The ab-initio simulation of Auger spectra*

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An efficient approach for the theoretical ab-initio simulation of the Auger spectra of polyatomic systems is reviewed. The theoretical and computational framework, based on a Green’s function method for the accurate calculation of dense double ionization spectra, includes methods for the quantitative evaluation of the two-hole density distribution in the final states and for the estimate of major nuclear dynamics effects on the Auger bandshapes. Some illustrative applications are discussed proving that these tools are of essential aid for the description and understanding of fundamental aspects of Auger spectroscopy. Recently discovered phenomena like foreign imaging and aggregation state effects are briefly discussed.

1. INTRODUCTION

Auger electron spectroscopy has long established itself as a powerful tool for chemical analysis [1]. With the advent of high resolution techniques based on the routine availability of synchrotron radiation, Auger spectroscopy has also received considerable new impetus as a method to access the doubly ionized states of free molecules and obtain valuable information on their energetics and dynamics [2]. Its recent developments have paralleled those of complementary techniques such as double charge transfer [2,3], coincidence Auger [4], double photoionization [5,6], and the advances in the experimental study of the decay of core excited states (resonant Auger) [7].

The necessary parallel development of theoretical tools for the reliable interpretation of the experimental data has progressed at a comparatively slower pace [8]. The calculation of Auger spectra of polyatomic molecules and materials at a level of accuracy sufficient to predict faithful bandshapes remains in fact a very difficult task, ultimately because of the lack of strict selection rules and the large number of electronic transitions from the decaying state to the final dicationic states which appear in the spectra. The need to compute these very many transition, quickly growing into the hundreds if not thousands already for molecules not much larger than triatomics, puts out of question the routine use of very accurate conventional methods of quantum chemistry and, on the other hand, demands that the electron correlation effects accompanying such density of final states and inducing substantial charge redistribution effects be accounted for to a sufficient degree. In addition to this, further key issues which must be handled reliably include at least the evaluation of Auger intensities and some account of the major nuclear dynamics effects on the bandshapes. Just as well, treating these aspects at the level of individual electronic states by accurate first-principles theory is a forbidding task.

To tackle these problems we have developed in recent years a specific theoretical and computational ab-initio approach [9], based on the two-particle Green’s function theory [10], which attempts to combine both accuracy and practicability, and thus to be usable for a wide range of applications. The present contribution focuses on the latest developments of this approach with the aim of outlining the current state of the art in the theoretical simulation of Auger spectra of polyatomic systems. After briefly sketching the theoretical and computational machinery, we shall illustrate, by discussing exemplary applications, some interesting key aspects and phenomena in Auger spectroscopy which the calculations have helped us to clarify.

*Work supported by the Progetto finalizzato CNR “Materiali speciali per tecnologie avanzate” and by the Deutsche Forschungsgemeinschaft.
2. THEORETICAL AND COMPUTATIONAL ASPECTS

2.1 The Green's function ADC method

For the study of simultaneous double ionization processes of an \(N\)-electron system the quantity of interest is the retarded part of the particle-particle propagator \([11]\), a particular projection of the two-body Green's function \([10]\), whose diagonal spectral representation in energy space reads

\[
P(\omega) = \mathbf{X}^\dagger (\omega \mathbf{1} - \Omega)^{-1} \mathbf{X}
\]  

(1)

where \(\Omega\) is the diagonal matrix of (negative) double ionization potentials (DIPs)

\[
\Omega_j = -(E_j^{N-2} - E_0^N)
\]  

(2)

for the \((N-2)\)-particle states \(|\Psi_j^{N-2}\rangle\) and \(\mathbf{X}\) is the matrix of residue amplitudes:

\[
X_{f,i,j} = \langle \Psi_j^{N-2} | a_i^\dagger a_j | \Psi_0^N \rangle
\]  

(3)

Here \(|\Psi_0^N\rangle\) is the molecular \(N\)-particle ground state of energy \(E_0^N\) (which we shall assume nondegenerate) and \(a_i^\dagger, a_i\) are creation and destruction operators, respectively, defined in some chosen one-particle basis.

To approximate the propagator, and thereby evaluate double ionization energies and spectroscopic factors, we use the Algebraic Diagrammatic Construction theory (ADC) \([12-14]\). This formalism couples in an efficient way the perturbation expansion of the neutral ground state \(|\Psi_0^N\rangle\) (starting from the unperturbed Hartree-Fock hamiltonian) with the configuration interaction expansion of the dicationic states \(|\Psi_j^{N-2}\rangle\). To this end, one writes a non-diagonal ansatz representing the propagator in the space of the unperturbed \((N-2)\)-particle configurations (classified as \((n+2)\)-hole-\(n\)-particle: \((n+2)hnp, n = 0, 1, \ldots\)):

\[
P(\omega) = \mathbf{F}^\dagger (\omega \mathbf{1} - \Gamma)^{-1} \mathbf{F}
\]  

(4)

with Eq. (1) and Eq. (4) being related through the hermitian eigenvalue problem for \(\Gamma\). The ADC formulation now determines the matrix elements of \(\Gamma\) and \(\mathbf{F}\) by conceptually requiring that, at any given order of perturbation theory of the ground state, \(\Gamma\) be the block-diagonal representation of an effective hamiltonian selecting the smallest possible configuration space which is physically required to yield double ionization energies and amplitudes correct at least up to the prescribed order for the main states. These are the states perturbatively derived from \(2h\) configurations, which have the largest spectroscopic amplitudes. Classes of higher excited (satellite) states, which have nonzero spectroscopic amplitudes as a consequence of relaxation and correlation effects, are treated at correspondingly decreasing orders of accuracy, according to their perturbation theory genealogy.

This design strategy is at the origin of the efficiency of the ADC method. Compared to a conventional configuration interaction (CI) approach (which in this context may be seen as \(\Gamma\) being the representation of \(E_0^N - H\), where \(H\) is the hamiltonian of the system) the size of its configuration space grows half as fast with the order of perturbation in units of the required configuration classes (at the comparatively little price, of course, that some blocks of matrix elements are nonlinear in the perturbation). This translates, in turn, into a much weaker power dependence on both the size of the molecular system under study and the basis set employed. For example, in the second and third order ADC schemes which we have implemented, the active configuration space comprises only the \(2h\) and \(3h1p\) configuration classes, i.e. it is smaller than the single plus double excitation CI required to obtain second order accuracy. Of course, for any individual state or small group of states, the CI method can be tailored to deliver results of higher accuracy by using relaxed or MCSCF orbitals and an appropriately selected configuration space. But this rapidly becomes impracticable for computing the whole double ionization spectrum of all but the smallest molecules, a task which is the prerequisite of theoretical Auger spectroscopy and which ADC is designed to accomplish with optimal cost-effectiveness.

On the computational side, ADC configures itself essentially as a large symmetric eigenvalue problem of which we wish to calculate many roots. Explicit construction of the \(\Gamma\) matrix is avoided by implementing a direct, integral driven, algorithm \([15]\) which, in the second order scheme ADC(2), is facilitated by the fact that only two-electron integrals having at most two virtual indices are required. In the diagonalization step, we are typically interested in computing all eigenvectors which have a non-negligible projection onto the \(2h\) configuration space, as these correspond to the spectroscopically most active dicationic states. This is accomplished by using a specifically optimized block-Davidson procedure which, for deep lying eigensolutions, incorporates a shifted inverse-operator technique \([16]\). For larger problems, where the density of active states in Auger spectra is typ-
ically of the order of several tens per eV, obtaining exact solutions for these selected roots is, besides forbidding, not necessary. It is sufficient to compute the envelope of the dense 2h pole strength distribution of the spectrum, which can be related to the Auger intensity distribution [17,18]. The calculation can be very effectively carried out by employing a moment-preserving block-Lanczos procedure iterated on the 2h space [19]. This technique can be shown [20] to provide a convergence rate on the “spectrum” of main space components of the eigenvectors which is exponential in the width of the lines making up the spectrum.

2.2 Two-hole density distribution in doubly ionized states

The ADC method enables us to compute a very large number of dicationic states and we must be able to understand in a simple and concise way their nature, spectroscopic and dynamic properties, which are essentially controlled by the distribution of the two-hole density. To describe this, we use a two-hole population analysis [18] similar in spirit to the familiar Mulliken analysis. By expanding the propagator amplitudes (or more simply the 2h part of the ADC eigenvectors) in the atomic orbital basis, we can express the total 2h pole strength as a sum of contributions describing the localization of the two-holes on single atomic centers (one-site terms) and on pairs of atoms each carrying one hole (two-site terms). From these calculations it is possible to describe in a quantitatively well defined way the character of the states in terms of charge (de)localization. Two-hole localization is flagged by the dominance of one particular contribution, of either one-site or two-site type, over all the others, while delocalization is characterized by a number of terms having comparable magnitude. This gives an immediate picture of the nature of the states and their distribution in the double ionization spectrum which has often been enlightening, as we shall review in Section 3.

The characterization of the states via the two-hole population analysis also offers a simple but qualitatively correct tool to estimate the essential features of the intensity distribution in the Auger spectra. This is very useful for the simulation of the Auger spectra of polyatomics, where the high density of states renders both prohibitive and statistically unnecessary [17] any more accurate level of computation of Auger transition rates. Because of the restricted space localization of the primary core hole at one atomic site, the Auger decay is an essentially intra-atomic process, populating preferentially final dicationic states where the valence two-hole density is larger at the initially core ionized site. Qualitatively, therefore, an Auger spectrum may be thought of as a rough measure of the relative extent of atomic two-hole localization in the final state manifold. This consideration immediately suggests that the one-site components of the pole strength should provide adequate estimates of the corresponding Auger spectra, at least where the density of states contributing to each observable band statistically averages out any not too large inaccuracy incurred at the level of individual transitions.

2.3 Nuclear dynamics effects on Auger bandshapes

The ADC calculations provide us with vertical double ionization spectra and before meaningful simulations of Auger spectra can be produced from these, one must be able to evaluate the major effects of nuclear dynamics on the Auger bandshapes, at least limited to the motion of the nuclei on the adiabatic potential energy surfaces of the decaying and final states [21,22]. Because of the high density of overlapping transitions in the spectra of polyatomic systems, vibrational progressions are usually not resolved and we can therefore usefully employ an approximate model to estimate the energy centroids and the broadenings of the bands, i.e. the lowest order moments of the vibrational spectra.

The required working equations have been derived from the general time-dependent theory of the nuclear dynamics of decay processes [23]. For a target system having M totally symmetric normal modes of vibration of harmonic frequencies \(\omega_i\), the expression for the first moment of an Auger transition reads

\[
\langle E \rangle = \Delta - \sum_{i=1}^{M} \xi_i \left[ 1 - \frac{\Gamma^2}{\Gamma^2 + \omega_i^2} \right]
\]

(5)

Here \(\Delta\) is the vertical transition energy at the target’s equilibrium geometry and \(\xi_i = \kappa_i \beta_i / \omega_i\), where \(\kappa_i\) is the slope of the decaying state surface along the \(i\)-th dimensionless normal mode and \(\beta_i\) is the difference between \(\kappa_i\) and the corresponding final state slope. \(\Gamma\) is the core hole lifetime width. The variance of the vibrational distribution is similarly given by

\[
\langle E^2 \rangle - \langle E \rangle^2 = \frac{1}{2} \sum_i \left\{ \beta_i^2 + \xi_i^2 \left[ 1 + \frac{\Gamma^2}{\Gamma^2 + 4\omega_i^2} - 2 \left( \frac{\Gamma^2}{\Gamma^2 + \omega_i^2} \right)^2 \right] \right\}
\]
In Eqs. (5) and (6) the non-totally symmetric vibration modes do not contribute since vibronic coupling effects are not considered and the energy derivatives vanish. By convoluting the Auger band with a Gaussian function, and including an experimental resolution parameter $\Gamma_\sigma$, its full width at half maximum $W$ is related to the second moment by:

$$W = \sqrt{8 \ln 2 \left( \langle E^2 \rangle - \langle E \rangle^2 \right) + \Gamma_\sigma^2}$$

These equations show that, through the effect of the $\kappa_i$ slopes and the $\Gamma_i$ lifetimes, the vibrational parameters depend on the intermediate state of the Auger decay, and thus can be very different, in general, in the different spectra of the same molecule. The "state specific" factors depending on the individual final states are instead identified with the final state energy derivatives appearing in the $\beta_i$ parameters. It is interesting to note that while the normal modes give additive independent contributions to the shifts induced by nuclear dynamics (see Eq. (5)), coupling terms between modes appear in the second and higher moments. These terms vanish in the limit of both very long and very short lifetime of the decaying state.

As is clear, the analysis requires the calculation of the gradient of the transition energies in normal coordinate space at the ground state equilibrium geometry, which can be done numerically by multiple ADC calculations. In addition, the core hole state slopes $\kappa_i$ along the normal modes must also be computed. This can be carried out by standard ab-initio calculations, e.g. CI. In the model outlined above we have assumed a process involving a single well defined decaying state and final adiabatic states. More complex cases involving vibronic coupling effects and non-totally symmetric contributions have also been analyzed [23].

3. PHENOMENA IN AUGER ELECTRON SPECTROSCOPY. SOME CASE STUDIES

3.1 Nuclear dynamics effects in the Auger spectra of carbonyl compounds

Simple carbonyl containing molecules, such as carbon monoxide itself, formaldehyde and acetaldehyde have been investigated in detail by Auger spectroscopy. Despite their small size, their carbon and oxygen KLL spectra present many interesting aspects of nontrivial description and permit a systematic study of the variations in the Auger profiles of the important CO group with the chemical environment. The carbon spectrum of CO [21c,24] already exhibits some remarkably distinctive features in the shape of the first two peaks, in particular the evidently composite nature of the first band and the extreme narrowness of the second. First indications of the importance of vibrational and interference effects in the Auger spectra of CO were given in refs. [21b,21c]. We studied with the ADC method the Auger spectra of CO [22] as a test example for our spectral moment analysis of the nuclear dynamics. To illustrate the quality of the results, we show in Fig. 1 the computed carbon spectrum along with the experimental one [24a]. The theoretical spectrum is very accurate in all details and in particular the characteristic shapes of the first (lowest ionization energy) peaks are reproduced exactly. As is clear, vibrational effects influence decisively both the widths and the energy positions of the peaks: the latter are reproduced in the simulation to within 0.2 eV, whereas the computed vertical transition ener-

![Figure 1: Experimental (upper) and theoretically simulated (lower) carbon Auger spectrum of carbon monoxide.](image)
gies differ by up to a few eV from experiment [22]. In addition, the shifts from the vertical energies, as well as the band broadenings, were found to differ by up to several eV between the oxygen and carbon spectra, indicating that the consideration of only intensity differences between different Auger spectra of the same system is in general insufficient to interpret them.

The Auger spectra of formaldehyde and, especially, acetaldehyde are already much more complex and for them previous theoretical calculations [25] could not satisfactorily reproduce the very characteristic band profiles and permitted only a tentative assignment of few principal features. For the low-symmetric acetaldehyde molecule, as many as ten vibrational modes must be taken into account in the calculation of nuclear dynamics effects, this fact alone emphasizing the intractability of even moderately sized systems by conventional theoretical routes. The ADC calculations [26,27] have shown that few hundred electronic states give non-negligible contributions to the spectra, and each observed band is the complex convolution of many transitions. Despite the evident complexity, the theoretical calculations reproduce unambiguously the overall shape and numerous details of the measured spectra. As an example, the theoretical [26,27] and experimental [25] carbon spectra are shown in Fig. 2 and Fig. 3. The computed relative energy of most peaks in both the carbon and oxygen spectra agrees with the observed values to within few tenths of eV. The effects of nuclear motion are found again to constitute the crucial factor in shaping the bands and explaining the very different appearance of the carbon and oxygen spectra. The computed shifts from the vertical transition energies often exceed 1 eV and all have the same sign in the carbon spectrum, while they are always much smaller and of varying sign in the oxygen case. In addition, the widths computed for the carbon transitions are generally much larger than those in the oxygen spectrum. It can be naturally expected that such diverse impact of nuclear dynamics effects in the different Auger spectra of the same system occur as a rule in polyatomic covalent systems. Our calculations indicate that the magnitude of these effects is unexpectedly large and the complex interplay of both energy shifts and band broadenings cannot safely be neglected in the interpretation of Auger spectra.

It is of particular interest that the carbon Auger spectrum of CH$_3$CHO results from the superposition of the the methylic and carbonylic carbon spectra, the two core binding energies differing by only 2.65 eV. This means that a doubled number of transitions, adding up to about 600, each with its own bandshape, underlies the observed convolution. The ADC calculations show [27] that the largest contributions come from methylic carbon transitions, which determine the overall broad profile of the spectrum. The carbonylic component is however responsible for the major part of the features and finer details which can be detected especially in the low energy side of the spectrum. Here again varying vibrational effects play a decisive role
in determining the visibility and appearance of these weaker features. The separately computed methylic and carbonylic spectra [27] clearly show a more pronounced atomic-like character of the former, with generally broader bands, and the more complex and structured appearance of the latter.

3.2 Two-hole localization effects and foreign imaging

The conceptually simple intra-atomic nature of the Auger decay discussed in Section 2 may be deceptive, suggesting models for the interpretation of the spectra which, although very useful in limited contexts, may spectacularly fail if overly generalized. It is clear for example that, to the extent that the electronic structure of an atom in its ground state is not vastly perturbed in the formation of the molecular system, its Auger spectrum must retain some atomic-like appearance. A more or less strict correspondence with the spectrum of the isolated atom is then observed, with the molecular environment causing characteristic perturbations of this underlying atomic structure. The idea of Auger spectroscopy as a tool to reveal atomic fingerprints is at the basis of its vast use in the chemical analysis of surfaces and materials [1]. This state of things, which we may call atomic self-imaging model of Auger spectroscopy, is of course also common among simple molecules and especially for the spectra of electronegative light atoms. In this situation the atomic model can also be usefully employed [28] for estimating molecular Auger intensities based on the known transition rates of the free ground state atom.

But the self-imaging model can break down completely for the Auger spectra of atoms which, in the molecular environment, undergo substantial electronic structure alterations, e.g. electron loss in ionic systems. This situation is most usually associated with strong two-hole density localization at other atomic sites in the molecule as is found, typically, in some polyatomic fluorides [18,19,29]. As an extreme example of this it is instructive to consider the silicon $LMM$ Auger spectrum of SiF$_4$, whose interpretation has puzzled researchers for a long time [30] before being conclusively settled with the aid of ADC calculations and the two-hole population analysis [19,29]. In contrast to the self-imaging model which applies very well to, e.g., the silicon spectrum of silane, this spectrum does not present three atomic-like band regions but at least six broad and equispaced bands. The ADC calculations have demonstrated that in all the dicaticonic states of SiF$_4$ the two electron vacancies are strongly localized at the fluorine sites. In roughly 3/4 of the states a pair of fluorine atoms carry each one hole, while in the other ones both holes are located around only one fluorine. The very small two-hole density at the silicon atom, and thus the intensity distribution of the corresponding Auger spectrum, is instead essentially uniform over all the states. This makes the relative energy of the states totally independent from the hole density at the silicon and entirely governed, via coulomb repulsion, by the two-site or one-site character of the hole localization and by the atomic shells of fluorine involved. It is easy to see [29] that, because of this, the states cluster in eight distinct groups, all of which appear in the silicon spectrum. Fig. 4 shows the excellent agreement between the experimental spectrum [30b] and the one obtained by convolution of the computed Si$^{2-}$ population. It is clear that the total absence of a recognizable Si$^{2+}$ species in the dicaticionic states signals the inapplicability of any atomic self-imaging model of the Si Auger spectrum. On the contrary, because of the total lack of selection rules, the spectrum is a complete and precise image of the surrounding environment where the electron holes are located. This is in remarkable contrast with the incompleteness of the fluorine Auger spectrum itself which, due to the strict selection rules imposed by hole localization, is an ideal self-imaging spectrum where only the relatively small number of one-site states have appreciable intensity. It seems clear that this foreign-imaging char-

![Figure 4: Experimental and theoretical silicon $LMM$ Auger spectrum of silicon tetrafluoride.](image-url)
acter of Auger spectra may dominate more frequently than is usually thought, emerging whenever the two-hole density at a particular atomic site is consistently small over a wide range of the double ionization spectrum. A two-hole population analysis is an indispensable tool to detect such situations.

3.3 Environmental effects. An example

In accord with the general picture, the effects of the chemical environment and the aggregation state on very atomic-like Auger spectra, such as fluorine $KLL$ spectra, are usually observed to consist essentially in a rigid energy shift of the spectrum [1]. Different life-time and vibrational effects may additionally cause detectable changes in band broadenings. One remarkable exception to this simple situation, whose interpretation provides interesting insights amenable to generalization, is provided by the fluorine $KLL$ Auger spectrum of solid KF. In this spectrum the usual intense Ne-like band at high kinetic energy is distinctly split into two well separated peaks [31]. Extensive Green’s function calculations on both the isolated KF molecule and a large cluster simulating the ionic crystal have conclusively clarified [32] that this is a pure solid state effect involving a strong interaction between close lying groups of one-site $F^{-2}$ and two-site $K^{-1}F^{-1}$ states. In the gas phase system these groups of states are well characterized and separated in energy. Consequently, the group of one-site $F^{-2}$ states gives rise to the usual intense atomic-like peak, while the two-site states are essentially inactive (see Fig. 5(A)). We found, however, that the two groups of states lie much closer in energy than in lighter alkaline or alkaline-earth fluorides. The main effect of the cubic crystal field in the solid is to stabilize the electrons of the $F^-$ ion, which is sorrounded by six neighboring $K^+$ ions, and correspondingly destabilize the potassium electrons. As a result, a large energy shift occurs of the $F^{-2}$ dicationic states towards the $K^{-1}F^{-1}$ states [32], with a consequent strong interaction and Auger intensity redistribution. Fig. 5(B) shows the observed band profile [31b] and the theoretical simulation reproducing this remarkably large aggregation state effect.

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