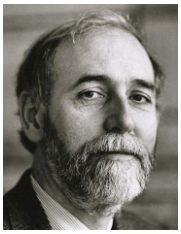
THE ROLE OF THE FERMI SURFACE IN ADSORBATE-METAL INTERACTIONS: AN ENERGY DECOMPOSITION ANALYSIS



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Abstract

The interpretation of chemical bonding and reactivity has been greatly aided by the development energy decomposition methods, which afford a quantification of concepts such as Pauli repulsion, electrostatic interaction, and (frontier) orbital interaction. The Kohn-Sham model of DFT uses molecular orbitals which are eminently suitable for this type of analysis.

We will discuss the extension of energy decomposition methods to extended systems, in particular for chemisorption of a molecule on a metal slab. It is known that an important repulsive contribution to a bond is the Pauli repulsion. At surfaces this energy component is modified. We introduce a new energy component, which we call the relief of the Pauli repulsion due to the existence of the Fermi level in the metal: antibonding levels that rise above the Fermi level can be depleted by electrons falling down into the Fermi sea. We will discuss how to quantify this effect and we will highlight the significance of this electronic structure feature of metallic systems as the key factor that gives them their singular reactivity properties, which are so much exploited in heterogeneous catalysis.

Reference and notes