Migration of holes: Formalism, mechanisms, and illustrative applications

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A hole created in a system, for instance by ionization, can migrate through the system solely driven by electron correlation. The theory describing this migration is derived and cast into a form amenable to *ab initio* calculations. Three different basic mechanisms of hole migration are presented and analyzed. The results of *ab initio* calculations on hole migration in realistic systems are discussed. In all cases studied the migration is ultrafast. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1540618]

I. INTRODUCTION

Charge transfer is a fundamental process in nature and has been subject to numerous scientific investigations. The term "charge transfer" stands for many different phenomena and generally describes the flow of electronic charge along extended chain molecules ("molecular wires") or between different molecules. A classic example of charge transfer in nature is photosynthesis.[1–3] In most charge transfer systems in nature an electron is transported from a donor to an acceptor in large molecules or proteins. In molecular electronics charge transfer is used for the storage and disposal of energy in large molecules.[4–6]

It is assumed that nuclear dynamics plays an important role in the course of charge transfer in molecular systems, in particular, that the transfer occurs via non-adiabatic couplings between nuclear and electronic dynamics.[6] In some descriptions of the phenomenon, a simple one-particle hopping mechanism is suggested.[7,8]

In contrast to the above-mentioned descriptions based on nuclear dynamics, we show here that charge transfer can be mediated solely by electron correlation. To distinguish our mechanism from the conventional ones it is referred to as *static geometry charge migration* or briefly *charge migration*. The migration of a (initially localized) charge is already active in a molecule at frozen nuclear geometry. In this work, we consider a charge prepared by ionizing the molecule, i.e., we investigate the propagation of a hole charge. These investigations are motivated by the availability of careful measurements by Weinkauf *et al.*[9,10] in which, after a localized ionization on one specific site of a peptide chain, the molecule fragmented rapidly at a remote site of the chain. The authors proposed that a fast electronic transfer mechanism is responsible for transporting the hole charge to the latter site of the molecule.

First *ab initio* investigations[11] based on calculations using the one-particle Green's function demonstrated that a pure electronic mechanism of charge migration is, in fact, possible. In that work, an *ultrafast* decay of the autocorrelation function of an initially generated hole in a molecule was obtained, thus establishing charge migration mediated solely by electron correlation. In the ultrashort time during which the charge migration takes place, nuclear motion does not play an important role and can therefore be neglected in a first step. The calculations in Ref. 11 also gave evidence of a directional charge migration from one end to the other end of the molecule. The important role of electron correlation is further supported by model calculations on peptides.[12] In these interesting calculations, each amino acid is described by one orbital within an extended Hubbard model Hamiltonian.

In the present work the electron-correlation-based theory of Ref. 11 is deepened to get precise information on the direction of the charge migration. The formulas deduced in the following are general and can be used in standard *ab initio* methods. In Sec. II the basic theory for the description of the time-dependent hole density of an initially created hole in a molecule is derived. Then, in Sec. III, a perturbation theoretical analysis is performed to obtain information about the important terms in the relevant formulas. In the fourth section several basic mechanisms of charge migration are described and analyzed, and related to the appearance of the ionization spectra of the corresponding systems. Numerical *ab initio* examples for these mechanisms in realistic systems are presented and briefly discussed in Sec. V. The results are summarized in Sec. VI.

II. THEORY

A. Derivation of basic equations

In this work we investigate charge migration following the removal of an electron from a neutral system, i.e., in the cation obtained by ionizing the neutral system. It should be noticed, however, that the terms neutral and cation are used only for the ease of discussion. The formalism discussed below also holds if the underlying system is not neutral, e.g., if the target system is an anion and the charge migration described takes place in the neutral product obtained by ionization. First of all, for the charge migration in a molecule to occur, we need an initially prepared nonstationary state. To be independent from any experimental conditions, this state

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is prepared by the sudden removal[13] of an electron from the neutral molecule in its ground state $|\Psi_0\rangle$. The cationic state $|\Phi_i\rangle$ prepared in this way is not an eigenstate of the system. Nonstationary behavior, due to electron correlation effects, will take place. If the resulting electronic motion is very fast (*ultrafast*), as preliminary calculations[11] indeed indicated in this case, the charge can arrive at its final destination before nuclear dynamics comes into play. Therefore, nuclear dynamics can be neglected in a first step. For this reason the present analysis is performed at fixed coordinates of the nuclei, i.e., only electronic motion will be taken into account in our calculations. Of course, after a sufficiently long time nuclear dynamics will also play an important role, but the migration driven by electron correlation is generally much faster. We would like to mention that the sudden removal of an electron is realized by ionizing the system with a high-energy photon or with a light pulse of very short duration. Since the present formalism is explicitly time dependent, it can be generalized to account for other modes of preparing the cation.

The density of a hole resulting from the ionization of a molecule in the ground state $|\Psi_0\rangle$ reads

$$Q(\vec{r},t) := \underbrace{\langle \Psi_0|\hat{\rho}(\vec{r},t)|\Psi_0\rangle}_{\rho_0(\vec{r})} - \underbrace{\langle \Phi_i|\hat{\rho}(\vec{r},t)|\Phi_i\rangle}_{\rho_i(\vec{r},t)}, \quad (1)$$

where $\hat{\rho}$ is the usual diagonal (local) density operator and $|\Phi_i\rangle$ is the generated initial cationic state. $Q(\vec{r},t)$ describes the density of the hole, or briefly *hole density*, at position $\vec{r}$ and time t. It is merely given as the difference between the density ρ_0 in the ground state of the neutral system and the density ρ_i in the produced cation. Since $|\Psi_0\rangle$ is the exact electronic ground state of the neutral molecule, the density ρ_0 is time independent. The second term on the right-hand side (rhs) of Eq. (1) is, of course, time-dependent, because the initial state $|\Phi_i\rangle$ is not an eigenstate of the cation. Consequently, migration of the hole density Q can take place. Since $Q(\vec{r},t)$ describes the difference in densities of a system with n particles and one having $n-1$ particles, this basic quantity fulfills the normalization condition

$$\int d\vec{r}\, Q(\vec{r},t) = 1 \quad (2)$$

at all times t.

To evaluate the hole density we insert the unit operator $\sum_I |I\rangle\langle I|$ into Eq. (1), where $\{|I\rangle\}$ is a complete set of stationary eigenstates of the cation. Using the time evolution of the density operator, the cationic density ρ_i takes on the following appearance

$$\rho_i(\vec{r},t) = \sum_{I,J} \langle \Phi_i|I\rangle\langle I|e^{iHt}\hat{\rho}(\vec{r},0)e^{-iHt}|J\rangle\langle J|\Phi_i\rangle$$

$$= \sum_{I,J} x_I^* \rho_{IJ}(\vec{r}) x_J e^{-i(E_J-E_I)t}. \quad (3)$$

Here, E_I is the *ionization energy* corresponding to the state $|I\rangle$ and $x_I = \langle \Phi_i|I\rangle$ is its *transition amplitude* with respect to

the initial (cationic) state $|\Phi_i\rangle$. $\rho_{IJ}(\vec{r}) = \langle I|\hat{\rho}(\vec{r},0)|J\rangle$ is the charge density matrix element between the states $|I\rangle$ and $|J\rangle$. Without loss of generality, one can assume the quantities x_I, ρ_{IJ} to be real and $\rho_i(\vec{r},t)$ then reads

$$\rho_i(\vec{r},t) = \langle \Phi_i|\hat{\rho}(\vec{r},0)|\Phi_i\rangle$$

$$- \sum_{I,J} x_I \rho_{IJ}(\vec{r}) x_J [1 - \cos((E_I - E_J)t)]$$

$$= \rho_i(\vec{r},0) - \Delta\rho(\vec{r},t). \quad (4)$$

Overall, the hole density is seen to consist of three parts,

$$Q(\vec{r},t) = \rho_0(\vec{r}) - \rho_i(\vec{r},0) + \Delta\rho(\vec{r},t). \quad (5)$$

The first two terms are time-independent and, since $\Delta\rho(\vec{r},0) = 0$, they describe the density of the initially created hole at $t=0$,

$$Q(\vec{r},0) = \rho_0(\vec{r}) - \rho_i(\vec{r},0). \quad (6)$$

The last term $\Delta\rho(\vec{r},t)$ is time-dependent and describes the migration of the charge driven by electron correlation. As can be seen in Eq. (4), its time dependence for short times is simple to obtain and one immediately finds $Q(\vec{r},t) - Q(\vec{r},0) \sim t^2$.

To proceed, we represent the density operator $\hat{\rho}(\vec{r},0) = \sum_{pq} \varphi_p^*(\vec{r})\varphi_q(\vec{r})a_p^+ a_q$ in a one-particle orbital basis of the molecule $\{\varphi_p\}$, where the a_p^+ and a_q are the corresponding electron creation and annihilation operators.[14] Using this representation, the three terms contributing to the hole density in Eq. (5) can be explicitly expressed as

$$\rho_0(\vec{r}) = \sum_p |\varphi_p|^2 n_p,$$

$$\rho_i(\vec{r},0) = \sum_{p,q} \varphi_p^* \varphi_q \langle \Phi_i|a_p^+ a_q|\Phi_i\rangle, \quad (7)$$

$$\Delta\rho(\vec{r},t) = \sum_{p,q} \varphi_p^* \varphi_q \sum_{I,J} x_I \langle I|a_p^+ a_q|J\rangle x_J$$

$$\times [1 - \cos((E_I - E_J)t)].$$

Note that the structure of $\rho_0(\vec{r})$ above implies that either orbitals of density functional theory or so-called natural orbitals that diagonalize the density are used.[15–17] In the former case, $n_p = 1$ if φ_p is occupied in the ground state and $n_p = 0$ otherwise, while in the latter case the n_p are noninteger numbers. In a general orbital basis, $\rho_0(\vec{r})$ possesses the usual bilinear structure similar to ρ_i above. Since all terms in Eq. (7) are bilinear in the orbitals, we can obviously collect all the coefficients, thus defining a Hermitian hole density matrix $\mathbf{N}(t)$ with elements N_{pq}, and obtain

$$Q(\vec{r},t) = \sum_{p,q} \varphi_p^*(\vec{r})\varphi_q(\vec{r}) N_{pq}(t). \quad (8)$$

The above equation explicitly reveals the density character of Q. The migrating hole charge is described by a time-dependent matrix $\mathbf{N}(t)$ in the time-independent natural orbital basis $\{\varphi_p\}$.

Diagonalization of the matrix $\mathbf{N}(t)$ for fixed points in time t leads to

$$Q(\vec{r},t)=\sum_p |\widetilde{\varphi}_p(\vec{r},t)|^2 \widetilde{n}_p(t), \qquad (9)$$

where both the resulting eigenvalues $\{\widetilde{n}_p(t)\}$ and the orthonormal eigenfunctions $\{\widetilde{\varphi}_p(\vec{r},t)\}$ depend on time. Clearly, the time dependence of the eigenpairs results from the time-dependence of the matrix $\mathbf{N}(t)$. In the following the eigenfunctions $\{\widetilde{\varphi}_p(\vec{r},t)\}$ will be called *natural charge orbitals* and the corresponding $\{\widetilde{n}_p(t)\}$ are their *hole occupation numbers*. Because of the conservation of hole charge, see Eq. (2), the hole occupation numbers fulfill the relation

$$\sum_p \widetilde{n}_p(t)=1. \qquad (10)$$

The eigenvalues $\{\widetilde{n}_p(t)\}$ should not be confused with the common $\{n_p\}$ introduced above for the ground state [see text below Eq. (7)]. $\widetilde{n}_p(t)$ tells us which part of the charge of the created hole is in the natural charge orbital $\widetilde{\varphi}_p(\vec{r},t)$ at time t.

The density of the initially created hole, i.e., at $t=0$, becomes particularly simple if the ionization of the neutral system is described by the removal of the electron out of a specific molecular orbital φ_i. This implies that $\widetilde{n}_i(t=0)=1$ and all other $\widetilde{n}_p(t=0)$ vanish. Consequently,

$$Q(\vec{r},0)=|\varphi_i(\vec{r})|^2 \qquad (11)$$

and the matrix $\mathbf{N}(t=0)$ is diagonal and has only a single nonvanishing element $N_{ii}(t=0)=1$, see Eq. (8). At time $t=0$ the natural charge orbitals can be chosen to be identical to the orbitals used, $\widetilde{\varphi}_p(\vec{r},t=0)=\varphi_p(\vec{r})$. Of course, all these quantities vary as time proceeds.

B. The hole density

To calculate the time-dependent part $\Delta\rho(\vec{r},t)=\sum_{pq}\varphi_p^*\varphi_q\Delta N_{pq}(t)$ of the hole density introduced in Eq. (5), the time-dependent part of the hole density matrix $\Delta\mathbf{N}(t)=\mathbf{N}(t)-\mathbf{N}(0)$ must be evaluated,

$$\Delta N_{pq}(t)=N_{pq}(t)-N_{pq}(0)$$

$$=\sum_{I,J} x_I\langle I|a_p^+ a_q|J\rangle x_J[1-\cos((E_I-E_J)t)]. \qquad (12)$$

Since the exact cationic states and energies are not at our disposal, appropriate approximations for these quantities have to be used. Let us start our discussion with a simple approximation and then move forward to a more realistic one. If the ground state of the neutral molecule is calculated using the Hartree–Fock method, an obvious approximation for the cationic states are the one-hole (1h) configurations of the Hartree–Fock ground state $|\Phi_0\rangle$. In this case, all cationic states are described by removing one electron from an occupied orbital using the annihilation operator a_j, i.e., $a_j|\Phi_0\rangle$ for all occupied orbitals φ_j. As long as Koopmans' theorem[15] is valid, the ionization energies of these states are

just the Hartree–Fock orbital energies ε_j. Inserting these states into $\langle I|a_p^+ a_q|J\rangle$ and identifying the indices I with the indices of the occupied orbitals of the neutral molecule leads to

$$\langle I|a_p^+ a_q|J\rangle=n_p\delta_{pq}\delta_{IJ}-n_p n_q\delta_{Iq}\delta_{Jp}. \qquad (13)$$

By substituting Eq. (13) into Eq. (12) one immediately finds that the first term on the rhs of Eq. (13) will not contribute to the time-dependent hole density matrix $\Delta\mathbf{N}(t)$, because the factor $[1-\cos((E_I-E_J)t)]$ is always zero for $|I\rangle=|J\rangle$. The remaining second term leads to the hole density matrix

$$\Delta N_{pq}(t)=-x_p x_q[1-\cos((\varepsilon_p-\varepsilon_q)t)]n_p n_q. \qquad (14)$$

Because of the factor $n_p n_q$ in Eq. (14), only occupied orbitals of the neutral molecule are involved in a possible charge migration. However, for a charge migration to occur, the involved orbitals φ_p need to have nonvanishing transition amplitudes $x_p=\langle\Phi_i|a_p\Phi_0\rangle$ mediating between the initial cationic state $|\Phi_i\rangle$ and the ground state $|\Phi_0\rangle$.

According to the preceding section we prepare the initial cationic state by the sudden ionization of the neutral molecule in its ground state. In the Hartree–Fock and Koopmans approximation this obviously implies that the initial cationic state is described by the annihilation of an electron associated with a specific orbital φ_i, i.e., $|\Phi_i\rangle=a_i|\Phi_0\rangle$. Then, the transition amplitudes $x_p=\langle\Phi_i|a_p\Phi_0\rangle=\delta_{ip}$ and Eq. (14) reduces to

$$\Delta\mathbf{N}(t)=0. \qquad (15)$$

The combined Hartree–Fock and Koopmans approximation defines the situation where electron correlation and electron relaxation are exactly absent.[15] Consequently, Eq. (15) leads to the straightforward but relevant statement that *in the absence of electron correlation and relaxation the hole charge will stay in the orbital in which it has been initially created and no charge migration will take place.*[11]

Of course, one could use some other one-particle theory and assume that the initial cationic state is differently prepared, for instance, by removing the electron from a fragment of the molecular system under investigation. Then Eq. (14) is still valid and fast oscillations between the orbitals will be found due to the values $x_p\neq\delta_{ip}$ used. These oscillations, however, have nothing in common with the charge migration discussed in this work which is driven by electron correlation and relaxation beyond the simple one-particle theory. As is well known, the combined Hartree–Fock and Koopmans approximation provides the best one-particle theory to describe the ionization, since many-body corrections to the ionization energies[15] and to the transition amplitudes[13] begin to contribute at a higher order of perturbation theory than with other choices of approximations. The Hartree–Fock and Koopmans approximation is thus a natural starting point, and a relevant point of reference where no migration takes place.

To obtain more precise results one has to go beyond the Hartree-Fock approximation for the ionic states $|I\rangle$, $|J\rangle$. One possibility is to expand the wavefunctions in electronic configurations as traditionally done in configuration interaction

(CI) calculations.[15] Using the Hartree–Fock based configurations, the CI expansion of a cationic state $|I\rangle$ reads

$$|I\rangle = \sum_j c_j^{(I)} a_j |\Phi_0\rangle + \sum_{r,k<l} c_{rkl}^{(I)} a_r^+ a_k a_l |\Phi_0\rangle + \cdots . \tag{16}$$

Here and in the following the indices $r, s, \ldots$ refer to orbitals unoccupied in the Hartree–Fock ground state $|\Phi_0\rangle$ of the neutral molecule and the indices $j, k, \ldots$ denote occupied orbitals in this state. p and q refer to general indices. Accordingly, the electronic configurations $a_j |\Phi_0\rangle$ are the so-called one-hole (1h) configurations where one electron has been removed from the neutral ground state $|\Phi_0\rangle$, and $a_r^+ a_k a_l |\Phi_0\rangle$ are two-hole one-particle (2h1p) configurations where one electron has been removed and another one excited into an unoccupied orbital of $|\Phi_0\rangle$. The quantities $c_j^{(I)}$ and $c_{rkl}^{(I)}$ are the corresponding CI coefficients.

Since the exact states $\{|I\rangle\}$ are eigenstates of the cationic Schrödinger equation, they can be chosen to be orthonormal, $\langle I|J\rangle = \delta_{IJ}$. This leads to the following orthonormality condition for the CI coefficients:

$$\delta_{IJ} = \langle I|J\rangle = \sum_j c_j^{(I)} c_j^{(J)} + \frac{1}{2} \sum_{rkl} c_{r[kl]}^{(I)} c_{r[kl]}^{(J)} + \cdots , \tag{17}$$

where $\langle \Phi_0|\Phi_0\rangle = 1$ has been used and $c_{r[kl]}^{(I)} = c_{rkl}^{(I)}$ for $k<l$, $c_{r[kl]}^{(I)} = -c_{rlk}^{(I)}$ for $k>l$ and zero otherwise. Inserting the CI expansion (16) into $\langle I|a_p^+ a_q|J\rangle$ and using the above orthonormality condition, one obtains

$$\langle I|a_p^+ a_q|J\rangle = n_p \delta_{pq} \delta_{IJ} - n_p n_q c_q^{(I)} c_p^{(J)}$$

$$+ n_p \bar{n}_q \sum_j c_j^{(I)} c_{q[pj]}^{(J)} + \bar{n}_p n_q \sum_j c_{p[qj]}^{(I)} c_j^{(J)}$$

$$+ \frac{1}{2} \bar{n}_p \bar{n}_q \sum_{jk} c_{p[jk]}^{(I)} c_{q[jk]}^{(J)}$$

$$- n_p n_q \sum_{rj} c_{r[qj]}^{(I)} c_{r[pj]}^{(J)} + \cdots . \tag{18}$$

The first term on the rhs of this equation does not contribute to $\Delta\rho(\vec{r},t)$ because of the factor δ_{IJ}, see Eq. (12).

Substituting the result (18) into the expression (12) for the time-dependent part of the hole density matrix leads to

$$\Delta N_{pq}(t) = \sum_{I,J} x_I x_J [1 - \cos((E_I - E_J)t)] \sum_{s=1}^4 A_{s,pq}^{(I,J)}, \tag{19}$$

where

$$A_{1,pq}^{(I,J)} = -n_p n_q c_q^{(I)} c_p^{(J)}, \tag{20a}$$

$$A_{2,pq}^{(I,J)} = n_p \bar{n}_q \sum_j c_j^{(I)} c_{q[pj]}^{(J)} + (p,I \leftrightarrow q,J), \tag{20b}$$

$$A_{3,pq}^{(I,J)} = \frac{1}{2} \bar{n}_p \bar{n}_q \sum_{jk} c_{p[jk]}^{(I)} c_{q[jk]}^{(J)}, \tag{20c}$$

$$A_{4,pq}^{(I,J)} = -n_p n_q \sum_{rj} c_{r[qj]}^{(I)} c_{r[pj]}^{(J)}, \tag{20d}$$

are the four different contributions arising from the 1h and 2h1p contributions to the wavefunctions. These are expected

to be the leading contributions but higher excited configurations, indicated in Eqs. (16)–(18) by "$\cdots$", may also contribute.

The time-dependent part of the hole density matrix can now be evaluated as a sum over time-independent matrices $\mathbf{A}_s^{(I,J)}$, $s=1,\ldots,4$, weighted by time-dependent coefficients. It is immediately clear that the matrices $\mathbf{A}_1^{(I,J)}$ and $\mathbf{A}_4^{(I,J)}$ only contribute if p and q are hole indices, i.e. if these are indices of occupied orbitals in the neutral molecule. The matrix $\mathbf{A}_3^{(I,J)}$ just contributes if both indices p and q are unoccupied orbitals (particle indices) and $\mathbf{A}_2^{(I,J)}$ contributes only if one of the two indices is a hole index and the other one is a particle index. Thus, Eq. (19) can be rewritten in a block matrix notation where the hole/hole indices are in the upper left block of the matrix and the particle/particle indices are in its lower right block,

$$\Delta\mathbf{N}(t) = \sum_{I,J} x_I x_J [1 - \cos((E_I - E_J)t)] \mathbf{A}^{(I,J)}, \tag{21}$$

where

$$\mathbf{A}^{(I,J)} = \begin{pmatrix} \mathbf{A}_1^{(I,J)} + \mathbf{A}_4^{(I,J)} & \mathbf{A}_2^{(I,J)} \\ (\mathbf{A}_2^{(I,J)})^\dagger & \mathbf{A}_3^{(I,J)} \end{pmatrix} . \tag{22}$$

One immediately recognizes that the matrix $\mathbf{N}(t)$ is Hermitian. An exchange of the indices $p \leftrightarrow q$ in the parts $\mathbf{A}_1^{(I,J)}$, $\mathbf{A}_3^{(I,J)}$, and $\mathbf{A}_4^{(I,J)}$ is identical to an exchange of the indices $I \leftrightarrow J$ and all other factors appearing in the summation are symmetric in I and J.

Equation (19) is easily seen to be a generalization of (14). In the Hartree–Fock approximation the 1h coefficients $c_p^{(I)}$ are replaced by δ_{pI} and the 2h1p coefficients are all zero. Because of the nonvanishing 2h1p coefficients in Eq. (19), virtual orbitals of the neutral molecule are involved in the charge migration. In contrast to the one-particle theory leading to Eq. (14) where only the occupied orbitals appear, a formally infinite number of virtual orbitals are involved in the many-body theory (19) of the charge migration. The charge can now truly migrate through the system and not simply oscillate. Since actual numerical calculations on the computer are performed using finite basis sets, care must be taken to include a sufficiently large number of virtual orbitals to describe the charge migration correctly. The finite basis set used actually defines the time scale on which the computed migration is reliable. The larger the basis set, the longer is this time scale.

Because of the block matrix form of Eq. (21), it is possible to investigate each of the terms $\mathbf{A}_s^{(I,J)}$, $s=1,\ldots,4$ separately, what helps to understand the mechanisms involved in the charge migration. The initially generated hole is in the subspace of the occupied orbitals. It is "located" in the upper left block of the initial matrix $\mathbf{N}(0)$, i.e., $\mathbf{N}(0)$ possesses non-vanishing elements in the upper left block and is zero otherwise. If the $\mathbf{A}_2^{(I,J)}$ matrix vanishes, the diagonalization of $\mathbf{N}(t)$ boils down to two separate diagonalizations of the upper left and the lower right block. The occupied and virtual orbitals would be treated completely separately in this case and there would be no interaction between the initial hole and the virtual space. The $\mathbf{A}_2^{(I,J)}$ matrix couples between

occupied and virtual orbitals in $\mathbf{N}(t)$. In Sec. III the four different matrices $\mathbf{A}_s^{(I,J)}$, $s=1,\dots,4$ are analyzed by perturbation theory in the electron–electron interaction in order to gain a better understanding of the relevance of these matrices in describing the charge migration.

Molecular symmetry has some impact on the form of the matrices in Eq. (21). For simplicity, we assume that the molecule belongs to an Abelian symmetry point group. If the initial state $|\Phi_i\rangle$ is chosen to belong to an irreducible representation of the symmetry group, only states $|I\rangle$ and $|J\rangle$ which belong to the same irreducible representation contribute to the hole density. This reduction is a consequence of the transition amplitude products $x_I x_J$ in Eq. (21). By examining the matrices $\mathbf{A}_s^{(I,J)}$, $s=1,\dots,4$ one recognizes that the supermatrix $\mathbf{A}^{(I,J)}$ for any index pair (I,J) takes on a block diagonal form in the orbital indices p,q, where each block corresponds to one irreducible representation of the symmetry group used. Consequently, the hole density matrix $\mathbf{N}(t)$ also takes on the same block diagonal appearance. It has to be explicitly mentioned that the blocks themselves are not diagonal. If the initial hole is, for instance, in an orbital of σ symmetry, it is located in the σ block of the matrix $\mathbf{N}(t)$. This does not imply, however, that only this σ block has to be considered in the calculation. The hole in the σ orbital will influence the π orbitals due to the interaction of the 1h and 2h1p configurations. This can be seen from Eqs. (20). Since both I and J are of σ symmetry, both indices p and q of $\mathbf{A}_1^{(I,J)}$ belong to σ orbitals, but can both belong to π orbitals in the other $\mathbf{A}_s^{(I,J)}$ terms. In other words, the π block of $\Delta\mathbf{N}(t)$ is also relevant for the charge migration. This leads to $\pi\pi^*$ excitations during the charge migration, even though the initial state is a σ state.

In the above analysis the contributing cationic states have been expanded in a CI scheme. We would like to mention that essentially equivalent results are obtained if the formalism of Green's functions[14,18] is used. In particular, the one-particle Green's function method allows one to directly calculate ionization spectra.[19–23] These methods, combined with efficient block-Lanczos algorithms,[24] make the calculation of the ionization spectrum of larger molecules possible.[25] Specifically, we mention the ADC(n) method[26] which calculates the Green's function correctly up to nth order perturbation theory and relevant terms of the expansion are considered up to infinite order. The ADC method leads to cationic eigenstates of the form (16). Here, however, the states on the rhs are 1h and 2h1p excitations with respect to the *exact* ground state of the neutral molecule $|\Psi_0\rangle$, i.e., $a_j|\Psi_0\rangle, a_r^+ a_k a_l|\Psi_0\rangle$, and not with respect to a single determinantal wave function $|\Phi_0\rangle$. The equation obtained with this method for the charge density matrix is essentially equivalent to the above Eq. (21). One only has to replace the CI coefficients in the definitions (20) by the corresponding ADC ones.

C. The direct ionization case

Our goal is to demonstrate that charge migration can be driven by electron correlation alone. Therefore, it is particularly useful to choose the initial state in such a way that in

absence of correlation no charge migration is possible. This can be done with an initial state $|\Phi_i\rangle\sim a_i|\Psi_0\rangle$ resulting from direct ionization out of a specific orbital φ_i. The experimental realization of direct ionization can, for instance, be realized by single photon excitation with a highly energetic photon (single-channel sudden approximation),[13] but other ways can also be anticipated. The following investigations assume a direct ionized initial state. As has been discussed in the preceding section, no charge migration will take place if electron correlation is neglected, see Eq. (15). Correlation is needed to trigger dynamics of a hole charge generated by direct ionization.

To make the discussion as transparent as possible, we assume $|\Psi_0\rangle\approx|\Phi_0\rangle$ for the ground state. Then, the initial density of the cation reduces to $\rho_i(\vec{r},0)=\Sigma_{p\neq i}|\varphi_p|^2 n_p$ and the initial hole density matrix $\mathbf{N}(t=0)$ takes on the trivial diagonal form $N_{pq}(0)=\delta_{ip}\delta_{iq}$. The natural charge orbitals at time $t=0$, which are obtained by the diagonalization of $\mathbf{N}(t=0)$, can be chosen to coincide with the Hartree–Fock orbitals of the neutral molecule. As expected, the initial hole charge density is described by $Q(\vec{r},0)=|\varphi_i(\vec{r})|^2$. For times $t>0$ the transition amplitudes $x_I=\langle\Phi_i|I\rangle$ play an important role, see (19). In the direct ionization case the transition amplitudes are described by $x_I=\langle a_i\Phi_0|I\rangle$. Inspecting the expansion (16) used for the cationic states, one finds $x_I=c_i^{(I)}$. The time-dependent part of the hole density matrix in the case of direct ionization now reads

$$\Delta\mathbf{N}(t)=\sum_{I,J} c_i^{(I)} c_i^{(J)}[1-\cos((E_I-E_J)t)]\,\mathbf{A}^{(I,J)}, \qquad (23)$$

where the matrix $\mathbf{A}^{(I,J)}$ is given in Eq. (22) and is discussed in the preceding section. It is seen that all quantities appearing in Eq. (23) follow immediately from a CI (or ADC) calculation of the cationic states of the molecule. Only the ionization energies E_I and the expansion coefficients $c_j^{(I)}, c_{r[kl]}^{(I)}$ are needed to describe the charge migration using Eq. (23).

III. PERTURBATION THEORETICAL ANALYSIS OF THE HOLE DENSITY

In this section we analyze the hole density $Q(\vec{r},t)$ by means of perturbation theory. Once an orbital basis $\{\varphi_p\}$ is specified, this basic quantity is directly connected with the hole density matrix $\mathbf{N}(t)=\mathbf{N}(0)+\Delta\mathbf{N}(t)$, see Eq. (8). In the following we choose the Hartree–Fock orbitals of the neutral molecule as our orbital basis. To have a concrete initial state and for the reasons already mentioned in Sec. II C, we choose the initial hole $|\Phi_i\rangle=a_i|\Phi_0\rangle$ created by direct ionization. This results in the hole density matrix given in Eq. (23) as the starting point of our perturbation analysis. Apart from the ionization energies, all quantities appearing in this equation can be expressed in terms of the coefficients of the CI expansion (16). These coefficients have to be analyzed in terms of the interaction between the Hartree–Fock particles.

The perturbation analysis depends on the nature of the underlying cationic state $|I\rangle$. At relatively low ionization energies it is generally possible to distinguish between main and satellite states, i.e., states which originate from a 1h con-

figuration and states which originate from higher order configurations, e.g., 2h1p, 3h2p, ... We will only take the first two terms of the expansion (16) into account and hence, in our case, satellite states are restricted to those which originate from 2h1p configurations. At higher ionization energies, a breakdown of the molecular orbital picture may occur[13] and the distinction between main and satellite states may not be possible. In such cases, perturbation theory fails. But even in these cases, perturbation theory can be used to assess the importance of the different terms contributing to the hole density and its migration.

The leading orders of the coefficients of the CI expansion (16) of the cationic states for a main state are

$$c_j^{(M)} = \delta_{jM} + \mathcal{O}(2),$$ (24a)

$$c_{rkl}^{(M)} = \mathcal{O}(1),$$ (24b)

and for a satellite state

$$c_j^{(S)} = \mathcal{O}(1),$$ (25a)

$$c_{rkl}^{(S)} = \delta_{(rkl)S} + \mathcal{O}(1).$$ (25b)

$\mathcal{O}(n)$ indicates a term of nth order in the interaction. It has to be pointed out that, as a consequence of Koopmans theorem,[15] the first order contribution to the coefficient $c_j^{(M)}$ vanishes. This will have impact on the leading orders of the contributions of the matrices $A_s^{(I,J)}$, $s = 1, \ldots, 4$ appearing in (23), depending on the nature of the states $|I\rangle$ and $|J\rangle$. Therefore, it is necessary to distinguish between the cases where the states $|I\rangle$ and $|J\rangle$ are both main states, both satellite states, or one of them is a main state and the other one a satellite state.

The terms $c_i^{(I)} c_i^{(J)}$ appearing in (23) as prefactors in the summation over $|I\rangle$ and $|J\rangle$ depend on the index of the initially ionized orbital φ_i and not on the $\Delta \mathbf{N}(t)$ matrix indices p, q. One easily sees from Eqs. (24) and (25) that these prefactors are of second order in perturbation theory in case where $|I\rangle$ and $|J\rangle$ are satellite states (sat/sat) and of first order if one of the states is a main state and the other one a satellite state (main/sat). If both I and J are main states (main/main) the prefactor is $c_i^{(I)} c_i^{(J)} = \delta_{IJ} \delta_{Ii} + \mathcal{O}(2)$, but since $(1 - \cos((E_I - E_J)t))$ is zero for $I = J$, the zeroth order part does not contribute to the matrix elements. Therefore, the main/main terms in the matrix summation of Eq. (23) are at least of second order.

Using these results and the expressions (20) for the matrices $A_s^{(I,J)}$, $s = 1, \ldots, 4$, the leading order contributions of the different terms in formula (23) can be obtained. Since the leading orders depend on the different type $s = 1, \ldots, 4$ of the matrices $A_s^{(I,J)}$ and on the nature of the states $|I\rangle$ and $|J\rangle$, it is useful to collect them in a table. In Table I the complete list of the leading order contributions of the matrices $A_s^{(I,J)}$, $s = 1, \ldots, 4$, multiplied by the prefactor $c_i^{(I)} c_i^{(J)}$, is shown.

We recall that the matrices $A_1^{(I,J)}$, $A_4^{(I,J)}$ are located in the upper left block and $A_3^{(I,J)}$ in the lower right block of $\Delta \mathbf{N}(t)$ in Eq. (22), thus involving only the occupied and virtual orbitals of the neutral molecule, respectively. $A_2^{(I,J)}$ is responsible for the coupling between the occupied and the

TABLE I. Leading order contributions to $\Delta \mathbf{N}(t)$. The columns refer to the different submatrices $c_i^{(I)} c_i^{(J)} A_s^{(I,J)}$, $s = 1, \ldots, 4$ and the rows to the different configurations of the states $|I\rangle$ and $|J\rangle$. main/main stands for both states being main states, sat/sat for both being satellite states. main/sat means contributions where one of the states is a main state and the other one is a satellite state.

I/J	$A_1^{(I,J)}$	$A_2^{(I,J)}$	$A_3^{(I,J)}$	$A_4^{(I,j)}$
main/main	2	3	4	4
main/sat	2	1	2	2
sat/sat	4	3	2	2

virtual orbitals in $\Delta \mathbf{N}(t)$. Inspection of Table I shows that the time dependence of the matrix elements in $\Delta \mathbf{N}(t)$ is dominated by terms which include satellite states. If no satellite states are taken into account, only the first row of Table I would determine the leading orders of $\Delta \mathbf{N}(t)$. In this case, the matrix elements between occupied orbitals would have a leading order of $\mathcal{O}(2)$ and the ones between virtual orbitals have a leading order of $\mathcal{O}(4)$ in $\Delta \mathbf{N}(t)$. Since the time dependence of the charge migration is strictly related to $\Delta \mathbf{N}(t)$, one can expect that the hole occupation in the subspace of the virtual orbitals would change less in time than in the subspace of the occupied orbitals. The coupling between the occupied and the virtual orbitals would start at a relatively high order ($\mathcal{O}(3)$). Including satellite states in the computation, all matrix elements within the subspace of occupied orbitals and within the one of virtual orbitals change in time with a leading order of $\mathcal{O}(2)$. Most important is the fact that the coupling between occupied and virtual states in $\Delta \mathbf{N}(t)$, mediated by $A_2^{(I,J)}$, is of $\mathcal{O}(1)$. As mentioned earlier in Sec. II B, the direct coupling of the occupied orbitals to the enormous number of virtual orbitals is needed for an efficient charge migration to take place.

In a block matrix notation, like the one used in Eqs. (23) and (22), the results of Table I can be transferred to $\Delta \mathbf{N}(t)$ giving

$$\Delta \mathbf{N}(t) = \left(\begin{array}{cc|c} \mathcal{O}(2) & \mathcal{O}(2) & \mathcal{O}(2) \\ \mathcal{O}(2) & \mathcal{O}(2) & \mathcal{O}(1) \\ \hline \mathcal{O}(2) & \mathcal{O}(1) & \mathcal{O}(2) \end{array} \right),$$ (26)

where the occupied orbitals of the neutral molecule are located in the upper left block of the matrix and the lower right block refers to the virtual orbitals. Since some elements $\Delta N_{ip}(t)$, where i is the index of the initially ionized orbital, respond differently to perturbations, these elements are shown explicitly in Eq. (26). They occupy the first row and column in the matrix $\Delta \mathbf{N}$. It is seen that the leading terms of i to all other orbitals are of second order.

In the direct ionization case considered, i.e., when $\mathbf{N}(0)$ has the form $N_{pq}(0) = \delta_{pi} \delta_{qi}$, the zeroth order terms of all matrix elements of $\mathbf{N}(t)$ vanish except for the element $N_{ii}(t)$. Therefore, it is not possible to use conventional matrix perturbation theory to diagonalize the hole density matrix $\mathbf{N}(t)$ and obtain the natural charge orbitals and the corresponding hole occupations. As seen in (26), the diagonal elements exhibit a higher leading order than some of the off-diagonal elements. The impact of the first order coupling

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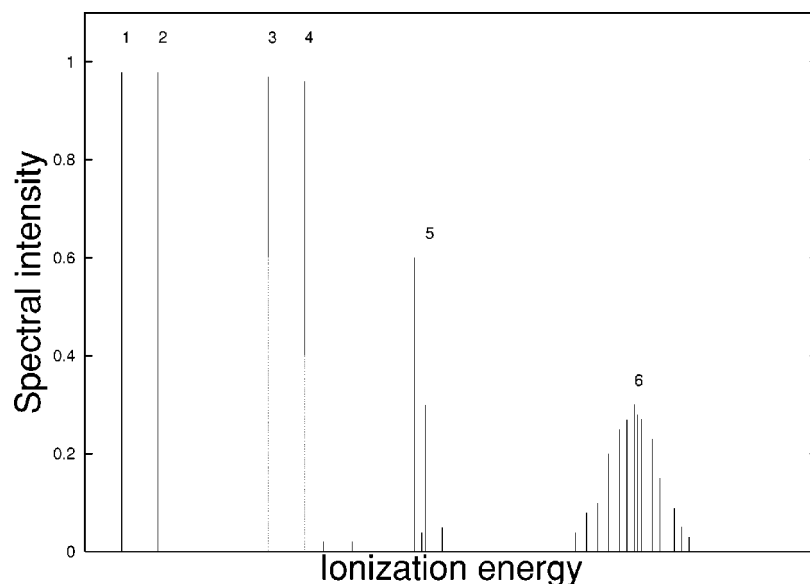
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FIG. 1. Schematic plot of a typical ionization spectrum of a molecule. Each vertical line shown is related to a final cationic state and is located at the corresponding ionization energy. At low energies, the outer valence lines appearing in the spectrum are dominated by a single 1h configuration (1,2) or by hole mixing (3,4). In the case of *hole mixing*, two (or more) lines in the spectrum are superpositions of two (or more) 1h configurations. At higher ionization energies, weak satellite lines originating from intensity losses of lines 1–4 may appear and valence ionizations may be accompanied by more intense individual satellites (5). Satellites appear because the 1h configuration is "spread" over several lines, due to interaction with 2h1p configurations. At high energies in the inner valence regime (6) this spreading is severe and a *breakdown of the molecular orbital picture* occurs, resulting in a quasicontinuum of lines.

between occupied and virtual orbitals is substantial. By diagonalizing $\mathbf{N}(t)$ it is seen that the first order contributions in the off-diagonal block in (26) lead to changes in first order of all hole occupation numbers except of $\tilde{n}_i(t)$.

IV. MECHANISMS OF CHARGE MIGRATION

The general case of charge migration driven by electron correlation is difficult to understand because many effects contribute. These make even a numerical calculation based on the above formulas cumbersome to analyze. For these reasons it is useful to concentrate on different cases where the charge migration is dominated by a single mechanism. We shall see that the specific mechanisms of charge migration considered in the following can be identified by the position and shape of the lines in the ionization spectrum. There is, in general, an intimate relationship between such spectra and charge migration. The knowledge and understanding of ionization spectra are helpful in identifying interesting cases of charge migration and in interpretating the findings. Since such spectra have been studied in detail while very little is known of charge migration, we briefly describe the appearance of a typical spectrum.

The ionization spectrum of a molecule consists of a series of vertical lines, where each line represents an eigenstate $|I\rangle$ of the cation. The energetic position of each line is given by the ionization energy E_I and the intensity of each line by its ionization cross section σ_I. Since the cross section depends on the experimental conditions, it is therefore convenient to find alternative quantities, which can be calculated entirely from the properties of the molecule under study. Such quantities will be considered in the following. The sudden ejection of an electron out of the orbital φ_i of a molecule in the ground state $|\Psi_0\rangle$ leads to the cationic nonstationary state $a_i|\Psi_0\rangle$. The overlap with the final ionic state $|I\rangle$ is given by the *transition amplitude* $x_I = \langle I|a_i\Psi_0\rangle$. It is obvious that the square $|x_I|^2$—the *spectroscopic factor*—is closely related to the cross section of the corresponding line in the ionization spectrum.[13]

In an independent-particle picture, the resulting cationic spectrum is very simple. For each occupied orbital φ_i there would be a line in the spectrum representing the ith cationic state with a spectroscopic factor equal to 1. Because of Koopmans' theorem[15] the energy of each line would be given by its orbital energy ε_i.

Because electrons are not independent particles, the interaction between them has to be taken into account. The exact cationic state can be expanded in a series of configurations which can be viewed as generalized excitations of the Hartree–Fock ground state of the neutral molecule, see Eq. (16). The first two terms in the series are the 1h excitations $a_j|\Phi_0\rangle$ and the 2h1p excitations $a_r^+ a_k a_l|\Phi_0\rangle$. If correlation effects are weak—and this is typically the case in the outer valence part of the spectrum—the molecular orbital picture of the ionization process outlined above remains approximately valid. The ionization spectrum is dominated by *main lines* which have large overlap with the 1h excitations. At somewhat higher energies in the ionization spectrum, weaker lines besides the main lines appear. These so called *satellite lines* have a small or moderate overlap with the 1h excitations. The cationic states of these lines are dominated by 2h1p excitations. Three kinds of satellite states can be distinguished in the spectrum:[13] *Relaxation satellites* where one of the two hole orbitals is identical to the hole orbital of the main line, *correlation satellites* where both hole orbitals differ from the hole orbital of the main line and satellites resulting from ground state correlation. At higher ionization energies—the inner valence region—the satellite lines acquire transition amplitudes similarly strong to those of the main lines and many of them appear in the spectrum. It is no longer possible to distinguish between main and satellite lines. This well-known phenomenon is called the *breakdown of the molecular orbital picture of ionization*.[13]

A schematic ionization spectrum is depicted in Fig. 1. In the outer valence region (lines 1–4) of the spectrum the molecular orbital picture remains valid. Each line has an intensity, i.e., spectroscopic factor, close to one and the corre-

sponding state is dominated by a single 1h configuration (lines 1,2), representing an ionization out of one specific molecular orbital, or by a few 1h configurations, a situation called *hole mixing*[27] (lines 3, 4). The energetic position of a line is approximately the orbital energy of the ionized orbital. In the case of hole mixing two (or more) states of the cation acquire relevant contributions from two (or more) 1h configurations. The holes are "mixed" in these ionization states. We will concentrate in the next section on the idealized case, where hole mixing involves two 1h configurations only, to make the analytical calculations transparent. At somewhat higher ionization energies, weak satellites originating from intensity losses of the outer valence ionization (lines 1–4) may appear.

In the low-energy inner valence region of the spectrum the ionization is accompanied by more intense individual satellites (lines 5). 2h1p configurations are close in energy to the 1h configuration and all these configurations can mix, i.e., the cationic states in the spectrum are superpositions of the 1h and 2h1p configurations. This leads to the appearance of satellite states. Typically, the two holes of the 2h1p configurations are located at outer valence orbitals. In Sec. IV B the special case of a main line accompanied by a single dominant satellite will be analyzed.

In the energetically higher region of the spectrum the phenomenon of the breakdown of the molecular orbital picture of ionization occurs. In this part of the ionization spectrum there are numerous 2h1p configurations which can overlap with the 1h configurations and it is no longer possible to distinguish between main and satellite states. The picture of single lines corresponding to 1h states is completely lost. The mixing of the 1h configurations with the many available 2h1p configurations can lead to a quasi-continuum of states which acquire intensity (lines 6). An idealized case of such a quasi-continuum is discussed in Sec. IV C.

A. Idealized case of hole mixing

Before treating the case of hole mixing, we briefly discuss the situation where the ionized state is well described by a single 1h configuration, i.e., $|I\rangle \approx |\Phi_i\rangle = a_i |\Phi_0\rangle$. The corresponding hole density matrix takes on the trivial form $N_{pq}(t) = \delta_{pi}\delta_{qi}$ and the hole density is simply given by $Q(\vec{r},t) = |\varphi_i(\vec{r})|^2$. Obviously, the ionization of this outer valence orbital $\varphi_i(\vec{r})$ does not lead to charge migration. The generated hole will not move through the molecule. Rather, it will stay in its initial position. Since the matrix $\mathbf{N}(t)$ is already diagonal, the natural charge orbitals can be identified with the orbitals φ_p of the neutral system.

The situation is more interesting if hole mixing appears. We discuss here the case of hole mixing of two states in the ionization spectrum which have comparable contributions of two 1h configurations $a_i |\Phi_0\rangle$ and $a_k |\Phi_0\rangle$ (lines 3, 4 in Fig. 1). In a CI expansion these states can be described as[27]

$$|I_{ik}\rangle = a|\Phi_i\rangle + b|\Phi_k\rangle + \dots ,$$

$$|I_{ki}\rangle = b|\Phi_i\rangle - a|\Phi_k\rangle + \dots . \tag{27}$$

In an idealized case of hole mixing all other contributions are

considered to be small enough and thus can be neglected, i.e., $a^2 + b^2 = 1$. For realistic examples, see Ref. 27. Under this assumption only the $A_1^{(I,J)}$ submatrix of Eqs. (22) and (23) contributes to the hole density matrix, giving rise to a 2×2-matrix $\mathbf{N}(t)$ in the basis (φ_i, φ_k). Here φ_i is the initially ionized orbital and φ_k is the other orbital involved in the hole mixing. This matrix reads

$$\mathbf{N}(t)$$
$$= \begin{pmatrix} 1 - 2(ab)^2(1 - \cos \omega t) & (a^2 - b^2)ab(1 - \cos \omega t) \\ (a^2 - b^2)ab(1 - \cos \omega t) & + 2(ab)^2(1 - \cos \omega t) \end{pmatrix}, \tag{28}$$

where ω is the difference between the ionization energies of the two lines in the spectrum, i.e., $\hbar\omega = E_{I_{ik}} - E_{I_{ki}}$. Diagonalization of this submatrix leads to the eigenvalues

$$\tilde{n}_{i/k}(t) = \tfrac{1}{2} \pm \tfrac{1}{2}\sqrt{1 - 4(ab)^2 \sin^2 \omega t}, \tag{29}$$

which are the hole occupations of the two resulting natural charge orbitals $\tilde{\varphi}_i(\vec{r},t)$ and $\tilde{\varphi}_k(\vec{r},t)$. As can be seen in Eq. (29), the hole is oscillating between the two natural charge orbitals. It has to be mentioned again that the hole occupations are the occupation numbers of the natural charge orbitals which differ at times $t \neq 0$ from the initial Hartree–Fock orbitals. In the case of strong hole mixing, a and b have nearly the same value and therefore the off-diagonal elements of (28) become very small. In this case, avoided crossings of the hole occupations $\tilde{n}_i(t)$ and $\tilde{n}_k(t)$ appear at $t = [(2n+1)/4]T$, n integer, and the two natural charge orbitals interchange their roles at each half cycle duration $T = 2\pi/\omega$, i.e., $\tilde{\varphi}_{i/k}(\vec{r},(n+\tfrac{1}{2})T) \approx \varphi_{k/i}(\vec{r})$ and $\tilde{\varphi}_{i/k}(\vec{r},nT) \approx \varphi_{i/k}(\vec{r})$.

Figure 2 is a visualization of formula (29). The eigenvalues $\tilde{n}_{i/k}(t)$, which are the time-dependent hole occupations of the corresponding eigenvectors (natural charge orbitals), are plotted (graphs "i" and "k") as functions of time. Since in reality none of the regarded mechanisms occurs in its pure form, all graphs in Fig. 2 are multiplied by a weakly exponentially decaying function to take care of a weak coupling to other configurations. The hole charge is oscillating between the two natural charge orbitals with the frequency ω, which is the energy difference of the two states involved in the hole mixing. If these states have a typical energy difference of about 1 eV, the time period of these oscillations would be about 4 fs.

If the two orbitals involved in the hole mixing are located at different sites of the molecule, the charge can oscillate through the whole molecule with the frequency ω, a situation illustrated in Fig. 3 for a long chain molecule. To show the motion of the hole charge through the chain molecule the hole density $Q(\vec{r},t)$ is integrated perpendicular to the axis of the molecule. If this axis is, e.g., the z axis, the resulting function $Q(z,t)$ can be easily plotted in a three-dimensional plot, where the hole density $Q(z,t)$ is a function of the coordinate z along the axis of the molecule and the time t.
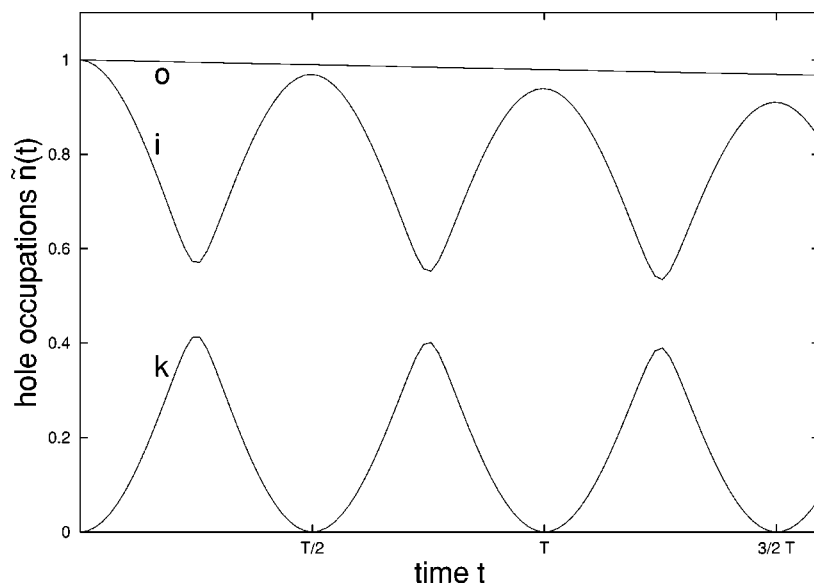
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FIG. 2. Time-dependent occupation numbers of the two orbitals (i,k) involved in the hole mixing and of an outer valence orbital not involved in the hole mixing (o). As expected, the hole occupation of the initially ionized outer valence orbital (o) will stay at "1". In the hole mixing case, the initially ionized orbital (i) will "lose" its hole charge, which is transferred to the other orbital involved in the hole mixing (k). To take care of other interactions not included in the analytically computed model, all plots are multiplied by a weakly exponentially decaying function.

For the example illustrated in Fig. 3, a hole charge initially located on the left-hand side of the molecule oscillates between the left and the other side of the molecule as time increases. Because of other contributing effects, the initially localized charge will eventually delocalize over the molecule at longer times.

B. Impact of a single dominant satellite

Dominant satellites often appear in the ionization spectrum (see Fig. 1, lines 5). These are satellite states, which have a single pronounced 1h weight besides some 2h1p ones. For simplicity, we take only one correlation satellite into account, i.e., there is one main state and one satellite state in the spectrum having overlap with the original 1h configuration, and both hole indices of the 2h1p configuration of the satellite state differ from the 1h configuration of the main state. The two states can be described in a CI expansion as

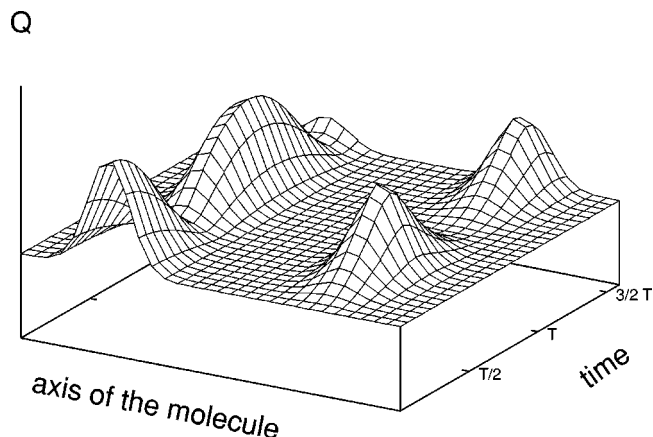$$|I_m\rangle = a|\Phi_i\rangle + b|\Phi_{rjk}\rangle, \tag{30a}$$

FIG. 3. Three-dimensional plot of a hole mixing, where the two orbitals involved are located at different sites of a long chain molecule. The total charge is integrated over the coordinates perpendicular to the axis (e.g., z axis) of the molecule and the resulting $Q(z,t)$ is plotted. The hole charge is oscillating through the whole molecule.
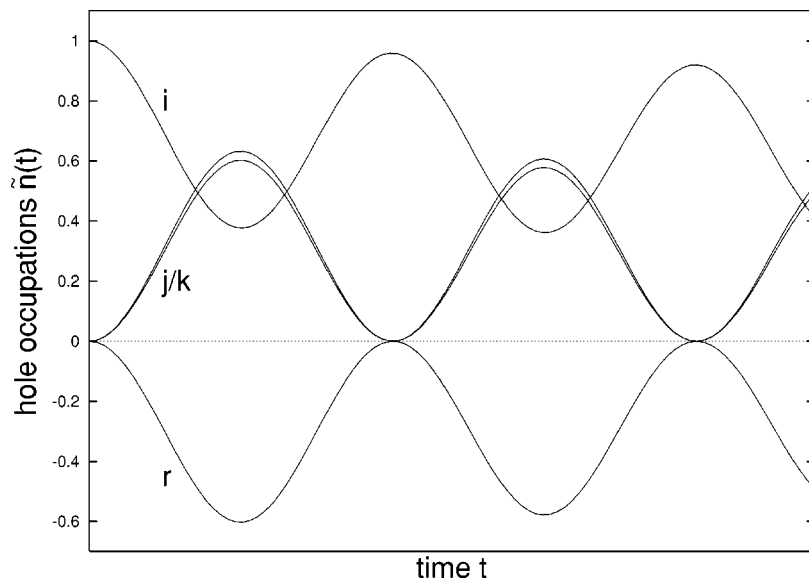
$$|I_s\rangle = b|\Phi_i\rangle - a|\Phi_{rjk}\rangle, \tag{30b}$$

where $|\Phi_{rjk}\rangle = a_r^+ a_j a_k |\Phi_0\rangle$ and $a^2 + b^2 = 1$. Using this ansatz in Eqs. (16), (19), and (20) produces the following nonvanishing elements in the matrix $\mathbf{N}(t)$:

$$N_{ii} = 1 - 2(ab)^2(1 - \cos \omega t), \tag{31a}$$

$$N_{jj} = N_{kk} = -N_{rr} = 2(ab)^2(1 - \cos \omega t). \tag{31b}$$

The hole density matrix $\mathbf{N}(t)$ is, thus, diagonal. We mention that this matrix would become nondiagonal if a second satellite was included. Since the hole density matrix is diagonal the natural charge orbitals are identical to the original, time-independent molecular orbitals. The occupation numbers of the four orbitals φ_i, φ_r, φ_j, φ_k are, of course, changing in time. Their values are given by the expressions (31): $\tilde{n}_i(t) = N_{ii}(t)$, etc. Following the ionization, the hole charge that is initially located in orbital φ_i will be transferred to the occupied orbitals φ_j, φ_k and this transfer is accompanied by an excitation of charge from the particle orbital φ_r to the latter hole orbitals. Figure 4 shows an illustration of this behavior, in which the *negative* hole occupation of the orbital φ_r has to be interpreted as an electron filling this virtual orbital.

Here, again, like in the hole mixing case, it is possible that the charge oscillates through the whole molecule, depending on the molecular position of the orbitals φ_i, φ_r, φ_j, and φ_k. If the involved orbitals are located at different sites of the molecule, this mechanism could lead to an efficient, and easy to interpret, charge migration process, due to the stationary natural charge orbitals.

Of course, the four orbitals φ_i, φ_r, φ_j, and φ_k need not belong to the same irreducible representation of the symmetry group of the molecule. For instance, φ_i and φ_j could be σ orbitals while φ_k and φ_r could be π orbitals. In this case the ionization out of the σ orbital φ_i is followed by a $\pi \rightarrow \pi^*$ charge excitation from orbital φ_k to φ_r, while the initial hole "moves" to the other σ-orbital, φ_j.

FIG. 4. Time-dependent occupation numbers in the case of a dominant satellite. The initially created hole (i) "loses" its hole charge to the orbitals j/k. At the same time an excitation from j/k to the virtual orbital r is observed. The negative hole occupation of the orbital φ_r has to be interpreted as an electron filling this virtual orbital. To take care of other interactions not included in the calculations, all occupation numbers are multiplied by a weakly decaying exponential function. For convenience, the $\tilde{n}_j(t)$ and $\tilde{n}_k(t)$ curves are artificially made to differ slightly from each other.

C. Breakdown of the molecular orbital picture

The last special case of charge migration investigated here is charge migration as the consequence of the breakdown of the molecular orbital picture of ionization, widely encountered in the ionization of inner valence orbitals.[13] Such a "breakdown" can be easily identified in the spectrum by a large number of dense lines having comparable 1h contributions. It is no longer possible to distinguish between main and satellite states. Standard perturbation theory cannot be used to calculate the CI coefficients of these states because of the strong interaction present.

To simplify the discussion we assume that the density of states in the breakdown region is high and the spectroscopic factors are uniformly distributed (see lines 6 in Fig. 1), and transform the summation of Eq. (23) into an integration

$$N_{ii}(t) = 1 - \int dE_I \int dE_J (1 - \cos((E_I - E_J)t)) \times c_i^2(E_I) c_i^2(E_J). \tag{32}$$

Here, $c_i(E_I) = c_i^{(I)}$ is the transition amplitude resulting from the state of energy E_I. For simplicity we consider only the matrix element $N_{ii}(t)$ which is the most interesting one because it describes the migration of the hole charge out of the initially ionized orbital. For a symmetric line shape $c_i^2(E)$ centered at energy E_0 Eq. (32) simplifies to

$$N_{ii}(t) = \left[\int dE \cos(Et) c_i^2(E + E_0) \right]^2. \tag{33}$$

In deriving Eq. (33) we have used the normalization condition for the $c_i^{(I)}$ coefficients. As can be seen, the time dependence of the matrix element $N_{ii}(t)$ is determined by the cosine transformation of the spectroscopic factors of the involved states. The cosine transformation can be replaced by the Fourier transformation, because $c_i^2(E + E_0)$ is a symmetric function around $E = 0$.

In the case of a Lorentzian line shape,

$$c_i^2(E) \sim \left(1 + \left(\frac{E - E_0}{\sigma} \right)^2 \right)^{-1}, \tag{34}$$

the matrix element reads

$$N_{ii}(t) \sim e^{-2\sigma t}. \tag{35}$$

The matrix element $N_{ii}(t)$ starts initially at 1 and decreases exponentially with a rate of 2σ. Since $N_{ii}(t)$ is the dominant part of the hole occupation $\tilde{n}_i(t)$ after the diagonalization of $\mathbf{N}(t)$, one can expect the same behavior for $\tilde{n}_i(t)$, see Fig. 5.

The "decay rate" obtained above is defined by the width of the line shape in the spectrum and, since this width is generally large, a very fast charge migration out of the initially ionized orbital takes place. Where does the charge go? The answer depends on the individual system studied. Nevertheless, we do have some expectations. Since many 2h1p configurations and probably also higher excited ones participate in the breakdown of the orbital picture and hence in the spectrum, we expect that the charge will more or less uniformly spread over large parts of the system. Another interesting situation occurs if the ionization energy of the ionization process is high and lies above the double ionization threshold. Then, double ionization can take place and the above-discussed mechanism can describe the decay of the ionized state, i.e., the emission of a second electron of the cation.[28]

V. REALISTIC EXAMPLES

In this section we briefly illustrate that the idealized mechanisms of charge migration discussed in Sec. IV above are not only interesting from a theoretical point of view, but may be realized in nature. We found manifestations of each of these mechanisms in three different molecules. Of course, one cannot expect that the mechanisms are found in their idealized form and there will always be some impact due to mixtures with other states. Surprisingly enough, these mechanisms of charge migration are observed in a relatively pure form in the examples we present below. The examples
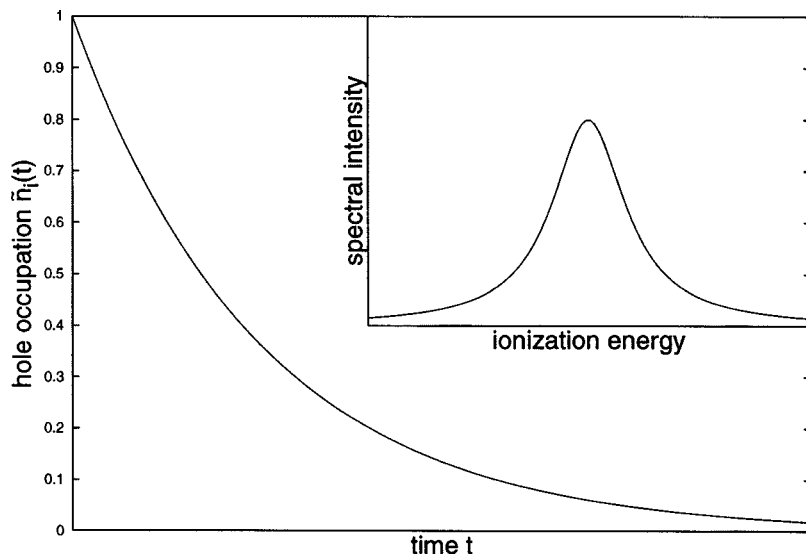
FIG. 5. Charge migration after ionization of an inner valence orbital. For a continuous Lorentzian line shape in the ionization spectrum the hole occupation $\tilde{n}_i(t)$ of the initially ionized orbital will decay exponentially.

are only meant to be an illustration of the above "dry" theory. We shall not present here a detailed description of the underlying involved numerical calculations of the charge migration in these molecules. The description of the calculations is presented here in a very brief form and details will be given elsewhere.

A. Hole mixing

An example for charge migration by hole mixing can be found in 2-propyn-1-ol for which hole mixing was already identified and investigated.[27] In the calculations presented here we used the DZP basis set[29] and the optimized geometry of the molecule which belongs to the C_s symmetry group. According to the calculation of the cationic states, hole mixing occurs between the 1h configurations $(4a')^{-1}$ and $(5a')^{-1}$. The corresponding orbitals are both localized at both ends of the molecule, i.e., at the CH moiety and at the COH moiety. The calculated cationic states $|I_{4a',5a'}\rangle$ and $|I_{5a',4a'}\rangle$ have an energetic difference of $\hbar\omega = 0.39$ eV and

the hole mixing is described by coefficients a and b in Eqs. (27) of similar size. For definiteness the calculations are performed such that initially we are ionizing the $4a'$ orbital. Starting with the ionization of the $5a'$ orbital will lead to equivalent results.

In Fig. 6 the hole occupations of the two involved natural charge orbitals are shown. At time $t = 0$ the natural charge orbital i with hole occupation equal to 1 is the $4a'$ orbital and the other one, k, is the $5a'$ orbital. As discussed in Sec. IV A, the natural charge orbitals vary strongly as a function of time in an ideal hole mixing situation. By investigating the natural charge orbitals at time $t = 5.25$ fs, i.e., at the time when $\tilde{n}_i(t)$ returns to its maximum, the initial orbitals are swapped. Now i is essentially the $5a'$ orbital and possesses the large hole occupation (≈ 0.8) and the k natural charge orbital is very similar to the $4a'$ orbital and has a small (< 0.2) hole occupation. The hole charge has migrated from the $4a'$ to the $5a'$ orbital in 5.25 fs. As expected, a full cycle of the oscillation lasts $T = 10.5$ fs and there are avoided crossings at times $t = [(2n + 1/4)]T$, where n is an integer.
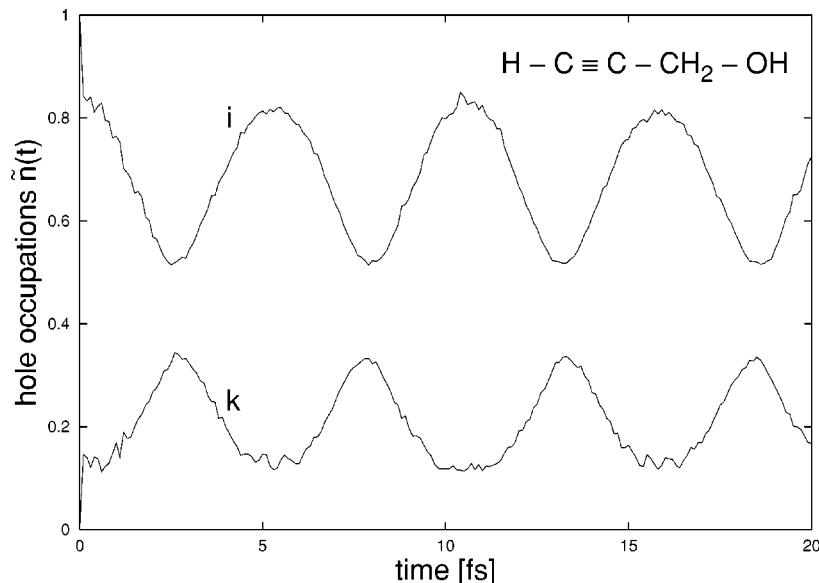

FIG. 6. Hole occupation numbers for hole mixing in the molecule 2-propyn-1-ol. The hole charge initially located in the $4a'$ orbital oscillates between the $4a'$ and the $5a'$ orbitals of the molecule. "i" denotes the natural charge orbital that is initially ionized, "k" denotes the other orbital involved in the hole mixing.
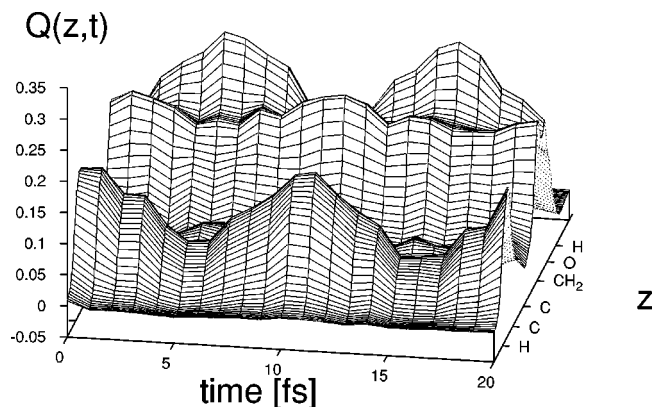
FIG. 7. Integrated charge density $Q(z,t)$ along the z axis in the case of hole mixing in the molecule 2-propyn-1-ol. The z axis is chosen along the triple bond of the molecule.

Unfortunately, in this molecule the two involved orbitals are not located at different sites of the molecule and the migration of the hole charge density is not very pronounced. Nevertheless, an oscillation of the hole charge between the two ends of the molecule takes place, see Fig. 7. A part of the hole charge is initially located at the HC moiety and oscillates to the other, i.e., COH, end of the molecule.

B. Dominant satellite

The linear molecule 3-fluoro-2-propynenitril (NC_3F) is an illustrative example for the mechanism of charge migration resulting from the presence of a dominant satellite. The molecule was calculated using the DZP basis set[29] and its geometry was optimized. The 5σ orbital is the orbital initially ionized. An investigation of the spectrum shows that the main $(5\sigma)^{-1}$ state mixes with the correlation satellites $(2\pi)^{-2}7\sigma^*$. The 5σ and 2π states involved are distributed over nearly the whole molecule. Most of the 7σ orbital is located on the fluorine atom and the central carbon atom. Because of the degeneracy of the π orbitals, there are two degenerate correlation satellites. This becomes particularly

transparent when using C_{2v} instead of $C_{\infty v}$ symmetry: Then the σ orbitals of both satellites belong to the a1 representation of the symmetry group and both holes of the first (second) satellite are generated in the π orbital belonging to the $b1$ ($b2$) representation. The energetic difference of the main state and the two degenerate satellite states is $\hbar\omega = 0.27$ eV, i.e., we expect a periodic dynamics with the period of $T = 15.5$ fs.

Figure 8 shows the result of our calculation of the charge migration in NC_3F. The initially ionized orbital 5σ loses its hole charge to the doubly degenerate 2π orbitals. At the same time the virtual orbital 7σ is being occupied. The 5σ orbital which is half empty at $t = 0$ is refilled by up to 0.7 of an electron while more than one electron are removed from the π orbitals. This becomes possible because more than 0.5 electrons can flow to the $7\sigma^*$ orbital which was empty at $t = 0$. The crossing which is seen in Fig. 8 is not an avoided crossing. The involved natural charge orbitals belong to different irreducible representations of the symmetry group and therefore appear in different uncoupled blocks of the matrix $\mathbf{N}(t)$, see explanation at the end of Sec. II B . For this reason, a crossing of these natural charge orbitals obtained by diagonalizing the hole density matrix is allowed.

C. Breakdown of the molecular orbital picture

A quasiexponential decrease of the initial hole charge is found in the linear molecule NC_5F after ionizing the 4σ orbital. This orbital is mainly localized at the triple bonds between the carbon atoms. Again, the molecule was calculated using the DZP basis set[29] and the geometry was optimized. The 1h configuration of this orbital can be found in a series of cationic states that form approximately a Lorentzian-type shape in the spectrum. Since it is not possible to distinguish between main and satellite states, we indeed encounter a breakdown of the molecular orbital picture of ionization. The width (FWHM) of this shape is about 1.2 eV, but this is only a rough estimate because the density of states is not sufficiently high. This width leads to a decay rate
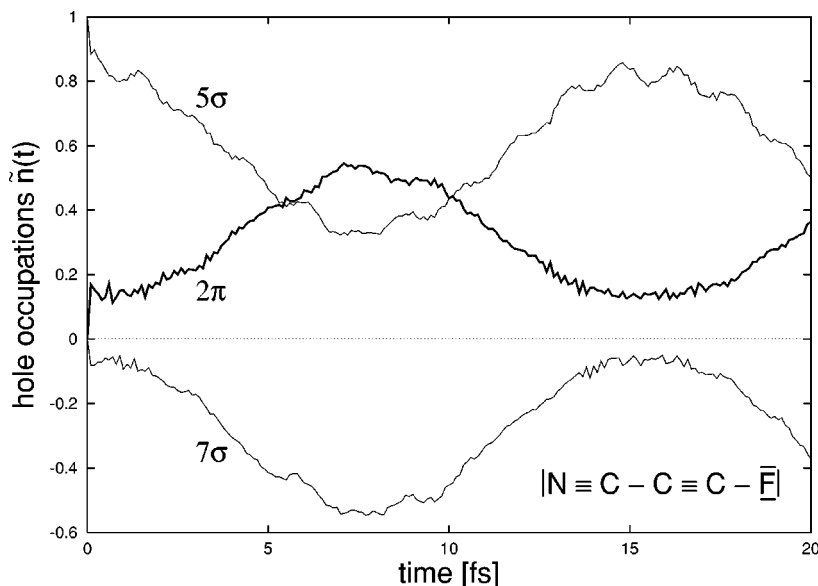

FIG. 8. Time-dependent hole occupation numbers for the molecule NC_3F. The initially ionized orbital 5σ loses its hole charge to the doubly degenerate 2π orbitals (marked by bold line). At the same time the 7σ orbital is filled by an electron. Obviously, the $(5\sigma)^{-1}$ 1h configuration mixes strongly with the degenerate 2h1p configuration $(2\pi)^{-2}7\sigma^*$.
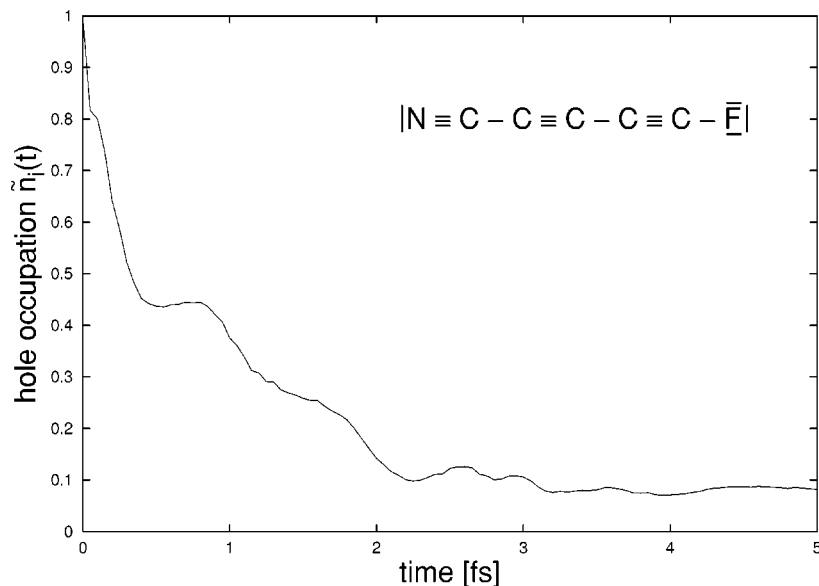
FIG. 9. Quasiexponential decrease of the hole occupation of the initially ionized 4σ orbital of the NC_5F molecule. The decay rate is $2\sigma \approx 1$ fs^{-1}.

of about $2\sigma = 1$ fs^{-1}, in agreement with the time-dependent calculations the results of which are depicted in Fig. 9.

We have also investigated the hole occupation numbers of the other orbitals of NC_5F. The calculations predict that the hole charge is distributed over many natural charge orbitals, resulting in an ultrafast delocalization of the hole density over large parts of the molecule.

It has to be mentioned that some of the states involved are energetically located above the double ionization threshold. According to our calculation the double ionization energy is 26.7 eV. This implies that the ionization out of the 4σ orbital can lead to a subsequent emission of an additional electron.

VI. SUMMARY AND CONCLUSIONS

In this work charge migration solely driven by electron correlation following the removal of an electron from a molecule is theoretically described and computed using *ab initio* methods. The hole density, defined as the difference between the density of the system and that of the ion, is the central quantity we analyze. This time-dependent quantity can be expressed in terms of the hole density matrix in the space spanned by the system's orbitals of our choice [see equation (8)]. The hole density matrix itself is explicitly expressed in terms of the ionization energies of the system under investigation and the expansion coefficients of the corresponding wavefunctions [see Eqs. (21) and (22)]. An easily understandable picture of the charge migration in the molecule is obtained by diagonalizing the hole density matrix as done in Eq. (9): The hole charge can be described by time-dependent hole occupation numbers of time-dependent natural charge orbitals.

To gain further insight into the charge migration process, the hole density based on the hole density matrix is further investigated using perturbation theory. It is shown that electron correlation is crucial for an electronic charge migration to take place. In an independent particle picture, no charge migration will occur. The most important terms of the hole density matrix are identified by perturbation theory and found to be the coupling terms between the occupied orbitals and the (formally) infinite set of virtual orbitals of the molecule. The leading orders of these coupling terms are mediated by satellite states in the ionization spectrum. In other words, by discarding the satellite states in the description of the charge migration the most important terms would be neglected.

Several specific mechanisms of charge migration are revealed and studied theoretically. Numerical examples for these are given and briefly discussed. These specific mechanisms of charge migration can be identified by the fingerprint of the corresponding electronic states in the ionization spectrum. If the ionization spectrum shows a hole mixing effect, it can be inferred that an efficient oscillation of the hole charge between the orbitals involved takes place. If, in addition, these orbitals are located at different sites of the molecule, an efficient charge migration through the whole molecule occurs. Investigating how the appearance of a dominant satellite in the ionization spectrum is reflected in the charge migration, we find another mechanism for an efficient charge migration of the hole charge to other orbitals. The electronic character of this satellite determines to which orbitals the hole charge flows. In the idealized case of a single dominant satellite, as investigated here, no mixture between the involved orbitals has been found. The natural charge orbitals are thus identical to the initial ones at all times, which makes the analysis particularly simple. Here, again, depending on the spatial distribution of these orbitals, an efficient charge migration through the molecule can take place. Finally we investigate a mechanism of charge migration which results from the breakdown of the molecular orbital picture of ionization. For a Lorentzian-type line shape in the ionization spectrum, an exponential decay of the hole occupation of the initially ionized orbital is obtained. The hole charge is distributed into many different natural charge orbitals, often resulting in a delocalization of the hole charge over the whole molecule. All of these three specific mecha-

nisms are identified in numerical examples of *real* systems which are briefly discussed.

It is shown that electron correlation is of primary importance for a rigorous description of charge migration. Charge migration solely driven by electron correlation can take place in real systems as shown by the examples discussed in this paper and in Ref. 11, and is seen to be ultrafast. For holes in inner valence orbitals this seems to be a particularly efficient mechanism: In the example studied more than half of the charge of the hole has flown out of its initial location in less than 0.5 fs (see Fig. 9). Obviously, the behavior of the initially generated hole charge depends strongly on the system in question. Because of the short time scales found in the examples we studied numerically, nuclear motion can be neglected in a first step. After a sufficiently long time, nuclear dynamics plays an important role in the description of the charge transfer. However, charge migration driven by electron correlation has already taken place and the hole charge can reach its final destination before nuclear dynamics sets in. For charge migration driven by nuclear dynamics, experimental observations should significantly depend on the nuclear masses and therefore significantly differ for different isotopes. If the charge migration is dominated by electron correlation, the isotopic effects are less important. In addition to the different time scales involved, this could be used to distinguish between electronic charge migration and charge migration due to nuclear motion. Another possibility to observe charge migration driven by electron correlation relates to site-specific probing. The ionization of a second electron from a given site of the cation is much more difficult, if the hole is located at this site.

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