

Time-dependent electron localization function

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(Received 27 April 2004; published 10 January 2005)

We present a generalization of the electron localization function (ELF) that can be used to analyze time-dependent processes. The time-dependent ELF allows the *time-resolved* observation of the formation, the modulation, and the breaking of chemical bonds, and can thus provide a visual understanding of complex reactions involving the dynamics of excited electrons. We illustrate the usefulness of the time-dependent ELF by two examples: the π - π^* transition induced by a laser field, and the destruction of bonds and formation of lone pairs in a scattering process.

DOI: 10.1103/PhysRevA.71.010501

PACS number(s): 31.70.Hq, 82.20.Wt, 31.15.Ew

The advent of ultrashort laser sources with pulse durations on the order of 10–100 fs [1] has paved the way to the analysis and control of chemical reactions [2]: By means of pump-probe spectroscopies with femtosecond laser pulses [3] one can follow, in the time domain, the nuclear motion which typically evolves on the picosecond time scale. One of the most important recent achievements has been the experimental realization of attosecond pulses [4]. These are produced by coherently superimposing high harmonics generated by a strong infrared laser pulse interacting with atoms. With this light source available, pump-probe spectroscopies using attosecond pulses allow the temporal resolution of the electronic motion which is governed by the femtosecond time scale. Questions like, “How does an electron travel from the highest occupied to the lowest unoccupied molecular orbital when excited by a laser?” may soon become experimentally accessible. This establishes the need for theoretical tools to analyze and interpret such data. Theoretical tools of this type will be developed in this article. We are mainly concerned with bonds, and how they break, form, or change during a time-dependent process.

The intuitive concept of a chemical bond is very simple and elegant: an electron pair shared between neighboring atoms that provides the necessary attraction to bind the molecule. However, it turns out to be very difficult to define exactly what a bond is, or even to visualize it. The one-electron molecular orbitals that stem from density-functional theory or Hartree-Fock usually have contributions from several atoms and do not represent a unique bond. The electronic density, on the other hand, does not easily reveal important features like lone pairs. The electron localization function (ELF) is a function crafted to bring into evidence the subtle bonding properties of an electronic system. It was originally applied to ground-state systems, in the study of atomic shells and covalent bonds [5]. Soon after, it was realized that the ELF could be also used to analyze lone pairs, hydrogen bonds [6], ionic and metallic bonds [7], etc. The systems studied include atoms [5], molecules [7], surfaces [7] and solids [7–9]. It is also possible to establish a rigorous topological classification of chemical bonds using the ELF [10]. Furthermore, the ELF has the advantage of being fairly

insensitive to the method used to calculate the wave functions of the system. In fact, Hartree-Fock, density-functional theory, or even simple approaches such as extended Hückel methods, yield qualitatively similar ELF's [7]. Approximate electron localization functions have also been obtained from experimental electron densities measured with x rays [9].

Up to now the ELF has only been used to study systems in their ground state. Clearly, an extension of the ELF to time-dependent processes appears quite desirable. Such an extension would allow the *time-resolved* observation of the formation, the modulation, and the breaking of chemical bonds, and thus provide a visual understanding of complex reactions involving the dynamics of excited electrons. That is exactly the goal of this communication.

The derivation of a time-dependent ELF (TDELFF) follows closely the derivation of Becke and Edgecombe of the ground-state ELF [5]. Our objective is to find a function, $D_\sigma(\mathbf{r}, t)$, that measures the probability of finding one electron in the near vicinity of a reference like-spin electron at position \mathbf{r} and time t . If this probability is high then the reference electron must be delocalized. On the other hand, a covalent bond consists of a localized electron pair (of opposite spins) between two neighboring atoms. The probability of finding a like-spin electron close to a reference electron in this region must then be very low. For a determinantal many-body wave function, the function $D_\sigma(\mathbf{r}, t)$ is given by

$$D_\sigma(\mathbf{r}, t) = \tau_\sigma(\mathbf{r}, t) - \frac{1}{4} \frac{[\nabla n_\sigma(\mathbf{r}, t)]^2}{n_\sigma(\mathbf{r}, t)} - \frac{j_\sigma^2(\mathbf{r}, t)}{n_\sigma(\mathbf{r}, t)}, \quad (1)$$

where σ denotes the spin, n_σ the spin density, j_σ the absolute value of the current density, and

$$\tau_\sigma(\mathbf{r}, t) = \sum_{i=1}^{N_\sigma} |\nabla \varphi_{i\sigma}(\mathbf{r}, t)|^2. \quad (2)$$

This last expression represents the kinetic-energy density of a system of N_σ electrons, described by the one-particle orbitals $\varphi_{i\sigma}$. These orbitals can be obtained, e.g., from time-dependent density-functional theory or from a time-dependent Hartree-Fock calculation.

Equation (1) is similar to the expression for the ground-state $D_\sigma(\mathbf{r})$ [5]. The main difference is the additional term proportional to j_σ^2 [11]. This term naturally arises when the analysis of Ref. [5] is carried out without assuming real-

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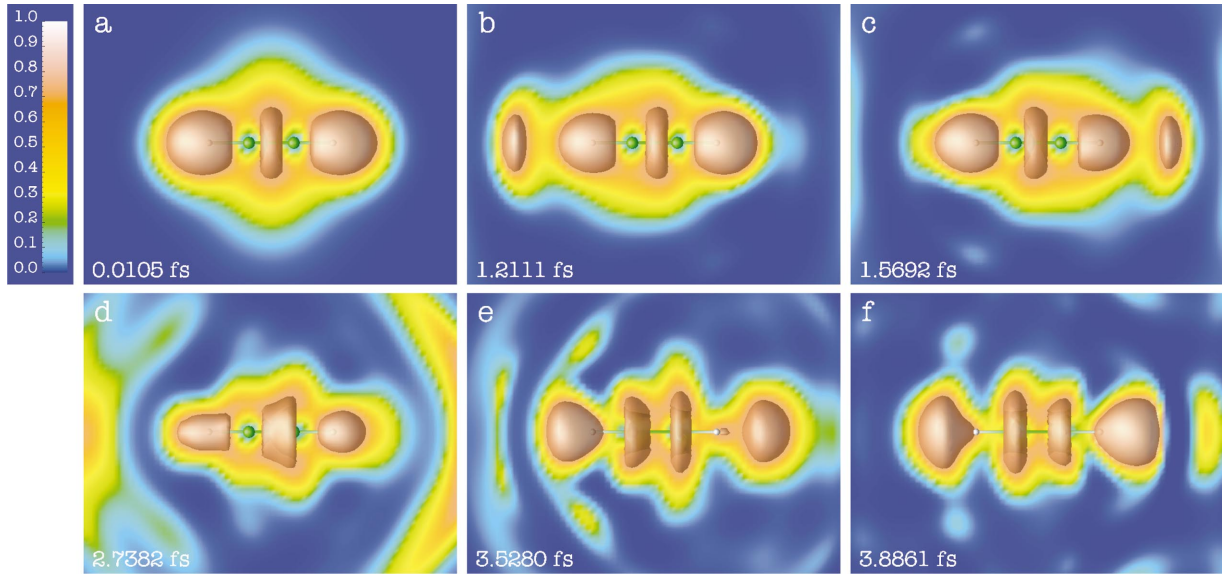


FIG. 1. (Color) Snapshots of the time-dependent ELF for the excitation of acetylene by a 17.15 eV laser pulse [12]. The pulse had a total length of 7 fs, an intensity of 1.2×10^{14} W cm $^{-2}$, and was polarized along the molecular axis. Ionization and the transition from the bonding π state to the antibonding π^* state are clearly visible.

valued orbitals, i.e., without assigning vanishing orbital currents. This was pointed out by Dobson [11] in his evaluation of the Fermi-hole curvature of a static current-carrying single-determinant state. It is easy to see that the derivation of Ref. [11] applies equally well to time-dependent determinantal wave functions, thus leading to Eq. (1).

The function $D_\sigma(\mathbf{r}, t)$ is always ≥ 0 , but it is not bounded from above. As usual, we define as an alternative measure of localization

$$f_{\text{ELF}}(\mathbf{r}, t) = \frac{1}{1 + [D_\sigma(\mathbf{r}, t)/D_\sigma^0(\mathbf{r}, t)]^2}, \quad (3)$$

with the definition $D_\sigma^0(\mathbf{r}, t) = \tau_\sigma^{\text{HEG}}(n_\sigma(\mathbf{r}, t))$, where

$$\tau_\sigma^{\text{HEG}}(n_\sigma) = \frac{3}{5}(6\pi^2)^{2/3} n_\sigma^{5/3} \quad (4)$$

is the kinetic-energy density of a homogeneous electron gas of density n_σ . Using this definition, f_{ELF} is dimensionless and lies between zero and one. A value of 1, i.e., $D_\sigma(\mathbf{r}, t)$ approaching zero, corresponds to high localization.

We illustrate the usefulness of the time-dependent ELF by two examples: (i) the excitation of acetylene by a strong laser pulse (Fig. 1), and (ii) the scattering of a high-energy proton from the ethene molecule (Fig. 2). The figures depict a slab of the ELF passing through the plane of the molecules, to which we superimposed an isosurface (Fig. 1) or contour lines (Fig. 2) at $f_{\text{ELF}}=0.8$. Movies of the time-dependent ELF and of the corresponding time-dependent density can be found in our website [13] or as supplementary material to this article [12]. All calculations were performed in the framework of time-dependent density-functional theory [14,15], using a real-space, real-time code [16], and employing the adiabatic local-density approximation [15] for the time-dependent exchange-correlation potential. This approximation is expected to overestimate ionization due to spurious self-interactions. This problem can be overcome by the use

of explicitly orbital-dependent functionals within the time-dependent optimized effective potential method [17].

In the beginning of the simulation (i) the acetylene molecule is in its ground state [Fig. 1(a)]. At this moment, the ELF exhibits three major features: a torus between the carbon atoms—typical of triple bonds—and the two characteristic blobs around the hydrogens. As the intensity of the laser increases, the system starts to oscillate, and then to ionize [Figs. 1(b) and 1(c)]. Note that the ionized charge leaves the system in fairly localized packets [the blob on the left in panel (b), and on the right in panel (c)], that then spread with time. The central torus then starts to widen until the moment it breaks into two separate tori, each around one carbon atom [Fig. 1(e)]. We interpret this finding as a transition from the π bonding state into the π^* nonbonding state. The system then remains in this excited state for some time. We emphasize that our calculation corresponds to one specific orientation of the molecule, namely the orientation where the polarization vector of the laser field is parallel to the molecular axis. A detailed analysis of the dependence of photoionization on the molecular orientation will be presented elsewhere [18].

To assess the importance of the j^2/n term, we compare, in Fig. 3, a snapshot of the proper time-dependent ELF [given by Eq. (1)] with the traditional ground-state expression (where the j^2/n term is absent). The plot shows clear differences in some regions of space, thus underlining the significance of the j^2/n term.

In our second example we send a fast, but still nonrelativistic, proton against one of the carbons of ethene (Fig. 2). The initial configuration is shown in panel (a). While approaching the carbon atom the proton accumulates some charge around it [Fig. 2(b)]. It then scatters and leaves the system picking up part of the electronic charge. The electron-nuclei system is thus excited (in total the electronic system absorbs around 20 eV). In panels (d) and (e) the leftmost carbon has already broken the two bonds with the hydrogens

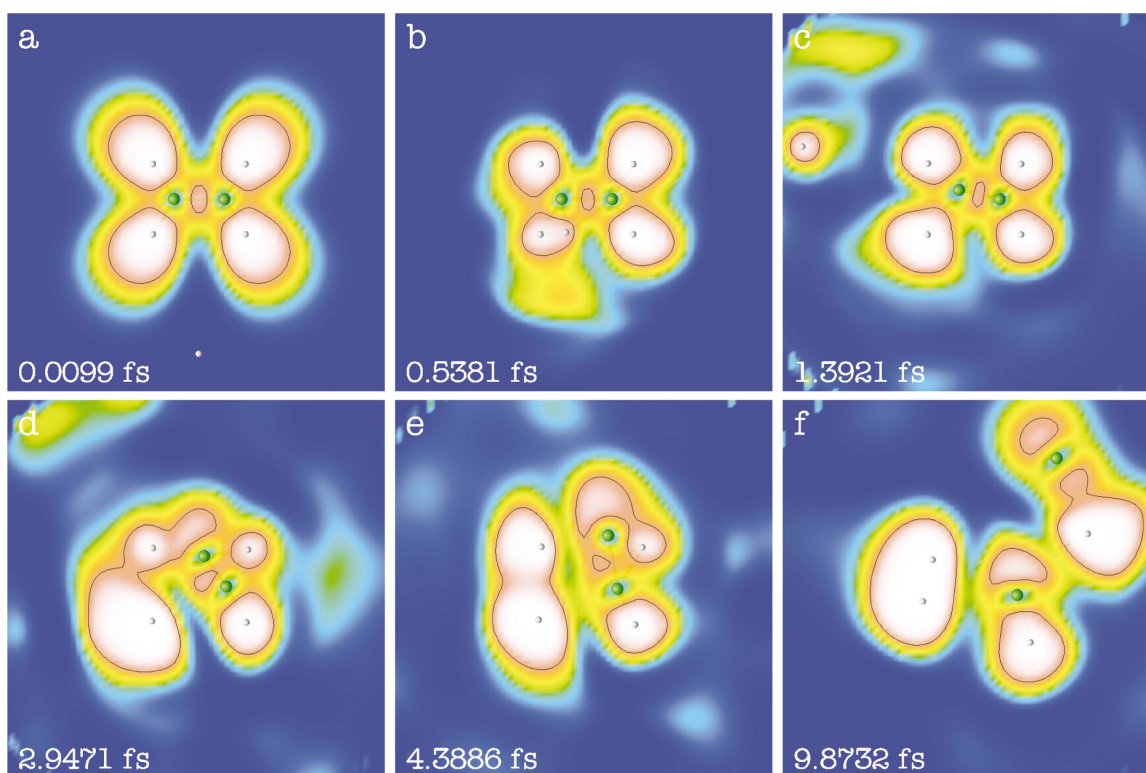


FIG. 2. (Color) Snapshots of the time-dependent ELF for the scattering of a fast, nonrelativistic proton ($E_{\text{kin}} \approx 2$ keV) by ethene [12]. The molecule breaks into several pieces. During this fragmentation process, the breaking of bonds and the subsequent creation of several lone pairs become clearly visible in the time-dependent ELF. The legend is the same as in Fig. 1.

(that will later form an H_2 molecule). Clearly visible is also the polarization of the carbon-carbon double bond, and the starting of the formation of a lone pair above the leftmost carbon. We emphasize once again that the formation of lone pairs cannot be visualized in movies of the time-dependent density. Only the TDELf allows one to observe this feature.

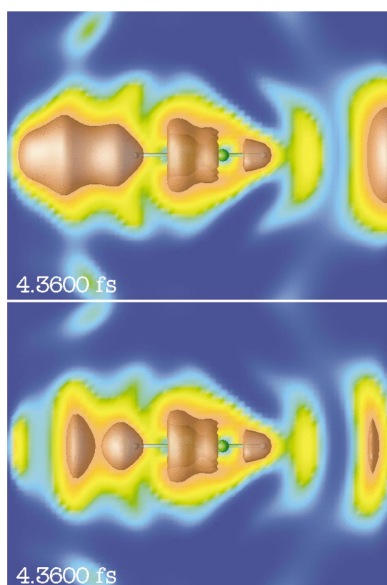


FIG. 3. (Color) Snapshot of the time-dependent ELF with (upper panel) and without (lower panel) the j^2/n term for the excitation of acetylene by a 17.15 eV laser pulse. The legend is the same as in Fig. 1.

At the end of the simulation [panel (f)] we can observe an H_2 molecule (left) and two CH fragments (middle and right). The rightmost CH fragment is again breaking to yield a carbon and a hydrogen atom. Note again the lone pairs characteristic of CH, localized near the carbon atoms.

These two examples illustrate the amount of information that can immediately be grasped just by looking at the time-dependent ELF, from π - π^* transitions, to the creation of lone pairs. One can infer the *time scale* and the *temporal order* of the various processes occurring, e.g., in a molecular collision: One can tell which bond breaks first and which breaks second, and how many attoseconds or femtoseconds it takes to form new bonds and new lone pairs. We emphasize once more that with the advent of attosecond pulses this information will soon become experimentally available. We expect the time-dependent ELF to be a valuable tool in the analysis of many physical processes. One example is the creation and decay of collective excitations or the scattering of electrons from atoms and molecules. Another example is the process of vision: light promotes the electrons of retinal into the first excited state, which by its turn induces the isomerization of the photo-receptor and eventually leads to the firing of a neuron. The key feature of the time-dependent ELF, in all cases, is the *time-resolved* observation of the formation, the modulation, or the breaking of chemical bonds, thus providing a visual understanding of the dynamics of excited electrons.

This work was supported in part by the NANOQUANTA Network of Excellence, by the EXC!TING Research and Training Network, and by the Deutsche Forschungsgemeinschaft within the Sonderforschungsbereich SFB450.

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