Program (lectures 1 and 2)

- Definitions (chemistry, photochemistry and photophysics)
- The Born-Oppenheimer approximation
- potential energy surfaces (PES)
- Methods for excited states in quantum chemistry
  - HF, TDHF
  - Configuration interaction, CI
  - Coupled Cluster, CC
  - MCSCF
- TDDFT: Why TDDFT in chemistry and biology?
- TDDFT: properties and applications in chemistry
- TDDFT failures
  - Accuracy and functionals
  - charge transfer excitations
  - topology of the PES
What’s quantum chemistry and photochemistry?

From Wikipedia:

Chemistry (from Egyptian kēme (chem), meaning "earth") is the science concerned with the composition, structure, and properties of matter, as well as the changes it undergoes during chemical reactions. Historically, modern chemistry evolved out of alchemy following the chemical revolution (1773). Chemistry is a physical science related to studies of various atoms, molecules, crystals and other aggregates of matter whether in isolation or combination, which incorporates the concepts of energy and entropy in relation to the spontaneity of chemical processes.

Perturbation theory or linear response in the nuclear coordinates are no longer valid solutions.

We need Molecular Dynamics.
What’s quantum chemistry and photochemistry?

We need dynamics to model chemical reactions ....

Atomic rearrangements: nuclear and electronic dynamics
What’s quantum chemistry and photochemistry?

... and a way to describe the interaction with the environment.
What’s quantum chemistry and photochemistry?

From Wikipedia:

**Chemistry** (from *Egyptian* kēme (chem), meaning "earth") is the *science* concerned with the composition, *structure*, and *properties of matter*, as well as the *changes* it undergoes during *chemical reactions*. Historically, modern chemistry evolved out of *alchemy* following the *chemical revolution* (1773). Chemistry is a *physical science* related to studies of various *atoms*, *molecules*, *crystals* and other aggregates of matter whether in *isolation or combination*, which incorporates the concepts of *energy* and *entropy* in relation to the *spontaneity* of *chemical processes*.

A theoretical/computational approach will therefore need:

> theoretical model for the study matter in the energy range [0 to few hundreds of eV]

> description of chemical reactions (structural changes)

> description of the interaction with the environment (condensed phase)
What’s quantum chemistry and photochemistry?

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…which translates into:

> theory of electronic structure and ways to solve the corresponding equations

> solution of the equations of motion for atoms and electrons + statistical mechanics (from the microcanonical to the canonical ensemble)

> approximate solutions for the description of the interactions with the rest of the universe
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…and in practice:

> HF, CI, MPn, CAS, …, DFT and corresponding theories for excited states

> time dependent theories for adiabatic and non adiabatic dynamics of atoms and electrons: mixed-quantum classical molecular dynamics

> periodic boundary conditions, PBC, for homogeneous systems and hybrid schemes, for inhomogeneous systems: QM/MM, coarse grained, hydrodynamics, …
What’s quantum chemistry and photochemistry?

From Wikipedia:

**Photochemistry**, a sub-discipline of **chemistry**, is the study of the **interactions between atoms**, **small molecules**, and **light** (or **electromagnetic radiation**). [...] *Photochemistry* may also be introduced to laymen as a **reaction** that proceeds with the absorption of light. Normally a reaction (not just a photochemical reaction) occurs when a molecule gains the necessary **activation energy** to undergo change. A simple example can be the **combustion** of **gasoline** (a **hydrocarbon**) into carbon dioxide and water. This is a chemical reaction where one or more molecules/chemical species are converted into others. For this reaction to take place **activation energy** should be supplied. The **activation energy** is provided in the form of heat or a spark. In case of photochemical reactions light provides the **activation energy**.
What’s quantum chemistry and photochemistry?

Light absorption → Electronic excitation

Radiative Dissipation mechanism → Radiationless

Radiative

1) Fluorescence
2) Phosphorescence

\[ h\nu \rightarrow h\nu' \]

Photophysics

Radiationless

Physical
1) Internal conversion
2) Intersystem crossing
3) Vibrational relaxation

\[ h\nu \rightarrow Q \]

Chemical
1) Singlet chemistry
2) Triplet chemistry

\[ h\nu \rightarrow \Delta G(+Q) \]

Photochemistry
What’s quantum chemistry and photochemistry?

Jablonski diagram
What's quantum chemistry and photochemistry?

(Electronic) Potential Energy Surfaces

grey: singlet states
dark: triplet state

a) singlet excitations
b) energetic minimum
c) saddle point
d) avoided crossing
e) conical intersection
f) fluorescence
g) phosphorescence
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The Born-Oppenheimer approximation

Central is the ratio: \( \frac{m_{el}}{M} \sim 10^{-4} \text{ to } 10^{-5} \)

Total molecular (electronic and nuclear) Hamiltonian

\[
\hat{H} = \hat{T}_N + \hat{H}_{el} = \hat{T}_N + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN}
\]

and corresponding time-independent Schrödinger equation

\[
\hat{H} \Psi^{e,n}(\mathbf{r}, \mathbf{R}) = E \Psi^{e,n}(\mathbf{r}, \mathbf{R})
\]

The point is that the nuclear kinetic energy, \( \sim 1/M \) is a very small term in the Hamiltonian, and we can compute the eigenstates and eigenvalues of \( \hat{H} \) by treating \( \hat{T}_N \) as a small perturbation.

In this picture, \( \mathbf{R} = \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N \) are no longer dynamical variables, but are considered merely as parameters.

(\( \mathbf{r} = r_1, r_2, \ldots, r_n \) collective variable for the position of the electrons)
The Born-Oppenheimer approximation

The basic Ansatz in BO

\[
\left[ T_N + T_e + V_{ee} + V_{eN} + V_{NN} \right] \Psi^{e,n}(r, R) = E \Psi^{e,n}(r, R)
\]

\[
\Psi^{e,n}(r, R) = \sum_n \varphi^n(R) \Phi^n(r, R)
\]

We proceed in 3 steps:

1. Solution of the electronic Schrödinger equation for fix nuclear coordinates $\hat{T}_N \to 0$

\[
\left[ \hat{T}_e + \hat{V}_{ee}(r) + \hat{V}_{eN}(r, R) \right] \Phi^n(r, R) = \left[ \varepsilon_n(R) - \hat{V}_{NN}(R) \right] \Phi^n(r, R)
\]

The eigenvalues $\varepsilon_n(R)$ defines the potential energy surfaces, PES

2. Derive equations for the expansion coefficients and the coupling matrix elements between PESs

3. Solution of the molecular time-independent Schrödinger equation at zero coupling
The Born–Oppenheimer approximation

2. Equation for the expansion coefficients and the coupling matrix elements between PES

Using the solution of the electronic Schrödinger equation for fixed nuclei,

\[
\sum_m \left( \varepsilon_m(R) + \hat{T}_N \right) \varphi^n_m(R) \Phi^e_m(r, R) = E \sum_m \varphi^n_m(R) \Phi^e_m(r, R)
\]

After some algebraic manipulations

\[
\left[ \hat{T}_N + \varepsilon_n(R) \right] \varphi^n_n(R) = E \varphi^n_n(R) - \sum_m A_{nm} \varphi^n_m(R)
\]

where

\[
A_{nm} \varphi^n_m(R) = -\sum_i^N \frac{1}{2M_i} \int dr \Phi^n_{e*}(r, R) \left[ 2\nabla_{R_i} \varphi^n_m(R) \cdot \nabla_{R_i} \Phi^e_m(r, R) + \varphi^n_m(R) \nabla^2_{R_i} \Phi^e_m(r, R) \right]
\]

are the terms that mix together different electronic wavefunctions in \( \Phi^e_m(r, R) \).
The Born–Oppenheimer approximation

3. Solution of the molecular time-independent Schrödinger equation at zero coupling

\[
\left[ \hat{T}_N + \varepsilon_n (\mathbf{R}) \right] \varphi_n (\mathbf{R}) = E \varphi_n (\mathbf{R}) \quad (A_{nm} \rightarrow 0)
\]

Now we can identify the expansion coefficients \( \varphi_n (\mathbf{R}) \) as the nuclear wavefunctions, the amplitude for the nuclei to be at a given position when the electrons are in state \( \Phi^e_n (\mathbf{r}, \mathbf{R}) \).

The total electronic energy \( \varepsilon_n (\mathbf{R}) \), which include the nuclear-nuclear potential, plays the role of an effective potential energy (PES) for the nuclei.

To lowest order in \( A_{nm} \) there is no mixing of the different electronic states and the molecular wavefunction is given by

\[
\Psi_n (\mathbf{r}, \mathbf{R}) = \varphi_n (\mathbf{R}) \Phi^e_n (\mathbf{r}, \mathbf{R})
\]
The Born-Oppenheimer approximation

Examples of potential energy surfaces


(a) Wave packets (yellow) on a typical molecular potential energy surface (red). The wave packet is the modulus squared of the wave function. (b) The wave packet changes shape due to diffraction and spreading as it moves in the potential. (eve.physics.ox.ac.uk/Personal/suominen/wpadv.html)

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Methods for the solution of the electronic Schrödinger equation in the excited states

1. Time-dependent Hartree-Fock
2. Post Hartree Fock methods (CI, CC, MCSCF)
3. Time-dependent density functional theory

There exist a number of other methods for the calculation of excited states energies and properties as for instance Complete Active Space SCF (CASSCF), but these methods require a deep understanding on how to construct the Active Space made of all relevant orbitals to use for an optimal representation of the molecular system. This is clearly beyond the scope of this lecture.
Excited state \textit{ab-initio} methods

There is a wide variety of wavefunction-based \textit{ab inito} methods for the calculation of excited states energies and properties of molecular systems.

In computational chemistry (but also physics and biochemistry) we need

- \textbf{Accuracy in the energies, forces (for MD) and properties in general}
- \textbf{Computational efficiency (scaling)}

The computational method should possess the following useful properties:

1. Variational (give an upper bound to the exact energy).
2. Size consistent (especially important in chemical reactions).
3. Correct ordering of the excited states energies.
4. Energies and wavefunction (density) should possibly be analytically differentiable with respect to external parameters (for instance nuclear displacements).
5. Should give a solution that corresponds to an eigenstate of the total spin operator.
Size consistency

Size consistency is a property that guarantees consistency of the energy behavior when interaction between the involved molecules is nullified (for instance increasing the intermolecular distance):

$$\omega(A + B) \xrightarrow{R \to \infty} \omega(A) + \omega(B)$$

In a truncated CI expansion (see figure) when the two systems A and B are treated as independent non-interacting moieties, they correspond to double-excited configurations. Instead, as a joined system, (A+B) is represented as a quadruple-excitation. The two calculations are not performed at the same level of theory and therefore dissociations energies computed with this method are not accurate.
Almost all post Hartree-Fock methods are based on the expansion of the many-electron wavefunction in a linear combination of “excited” Slater determinants:

\[ |\Psi\rangle = c_0 |\Phi_0\rangle + \sum_{ra} c^r_a |\Phi^r_a\rangle + \sum_{a<b, r<s} c^{rs}_{ab} |\Phi^{rs}_{ab}\rangle + \sum_{r<s<t, a<b<c} c^{rst}_{abc} |\Phi^{rst}_{abc}\rangle + \ldots \]

The different quantum chemical methods for the electronic structure (ground and excited states) differ in the way this (infinite) sum is approximated.

The correlation energy

The correction to the HF energy introduced in this way contributes to the so-called correlation energy:

\[ E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} \]
Most of the wavefunction based methods in quantum chemistry are MORE accurate than TDDFT with the usual approximations for the exchange and correlation functional, BUT their use is limited to small systems (up to 10-20 atoms).

### The ZOO of quantum chemical methods

<table>
<thead>
<tr>
<th>Wavefunction based methods suited for excited states calc.</th>
<th>SR (single reference = 1 Slater determinant)</th>
<th>MR (multi reference = more than 1 Slater determinant used to describe the system wavefunction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI (Configuration Interaction)</td>
<td>CIS(D) (In bracket extension via perturb.)</td>
<td>Full CI, MRCI</td>
</tr>
<tr>
<td></td>
<td>CISD, QCISD</td>
<td></td>
</tr>
<tr>
<td>CC (coupled-cluster)</td>
<td>CCSD, CCSD(T), CC2 (SRCC with approximated second order corrections)</td>
<td>MRCC</td>
</tr>
<tr>
<td>SCF (self-consistent field. Orbitals optimized like in HF)</td>
<td>HF</td>
<td>MCSCF, CASSCF</td>
</tr>
<tr>
<td>MPn (Møller-Plesset)</td>
<td>MP2 and MP4</td>
<td>GMCQDPT2, CASPT2</td>
</tr>
</tbody>
</table>
The Configuration Interaction Method

The scope of CI is to improve the HF solution by increasing the space of all possible many-electron wavefunction from a single Slater determinant (in Hartree-Fock theory) to a set of, in principle infinite, Slater determinants.

\[ |\Psi\rangle = c_0 |\Phi_0\rangle + \sum_{ra} c^r_a |\Phi^r_a\rangle + \sum_{a<b,r<s} c^{rs}_{ab} |\Phi^{rs}_{ab}\rangle + \sum_{r<s<t,a<b<c} c^{rst}_{abc} |\Phi^{rst}_{abc}\rangle + \ldots \]

where \( |\Phi_0\rangle \) is the HF Slater determinant and \( |\Phi^r_a\rangle, |\Phi^{rs}_{ab}\rangle, |\Phi^{rst}_{abc}\rangle, \ldots \) refer to singly, doubly, triply, … excited determinants, constructed from optimized HF orbitals.

The CI method consists in finding all coefficients \( c_0, c^r_a, c^{rs}_{ab}, c^{rst}_{abc}, \ldots \) in the expansion.

Minimize the expectation value of the total energy:

\[ E_{CI} = \min_{c_0, c^r_a, \ldots} \frac{\langle \Psi_{CI} | \hat{H} | \Psi_{CI} \rangle}{\langle \Psi_{CI} | \Psi_{CI} \rangle} \]
The Configuration Interaction Method

CIS for excited states

\[ |\psi_I\rangle = \sum_{b} C_{jb}^{I} \hat{b}^{\dagger} |\phi_0\rangle \]

Ansatz:

Minimizing

\[ E_I = \frac{\langle \psi_I | \hat{H} | \psi_I \rangle}{\langle \psi_I | \psi_I \rangle} \]

gives

\[ \sum_{ijab} \langle \phi_0 | \hat{i}^{\dagger} \hat{a} \hat{b}^{\dagger} \hat{j} | \phi_0 \rangle C_{jb}^{I} = E_I C_{ia}^{I} \]

In matrix notation

\[ \sum_{jb} A_{ia,jb} C_{jb}^{I} = (E_I - E_{HF}) C_{ia}^{I} \]

with

\[ A_{ia,jb} = \delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i) + (j b | f_H | a i) - (a b | f_H | j i) \]

The oscillator strength are

\[ f_I = \frac{2}{3} \omega_I (|\langle \phi_0 | x | \psi_I \rangle|^2 + |\langle \phi_0 | y | \psi_I \rangle|^2 + |\langle \phi_0 | z | \psi_I \rangle|^2) \]

Notation:

\[ (j b | f_H | a i) = \int \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_{j}^*(\mathbf{r}_1) \phi_{a}(\mathbf{r}_2) r_{12}^{-1} \phi_{b}^*(\mathbf{r}_2) \phi_{i}(\mathbf{r}_2) \]
CIS vs time-dependent Hartree-Fock

Solution of the time-dependent Hartree-Fock equations

Using the HF Hamiltonian in second quantization

\[ \hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} (\phi_p \phi_q | f_H | \phi_r \phi_s) \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q \]

the excitation energies are obtained from the solution of the eigenvalue equation

\[
\begin{bmatrix}
A & B \\
B^* & A^*
\end{bmatrix}
\begin{bmatrix}
\vec{X} \\
\vec{Y}
\end{bmatrix} = \omega
\begin{bmatrix}
1 & 0 \\
0 & -1
\end{bmatrix}
\begin{bmatrix}
\vec{X} \\
\vec{Y}
\end{bmatrix}
\]

with

\[ A_{ia,jb} = \delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i) + (ia|f_H|bj) - (ij|f_H|ba) \]
\[ B_{ia,jb} = (ia|f_H|jb) - (ib|f_H|ja) , \]
\[ (\phi_p \phi_q | f_H | \phi_r \phi_s) = \int dr_1 dr_2 \phi_p^*(r_1)\phi_q(r_1) \frac{1}{|r_1 - r_2|} \phi_r^*(r_2)\phi_s(r_2) \]

> CIS is TDHF within the Tamm-Dancoff approximation (TDA) that \( B = 0 \).
CIS vs time-dependent Hartree-Fock

CIS properties

> TDHF with in the Tamm-Dancoff approximation (B=0) is equivalent to the CIS

> CIS is size consistent

> CIS can produce pure spin states

> For CIS analytic energy gradients are available

> Both TDHF and CIS suffer from an unbalanced description of the correlation. The ground state remains “uncorrelated” while the excited states miss important static and dynamic correlation contributions.

> Typical errors for TDHF in the range 0-3.0 eV (usually too high compared to experiments). Wrong ordering for states of different electronic character are not unusual.

> Formally CIS scales like O(n₄) with n=n_{occ}+n_{virt}. When restricted to the first singlet excited states the scaling can be reduced to O(n²) using the Davidson diagonalization scheme.
Coupled Cluster Method

CC is also based on the CI expansion, but has the advantage that it provides a size-consistent description even at truncated level and converges faster to the full CI limit than truncated CI.

\[ |\Psi_{CC}\rangle = \exp(\hat{T}) |\Phi_{HF}\rangle \]

where the cluster operator is defined as

\[ \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_N = \sum_{\mu} t_{\mu} \hat{\tau}_{\mu} \]

the excitation operator \( \hat{T} \) correspond to different level of excitations. In second quantization notation

\[ \hat{T}_1 = \sum_{ai} t^a_{i}\hat{a}_i\hat{a}^{\dagger}_a = \sum_{ai} t^a_{i} \hat{\tau}^a_{i} \]

\[ \hat{T}_2 = \frac{1}{4} \sum_{i,j} \sum_{a,b} t^{ab}_{ij} \hat{a}_j\hat{a}^{\dagger}_j \hat{a}^{\dagger}_a \hat{a}_b = \sum_{aibj} t^{ab}_{ij} \hat{\tau}^{ab}_{ij} \]

The faster convergence to the full CI limit of CC arises from the fact that even if the series for the cluster operator is truncated at a given level, say \( \hat{T}_n \), the CC expansion still contains contribution to the full CI expansion (through the indirect or disconnected clusters).
Consider the following reordering of the contributions

\[ |\Psi_{CC}\rangle = \exp(\hat{T}) |\Phi_{HF}\rangle = \sum_{i=1}^{N} \hat{C}_i |\Phi_{HF}\rangle \]

where \( \hat{C}_i \) is the operator that group all the excitation of order \( i \).

\[
\begin{align*}
\hat{C}_0 &= 0 \\
\hat{C}_1 &= \hat{T}_1 \\
\hat{C}_2 &= \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \\
\hat{C}_3 &= \hat{T}_3 + \hat{T}_1 \hat{T}_2 + \frac{1}{6} \hat{T}_1^3 \\
\hat{C}_4 &= \hat{T}_4 + \hat{T}_1 \hat{T}_3 + \frac{1}{2} \hat{T}_2^2 + \frac{1}{2} \hat{T}_1^2 \hat{T}_2 + \frac{1}{24} \hat{T}_1^4 \\
\end{align*}
\]

\[
\vdots
\]

Truncation at \( N=2 \) \( (\hat{T} = \hat{T}_1 + \hat{T}_2) \) will also give contributions to quadruple excitations \( (\hat{C}_4) \) via “disconnected” clusters.

Nomenclature:

\[
\begin{align*}
\hat{T} &= \hat{T}_1 & \text{CCS} \\
\hat{T} &= \hat{T}_1 + \hat{T}_2 & \text{CCSD} \\
\hat{T} &= \hat{T}_1 + \hat{T}_2 + \hat{T}_3 & \text{CCSDT}
\end{align*}
\]
Consider the following reordering of the contributions

\[ |\Psi_{CC}\rangle = \exp(\hat{T}) |\Phi_{HF}\rangle = \sum_{i=1}^{\infty} \hat{C}_i |\Phi_{HF}\rangle \]

where \( \hat{C}_i \) is the operator that group all the excitation of order \( i \).

\[
\begin{align*}
\hat{C}_0 &= 0 \\
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\hat{C}_4 &= \hat{T}_4 + \hat{T}_1 \hat{T}_3 + \frac{1}{2} \hat{T}_2^2 + \frac{1}{2} \hat{T}_1^2 \hat{T}_2 + \frac{1}{24} \hat{T}_1^4 \\
\ldots
\end{align*}
\]

Truncation at \( N=2 \) (\( \hat{T} = \hat{T}_1 + \hat{T}_2 \)) will also give contributions to quadruple excitations (\( \hat{C}_4 \)) via "disconnected" clusters.

Nomenclature:

- \( \hat{T} = \hat{T}_1 \) \hspace{1cm} CCS
- \( \hat{T} = \hat{T}_1 + \hat{T}_2 \) \hspace{1cm} CCSD
- \( \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \) \hspace{1cm} CCSDT
CC excited state energies

CC excitation energies are derived from linear response time-dependent perturbation theory applied to the CC equations (H. Koch, P. Jørgensen, JCP, 93, 3333 (1990)).

The CCLR eigenvalue equations are

\[(A - \omega_j S)X_j = 0\]

\[A_{\mu,\nu} = \langle \mu | e^{-\hat{T}} [\hat{H}, \hat{\tau}_\nu] | \Phi_{CC} \rangle\]
\[S_{\mu,\nu} = \langle \mu | e^{-\hat{T}} \hat{\tau}_\nu | \Phi_{CC} \rangle = \langle \mu | \hat{\tau}_\nu | \Phi_{HF} \rangle\]

where \( | \Phi_{CC} \rangle = e^{\hat{T}} | \Phi_{HF} \rangle \) is the CC reference state,

\[\hat{T} = \sum_\mu \hat{T}_\mu = \sum_\mu t_\mu \hat{\tau}_\mu\]

is the cluster operator

and \( \langle \mu | = \langle \Phi_{HF} | \hat{\tau}_\mu^\dagger \) represents the excited manifold.

The solutions of the eigenvalue equations are the excitations energies \( \omega_j \) and the corresponding eigenvectors \( X_j \).
Efficient CC excited state energies

Using perturbation theory, excitations of higher order than the actual truncation level can be estimated leading to approximated CCSD (CC2) and approximated CCSDT (CC3).

CC2 gives good precision at a modest computational cost (compared to CCSD for example).

Computational costs:

CC2 $O(n^4) - O(n^2)$ while CCSD $O(n^6)$ where $n$ is the number of orbitals.
Examples: Excitation energies

Benzene excitation energies

Comparison of different methods:

<table>
<thead>
<tr>
<th>Basis</th>
<th>Exp. $^b$</th>
<th>aug-cc-pVTZ-CM2</th>
<th>ANO1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^1\text{B}_{2u} (\pi-\pi^*)$</td>
<td>4.90</td>
<td>5.232</td>
<td>4.80</td>
</tr>
<tr>
<td>$1^1\text{B}_{1u}$</td>
<td>6.20</td>
<td>6.463</td>
<td>7.32</td>
</tr>
<tr>
<td>$1^1\text{E}_{1u}$</td>
<td>6.94</td>
<td>7.070</td>
<td>8.53</td>
</tr>
</tbody>
</table>

Examples : Quality of a PES

4-N,N-dimethylaminobenzonitrile (DMABN)

Examples

Excitation energies and bond lengths of diatomic molecules (first triplet state)

(Hättig C., Advances in Quantum Chemistry : Response theory and molecular properties, Vol. 50, pp. 37-60)

Energies in eV (first triplet state):

<table>
<thead>
<tr>
<th>Molecule</th>
<th>CIS</th>
<th>CC2</th>
<th>CCSD</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>5.3</td>
<td>6.54</td>
<td>6.33</td>
<td>6.22</td>
</tr>
<tr>
<td>CO</td>
<td>5.78</td>
<td>6.08</td>
<td>6.17</td>
<td>6.04</td>
</tr>
</tbody>
</table>

Bond length in pm (first triplet state):

<table>
<thead>
<tr>
<th>Molecule</th>
<th>CIS</th>
<th>CC2</th>
<th>CCSD</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>122.8</td>
<td>131.5</td>
<td>126.8</td>
<td>128.7</td>
</tr>
<tr>
<td>CO</td>
<td>117.5</td>
<td>122.7</td>
<td>119.4</td>
<td>120.6</td>
</tr>
</tbody>
</table>

CC2 tends to overestimate the correlation. So bond lengths are usually overestimated (in contrast with CCSD which underestimate the bond length).
**Coupled Cluster Method**

**CC2 properties**

> is size consistent

> Typical errors for the CC2 singlet excited energies are in the range 0-0.5 eV (usually too high compared to high level calculations). [Schreiber et al, JCP, 128, 134110 (2008)]. The quality deteriorates for open shell systems and electronically more demanding cases such as transition metals

> as consequence of the approximations for the “doubles”, CC2 provides a better description of excited state properties rather than energies.

> can describe charge transfer states (CT)

> can produce pure spin states

> analytic energy gradients are available

> scales like $O(n^5)$ with n the number of basis functions ($O(n^6)$ for CCSD) (> 50 atoms)
MCSCF Methods

Multi-Configurational Self-Consistent Field Method

MCSCF uses the same multi-determinantal series as in CI, with the difference that also the orbitals that enter the Slater determinants are optimized.

\[ E_{MCSCF} = \min_{c_0,c_1,\ldots,c_i} \frac{\langle \Psi_{MCSCF} | \hat{H} | \Psi_{MCSCF} \rangle}{\langle \Psi_{MCSCF} | \Psi_{MCSCF} \rangle} \]

A chemical active space (AS) is defined, which contained a limited number of occupied and unoccupied orbitals important for the system.

Choice of the active space: Iterative Natural Orbital (INO) for example.

For excitation energy: State-averaged MCSCF (average optimization of the orbitals for different excited roots)

Complete Active Space Self-Consistent Field method (CASSCF)

This is a special version of MCSCF in which all excitations inside the active space are allowed. CASSCF(M,N) refers to an active space of M electrons in N orbitals.
End of part I

THANK YOU FOR YOUR ATTENTION!