Electron emission to analyze cluster dynamics

P M Dinh¹, J Messud¹, P G Reinhard², E Suraud¹, S Vidal¹ and Z Wang¹

¹ Laboratoire de Physique Théorique, IRSAMC, UPS and CNRS, Université de Toulouse, 118 Route de Narbonne, F-31062 Toulouse, cedex, France
² Institut für Theoretische Physik, Universität Erlangen, Staudtstrasse 7, D-91058 Erlangen, Germany

E-mail: dinh@irsamc.ups-tlse.fr

Abstract. We present a brief review of typical theoretical methods used to analyze cluster dynamics on the basis of electronic emission. After putting the various possible theories in perspective, we focus on a few examples of application, concerning in particular photoelectron spectroscopy and photoelectron angular distributions. We finally conclude by considering the case of high laser frequencies as delivered by free electron lasers and investigate the impact of such frequencies on cluster ionization.

1. Introduction
The physics of metal clusters has attracted much attention in the past decades. Early works were mostly devoted to structure properties [1, 2, 3]. Meanwhile, dynamical studies become increasingly important [4]. Observables from the electronic dynamics of clusters turn out to provide useful information on the underlying cluster properties. That holds in all dynamical regimes ranging from the linear to the strongly non-linear one.

Optical absorption spectra are the typical examples in the linear domain providing useful insights into structure properties of clusters. They have been successfully exploited in the early decades of cluster physics, for overviews see e.g. [1, 5, 6, 7, 8]. But optical response also plays an important role in many dynamical scenarios, as for example in the case of pump-probe dynamics [9, 10, 11, 12].

As another key example let us mention Photo-Electron Spectra (PES), i.e. the distribution of kinetic energies of the emitted electrons for which exist several interesting experimental results, see e.g. [13, 14, 15]. These allow to gain an almost direct insight into the electronic shell structure of the cluster. They have also been explored in truly dynamical situations both experimentally [16] and theoretically [17, 18, 19]. Further complementing information can be obtained from the angular distributions of the emitted electrons (Photoelectron Angular Distribution, PAD). There exist already a few very promising measurements [20, 21, 22].

Angular distributions, for example, allow to distinguish between direct and thermal electron emission [20, 23]. Direct emission prevails for short laser pulses or low intensities and one can expect that angular distributions from direct emission carries information on the spatial structure of the initial electron states [24, 21] similar as PES reveal the electronic energy spectrum. The recent availability of high frequency photons in Free Electron Laser facilities [25] adds further
new aspects in the studies of electronic dynamics in clusters. These aspects have just started to be explored and it is an interesting challenge to consider such cases.

We discuss in this paper theoretical methods used for describing electronic emission used to analyze cluster dynamics. We take as typical examples PES and PAD signals from irradiated metal clusters. We also discuss examples of irradiation by VUV-FEL frequencies as a first step in the direction of ionization dynamics by high frequency photons but moderate laser intensities. The paper is organized as follows. After a brief review of theoretical methods used in the field, we show a few examples of PES and PAD. We finally analyze an example of irradiation with VUV-FEL photons.

2. Possible theories

Clusters are finite many-body systems in which size may be varied almost arbitrarily. Dynamics adds an extra piece of complexity which requires some more efforts. One wants to deal with possibly large numbers of degrees of freedom involved in strongly dynamical scenarios and all that at the best level of microscopic detail. There does not yet exist any theory fulfilling that high goal. In order to be able to describe such involved situations, one is forced to make compromises. There thus exists a rich spectrum of applicable methods, especially for the treatment of electrons which require most of the effort, ions being usually safely treated at a classical level.

Figure 1 sketches typical theories used in the field. They are sorted according to their relevance both in terms of size (vertical axis) and excitation energy per electron (horizontal axis). The latter axis represents, so to say, a scale of increasing dynamics. This is also illustrated by the two upper arrows in which excitation energies are converted, as an illustration, into typical laser intensity in the optical domain, still taking care of resonant or non-resonant frequencies. In other words, features of the irradiated system play also a role in such a correspondence. In the same spirit, one should consider the boundaries shown in the figure as mostly qualitative and with rather large zones of overlap between models. The degree of microscopic detail more or less corresponds, not surprisingly, to an axis along the diagonal of the figure. The more detailed microscopic theories corresponding to small size/excitation energies.

The class of “ab initio” theories covers a huge range of treatments somewhat depending on the size of the underlying basis space [4]. This is especially true for the configuration interaction (CI) and the multi-configuration time-dependent Hartree-Fock (MC-TDHF) approach. The most general methods, i.e. exact time-dependent Schrödinger equation (TDSE) and Quantum Monte-Carlo (QMC), are still restricted to very few electrons and presently not practically applicable to clusters.

The vast majority of theoretical investigations of cluster dynamics still accounting for quantum aspects relies on density-functional theory (DFT) based methods, with quantum mechanical (QM) or semiclassical propagation. The latter case is labeled Vlasov- or Vlasov-Uehling-Uhlenbeck (VUU) [26, 27] schemes where VUU allows also to account for dynamical electron-electron correlations by means of a Boltzmann-like collision term. In the few examples below, we shall use such a DFT approach, at the simplest Local Density Approximation (LDA) in the time domain (TDLDA) and at sufficiently moderate excitation so that a quantum treatment is still relevant. Details of the model can be found in [28]. In fact, close to emission threshold the pure LDA picture has to be complemented by a Self-Interaction Correction (SIC). We have used here the simple ADSIC method [29] which is well suited for metals. But the general case, in particular of covalent clusters, such as carbon systems, requires more elaborate methods, especially when one wants to be able to analyze dissociation properties following large energy deposit. Preliminary results of such theories are under publication [30].

Very violent processes exceed the capability of DFT methods and are usually treated in a purely classical manner, either with Molecular Dynamics (MD) [31, 32] or, more simply, with rate equations [33, 34]. The upper limits in energy and/or laser intensity are finally given by the
Figure 1. Sketch of various theories developed to analyze cluster dynamics. The axes correspond to the deposited excitation energy per electron (horizontal axis) and the cluster size (vertical axis). The higher the excitation energy the more dynamical the situation so that the horizontal axis represents so to say a dynamical arrow. The various theories are represented by overlapping grey squares. The boundaries are of course only indicative and mostly qualitative. The typical excitation energies can be loosely related to typical laser intensities in the optical range, as indicated by the intensity scales on top, which are, however, also strongly dependent on the response of the particular system, i.e. resonant or non-resonant.

onset of the relativistic regime, where retardation effects within the coupling begin to severely influence the dynamics.

3. Example of electronic emission
As discussed in the introduction, electronic emission constitutes a key tool of investigation of cluster properties. We take here two typical examples for illustration.

3.1. Photoelectron spectroscopy (PES)
Examples of PES are presented in Figure 2 which compares experimental results [35] to TDLDA calculations. Experiments were performed with photons in the UV range, $\omega_{\text{photon}} = 6.42$ eV, obtained from frequency tripling of a high-intensity laser pulse. That energy is above the ionization potential (IP) so that we are considering "simple" one-photon processes in this case. The TDLDA analysis of the emission pattern is here performed at specific "measuring points". Two choices are demonstrated in the figure: A doublet of points along the polarization axis (forward plus backward emission) and one point for outflow, orthogonal to the axis. Both
Figure 2. Examples of PES in the case of sodium cations. Experimental values are taken from [35]. The PES is analyzed along the laser polarization axis and perpendicular to it, which provides a first clue to angular distributions. From [19].

Measuring points show different patterns due to a different selectivity on angular momentum \( l_z \) as can be seen from the figure. The effect is visible in both cation clusters presented, namely \( \text{Na}_{41}^+ \) and \( \text{Na}_{93}^+ \). This preliminary example of angular resolved PES taken at two different directions hints that much more information could be disentangled when measuring angular distributions of PES. This is illustrated below.

3.2. Photoelectron angular distributions (PAD)

Figure 3 shows examples of angular distributions for \( \text{Na}_{93}^+ \) and for two photon frequencies, a very low one and another one somewhat above ionization threshold. Note that the system contains eight electrons which corresponds to electronic shell closure. The electronic distribution is thus, up to small perturbations from the detailed ionic background, close to spherical. The PAD have been furthermore disentangled with respect to the electron state from which they are emitted. This thus corresponds to an energy-resolved measurement of angular distributions (or a double differential cross-section, with respect to angle and energy), as is presently measured [21]. In addition, calculations have been performed for a thermal ensemble of ionic configurations. The faint lines in the figures show results from a few single members of the ensemble. They generally share the same pattern. The thermally averaged results with ionic structure are shown with heavy lines and filled dots as symbols. The low-frequency case shows overall pattern for each state almost as from a spherical system. Note, e.g., the pronounced zero at \( \theta = 0^\circ \) and \( 180^\circ \) for the 1p state with \( l_z = 1 \). Interestingly, the corresponding jellium results are very similar. In that case the ionic background potential has been modeled with exact spherical symmetry. The high-frequency case, on the other hand, looks much different. The angular distributions show marked structure which very much differ from jellium results (mind the logarithmic scales). These distributions are obviously strongly influenced by detailed ionic structure and, in turn, they carry information on structure. This raises two interesting questions: How to explicitly extract ionic effects from the PAD, and do higher frequencies enhance such an effect? The answer to the second might help to analyze the first one. We shall thus focus on the second issue. The analysis of the PAD obtained with even larger frequencies is in progress and we shall thus only focus on the simpler analysis of how levels are depleted in high frequency fields as a first clue to understand the impact of VUV-FEL laser on electronic emission.
Figure 3. Example of PAD in a small sodium cluster. Calculations with an explicit account of ionic structure at a temperature of 1000 K are compared to jellium ones. They match in the low laser frequency case but significantly differ in the high frequency case. From [24].

4. New dynamics with free electron lasers

The recent progress in the development of Free Electron Lasers allow the use of high frequency laser beams with possibly large intensities. The nature of the laser cluster coupling fundamentally changes when going from the IR regime towards excitation with VUV-, XUV-, or even X-ray pulses. This concerns ionization processes as well as the mechanisms of energy absorption. Still, we shall not discuss these details here and only illustrate the impact of large frequencies on the ionization of a small sodium cluster. The test case is Na$_{13}$ cluster and we remain in a regime of small ionization to comply with the PAD case of the previous section. Such a study complements earlier results obtained in rare gases, both experimentally [36] and theoretically [32], and in which it was shown that moderate intensities already allow to attain large ionization states at the side of the atoms inside the cluster.

Figure 4 shows the level depletion for various laser frequencies between 0.1 and 2.4 Ry as a function of total ionization. The larger the frequency, the larger the intensity required for a given net ionization, whence this choice of plotting. The depletion is simply computed as the number of electrons emitted from a given level. We consider two particular levels in Figure 4, namely the most deeply bound one (with 0.62 Ry binding) and the least bound one (0.44 Ry binding). The most striking feature of this figure is the difference in depletion observed between the various laser frequencies. For low frequencies, ionization dominantly comes from the least bound state, while the most bound state contributes very little (typically one order of magnitude less). The situation is the reverse in the case of high laser frequencies, in which ionization from
the most bound state dominates. This case is not accidental. We checked a similar trend in a neutral Na$_8$ cluster and the case of small organic molecules exhibits similar patterns. The example indicates that low frequency pulses withdraw the electrons preferably from the surface while high frequency pulses allow to explore the whole volume of the cluster.

5. Conclusions and perspectives

We have presented a short theoretical review of the description of electron emission to analyze cluster dynamics, concentrating on a few examples in simple metal clusters. After a brief sketch of available theories, we focused on the most flexible and robust TDLDA which allows to make numerous exploratory studies. We have illustrated our point on the especially interesting cases of photoelectron spectra and photoelectron angular distribution for which several experimental results have been recently obtained. Finally we have roughly discussed the case of VUV-FEL frequencies in the moderate ionization regime and found interesting behaviors which will deserve more extensive investigations. Work along that direction is in progress.
Acknowledgements
This work was supported, by Agence Nationale de la Recherche (ANR-06-BLAN-0319-02), the Deutsche Forschungsgemeinschaft (RE 322/10-1), and the Humboldt foundation.

References

[1] Haberland H (ed) 1994 *Clusters of Atoms and Molecules 1- Theory, Experiment, and Clusters of Atoms* vol 52 (Berlin: Springer Series in Chemical Physics)
[2] Haberland H (ed) 1994 *Clusters of Atoms and Molecules 2- Solvation and Chemistry of Free Clusters, and Embedded, Supported and Compressed Clusters* vol 56 (Berlin: Springer Series in Chemical Physics)
[3] Sugano S 1998 *Microclusters Physics* (Berlin: Springer)
[4] Reinhard P G and Suraud E 2003 *Introduction to Cluster Dynamics* (New York: Wiley)
[5] de Heer W A 1993 *Rev. Mod. Phys.* 65 611
[6] Brack M 1993 *Rev. Mod. Phys.* 65 677
[7] Kreibig U and Vollmer M 1993 *Optical Properties of Metal Clusters* vol 25 (Springer Series in Materials Science)
[8] Bjørnholm S and Borggreen J 1999 *Phil. Mag.* 79 1321
[9] Seifert G, Kaempfe M, Berg K J and Graener H 2000 *Appl. Phys. B* 71 795
[10] Andrae K, Reinhard P G and Suraud E 2002 *J. Phys. B* 35 1
[11] Andrae K, Reinhard P G and Suraud E 2004 *Phys. Rev. Lett.* 92 173402
[12] Andrae K, Dinh P M, Reinhard P G and Suraud E 2006 *Comp. Mat. Sci.* 35 169
[13] McHugh K M, Eaton J G, Lee G H, Sarkas H W, Kidder L H, Snodgrass J T, Manaa M R and Bowen K H 1980 *J. Chem. Phys.* 91 3792
[14] Hoffmann M A, Wrigge G, v Issendorff B, Muller J, Gantefor G and Haberland H 2001 *Euro. Phys. J. D* 16 9
[15] Hergenhahn U, Kolmakov A, Riedler M, de Castro A R B, Lofken O and Moller T 2002 *Chem. Phys. Lett.* 351 235
[16] Campbell E E B, Hansen K, Hoffmann K, Korn G, Tchaplyguine M, Wittmann M and Hertel I V 2000 *Phys. Rev. Lett.* 84 2128
[17] Pohl A, Reinhard P G and Suraud E 2000 *Phys. Rev. Lett.* 84 5090
[18] Pohl A, Reinhard P G and Suraud E 2001 *J. Phys. B* 34 4969
[19] Pohl A, Reinhard P G and Suraud E 2004 *J. Phys. B* 37 3301
[20] Baguenard B, Pinar J C, Bordacs C and Broyer M 2001 *Phys. Rev. A* 63 023204
[21] Koetko O, Huber B, Mostler M and von Issendorff B 2007 *Physical Review Letters* 98 043401 (pages 4) URL http://link.aps.org/abstract/PRL/v98/e043401
[22] Fennel T, Döppner T, Paesing J, Schaal C, Tiggesbäumker J and Meiwe-Broer K H 2007 *Phys. Rev. Lett.* 98 143401
[23] Giglio E, Döppner T, Paesing J, Schaal C, Tiggesbäumker J and Meiwe-Broer K H 2007 *Phys. Rev. A* 67 43202
[24] Pohl A, Reinhard P G and Suraud E 2004 *Phys. Rev. A* 70 023202
[25] Gruber F, Becker S, Schramm U, Eichner T, Fuchs M, Weingartner R, Haber B, Meyer-Ter-Vehn J, Geistler M, Ferrario M, Serafini L, van der Geer B, Backe H, Reiche S and Lauth W 2007 *Appl. Phys. B* 86 431
[26] Domps A, Reinhard P G and Suraud E 1998 *Phys. Rev. Lett.* 80 5520
[27] Fennel T, Bertsch G F and Meiwe-Broer K H 2004 *Eur. Phys. J. D* 29 367
[28] Calvayrac F, Reinhard P G, Suraud E and Ulrich C A 2000 *Phys. Rep.* 337 493
[29] Legrand C, Suraud E and Reinhard P G 2002 *J. Phys. B* 35 1115
[30] Menou J, Dinh P M, Reinhard P G and Suraud E 2008 *Chem. Phys. Lett.* In press
[31] Roez-Petruck C, Schafot K J, Wilson K R and Barty C P J 1997 *Phys. Rev. A* 55 1182
[32] Saalmann U, Siedschlag C and Rost J M 2006 *J. Phys. B* 39 R39
[33] Ditmire T, Donnelly T, Rubenchik A M, Falcone R W and Perry M D 1996 *Phys. Rev. A* 53 3379
[34] Micheau S, Bonté C, Dorchies F, Fourment C, Harmand M, Jouin H, Peyrusse O, Pons B and Santon J 2007 *High Energy Density Physics* 3 191
[35] Wrigge G, Hoffmann M A and von Issendorff B 2002 *Phys. Rev. A* 65 063201
[36] Wabnitz H, Bittner L, de Castro A R B, Döhrmann R, Gürtler P, Laarmann T, Laesch W, Schulz J, Swiderski A, von Haftens K, Möller T, Faatz B, Fateev A, Feldhaus J, Gerth C, Hahn U, Saldin E, Schneidermiller E, Sytchev K, Tiedtke K, Treusch R and Yurkov M 2002 *Nature* 420 482