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Proof that $\partial E/\partial n_i = \epsilon_i$ in density-functional theory

J. F. Janak
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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It is shown that the variation of the total energy, as constructed in density-functional theory, with respect to an orbital occupation is equal to the eigenvalue of that orbital, independent of the detailed form of the exchange-correlation functional. This leads to a rigorous connection between the ground-state energies of N- and $(N+1)$-particle systems, which is useful in the calculation of certain excitation energies.

In the density-functional theory (DFT) of Hohenberg, Kohn, and Sham[1-3] it is shown that the total energy is a unique functional of the charge density $p(\vec{r})$, and is minimized when evaluated for the true ground-state charge density. These theorems have been proven only for the ground state, and it is not known whether, or how well, the density-functional formalism applies to properties of excited states. Nevertheless, the theory can be used to calculate some excitation energies; for example, the ionization potential of an atom is the difference of the ground-state energies of the atom and of the ion. In this Comment, a simple proof is given that the derivative of a generalization of the total energy with respect to the occupation of an orbital is equal to the eigenvalue of the effective one-electron Hamiltonian for the orbital. This is the DFT version of a theorem originally proved by Slater[4] for the $X\alpha$ method, which he applied to the calculation of excitation energies by introducing the "transition state."[5] Apparently,[6] it is not universally realized that a similar statement is true in DFT, regardless of the detailed form of the exchange-correlation functional $E_{xc}[\rho]$. This extension of the transition-state concept to DFT has applications for a broad class of problems, such as ionization potentials and electron affinities of atoms and molecules, and the work function of solid surfaces.

We first give a short summary of DFT, then introduce a generalization of the total energy $\tilde{E}$, which is defined for fractional total number of particles. This permits the investigation of derivatives of $\tilde{E}$ with respect to occupation number. We then use $\tilde{E}$ to connect the ground-state energies of N- and $(N+1)$-particle systems, and to investigate an unusual situation which arises in "local-density" calculations for atoms.

In DFT, the total energy is a functional of the electron density $\rho(\vec{r})$:

$$E[\rho]=T_s[\rho]+U[\rho]+E_{xc}[\rho], \qquad (1)$$

where T_s is the kinetic energy of a noninteracting electron system with the same density $\rho(\vec{r})$, U is the classical Coulomb energy, and $E_{xc}[\rho]$ is the exchange-correlation functional. While E_{xc} is at present only imperfectly known, the utility of DFT lies in the fact that E_{xc} is amenable to approximation, e.g., in local-density theory it is taken to be the integral over $\vec{r}$ of the same function of $\rho(\vec{r})$ as it would be of this local electron density in the homogeneous electron gas.[2,7]

Minimization of the total energy with respect to $\rho(\vec{r})$ leads to the effective one-particle equation (in rydberg units)

$$[-\nabla^2+V_H(\vec{r})+v_{xc}(\vec{r})]\psi_i=\epsilon_i\psi_i, \qquad (2)$$

where $V_H(\vec{r})\equiv\delta U/\delta\rho(\vec{r})$ is the classical Coulomb potential and $v_{xc}\equiv\delta E_{xc}/\delta\rho(\vec{r})$ is the exchange-correlation potential. Equation (2) is to be solved self-consistently given the condition

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

where the sum goes over the lowest N normalized solutions of Eq. (2) for an N-electron system. If v_{xc} were the exact exchange-correlation potential, the self-consistent solution of Eqs. (2) and (2a) would lead to the *exact* ground-state charge density of the system. We introduce the quantity

$$t_i=\int\psi_i^*(-\nabla^2)\psi_i\,d\vec{r}=\epsilon_i-\int\psi_i^*(V_H+v_{xc})\psi_i\,d\vec{r} \qquad (3)$$

in terms of which the kinetic-energy functional $T_s[\rho]$ is defined by

$$T_s[\rho]=\sum_{i=1}^{N}t_i$$

for an N-electron system (in other words, given the self-consistent solutions of Eq. (2), one constructs the t_i from Eq. (3), and then constructs $T_s[\rho]$ by summing up the t_i of the lowest N states). Since the definition of T_s is important in all that follows, we emphasize that it is defined only in terms of the lowest N solutions of Eq. (2), under the self-consistency condition given in Eq. (2a).

The theory outlined above applies only to the ground state; since the state in which the occupation of one of the single-particle states has been infinitesimally changed is not necessarily a ground state, this theory cannot be used directly for the calculation of derivatives with respect to occupation. However, a suitable generalization of the theory can be constructed by introducing occupation numbers n_i for each of the states, and defining a charge density by

$$\rho(\vec{r}) = \sum_i n_i |\psi_i(\vec{r})|^2 . \tag{4}$$

If we think of the n_i's as parameters, it is clear that a self-consistent solution of Eqs. (2) and (4) can be found for *almost any*[8] given set of n_i's, including nonintegral values of some of the n_i. We define

$$\tilde{T} \equiv \sum_i n_i t_i .$$

Then, for a given set of n_i, the self-consistent solution of Eqs. (2) and (4) will make

$$\tilde{E} \equiv \tilde{T} + U[\rho] + E_{xc}[\rho] \tag{5}$$

stationary [U and E_{xc} depend on the n_i's through Eq. (4)]. This is easily proved by varying $\tilde{E}$ with respect to ψ_i^*, subject to the constraint that all the ψ_i are normalized. While it is well-defined mathematically, $\tilde{E}$ is *not* equal to the total energy E in general, because $T_s[\rho]$ is not equal to $\tilde{T}$ for an arbitrary set of n_i.[9] When the n_i have the form of the Fermi-Dirac distribution, however, $\tilde{E}$ is numerically equal to the total energy E by construction. Thus Eq. (5) defines a quantity which is a continuous function of the n_i, which is stationary with respect to variations in electron density for an arbitrary set of n_i (*including* nonintegral values) whenever Eqs. (2) and (4) are satisfied, and which takes on a value equal to the true total energy whenever the n_i assume the form of the Fermi distribution. $\tilde{E}$ plays an important role in any problem in which it is useful to introduce fractional occupations or a fractional total number of electrons (The Hohenberg-Kohn[1] total energy is defined only for integral total number of electrons, being the total energy of a real electron system.) For example, $\tilde{E}$ defines a function which can be used to make an *exact*, continuous connection between the ground-state energies of the N- and $(N+1)$-particle systems, by introducing a gradually increasing fraction of an electron into the lowest unoccupied level of the N- particle system. As in Slater's transition state,[5] an "interpolating" approximation to the difference between the ground-state energies of the N- and $(N+1)$-particle systems can be obtained from partial derivatives of $\tilde{E}$ evaluated at a state halfway between. Since $\tilde{E}$ is an auxiliary mathematical quantity, defined for fractional occupations, this is a perfectly legitimate procedure[10] within the framework of DFT.

We now prove some useful properties of $\tilde{E}$. Consider the variation of $\tilde{E}$ with respect to one of the n_i, allowing the orbitals to relax [i.e., solving Eqs. (2) and (4) self-consistently in the presence of the variation]. From Eq. (5), we have

$$\frac{\partial \tilde{E}}{\partial n_i} = t_i + \sum_j n_j \frac{\partial t_j}{\partial n_i} + \int (V_H + v_{xc}) \left(|\psi_i|^2 + \sum_j n_j \frac{\partial |\psi_j|^2}{\partial n_i} \right) d\vec{r} . \tag{6}$$

Introducing the second part of Eq. (3) into this,

$$\frac{\partial \tilde{E}}{\partial n_i} = \epsilon_i + \sum_j n_j \left(\frac{\partial t_j}{\partial n_i} + \int (V_H + v_{xc}) \frac{\partial |\psi_j|^2}{\partial n_i} d\vec{r} \right) . \tag{7}$$

Now, according to the first part of Eq. (3),

$$\frac{\partial t_j}{\partial n_i} = \int \frac{\partial \psi_j^*}{\partial n_i} (-\nabla^2) \psi_j \, d\vec{r} + \text{c.c.} , \tag{8}$$

where c.c. denotes the complex conjugate of the preceding term. Putting this into Eq. (7), one finds

$$\frac{\partial \tilde{E}}{\partial n_i} = \epsilon_i + \sum_j n_j \left(\int \frac{\partial \psi_j^*}{\partial n_i} (-\nabla^2 + V_H + v_{xc}) \psi_j \, d\vec{r} + \text{c.c.} \right) . \tag{9}$$

However, according to Eq. (2), the last term is

$$\sum_j n_j \epsilon_j \frac{\partial}{\partial n_i} \int |\psi_j|^2 d\vec{r} = 0 ,$$

because ψ_i are normalized. Thus one has

$$\frac{\partial \tilde{E}}{\partial n_i} = \epsilon_i \tag{10}$$

independent of the detailed form of $E_{xc}[\rho]$.

An alternative derivation of this result can be given: thinking of $\tilde{E}$ as a function of the n_i and as a functional of ρ, one has

$$\frac{\partial \tilde{E}}{\partial n_i} = \left(\frac{\partial \tilde{E}}{\partial n_i} \right)_\rho + \int \frac{\delta \tilde{E}}{\delta \rho(\vec{r})} \frac{\partial \rho}{\partial n_i} d\vec{r} . \tag{11}$$

Now, $\tilde{E}$ is stationary with respect to variations in ρ when Eqs. (2) and (4) are satisfied; it follows that $\delta \tilde{E} / \delta \rho(\vec{r}) = 0$. Thus, only the first term in Eq. (11) survives, and it can be shown [either from Eqs. (6)–(9) or from first-order perturbation theory] that this term is equal to ϵ_i. Since the Hohenberg-Kohn[1] theorem applies only to variations in which the total particle number is fixed, this derivation shows explicitly how Eq. (10) is an extension[11] of Hohenberg-Kohn-Sham theory, because the first term in Eq. (11) is the change in $\tilde{E}$ due to the change in the particle number (the second term in the change in $\tilde{E}$ due to the change in the charge density).

The minimum value of $\tilde{E}$ for fixed total number of electrons (and for each n_i between zero and one) occurs *either* when

$$\frac{\partial \tilde{E}}{\partial n_i}+\lambda=0$$

(λ being a Lagrange multiplier arising from the constraint on the total particle number) or at the "end points" (each n_i equal to zero or one). It follows from Eq. (10), however, that $\tilde{E}$ is minimized at the end points, when the n_i have the form of the Fermi-Dirac distribution (and, by construction, it is then equal to the true ground-state total energy of the system). This is true because, according to Eq. (10), transferring an infinitesimal amount of charge from an occupied to an unoccupied state can only increase $\tilde{E}$, inasmuch as the eigenvalue of the unoccupied state must be higher than that of the occupied one. Conversely, no configuration with holes below the highest occupied level can correspond to the minimum value of $\tilde{E}$, because the value of $\tilde{E}$ for any such configuration can be lowered by transferring an infinitesimal amount of charge into one of the empty states. Suppose this is done, and Eqs. (2) and (4) are are solved self-consistently for this new configuration. The eigenvalues ϵ_i will shift positions, but $\tilde{E}$ can be lowered still more if any holes remain below the highest occupied level; this argument can be continued until no holes remain, where $\tilde{E}$ assumes its lowest value (one can lower $\tilde{E}$ still more by introducing more than one electron into the lowest occupied state, but at this point the connection with the true total energy of Fermi systems is lost; since the n_i's no longer correspond to a Fermi distribution in this case, $\tilde{E}\neq E$).

Consider using Eq. (10) to connect the ground states of the N- and $(N+1)$-particle systems, by introducing n $(0\leqslant n\leqslant 1)$ electrons into the lowest unoccupied level. Since $\tilde{E}$ is equal to the true total energies for $n=0$ or 1, one has exactly

$$E_{N+1}-E_N=\int_0^1 \epsilon_i(n)\,dn. \tag{12}$$

Rather than actually calculating $\epsilon_i(n)$ for all values of n between 0 and 1, approximations based on numerical techniques for performing integrals can be introduced; for example, the transition state[5] corresponds to the lowest-order approximation of evaluating the function inside the integral at only the midpoint $n=\frac{1}{2}$. Higher-order approximations can also be used.[12]

It follows from Eq. (10) or Eq. (12) that the Fermi energy of an extended system (ϵ_i for the highest occupied state relative to vacuum) and the chemical potential $(E_{N+1}-E_N)$ are equivalent,[13] because ϵ_i for the highest occupied state will change only infinitesimally upon the addition of a single extra electron to an extended system already containing a large number of electrons.

We now turn to an interesting situation which, in contrast to the derivations given above, is not yet completely understood. This situation (in which $\tilde{E}$ is of use as conceptual tool) arises in the application of the spin-polarized local-density approximation[14] to finding the ground-state energy of atoms when the calculations assume spherical symmetry.[15] In some cases, notably iron and cobalt,[16] a self-consistent solution of Eqs. (2) and (4) for the d^ns^1 configuration leads to an empty s state below the partially filled d states, while a calculation for the $d^{n-1}s^2$ configuration puts the d levels below the s levels, so that the d levels have holes. Since neither of these configurations corresponds to the Fermi distribution, neither gives the minimum value of $\tilde{E}$, and neither gives the local-density approximation to the ground-state energy following from Eq. (1) (because $T_s\neq\tilde{T}$ in either case). It is not clear whether this situation arises because of the use of the local-density approximation, or whether it is due to the assumption of spherical symmetry. However, as was first done by Slater and co-workers,[17] the situation can be investigated by studying $\tilde{E}$ for the configuration $d^{n-x}s^{1+x}$ for x between zero and one, introducing these fractional occupations (with Σn_i fixed) in order to search for a minimum of $\tilde{E}$. What happens is that the s and d levels cross for some nonintegral value of x.[18] At this point, $\tilde{E}(x)$ is minimized, since its derivative with respect to x vanishes according to Eq. (10). The true total energy is still not necessarily equal to $\tilde{E}$ at this value of x, however, because this configuration is a generalization of the Fermi distribution, with unequal fractional occupations of the highest levels, and it has not been proven that $\tilde{T}$ for such a configuration is equal to T_s for the corresponding charge density. In a strict interpretation of Kohn-Sham[2] theory, this means that there is *no* charge density for this problem which minimizes the total energy and which is generated from a Fermi distribution.

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[8] There may be pathological sets of n_i's for which a self-consistent solution of Eqs. (2) and (4) cannot be found. In all practical cases, however, a self-consistent solution in fact exists.

[9] By way of example, suppose the ψ_i are plane waves. Then, for N electrons, the charge density obtained from Eq. (4) will be a constant, independent of the values of the n_i. The value of $\sum n_i t_i$, on the other hand, clearly depends on the choice of the n_i. Thus, $\sum n_i t_i$ is not a unique functional of the electron density ρ, unless the n_i have fixed values, and is not equal to T_s unless the n_i have the form of the Fermi distribution.

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