

Notes GPS II Intro

Philosophy of chemistry: the rise of quantum chemistry

Valence bond theory: explained chemical bonds in terms of electron pairs

Each element is considered to have a certain number of “valences” or free electrons and can bond with another element that has free electrons

E.g., water $2\text{H}\cdot + \text{O}\cdot \rightarrow \text{H}-\text{O}-\text{H}$

Or ethylene $2\text{C}:: + 4\text{H}\cdot \rightarrow \text{H}_2-\text{C}=\text{C}-\text{H}_2$

Some difficult cases:

Benzene C_6H_6 , arranged hexagonally

Q: Where place the double bonds? Due to the high symmetry of the molecule, there are two equally stable configurations.

It was first postulated that the double bonds flip back and forth in the benzene molecule, which would be consistent with the valence bond theory. But there was no evidence for this flipping; it's only advantage was that it saved the valence bond theory

Early attempts to explain electron pair-bonding:

The negatively charged electrons orbit the positively charged nucleus. An electrostatic attraction between the nucleus of one atom and the free electrons of the neighboring atom “glues” the molecule together.

But why does it always need exactly two free electrons? And why are some electrons “free” and others not?

In the older atomic models (Bohr), electrons were considered to orbit the nucleus. It was observed that each orbit can take exactly two electrons, which was explained by appealing to the electron spin. Each orbit can take an electron with spin up and one with spin down (Pauli's Exclusion Principle, simplified). “Free” electrons are thus unpaired, single electrons in the outermost orbit (the lower orbits are filled first before there can be an unpaired electron).

Molecules with free electrons are called “radicals” and are typically chemically highly reactive. According to some biological theories, free radicals are a major cause of aging and death.

The Exclusion Principle was already formulated and explained in quantum-mechanical terms (1925), thus before QM there was no good explanation really for why the valence bond theory worked so well in chemistry.

Nonetheless, as Gavroglu and Simoes argue, there was a real question for chemists after the advent of QM to what extent this new physics would be relevant for them, and why they should rely on this theory which had some rather strange features after all.

There was also a question as to what a “theory” should do in chemistry. The valence bond theory could be seen as a very economical way of summarizing a vast pool of empirical findings (c.f. Duhem’s instrumentalist understanding of scientific theories), and perhaps this was all that a chemist needed.

1929: Eminent physicist Paul Dirac publishes a highly influential article titled “Quantum Mechanics of Many-electron systems”

In this article, Dirac pushed a very ambitious reductionistic program according to which all of chemistry would be eventually be absorbed by QM. Of course, he realized that applying QM to many-electron systems generated equations that were impossible to solve. Therefore, he suggested the use of mathematical approximation methods. He expressed the hope that this could be done “without too much computation”.

It rapidly became clear that only some very simple systems such as the dihydrogen cation H_2^+ can be calculated in this way, and perhaps some special cases. In general, solving the QM equations for molecules requires numerical methods and gigantic computational power.

With the emergence of fast computers in the 1970s came the hope that one the computer might replace the chemical laboratory. And indeed, many chemists today spend their days with supercomputers rather than with beakers and flasks.

Questions:

- Has chemistry been reduced to QM? Problem: there is no derivation of any laws, at best a piecemeal treatment of disparate systems. Actually, no derivations at all, not even approximations, but numerical simulations for the most part.
- Given the enormous success of the valence bond theory in guiding chemical synthesis as well as in explaining the stability of compounds, why should chemists have been interested in QM in the 1920s? Why should they even accept the theory as fundamental?
- If QM is fundamental, in what sense?
- Does chemistry have autonomous explanatory principles, and if it does how can we account for it?