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Perspective

Perspective on "Density-functional theory for fractional particle number: derivative discontinuities of the energy"

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Abstract. This paper provides an overview of the title paper by Perdew, Parr, Levy and Balduz [*Phys Rev Lett* 49:1691 (1982)]. The title paper extended density functional theory to fractional electron number by an ensemble approach and proved that the energy is a series of straight lines interpolating its values at integer numbers of electrons. It also established that the highest-occupied exact Kohn–Sham orbital energy is the negative of the ionization energy, and showed that the exchange-correlation potential jumps by a constant as the number of electrons increases by an integer. These results are fundamental and continue to inspire developments in density functional theory.

Key words: Density functional theory – Exchange-correlation functional – Fractional number of electrons – Self interaction error – Derivative discontinuity

The original density functional theory (DFT), based on Hohenberg–Kohn theorems [1], Kohn–Sham equations [2] and the Levy constrained search formulation [3], is a rigorous approach for determining the ground-state density and ground-state energy for any N-electron system. Here the electron number

$$N = \int d^3 r \rho(\mathbf{r}) \tag{1}$$

is an integer. The electronic ground-state energy of the system is a functional of the electron density ρ,

$$E[\rho] = F[\rho] + V_{\mathrm{ne}}[\rho] \ , \tag{2}$$

where $F[\rho]$ is the universal density functional and $V_{\mathrm{ne}}[\rho]$ is the electron-nuclear interaction. $F[\rho] = T_{\mathrm{s}}[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho]$, where $T_{\mathrm{s}}[\rho]$ is the kinetic energy of the Kohn–Sham non-interacting reference system with the same density ρ, $J[\rho] = \frac{1}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'$ is the classical electron–electron repulsion energy, and $E_{\mathrm{xc}}[\rho]$ is the exchange-correlation energy functional.

Since DFT uses the electron density as the basic variable, instead of the wave function in the conventional quantum theory of electronic structure, not only would it be advantageous to have the energy functional and derivatives defined for densities with fractional number of electrons, but it is also necessary to treat systems with a fractional number of electrons. To show this necessity, one only needs to consider the dissociation of H_2^+. In the exact quantum-mechanical theory, at the dissociation limit, H(a)–H(b)$^+$ and its nuclear permutation H(a)$^+$ – H(b) are two degenerate states. Any linear combination of these two states is also a ground state of the dissociation, including the state $\mathrm{H}^{0.5+} - \mathrm{H}^{0.5+}$. At this limit, we have two independent systems each with fractional numbers of electrons. As in Fig. 1, which shows results, obtained from a typical ab initio calculation, we can see that the one-electron system becomes two half-electron fragments when H_2^+ becomes dissociated. The foregoing argument also holds true for the dissociation of any homonuclear diatomic molecular ion A_2^+.

In the title paper by Perdew, Parr, Levy and Balduz (PPLB) [4], DFT was extended to a fractional number of electrons based on the zero-temperature grand canonical ensemble theory. Note that the ensemble description of electronic structure problems goes back to Gyftopoulos and Hatsopoulos [5]. PPLB [4] showed that at zero temperature the ground state of a system with a noninteger numbers of electrons is an ensemble of two pure states with integer numbers of electrons and E^{g}_{N+q}, the ground-state energy of a $(N+q)$-electron system, is a linear combination of E^{g}_{N} and E^{g}_{N+1}, the ground-state energies of the corresponding N- and $(N+1)$-electron systems; namely

$$E^{\mathrm{g}}_{N+q} = (1-q)E^{\mathrm{g}}_{N} + qE^{\mathrm{g}}_{N+1} \ , \tag{3}$$

where $0 < q < 1$. The energy functional was also formulated in exactly the same form as in Eq. (2), with the

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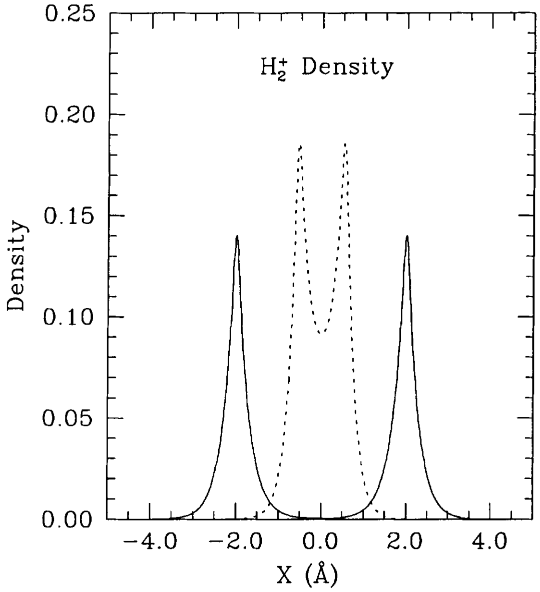

Fig. 1. Hartree–Fock electron density for H_2^+ along the bond axis with the bond middle point at zero. *Solid line* for H_2^+ with bond length 4.0 Å and dashed line for H_2^+ with bond length 1.1 Å

universal density functional defined for a fractional number of electrons by the Levy constrained search [3]

$$F[\rho_{N+q}] = \min_{\hat{\Gamma}\to\rho_{N+q}} \mathrm{Tr}[\hat{\Gamma}(\hat{T}+\hat{V}_{\mathrm{ee}})] \ , \tag{4}$$

where $\hat{T}$ and $\hat{V}_{\mathrm{ee}}$ are the kinetic and electron–electron repulsion operators, and $\hat{\Gamma}$ is any many-electron density operator that delivers the density ρ_{N+q} with fractional numbers of electrons. The type of $\hat{\Gamma}$ allowed is a statistical mixture of N- and $(N+1)$-electron systems. The electron density entering the definition of the energy functional is also an ensemble sum

$$\rho_{N+q} = (1-q)\rho_N + q\rho_{N+1} \ . \tag{5}$$

These are fundamental results in DFT. The density functional extended for a fractional number of electrons based on the ensemble approach gives the correct description for fractional electron number systems in the dissociation limit of H_2^+. A great challenge remains to construct an energy functional $E[\rho]$ that would have the correct behavior for fractional electron number systems, as described in Eq. (3).

Based on PPLB's work, Perdew [6] generalized the sum rule for the exchange-correlation hole to the fractional number of electrons, and Perdew and Levy [7] reached the conclusion that the local density approximation (LDA) and the generalized gradient approximation (GGA) energies were too low for systems with fractional numbers of electrons by analyzing this generalized sum rule.

Functionals with electron self-interaction excluded do very well in approximating the exact relation of Eq. (3) [7]. Based on the Eqs. (3) and (5), Zhang and Yang [8] have recently derived a new scaling relation necessary for the exchange-correlation functional to be self-interaction-error free.

$$E_{\mathrm{xc}}[q\rho_1] = q^2 E_{\mathrm{xc}}[\rho_1] \ , \tag{6}$$

for $0 < q < 1$; however, all widely used GGA and hybrid GGA/exact-exchange functionals [9–12] fail to obey this relation. This failure leads to the consequence that even when the self-interaction error of a functional for systems with integer numbers of electrons is quite small, this error will significantly increase for fragments with noninteger numbers of electrons and so the resulting total energy can be too negative. This is demonstrated to be the main reason for the widely used functionals' failure to describe the dissociative behavior of some radicals correctly, such as H_2^+, He_2^+, CO^-; and it has been pointed out that the large self-interaction error for fractional numbers of electrons also accounts for the difficulty of approximate DFT to describe transition states of some chemical reactions and some charge-transfer complexes [8].

PPLB [4] have also given the physical meaning of the highest-occupied Kohn–Sham orbital energy. The Kohn–Sham orbital energies usually have no physical meanings; however, PPLB showed that for the exact density functional, the highest-occupied Kohn–Sham eigenvalue for all electron numbers M between the integers $N-1$ and N is the negative of the exact ionization energy of the N-electron system, i.e.,

$$\varepsilon^M_{\max} = -I_N, \quad (N-1 < M < N) \tag{7}$$

$$\varepsilon^M_{\max} = -A_N, \quad (N < M < N+1) \ , \tag{8}$$

where I_N and A_N are the ionization energy and electron affinity of the N-electron system. Recently, there have been some debates on this subject [7, 13, 14] and two new independent proofs have been provided [7, 15]. From an exact solution of a two-electron problem, Hooke's atom, this ionization energy theorem is confirmed [7].

Another major result from the PPLB paper [4] is the derivative discontinuities of the energy and functional, i.e., as M increases by an integer N, the chemical potential and the Kohn–Sham potential both jump by a constant. The discontinuity of the chemical potential resolved a paradox of the chemical potential equalization principle [4, 16, 17]. The discontinuity of the exact Kohn–Sham potential, which recently has also been "exactly" constructed by Harbola [18], represents an important feature of the ground-state energy functional and is crucial for describing the band gap in an insulator or semiconductor [17, 19, 20]. Continuum approximations to exchange-correlation functionals, including all current widely used LDA and GGA functionals, fail to produce the correct derivative discontinuity. This failure accounts for the difficulty of LDA and GGA to describe the band gap correctly. Recently this property of derivative discontinuity has been used by Tozer and Handy [21] to design new exchange-correlation functionals.

In summary, the title paper is a seminal contribution that extended DFT to a fractional number of electrons. All the theorems, relations and properties for the exact DFT mentioned above, which are either presented in the PPLB paper or were developed later based on it, are not only very interesting in theory, but have also become more and more important from the practical viewpoint, especially in the development of a new generation of the exchange-correlation functional. Some well-known difficulties for the widely used functionals, such as the dissociate behavior of some radicals, the reaction barrier of some reactions and the band gap, are found to originate from the failure to satisfy these exact relations. This kind of difficulty for approximate functionals cannot be solved in the present framework of GGAs. We believe that the future breakthrough to further extend the applicability of density functional calculations needs a novel approach to construct the exchange-correlation functional that has the correct behavior for a fractional electron number, as shown by this title paper.

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