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Phys. Rev. Lett. **117**, 093002 — Published 23 August 2016

DOI: [10.1103/PhysRevLett.117.093002](https://doi.org/10.1103/PhysRevLett.117.093002)

Core ionization initiates sub-femtosecond charge migration in the valence shell

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(Dated: August 4, 2016)

After ionization of a valence electron, the created hole can migrate ultrafast from one end of the molecule to another. Due to the advent of attosecond pulse techniques, the measuring and understanding of charge migration has become a central topic in attosecond science. Here, we pose the hitherto unconsidered question whether ionizing a core electron will also lead to charge migration. It is found that the created hole in the core stays put, but in response to this hole interesting electron dynamics takes place which can lead to intense charge migration in the valence shell. This migration is typically faster than that after ionization of a valence electron and transpires on a shorter time scale than the natural decay of the core hole by the Auger process, making the subject very challenging to attosecond science.

PACS numbers: 34.70.+e, 33.60.+q, 32.80.Aa, 31.15.vq

The investigation of ultrafast electron dynamics has become popular in recent years not least due to advances in time-resolved spectroscopic techniques and the advent of attosecond laser pulses. A particularly attractive process to study is charge migration following the ionization of a molecular system. Ultrafast ionization creates a ‘hole’ in the electronic cloud and this hole can migrate through the system. Theory shows that the created hole can migrate ultrafast driven solely by electron correlation and electron relaxation [1]. The phenomenon is termed charge migration to underline the difference to standard electron and hole transfer which is driven by nuclear motion [2, 3] and is consequently much slower in general. By now there are ample computational examples [4–6] and a number of experimental studies [7, 8] of charge migration (see a recent review [9] and Refs. [10, 11]). Charge migration has been found to exhibit many facets and is a rich phenomenon depending on the electronic properties of the molecule, its geometry and on the specific site from which the electron has been removed to create the hole. Even different conformers of the same system may exhibit totally different electron dynamics.

Until now charge migration has been considered only for the case of valence ionization, i.e., the hole is created by removing an electron from the valence shell of a molecule. At first sight this restriction seems to be natural and self evident as the ionization of the core leads to a very short-lived hole. The core hole is well known to decay by the Auger effect [12] on the fast time scale of typically a few femtoseconds [13, 14]. Therefore, to observe charge migration this migration must be extremely fast, well faster than the hole’s lifetime. Another apparent reason for not considering charge migration after core ionization is the anticipation that the resulting hole is not expected to migrate through the molecule and thus not expected to be of interest. In this work we present general arguments that the contrary is true, i.e., charge migration after core ionization is particularly interesting, and document this statement by an explicit example.

Let us start by making clear that electron dynamics of the valence electrons can be particularly fast after ionization of a core electron. Core electrons are strongly localized at a nucleus and hence when a core electron is removed, the valence electrons see a new potential which resembles that of a nucleus with a charge enhanced by one and adjust to this potential. This relaxation gives rise to the appearance of so-called shake-up satellite states in the ionization spectrum [15]. A typical core ionization spectrum exhibits an intense main line – the core level – accompanied by shake-up satellite lines of lower intensity at higher binding energies. The energy gap between the main line and the satellites is typically rather large as it is related to the excitation energy of the system with a core vacancy. The time Δt of a population transfer between a satellite and the main line is dictated by the energy gap ΔE between them according to Δt (fs) = $2.07/\Delta E$ (eV). In the O1s ionization spectrum of the water molecule, for example, the first shake-up satellite appears at 16.96 eV above the main line [16] and Δt is as short as 0.12 fs, i.e., it is in the attosecond (as) regime.

The investigation of charge migration after core ionization possesses additional favorable features. The initial core hole is strongly localized at a well-defined atomic site. This hole will not migrate but will stay localized at the respective atomic site [17]. This enables one to study the electron dynamics in the valence shell caused by the sudden creation of a core vacancy. If the core hole would also have its own dynamics, this dynamics will interfere with that of the valence electrons and make the investigation much more complex. It is well-known that the sudden approximation applies to core ionization and that the electron is removed from a specific core orbital [18]. Furthermore, the ionization cross-section with high photon energies is typically much larger for core than for valence electrons [19]. All these facts simplify the preparation of the core hole and its characterization considerably. We remind here that the preparation of the initial valence hole in the former studies of charge migration has always

been a delicate and not yet fully resolved issue [9, 20]. In the case of a core, one just has to ionize the electron with a high energy photon and the valence-electron dynamics solely driven by electron relaxation will automatically set in.

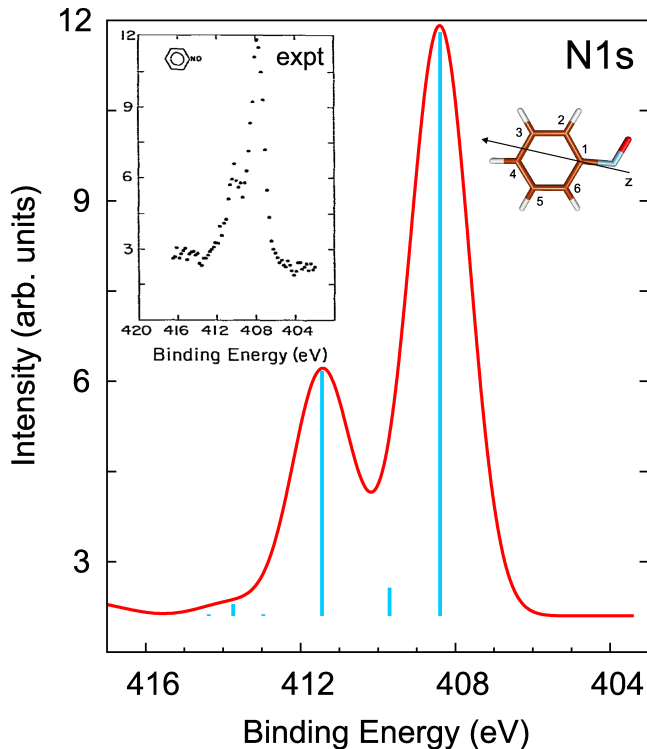


FIG. 1. (Color online) Nitrogen 1s ionization spectrum of nitrosobenzene computed with the accurate *ab initio* Green's function ADC(4) approach (blue bars). The spectral envelope (red curve) is obtained by convoluting each computed line with a Gaussian with FWHM of 1.8 eV, which accounts for the natural linewidth, vibrational broadening, and experimental resolution. For comparison, the experimental N1s XPS spectrum of nitrosobenzene is shown in the inset (taken from Ref. [22]). The value of 1.8 eV used in the convolution was extracted from the main peak of that spectrum.

In the following we demonstrate the above general considerations by an explicit example. There is an intimate relationship between the ionization spectrum and the possible charge migration taking place after ionization [21]. In the core, the larger the intensity of a shake-up satellite is, the larger is the amount of charge migrating. Since this intensity is borrowed from the main line, it decreases with the energy gap between them. We thus have to compromise between the gap size, which determines the fastness of the charge migration, and the relative intensity of the satellite. We have chosen nitrosobenzene which is a common molecule as our example. This molecule possesses a single nitrogen atom which makes the study simpler as there is only a single N1s core orbital which can be ionized. Moreover, the N1s ionization

spectrum of this molecule has been measured [22]. This spectrum is difficult to compute and will serve as a stringent test for our calculation.

Figure 1 depicts the N1s ionization spectrum of nitrosobenzene computed using the high-level *ab initio* ADC(4) propagator method [23] which has been shown many times to yield highly accurate results [24]. For more details on the calculations, see the Supplemental Material (SM) [25]. As seen, the calculation reproduces very well the experimental spectrum [22] shown in the inset. Analyzing the computational findings, this spectrum can now be well understood. The spectrum consists of a main line, the core level, at 408.4 eV binding energy, a dominant satellite line at 411.4 eV, and a few weak satellite lines.

Although the calculations on the electron dynamics to be discussed below take account of all the computed satellites, we concentrate here on the main line and the dominant satellite which give rise to most of the electron dynamics phenomena. The many-electron wavefunctions of the core level and the satellites are rather complex and involve many configurations. We may, however, for the sake of discussion boil down these wavefunctions to just three dominating configurations. The first one is the core-hole configuration $|\Phi_{N1s}\rangle = \hat{a}_{N1s}|0\rangle$, where the annihilation operator \hat{a}_{N1s} removes an electron from the N1s Hartree-Fock core orbital of the electronic ground state $|0\rangle$ of nitrosobenzene. In addition to this so-called one-hole (1h) configuration, two so-called two-hole one-particle (2h1p) configurations strongly contribute. They are characterized by $|\Phi_{L,H-1,N1s}\rangle = \hat{a}_L^\dagger \hat{a}_{H-1} \hat{a}_{N1s}|0\rangle$ and $|\Phi_{L+2,H-3,N1s}\rangle = \hat{a}_{L+2}^\dagger \hat{a}_{H-3} \hat{a}_{N1s}|0\rangle$ which are spin-adapted configurations made to be eigenfunctions of the spin operator as all contributing configurations have to describe a spin doublet state resulting upon ionization of the closed-shell nitrosobenzene. As usual, the highest occupied valence orbital is called HOMO (highest occupied molecular orbital) and the unoccupied orbital lowest in energy is called LUMO (lowest unoccupied molecular orbital) and the other occupied and unoccupied orbitals are successively named HOMO-1, HOMO-2, etc., and LUMO+1, LUMO+2, etc.. Accordingly, \hat{a}_{H-1} above removes a valence electron from the Hartree-Fock HOMO-1 and \hat{a}_L^\dagger adds an electron to the LUMO, and so on. The orbitals participating in the above relevant configurations are depicted in Fig. 2.

The core level is found to be

$$|\text{Main state}\rangle \approx -0.63|\Phi_{N1s}\rangle + 0.33|\Phi_{L,H-1,N1s}\rangle + 0.15|\Phi_{L+2,H-3,N1s}\rangle, \quad (1a)$$

and similarly the dominant-satellite's state reads

$$|\text{Sat. state}\rangle \approx 0.49|\Phi_{L,H-1,N1s}\rangle - 0.15|\Phi_{L+2,H-3,N1s}\rangle + 0.41|\Phi_{N1s}\rangle. \quad (1b)$$

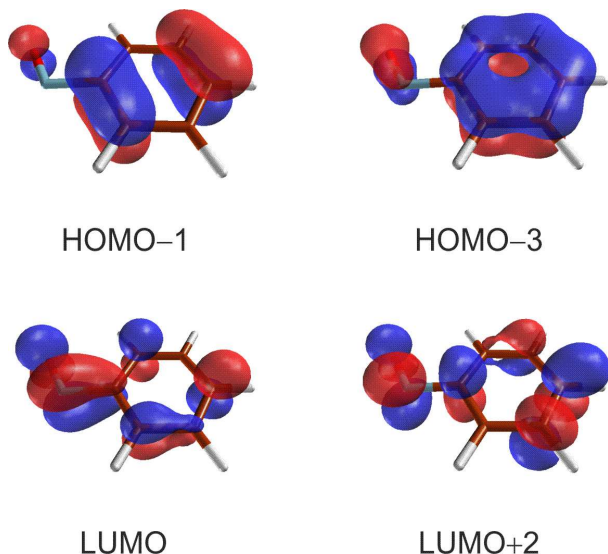


FIG. 2. (Color online) The four relevant valence molecular Hartree-Fock orbitals participating in the ionization spectrum of nitrosobenzene. Shown are the HOMO-1 and HOMO-3 orbitals occupied in the electronic ground state of this molecule and the unoccupied orbitals LUMO and LUMO+2 (see text).

The emerging physical picture behind the N1s core ionization is thus found to be rather transparent. Both HOMO-1 and HOMO-3 are mostly distributed over the phenyl ring of the molecule while LUMO+2 and in particular LUMO have substantial contributions on the CNO moiety. By removing an electron from the nitrogen core, excitations in the valence space of the π electrons are generated to screen the core hole. These excitations thus correspond to charge moving from the phenyl ring to the CNO moiety.

To visualize the electron dynamics following the core ionization and to be able to discuss in quantitative terms the resulting charge migration, we have computed the *hole density* $Q(\vec{r}, t)$ which is defined [1] as the difference between the electron density $\rho_0(\vec{r})$ in the ground state of the system and that of the ion, $\rho_c(\vec{r}, t)$, obtained by removing a N1s core electron from this ground state. The latter is the expectation value of the usual density operator taken with $|\Phi_{N1s}\rangle = \hat{a}_{N1s}|0\rangle$. Since the $|\Phi_{N1s}\rangle$ is not an eigenstate of the ion and contains information on all ionic states produced by the removal of a N1s electron, $\rho_c(\vec{r}, t)$ and hence the hole density $Q(\vec{r}, t)$ are time-dependent reflecting the underlying electron dynamics. The general theory including the basic mechanisms of charge migration can be found in [21, 26]. Here, we only dwell briefly on the case of a dominant relaxation satellite. Originally, the theory was meant for valence holes [17], but it applies as well to the current study of a core hole. Accordingly, we expect the core hole initially created by the ionization to stay put where it is created

without exhibiting any dynamics itself. However, there is substantial electron dynamics in the valence shell at later times. It is easy to show that this finding [17] applies generally to core ionization as within the excellent approximation of core-valence separation all contributing electronic configurations contain a core hole [27]. This can also be seen in Eq. (1) above.

We have computed the time evolution of the hole density by first calculating the multi-electron wavepacket produced by removing an N1s electron using the technique developed in [21, 26] and subsequently constructing $Q(\vec{r}, t)$ employing this wavepacket. The technique used until now was based on the ADC(3) approach [28, 29] and had to be extended extensively to allow for using the much more involved ADC(4) approach [23] required to compute accurately the satellite levels appearing in core ionization.

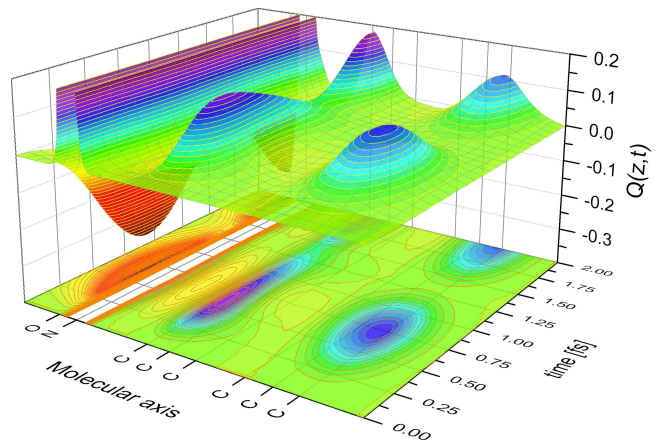


FIG. 3. (Color online) Evolution of the hole density $Q(z, t)$ of nitrosobenzene after ionization out of an N1s orbital. The z axis, denoted as “molecular axis”, passes through the nitroso carbon (C1) and through the bond between C3 and C4 (see Fig. 1). The positions of the atoms along the molecular axis are also indicated. Note that the hole density is positive where electrons are deficient and negative where they are surplus.

The time evolution of the hole density after N1s ionization of nitrosobenzene is depicted in Fig. 3. More precisely, the hole density $Q(z, t)$, where z is the molecular axis indicated in Fig. 1, is shown. This quantity is obtained by integrating the three dimensional and difficult to visualize quantity $Q(\vec{r}, t)$ over all directions perpendicular to z . One can see that at time $t = 0$ a core hole is created at the nitrogen site and this hole stays unchanged at all times. Very soon valence electrons start flowing from the carbon ring to the CNO moiety. Note that the hole density is positive where electrons are deficient and negative where they are surplus. After a short time the electrons flow back to the ring and the whole process begins again. This all happens on a sub-femtosecond time scale dictated by the energy gap between the core level

and the satellite as discussed above. We shall return to this point below.

To breakdown the hole density $Q(\vec{r}, t)$ further into orbital contributions, we make use of the fact that it can be expressed as a sum over orbital densities [21] (see also the SM [25])

$$Q(\vec{r}, t) = \sum_p |\tilde{\varphi}_p(\vec{r}, t)|^2 \tilde{n}_p(t). \quad (2)$$

The orbitals $\tilde{\varphi}_p(\vec{r}, t)$ are denoted *natural charge orbitals* and depend on time, reflecting the fact that electron dynamics is a many-electron phenomenon. The weights $\tilde{n}_p(t)$ of each of these orbital densities are the *hole-occupation numbers* and are also time-dependent. Since each natural charge orbital is normalized to unity at any time t , their occupation numbers tell us how the dynamics proceeds on an orbital level.

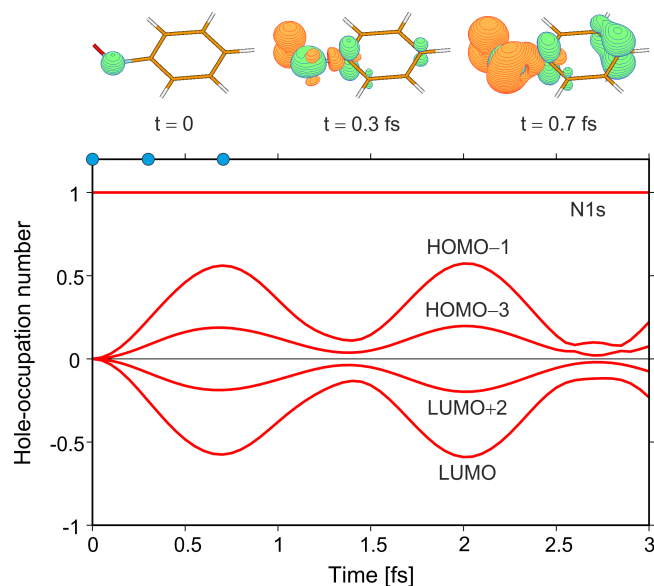


FIG. 4. (Color online) The dominating hole-occupation numbers of nitrosobenzene after the ionization of an N1s electron are shown as a function of time. In addition, snapshots of the three-dimensional hole density $Q(\vec{r}, t)$ at the times $t = 0$, 0.3, and 0.7 fs (marked with blue dots on the upper axis) are depicted at the top of the figure. The positive hole density is shown in green and the negative electron density is depicted in orange.

The time evolution of the largest hole-occupation numbers is shown in Fig. 4. It is nicely seen that at time $t = 0$ only one orbital contributes and this is the N1s orbital as expected. The respective occupation number stays unity at all times. This underlines again the statement that the core hole itself does not participate in the dynamics. As time proceeds, two pairs of orbitals acquire non-vanishing occupation numbers. We remind that positive occupation numbers mean that valence holes are created and negative numbers imply that electrons appear

at the respective orbitals. It is clearly seen that one pair is HOMO-1 and LUMO and the other HOMO-3 and LUMO+2 indicating charge migration from the first to the second one in each pair. This is in accord with the analysis of the ionization spectrum in Fig. 1 discussed above. Because of the presence of a single dominant satellite, the two contributing pairs of natural charge orbitals oscillate essentially in consonance; it is only after the second oscillation at about $t = 2.5$ fs that one can clearly see the influence of other weakly contributing satellites. If several intense satellites would appear in the ionization spectrum, this will show up in a more complex pattern of the time evolution of the occupation numbers.

Although the charge migration can be well understood from the hole density $Q(z, t)$ shown in Fig. 4, it is illuminating to see the evolution of the charge migration in three dimensions. For that purpose we depicted $Q(\vec{r}, t)$ on the top of Fig. 4 for three distinct values of time t marked with blue dots on the upper axis. At time $t = 0$ the core hole is created on the nitrogen atom. Already after 300 as, valence π electron density has migrated from essentially only two carbon atoms of the phenyl ring to the vicinity of the nitrogen atom. After only 700 as, about 0.7 electrons have migrated from the ring to this vicinity. This time span is consistent with the energy gap between the core level and the dominant satellite in the ionization spectrum in Fig. 1.

We may conclude that intense charge migration of valence electrons can in general take place triggered by ionization of a core electron well within the lifetime span of the core hole which decays rather fast by the Auger effect. In the case of an N1s hole, the lifetime is known to be about 6 fs [30]. Our accurate calculations on nitrosobenzene which also reproduce well the ionization spectrum show that the charge migration is completed on the substantially shorter time scale of 700 as. This implies that this interesting charge migration from the phenyl ring to the vicinity of the nitrogen atom should be, in principle, measurable much before the core hole state has decayed. Moreover, several oscillations of the migration should be detectable as well. Since time-resolved measurements are desirable and the time scale is short, such measurements are a great challenge to attosecond techniques. Substantial advances have been achieved in this direction. If we envisage pump-probe experiments with attosecond pulses only, suitable probe pulses are available already [31], as the probe pulse is needed to study the valence shell and thus does not require particularly high photon energies. The pump pulse requires, however, energies above the ionization energy of the core electron in question. In the case of the nitrogen atom, above 400 eV (see also Fig. 1). It is encouraging that attosecond pulses with even much higher photon energies have been reported [32]. Attosecond transient absorption spectroscopy [33] appears as a promising technique to trace the ultrafast dynamics initiated by the core ionization of the molecule.

Financial support by DFG (under QUTIF Priority Programme) and by US ARO (under grant No W911NF-14-1-0383) is gratefully acknowledged.

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