

# Studying and Exploring the Potential Energy Surfaces of Compressed Molecules: a fresh Theory from the eXtreme Pressure Polarizable Continuum Model (XP-PCM)

**Roberto Cammi<sup>1</sup> and Bo Chen<sup>2</sup>**

<sup>1</sup>*Department of Chemical Science, Life Science and Environmental Sustainability, University of Parma Viale Parco Area delle Scienze. 17/a, Parma, 43100 (Italy)*

<sup>2</sup>*Donostia International Physics Center, Paseo Manuel de Lardizabal 4, 20018 Donostia-San Sebastian, Spain*

We present a new theory for studying and exploring the potential energy surface of compressed molecular systems as described by the XP-PCM method [1,2]. The effective potential energy surface is defined in terms of the sum of the electronic energy of the compressed system and the pressure-volume work necessary to create the compression cavity at the given condition of pressure. Then, we show that the resulting total energy,  $G_t$ , is related to the electronic energy by a Legendre transform, in which the pressure and volume of the compression cavity are the conjugate variables. Furthermore, we present an analytical expression for evaluating the gradient of the total energy  $G_t$  to be used for the geometry optimization of equilibrium geometries and transition states of compressed molecular systems. Due to the Legendre transform property, we also show that the potential energy surface can be studied explicitly as a function of the pressure, leading to an explicit connection with the well-known Hammond postulate. Finally, we present the application of the theory to the geometry optimization of compressed methane and the compressed transition states of electrocyclic ring-closure of hexatriene and hydrogen transfer between methane and methyl radical.

## References:

- [1] R. Cammi, "Quantum Chemistry at the High Pressures: The eXtreme Pressure Polarizable Continuum Model (XP-PCM)", in "Frontiers of Quantum Chemistry" Wójcik, M.J., Nakatsuji, H., Kirtman, B., Ozaki, Y. (Eds.), Springer (2018).
- [2] B. Chen. R. Hoffmann, R. Cammi, *Angew. Chem. Int. Ed.*, **56**, 1126 (2017)
- [3] G.S. Hammond, *J. Am. Chem. Soc.*, **77**,334 (1955)