

Total energy density as an interpretative tool

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We present a formulation for the total-energy density within density-functional theory which is physically transparent and computationally feasible. We propose that it be used as a tool for the interpretation of computed energy and electronic structure changes during structural transformations and chemical reactions, augmenting the present use of changes in the electron density, in the Kohn–Sham local density of states, and in the Kohn–Sham energy density. © 2000 American Institute of Physics. [S0021-9606(00)30131-3]

Changes in the electron density of a system undergoing a structural transformation or a chemical reaction have long been used to understand the forces driving the transformation or the reaction. Indeed, the electron density itself has been regarded as one of the most significant descriptors of a system of electrons and nuclei since the advent of quantum mechanics. This view of the importance of the electron density was greatly strengthened by the emergence of density-functional theory. The Hohenberg–Kohn theorem¹ shows that the total energy of a system can be treated as a functional of the electron density. The Kohn–Sham theory² makes possible the construction of the true ground-state electron density of an N -electron system from the N one-electron orbitals of lowest energy of a particular independent electron system. This rigorous decomposition of the electron density into contributions from one-electron orbitals, the Kohn–Sham orbitals, greatly increases its power as an interpretive tool.

At present, methods based on density-functional theory are dominant in first-principles calculations for condensed matter and for much of quantum chemistry. The electron density and its Kohn–Sham orbital decomposition, fundamental outputs of the computations, are typically used to enrich understanding of the resulting energies. For example, studies of the isosurfaces of electron-density changes along a reaction pathway for the dissociation of H_2 on the Pd (100) surface³ have revealed the formation of bridge bonds between the s – p tails of the metallic surface electron density and the σ_g and σ_u^* molecular orbitals. These bridge bonds mediate the hybridization of the molecular orbitals with the metallic d -orbitals before they actually overlap. It is the bridge bonds which evolve into the bonds between the dissociated hydrogen atoms and the metal.

The Kohn–Sham (KS) theory enables one to go still

deeper into the interpretation of the results of the electronic structure computations. For extended systems, one can construct the Kohn–Sham density of states,

$$g(\epsilon) = \sum_{i=1}^{\infty} \delta(\epsilon - \epsilon_i), \quad (1)$$

where ϵ_i is the i th Kohn–Sham eigenvalue, and use it to tease out the energetics associated with the electron-density changes. For example, in studies of the interaction of chemisorbed O and H to form OH and H_2O on the (111) surfaces of Rh and Pt,⁴ the resonances and bound states associated with the bonding and antibonding orbitals of the atoms, radicals, or molecules to the surface are shown to be clearly visible in $g(\epsilon)$. Even more revealing is the local density of states,

$$g(\mathbf{r}, \epsilon) = \sum_{i=1}^{\infty} |\phi_i(\mathbf{r})|^2 \delta(\epsilon - \epsilon_i), \quad (2)$$

where $\phi_i(\mathbf{r})$ is the i th Kohn–Sham orbital, which enables one to associate a particular resonance or bound state in the Kohn–Sham spectrum, Eq. (1), with a particular atom or molecule. It allows one to make a resolution with respect to the Kohn–Sham energy of the changes of electron density accompanying structural transitions or chemical reactions.

Nevertheless, what drives a transformation or a reaction is the dependence of the total energy on the nuclear coordinates. Thus, what one needs as an additional interpretive tool is a physically transparent, computationally feasible total-energy density $e(\mathbf{r})$, such that

$$E = \int d^3r e(\mathbf{r}), \quad (3)$$

where E is the total energy. With $e(\mathbf{r})$ one could explore the relation between local changes in the electron density and the spatial dispersion of the total energy changes through the corresponding changes in $e(\mathbf{r})$.

To be more specific, in Ref. 3, evidence was found for the simultaneous presence of all the specific mechanisms commonly cited as playing important roles in the dissociation of H_2 on a transition metal surface. These included the formation of an orthogonality hole in the s - p tail of the metallic electron density, with concomitant flow of screening charge into the d -states, as emphasized by Harris and Andersson;⁵ the hybridization of the d -states with the occupied σ_g bonding orbital of the H_2 , as emphasized by Hammer and Scheffler,⁶ and the hybridization of the unoccupied σ_u^* antibonding orbital of the H_2 with associated backbonding, as emphasized by Hammer and Nørskov.^{7,8} Each of these processes introduced distinct, easily recognized characteristic changes in the electron density, which occurred in distinct regions of space. One could therefore utilize $e(\mathbf{r})$ to order the relative importance of each of these mechanisms as well as of bridge-bond formation at different locations along the dissociation pathway, garnering thereby a detailed, intimate quantitative understanding of the breaking of the intramolecular bond and the formation of metal-atom bonds in the course of the dissociation.

There are several issues to be confronted in constructing a useful and computationally-feasible expression for $e(\mathbf{r})$. The first and most important issue is that $e(\mathbf{r})$ is not unique. Any function of position which integrates to zero can be added to $e(\mathbf{r})$ in Eq. (3) without changing the total energy. Thus, there is a freedom of choice⁹ in the form of $e(\mathbf{r})$ which allows for selection on the basis of computational convenience and physical utility as an interpretative tool. For example, the kinetic-energy density for one electron can be expressed simply either in terms of the square of the magnitude of the gradient of the wave function or of the complex conjugate of the wave function times the Laplacian of the wave function, each of which has its own particular advantages. With the former choice, the kinetic-energy density is always positive, as it is classically. With the latter choice, one understands that the kinetic-energy density is negative in the classically forbidden regions and relates it to the decay of the wave function in those regions. Both choices are useful for interpretation, but if one, e.g., the Laplacian form, were immediately accessible from preexisting computations, one would use it.

In Ref. 4, the Kohn-Sham energy density $e_s(\mathbf{r})$,

$$e_s(\mathbf{r}) = \sum_{i=1}^N \epsilon_i |\phi_i(\mathbf{r})|^2 = \int \epsilon_N^+ d\epsilon g(\mathbf{r}, \epsilon), \quad (4)$$

was used as an interpretative tool. This choice was made primarily because the authors had at the time no means of computing the full $e(\mathbf{r})$ itself, but also because the ϵ_i and $\phi_i(\mathbf{r})$ are part of the output of a Kohn-Sham computation, so that construction of $e_s(\mathbf{r})$ does not increase computational complexity. In Ref. 4, $e_s(\mathbf{r})$ was found to be a useful interpretative tool. Moreover, there is also reason to believe that it is an important part of $e(\mathbf{r})$, as discussed more fully below. Accordingly, in the present paper we present a formu-

lation for $e(\mathbf{r})$ in which $e_s(\mathbf{r})$ is present explicitly, which is computationally feasible, and which remains physically transparent. We note parenthetically that the Laplacian form of the Kohn-Sham kinetic-energy density is thus implicitly chosen in Eq. (4).

The total energy can be represented as a density functional in the form

$$E = T + V_{ee} + V_{en} + V_{nn}, \quad (5)$$

where T , V_{ee} , and V_{en} are the functionals for the electron kinetic energy, the electron-electron interaction, and the electron-nuclear interaction. V_{nn} is the Coulomb interaction between the nuclei. In Kohn-Sham density-functional theory,^{10,11} the expression Eq. (5) is rewritten as

$$E = T_s + U + E_{XC} + V_{en} + V_{nn}. \quad (6)$$

Here T_s is the kinetic energy of the independent Kohn-Sham particles, U is the Hartree electrostatic energy,

$$U = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \quad (7)$$

where $n(\mathbf{r})$ is the electron density, and E_{XC} is the exchange-correlation energy,

$$E_{XC} = T - T_s + V_{ee} - U. \quad (8)$$

To achieve our goal of having $e_s(\mathbf{r})$ present explicitly in $e(\mathbf{r})$, we must first arrange Eq. (5) so that the total Kohn-Sham energy of the system,

$$E_s = \sum_{i=1}^N \epsilon_i = T_s + \int d^3r n(\mathbf{r})v_s(\mathbf{r}), \quad (9)$$

appears explicitly. In Eq. (9), $v_s(\mathbf{r})$ is the Kohn-Sham potential,

$$v_s(\mathbf{r}) = v_{en}(\mathbf{r}) + v_H(\mathbf{r}) + v_{XC}(\mathbf{r}), \quad (10)$$

where $v_{en}(\mathbf{r})$ is the Coulomb potential produced by the nuclei at \mathbf{r} , which enters V_{en} as well:

$$V_{en} = \int d^3r n(\mathbf{r})v_{en}(\mathbf{r}), \quad (11)$$

and $v_H(\mathbf{r})$ is the Hartree potential, the mean electrostatic potential produced by the electrons,

$$v_H(\mathbf{r}) = \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|} n(\mathbf{r}'), \quad (12)$$

which enters the Hartree energy functional,

$$U = \int d^3r e_H(\mathbf{r}), \quad e_H(\mathbf{r}) = \frac{1}{2} n(\mathbf{r})v_H(\mathbf{r}). \quad (13)$$

Finally, $v_{XC}(\mathbf{r})$ is the functional derivative of E_{XC} :

$$v_{XC}(\mathbf{r}) = \frac{\delta E_{XC}}{\delta n(\mathbf{r})}. \quad (14)$$

Thus Eq. (9) can be transformed into

$$E_s = T_s + 2U + V_{en} + \int d^3r n(\mathbf{r})v_{XC}(\mathbf{r}). \quad (15)$$

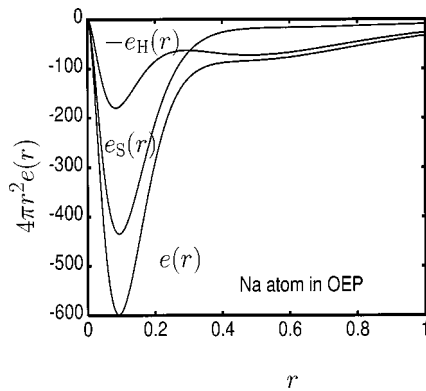


FIG. 1. Radial contributions to the total electronic energy density for the Na atom (atomic units).

Inserting Eq. (15) into Eq. (6) allows us to eliminate T_s , resulting in

$$E = E_s - U + V_{\text{nn}} + E_{XC} - \int d^3r n(\mathbf{r}) v_{XC}(\mathbf{r}). \quad (16)$$

Each of the above terms can be written as an integral over an energy density so that

$$e(\mathbf{r}) = e_s(\mathbf{r}) - e_H(\mathbf{r}) - \frac{1}{2} \rho_n(\mathbf{r}) v_{\text{en}}(\mathbf{r}) + e_{XC}(\mathbf{r}) - n(\mathbf{r}) v_{XC}(\mathbf{r}). \quad (17)$$

With the exception of the exchange-correlation energy density $e_{XC}(\mathbf{r})$, each term in Eq. (17) has already been given a physically clear interpretation. Turning now to the issue of computational feasibility in Eq. (17), $e_s(\mathbf{r})$ is given by Eq. (4) and can readily be constructed from the output of the standard codes which solve the Kohn–Sham equations. The electron density $n(\mathbf{r})$ is a fundamental output of such computations. The potentials $v_H(\mathbf{r})$ and $v_{\text{en}}(\mathbf{r})$ must be constructed during the computations, as must be $v_{XC}(\mathbf{r})$. The number density of the nuclei weighted by their respective atomic numbers is

$$\rho_n(\mathbf{r}) = \sum_{\alpha} Z_{\alpha} \delta(\mathbf{r} - \mathbf{R}_{\alpha}), \quad (18)$$

where \mathbf{R}_{α} is the position and Z_{α} the charge of nucleus α . We note that the third term in Eq. (17), though singular at the nuclei, vanishes away from the nuclei.

There remains the choice of a form for $e_{XC}(\mathbf{r})$. Each of the working approximations for E_{XC} (e.g., LDA,² GGA,^{12–14} or hybrid forms)^{15–17} are (or can be) expressed as an integral over an energy density, which we term the conventional one. Calculations employing these approximations can thus yield results for the conventional $e_{XC}(\mathbf{r})$ directly. However, during the construction of such approximations, procedures may be followed which have the effect of introducing an addition to the energy density which integrates to zero. Thus the conventional results from different approximations cannot be meaningfully compared. For example, deep in the derivations of PW91,^{18,19} an integration by parts occurs which eliminates the possibility of comparing results for $e_{XC}(\mathbf{r})$

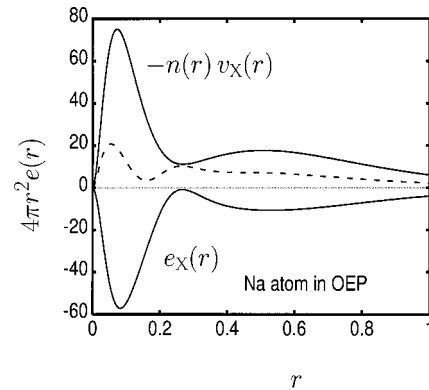


FIG. 2. Radial exchange contributions to the total electronic energy density for the Na atom (atomic units); the dashed curve is the sum of the other two.

with that of LDA. This nonuniqueness of $e_{XC}(\mathbf{r})$, however, does not affect $v_{XC}(\mathbf{r})$ which is unique, i.e., invariant to such additions. We therefore choose to define $e_{XC}(\mathbf{r})$ in terms of $v_{XC}[n](\mathbf{r})$ via the procedure of Burke, Cruz, and Lam (BCL),²⁰ an extension of the original ideas of Engel and Vosko,²¹

$$\nabla^2 e_{XC}(\mathbf{r}) = 3 \nabla(n(\mathbf{r})) \nabla \tilde{v}_{XC}(\mathbf{r}), \quad (19)$$

where

$$\tilde{v}_{XC}[n](\mathbf{r}) = \int_0^1 \frac{d\gamma}{\gamma} v_{XC}[n_{\gamma}]\left(\frac{\mathbf{r}}{\gamma}\right), \quad (20)$$

and $n_{\gamma}(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$. Thus, Eqs. (19) and (20) yield $e_{XC}(\mathbf{r})$ as a computationally feasible mapping of $v_{XC}(\mathbf{r})$, an output of the standard codes. This mapping has additional attractive features. It can be constructed for any approximate functional $E_{XC}[n]$. Within the local density approximation (LDA), this procedure reproduces simply $e_{XC}^{\text{unif}}(n(\mathbf{r}))$, the exchange-correlation energy density of a uniform electron gas of density $n(\mathbf{r})$. This is just the conventional exchange-correlation energy density within LDA, and so is already calculated in standard LDA Kohn–Sham calculations, for which the mapping of Eqs. (19)–(20) is unnecessary. Within any generalized gradient approximation (GGA) such as PBE,¹⁴ or BLYP,^{12,13} the procedure defines a different exchange-correlation energy density from the conventional one. This exchange-correlation energy density includes dependence on the Laplacian and other higher derivatives of $n(\mathbf{r})$, and so is far more sensitive to details in $n(\mathbf{r})$ than the conventional GGA forms. The scaling defined in Eq. (20) is easily performed on any approximate density functional. Finally, the BCL procedure can be used to define an exact exchange energy density, so that it can be applied even to hybrids of GGA with exact exchange.²⁰ Meaningful comparison of the results of different approximations is thus generally achievable.²⁰

To illustrate use of the total energy density, we plot the various contributions to the total energy density for the Na atom. Our calculations are all for exact exchange only, using the atomic optimized effective potential (OEP) code of Engel.²² From Figs. 1 and 2, we see that the total energy

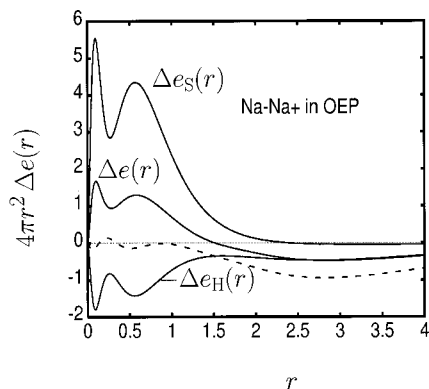


FIG. 3. Same as Fig. 1, but for the difference between the neutral atom, Na, and the ion, Na^+ ; the dashed curve is $\Delta e(r) - \Delta e_H(r)$.

density is usually dominated by two terms: the Kohn–Sham eigenvalue contribution and the electrostatic energy correction. The two exchange terms of Eq. (17) are small, and largely cancel, as shown in Fig. 2. This cancellation is already apparent in LDA exchange, where the sum of these terms is only $1/3$ of e_X^{unif} . This agrees with arguments^{23–25} that changes in the energy can be largely understood in terms of changes in KS eigenvalues and the electrostatic potentials, and reinforces our decision to make $e_s(\mathbf{r})$ an explicit part of $e(\mathbf{r})$, having based our formulation for $e(\mathbf{r})$ on Eq. (16) instead of Eq. (6). The present analysis also allows comparison between results from approximate functionals and theoretically exact²⁶ or accurate wave function computations.²⁰

To illustrate the importance of the electrostatic energy correction, consider Fig. 3, which shows energy-density differences between neutral Na and its ion. The Kohn–Sham contribution is dominated by the core ($r \leq 0.2$, roughly). This is because the $3s$ electron in Na induces an almost constant shift in the core Hartree potential, so that all eigenvalues are about 0.29 higher in the neutral relative to the ion. When the Hartree correction is made, and the total energy density difference plotted, we find that there are two almost equal and opposite contributions to the energy difference. To see that these are entirely electrostatic effects, we further subtract $e_H(r)$ from the total (dashed line), showing that, in the absence of Hartree contributions, the total energy density lies almost entirely in the valence region. This simple analysis demonstrates both the importance of electrostatic contributions to the energy density, and how the various terms are needed in Eq. (17) to produce the final physical picture. [For example, overall shifts in KS eigenvalues do not contribute to $e(\mathbf{r})$, but do show up in $e_s(\mathbf{r})$.] The electrostatic energy correction is omitted in the generalized perturbation method²⁷ widely used in the theory of alloys.²⁸ The present analysis allows us to explore the role of exchange–correlation energy differences in chemical systems.

Note that $v_H(\mathbf{r})$ and $v_{\text{en}}(\mathbf{r})$ each diverge separately in the thermodynamic limit for extended systems. The divergences cancel each other in $v_s(\mathbf{r})$, Eq. (10), because only their sum enters. The divergences similarly cancel in E , Eqs. (5), (6), and (16) and in E_s , Eq. (9). They do not cancel in $e(\mathbf{r})$ as written in Eq. (17). This difficulty should be obviated

by the methods of eliminating the singular parts of $v_H(\mathbf{r})$ and $v_{\text{en}}(\mathbf{r})$ which are standard in the theory of the electron structure of extended systems. That is, $v_H(\mathbf{r})$ and $v_{\text{en}}(\mathbf{r})$ should be interpreted as the nonsingular part of the Hartree and nuclear potential, respectively, in Eq. (17) for extended systems.

In conclusion, we propose that the total energy density away from the nuclei be constructed from the output of Kohn–Sham computations augmented by the procedure of Ref. 20 and used as an interpretive tool in analyzing energy and electronic structure changes during transformations and reactions when the focus is on the study of bond formation in the spaces between atoms. In addition, the full expression for $e(\mathbf{r})$, Eq. (17), can be coarse-grained by integration over a small sphere containing a particular nucleus to examine the role of the corresponding atom in chemical bonding or structural transformation. Such spheres are already present in, e.g., linear-augmented plane-wave, muffin-tin, and Korringa–Kohn–Rostocker codes, and can be readily introduced into other procedures. When used in this way, the total energy density, Eq. (17), together with the definitions we have given for the individual terms within it, should prove to be a computationally feasible, physically informative interpretive tool for use with electronic structure calculations in a wide variety of systems.

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