Novel Approach for Predicting Vertical Electron Attachment Energies in Bulk-Solvated Molecules

KIATAKI, Matheus B.;[A,B] **do N. VARELLA Marcio T.;**[B] **COUTINHO, Kaline;**[B] **THIAM Guillaume;**[C]
RABILLOUD Franck[A]

A) Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, UMR 5306, Villeurbanne, France ; B) Instituto de Fisica, Universidade de São Paulo, São Paulo, Brazil; C) Università degli Studi di Perugia, UNIPG, Perugia, Italy

franck.rabilloud@univ-lyon1.fr

When low-energy electrons interact with molecules, they can give rise to transient anion states, commonly known as resonances. These states are formed through vertical electron attachment processes and have the potential to induce various forms of DNA lesions, including base damage, single- and double-strand breaks, crosslinks, and clustered lesions that are challenging to repair. So far, most experimental and theoretical studies have investigated the formation of resonances of (bio)molecules in gas phase or in microsolvated environments.

Since cellular environments are mainly composed of water molecules, it is crucial to understand how bulk water affects the resonances of (bio)molecules. Given the existing gap of studies on resonances of bulk-solvated molecules, we propose a novel theoretical-computational approach [1] to address this void, in the framework of DFT and TDDFT, which were recently shown to be able to describe the attachment of an extra electron whether it is located in a valence state [2] or in a long-range state [3], and a QM/MM scheme taking into account solvation effects. Our approach combines the Multi-Basis-Set (TD-)DFT [2] and self-consistent sequential quantum mechanics/molecular mechanics polarizable electrostatic embedding (scPEE-S-QM/MM) [4] methods.

We apply this combined methodology to predict the vertical electron attachment energies of 1-methyl-5-nitroimidazole (1M5NI), a well-known radiosensitizer model, in bulk water. We analyze the rapid mutual polarization between the resonances (both shape and core-excited) of 1M5NI and the surrounding bulk water environment. Overall, while the polarization of the environment is clearly sensitive to the solute charge, causing a significant impact on the vertical electron affinity and consequently on the attachment electron energies, it does not have a significant impact on the excitation energies of the anion.

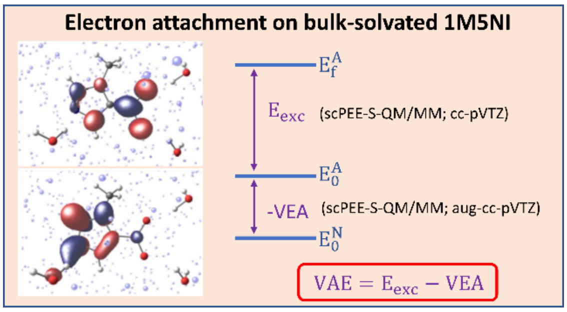

Figure 1. Depiction of the vertical electron attachment energy (VAE) computed with the combination of the Multi-Basis-Set (MBS) and scPEE-S-QM/MM methods.[1]

Keywords: Resonance, Electron Attachment, TDDFT, QM/MM, solvation

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[1] M. B. Kiataki, M. T. do N. Varella, K. Coutinho, F. Rabilloud, Novel Approach for Predicting Vertical Electron Attachment Energies in Bulk-Solvated Molecules, *J. Chem. Theory Comput.* (2024).

[2] G. Thiam, F. Rabilloud, Multi-basis set (TD-)DFT methods for predicting electron attachment energies, *J. Phys. Chem. lett.* 12 (2021) 9995.

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[4] Kiataki, M.; do N. Varella, M. T.; Coutinho, K. New approach to instantaneous polarizable electrostatic embedding of the solvent, *Journal of Molecular Liquids* 389 (2023) 122861.