

Is it impossible to find the universal density functional? Or is it just well-hidden?

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We review information on methods for constructing the exact density functional mathematically and computationally. While it is generally accepted that no explicit analytic form for the exact functional exists, we argue, based on what is known about the classical many-body problem, that this is not necessarily the case.

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Is the Universal Density Functional Unknown?

Density functional theory is an exact framework for computing the ground-state electronic energy and electron density for any electronic system, including atoms, molecules, and solids.¹⁻⁴ The fundamental theorems of Hohenberg & Kohn⁵ provide a quite simple mathematical framework, and it is commonly stated that the only problem is that the exact density functional is unknown, and probably unknowable.

However, the form of the universal functional is not unknown. On the contrary, explicit formulas for computing the functional are well-known, including the Levy wavefunction constrained search,^{6,7} the Levy-Valone ensemble constrained search,⁸ and the Lieb Legendre transform^{9,10} (foreshadowed in the work of Nalewajski & Parr¹¹). These forms have, in some cases, even been implemented numerically. For example, Colonna & Savin¹², and later Teale & Helgaker^{13,14}, implemented the Legendre transform. Freed & Levy¹⁵, and later Cioslowski¹⁶, presented algorithms based on the constrained search. In the Kohn-Sham context,¹⁷ the exact functional has been constructed, and even optimized, by Burke & his coworkers^{18,19} (for a discretized one-dimensional system). All of these approaches are even more expensive than solving the Schrödinger equation, in a specified basis, directly. However, they are not only exact in principle, but also exact in practice.

There are other, more unconventional, approaches to the exact functional. Ludena²⁰⁻²³ has developed ways to construct the exact functional using non-uniform coordinate scaling; this is related to

approaches based on line-integration.^{24,25} The present authors worked, within the context of moment expansions, to find, and then solve, a first-order partial differential equation that writes the exact functional as a function of the moments of the electron density.^{26,27} So there are ways to construct the exact functional. It is just that they are less efficient than solving the Schrödinger equation directly. The methods theorists use to construct the exact functional are designed to provide insight, not numbers.

Might There Be Practical Expressions for the Universal Density Functional?

Finding the universal density functional is not impossible. On the contrary, as described above, we know of many (perhaps too many) different ways to write the universal functional (many of which are equivalent to the ensemble constrained search, and none of which are computationally practical).^{7,9,28} When we talk about the unknown density functional, we usually mean that we do not know how to write the universal functional as a simple and explicit functional of the density, without any reference to the wavefunction (or wavefunction-related quantities). Can we express the exact density functional as a simple and explicit functional of the electron density?

This is a more challenging quest. One may argue that it is quixotic, and most researchers in density functional theory believe that it is impossible to find practical formulations for the exact density functional. For example, it is known that the exact Hohenberg-Kohn density functional is non-differentiable²⁹⁻³² and that it may

even be discontinuous (though it is at least lower semicontinuous⁹). It is difficult to find explicit density functionals that are non-differentiable, but some implicit orbital-based density functionals are non-differentiable. (The most important example of a non-differentiable implicit density functional is the Becke's functional for static correlation.³³) Even so, all known functionals that are explicit in and use only the occupied Kohn-Sham orbitals have deep problems (which may or may not be insurmountable). Full configuration interaction (full-CI) can be written as a functional that depends explicitly on both the occupied and the unoccupied Kohn-Sham orbitals, so that it is possible to write an explicit orbital functional if one allows oneself to use the virtual orbitals. But then we are now back where we started from: we are using information about the exact wavefunction, and constructing the universal functional in a way that is even more costly than directly solving of the Schrödinger equation.

It is possible that no computationally tractable form for the exact density functional exists. While most density functional workers seem to believe this to be true, it has not been proven. The argument is normally that the quantum many-body problem is intractable (which is, itself, a debatable assumption), therefore no universal density functional can exist. (subuniversal functionals—e.g., for 1-electron systems or uniform electron gasses—obviously exist.)

Traditionally, one argues that there are no explicit solutions to the quantum many-body problem because there are no explicit solutions to the classical many-body problem, and the quantum many-body problem is even more difficult. The problem with this argument is that, in many interesting cases, the classical many-body problem is not unsolvable.^{34, 35} For example, for N masses interacting through gravitation alone, there are analytic, and convergent, expansions.³⁶⁻³⁸ (The 3-body solution is more than one hundred years old;^{39, 40} the N -body solution is more recent.³⁶⁻³⁸ In both cases, one typically makes a small additional assumption, namely that there are no "collisions" between the masses (so that the potential does not diverge). At least for the 3-body problem, this assumption can be relaxed.) These solutions to the classical many-body problem are analytic, but they are not "nice": the convergence is so slow as to be useless. However, the classical N -body problem is not "impossible" at a mathematical level.

Furthermore, the 3-body⁴¹ and 4-body⁴² quantum problems can be generically solved (and in a way that is

sometimes used numerically), using techniques developed by Faddeev.⁴³ So, we should not be too hasty to discard the possibility of finding an analytic (albeit perhaps not practically useful) formula for the universal density functional, at least for systems with four or fewer electrons. An explicit expression for the universal density functional might exist; it might just be well-hidden.

If an analytic expression for the universal functional is available, might it be useful? Consider that the classical density functional theory problem is almost certainly easier than the conventional classical many-body problem. In the classical many-body problem, one has to trace the detailed trajectory of the positions of the N bodies. In the classical density functional theory problem, one may assume that all the masses are equal, and then one must compute, from the time-averaged mass density, the total energy. The problem is much simpler than the classical N -body problem because all the point-masses are equivalent and the detailed, possibly chaotic, time-dependent trajectory is not required! However, the problem is also more complicated, because one wishes to consider cases where the point-masses are bound by an external gravitational potential. To the best of our knowledge, no analytic expression for the classical density functional has ever been found.

There is one case of quantum density functional theory that closely resembles the solvable classical case: density functional theory for nucleons.⁴⁴⁻⁴⁶ With nucleons, there is no external potential, and the nucleons are often modeled as point-particles, interacting by a pairwise attractive (albeit not $1/r$) potential. This problem is a close analogue to the gravitational classical many-body problem for which solutions are known. If there are ways to write the universal functional as an explicit functional of the density, or an implicit functional of only the occupied Kohn-Sham orbitals, the functional is probably least-hidden for the nuclear density functional problem.

Conclusions

We conclude with an optimistic note: if we assume that there might be expressions for the classical density functional, then perhaps there may be functionals in the quantum case also. If we assume that the expressions for the classical density functional are more computationally facile than the trajectories of the classical many-body problem, then perhaps the expressions for the quantum density

functional are tractable also. The analytic form for the universal density functional may exist; it might even be useful, but it is certainly well-hidden.

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References

- 1 Kohn W, Becke A D & Parr R G, *J Phys Chem*, 100 (1996) 12974.
- 2 Parr R G & Yang W, *Density-Functional Theory of Atoms and Molecules*, (Oxford UP, New York) 1989.
- 3 Ayers P W & Yang W, *Density Functional Theory*, in *Computational Medicinal Chemistry for Drug Discovery*, edited by P Bultinck, H de Winter, W Langenaeker & J P Tollenaere (Dekker, New York) 2003, pp. 571.
- 4 Kohn W, *Rev Mod Phys*, 71 (1999) 1253.
- 5 Hohenberg P & Kohn W, *Phys Rev*, 136 (1964) B864.
- 6 Levy M, *Proc Natl Acad Sci*, 76 (1979) 6062.
- 7 Levy M & Perdew J P, *NATO ASI Series, Series B*, 123 (1985) 11.
- 8 Valone S M, *J Chem Phys*, 73 (1980) 4653.
- 9 Lieb E H, *Int J Quant Chem*, 24 (1983) 243.
- 10 Lieb E H, *NATO ASI Series, Series B*, 123 (1985) 31.
- 11 Nalewajski R F & Parr R G, *J Chem Phys*, 77 (1982) 399.
- 12 Colonna F & Savin A, *J Chem Phys*, 110 (1999) 2828.
- 13 Teale A M, Coriani S & Helgaker T, *J Chem Phys*, 130 (2009) 104111.
- 14 Teale A M, Coriani S & Helgaker T, *J Chem Phys*, 132 (2010) 164115.
- 15 Freed K F & Levy M, *J Chem Phys*, 77 (1982) 396.
- 16 Cioslowski J, *Phys Rev Lett*, 60 (1988) 2141.
- 17 Kohn W & Sham L J, *Phys Rev*, 140 (1965) A1133.
- 18 Stoudenmire E M, Wagner L O, White S R & Burke K, *Phys Rev Lett*, 109 (2012) 056402.
- 19 Wagner L O, Stoudenmire E M, Burke K & White S R, *Phys Rev Lett*, 111 (2013) 093003.
- 20 Kryachko E S & Ludena E V, *Phys Rev A*, 43 (1991) 2179.
- 21 Ludena E V, Lopez-Boada R, Maldonado J E, Valderrama E, Kryachko E S, Koga T & Hinze J, *Int J Quant Chem*, 56 (1995) 285.
- 22 Ludena E V & Lopez-Boada R, *Density Functional Theory I*, 180 (1996) 169.
- 23 Ludena E V, Gomez D, Karasiev V & Nieto P, *Int J Quant Chem*, 99 (2004) 297.
- 24 van Leeuwen R & Baerends E J, *Phys Rev A*, 51 (1995) 170.
- 25 Gaiduk A P & Staroverov V N, *J Chem Phys*, 131 (2009) 044107.
- 26 Ayers P W, Lucks J B & Parr R G, *Acta Chim Phys Debr*, 34-35 (2002) 223.
- 27 Ayers P W & Rodriguez J I, *Can J Chem-Rev Can Chim*, 87 (2009) 1540.
- 28 Ayers P W, *Phys Rev A*, 73 (2006) 012513.
- 29 Perdew J P, Parr R G, Levy M, Balduz J L & Jr, *Phys Rev Lett*, 49 (1982) 1691.
- 30 Yang W T, Zhang Y K & Ayers P W, *Phys Rev Lett*, 84 (2000) 5172.
- 31 Ayers P W, *J Math Chem*, 43 (2008) 285.
- 32 Mori-Sanchez P, Cohen A J & Yang W T, *Phys Rev Lett*, 102 (2009) 066403.
- 33 Becke A D, *J Chem Phys*, 122 (2005) 064101.
- 34 Diacu F, *Math Intell*, 18 (1996) 66.
- 35 Diacu F, *Mathl Intell*, 22 (2000) 19.
- 36 Babadzanjanz L K, *Celest Mech*, 20 (1979) 43.
- 37 Wang Q D, *Celest Mech Dynam Astron*, 50 (1990) 73.
- 38 Babadzanjanz L K, *Celest Mech Dynam Astron*, 56 (1993) 427.
- 39 Sundman K F, *Acta Math*, 36 (1912) 105.
- 40 McCord C K, Meyer K R & Wang Q D, *Mem Amer Math Soc*, 132 (1998) 1.
- 41 Faddeev L D, *Soviet Phys, JETP*, 12 (1961) 1014.
- 42 Yakubovsky O A, *Soviet J Nucl Phys*, 5 (1967) 971.
- 43 Faddeev L D & Merkuriev S P, *Quantum Scattering Theory for Several Particle Systems*, (Springer, Dordrecht) 1993.
- 44 Bender M, Heenen P H & Reinhard P G, *Rev Mod Phys*, 75 (2003) 121.
- 45 Dobaczewski J, *Int Nucl Phys Conf 2010 (Inpc): Nucl Struct*, 312 (2011) 092002.
- 46 Petkov I Z & Stoitsov M V, *Nuclear Density Functional Theory*, (Clarendon, Oxford) 1991.