Coincidence and *Total* Photoelectron Spectra and their Differences Induced by Internal Degrees of Freedom

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Recent progress in experimental techniques have made it possible to measure photoelectron spectra in coincidence with particles emitted during the decay of the photoionized species. In this work it will be shown that, contrary to intuition, these coincident photoelectron spectra can be qualitatively different from the photoelectron spectra resulting when all photoelectrons are detected. In particular they carry information on the decay mechanism following photoionization as soon as the decay is influenced by internal degrees of freedom of the photoionized system. This is shown explicitly for the case of vibrational degrees of freedom of molecules and demonstrated with a model study.

Because of recent advances in experimental techniques [1–4], today it is possible to measure photoelectron spectra with unprecedent energy resolution. Most of the ionized states created in a photoelectron experiment are nonstationary and decay by the emission of photons or, if their energy is sufficiently high, of electrons. In traditional photoelectron spectroscopy one measures just the distribution of the photoelectrons and does not pay attention to the secondary particles emitted by the decay of the ionized state. On the other hand, it is nowadays feasible to measure photoelectrons in coincidence with one type of particles, photons or electrons, emitted during the decay of the ionized state and even restrict the energy of these particles to a given range of interest. This is done, for example, employing the x-ray-emission-threshold-electron coincidence (XETECO) technique [4], and in coincidence with electrons using Auger-photoelectron coincidence spectroscopy (APECS) [5–7].

One calls a photoelectron spectrum (PES) measured in coincidence a coincidence PES, in contrast to the usual PES which might then be addressed as the total PES. Experimental evidence for possible differences between coincidence and total spectra is very rare and essentially restricted to a few specific examples in condensed matter [5–7].

We concentrate here on coincidence PES where the photoelectrons are measured in coincidence with all secondary particles of one type, either electrons or photons, regardless of their energy. Such experiments are reported, e.g., in Refs. [3,4]. There are several reasons for this choice. First, it makes the discussion more transparent as one does not have to deal with the additional dependence on the specific final state of the decay. Second, if one measures secondary particles of a given energy, one may encounter differences between the spectra which have a rather trivial origin. For instance, the density of final states then enters as a prefactor. Another example emerges when accidentally the contribution of two overlapping electronic states to the spectrum cannot be resolved in the total spectrum and these states decay to different final states. By setting the secondary particle analyzer on one of these final states, one selectively counts only the photoelectrons coming from the electronic state decaying to the chosen final state. Third, if we find a physical mechanism which invariably leads to differences between the coincidence PES measured regardless of the secondary particle energy and the total spectrum, we may expect that this mechanism leads to even more marked differences when the secondary particle analyzer is set on a specific energy range.

At first sight, one would expect that the coincidence spectra do not contain additional information on the states involved to that already contained in the total spectra. This view is further substantiated by the fact that the widths of lines in the spectra are determined by the total lifetime of the decaying state. Consider, for instance, a photoionized system which can decay both radiatively and via electron emission and that the photoelectrons correlated with the emitted photons can be distinguished from those correlated with the secondary electrons. Intuitively, one would expect that apart from an overall prefactor determining the ratio of the numbers of emitted photons and secondary electrons, the two coincidence PES associated with radiative decay and with electron emission would have the same shape and that this shape would coincide as well with that of the total PES. Indeed, if the photoelectron is fast and already gone when the decay takes place, the photoionization and successive decay of a system can be viewed as a two step process, where the first step is instantaneous and not influenced by the second step.

In this work we demonstrate that while the above intuitive picture is true for atoms, in general it does not hold for more complicated systems like molecules. We have developed a formalism which allows one to describe coincidence PES. In the following we clarify the origin of the differences between coincidence and total PES and show that the former provide additional sources of information

on the photoionized system. In particular, we elucidate the fundamental role played by the internal degrees of freedom of the system. In the derivations we specifically consider molecular systems and focus on the role played in the process by the vibrational degrees of freedom. Our conclusions, though, are of general validity and by no means restricted to molecules.

Consider the process of photoionization of a system and the decay of the resulting ion. Since in general the photoionized system can undergo different decay mechanisms and since, for a given decay mechanism, several final states are in principle present, it is useful to introduce the notion of decay channel and of the partial transition probability associated with it. Indicating the different decay mechanisms with the index j, the possible final states to be reached via j are denoted by $F_i^{(j)}$, corresponding to the decay channel (i, j). Then, the partial transition probability $P_{F_i I}^{(j)}$ for going from the initial state I to the final state F_i via the decay mechanism j, is

$$P_{F_i I}^{(j)} = |\langle F_i^{(j)} | \hat{T}_i^{(j)} | I \rangle|^2 \delta(E_I - E_{F_i^{(j)}}), \qquad (1)$$

where $\hat{T}$ is the transition operator and E_I and $E_{F_i^{(j)}}$ denote the energies of the system in the initial and final state, respectively. The probability $P_{FI}^{(j)}$ of a transition from I to any final state F_i reachable via a specific decay mechanism j is $P_{FI}^{(j)} = \sum_i P_{F_i I}^{(j)}$. This allows us to introduce the notion of coincidence PES $\sigma^{(j)}$, which is the spectrum obtained detecting only the photoelectrons which are associated with a decay of the photoionized system via the mechanism j. For instance, if a photoionized system can decay both via photoemission ($j = PE$) or electron emission ($j = EE$), $\sigma^{(PE)}$ and $\sigma^{(EE)}$ would be the photoelectron spectra obtained collecting all the photoelectrons emitted in coincidence with the secondary electrons and photons, respectively. The coincidence spectrum $\sigma^{(j)}$ can be easily derived from the transition probabilities $P_{F_i I}^{(j)}$ by summation and integration over the final states and energies, respectively. In principle, one could also restrict the energies of the emitted particle to some specified energy range, but this is essentially a trivial extension of the following theory. The total PES, i.e., the one obtained by detecting all photoelectrons independently of the decay channel of the photoionized system, is given by the sum of the coincidence ones: $\sigma_{\text{tot}} = \sum_j \sigma^{(j)}$.

If we consider a molecule described in the framework of the Born-Oppenheimer approximation, and work in the local approximation, this procedure furnishes the following expressions for the total [8] and the coincidence PES:

$$\sigma_{\text{tot}} = \langle 0 | V^\dagger (\omega_p - \mathcal{H}^\dagger)^{-1} \Gamma_{\text{tot}} (\omega_p - \mathcal{H})^{-1} V | 0 \rangle, \quad (2)$$

$$\sigma^{(j)} = \langle 0 | V^\dagger (\omega_p - \mathcal{H}^\dagger)^{-1} \Gamma^{(j)} (\omega_p - \mathcal{H})^{-1} V | 0 \rangle. \quad (3)$$

Here, it is assumed that before photoionization the molecule is in the vibrational state $|0\rangle$ of a given electronic state (typically the ground state); the energy of the state $|0\rangle$ has

been taken as zero of the energy scale. ω_p is the energy of the incident photon minus the kinetic energy of the photoelectron (or, equivalently, the binding energy of the photoelectron) and V is the dipole matrix element between the electronic wave functions of the initial and photoionized states. V may thus depend on the internuclear coordinates. In Eqs. (2) and (3), $\mathcal{H}$ is the non-Hermitian nuclear Hamilton operator governing the nuclear dynamics in the ionized state. It is defined as $\mathcal{H} = H - i\Gamma_{\text{tot}}/2$, where $\Gamma_{\text{tot}} = \Gamma_{\text{tot}}(R)$ is the total decay rate of the state, obtained as sum of all the partial decay rates associated with the available decay channels $\Gamma_{\text{tot}} = \sum_{i,j} \Gamma_i^{(j)} = \sum_j \Gamma^{(j)}$.

Let us first dicuss the simpler case of the total PES. Here, one often assumes that the total decay rate depends only weakly on the internuclear coordinates and adopts a constant value for Γ_{tot} which is determined via considerations related to the Franck-Condon principle [8,9]. When Γ_{tot} is constant, the non-Hermitian Hamiltonian $\mathcal{H}$ can be obtained from the Hermitian one, H, by a simple shift of the constant $-\Gamma_{\text{tot}}/2$ into the complex plane. It is, therefore, sufficient to consider the eigenstates and eigenvalues of H, $H|m\rangle = E_m |m\rangle$, as $\mathcal{H}$ and H share the same set of eigenstates. The eigenvalues of $\mathcal{H}$ are simply given by $E_m - i\Gamma_{\text{tot}}/2$. By inserting in Eq. (2) the resolution of the identity in terms of the eigenstates of H, one promptly obtains

$$\sigma_{\text{tot}}(\omega_p) = \Gamma_{\text{tot}} \sum_m \frac{|\langle m | V | 0 \rangle|^2}{(\omega_p - E_m)^2 + (\Gamma_{\text{tot}}/2)^2}. \quad (4)$$

The photoelectron spectrum is therefore given by a sum of Lorentzians each centered at the energy of the respective ionic vibrational state and having its own weight (Franck-Condon factor), but all characterized by the same width.

The situation becomes more involved as soon as the coordinate dependence of the decay width becomes pronounced. To some extent this is the case in Auger decay [10] and certainly in the interatomic Coulombic decay [11–14] where it is a fundamental characteristic that cannot be ignored. The major complication arises from the fact that the decay width is now an operator in nuclear space and cannot be moved outside the expectation value of Eq. (2) as was the case for a constant decay width. Now one has to work directly with the eigenstates $\{|\tilde{m}\rangle\}$ and complex eigenenergies $\{\mathcal{E}_m\}$ of the non-Hermitian Hamiltonian $\mathcal{H}$, which indeed can no more be derived from those of H. One has $\mathcal{H}|\tilde{m}\rangle = \mathcal{E}_m |\tilde{m}\rangle$ with $\mathcal{E}_m = e_m - i\Gamma_m/2$. It is well-known that $\mathcal{H}$ can be represented as a complex symmetric matrix and that its left and right hand eigenstates $\langle \tilde{m}|$ and $|\tilde{m}\rangle$ are not adjoints of each other as is the case for eigenstates of Hermitian Hamiltonians [15]. The orthogonality relation now reads $(\tilde{m}|\tilde{m}') = \delta_{m,m'}$ and the resolution of the identity is given by $\sum_m |\tilde{m})(\tilde{m}| = 1$.

By observing that $i\Gamma_{\text{tot}} = (\omega_p - \mathcal{H}) - (\omega_p - \mathcal{H}^\dagger)$ the expression for the total PES, Eq. (2), takes on the form $\sigma_{\text{tot}}(\omega_p) = -2 \operatorname{Im} \langle 0 | V^\dagger (\omega_p - \mathcal{H})^{-1} V | 0 \rangle$, which can be explicitly rewritten as

$$\sigma_{\text{tot}}(\omega_p) = -2 \operatorname{Im} \sum_m \frac{V_{0m0}(\omega_p - \mathcal{E}_m^*)}{(\omega_p - e_m)^2 + (\Gamma_m/2)^2}, \quad (5)$$

where $V_{0m0} = \langle 0|V^\dagger|\tilde{m}\rangle(\tilde{m}|V|0\rangle$. We note that the denominator of each term contributing to σ_{tot} exhibits its own width. Because the V_{0m0} can now be complex numbers, σ_{tot} is not anymore given by a superposition of Lorentzians. This indicates that the use of non-Hermitian quantum mechanics can be imperative also for photoelectron spectra, as already shown in Ref. [16] for the case of Auger and x-ray emission spectra. This result is of interest by itself.

What happens if coincidence PES are considered? Assume first that the decay is independent of the internal degrees of freedom; i.e., that both the total and the partial decay rates, Γ_{tot} and $\Gamma^{(j)}$, are constants. Then, it is promptly shown that $\sigma^{(j)}$ is identical to σ_{tot} except for a trivial overall factor: $\sigma^{(j)} = f^{(j)}\sigma_{\text{tot}}$, where $f^{(j)} = \Gamma^{(j)}/\Gamma_{\text{tot}}$. This result, of course, also applies to the atomic case.

The situation changes as soon as the internal degrees of freedom influence the decay, i.e., when either Γ_{tot} or/and $\Gamma^{(j)}$ are coordinate dependent. Consider first for the sake of transparancy the case of a constant Γ_{tot} and a coordinate dependent $\Gamma^{(j)}$. Then, the eigenstates and eigenvalues $\{|m\rangle\}$ and $\{E_m\}$ of H can be used. By inserting in Eq. (3) the resolution of the identity, one now obtains the following explicit expression:

$$\sigma^{(j)} = \sum_{m,m'} \frac{\langle 0|V^\dagger|m\rangle\langle m|\Gamma^{(j)}|m'\rangle\langle m'|V|0\rangle}{(\omega_p - E_m - i\Gamma_{\text{tot}}/2)(\omega_p - E_{m'} + i\Gamma_{\text{tot}}/2)}. \quad (6)$$

Since $\Gamma^{(j)}$ is coordinate dependent, the orthogonality between different eigenstates of H cannot be exploited and, consequently, also the terms with $m \neq m'$ do contribute. The different contributions to the spectrum can be better interpreted by splitting Eq. (6) into two distinct terms

$$\sigma^{(j)}(\omega_p) = \sum_m \frac{|\langle 0|V^\dagger|m\rangle|^2\langle m|\Gamma^{(j)}|m\rangle}{(\omega_p - E_m)^2 + (\Gamma_{\text{tot}}/2)^2} + 2\operatorname{Re}\sum_{m>m'} \frac{\langle 0|V^\dagger|m\rangle\langle m|\Gamma^{(j)}|m'\rangle\langle m'|V|0\rangle}{(\omega_p - E_m - i\Gamma_{\text{tot}}/2)(\omega_p - E_{m'} + i\Gamma_{\text{tot}}/2)}. \quad (7)$$

It is now clearly seen that the structure of the coincidence PES differs qualitatively from that of the total spectrum, Eq. (4). Indeed, $\sigma^{(j)}$ is now given by a term which is a sum of Lorentzians, all characterized by the same width [as is the case in Eq. (4)] and an additional second term exhibiting interference-like contributions. In practice, the largest structural deviations of $\sigma^{(j)}$ from σ_{tot} are expected when the coordinate dependence of $\Gamma^{(j)}$ is substantial. On the other hand, when $\Gamma^{(j)}$ is a very slowly varying function of the nuclear coordinates, $\langle m|\Gamma^{(j)}|m'\rangle$ can be approximately replaced in Eq. (7) by $\delta_{m,m'}$ times an average value of $\Gamma^{(j)}$, and $\sigma^{(j)}$ then reduces to σ_{tot} in Eq. (4) times a factor $\Gamma^{(j)}/\Gamma_{\text{tot}}$.

Finally, we turn to the general case where also Γ_{tot} is coordinate dependent. The expression for the coincidence PES can be similarly split into two terms as done above and reads

$$\sigma^{(j)}(\omega_p) = \sum_m \frac{|\langle 0|V^\dagger|\tilde{m}^*\rangle|^2(\tilde{m}^*|\Gamma^{(j)}|\tilde{m})}{(\omega_p - e_m)^2 + (\Gamma_m/2)^2} + 2\operatorname{Re}\sum_{m>m'} \frac{\langle 0|V^\dagger|\tilde{m}^*\rangle(\tilde{m}^*|\Gamma^{(j)}|\tilde{m}')(\tilde{m}'|V|0\rangle}{(\omega_p - \mathcal{E}_m^*)(\omega_p - \mathcal{E}_{m'})}. \quad (8)$$

It should be noted that now, even when $\Gamma^{(j)}$ is coordinate independent, $\sigma^{(j)}$ still qualitatively differs from σ_{tot}. This is due to $(\tilde{m}^*|\tilde{m}') \neq \delta_{m,m'}$. The markedness of the difference is determined by the functional dependence of Γ_{tot} and eventually of $\Gamma^{(j)}$ on the internuclear coordinates. Furthermore, the magnitude of Γ_{tot} now plays a more important role than in Eq. (7). The reason is that a larger total decay width now increases the overlap between eigenstates $\{|\tilde{m}\rangle\}$ with different m while this was not the case in Eq. (7), where the eigenstates $\{|m\rangle\}$ of H could be utilized.

The kind of structural differences between σ_{tot} and $\sigma^{(j)}$ one might expect is shown by the following simple and illustrative numerical example. As model system we consider a diatomic molecule. For the decay widths, the easiest possible scenario has been chosen, characterized by a constant total decay rate and a coordinate dependent partial decay width. The potential energy curves of the initial and the photoionized state are plotted in Fig. 1 together with the total and a partial decay rate. Since Γ_{tot} is constant, all the vibrational levels of the photoionized state have the same energy width. This width is chosen to be comparable to the spacings of the levels inside the Franck-Condon

zone. As can be inferred from Eqs. (7) and (4), the differences between the total and coincidence spectra are insensitive to the magnitude of this constant width. $\Gamma^{(j)}$ is taken to be a decreasing function of the internuclear distance R, with a functional behavior of R^{-6} as is the case in electronic interatomic decay processes at large distances [17].

The computed total and coincidence PES obtained using Eqs. (4) and (7) are shown in Fig. 2. The difference between them is evident. The centroid of $\sigma^{(j)}$ is shifted toward smaller energies in comparison to that of σ_{tot}. This reflects the structure of $\Gamma^{(j)}$ which is larger at smaller internuclear distances. As a result, the expectation values $\langle m|\Gamma^{(j)}|m\rangle$ decrease with growing m and hence the lower vibrational levels among the populated ones have a stronger weight in the spectrum [see Eq. (7)]. Similarly, if $\Gamma^{(j)}$ were an increasing function of R, one would expect a shift of the centroid of $\sigma^{(j)}$ towards larger energies.

The impact of the increase in intensity of the vibrational peaks at lower energy is substantial. As seen in Fig. 2, the most intense peaks of σ_{tot} and $\sigma^{(j)}$ do not coincide. While in σ_{tot} the 7th visible peak is the highest one, the 6th peak
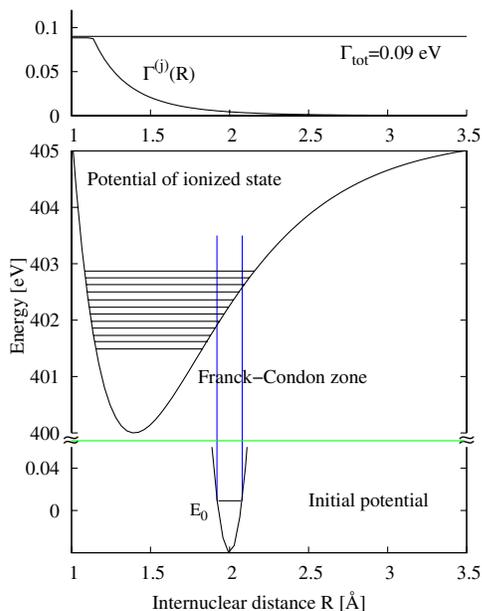
FIG. 1 (color online). Lower panel: Potential energy curves of the initial and photoionized electronic states. The vibrational ground state of the initial electronic state is shown, as well as the most populated vibrational levels of the ionized state, which lie inside and nearby the Franck-Condon zone. Upper panel: a partial and the total decay rate of the photoionized state.

FIG. 2 (color online). Total (σ_{tot}) and coincidence ($\sigma^{(j)}$) PES. The former has been divided by a factor 6.2 to facilitate the comparison. The difference between the two spectra is evident: the centroid of $\sigma^{(j)}$ is at lower energy and the most intense peaks in $\sigma^{(j)}$ and σ_{tot} do not coincide. Shown are also the contributions to the coincidence PES coming from the Lorentzian and interference-like terms in Eq. (7). The latter is destructive..

dominates $\sigma^{(j)}$. In spectroscopy, the overall location of a spectrum and the vibrational level m at which the intensity is highest are often used to deduce information on the potential energy curve and nuclear dynamics of the ion. It is demonstrated here that more information is contained in analyzing both the coincidence and the total spectra.

In Fig. 2 we also show the breakup of σ_{tot} into its Lorentzian and interference-like terms. It is interesting to notice that in this example the difference between $\sigma^{(j)}$ and σ_{tot} derives mainly from the Lorentzian term. The contribution to $\sigma^{(j)}$ coming from the interference-like term is destructive and smaller in magnitude; it is important for the finer details of the spectrum.

Summarizing, coincidence and total photoelectron spectra have been discussed and their difference analyzed. The dependence of the decay rates on internal degrees of freedom has a marked influence on the spectra. If the decay rates are essentially constants, the coincidence spectra do not contain additional information. On the other hand, as soon as the internal degrees of freedom play a role in the decay, the structure of the coincidence PES is qualitatively different from that of the total one. Our results demonstrate that the measurement of coincidence PES, for instance via the XETECO and APECS techniques, represents an important tool to obtain new and important information which cannot be extracted from the total PES alone. Most importantly and surprisingly, this information is useful not only to better characterize the photoionized system itself, but also to better understand the properties of the decay

mechanisms following photoionization. In particular, we believe that very interesting effects could be observed in photoionized systems undergoing, e.g., Auger or interatomic Coulombic decay. Finally, we emphasize that the example shown, though already informative, relates to a rather simple scenario. The differences between σ_{tot} and $\sigma^{(j)}$ as well as the role of the interference-like term are expected to become even more interesting in polyatomic molecules, where several vibrational degrees of freedom participate and often electronic states exhibiting conical intersections may be present giving rise to nonadiabatic effects.

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