Séminaire de groupe :

"Generalized Density-Functional Theory."

Prof. Paul W. AYERS

Department of Chemistry; McMaster University

Mardi 7 décembre 2004 à 11 heures

Salle RAPHAEL 1 – site d'Ivry-sur-Seine

Density-functional theory has become the method of choice for computations on large or complex systems because it combines the virtues of reasonable accuracy with relative computational ease. Unfortunately, approximate density functionals are not uniformly accurate and, when they fail, there is no systematic way to improve their results. This has led to some interest in "generalized density functional theories;" these methods are motivated by the premise that if using the electron density is good, then using some quantity more complicated than the density is bound to be better.

The practical success of density-functional theory rests on three pillars, two of which are theoretical and one of which is practical:

1. *The First Hohenberg-Kohn Theorem, which tells us that every property of any electronic system can be expressed in terms of its electron density.*
2. *The Second Hohenberg-Kohn Theorem, which tells us that the ground state energy and electronic density of a system may be determined by minimizing the energy with respect to the density.*
3. *Accurate functionals for the electronic energy of the system (invariably constructed through the Kohn-Sham ansatz), which provide the practical tools by which the variational procedure for determining the electronic energy and density is performed.*

In order to be useful, a "generalized" density-functional theory must also address these three issues. Probably the simplest "generalized" density-functional theory is one constructed using the pair electron density, $r_2(r_1, r_2)$, which is simply the probability of observing one electron at r_1, given that another electron is at r_2. This function contains most (perhaps all?) of the "chemically relevant" information about electron pairing, chemical binding, and other properties of interest. In addition, if one knows $r_2(r_1, r_2)$, then one can construct every component of the energy except the kinetic energy. Theories based on the

pair-density will not be practically useful unless there are accurate kinetic energy functionals. Accordingly, we will start by constructing

> *3'. Accurate functionals for the kinetic energy in terms of the electron pair density, which can be used to determine the kinetic energy (ergo the total energy) to any accuracy.*

Given that there seem to be reasonable energy functionals of the pair-density, the next question is whether the pair density can be used to determine other properties of electronic systems. This is obviously true since the pair-density determines the density.

> 1'. The rigorous mathematical analysis of Lieb can be extended to the pair density, formally eliminating the v-representability *and* N-representability problems.

The N-representability problem is particularly problematic, because it bears on the variational procedure. We cannot simply minimize the electronic energy as a functional of the pair density; rather, we must minimize the electronic energy over the set of N-representable pair densities. Unfortunately, the literature does not seem to contain a characterization of the set of N-representable pair densities.

> 2'. A necessary and sufficient condition for the N-representability of the electron pair density will be derived. This allows us to determine the ground state electronic energy and pair density using a variational approach.