Beyond DFT —
Wavefunction-based Correlation Methods

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1 Introduction:

Adsorption on surfaces - with which bonding situation we have to deal with?

2 What are ab initio methods?

   Hamilton operator
   Mean-field treatment
   Basis sets
   Density functional theory
   Wavefunction-based correlation methods
   Results for pyridin-gold interaction

3 Wavefunction-based correlation methods for periodic systems

   The method of increments
   Applied to adsorption energy
   CO on MgF$_2$ surface
   H$_2$O on graphene
1 Introduction

Pyridine on gold (111) surface
Which kind of bond is formed?

- covalent bond
dissociation energy: H₂: 104 kcal/mol; N₂ 227 kcal/mol; Na₂ 18 kcal/mol

- ionic bond
dissociation energy: NaCl: 98 kcal/mol

- hydrogen bonds
dissociation energy: (H₂O)₂: 5.4 kcal/mol

- van der Waals bonds
dissociation energy: (CO₂)₂: 1.3 kcal/mol; Ar₂: 0.3 kcal/mol

(100 kcal/mol = 4.33 eV)

*All intermediate bonding situations are possible in chemistry!*
Adsorption of molecules on surfaces:

1. **Chemisorption:**
   Formation of covalent bonds between molecule and the surface
   e.g. OH\(^{-}\) on alumina surface (hydroxylation)
   Adsorption energy larger as 0.5 eV

2. **Physisorption:**
   Dispersion interaction and electrostatic interaction
   e.g. CO on copper, CO on MgO, H\(_2\)O on graphene
2 Ab initio methods

2.1 Hamilton operator

Chemical bonds are formed by electrons
→ electrons are quantum mechanical particles
→ nuclei are kept fixed for the treatment of the electrons
  (Born-Oppenheimer approximation)
→ Electronic Hamiltonian (in atomic units):

\[
H = \sum_i \left(\frac{1}{2} \Delta_i - \sum_{\alpha}^{K} \frac{Z_\alpha}{|\vec{r}_i - \vec{R}_\alpha|} \right) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|}
\]

- **Kinetic energy**
- **Electron-nucleus interaction**
- **Electron-electron interaction**
  ⇒ Many-body effect, makes life hard, but interesting
2.2 Mean-field treatment

Solving the problem in an effective single-particle picture:
(That means: independent electrons, effective average mean field interaction between the electrons)

Hartree-Fock Treatment
(D.R. Hartree, Proc. Cambridge Philos. Soc. 24, 89 (1928); V. Fock, Z. Phys. 61, 126 (1930); J.C. Slater, Phys. Rev. 35, 210 (1930))

- ansatz for the wavefunction (obeys Pauli principle)
  \[ \Psi_{HF} = \frac{1}{\sqrt{N!}} \det[\Phi_i(\vec{x}_j)] \]
  \[ \Phi_i(\vec{x}_j) \text{ One-particle orbitals = molecular orbitals = Bloch functions} \]

- single-particle density \[ \rho(\vec{x}) = \sum_i |\Phi_i(\vec{x})|^2 \]
Molecular orbitals of H$_2$O (Hartree-Fock orbitals)

molecular structure

spatial electron density $\rho(\vec{r})$

(Isolated value 0.2 1/$\text{Å}^3$)
individual molecular orbitals $|\Phi_i(\vec{x})|^2$, obey the symmetry of the molecule

Orbital energy: -36.9 eV = -851 kcal/mol

Orbital energy: -18.8 eV

Orbital energy: -15.3 eV

Orbital energy: -14.2 eV
localized orbitals (squared in the plots): “correspond” to the Lewis structure
bonding orbitals
lone pair orbitals
Modeling adsorption in a periodic arrangement:

Single molecule adsorption on a periodic, infinite 2-dimensional surface:
Construction of a unit cell and periodically repeating in 2 dimensions: Generating a slab (also a model for the monolayer coverage)
Repeating the slab in the 3. dimension — 3-dimensional periodicity achieved
Bloch functions and Wannier functions for periodic systems:

Bloch function: \( \phi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}} \) with \( u_{\vec{k}}(\vec{r}) \) translational symmetric
Wannier function: Localization of the Bloch function (Fourier transform) centered at a specific lattice vector $\vec{R}_l$: $\psi_l(\vec{r}) = \frac{1}{\sqrt{N}} \sum_k e^{i\vec{k} \cdot \vec{R}_l} \phi_k(\vec{r})$
(Wannier function obtained with CRYSTAL code)
How to obtain molecular orbitals or Bloch functions?

**Hartree-Fock Treatment**

- **ansatz for the wavefunction (obeys Pauli principle)**
  \[ \Psi_{HF} = \frac{1}{\sqrt{N!}} \det[\Phi_i(\vec{x}_j)] \quad \Phi_i(\vec{x}_j) \text{ One-particle orbitals } = \text{ molecular orbitals} \]

- **Coulomb term correspond to the classical interaction of charge densities**
  \[ \int d\vec{x}^3 d\vec{x}'^3 \Phi_i(\vec{x}) \Phi_j(\vec{x}') \frac{1}{|\vec{x} - \vec{x}'|} \Phi_i(\vec{x}') \Phi_j(\vec{x}) \]

- **non-local exchange term is treated explicitly**
  \[ \int d\vec{x}^3 d\vec{x}'^3 \Phi_i(\vec{x}) \Phi_j(\vec{x}') \frac{1}{|\vec{x} - \vec{x}'|} \Phi_i(\vec{x}') \Phi_j(\vec{x}) \]

- **Solving the Hartree-Fock problem by applying the variational principle**
  \[ \Rightarrow \text{ best possible effective one-particle treatment} \]
2.3 Basis sets

2.3.1 Atom-like orbitals as basis sets

Describing the molecular orbitals $\Phi_i(\vec{r})$ forming the Hartree-Fock space with atomic basis functions $\psi_\mu(\vec{r})$: MO-LCAO Ansatz

- Hydrogen atom: Slater orbitals $\psi^\text{STO}_\mu(\vec{r}) = Y_{lm}(\theta, \phi)r^{n-1}e^{-\xi_\mu r}$

- Quantum chemistry: primitive Gaussian orbitals $\psi^\text{PGTO}_\mu(\vec{r}) = Y_{lm}(\theta, \phi)x^a y^b z^c e^{-\beta_\mu r^2}$

for a better approximation of the long-range behaviour:

Contracted Gaussian Functions (cGTO): $\psi^\text{cGTO}_\mu(\vec{r}) = \sum_{\mu=1}^{K} C_{i\mu} \psi^\text{PGTO}_\mu(\vec{r})$

\[ s \quad p \quad d \]
Description of a particular basis set:
e.g. for Germanium $1s^2 2s^2 p^6 3s^2 p^6 d^{10} 4s^2 p^2$:

cc-p-avdz $(15s12p5d2f)/[6s4p3d2f]$

- **cc**: correlation consistent made for correlation calculations
- **p**: polarization functions higher angular momentum
- **a**: augmented additional diffuse functions are supplied
- **vdz**: valence double-$\zeta$ for the valence orbitals twice as much cGTO are supplied as occupied
- **vtz**: valence triple-$\zeta$ three times as much cGTO as occupied
2.3.2 Plane wave basis sets

Especially useful for periodic calculations:
Taking into account all plane waves up to a defined energy cut-off: \( E = \frac{\hbar^2 \vec{k}^2}{2m} \)

But to describe rapid varying potential near nuclei many plane waves are necessary:

Solution: Use of pseudopotentials
Hartree-Fock-Roothaan-Hall procedure

MO-LCAO Ansatz for the HF orbitals in the Hartree-Fock equations

⇒ Hartree-Fock-Roothaan-Hall equations:

\[ FC = \epsilon SC \]

with the Fock matrix

\[ F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} (2(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)) \]

where \( P \) is the density matrix

\[ P_{\lambda\sigma} = \sum_{b=1}^{\frac{n}{2}} c_{b\lambda} c_{b\sigma}^* \]

with the one-electron matrix elements

\[ h_{\mu\nu} \]

with the two-electron integrals

\[ (\mu\nu|\sigma\lambda) \]

with the Coefficient matrix

\[ C_{\mu\nu} \] determine molecular orbitals

with the eigen value matrix

\[ \epsilon \] molecular orbital energies

with the overlap matrix

\[ S_{\mu\nu} = \langle \psi_\mu | \psi_\nu \rangle \]
Procedure to solve the Hartree-Fock-Roothaan-Hall equations:

1. Choose geometry of the molecule (BOA)
2. Choose basis functions $\psi_\mu$
3. Calculate integrals $h_{\mu\nu}$, $(\mu\nu||\sigma\lambda)$, $(\mu\lambda||\sigma\nu)$
4. Select initial guess for the density matrix $P_{\lambda\sigma}$
5. Calculate Fock operator with this density matrix
6. Solve Hartree-Fock-Roothaan-Hall equations
7. Get new density matrix
8. Iterate 5-7 until density matrix and energy is converged
2.4 Wavefunction-based correlation methods

What is missing?
Hartree-Fock yields the best possible (variational principle) many-body wavefunction built from single-particle wavefunctions (orbitals)
But only effective interaction between the electrons — via a mean field
Instantaneous “motion” of the electrons not take into account
Definition: Electron correlation \( E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} \)
“All what is missing beyond Hartree-Fock”
Example: Calculation of the dissociation of H\(_2\) in two hydrogen atoms:
Configuration-Interaction (CI) ansatz for the ground-state wavefunction:

\[ |\Psi > = (1 + \Omega)|\Psi_{HF} > \quad \text{with} \quad \Omega = \sum_{i,\mu} n_i^\mu c_i^{\dagger} c_\mu + \frac{1}{2} \sum_{ij\mu\nu} n_{ij}^{\mu\nu} c_i^{\dagger} c_j^{\dagger} c_\mu c_\nu + \cdots \]

\(\Omega\) contains all single, double, triple, \cdots excitations out of all occupied Hartree-Fock orbitals \(\mu, \nu\) into all unoccupied (virtual) Hartree-Fock orbitals \(i, j\)

Including all possible excitations: Full Configuration Interaction (FCI)
Density and pair density:

Example: \( \text{H}_2 \) two-electron system

**Density:** Probability to find an electron at place \( \vec{r}_1 \), when the other electron can be somewhere is space (integrated out)

\[
\rho(\vec{r}_1) = \int |\Psi(\vec{r}_1, \vec{r}_2)|^2 d\vec{r}_2
\]

**Pair density:** Probability to find an electron at place \( \vec{r}_1 \), when the other electron is sitting at place \( \vec{r}_2 \) (conditional probability)

\[
P(\vec{r}_1, \vec{r}_2) = |\Psi(\vec{r}_1, \vec{r}_2)|^2
\]
Density and pair density of $\text{H}_2$ in the HF treatment:

(figures from Helgaker, electronic structure theory)
Density and pair density of $H_2$ in the FCI treatment
For larger systems a Full CI treatment is computational not possible:

**Truncated CI Ansatz (e.g. Singles and Doubles, CISD):**

(not size-consistent and not size-extensive)

size-consistent: for large distance correct dissociation limit:

\[ E(A + B) = E(A) + E(B) \]

size-extensive: correct scaling with the particle number \( N \):

\[ E(N \cdot A) = N \cdot E(A) \]

**Solution:**


(size-consistent and size-extensive)

\[ |\Psi_{CCSD} > = e^\Omega |\Psi_{HF} > \]
Can we treat the electronic correlations in a different way? Computational cheaper?

2.5 Density-Functional Theory (DFT)


Nobel prize 1998 in Chemistry “to Walter Kohn for his development of the density-functional theory and to John Pople for his development of computational methods in quantum chemistry”

- based on the single-particle density \( \rho(\vec{x}) \)

- many-body effects are treated implicitly via an exchange-correlation functional \( E_{xc}[\rho(\vec{x})] \)
• approximations are necessary for the exchange-correlation functional in realistic systems
  – Local density approximation (LDA)
  – Generalized Gradient-corrected approximation (GGA)
    Different parametrizations: e.g. PW86, PW91, PBE, ...
  – Hybrid functionals
    (exchange term is explicitly evaluated and included partially)
    Different parametrizations: mixing coefficient of exchange term
    B3LYP, B3PW, ...
  – Orbital-dependent functionals
  – Dispersion corrected functionals

• systematic improvement is difficult
Also DFT-B3LYP can not describe the dissoziation of H₂, but very good in the region around the equilibrium
2.6 Results for Pyridin-Gold interaction
Binding energy [mH] vs. Au-middle of ring [Ångstroms]

- CCSD(T)
- CCSD (+34%)
- MP2 (-84%)
- B3LYP (no binding)
- PBE (+72%)
- PW91 (+62%)
- LDA (-176%)
- HF (no binding)
3 Wavefunction-based correlation methods for periodic systems

How to apply quantum chemical correlation methods to infinite systems?

Idea: Electronic correlations are of short range: Far away electrons interact only via mean-field

- Hartree-Fock calculation for the infinite solid
- Generating localized orbitals (e.g. Wannier orbitals)
- Dividing the correlation energy into transferable contributions of localized orbital groups
3.1 The Method of increments

Coupled cluster ansatz for the ground-state wavefunction:

\[ |\Psi\rangle = e^{\Omega} |\Psi_{HF}\rangle \quad \text{with} \quad \Omega = \sum_{i,\mu} n_i^\mu c_\mu^\dagger c_i^\dagger + \frac{1}{2} \sum_{ij\mu\nu} n_{ij}^{\mu\nu} c_\mu^\dagger c_\nu^\dagger c_i c_j + \cdots \]

\(i, j, \ldots\) label the localized orbitals at centre \(i, j\)
\(\mu, \nu, \ldots\) label the virtual orbitals (delocalized)
Incremental scheme:

- Correlating (size-extensive method) orbitals at centre $i$ (independent centres), e.g. excitations from $i$ into the whole virtual space

$$
\epsilon_i = E_i - E_{HF} = \langle \Psi_{HF} e^{-\Omega_i} | H_{corr} | e^{\Omega_i} \Psi_{HF} \rangle
$$

$$
\Rightarrow E_{corr}^{(1)} = \sum_{i \in u.c.} \epsilon_i
$$
• Correlating localized orbitals at two centres $i$ and $j$

$$\epsilon_{ij} = E_{ij} - E_{HF} = \langle \Psi_{HF} e^{-\Omega_{ij}} | H_{corr} | e^{\Omega_{ij}} \Psi_{HF} \rangle$$

Energy increment $\Delta \epsilon_{ij}$: non-additive contribution of the two centres $i$ and $j$

$$\Delta \epsilon_{ij} = \epsilon_{ij} - (\epsilon_i + \epsilon_j)$$

• Correlating three centres $i$, $j$ and $k$

$$\Delta \epsilon_{ijk} = \epsilon_{ijk} - (\epsilon_i + \epsilon_j + \epsilon_k) - (\Delta \epsilon_{ij} + \Delta \epsilon_{jk} + \Delta \epsilon_{ik})$$

• Correlation energy for the infinite system

$$E_{corr} = \sum_{i \in \text{u.c.}} \epsilon_i + \frac{1}{2!} \sum_{i \neq j \atop i \in \text{u.c.} \atop j \in \text{solid}} \Delta \epsilon_{ij} + \frac{1}{3!} \sum_{i \neq j \neq k \atop i \in \text{u.c.} \atop j, k \in \text{solid}} \Delta \epsilon_{ijk} + \cdots$$
Incremental expansion will be useful if

- it converges with increasing distance of the localized orbitals
- it converges with respect to the order of the increments
- the increments can be calculated in small embedded clusters

These properties have to be tested for the individual system: Dependent of the choice of localized orbitals and of their grouping to the centres

3.2 Method of increments for the adsorption on surfaces

3.2.1 Formalism

Incremental expansion for the adsorption energy

Localized orbital groups:

- localized orbitals of the adsorbed molecule
- localized orbitals of the individual atoms/ions in the surface
Definition of the adsorption energy:

\[ E_{\text{adsorb}} = E_{\text{joint system}} - E_{\text{surface}} - E_{\text{molecule}} = E_{\text{HF}} + E_{\text{corr}} \]

Incremental expansion for the correlation contribution to the adsorption energy:

\[ E_{\text{corr}} = \eta_{\text{mol}} + \sum_{i \in \text{surface}} \eta_i + \sum_{i \in \text{surface}} \eta_{\text{mol},i} + \frac{1}{2!} \sum_{i \neq j} \eta_{ij} + \cdots \]

with

- \( \eta_{\text{mol}} \): change in correlation energy of the molecule due to adsorption
- \( \eta_i \): change in the individual correlation increments of the surface
- \( \eta_{\text{mol},i} \): correlation energy increments between molecule and surface
- \( \eta_{ij} \): changes in the two-body increments of the surface
3.2.2 Results for CO on the MgF$_2$ 110 surface:


MgF$_2$ in the rutile structure

Most stable surface 110 with terminating F
B. Paulus, Wavefunction-based correlation methods

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{\text{ads}}$ / meV</th>
<th>$r$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-193</td>
<td>$r(C-O)$</td>
</tr>
<tr>
<td>B3LYP(^a)</td>
<td>-272</td>
<td>$r(O-Mg)_{\text{surface}}$</td>
</tr>
<tr>
<td>MP2</td>
<td>-384</td>
<td>$r(C-O)_{\text{surface}}$</td>
</tr>
<tr>
<td>MP2(_{\text{incr}})</td>
<td>-386</td>
<td></td>
</tr>
<tr>
<td>CCSD(T)(_{\text{incr}})</td>
<td>-378</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) optimized $r(C-O-Mg)$, all others single point

\(^b\) B3LYP optimized
3.2.3 Adsorption of H$_2$O on Graphene:

Elena Voloshina et al. PCCP 13, 12041 (2011)

Water molecule on graphene:

$C_{58}H_{20}$ cluster with different adsorption geometries of H$_2$O
Results for different adsorption geometries and different methods:
(Energy in meV, distance in Å)

<table>
<thead>
<tr>
<th>Structure</th>
<th>CCSD(T)</th>
<th>MP2</th>
<th>PBE</th>
<th>PBE-D2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(d_0)</td>
<td>(E_{ads})</td>
<td>(d_0)</td>
<td>(E_{ads})</td>
</tr>
<tr>
<td>C-UP</td>
<td>3.06</td>
<td>-108</td>
<td>3.09</td>
<td>-98</td>
</tr>
<tr>
<td>C-DOWN</td>
<td>2.61</td>
<td>-123</td>
<td>2.66</td>
<td>-106</td>
</tr>
<tr>
<td>B-UP</td>
<td>3.05</td>
<td>-102</td>
<td>3.09</td>
<td>-99</td>
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<tr>
<td>B-DOWN</td>
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<td>-118</td>
<td>2.69</td>
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<tr>
<td>T-UP</td>
<td>3.06</td>
<td>-110</td>
<td>3.08</td>
<td>-101</td>
</tr>
<tr>
<td>T-DOWN</td>
<td>2.69</td>
<td>-135</td>
<td>2.70</td>
<td>-116</td>
</tr>
</tbody>
</table>

- T-down configuration is most stable in CCDS(T) and MP2
- PBE-D2 improves PBE but C-down more stable, all up-configurations much less stable
Distance dependence for C up adsorption geometry:

\[
C_{58}H_{20} \text{ cluster with different adsorption geometries of } H_2O
\]

• Comparison with periodic DF-LMP2 (Denis Usvyat) is excellent (deviation 3 meV)
• VTZ basis at H\textsubscript{2}O yields an increase in the adsorption energy of 2 meV
Thanks to my group