

## Chemical Bonding Models – and some Applications

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Science requires effective models in order to understand empirical observations. Folk molecular theory inherits models from successful chemical theories of the 19th and 20th centuries, whereas quantum chemistry established new successful models such as molecular orbital theory. Very popular concepts from folk theories can not be defined rigorously and univocally in quantum terms, but remain extremely useful and harness predictive power nevertheless.

Molecular orbital theory has achieved remarkable breakthroughs (e.g. Woodward–Hoffman rules) but suffers from a number of shortcomings. On the other hand, real-space based approaches are defined in the exact many-body theory and are more robust with respect to basis set size. However, they lack predictive power. The underlying reason is the lack of simple models connecting scalar fields derived from the density and the energy.

In this presentation a new model will be presented that considers chemical bonds as explicit entities. In its construction, the spectroscopic Bond Charge Model (BCM) is combined with the Electron Localization Function (ELF) from quantum chemical topology. The model will be discussed and validated empirically, showcasing its adequacy for describing covalent bonds and its understandable failure in metallic bonds. Then, it will be applied exemplarily to model the intrinsic bond energy of C–C bonds, achieving remarkable accuracy.

Finally, the density error conundrum in density functional theory will be assessed using the toolkit of our model. In particular, it will be shown that local descriptors are necessary in order to evaluate density errors, and some open questions will be put forward regarding current parametrization strategies.

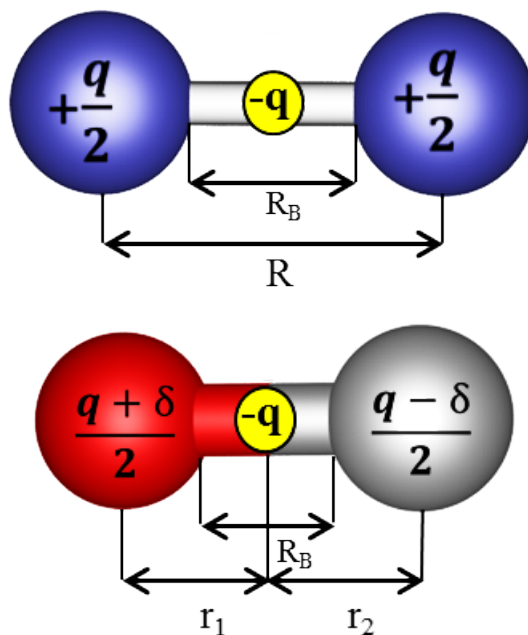


Figure 1: Schematised bond charge model for an homonuclear (top) and heteronuclear (bottom) diatomic molecule.