In this set of exercises, you will assess the performance of various state-of-the-art density functionals in the prediction of geometric properties, and you will again compare your results to both wavefunction theory and experimental data. The second part of this exercise script constitutes a brief *résumé* of DFT and a description of the various *exchange-correlation* approximations used.

6.2 Structural Parameters of $NO_3\cdot$: Performance of DFT, HF and MP2

Before diving into the theoretical aspects of exchange-correlation functionals, you will put a representative selection of functionals to good use in a notoriously tricky system, the $NO_3\cdot$ radical. Nitrite radicals are highly reactive species that are rapidly destroyed by sunlight, but as the sun sets, they start to play an important role in chemical transformations (in what is called the night-time chemistry of the atmosphere). There exist various experimental and theoretical studies of $NO_3\cdot$ (*Phys. Chem. Chem. Phys.*, **2014**, 16, *19437*), with the experiment indicating a fully symmetric D_3^h structure with equal N-O bond lengths of 1.24 Å and O-N-O bond angles of 120°. In this exercise, you will be comparing the performance of various DFT exchange-correlation functionals, Hartree-Fock theory and MP2 in predicting these structural parameters. Your input file should contain the following coordinates:

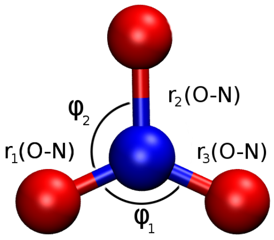
```
%NProcShared=2
%Mem=1GB
%Chk=CHECKPOINTNAME
#P GFINPUT IOP(6/7=3) METHOD/6-31+G* Opt Symmetry=None

NO3

0 2
N  0.000  0.000  0.000
O  1.400  0.000  0.000
O -1.000  1.000  0.000
O -1.000 -1.000  0.000
```

The new keywords `GFINPUT` and `IOP(6/7=3)` will force Gaussian to write additional orbital information to the output file, which makes it possible to visualise the orbitals with Molden. Do not forget to change the name for the Checkpoint file for each method.

a) Create inputs for MP2, HF and two of the following density functionals (where the Gaussian keyword differs from the functional abbreviation, it is given in parentheses): LDA (SVWN5), BLYP, BP86, PBE (PBEPBE), B3LYP, B97-2 (B972), M06-L (M06L), mPW (mPW1PW91). Your assistants will assign to you which functionals to use. For this small system, Hartree-Fock and MP2 will be surprisingly fast; however, you may rest assured that for larger molecules and basis sets, all the DFT methods will outperform MP2 in computational efficiency, with some of them even beating Hartree-Fock. Make sure just to submit *one job at once*. Open the output files in Molden and complete the following table (you can again easily extract this structural information from the `ZMAT Editor`):



Method:	ϕ_1 [°]	ϕ_2 [°]	$\mathbf{r}_1(O-N)$ [Å]	$\mathbf{r}_2(O-N)$ [Å]	$\mathbf{r}_3(O-N)$ [Å]	Symmetry
Exp.	120	120	1.24	1.24	1.24	D_3^h
HF						
MP2						
SVWN5						
BLYP						
BP86						
PBE						
B3LYP						
B97-2						
M06-L						
mPW1PW91						

b) Compare the performance of the methods in predicting accurate structures. For the DFT methods, specify what approximations are used in the exchange functional (you may refer to chapter 5.3 to obtain this information). Is there a trend relating the complexity of the exchange-correlation functional (LDA, GGA, hybrid, . . .) to the quality of your results?

In order to assess the reliability of an electronic structure calculation, it is usually not sufficient to simply glance at the optimised structure and energies. One should as well examine the orbitals. This is also valid for DFT: Although the Kohn-Sham orbitals lack, in a strict sense, any physical interpretation, experience shows that they are *very close* to wavefunction-based single particle orbitals (*cf.* chapter 5.3). Thus, the DFT Kohn-Sham orbitals provide a useful interpretative tool to visualise changes in the electronic structure between different species (or in a chemical transformation), but one should bear in mind that they have to be interpreted with care.

Molden comes with the built-in capability of reading the orbitals from the Gaussian output, given that the input modifications specified before are made. Open your MP2 output file in Molden:

```
molden outputfile.log
```

In *Molden Control*, click on `Dens. Mode`. Then, in *Plot Mode*, click on the symbol with the dashed circles on it. Molden will now visualise the HOMO. Return to `Mol. Mode`, and you will now be able to turn your molecule and view it from different angles by clicking on it with the left mouse button and moving your mouse. To get a nicer representation, change the *Draw Mode* to `Solid` and `Ball & Stick`.

c) Take a screenshot of the MP2 orbital and include it in your report. Then, open a DFT outputfile of your choice in Molden and repeat the orbital visualisation. Take a screenshot of the DFT HOMO as well. How do the orbitals differ from each other? How does the symmetry of the HOMO relate to the predicted structure?

d) Explain the difference between static and dynamic correlation. Relate this to the different results you obtained for the nitrate radical. What kind of correlation do HF, MP2 and DFT take into account?

e) If you needed a highly accurate structure and energy for $NO_3\cdot$, which method would you use?

6.3 Exact Theory and Approximate Functionals: Comparison of Various Density Functionals

The successful application of DFT requires some knowledge on where, why and how approximations to the density functional are made. The following is a brief review of the *Kohn-Sham Density Functional Theory* as it is ubiquotously used today.

The Hohenberg-Kohn Theorems

In 1964, Hohenberg and Kohn provided two theorems for 'the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$' (such as the external potential that is due to the nuclei). The first theorem states that an external potential $v_{ext}(\mathbf{r})$ is, up to a constant, uniquely determined by the density $\rho(\mathbf{r})$. Since $v_{ext}(\mathbf{r})$ fixes the Hamiltonian of the system, *the many-particle ground state is a unique functional of the density.* Therefore, a density functional $F[\rho]$ exists such that the energy E_v of a system subjected to the potential v_{ext} is given by

$$E_v[\rho] = \int v_{ext}(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r} + F[\rho]. \tag{89}$$

Hohenberg and Kohn also provided a variational principle stating that *the density minimising the total energy corresponds to the ground-state density* (*cf.* course script, chapter 4.3):

$$E_v^{GS}[\rho] = \min_{\Psi \to \rho} \langle \Psi[\rho] | \, \hat{\mathrm{H}} \, | \Psi[\rho] \rangle \tag{90}$$

The Kohn-Sham Formalism

Although the exact density functional exists, it is not known, and finding approximations to it is quite a formidable task. In 1965, Kohn and Sham introduced a formalism that, in practice, considerably simplifies the determination of the functional $F[\rho]$. According to Hohenberg and Kohn, one may separate the Coulomb energy J out of eq. 89:

$$E_v[\rho] = \int v_{ext}(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r} + J[\rho] + G[\rho], \tag{91}$$

which leaves a functional $G[\rho]$ that takes all the non-classical terms into account. Kohn and Sham suggested to further split this term:

$$G[\rho] \equiv T_s[\rho] + E_{xc}[\rho], \tag{92}$$

where T_s is the kinetic energy of a system of non-interacting particles (s stands for 'single particle') , and E_{xc} is taking care of all non-classical *exchange-correlation* effects. This *exchange-correlation* energy will thus be given by the difference between the non-interacting kinetic energy T_s and the (true) interacting kinetic energy T of the system, as well as the difference between classical (J) and (true) quantum mechanical interaction (potential) energy (V_{ee}) of the electrons:

$$E_{xc}[\rho] \equiv \underbrace{T[\rho] - T_s[\rho]}_{\text{kinetic terms}} + \underbrace{V_{ee}[\rho] - J[\rho]}_{\text{potential terms}} \tag{93}$$

The use of the non-interacting T_s allows for a simple evaluation of the dominant part of T. In order to determine T_s, Kohn and Sham introduced *auxiliary single-particle wavefunctions* $\psi^{(KS)}$, the purpose of which is to simply yield the correct density ρ. The total energy is then obtained from the density:

$$\rho(\mathbf{r}) = \sum_i^N \left|\psi_i^{(KS)}(\mathbf{r})\right|^2 \quad ; \quad \int \psi_i^{(KS)*}(\mathbf{r})\,\psi_i^{(KS)}(\mathbf{r})\,d\mathbf{r} = \delta_{ij}. \tag{94}$$

These single-particle wavefunctions minimise T_s for a given density ρ; they have *no other physical interpretation* (*cf.* the following section) - they are simply an auxiliary tool, based on the assumption that the difference $T - T_s$ is much easier to account for in a functional than the complete T at once. The $\psi^{(KS)}$ are orbitals that correspond to a system of *non-interacting electrons* which has the same *density* as the true, physical system. Since the true ground-state energy of a system is solely given by its density, the use of an auxiliary (*i.e.* non-physical) wavefunction does not introduce any error and still yields the exact result.

Taking advantage of the now known expression for the non-interacting kinetic energy T_s, one finds for the energy that:

$$E_v[\rho] = \sum_i^N \int \psi_i^{(KS)*}(\mathbf{r})\left(-\frac{1}{2}\nabla^2\right)\psi_i^{(KS)}(\mathbf{r})\,d\mathbf{r} + J[\rho] + E_{xc}[\rho] + \int v_{ext}(\mathbf{r})\,\rho(\mathbf{r})\,d\mathbf{r}. \tag{95}$$

We note that T_s, although expressed in terms of an auxiliary wavefunction, is still an implicit functional of the density, as the auxiliary wavefunctions or *Kohn-Sham orbitals* $\psi^{(KS)}(\mathbf{r})$ are themselves determined by the density.

By subjecting eq. 95 to a constrained minimisation, *i.e.* by applying the variational principle, Kohn and Sham derived a set of *single particle equations* for the Kohn-Sham orbitals $\psi^{(KS)}$ that yield the ground-state density:

$$\left[-\frac{1}{2}\nabla^2 + \upsilon_{eff}\right]\psi_i^{(KS)} = \epsilon_i \psi_i^{(KS)}, \tag{96}$$

where υ_{eff} is an effective potential given by:

$$\upsilon_{eff} = \upsilon_{ext}\left(\mathbf{r}\right) + \frac{\delta J[\rho]}{\delta\rho\left(\mathbf{r}\right)} + \frac{\delta E_{xc}[\rho]}{\delta\rho\left(\mathbf{r}\right)} \tag{97}$$

or, alternatively,

$$\upsilon_{eff} = \upsilon_{ext}\left(\mathbf{r}\right) + \int \frac{\rho\left(\mathbf{r}'\right)}{\left|\mathbf{r}-\mathbf{r}'\right|} d\mathbf{r}' + \upsilon_{xc}\left(\mathbf{r}\right). \tag{98}$$

By definition,

$$\upsilon_{xc} \equiv \frac{\delta E_{xc}[\rho]}{\delta\rho\left(\mathbf{r}\right)} \tag{99}$$

is the *exchange-correlation potential*, the part of the potential that is due to non-classical effects. Besides the external potential υ_{ext} that uniquely determines the ground-state density, the single-particle equations contain an additional potential due to the electron-electron interaction (the Coulomb term), as well as a local ficticious potential for all non-classical effects υ_{xc}.

The sum of all the potentials in eq. 98 can be regarded as a ‘new’ υ'_{ext} that fixes the density and thus the ground-state energy, as proven by Hohenberg and Kohn. To stress its ficticious nature, this new Kohn-Sham single particle potential is denoted the *effective potential* υ_{eff}, and the corresponding Hamiltonian is referred to as the *effective Hamiltonian* $\hat{\mathrm{H}}_{eff}$. Given an expression for the *exchange-correlation functional* $E_{xc}[\rho]$, eq. 96 is now easily solved self-consistently (*cf.* course script, chapter 8.4.2). The exchange-correlation potential as defined by eq. 99 and used in eq. 96 is obtained from the exchange-correlation energy computed in the *previous* cycle; hence, the procedure calls for a self-consistent solution. (Recall that in Hartree-Fock theory, this was made neccessary by the dependence of the Fock operator on the previous iteration; in Kohn-Sham DFT, it is the functional derivative of the exchange-correlation functional that imposes this requirement.)

The beauty of the Kohn-Sham approach lies in the mapping of an interacting, physical problem, onto an artificial, but easy-to-solve auxiliary non-interacting problem. The real interacting system and the Kohn-Sham non-interacting system just share the same N-electron density. The link (mapping) between the two systems is accounted for by the exchange-correlation functional $E_{xc}[\rho]$.

Interpretation of the Kohn-Sham Orbitals

In the early years of Kohn-Sham DFT, great emphasis was put on the fact that, based on their derivation, Kohn-Sham orbitals are *physically meaningless.* As single-particle orbitals from wavefunction theory are often the base of a more intuitive interpretation of chemical processes, this could be regarded as a severe drawback. However, experience shows that Kohn-Sham orbitals are in praxis very close to the orbitals obtained from wavefunction-based methods; and they have been used as an illustrative tool for *e.g.* chemical transformations for many years. It has been demonstrated that the Kohn-Sham orbitals have an intriguing interpretation, which is linked to their response to changes of the exchange-correlation hole (the exchange-correlation hole is quite an important concept both in wavefunction and density functional theory; *J. Am. Chem. Soc.*, **1999**, 121, *3414*). We do, however, note *en passant* that the meaning of single-particle orbitals in general is quite limited; even in Hartree-Fock theory, the meaningful quantity is the total wavefunction, *i.e.* the Slater determinant over all occupied orbitals.

Approximations

Until this point, no approximations were invoked at all. The Kohn-Sham equations will still yield the exact ground-state energy and ground-state density for a system, given that E_{xc} is known - but this is not the case. Although more and more properties of the exact exchange correlation functional were established over the years, there is no universal analytical expression for it. This is where one needs to approximate.

An approximate expression for the exchange-correlation functional will, however, pose a formal problem. Although the Hohenberg-Kohn variational principle guarantees that the energy of a trial density will always be an upper boundary to the ground-state energy, this holds only for the exact density functional. If approximate functionals are to be used, the variational theorem just holds *for this specific Hamiltonian* (recall from the preceeding section that the effective potential v_{eff} fixes the Hamiltonian; since v_{eff} depends on the exchange-correlation functional, the exchange-correlation functional determines the Hamiltonian). If the exchange-correlation functional is approximate, the Hamiltonian is approximate as well, and *the ground-state energy for a system with an approximate Hamiltonian may be lower than the physical ground-state energy.* This violates the general form of the variational theorem, that strictly calls for an upper boundary for the *physical* system. However, it has to be stressed that this is not a problem of Density Functional Theory, but of the approximate exchange-correlation functionals.

Still, the variational theorem holds in a less general sense, such that, within the *approximate* Hamiltonian, the Kohn-Sham equations will yield the density that minimises the energy, and thus a ground-state density (for this specific Hamiltonian). The accuracy is then determined by how well the approximate Hamiltonian is able to describe the true, physical Hamiltonian.

Local Density Approximation: LDA/LSDA

The question left standing is how to find a reasonable approximation to the exchange-correlation functional. A first simplification of the problem can be achieved by splitting the exchange-correlation functional into an exchange and a correlation functional:

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho], \tag{100}$$

which allows for a convenient separation of the problem. Because the exchange contribution dominates over correlation effects, exchange-correlation functionals are usually classified according to the derivation of the exchange functional.

In order to establish an approximation for the exchange functional, one may refer to the electron gas (*cf.* the Hohenberg-Kohn Theorem). Namely, for a *uniform*, homogenuous (interacting) electron gas, there exists an analytical expression for the exchange energy per volume element. By assuming that the density of a non-homogenuous system can locally (meaning, at any point $\mathbf{r}$ in space) be described by that of the uniform electron gas, one arrives at the following expression for the exchange functional:

$$E_x^{LDA}[\rho] = -\frac{3q_e^2}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int \rho^{\frac{4}{3}} \mathrm{d}\mathbf{r}, \tag{101}$$

which is known as the *Local (Spin) Density Approximation* or LDA (LSDA if spin is taken into account). The term for the correlation functional is substantially more complicated and will not be shown here. LDA was one of the first successful approaches towards an exchange-correlation functional, with results for molecules and especially solid state systems being mostly superior to Hartree-Fock, all whilst having a lower computational cost. The term LDA is frequently used to denote both the approximation and the functional. For the functional, there exist different parametrisations for the correlation energy of the uniform electron gas: They may either be based on analytical expressions, or on Quantum Monte Carlo results.

With multiple parametrisations for the same approximation, an appropriate naming scheme is required. Usually, to denote an exchange-correlation functional, an abbreviation for the exchange functional is contracted with one for the correlation functional. Unequivocally, the Slater exchange functional (abbreviated S) is used for the exchange part of all LDA functionals. The LDA correlation functional that is predominantely used is based on a parametrisation by Vosko, Wilk and Nusair, who obtained the correlation energy from Quantum Monte Carlo results for the uniform electron gas (the Ceperley-Alder solution). This correlation functional is denoted VWN5. The full exchange-correlation functional is then abbreviated as SVWN5.

Generalised Gradient Approximation: GGA

LDA will perform reasonably well for systems with a slowly varying density, because in such systems, the density will be almost homogenous between two infinitesimally close points in space. For more fluctuating densities, however, the assumption that a local description based on the electron gas is sufficient starts to break down. An additional term in the exchange functional that is able to describe the local shape of the density would seem promising. An intuitive approach could include the gradient of the density; however, such an expression turns out to be divergent. Instead, a *generalised gradient expansion* can be derived, resulting in the *Generalised Gradient Approximation* (GGA):

$$E_x^{GGA}[\rho] = E_x[\rho, \nabla\rho] = \int f(\rho, \nabla\rho)\mathrm{d}\mathbf{r}, \tag{102}$$

However, the general form for a GGA contains parameters that are undetermined. How they are obtained is a matter of choice (and dispute); they may either be recovered from imposing certain limits and conditions on the functional, or by fitting to experimental or accurate quantum chemical data to minimise the error made by the functional. The former group of GGAs are referred to as non-empirical, the latter as (semi-)empirical. The exact limits that the functional should adhere to may be given by one or several basic physical concepts, including the exchange hole, the requirement that the uniform electron gas be recovered, the recovery of a gradient term of a certain order, *etc.*

An example of a popular non-empirical GGA is the exchange functional due to Perdew, Burke and Ernzerhof (PBE). The modified Perdew-Wang functional (mPW91) is an example of a GGA where a functional form was designed to fit *analytical* data. The missing parameters for other GGA exchange functionals, like the Becke exchange (B), were instead determined by a semi-empirical fit to exact exchange energies of rare gas atoms.

Gradient corrected exchange functionals can be combined with various elaborate correlation functionals, the most popular of which are the Lee-Yang-Parr correlation functional (LYP), the Perdew correlation functional from 1986 (P86), the Perdew-Wang correlation functional of 1991 (PW91) and the PBE correlation functional (PBE). In principle, any correlation functional could be combined with any exchange functional, but certain combinations will outperform others based on a remarkable *error cancellation* between the two exchange and correlation part. Therefore, functionals derived with similar targets and philosophies will often work better together, whereas mixing of philosophies may give catastrophic results (for instance, the combination B-PBE will be ridiculously off). Popular combinations of GGA exchange with correlation functionals include BLYP, PBE (acronym for PBEPBE), mPWPW91 and BP86.

Kinetic Energy Density: Meta-GGA

One step beyond the GGA is given by including the second derivative of the density. In practice, the *kinetic energy density* τ:

$$\tau = \sum_i \left\langle \psi_i^{(KS)*} \middle| \nabla^2 \middle| \psi_i^{(KS)} \right\rangle, \tag{103}$$

is used and the general functional form for a *meta-GGA* follows:

$$E_x^{meta-GGA}[\rho] = E_x[\rho, \nabla\rho, \tau] = \int f(\rho, \nabla\rho, \tau)\mathrm{d}\mathbf{r}. \tag{104}$$

Although these functionals are still completely local, they are in a way able to sense long-range effects due to the second derivative information. Whereas LDA and GGA are plagued by a self-interaction error in certain systems, meta-GGAs are already much less prone to this pitfall. Examples include the TPSS exchange-correlation functional (due to Tao, Perdew, Staroverov and Scuseria), and the local *Minnesota functionals* M05-L and M06-L (developed by Donald Truhlar). Whereas TPSS was derived purely based on theoretical considerations, the Minnesota functional parameters were determined by a fit to an experimental database, resulting in a remarkable accuracy for all systems that are sufficiently close to the training set.

Hybrid Functionals: Including Exact Exchange

From Hartree-Fock theory, the expression for the exchange energy of a single Slater determinant is known:

$$E_x^{HF} = \sum_i \sum_{j \neq i} \iint \frac{\phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_2 \mathrm{d}\mathbf{r}_1. \tag{105}$$

In DFT, this expression is evaluated based on the Kohn-Sham orbitals, and is usually denoted the *exact exchange* functional (given that $\rho \to \psi^{(KS)}$, E_x^{HF} is still an implicit functional of the density). It can be shown that the exact exchange expression corresponds to a certain limit in the non-interacting Kohn-Sham system (this relation is given by the *adiabatic connection theorem*). Therefore, *hybrid* density functionals may be constructed by including both contributions from (meta)-GGA and the exact exchange term:

$$\begin{aligned} E_x^{hybrid}\left[\rho, \nabla\rho, \left\{\psi^{(KS)}\right\}(,\tau)\right] &= \lambda E_x^{(meta-)GGA}\left[\rho, \nabla\rho(,\tau)\right] + (1-\lambda) \\ &\times \sum_i \sum_j \iint \frac{\psi_i^{(KS)*}(\mathbf{r}_1)\psi_j^{(KS)*}(\mathbf{r}_2)\psi_j^{(KS)}(\mathbf{r}_1)\psi_i^{(KS)}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_2 \mathrm{d}\mathbf{r}_1. \end{aligned} \tag{106}$$

Again, the fractional contribution λ of the exact exchange to the total exchange functional can be derived based on theoretical considerations or empirical fitting. Hybrid functionals have constituted a tremendous breakthrough, as they especially improved the performance of DFT on barrier heights. The first successful generation of these functionals combined GGA and the exact exchange term. This generation includes the probably most popular B3LYP, the Becke three-parameter hybrid, which combines Becke exchange, the exact exchange term, the LYP and the VWN correlation functional into one functional (with three empirically determined fitting parameters). An analytically derived example is given by the PBE0 hybrid (also named PBE1PBE), the derivation of which is rather involved in terms of the adiabatic connection theorem. Especially for barrier heights, the mPW1PW91 functional has been rather popular, adding exact exchange to the mPWPW91 GGA. The B3PW91 functional constitutes a further notable example.

The second generation of hybrid-GGAs (*e.g.* B97 due to Becke) were presented towards the end of the 1990ies and have improved accuracy over the first generation. The quite recent (2005 and 2006) Minnesota functionals M05 and M06 combine a meta-GGA expression with the exact exchange functional, and all the free parameters were fit to a benchmarking set of molecules. These highly empirical functionals are of remarkable accuracy over a wide range of systems, further improving over the M05-L and M06-L functionals.

a) The LDA is the simplest approximation to an exchange-correlation functional. In what cases would it perform well, and when would you expect it to fail?

b) What is a self-interaction error, and which of the methods that you used so far will suffer from it?

c) What is the meaning and physical interpretation of the Kohn-Sham orbitals?

d) Density Functional Theory is sometimes referred to as being a semi-empirical method. Comment on this.

e) In a related matter, it may be mentioned that DFT is non-variational. Comment on this statement.

f) Derive a flow chart describing the self-consistent solution of the Kohn-Sham equations (eq. 95 to 99). Indicate which terms are obtained from the results of the previous cycle, and which terms are obtained in the new cycle. For which terms is the initial Kohn-Sham orbital guess $\psi^{(KS)}_{guess}$ used?

g) **Bonus:** In Kohn-Sham DFT, the total energy is *not* simply given by a sum over orbital eigenvalues (recall that this is a situation similar to what one encounters in Hartree-Fock theory). Instead, one finds that

$$E = \sum_i^N \epsilon_i - J[\rho] + E_{xc}[\rho] - \int \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \rho(\mathbf{r}) \mathrm{d}\mathbf{r}. \tag{107}$$

Explain why this expression is not equal to

$$E = \sum_i^N \epsilon_i - J[\rho], \tag{108}$$

i.e. why the last two terms in eq. 107 do not cancel.

h) **Bonus:** The energy minimisation in DFT is given by the functional:

$$E_v[\rho] = T[\rho] + V_{ee}[\rho] + \int v_{ext}(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r}. \tag{109}$$

Specify where approximations are made. Compare these terms to the Kohn-Sham effective single-particle Hamiltonian:

$$\hat{\mathrm{H}}_{eff} = \hat{\mathrm{T}}_s + v_{eff}(\mathbf{r}), \tag{110}$$

and elaborate on the connection between the approaches.