DENSITY FUNCTIONAL THEORY: A BRIEF COURSE
DENSITY FUNCTIONAL
THEORY: A BRIEF COURSE

Juan Carlos Sancho García
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J’écris \( \mathbf{F} = m\gamma \)
et la flèche prend son essor.
J’écris \( E_2 - E_1 = h\nu \)
et la feuille boit le soleil.

\[ \cdots \cdots \]

J’écris \( A_\mu = j_\mu; \quad F_{\mu\nu} = \delta_\mu A_\nu - \delta_\nu A_\mu \)
et la lumière EST.
J’écris \( i\hbar \frac{\partial \Psi}{\partial t} = \left( -\hbar^2 \sum_k \frac{\Delta_k}{2m_k} + \sum_i \sum_j \frac{e_i e_j}{|r_i - r_j|} \right) \Psi \)
et le sel se fait cristal.

\[ \cdots \cdots \]

J’écris \( \left( \frac{\partial^2}{\partial t^2} - c^2 \Delta^2 \right) p(r, t) = 0 \)
et j’entends ta voix. J’écris, je décris, je décrête.
L’univers se plie à la lettre.
Nul atome n’est censé ignorer la Loi.

Jean-Marc Lévy-Leblond (*Lois de la Nature*)
Introduction

In 1964, P. Hohenberg and W. Kohn\(^1\) published a pair of theorems constituting the basis for Density Functional Theory (DFT). Only one year later, the development of the Kohn-Sham (KS) scheme allowed to make the DFT a practical theory for all kind of (intended) calculations, as it is known today (KS-DFT). These authors showed that there always exists a one-to-one relation (correspondence) between the energy and the electron density of a system, i.e. it is in principle possible to obtain directly the exact energy from this density through an universal functional. However, the mathematical formulation that delivers this energy is still unknown, although some examples have showed that it can be numerically constructed from an exact (accurate) wavefunction for some model systems. Note how this approach completely circumvents the paths classically forming the core of Quantum Chemistry: the wavefunction is no longer needed and the associated Schrödinger equation does not need to be correspondingly solved. The key is thus to model or mimic the subtle effects dominating matter at the quantum scale by means of a functional of the electronic density. The machinery should accurately include exchange and correlation effects, in order to address structure and bonding of molecules, and it should be more advantageous than the \textit{ab initio} methods, either by reducing the computational cost associated to any calculation or by introducing theoretical concepts able to rationalise chemical reactivity or morphologies.

\(^1\)In 1998, Walter Kohn received (shared with John A. Pople) the Nobel prize in Chemistry for his work on DFT.
It was not until the 1980s that the first reasonable approximations to that universal functional were proposed. That means to dispose of expressions able to deliver the stabilising effects of matter arising from a purely quantum-mechanical (non-classical) origin after inserting the density of any system into the specific chosen mathematical form. The development of these expressions (the density functionals) is normally a hard and painstaking work, and often underestimated by the community. Apart from the older Local Density Approximation (LDA), which is, however, still appreciated in some fields of Physics, the extension coined as Generalized Gradient Approximation (GGA), the hybrid functionals containing a portion of exact-like (Hartree-Fock) exchange, but calculated with the KS orbitals, the meta-GGA functionals, the double hybrid functionals also containing a portion of the nearly exact (perturbative) correlation, local hybrid functionals, and the recently developed range-separated hybrid functionals are available today for running any calculation. The (admittedly) proliferation of functionals have provoked two (apparently contradictory) effects: (i) routine calculations plague nowadays almost all existing fields; and (ii) cautions must be taken and experience in use is needed more than ever. Furthermore, since the codes, where density functionals are implemented, are sometimes obscure, one needs to calibrate first the methodology before next tackling the interested systems. Also note that the results are sometimes system-dependent and/or property-dependent, which implies to analyse carefully how the results evolve or compare with closely related data before concluding, and that comparison with experimental data may need to model solvent effects or nanostructured systems, which complicate the task further.

We would also like to mention that, before any attempt to apply DFT further in your career and in connection with previous warnings, a successful research strategy in Quantum and Computational Chemistry, independently of the theory involved behind that statement, needs to provide a manifold of results with: (i) predictive character (high accuracy); and (ii) independent to any experimental information. The following flowchart tries to summarise the main steps that need to be followed:
First, one should clearly define the aim of the study, as precisely as possible. This is probably one of the most important parts of any research and should not be underweighted. Then, extensive literature reviewing would provide the scientific background of the topic. The analysis of previous information has to be reviewed with an open mind, trying to summarise previous levels of theory used and its achievements. The review includes the computational packages which were used and why. Once the actual computations take place at a given level of the theory, and the results have been carefully analysed and double-checked for errors, two key questions arise: (i) might the conclusions be improved by further theoretical improvements?; and (ii) do they accomplish the initial objective? If not, keep fighting! Proper actions have to be taken if the calculations do not guarantee the required levels of quality or do not provide unbiased conclusions.
Last but not least, Science is the foundation of technology that drives much of the modern economy and the well-being of nations and their citizens. The second half of the 20th century and, in particular, the first decade of the 21st century has seen a near-exponential growth in worldwide science. Therefore, we can not avoid to relate the research sketched through these lines and the Nanotechnology issue. Nanotechnology is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to investigating whether we can directly control matter on the atomic scale. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials and energy production.

Nanotechnology is the study of manipulating matter on an atomic and molecular scale. Generally speaking, nanotechnology deals with structures sized\(^2\) between 1 to 100 nm in at least one dimension, and involves developing materials or devices possessing at least one dimension within that size. A number of physical phenomena become pronounced as the size of the system decreases. These include statistical mechanical effects, as well as quantum mechanical effects, which is in the quantum realm. We hasten to say that mechanical, electrical, optical, etc. properties change when compared to macroscopic systems.

The first use of the concepts found in 'nano-technology' (but predating the use of that name) was in "There’s Plenty of Room at the Bottom", a talk given by physicist Richard Feynman at an American

---

\(^2\)1 nm is one billionth, or \(10^{-9}\), of a metre. In comparison, typical C-based bond lengths, are in the range 0.10 – 0.15 nm, and a DNA double-helix has a diameter around 2 nm. On the other hand, the smallest cellular life-forms, the bacteria of the genus Mycoplasma, are around 200 nm in length. By convention, nanotechnology is taken as the scale range 1 to 100 nm following the definition used by the National Nanotechnology Initiative in the US. The lower limit is set by the size of atoms (hydrogen has the smallest atoms, which are approximately a quarter of a nm diameter) as nanotechnology must build its devices from atoms and molecules. The upper limit is more or less arbitrary, but it is around the size that phenomena not observed in larger structures start to become apparent and can be made use of in the nano device.
Physical Society meeting at the California Institute of Technology (Caltech) on December 29, 1959. Feynman described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, and so on down to the needed scale. In the course of this, he noted, scaling issues would arise from the changing magnitude of various physical phenomena: for instance, gravity would become less important while van der Waals attraction would become increasingly more significant.

Today, modern synthetic chemistry has reached the point where it is possible to prepare small molecules to almost any structure. This ability raises the question of extending this kind of control to the next-larger level, seeking methods to assemble these single molecules into supramolecular assemblies consisting of many molecules arranged in a well defined manner through a bottom-up approach. The concept of molecular recognition is especially important: molecules can be designed so that a specific configuration or arrangement is favoured due to inter-molecular forces. We believe that any reader could infer from this short description on how important (an will endless be) the quantum physical effects at this stage are and how precise a quantum-chemical method needs to be. Let's try to also pave the way in this direction.

Finally, it would also be convenient to announce in advance the sources of this work. The M.Sc. course “Introduction to Density Functional Theory” is part of a larger block of knowledge called “Theory and simulations in Materials Science” of the M.Sc., and developed by the Faculty of Science at the University of Alicante. This 3 ECTS course combines lectures, questions and answers, exercises and problems (test of knowledge), hand-on experiments, self-evaluation tests, reading key papers and chapters, etc. Also note that the content of each lecture is later illustrated through real-world (published) results by the author. Thus, this material is intended to be used as notebook rather than as a textbook by the audience. Also note that it is completely unreliable to cover every detail within the rich field of DFT just in 30 h. of in-person teaching activities. We thank the reader in advance for, if you will forgive the repetition, the reading
of this material.

We hope to introduce to you to this fascinating adventure through the use of DFT; your efforts are highly welcome now and forever!

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Department of Physical Chemistry

University of Alicante, 2013
Chapter 1

Quantum Chemists: searching for the right answer for the right reason

1.1 Who we are

- The purpose of our work: provide new and reliable knowledge, through formulating driven hypothesis, gathering and analysing data, as well as its later critical assessment.

- The ambition of our work: acquire and disseminate such knowledge, without any prejudice, and without any restriction far beyond those dictated by the most rigorous quality assessment, ruling scientific research at an international and competitive framework.

- The intention of our work: serve the citizenship, the social welfare state, and to achieve a clean and sustainable development; without infringing or recognising research as an essential element of our society and human condition as an intelligent being.

1.2 What we do

- Talking about what?
  - P. A. M. Dirac (1929): “The fundamental laws necessary for
the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies in the fact that the application of these laws leads to equations that are too complicated to be solved”.

○ H. Eyring et al. (1944): “Problems in chemistry had been converted by quantum mechanics into problems in applied mathematics”.

○ P. A. M. Dirac (1963): “If one has really a sound insight, one is on a sure line of progress. If there is not a complete agreement between the results of one’s work and experiment, one should not allow oneself to be discouraged, because the discrepancies will be cleared up with further developments of the theory”.

• Quantum and Computational Chemistry: state-of-the-art (I)

  ○ Fast emerging area which is used for the **modeling and simulation** of chemical and biological systems in order to understand and predict their behaviour at the molecular level.

  ○ It has also an envisioned wide range of applications in **many disciplines**: materials science, chemical engineering, biomedicine, etc. It can assist in the design and optimisation of new and existing processes and products.

  ○ It is probably the easiest route or gateway to the fast-growing discipline of nanoscience and **nanotechnology**, which is expected to revolutionise the industrial sector in the coming decades.

  ○ Experimentally deal nanometer-sized objects usually need expensive techniques; however, simulations of nanosystems can be today performed on **not-so-costly** Symmetric Multiprocessing Architectures or the recent deployment of GPU technology.

• Quantum and Computational Chemistry: state-of-the-art (II)

  ○ As we progress into the 21st century, industry will continue to emphasise a shareholder return, globalisation and capitalism-based efficiency; **modeling and simulation** will progressively
become critical technologies. Acquiring such knowledge might be a driving force for further career development.

○ From an economical point of view, it can be used to reduce the costs of development, improve energy efficiency and environmental performance, and increase productivity and profitability.

○ According to these features, this discipline is being taught presently as a course at (mainly) the postgraduate and research level in many universities all around the world. It is (fortunately) included in the education curricula for chemists, physicists and pharmacists.

• Quantum and Computational Chemistry: barriers

○ Considerable efforts need to be applied to develop new theories, increase computational capability, remove predictive uncertainties, and educate decision makers about the benefits of these potentially powerful tools.

○ Work to be still done is turning disparate information, or result from individual contributors, into organised, exploitable, and implementable knowledge.

○ The main challenges can thus be enumerated as follows:

  □ Applicable to a wider range of systems and situations: larger or complicated systems, over greater time scales, liquids or solids, etc.
  □ Flexible: inter-operable between various computing platforms and software, easy graphical interfaces, etc.
  □ Affordable: capable of running on desktops or lower-cost parallel computing platforms.
  □ User friendly: expert systems for non-experts upon expert guidance.
  □ Widely publicised: publication of periodic benchmarks, computations validated through further experiments, etc.

\footnote{That’s one of the reasons why this material comes to light!}
• Quantum and Computational Chemistry: experiments

  ○ When we are using computational chemistry to answer a chemical question, the first requirement is to know how to use the software. Furthermore, we need to know how good the answer is going to be.

  ○ Preliminary questions thus are:

    □ What do we need to infer from computations?
    □ Why do we stick to computational tools?
    □ What should be the permissible accuracy level?
    □ Do I have these tools implemented or should I find better tools?

  ○ A further step is to ask oneself: how should I bracket the error of the computational experiments? Repeating the same experiment will give the same number, contrarily to the rest of chemistry fields.

  ○ Thus one needs to study known systems (literature & own benchmarks) and make a proper calibration of the method before applying it to unknown systems.
Chapter 2

Quantum Chemistry: \textit{ab initio} and/or DFT methods

2.1 General comments & framework

- Generalities (1): Chemistry implies various size scales
  - **QUANTUM SCALE**: quantum effects truly manifest in a complex way (\textit{ab initio} or DFT), but the price to be paid is the size of the systems tackled ($10^2 - 10^3$ non-H atoms),

\[
E_0[\Psi] = \inf_{\Psi \in W_N} \left\langle \Psi | \hat{H} | \Psi \right\rangle ; \quad |\Psi\rangle = \hat{O}|\Psi_0\rangle ; \quad \hat{O} : \text{CC, CI, PT}
\]

(2.1)

- **ATOMISTIC SCALE**: a certain degree of empiricism is introduced (QM/MM, MD, Monte-Carlo \ldots) allowing the treatment of larger systems ($10^3 - 10^6$ non-H atoms),

\[
E = \sum_{AB} E_{AB} + \sum_{ABC} E_{ABC} + \cdots + \sum_{AB} E_{QAB} + \sum_{AB} E_{vdW} + \cdots
\]

(2.2)

- Semi-empirical methods (AM1, PM3, PM6, INDO/S, \ldots) lying in the middle point between the two scales.
• Generalities (II): Technology Roadmap (2020)

○ A panel of experts have even proposed the following envisioned goals for the two sized scales, respectively,

<table>
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<tr>
<th>Size</th>
<th>Accuracy</th>
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<tr>
<td>30 atoms</td>
<td>0.2 kcal/mol</td>
</tr>
<tr>
<td>500 atoms</td>
<td>1–2 kcal/mol</td>
</tr>
<tr>
<td>Intermolecular</td>
<td>Increase by a</td>
</tr>
<tr>
<td>energies</td>
<td>factor 5–10</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Size</th>
<th>Time</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^6$ atoms</td>
<td>1 µs</td>
<td>Increased</td>
</tr>
</tbody>
</table>

○ However, advances in computing will not only serve to satisfy these requirements! Better algorithms, data sets and calibration results are thus needed!

• Framework (I): *ab initio* vs. DFT

○ *ab initio* methods: to describe rigorously the electronic structure of chemical systems, using the postulates of quantum mechanics, and solving (approximately) the associated *Schrödinger*
The equation \( \hat{H} |\Psi(x; R)\rangle = E(R) |\Psi(x; R)\rangle \), with

\[
\hat{H} = \frac{1}{2} \sum_{i} \nabla_{i}^{2} - \sum_{i} \sum_{A} \frac{Z_{A}}{|r_{i} - R_{A}|} + \frac{1}{2} \sum_{i} \sum_{j} \frac{1}{|r_{i} - r_{j}|} \sum_{i} h(i) \sum_{j} g(i,j) \\
+ \frac{1}{2} \sum_{A} \sum_{B} \frac{Z_{A}Z_{B}}{|R_{A} - R_{B}|},
\]

and \( |\Psi(x; R)\rangle \) the exact wavefunction of the system. Note the dependence on \( E(R) \) which defines the corresponding energy hypersurface before invoking the Born-Oppenheimer approximation.

- The Density Functional Theory: to describe rigorously the electronic structure of chemical systems, avoiding the resolution of the Schrödinger equation, after invoking and showing the existence of a universal functional of the density for any known system \( (E[\rho]) \).

- Framework (II): Variety and diversity
  - \textit{ab initio} methods (acronyms) for both Single-Reference and Multi-Reference (MR) variants:
    - Starting point \( (|\Psi_{0}\rangle) \): HF\(^1\) & MR variants such as GVB or CASSCF(N,M).
    - The CI-based family: CIS, CISD, QCISD, QCISD(T),... & MR variants known as MR-CI.
    - The CC-based family: CCSD, CCSD(T), pCCSD, CCSDT, CCSDT-1b, ... & MR variants known as MR-CCSD.
    - The perturbative MPn-based family: MP2, MP2.5, MP4, SCS-MP2, SOS-MP2, ... & MR variants known as MR-MP2 (CASPT2 being probably the most employed one)

\(^{1}\)A single Slater determinant by definition. The HF model also provides, again by definition, the exchange energy exactly once the associated orbitals are considered; thus, any theory dealing with it, even using other orbitals arising from different equations, is also known as a Exact-like EXchange (EXX) theory.
DFT approach (I): pure and hybrid \((w_1 \neq 0)\) functionals;

\[ E_{xc}[\rho] = w_1 E_x^{\text{EXX}} + (1 - w_1) E_x[\rho] + E_c[\rho], \]
with: \(E_x[\rho] = \text{B88, PW91, mPW, G96, PBE, revPBE, OPTX, TPSS, ...;}\)
\(E_c[\rho] = \text{P86, LYP, WL, PW91, B95, PBE, OPTC, TPSS, ...; or standalone } E_{xc}[\rho] = \text{B97, B98, HCTH, BBX, MPWX, XLYP, M06-2X, ...}\)

DFT approach (II): double-hybrid \((w_1, w_2 \neq 0)\) functionals;

\[ E_{xc}[\rho] = w_1 E_x^{\text{EXX}} + (1 - w_1) E_x[\rho] + w_2 E_c^{\text{MP2}} + (1 - w_2) E_c[\rho], \]
with: \(E_{xc}[\rho] = \text{B2-PLYP, B2GP-PLYP, XYG3, DSD-BLYP, PBE0-DH ...}\)

Framework (III): Some points of concern affecting routine DFT calculations:

- Self-interaction (one-electron & unpaired) error: \(E_{xc}[\rho] \neq -U[\rho]\)
- The errors increase disproportionately with increasing molecular size (non size-extensive).
- Correlation effects are usually too short-sighted due to the dependence on \(\rho\) and its higher derivatives: \(E[\rho(\mathbf{r}), \nabla \rho(\mathbf{r})...]\)
- Poor description of interactions between weakly interacting fragments or densities.

\[ \Rightarrow \] The mixture of EXX and \(E_x[\rho]\) only partly alleviate them, and possible solutions are being lately pursued:

- Non-covalent interactions: \textbf{DFT-D(3)}, \(E_c[\rho] + f(R^{-6})\)
or non-local \textbf{vdW-DFT}, \(E_c[\rho] = \int \rho(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') d\mathbf{r}\)
- \textbf{Local} admixture of \textbf{Exact-like EXchange (EXX)}: \(E_{xc}[\rho] = \int \rho(\mathbf{r}) \{ a(\mathbf{r}) e_x[\rho] + (1 - a(\mathbf{r})) e_x^{\text{EXX}} \} d\mathbf{r} + E_c[\rho]\)
- \textbf{Range-separation} of exchange-correlation effects:\n\(E_{xc}[\rho] = f(\text{short-range } e_{xc}[\rho]) + f(\text{long-range } e_{xc}[\rho], e_x^{\text{EXX}}).\)
- \textbf{Doubly-hybrid} (non-local) exchange-correlation kernels:\n\(E_{xc}[\rho] = f(e_x[\rho], e_x^{\text{EXX}}, e_c[\rho], e_c^{\text{MP2}})\)
2. Quantum Chemistry: ab initio and/or DFT methods

- Some recent thoughts (2005-2010)
  - “...the happy days of ‘black-box’ usage are over, at least for energy calculations. Confidence has been undermined. No available density functional is reliable for large molecules”
    Paul von R. Schleyer
  - “...we are not questioning the exactness and usefulness of DFT, but just the human ability to find accurate density functionals in practice”
    Stefan Grimme
  - “In the meantime, the recommendation is therefore to utilize DFT approaches for structure optimisations but to use higher levels for energy comparisons”
    Peter Schreiner

2.2 Modern ab initio methods

2.2.1 Correlation effects and associated energy

- Some preliminary issues:
  - Ground-state energy: $E_0[\Psi] = \inf_{\Psi \in \mathcal{W}_N} \left\langle \Psi | \hat{H} | \Psi \right\rangle$.
  - Methods arise from the way in which $|\Psi\rangle = \hat{O}|\Psi_0\rangle$, giving rise to the CI, CC o MPn families,
    \[ \hat{O}_{CI} \sim \hat{C}|\Psi_0\rangle = \left( 1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \cdots \right)|\Psi_0\rangle; \]
    \[ \hat{O}_{CC} \sim e^{\hat{t}}|\Psi_0\rangle = \left\{ 1 + \left( \hat{T}_1 \right) + \left( \hat{T}_2 + \frac{1}{2!}\hat{T}_1^2 \right) + \left( \hat{T}_3 + \hat{T}_2\hat{T}_1 + \frac{1}{3!}\hat{T}_1^3 \right) + \cdots \right\}|\Psi_0\rangle; \]
    \[ \hat{O}_{MPn} \sim \hat{P}|\Psi_0\rangle = \left\{ 1 + \hat{\Omega}_1^{(1)} + \hat{\Omega}_2^{(2)} + \hat{\Omega}_3^{(3)} + \cdots \right\}|\Psi_0\rangle \]
  - Truncation of the operator leads to a hierarchy of methods: CISD, CISDT . . . ; CCSD, CCSDT . . . ; MP2, MP4 . . .
2.2. Modern ab initio methods

- **Multi-reference extensions** of the methods (MR-CI, MR-CC, MR-PT) are also possible: \( |\Psi_0\rangle \) is no longer described by a single Slater determinant but by a few of them (adequately selected and well-rooted).

- All correlation effects can be introduced in a systematic way. The methods are improvable!

**Definition of correlation effects:**

\[ \Rightarrow \text{The term } \sum_{i<j} \frac{1}{r_{ij}} \text{ introduces correlation effects}^2 \text{ that are often partitioned into DYNAMIC } (\varepsilon_c^D) \text{ and NON-DYNAMIC } (\varepsilon_c^{ND}) \text{ effects:} \]

\[ E_c = E_{\text{exact}} - E_{\text{HF}} = \varepsilon_c^D + \varepsilon_c^{ND} \quad (2.4) \]

\[ \Rightarrow \text{Dynamic: short-range, including the so-called "in-out" or "angular" } (s \rightarrow s', p \rightarrow p', \sigma \rightarrow \sigma' \ldots) \]

- Introduce as many excitations as possible (\( \hat{\text{O}} \)) from the starting \( |\Psi_0\rangle \).
- It modifies HF results in a quantitative manner.

\[ \Rightarrow \text{Non-Dynamic: long-range or static, including the so-called "left-right"} \]

- Due (often) to near-degeneracies, bond(s)-breaking...
- It modifies HF results in a qualitative manner.
- It introduces very few yet well-chosen \( |\Psi_\mu\rangle \) needed to qualitatively describe the problem (MCSCF).

- Still more related definitions...

\[ \Rightarrow \text{Radial ("in-out"): if an electron is close to a nucleus it is more probable for the other electron to be far out from that nucleus.} \]

---

2If \( |\Psi_{\text{exact}}\rangle = |\Psi_{\text{HF}}\rangle + |\Psi'\rangle \), then \( E' = E_c = E_{\text{exact}} - E_{\text{HF}} \). Note also that \( \Psi_{\text{HF}} = \Psi_0 \) since it implies a kind of 0th-order solution for further theoretical treatments.
Angular: if an electron is on one side of a nucleus it is more probable for the other electron to be on the opposite side of that nucleus.

Left-right: if an electron is close to a nucleus on the left side on a chemical bond it is more probable for the other electron to be close to the nucleus on the right.

A strict distinction (or separability) between the terms is not possible in general. And some confusion might further arise from it:

Fermi correlation: energy stabilisation by obeying Fermi statistics, which requires that the wavefunction of indistinguishable particles was antisymmetric with respect to their exchange.

Coulomb correlation: electrons interact through a repulsive Coulomb force \( \frac{1}{r_{ij}} \).

The non-dynamic term is difficult to define rigorously:

<table>
<thead>
<tr>
<th>System</th>
<th>( \varepsilon_c^D )</th>
<th>( \varepsilon_c^{ND} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 \ (R \rightarrow \infty) )</td>
<td>-</td>
<td>( E^{\text{He,Ne}}<em>{\text{exact}} - E^{\text{He,Ne}}</em>{\text{HF}} )</td>
</tr>
<tr>
<td>( \text{He, Ne} )</td>
<td>( E^{\text{He,Ne}}<em>{\text{exact}} - E^{\text{He,Ne}}</em>{\text{HF}} )</td>
<td>-</td>
</tr>
</tbody>
</table>

What to do for other challenging yet chemically interesting systems? We need to resort to a CASSCF(N,M) wavefunction:

\[
|\Psi_{\text{CASSCF}}\rangle = \sum_{\mu} \varepsilon_{\mu} |\Psi_{\mu}\rangle , \quad \text{being} \quad |\Psi_{\mu}\rangle = |(\text{core}) \phi_i \rightarrow \phi_{i+k}\rangle \quad (2.5)
\]

How to perform a CASSCF(N,M) calculation:

- Define N e^- and M valence orbitals, and thus \( |\Psi_{\text{CASSCF}}\rangle \).
- Note that indeed a full-CI of N e^- in M orbitals is still very costly. (N!).
- Add the remaining correlation energy by selecting the operator \( \hat{O} \) (CASPT2, MR-CI, MR-CC) according to hard- and software availability.
2.2.2 Convergence of \textit{ab initio} methods

• Choice of a model chemistry (I):
  
  ° A hierarchy of basis sets for electron correlation methods is needed: cc-pVnZ and further extensions (aug-cc-pVnZ, cc-pwCVnZ) to achieve the Complete Basis Set (CBS) limit.
  
  ° A dual-convergence\textsuperscript{3} towards the exact solution is thus expected:

\begin{center}
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{Cost} & \textbf{Method} & \textbf{n=D} & \textbf{n=T} & \ldots & \textbf{CBS} \\
\hline
N\textsuperscript{4} & HF & & & & \\
N\textsuperscript{5} & MP2, CCD & → → & & & \\
N\textsuperscript{6} & CCSD \simeq MP4 & \downarrow & & & \\
N\textsuperscript{7} & CCSD(T), QCISD(T) & \downarrow & & & \\
N\textsuperscript{8} & CCSDT, CCSD(TQ) & \downarrow & & & \\
\vdots & & & & & \\
N! & FCC \equiv FCI & & & & EXACT \\
\hline
\end{tabular}
\end{center}

° A model chemistry is indicated by a specific notation such as CCSD(T)/cc-pVTZ//MP2/cc-pVDZ. Note what is implied by the scaling of the methods since $N^k$ means that going from $N$ to $2N$ atoms, the computational cost and associated use of resources increases by a factor of $2^k$.

• Choice of a model chemistry (II):

\[ \Longrightarrow \text{The choice of a model chemistry introduces two errors:} \]

° Basis sets truncation: $\Delta \epsilon_n = E_n - E_\infty$

° Truncation of $\hat{O}$: $\Delta \epsilon^M = E^M - E^{\text{FCC}=\text{FCI}}$

\textsuperscript{3}This also applies to the def2-nVP sequence of basis sets or any other built under this prescription.
The goal is to reduce as much as possible the combined $\Delta \varepsilon^M_n = E^M_n - E^\text{exp.}_{\text{FCC}}$ to achieve the so-called “chemical accuracy” ($\varepsilon^M_n \leq 1$ kcal/mol) or even the “calibration accuracy” ($\varepsilon^M_n \leq 1$ kJ/mol). To that end, we use extrapolation techniques to reduce separately both $\Delta \varepsilon^M_n / \Delta \varepsilon^n$:

$$E^\text{FCC} = \frac{E_1}{1 - E_2^2 / E_3^2}; \quad E_\infty = E(n + 1) + f(n) \Delta E$$

with $\Delta E = [E(n + 1) - E(n)]$

$E_1 = \text{HF}$, $E_2 = \text{CCSD} - \text{HF}$

$E_3 = \text{CCSD(T)} - \text{CCSD} \ldots$

$E \equiv \text{HF energy: } f(n) = n^{-5}$

$E_c \equiv \text{MPn o CC: } f(n) = n^{-3}$

Note that one always aims at pursuing the right answer for the right reason!

• Choice of a model chemistry (III):

$$E_\infty = E(n + 1) + f(n) \left[ E(n + 1) - E(n) \right], \text{ with } f(n) = n^{-3}$$
\( \Rightarrow \) **CAUTION:** Whereas the error is \( \propto n^{-3} \), the computing time is \( \propto n^{12} \), and the convergence is rather slow.

- **Properties:** Size-extensivity and size-consistency
  
  - **Size-consistency:** right molecular dissociation\(^4\),
    \[
    E_{AB} (R_{AB} \to \infty) = E_A + E_B. \tag{2.6}
    \]
  
  - **Size-extensivity:** right scaling with system size\(^5\),
    \[
    E (S_1 + S_2 + \cdots + S_m) = E (S_1) + E (S_2) + \cdots + E (S_m),
    \]
    \[
    E(mS) = mE(S) \tag{2.7}
    \]

  \( \Rightarrow \) **CONSEQUENCE:** Predominance of \( \hat{O}_{CC} \) [CCSD, CCSD(T)]
  and \( \hat{O}_{MPn} \) (MP2, MP4) vs \( \hat{O}_{CI} \) [CISD, QCISD(T)].

  \( \Rightarrow \) **REASON:** \( E_{\text{CISD}}(mS) \propto \sqrt{m} E_{\text{CISD}}(S) \) while \( E_{\text{CCSD}}(mS) \propto m E_{\text{CCSD}}(S) \), and the CISD error will increase with system size.

- **Modern MP2-based theories:**
  
  - We can scale also directly pair correlation effects to achieve better accuracy than MP2 at the same computational cost:
    \[
    E^{\text{MP2}} = E^{\text{HF}} + E_{c}^{\text{PT2}} = E^{\text{HF}} + c_{\uparrow\downarrow} E_{c}^{\uparrow\downarrow} + \frac{1}{2}c_{\uparrow\uparrow} E_{c}^{\uparrow\uparrow} + \frac{1}{2}c_{\downarrow\downarrow} E_{c}^{\downarrow\downarrow} \tag{2.8}
    \]

  - This leads to a family of Spin-Component-Scaled (SCS) MP2-based variants,

\(^4\)To simulate chemical reactions.
\(^5\)To deal with crystals, polymers, etc.
2. Quantum Chemistry: \textit{ab initio} and/or DFT methods

<table>
<thead>
<tr>
<th>Method</th>
<th>(c_{11} )</th>
<th>( c_{11} = c_{11} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP2</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>FE2-MP2</td>
<td>1.12</td>
<td>0.84</td>
</tr>
<tr>
<td>SCS-MP2</td>
<td>1.20</td>
<td>0.33</td>
</tr>
<tr>
<td>SOS-MP2</td>
<td>1.30</td>
<td>0.00</td>
</tr>
<tr>
<td>SCS-MI-MP2</td>
<td>0.40</td>
<td>1.29</td>
</tr>
<tr>
<td>SCSN-MP2</td>
<td>0.00</td>
<td>1.76</td>
</tr>
<tr>
<td>SCS-S66-MP2</td>
<td>0.28</td>
<td>1.56</td>
</tr>
</tbody>
</table>

- Further extensions to all \textit{ab initio} methods: SCS-MP3, SCS-CCSD, SCS-CC2, SCS-CIS(D) ... 

### 2.3 Summary and conclusions

1. \textit{ab initio} methods: use and hierarchy

- **BARRIERS**
  - scaling with size: \( N^k \)
  - assessment / calibration
  - high-performance computing
  - experience in use
  - disentangle dual-convergence

- Ab initio
- High accuracy (low- to medium-size)

2. The goal is to bracket the errors associated to the model chemistry chosen:

\[
\Delta \epsilon_n = E_n - E_\infty, \quad \Delta \epsilon^M = E^M - E^{\text{FCC}}, \quad (2.9)
\]

which combine into \( \Delta \epsilon^M_n = E^M_n - E_{\exp}. (E^{\text{FCC}}_\infty) \leq \pm 1 \text{ kcal/mol} \).
3. Note the large basis set dependence of the results and other basis set incompleteness issues as the Basis Set Superposition Error (BSSE), for example.
Chapter 3

The electronic density is the key (I): fundamental definitions and concepts

3.1 General comments

3.1.1 Could density $\rho(r)$ be considered a state variable?

- State variable (I): a state variable is one of the set of variables able to describe the state of a system and to determine its evolution. They divide into extensive (its value is proportional to the size of the system) and intensive (its value is the same at all points).

  $$\implies$$ Can one consider $\rho(r)$ as a state variable in Quantum Chemistry? $$\iff$$

- State variable (II): the experience shows that not all state variables are independent: a subset of them normally suffices to fully characterise the state under scrutiny.

  $$\implies$$ Will $\rho(r)$ serve to legitimately identify and characterise the state of any system? $$\iff$$

- State variable (III): an equation of state is a functional relation

17
between state variables that allows to express any property of the
system as a function of these independent variables.

\[ \Rightarrow \text{Will such a relation } \rho(r) \text{ and the energy of any known system exist?} \]

### 3.1.2 Some mathematical aspects and notations

- **Function:** mathematical prescription associating exactly one quantity, the argument, with another quantity, the value; i.e., usually relating numbers with numbers. E.g.: the function \( y = f(x) = x^2 \) takes a number and multiplies by itself.

- **Operator:** mathematical prescription associating exactly (biunivocally) one function with another function. E.g.: the operator \( \dot{F} = \frac{\partial^2}{\partial x^2} \) calculates the second derivative of a function with respect to \( x \), \( \dot{F} f(x) = \frac{\partial^2}{\partial x^2} f(x) = g(x) \).

  - Example (I): the operator \( \nabla \) is a common 3D operator, \( \nabla = \left( \frac{\partial}{\partial x} \mathbf{i} + \frac{\partial}{\partial y} \mathbf{j} + \frac{\partial}{\partial z} \mathbf{k} \right) \), used normally to calculate forces from potential energies, \( F = -\nabla V \).

  - Example (II): the operator \( \nabla^2 \) appears in the Hamiltonian operator (\( \hat{H} \)), being \( \nabla^2 = \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \), in the term describing the kinetic energy of a system of particles.

- **Functional (I):** mathematical prescription taking one function and providing one value, normally a number. For instance, the functional \( F[\phi(x)] = \int_{-\infty}^{\infty} \phi(x) dx \) integrates the function \( \phi(x) \) to give its value. The set of all functions \( \phi(x) \) is called its domain.

- **Notation:** to clearly distinguish a functional from a function we will employ the notation \( F[\phi(x)] \), which specifies that the argument is a function depending on \( x \), and providing a certain value \( I \) once the form of \( F \) is mathematically fixed: there should also exists a biunivocal relation \( \phi(x) \rightarrow F[\phi(x)] \rightarrow I \). If the functional depends on few variables, it will be coined as \( E[\phi, \varphi, \ldots] \).
• Functional (II): the Schrödinger equation can be expressed as:

\[
E = \langle \Psi | \hat{H} | \Psi \rangle = \int \cdots \int \Psi(x_1, x_2, \ldots, x_N) \hat{H} \Psi^*(x_1, x_2, \ldots, x_N) \, dx_1 \, dx_2 \cdots dx_N
\tag{3.1}
\]

and, therefore, we can affirm that \( E = E[\Psi] \) which has a domain that is the set of well-behaved functions \( \Psi \). The minimisation of \( E[\Psi] \) will give the energy \( E_0 \) of the ground state and its corresponding \( \Psi_0 \), with \( E_0 = E[\Psi_0] \leq E[\Psi] \).

• Variation (I): the variation \( \delta F[\phi] \) of the functional \( E[\phi] \) is the expression which is linear in \( \delta \phi \) upon expanding the functional with respect to variations in the function \( \phi + \delta \phi \). We have then:

\[
\delta F[\phi] = F[\phi + \delta \phi] - F[\phi] = \int \frac{\delta F[\phi]}{\delta \phi(x)} \delta \phi(x) \, dx \tag{3.2}
\]

functional derivative

• Variation (II): the aim is to describe how the functional \( F[\phi] \) will change upon small changes suffered by the function \( \phi \). The condition that \( F[\phi] \) is stationary with respect to variations in the function \( \phi + \delta \phi \) implies that the functional derivative needs to be:

\[
\frac{\delta F[\phi]}{\delta \phi(x)} = 0,
\tag{3.3}
\]
a condition known as Euler-Lagrange equation.

• Functional derivative (I): if the functional derivative exists, the functional is said to be differentiable. With the functional derivative we operate similarly to the derivatives of a function,

\[
\frac{\delta}{\delta \phi} (c_1 F_1 + c_2 F_2) = c_1 \frac{\delta F_1}{\delta \phi} + c_2 \frac{\delta F_2}{\delta \phi} \tag{3.4}
\]

\[
\frac{\delta}{\delta \phi} (F_1 \, F_2) = \frac{\delta F_1}{\delta \phi} F_2 + \frac{\delta F_2}{\delta \phi} F_1 \tag{3.5}
\]
• Functional derivative (II): the functional derivative $\frac{\delta F[\phi]}{\delta \phi}$ can be another functional. Some applications to known (vide infra) examples are:

$$T_{TF}[\rho] = C_{TF} \int \rho^{5/3}(r) \, dr \quad \rightarrow$$

$$\frac{\delta T_{TF}[\rho]}{\delta \rho} = \frac{5}{3} C_{TF} \rho^{2/3}(r)$$

(3.6)

$$U[\rho] = \frac{1}{2} \int \frac{\rho(r) \rho(r')}{|r - r'|} \, dr \, dr' \quad \rightarrow$$

$$\frac{\delta U[\rho]}{\delta \rho} = \int \frac{\rho(r')}{|r - r'|} \, dr'$$

(3.7)

$$T_W[\rho] = \frac{1}{8} \int \frac{\nabla \rho(r) \cdot \nabla \rho(r)}{\rho(r)} \, dr \quad \rightarrow$$

$$\frac{\delta T_W[\rho]}{\delta \rho} = \frac{1}{8} \left( \frac{\nabla \rho(r)}{\rho(r)} \right)^2 - \frac{1}{4} \nabla^2 \rho(r)$$

(3.8)

3.1.3 Probabilistic interpretation of $|\Psi|^2$

• Postulates of quantum mechanics (I): the first postulate affirms that “the state of a quantum-mechanical system is completely specified by a state vector $|\Psi\rangle$ that depends upon the coordinates of the particles. All possible information about the system can be derived from it. This function, called the wave function or the state function, has the important property that $\Psi^*\Psi$ is related with the probability of finding the particles at defined regions in coordinate space”

• Analysis: the value of $\Psi$ does not (apparently) contain information, BUT:

$$\Psi^*(r_1, r_2, \ldots, r_N) \Psi(r_1, r_2, \ldots, r_N) \, dr_1 \, dr_2 \cdots \, dr_N$$

probability distribution

represents the probability that particle 1 lies in the interval $dr_1$ located at $r_1$, particle 2 lies in the interval $dr_2$ located at $r_2$, and so.
3. The electronic density is the key (I): fundamental definitions and concepts

\[ \implies \text{Equivalent notation: } |\Psi|^2 \equiv \Psi^*\Psi \equiv |\Psi\rangle\langle \Psi|. \]

- Postulates of quantum mechanics (II): the probability of finding the \( N \) particles of the system located at any point in the space at a given time \( t \) must be the sum over all possible probabilities:

\[
\int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \Psi^*(r_1, r_2, \ldots, r_N)\Psi(r_1, r_2, \ldots, r_N)dr_1dr_2 \cdots dr_N = 1
\]

(3.10)

\[ \implies \text{This functional can be seen as the probability of finding any of the } N \text{-electrons within a volume element } d\mathbf{r} \text{ with arbitrary spin. The volume element } d\mathbf{r} = dx dy dz \text{ as the form:} \]

\[ \implies \text{The } \textbf{electronic density} \text{ is defined as the number of electrons per unit volume in a given state. It is designated by } \rho(r) \text{: the electronic density } \rho(r) \text{ must be related in some way with } \Psi^*\Psi \]
3.2 Density matrices

3.2.1 Reduced density matrices

- The ultimate goal of Quantum Chemistry is to solve the Schrödinger equation:

\[
\hat{H} |\Psi (x_1, x_2, \ldots, x_N)\rangle = E |\Psi (x_1, x_2, \ldots, x_N)\rangle = \begin{cases} 
|\Psi\rangle \equiv \text{Wavefunction} \\
\hat{H} \equiv \text{Hamiltonian operator} \\
E \langle \Psi \rangle \equiv \text{Functional of } \Psi
\end{cases}
\]

**Motivation:** the wavefunction \( \Psi \) depends on the spatial and spin coordinates of the \( N + M \) particles of the system \( (N+M) \) while \( \hat{H} \) is a two-body operator only:

\[
\hat{H} = -\frac{1}{2} \sum_{i}^{N} \nabla_{i}^{2} - \sum_{A}^{M} \sum_{i}^{N} \frac{Z_{A}}{r_{iA}} + \sum_{i<j}^{N} \frac{1}{r_{ij}}
\]

Does it sound reasonable to deal with a two-particle \((r_1, r_2)\) function coming from \( \Psi \), yet containing all the relevant physical information?

- The **density matrix** of order \( N \) and \( p \), respectively, is conveniently defined as:

\[
\gamma_{N} (x_1', x_2', \ldots, x_N'; x_1, x_2, \ldots, x_N) = \Psi (x_1', x_2', \ldots, x_N') \Psi^* (x_1, x_2, \ldots, x_N), \quad (3.11)
\]

and

\[
\gamma_{p} (x_1', \ldots, x_p'; x_1, \ldots, x_p) = \left( \begin{array}{c}
N \\
p
\end{array} \right) \int \cdots \int \gamma_{N} (x_1', x_2', \ldots, x_N'; x_1, x_2, \ldots, x_N) \, dx_{p+1} \cdots dx_{N} \quad (3.12)
\]
\[ \Rightarrow \text{If } p < N, \text{ one deals with } \textbf{reduced density matrices} \text{ instead.} \]

- Most importantly, we mention:

\[
\begin{align*}
\gamma_2 (x'_1, x'_2; x_1, x_2) &= \frac{N(N-1)}{2!} \int \cdots \int \Psi (x'_1, x'_2, \ldots, x_N) \Psi^* (x_1, x_2, \ldots, x_N) dx_3 \ldots dx_N, \\
\gamma_1 (x'_1; x_1) &= N \int \cdots \int \Psi (x'_1, x_2, \ldots, x_N) \Psi^* (x_1, x_2, \ldots, x_N) dx_2 \ldots dx_N
\end{align*}
\]  

- Integrating over spin, they simplify to:

\[
\begin{align*}
\rho_2 (r'_1, r'_2; r_1, r_2) &= \int \gamma_2 (r'_1 s_1, r'_2 s_2; r_1 s_1, r_2 s_2) ds_1 ds_2, \\
\rho_1 (r'; r) &= \int \gamma_1 (r'_1 s_1; r_1 s_1) ds_1
\end{align*}
\]

having as diagonal elements, \( r'_i = r_i \), the functions \( \rho(r) \) and \( \rho_2 (r_1, r_2) \), which integrates to \( \frac{N(N-1)}{2} \) and \( N \), respectively.

- The expectation value \( E = \langle \Psi | \hat{H} | \Psi \rangle \) transforms now into:

\[
E = -\frac{1}{2} \int [\nabla^2 \rho_1 (r'; r)]_{r'=r} dr + \int v(r) \rho(r) dr \\
+ \int \int \frac{1}{r_{12}} \rho_2 (r_1, r_2) dr_1 dr_2,
\]

noticing that \( E [\rho_2] \). Problem: \( \rho_2 \) must come from a function \( |\Psi\rangle \) physically well-behaved \((N\text{-representability})\), but we do not know the necessary and sufficient conditions for it yet.
\textbf{Representation:} the expectation value of the kinetic energy operator, $\hat{T} = -\frac{1}{2} \sum_i^N \nabla_i^2 = \sum_i^N \hat{t}(r_i)$ can be expressed as:

$$\langle \Psi | \hat{T} | \Psi \rangle = \int \cdots \int \Psi^* (x_1, x_2, \ldots, x_N) \left| \sum_i^N \hat{t}(r_i) \right| \Psi (x_1, x_2, \ldots, x_N) dx_1 dx_2 \ldots dx_N$$

$$= N \int d\mathbf{x} \left[ \hat{t}(\mathbf{r}) \int \Psi^* (\mathbf{x}', x_2, \ldots, x_N) \Psi (\mathbf{x}_1, x_2, \ldots, x_N) dx_2 \ldots dx_N \right]_{\mathbf{x}' = \mathbf{x}}$$

$$= \sum_{s_i} \int \left[ \hat{t}(\mathbf{r}) \gamma_1 (\mathbf{r}', \mathbf{r}) \right]_{\mathbf{r}' = \mathbf{r}} d\mathbf{r} = -\frac{1}{2} \int \left[ \nabla^2 \gamma_1 (\mathbf{r}', \mathbf{r}) \right]_{\mathbf{r}' = \mathbf{r}} d\mathbf{r}$$

\[ \hat{T} = \frac{1}{2} \sum_i^N \nabla_i^2 \]

\[ \gamma_1 (\mathbf{r}', \mathbf{r}) = \rho (\mathbf{r}) \sum_{s_i} \int \left[ \hat{t}(\mathbf{r}) \gamma_1 (\mathbf{r}', \mathbf{r}) \right]_{\mathbf{r}' = \mathbf{r}} d\mathbf{r} \]

$\rho (\mathbf{r})$ is the individual particle density, $\gamma_1 (\mathbf{r}', \mathbf{r})$ is the pair density.

- Physical interpretation of $\rho_2 (\mathbf{r}_1, \mathbf{r}_2)$: \textbf{electronic pair density}, that is, the number of pairs multiplied by the probability density of finding a particle at $\mathbf{r}_1$ when there is another at $\mathbf{r}_2$. Clearly,

$$\int \int \rho_2 (\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \frac{N(N-1)}{2}, \quad (3.18)$$

with the further factorisation:

$$\frac{1}{2} \rho_2 (\mathbf{r}_1, \mathbf{r}_2) = \rho (\mathbf{r}_1) \rho (\mathbf{r}_2) [1 + F (\mathbf{r}_1, \mathbf{r}_2)]$$

- The motion of two particles is said to be \textit{statistically uncorrelated} if:

$$\rho_2 (\mathbf{r}_1, \mathbf{r}_2) = \rho (\mathbf{r}_1) \rho (\mathbf{r}_2) \quad (3.19)$$

$\Rightarrow$ Thus, $F (\mathbf{r}_1, \mathbf{r}_2)$ is a \textit{pair correlation function} incorporating all non-classical effects.

- The conditional probability of finding a particle at $\mathbf{r}_2$ \textit{if there is another particle at $\mathbf{r}_1$} is defined as:

$$\Omega (\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho_2 (\mathbf{r}_1, \mathbf{r}_2)}{\rho (\mathbf{r}_1)} \quad (3.20)$$
• The **exchange-correlation hole** encodes a great deal of information, and it is defined as:

\[
h_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)} - \rho(\mathbf{r}_2) = \rho(\mathbf{r}_2) F(\mathbf{r}_1, \mathbf{r}_2) \tag{3.21}
\]

• The \(h_{xc}\) has been thoroughly employed to develop physically acceptable models since:

\[
\int h_{xc}(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_2 = \int \frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)} \, d\mathbf{r}_2 - \int \rho(\mathbf{r}_2) \, d\mathbf{r}_2 = -1 \tag{3.22}
\]

\(\Rightarrow\) Physical interpretation: if an electron is known to be at position \(\mathbf{r}_1\), it must be missing from everywhere else in the system.

• The hole can be split into an exchange and a correlation part, also known as the **Fermi hole** and **Coulomb hole**, \(h_{xc}(\mathbf{r}_1, \mathbf{r}_2) = h_x(\mathbf{r}_1, \mathbf{r}_2) + h_c(\mathbf{r}_1, \mathbf{r}_2)\), satisfying:

\[
\int h_x(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_2 = -1, \quad \int h_c(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_2 = 0 \tag{3.23}
\]

\(\Rightarrow\) This is motivated by the HF picture (only the total hole has a real meaning).

• The Fermi hole is mainly due to the antisymmetry of the wavefunction and affects the behaviour of electrons of the same spin. The Coulomb hole contains all remaining many-body effects (which also affect electrons of the opposite spin) and describes how electrons try to avoid one another due to their Coulomb repulsion.

• The electron-electron term of \(E = \langle \Psi| \hat{H} |\Psi \rangle\) had been transformed into:

\[
V_{ee} = \int \int \frac{1}{r_{12}^2} \rho_2(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2 \tag{3.24}
\]
• The electron-electron interacting energy $V_{ee}$ can be expressed now as:

$$
\int \int \frac{1}{r_{12}} \rho_2 (r_1, r_2) \, dr_1 \, dr_2 = \frac{1}{2} \int \int \frac{\rho (r_1) \rho (r_2)}{r_{12}} \, dr_1 \, dr_2 \quad (3.25)
$$

$$
+ \frac{1}{2} \int \int \frac{\rho (r_1) h_{xc} (r_1, r_2)}{r_{12}} \, dr_1 \, dr_2
$$

• In short, we can decompose $V_{ee} = U [\rho] + E_{xc}[\rho, h(\rho)]$ as a sum of a classical and a non-classical term.

$$
\implies \text{The concept of the exchange-correlation hole has been widely used for the derivation of many of the coded expressions.}
$$

### 3.2.2 The electronic density and its properties

• Motivation: if the computational cost for a molecule A is $N^k$, for the corresponding dimer A $\cdots$ A will be $(2N)^k$, $k$ depending on the chosen method,

<table>
<thead>
<tr>
<th>Method</th>
<th>CCSDT</th>
<th>CCSD(T)</th>
<th>CCSD</th>
<th>$E[\rho_2]$</th>
<th>MP2</th>
<th>HF</th>
<th>$E[\rho]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$:</td>
<td>8</td>
<td>7</td>
<td>6</td>
<td>6</td>
<td>5</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>

• The electronic density corresponding to a normalized wavefunction $\Psi$ is defined by the expectation value of the operator $\hat{\rho}(r) =$
\[ \sum_i^N \delta (\hat{r}_i - \mathbf{r}), \] that is:

\[ \rho(\mathbf{r}) = \langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle = \int \cdots \int \Psi^* (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \hat{\rho} (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \ldots d\mathbf{r}_N, \]

\[ = \sum_i^N \int \cdots \int \Psi^* (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \delta (\hat{r}_i - \mathbf{r}) \Psi (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \ldots d\mathbf{r}_N, \]

\[ = \sum_i^N \int \cdots \int \Psi^* (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \delta (\hat{r}_i - \mathbf{r}) \Psi (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \ldots d\mathbf{r}_N, \]

\[ = N \int \cdots \int \Psi^* (\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \Psi (\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \, d\mathbf{r}_2 \ldots d\mathbf{r}_N \quad (3.26) \]

\[ \Rightarrow \text{Note that the definition of the } \delta \text{-function used is:} \]

\[ \int \delta (\hat{r}_1 - \mathbf{r}) \, f(\mathbf{r}_1) \, d\mathbf{r}_1 = f(\mathbf{r}) \quad (3.27) \]

\[ \Rightarrow \text{Also note that: (i) the last steps stem from the Pauli principle, all particles are indistinguishable, and then we can replace } \mathbf{r}_i \text{ by } \mathbf{r}_1; \text{ and (ii) the sum is over identical numbers, so it becomes a mere multiplication by } N. \]

- **Interpretation:** The electronic density integrates a huge amount of information, and only the data concerning the density distribution of a single electron remains. When one multiplies by \( N \), then \( \rho(\mathbf{r}) \) indeed accounts for the combined density of all electrons.

- **Properties:** The electronic density offers large and valuable informa-
tion about the $N$-electron system, such as

\begin{align*}
  i) & \quad \int \rho(\mathbf{r}) d\mathbf{r} = N, \quad \text{(normalisation condition)} \\
  ii) & \quad \frac{\partial}{\partial r} \tilde{\rho}(r)|_{r=R_i} = -2Z_i \tilde{\rho}(r), \quad \text{(nuclear cusp)} \\
  iii) & \quad \frac{1}{2} \int \left( \nabla \sqrt{\rho(\mathbf{r})} \right)^2 \leq T, \quad \text{(bracketing kinetic energy)} \\
  iv) & \quad \rho(r)|_{r=0} \sim e^{-2Zr}, \quad \text{(asymptotic behaviour)} \\
        & \quad \rho(r)|_{r=\infty} \sim e^{-2\sqrt{2}r}
\end{align*}

• Simply stated, it seems that $\rho(\mathbf{r})$ contains \textit{a priori} enough information to build the Hamiltonian operator $\hat{H}$:
  \begin{itemize}
    \item Its cusps will occur at the positions of the nuclei.
    \item Its gradients at the nuclei would provide the nuclear charge $Z$.
    \item Its integration over all the space will lead to $N$.
  \end{itemize}

• Contrarily to $\Psi$ or $\rho_2$, $\rho(\mathbf{r})$ is \textbf{observable}, and can be accessed by X-ray diffraction patterns:

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{image1.png}
\caption{X-ray diffraction patterns of the density $\rho(\mathbf{r})$.}
\end{figure}

• The density $\rho(\mathbf{r})$ is further related with other interesting properties as the \textbf{molecular electrostatic potential} (MEP):

\begin{equation}
  V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (3.28)
\end{equation}

with $\mathbf{r}'$ the position vector of the charge distribution leading to the electrostatic potential at $\mathbf{r}$. Some criteria is still needed:
- $V(r) > 0$ (Red: $e^-$-richest regions)
- $V(r) < 0$ (Blue: $e^-$-poorest regions)

- The MEP is a useful magnitude for explaining supramolecular issues. For the unsubstituted tetracene (right) and selectively functionalised dicyano-tetracene (left), the difference in packing (slipped cofacial vs. herringbone structures, bottom) can be rationalised by the analysis of the MEP contour plots (ie. leading interactions, top).
Example: show that the ground state \((^1S)\) of the He atom fulfills the above properties of the density, with \[\phi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}\]. A common starting point is to write:

\[\rho(r) = N \int \cdots \int |\Psi|^2 dr_2 \ldots dr_N;\]

and

\[|\Psi\rangle = \phi_{1s}(1)\phi_{1s}(2)\frac{1}{\sqrt{2}} \left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right],\]

restricted to \(\langle \phi_{1s}|\phi_{1s}\rangle = 1\) and \(\langle \alpha|\beta\rangle = \delta_{\alpha\beta}\). Furthermore,

\[|\Psi|^2 = \phi_{1s}^2(1)\phi_{1s}^2(2), \quad \text{and} \quad \rho(r) = N\phi_{1s}^2(1) \int \phi_{1s}^2(2) dr_2 = 2\phi_{1s}^2\]

Hence, if \(\int \rho(r) dr = N\) equivalates in this case to demonstrate \(\langle \phi_{1s}|\phi_{1s}\rangle = 1\),

\[\langle \phi_{1s}|\phi_{1s}\rangle = 4\pi \int_0^\infty r^2 \phi_{1s}^* r \phi_{1s} dr = 4 \left(\frac{Z}{a_0}\right)^3 \int_0^\infty r^2 e^{-2Zr/a_0} dr = 1\]

\[\implies \text{Corollary: readily following the previous statement, it can be shown if } |\Psi\rangle \text{ is a Slater determinant, } \]

\[\rho(r) = \sum_i^N |\phi_i(r)|^2.\]

If we define the radial density \(D(r)\) for the He atom as:

\[D(r) = r^2 \int_0^{2\pi} \int_0^\pi \sin \theta d\theta d\phi \rho(r), \quad \text{then} \quad \bar{\rho}(r) = \frac{D(r)}{4\pi r^2},\]

that allows us to choose as origin \((r = 0)\) the position of atomic nuclei. The concept of \(\bar{\rho}\) is applicable now to spherically symmetrical atoms as well as to atoms embedded in molecules. Thus,

\[\frac{\partial}{\partial r} \bar{\rho}(r) = \frac{1}{4\pi r^2} \left[ \frac{\partial D(r)}{\partial r} - \frac{2}{r} D(r) \right],\]

with

\[D(r) = 8r^2 \left(\frac{Z}{a_0}\right)^3 e^{-2Zr/a_0},\]

showing easily than \(\lim_{r \to 0} \left[ \frac{\partial}{\partial r} + 2Z \right] \bar{\rho}(r) = 0\).
3. The electronic density is the key (I): fundamental definitions and concepts

3.3 Summary and conclusions

1. Key concepts: functions, operators, functionals, $\Psi^*\Psi$, etc.

2. Importance of magnitudes as $\rho(r)$ and $\rho_2(r_1, r_2)$ in Quantum Chemistry, which, of course, keep known hierarchical relationships:

$$\rho(r) = \frac{2}{N-1} \int \rho_2(r_1, r_2) \, dr_2$$

$\implies$ They are known to contain relevant information about the $N$-electron system.

3. The Schrödinger equation can be reformulated as:

$$\left\langle \frac{E[\Psi]}{E[\rho_2]} \right\rangle \equiv E[\rho^2] \equiv E[\rho] \ ?$$

$\text{cost: } 4^{N+M} \rightarrow N^k \ (k \geq 5)$  $\text{cost: } N^6$  $\text{cost: } N^4$

4. The next step emerges in a natural way: try to infer if $E[\rho]$ is a valid (praiseworthy) idea.
Chapter 4

The electronic density is the key (II): primitive models

4.1 Historic evolution

4.1.1 Milestones in the development of DFT

- **1927.** Thomas-Fermi model (kinetic energy $T_{TF}[^{\rho}]$).
- **1930.** Thomas-Fermi-Dirac model (exchange energy $E_{x}[^{\rho}]$).
- **1951.** Slater $X_{\alpha}$ method (improved exchange energy $E_{x}[^{\rho}]$).
- **1964.** Hohenberg-Kohn theorems: rigorous proof than $E[^{\rho}]$.
- **1965.** Kohn-Sham approach: prescriptions for the mathematical form of $E[^{\rho}]$. Introduction of $E_{c}[^{\rho}]$ and $T[\phi(^{\rho})]$ functionals.
- **1980-1990.** More accurate and sophisticated models for $E_{x}[^{\rho}]$ and $E_{c}[^{\rho}]$. A lot of knowledge about its expression is gained.
- **From 1993.** A new class of methods emerges: hybrid functionals. Blooming of applications to all kind of systems.
- **1998.** NOBEL prize of Chemistry to W. Kohn recognising the deep impact of DFT in the whole scientific community.
- **From 2000.** High-degree of sophistication for $E_{x}[^{\rho}]$ y $E_{c}[^{\rho}]$. Nanotechnological and materials science applications.

4.2 Thomas–Fermi–Dirac model

4.2.1 Starting point: Thomas-Fermi

- A pioneering semi-classical theory:
  - A semi-classical theory (statistics of particles): forerunner of modern DFT thanks to the introduction of $\rho(r)$ (circumventing $\Psi$) for the first time in history.
  - Correct behaviour in the limit of $Z \rightarrow \infty$.
  - Developed independently, although almost simultaneously, of the Schrödinger equation.
  - Poor quantitative predictions in real systems, despite (hopefully) being a sound educational model.


- Derivation of the theory:
  - The energy\(^1\) of a classical particle (actually the fastest) in a common field $V(r)$ is $E = \frac{1}{2} p^2(r) + V(r)$. Consider next than\(^2\) $dN = 2d\nu dp$: the maximum number of particles allowed, if each one can be housed in a sphere of radius $p_i$, is $N = 2V (\sum \frac{4 \pi}{3} p_i^3) = 2V \frac{4 \pi}{3} p^3$.

\(^1\) Atomic units: $e^2 = \hbar = m = 1$

\(^2\) Every cell in phase space houses up to 2 electrons with opposite spins
○ Consider a region of the electronic cloud close to the position given by \( \mathbf{r} \), thanks to the fact that \( N = \rho(\mathbf{r})V \), the number of particles per unit volume is

\[
\rho(\mathbf{r}) = \frac{N}{V} = \frac{8\pi}{3} p^3(\mathbf{r}).
\]

○ Inverting the above equation, \( p = \left( \frac{3}{8\pi} \right)^{1/3} \rho(\mathbf{r})^{1/3} \), and substituting into the energy expression, one has:

\[
E = \frac{1}{2} \left( \frac{3}{8\pi} \right)^{2/3} \rho(\mathbf{r})^{2/3} + V(\mathbf{r}) \quad (4.1)
\]

\( \implies \) Consequence: the density \( \rho \) at position \( \mathbf{r} \) seems to be solely determined by the potential energy at the same point (plus knowledge of \( E \)); a local relation which is not completely correct.

○ The kinetic energy density \( (t = \frac{\mathbf{p}^2}{2}) \) of the \( N \) particles will be:

\[
t = \frac{1}{V} \int \frac{p^2}{2} dN = \frac{1}{V} \int_0^p \frac{p^2}{2} 8\pi p^2 V dp = 4\pi \int_0^p p^4 dp = \frac{4\pi}{5} p^5; \quad (4.2)
\]

note that \( \rho = \frac{N}{V} = \frac{8\pi}{3} p^3 \) (to go from \( dN \) to \( dp \)).

○ Substituting \( p = \left( \frac{3}{8\pi} \right)^{1/3} \rho(\mathbf{r})^{1/3} \) in the above expression, one has:

\[
t(\mathbf{r}) = \frac{3}{10} \left( \frac{3}{8\pi} \right)^{2/3} \rho(\mathbf{r})^{5/3} \quad (4.3)
\]

○ The kinetic energy can be recovered upon integration:

\[
T = \int t(\mathbf{r}) d\mathbf{r} = C_{TF} \int \rho(\mathbf{r})^{5/3} d\mathbf{r} \quad (4.4)
\]

• The corresponding variational principle is:

○ The potential energy is due to the interaction with an external field, \( V_{Ne}(\mathbf{r}) = -\frac{Z}{r} \), and electrostatic interaction of the electron
density with itself, \( V_{ee}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \), so that the total energy of the electron system is:

\[
E = C_{TF} \int \rho(\mathbf{r})^{5/3} d\mathbf{r} + \int V_{Ne}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \rho(\mathbf{r})V_{ee}(\mathbf{r})d\mathbf{r}
\]

(4.5)

- We now search for the particle distribution minimising the energy, subject to the normalisation condition \( \int \rho(\mathbf{r})d\mathbf{r} = N \), that is \( \delta (E - \mu N) = 0 \). The condition becomes:

\[
\frac{5}{3} C_{TF} \rho(\mathbf{r})^{2/3} - \frac{Z}{r} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \mu,
\]

(4.6)

with \( \mu \) a constant and \( \phi(\mathbf{r}) \) the electrostatic potential at point \( \mathbf{r} \) due to the nucleus and the entire electron distribution.

\[ \implies \text{Even when reality is oversimplified, this is an exquisitely simple model!} \]

### 4.2.2 Exchange: Thomas-Fermi-Dirac

- What is wrong with the Thomas-Fermi theory?

  - So far, we have considered electrostatic interactions of each electron with the whole background charge.

  - Consequence: although some statistics of particles are introduced, an effect of a purely quantum-mechanical origin (anti-symmetry principle) is fully neglected (semi-classical theory).

    - We have neglected the Pauli principle, in a sense that there is no preference in electron-electron interaction with respect to spin.

    - For an electron with spin “up”, the charge density of spin “down” should be reduced in its neighbourhood.

    - Since this “down” density is not due to the electron in question, it can be handled as a smooth distribution of charge.
This additional interaction (the exchange energy) lowers the total energy since it puts the electron more apart.

This energy can be casted, at least approximately, in a form explicitly dependent on density too.

- Derivation of the theory:
  - Let’s assume that the exchange energy density $e_x$ can be also expressed as a power law of $\rho(r)$, in the form:
    \[ e_x \propto (e^2)^l (\rho)^n \]  
    The energy density $(e_x)$ must have the dimension $[\text{ML}^2\text{T}^{-2}]$ per unit volume $[\text{ML}^{-1}\text{T}^{-2}]$.
  - On the other hand, from Coulomb’s law, the dimension of $e^2$ should be $[\text{ML}^3\text{T}^{-2}]$. Since $\rho$ is a number per unit volume, its dimensionality is $[L^{-3}]$. Then, the second member above has dimensions $[(\text{ML}^3\text{T}^{-2})^l L^{-3n}]$.
  - Equating powers of $M$ or $T$, we arrive to the result $l = 1$. Furthermore, equating powers of $L$ we have that $L^{-1} = L^3L^{-3n}$, and then $n = 4/3$:
    \[ e_x = -C_x \rho(r)^{4/3}, \text{ and again } E_x = -C_x \int \rho(r)^{4/3} dr \]  
    (4.8)
  - Consequence: $C_x$ cannot be obtained from dimensional analysis. Further modeling leads to $C_x = \frac{2}{3} \left( \frac{3}{\pi} \right)^{1/3}$.

- Further refinements of the model:
  - Gradient expansions: von Weizsäcker (1935) used plane waves to have an inhomogeneous situation and found the gradient correction term for two particles occupying the same orbital,
    \[ T_W[\rho] = \frac{1}{2} \int \left[ \nabla \rho^{1/2}(r) \right]^2 dr = \frac{1}{8} \int \frac{\nabla \rho(r) \cdot \nabla \rho(r)}{\rho(r)} dr \]  
    (4.9)
    \[ \Rightarrow \text{The kinetic energy density can be thus approached as:} \]
    \[ t(r) = C_{TF} \rho(r)^{5/3} + \frac{1}{8} \frac{\nabla \rho(r) \cdot \nabla \rho(r)}{\rho(r)} + \ldots \]  
    (4.10)
○ Corrections to $E_x (X_\alpha)$: J. Slater (1951) proposed to introduce an adjustable parameter ($\alpha$), depending on each atom, to improve the exchange energy:

$$E_x = -\frac{9}{4} \alpha \left( \frac{3}{4\pi} \right)^{4/3} \int \rho(r)^{4/3} dr,$$

which can be optimised (averaged) to become $\alpha = 0.667$

4.3 Summary and conclusions

• Essential limitations of the Thomas-Fermi-Dirac model

1. There is no chemical binding in the Thomas-Fermi theory, the total energy of two close (interacting) atoms is never lower than that of two distant atoms (1962): $E_{\text{molecule}} > \sum E_{\text{atoms}}$.

2. A solution for neutral and positively charged ions (no bounded solutions for negative ions) always exists.

3. The total atomic energy is too low (54 % for H, 35 % for He, $\sim 15 \%$ for heavy atoms $Z \sim 100$). No shell structure of atoms appears.

4. Asymptotic is wrong: $\rho \propto r^{-6}$ for $r \to \infty$, in reality $\rho \propto e^{-r}$; $\rho \propto r^{-3/2}$ (diverges) for $r \to 0$, in reality $\rho(0)$ is finite.

5. In Thomas-Fermi-Dirac the exchange energy is underestimated by around 10 % BUT the total energy (already too low) is lowered even further. There are still no bound negative ions.

6. The correction due to von Weizsäcker works better: asymptotics are right now, negative ions are formed and molecules may bind. However, further gradient expansions diverge and quantitative applications are not accurate enough.

• Main features to be remarked:

1. It seems that the variable $\rho(r)$ enters in a natural way into any intended microscopic treatment of matter (even at a semi-classical level).
2. We have seen how both the kinetic and exchange energies can be expressed as true density functionals, $T[\rho]$ and $E_x[\rho]$, missing correlation effects at this point. It might be supposed that the total energy will be a functional of the density too.

3. The next step appears clear: to show that $E[\rho]$ uniquely exists and provide formal frameworks to extract accurate expression to calculate it.
Chapter 5

Hohenberg-Kohn-Sham
formalism (I): theoretical
framework

5.1 Hohenberg-Kohn theorems

5.1.1 First Hohenberg-Kohn theorem: existence

- Statement: the ground state density $\rho(r)$ uniquely determines the
  external potential, and then the ground state of a system completely.

- Consequence: any expectation value for the ground state of an $N$-
  electron system, including the energy, can be in principle exactly
  calculated from the ground state density.

- Proof: it is (disarmingly simple) established from *reductio ad
  absurdum* and following the steps:

1. Let’s assume that $\rho_0(r)$ is the exact density for a non-degenerate
  ground-state.

2. Let’s assume that for such density there exist two external
  potentials, $v(r)$ and $v'(r)$, obviously corresponding to two dif-
  ferent Hamiltonians, $\hat{H}$ and $\hat{H}'$, also existing two di-
  ments wave-
  functions: $|\Psi_0\rangle$ and $|\Psi'_0\rangle$. The corresponding energies will be
given by:

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \quad \text{and} \quad E_0' = \langle \Psi_0' | \hat{H}' | \Psi_0' \rangle \quad (5.1)$$

3. Let’s calculate the expectation value for the energy of $|\Psi_0'\rangle$ with the Hamiltonian $\hat{H}$, using the variational principle:

$$E_0 < \langle \Psi_0' | \hat{H} | \Psi_0' \rangle = \langle \Psi_0' | \hat{H}' | \Psi_0' \rangle + \langle \Psi_0' | \hat{H} - \hat{H}' | \Psi_0' \rangle \quad (5.2)$$

$$= E_0' + \int \rho_0(r) [v(r) - v'(r)] \, dr$$

4. Let’s exchange now the superscripts:

$$E_0' < \langle \Psi_0 | \hat{H}' | \Psi_0 \rangle = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 | \hat{H}' - \hat{H} | \Psi_0 \rangle \quad (5.3)$$

$$= E_0 + \int \rho_0(r) [v'(r) - v(r)] \, dr$$

5. Adding equations (5.2) and (5.3) we get a contradiction:

$$E_0 + E_0' < E_0' + E_0', \quad 0 < 0 \quad (5.4)$$

and the external potential is thus a unique functional of $\rho_0(r)$.

In other words: two $N$-electron systems described by their respective $\hat{H}$, and whose external potentials differ in more than a constant, cannot have a ground state with the same electronic density.

P. Hohenberg (1934–) W. Kohn (1923–)
• Analysis (I):
  ○ In a schematic-like picture, we have that:

  \[ \text{known } \rho(\mathbf{r}) \rightarrow v(\mathbf{r}), N \rightarrow \hat{H} \rightarrow E[N, v(\mathbf{r})] \rightarrow E[\rho(\mathbf{r})] \]

  ○ Hence, we can represent the energy as a density functional:

  \[
  E[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F[\rho(\mathbf{r})] \\
  = \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + T[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})]
  \]

  ○ And knowing additionally that \( U[\rho(\mathbf{r})] \equiv J[\rho(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r} \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \), we can decompose \( V_{ee}[\rho] \) into:

  \[
  V_{ee}[\rho(\mathbf{r})] = U[\rho(\mathbf{r})] + E_{ee}[\rho(\mathbf{r})]
  \]

• Analysis (II):

  ○ Remarks: the 1st. theorem forbids that two different systems share the same density, but does not guarantee that, given a certain density, there exists a system with such \( \rho \).

  \[ \Rightarrow \text{In such a case, both the functionals } E[\rho] \text{ and } F[\rho] \text{ will remain as undefined.} \]

  \[ \Rightarrow \text{In principle, all but few pathological densities, could be the densities of some physical or hypothetical system.} \]

  ○ Remarks: \( v \)- and \( N \)-representability of \( \rho(\mathbf{r}) \). If \( \rho \in \mathcal{S}_N \),

  \[ \mathcal{S}_N = \{ \rho(\mathbf{r}) | \rho(\mathbf{r}) \text{ comes from a non-degenerate ground-state} \} \]
is \( \nu \)-representable\(^1\) (barely known conditions). If \( \rho \in S'_N \),
\[
S'_N = \left\{ \rho(r) \mid \rho(r) \geq 0; \int \rho(r) dr = N; \rho(r)^{1/2} \in L^2 = \int |\nabla \rho(r)^{1/2}|^2 dr < \infty \right\},
\]
is \( N \)-representable\(^2\). The \( N \)-representability is always assured when \( \rho \leftarrow |\Psi\rangle \).

\section*{5.1.2 Second Hohenberg-Kohn theorem: variational principle}

- **Statement**: for any trial density, \( \tilde{\rho}(r) \), such as \( \tilde{\rho}(r) \geq 0 \) and for which \( \int \tilde{\rho}(r) dr = N \), we have that \( E_0 \leq E[\tilde{\rho}(r)] \).
- **Consequence**: the minimal value for the functional \( \int v(r) \rho(r) dr + F[\rho(r)] \) is obtained when \( \rho(r) \) is the correct (ground state) density associated to the external potential \( v(r) \).
- **Proof**: it is established from the conventional variational principle and following the steps:

1. Let’s assume that certain trial density \( \tilde{\rho}(r) \) comes from the corresponding \( |\tilde{\Psi}\rangle \).
2. Let’s apply the variational principle to warrant that \( \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle \geq \langle \Psi | \tilde{\hat{H}} | \Psi \rangle \).
3. Let’s replace the operator \( \hat{H} \) by \( \tilde{\hat{H}} = \hat{H} - \sum_i N_i [\tilde{v}(r_i) - v(r_i)] \) to obtain:
\[
\langle \tilde{\Psi} | \tilde{\hat{H}} | \tilde{\Psi} \rangle - \int [\tilde{v}(r) - v(r)] \tilde{\rho}(r) dr \geq \langle \Psi | \tilde{\hat{H}} | \Psi \rangle \quad (5.7)
\]
4. Using the result of the 1st theorem, we can write:
\[
E[\tilde{\rho}(r)] - \int [\tilde{v}(r) - v(r)] \tilde{\rho}(r) dr \geq E[\rho(r)] \quad (5.8)
\]

\(^1\)How do I know that \( \rho(r) \) is the ground-state density of some \( v(r) \)?
\(^2\)How do I know that \( \rho(r) \) comes from a well-behaved \( \Psi \)?
5. By means of the definition $E[\rho(r)] = \int \rho(r)v(r)dr + F[\rho(r)]$, we finally arrive to:

$$
\int \tilde{\rho}(r)\tilde{v}(r)dr + F[\tilde{\rho}(r)] - \int [\tilde{v}(r) - v(r)]\tilde{\rho}(r)dr \geq E[\rho(r)]
$$

$$
F[\tilde{\rho}(r)] + \int v(r)\tilde{\rho}(r)dr \geq E[\rho(r)]
$$

- Analysis (I):
  - If the energy can be made stationary with respect to changes in the density, the use of a Lagrange multiplier,

$$
\delta \{ E[\rho(r)] - \mu N \} = 0,
$$

allows to introduce the electronic **chemical potential** as $\mu = \left( \frac{\delta E}{\delta N} \right)_{v(r)}$

- Analysis (II): The variational principle

  - Starting from $\delta \{ E[\rho(r)] - \mu N \} = 0$,

$$
\delta E[\rho(r)] - \mu \delta \left\{ \int \rho(r)dr \right\} = 0
$$

  - Applying the principles of variational calculus\(^3\) we obtain:

$$
\int \frac{\delta E[\rho(r)]}{\delta \rho(r)} \delta \rho(r)dr - \mu \int \delta \rho(r)dr = \int \left\{ \frac{\delta E[\rho(r)]}{\delta \rho(r)} - \mu \right\} \delta \rho(r)dr = 0
$$

  - Goals: (i) to establish the appropriate conditions for the minimisation; and (ii) to define the value of $\mu$ at the global minimum.

$$
\mu = \frac{\delta E[\rho(r)]}{\delta \rho(r)} = v(r) + \frac{\delta F[\rho(r)]}{\delta \rho(r)}
$$

\(^3\)We remind that $\delta F[\phi] = F[\phi + \delta \phi] - F[\phi] = \int \frac{\delta F}{\delta \phi} \delta \phi(x)dx$. 
An analogy with (chemical potential) the field of thermodynamics:

$$\mu = \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_j \neq n_i} = \left( \frac{\partial H}{\partial n_i} \right)_{S,P,n_j} = \left( \frac{\partial A}{\partial n_i} \right)_{T,V,n_j} = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j}$$

- Analysis (III):

  - Remarks: the domain of the functional $F[\rho(r)]$ has been restricted to the space $S'_N$, $F[\rho(r)]$, in a way so that the functional:

    $$E[\Psi] = \min_{|\Psi|} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V}_{Ne} | \Psi \rangle$$  

    is replaced now by:

    $$E[\rho] = \min_{\rho} \left\{ F[\rho(r)] + \int v(r)\rho(r)dr \right\},$$

    with:

    $$F[\rho(r)] = \min_{|\Psi| - \rho} \langle \Psi[\rho(r)] | \hat{T} + \hat{V}_{ee} | \Psi[\rho(r)] \rangle$$

    By the 2nd theorem:

    $$F[\rho(r)] + \int v(r)\rho(r)dr \geq F[\rho_0(r)] + \int v(r)\rho_0(r)dr,$$

    but for arbitrary, $N$-representables, densities which is known as Levy-Lieb constrained search.

  - Remarks: the expressions for $T[\rho]$, $V_{ee}[\rho]$ and, therefore, $F[\rho]$

- $F[\rho]$ are unknown yet.

### 5.2 The Kohn-Sham orbitalic approach

#### 5.2.1 The Kohn-Sham (KS) hypothesis

- Basic premises: Kohn-Sham hypothesis (1)
5. Hohenberg-Kohn-Sham formalism (I): theoretical framework

- On $T$ (I): its estimate is particularly thorny, but the HF kinetic energy is largely accurate with respect to the exact energy, whose expression is,

$$T = \sum_{i}^{N} \langle \phi_{i} | -\frac{1}{2} \nabla_{i}^{2} | \phi_{i} \rangle$$  \hspace{1cm} (5.17)

- On $T$ (II): on the other hand, the kinetic energy of the early models,

$$T[\rho] = C_{TF} \int \rho(\mathbf{r})^{5/3} d\mathbf{r} + \ldots$$  \hspace{1cm} (5.18)

was affected by large errors and the gradient expansions did not converge (rail siding).

**Motivation:** would it not be possible to take advantage of the orbitalic Hartree-Fock formalism without contradicting any of the Hohenberg-Kohn theorems?

- Basic premises: Kohn-Sham hypothesis (II)

  - On $\{\phi_{i}\}$: if we take a **non-interacting particle system**\(^4\) as a reference, acting under the influence of an external potential $v_{e}(\mathbf{r})$, and satisfying\(^5\),

$$|\Psi_{KS}\rangle = (N!)^{-1/2}|\phi_{1}\phi_{2}\ldots\phi_{N}|,$$  \hspace{1cm} (5.19)

it is able to generate a $N$-representable density,

$$\rho_{KS}(\mathbf{r}) = \sum_{i}^{N} |\phi_{i}|^{2},$$  \hspace{1cm} (5.20)

\(^4\hat{H}_{s} = -\frac{1}{2} \sum_{i}^{N} \nabla_{i}^{2} + v_{e}(\mathbf{r})\)
\(^5\)Pauli principle
its energy will be given by:

\[ E = \sum_i^N \langle \phi_i | -\frac{1}{2} \nabla_i^2 | \phi_i \rangle + \sum_i^N \langle \phi_i | v_s(r) | \phi_i \rangle \]
\[ = \sum_i^N \langle \phi_i | -\frac{1}{2} \nabla_i^2 | \phi_i \rangle + \int v_s(r) \rho(r) dr \] (5.21)

○ On \( v_s(r) \): the system of \( N \) pseudo-particles remains tied thanks to the external potential \( v_s(r) \), and the \( \phi_i \) obey an SCF-like equation,

\[ \left\{ -\frac{1}{2} \nabla_i^2 + v_s(r) \right\} \phi_i = \epsilon_i \phi_i \] (5.22)

**In other words:** suppose that the particles move in some potential that give the same density \( \rho_{KS}(r) \) (fictitious, non-interacting particle system) as the real system \( \rho(r) \) (real, interacting particle system)

### 5.2.2 Basic equations of the Kohn-Sham model

- Kohn-Sham model: basic equations (I)

○ For a real system:

\[ E[\rho(r)] = \int \rho(r)v(r)dr + T[\rho(r)] + V_{ee}[\rho(r)], \] (5.23)

by the condition \( \rho_{KS}(r) = \rho(r) \), the Hohenberg-Kohn theorem
allows us to write:

\[
E[\rho(r)] = \int \rho(r)v(r)dr + T[\rho(r)] + V_{ee}[\rho(r)]
\]

(5.24)

\[
\equiv \sum_i \langle \phi_i | -\frac{1}{2}\nabla_i^2 | \phi_i \rangle + \int v_s(r)\rho(r)dr,
\]

\[\underbrace{T_s[\rho]}_{E_{xc}[\rho(r)]}\]

and to rewrite \(E[\rho(r)]\), after using \(v_s(r)\) as a fitting variable, like:

\[
E[\rho(r)] = \int \rho(r)v(r)dr + T_s[\rho(r)] + U[\rho(r)]
\]

: known

\[
+ (T[\rho(r)] - T_s[\rho(r)]) + (V_{ee}[\rho(r)] - U[\rho(r)])
\]

: unknown

\[
\frac{\delta E[\rho(r)]}{\delta \rho(r)} = v(r) + \delta T_s[\rho(r)] + \delta U[\rho(r)] + \delta E_{xc}[\rho(r)]
\]

: Kohn-Sham model: basic equations (II)

- Recovering\(^6\) the variational principle, \(\mu = \frac{\delta E[\rho(r)]}{\delta \rho(r)} = v(r) + \frac{\delta T_s[\rho(r)]}{\delta \rho(r)} + \frac{\delta U[\rho(r)]}{\delta \rho(r)} + \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)}\), we have that:

\[
\mu = \frac{\delta T_s[\rho(r)]}{\delta \rho(r)} + v(r) + \frac{\delta U[\rho(r)]}{\delta \rho(r)} + \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)}
\]

(5.25)

- Combining eqs. (5.21)-(5.22) with the above expression, the orbitals \(\phi_i\) must now obey the well-known **Kohn-Sham equations**:

\[
\left\{ -\frac{1}{2}\nabla_i^2 + v(r) + \int \frac{\rho(r')}{|r - r'|}dr' + v_{xc}(r) \right\} \phi_i = \epsilon_i \phi_i,
\]

(5.26)

with \(v_{xc} = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}\) the corresponding **exchange-correlation potential** and:

\[
v_s = v(r) + \int \frac{\rho(r')}{|r - r'|}dr' + v_{xc}(r)
\]

(5.27)

\(^6\)We remind that \(E[\rho(r)] = \int \rho(r)v(r)dr + T_s[\rho(r)] + U[\rho(r)] + E_{xc}[\rho(r)]\)
• Kohn-Sham model: basic equations (III)
  
  - Starting from $\hat{h}_{\text{eff}} \phi_i = \epsilon_i \phi_i$, multiplying by $\langle \phi_i^* \rangle$ and integrating, one arrives at:
    \[
    \langle \phi_i^* \rangle - \frac{1}{2} \nabla_i^2 \phi_i + \langle \phi_i^* \rangle v(r) \phi_i + \langle \phi_i^* \rangle \int \frac{\rho(r')}{|r - r'|} dr' \phi_i + \\
    \langle \phi_i^* \rangle v_{\text{xc}}(r) \phi_i = \epsilon_i,
    \]
    (5.28)
  
  - Summing up the $N$ values leads to:
    \[
    \sum_i \epsilon_i = T_s[\rho] + \int \rho(r)v(r)dr + 2U[\rho] + \int \rho(r)v_{\text{xc}}(r)dr,
    \]
    (5.29)
    and noticing that $E[\rho(r)] = T_s[\rho] + \int \rho(r)v(r)dr + U[\rho] + E_{\text{xc}}[\rho]$, the total energy also becomes:
    \[
    E[\rho(r)] = \sum_i \epsilon_i - U[\rho] - \int \rho(r)v_{\text{xc}}(r)dr + E_{\text{xc}}[\rho]
    \]
    (5.30)

• Kohn-Sham vs. Hartree-Fock model
  
  - If we compare both (HF and KS) one-particle equations, the exchange operator $\hat{K}(r, r')$ has been substituted by $v_{\text{xc}}(r)$:
    \[
    \text{HF:} \quad \left\{ -\frac{1}{2} \nabla_i^2 - \sum_{A,\alpha} Z_A Z_A \frac{\rho(r')}{|r - r'|} d_\alpha + \sum_j \int \phi_j(r') \phi_i(r) d_\alpha d_\alpha d_\alpha \right\} \phi_i = \epsilon_i \phi_i,
    \]
    (5.31)
    \[
    \text{KS:} \quad \left\{ -\frac{1}{2} \nabla_i^2 - \sum_{A,\alpha} Z_A Z_A \frac{\rho(r')}{|r - r'|} d_\alpha + \int v_{\text{xc}}(r) d_\alpha d_\alpha d_\alpha \right\} \phi_i = \epsilon_i \phi_i
    \]
    (5.32)
  
  - The similarities between models allows one to:

    (i) Take advantage of existing codes and implementation tricks, sharing a necessarily iterative resolution;
(ii) Treating closed- \( (N\) even: RKS) and open-shell systems 
\((N\) odd: UKS), which allows to apply the equations to the 
lowest energy system of a given symmetry (singlet, doublet, 
etc.)

- However, some **differences** still persist:
  
  (i) The KS wavefunction \( \Psi_{KS} = (N!)^{-1/2} |\phi_1 \phi_2 \ldots \phi_N| \) differs 
  from the HF one, as well as the corresponding \( \phi_i \)'s do.

  (ii) The meaning of the KS orbitals is unclear; however, they 
  are used as interpretative tools (as other one-electron orbitals).

  (iii) The HF exchange potential (non-local and non-multiplicative) 
  is substituted by an exchange-correlation potential (local and 
  multiplicative).

  (iv) In the HF theory, the diagonal elements\(^7\) \( K_{ii} \) \( U_{ii} \) mutually 
  cancel in an exact way, which does not usually happen 
  with the corresponding terms \( E_{xc}[\rho] \) and \( U[\rho] \): **self-interaction error**.

  (v) The spin contamination \( \langle \Psi | \hat{S}^2 | \Psi \rangle \) in unrestricted calculations is clearly not defined since \( |\Psi_{KS}\rangle \) is just a fiction to 
  describe the density.

  (vi) The computational cost of the HF methods is \( N^4 \), \( \langle \phi_i \phi_j || \phi_i \phi_j \rangle \), 
  while any \( F[\rho] \)-like term scales as \( N^3 \).

### 5.3 Summary and conclusions

1. Computational methodology applicable to every class of \( N \)-electron 
   system: universal functionals (in principle).

\(^7\)\( K_{ij} = \iint \hat{\phi}_i^*(r) \phi_j^*(r') \hat{\phi}_i(r') \phi_j(r) \ \frac{drdr'}{|r-r'|} \); \( U_{ij} = \iint \hat{\phi}_i^*(r) \phi_j^*(r') \phi_i(r) \phi_j(r') \ \frac{drdr'}{|r-r'|} \)
2. Key: to find a physically sound and easy to handle approach to $E_{xc}[\rho] \leftarrow E[\rho]$ and, consequently $u_{xc} = \delta E_{xc}[\rho]/\delta \rho(\mathbf{r})$.

3. We dispose of a quantum-chemical formalism $(\mu, \{\phi_i, \epsilon_i\})$ that can be used as an interpretative tool (chemical reactivity) and extended to excitation energies.

4. Computational advantages: (i) acceptable cost ($N^3$: $\int e_i[\rho]d\mathbf{r}$); (ii) parallelism (HF vs. KS) with existing codes; etc.
Chapter 6

Hohenberg-Kohn-Sham formalism (II): the exchange-correlation functional

6.1 Exchange-correlation modeling

6.1.1 LDA, GGA and meta-GGA approximations

- Approaching the exact $E_{xc}[\rho]$: LDA (I)
  - Starting point (I): one postulates that exchange-correlation effects might have the form,

$$
E_{xc}[\rho] = \underbrace{\mathcal{F}[\rho_s]}_{\text{unknown}} - U[\rho] - T_s[\rho] = \cdots = \int \rho(\mathbf{r}) e_{xc}[\rho(\mathbf{r})] d\mathbf{r},
$$

(6.1)

with the possible separability of terms $e_{xc} = e_x + e_c$.

- Starting point (II): analytically solvable model known as “jellium”

$\implies$ $N$ electrons in a box, volume $V = l^3$, throughout which a positive charge $N$ is uniformly spread out to ensure neutrality.
The limit $N \to \infty$, $V \to \infty$, but $\rho = N/V$ tending to a finite limit, defines the isotropic system known as Uniform Electron Gas (UEG).

- For the UEG one obtains:

\[
E_x[\rho] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int_{C_s} \rho^{4/3}(r) d\mathbf{r}; \quad (6.2)
\]
\[
T_s[\rho] = -\frac{3}{10} \left(3\pi^{2}\right)^{2/3} \int_{\approx C_{TF}} \rho^{5/3}(r) d\mathbf{r} \quad (6.3)
\]

- Approaching the exact $E_{xc}[\rho]$: LDA (II)

  - Further proposal of approximate\(^1\) models for $E_c[\rho]$ such as:

\[
E_{c}^{\text{LDA}}[\rho] = -\int \rho(r) \frac{0.44}{r_s + 7.8} dr, \quad \text{with} \quad \frac{4}{3}\pi r_s^3 = \frac{1}{\rho}, \quad (6.4)
\]

defines entirely the approach called **Local Density Approximation (LDA)**

- For the correlation energy of the UEG, reliance is placed on numerical simulations for different values of $r_s$ (the Vosko-Wilk-Nussair model) from $r_s < 1$, high-density limit, and $r_s \geq 1$, low-density limit, after subtracting kinetic and exchange energies given by eqs. (6.2)-(6.3).

\[
\Rightarrow \text{The (often referred) SVWN model} = E_{xc}^{\text{LDA}}[\rho] \text{ (S + VWN).}
\]

- Problems:

\[
\Rightarrow E_{c}^{\text{LDA}}[\rho] \text{ (} E_{x}^{\text{LDA}}[\rho] \text{) (under)overestimates} \quad E_c \text{ (} E_x \text{) around } \sim 100\% \text{ (10 - 15 %)}
\]

\(^1\)The correlation energy density is not exactly known in analytic form.
Homogeneous systems (metals) are naturally favoured with respect to inhomogeneous ones (molecules).

- Approaching the exact $E_{xc}[\rho]$: LSDA
  
  - In magnetic or polarised systems, when $N_{\uparrow} \neq N_{\downarrow}$, the spin polarisation needs to be introduced:
    
    $$E_{xc}^{\text{LSDA}}[\rho_{\uparrow}, \rho_{\downarrow}] = C_x \int \left[ \rho_{\uparrow}^{4/3}(\mathbf{r}) + \rho_{\downarrow}^{4/3}(\mathbf{r}) \right] d\mathbf{r}.$$  

  - For more complicated expressions, the function $f(\xi)$ is used, with $\xi(\mathbf{r}) = \frac{\rho_{\uparrow} - \rho_{\downarrow}}{\rho_{\uparrow} + \rho_{\downarrow}}$ (spin polarisation):
    
    $$f(\xi) = \frac{(1 + \xi)^{4/3} + (1 - \xi)^{4/3} - 2}{2(2^{1/3} - 1)},$$

    that allows us to interpolate between the un- ($\xi = 0$) and polarised ($\xi = 1$) limits:

    $$e_{xc}[\rho, \xi] = e_{xc}[\rho, \xi = 0] + \{ e_{xc}[\rho, \xi = 1] - e_{xc}[\rho, \xi = 0] \} f(\xi)$$


- Approaching the exact $E_{xc}[\rho]$: GGA (I)

  - Molecules and real systems deviate from the homogeneity implicitly included in the UEG. But, how do we reliably introduce the inhomogeneity of matter?

    $$E_{xc}^{\text{GGA}}[\rho] = E_{xc}^{\text{LDA}}[\rho] + \Delta E_{xc}[\rho, \nabla \rho],$$

    mathematical modeling of $\Delta E_{xc}$: constraints, limiting values, (multi)parameters fitting, etc.
\[ \Delta E_{xc}[\rho] = \int \rho(r) F_{xc}(s) \, dr, \quad \text{con} \quad s = \frac{\nabla \rho(r)}{\rho^{\beta/3}(r)}, \quad (6.8) \]

defining the approach called **Generalized Gradient Approximation (GGA)**.

- A step further: forms exist depending on \( \nabla^2 \rho(r) \),

\[ E_{xc}^{m-GGA}[\rho] = \int e_{xc}(\rho, |\nabla \rho|, \nabla^2 \rho) \, dr \quad (6.9) \]

defining the approach called **meta-** Generalized Gradient Approximation (m-GGA).

- Approaching the exact \( E_{xc}[\rho] \): GGA (II)
  - Some very successful cases when modeling \( \Delta E_x[\rho, \nabla \rho] \):

\[
F_{DK87}^x(s) = s^2 \left( \frac{1 + \alpha s}{1 + \alpha' s^2} \right) \quad (6.10)
\]

\[
F_{B88}^x(s) = -\beta s^2 \left( \frac{1}{1 + 6 \beta s \sinh^{-1}(s)} \right) \quad (6.11)
\]

\[
F_{PBE96}^x(s) = \kappa - \frac{\kappa}{1 + \mu \kappa s^2} \quad (6.12)
\]

with \( \alpha, \alpha', \beta, \kappa \) and \( \mu \) well-fitted (training set) parameters.

- Reasons for the **success of GGA**: \( F_{xc}(\rho, \nabla \rho) \) is obliged to satisfy a set of exact conditions and limiting values.

\[ \implies \text{Ex.: The integrand of } E_{x}^{B88} \text{ functional behaves correctly when } \lim_{r \to \infty} e_x(r) \sim -1/2r \text{ (asymptotic behaviour } \neq \text{ LDA).} \]

\[ \implies \text{Ex.: The integrand of } E_{x}^{PBE} \text{ functional gives } F_x(0) = 0 \text{ (reduces correctly to the UEG limit).} \]

- Approaching the exact \( E_{xc}[\rho] \): GGA (III)
\( \bullet \) Possibilities for the (admittedly) elusive \( e_{xc}[\rho(\mathbf{r})] \):

1.\(-\) \( E_x < 0, \quad E_c \leq 0 \)
2.\(-\) \( E_x \geq E_{xc} \geq C_{LO} \int \rho(\mathbf{r})^{4/3} d\mathbf{r}, \) with \(-1.44 \geq C_{LO} \geq -1.68 \)
3.\(-\) If \( N = 1, \) \( E_x[\rho] + U[\rho] = 0, \) \( E_c[\rho] = 0 \)
4.\(-\) If \( r \to \infty, \) \( e_x \sim -\frac{1}{2r}, \) \( v_x \sim -\frac{1}{r} \)
5.\(-\) \( E_x[\rho] = \int [3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla \rho(\mathbf{r})] v_x[\rho] d\mathbf{r} \)
6.\(-\) If \( s = \frac{|
abla \rho(\mathbf{r})|}{\rho^{4/3}(\mathbf{r})} \to 0, \) \( E_{xc}(s) \to 0 \)
7.\(-\) \( -\frac{1}{8} \frac{|
abla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \leq -\frac{1}{2} \sum_i |
abla \phi_i(\mathbf{r})|^2 \)

\( \bullet \) Approaching the exact \( E_{xc}[\rho] \): range-separation

\( \circ \) Range-separation (RS) is based on:

\[
\frac{1}{r_{ij}} = \frac{f(\omega r_{ij})}{r_{ij}} + \frac{1 - f(\omega r_{ij})}{r_{ij}}
\]

(6.13)

\( \Rightarrow \) The function \( f \) has the properties \( f(\omega x \to 0) = 1 \) and \( f(\omega x \to \infty) = 0. \) Examples: \( f(\omega x) = e^{-\omega x} \) or the error function (simplicity in calculating integrals for common basis sets).

\( \Rightarrow \) The key is to treat long- and short-range parts with different functionals.

\( \circ \) Since the HF potential is known to have the correct asymptotic behaviour \( (\frac{1}{r}) \), one can mix long-range HF with short-range GGA to give (the simplest) form:

\[
E_{xc}^{RS} = E_{x}^{\text{short-range GGA}} + E_{x}^{\text{long-range EXX}} + E_{c}^{\text{GGA}}
\]

(6.14)
Although these functionals may not improve thermochemistry, other properties (excitation energies) are often improved.

- This framework continues to gain many followers: CAM-B3LYP, HSE, ωPBE, ωPBEh, ωB97, ωB97X, HISS, etc.

6.1.2 The adiabatic connection functionals

- Approaching the exact $E_{xc} [\rho]$: The adiabatic connection (I)

  - In this model, the functional $E_{xc} [\rho]$ is reexpressed for a model which replaces the exact $\hat{V}_{ee}$ by a parameterised one, $\lambda \hat{V}_{ee}$ (\( \lambda \in [0,1] \)), thus connecting the non-interacting particle system ($\lambda = 0$) with the real one ($\lambda = 1$),

  \[
  \hat{V}_{ee} = \sum_{i<j} \frac{\lambda}{r_{ij}} \tag{6.15}
  \]

  - We remind that for $N$-representable densities,

  \[
  F[\rho(r)] = \min_{\left|\Psi\right\rangle \rightarrow \rho} \langle \Psi[\rho(r)]|\hat{T} + \hat{V}_{ee} |\Psi[\rho(r)]\rangle, \tag{6.16}
  \]

  a condition which now translates into:

  \[
  F_{\lambda}[\rho(r)] = \min_{\left|\Psi_{\lambda}\right\rangle \rightarrow \rho} \langle \Psi_{\lambda}|\hat{T} + \lambda \hat{V}_{ee} |\Psi_{\lambda}\rangle, \tag{6.17}
  \]

  with $\Psi_{\lambda}$ the wavefunction which minimises $\hat{T} + \lambda \hat{V}_{ee}$ and which gives the exact density.

- Approaching the exact $E_{xc} [\rho]$: The adiabatic connection (II)

  - The exchange-correlation energy will be given by:

  \[
  E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - U[\rho] = \{ F_{\lambda=1}[\rho] - U[\rho] \} - F_{\lambda=0}[\rho]
  \]

  \[
  = \int_0^1 \frac{\partial F_{\lambda}[\rho]}{\partial \lambda} d\lambda - U[\rho] \tag{6.18}
  \]
We may then use the Hellmann-Feynmann theorem (since there is a parameter $\lambda$ in $\hat{H}$) to give:

$$E_{xc}[\rho] = \int_0^1 W_\lambda[\rho] \, d\lambda, \quad \text{con} \quad W_\lambda[\rho] = \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle - U[\rho].$$

(6.19)

The limiting values reached by $\lambda$ situate two extremes:

$$W_0 = \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle - U[\rho] = E_{xx}^{\text{EXX}}$$

(6.20)

$$W_1 = \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle - U[\rho] = V_{ee}[\rho] - U[\rho] = E_{xc}^{\text{exact}},$$

(6.21)

and, hence, the task is trying to find a path interpolating them.

- Approaching the exact $E_{xc}[\rho]$: The adiabatic connection (III)

**Significance:** the adiabatic connection shows that any functional $E_{xc}[\rho]$ might include (at least) a fraction of the exact-exchange:

$$E_x^{\text{EXX}} = -\frac{1}{2} \sum_{i,j}^{\text{occupied}} \frac{1}{|r - r'|} \phi_i(r) \phi_j^*(r') \phi_j(r) \phi_i^*(r') dx \, dr'$$

The simplest conceivable form for the interpolating function $W_\lambda$ will be:

$$W_\lambda[\rho] = a[\rho] + \lambda b[\rho],$$

(6.22)

and, consequently,

$$E_{xc}[\rho] = \int_0^1 W_\lambda[\rho] \, d\lambda = a[\rho] + \frac{1}{2} b[\rho],$$

(6.23)

being $a[\rho] = W_0 = E_x^{\text{EXX}}$ and $b[\rho] = W_1 - a = E_{xc}^{\text{exact}} - E_x^{\text{EXX}}.$
Hence,

\[ E_{xc}[\rho] = E_{xx}^{\text{EXX}} + \frac{1}{2} (E_{xx}^{\text{exact}} - E_{xx}^{\text{EXX}}), \]

(6.24)

The above relation inspired the pioneering hybrid method known as “Half-and-Half”:

\[ E_{xc}[\rho] = \frac{1}{2} E_{xx}^{\text{EXX}} + \frac{1}{2} E_{xc}^{\text{LDA}} \]

(6.25)

Then, a further extension (the famous B3LYP) comes from:

\[ \Rightarrow \text{Introducing more sophisticated GGA-like forms, and} \]

\[ \Rightarrow \text{Introducing some semi-empirical mixing of the allowed ingredients.} \]

\[ E_{xc}[\rho] = a E_{xx}^{\text{EXX}} + (1-a) E_{xc}^{\text{LDA}}[\rho] + b \Delta E_{xx}^{\text{B88}}[\rho] + (1-c) E_{xc}^{\text{LDA}}[\rho] + c E_{c}[\rho]^{\text{LYP}}, \]

(6.26)

with

\[ (a, b, c) = (0.20, 0.72, 0.81) \]

(6.27)
• Approaching the exact $E_{xc}[\rho]$: The adiabatic connection (IV)
  
  ○ In general, for any arbitrary point in the $\lambda$ space the exact value and its derivatives are unknown. We need to consider additional information for the weak interacting limit $\lambda \to 0$, such as:
  
  \[
  W'_0 = \left( \frac{\partial W_\lambda}{\partial \lambda} \right)_{\lambda=0} = 2E^{PT2}_c, \tag{6.28}
  \]
  
  together with other known conditions: $\frac{\partial W_\lambda}{\partial \lambda} < 0 \forall \lambda$; $\lim_{\lambda \to \infty} W_\lambda =$ finite, ...
  
  ○ The meaning of $E^{PT2}_c$ in the DFT framework is based on Görling-Levy’s perturbation theory:

  \[
  E = E^{KS} + \sum_{i=2}^{\infty} E^{PT_i}_c, \tag{6.29}
  \]

  \[
  E^{PT_i}_c = \frac{1}{4} \sum_{p,p'} \sum_{q,q'} \frac{|\langle qq'|pp' \rangle|^2}{(\epsilon_q + \epsilon_{q'}) - (\epsilon_p + \epsilon_{p'})}, \tag{6.30}
  \]

  with $\langle qq'|pp' \rangle = \langle qq'|pp' \rangle - \langle qq'|p'p \rangle$.

  ○ The two-electron integrals depend on both occupied and virtual KS orbitals,

  \[
  \langle qq'|pp' \rangle = \iint \phi_q^*(r)\phi_{q'}^*(r') \frac{1}{|r - r'|} \phi_p(r)\phi_{p'}(r') dr dr' \tag{6.31}
  \]

  \[
  \langle qq'|p'p \rangle = \iint \phi_q^*(r)\phi_{q'}^*(r') \frac{1}{|r - r'|} \phi_p(r)\phi_{p'}(r') dr dr' \tag{6.32}
  \]

  $\Rightarrow$ Key issue: introduction of excitations from occupied to virtual orbitals (as what happens in ab initio theories).

  ○ The incorporation of this further key feature needs to rely on functional forms\(^2\) for $W_\lambda$ depending on:

  \[
  W_\lambda[\rho] = f(a[\rho], b[\rho], c[\rho]) \rightarrow a[\rho] + \lambda b[\rho] + \lambda^2 c[\rho], \tag{6.33}
  \]

\(^2\)Note that now $E_{xc}[\rho] = a[\rho] + \frac{1}{2} b[\rho] + \frac{1}{3} c[\rho]$.,
for which we find:

\[ a[\rho] = E_x^{\text{EXX}}, \quad b[\rho] = E_c^{\text{PT2}}, \quad c[\rho] = E_{xc}^{\text{exact}} - E_x^{\text{EXX}} - E_c^{\text{PT2}} \]

(6.34)

\( \circ \) Again, if we allow some flexibility for the mixing,

\[ E_{xc}[\rho] = \underbrace{w_{\text{EXX}} E_{xc}^{\text{EXX}}}_{a_1} + \underbrace{(1 - w_{\text{EXX}}) E_{xc}^{\text{DFT}}[\rho]}_{a_2} + \underbrace{w_{\text{PT2}} E_{xc}^{\text{PT2}}}_{b_1} + \underbrace{(1 - w_{\text{PT2}}) E_{xc}^{\text{DFT}}[\rho]}_{b_2} \]

(6.35)

with now,

\[ (w_{\text{EXX}}, w_{\text{PT2}}) = (0.53, 0.27) \]

(6.36)

giving rise to the double-hybrid functionals, as the B2-PLYP.

\( \bullet \) Approaching the exact \( E_{xc}[\rho] \): The adiabatic connection \((V)\)

\( \circ \) General framework:

\[ E_{xc}[\rho] = a_1 \underbrace{E_{xc}^{\text{EXX}}}_{N^4} + a_2 \underbrace{E_{xc}^{\text{DFT}}[\rho]}_{N^3} + b_1 \underbrace{E_{xc}^{\text{PT2}}}_{N^5} + b_2 \underbrace{E_{xc}^{\text{DFT}}[\rho]}_{N^3} \]

(6.37)

\( \circ \) In short, we have at our disposal nowadays:

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Acronym</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_2 = (1 - a_1) ) ( b_1 = 0 ) ( b_2 = (1 - b_1) )</td>
<td>B1LYP</td>
<td>hybrid</td>
</tr>
<tr>
<td>( a_2 \neq (1 - a_1) ) ( b_1 = 0 ) ( b_2 \neq (1 - b_1) )</td>
<td>B3LYP</td>
<td>hybrid</td>
</tr>
<tr>
<td>( a_2 = (1 - a_1) ) ( b_1 \neq 0 ) ( b_2 = (1 - b_1) )</td>
<td>B2-PLYP</td>
<td>double-hybrid</td>
</tr>
<tr>
<td>( a_2 \neq (1 - a_1) ) ( b_1 \neq 0 ) ( b_2 \neq (1 - b_1) )</td>
<td>XY3</td>
<td>double-hybrid</td>
</tr>
<tr>
<td>( a_2 = (1 - a_1) ) ( b_1 \neq 0 ) ( b_2 \neq (1 - b_1) )</td>
<td>B2\pi-PLYP</td>
<td>double-hybrid</td>
</tr>
</tbody>
</table>

\( \circ \) Evidently, each category also takes the denomination GGA or m-GGA, depending on the final forms chosen for \( E_x[\rho] \) and \( E_c[\rho] \).
6.1.3 Variety of forms: real or not?

- Approaching the exact $E_{xc}[\rho]$: real variety (I)
  - We can establish a kind of hierarchy, although admittedly not so marked as that existing for \textit{ab initio} methods:

  
  ![Diagram of hierarchy]

  - Moving up and down across the hierarchy may be useful to bracket the accuracy at each level, keeping the same exchange-correlation form:

<table>
<thead>
<tr>
<th>Type</th>
<th>$e_{xc}(r)$</th>
<th>Cost</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1o.</td>
<td>$\rho(r)$</td>
<td>$N^3$</td>
<td>SVWN</td>
</tr>
<tr>
<td>2o.</td>
<td>$\rho(r), \nabla \rho(r)$</td>
<td>$N^3$</td>
<td>BLYP, PBE</td>
</tr>
<tr>
<td>3o.</td>
<td>$\rho(r), \nabla \rho(r), \nabla^2 \rho(r), \ldots$</td>
<td>$N^3$</td>
<td>BB95, TPSS</td>
</tr>
<tr>
<td>4o.</td>
<td>$\rho(r), \nabla \rho(r)/\phi_i^{\text{occupied}}(r')$</td>
<td>$N^4$</td>
<td>B3LYP, PBE0</td>
</tr>
<tr>
<td>5o.</td>
<td>$\rho(r), \nabla \rho(r)/\phi_i^{\text{occupied}}(r'), \phi_i^{\text{virtual}}(r')$</td>
<td>$N^5$</td>
<td>B2-PLYP, PBE0-DH</td>
</tr>
</tbody>
</table>

- However, in practice, it is sometimes difficult to disentangle leading effects and/or to compare with previously published results: the functional zoo (see the following examples).
### 6.1. Exchange-correlation modeling

<table>
<thead>
<tr>
<th>$E_x[\rho]$</th>
<th>$E_c[\rho]$</th>
<th>$E_{xc}[\rho]$ (hybrid)</th>
<th>$E_{xc}[\rho]$ (double-hybrid)</th>
<th>Basis set</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS8</td>
<td>PS6</td>
<td>B3LYP</td>
<td>BMK</td>
<td>B2-PLYP</td>
</tr>
<tr>
<td>PW91</td>
<td>LYP</td>
<td>X3LYP</td>
<td>B97</td>
<td>mPW2-PLYP</td>
</tr>
<tr>
<td>mPW</td>
<td>PW91</td>
<td>O3LYP</td>
<td>B98</td>
<td>B2GP-PLYP</td>
</tr>
<tr>
<td>PBE</td>
<td>PBE</td>
<td>CAM-B3LYP</td>
<td>?HCTH</td>
<td>XYG3</td>
</tr>
<tr>
<td>G96</td>
<td>B95</td>
<td>BH&amp;HLYP</td>
<td>M06</td>
<td>B2-P3LYP</td>
</tr>
<tr>
<td>OPTX</td>
<td>OPTC</td>
<td>B1LYP</td>
<td>M06-2X</td>
<td>B2-OS3LYP</td>
</tr>
<tr>
<td>BRx</td>
<td>BRc</td>
<td>B1B95</td>
<td>M06-HF</td>
<td>XYG3s</td>
</tr>
<tr>
<td>PKZB</td>
<td>PKZB</td>
<td>PBE0</td>
<td>wB97</td>
<td>B2T-PLYP</td>
</tr>
<tr>
<td>TPSS</td>
<td>TPSS</td>
<td>TPSSh</td>
<td>wB97X</td>
<td>B2K-PLYP</td>
</tr>
<tr>
<td>HSE</td>
<td>KCIS</td>
<td>mPW1k</td>
<td>LC-ω-PBE</td>
<td>B2ω-PLYP</td>
</tr>
</tbody>
</table>

- $w_{\text{EXX}}$ (% of exact-like exchange) widely varies: 10–80 %
- $w_{\text{PT2}}$ (% of perturbation-like correlation) seems to be lightly more restricted: 25–50 %
- Allowed combinations $E_x[\rho] + E_c[\rho]/$Basis functions = $10^k$

- Approaching the exact $E_{xc}[\rho]$: real variety (II)

6.2 Precautions to be taken

6.2.1 Accuracy and validity domain

- Accuracy and validity domain of $E_{xc}$ (I):
  - Although every step of the approximate hierarchy has its own advantages and disadvantages; generally speaking, we can roughly establish\(^3\) that:
    
    $$\text{double-hybrid} > \text{hybrid} > \text{m-GGA} \sim \text{GGA} > \text{LDA}$$
  
  - However, the behaviour of each model might depend on property or system (calibration is always needed).

- A good piece of news is that the basis sets dependence is not so marked as for the \textit{ab initio} methods: 6-31G**, def2-TZVP or cc-pVTZ are (often) good compromises.

---

\(^3\)A great challenge is still to develop a functional that performs uniformly better than B3LYP or B2-PLYP.
6.2. Precautions to be taken

- **Structural** properties:
  - Molecules (1st/2nd period): < 0.01 Å, 1 – 2°.
  - Metallic compounds: < 0.2 Å.
  - Weak interactions: ~ 1 Å.
  - Vibrational frequencies: 20 – 50 cm⁻¹.

- **Thermochemical** properties:
  - Atomisation energies (metallic dimers): 5–25 kcal/mol.
  - Ionisation potentials: 2–5 kcal/mol.
  - Electron affinities: 2–3 kcal/mol.
  - Enthalpies of formation: 3–30 kcal/mol.

- **Non-covalent** (I) interactions (electrostatic-like: hydrogen bond, dipole-dipole, . . .):
  - Association energies: < 2 kcal/mol.

- **Non-covalent** (II) interactions (dispersion, π-π, . . .):
  - Association energies: 1–10 kcal/mol.

- **Accuracy and validity domain of** \( E_{xc} \) (III):

- **Additional warning**: if the system or property under study is (or is expected to be) dominated by

  - non-covalent or dispersive-like interactions,
  - large electronic delocalisation (π-electron conjugation),
  - degeneracies or near-degeneracies of frontier orbitals,
  - marked stereoelectronics effects,
  - charge-transfer involved processes.

- **Working approach**: try to perform or discuss with

  - exhaustive literature and code search,
  TOGETHER with
(hopefully) calibration with *ab initio* methods, TOGETHER with

experts advice or discussion (friendly peer-review), TOGETHER with

*ad-hoc* developed solutions (i.e., B3LYP-D or CAM-B3LYP might be more suited than B3LYP), TOGETHER with

bracketing errors across the (approximate) hierarchy of existing methods (i.e., BLYP < B3LYP < B2-PLYP).

### 6.2.2 The self-interaction error

- The Self-Interaction-Error (SIE):
  - Definition: spurious self-interaction of an \( e^- \) with itself \((U[\rho_i] + E_{xc}[\rho_i,0] \neq 0)\). The consequence is an artificial stabilisation of delocalised states (highly overestimated energy differences, too low alternation between single and double bond in polyenes, underestimated fundamental gaps ...)
  - Origin: localised have larger self-repulsion than delocalised densities\(^4\)

![](image)

- Origin: but at the same time, due to the leading \( \rho^{4/3} \) (LDA) dependence of common \( E_x[\rho] \)

\(^4\)Note that \( U[\rho] = \iint \rho(r)\rho(r')/|r - r'|drdr' \)
○ Consequence: larger and larger difference (SIE) \( U[\rho] - E_x[\rho] \)
the more delocalised the state becomes!

<table>
<thead>
<tr>
<th>SIE: ( \frac{1}{2} U[\rho] - \frac{1}{2} \pi E_x[\rho^{4/3}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>localised</td>
</tr>
</tbody>
</table>

• The importance of EXact-like Exchange (EXX):

○ 1st framework: since EXX is by definition SIE-free, global hybrid functionals partly alleviate it,

\[
E^\text{hybrid}_{xc}[\rho] = w_{\text{EXX}} E^\text{EXX}_x + (1 - w_{\text{EXX}}) E_x[\rho] + E_c[\rho], \quad E^\text{EXX}_x \text{ cancels } U[\rho].
\]

\[\implies \text{KNOWN: } w_{\text{EXX}} \text{ is a system-/property-dependent value for } \pi\text{-conjugated systems.}\]

○ 2nd framework: a range-separated (RS) hybrid functional is based on splitting\(^5\) \( r_{ij}^{-1} \), giving rise to (exchange-only):

\[
E^\text{RS}_x[\rho] = w_{\text{SR-EXX}} E^\text{SR-EXX}_x(\omega) + (1 - w_{\text{SR-EXX}}) E_x[\rho](\omega) \\
+ w_{\text{LR-EXX}} E^\text{LR-EXX}_x(\omega) + (1 - w_{\text{LR-EXX}}) E_x[\rho](\omega)
\]

\[\implies \text{Recent NEW: } \omega \text{ depends also on the characteristics of the system.}\]

○ 3rd framework: local hybrid functionals, for which \( w_{\text{EXX}}(r) \)
(position-dependent), which are, however, very costly and technically challenging.

\(^5\) \( r_{ij}^{-1} = [1 - \text{erf}(\omega r_{ij})]/r_{ij} + [\text{erf}(\omega r_{ij})]/r_{ij} = \text{short-range} + \text{long-range} \)
6.2.3 Some successful stories: DFT–D and beyond

• Intermolecular forces (I): Generalities
  ○ Aggregated states of the matter: balance between repulsive ($e^{-R}$) and attractive ($R^{-n}$) forces. The use of the intermolecular potential energy, related with force through $F = -\nabla V$ is longer preferred.
  ○ To notably simplify the treatment, we rely on pairwise additive schemes:
    \[ V \approx \sum_{A \in a} \sum_{B \in b} V_{AB}(R_{AB}, \Omega_{AB}), \]  
    \[ \text{(6.38)} \]
    with $V_{AB}$ the (two-centre)\(^6\) interaction potential ($R_{AB}$: distance; $\Omega_{AB}$: orientation).
  ○ Summary of attractive interactions:

<table>
<thead>
<tr>
<th>Type</th>
<th>$V(R, \Omega)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ion - ion</td>
<td>$-\frac{2a_{vdW}}{4\pi\epsilon R}$</td>
</tr>
<tr>
<td>ion - dipole</td>
<td>$-\frac{2\mu_1\mu_2}{3k_B T} \left( \frac{1}{\epsilon} \right)^2$</td>
</tr>
<tr>
<td>dipole - dipole</td>
<td>$-\frac{2\mu_1\mu_2}{3k_B T} \left( \frac{1}{\epsilon} \right)^2$</td>
</tr>
<tr>
<td>dipole - dipole (induced)</td>
<td>$-\frac{2\mu_1\mu_2}{3k_B T} \left( \frac{1}{\epsilon} \right)^2$</td>
</tr>
<tr>
<td>dipole (induced) - dipole (induced)</td>
<td>$-\frac{2\mu_1\mu_2}{3k_B T} \left( \frac{1}{\epsilon} \right)^2$</td>
</tr>
</tbody>
</table>

dipole moment ($\mu$), ionisation pot. ($f$), and polarizability ($\alpha$)

• Intermolecular forces (II): Approximations
  ○ J. D. van der Waals first recognised (1873) that certain forces operate at small yet pervasive scale: \( p + \frac{a_{vdW} N^2}{V^2} \left( \frac{V}{N} - b_{vdW} \right) = k_B T \)
  ○ Mimic of van der Waals interactions: contributions depending on $R^{-6}$ (dipole - dipole, dipole - induced dipole, London ).

\(^6\)3-body effects and beyond are neglected.
In practice (DFT–D) we can learn from molecular-mechanics:

\[ E_{\text{final}} = E_{\text{DFT}} + E_{\text{vdW}}, \quad E_{\text{vdW}} = -s_6 \sum_{A,B} f\left(R_{AB}, R_{\text{vdW}}^\text{AB}\right) \frac{C_{AB}^6}{R_{AB}^6}, \]

\[ C_{AB}^6 = \sqrt{C_A^6 C_B^6}; \quad f\left(R_{AB}, R_{\text{vdW}}^\text{AB}\right) = \frac{1}{1 + e^{-\alpha \left(\frac{R_{AB}}{R_{\text{vdW}}^\text{AB}} - 1\right)}} \]

- Intermolecular forces (III): Approximations
  - What is the specific shape of the contributions like? See the evolution of the dispersion energy (DFT–D) for different atomic pairs (left) or for the same pair (right) according to the considered functional \( (s_6) \).
Some nice features: (i) correct asymptotic behaviour \( R_{AB}^{-6} \); (ii) maximum vdW energy peaking at \( R_{AB}^{-w} \); (iii) less energy for less polarisable atoms; (iv) the \( s_0 \) parameter decreases along the hierarchy, and consequently the energy, as expected.

- Intermolecular forces (IV): Microscopic approximation
  - Origin: correlated instantaneous fluctuations of electronic densities at \( \mathbf{r} \) and \( \mathbf{r}' \);

  \( \implies \) CCSD(T) (MP2) is able to fully (partly) introduce them by default.

  \( \implies \) DFT is unable to do it without further modifications.

\[ a) \text{ Statically-interacting densities} \]

\[ 1/R_{AB}^6 \] 

(\( \text{center-to-center distance} \))

\[ a) \text{ Dynamically-interacting (electronic distortions)} \]

- Treatment: non-local correlation functionals \( E_{\text{c}}[\rho] = E_{\text{c}}^{\text{semi-local}} + E_{\text{c}}^{\text{NL}} \), with,

\[
E_{\text{c}}^{\text{NL}} = \int \int \rho(\mathbf{r}) \Phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad (6.39)
\]

being the most used form for \( E_{\text{c}}^{\text{NL}} \) that is coined as VV10.
6.2.4 Density fitting (RI) and numerical quadrature

- Density fitting\textsuperscript{7}: significant speed up of the calculations for the terms $E^\text{EXX}_x$ and $E^\text{PT2}_e$ entering into the hybrid or double-hybrid forms.

  - Evaluation of four-index two-electron integrals:

$$
\left< pq \mid \hat{O} \mid rs \right> = \int \int \varphi_p(r_1)\varphi_q(r_1) \hat{O}(r_1, r_2) \varphi_s(r_2) \varphi_r(r_2) d\tau_1 d\tau_2, \tag{6.40}
$$

will soon become (large orbital basis sets) highly linear dependent, and can thus be expanded in an auxiliary basis of fitting functions \{Q\}:

$$
\varphi_p(r)\varphi_q(r) \approx \sum_Q c_{Q,pq} Q(r) \tag{6.41}
$$

- The result is a scaling of $O(N^3)$ (two- and three-centre two-electron integrals) instead of the original $O(N^4)$:

$$
\left< pq \mid \hat{O} \mid rs \right> = \sum_{PQ} (pq \mid P) V^{-1}_{PQ} (Q \mid rs), \tag{6.42}
$$

with:

$$
(Q \mid P) = \int \int Q(r_1)\hat{O}P(r_2) d\tau_1 d\tau_2, \tag{6.43}
$$

$$
(Q \mid pq) = \int \int Q(r_1)\hat{O}\varphi_p(r_2)\varphi_q(r_2) d\tau_1 d\tau_2 \tag{6.44}
$$

- Implementation of DFT:

\textsuperscript{7}Or Resolution-of-the-Identity (RI)
○ The new integrals which arise in the KS equation may not be analytically evaluated. Thus,

\[
I = \int f(r) dr \approx \sum_i w_i f(r_i), \quad N^3 \text{ scaling} \quad (6.45)
\]

generating a **numerical** 3-dimensional grid of points \((w_i)\) are the weights).

⇒ The integration grid should be adapted to the shape of the molecular density (high and nearly spherically symmetric near the nuclei; lower and less symmetric between them).

⇒ The grid of \(w_i\) are centered on every nuclei; needing to define a *radial* and an *angular* quadrature scheme. The atomic grids then generate the molecular mesh used.

○ A good test on the accuracy\(^8\) of a quadrature scheme may just be judged by \(N = \int \rho(r) dr\). Example:

<table>
<thead>
<tr>
<th>Grid</th>
<th>(N)</th>
<th>(E_{xc})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid 3</td>
<td>29.997204</td>
<td>-19.329346</td>
</tr>
<tr>
<td>Grid 4</td>
<td>29.999728</td>
<td>-19.329311</td>
</tr>
<tr>
<td>Grid 5</td>
<td>30.000017</td>
<td>-19.329297</td>
</tr>
<tr>
<td>Grid 6</td>
<td>30.000074</td>
<td>-19.329439</td>
</tr>
<tr>
<td>Grid 7</td>
<td>30.000016</td>
<td>-19.329378</td>
</tr>
</tbody>
</table>

○ Clear need to increase the default thresholds when one is concerned with:
  - Flat potential energy surfaces and/or vibrational frequencies.
  - Diffuse functions in both ground- and excited-states.
  - Any property based on population analysis.
  - The density fitting (RI) or related techniques.

\(^8\)\(\text{C}_4\text{H}_6, \text{B3LYP}/6-31G^* \text{(ORCA 2.8.0); error in } E_{xc} \text{ up to 0.1 kcal/mol}\)
Chapter 7

Chemical concepts and reactivity

7.1 The chemical potential

- Chemical concepts:

  - One of the most striking successes of DFT lies on its ability to (re)define key concepts, historically employed to dilucidate the existing relationships between molecular structure and reactivity.

  - By means of ab initio methods, this work is however not exempted from difficulties.

  - On the other hand, this is certainly possible in DFT thanks to the main role played by variables $\rho(r)$ y $N$. After all, Chemistry is related with electron(s) transfer(s) from one region to another region of space.
Significance: we recall the following definitions

Ionisation energy \((I)\): minimum energy needed to remove an electron from a gaseous isolated system in its vibrational ground-state,

\[
X(g) + I \rightarrow X^+(g) + e^-, \quad I = E(X^+) - E(X) > 0 \quad (7.1)
\]

Electron affinity \((A)\): amount of energy released when an electron is added to a gaseous, generally neutral, system,

\[
X(g) + e^- \rightarrow X^-(g) + A, \quad A = E(X) - E(X^-) > 0 \quad (7.2)
\]

7.1.1 Definitions and derivations

- The chemical potential \((\mu)\):
  - Since \( E[N,v(r)] \), differentiating with respect to the variables to what depends on:
    \[
dE = \left( \frac{\partial E}{\partial N} \right)_{v(r)} dN + \int \left( \frac{\delta E[\rho(r)]}{\delta v(r)} \right)_{N} \delta v(r) dr \quad (7.3)
    \]
  - In turn, it is known\(^1\) that \( N = N[\rho] \):
    \[
dE = \int \left( \frac{\delta E[\rho(r)]}{\delta \rho(r)} \right)_{v(r)} \delta \rho(r) dr + \int \left( \frac{\delta E[\rho(r)]}{\delta v(r)} \right)_{\rho} \delta v(r) dr \quad (7.4)
    \]
  - From the fundamental equation of DFT, \( \mu = \frac{\delta E[\rho(r)]}{\delta \rho(r)} \), and how \( dN = \int \delta \rho(r) dr \), we arrive at:
    \[
dE = \mu dN + \int \left( \frac{\delta E[\rho(r)]}{\delta v(r)} \right)_{\rho} \delta v(r) dr \quad (7.5)
    \]

---

\(^1\)Remember that \( \int \rho(r) dr = N \)
Comparing both eqs. (7.3) and (7.5) we obtain a new definition for \( \mu \):
\[
\mu = \left( \frac{\delta E[\rho(r)]}{\delta \rho(r)} \right)_{\nu(r)} = \left( \frac{\partial E}{\partial N} \right)_{\nu(r)} \tag{7.6}
\]
\( \Rightarrow \) \( \mu \) indicates how the energy changes upon changing the number of electrons.

Starting from \( E[\rho(r)] = \int \rho(r)v(r)dr + T[\rho(r)] + V_{ee}[\rho(r)] \), we will analyse now how this energy is modified after varying the external potential\(^2\):
\[
dE = \int \rho(r)\delta v(r)dr + \int \left( \frac{\delta T[\rho(r)]}{\delta v(r)} \right)_{\rho(r)} \delta \rho(r)dr \tag{7.7}
\]
\[
+ \int \left( \frac{\delta V_{ee}[\rho(r)]}{\delta v(r)} \right)_{\rho(r)} \delta \rho(r)dr = \int \rho(r)\delta v(r)dr
\]

If one does the same from eq. (7.3), we arrive to the expression:
\[
dE = \int \left( \frac{\delta E[\rho(r)]}{\delta v(r)} \right)_{N} \delta v(r)dr \tag{7.8}
\]

Since \( E[N, v(r)] \), comparing the former eqs. for \( dE \), we see that \( \rho(r) = \left( \frac{\delta E[\rho(r)]}{\delta v(r)} \right)_{\rho} \), and after being introduced into eq. (7.5):
\[
dE = \mu dN + \int \rho(r)\delta v(r)dr \tag{7.9}
\]
\( \Rightarrow \) An expression known as fundamental equation of the chemical change.

In practice\(^3\), we start from:
\[
\mu = \left( \frac{\partial E}{\partial N} \right)_{\nu(r)} \simeq \frac{\Delta E}{\Delta N} = \frac{E(N + 1) - E(N - 1)}{(N + 1) - (N - 1)}
\]
\[
= \frac{[E(N) - A] - [E(N) + I]}{2} = - \frac{I + A}{2} \tag{7.10}
\]

\(^2\)Keeping \( \rho(r) \) constant.
\(^3\)Remember that \( I = E(N - 1) - E(N) \) and \( A = E(N) - E(N + 1) \)
One can thus uses experimental or calculated values of $I$ and $A$ (in eV).

- The chemical potential (II):
  - R. A. Mulliken (1934) considered the following reactions:
    \begin{align*}
    X + Y & \rightarrow X^+ + Y^- \\
    X + Y & \rightarrow X^- + Y^+,
    \end{align*}
    \hspace{1cm} (7.11) \hspace{1cm} (7.12)
  
  and defined the electronegativity ($\chi$) as the average tendency of an element to give or attract electrons:
  \[ \chi = \frac{I + A}{2} \]
  \hspace{1cm} (7.13)
  
  since, in that way, $X$ and $Y$ have the same $\chi$; note how they are equally inclined to win or lose electrons: $I(X) + A(Y) = I(Y) + A(X)$.

  - Hence:
    \[ \mu = -\chi = \left( \frac{\partial E}{\partial N} \right)_v = -\frac{I + A}{2} \]
    \hspace{1cm} (7.14)

  - For a chemical reaction between systems $A$ and $B$, assuming that $v(r)$ is kept constant, and for a charge transfer given by $\Delta N$, the eq. (7.9) becomes now $\Delta E \simeq \mu \Delta N$. Since normally $\Delta E = \Delta E_A + \Delta E_B$, being $\Delta N_A = -\Delta N_B = \Delta N > 0$, we have that:
    \[ \Delta E = (\mu_A - \mu_B) \Delta N \]
    \hspace{1cm} (7.15)
    
    \[ \implies \text{Matter flows from higher to lower values of } \mu. \]
    
    \[ \implies \text{Matter flows from lower to higher values of } \chi. \]
    
    \[ \implies \text{Continuous and spontaneous process to get the same homogeneous value of } \mu \text{ in all subparts of the system.} \]

\footnote{Remember that $dE = \mu dN + \int \rho(r) \delta v(r) dr$}
implies $\mu$ thus measures the tendency of electrons to escape from the system.

implies Large differences of $\mu$ between system favours the electronic transfer.

### 7.2 Related concepts

#### 7.2.1 Hardness and Fukui functions

- Hardness and Fukui functions (I):
  
  - Differentiating $\mu[N, v(r)]$, we have that:

  $$d\mu = \left(\frac{\partial \mu}{\partial N}\right)_{v(r)} dN + \int \left(\frac{\delta \mu}{\delta v(r)}\right)_{N} \delta v(r) dr$$  

  \hspace{1cm} (7.16)

  - We define the following functions:

  \hspace{1cm} $$\eta = \left(\frac{\partial \mu}{\partial N}\right)_{v(r)} = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)}$$  

  \hspace{1cm} $$f(r) = \left(\frac{\delta \mu}{\delta v(r)}\right)_{N} = \frac{\delta^2 E}{\partial N \delta v(r)} = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)}$$  

  \hspace{1cm} (7.17)

  \hspace{1cm} (7.18)

  - $\eta$: **Hardness** (reciprocal $s = \frac{1}{\eta}$: Softness)

  - $f(r)$: **Fukui functions** (chemically interesting)

  - The fundamental equation of chemical change, $dE = \mu dN + \int \rho(r) \delta v(r) dr$, now transforms into:

  $$d\mu = \eta dN + \int f(r) \delta v(r) dr,$$  

  \hspace{1cm} (7.19)
showing how $\mu$ varies upon changes in $N$ and the external potential.

- In practice, we start from:

$$\eta = \left( \frac{\partial^2 E}{\partial N^2} \right)_{v(r)} \simeq \frac{E(N + 1) - 2E(N) + E(N - 1)}{[(N + 1) - (N - 1)]^2}$$

$$= [E(N) - A] - 2E(N) + [E(N) + I] = I - A \quad (7.20)$$

$\implies$ $\eta$ is proportional to the band gap of a chemical system.

$\implies$ The definition $\eta = \frac{I-A}{2}$ is usually preferred.

$\implies$ Again using experimental or calculated values of $I$ and $A$ (in eV).

$\implies$ $\eta$ measures how the system opposes to charge transfers: trying to change $N$ in a hard system will not be easy (resistance to deformation).

- Hardness and Fukui functions (II):

  - The **principle of maximum hardness**: a chemical system at a given temperature will evolve to a state of maximum hardness, provided that $\mu$ and $v(r)$ remain constant. The highest value of $\eta$ reflects the highest possible band gap; this value correlates with stability.

  - **HSAB (Hard-Soft-Acid-Bases) principle**: it assigns the terms ‘hard’ or ‘soft’, and ‘acid’ or ‘bases’, to chemical species, to establish that hard acids prefer hard bases, giving rise to compounds with essentially ionic bonds, and soft acids prefer soft bases, giving rise to compounds with essentially covalent bonds.
    - **Hard** applies to species which are small, have high charge state, and are weakly polarisable.
    - **Soft** applies to species which are big, have low charge state,
and are strongly polarisable.

- **Acid** (Lewis) is a molecular entity containing an electron-pair acceptor centre.
- **Base** (Lewis) is a molecular entity containing an electron-pair donor centre.

- **Hardness and Fukui functions (III):**
  - Recovering the definition, \( f(r) = \left( \frac{\delta \mu}{\delta v(r)} \right)_N = \left( \frac{\partial \rho(r)}{\partial N} \right)_{v(r)} \), indicating that \( f(r) \) can be interpreted as a:
    
    \[ \implies \text{Measure how sensitive the chemical potential is to a change in the external potential, or} \]
    
    \[ \implies \text{Measure how the electronic density varies upon increasing the number of electrons of the system.} \]

  - Again, in practice, we start from:
    
    \[
    f(r) = \left( \frac{\partial \rho}{\partial N} \right)_{v(r)} \approx \frac{\Delta \rho}{\Delta N} = \frac{\rho_{(N+1)}(r) - \rho_{(N-1)}(r)}{(N + 1) - (N - 1)}
    \]
    
    \[ = f^+(r) + f^-(r) = \frac{\rho_{(N+1)}(r) - \rho_N(r)}{(N + 1) - N} + \frac{\rho_N(r) - \rho_{(N-1)}(r)}{N - (N - 1)} \]  \( (7.21) \)

  - If \( \rho(r) = \sum_i^N |\phi_i|^2 \), then \( \rho_{(N+1)} - \rho_N = \rho_{\text{LUMO}} \) and \( \rho_N - \rho_{(N-1)} = \rho_{\text{HOMO}} \), so we have:
    
    \[
    f^+(r) = \rho_{\text{LUMO}}(r); \quad f^-(r) = \rho_{\text{HOMO}}(r); \quad f^0(r) = \frac{f^+(r) + f^-(r)}{2}
    \]  \( (7.22) \)  \( (7.23) \)  \( (7.24) \)

  - Physical significance (chemical reactivity indices):
\[ \implies f^+(\mathbf{r}) \text{ appreciates a change of } N \text{ through } \rho_{\text{LUMO}}(\mathbf{r}) \text{ (measures the reactivity towards a nucleophilic attack).} \]

\[ \implies f^-(\mathbf{r}) \text{ appreciates a change of } N \text{ through } \rho_{\text{HOMO}}(\mathbf{r}) \text{ (measures the reactivity towards an electrophilic attack).} \]

- Applied to atoms \((k)\), in a condensed form:

\[
f_k^+(\mathbf{r}) = q_k(N + 1) - q_k(N), \quad f_k^-(\mathbf{r}) = q_k(N) - q_k(N - 1);
\]

with \(q_k\) the electronic population on the \(k\) atom. If \(f_k^+ > f_i^+\), that \(k\) atom will probably act as electrophilic (suffering thus a nucleophilic attack).

### 7.2.2 Curvature, frontier orbital energies and band gaps

- The effect of adding \(N\):

  - In a seminal paper (1985) Perdew, Parr, Levy and Balduz discovered that exact DFT must obey:

\[
\text{Energy change [F: CCSD(T)/6-311+G\ast\ast]}
\]
The exact total energy must be a series of linear segments between integer electron points.

Different slopes reflect discontinuities in \( \mu \), that is, the fact that electron removal energy is not the same as the electron insertion energy.

Total slope: \( \frac{dE}{dN} = -\frac{I + A}{2} \)

\( \Delta N = 1 \), but if the curve is made continuous: \( E(N) = aN^2 + bN + c \) for fractional charges \( (N \pm x, -1 \leq x \leq 1) \) the curvature is then \( \frac{d^2E}{dN^2} = I - A \).

- Analogous of Koopmans’ theorem in DFT: Janak’s theorem

**Significance:** the eigenvalues associated to the highest (lowest) occupied (virtual) \( \phi_i \)'s, with the opposite sign, equals (is related to) the ionisation energy (the electron affinity), respectively.

Consequence: \( I = -\epsilon_{N}(N) = -\epsilon_{\text{HOMO}} \) and \( A = -\epsilon_{N+1}(N+1) \approx -\epsilon_{\text{LUMO}} \)

This opens a new way to calculate \( \mu, \chi \) and \( \eta \) in KS calculations:

\[
\mu (-\chi) = -\frac{I + A}{2} = \frac{\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}}}{2} \quad (7.26)
\]

\[
\eta = \frac{I - A}{2} = \frac{\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}}{2} \quad (7.27)
\]

While these are exact statements, the use of approximate \( E_{xc}[\rho] \) makes the calculated energies approximate. As in HF theory, \( A \) calculated in this way is less accurate than \( I \).
• The band gap in chemical systems:
  
  o The excitation gap (also known as \textbf{optical gap}) can be probed by optical spectroscopy. It refers to the energy difference between the electronic ground state and the first excited state of a system for a \textit{fixed} particle number $N$.

  $\implies$ Optical gaps can be successfully calculated by TD-DFT.

  o The fundamental gap (also known as band or \textbf{particle gap}) plays an important role in transport phenomena or electron-transfer reactions, involving ground-state energies of systems with \textit{different} particle numbers $N$; it is defined as:

  $$E_g(N) = \epsilon_{N+1}(N+1) - \epsilon_N(N),$$  
  (7.28)

  with $\epsilon$ the occupied KS eigenvalues.

  o The particle gap in a non-interacting system (also known as \textbf{KS gap}) is:

  $$E_g^{KS}(N) = \epsilon_{N+1}(N) - \epsilon_N(N) = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}},$$  
  (7.29)

  while we can relate the latter two gaps by:

  $$\Delta_{xc} = E_g(N) - E_g^{KS}(N) = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N),$$  
  (7.30)

  that is, the many-body correction to the KS gap.

  o It turns out that the $\Delta_{xc}$ can be related to a \textbf{VERY FUNDAMENTAL} property of density functionals, known as the \textbf{derivative discontinuity}.

  $\implies$ Note that \textit{“True (or measured) gap = KS prediction + $\Delta_{xc}$”}

  $\implies$ Numerical estimates show that $\Delta_{xc}$ can be large (i.e., $\sim 0.5$ eV in bulk Si).
Graphically, we have that:

<table>
<thead>
<tr>
<th>Initial state</th>
<th>Final state</th>
<th>( \Delta E = E_{\text{UKS}} (T_1) - E_{\text{RKS}} (S_0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \circ \circ )</td>
<td>( \times \circ )</td>
<td>( \Delta E = E_{\text{TD-DFT}} (S_i, T_i) - E_{\text{DFT}} (S_0) )</td>
</tr>
<tr>
<td>( \circ \circ )</td>
<td>( \circ \circ )</td>
<td>( E_g(N) = I(N) - A(N) = \varepsilon_{N+1}(N+1) - \varepsilon_N(N) )</td>
</tr>
<tr>
<td>( \circ \circ )</td>
<td>( \circ \circ )</td>
<td>( E_g^\text{KS}(N) = \varepsilon_{N+1}(N) - \varepsilon_N(N) )</td>
</tr>
</tbody>
</table>

The derivative discontinuity (I):

- Let us consider an open system \((N)\) with a gap and connected to a particle reservoir with fixed \(\mu\),

\[ \Rightarrow \text{Assume that } \varepsilon_{\text{LUMO}} < \mu < \varepsilon_{\text{HOMO}} \]

\[ \Rightarrow \text{For small enough changes, } \mu \text{ remains within the gap, and nothing interesting happens.} \]

\[ \Rightarrow \text{But as soon as, say, } \mu < \varepsilon_{\text{LUMO}}, \text{ an additional particle is allowed to come (the total number changes from } N \text{ to } N+1). \]
○ To reflect this new situation, \( \mu \) must take a new value compatible with \( N + 1 \); thus, \( \mu \) is a piecewise constant function of the particle number,

\[
\begin{array}{c}
\begin{array}{c}
N \\
N^{-1} \\
N+1
\end{array}
\end{array}
\]

\[
\begin{array}{c}
\begin{array}{c}
\mu
\end{array}
\end{array}
\]

- The derivative discontinuity (II):
  ○ Since \( I(N) = E(N - 1) - E(N) \) and \( A(N) = E(N) - E(N + 1) \), taken into account that \( \mu = \left( \frac{\delta E[\rho]}{\delta \rho(r)} \right) v(r) = \left( \frac{\partial E[\rho]}{\partial \rho(r)} \right) v(r) \), the fundamental gap \(^5\) is:

\[
E_g(N) = I(N) - A(N) = \frac{\delta E[\rho]}{\delta \rho(r)} \bigg|_{N^{-}} - \frac{\delta E[\rho]}{\delta \rho(r)} \bigg|_{N^{+}}, \quad (7.31)
\]

since the discontinuity in \( \mu \) must be translated to it.

○ Since the total energy is \( E[\rho] = \int \rho(r)v(r)dr + T_s[\rho] + U[\rho] + E_{xc}[\rho] \), the above condition is:

\[
E_g(N) = \frac{\delta T_s[\rho]}{\delta \rho(r)} \bigg|_{N^-} + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \bigg|_{N^-} - \frac{\delta T_s[\rho]}{\delta \rho(r)} \bigg|_{N^+} - \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \bigg|_{N^+}, \quad (7.32)
\]

\(^5\) \( N^\pm = \lim_{\delta \to 0} N \pm \delta \)
However, for the KS system, \( \mu = \frac{\delta T_s[\rho]}{\delta \rho(r)} + v_s(r) \), and then,

\[
E_{g}^{KS}(N) = \frac{\delta T_s[\rho]}{\delta \rho(r)} \bigg|_{N^-} - \frac{\delta T_s[\rho]}{\delta \rho(r)} \bigg|_{N^+},
\]

(7.33)

Hence, \( \Delta_{xc} = E_{g}(N) - E_{g}^{KS}(N) \) and then,

\[
\Delta_{xc} = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \bigg|_{N^-} - \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \bigg|_{N^+},
\]

(7.34)

is the (in)famous **derivative discontinuity** of the exchange-correlation potential. Its importance relies on:

\[\implies\] Giving a contribution to the band gap in solids and extended systems.

\[\implies\] Ensuring that heteroaromatic molecules dissociate into neutral fragments.

\[\implies\] Providing physical quality and content of the KS eigenvalues.

The derivative discontinuity must be related with the asymptotic \( (r \to \infty) \) behaviour\(^6\) of the \( v_{xc} \).

\[\implies\] Far from the nucleus, an electron (escaping) should feel an effective \( Z - (N - 1) \) charge.

\[\implies\] Since \( v(r) \to -\frac{Z}{r} \), and \( u[\rho] = \int \frac{\nu(r')}{|r-r'|} dr' \to \frac{N}{r} \), this implies \( v_{xc} \to -\frac{1}{r} \).

\[\implies\] Note that wrongly \( \lim_{r \to \infty} v_{xc}^{LDA} = e^{-r} \) or \( \lim_{r \to \infty} v_{xc}^{GGA(B88)} = -\frac{1}{r} \).

\(^6\)Hybrids and range-separated functionals must work better!
7.3 Size-extensivity

- Separability of the energy in DFT:
  - The separability implies\(^7\):
    \[
    E[N_A + N_B, v_A(r) + v_B(r)] = E[N_A, v_A(r)] + E[N_B, v_B(r)]
    \]
  - In DFT, common expressions are \(\int e(\rho, \nabla \rho, \ldots) d\mathbf{r}\), which translates into the proof:
    \[
    \int e(\rho_A + \rho_B, \ldots) d\mathbf{r} = \int e(\rho_A, \ldots) d\mathbf{r} + \int e(\rho_B, \ldots) d\mathbf{r}
    \]
  - However, if the functional explicitly depends on \(N\),
    \[
    \int e(N_A + N_B, \rho_A + \rho_B, \ldots) d\mathbf{r}
    \]
    \[
    \neq \int e(N_A, \rho_A, \ldots) d\mathbf{r} + \int e(N_B, \rho_B, \ldots) d\mathbf{r}
    \]
    \[
    = \int e(N_A + N_B, \rho_A, \ldots) d\mathbf{r} + \int e(N_A + N_B, \rho_B, \ldots)
    \]  
  - **Case 1.** He \ldots He \((R \to \infty)\). Functional: \(U[\rho(r)]\)
    \[
    U[\rho_{\text{He}(A)} + \rho_{\text{He}(B)}] = U[\rho_{\text{He}(A)}] + U[\rho_{\text{He}(B)}]
    \]  
  - **Case 2.** He \ldots He \((R \to \infty)\). Functional: \(\tilde{U}[\rho(r)] = U[\rho(r)] - \frac{1}{N} U[\rho(r)]\)
    \[
    \tilde{U}[\rho_{\text{He}(A)} + \rho_{\text{He}(B)}] \neq \tilde{U}[\rho_{\text{He}(A)}] + \tilde{U}[\rho_{\text{He}(B)}]
    \]

\(\implies\) **Separability:** for a system composed of two or more objects separated by great distances of empty space, the total energy is the sum of the energy of the separated objects.

\(^7\)\(v_A\) and \(v_B\) are separated by a large distance, in such a way that any electron will feel at any point of the space only one of these potentials.
⇒ Integer preference: in a collection of separated objects, nature prefers to locate an integer number of electrons on each object: \[ \text{Na}^+ \cdots \text{Cl}^- (\text{Na} \cdots \text{Cl}) \text{ for } R < 10 \, \text{Å} \ (R > 10 \, \text{Å}). \]

⇒ Common approximations (LDA, GGA, ...) respect the separability principle BUT the integer preference is not respected by any practical approximation.

7.4 Summary and conclusions

1. We dispose of a set of useful and rationalised expressions:

⇒ Chemical potential (electronegativity):

\[
\mu (-\chi) = \left( \frac{\partial E}{\partial N} \right)_{v(r)} = \frac{-I + A}{2} = \frac{\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}}}{2}
\]

⇒ Hardness:

\[
\eta = \left( \frac{\partial^2 E}{\partial N^2} \right)_{v(r)} = \frac{I - A}{2} = \frac{\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}}{2}
\]

⇒ Fukui functions:

\[
f(r) = \left( \frac{\delta \mu}{\delta v(r)} \right)_N = \left( \frac{\partial \rho(r)}{\partial N} \right)_{v(r)} = f^+(r) + f^-(r)
\]

\[
= \phi_{\text{LUMO}}^2(r) + \phi_{\text{HOMO}}^2(r)
\]

⇒ \( E_g(N) = I(N) - A(N) = E_{\text{KS}}^{\text{g}} + \Delta_{\text{xc}} \); \( \Delta_{\text{xc}} \to 0 \) if approximate \( E_{\text{xc}}[\rho] \to \text{true (nearly-exact) } E_{\text{xc}}[\rho] \).
2. The variations of the energy with respect to \( N \) (global property) generate a set of (customarily) global properties which govern the reactivity of the system.

3. The variations of the energy with respect to \( v(r) \) (local property) generate a set of local properties which govern the selectivity (topology) of the system.
Chapter 8

Extensions to excited-states: TD-DFT

8.1 Extension to excited-states: some preliminaries

- Framework (I):
  - An electronically excited state is obtained when a molecule is in a higher-than-ground-state energy level, after absorption of one or more photons: Photochemistry and Photophysics.
  - The most popular extension of (ground-state oriented) DFT to the calculation of excited-states is the time-dependent (TD-DFT); the excited-states are sought after applying a time-dependent (weak) electric field.
  - TD-DFT heritages all the advantages and disadvantages of DFT, including a frequently erratic performance depending on the functional chosen.
  - The flaws of the method are also known: (i) poor description of charge-transfer states; (ii) single-excitation method, thus lacking doubly excited states; (iii) systematic errors in valence states of large $\pi$-extended systems; (iv) impossibility to deal with conical intersections (degeneracies); (v) appearance of intruder (ghost) states . . .
● Framework (II):

○ Looking at what causes the system to get excited, there should always be some time-dependent perturbation of the Hamiltonian. Therefore, we should consider the response of the system to an external stimulus.

\[ \implies \text{The standard approach is to consider the response to a monochromatic perturbation of frequency } \omega . \]

○ The family of TD-methods originates from the variation form of the time-dependent Schrödinger equation:

\[ \delta \int \left[ \Psi^\dagger \hat{H} \Psi - \Psi^\dagger \left( i \frac{\partial \Psi}{\partial t} \right) \right] dt = 0, \quad (8.1) \]

which is merely a consequence of the fifth postulate:

\[ i \hbar \frac{\partial}{\partial t} |\Psi(x, t)\rangle = \hat{H}(x, t)|\Psi(x, t)\rangle, \quad (8.2) \]

with \( \lim_{t \to -\infty} |\Psi(x, t)\rangle = |\Psi(x, 0)\rangle \), showing how a wavefunction evolves with time, being \( |\Psi(x, 0)\rangle \) the corresponding groundstate.

○ An electron excited to a higher state, will return to its groundstate after some time. The finite lifetime (\( \tau \)) gives rise to a finite width of the energy spectrum, according to the uncertainty principle:

\[ \tau \frac{\Delta E}{\hbar c \Delta \nu} \geq \frac{\hbar}{2}, \quad \Delta \nu \text{ (cm}^{-1}) \propto \frac{1}{\tau} \quad (8.3) \]

\[ \implies \text{We just look at the fingerprint of the spectrum through the use of macroscopic dielectric functions exhibiting peaks as a function of } \omega . \]
In practice, the system is perturbed by an electromagnetic field, with:

\[ V = -\mu \cdot E = E_0 \cos(\omega t) \sum_i r_i \alpha, \quad (8.4) \]

and the answer of the system is found.

\[ \Rightarrow \text{For some frequencies, in particular of each system, the answer found is out of proportion (resonance).} \]

8.1.1 Runge-Gross-Kohn-Sham exact formalism

- Runge-Gross theorem:
  
  - Goal: extend the Hohenberg-Kohn theorem (existence and uniqueness of solutions).
  
  - The TD-Schrödinger equation formally defines the map:
    
    \[ v(r, t) \rightarrow i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H}(t) |\Psi\rangle \rightarrow \Psi(t) \rightarrow \langle \Psi(t) | \hat{\rho} | \Psi(t) \rangle \rightarrow \rho(r, t) \]
    
    \[ \Rightarrow \text{However, we need to show that } \rho(r, t) \text{ is equally valid as a variable to completely determine the dynamics of the system.} \]
    
    \[ \Rightarrow \text{Again, it must be proved that a unique, one-to-one, correspondence between } v(r, t) \text{ and } \rho(r, t) \text{ exists.} \]

  - First, the analytical structure of admissible time-dependent external potentials must be of the form:
    
    \[ v(r, t) = \sum_{k=0}^{\infty} (t - t_0)^k \frac{1}{k!} \frac{\partial^k}{\partial t^k} v(r, t)|_{t=t_0}; \quad (8.5) \]
    
    i.e., they can be Taylor-like expanded around the initial time \( t_0 \).
It is shown that if two potentials \( v(r, t) \) and \( v'(r, t) \) differ in more than a constant, \( c(t) \), they cannot lead to the same density \( \rho(r, t) \), that is:

\[
v(r, t) \neq v'(r, t) + c(t), \quad \implies \quad \rho(r, t) \neq \rho'(r, t), \quad (8.6)
\]

which newly implies the biunivocal relation \( v(r, t) \iff \rho(r, t) \).

This means that \( \hat{H}(t) \) and \( \Psi(t) \) are functionals of \( \rho(r, t) \) as well:

\[
v(r, t) \equiv v[\rho, \Psi_0](r, t) \implies \hat{H}(t) = \hat{H}[\rho, \Psi_0](t) \implies \Psi(t) = \Psi[\rho, \Psi_0](t)
\]

In time-dependent systems, the quantum-mechanical action\(^1\) is defined as:

\[
A[\Psi] = \int_{t_0}^{t_1} \langle \Psi(t) | i \frac{\partial}{\partial t} - \hat{H}(t) | \Psi(t) \rangle dt, \quad (8.7)
\]

since a corresponding energy-based variation principle does no longer exist.

- Kohn-Sham equations (I):
  
  The \( N \)-particles automatically satisfy a time-dependent (TD-KS) equation:

  \[
i \frac{\partial}{\partial t} \phi_i(r, t) = \left\{ -\frac{1}{2} \nabla_i^2 + v_s(r, t) \right\} \phi_i(r, t), \quad (8.8)
  \]

  \[
  \rho(r, t) = \sum_i |\phi_i(r, t)|^2, \quad (8.9)
  \]

  with \( v_s(r, t) \) the KS potential\(^2\), given now by:

  \[
v_s(r, t) = v(r, t) + \int \frac{\rho(r', t)}{|r - r'|} dr' + v_{zc}(r, t) \quad (8.10)
  \]

\(^1\)\( \delta A[\Psi] / \delta \Psi(t) \) leads to the TD-Schrödinger equation.

\(^2\)A functional of the entire history of the density.
Contrary to DFT, where $v_{xc} = \frac{\delta E_{xc}}{\delta \rho(r)}$, the potential $v_{xc}(r, t)$ is written as:

$$v_{xc}(r, t) = \frac{\delta A_{xc}}{\delta \rho(r, t)},$$

with $A_{xc}$ the exchange-correlation part of the action function. In contrast to stationary-state DFT, where very good functionals exist, approximation to $v_{xc}(r, t)$ are still in their infancy.

- Kohn-Sham equations (II):
  - The initial condition is $\phi_i(r, t_0) = \phi_i^{(0)}(r)$, which means that we time-propagate via the TD-KS equations only those orbitals initially occupied.
  - The TD-KS formalism implies several steps\(^3\) to become a workable scheme in practice:
    - $\Rightarrow$ Preparation of the initial state of the system by solving the KS equations with some $v_{xc}^{(0)}(r)$.
    - $\Rightarrow$ Time-propagation of the $N$ initially occupied $\phi_i(r, t)$ from $t_0$ to the chosen $t_f$. This requires an approximation to the $v_{xc}(r, t)$.
    - $\Rightarrow$ Self-consistency of the TD-KS equations (numerical time propagation) to obtain $\rho(r, t)$.
    - $\Rightarrow$ Use $\rho(r, t)$ as input for other physical observables based on density functionals [i.e., $N(t) = \int \rho(r, t) dr$].

- The adiabatic approximation: ALDA
  - Key approach (I): to rely on the large number of existing (apparently accurate) expressions for $E_{xc}[\rho]$. If $v_{xc}^{(0)}[\rho]$ is defined

\(^3\)Each step has its own approximations!
for the ground-state, it is readily used in TD-DFT after doing:

\[ v_{xc}^{\text{adiabatic}}[\rho(r, t)] = v_{xc}^{(0)}[\rho(r)]|_{\rho(r) = \rho(r, t)}, \quad (8.12) \]

which receives the name of adiabatic approximations (the most basic one).

- In short, we employ the same functional form\(^4\) but evaluated at each time with the density \(\rho(r, t)\); i.e., we ignore all dependence on the past.

\[ \implies \text{The functional is thus again local \(t, \text{and not} \ t'\), which is often a too crude approximation unless for weak interactions (the perturbed system is close to equilibrium).} \]

- Key approach (II): if for \(v_{xc}^{(0)}[\rho]\) we use the LDA expression, the approach will assume the UEG expression for every point of both position and time spaces: ALDA (Adiabatic LDA).

- Reason: the GGA’s expressions give of course better energetics than LDA but, however, the corresponding potential is not significantly better yet more time-consuming.

### 8.1.2 Lineal response regime: escape from TD-KS equations

- Lineal response regime: Basic theory (I)

  - Suppose a quantum-mechanical observable,

    \[
    \begin{align*}
    \text{GS expectation:} & \quad \alpha^{(0)} = \langle \Psi^{(0)} | \hat{\alpha} | \Psi^{(0)} \rangle \quad (8.13) \\
    \text{TD-perturbation:} & \quad \alpha(t) = \langle \Psi(t) | \hat{\alpha} | \Psi(t) \rangle, \quad (8.14)
    \end{align*}
    \]

    the difference \(\alpha(t) - \alpha^{(0)}\) is called the response of \(\hat{\alpha}\) to the perturbation.

\(^4\)Note that \(v_{xc}^{(0)}[\rho]\) is a ground-state property.
The response can be expanded as \( \alpha(t) - \alpha^{(0)} = \alpha_1(t) + \alpha_2(t) + \ldots \), where \( \alpha_1(t) \) is the linear-response, \( \alpha_2(t) \) the quadratic (or second-order) response, \ldots

The expression for \( \alpha_1(t) \) is:

\[
\alpha_1(t) = \int dt' \chi(t - t') F(t'),
\]

with \( F(t') \) the external field provoking the perturbation.

It is far more common to work in frequency space that in real time, with the Fourier transform:

\[
F(\omega) = \int dt F(t) e^{i\omega t},
\]

since replacing the time with \( \omega \) is the key to extracting the **excitation energies** of a system from its linear response.

- **Lineal response regime: Basic theory (II)**

  At \( t_0 \) we turn on a perturbation to the external potential, \( v_s = v_s(r) + \delta v_s(r, t) \Theta(t - t_0) \), that will induce a change in the density:

\[
\rho(r, t) = \rho(r) + \delta \rho(r, t) + \ldots
\]

where \( \delta \rho \) is the component of \( \rho(r, t) \) that depends linearly on \( \delta v_s \).

As the perturbation is weak, only the linear term will concern us:

\[
\delta \rho(r, t) = \int dt' \int dr' \chi(r, r', t - t') \delta v_s(r', t'),
\]

with \( \chi \) the response of the ground-state to a small change in the external potential.
\[ \chi_s(r, r', t - t') \] tells you how the density will change at point \( r \) and time \( t \) if you make a small change in the external potential at point \( r' \) and time \( t' \).

- The linear change of \( \delta v_s(r', \omega) \) can be calculated from:

\[ \delta v_s(r', \omega) = \delta v(r, t) + \int \frac{\delta \rho(r', t)}{|r - r'|} dr' + \delta v_{xc}(r, t), \quad (8.19) \]

with

\[ \delta v_{xc}(r, t) = \int dt' \int dr' \frac{\delta v_{xc}(r, t)}{\delta \rho(r', t')} \delta \rho(r', t'), \quad (8.20) \]

where we introduce the exchange-correlation kernel \( f_{xc} \) evaluated at the ground-state density, a complex quantity that hides all non-classical many-body effects.

- Its relation to the static case is \( \lim_{\omega \to 0} f_{xc}(r, r', t - t') = \frac{\delta^2 E_{xc}}{\delta \rho(r) \delta \rho(r')} \)

- The simplest form (frequency-independent and local) is:

\[ f_{xc}^{ALDA}(r, r', t - t') = \delta(r - r') \delta(t - t') f_{xc}^{LDA}[\rho]|_{\rho=\rho(r)} \quad (8.21) \]

- Linear response regime: Basic theory (III)

- The \( \chi(r, r', t - t') \) is given (in frequency space) in terms of the unperturbed stationary KS orbitals,

\[ \chi_s(r, r', \omega) = \lim_{\eta \to 0} \sum_{jk} \infty \left( f_k - f_j \right) \frac{\phi_j(r) \phi_j^*(r') \phi_k(r') \phi_k^*(r)}{\omega - (\epsilon_j - \epsilon_k) + i\eta}, \quad (8.22) \]

with \( f_i \) the occupation numbers (0 or 1) of the corresponding orbitals, and \( \omega_{KS} \) represents a transition from occupied \( k \) to
unoccupied $j$ KS orbitals.

\[ \Rightarrow \text{Thus, } \chi \text{ is purely a product of the ground-state KS calculation. Note that when } \omega \text{ matches a true transition energy of the system } \omega = \omega_{KS}, \text{ the response function blows up.} \]

\[ \Rightarrow \text{We see that the response function } \chi_s \text{ has poles at the excitation energies of the KS system.} \]

• Lineal response regime: Excitation energies

  ○ The solution (1996) to the (interacting) density response function goes to:

  \[
  \chi(r, r', \omega) = \lim_{\eta \rightarrow 0} \sum_m \frac{\langle 0|\hat{\rho}(r)|m\rangle \langle m|\hat{\rho}(r')|0\rangle}{\omega - (E_m - E_0) + i\eta} - \frac{\langle 0|\hat{\rho}(r')|m\rangle \langle m|\hat{\rho}(r)|0\rangle}{\omega + (E_m - E_0) + i\eta},
  \]

  \[ (8.23) \]

  where $|m\rangle$ is a complete set of many-body states with energy $E_m$.

  ○ From this expansion, $\chi(r, r', \omega)$ has poles at frequencies that correspond to the excitation energies of the real system, $\Omega = E_m - E_0$.

  ○ In general, $\omega_{KS} = \epsilon_j - \epsilon_k \neq \Omega = E_m - E_0$. But, how large are the deviations between KS and true excitations?; indeed\(^5\), $\Omega = \omega_{KS} + \Delta f_{xc}$.

  ○ The poles come in pairs ($\Omega_m, -\Omega_m$) corresponding to the excitations and deexcitations of the system. If all the deexcitations are neglected (reduction of computational time) this is the Tamm-Dancoff approximation. In the context of the TD-HF theory, this will be equivalent to dealing with CIS.

\(^5\) $f_{xc}$ is the exchange-correlation kernel
8.1.3 The importance of the exchange-correlation potential

- The shape of the exchange-correlation potential (I):
  - For the He atom, it is easy to verify that:

  \[ v_{xc}[\rho] = \epsilon_{\text{HOMO}} + \frac{1}{2} \nabla^2 \left( \sqrt{\rho(r)} \right) - v(r) - \int \frac{\rho(r')}{|r - r'|} dr', \tag{8.24} \]

  and use a near-exact density to obtain its value for a set of GGA-like models\(^6\).

\[ v_{xc}(\rho) = \epsilon_{\text{HOMO}} \phi_{\text{HOMO}}, \tag{8.25} \]

\(\delta E_{xc}(\rho)\) provides a way to measure the performance of different functionals.

\(\delta E_{xc}(\rho)\) can be used to evaluate the accuracy of different functionals.

\(\delta E_{xc}(\rho)\) is crucial for determining the quality of exchange-correlation potentials.

\(\delta E_{xc}(\rho)\) is a measure of the error in the exchange-correlation energy.

\(\delta E_{xc}(\rho)\) is essential for validating the reliability of computational methods.

\(\delta E_{xc}(\rho)\) is a key component in the development of advanced computational models.

\(\delta E_{xc}(\rho)\) is a fundamental quantity in the study of electronic structure.

\(\delta E_{xc}(\rho)\) is a significant factor in understanding the behavior of materials.

\(\delta E_{xc}(\rho)\) is a critical element in the design of new materials.

\(\delta E_{xc}(\rho)\) is a vital parameter in the exploration of novel systems.

\(\delta E_{xc}(\rho)\) is a key parameter in the study of chemical reactions.

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\(\delta E_{xc}(\rho)\) is a critical parameter in the exploration of new materials.
as \( r \to \infty \). Note that we also know that \( v_{xc} \to -\frac{1}{r} \) in that region.

- Since \( \phi_{\text{HOMO}}(r) |_{r \to \infty} \sim e^{-\sqrt{2}r} \), the KS equation yields,
  \[
  -I + v_{xc}(\infty) = \epsilon_{\text{HOMO}},
  \]
  or, equivalently, \( v_{xc}(\infty) = I + \epsilon_{\text{HOMO}} \).

- Combining the aforesaid features, asymptotically\(^7\) \( v_{xc} \to -\frac{1}{r} + I + \epsilon_{\text{HOMO}} \), which is unfortunately not respected by any (unmodified) functional.

\[\implies\] Note how the exact exchange-correlation potential fulfills the above requirement just by definition: \( I = -\epsilon_{\text{HOMO}} \).

- The wrong behaviour of the \( v_{xc} \) in TD-DFT:

<table>
<thead>
<tr>
<th>( v_{xc}[\rho] )</th>
<th>Far from nucleus</th>
<th>Close to nucleus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact ( v_{xc}[\rho] )</td>
<td>( -\frac{1}{r} + \Delta )</td>
<td>Finite</td>
</tr>
<tr>
<td>Model GGAs</td>
<td>rapidly goes to 0</td>
<td>Divergence</td>
</tr>
<tr>
<td>Hybrid GGAs</td>
<td>intermediate ( -\frac{w_{\text{EXX}}}{r} )</td>
<td>Divergence</td>
</tr>
<tr>
<td>Importance (TD-DFT)</td>
<td>Enormous</td>
<td>Negligible</td>
</tr>
</tbody>
</table>

- Note that a wrong \( v_{x} \) does not imply a wrong energy, since we can obtain:

\[
E_{\text{virial}}^x[\rho] = \int dr \left[ 3\rho(r) + \mathbf{r} \cdot \nabla \rho(r) \right] v_{x}[\rho]
\]

<table>
<thead>
<tr>
<th>( E_{\text{virial}}^x ) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B88</td>
</tr>
<tr>
<td>PW91</td>
</tr>
<tr>
<td>PBE</td>
</tr>
<tr>
<td>Exact</td>
</tr>
</tbody>
</table>

\(^7\)Since \( v_c << v_x \), the latter term dominates the shape of the entire \( v_{xc} \).
8.1.4 Charge transfer and related issues

- Charge transfer excitations (I): Generalities
  - Charge is physically transferred to one region to a second (spatially separated) one: weakly bound complexes, functionals groups within the same molecule, etc.

  \[ \Rightarrow \text{Charge transfer (CT) excitations are notoriously predicted too low in energy (by up to } 1 - 2 \text{ eV).} \]

  \[ \Rightarrow \text{Furthermore, in chain-like systems (conjugated polymers) the error in CT excitation energies increases with the chain length.} \]

  - The CT error can be traced back first to the linear-response theory of TD-DFT:
    
    (i) when an excitation moves charge from one region to another, geometry relaxations must concomitantly occur, BUT

    (ii) TD-DFT must deduce those transitions by (infinitesimal) perturbations around the ground-state, without relaxation.

- Charge transfer excitations (II): limit of large separation
Donor ($D$) and acceptor ($A$) subsystems separated by $R$. When $R \to \infty$,
\[ \Omega_{CT}^{\text{exact}} = I_D - A_A - \frac{1}{R} \quad (8.28) \]

However, in TD-DFT treatment:
\[ \Omega_{CT} = \epsilon_{\text{LUMO}}^A - \epsilon_{\text{HOMO}}^D \quad (8.29) \]
\[ + 2 \int \int \phi_{\text{LUMO}}^A(r) \phi_{\text{HOMO}}^D(r) f_{xc}(r, r', \omega) \phi_{\text{LUMO}}^A(r') \phi_{\text{HOMO}}^D(r') d\mathbf{r} \, d\mathbf{r}', \]
but $\phi_i \to 0$ (exponential vanishing overlap in the limit of large separation), so it simply collapses to:
\[ \Omega_{CT}^{\text{TD-DFT}} = \epsilon_{\text{LUMO}}^A - \epsilon_{\text{HOMO}}^D \quad (8.30) \]

Two errors for $\Omega_{CT}^{\text{TD-DFT}}$: (i) it misses the $-1/R$ component; and (ii) $I_D - A_A$ is exactly $\epsilon_{\text{LUMO}}^A - \epsilon_{\text{HOMO}}^D + \Delta_{xc}$, with $\Delta_{xc}$ the correction to the KS gap or the derivative discontinuity. This explains why CT excitations are dramatically underestimated.

- Charge transfer excitations (III): Remedies
  
  - Experience shows that:
    
    \[ \implies \text{For short-range CT between overlapping subsystems, hybrid functionals can partly remedy the problem.} \]
    
    \[ \implies \text{For long-range CT, range-separated schemes (full EXX at long-range) seems to work efficiently.} \]
  
  - The reason can be traced back to TD-HF, for which at large separations:
    
    \[ \Omega_{CT}^{\text{TD-HF}} = \epsilon_{\text{LUMO}}^A - \epsilon_{\text{HOMO}}^D \]
    
    \[ - \int \int \frac{\phi_{\text{LUMO}}^A(r) \phi_{\text{HOMO}}^D(r) \phi_{\text{LUMO}}^A(r') \phi_{\text{HOMO}}^D(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} \, d\mathbf{r}' \]
    
    \[ \to \epsilon_{\text{LUMO}}^A - \epsilon_{\text{HOMO}}^D - \frac{1}{R} \quad (8.31) \]
    
    reproducing (qualitatively) the CT excitations.
8.2 Summary and conclusions

1. Overview of \textit{ab initio} methods:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF</td>
<td>TD-HF ([N^3])</td>
<td>CASSCF</td>
</tr>
<tr>
<td>CI</td>
<td>CIS ([N^3]), CISD ([N^6]) ...</td>
<td>MR-CISD, CAS-CI</td>
</tr>
<tr>
<td>CC</td>
<td>CC2 ([N^3]), CCSD ([N^6]), CC3 ([N^7]) ...</td>
<td>MR-CC</td>
</tr>
<tr>
<td>PT</td>
<td></td>
<td>CASPT2</td>
</tr>
</tbody>
</table>

(a) MR-methods requires much more user intervention; \textit{less "black-box"}. One typically chooses an active space, in which the full variational optimisation is performed.

(b) In practice, we have a linear combination of Slater determinants containing excited-states configurations (single, double, etc.). One needs to optimise both the single-particle orbitals and the expansion coefficients.

(c) The computational cost increases exponentially with the size of the active space, which is \textbf{very time consuming}.

2. On the other hand, \textbf{TD-DFT} delivers a compromise between accuracy and efficiency. However, a straightforward recommendation about the performance of a functional is not always possible...

(a) The Runge-Gross theorem exists for time-dependent systems; and application of this theorem to a non-interacting system yields the Kohn-Sham equations generalised to the time-dependent case.

(b) In the ground state, the energy satisfies a minimisation principle; the time-dependent analog is the action, which satisfies a stationary condition. However, the actual value of action is never of interest, but only its functional derivative.
(c) If the time-dependent phenomena can be treated as a weak perturbation of the ground state, the linear response theory gives excitation energies as the poles of the interacting susceptibility.

(d) Whenever a method is shown to work well, it inevitably gets applied to many fields, and (again inevitably) some failures then appear.

(e) Linear-response TD-DFT works best for: (i) low-energy transitions, which (ii) involves mainly one-electron excitations, with (iii) little or no charge transfer, and in (iv) not too delocalised systems.

3. Sources of errors in predictions from TD-DFT:

(a) The sin of ground-state: errors in the underlying DFT (ground-state) calculations; if KS eigenvalues and eigenorbitals miss accuracy, TD-DFT can not overcorrect it.

⇒ Overall, the ground-state potential appears to be the most important factor determining the quality of TD-DFT excitation energies.

(b) The sin of sightedness: errors due to local (or semilocal) approximations (LDA, GGA, etc.) to the kernel $f_{\text{xc}}(\mathbf{r}, \mathbf{r}')$ which may require nonlocality in $|\mathbf{r} - \mathbf{r}'|$. 

(c) The sin of forgetfulness: errors due to the local approximations in time (memory is missed) for phenomena requiring nonlocality in $t - t'$. 

(d) The sin of wavefunction: the TD-KS wavefunction is an approximated construct, and may differ from the real one; thus, observables evaluated on the former may be inaccurate.

In other words: it is completely science-fictioned to claim an accuracy in practical calculations larger than $0.1 - 0.2 \text{ eV}$.
Chapter 9

Tests of knowledge

9.1 Tests of knowledge (I)

The following are some questions that will help you refresh the memory about undergraduate chemistry/physics courses dealing with quantum-mechanical aspects, and that will allow you to exercise the main features shown across the first lecture focused on ab initio methods; more specifically, on their features differing from DFT. Some basics on postulates of quantum mechanics, including bra-ket notation, are encouraged.

1. Answer right or wrong to the following questions:

   (a) The computational cost of the CCSD method lies between that of CCSD(T) and CCSDT

   (b) All the methods based in perturbation theory up to second order (MP2, SCS-MP2, ...) formally scale similarly with the size of the system

   (c) The correlation energy is always a stabilising effect ($E_c < 0$)

   (d) Particle-particle correlations can be systematically added towards the exact solution by excitation operators, starting from a 0th-order solution

   (e) Basis set truncation error refers to the difference between the calculated solution to the Schrödinger equation and the experimental value
(f) Any quantum-chemical method depending explicitly on the interelectronic distance \( r_{ij} = | \mathbf{r}_i - \mathbf{r}_j | \) introduces mainly “dynamic correlation”

(g) The “chemical accuracy” is more difficult to achieve than the “calibration accuracy” in practical calculations

(h) A method is said to be size-consistent if the energy of the system AB, if A and B are very far apart, is the same as the energy of A plus the energy of B evaluated separately

2. Let’s suppose that our method of choice scales with the size of the system (\( N \)) as \( N^6 \). After applying it to calculate the energy of a monomer of a polymer-like compound, one needs a total CPU time of about 15000 s. If one switches now to a dimer or a trimer of the same compound, how much total CPU time would the same type of calculation consume? Does this sound reasonable? How many cores one would need to run in parallel the new calculations to consume the same time than for the monomer?

3. To get an impression of the “exponential wall” one always encounters when dealing with many-body wavefunctions, let us imagine that we represent the wavefunction of a four-electron system described by the minimal STO-3G basis set, which implies three parameters (coefficients of basis functions) for each particle, and a variety of theoretical methods ranging from \( N^2 \) (semi-empirical) to \( N^7 \) [CCSD(T) or MP5]. Show that the CPU time will behave as:

![Graph showing CPU time vs. k (from a N scaling)]
concerning now the storage requirement, consider a one-electron system whose wavefunction needs 10 parameters (be them grid points, coefficients...) for each spatial coordinate and therefore would require $10^3 = 1000$ numbers to fully represent it. In single precision, this corresponds to 1kb of data that needs to be stored. How many bytes would you need to store the wavefunction of a two-electron system, and how many for a 10-electron system? Assume that a hard drive has a capacity of 1 Terabyte, how many hard drives do you need?

4. If an experimentally measured magnitude at 300 K happens to be of the order of the thermal energy $k_B T$, which criteria for accuracy (“chemical”, “calibration” or “spectroscopy”) should one impose to our calculation to accurately reproduce that magnitude?

5. Given a certain well-behaved wavefunction $\Psi(r) = A \sin(kr)$ find the eigenvalues (if any) of the following operator $\hat{O}_1 = \frac{d}{dr}$ and $\hat{O}_2 = \frac{d^2}{dr^2}$. Calculate also the value $[\hat{O}_1, \hat{O}_2]$.

6. Consider now a spherically symmetric monoelectronic atom, for which the Hamiltonian operator takes the form $\hat{H} = -\frac{1}{2} \frac{1}{r^2} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{1}{r}$, and apply it to the trial function $\phi(r) = Ne^{-\beta r}$ with $\beta$ a parameter and $N$ some normalisation constant. Apply the variational principle to find the optimal value of $\beta$ and hence the lowest possible energy of the system.

7. Consider now the ground state of the H atom, being $\phi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$ an hydrogen-like orbital, and calculate\(^1\) the following terms as the mean value of the corresponding operator:

(a) The kinetic energy, as given by $\langle T \rangle = -\frac{1}{2} \int \phi_{1s}^* \nabla^2 r \phi_{1s} dr$, with $\nabla^2 r = \left( \frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} \right)$.

(b) The potential energy, as given by $\langle V \rangle = \int \phi_{1s}^* \left( -\frac{Z}{r} \right) \phi_{1s} dr$.

\(^1\)The following integral is needed: $\int_0^\infty x^a e^{-\alpha x} dx = \frac{\alpha^a}{\alpha^{a+1}}$
After that, add them to have the total exact-like energy $\langle E \rangle$. Next show how the virial theorem is indeed fulfilled, $\langle T \rangle = -\frac{1}{2}\langle V \rangle$. Give (in eV) the ionisation potential of the system.

8. Let’s consider a system AB composed of two non-interacting subsystems A and B. For this system, there is a certain magnitude $F$ which can be shown to behave as $F_{AB} = F_A + F_B$, a property known as “additive separability”. If we now define the magnitude $G = e^F$ and apply it to our system, try to infer the kind of separability we have now.

9. It is well-known that the exponential operator $\hat{\Omega} = e^T$ automatically satisfies the requirement of proper separability, as it is shown before. Show that, after rearranging a supersystem (AB) eigenvalue problem as:

$$\hat{H}_{AB} \hat{\Omega}_{AB} |\Psi_0\rangle = E_{AB} |\Psi_0\rangle,$$

the energy is $E_{AB} = \langle \Psi_0 | \hat{H}_{AB} \hat{\Omega}_{AB} |\Psi_0\rangle = E_A + E_B$ for two non-interacting subsystems. Note that $\hat{T}_{AB} = \hat{T}_A + \hat{T}_B$ and that $\hat{T}_i$ acts only on the subsystem A or B. Relate this feature with practical calcula tions employing hierarchical CC methods.

10. Now consider a trial wavefunction for the He atom involving one double replacement from occupied ($\phi_1$) to virtual orbitals ($\phi_j$, $j > 1$), such as $|\Psi\rangle = |\Psi_0\rangle + c |\Psi_{ij}\rangle$. For two such He atoms (A and B) represented by such a wavefunction a long way apart, obtain the corresponding wavefunction (given by $|\Psi_{A-B}\rangle = |\Psi_A\rangle \cdot |\Psi_B\rangle$ after imposing right separability). Note that the resulting wavefunction involves up to four-fold replacements of the reference wavefunction. Relate this feature with practical calculations employing hierarchi cal CI methods.

11. A simple way to introduce correlation effects is to force a dependence of the wavefunction on the distance between particles $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, the motions of the electrons is therefore naturally correlated. Consider a two-electron system, $r_{ij} = r$ here, and write the
Schrödinger equation in spherical polar coordinates as:

\[
\left(-\frac{\partial}{\partial r^2} - 2\frac{\partial}{r \partial r} + \frac{1}{r}\right) |\Psi\rangle = E |\Psi\rangle.
\]

Now expand the wavefunction \( \Psi(r) \) as \( \Psi(r) = a + br + cr^2 + \ldots \), substitute in the equation, and after equating the coefficients of \( r^{-1} \) to zero, get the resulting expression for the wavefunction. The solution to be found means that near the coalescence point (electron coincidence) the wavefunction depends linearly on \( r \), and thus we have the correct reduction in probability as two electrons approach one another.

12. A four-electron system has the following orbital energies:

![Diagram of orbital energies](image)

Note that \( \phi_2 \) and \( \phi_3 \) are completely degenerate in this case. Write the, necessarily Multi-Configurational (MC), wavefunction corresponding to the singlet ground state of the system as \( |\Psi\rangle = \sum_I c_I |\Phi_I\rangle \), where the different \( \Phi_I \) arises from all the possible orbital occupancies, excluding \( \phi_2^2 \phi_3 \phi_3 \) by symmetry grounds. Note also that \( \langle \Phi_I | \Phi_J \rangle \neq \delta_{IJ} \) and that \( \sum_I c_I^2 = 1 \). Then, what is the expectation value of \( \hat{H} \)? Show that this energy is indeed lower than if we remove the existing degeneracy. This lowering is known as “static (non-dynamic) correlation” and it is always present when more than a Slater determinant is needed to properly represent (even qualitatively) the system under study, and independently of the post-MC treatment performed.
13. The only way forward to continue, after having introduced analytical basics for both existing correlation effects, is to continue with the use of excited determinants. It can be easily shown that taking a linear combination of determinants we introduce naturally the square of $r_{ij}$. Consider a four-determinant wavefunction for the He atom:

$$\Psi = c_1|\phi_1\overline{\phi}_1\rangle + c_2|\phi_2\overline{\phi}_2\rangle + c_3|\phi_3\overline{\phi}_3\rangle + c_4|\phi_4\overline{\phi}_4\rangle,$$

where:

$$c_1 = 1; \quad c_2 = c_3 = c_4 = c;$$

and (spatial part only):

$$\phi_1 = e^{-2r}, \quad \phi_2 = xe^{-2r}, \quad \phi_3 = ye^{-2r}, \quad \phi_4 = ze^{-2r}.$$

Obtain the final form of the wavefunction. Note that the 2nd, 3rd, and 4th determinants in the above example are each double replacement of the first one, showing that double excitations\(^2\) introduce the square of the interelectronic distance in a natural way, and therefore correlation effects into the wavefunction. In practice, it is found that the CI method is very slowly convergent, needing very large basis sets to generate a large number of virtual orbitals to use in the double replacement determinants.

### 9.2 Tests of knowledge (II)

The following are some questions infinitely related to the concepts forming the core of DFT, developed across the different lectures given.

1. The potential energy operator, $\hat{v}(\mathbf{r}) = -\sum_A^M \sum_i^N \frac{Z_i}{|\mathbf{r}_i - \mathbf{R}_A|}$, where

$M$ ($N$) refers to nuclei (electrons) can be decomposed, as the kinetic energy expression, as follows: $\hat{v}(\mathbf{r}) = \sum_i \hat{v}(\mathbf{r}_i)$, due to its

\(^2\)Take home message: double excitations really matter, and help to explain the historical success of methods like CI$+$SD or MP2.
dependence solely on one-electron coordinates \( r_{iA} \). Normally, it is further simplified to write \( v(r) = \sum_i v(r_i) \). Try thus to obtain the representation (mean value) of such operator: \( \langle \Psi | v(r) | \Psi \rangle \)

2. About the functional derivative (I):

(a) Given a function of one variable, \( y = f(x) \), the differential of such function, \( dy \), measures the change induced for \( y \) produced by the variation \( x \to x + dx \) of the variable \( x \). The derivative, \( \frac{dy}{dx} \), measures the changes up to first order of \( y = f(x) \) upon changes of \( x \), that is, the slope of the function \( f(x) \) in \( x \):

\[
    f(x + dx) = f(x) + \frac{df}{dx} dx + O(dx^2).
\]

The functional derivative represents, similarly, first-order changes in the functional \( F[f(x)] \) upon changes in its argument,

\[
    F[f(x) + \delta f(x)] = F[f(x)] + \int s(x)\delta f(x)dx + O(\delta f^2),
\]

where the integral indicates that the variation of the functional \( F[f(x)] \) is determined by the variation of the function in all points of the space. The “slope of the functional”, \( s(x) \) is defined now as the functional derivative \( \frac{\delta F[f]}{\delta f(x)} \). This functional derivative allows one to study how a functional change upon changes in the function to which depends.

(b) One classical technique to find the functional derivative is to force first an explicit dependence of the variation on a parameter \( \alpha \), and then to derive with respect to this parameter when its value tends to zero:

\[
    \frac{\delta F[f]}{\delta f(x)} = \frac{d}{d\alpha} F[f(x) + \alpha \delta f(x)] \bigg|_{\alpha \to 0}
\]

If we apply the later technique to the well-known functional
\[ T[\rho] = \int \rho(r)^{5/3} \, dr, \] we find:

\[
T[\rho + \alpha \delta \rho] = \int (\rho + \alpha \delta \rho)^{5/3} \, dr
\]

\[
\frac{d}{d\alpha} T[\rho + \alpha \delta \rho] = \frac{5}{3} \int (\rho + \alpha \delta \rho)^{2/3} \delta \rho \, dr
\]

\[
\frac{d}{d\alpha} T[\rho + \alpha \delta \rho] \big|_{\alpha=0} = \frac{5}{3} \int \rho(r)^{2/3} \delta \rho(r) \, dr,
\]

and thus the term which is linear in \( \delta \rho(r) \) is the corresponding functional derivative:

\[
\frac{\delta T[\rho]}{\delta \rho(r)} = \frac{5}{3} \rho(r)^{2/3}.
\]

(c) The task is now to find yourself the functional derivative of the following classical expressions:

\[
E_{x}^{\text{LDA}}[\rho] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int \rho(r)^{4/3} \, dr
\]

\[
E_{c}^{\text{LDA}}[\rho] = -\int \frac{0.44}{7.8 + \rho(r)^{1/3}} \, dr
\]

3. About the functional derivative (II)

(a) For the class of functionals commonly encountered in DFT applications, having the form:

\[
F[\rho] = \int e(\rho(r), \nabla \rho(r)) \, dr,
\]

it can be shown that the functional derivative can be written as:

\[
\frac{\delta F[\rho]}{\delta \rho(r)} = \frac{\partial e}{\partial \rho} - \nabla \cdot \frac{\partial e}{\partial \nabla \rho}.
\]

If we now apply this definition to the functional \( T[\rho] = \int \rho(r)^{5/3} \, dr \), we immediately find:

\[
\frac{\delta T[\rho]}{\delta \rho(r)} = \frac{\partial \rho(r)^{5/3}}{\partial \rho} \frac{5}{3} \rho(r)^{2/3},
\]

which, of course, coincides with the former result.
(b) The task is now to find yourself, using the above expression, the functional derivative of the following functionals:

\[ J[\rho] = \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' \]

\[ T_w[\rho, \nabla \rho] = \frac{1}{8} \int \frac{\nabla \rho(r) \cdot \nabla \rho(r)}{\rho(r)} dr \]

Note the dependence of \( T_w \) in \( \nabla \rho \) too.

4. The last term in the famous LYP correlation functional reads:

\[ \int \omega \rho^3(r)|\nabla \rho(r)|^2 dr \]

Evaluate the functional derivative of this term with respect to the density function. For simplicity treat \( \omega \) as a constant.

5. The Fermi hole is due to the antisymmetry of the wavefunction and affects the behaviour of electrons of the same spin: because of the Pauli principle, the conditional probability for electrons of spin \( \sigma \) must integrate to \( N_\sigma - 1 \) rather than to \( N - 1 \) because there can be no other electrons of spin \( \sigma \) at position \( r_1 \). Using this information, show that:

\[ \int h_x (r_1, r_2) dr_2 = -1, \]

and, consequently, \( \int h_c (r_1, r_2) dr_2 = 0 \). Show also that again due to the Pauli principle, which ensures that two electrons of the same spin cannot be at the same position in space, the Fermi hole has to become equal to minus the density of electrons with this spin at the position of the reference electron for \( r_2 \rightarrow r_1 \),

\[ h_x (r_1, r_2 \rightarrow r_1) = -\rho (r_1). \]

6. The Thomas-Fermi total energy of an electron system is given by:

\[ E = C_{TF} \int \rho(r)^{5/3} dr + \int V_{ext} \rho(r) dr + \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr', \]
with $V_{ext}$ the external potential being felt by the particles. Find the corresponding $\frac{dE}{d\rho}$. Find how adding the exchange energy provided by Dirac modified its expression.

7. To simply show how it might make sense that a property such as the kinetic energy of a system of particles can be related to the electron density, consider a system of $N$ non-interacting electrons moving in a 3D cubic box. The energy states of such particles is known to be:

$$E = \frac{\hbar^2}{8m_eL^2} (n_x^2 + n_y^2 + n_z^2),$$

with $L$ the length of the box along the three axes, and $n_i$ the quantum numbers describing the state. We can view $n_x^2 + n_y^2 + n_z^2 = R^2$ as the squared radius of a sphere in the quantum numbers space. Follow the steps: (i) find the volume of the sphere of radius $R$ as a function of $E$, which is called the integrated density of states $\Phi(E)$; (ii) next find the number of states with energy between $E$ and $E+dE$, given by $g(E) = \frac{d\Phi}{dE}$; (iii) calculate the total energy for $N$ electrons that doubly occupy all states having energies up to the HOMO (or Fermi) level, as given by $E = 2 \int_{E_0}^{E} g(E)E dE$; (iv) calculate the total number of electrons, $N = 2 \int_{E_0}^{E} g(E)dE$; and (v) finally solve for $E_0$ in terms of $N$ to express $E$. As the potential energy is zero within the box, the kinetic energy obtained leads to $E \propto \rho^{5/3}$.

8. Now consider the ground state of the H atom, being $\phi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$ and $\rho(r) = \phi_{1s}^2(r)$, and calculate\(^3\) the following terms:

(a) The kinetic energy as given by the Thomas-Fermi expression, $T[\rho] = C_{TF} \int \rho^{5/3}(r)dr$.

(b) The exchange energies as given by the Dirac, $E_x[\rho] = C_x \int \rho^{4/3}(r)dr$, and the $X_a$ (Slater) expressions

Show and discuss if any self-interaction-error (SIE) in this system exists (note that for an uncorrelated one-electron system the ex-

---

\(^3\)The following integral is needed: $\int_0^\infty x^ne^{-ax}dx = \frac{n!}{a^{n+1}}$
change energy should exactly vanish in an exact theory. Now calculate the extra exchange energy given by an hypothetical (but strong) gradient correction like this:

\[ \Delta E_x[\rho] = -C_x \int |\nabla \rho(\mathbf{r})|^2 d\mathbf{r}, \]

and relate it to the former (LDA) value. Recalculate the SIE.

9. A simple way to tune down the SIE in one-electron systems is to remove that spurious interaction of an electron with itself. Show that for the exchange functional \( E_x[\rho] = C_x \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \), the way to correct it is through the modification \( E_x \left[ \frac{\rho}{N} \right] \) in such a form that the new expression gives:

\[ E_x[\rho]' = E_x[\rho] - E_x \left[ \frac{\rho}{N} \right] = 0, \]

as it should be. However, this is a very rough approximation for heavier atoms and is not considered for practical calculations.

10. Write carefully the exact Kohn-Sham and Hartree-Fock equations for the Hydrogen atom. Compare and comment.

11. Consider a two-electron system with a doubly occupied Kohn-Sham orbital (i.e., the Helium atom) and show that the exact exchange energy is minus one-half of the Coulomb energy in this case. Derive the corresponding exchange and Coulomb potentials as well as, using these results, the corresponding exchange-correlation and correlation potentials.

12. The output (some part) of a HF-LYP calculation, note that the correlation potential is added to a Hartree-like exchange potential, reads as:

\[ E_{\text{ex}} \left[ \frac{\rho}{N} \right] = E_x[\rho] - E_x \left[ \frac{\rho}{N} \right] = 0, \]

\[ \Delta E_x[\rho] = -C_x \int |\nabla \rho(\mathbf{r})|^2 d\mathbf{r}, \]

\[ E_x[\rho]' = E_x[\rho] - E_x \left[ \frac{\rho}{N} \right] = 0, \]

\[ E_{\text{ex}} \left[ \frac{\rho}{N} \right] = E_x[\rho] - E_x \left[ \frac{\rho}{N} \right] = 0, \]

\[ \Delta E_x[\rho] = -C_x \int |\nabla \rho(\mathbf{r})|^2 d\mathbf{r}, \]

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\[ E_x[\rho]' = E_x[\rho] - E_x \left[ \frac{\rho}{N} \right] = 0, \]

\[ E_{\text{ex}} \left[ \frac{\rho}{N} \right] = E_x[\rho] - E_x \left[ \frac{\rho}{N} \right] = 0, \]
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<tr>
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<tr>
<td>Nuclear Repulsion</td>
<td>0.000000000 Eh</td>
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<td>One Electron Energy</td>
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<td>Two Electron Energy</td>
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<table>
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<tr>
<th>DFT components</th>
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<tbody>
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<tr>
<td>N(Beta)</td>
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<td>E(C)</td>
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</tr>
<tr>
<td>E(XC)</td>
<td>-0.000000000000000 Eh</td>
</tr>
</tbody>
</table>

If we now repeat the calculations with the PBE correlation counterpart, and, of course, under the same technical conditions and with the same software, the output is:
9. Tests of knowledge

<table>
<thead>
<tr>
<th>Components:</th>
<th>Value</th>
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<tbody>
<tr>
<td>Total Energy</td>
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<tr>
<td>Nuclear Repulsion</td>
<td>0.00000000 Eh</td>
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<tr>
<td>Virial Ratio</td>
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</table>

DFT components:

- \( N(\text{Alpha}) \) = 1.000000000075 electrons
- \( N(\text{Beta}) \) = 0.000000000008 electrons
- \( N(\text{Total}) \) = 1.000000000083 electrons
- \( E(X) \) = 0.0000000000000 Eh
- \( E(C) \) = -0.006045887431 Eh
- \( E(XC) \) = -0.006045887431 Eh

Comment all the valuable information that can be extracted from the calculations. Compare the two calculations with exact values \([-0.5 \text{ Eh}; E(XC): 0.0 \text{ Eh}]\), and indicate the origin of the (if any) SIE.

13. The Hellmann-Feynman theorem relates the derivative of the total energy with respect to a parameter, to the expectation value of the derivative of the Hamiltonian with respect to that same parameter:

\[
\frac{\partial E}{\partial \lambda} = \langle \Psi | \frac{d\hat{H}_\lambda}{d\lambda} | \Psi \rangle.
\]

In the adiabatic connection approach, the exchange-correlation functional is reexpressed as:

\[
E_{xc}[\rho] = \int_0^1 \frac{\partial F_\lambda}{\partial \lambda} d\lambda - U[\rho].
\]

Find the expression of the functional after applying the above theorem to \( E_{xc}[\rho] \).
14. One of the last conjectured expression [J. Chem. Phys. 124 (2006) 091102] for the \( W_\lambda \) functional entering into the adiabatic connection approach takes the form:

\[
W_\lambda = a + \frac{\lambda b}{1 + \lambda c},
\]

where \( a, b, \) and \( c \) are to be constructed as functionals of the density or the orbitals, which necessarily must be related to non-classical physical effects. Perform the corresponding analytical integration to derive the associated form of the \( E_{xc}[\rho] \):

\[
E_{xc}[\rho] = \int_0^1 W_\lambda[\rho] \, d\lambda
\]

Furthermore, show that the \( W_\lambda \) fulfills some other known conditions: (i) the curve monotonically decreases with increasing \( \lambda \), \( \frac{\partial W_\lambda}{\partial \lambda} < 0 \) \( \forall \lambda \); and (ii) \( \lim_{\lambda \to \infty} W_\lambda = \text{finite} \).

15. Suppose that the energy of a system varies with respect to its number of particles \( N \) through an equation like \( E(N) = aN^2 + bN + c \). If a chemical system in a charged state \( M^+ (N) \) goes to \( M^- (N+2) \), passing through the neutral state \( M (N+1) \), show that the hardness takes the expression:

\[
\eta = \left( \frac{\partial^2 E}{\partial N^2} \right)_{v(r)} = I - A,
\]

being \( I \) the ionisation energy, defined as \( E(M^+) - E(M) \), and \( A \) the electron affinity, defined as \( E(M) - E(M^-) \).

16. We also know that the variation of the energy \( \Delta E \) up to second order for a system with a fixed external potential, and for an electron transfer \( \Delta N \), satisfies the expression:

\[
\Delta E = \mu \Delta N + \frac{1}{2} \eta \Delta N^2,
\]

where \( \mu \) and \( \eta \) are the chemical potential and the hardness, respectively. Show that in the so-called ‘saturation point’, when \( \frac{\Delta E}{\Delta N} = 0 \),
we have that $\Delta E = -\frac{u^2}{2\theta}$, which is also coined as “electrophilicity index”. Using DFT, in your favourite flavour, calculate this index for the system you are investigating now and compare the value with that of your (again favourite) colleague.

17. The problem of calculating the tiny binding forces between neutral entities at close range relies mainly on correlation effects. Consider two neutral rare-gas atoms A and B, at a distance apart so that $\rho_{AB} = \rho_A + \rho_B$, although $\int \rho_A(r)\rho_B(r)dr \neq 0$ but small. Obviously, the binding energy of the complex at a distance $R$ is given by $\Delta E_{AB} = E_{AB}(R) - E_A - E_B$. Use Thomas-Fermi formula for kinetic energy, the Dirac expression for exchange, and some general expressions (i.e., $\int \rho(r)e^2c[\rho]dr$) for correlation to find the corresponding expression for $\Delta E_{AB}$. The use of the above two conditions for the densities allows one to isolate the correlation energy as the (main) physical source of the (if any) binding.

18. Show, as explicitly as possible, using the functionals $U[\rho]$ and $\tilde{U}[\rho] = U[\rho] - \frac{1}{N}U[\rho]$, the expected separability of this energy for the case of two He atoms (A and B) infinitely separated, that is:

$$U[\rho_{\text{He}(\text{A})} + \rho_{\text{He}(\text{B})}] = U[\rho_{\text{He}(\text{A})}] + U[\rho_{\text{He}(\text{B})}],$$

$$\tilde{U}[\rho_{\text{He}(\text{A})} + \rho_{\text{He}(\text{B})}] \neq \tilde{U}[\rho_{\text{He}(\text{A})}] + \tilde{U}[\rho_{\text{He}(\text{B})}]$$

Note that $N = 4$ for the system He $\cdots$ He ($R \rightarrow \infty$) although $N = 2$ was for each of the subysystems. This result means that any functional containing an explicit dependence on $N$ is not size-extensive. In fact, since $N = N[\rho]$, some experts have recently questioned the ability of common functionals to provide results not degrading with the size of the system, as indeed happens for increasingly larger $\pi$-conjugated systems.

19. Let us clarify what it meant by “different potentials” in TD-DFT.

If two potentials differ only by an additive time-dependent scalar

---

5This correction is due to Fermi-Amaldi (1934), whose purpose was to correct approximately the self-interaction of an electron with itself, a common drawback of almost all functionals in use today as seen before.
function \( c(t) \), then the corresponding wavefunctions differ only by a simple time-dependent phase factor,

\[
v'(\mathbf{r}, t) = v(\mathbf{r}, t) + c(t); \quad \Psi'(t) = e^{-i\alpha(t)}\Psi(t),
\]

with \( da(t)/dt = c(t) \) (this result follows from the time-dependent Schrödinger equation). Show that the resulting densities, \( \rho'(\mathbf{r}, t) \) and \( \rho(\mathbf{r}, t) \), will be strictly identical (hint: start from \( \rho'(\mathbf{r}, t) = \langle \Psi'(t)|\hat{\rho}(\mathbf{r})|\Psi'(t)\rangle \)).
Appendix A

Valuable books

Through these books the reader may expand any topic dealt with, as well as to go deeper inside into his/her specific area of research. It is also gratifying to deeply recognise the great work done by their authors since, of course, many of the present lecture notes are inspired by these sources. The books are listed within each category in reverse chronological order, without any other further intention.

- Some of the most useful Computational Chemistry and Molecular Modeling books:


• Some of the most useful Density Functional Theory books:


• Some of the most useful (Time-Dependent) Density Functional Theory books:

Appendix B

Keynotes and self-evaluation

⇒ Write short sentences (up to 3) summarising the main features developed across the different lectures given, according to your (necessarily subjective) opinion:

• Lecture 1.- Quantum Chemistry: *ab initio* and/or DFT methods
  1. .................................................................
  2. .................................................................
  3. .................................................................

• Lecture 2.- The electronic density is the key: definitions and primitive models
  1. .................................................................
  2. .................................................................
  3. .................................................................
• **Lecture 3.** Hohenberg-Kohn-Sham formalism: the exchange-correlation functional

1. .................................................................

2. .................................................................

3. .................................................................

• **Lecture 4.** Chemical concepts and reactivity

1. .................................................................

2. .................................................................

3. .................................................................

• **Lecture 5.** Extensions to excited-states: TD-DFT

1. .................................................................

2. .................................................................

3. .................................................................

• Try now to summarise in no more than 50 words what is DFT:
Evaluate numerically from 0 (not fulfilled) to 10 (fully fulfilled) the following items, briefly reasoning the score given:

1. Knowing the theoretical foundations of Density Functional Theory as applied to Chemistry and Physics nowadays.

2. Being able to identify in advance the accuracy and limitations of Density Functional Theory for quantitative and productive research.

3. Being able to perform state-of-the-art computational experiments by yourself, bracketing the associated experimental (computationally speaking) error.
Additional features related to the course: comments, suggestions, missed contents, etc.
Appendix C

Ethical Guidelines

The present chapter is based on the guidelines for good scientific practice elaborated by the Danish Committees on Scientific Dishonesty. The guidelines focus on health, natural and technical science, but should be applicable to other areas as well. Hopefully, scientists will consider the guidelines supportive to their work and supportive to introducing younger scientists to good scientific practice for the overall purpose of raising the scientific quality of the research process. The Committee recommended that managers and project supervisors in all research institutions make all scientists aware of the guidelines, or produce local guidelines based on similar principles.

More information can be found in the following link:

http://en.fi.dk/councils-commissions/the-danish-committees-on-scientific-dishonesty

C.1 Guidelines for agreements at the initiation of research projects

The following list comprises items which it might be advantageous to have discussed and formally agreed upon at the initiation of research projects, especially when several centres or departments participate. Such agreements may be based on a selection or all the items on the list.
Smaller research groups may not need formal agreements, but the more complex the collaboration, the greater the need for agreements. The scope of the contract/agreements must depend on the research group’s concrete evaluation. The list may serve as a check-list for agreements as well as for the many activities necessary during the course of the project.

Basic elements of collaborative agreements:

- Title, participants, objectives and timeline of the research project.
- Project management and rules of procedure.
- Research protocol/study plan.
- Internal information about project progress.
- Allocation of functions.
- Access to equipment, assistance and other facilities.
- Planned publications and academic theses.
- Preparation of publications and allocation of authorships.

We remind you that the overall ambition for research is the acquisition of new knowledge and spreading of the knowledge thereof, unprejudiced and with no other restriction than as followed from quality assessment. This is incompatible with ownership which usually means that the owner may also destroy or keep the research results a secret and data as he or she deems appropriate. Thus, we better speak about the right and duty to use them in a responsible way and have them in custody.

Scientists shall have right of use of analysis and publication of the data they have produced or assisted in producing by creative efforts. However, other scientists shall only apply such unpublished data in own publications upon prior agreement with the scientists who have produced them. Political, administrative and scientific managers or supervisors who are not directly involved in the research process may be co-responsible for the quality of the work and the resulting publications, but they should
not prevent or delay the publication for the reason that the results are unexpected or unwanted.

Universities and similar institutions usually do not exercise influence on the publishing process, but usually assume that publishing is made in scientific journals or books. The rights and responsibilities of scientists in relation to a publication which appears scientific should be considered independent of the manner of publication. The individual scientist’s right to the use of data should be exercised within the framework of the cooperation with the other participants according to the agreements entered into, fully open and respecting the other members’ duties and rights. On the use of data, the scientists in cooperation should seek to avoid unnecessary delays.

C.2 Guidelines on publication matters

When scientific work is published, it either appears as the work of one person or as the work of a group of authors of which one has main author status, while the others are co-authors. If it is not a situation of single authorship, unclarity may arise about who is entitled to an authorship. However, it is internationally acceptable that the right to authorship is acquired by creative efforts and only thereby.

In order to obtain the right to become an author, the following three requirements must be met:

1. An author must have contributed significantly to the creative process, usually within more than one of the following elements: idea, planning, experimental work, collection of data, data analysis and interpretation.

2. An author must have contributed to the preparation of the final article by participating in the preparation of the draft manuscript and/or through critical revision signifying the appearance of the article.
3. An author must have approved the final version of the manuscript in writing.

Note that in some journals, prior to submission of the manuscript, a common authorship declaration ought to be prepared, which precisely indicates the nature and volume of each author’s contribution without the use of stereotypes. In all other respects, an author shall be able to indicate in detail his or her own contribution and must have participated to such degree in the entirety of the work, that the relevant party is able to indicate the full contents of the manuscript and be able to discuss fundamental aspects of the remaining contributions. Furthermore, all authors of an article –within the limits of what is possible and fair– are co-responsible for it being based on honest research so as for the risk of fraud to be minimised.

As predominantly creative efforts give access to authorship, individual instances in the form of, e.g. the head of institute’s provision of framework conditions, specialist departments’ services of routine data or mere help in the collection of data, should not be rewarded by authorship, but such institutions/people should be acknowledged in a special section for providers of non-authorship-entitling contributions, usually named acknowledgements.

The guidelines may give rise to problems for supervisors accustomed to gift-authorships. However, the right to authorship must follow the usual rules, also in this relation, and accordingly, only supervisor(s), who meet the above three requirements should be co-author(s).

Obtaining right to authorship is not related to specific positions, professions or training and does not depend on whether the efforts of the relevant person are salaried or unsalaried. If the creative efforts meet the above three conditions, they are entitled to authorship.

For reviewing articles, it also applies that the authors are to have performed the work on collecting, reading and critically assessing the referred literature. Accordingly, it does not entitle to authorship to merely
having reviewed a manuscript prepared by others nor if corrections are proposed in this connection.

The order of authors has added different significance in the international scientific sphere, and no consensus seems possible. The generally applied practice, which however is not subject to international unanimity, is that the participant contributing the most significant work efforts and preparing the first manuscript is indicated as first author, while the often senior participant, who is overall responsible for the project, but who meets the previously stated criteria for co-authorship, is indicated as final author.

Preparation of manuscripts for publications should take place within the framework of the cooperation in the group of scientists, fully open and in accordance with agreements entered into. Furthermore, by reason of, among others, a recent scandal, it is recommended that all co-authors receive confirmation e-mail from the editorial office or from the main author when a manuscript has been submitted.

Reference to published works within the processed area of subjects has the purpose of partly connecting the current work with the other research on the area, partly to give other scientists the recognition due to them. These purposes are closely connected, and careful handling of them is significant to the quality of work. No reference should be made to own work or the work of colleagues apart from what the compliance of the said purposes requires, and references should not be applied for artificial increase in the frequency of quotes or the work of others or for systematic omission of the references of others.
Appendix D

Hardware & Software issues

D.1 Beowulf clusters

A Beowulf is a class of computer clusters deployed worldwide, chiefly in support of scientific computing. They are high-performance parallel computing clusters, which are running a Free and Open Source Software Unix-like operating system, such GNU/Linux. They are networked into a small TCP/IP LAN, and have libraries and programs installed which allow processing to be shared among them. There is no particular piece of software that defines a cluster as a Beowulf. Commonly used parallel processing libraries include Message Passing Interface (MPI), which permits the programmer to divide a task among a group of networked computers, and collect the results of processing. Examples of MPI software include OpenMPI or MPICH.

The typical setup of a Beowulf cluster is illustrated next. We can easily see a multi-computer architecture, which can be used for parallel computations, usually consisting of one server (master) node, and one or more client (slaves) nodes connected together via Ethernet or some other network. In most cases client nodes do not have keyboards or monitors, and are accessed only via remote login or possibly serial terminal. Beowulf nodes can be thought of as a CPU + memory package which can be plugged into the cluster, just like a CPU or memory module can be plugged into a motherboard.
Because there is no need for client nodes to access machines outside the cluster, nor for machines outside the cluster to access client nodes directly, it is a common practice for the client nodes to use private IP addresses like 192.168.XXX.XXX. Usually the only machine that is also connected to the outside world using a second network card is the server node. The most common ways of using the system is to access the server’s console directly, or remote login to the server node from personal workstation. Once on the server node, users can edit and compile their code, and also spawn jobs on all nodes in the cluster.

A typical Beowulf is a collection of single CPU machines connected using fast Ethernet and is, therefore, a local memory machine. But if each machine has a Symmetric Multi-Processor (SMP) architecture, a multiprocessor computer hardware architecture where two or more identical processors are connected to a single shared main memory and are controlled by a single OS instance, we have a cluster of workstation better than a Beowulf. SMP systems allow any processor to work on any task no matter where the data for that task is located in memory, provided that each task in the system is not in execution on two or more processors at the same time; with proper operating system support, SMP systems can easily move tasks between processors to balance the workload efficiently.

Furthermore, the most recent machines are able to profit the technol-
ogy called multithreading. In computer science, a thread of execution is the smallest unit of processing that can be scheduled by an operating system. It generally results from a fork of a computer program into two or more concurrently running tasks. Multiple threads can exist within the same process and share resources such as memory, while different processes do not share these resources. On a single processor, multithreading generally occurs by time-division multiplexing: the processor switches between different threads. This context switching generally happens frequently enough that the user perceives the threads or tasks as running at the same time. On a multiprocessor or multi-core system, the threads or tasks will actually run at the same time, with each processor or core running a particular thread or task. The following picture illustrates it:

![Diagram of a process and threads](image)

Concerning the details of the cluster, one can mainly choose between AMD or Intel vendors. Examples of the latter is the Xeon brand of multiprocessor- or multi-socket-capable x86_64 microprocessors. We currently have in our laboratory the 5440-series “Harpertown” (quad-core), the X5670-series “Westmere” (six-core) and the E5-2670-series “Sandy Bridge” (ten-core). Additionally, we adopt the BogoMips as measure for computing performance. BogoMips (from "bogus" and MIPS) is an unscientific measurement of CPU speed made by the Linux kernel when it boots, to calibrate an internal loop. BogoMips can be used to
see whether it is in the proper range for the particular processor, and although it is not usable for a quantitative performance comparison between different CPUs, it serves nonetheless to give an estimate of the expected CPU power.

D.2 The Debian operating system

Technical variations of Linux distributions include support for different hardware devices and systems or software package configurations. Organisational differences may be motivated by historical reasons. Other criteria include security, including how quickly security upgrades are available, ease of package management, and number of packages available. From the year 2005, we strongly adhere to one of these distributions named Debian.

Debian is a free operating system (OS) for any computer. An operating system is the set of basic programs and utilities that make the computer run. Debian uses the Linux kernel (the core of an operating system), but most of the basic OS tools come from the GNU project; hence the complete name GNU/Linux. Debian GNU/Linux provides more than a pure OS: it comes with an enormous list of packages, precompiled software bundled up in a nice format for easy installation on machines. It is distributed with access to repositories containing thousands of software packages ready for installation and use. Debian is known for relatively strict adherence to the Unix and free software philosophies as well as using collaborative software development and testing processes. Debian can be used as a desktop as well as a server operating system. It focuses on stability and security and is used as a base for many other distributions. The OS is also extraordinarily stable. There are many cases of machines that run for over a year without rebooting. Even then, they are only rebooted due to a power failure or a hardware upgrade. Compare that to other systems that crash multiple times a day.
Debian surpasses all other distributions in how well its packages are integrated. Since all software is packaged by a coherent group, not only can all packages be found at a single site, but you can be assured that the developers have already worked out all issues regarding complicated dependencies. Additionally, due to the packaging system, upgrading to new versions is an easy-to-handle task. Debian and distributions based on it use the .deb package format and the dpkg package manager.

The Debian standard install makes use of the GNOME desktop environment. It includes popular programs such as OpenOffice.org, Ieweasel (a rebranding of Firefox), Evolution mail, CD/DVD writing programs, music and video players, image viewers and editors, and PDF viewers. It is quite true that some popular software is not available for GNU/Linux. There are, however, replacement programs for most of those, designed to mimic the best features of the proprietary programs, with the added value of being free software. Lack of popular office programs such as Word or Excel should no longer be a problem, because Debian includes three office suites composed entirely of free software, OpenOffice, KOOffice, and GNOME Office. Debian always has at least three releases in active maintenance: "stable", "testing" and "unstable". The "stable" distribution contains the latest officially released distribution of Debian; this is the production release of Debian, the one which we primarily recommend using.

Many distributions are based on Debian, including Ubuntu and Knoppix. The original aim of the Ubuntu team was to create an easy-to-use (freedom for users rather than freedom for programmers) Linux desktop. Ubuntu gives you a clean and streamlined Desktop that you can really
make your own. A built-in firewall and virus protection come as standard, and thanks to Firefox and gnome-keyring, Ubuntu helps you keep your private information private.

More information can be found in the following links:

<table>
<thead>
<tr>
<th>URL</th>
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<tbody>
<tr>
<td><a href="http://www.debian.org">http://www.debian.org</a></td>
</tr>
<tr>
<td><a href="http://www.ubuntu.com">http://www.ubuntu.com</a></td>
</tr>
<tr>
<td><a href="http://packages.debian.org/stable/science">http://packages.debian.org/stable/science</a></td>
</tr>
</tbody>
</table>

### D.3 Scientific software

Fortunately enough, new developments and algorithms are progressively incorporated into existing codes with great success, and that include those based on DFT. However, depending on the background and profile of developers, each code normally focuses on few methodologies and/or properties, which bring us with the need of being updated according to our own interests. Additionally, the strongest features of one code are usually the weakest in others; thus, it is largely difficult to deal with only one (master code). Furthermore, we rely once more on Free and Open Source Software (FOSS) since one can save a substantial amount of public money from OS licenses and extra software. We therefore provide herein a (necessarily biased and incomplete) alphabetical list of the software currently installed in our cluster, together with a short explanation of capabilities\(^1\), which can be viewed just as an example of current\(^2\) possibilities:

\(^1\)The text accompanying each program has been taken directly from the own sources, see the enclosed links, deeply appreciating the efforts by the developers of each code or visualiser. We here reproduce the main features of each one, attempting to facilitate its choice when needed.

\(^2\)Note that these examples are periodically updated, so that we avoid mentioning the present version of distribution.
**ABINIT: A package for electronic structure calculations.** ABINIT is a package which has a main program that allows one to find the total energy, charge density and electronic structure of systems made of electrons and nuclei (molecules and periodic solids) within Density Functional Theory (DFT), using pseudopotentials and a planewave basis. ABINIT also includes options to optimise the geometry according to the DFT forces and stresses, or to perform molecular dynamics simulations using these forces, or to generate dynamical matrices, Born effective charges, and dielectric tensors. Excited states can be computed within the Time-Dependent Density Functional Theory (for molecules), or within Many-Body Perturbation Theory (the GW approximation). In addition to the main ABINIT code, different utility programs are provided.

More information can be found in the following link:


**AVOGADRO: Molecular Graphics and Modelling System.** Avogadro is a molecular graphics and modelling system targeted at molecules and biomolecules. It can visualise properties like molecular orbitals or electrostatic potentials and features an intuitive molecular builder. Features include:
* Molecular modeller with automatic force-field based geometry optimisation
* Molecular Mechanics including constraints and conformer searches
* Visualisation of molecular orbitals and general isosurfaces
* Visualisation of vibrations and plotting of vibrational spectra
* Support for crystallographic unit cells

File formats Avogadro can read include PDB, XYZ, CML, CIF, Molden, as well as Gaussian, GAMESS and MOLPRO output.

More information can be found in the following link:

[http://avogadro.openmolecules.net](http://avogadro.openmolecules.net)
**CFOUR: Coupled-Cluster techniques for Computational Chemistry.**

CFOUR (Coupled-Cluster techniques for Computational Chemistry) is a program package for performing high-level quantum chemical calculations on atoms and molecules. The major strength of the program suite is its rather sophisticated arsenal of high-level \textit{ab initio} methods for the calculation of atomic and molecular properties. Virtually all approaches based on Möller-Plesset (MP) perturbation theory and the coupled-cluster approximation (CC) are available; most of these have complementary analytic derivative approaches within the package as well. Studies of excited electronic states and other "multireference" problems are possible using the equation-of-motion (EOM) coupled-cluster techniques. These techniques which are closely related to (and in some cases identical to) so-called Fock space multireference coupled-cluster theory, offer a powerful means to study open-shell systems and decided advantages when configuration mixing is important. At present, these include the EOMEE approach for singlet and triplet excited states, and the EOMIP and EOMEA methods that are best applied to low-spin doublet states. Analytic derivatives are available for these methods. A number of methodological developments have been added to the program in the last two decades. These include: analytic second derivatives for all coupled-cluster approaches up to full CCSDT; the calculation of NMR chemical shifts at MP and CC levels of theory; the calculation of anharmonic force fields (via numerical differentiation of analytic derivatives); relativistic corrections; corrections to the Born-Oppenheimer approximation at the CC level; nonadiabatic coupling within the EOM framework, and several others.

More information can be found in the following link:

[http://www.cfour.de/](http://www.cfour.de/)

**CHEMTOOL: Chemical structures drawing program.** Chemtool is a GTK+ based 2D chemical structure editor for X11. It supports
many bond styles, most forms of text needed for chemical typesetting and splines/arcs/curved arrows. Drawings can be exported to MOL and PDB format, SVG or XFig format for further annotation, as a PiCTeX drawing, as a bitmap or as Postscript files (several of these through XFig’s companion program transfig). The package also contains a helper program, cht, to calculate sum formula and (exact) molecular weight from a chemtool drawing file.

More information can be found in the following link:

http://ruby.chemie.uni-freiburg.de

EASYCHEM: Draw high-quality molecules and 2D chemical formulas.

EasyChem is a program that helps you creating high quality diagrams of molecules and 2D chemical formulas that can be exported to PDF, PS, LaTeX and fig. EasyChem was originally developed to create diagrams for chemistry books and is now frequently used for this purpose in commercial and non-commercial chemistry-related books.

More information can be found in the following link:

http://easychem.sourceforge.net/

GABEDIT: Graphical user interface to ab Initio packages.

Gabedit is a graphical user interface to computational chemistry packages like GAMESS-US, Gaussian, Molcas, Molpro, MPQC, OpenMopac, Orca, PCGAmess and Q-Chem. It can display a variety of calculation results including support for most major molecular file formats. The advanced "Molecule Builder" allows to rapidly sketch in molecules and examine them in 3D. Graphics can be exported to various formats, including animations. Features include:
* Molecular orbitals.
* Surfaces from the electron density, electrostatic potential, NMR
shielding density, and other properties.
* Surfaces may be displayed in solid, translucent and wire mesh modes. They are can be colourcoded by a separate property.
* Contours (colourcoded), Planes colourcoded, Dipole. XYZ axes and the principal axes of the molecule.
* Animation of the normal modes corresponding to vibrational frequencies.
* Animation of the rotation of geometry, surfaces, contours, planes colourcoded, xyz and the principal axes of the molecule.
* Display UV-Vis, IR and Raman computed spectra.
Simulated Annealing with Molecular Dynamics is implemented in Gabedit (using Amber 99 molecular mechanics parameters).

More information can be found in the following link:

http://gabedit.sourceforge.net/

**GAMESS: The General Atomic and Molecular Electronic Structure System.**
GAMESS is a program for *ab initio* molecular quantum chemistry. Briefly, GAMESS can compute SCF wavefunctions ranging from RHF, ROHF, UHF, GVB, and MCSCF. Correlation corrections to these SCF wavefunctions include Configuration Interaction, second order perturbation Theory, and Coupled-Cluster approaches, as well as the Density Functional Theory approximation. Nuclear gradients are available, for automatic geometry optimisation, transition state searches, or reaction path following. Computation of the energy hessian permits prediction of vibrational frequencies, with IR or Raman intensities. Solvent effects may be modeled by the discrete Effective Fragment potentials, or continuum models such as the polarizable Continuum Model. Numerous relativistic computations are available, including third order Douglas-Kroll scalar corrections, and various spin-orbit coupling options. The Fragment Molecular Orbital method permits use of many of these sophisticated treatments to be used on very large systems, by dividing the computation into small fragments. A variety of molecular properties, ranging
from simple dipole moments to frequency dependent hyperpolarisabilities may be computed. Many basis sets are stored internally, together with effective core potentials or model core potentials, so that essentially the entire periodic table can be considered.

More information can be found in the following link:

http://www.msg.ameslab.gov/gamess/

**GDIS: Molecular and crystal model viewer.** GDIS is a scientific visualisation program for the display, manipulation, and analysis of isolated molecules and periodic structures. It has the following features:
* Support for many common file formats (CIF, PDB, XTL, XYZ, and many more).
* Job submission tools for computational chemistry packages: GAMESS, GULP, ReaxMD, and SIESTA.
* Job analysis and graphing tools for dynamics simulations.
* Useful manipulation tools, including matrix transformations and supercell construction.
* Powerful surface generation and crystal morphology tools.
* Diffraction pattern generation and plotting.
* Animation of multi-frame files.
* Assorted tools for visualisation (measurements, ribbons, polyhedral display).

More information can be found in the following link:

http://gdis.sourceforge.net/

**GHEMICAL: A GNOME molecular modelling environment.** Ghemical is a computational chemistry software package written in C++. It has a graphical user interface and it supports both quantum-mechanics (semi-empirical) models and molecular mechanics models.
Geometry optimisation, molecular dynamics and a large set of visualisation tools using OpenGL are currently available. Chemical relies on external codes to provide the quantum-mechanical calculations. Semi-empirical methods MNDO, MINDO/3, AM1 and PM3 come from the MOPAC7 package (Public Domain), and are included in the package. The MPQC package is used to provide *ab initio* methods: the methods based on Hartree-Fock theory are currently supported with basis sets ranging from STO-3G to 6-31G**.

More information can be found in the following link:

http://www.bioinformatics.org/chemical/

**GNUPLLOT: A command-line driven interactive plotting program.**

Gnuplot is a portable command-line driven interactive data and function plotting utility that supports lots of output formats, including drivers for many printers, (La)TeX, (x)fig, Postscript, and so on. The X11-output is packaged in gnuplot-x11. Data files and self-defined functions can be manipulated by the internal C-like language. Can perform smoothing, spline-fitting, or nonlinear fits, and can work with complex numbers.

More information can be found in the following link:

http://gnuplot.sourceforge.net/

**GPAW: Grid-based projector-augmented wave method.** GPAW is a Density-Functional Theory (DFT) Python code based on the projector-augmented wave (PAW) method. It uses real-space uniform grids and multigrid methods or atom-centered basis-functions. All the functionals from the libxc library can be used. The code has been designed to work together with the atomic simulation environment (ASE). ASE provides:

* Structure optimisation.
* Molecular dynamics.
* Nudged elastic band calculations.
* Maximally localised Wannier functions.
* Scanning tunneling microscopy images.
* Transport calculations.
Parallelisation is done by distributing k-points, spins, and bands over all processors.

More information can be found in the following link:

https://wiki.fysik.dtu.dk/gpaw/

GPDC: Visualiser of molecular dynamic simulations. Gpdc is a graphical program for visualising output data from molecular dynamics simulations. It reads input in the standard xyz format, as well as other custom formats, and can output pictures of each frame in JPG or PNG format.

More information can be found in the following link:

http://www.frantz.fi/software/gdpc.php

GRACE: An XY plotting tool. Grace is a point-and-click tool that allows the user to draw X-Y plots. This is the program formerly known as Xmgr.

More information can be found in the following link:

http://plasma-gate.weizmann.ac.il/Grace/

GROMACS: Molecular dynamics simulator, with building and analysis tools. GROMACS is a versatile package to perform molecular dynamics, i.e. simulate the Newtonian equations of motion for systems with
hundreds to millions of particles. It is primarily designed for bio-
chemical molecules like proteins, lipids and nucleic acids that have
a lot of complicated bonded interactions, but since GROMACS is
extremely fast at calculating the nonbonded interactions (that usu-
ally dominate simulations) many groups are also using it for research
on non-biological systems, e.g. polymers. GROMACS provides ex-
tremely high performance compared to all other programs and is
user-friendly, with topologies and parameter files written in clear
text format.

More information can be found in the following link:

http://www.gromacs.org/

MOPAC7: Semi-empirical Quantum Chemistry Library. MOPAC
provides routines to solve the electronic structure of molecules on a
semi-empirical level. Available methods include MNDO, MINDO/3,
AM1 and PM3.

More information can be found in the following link:

http://sourceforge.net/projects/mopac7/

MPQC: The Massively Parallel Quantum Chemistry Program.
MPQC is an ab-initio quantum chemistry program. It is especially
designed to compute molecules in a highly parallellised fashion. It
can compute energies and gradients for the following methods:
* Closed shell and general restricted open shell Hartree-Fock (HF)
* Density Functional Theory (DFT)
* Closed shell Moeller-Plesset pertubation theory (MP2)
Additionally, it can compute energies for the following methods:
* Second order open shell pertubation theory (OPT2[2])
* Z-averaged pertubation theory (ZAPT2)
It also includes a robust internal coordinate geometry optimiser
that efficiently optimises molecules with many degrees of freedom. Nearly an arbitrary internal coordinate constraints can be handled.

More information can be found in the following link:

http://www.mpqc.org/

**NWChem: Delivering High-Performance Computational Chemistry to Science.**

NWChem aims to provide its users with computational chemistry tools that are scalable both in their ability to treat large scientific computational chemistry problems efficiently, and in their use of available parallel computing resources from high-performance parallel supercomputers to conventional workstation clusters. The local basis implementation of DFT in NWChem uses GTO-type orbitals and can be used to study molecular, finite clusters and nanosystems. An exhaustive list of exchange-correlation functionals are supported including: traditional DFT, hybrid functionals, meta-type functionals, range-separated forms, double-hybrid functionals and dispersion corrections. All the available exchange-correlation functionals have associated analytic first derivatives and most functionals have associated second derivatives. Relativistic effects can also be included in DFT/HF calculations. NWChem offers several variants of the EOMCC formalism: from rudimentary EOMCC model with singles and doubles (EOMCCSD) to more sophisticated methods accounting for the effect of triple excitations such as the non-iterative CR-EOMCCSD(T) method and the iterative EOM-CCSDT approach and its active-space variant. These accurate formalisms can be used not only for calculations of vertical excitation energies but also to characterise excited-state potential energy surfaces. The new QM/MM module provides a seamless integration between molecular mechanics and most quantum-mechanical theories in NWChem. It boasts an extensive array of capabilities for comprehensive description of large molecular systems for chemistry and biology, including ground and excited state calculations, properties, efficient large scale optimisations, reaction pathways, dynamics, and
free energy. The NWChem highly scalable Plane-Wave module now enables users to use exact exchange and the Self-Interaction Correction (SIC) within its framework for complex molecular, liquid, and solid-state systems. The Molecular Dynamics (MD) module of NWChem is designed for the simulation of biomolecular systems, with special features that facilitate the setup of complex systems.

More information can be found in the following link:

http://www.nwchem-sw.org/

OPENMX: Package for nano-scale material simulations. OpenMX (Open source package for Material eXplorer) is a program package for nano-scale material simulations based on density functional theories (DFT), norm-conserving pseudopotentials and pseudo-atomic localised basis functions. Since the code is designed for the realisation of large-scale \textit{ab initio} calculations on parallel computers, it is anticipated that OpenMX can be a useful and powerful tool for nano-scale material sciences in a wide variety of systems such as biomaterials, carbon nanotubes, magnetic materials, and nanoscale conductors.

More information can be found in the following link:

http://www.openmx-square.org/

ORCA: An \textit{ab initio}, DFT and semiempirical SCF-MO package. ORCA is a flexible, efficient and easy-to-use general purpose tool for quantum chemistry with specific emphasis on spectroscopic properties of open-shell molecules. It features a wide variety of standard quantum chemical methods ranging from semiempirical methods to DFT to single- and multireference correlated \textit{ab initio} methods. It can also treat environmental and relativistic effects. ORCA is able to carry out geometry optimisations and to predict a large num-
ber of spectroscopic parameters at different levels of theory. As the special highlights of ORCA we remark: user friendliness, flexibility, efficiency, parallelisation, interface to graphics programs, and rapid integration of most modern methodological developments.

More information can be found in the following link:

http://www.thd.uni-bonn.de/te/orca/

**PSI3: Quantum Chemical Program Suite.** PSI3 is an *ab initio* quantum chemistry program. It is especially designed to accurately compute properties of small to medium molecules using highly correlated techniques. It can compute energies and gradients for the following methods:

* Closed shell and general restricted open shell Hartree-Fock (RHF/ROHF)
* Complete active space SCF (CASSCF)
* Coupled-cluster (RHF/ROHF/UHF) singles doubles (CCSD)
* Coupled-cluster (UHF) singles doubles with pertubative triples (CCSD(T))

Additionally, it can compute energies for the following methods:

* Unrestricted open shell Hartree-Fock (UHF)
* Closed/open shell Moeller-Plesset pertubation theory (MP2)
* Closed shell linear R12 Moeller-Plesset pertubation theory (MP2-R12)
* Multireference configuration-interaction (MRCI)
* Coupled-cluster singles doubles with pertubative triples (CCSD(T))
* Second-order approximate coupled-cluster singles doubles (CC2)
* Closed shell and general restricted open shell equation-of-motion coupled-cluster singles doubles (EOM-CCSD)

Further features include:

* Flexible, modular and customisable input format
* Arbitrarily high angular momentum levels in integrals and derivative integrals.
* Excited state calculations with the CIS(D), CC2, EOM-CCSD, CASSCF and MRCI methods
* Internal coordinate geometry optimiser
* Harmonic frequencies calculations
* Diagonal Born-Oppenheimer correction (DBOC) for RHF, ROHF, UHF, and CI wave functions.
* One-electron properties like dipole/quadrupole moments, natural orbitals, electrostatic potential, hyperfine coupling constants or spin density
* Utilisation of molecular point-group symmetry to increase efficiency

More information can be found in the following link:


**PYMOL: Molecular Graphics System.** PyMOL is a molecular graphics system targeted at medium to large biomolecules like proteins. It can generate high-quality publication-ready molecular graphics images and animations. Features include:
* Visualisation of molecules, molecular trajectories and surfaces of crystallography data or orbitals
* Molecular builder and sculptor
* Internal raytracer and movie generator
* Fully extensible and scriptable via a Python interface
File formats PyMOL can read include PDB, XYZ, CIF, MDL Molfie, ChemDraw, CCP4 maps, XPLOR maps and Gaussian cube maps.

More information can be found in the following link:

[http://www.pymol.org/](http://www.pymol.org/)

**VIEWMOL: A graphical front end for computational chemistry program.** Viewmol is a graphical front end for computational chemistry programs. It is able to graphically aid in the generation of molecular structures for computations and to visualise their results. At
present Viewmol includes input filters for Discover, DMol3, Gamess, Gaussian 9x/03, Gulp, Mopac, PQS, Turbomole, and Vamp outputs as well as for PDB files. Structures can be saved as Accelrys’ car-files, MDL files, and Turbomole coordinate files. Viewmol can generate input files for Gaussian 9x/03. Viewmol’s file format has been added to OpenBabel, so that OpenBabel can serve as an input as well as an output filter for coordinates.

More information can be found in the following link:

http://viewmol.sourceforge.net/

XDRAWCHEM: Chemical structures and reactions editor. Xdrawchem is a 2D editor for chemical structures and reactions. It mirrors the abilities of the commercial ChemDraw suite and has file compatibility with it as well as other chemical formats through OpenBabel.

More information can be found in the following link:

http://xdrawchem.sourceforge.net/

XMAKEMOL: A program for visualising atomic and molecular systems. XMakemol is an application for the visualisation and manipulation of atomic, molecular, and other chemical systems. Features include:
* Animating multiple frame files
* Interactive measurement of bond lengths, bond angles and torsion angles
* Control over atom/bond sizes
* Exporting to Xpm, Encapsulated PostScript and XYZ formats
* Toggling the visibility of groups of atoms
* Editing the positions of subsets of atoms
XMakemol is principally a mouse-based application with menus and pop up dialog boxes with buttons, scrollbars etc.
More information can be found in the following link:

http://www.nongnu.org/xmakemol/

**V-SIM: Visualise atomic structures.** V-Sim visualises atomic structures such as crystals, grain boundaries, molecules and so on (either in binary format, or in plain text format). The rendering is done in pseudo-3D with spheres (atoms) or arrows (spins). The user can interact through many functions to choose the view, set the bindings, draw cutting planes, compute surfaces from scalar fields, duplicate nodes, measure geometry, etc. Moreover V-Sim allows to export the view as images in PNG, JPG, PDF (bitmap), SVG (scheme) and other formats. Some tools are also available to colorize atoms from data values or to animate on screen many position files.

More information can be found in the following link:

http://inac.cea.fr/L_Sim/V_Sim/

### D.4 LaTeX and related utilities

LaTeX is a document markup language and document preparation system for the TeX typesetting program. The term LaTeX refers only to the language in which documents are written, not to the editor used to write those documents. In order to create a document in LaTeX, a .tex file must be created using some form of text editor (e.g. gvim). While most text editors can be used to create a LaTeX document, a number of editors have been created specifically for working with LaTeX. LaTeX is used because of the high quality of typesetting achievable by TeX. The typesetting system offers programmable desktop publishing features and extensive facilities for automating most aspects of typesetting and desktop publishing, including numbering and cross-referencing, tables and figures, page layout and bibliographies. The current version is LaTeX2e.
We strongly adhere to the use of LaTeX, as shown in this document.

LaTeX is based on the idea that authors should be able to focus on the content of what they are writing without being distracted by its visual presentation. In preparing a LaTeX document, the author specifies the logical structure using familiar concepts such as chapter, section, table, figure, etc., and lets the LaTeX system worry about the presentation of these structures. It therefore encourages the separation of layout from content while still allowing manual typesetting adjustments where needed. When TeX “compiles” a document, the processing sequence (from the user’s point of view) goes like this: Macros > TeX > Driver > Output. Different implementations of each of these steps are typically available in TeX distributions. Traditional TeX will output a DVI file, which is usually converted to a PostScript file, and this to a PDF file if needed.

BibTeX is reference management software for formatting lists of references. The BibTeX tool is typically used together with the LaTeX document preparation system. BibTeX uses a style-independent text-based file format for lists of bibliography items, such as articles, books, and theses. BibTeX bibliography file names usually end in .bib. BibTeX formats bibliographic items according to a style file, typically by generating TeX or LaTeX formatting commands. Most journals or publishers that support LaTeX have a customised bibliographic style file for the convenience of the authors. This ensures that the bibliographic style meets the guidelines of the publisher with minimal effort.

Beamer is a LaTeX class for creating presentations that are held using a projector, but it can also be used to create transparency slides. A Beamer presentation is created like any other LaTeX document: it has a preamble and a body, the body contains sections and subsections, the different slides (called frames in Beamer) are put in environments, they are structured using itemise and enumerate environments, and so on. The obvious disadvantage of this approach is that you have to know LaTeX in order to use Beamer. The advantage is that if you know LaTeX, you can use your knowledge of LaTeX also when creating a presentation,
not only when writing papers or reports. The final output is typically a PDF file. Viewer applications for this format exist for virtually every platform. When bringing your presentation to a conference on a memory stick, you do not have to worry about which version of the presentation program might be installed there. Also, your presentation is going to look exactly the way it looked on your computer, isn’t it nice?

**XyMTeX** is a macro package for TeX (TeX) which renders high-quality chemical structure diagrams. The commands have a set of systematic arguments for specifying substituents and their positions, endocyclic double bonds, and bond patterns; in some cases there are additional arguments for the hetero-atoms on the vertices of heterocycles. It is believed that this systematic design allows XyMTeX to operate as a practical (device-independent) tool to use with LaTeX.

More information can be found in the following links:

http://en.wikipedia.org/wiki/LaTeX
http://en.wikipedia.org/wiki/Beamer
http://en.wikipedia.org/wiki/XyMTeX