Q&A Lecture 7

Is it for simple systems possible to get an exact exchange correlation term for simple systems? If not, is the LDA the only way of estimating a term or are there also different methodologies?

Unfortunately, I [Edrick] am not an expert on the field but here are some comments.
I could not find an analytical expression for the *correlation* contribution of any system (if I find one I will let you know!). It seems that this contribution is usually estimated using quantum Monte Carlo methods, as in the homogeneous electron gas that we saw during the tutorial. On the other hand, one example of an analytical expression for the *exchange* contribution is the homogeneous electron gas, as we also saw in the tutorial. I found another interesting approach for the exchange contribution is in this paper (https://rsc.anu.edu.au/~pgill/papers/033GP93.pdf), where, as far as I understand, they are using an "inverse" approach, finding a function such that results for the hydrogen atom are reproduced.
I am not quite sure about understanding the link that you are making between the two questions, but regarding the second question, you can think that each rung of the Jacob's ladder is a different methodology. In the tutorial, we only saw in detail the rationale behind the LDA approximation, but each rung has its own rationale. We saw for example that hybrid functionals are linear combinations between the exchange from Hartree-Fock and the exchange from lower rungs. Something that I did not mention in the tutorial was the fact that for each rung there are *empirical* and *non-empirical* functionals; you can find a bit more on this in the pdf that I uploaded to the moodle called *Which functional should I choose?*

The nuclei–nuclei repulsion term seems straightforward to express in the same manner as the electron–nuclei and electron–electron terms. However, I am unsure how the analysis proceeds for the electronic kinetic energy operator. What form do we obtain when we carry out an analogous derivation for the kinetic energy contribution in the energy functional?

The fact that the kinetic energy can be expressed as a functional of the density follows from a theorem (by Walter Kohn) that proves that the whole energy is. The derivation using our “explicit methods” is not straightforward, except for simple systems like the Fermi electron gas (i.e. a gas of free electrons) for which one finds that the kinetic energy is proportional to a power of the density. I plan to say a few more words on this in the next class.

We saw that the rho and rho_2 could be interpreted as the density distribution of finding an electron in a certain r position (or two electrons in two positions), given a quantum state. But how can we interpret the g_2? Is it like a conditional probability?

g_2 is what is called a likelihood ratio or correlation coefficient depending on the communities. It measure the probabilistic correlation between the two variables in rho_2. If they are independent, then g_2 = 1. If there is a dependency g_2 is not equal to one and is “bigger” for more strongly correlated variables.

If the density defines the ground-state (energy) uniquely, can excited states also be described as functionals of the density or is this limited to the ground-state only?

as the energy (i.e. the Hamiltonian) is a functional of the density in the coordinate basis, all eigenstates of the Hamiltonian can be thought of as functionals of the density. The issue is that, for excited states, the variational theory is much weaker/essentially useless. There are, however, extension of density functional theory (for example time-dependent DFT) that bypass this problem by avoiding to invoke a minimisation to compute the excited states. Good parametrisation of functionals - e.g. exchange correlation- that is valid at the same time for the ground and excited states, however, is difficult.

If we look at the final expression of $\langle\varphi|\hat{U}_{ee}|\varphi\rangle$, can we derive that the self-interaction error appears for not statistically dependent electrons? So that in the presence of exchange and correlation we might have self-interaction error? What can we do to correct/remove SIE?

Self-interaction error comes from a non exact cancellation of the self energy between the coulomb and exchange-correlation. It is usually present to some extend in DFT. Alternative methods, e.g. many body perturbation theory, avoid this but at considerable additional numerical cost. Recent developments, e.g. Koopmans theory, in DFT mitigate the self interaction problem.

The electron density functions $\rho(r)$ should be different for different electrons(ex. one electron in 1s orbital, one in 2p).yes, electrons are not distingushable, then why we still write r1,r2..., and use them to represent different electron?

All these variables are integrated out so you can think about them as labels that we use to keep track of a count as in “position in space in which an electron that we label as 1 is found”. In the end, we are left only with an “unassigned” set of space coordinates where we can find “one of the electrons irrespective of where the others are"

Why is the probability density a function of x y z and not r? Also, this approach uses the full probability density allowing us to just multiply by the number of electrons, but for Hartree-fock for example we use the single orbital probability density then we must solve for each electron and we cannot just multiply by the number of electrons. Am I correct in thinking this way? If so, is one considered more accurate than the other?

Not sure I understand: x,y,z are the three Cartesian components of r. If the question is why does it depend on all three and not, e.g. on the modulus of r, the reason is that we wrote the density in the most general form possible: sometimes it will be possible to use only the modulus but this depends on the specific problem.
It is correct that in H-F we are still looking at the level of the single electrons to construct the trial states. The modulus square of the trial state is the probability as a function of 3N electronic positions for the full system. In DFT we are looking at the probability to find "one" electron somewhere in space. Accuracy is usually greater at the DFT level, but this depends on the system and on the choice of the exchange correlation functional.

When we marginalize over all but one coordinate in $|\Phi(r1,r2,\cdots,rN)|2$ *to obtain the one-electron density* $\rho(r)$*, what does this operation represent physically? Does the information about the other coordinates remain encoded in* $\rho(r)$*, and what is the physical meaning of this reduction?*

I would say that we shift point of view from the statement "electron 1,2,…N" have a certain probability to be found around "r_1,r_2,…,r_N" to the distribution of charge around the space point "r" is…Of course, this distribution of charge originates from the positioning of the electrons in space, but we now look at space similar to what is done in classical electromagnetism when considering any charge density. I'll say a bit more about this in class. Yes it remains encoded: different $|\Phi(r1,r2,\cdots,rN)|2$ lead to different densities. The interpretation is that the energy is not an explicit function of the position of each electron in space but only on the charge density that these positions determine at a position in space.

We say that the ground-state energy can be obtained by minimizing an energy functional of the density, but in fact this functional itself isn't known exactly. Are we essentially reformulating the original unknown exact wavefunction problem into an unknown exact functional problem, or is there a concrete sense in which the density formulation is still easier (more constrained, more systematically improvable, less variables) than the full many-electron wavefunction?

The density formulation comes with the advantage that we reduce the dimensionality of the function to "guess" in the variational principle to the three Cartesian coordinates (not 3N Cartesian coordinates as in a full wave function optimisation). Guessing in three d is "easier" than guessing in 3N d. The price that we pay in this process is the fact that we have to deal with an unknown exchange correlation functional. There are, however, more than 60 years of work on finding good approximations for these objects as I believe you have seen in the discussion session. The work on developing exchange correlation functional that are progressively more accurate is on-going but there are criteria to determine their quality (e.g. by checking results different choices and stopping at a level of complexity that does not

change the quality of the results - either because no computational difference is observed or because comparison with experimental references is satisfactory).

What is the necessarity to introduce the correlation function? We are just changing the forms of the integral, but there is no simplification for our calculation. In practice, how do people calculate the exchange-correlation term? Do they directly calculate the integral, or there are better ways to estimate it?

The advantage comes mainly from isolating the "classical like Coulomb" term that is - usually - the largest contribution to the interaction and is a simple functional of the density. The integral with the correlation function is then modelled as you have seen in the discussion session so there is a simplification that comes from the fact that we don't treat it exactly but via controlled approximate forms that are quite accurate for many applications. Testing functionals of increasing complexity and checking that from a certain point on results are not affected is a criterion to verify the quality of the approximation.
Different forms for the term are introduced (LDA, GGA…the Jacob's ladder of functionals, etc. as you should have seen in the discussion session). These have know forms that can be computed "exactly" together with their derivatives.
It depends on the form chosen for the functional. Typically, the integrals are evaluated numerically but this does not pose the greatest computational challenge in the process.

Is there ever a case when the magnitude of the Coulomb term is much greater than the Exchange-Correlation term such that the evaluation of the Exchange-Correlation term is not as significant, reducing computational costs/accuracy needed for the Exchange-Correlation?

This is in fact generally the case. Direct Coulomb is almost always the dominant term (the exception being the so-called strongly correlated systems (e.g transition metal oxides) and existing approximations of the exchange correlation are good enough to capture the main corrections. Note, however, that these corrections - while "small" - can still significantly affect the properties of the system (e.g. bound vs unbound state) and cannot be completely neglected.

When computing the integrals numerically, how are the singularities at $|r_1-r_2|=0$ handled?

In practice, this singularity never occurs due to the repulsive components of the interactions that prevent $r_1=r_2$.

I am a bit confused about the kinetic term, expressing it as a functional of the electron density is not obvious to me. How is this term expressed as a functional of the electron density ?

The fact that the kinetic energy can be expressed as a functional of the density follows from a theorem (by Walter Kohn) that proves that the whole energy is. The derivation using our "explicit methods" is not straightforward, except for simple systems like the Fermi electron gas (i.e. a gas of free electrons) for which one finds that the kinetic energy is proportional to a power of the density. I plan to say a few more words on this in the next class.

We saw the problem reduced from 3N to 3 variables but I am still not convinced because I see the integral of ϱ which has all other variables. We still need some way to do that integral or not? Why? Why not?

We never do the integrals in practice. In the variational principle we "guess" a form for the 3d density directly and work with it and only the 3d integrals that we mentioned in class.

Since we do not know the exact many-electron wavefunction, how do we actually calculate the electron density in practice?

The mathematical definition of the density is obtained via integration of the wave function but once we understand that the density is our focus, we treat it as the basis of the variational approach. So, we "guess" trial densities on the basis of, e.g. symmetries and/or chemical intuition (as we would "guess" trial wave functions), and proceed from there.

In the framework of DFT, since the energy of the system is a functional of the electron density, how can the electron density be determined? Are there analytical models that determine this quantity (except from deriving it from the wavefunction of the system, which would remove the advantage of cheap storing in DFT since it would be necessary to store the wavefunction), or is it determined experimentally?

The mathematical definition of the density is obtained via integration of the wave function but once we understand that the density is our focus, we treat it as the basis of the variational approach. So, we "guess" trial densities on the basis of, e.g. symmetries and/or chemical intuition (as we would "guess" trial wave functions), and proceed from there. Of course validation, e.g. of the variational ground state energy for a given trial density, vs experiments is important.

You had mentioned in the end of the lecture that this density functional representation of the energy works better (or is preferable) for solids, not molecules - I was wondering why this was the case? And what would we use for studying molecules instead?

If I remember correctly my statement - or in any case the intent behind it - I meant that the practical implementation of DFT (and the creation of approximate exchange correlation functionals) is used most often for solid. This comes mainly from the fact that several codes

typically use a plane wave basis to represent the density - and then the coefficients of the expansion in this basis as the variational parameters. This basis is better adapted to periodic systems like crystals. There are versions of DFT that use basis, e.g. Gaussians, that are localised on ions and that can be used for molecules. Examples of codes in the two "domains" are Quantum Espresso (plane waves) and CP2K (localised basis).
So, the theory is the same in both cases, but implementations differ and can be more adapted to one situation or the other.

This whole simplification is to get the the coulomb interaction because then we can calcultated, using basis set, the correlation, but I don't really get how we can add together everything that we can't calculate and then with some computation get really close to an accurate answer. Sorry my question is not really clear but I don't get this "we put everything we don't get in a box and then with some model get close to the real value".

The idea is that the term we don't know is a (relatively small) correction to the "classical Coulomb" interaction. Therefore we - meaning the people who have developed approximate exchange correlation functionals in the last 60 or so years - can obtain this correction via physically based approximations (e.g. the exchange correlation kernel is a local functional of the density (LDA, I think you saw this in the discussion session) or we can improve on this by saying that it also depends on changes, gradients, of the density (GGA…)) and experimental information (by adding, for example, parametrizations that are tuned to match experimental spectra). There is certainly a bit of "cooking" in all of this, but the results are very accurate. There is also quite a bit of theoretical work to determine (e.g. based on symmetry) general mathematical forms for the exchange correlation functionals.