

Reactivity Indices from Conceptual Density Functional Theory: Analytical and Data-Based Evaluation and Extension to Excited States

Frank De Proft

fdeprof@vub.be

Research Group of General Chemistry (ALGC), Vrije Universiteit Brussel (VUB), Pleinlaan 2, B-1050 Brussels, Belgium.

Chemical concepts from Density Functional Theory have been highly successful in the scrutiny of atomic, molecular and solid-state properties and chemical reactivity.^[1] The majority of these concepts are introduced as response functions of the system's energy E with respect to changes in the number of electrons N , the external potential $v(\mathbf{r})$ or both. These definitions have afforded the non-empirical calculation of these reactivity indices and applications in many fields of chemistry have been studied. Many of the computed values of these indices have been obtained using the so-called finite difference approach.

We now present an analytical approach to obtain these concepts up to the second order.^[2-5] Next, we discuss their evaluation using machine learning methods from computed reactivity index data.^[6] In a final part, we present the extension of the framework to investigate reactivity of excited states.^[7]

[1] (a) R. G. Parr, W. Yang, *Annu. Rev. Phys. Chem.* **1995**, *46*, 701-728. (b) H. Chermette, *J. Comput. Chem.* **1999**, *20*, 129-154. (c) P. Geerlings, F. De Proft, W. Langenaeker, *Chem. Rev.* **2003**, *103*, 1793-1874. (d) P. W. Ayers, J. S. M. Anderson, L. J. Bartolotti, *Int. J. Quantum Chem.* **2005**, *101*, 520-534. (e) S. Liu, *Conceptual Density Functional Theory: Towards a New Chemical Reactivity Theory*; Wiley-VCH, 2022.

[2] B. Wang, P. Geerlings, C. Van Alsenoy, F. Heidar-Zadeh, P. W. Ayers, F. De Proft, *J. Chem. Theory Comput.* **2023**, *19*, 3223-3236.

[3] B. Wang, P. Geerlings, S. Liu, F. De Proft, *J. Chem. Theory Comput.* **2024**, *20*, 1169-1184.

[4] B. Wang, P. Geerlings, F. Heidar-Zadeh, P. W. Ayers, F. De Proft, *J. Phys. Chem. Lett.* **2024**, *15*, 11259-11267.

[5] B. Wang, P. Geerlings, F. Heidar-Zadeh, P. W. Ayers, F. De Proft, *J. Chem. Theory Comput.* **2025**, *21*, 1695-1708.

[6] A. Bajaj, B. Deng, P. Kumar, T. Stuyver, S. Habershon, F. De Proft, in preparation.

[7] B. Wang, P. Geerlings, F. De Proft, submitted.