

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 $E[\rho]$ with respect to $\rho(x_i)$, the one-body particle density¹,

$$E[\rho] = F_{\hbar}^{HK}[\rho] + \int_{\mathbb{R}^3} V(x)\rho(x)dx, \quad \rho(x_i) = N \int_{\mathbb{R}^{3(N-1)}} |\psi(x_1, x_2, \dots, x_N)|^2 dx_1 \dots d\hat{x}_i \dots x_N,$$

where N denote the number of electrons, ψ is the wave-function, V an external potential, which is due to the nuclei, and $F_{\hbar}^{HK}[\rho]$ 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 $F_{\hbar}^{HK}[\rho]$ is defined as a minimization problem on a space of wave functions subject to a highly non-linear constraint $\psi \mapsto \rho$

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

and $\psi \mapsto \rho$ stands for $\int_{\mathbb{R}^{3(N-1)}} |\psi(x_1, \dots, \hat{x}_j, \dots, x_N)|^2 dx_1 \dots d\hat{x}_j \dots dx_N = \rho(x_j), \forall j = 1, \dots, N$.

Although the Hohenberg-Kohn theory guarantees the existence of such functional $F_{\hbar}^{HK}[\rho]$, 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 $T_s[\rho]$, corresponding to the minimum of the expectation value of the kinetic energy alone over all fermionic wave functions yielding the given ρ . The remaining part of the exact energy functional, $E_{Hxc}[\rho] = F_{\hbar}^{HK}[\rho] - T_s[\rho]$, 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.

¹The idea of formulate the ground state problem in terms of the electronic density alone comes from Thomas-Fermi (TF) model [4, 15]. L. H. Thomas and E. Fermi are viewed as precursors of the modern Density Functional Theory.

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 $\hbar \rightarrow 0$ 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) μ_1, \dots, μ_N and Coulomb cost:

$$V_{ee}[\rho] = \inf \left\{ \int_{(\mathbb{R}^d)^N} V_{ee}(x_1, x_2, \dots, x_N) d\gamma(x_1, \dots, x_N) : \begin{array}{l} e_i : (\mathbb{R}^d)^N \rightarrow \mathbb{R}^d \\ (e_i)_\# \gamma = \mu_i \end{array} \text{ and } 1 \leq i \leq N \right\}, \quad (2)$$

where $e_1, \dots, e_N : (\mathbb{R}^d)^N \rightarrow \mathbb{R}^d$ denotes the canonical projections. The probability measure γ are called couplings or transport plans, and give the joint probability distribution of the marginals μ_1, \dots, μ_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].

3 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 asymptotic behavior 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.

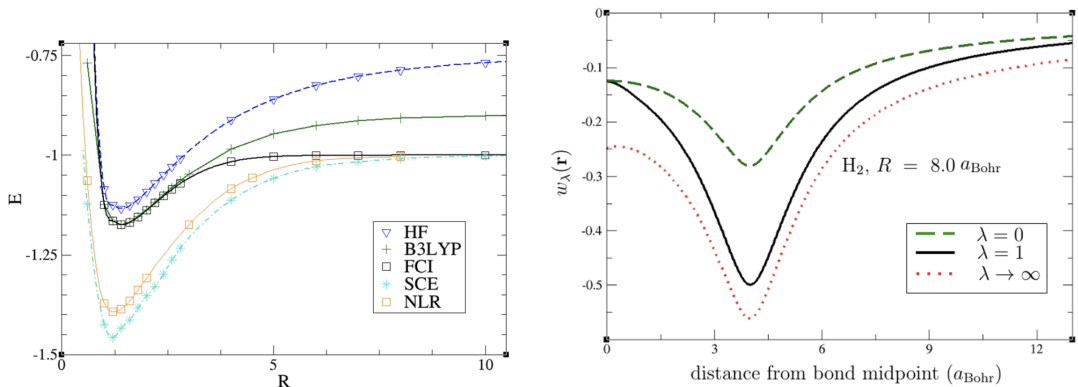


Figure 1: From [16] [Left] H_2 dissociation curves obtained by different methods, including Hartree-Fock, B3LYP, FCI, LDA and SCE. [Right] Energy densities in the xc hole of eq 30 for H_2 at $R = 8.0$ at different strength \hbar values: 0, 1, and ∞ . (for all details see [16])

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 ρ , 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 α and β .

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

- [1] Giuseppe Buttazzo, Luigi De Pascale, and Paola Gori-Giorgi. Optimal-transport formulation of electronic density-functional theory. *Physical Review A*, 85(6):062502, 2012.
- [2] Codina Cotar, Gero Friesecke, and Claudia Klüppelberg. Density functional theory and optimal transportation with coulomb cost. *Comm. Pure Appl. Math.*, 66:548–599, 2013.
- [3] Codina Cotar, Gero Friesecke, and Claudia Klüppelberg. Smoothing of transport plans with fixed marginals and rigorous semiclassical limit of the Hohenberg-Kohn functional. *Archive for Rational Mechanics and Analysis*, 228(3):891–922, 2018.
- [4] Enrico Fermi. Un metodo statistico per la determinazione di alcune proprietà dell’atomo. *Rend. Accad. Naz. Lincei*, 6:602–607, 1927.
- [5] Paola Gori-Giorgi, Michael Seidl, and Giovanni Vignale. Density-functional theory for strongly interacting electrons. *Physical review letters*, 103(16):166402, 2009.
- [6] Pierre Hohenberg and Walter Kohn. Inhomogeneous electron gas. *Phys. Rev.*, 136(B864), 1964.
- [7] Walter Kohn. Nobel lecture: Electronic structure of matter-wave functions and density functionals. *Reviews of Modern Physics*, 71(5):1253–1266, 1999.
- [8] Walter Kohn and Lu J. Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, 140(A1133), 1965.
- [9] Chengteh Lee, Weitao Yang, and Robert G Parr. Development of the colle-salvetti correlation-energy formula into a functional of the electron density. *Physical review B*, 37(2):785, 1988.
- [10] Mel Levy. Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v-representability problem. *Proceedings of the National Academy of Sciences*, 12:6062–6065, 76.
- [11] Mathieu Lewin. Semi-classical limit of the Levy-Lieb functional in density functional theory. *Comptes Rendus Mathematique*, 356(4):449–455, 2018.
- [12] Elliott H. Lieb, , and Walter E. Thirring. Universal nature of van der waals forces for coulomb systems. In *The Stability of Matter: From Atoms to Stars*, pages 113–119. Springer, 1997.

- [13] Elliott H Lieb. Density functionals for coulomb systems. In *Inequalities*, pages 269–303. Springer, 2002.
- [14] Michael Seidl. Strong-interaction limit of density-functional theory. *Physical Review A*, 60(6):4387, 1999.
- [15] Llewellyn H. Thomas. The calculation of atomic fields. *Proc. Cambridge Phil. Soc.*, 5(23):542–548, 1927.
- [16] Stefan Vuckovic, Lucas O Wagner, André Mirtschink, and Paola Gori-Giorgi. Hydrogen molecule dissociation curve with functionals based on the strictly correlated regime. *Journal of chemical theory and computation*, 11(7):3153–3162, 2015.