Decay processes mediated by long-range electron correlation

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Electronically excited states of atoms and molecules embedded in an environment may efficiently decay by ionising neighbouring species in the energy or charge transfer mediated processes. Both kinds of processes become possible due to the correlation between the electrons on the excited moiety and on the surrounding species. The energy transfer driven interatomic Coulombic decay (ICD) [1] has been shown to proceed on a femtosecond timescale in a variety of weakly bonded systems (such as rare-gas or water clusters) following a localised electronic excitation in a photoionisation or Auger decay event [2, 3]. Related electron transfer mediated decay (ETMD) proceeds in a few picoseconds timescale and becomes an important relaxation pathway whenever ICD channel is unavailable [4]. In this talk we will give a short overview and discuss the importance of ICD and ETMD processes. In particular, we demonstrate that ETMD provides an efficient neutralisation pathway for the majority of the multiply charged ions produced by Auger decay in an environment [5]. As an example we show the results of an ab initio study of the $NeKr_2$ cluster following the Auger decay of 1s vacancy of Ne. The ETMD rates even at the frozen nuclei configuration can be as large as 0.130 ps^{-1}. We also show that nuclear dynamics may increase the rate by about an order of magnitude. The generality of the mechanism makes this neutralisation pathway important in weakly bonded environments.

[1] L.S. Cederbaum, J. Zobeley and F. Tarantelli, *Phys. Rev. Lett.* **79**, 4778 (1997).

[2] V. Averbukh *et al*, *J. Electron Spectrosc. Relat. Phenom.* **183**, 36 (2011).

[3] U. Hergenhahn, *J. Electron Spectrosc. Relat. Phenom.* **184**, 78 (2011).

[4] E. Faßhauer, M. Pernpointner and K. Gokhberg, *J. Chem. Phys.* **138**, 014305 (2011).

[5] V. Stumpf, P. Kolorenč, K. Gokhberg and L.S. Cederbaum *Phys. Rev. Lett.* **110**, 258302 (2013).