Two ways of looking at chemical bonding

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Abstract

Chemical bonding can be described using either the electrostatic potential or the electrostatic field. The former gives the energy, the latter describes the electrostatic flux which is the same as the bond valence. Energies cannot be calculated from the bond flux nor can bonds be found in the electrostatic potential, but in this issue of the American Mineralogist [ref?] Bickmore and his collaborators show, that if electronegativity is taken into account, the empirical correlation between bond valence and energy can be used to understand complex bonding preferences.

Keyword

Bond energy

bond valence

electronegativity

Text

It is two hundred years since chemists first recognized that electricity is what causes atoms to stick together, but early attempts to quantify this process were unproductive. Instead chemists devised an empirical model in which neighboring atoms were connected by bonds but without specifying what forces were involved. A hundred years later physicists discovered atoms and learned how to use the Schrödinger equation with the electrostatic potential to examine the interactions between the atoms, but the resulting picture of an array of nuclei surrounded by negative charge showed no sign of the chemists' bonds, nor did it suggest a natural way to define an atom once it is incorporated into a molecule or a crystal. Atoms and bonds only appear when the description is formulated in terms of the electrostatic field rather than the electric potential. The Faraday lines of electric field represent the bond linking a cation to a neighboring anion in the ionic model, with the number of such lines being a measure of the electrostatic flux that forms the bond (Brown, 2016). Identifying the flux with the bond valence allows the theorems of electrostatics to be used to derive the rules obeyed by atoms and bonds, but just as it is impossible to define a bond using the electric potential, so it is impossible to define the energy using the electrostatic flux. A complete description of bonding requires both the potential and flux.

Is it possible to reconcile the energy and flux approaches when they have so few concepts in common? Does it even make sense to talk of the energy of a bond? Attempts to derive bond energies from quantum mechanics involve simplifying assumptions that severely restrict their usefulness, but in this issue of the American Mineralogist, Bickmore and his collaborators (Bickmore et al. xxxx) describe an alternative approach in which they look for an empirical correlation between the energy, the electronegativities of the atoms and the bond valence. The correlation is not perfect, but there are useful trends. For example, by noting that covalent bonds increase their energy more rapidly than ionic bonds as the valence of the bond increases, they can account for the different pKa values of various oxy-acid and hydroxy-acid species. This and similar correlations have the potential to create a more unified picture in which both bonds and energy can work together in our understanding of structure and bonding.

References

Bickmore, B.R., Craven, R., Wander, M.C.F., Checketts, H., Whitmer, J., Shurtleff, C., Ernstrom, K., Andros, C. and Thompson, H. (xxxx) American Mineralogist. XXX, pp xxx.

Brown, I.D. (2016) ‘The chemical bond in inorganic chemistry: the bond valence model’ 2nd edn. Oxford: Oxford University Press.