Dispersion Interactions via Optimal Transport

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2 Overview of the Field

Accurately predicting electronic structure from first principles is crucial for many research areas such as chemistry, solid-state physics, biophysics and material sciences. In principle, the electronic structure is determined by the Schrödinger equation, which can only be solved in practice for few electrons. Kohn-Sham (KS) Density functional theory (DFT) has been a real breakthrough for electronic structure calculations. KS DFT uses the one-electron density and a non-interacting wave function as basic variables, much simpler quantities than many-electron wave-functions, allowing to treat realistic large systems \[2, 6, 7, 8, 9, 10, 13\].

In the Hohenberg and Kohn formulation of DFT \[6, 10, 13\] the electronic-ground state properties are calculated by minimizing a functional

\[
E[\rho] = F_{HK}[\rho] + \int_{\mathbb{R}^3} V(x)\rho(x)dx, \quad \rho(x) = N \int_{\mathbb{R}^3(N-1)} |\psi(x_1, x_2, \ldots, x_N)|^2 dx_1 \ldots dx_i \ldots x_N,
\]

where \(N\) denote the number of electrons, \(\psi\) is the wave-function, \(V\) an external potential, which is due to the nuclei, and \(F_{HK}[\rho]\) is an universal functional, the so-called Hohenberg-Kohn functional (or Levy-Lieb functional) \[2, 10, 13\].

For every density \(\rho \geq 0\) in \(\mathbb{R}^3\) the functional \(F_{HK}^{H}[\rho]\) is defined as a minimization problem on a space of wave functions subject to a highly non-linear constraint

\[
F_{HK}^{H} = \inf_{\psi \mapsto \rho} \int_{\mathbb{R}^3(N-1)} \frac{1}{2} |\psi|^2 dx, \quad V_{ee}(x_1, x_2, \ldots, x_N) = \sum_{j=1}^{N} \sum_{i=j+1}^{N} \frac{1}{|x_j - x_i|}, \quad (1)
\]

and \(\psi \mapsto \rho\) stands for

\[
\int_{\mathbb{R}^3(N-1)} |\psi(x_1, \ldots, x_j, \ldots, x_N)|^2 dx_1 \ldots dx_j \ldots dx_N = \rho(x_j), \quad \forall j = 1, \ldots, N.
\]

Although the Hohenberg-Kohn theory guarantees the existence of such functional \(F_{HK}^{H}[\rho]\), in practical, approximations are needed. In classical Kohn-Sham DFT, the minimization of \(E[\rho]\) is done under the assumption that the kinetic energy dominates over the electron-electron interaction by introducing the functional \(F_{HK}^{T}[\rho]\), corresponding to the minimum of the expectation value of the kinetic energy alone over all fermionic wave functions yielding the given \(\rho\). The remaining part of the exact energy functional, \(E_{Hxc}[\rho] = F_{HK}^{T}[\rho] - T_s[\rho]\), is usually approximated by splitting it into the sum of the classical Hartree functional and the exchange-correlation \((xc)\) energy \(E_{xc}\), that is the crucial quantity to be approximated.

The idea of formulate the ground state problem in terms of the electronic density alone comes from Thomas–Fermi (TF) model \[4, 5\]. L. H. Thomas and E. Fermi are viewed as precursors of the modern Density Functional Theroy.
In addition, Kohn-Sham DFT obviously encounters difficulties when particle-particle interactions play a more prominent role. In such cases, the physics of \( F_h^{HK}[\rho] \) is completely different than the one of the Kohn-Sham non-interacting system.

An alternative approach, more suitable to study strongly-correlated electrons (SCE), were introduced by M. Seidl, P. Gori-Giorgi and co-authors (e.g. [1, 5, 14]). The so-called SCE limit is defined as the semi-classical limit \( \hbar \to 0 \) of \( F_h^{HK}[\rho] \) keeping the one-body density fixed. In [2, 3, 11] this limit was shown to be equal to an optimal transport problem with finitely many probability measures (marginals) \( \mu_1, \ldots, \mu_N \) and Coulomb cost:

\[
V_{ee}[\rho] = \inf \left\{ \int_{(\mathbb{R}^d)^N} V_{ee}(x_1, x_2, \ldots, x_N) d\gamma(x_1, \ldots, x_N) : \begin{array}{l}
e_1 : (\mathbb{R}^d)^N \to \mathbb{R}^d \\
(\varepsilon_i)_+ \gamma = \mu_i \quad \text{and} \quad 1 \leq i \leq N \end{array} \right\},
\]

where \( \varepsilon_1, \ldots, \varepsilon_N : (\mathbb{R}^d)^N \to \mathbb{R}^d \) denotes the canonical projections. The probability measure \( \gamma \) are called couplings or transport plans, and give the joint probability distribution of the marginals \( \mu_1, \ldots, \mu_N \). In the DFT context, the multi-marginal optimal transportation problem with Coulomb cost is a lower bound for the internal part of the ground state energy (Hohenberg-Kohn functional) of a time-independent Electronic Schrödinger equation describing the evolution of a molecular system of \( N \)-electrons under Coulomb electron-electron interaction [2].

\section{Objectives of the meeting}

The goal of this team meeting is to boost up progress in the very early stage of the proposed research program we have recently initiated. Augusto Gerolin is a mathematician working at the Theoretical Chemistry Department at Vrije Universiteit Amsterdam (VU Amsterdam), which has been developing Optimal Transport methods in Density Functional Theory: Mircea Petrache is a mathematician working at the Pontificia Universidad Católica de Chile, which among other interests have been studying ground state energies and assymptotic behaviour of clusters of molecules in different contexts.

Augusto Gerolin together with Quantum Matter research group at the VU Amsterdam has been developing physical models on dispersion interaction via the SCE-formalism in DFT. The main goal of this team meeting is to start a rigorous mathematical framework, based on Optimal Transport Theory, to describe quantum interactions between molecules (e.g. Hydrogen bond, van der Waal’s, dipole-dipole force) in the so-called strong-interaction limit. Although we have been done several online meetings, it was fundamental for both of us to meet personally and to focus on full week in the problem.

Figure 1: From [16] [Left] \( H_2 \) dissociation curves obtained by different methods, including Hartree-Fock, B3LYP, FCI, LDA and SCE. [Right] Energy densities in the xc hole of eq 30 for \( H_2 \) at \( R = 8.0 \) at different strength \( \hbar \) values: 0, 1, and \( \infty \). (for all details see [16])
4 Scientific Progress Made

In the physical-chemistry literature, dispersion interactions, have been always considered out of the realm of the strong-interaction limit, and, more generally, have been usually treated in a conceptually separate framework from the problem of strong correlation. During the meeting, we make the first step in understanding the mathematical framework allowing to study Dispersion interaction in the strongly-correlated limit.

The relevance of the strong-interaction limit for dispersion is already hinted in the fundamental work of E. Lieb and W. Thirring [12]. The conceptual difference with respect to other physical and theoretical investigations available in the literature is that during the meeting the analysis were done with the density constraint $\rho$, using the a highly non-local functional $V_{ee}[\rho]$ and to study the asymptotic behaviour of the ground state energy of the coupled system $\alpha\beta$ in function of the distance of the molecules $\alpha$ and $\beta$.

5 Outcome of the Meeting

The work developed at BIRS allowed us to be one step forward in understanding dispersion interactions via Optimal Transportation techniques. We will continue developing the theory and we plan to write a paper containing the results obtained at Banff.

References


