Quantum Chemistry on the time axis: Electron correlations and rearrangements on femtosecond and attosecond scales

Cleanthes A. Nicolaides December 28, 2014

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vasileos Constantinou Avenue, Athens 11635, Greece **caan@eie.gr**

Science and technology have been making impressive progress toward the production and laboratory use of pulses of high intensity, and/or of very high frequency, and/or of ultrashort duration, going down to the ***attosecond scale*** (*as-sc*). Such developments are challenging to theory and methods that are in the realm of Quantum Chemistry, since now the many-electron nature of dynamics must be formulated and understood quantitatively via the solution of the *many-electron time-dependent Schrödinger equation* (METDSE), while the continuous spectrum cannot be ignored [1]. The non-perturbative solution of the METDSE is achievable via the ***state-specific expansion approach*** (SSEA) [1, 2].

The lecture focuses on the judicious implementation of the SSEA to issues that are covered by the theme of this plenary session: In 2002 [3], soon after the announcement of the first preparation of single and of train attosecond pulses [4], it was proposed, and demonstrated via the SSEA, that effects due to **state-specific SCF orbitals and strong electron correlations** in doubly excited or inner-hole states can be *time-resolved* on the *as-sc*. For example, it was pointed out that the 'geometrical motion' of pairs of electrons in strongly mixing excited configurations is resolvable on the *as-sc* [5]. The relevance of such resolution had already been pointed out in the 1990s, in the first study exploring from first principles (including many-electron interactions) the 'law' of exponential decay (ED) in unstable states [6]. Indeed, a few years later, the first experimental application of attosecond techniques involved the measurement of the ED of an inner-hole autoionizing state, with attosecond time-resolution [7].

Subsequent applications of the SSEA in connection with prototypical problems of time-resolved ***ultrafast electron rearrangements*** have to do with electron-correlation 'beats', with the coherent excitation and decay of autoionizing states into distinct channels, with the dynamics of the creation of resonance states of multielectron systems, etc. [2, 8]. Also, the SSEA was employed in the first theoretical contribution and analysis that accompanied the pioneering pump-probe experiment, conceived and executed at the Max Planck Institute - Garching, concerning the intriguing question of a possible ***time delay (td)*** in the photoemission of electrons from different atomic subshells [9]. The SSEA calculation of the accumulated phase during photoionization of the 2s and 2p electrons of Neon by the *as* XUV pulse, took into account initial and final state correlations, including interchannel coupling. The result for the pump 2p-2s *td*, (6.4 *as*), demonstrated via many-electron QM that, indeed, there **is** ***td*** in atomic photoionization, [9] and SOM

[1] C. A. Nicolaides, "***Quantum Chemistry and its 'Ages'***", Int. J. Quantum Chem. **114**, 963 (2014).
[2] Th. Mercouris, Y. Komninos and C. A. Nicolaides, Adv. Quantum Chem. **60**, 333 (2010).
[3] C. A. Nicolaides, Th. Mercouris and Y. Komninos, "***Attosecond dynamics of electron correlation in doubly excited atomic states***", J. Phys. **B 35**, L271 (2002).
[4] M. Hentschel, et al, Nature **417**, 509 (2001); P. M. Paul, et al, Science **292**, 1689 (2001).
[5] Th. Mercouris, Y. Komninos and C. A. Nicolaides, Phys. Rev. A **69**, 032502 (2004).
[6] C. A. Nicolaides and Th. Mercouris, J. Phys. B **29**, 1151 (1996); ibid, **30**, 811 (1997).
[7] M. Drescher, et al, "***Time-resolved atomic inner-shell spectroscopy***", Nature **419**, 803 (2002).
[8] Th. Mercouris, Y. Komninos and C. A. Nicolaides, Phys. Rev. **A 75**, 013407; **76**, 033417 (2007).
[9] M. Schultze, et al, "***Delay in Photoemission***", Science **328**, 1658 (2010).