

Chemical reactivity indices in thermodynamic extension of the spin density functional theory and its zero-temperature limit.

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Abstract of PhD Thesis

The focus of the present dissertation is concentrated on two subjects: conceptual one and computational one, both of them related to the finite-temperature (FT) extension of the density functional theory (DFT). The FT-DFT allows to extend domain of DFT to non-integer electron number and spin number, \mathcal{N} and \mathcal{S} . This extension is crucial for two reasons: to ensure that all functional derivatives of state functions, and hence all potentials, are completely defined; to describe an open system which can exchange electrons with its environment.

In the conceptual part, a systematic derivation of a complete set of response functions in FT-DFT formalism up to the third-order is presented (the obtained formalism is valid for any computational chemistry method). Based on them, the role of classical reactivity indices such as the Mulliken electronegativity μ_{MP} and the Pearson-Parr hardness η_{PP} is analyzed by means of thermal extension of the reactivity indices in the spinless case. This investigation overthrows the traditional link between η_{PP} and the second derivative of the energy. The new interpretation of η_{PP} is the amplitude of the thermal admixture to the ground state energy and regulator of the thermal factor damping. Based on these two quantities, μ_{MP} and η_{PP} , the set of the response functions up to third derivatives with respect to temperature (strictly, inverse of the temperature) and with respect to electron numbers are constructed. Finally in this part, many discontinuity patterns of the energy derivative with respect to electron and spin numbers in the vicinity of the singlet state are obtained and discussed.

In the computational part, the quality of various exchange-correlation functionals is investigated by checking satisfaction of four properties related to the fractional electron number on example of a few atoms. In the last part, an overview of different approaches and their accuracy in the assessment of Fukui function (FF) is done. Within the DFT method, it is found that finite difference approach for evaluation of FF has better performance than analytical approach, seen well when results are compared with FF calculated by means of the full configuration interaction method. It is found here that PBE functional has the best performance for predicting FF for the set of molecules. Previously it was found for atoms that deviations from the linearity and constancy conditions stemming from application of the PBE functional are much higher than ones from the CAM-B3LYP and rCAM-B3LYP functionals.