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Constructive definition of functional derivatives in density-functional theory

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Abstract

It is shown that the functional derivatives in density-functional theory (DFT) can be explicitly defined within the domain of electron densities restricted by the electron number, and a constructive definition of such restricted derivatives is suggested. With this definition, Kohn–Sham (KS) equations can be established for an N -electron system without extending the functional domain and introducing a Lagrange multiplier. This may clarify some of the fundamental questions raised by Nesbet (1998 *Phys. Rev. A* **58** R12). The definition naturally leads to the fact that the KS effective potential is determined only to within an additive constant, thus the KS levels can shift freely and the relation between the highest occupied molecular orbital (HOMO) energy and the ionization potential of the system depends on the choice of the constant. On the other hand, if the domain of functionals is indeed extended beyond the electron number restriction, conclusions depend on whether the extended functionals have unrestricted derivatives or not. It is shown that the ensemble extension of DFT to open systems of mixed states (Perdew *et al* 1982 *Phys. Rev. Lett.* **49** 1691) leads to an energy functional which has no unrestricted derivative at integer electron numbers. Hence after this extension, the relation between the HOMO energy and the ionization potential for an N -electron system is still uncertain. Besides, there are different extensions of the energy functional to a domain of densities unrestricted by the integer electron number, resulting in different unrestricted derivatives and electron systems with different chemical potentials. Even for the exact exchange-correlation potential, there is still an undetermined constant, whether it is a restricted or unrestricted derivative.

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1. Introduction

Density-functional theory (DFT) of Hohenberg, Kohn and Sham [1, 2] has become one of the mainstays for electronic structure calculations of solids and molecules. In DFT, the energy functional $E_v[\rho]$, where $\rho(\vec{r})$ is the electron density of an N -electron system moving in the region Ω and the external potential $v(\vec{r})$, plays the central role. The ground-state electron density minimizes the energy functional, thus variational principles are applied and the functional derivative with respect to the electron density is necessary. Because the electron density must satisfy

$$\int_{\Omega} \rho(\vec{r}) d\vec{r} = N, \quad (1)$$

a Lagrange multiplier μ is introduced and the variational process is carried out by letting

$$\delta \left\{ E_v[\rho] - \mu \int_{\Omega} \rho(\vec{r}) d\vec{r} \right\} = \int_{\Omega} \left\{ \frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} - \mu \right\} \delta \rho(\vec{r}) d\vec{r} = 0 \quad (2)$$

where $\delta \rho(\vec{r})$ is an arbitrary variation of $\rho(\vec{r})$, $E_v[\rho]$ is implicitly considered as a functional defined in a larger domain of $\rho(\vec{r})$ unrestricted by equation (1) and μ is believed to be the chemical potential. Through the introduction of an auxiliary non-interacting electron system, equation (2) leads to a set of single-electron Schrödinger equations, the Kohn–Sham (KS) equations.

This scheme is not unquestionable. Perdew *et al* [3] listed the question of whether $E_v[\rho]$ is defined for $\rho(\vec{r})$ unrestricted by equation (1) as a fundamental one which lies obscured beneath equation (2). They extended the domain of $E_v[\rho]$ by introducing the ensemble of an open system described by statistical mixtures. However, one of their results, the relation between the highest occupied molecular orbital (HOMO) energy and the ionization potential, gave rise to a debate [4–6], and has been intensively studied [7–12]. The crux of the problem seems to lie in the definition of the functional derivative. Later Nesbet [13], among other things, queried whether the functional derivative of the kinetic energy of a non-interacting electron system is equivalent to a local potential function and claimed that equation (2) is inconsistent with KS equations. Nesbet's claims were followed by many works either demonstrating that the derivative of the kinetic energy functional of the non-interacting electrons is a local function or studying the functional derivative of DFT [14–21]. Lindgren *et al* [22] in their review article discussed two different kinds of functional derivatives and demonstrated that the KS scheme actually can be established with the densities restricted by equation (1). However, apart from an existence statement, there still lacks an explicit constructive definition for the derivative of a functional defined in the domain of densities restricted by equation (1). As we shall see, such a definition may help to clarify some of the obscure and disputed fundamental questions in DFT.

For simplicity, we hereafter call a functional defined in the domain of densities restricted by equation (1) as a restricted functional, its derivative as a restricted derivative, and a functional defined in an extended domain of densities unrestricted by equation (1) as an unrestricted functional, its derivative in the extended domain as an unrestricted derivative. In this paper, we suggest a constructive definition for the restricted derivative of a restricted functional defined in a domain of densities restricted by equation (1). With this definition, the stationary condition for the DFT energy functional to take a minimum value is obtained and KS equations can be established for an N -electron system, without extending the functional domain and introducing a Lagrange multiplier. This may clarify some of the questions raised by Nesbet [13]. The definition also naturally brings about the fact that the functional derivative is determined only to within an additive constant, which leads to the resulting non-determinacy

of the KS effective potential with a constant and the shift of KS energies. Thus, the relation between the HOMO energy and the ionization potential of the system depends on the choice of the constant in the derivative of the exchange-correlation energy. On the other hand, if DFT functionals are indeed extended so that they have definitions in a domain of densities unrestricted by equation (1), conclusions depend on whether or not the extended functionals have unrestricted derivatives. If they have, then the derivative of the energy functional at the ground-state density is the chemical potential of the system, the KS effective potential and KS energies are uniquely determined, and there is a definite relation between the HOMO energy and the ionization potential. Otherwise, the derivative of the energy functional has no physical meaning, the KS effective potential and KS levels are not uniquely determined, and the relation between the HOMO energy and the ionization potential is uncertain. It is shown that the ensemble extension of Perdew *et al* [13] leads to the energy functional which has no unrestricted derivative at integer electron numbers. Thus after the ensemble extension, the relation between HOMO energy and the ionization potential for the N -electron system still remains uncertain. Besides, there are different extensions of the energy functional which lead to different unrestricted derivatives and electron systems with different chemical potentials. Even for the exact exchange-correlation potential, there is still an undetermined constant, whether it is a restricted or unrestricted derivative.

2. Constructive definition of restricted functional derivatives

For an unrestricted functional $F[\rho]$, its derivative is usually defined by the following existence statement, that is, if there exists a function $\delta F[\rho]/\delta\rho(\vec{r})$ of space positions such that for any variation $\delta\rho(\vec{r})$ of $\rho(\vec{r})$,

$$F[\rho + \delta\rho] - F[\rho] = \int_{\Omega} \delta\rho(\vec{r}) \frac{\delta F[\rho]}{\delta\rho(\vec{r})} d\vec{r} + o(\|\delta\rho\|), \quad (3)$$

where $\|\delta\rho\|$ is some kind of norm of $\delta\rho(\vec{r})$ and $o(\|\delta\rho\|)$ is a higher order infinitesimal quantity, that is $\lim_{\|\delta\rho\| \rightarrow 0} o(\|\delta\rho\|)/\|\delta\rho\| = 0$, then this function is defined as the functional derivative of $F[\rho]$ at $\rho(\vec{r})$. Equation (3) defines the so-called Fréchet derivative [17, 18, 22], and this definition is equivalent to the following constructive alternative: one takes a small region $\Delta\Omega$ at the position \vec{r} and chooses a variation $\delta\rho(\vec{r})$ such that $\delta\rho(\vec{r})$ has the same sign in $\Delta\Omega$ and is zero outside $\Delta\Omega$, then one defines the derivative value at position \vec{r} to be

$$\frac{\delta F[\rho]}{\delta\rho(\vec{r})} = \lim_{\Delta\Omega \rightarrow \vec{r}, \delta\rho \rightarrow 0} \frac{F[\rho + \delta\rho] - F[\rho]}{\int_{\Delta\Omega} \delta\rho(\vec{r}) d\vec{r}}, \quad (4)$$

where $\Delta\Omega \rightarrow \vec{r}$ means that the volume $\Delta\Omega$ shrinks to the point \vec{r} . Equation (4) indicates that $\delta F[\rho]/\delta\rho(\vec{r})$ is a single-valued function of \vec{r} .

For a restricted functional $F[\rho]$, the definition by the existence statement of equation (3) is also adopted, only the restriction

$$\int_{\Omega} \delta\rho(\vec{r}) d\vec{r} = 0 \quad (5)$$

must be applied to the variation of $\rho(\vec{r})$. This brings about the fact that the derivative is now not uniquely determined: for any constant C , $\delta F[\rho]/\delta\rho + C$ satisfies equations (3) and (5) and can be defined as a derivative as well. Conversely, if another function satisfies equations (3) and (5), then this function can differ from $\delta F[\rho]/\delta\rho$ only by an additive constant. The constructive definition, equation (4), however, is no longer applicable, because $\int_{\Delta\Omega} \delta\rho(\vec{r}) d\vec{r} \neq 0$, and $\rho + \delta\rho$ will go out of the functional domain. Here, we suggest a constructive definition for the derivative of the restricted functional $F[\rho]$ as follows. We first choose a fixed position \vec{r}_0

in Ω . For $\vec{r} \neq \vec{r}_0$, we take a small region $\Delta\Omega$ at \vec{r} and a small region $\Delta\Omega_0$ at \vec{r}_0 , respectively, and let $\Delta\Omega \cap \Delta\Omega_0 = \emptyset$. We then choose the variation $\delta\rho(\vec{r})$ such that

$$\begin{cases} \delta\rho(\vec{r}) > 0 (\vec{r} \in \Delta\Omega) \\ \delta\rho(\vec{r}) < 0 (\vec{r} \in \Delta\Omega_0) \\ \delta\rho(\vec{r}) = 0 (\vec{r} \notin \Delta\Omega \cup \Delta\Omega_0) \end{cases} \quad \text{or} \quad \begin{cases} \delta\rho(\vec{r}) < 0 (\vec{r} \in \Delta\Omega) \\ \delta\rho(\vec{r}) > 0 (\vec{r} \in \Delta\Omega_0) \\ \delta\rho(\vec{r}) = 0 (\vec{r} \notin \Delta\Omega \cup \Delta\Omega_0), \end{cases} \quad (6)$$

and

$$\int_{\Delta\Omega} \delta\rho(\vec{r}) \, d\vec{r} + \int_{\Delta\Omega_0} \delta\rho(\vec{r}) \, d\vec{r} = 0. \quad (7)$$

The restricted derivative now can be defined by

$$\frac{\delta F[\rho]}{\delta\rho(\vec{r})} = \lim_{\substack{\Delta\Omega \rightarrow \vec{r}, \Delta\Omega_0 \rightarrow \vec{r}_0 \\ \delta\rho \rightarrow 0}} \frac{F[\rho + \delta\rho] - F[\rho]}{\int_{\Delta\Omega} \delta\rho(\vec{r}) \, d\vec{r}} + C, \quad (8)$$

where C is an arbitrary constant. The derivative value at the position \vec{r}_0 can be determined by letting $\delta F[\rho]/\delta\rho(\vec{r}_0) = \lim_{\vec{r} \rightarrow \vec{r}_0} \delta F[\rho]/\delta\rho(\vec{r})$. The limit value in equation (8) depends on the choice of \vec{r}_0 . However, as will be proved later, for a different choice of the fixed position, the limit value only changes by a constant independent of \vec{r} . Similar to primitive functions in the case of indefinite integral, the restricted functional derivative is a family of functions. Due to this fact, a constant C is added to the definition for a specifically chosen \vec{r}_0 and this will give the whole family of the functions. In practical use, a specific value of C may be adopted and the derivative becomes a single local function. Let

$$\alpha = \frac{F[\rho + \delta\rho] - F[\rho]}{\int_{\Delta\Omega} \delta\rho(\vec{r}) \, d\vec{r}} - \frac{\delta F[\rho]}{\delta\rho(\vec{r})} + C; \quad (9)$$

then α is an infinitesimal quantity,

$$\lim_{\substack{\Delta\Omega \rightarrow \vec{r}, \Delta\Omega_0 \rightarrow \vec{r}_0 \\ \delta\rho \rightarrow 0}} \alpha = 0, \quad (10)$$

and

$$F[\rho + \delta\rho] - F[\rho] = \left\{ \frac{\delta F[\rho]}{\delta\rho(\vec{r})} + \alpha - C \right\} \int_{\Delta\Omega} \delta\rho(\vec{r}) \, d\vec{r}. \quad (11)$$

We briefly prove that equations (3) and (8) are equivalent for a restricted functional. To get equation (8) from equation (3) is direct. We only need to choose $\delta\rho(\vec{r})$ in equation (3) according to equations (6) and (7), and a limit process will lead to equation (8), provided we take C as $\delta F[\rho]/\delta\rho(\vec{r}_0)$. To get equation (3) from equation (8), for any variation $\delta\rho(\vec{r})$ satisfying equation (5), we divide Ω into $K + 1$ small regions $\Delta\Omega_i$, $i = 0, 1, 2, \dots, K$, of which $\Delta\Omega_0$ is the region containing the position \vec{r}_0 . The division can always be realized such that in each $\Delta\Omega_i$, $i = 1, 2, \dots, K$, $\delta\rho(\vec{r})$ keeps its sign. If we define

$$\delta\rho_i(\vec{r}) = \begin{cases} \delta\rho(\vec{r}) & (\vec{r} \in \Delta\Omega_i) \\ 0 & (\vec{r} \notin \Delta\Omega_i) \end{cases} \quad (12)$$

for $i = 0, 1, 2, \dots, K$, then $\delta\rho(\vec{r}) = \sum_{i=0}^K \delta\rho_i(\vec{r})$. For each $\delta\rho_i(\vec{r})$, $i = 1, 2, \dots, K$, we construct a function $\delta\rho'_i(\vec{r})$ in $\Delta\Omega_0$, such that $\delta\rho'_i(\vec{r})$ has the opposite sign of $\delta\rho_i(\vec{r})$, $\delta\rho_0(\vec{r}) = \sum_{i=1}^K \delta\rho'_i(\vec{r})$, and

$$\int_{\Delta\Omega_i} \delta\rho_i(\vec{r}) \, d\vec{r} + \int_{\Delta\Omega_0} \delta\rho'_i(\vec{r}) \, d\vec{r} = 0. \quad (13)$$

The functional variation can be expressed as

$$\begin{aligned}
 F[\rho + \delta\rho] - F[\rho] &= F[\rho + \delta\rho_0 + \dots + \delta\rho_{K-1} + \delta\rho_K] - F[\rho + \delta\rho_0 + \dots + \delta\rho_{K-1} - \delta\rho'_K] \\
 &\quad + F[\rho + \delta\rho_0 + \dots + \delta\rho_{K-1} - \delta\rho'_K] - F[\rho + \delta\rho_0 + \dots + \delta\rho_{K-2} - \delta\rho'_{K-1} - \delta\rho'_K] \\
 &\quad + \dots + F[\rho + \delta\rho_0 + \delta\rho_1 - \delta\rho'_2 - \dots - \delta\rho'_K] \\
 &\quad - F[\rho + \delta\rho_0 - \delta\rho'_1 - \delta\rho'_2 - \dots - \delta\rho'_K].
 \end{aligned}
 \tag{14}$$

Due to equation (13), densities in the square brackets all satisfy equation (1). According to equation (11), we get

$$\begin{aligned}
 F[\rho + \delta\rho] - F[\rho] &= \left\{ \frac{\delta F[\rho + \delta\rho_0 + \dots + \delta\rho_{K-1} - \delta\rho'_K]}{\delta\rho(\vec{r}_K)} + \alpha_K - C \right\} \\
 &\quad \times \int_{\Delta\Omega_K} \delta\rho(\vec{r}) \, d\vec{r} + \left\{ \frac{\delta F[\rho + \delta\rho_0 + \dots + \delta\rho_{K-2} - \delta\rho'_{K-1} - \delta\rho'_K]}{\delta\rho(\vec{r}_{K-1})} + \alpha_{K-1} - C \right\} \\
 &\quad \times \int_{\Delta\Omega_{K-1}} \delta\rho(\vec{r}) \, d\vec{r} + \dots + \left\{ \frac{\delta F[\rho]}{\delta\rho(\vec{r}_1)} + \alpha_1 - C \right\} \int_{\Delta\Omega_1} \delta\rho(\vec{r}) \, d\vec{r},
 \end{aligned}
 \tag{15}$$

where α_i are the infinitesimal quantities and each \vec{r}_i is a position in $\Delta\Omega_i$, $i = 1, 2, \dots, K$. By employing the continuous assumption, through a limit process it can be proved that equation (15) leads to $F[\rho + \delta\rho] - F[\rho] = \int_{\Omega} \delta\rho(\vec{r}) \{ \delta F[\rho] / \delta\rho(\vec{r}) \} \, d\vec{r} + o(\int_{\Omega} |\delta\rho(\vec{r})| \, d\vec{r})$, thus equation (3) holds. For simplicity, the over-elaborations are omitted. Similarly, for three positions \vec{r}, \vec{r}_0 and \vec{r}'_0 , we can respectively take $\delta\rho$ and $\delta\rho'$ according to equations (6) and (7). By writing $F[\rho + \delta\rho'] - F[\rho] = F[\rho + \delta\rho + \delta\rho' - \delta\rho] - F[\rho + \delta\rho] + F[\rho + \delta\rho] - F[\rho]$, it can be proved that the limit value in equation (8) only varies a constant independent of \vec{r} , if the fixed position is chosen to be \vec{r}'_0 . Because equations (3) and (5) lead to

$$\lim_{\lambda \rightarrow 0} \frac{F[\rho + \lambda\delta\rho] - F[\rho]}{\lambda} = \int_{\Omega} \delta\rho(\vec{r}) \frac{\delta F[\rho]}{\delta\rho(\vec{r})} \, d\vec{r},
 \tag{16}$$

where λ is a real variable, equation (8) gives a constructive definition of the Gâteaux derivative of a restricted functional $F[\rho]$ [18, 22].

The key to the constructive definition equation (8) is the formation of $\delta\rho(\vec{r})$ satisfying equation (5). Apart from equations (6) and (7) suggested in this paper, there might be other formations. However, whatever the formations are, any constructive definition of restrictive functional derivatives must satisfy equation (3). Different definitions thus should give the same family of functions. The additive constant is inherent to the restrictive derivatives and its implications to DFT.

3. Restricted functional derivatives and Kohn–Sham equations

With the constructive definition, the variational principles can be applied to a restricted functional $F[\rho]$, without extending its domain and introducing a Lagrange multiplier, because a stationary condition can be obtained through equation (8) for the functional to take an extreme value. If $F[\rho]$ takes a minimum value at $\rho(\vec{r})$, then in equation (8), for $\delta\rho(\vec{r}) > 0$ in $\Delta\Omega$, we have

$$\lim_{\substack{\Delta\Omega \rightarrow \vec{r}, \Delta\Omega_0 \rightarrow \vec{r}_0 \\ \delta\rho \rightarrow 0}} \frac{F[\rho + \delta\rho] - F[\rho]}{\int_{\Delta\Omega} \delta\rho(\vec{r}) \, d\vec{r}} \geq 0,
 \tag{17}$$

but for $\delta\rho(\vec{r}) < 0$ in $\Delta\Omega$, we have

$$\lim_{\substack{\Delta\Omega \rightarrow \vec{r}, \Delta\Omega_0 \rightarrow \vec{r}_0 \\ \delta\rho \rightarrow 0}} \frac{F[\rho + \delta\rho] - F[\rho]}{\int_{\Delta\Omega} \delta\rho(\vec{r}) \, d\vec{r}} \leq 0,
 \tag{18}$$

hence the limit value must be zero, equation (8) becomes

$$\frac{\delta F[\rho]}{\delta \rho(\vec{r})} = C, \quad (19)$$

meaning the derivative has the constant value at any position \vec{r} in Ω . Equation (19) is only a necessary condition for $F[\rho]$ to take an extreme value. However, as in the usual extreme-value problems, if there is only one $\rho(\vec{r})$ satisfying equation (19), then $F[\rho]$ takes the extreme value only at this $\rho(\vec{r})$.

Kohn and Sham [1, 2] and later Levy [23] established the restricted universal functional $F[\rho]$ and restricted energy functional $E_v[\rho]$ of DFT. According to Levy,

$$F[\rho] = \min_{\psi \rightarrow \rho} \langle \psi | \hat{T} + \hat{U} | \psi \rangle, \quad (20)$$

and

$$E_v[\rho] = \int_{\Omega} v(\vec{r}) \rho(\vec{r}) d\vec{r} + F[\rho], \quad (21)$$

where $\hat{T} = (-1/2) \sum_{i=1}^N \nabla_i^2$ and $\hat{U} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N 1/|\vec{r}_j - \vec{r}_i|$ are the kinetic and electron–electron repulsion operators for the N -electron system, respectively, and ψ is an arbitrary normalized wavefunction which has the electron density $\rho(\vec{r})$. At present, the only result about the derivatives of $F[\rho]$ and $E_v[\rho]$ is that for a given v -representable electron density $\rho(\vec{r})$,

$$\frac{\delta F[\rho]}{\delta \rho(\vec{r})} = -v(\vec{r}) + \text{const}, \quad (22)$$

where $v(\vec{r})$ is the external potential that produces the electron density $\rho(\vec{r})$, which is usually unknown [22]. With the constructive definition, as long as the minimum search of equation (20) is realized, the derivatives $\delta F[\rho]/\delta \rho(\vec{r})$ and $\delta E_v[\rho]/\delta \rho(\vec{r})$ can be calculated through equation (8).

Because the true ground-state electron density $\rho(\vec{r})$ minimizes $E_v[\rho]$, according to equation (19), the restricted derivative of $E_v[\rho]$ must be a constant at $\rho(\vec{r})$,

$$\frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} = C. \quad (23)$$

According to KS [2], the energy functional is expressed as

$$E_v[\rho] = T_s[\rho] + \int_{\Omega} \rho(\vec{r}) v(\vec{r}) d\vec{r} + \frac{1}{2} \iint_{\Omega \times \Omega} \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + E_{xc}[\rho], \quad (24)$$

where $T_s[\rho]$ is the kinetic energy of the non-interacting electrons, which can be defined through equation (20) by letting $\hat{U} = 0$, and $E_{xc}[\rho]$ is the exchange–correlation energy. Equation (23) then becomes

$$\frac{\delta T_s[\rho]}{\delta \rho(\vec{r})} + v(\vec{r}) + \int_{\Omega} \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} = C. \quad (25)$$

Now all the derivatives in equation (25) are restricted ones. Also according to KS, an effective potential is defined as

$$v_{\text{eff}}(\vec{r}) = v(\vec{r}) + \int_{\Omega} \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})}, \quad (26)$$

where the density $\rho(\vec{r})$ is a fixed function, the ground-state density of the N -electron system. Let the energy functional of the non-interacting electrons moving in the region Ω and the

external potential $v_{\text{eff}}(\vec{r})$ be $E_s[\rho] = T_s[\rho] + \int_{\Omega} v_{\text{eff}}(\vec{r})\rho(\vec{r}) d\vec{r}$, according to equation (25), $\rho(\vec{r})$ also satisfies

$$\frac{\delta E_s[\rho]}{\delta \rho(\vec{r})} = C. \quad (27)$$

If $\rho(\vec{r})$ is the only solution of both equations (23) and (27), then the ground-state density of the interacting N -electron system moving in the external potential $v(\vec{r})$ is also the ground-state density of the non-interacting N -electron system moving in the external potential $v_{\text{eff}}(\vec{r})$. The latter, however, can be calculated from orthonormal single-electron wavefunctions $\psi_i(\vec{r})$ by

$$\rho(\vec{r}) = \sum_{i=1}^N |\psi_i(\vec{r})|^2, \quad (28)$$

where $\psi_i(\vec{r})$ are the energy eigenfunctions determined by the KS equations:

$$-\frac{1}{2}\nabla^2\psi_i(\vec{r}) + v_{\text{eff}}(\vec{r})\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r}). \quad (29)$$

The only thing in common for the interacting electron system in $v(\vec{r})$ and the non-interacting electron system in $v_{\text{eff}}(\vec{r})$ is that they have the same ground-state electron density.

4. Restricted, unrestricted functional derivatives and some fundamental problems in DFT

4.1. Ionization energy, Kohn–Sham orbital energies and chemical potential

Thus, the KS scheme of DFT can be established based on the definition of restricted functional derivatives. Due to the multiple values of $\delta E_{\text{xc}}[\rho]/\delta \rho(\vec{r})$, $v_{\text{eff}}(\vec{r})$ is only determined to within an additive constant. However, the multiple values of the derivative do not affect the ground-state electron density, because adding a constant to the effective potential will not change the single-electron eigenfunctions $\psi_i(\vec{r})$. The KS eigenenergies, ε_i , on the other hand, will shift with the different choice of the constant. The physical meaning of ε_i , such as the relation between the HOMO energy ε_N and the ionization potential of the system $I(N) = E(N-1) - E(N)$, where $E(N-1)$ and $E(N)$ are the ground-state energies of the $(N-1)$ - and N -electron systems, respectively, thus depends on the choice of the constant in $\delta E_{\text{xc}}[\rho]/\delta \rho(\vec{r})$.

To get equation (23), it is not necessary to extend the functional domain, introduce a Lagrange multiplier and conduct the variational process for the extended functional. Here, the constant C generally has no physical meaning and need not to be the chemical potential of the system. However, if the domain is indeed extended such that the energy functional is defined for densities unrestricted by the electron number as well, then the results depend on whether the extended functional has the unrestricted derivative or not. If the unrestricted derivative exists, it is also a restricted derivative of the restricted functional. Hence in equation (23), $\delta E_v[\rho]/\delta \rho(\vec{r})$ can be chosen as the unrestricted derivative, and this uniquely determines the constant C , which now must be the chemical potential μ . The proof is as follows: suppose $E(N)$ and $E(N+dN)$ are the ground-state energies of the N - and $(N+dN)$ -electron systems, respectively, where dN is a small quantity. According to equations (3) and (23), $E(N+dN) - E(N) = CdN + o(\|\delta\rho\|)$, a limit process leads to

$$C = \frac{dE(N)}{dN} = \mu. \quad (30)$$

However, there are different extensions which lead to unrestricted derivatives differing by a constant. Suppose an extension of the functional $E_v[\rho]$ leads to the unrestricted derivative $\delta E_v[\rho]/\delta \rho(\vec{r})$, we can make another extension $E'_v[\rho]$ by defining

$$E'_v[\rho + \delta\rho] = E_v[\rho + \delta\rho] + D \int_{\Omega} \delta\rho(\vec{r}) d\vec{r}, \quad (31)$$

where $\rho(\vec{r})$ is the ground-state electron density of the N -electron system and D is a constant. According to equation (3) or (4), the unrestricted derivative of $E'_v[\rho]$ will be

$$\frac{\delta E'_v[\rho]}{\delta \rho(\vec{r})} = \frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} + D. \quad (32)$$

As a result, different extensions of $E_v[\rho]$ may lead to electron systems with different chemical potentials. The difference between some extensions of $E_v[\rho]$ has already been noted [2]. However, equation (32) indicates that for different extensions, the $\delta E_{xc}[\rho]/\delta \rho(\vec{r})$, hence $v_{\text{eff}}(\vec{r})$, could differ by a constant, thus the relation between ε_N and $I(N)$ will not be the same, contrary to what is commonly believed [8].

On the other hand, if the extended energy functional has no unrestricted derivative, then $\delta E_v[\rho]/\delta \rho(\vec{r})$ in equation (23) must remain a restricted derivative and C is a meaningless constant. In particular, $C \neq dE(N)/dN$, because equation (3) may no longer hold for $E(N + dN) - E(N)$. This is consistent with the conclusion of Parr *et al* [24] that it is impossible to determine the chemical potential solely from the ground-state electron density of the N -electron system. The chemical potential depends on how the energy functional is extended to the domain of electron densities unrestricted by equation (1).

4.2. Exact and approximate exchange-correlation energy functional

For the important functional derivatives in DFT, three additive constants respectively in $\delta E_v[\rho]/\delta \rho(\vec{r})$, $\delta T_s[\rho]/\delta \rho(\vec{r})$ and $\delta E_{xc}[\rho]/\delta \rho(\vec{r})$ need to be determined. According to equation (24), the determination of any two of them will fix the third one. In particular, if an extension results in unrestricted derivatives of $E_v[\rho]$ and $T_s[\rho]$, then $\delta E_v[\rho]/\delta \rho(\vec{r})$ and $\delta T_s[\rho]/\delta \rho(\vec{r})$ can be chosen as the unrestricted derivatives. $\delta E_{xc}[\rho]/\delta \rho(\vec{r})$, then, is automatically determined through equation (24). However, because different extensions may lead to different $\delta E_v[\rho]/\delta \rho(\vec{r})$ and $\delta T_s[\rho]/\delta \rho(\vec{r})$, the resulting unrestricted $\delta E_{xc}[\rho]/\delta \rho(\vec{r})$ can still differ by a constant. This may clarify an obscurity about the so-called exact exchange-correlation energy and the exact exchange-correlation potential: one can define and uniquely determine the exact exchange-correlation energy through equation (24), but even for the exact $E_{xc}[\rho]$, the exchange-correlation potential $\delta E_{xc}[\rho]/\delta \rho(\vec{r})$ can still vary by an additive constant, whether it is a restricted or unrestricted derivative. In the case of restricted derivative, this is due to the constant C in equation (8), and in the case of unrestricted derivative, due to the constant D in equation (31).

Approximate exchange-correlation energy functionals, such as in local density approximation (LDA) and general gradient approximation (GGA), directly give an extension of $E_{xc}[\rho]$, without the need of knowledge of $E_v[\rho]$ and $T_s[\rho]$, and the constant in $\delta E_{xc}[\rho]/\delta \rho(\vec{r})$ is implicitly determined. For instance, GGA defines the exchange-correlation potential as [25]

$$E_{xc}[\rho] = \int_{\Omega} f(\rho, \nabla \rho) d\vec{r}, \quad (33)$$

where $f(\rho, \nabla \rho)$ is a certain function. Thus, in equation (4)

$$E_{xc}[\rho + \delta \rho] - E_{xc}[\rho] = \int_{\Delta \Omega} [(\partial f / \partial \rho) \delta \rho + \nabla_{\nabla \rho} f \cdot \nabla(\delta \rho)] d\vec{r} + o(\|\delta \rho\|),$$

and

$$\frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} = \frac{\partial f(\rho, \nabla \rho)}{\partial \rho}. \quad (34)$$

The relation between ε_N and $I(N)$ for GGA is then determined by the function $f(\rho, \nabla \rho)$. According to equation (4), for a fixed \vec{r} , $\delta E_{xc}[\rho]/\delta \rho(\vec{r})$ is a functional of $\rho(\vec{r})$, thus the

exchange-correlation potential at a position \vec{r} may depend on the electron densities far distant from this position. In LDA and GGA, however, the value of $\delta E_{xc}[\rho]/\delta\rho(\vec{r})$ at \vec{r} is solely determined by the electron densities in an infinitesimal volume around this position. In this case, for a finite system,

$$\lim_{r \rightarrow \infty} \frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})} = \lim_{\rho \rightarrow 0, |\nabla\rho| \rightarrow 0} \frac{\partial f(\rho, \nabla\rho)}{\partial\rho} = \text{const.} \quad (35)$$

However, the conclusion may be different for the exact exchange-correlation potential. In fact, in the original paper of Hohenberg and Kohn [1], they were considering an N -electron system enclosed in a large box. Thus the KS scheme is established for the N -electron system moving in a region Ω . In principle, any quantity as a function of position \vec{r} can be defined in and limited to Ω , and all the integrations in DFT are also conducted in Ω . There is no need to consider positions outside this region. Strictly speaking, the functional derivatives in DFT have no definition outside Ω . Although on the boundary, the electron density approaches zero, in general $\delta E_{xc}[\rho]/\delta\rho(\vec{r})$ or $v_{\text{eff}}(\vec{r})$ may be different at different positions.

4.3. Disputed problems in references

With the definition of restricted functional derivatives and the establishment of KS equations described above, some of the questions raised by Nesbet [13] might be clarified. First, equation (2) of [13] holds, but can be derived through another way, not necessarily from equation (1) of [13], and there is no need to establish the meaning of functionals and functional derivatives for non-integer electron numbers. Second, KS equations or equation (3) of [13] also hold, but their only role is to give the electron density. According to equation (8), the derivative $\delta T_s[\rho]/\delta\rho(\vec{r})$ is a local function, not the operator $(-1/2)\nabla^2$, as it is in equation (3) of [13]. Thus, the notation $\delta E/\delta\rho$ has different meaning in equations (2) and (3) of [13]. These two equations give the same electron density, but this does not mean that the values of equations (4) and (5) in [13] must be equal, especially, μ could be a meaningless constant, not necessarily the chemical potential. Finally, if the non-interacting electrons are described by the normalized single-electron orbitals $\psi_i(\vec{r})$ which satisfy equation (29) and generate the electron density $\rho(\vec{r})$ through equation (28), then [13, 19]

$$T_s[\rho + \delta\rho] - T_s[\rho] = - \int_{\Omega} v_{\text{eff}}(\vec{r})\delta\rho(\vec{r}) d\vec{r} + o(\|\delta\rho\|). \quad (36)$$

According to equation (8),

$$\begin{aligned} \frac{\delta T_s[\rho]}{\delta\rho(\vec{r})} &= \lim_{\substack{\Delta\Omega \rightarrow \vec{r}, \Delta\Omega_0 \rightarrow \vec{r}_0 \\ \delta\rho \rightarrow 0}} \frac{- \int_{\Delta\Omega} v_{\text{eff}}(\vec{r})\delta\rho(\vec{r}) d\vec{r} - \int_{\Delta\Omega_0} v_{\text{eff}}(\vec{r})\delta\rho(\vec{r}) d\vec{r}}{\int_{\Delta\Omega} \delta\rho(\vec{r}) d\vec{r}} + C \\ &= -v_{\text{eff}}(\vec{r}) + v_{\text{eff}}(\vec{r}_0) + C = -\frac{\nabla^2\psi_i(\vec{r})}{2\psi_i(\vec{r})} + \frac{\nabla^2\psi_i(\vec{r}_0)}{2\psi_i(\vec{r}_0)} + C. \end{aligned} \quad (37)$$

Equation (37) reveals the relation between the restricted derivative $\delta T_s[\rho]/\delta\rho(\vec{r})$ and the operator $(-1/2)\nabla^2$ of single-electron orbitals. Because the chain rule used in [13] and [15], $\delta T_s/\delta\psi_i^* = (-1/2)\nabla^2\psi_i = \psi_i\delta T_s/\delta\rho$, does not hold, there is no such paradox as $\delta T_s[\rho]/\delta\rho(\vec{r}) = \varepsilon_i - v_{\text{eff}}(\vec{r})$ for all the orbitals [15]. We note that the chain rule no longer holds because $\psi_i(\vec{r})$ are also restricted by the normalization condition. On the other hand, the relationship between $\delta T_s[\rho]/\delta\rho(\vec{r})$ and $(-1/2)\nabla^2$ plays no role in deducing KS equations, since $(-1/2)\nabla^2$ comes into KS equations just because for a non-interacting electron system, its electron density can be calculated by solving single-electron Schrödinger equation. There is more discussion about the chain rule in [17] and [26].

Perdew *et al* [3, 5] gave the ensemble extension of the closed N -electron system. An $(N + \omega)$ -electron system is the statistical mixture of an N -electron pure state with probability $1 - \omega$ and an $(N + 1)$ -electron pure state with probability ω , where $0 < \omega < 1$. The electron density $\rho(\vec{r})$ now satisfies $\int_{\Omega} \rho(\vec{r}) d\vec{r} = (1 - \omega)N + \omega(N + 1) = N + \omega$. Perdew *et al* demonstrated that the energy of the mixed state is

$$E(N + \omega) = (1 - \omega)E(N) + \omega E(N + 1), \quad (38)$$

where $E(N)$ and $E(N + 1)$ are the ground-state energies of the N - and $(N + 1)$ -electron systems, respectively. Similarly, for the mixture of an $(N - 1)$ -electron pure state with probability $1 - \omega$ and an N -electron pure state with probability ω , $0 < \omega < 1$, its energy is

$$E(N - 1 + \omega) = (1 - \omega)E(N - 1) + \omega E(N), \quad (39)$$

where $E(N - 1)$ is the ground-state energy of the $(N - 1)$ -electron system. From equations (38) and (39), Perdew *et al* discovered the discontinuity of the functional derivative $\delta E_v[\rho]/\delta\rho(\vec{r})$ at the integer N and pointed out that $\delta E_v[\rho]/\delta\rho(\vec{r})$ may not be defined there [3]. In fact, in the ensemble extension, $E_v[\rho]$ has no unrestricted derivative at integer electron numbers. The proof is as follows: in equation (4), let $\rho(\vec{r})$ be the ground-state electron density of the N -electron system. If $\delta\rho(\vec{r}) > 0$ and $\int_{\Delta\Omega} \delta\rho(\vec{r}) d\vec{r} = \omega > 0$, then, due to the minimum character of $E(N + \omega)$, we have $E_v[\rho + \delta\rho] \geq E(N + \omega)$. Hence,

$$E_v[\rho + \delta\rho] - E_v[\rho] \geq E(N + \omega) - E(N) = \omega[E(N + 1) - E(N)],$$

and

$$\lim_{\Delta\Omega \rightarrow \vec{r}, \delta\rho \rightarrow 0} \frac{E_v[\rho + \delta\rho] - E_v[\rho]}{\int_{\Delta\Omega} \delta\rho(\vec{r}) d\vec{r}} \geq E(N + 1) - E(N). \quad (40)$$

Similarly, for $\delta\rho(\vec{r}) < 0$ and $\int_{\Delta\Omega} \delta\rho(\vec{r}) d\vec{r} = -(1 - \omega) < 0$, we have $E_v[\rho + \delta\rho] \geq E(N - 1 + \omega)$. Hence,

$$E_v[\rho + \delta\rho] - E_v[\rho] \geq E(N - 1 + \omega) - E(N) = (1 - \omega)[E(N - 1) - E(N)],$$

and

$$\lim_{\Delta\Omega \rightarrow \vec{r}, \delta\rho \rightarrow 0} \frac{E_v[\rho + \delta\rho] - E_v[\rho]}{\int_{\Delta\Omega} \delta\rho(\vec{r}) d\vec{r}} \leq E(N) - E(N - 1). \quad (41)$$

As pointed out by Perdew *et al*, the upward concavity of the plot of $E(N)$ versus N leads to $2E(N) < E(N - 1) + E(N + 1)$, thus $E(N) - E(N - 1) < E(N + 1) - E(N)$, and equations (40) and (41) mean that the unrestricted $\delta E_v[\rho]/\delta\rho(\vec{r})$ does not exist at N .

If the ensemble energy functional $E_v[\rho]$ and the kinetic energy functional $T_s[\rho]$ have unrestricted derivatives at fractional electron numbers $N - 1 + \omega$ or $N + \omega$, then the disputed conclusion of Perdew *et al*, equation (14) of [3],

$$\varepsilon_{\max} = \mu = \begin{cases} -I(N) = E(N) - E(N - 1) & (N - 1 < N - 1 + \omega < N) \\ -A(N) = E(N + 1) - E(N) & (N < N + \omega < N + 1), \end{cases} \quad (42)$$

is correct. According to equation (30), $\delta E_v[\rho]/\delta\rho(\vec{r})$ is now indeed the chemical potential μ . For the non-interacting electron system, we may let $\delta E_s[\rho]/\delta\rho(\vec{r}) = \delta E_v[\rho]/\delta\rho(\vec{r}) = \mu$ and then determine the effective potential by

$$v_{\text{eff}}(\vec{r}) = \mu - \frac{\delta T_s[\rho]}{\delta\rho(\vec{r})}, \quad (43)$$

where $\delta T_s[\rho]/\delta\rho(\vec{r}) = dT_s/d\omega$ is the unrestricted derivative. Once the effective potential is determined, one has $E_s(\omega) = (1 - \omega) \sum_{i=1}^{N-1} \varepsilon_i + \omega \sum_{i=1}^N \varepsilon_i$ or $E_s(\omega) = (1 - \omega) \sum_{i=1}^N \varepsilon_i + \omega \sum_{i=1}^{N+1} \varepsilon_i$, this choice of $v_{\text{eff}}(\vec{r})$ will lead to $\mu = \delta E_s[\rho]/\delta\rho(\vec{r}) = dE_s/d\omega = \varepsilon_{\max}$. However,

since $E_v[\rho]$ has no unrestricted derivative at the integer N , the determination of $v_{\text{eff}}(\vec{r})$ by equation (43) fails to apply here, and equation (26) should be used, in which $\delta E_{\text{xc}}[\rho]/\delta\rho(\vec{r})$ remains the restricted derivative and the constant in the effective potential is undetermined. Thus for the N -electron system, ε_N is also undetermined and the relation between ε_N and $I(N)$ depends on the choice of the constant in $\delta E_{\text{xc}}[\rho]/\delta\rho(\vec{r})$. Of course, one may determine the effective potential for the N -electron system through equation (43) by letting the electron density $\rho(\vec{r})$ approach that of the N -electron system from below, thus keeping $\varepsilon_N = -I(N)$, but this is just one choice.

5. Summary

A constructive definition for the derivative of functionals in DFT defined in the domain of densities restricted by the electron number is suggested. From this definition, the KS scheme can be established without extending the domain of DFT functionals. This definition may help to clarify some fundamental but still obscure or disputed problems of DFT.

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