The Fifth Age of Quantum Chemistry?

(Theory and Computation of effects of Electron Correlations as they happen!)

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A recent publication by **Császár et al**, (2012), which discusses methods for the computation of spectroscopic effects of nuclear motion, delineated this type of modern activity in Quantum Chemistry (QC) from others, which were considered as representing "*the first three ages [of QC], principally defined by developments in electronic structure techniques*" (**Richards**, 1979). Such a categorization makes the point that the technological-experimental-theoretical progress which brought us real-time *femtosecond* spectroscopy, ushered QC (or, theoretical Chemical Physics), into a new research area, that of trying to obtain accurate potential energy surfaces in terms of which to determine the time-dependent dynamics of the motion of nuclei, viewed as classical objects.

At the very dawn of the 21st century, the first announcement of the creation of well-characterized *attosecond* (*as*) pulses (1 *as* = 10^{-18} sec) was made. Obviously, by using such pulses in pump-probe type experiments, the possibility of observing nuclear motion remains. However, now, electronic relative motion may become the object of investigation as well. One fundamental difference is that the observation of electronic relative 'motions' inside atoms and molecules cannot be rigorously described classically. The first application of single *as* pulses with spectroscopic information was reported by **Drescher et al** (2002) on the time-resolved Auger decay.

The time-resolution of such a dynamical process of electronic rearrangements had already been demonstrated theoretically-computationally by **Nicolaides and Mercouris** (1996), via the ab initio solution of the many-electron time-dependent

Schrödinger equation. Upon the first publications of the successful creation of *as* pulses, we argued and demonstrated quantitatively that, by utilizing state-specific wavefunctions, one could prepare and probe the relative 'motion' of pairs of electrons even within the same atom, (of course, the same holds for interatomic dynamics). (**Nicolaides et al** 2002, **Mercouris et al** 2004). Such problems involve the possibility of new types of spectroscopy, where excitation of *strongly correlated electronic motions* could be studied, experimentally and theoretically, within a time-dependent context, and where *the continuous spectrum and resonances within it*, play a dominant role.

The past decade has seen an increasing number of theoretical investigations of time-resolved effects of both nuclear and electronic 'motions' at the attosecond time scale. Obviously, a serious desideratum is for theory to be able to deal with systems of arbitrary electronic structures and for a variety of real-time excitation-de-excitation schemes. In that respect, the requirements of the 5^{th} age (?) of QC are more sophisticated, formally and computationally, than those of the previous ages. In my lecture, I will provide key elements of the theoretical framework in which our work has been carried out.

Császár A. et al. **2012**, Phys. Chem. Chem. Phys. 14, 1057 "*The fourth age of Quantum Chemistry: molecules in motion*".

Drescher M. et al. **2002**, NATURE 419, 803 "*Time-resolved atomic inner-shell spectroscopy*".

Mercouris Th. et al. **2004**, Phys. Rev. A 69, 032502 "*Theory and computation of the attosecond dynamics of pairs of electrons excited by high-frequency short light pulses"*.

Nicolaides C. A. and Mercouris Th. **1996**, J. Phys. B 29, 1151 "*On the violation of the xponential decay law in atomic physics: Ab initio calculation of the time-dependence of the* He^- *1s2p*^{2} ^{4}*P nonstationary state*".

Nicolaides et al. **2002**, J. Phys. B 35, L271 "*Attosecond dynamics of electron correlation in doubly excited atomic states*".

Richards G. **1979**, NATURE 278, 507 "*Third age of Quantum Chemistry*".