Are covalent bonds really directed?

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ABSTRACT

The flux theory of the chemical bond, which provides a physical description of chemical structure based on classical electrostatic theory, correctly predicts the angles between bonds, to the extent that they depend on the intrinsic properties of the bonded atoms. It is based on the justifiable assumption that the charge density around the nucleus of an atom retains most of its spherical symmetry even when bonded. A knowledge of these intrinsic bond angles permits the measurement and analysis of the steric angular strains that result from the mapping of the bond network into three-dimensional space. The work ends by pointing out that there are better ways of characterizing bonds than describing them as covalent or ionic.

Keywords: Bond angles, flux bonding theory, directed bonds, Invited Centennial article

INTRODUCTION

It is often said that “covalent bonds are directed but ionic bonds are not.” This is presented as if it were a profound observation about the nature of chemical bonding, but it depends on the questionable assumption that bonds can be neatly divided into two clearly distinguishable classes, covalent and ionic, even though it is widely accepted that bonds lie on a single continuum and such a distinction is difficult to make.

The purpose of this paper is to examine to what extent bonds can be said to be directed. Using the flux theory of the chemical bond, more fully described by Brown (2014), it argues that bond directions are determined by the spherical symmetry of the atoms and no distinction needs to be made between bonds of different character. The flux theory is first briefly reviewed as it involves few if any of the concepts commonly used to describe chemical bonding.

THE FLUX THEORY OF THE CHEMICAL BOND

For many years it has been fashionable to discuss chemical bonding as a quantum phenomenon, but the idea of a chemical bond predates quantum mechanics by half a century; its properties are rooted in classical physics, yet in our search for a quantum explanation of bonding we have failed to appreciate the extent to which classical electrostatic theory gives a physically correct description of the chemical structures formed by the quantum atom. While there is no doubt that quantum mechanics is essential for understanding atomic spectra, chemical structure generally involves only the ground state of the atom so that the greater part of structure theory is readily derived using only classical electrostatics. The key is to recognize that the chemical bond and the electrostatic flux have the same properties. Both depend only on the amount of charge (the valence) that is used to form the bond and neither depends on where that charge is located.

This contrasts with quantum mechanical descriptions, which supply exactly the information that the bond theory does not require. Quantum mechanics accurately describes the location of the charge between the atoms, but is unable to identify how much charge is used to form a given bond. Quantum mechanics cannot be entirely ignored in such a classical approach, but in most cases the essential constraints that it describes can easily be introduced via a few plausible ad hoc rules and a small number of empirically determined atomic and bond parameters. This is not to say that quantum calculations do not properly describe chemical bonding, only that the flux picture provides a complementary, simpler, yet physically accurate picture that has many advantages in predicting structure and geometry. This section describes the features of the flux model that are necessary to understand how the flux can be used to determined bond angles. It is a particularly simple theory because it uses only concepts that are introduced early into the physics curriculum at about the same time that the chemical curriculum introduces the concept of the chemical bond.

An important heuristic that underlies the flux theory of the chemical bond is the principle of maximum symmetry, which states that:

\[ \text{A system in stable static equilibrium adopts the highest symmetry that is consistent with the constraints acting on it (Brown 2009).} \]

The justification for this principle is that the presence of a symmetry element in such a system is necessarily an energy minimum with respect to any deformation of the system that breaks this symmetry. By definition, a system in stable static equilibrium is at an energy minimum, and displacing an atom in such a system from a mirror plane (for example) in either direction must result in an increase in the energy. An equilibrium system with mirror symmetry has a lower energy than the same system in which this mirror plane is lost, unless there is some