Impact of Interatomic Electronic Decay Processes on Xe 4d Hole Decay in the Xenon Fluorides

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A hole in a 4d orbital of atomic xenon relaxes through Auger decay after a lifetime of 3 fs. Adding electronegative fluorine ligands to form xenon fluoride molecules, results in withdrawal of valence-electron density from Xe. Thus, within the one-center picture of Auger decay, a lowered Xe 4d Auger width would be expected, in contradiction, however, with experiment. Employing extensive ab initio calculations within the framework of many-body Green’s functions, we determine all available decay channels in XeFₙ and characterize these channels by means of a two-hole population analysis. We derive a relation between two-hole population numbers and partial Auger widths. On this basis, interatomic electronic decay processes are demonstrated to be so strong in the xenon fluorides that they overcompensate the reduction in intra-atomic Auger width and lead to the experimentally observed trend. The nature of the relevant processes is discussed. These processes presumably underlie Auger decay in a variety of systems.

I. INTRODUCTION

The Auger effect provides a magnificent means to study atoms, molecules, and surfaces. It is caused by a special type of electronic resonance, i.e., the decay by electron emission of core-ionized atoms, molecules, or solids. Since its discovery it has received much attention, because it is a fundamental process yielding deep insights into complex many-body effects in matter. Moreover, the Auger effect has proven to be useful in many experimental situations and can be used as an analytical tool. Therefore, an in-depth understanding of the Auger effect is important both for fundamental and practical reasons.

A particularly interesting situation arises when systems consisting of more than one atom are considered. Can the Auger decay rate of a core hole in an atom be influenced—or maybe even adjusted at will—by modifying the chemical environment of that atom? If yes, what are the underlying mechanisms? Early experiments on gas-phase molecules and ionic solids hinted at a simple correlation between the binding energy of a core electron and the Auger width of the associated core hole. For instance, withdrawal of valence electrons by electronegative ligands induces a chemical shift of the core level toward higher binding energies; at the same time, a smaller number of valence electrons is available for Auger decay, if a local, atomic mechanism is assumed. Hence, within the one-center picture of Auger decay, an increase in binding energy is accompanied by a decrease in Auger width.

Citrin, however, analyzed x-ray photoemission measurements in a number of metal oxides and halides, and found convincing evidence for interatomic processes, which can lead to a trend in contradiction to the one-center model. Citrin’s work stimulated theoretical work on interatomic Auger decay in crystalline NaCl and NaF. Matthew and Komninos were the first to present a formal examination of interatomic Auger processes. Using strong approximations they concluded that these transitions have a small impact on the Auger rate, except in low-energy Auger processes. In fact, recent theoretical and experimental investigations show that in the low-energy case the effect of the chemical bond can be dramatic.

In this work, we argue that interatomic electronic decay processes can have an even greater impact than previously assumed. We investigate as an example Auger decay of a Xe 4d hole in Xe, XeF₂, XeF₄, and XeF₆. It is demonstrated that the Auger width in the series XeFₙ, \( n = 0, 2, 4, 6 \), would decrease drastically if only intra-atomic decay played a role. By contrast, the experimentally observed linewidths display—in clear contradiction to the one-center picture mentioned previously—a monotonic increase from Xe to XeF₆. This is illustrated...
We show that interatomic Auger processes are responsible for the discrepancy. Vibrational broadening, which could cause a similar effect, is very likely to be insignificant. Single ionization spectra of the xenon fluorides, which we have calculated recently, provided a first theoretical indication of an entirely electronic mechanism.

The xenon fluorides constitute, from our point of view, an ideal example, because of the relatively weak bonding between the central noble-gas atom and the fluorine ligands. This allows us to identify various interatomic electronic decay mechanisms that govern the inner-valence physics in weakly bound clusters of atoms or molecules.23,24,25,26,27,28,29 provide a conceptual framework for our analysis. Therefore, a short summary of these processes is given in Sec. III.

The nature of Auger decay in a molecule can be assessed most clearly by characterizing the available decay channels. To this end, Sec. III introduces a many-body Green’s function method—the algebraic diagrammatic construction scheme.26,29—for calculating double ionization spectra of molecules at a highly correlated level. A two-hole population analysis30 is discussed that serves as an important tool for determining the localization properties of the two holes in an Auger decay channel. Using Wigner-Weisskopf theory32,33 we derive a relationship between final-state population numbers and partial Auger widths. The calculated double ionization spectra are analyzed in Sec. IV and the relevance of interatomic decay processes for the decay of Xe 4d vacancies is elucidated. Concluding remarks are the subject of Sec. V.

II. ELECTRONIC DECAY PROCESSES IN WEAKLY BOUND SYSTEMS

In this section, we review the knowledge obtained in the study of the electronic decay of inner-valence ionized clusters. The decay processes discovered in clusters, and the associated terminology we use in order to emphasize the nature of the underlying mechanisms, allow a succinct classification of the Auger processes in XeFₙ. We mention that the decay processes discussed in the following for singly ionized systems can be generalized to describe the decay of inner-valence vacancies of multiply ionized clusters.32,33

Intra-atomic electronic decay (IAED) is usually the most prominent electronic decay process of core-ionized atoms embedded in molecules or clusters. IAED is, of course, the only Auger process that can take place in an isolated atom. In atoms, this mechanism is well understood.1,2,3,4,5 The initial core hole is filled by a (valence) electron and the excess energy is transferred via Coulomb interaction to a second (valence) electron, which is emitted subsequently [Fig. 2(a)]. In molecules or clusters, intra-atomic decay is not the only decay process, because other processes can occur that involve neighboring atoms or molecules.

If one removes an inner-valence electron from an isolated atom or molecule, the ionized system cannot, in general, decay by electron emission, for it lies energetically below the double ionization threshold. The situation changes if the monomer is part of a cluster.

The initial inner-valence vacancy is filled by a valence electron of the same monomer and the excess energy is transferred to a second valence electron of a neighboring monomer. This electron is emitted subsequently. See Fig. 2(b) for a schematic representation. The decay process is termed interatomic or intermolecular Coulombic decay (ICD) for clusters of atoms or clusters of molecules, respectively. It was identified theoretically in several weakly bound clusters: (HF)ₙ clusters,23,25,27,29 the HF(H₂O)₂ cluster,36 (H₂O)ₙ clusters,23 Neₙ clusters,24,28,37 and the NeAr dimer.28 Further we would like to point out studies of electronic decay after inner-valence ionization of CN− and of fluorinated carbanions and their acids.39

ICD of inner-valence holes in clusters is ultrafast, typically taking place on a time scale of the order of 10 fs (see Ref. 40 for a review). Experimental evidence for ICD has been found recently in neon clusters.24,28,37 In the context of this paper, it is especially important to note that ICD is highly sensitive to cluster size: The ICD width in Neₙ clusters, for instance, increases strongly with the central neon atom carries the initial inner-valence vacancy and the surrounding atoms converge with it to the shape of the first coordination sphere in solid neon.38

Clearly, a larger number of nearest neighbors translates into a larger number of dicationic decay channels available for ICD.

The ionization spectra of neon and argon are quantitatively very different from one another (Ref. 25 and references therein). Neon has significantly higher lying single (IP) and double ionization potentials (DIP) compared to argon. The inner-valence Ne 2s IP is larger than the Ne 1s Ar−1 DIP in the NeAr dimer.25 Therefore, an initial Ne 2s vacancy can lead to ICD. However, the Ne 2s vacancy in NeAr can decay in another way, too, because the Ne 2s IP is also larger than the NeAr−2 DIP. In this case, a valence electron from argon drops into the Ne 2s hole and the excess energy is transferred to another valence electron of argon. Upon electron emission, the dimer is left in a NeAr−2 state. This process is called electron-transfer mediated decay (ETMD).25 A schematic representation of the ETMD process is shown in Fig. 2(c). In Ref. 25 it is shown that the contribution of ETMD to the total electronic decay width of an initial Ne 2s vacancy in NeAr is appreciably smaller than the contribution of ICD. In light of the vastly increasing ICD width in neon clusters,28 we expect a similar size effect for ETMD, too. In the ETMD described, only two atoms are involved. It is called two-monomer ETMD (ETMD2).

A three-monomer ETMD (ETMD3) has been sug-
FIG. 2: Principles of electronic decay processes in weakly bound systems: (a) intra-atomic electronic decay (IAED), (b) interatomic Coulombic decay (ICD), (c) two-monomer electron-transfer mediated decay (ETMD2), (d) three-monomer electron-transfer mediated decay (ETMD3). Common to all electronic decay processes is that the initial vacancy is filled by a valence electron from the same or a neighboring atom. The excess energy is transferred to a second valence electron of the same or a neighboring atom. Emission of this electron results in distinct dicationic charge distributions that allow one to characterize the underlying decay process.

...gested to occur for an initial Ne 2s vacancy in NeAr₂. A schematic representation of this (proposed) process is given in Fig. 2(d). A valence electron of one of the two argon atoms is transferred into the initial Ne 2s hole. Energy is released, and a valence electron is ejected from the second argon atom, leaving the trimer in a NeAr⁻²Ar⁻² state.

We would like to study a new example for the surprising impact of the ideas presented so far. To this end, we examine the decay of Xe 4d vacancies in XeFₙ and demonstrate how interatomic processes lead to an increase in Auger width. In order to pursue this issue, we need to introduce a few computational techniques and useful relations in the ensuing section.

III. COMPUTATIONAL METHODS AND BASIC RELATIONS

A. Algebraic Diagrammatic Construction and Two-Hole Population Analysis

Many-body Green’s functions are ideal tools for investigating excitation spectra of molecular matter at various stages of ionization. The two-particle Green’s function, specifically, provides direct access to double ionization spectra and associated eigenstates. Algebraic diagrammatic construction (ADC) is an advanced perturbation-theoretical approximation scheme for evaluating many-body propagators. ADC sums all Feynman diagrams up to nth order as well as certain classes of diagrams up to infinite order. There is no Dyson equation for the two-particle Green’s function. The two-particle ADC evaluates the two-particle propagator directly in terms of a Hermitian eigenvalue problem. The program we use to calculate double ionization potentials implements the two-particle ADC(2) scheme.

The two-hole population analysis, utilized in combination with the ADC(2) program, is a means to reveal the spatial localization of the two holes resulting from double ionization. The analysis is carried out in a Mulliken-type fashion by determining the atomic two-hole (2h) contributions to the dicaticonic eigenstates. To this end, a dicaticonic eigenstate in the ADC(2) scheme is first expanded in terms of 2h configurations in molecular orbital basis,

\[ |\Psi_{N-2}^n\rangle = \sum_{ij} (\tilde{X}_n)_{ij} |ij\rangle + \cdots, \]  

where \( \tilde{X}_n \) is the 2h part of the ADC eigenvector of the nth dicaticonic state |\( \Psi_{N-2}^n \rangle \). The symbol |ij\rangle denotes...
a spin-adapted $2h$ configuration with holes in molecular (spin) orbitals $i$ and $j$, both of which are occupied in the Hartree-Fock ground state of the $N$-electron system. Note that $ij$ runs only over distinguishable $2h$ configurations. Each $2h$ configuration in molecular orbital basis, $|ij\rangle$, can now be expanded in terms of $2h$ configurations $|\mu\nu\rangle$ deriving from the atomic orbital basis:

$$|ij\rangle = \sum_{\mu\nu} U_{\mu\nu,ij} |\mu\nu\rangle .$$  \hspace{1cm} (2)

Using this transformation, the total $2h$ weight $\bar{X}_n^i \bar{X}_n^j$ $(2h$ pole strength) of the $n$th dicaticonic eigenstate can be written as:

$$\bar{X}_n^i \bar{X}_n^j = \bar{Y}_n^i \bar{Y}_n^j = \sum_{\mu\nu} Y_{\mu\nu,nn} \sum_{\rho\sigma} O_{\mu\nu,\rho\sigma} Y_{\rho\sigma,nn} .$$  \hspace{1cm} (3)

with eigenvector expansion coefficients $\bar{Y}_n := U \bar{X}_n$ in atomic orbital basis. $O$ represents the overlap matrix between atomic $2h$ configurations, which satisfies $U^\dagger OU = \mathbb{1}$.

On choosing suitable sets of atomic basis functions $A$ and $B$, one obtains population numbers $Q_{AB,n} = \sum_{\nu \in A} Q_{\mu\nu,nn}$. Frequently, as is done in this work, $A$ and $B$ represent the atomic basis functions associated with two not necessarily distinct atoms within a molecule. In this sense, $A$ and $B$ can be identified with individual atoms. This provides a clear picture of the localization properties of the two holes.

### B. Relation between Two-Hole Population Numbers and Partial Decay Widths

A useful approximation to the decay width of a resonance is given within the framework of Wigner-Weisskopf theory \cite{Wigner1935, Weisskopf1935} which is based on time-dependent perturbation theory. Applications of Wigner-Weisskopf theory to the electronic decay of inner-valence-ionized clusters can be found in Refs. \cite{Chandler1992, Chandler1994}. There, single Hartree-FOck determinants were employed to describe both initial and final states. For more complicated systems like XeF$_2$ and on the energy scale of core levels, however, the final states in particular require a more sophisticated treatment.

Let the initial state $|\Psi_1^{N-1}\rangle$ be a discrete, singly ionized state approximating the core-hole resonance and a final state be a doubly ionized state $|\Psi_n^{N-2}\rangle$ together with a decay electron of momentum $\vec{k}$. For simplicity we employ the sudden approximation (Ref. \cite{SuddenApproximation} and references therein) and express such a final state by the antisymmetrized product $\hat{c}_{\vec{k}}^\dagger |\Psi_n^{N-2}\rangle$, where $\hat{c}_{\vec{k}}^\dagger$ is a fermionic creation operator. The decay width is then given by:

$$\Gamma = 2\pi \sum_n \sum_{\vec{k}} \left| \langle \Psi_n^{N-2} | \hat{c}_{\vec{k}} \hat{H} | \Psi_1^{N-1} \rangle \right|^2 \delta(E_n - E_1) .$$  \hspace{1cm} (4)

This equation contains three types of matrix elements: transition matrix element $\langle \Psi_n^{N-2} | \hat{c}_{\vec{k}} \hat{H} | \Psi_1^{N-1} \rangle$, initial-state energy $E_1 := \langle \Psi_1^{N-1} | \hat{H} | \Psi_1^{N-1} \rangle$, and final-state energy $E_{n\vec{k}} := \langle \Psi_n^{N-2} | \hat{c}_{\vec{k}} \hat{H} | \Psi_n^{N-2} \rangle$. The operator $\hat{H}$ is the Hamiltonian in fixed-nuclei approximation. The $\delta$ function in Eq. (4) ensures that the contribution to the total decay width of only those accessible final states is summed that conserve energy in the decay.

Using Eq. (1), we obtain:

$$\langle \Psi_n^{N-2} | \hat{c}_{\vec{k}} \hat{H} | \Psi_1^{N-1} \rangle = \sum_{ij} (\bar{X}_n^i)_ij \langle ij | \hat{c}_{\vec{k}} \hat{H} | \Psi_1^{N-1} \rangle + \ldots$$  \hspace{1cm} (5)

for the transition matrix elements in Eq. (4). Let us assume that the initial state can be approximated by a single determinant $|\Psi_1^{N-1}\rangle = \hat{c}_l |\Phi_0^N\rangle$, where $l$ indicates a core orbital and $|\Phi_0^N\rangle$ the $N$-electron Hartree-Fock ground state. Let us further exploit the fact that excitations of core orbitals are, to a good approximation, negligible in all expansion terms of the dicaticonic final state $|\Psi_n^{N-2}\rangle$. The terms indicated in Eq. (5) with "..." then vanish exactly due to the Slater-Condon rules.

To proceed, we express the dicaticonic electronic configurations in terms of atomic $2h$ vectors $|\mu\nu\rangle$. The configurations $|ij\rangle$ appearing in Eq. (5) form an orthonormalized set of functions, and by using the relation:

$$|ij\rangle = \sum_{\mu\nu,\rho\sigma} (O_{\mu\nu,\rho\sigma})^* \sum_{\rho\sigma} U_{\mu\nu,ij} |\mu\nu\rangle,$$  \hspace{1cm} (6)

we introduce an orthonormalized set of configurations $|\mu\nu\rangle$ referring to atomic orbitals. Notice that the atomic configurations in Eq. (6) are not orthonormalized. Inserting Eq. (6) into Eq. (5) leads to:

$$\langle \Psi_n^{N-2} | \hat{c}_{\vec{k}} \hat{H} | \Psi_1^{N-1} \rangle = \sum_{\mu\nu} (\bar{Y}_n^i)^\dagger \langle \mu\nu | \hat{c}_{\vec{k}} \hat{H} | \Psi_1^{N-1} \rangle ,$$  \hspace{1cm} (7)

where $\bar{Y}_n^i := O_{\mu\nu,\rho\sigma}^\dagger U \bar{X}_n^i$. This equation relates the transition matrix element to a superposition of atomic-like quantities.

We now insert the transition matrix element (7) into the basic Eq. (4) for the decay width, integrate over the momentum $\vec{k}$ of the emitted electron, and neglect interference terms (cross terms). The result reads:

$$\Gamma = \sum_n \Gamma_n ,$$  \hspace{1cm} (8)

$$\Gamma_n = \sum_{\mu\nu} |T_{\mu\nu}|^2 |\bar{Y}_n^\mu\nu|^2 .$$

The partial width $\Gamma_n$ associated with the final dicaticonic state $|\Psi_n^{N-2}\rangle$ is expressed as a sum over atomic $2h$ configurations. Each contributing term consists of a state-specific factor $|\bar{Y}_n^\mu\nu|^2$, which we have calculated earlier.
The other factor,
\[ |T_{\mu\nu}|^2 = 2\pi \sum_k \left| \langle \mu \nu | \hat{c}_k \hat{H} | \Psi_1^{N-1} \rangle \right|^2 \delta(E_n - E_1), \]  
(9)
depends on the dicationic state \( |\Psi_2^{N-2} \rangle \) only via the \( \delta \) function and is termed transition strength. Since we consider the decay of a core level, implying that the energy of the emitted electron is relatively high, this dependence on \( n \) is weak and can be neglected to a good approximation.

The state-specific quantities \( |Y_{\mu\nu,n}|^2 \) are closely related to the occupation numbers discussed in Sec. II A. In principle, they could be used as an alternative definition of occupation numbers in the spirit of Löwdin’s population analysis. In particular, if the atomic basis functions are well localized, each on its atom, we may put \( |Y_{\mu\nu,n}|^2 = Q_{\mu\nu,n} \) and obtain
\[ \Gamma_n = \sum_{\mu\nu} |T_{\mu\nu}|^2 Q_{\mu\nu,n}. \]  
(10)
For a given molecule the quantities \( |T_{\mu\nu}|^2 \) are universal, and the only information that is state-specific is contained in the occupation numbers \( Q_{\mu\nu,n} \). We are able to compute the occupation numbers of the molecules studied in this work, and hence Eq. (10) is already a useful tool of analysis.

We note, however, that many elements \( |T_{\mu\nu}|^2 \) can be of similar magnitude, e.g., if \( \mu \) denotes a \( p \)-type atomic orbital on atom \( A \) and \( \nu \) a \( p \)-type atomic orbital on atom \( B \). We therefore group together in Eq. (10) the corresponding contributions:
\[ \Gamma_n = |T_{AB}|^2 \sum_{\mu,\nu} Q_{\mu\nu,n} + \cdots. \]
The \( |T_{\mu\nu}|^2 \) grouped together are not identical, the average quantity \( |T_{AB}|^2 \) will depend somewhat on the dicationic state index \( n \). Computing \( \Gamma = \sum_n \Gamma_n \) amounts to averaging over the slightly varying \( |T_{AB}|^2 \) and thus leads to a more stable result.

Highly localized dicationic final-state holes, for example those that result from ICD in weakly bound clusters, lead to similar contributions to the overall decay width of the initially ionized state. By classifying the atomic pairs \( (\mu\nu) \) by their localization characteristics, we can form sets of atomic orbitals where \( |T_{AB}|^2 \) is only a slightly varying quantity. Let us denote with \( A \) the atom on which the initial core hole is localized. Then, if \( \mu \) and \( \nu \) denote atomic orbitals on \( A \), \( |T_{\mu\nu}|^2 \) obviously corresponds to IAED (Sec. II). Analogously, if \( \mu \) belongs to atom \( A \) and \( \nu \) to atom \( B \), we are dealing with ICD, and if neither \( \mu \) nor \( \nu \) belong to \( A \), \( |T_{\mu\nu}|^2 \) describes either ETMD2 or ETMD3, depending on whether \( \mu \) and \( \nu \) belong to the same atom \( B \) or to two atoms \( B \) and \( C \). Thus, the minimal dissection of \( \Gamma \) into its various contributions, in the spirit of the above discussion, reads
\[ \Gamma = \Gamma_{\text{IAED}} + \Gamma_{\text{ICD}} + \Gamma_{\text{ETMD2}} + \Gamma_{\text{ETMD3}}, \]  
(11)
where
\[ \begin{aligned}
\Gamma_{\text{IAED}} &= |T_{\text{IAED}}|^2 Q_{\text{IAED}}, \\
\Gamma_{\text{ICD}} &= |T_{\text{ICD}}|^2 Q_{\text{ICD}}, \\
\Gamma_{\text{ETMD2}} &= |T_{\text{ETMD2}}|^2 Q_{\text{ETMD2}}, \\
\Gamma_{\text{ETMD3}} &= |T_{\text{ETMD3}}|^2 Q_{\text{ETMD3}},
\end{aligned} \]
(12)
and
\[ \begin{aligned}
Q_{\text{IAED}} &= \sum_n \sum_{\mu,\nu} Q_{\mu\nu,n}, \\
Q_{\text{ICD}} &= \sum_n \sum_{\nu,\mu} Q_{\mu\nu,n}, \\
Q_{\text{ETMD2}} &= \sum_n \sum_{\nu,\mu} Q_{\mu\nu,n}, \\
Q_{\text{ETMD3}} &= \sum_n \sum_{\nu,\mu} Q_{\mu\nu,n}.
\end{aligned} \]
(13)
If necessary, further dissections of \( \Gamma \) into more detailed contributions are readily done. For instance, grouping together separately the contributions of \( \mu \) and \( \nu \), both being atomic orbitals of \( s \)-type, both of \( p \)-type, or one of \( s \) and one of \( p \)-type, etc. A distinction between the decay into singlet and triplet final dicationic states is also possible. Finally, we mention that the individual transition strengths, \( |T_{\text{ICD}}|^2 \), etc., may be similar in a series of related molecules.

IV. RESULTS AND DISCUSSION

A. Double Ionization Spectra

The computed double ionization spectra for the xenon atom, the fluorine molecule, and the series \( \text{XeF}_n \), \( n = 2, 4, 6 \), are shown in Fig. 3. The molecular ground-state geometries used in the calculations are described in Refs. 21 and 22. It has to be stressed, however, that the double ionization spectrum of \( \text{XeF}_6 \), unlike the single ionization spectrum in Refs. 21 and 22, has been calculated assuming a geometry of \( O_h \) symmetry, instead of \( C_{3v} \) symmetry, in order to make the calculation feasible with the available computer resources. We also refer the reader to Refs. 21 and 22 for details regarding the Gaussian basis sets employed.

The ADC \( 2h \) pole strength plotted in Fig. 3 characterizes how well the dicationic states are described by \( 2h \) configurations. The deviation of the \( 2h \) pole strength from unity yields the total contribution of three-hole–one-particle configurations to the state in question. Our focus in this work is on the energy regime below the \( \text{Xe} \text{F}_4 \) single ionization threshold, which ranges from almost 68 eV in atomic Xe to a little less than 76 eV in \( \text{XeF}_6 \). The double ionization spectra below 80 eV in Fig. 4 comprise ionization out of the outer and inner valence of Xe, \( \text{F}_2 \), and \( \text{XeF}_n \). Since mean-field and correlation effects, as revealed by the ADC scheme, dominate
in the valence region, the spectra have not been corrected for relativistic effects, which are expected to be negligible.

Double ionization from the outer valence of the xenon atom takes place between 30 and 40 eV, and three distinct DIPs are found in Fig. 3. The spectra of the series XeF\(_n\), \(n = 2, 4, 6\), display in this region increasingly dense lying DIPs, which is attributed to a growing number of outer-valence states due to a higher delocalization of the two final-state holes. The double ionization spectrum of F\(_2\) in Fig. 3 shows outer-valence ionization of F\(_2\) in the range between 40 and 55 eV. With an increasing number of fluorine ligands, the general trend in the spectra, especially at DIPs above 40 eV, is a decrease of the validity of the two-hole description of dicaticonic states of XeF\(_n\). As all fluorine atoms in XeF\(_n\) are equivalent (the double ionization spectrum of XeF\(_6\) is obtained in \(O_h\) symmetry), a dicaticonic state with a hole on xenon and a hole on a fluorine atom is in fact a linear combination of configurations involving a hole on xenon and a hole on one of the \(n\) fluorine atoms in XeF\(_n\). The coefficients of the linear combinations are determined by the strength of the interaction among the fluorine ligands, being the weakest in XeF\(_2\).

The triple ionization threshold of the xenon atom\(^{53}\) is 66.2 eV; for the xenon fluorides, the triple ionization threshold is at least that low. Therefore, many of the dicaticonic states we have calculated can decay to tricationic ones. Owing to the discrete basis set used, the appearance of a decaying state mimics a discretized Lorentzian curve as can be seen in Fig. 3 such curves may indeed be identified for XeF\(_n\) above 50 eV. Interestingly, the Xe 4\(d\) lines in the single ionization spectra of xenon and its fluorides\(^{19,21,22}\) are thus above the triple ionization threshold. This indicates that there is some probability for the Xe 4\(d\) holes to decay by emitting two electrons. According to a measurement by Kämmerling et al.\(^{54}\) this probability amounts to about 20% in atomic xenon.
When analyzing the DIPs, one has to keep in mind that essentially there are four contributions to a dicaticonic state that determine its character. The two holes in the dicaticonic state can be localized on one atom, either Xe or F, or on two atoms, Xe and F or two different F atoms. The one-site states have a large dicaticonic population number on either xenon (Xe$^2^-$) or a single fluorine (F$^2^-$), and the two-site states are of either Xe$^1^-F^{-1}$ or F$^1^-F^2^-$ character. For each dicaticonic state appearing in the spectra of the xenon fluorides, the data of the population analysis for equivalent fluorine atoms are summed up to yield the population numbers. In XeF$_2$, for example, the Xe$^{-1}F1^-1$ and Xe$^{-1}F2^-1$ population numbers are added to give a single Xe$^{-1}F^{-1}$ contribution for each dicaticonic state in the spectrum of XeF$_2$.

B. One-site Population Numbers

The one-site population numbers for the xenon fluorides are plotted in Fig. 1. For the graphical representation in Fig. 1 and in Fig. 1, the population numbers have been normalized, i.e., the sum of the contributions of Xe$^2^-$, F$^{-2}$, Xe$^{-1}F^{-1}$, and F$1^-F^{-2}$ character equals unity for each dicaticonic eigenstate. The spectra are compared to study the effect of the increasing number of fluorine atoms. The first states in the double ionization spectra possess DIPs of $\approx$ 30 eV. The major contribution of the one-site population Xe$^{-2}$ is at the lower energy part of the spectrum. Obviously, the density of states with a considerable F$^{-2}$ population increases due to the increasing number of fluorine atoms. The overall distribution of these states does not change much in the different compounds. Certain regions are visible where the states have a high F$^{-2}$ population. These regions shift slightly to higher DIPs due to the reduced excess charge that the individual fluorine atoms acquire from the central xenon atom in the molecular ground state.$^{21,22}$

Conversely, the importance of Xe$^{-2}$ contributions to the dicaticonic states is extremely reduced due to the withdrawal of valence electron density on the xenon atom. In XeF$_6$, the contributions of Xe$^{-2}$ character have nearly vanished.

C. Two-site Population Numbers

The two-site population numbers for the xenon fluorides are plotted in Fig. 1. The impact of the increasing number of fluorine atoms is seen here as well. The states with a large F$1^-F^{-2}$ population in the spectrum of XeF$_2$ are clearly separated into distinct groups of lines originating from F1$2p^-1$ F2$2p^-1$, F1$2p^-1$ F2$2s^-1$, and F1$2s^-1$ F2$2s^-1$ populations. This can be concluded from a simple energy consideration. The IPs for ionization from molecular orbitals with F$2p$ character are located at $\approx$ 20 eV, those for ionization from molecular orbitals with F$2s$ character are located at $\approx$ 40 eV.$^{21,22}$ In the spectrum of XeF$_2$ in Fig. 1, the groups are approximately at 40, 60, and 80 eV. XeF$_2$ is a linear molecule, the two fluorine atoms being separated by the central xenon atom. Such states with a large F$1^-F^{-2}$ population are termed opposite F$1^-F^{-2}$ states.

The situation changes in XeF$_4$ and XeF$_6$. There are adjacent and opposite F$1^-F^{-2}$ states, and the clear separation between the groups seen in the spectrum of XeF$_2$ is lost. One reason for this effect is the interaction between adjacent fluorine atoms, which is stronger than the interaction between opposite ones. This leads to a splitting of the fluorine lines, which is also observed in the single ionization spectra.$^{21,22}$

The F1–F2 distance in adjacent F$1^-F^{-2}$ states is considerably reduced in comparison to the F1–F2 distance in opposite states, and the hole–hole repulsion energy varies accordingly. Of course, one has to compare states which have a large F$1^-F^{-2}$ population that arises from the same types of orbitals. Such F$1^-F^{-2}$ states are distributed over a small energy range in the double ionization spectrum. Corresponding lines in XeF$_2$ mark the lower ends of such DIP ranges, due to the maximum distance between the two vacancies. Coulomb repulsion between holes on adjacent fluorine ligands in XeF$_4$ and XeF$_6$ results in shifts toward higher DIPs.

States with a large Xe$^{-1}F^{-1}$ population do not group like those of F$1^-F^{-2}$ character. The density of these Xe$^{-1}F^{-1}$ states also increases with an increasing number of fluorine atoms, but they are distributed more uniformly over the whole spectral range. In XeF$_2$ and XeF$_6$, these states are dominant with respect to population number, and in XeF$_4$ they are comparable to the F$1^-F^{-2}$ states. The DIPs of the Xe$^{-1}F^{-1}$ states are not subject to a change of the hole–hole repulsion energy (in contrast to those of the F$1^-F^{-2}$ states) because the Xe–F distance is the same for all fluorine ligands within a molecule (remember that the double ionization spectrum of XeF$_6$ was calculated assuming octahedral symmetry).

D. Xe 4d Linewidth

The electronic decay processes presented in Sec. 11 are characterized in Sec. 1111 according to their final-state population. Using Eqs. (11), (12), and (13), the analysis of the final-state population numbers allows one to determine the relative importance of IAED, ICD, ETMD2, and ETMD3 for the electronic decay of a Xe 4d hole in XeF$_4$. The partial decay width associated with a given decay process can be viewed, according to Eq. (12), as a product of an averaged Coulomb matrix element and a two-hole population factor related to that process.

We calculated the population factors, as defined by Eq. (13), by summing population numbers up to the energy of the Xe 4d lines obtained in Ref. 22. The results are collected in Table 1.$^p$ We see that $Q_{IAED}$ is rather low in the xenon fluorides, especially when compared to the
FIG. 4: (Color) One-site population numbers of the double ionization spectra of XeF$_2$, XeF$_4$, and XeF$_6$. Each line shown is related to a dicationic state in the double ionization spectra in Fig. 3. The height of the line gives the one-site population number. Note that the contributions on xenon decrease drastically as the number of fluorine atoms increases.

TABLE I: Two-hole population factors for intra-atomic electronic decay (IAED) and for the interatomic decay processes ICD, ETMD$_2$, and ETMD$_3$ in xenon and its fluorides. The two-hole population factors are defined in Eq. (13).

| Compound | $Q_{\text{IAED}}$ | $Q_{\text{ICD}}$ | $Q_{\text{ETMD}_2}$ | $Q_{\text{ETMD}_3}$ |
|----------|------------------|-----------------|---------------------|---------------------|
| Xe       | 14.6             | 0               | 0                   | 0                   |
| XeF$_2$  | 10.4             | 43.8            | 19.4                | 22.7                |
| XeF$_4$  | 7.1              | 68.1            | 34.3                | 124.1               |
| XeF$_6$  | 4.8              | 80.2            | 45.5                | 288.6               |

population factors $Q_{\text{ICD}}$, $Q_{\text{ETMD}_2}$, and $Q_{\text{ETMD}_3}$. Hence, as far as population numbers are concerned, IAED is suppressed, and interatomic decay processes dominate the electronic decay of a Xe 4$d$ hole. Also note the sensitive dependence of all population factors on the number of fluorine ligands.

In order to arrive at a complete picture, the transition strengths in Eq. (12) have to be determined. For this purpose, we make a reasonable assumption: The transition strengths $|T_{\text{IAED}}|^2$, $|T_{\text{ICD}}|^2$, $|T_{\text{ETMD}_2}|^2$, and $|T_{\text{ETMD}_3}|^2$ are universal for xenon and its fluorides. This allows us—utilizing Eqs. (11) and (12)—to take the averaged experimental Xe 4$d$ linewidths, displayed in Fig. 1 and reproduced in Table II and the population factors in Table I to set up a linear system of four equations for the four unknown transition strengths. The matrix of population factors, however, is extremely ill-conditioned, as its $L^2$ condition number, for instance, is 945, which is much larger than unity. This means that the solution of the linear system depends strongly on the accuracy of the population factors.

Therefore, we first determine $|T_{\text{IAED}}|^2$ by solving Eqs. (11) and (12) for the xenon atom. We then exploit that both $|T_{\text{ETMD}_2}|^2$ and $|T_{\text{ETMD}_3}|^2$ are based on electron transfer between Xe and a fluorine ligand. They are thus expected to be of similar magnitude, so we set $|T_{\text{ETMD}_2}|^2 = |T_{\text{ETMD}_3}|^2$. The remaining linear system of three equations and two unknowns can be solved in a stable fashion by a least-squares procedure. The calculated transition strengths for Xe and XeF$_n$ are displayed in Table III. The results are in line with expectations: The transition strength associated with intra-atomic decay is greater by an order of magnitude than the interatomic energy-transfer strength of ICD. $|T_{\text{ETMD}_2}|^2$ and $|T_{\text{ETMD}_3}|^2$, which require interatomic orbital overlap for electron transfer, are even smaller.

Finally, by combining the population factors from Table I and the transition strengths from Table II, the par-
FIG. 5: (Color) Two-site population of the double ionization spectra of XeF$_2$, XeF$_4$, and XeF$_6$.

| Decay Process | $|T|^2$ [eV] |
|---------------|-------------|
| IAED          | $1.4 \times 10^{-2}$ |
| ICD           | $1.9 \times 10^{-3}$ |
| ETMD2/ETMD3   | $2.1 \times 10^{-4}$ |

TABLE II: Transition strengths for electronic decay of a Xe 4$d$ hole in XeF$_n$.

We have shown that interatomic electronic decay processes are of prime importance for understanding relaxation of a Xe 4$d$ vacancy in the xenon fluorides. The experimentally observed trend of increasing Auger width in the series XeF$_n$, $n = 0, 2, 4, 6$, is an impressive consequence of the fact that interatomic Coulombic decay and electron-transfer mediated decay not only cancel out the drop in intra-atomic Auger rate: Interatomic decay dominates by far in the larger xenon fluorides. In XeF$_6$, for example, 76% of the total Xe 4$d$ linewidth is due to the combined effect of ICD, ETMD2, and ETMD3.

ICD in XeF$_n$ takes place on an ultrashort time scale of less than 10 fs. This is of the same order of magnitude as the ICD lifetimes calculated for a 2$s$ hole in a Ne atom surrounded by at least six neon monomers. Our finding that, in XeF$_6$, $\Gamma_{\text{ICD}}$ is only a little more than two times greater than $\Gamma_{\text{ETMD3}}$, affords a new impulse for cluster and condensed-matter research. We anticipate ETMD3 to be a major decay mechanism for an inner-valence hole, for instance, in a neon atom embedded in an argon matrix.

There are obvious consequences of our investigation for molecules bearing a similarity to XeF$_n$. An interesting example is Auger decay of a Si 2$p$ hole in SiF$_4$. It was shown in Refs. 15 and 16 that virtually not a single di-
cationic (valence) eigenstate in SiF$_4$ is, at a significant level, of Si$^{-2}$ character. The occurrence of primarily multi-center decay channels is termed foreign imaging. It is these channels to which ICD, ETMD2, and ETMD3 provide access. In light of the present study, we may conclude that the calculation by Larkins based on the one-center model, must be expected to appreciably underestimate the Si$^{2p}$ Auger width in SiF$_4$. A recent measurement by Thomas et al. proves this expectation to be justified: The experimental Si$^{2p}$ Auger width is more than five times greater than the prediction of the one-center model. The authors of Ref. 18 also interpret this discrepancy in terms of interatomic electronic processes.

Our approach to molecular Auger decay, as presented in this paper, lays its emphasis on the decay channels. Though not impossible, an actual computation of Auger widths in such complicated many-electron systems as the xenon fluorides still cannot be carried out in a very reliable and accurate manner. We therefore put to use two highly powerful theoretical tools: the ADC scheme for the two-particle propagator and the two-hole population analysis of dicationic eigenstates. These two methods allow us to concentrate on the mechanisms underlying Auger decay by yielding detailed information about the nature of the available decay channels.

The key relations (11), (12), and (13) between two-hole population numbers and partial Auger widths are, strictly speaking, only valid for molecules with pronounced charge localization characteristics. The xenon fluorides satisfy this criterion well. We are convinced, however, that the basic picture is much more general. In order to understand Auger decay in arbitrary molecules, it is usually insufficient to restrict the analysis to local valence electron densities. The physics may be even more complicated, but a qualitative decomposition into interatomic processes ICD, ETMD2, and ETMD3 is most likely still possible.

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| Compound  | $\Gamma_{\text{IAD}}$ [eV] | $\Gamma_{\text{ICD}}$ [eV] | $\Gamma_{\text{ETMD2}}$ [eV] | $\Gamma_{\text{ETMD3}}$ [eV] | $\Gamma_{\text{expt}}$ [eV] |
|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Xe        | 0.20            | 0.00            | 0.00            | 0.00            | 0.20            |
| XeF$_2$   | 0.15            | 0.08            | 0.00            | 0.00            | 0.24            |
| XeF$_4$   | 0.10            | 0.13            | 0.01            | 0.03            | 0.26            |
| XeF$_6$   | 0.07            | 0.15            | 0.01            | 0.06            | 0.29            |

TABLE III: Decomposition of the mean experimental electronic decay width, $\Gamma_{\text{expt}}$, of the Xe$4d$-lines in Xe and XeF$_n$ into contributions from intra-atomic and interatomic decay processes. $\Gamma_{\text{expt}}$ is taken from Fig. 1.
