

THE HAMMOND POSTULATE IN THE THEORY OF MECHANICAL BEHAVIOR

M. E. Eberhart¹, T. E. Jones

Molecular Theory Group, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden CO., 80401, USA, E-mail: meberhar@mines.edu

The Hammond Postulate [1] has proved invaluable in extending our understanding of the atomic mechanisms responsible for chemical processes. This postulate, as originally posed, asserts, "If two states, as for example, a transition state and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their interconversion will involve only a small reorganization of the molecular structures." The more modern corollary posits that for two similar reactions, the one in which the transition state "more closely resembles" the reactants will be the one of lower activation energy. Though this postulate is most often used to explain the relative rates of complex chemical reactions, particularly those between organic molecules, it has seldom been employed in the study of condensed phase phenomena. Perhaps this is due to the absence of a framework to compare solid-state structures and identify those where small reorganizations have occurred. In chemistry, the essential ingredient necessary for this task is a representation of the chemical bond (usually that provided by conceptual valence bond theory) described by a conceptual "strength" parameter that varies continuously along a reaction coordinate.

A more rigorous representation of a chemical bond, and one that is applicable to all molecular and condensed phase systems, is provided by Bader's topological and geometric theory of molecular structure, Atoms in Molecules (AIM) [2], and its recent extensions. Within AIM, one uses various geometric measures of the charge density at its topological critical points (CPs) as continuous parameterizations of molecular structure. The CPs are the zeros of the gradient of the charge density and are of four types: local minima, local maxima and two kinds of saddle points. The locations, curvatures and values of the charge density at CPs change as nuclear positions change, providing a means to assess similarity between the structure of two atomic systems and thus a means to apply the Hammond Postulate.

In this talk I will review the research of the Molecular Theory Group that permits us to use extend-AIM theory to study condensed phase phenomena. I will argue that when used to interpret the results of first principle calculations the Hammond postulate reveals that, for example, dislocation motion and fracture, involve the transfer of electrons between Fermi energy electronic states, and further that this transfer is governed by quantum mechanical selection rules. Ultimately, any attempt to control the many crack tip processes of importance to materials performance will need to take these quantum mechanical selection rules into account.

[1] Hammond, George S., A Correlation of Reaction Rates. *Journal of the American Chemical Society* **1955**, 77, (2), 334-338

[2] R.F.W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press: Oxford, (1990).