Electrons on a Leash: Topology-Based Charge Partitioning and Rigorous Definition of Oxidation States in Solids

L. Jiang, S. V. Levchenko, and A. M. Rappe

The Makineni Theoretical Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, USA.

The concept of oxidation states (OS) is widely used in all disciplines of physical sciences to explain and predict properties and phenomenons. Its definition stems from a simple ionic charge transfer mechanism and lacks justification in systems with covalent or metallic characters. In fact it has been shown that in some transition metal complexes charge transfer does not occur upon changing the OS [1]. In the theoretical front, there are more versatile and accurate definitions of OS, such as charge integration in real-space, and wavefunction projection onto atomic orbitals. However, these traditional methods all have intrinsic ambiguity (e. g. the choice of integration boundaries and atomic basis sets, respectively) and also usually result in non-integer quantities. We propose a method that definitively partitions integer number of electrons to a certain nucleus in solid state insulators based solely on the topology of the electronic wavefunctions [2]. When an atomic sublattice (an atom and all of its periodic images) is moved by a lattice vector $\vec{R}$ along a path that keeps the system insulating, the polarization change $\Delta\vec{P}$ can be obtained by calculating the Berry phase polarization $\vec{P}$ of each intermediate structure [3]. Such cyclic evolution of the Hamiltonian produces a quantized $\Delta\vec{P}$ that characterizes the charge carried by the sublattice [4]. The integer quantity $N = \frac{V}{e}\frac{\Delta\vec{P}\cdot\vec{R}}{\vec{R}^2}$, where V is the volume of the unit cell, only depends on the atomic sublattice in its initial configuration and is therefore defined as the OS of that sublattice. In its essence, the sublattice movement identifies the number of Wannier state centers that move with the sublattice, therefore the belong to the nucleus. As such, each electron can be considered as on an invisible "leash" attached to a certain nucleus and the OS can be uniquely assigned with mathematical rigor. We present results from a broad range of test systems to show that our method not only agrees with conventional chemistry knowledge, but also possesses the ability to resolve real-world ambiguity where experiment falls short.

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Contact: rappe@sas.upenn.edu