Checks-and-balances: orbital symmetry and quantitative methods in late twentieth century quantum chemistry

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Since the early twentieth century chemists have sought to account for a number of organic reactions of crucial importance to synthetic chemistry, ranging from the relatively simple reaction between two ethylene molecules to the Diels-Alder reaction, and reactions within the fundamental carbon skeleton such as the Cope and Claisen rearrangements. By the mid 1960's, developments in quantum chemical theories of chemical bonding resulted in the application the molecular orbital theory to these important organic reactions in the form of a relatively simple, qualitative modelling technique. R.B. Woodward and Roald Hoffmann's orbital symmetry approach proved a remarkably successful technique to predict broad trends in chemical data of particular use in synthetic chemistry. The fundamental property governing the course of "pericyclic reactions", as Woodward and Hoffmann called them, was the relative phase symmetry of the molecular orbitals representing the bonds that contributed most to a reaction. When the symmetry of the molecular orbitals is conserved in the transition from reactants to products, a reaction is "allowed" because it requires less energy. Woodward and Hoffmann's relatively simple, qualitative quantum chemical approach had great utility not only because it worked well as a predictive tool, but also because of its intelligibility to theoretically inclined experimentalists who lacked the requisite knowledge of quantum mechanics to engage in the computationally daunting task of applying fundamental physical theory to quantitative studies of molecules and their reactions.

Given the importance of the orbital symmetry approach to modern chemistry and its potential historical and philosophical interest, it is remarkable that it has received so little attention. Although the orbital symmetry approach is mentioned by Brush (1999), for example, a dedicated investigation of its role in forging a contemporary understanding of organic reactions seems to be absent in the historical and philosophical literature. Moreover, there appears to be very little cognisance of the broader epistemic impact, methodological repercussions, and controversies that followed the introduction of Woodward and Hoffmann's ideas. Applying quantum mechanics to the study of organic reactions is challenging because of the complexity of the target systems. But it is also challenging for a more subtle reason. One might suppose that whatever method of approximation is employed, the quantitative results might differ in terms of their precision but not in terms of their consistency. However, different approximation methods give different answers, and this led experimental chemists to infer that the numerical results were merely artefacts of the approximation methods. It is no over-statement to say that this controversy of quantitative methods has proved to be one of the most important and divisive issues in modern chemistry although like orbital symmetry itself there appears to be very little awareness of it outside of chemistry.

This paper investigates the historical and philosophical significance of orbital symmetry, and probes its epistemic status and function within the context of a controversy of immense importance to contemporary chemistry. One central issue concerns how models are evaluated in their historical context, and how these situated criteria of assessment mesh with philosophical analyses of model evaluation. For example, orbital symmetry is renowned for its predictive abilities. The "Woodward-Hoffmann rules" are selections rules that have enormous utility because they provide experimental chemists with the means to anticipate the stereochemical course of the appropriate class of organic reactions in spite of a degree of imprecision in their results. Perhaps this is typical in chemistry. For example Slater (2002) has dubbed Woodward and Hoffmann's approach a "rule-based theory". One might cash-out such an idea by appeal to the practice of “trade-offs” in science. Drawing from Hoffmann’s ideas on idealization in chemistry, Weisberg (2004) argues that while highly idealized (“qualitative”) models in chemistry may not be as accurate as quantitative predictions, precision can be traded off against generality. One of us has argued that trade-offs between manageability and accuracy are a notable feature in the development of computational methods in twentieth century quantum chemistry (Park 2009). A finer-grained analysis of trade-offs can be advanced by looking to the specific historical development of orbital symmetry, by considering the various kinds of trade- offs employed by practioners working within the frameworks of quantitative theory, qualitative modelling and experimentation, and the motivations and justifications for these trade-offs.

This paper also considers the broader context of the application of quantum mechanics to the study of organic reaction mechanisms: the interplay of models and computational methods in the controversies surrounding legitimate applications of fundamental theory. The orbital symmetry approach and ab initio computational methods used to study organic reactions tend to agree in their independently derived results. The convergence of orbital symmetry predictions and the more precise ab initio methods calls for an investigation of the use of robustness analysis in quantum chemistry. Robustness analysis was developed in population biology (Levins 1966), and its applicability to the assessment of models making different idealizations and/or approximations in chemistry has been pursued by Weisberg (2008). This paper looks to the specific moves made by the historical actors engaged with the controversy of methods and the significance of robustness analysis in settling methodological disputes regarding standards of rigour in quantum chemistry. In a delicate process of epistemological checks-and-balances, qualitative models and quantitative methods emerged as a means to coordinate the difficult task of extending quantum mechanics from the study of molecular structure to molecular dynamics.

References

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