Introduction to Quantum Chemical Methods

Frank Neese

Max Planck Institut für Kohlenforschung
Kaiser-Wilhelm Platz 1
D-45470 Mülheim an der Ruhr
Frank.Neese@kofo-mpg.de
The Big Promise

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“

.. but not like this please!

We can calculate everything!
(1975)

Enrico Clementi
(born 1931)
„All science begins by wondering why the things are as they are“

„Science starts by being curious“
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)

• Have fun with computers, study algorithms, approximations and other „inner theoretical reasons to do it“, …
… but not like this please

Note: 1. au. = 27.21 eV  
1 eV = 8065 cm\(^{-1}\) = 23.06 kcal/mol  
1 cm\(^{-1}\) = 29979 MHz
Seeking Feedback from Experiment

R-H \xrightarrow{k_1} I_1 \xrightarrow{k_2} I_2 \xrightarrow{k_n} I_n \xrightarrow{k_{n+1}} R-OH

Kinetics \(k_i\)  Thermodynamics \(\Delta G\)

Spectroscopy

Compare \xrightarrow{\text{Improve}} \xrightarrow{\text{Calculate}} \xrightarrow{\text{Imagine!}}
... but I shall certain admit a system as empirical or scientific only if it is capable of being tested by experience. These considerations suggest that not verifiability but the falsifiability of a system is to be taken as a criterion of demarcation.

The logic of scientific discovery (1959)
„Experiments are the only source of knowledge at our disposal. The rest is poetry, imagination“


Max Planck
(1858-1947)
Observables

- Dissociation energy
- Dipole moment
- Chemical shift
- Molecular mass
- Excitation energy

Interpretation Aids

- Resonance
- Hybridization
- Orbitals
- Partial charge
- Bond order
- Ligand Field
- $\pi$-system
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

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

\[ E = T_e + T_N + V_{eN} + V_{NN} + V_{ee} \]
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:
\[ p_i \rightarrow -i\hat{\nabla}_i \quad \hat{\nabla} = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \quad \hat{i} = \text{imaginary unit} \quad \hat{i}^2 = -1 \]

★ 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 \( x \).

★ Schrödinger‘s equation for the many particle wavefunction \( \Psi(x_1,\ldots,x_N,R_1,\ldots,R_M,t) \equiv \Psi(x,R,t) \) 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.

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

★ **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!

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

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

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
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:

\[ \Delta E_{\text{reaction}} \rightarrow \text{Reaction Energy} \]
\[ \Delta E^\infty \rightarrow \text{Equilibrium Constant} \]
\[ \Delta E^\infty \rightarrow \text{Reaction Rate} \]
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")

$$I \propto \left| \langle \Psi_{initial} | H_1 | \Psi_{final} \rangle \right|^2$$
**Spectroscopic Techniques**

<table>
<thead>
<tr>
<th></th>
<th>Gamma</th>
<th>X-Ray</th>
<th>UV/vis</th>
<th>Infrared</th>
<th>Microwave</th>
<th>Radiowave</th>
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<td>8000</td>
<td>2000</td>
<td>4 - 1</td>
<td>0.1-0.01</td>
<td>10^{-4} - 10^{-5}</td>
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<td>10^{-6} - 10^{-7}</td>
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</table>

**Note:**
- 1 au. = 27.21 eV
- 1 eV = 8065 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

**cost**

**accuracy**
Ideally we would always solve the relativistic many particle Schrödinger equation combined with quantum dynamics for the entire system including its environment at finite temperature and inclusion of radiative corrections ...

.... but we cannot do that

.... neither do we need that to answer many useful chemical questions

➡ Be accurate where it matters!

➡ Be interested in your error sources!
An error of only 1.3 kcal/mol ($=0.056 \text{ eV} = 450 \text{ cm}^{-1}$) is equivalent to:

- $pK_a$-value: One log-unit
- Redox Potential: 56 mV
- Reaction Rate: Factor 10

Possible Consequences:

a) **Need extremely accurate theory**
b) **Need very good error compensation**
c) **Care about properties other than $E_{\text{tot}}$**
Where it matters $\text{NH}_3$: rovibrational bands at $T=300$ K

Where it matters: Enantioselective Hydrogenation of Prochiral Enamides

DLPNO-CCSD (=LPNO-QCISD)

B3LYP

Relative Energy (kcal mol\(^{-1}\))

How accurate is accurate enough?

DLPNO-CCSD(T)/def2-TZVPP // B3LYP-D3/def2-TZVP/CPCM
B3LYP-D3/def2-TZVPP // B3LYP-D3/def2-TZVP/CPCM
Where efforts may not be well spent

Example: Host/guest or Drug/Receptor complexes:

Complex organic reaction mechanisms

In both cases, overall not much overall improvement over DFT due to limitations in entropy and solvation contributions
Approximations: The Variational Principle

Given a trial wavefunction that depends on some parameters $p$: $\Psi_{\text{trial}}(x | R, p)$

The "Ritz-functional" is:

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

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 obtain 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 fulfil the Pauli principle. Hence, one employs a „Slater determinant“

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

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“

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

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:

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

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

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

$$
\varepsilon_i = \langle \psi_i \mid F \mid \psi_i \rangle = \left\langle \psi_i \mid \frac{T_e + V_{eN}}{\hbar} \mid \psi_i \right\rangle + \sum_j \left\langle \psi_i \psi_j \mid \psi_i \psi_j \right\rangle
$$

Where the „two-electron integral“ is:

$$
\left\langle \psi_i \psi_j \mid \psi_i \psi_j \right\rangle = \left\langle \psi_i \psi_j \mid \psi_i \psi_j \right\rangle - \left\langle \psi_i \psi_j \mid \psi_j \psi_i \right\rangle
$$

$$
= \int \int \frac{\left| \psi_i(x_1) \right|^2 \left| \psi_j(x_2) \right|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{x}_1 d\mathbf{x}_2 - \int \int \frac{\psi_i(x_1)\psi_j(x_1)\psi_i(x_2)\psi_j(x_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{x}_1 d\mathbf{x}_2
$$

**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

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></th>
<th>Exact HF Energy</th>
<th>Exact Experimental Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-128.547 Eh</td>
<td>-129.056 Eh</td>
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</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)
Interpretation of the Hartree-Fock Solutions

The primary result of Hartree-Fock calculation (once converged) is the \textbf{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 \textbf{many-electron wavefunction}

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

But what about the „secondary quantities“, the \textbf{orbital energies}

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

And the \textbf{orbitals} themselves:

\[
\psi_i(x) = \sum_{\mu} c_{i\mu} \varphi_\mu(x) \quad \text{Rigorous: No fundamental importance despite frequent use of HOMO/LUMO and related arguments}
\]

\[
\text{In practice: Describes the „electronic structure“ of the molecule in terms of bonding orbitals, antibonding orbitals or lone pairs.}
\]

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

- Weakly structured
- Always positive
- Insensitive to bonding

In HF Theory:

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

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

\[
= \sum_{\mu\nu} (P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta) \varphi_{\mu}(\mathbf{r})\varphi_{\nu}(\mathbf{r})
\]
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:

\[
N_A = \sum_{\mu \nu \in A} P_{\mu \nu}^{AA} S_{\mu \nu}^{AA} + \sum_{B \neq A} \sum_{\mu \in A \nu \in B} P_{\mu \nu}^{AB} S_{\mu \nu}^{AB} \\
Q_A = Z_A - N_A
\]

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:

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

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

\[
= \sum_{\mu\nu} (P^\alpha_{\mu\nu} - P^\beta_{\mu\nu}) \varphi_\mu(r)\varphi_\nu(r)
\]
What is missing from Hartree-Fock Theory?

Exact Energy = “Mean Field” Hartree-Fock

Correlation energy = \[ \frac{1}{2} \sum_{i,j} \epsilon_{ij}(\uparrow \uparrow) + \epsilon_{ij}(\uparrow \downarrow) \]

Fermi-Correlation

Coulomb-correlation

Relatively easy due to “Fermi hole” in the mean-field

Extremely hard to calculate due to interelectronic cusp at the coalescence point \( r_1 = r_2 \)
\[ |\Psi\rangle = |\Psi_0\rangle + \sum_{ia} C^{i}_{a} |\Psi^{a}_{i}\rangle + \frac{1}{4} \sum_{ijab} C^{ij}_{ab} |\Psi^{ab}_{ij}\rangle + \frac{1}{36} \sum_{ijkabc} C^{ijk}_{abc} |\Psi^{abc}_{ijk}\rangle + \ldots \]
Coupled Cluster Theory in a Nutshell

\[ \Psi = \exp(T) \Psi_0 \quad \Psi_0 = |\phi_1 ... \phi_N| \quad \phi_i (\mathbf{r}) = \sum_{\mu} c_{\mu i} \varphi_\mu (\mathbf{r}) \]

\[ \text{Ansatz (Coester & Kuemmel)} \]

Reference determinant

MOs

MO coefficients

BFs

Cluster Operator

\[ T = T_1 + T_2 + T_3 + ... \]

\[ T_1 = \sum_{ia} t^i_a a^+_a a_i \quad T_2 = \frac{1}{4} \sum_{ijab} t^{ij}_{ab} a^+_b a^+_a a_i a_j \]

Cluster Amplitudes

CC wavefunction

\[ \Psi = \left( 1 + \left( T_1 + T_2 + ... \right) + \frac{1}{2} \left( T_1 + T_2 + ... \right)^2 + ... \right) \Psi_0 \]

\[ = \left( 1 + T_1 + T_2 + \frac{1}{2} T_1^2 + T_1 T_2 + \frac{1}{2} T_2^2 + ... \right) \Psi_0 \]

connected excitations

like CI, linear

disconnected excitations

(statistically uncorrelated)

Determination of the energy and the cluster amplitudes

\[ E_{CC} = \left\langle \Psi_0 \mid e^{-T} \hat{H} e^T \mid \Psi_0 \right\rangle \]

\[ R_K = \left\langle t_K \Psi_0 \mid e^{-T} \hat{H} e^T \mid \Psi_0 \right\rangle = 0 \]

Gold Standard:

CCSD(T)

Nonlinear equation set, not hard to solve; up to 4th power of amplitudes
Accurate Solutions

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W4 theory for computational thermochemistry: In pursuit of confident sub-kJ/mol predictions

Amir Karton, Elena Rabinovich, and Jan M. L. Martin
Department of Organic Chemistry, Weizmann Institute of Science, IL-76100 Rehovot, Israel

Branko Ruscic
Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

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main group systems, to be known as W4 theory, is proposed. Its computational cost is not insurmountably higher than that of the earlier W3 theory, while performance is markedly superior. Our W4 atomization energies for a number of key species are in excellent agreement (better than 0.1 kcal/mol on average, 95% confidence intervals narrower than 1 kJ/mol) with the latest experimental data obtained from Active Thermochemical Tables. Lower-cost variants are proposed:

... meaning the (non-relativistic) Schrödinger equation is solved to an accuracy of \(0.0001 \text{ Eh}\) which is \(\sim 99.9999\%\) or \(\sim 1\) part in \(10^6\)!

... For **really** small systems (1-6 electrons), we can today reach „crazy accuracy“, e.g. Nakatsuji calculated the \(\text{H}_2^-\) ground state energy to be \(-0.597 139 063 123 405 074 834 134 096 025 974 142\) a.u. (36 significant digits!)

Problems with Coupled Cluster Theory

So why don’t we use these accurate ab initio methods for our everyday theoretical chemistry?

Explosive cost

Wall clock time $\propto O(N^7)$
Saving Time in Electronic Structure Calculations

Exploit Sparsity!

Density Matrix

$10^{-10}$

Pair Correlation Energy

Correlation

Compress Data!

$M = \begin{pmatrix} M' = U^\dagger MU \end{pmatrix}$

$M' = \begin{pmatrix} \text{dense matrix} & 0 \\ 0 & 0 \end{pmatrix}$
Approximation 1: Pair Approximation

\[ E_{corr} = \frac{1}{4} \sum_{i,j,a,b} C^{ij}_{ab} \langle ij \parallel ab \rangle = \frac{1}{2} \sum_{ij} \epsilon_{ij} \]

Exploit locality by cutting pairs with estimated \( \epsilon_{ij} < T_{CutPairs} \)

Approximation 2: Virtual Space truncation

\[ \epsilon_{ij} \approx \frac{1}{2} \sum_{a,b \in \text{pair-domain } ij} C^{ij}_{ab} \langle ij \mid \mid ab \rangle \]

✓ Truncated canonical virtual orbitals?

→ BAD idea!

✓ Projected atomic orbitals (Pulay, Werner, Schütz), localized virtual orbitals (Förner, Jørgensen, …)

→ It works, but for high accuracy (99.9%) the domains become impractically large
→ Need „compaction“ of the space
Most Compact Expansion: Natural Orbitals

Shortest possible accurate virtual space expansion through neglecting natural orbitals with occupation number $T_{\text{CutNO}} (<10^{-7})$
Huge Calculations with linear DLPNO-CCSD(T)

Crambin/def2-TZVP
644 atoms
12705 Basis functions
10 d/4 cores

C\textsubscript{350}H\textsubscript{702}/def2-TZVP
1052 atoms
15062 Basis functions
18h/4 cores

Integrase/cc-pVDZ
2380 atoms
22621 Basis functions
62h/64 cores

(CIM-DLPNO-CCSD(T))
DFT: 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.

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

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

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.
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!

1) The existence 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 “**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!
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):

\(V_{eN}[\rho] = - \sum_A Z_A \int \rho(\mathbf{r}) r_{iA}^{-1} d\mathbf{r}\)  
Electron-Nuclear Attraction (ok)

\(J[\rho] = \frac{1}{2} \sum_{ij} \langle ij | ij \rangle = \frac{1}{2} \int \int \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2\)  
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)

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

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


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:

\[ v_{\text{eff}} (\mathbf{r}) = -\sum_A Z_A r_A^{-1} + \int \rho (\mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_2 + V_{\text{XC}} (\mathbf{r}) \]

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.
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 ...
# 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></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.