Q&A Lecture 8

What exactly are the Kohn-Sham orbitals and how do they participate in what we discussed?

At this stage, I'll say that they are used to provide a (very) convenient reference system to be used to obtain an expression for the kinetic energy functional that is easy to manipulate. As mentioned in class, they are not critical to understand today's discussion and we'll rediscuss them in the future.

- *How do we choose which model to use for the exchange-correlation functional? Is there a way to predict which model is adapted to which system?;*
- *How can the exchange term be approximated as accurately as possible ?*

Here is a chapter of a book that addresses exactly this question (https://dft.uci.edu/pubs/RCFB08.pdf).
The choice of an exchange-correlation energy depends on the system and the properties that you are interested in. For example, the LDA approximation does well by approximating structural properties but not so well for computing dissociation energies (attached an extract of the book of Giustino, which I mentioned in the exercise session, where the LDA and the GGA are compared for a specific molecule). There are studies where different exchange-correlation functional are compared. Here some examples for band gaps (https://www.nature.com/articles/s41524-020-00360-0), molecules (https://pubs.aip.org/aip/jcp/article/107/13/5007/477066/Exchange-and-correlation-energy-in-density), and some chemical reactions (https://onlinelibrary.wiley.com/doi/full/10.1002/jcc.26985)

What factors significantly impact the performance and the accuracy of this method (is there anything else than the model chosen for the exchange-correlation energy) ? When should we prefer Hartree-Fock over DFT ?

The exchange-correlation is by far the most relevant factor in accuracy, also van der Waals interactions are difficult to capture in DFT and specific correction schemes have been adopted. Furthermore, the theory assumes that electrons are in the ground state, so, e.g. non-adiabatic phenomena are tricky to model. That said DFT is currently the best compromise between accuracy and performance for "large" (some hundreds) of atoms and is usually preferred to HF. Machine learned potentials trained on more accurate quantum chemistry protocols might change that in the near future.

Why is it that an explicit form for the kinetic energy functional in DFT is not available? Is this limitation dependent on the choice of basis, and could using a momentum (reciprocal space) basis help simplify or resolve this issue?

In the coordinate representation, the kinetic energy is a laplacian (second derivative) operator of the wavefunction and it is very difficult (read impossible) to determine its analytical form as a functional of the density. Using a momentum basis would simplify this term but the other terms in the energy would become really ugly.

In the lecture, we said that exchange-correlation term is a functional of one-body function. However, this term implicitly depends on two-body electron density. Does this imply that expressing energy functional in terms of one-body density is an approximation which works well for the systems where electron correlations are weak?

The writing of energy as a functional fo the one-body density is an EXACT result. The problem is that, while we know that this rewriting is possible, in practice we don't know the exact expression for the individual terms in which we have separated the energy (kinetic, standard Coulomb, exchange correlation). The approximations come in when specific (approximate) forms for these terms, and in particular for the exchange correlation term, are adopted.

I don't quite understand marginal probabilities in this context (one and two body probability), what do they represent?

Not sure I understand the difficulty…here is an attempt to answer. The two boby probability represents the probability to find one of the electrons of the system at position r AND another electron of the system at position r', irrespective of where the remaining N-2 electrons are in space. The one body probability represents the probability to find one of the electrons of the system at position r, irrespective of where the remaining N-1 electrons are in space.

Moreover, it seems to me that these marginal probabilities only make sense if we label the electrons, distinguishing them from each other, but aren't electrons indistinguishable?

In the probabilities above, say the two body, we never specify (or care, or even can say due to indistinguishability) WHICH electron (i.e. a labeled one) is at position r and WHICH electron is in r'…we only discuss the probabilty that one (anyone) of the electrons is somewhere…

The Hohenberg-Kohn theorem applies to the ground state of the system, what should we do when considering excited states ?

There is an extension of DFT, known as time-dependent DFT, that can be used in this case. It is, however, a bit more expensive and less reliable.