV

How accurate do we need it?
If we want to have energy differences accurate to ~1 kcal/mol then we need to have it accurate to 0.05 eV or in other words: better than 1 ppm!

Note: 1 atomic unit (a.u.) ~27.21 eV ~627 kcal/mol
Ground and Excited States

The BO eigenvalue equation (like any other eigenvalue equation) has an infinite number of solutions. If we order, the solutions according to increasing energy and start labelling by ’0‘:

- $E_0(R)$ is the **ground state** total energy of the system
- $E_I(R)$ for $I>0$ are the **excited states** of the system
- NOTE: Each state has its own eigenfunction $\Psi_I(x|R)$
- If two or several eigenvalues are identical (say $n$), we say that the state is $n$-fold **degenerate**. The eigenfunctions belonging to the same degenerate eigenvalue are only determined up to an arbitrary unitary transformation.
- The eigenfunctions can be classified at least according to three criteria:
  - Their total spin $S$ (to be discussed later)
  - Their spin-projection quantum number $M$ (to be discussed later)
  - Their overall spatial symmetry with irreducible representation $\Gamma$ (not discussed here)
Chemistry and Potential Energy Surfaces

Chemistry (reactions) occur typically only on the ground or at most on a few low-lying potential energy surfaces. Thus, the most important feature is the variation of the total energy with changes in the nuclear coordinates:

- Local Minimum ("reactants")
- Saddle point ("Transition State")
- Global Minimum ("products")

\[ \Delta E_{\text{reaction}} \rightarrow \text{Reaction Energy} \]
\[ \Delta E^\infty \rightarrow \text{Reaction Rate} \]
Apply some kind of oscillating perturbing field with Hamiltonian $H_1(\omega)$ in order to induce transitions between different states of the system.

**Transition Probability**

["Fermi’s Golden Rule"]

\[ I \propto \left| \langle \Psi_{\text{initial}} | H_1 | \Psi_{\text{final}} \rangle \right|^2 \]
Spectroscopic Techniques

<table>
<thead>
<tr>
<th>Gamma</th>
<th>X-Ray</th>
<th>UV/vis</th>
<th>Infrared</th>
<th>Microwave</th>
<th>Radiowave</th>
</tr>
</thead>
<tbody>
<tr>
<td>eV</td>
<td>14000</td>
<td>8000</td>
<td>2000</td>
<td>4 - 1</td>
<td>0.1-0.01</td>
</tr>
</tbody>
</table>

Note: 1.au. = 27.21 eV  
1 eV = 8095 cm\(^{-1}\) = 23.06 kcal/mol  
1 cm\(^{-1}\) = 29979 MHz
Solving the Born-Oppenheimer Equation

★ How do we solve the many-particle Born-Oppenheimer equation?

NOT AT ALL!

➡ The Born-Oppenheimer Schrödinger equation can not be solved in closed form for more than one electron. Not even for the simplest two electron cases.

➡ We need approximation methods
Approximate Quantum Mechanical Methods

\[ \hat{H}(x, R)\Psi(x_1, \ldots, x_N | R) = E(R)\Psi(x_1, \ldots, x_N | R) \]

- Hartree-Fock
- Density Functional Theory
- Semi-Empirical
  - Force Fields
  - Configuration Interaction
  - Many Body Perturbation
  - Coupled Cluster
- Multireference CI, PT, CC

Exact Solution of the BO-Problem
Approximations: The Variational Principle

Given a trial wavefunction that depends on some parameters \( p \):

\[ \Psi_{\text{trial}}(x \mid R, p) \]

The "Ritz-functional" is:

\[ E[\Psi] = \frac{\langle \Psi_{\text{trial}} \mid H \mid \Psi_{\text{trial}} \rangle}{\langle \Psi_{\text{trial}} \mid \Psi_{\text{trial}} \rangle} \]

For the exact wavefunction \( E[\Psi] \) is the exact energy. For any other wavefunction it is readily shown that:

\[ E[\Psi] \geq E_{\text{exact}} \]

Hence, we can search for a minimum of \( E[\Psi] \) with respect to the parameters \( p \) to obtain the best possible approximation within the given Ansatz. The condition for a stationary point is:

\[ \frac{\partial E[\Psi]}{\partial p_I} = 0 \quad (\text{all } I) \]
Ansatz: The Hartree-Fock Method

The **Hartree-Fock** (HF) method is obtained by a specific Ansatz for the trial wavefunction. It is inspired by the form the wavefunction would have, if the electron-electron interaction would not be there ("independent particle model")

In this case, the wavefunction would be a simple product of one-electron functions. However, the overall wavefunction needs to fulfill the Pauli principle. Hence, one employs a **Slater determinant**

\[
\Psi_{HF} = \frac{1}{\sqrt{N!}} \left| \begin{array}{cccc}
\psi_1(x_1) & \psi_1(x_2) & \cdots & \psi_1(x_N) \\
\psi_2(x_1) & \psi_2(x_2) & \cdots & \psi_1(x_N) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_N(x_1) & \psi_N(x_2) & \cdots & \psi_N(x_N)
\end{array} \right| \equiv | \psi_1 \psi_2 \cdots \psi_N |
\]

The "auxiliary" one-electron functions that have been introduced are called "orbitals". They are the objects to be varied in order to find the best possible approximation to the true wavefunction.
The Hartree-Fock Roothaan Method

It is difficult to vary the orbitals themselves. Rather what one does is to expand the orbitals in another set of auxiliary functions, the "basis set"

\[ \psi_i(x) = \sum_{\mu} c_{\mu i} \varphi_\mu(x) \]

If the basis set \( \{\phi\} \) would be mathematically "complete", the expansion would be exact. In practice, we have to live with less than complete basis set expansions.

Carrying out the variation now with respect to the unknown "MO coefficients" \( c \) leads to the famous Hartree-Fock Roothaan equations. The MO coefficients must satisfy the following coupled set of nonlinear equations:

\[ F \psi_i = \varepsilon_i \psi_i \quad \Leftrightarrow \quad \sum_{\nu} F_{\mu \nu}(c) c_{\mu i} = \varepsilon_i \sum_{\nu} c_{\nu i} S_{\mu \nu} \quad (\text{all } \mu, i) \]

\[ \varepsilon_i = \text{Orbital Energy of Orbital } i \]
\[ F = \text{Fock Operator} \]
\[ S = \text{Overlap Matrix} \]
The Fock Operator

The orbital energy is the expectation value over the Fock operator and describes the average energy of the electron in orbital $i$:

$$\varepsilon_i = \langle \psi_i | F | \psi_i \rangle = \left( \langle \psi_i | T_e + V_{eN} | \psi_i \rangle \right) + \sum_j \langle \psi_i \psi_j | \psi_i \psi_j \rangle$$

Where the "two-electron integral" is:

$$\langle \psi_i \psi_j | \psi_i \psi_j \rangle = \langle \psi_i \psi_j | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \psi_j \psi_i \rangle$$

$$= \int \int \frac{\left| \psi_i (x_1) \right|^2 \left| \psi_j (x_2) \right|^2}{|r_1 - r_2|} \, dx_1 \, dx_2 - \int \int \frac{\psi_i (x_1) \psi_j (x_1) \psi_i (x_2) \psi_j (x_2)}{|r_1 - r_2|} \, dx_1 \, dx_2$$

**Coulomb integral**

- Electrostatic interaction between "smeared" out charge distributions $|\psi|^2$ and $|\psi|^2$
- "classical" interaction
- Always positive

**Exchange integral**

- Electrostatic self-interaction of the "smeared" out "interference density" $\psi \psi_j$
- Purely quantum mechanical
- Arises from the Pauli principle
- Always positive (not trivial)
- Does NOT describe a genuine "exchange interaction"
Interpretation of the Hartree-Fock Model

Each electron moves in the field created by the nuclei and the average field created by the other electrons („mean field model“) - this also called the „Hartree-Fock sea“
Solving the Hartree-Fock Equations

The Fock operator depends on its own eigenfunctions! Hence, the Hartree-Fock equations are highly nonlinear and can only be solved by an iterative process:

1. Guess some starting orbitals
2. Calculate the Fock operator with the present orbitals
3. Diagonalize the Fock operator to obtain new orbitals
4. Calculate the total energy
5. Check for convergence
   - Not converged
     - 2. Calculate the Fock operator with the present orbitals
     - 3. Diagonalize the Fock operator to obtain new orbitals
     - 4. Calculate the total energy
     - 5. Check for convergence
   - Converged (Hurray!)
     - Print results and/or do additional calculations

 Disclaimer
Convergence may be slow, may not occur at all or may occur to a high energy solution that may or may not be physically sensible! Special techniques are often required to reach convergence
How Good is Hartree-Fock Theory?

Consider a Hartree-Fock calculation on the Neon atom (10 electrons)

<table>
<thead>
<tr>
<th>Exact HF Energy</th>
<th>-128.547 Eh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact Experimental Energy</td>
<td>-129.056 Eh</td>
</tr>
</tbody>
</table>

(NOTE: exact experimental energy= sum of the ten ionization potentials)

**Good News:** HF recovers 99.6% of the exact energy (after subtraction of relativistic effects ~99.8%)

**Bad News:** The conversion factors work against us!

1 Eh = 27.21 eV
1 eV = 23.06 kcal/mol
= 8065 cm$^{-1}$

Thus, the small HF error amounts to the huge number of 319 kcal/mol error! In chemistry one aims at 1 kcal/mol accuracy.

✓ Very hard to achieve for absolute energies
✓ We usually want relative energies (much easier but still hard)
What is missing from Hartree-Fock Theory?

Exact Energy =

"Mean Field" Hartree-Fock

\[ \sum_{i,j} \text{Electron pairs} \epsilon_{ij}(↑↑) + \epsilon_{ij}(↑↓) \]

Fermi-Correlation

Coulomb-correlation

Correlation energy = \( \frac{1}{2} \sum_{i,j} \) Electron pairs

Relatively easy due to "Fermi hole" in the mean-field

Extremely hard to calculate due to interelectronic cusp at the coalescence point \( r_1=r_2 \)
\[
\left| \Psi \right> = \left| \Psi_0 \right> + \sum_{ia} C_{ia}^i \left| \psi_i \right> + \frac{1}{4} \sum_{ijab} C_{ijab}^{ij} \left| \psi_{ij} \right> + \frac{1}{36} \sum_{ijabc} C_{ijabc}^{ijk} \left| \psi_{ijk} \right> + \ldots
\]

\[
\frac{1}{2} P_{ij} P_{ab} \sum_{klcd} \langle kl \parallel cd \rangle t_{ac}^{ik} t_{db}^{lj}
\]
Interpretation of the Hartree-Fock Solutions

The primary result of Hartree-Fock calculation (once converged) is the **Total energy**

\[ E = V_{NN} + \sum_i \langle \psi_i | h | \psi_i \rangle + \frac{1}{2} \sum_{i,j} \langle \psi_i \psi_j | | \psi_i \psi_j \rangle \]

And the approximate **many-electron wavefunction**

\[ \Psi_{HF}(x_1, \ldots, x_N) = | \psi_1 \ldots \psi_N | \]

But what about the „secondary quantities“, the **orbital energies**

\[ \varepsilon_i = \text{roughly the energy it takes to remove the electron from the molecule ('ionization potential')} \] *(Koopman’s Theorem)*

And the **orbitals** themselves:

\[ \psi_i(x) = \sum_{\mu} c_{\mu i} \varphi_{\mu}(x) \]

**Rigorous:** No fundamental importance despite frequent use of HOMO/LUMO and related arguments

**In practice:** Describes the „electronic structure“ of the molecule in terms of bonding orbitals, antibonding orbitals or lone pairs.

→ Subject of endless fights and debates. However, please remember: **Orbitals are NOT observable.**
The Electron Density

- Weakly structured
- Always positive
- Insensitive to bonding

In HF Theory:

\[
\rho(r) = \sum_i |\psi_i^{\alpha}(r)|^2 + \sum_i |\psi_i^{\beta}(r)|^2
\]

\[
= \rho^{\alpha}(r) + \rho^{\beta}(r)
\]

\[
= \sum_{\mu\nu} \left( P_{\mu\nu}^{\alpha} + P_{\mu\nu}^{\beta} \right) \varphi_{\mu}(r)\varphi_{\nu}(r)
\]
Partial Charges and Bond Orders

As (bio)chemists we want to think of „polar groups“ and „partial charges“ and „ionic character“ and all that. Hence, we have a desire to divide the total electron density such that parts of it are „assigned“ to individual atoms.

This is the subject of „population analysis“. It is never unique and hence very many different schemes exist.

The easiest is due to Mulliken:

\[ N_A = \sum_{\mu \in A} P_{\mu \nu} S_{\mu \nu} + \sum_{B \neq A} \sum_{\mu \in A, \nu \in B} P_{\mu \nu} S_{\mu \nu} \]

\[ Q_A = Z_A - N_A \]

Refined Schemes are the „Natural Population Analysis“ (NPA) and the „Atoms in Molecules (Bader)“ Analysis.

NOTE: Since partial charges are NOT observables there is no „best“ charge. One should stick to one scheme and then look at trends.
The Spin Density

✓ Strongly structured
✓ Positive or negative
✓ Highly sensitive to bonding

In HF Theory:

\[ \rho^{\alpha-\beta}(\mathbf{r}) = \sum_i \left| \psi^\alpha_i(\mathbf{r}) \right|^2 - \sum_i \left| \psi^\beta_i(\mathbf{r}) \right|^2 \]

\[ = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r}) \]

\[ = \sum_{\mu\nu} \left( P^\alpha_{\mu\nu} - P^\beta_{\mu\nu} \right) \varphi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r}) \]
The Basis for the Hohenberg-Kohn Theorems

We can reconstruct the nuclear positions and charges from the electron density. This means, we can reconstruct the BO Hamiltonian of the molecule from $\rho(r)$ alone.

$$\lim_{r \to 0} \left[ \frac{\partial}{\partial r} + 2Z_A \right] \rho(r) = 0$$

$$\int \rho(r) dr = N$$

We can reconstruct the nuclear positions and charges from the electron density.

This means, we can reconstruct the BO Hamiltonian of the molecule from $\rho(r)$ alone.

Electron Density of the CO molecule
The Hohenberg Kohn-Theorems

If we know the BO Hamiltonian of the molecule we could (in principle) solve the Schrödinger equation. Hence, the exact $N$-particle wavefunction, the exact energy and all expectation values are **functionals** of the electron density!

Knowing $\rho(r)$  
\[ \rightarrow \] \( V_{eN}, N \)  
\[ \rightarrow \] \( H_{BO} \)  
\[ \rightarrow \] \( E, \Psi \)  

Somehow possible

The “**big dream**” is to go directly from the electron density to the exact energy. From the DFT logics this must be “somehow” possible, but we don’t know how!

1) The existance of the “universal” functional $E[\rho]$ is guaranteed by the **first Hohenberg-Kohn** (HK) theorem.

2) The **second HK theorem** establishes a variational principle that states that $E[\rho']$ ($\rho'$ being a test density) $\geq E[\rho]$
The DFT Functional

We can start to approach the functional by separating the parts inspired by HF theory that we know we can write exclusively in terms of the density:

\[
\]

- \(V_{NN}\)  
  Nuclear Repulsion (trivial):

- \(V_{eN}[\rho] = -\sum_A Z_A \int \rho(r) r_i^{-1} dr\)  
  Electron-Nuclear Attraction (ok)

- \(J[\rho] = \frac{1}{2} \sum_{ij} \langle ij | ij \rangle = \frac{1}{2} \int \int \rho(r_1) \rho(r_2) r_{12}^{-1} dr_1 dr_2\)  
  Coulomb Energy (ok)

- \(T[\rho]\)  
  Kinetic Energy (unknown)

- \(E'_{XC}[\rho] = K[\rho] + C[\rho]\)  
  Exchange and Correlation (unknown)
The Kohn-Sham Construction (I)

DFT only became a practical tool after an ingenious trick of Kohn-Sham. They have considered a fictitious model system of independent particles that share the exact electron density with the real system.

The wavefunction for such a system is a single Slater determinant (Kohn-Sham determinant)

$$\rho_{KS}(r) = \sum_i \int |\psi_i(x)|^2 \, ds \equiv \rho_{exact}(r)$$

Re-inserting $\rho(r)$ into the energy expression yields the exact $E$.

$$E[\rho] = V_{NN} + T_s[\rho] + V_{eN}[\rho] + J[\rho] + E_{XC}[\rho]$$

The “noninteracting” kinetic energy is:

$$T_s[\rho] = -\frac{1}{2} \sum_i \langle \psi_i | \nabla^2 | \psi_i \rangle$$

But now the exchange correlation contains the missing part of the kinetic energy:

$$E_{XC}[\rho] = E'_{XC}[\rho] + T[\rho] - T_s[\rho]$$
The Kohn-Sham Construction (II)

The Kohn-Sham orbitals are found from the Kohn-Sham equations:

\[
\left\{-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r})\right\}\psi_i(\mathbf{x}) = \varepsilon_i \psi_i(\mathbf{x})
\]

The effective Kohn-Sham potential is defined by:

\[
v_{\text{eff}}(\mathbf{r}_i) = -\sum_A Z_A r_{Ai}^{-1} + \int \rho(\mathbf{r}_2) r_{i2}^{-1} d\mathbf{r}_2 + V_{\text{XC}}(\mathbf{r})
\]

And the XC contribution is defined by a “functional derivative”:

\[
V_{\text{XC}}(\mathbf{r}) = \frac{\delta E_{\text{XC}}}{\delta \rho(\mathbf{r})}
\]

This is the celebrated formal apparatus of DFT! If we would know \(E_{\text{XC}}\), these equations would constitute an exact framework. But we don’t (and likely never will)!

However, much progress has been made by guessing approximate \(E_{\text{XC}}[\rho]\) and inserting them into the Hohenberg-Kohn-Sham machinery.
Ab Initio DFT Potentials

There are (expensive!) ways to construct very good KS potentials from accurate densities (red). These can be compared with “typical” present day potentials (blue).

The presently used potentials are far from being correct and all present day DFT results rely on cancellation of large errors.
Big Problems may still exist ...

\[ \Delta E = +1.9 \pm 0.5 \text{ kcal/mol} \quad \text{Exp.} \]
\[ +1.4 \quad \text{kcal/mol} \quad \text{SCS-MP2} \]
\[ -11.5 \quad \text{kcal/mol} \quad \text{HF} \]
\[ -8.4 \quad \text{kcal/mol} \quad \text{B3LYP} \]
\[ -9.9 \quad \text{kcal/mol} \quad \text{BLYP} \]
### Numerical Results

Total, correlation and exchange energies of the Neon atom using the *ab initio* CCSD(T) method and various standard functionals (deviations from the wavefunction results in mEh).

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{\text{tot}}$</th>
<th>$E_{\text{corr}}$</th>
<th>$E_{\text{x}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD(T)</td>
<td>-128.9260</td>
<td>-0.379</td>
<td>-12.098</td>
</tr>
<tr>
<td></td>
<td>-129.0640 (rel)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP86</td>
<td>-128.9776 (-52)</td>
<td>-0.388 (- 9)</td>
<td>-12.104 (-6)</td>
</tr>
<tr>
<td>PBE</td>
<td>-128.8664 (+60)</td>
<td>-0.347 (+32)</td>
<td>-12.028 (+70)</td>
</tr>
<tr>
<td>BLYP</td>
<td>-128.9730 (-47)</td>
<td>-0.383 (- 4)</td>
<td>-12.099 (-1)</td>
</tr>
<tr>
<td>TPSS</td>
<td>-128.9811 (-55)</td>
<td>-0.351 (+28)</td>
<td>-12.152 (-54)</td>
</tr>
<tr>
<td>B3LYP</td>
<td>-128.9426 (-17)</td>
<td>-0.452 (-73)</td>
<td>-12.134 (-36)</td>
</tr>
<tr>
<td>B2PLYP</td>
<td>-128.9555 (-30)</td>
<td>-0.392 (-13)</td>
<td>-12.103 (-5)</td>
</tr>
<tr>
<td>Exp</td>
<td>-129.056</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Wavefunction theory is very accurate (but also very expensive). DFT results vary widely among different functionals and either over- or undershoot. However, total energies are not important in chemistry – relative energies matter.
Summary of Lecture 1

✓ Chemistry is described by the many particle Schrödinger equation

✓ The Born-Oppenheimer approximation is a cornerstone of molecular theory and is (most of the time) accurate enough

✓ The many particle Schrödinger equation cannot be solved exactly

✓ Hartree-Fock theory is a useful first step and recovers more than 99.8% of the exact energy. The remaining error is still too large for chemistry!

✓ „Post-HF“ methods can approach chemical accuracy but are computationally still too expensive for widespread application

✓ Density functional theory offers an efficient and pragmatic route towards usefully accurate chemical results but the presently available models are semi-empirical in nature and all involve the cancellation of very large errors.