Diagnostics and the ‘deconstruction’ of models.

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Abstract: This paper argues that a significant focus in computational organic chemistry, alongside the construction and deployment of models, is the “deconstruction” of computational models. This practice has arisen in response to difficulties and controversies resulting from the use of plural methods and computational models to study organic reaction mechanisms. *Diagnostic controllability* is the capacity of cognitive agents to gain epistemic access to grey-boxed computational models, to identify and explain the impact of specific idealizations on results, and to demonstrate the applicability of computational methods to target systems.

1. Introduction.

In quantum chemistry, providing solutions to the non-relativistic Schrödinger equation for molecules in the ground state from so-called first principles of quantum mechanics has been an acute problem well documented by historians of chemistry (for example Gavroglu & Simões 2012; Park 2009). Recently, attention has been brought to the “computational turn” in quantum chemistry and how it is not merely a matter of technological augmentation but a new discipline of computational quantum chemistry with particular emphasis placed on developments in computational modelling (Lenhard 2014). My aim in this paper is to explore how computational organic chemists attempt to “deconstruct” computational models by diagnosing sources of errors resulting from the use of tractable computational models to study the important organic reactions such as the Diels-Alder reaction. This amounts to modelers attempting to gain epistemic access to grey-boxed computational processes performed on digital computers by investigating modular computational procedures. These modular procedures include various approximations, tools, and base-line theoretical models. Much contemporary research in contemporary computational organic chemistry is focused on modular computational procedures and their comparative performance with respect to classes of target systems in line with various computational goals as well as constraints like computational speed and cost. While accuracy is a desideratum in computational chemistry a considerable focus of research is the *diagnostic controllability* of modular procedures. Controllability is focused on the applicability of modular procedures to specific classes of target systems and focuses on stability or consistency of result. It is cognitively prior to determining the accuracy of results. Although diagnostics of modular computational procedures is a distinctive practice in contemporary computational chemistry, there are important connections to some of the recent literature on simulations in philosophy of science. Some chemists regard computational modeling as a kind of chemical "experimentation". But even before practitioners can generate simulated "data", what stands out in contemporary computational chemistry is the degree to which practitioners focus on legitimating the application of computational models. I will briefly consider the significance of this issue for computational chemistry and how it might relate to the "verification" and "validation" of computational models.

2. The configuration problem.

In order to compute the activation energies of molecules in organic reactions one has to pay particular attention to the correlation energies associated with different configurations of electrons occupying molecular orbitals. Different interactions between configurations of electrons can lead to changes in excitation levels crucial when investigating molecules in the activated state. To study these systems, theoretical chemists make use of computational models using digital computers where approximation procedures and idealizations convert equations lacking an analytic solution into a tractable form, resulting in computable algorithms whose outputs permit practitioners to draw inferences about the mechanisms of reactions that are otherwise difficult to access experimentally.

A significant area of early computational organic chemistry addressed pericyclic reactions like the Diels-Alder reaction and the Cope rearrangement. These are reactions are thought to pass through a transition state formed of a closed circle of bonds and are “allowed” when the symmetry of the molecular orbital wave functions corresponding to bonds broken and formed during the reaction is conserved. Michael Dewar was one of the first chemists to propose that digital computers should be used to semiempirically calculate the activation energies and geometries of transition structures for pericyclic reactions. He argued that ab initio methods – that is, calculations supposedly performed from first principles of quantum mechanics – were simply inapplicable to systems of chemical interest because they effectively ignored electron correlations (Dewar & Jie 1992, p. 538). The first semiempirical computational models of pericyclic reactions used approximation methods taking some electron correlations into account while taking many of the core and electron repulsion integrals to be zero so they are not calculated from an explicit Hamiltonian or basis functions. One approximation is called neglect of diatomic differential overlap (NDDO), a powerful semiempirical tool that ignores only the overlap integrals associated with atomic orbitals on different atoms. Other complex integral calculations are replaced by parameters adjusted with reference to experimental data.

Early ab initio calculations in quantum chemistry were based on the Hartree-Fock-Self-Consistent-Field-approach. Electrons are assumed to move in an average potential field comprising the other electrons. One chooses an electron, computes it potential energy, the result is used to compute the next electron, and so on until the calculated potential fields are "self-consistent". Although semiempirical approaches adopted the same base-line model, ab initio methods were restricted to very simple systems without parametrization. But as it became possible to perform ab initio calculations of activation energies using digital computers in the mid-1970s, ab initio and semiempirical computational approaches produced conflicting results. Ab initio models generated results supporting the idea of symmetric transition states in which bonds break and form in unison (synchronously) in a closed circle of bonds. But semiempirical chemists defended alternative reaction profiles tending to suggest asymmetric transition states in which bonds break and form asynchronously.[1] This came to be known as a "dichotomy of methods" because ab initio and semiempirical methods predicted incompatible mechanisms.

Although contemporary chemists tend to play down the seriousness of this dispute, there is recognition that it has done much to shape the character of contemporary computational organic chemistry. That plural approximation approaches to computational modelling resulted in conflicting reaction mechanisms has raised questions about the applicability of various approximation procedures to chemical systems and their reliability given potential errors. Although the computational chemistry community tends to accept the veracity of the ab initio results for pericyclic reactions, that there has been divergence of results for computational

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[1] Dewar proposed two alternative mechanisms: reactions either occurred in two distinct kinetic steps via a stable intermediate, or even if in a single step, bonds break and form asynchronously. Both conflict with ab initio results.

models that share the same background theoretical models within molecular orbital theory, but differ in specific model assumptions and the use of parameterization, has resulted in practices of error determination and justification of methods via the “deconstruction” of models.

3. Modular procedures, pluralism, and diagnostics.

Computational modelers aim to generate computational models resulting in algorithms that are tractable in the sense that they are capable of rendering equations that lack analytic solution into computable form. As computational models eschew the intervention of epistemic agents in the computational process, computational models are, as Paul Humphreys (2004; 2009) has argued, at least partially epistemically opaque. In what Humphreys calls “hybrid scenarios”, where cognitive agents must “balance the needs of the computational tools with human consumers” (2009, p. 617), not only is this balance to be achieved in terms of computational tractability constrained by computational speed and cost. Consumers aim to deconstruct grey-boxed computational models by cognitively accessing them in order to identify errors resulting from approximations procedures and to determine how they might contribute to the generation of incompatible results. This does not mean that one attempts “full” epistemic access and all errors are eradicated. The idea is that errors resulting from approximations should be “controllable” in the sense to be discussed shortly.

Computational organic chemistry can facilitate epistemic access to computational models due to its methodological characteristics, which include *modularity* and *pluralism*. It is modular in the sense that there are various components parts with specific functional roles used in computational modelling as well as in classifying and organising the tools of the trade. These modules will include what Humphreys (2004) calls “computational templates”. But modular procedures and tools, unlike templates, will also include techniques that are more specific to computational chemistry. The main kinds of modular tools include minimal or extended basis sets (atom centred functions describing atomic orbitals used to construct molecular orbitals from linear combinations of atomic orbitals) of varying kinds (Slater or Gaussian-type), semiempirical procedures that leave out or approximate the two electron integrals associated with exchange interaction and the correlation interactions using the neglect of differential overlap approximation and correcting the resulting errors using parameters drawn from experiment. These two-electron integrals are a central focus for ab initio procedures and there are various ab initio modular procedures available depending on how practitioners want to tackle electron correlations. Modules include: configuration interaction, Möller-Plesset perturbation theory, multiconfiguration self-consistent field theory, and coupled cluster theory. Some modular tools are employed by both semiempirical and ab initio approximation procedures. For example, a standard theoretical model would be the Hartree-Fock model, employing a mean-field approximation that averages out the effect of electron-electron repulsions. This is a base-line model from which corrections to errors resulting from the mean field approximation are then made iteratively and by augmentation using ab initio or semiempirical procedures. There are also “model chemistries” such as the Gaussian-*n* theories used to benchmark computational results. And as Lenhard (2014) has pointed out, since the 1990s, practitioners have increasingly used density functional theory (DFT) to approximate total energy in terms of the total electron density rather than the wavefunction. The use of DFT is central to the development of computational quantum chemistry.

Computational chemistry is pluralistic because the choice of modular procedure is in part contextual, depending on the extent to which practitioners seek to tradeoff accuracy of computational results for computational speed and cost. Computational studies of the Diels-Alder reaction or the Cope rearrangement are covered in some depth in contemporary research and review articles as well as textbooks where the student and researcher can examine the strengths and weaknesses of what have become “off-the-shelf” computational procedures (see for example Bachrach 2014). This complex modularity has resulted in organization of procedures into hierarchies (“levels of theory”) where increasing accuracy demands increasing consumption of resources. The drive towards modularization is important because it represents not only many key developments in computational chemistry, it also facilitates access to partially epistemic opaque computational models. On one level, this is a matter of practitioners diagnosing the sources of errors understood in terms of the contribution made by specific modular procedures to computational results. But this is only made possible by the pooling of comparative studies of computational models and their relative performance across research groups. The general idea of deconstruction is that it is only by first constructing a computational model that delivers solutions comparable to data sets obtained by model chemistries and experimentally determined values that modellers can then go back to the model and diagnose sources of error. The evidence of error is the extent to which results depart from model data or when choice of modular procedures deliver results considered incompatible with computational models making alternative modular choices. Deconstruction is diagnostics. It consists of the collective strategies used to determine the effects of using specific modular components for the study of molecular systems using computational models.

Diagnostics aims at enabling practitioners to isolate, articulate, and quantify error so that they can determine the extent to which computational modules are *controllable*. Here I borrow from Ronald Laymon's (1983, 1987) and Jeffery Ramsey (1992). Both adopt a view of approximation that goes beyond merely assessing approximation validity in terms of the extent to which results depart from experimental data. But there are significant difference between the two authors because for Ramsey "[a]n approximation is an act and not a relation" and will amount to "any methodological strategy which is used to generate or interpolate a result due to underresolved data or deficits of analytic or calculational power" (Ramsey 1992, p. 157). Controllability for Laymon, as I understand it, is essentially being able to give an account of the effect of idealizations of data (Laymon calls these "counterfactual initial conditions") have on the accuracy of predictions such that we are able to seek procedures to "improve" upon them and so improve our predictions. This is central to Laymon's account of confirmation. If one can relax the counterfactuality of the initial conditions used to derive testable consequences from our theories, and the predictions become more accurate, then that theory is better confirmed because it is "monotonic towards truth". A theory is disconfirmed if it does not lead to better approximations (Laymon 1987, p. 211).

My aim here is not engage in the details of the differences between Laymon and Ramsey's respective accounts of approximation and idealization. Both accounts are instructive in that they depart from the idea that approximations should be judged merely in terms of how they might depart from experimental values. But "controllability" in a *diagnostic* sense departs from Laymon's account of confirmation in both its content and its aims (Fisher 2016). First, controllability does not take place in the context of theory-testing but it is nonetheless concerned with other important epistemic goals in computational modelling. To call a modularized computational procedure *diagnostically controllable* is to claim that one knows how and by how much the distortions introduced will affect computational results given that there are no actual target systems in which the distortions are realized. We want to know what effect, if any, model distortions and other counterfactual assumptions would have in actual cases (this seems to be necessary even before we could say that we can “monotonically improve” upon them). It is important to emphasise that the aim of diagnostic controllability is not necessarily to remove errors nor even to generate accurate results (at this stage at least) but instead to demonstrate that, in spite of the errors, which are to some extent inevitable, computational procedures generate predominantly stable results for a given class of target systems in light the contextual goals of the model users.

For example, ab initio calculations of the Diels-Alder reaction turned out to be controllable because chemists could learn what errors to expect when using the Hartree-Fock model and furthermore that the results would be more or less stable under augmentations to the base line approximation by iterative improvements to the models using some of the modular procedures used to take into account electron correlations. Although improving predictive accuracy is ultimately an epistemic goal in much modelling, controllability demonstrated by relative stability of results under modular iterations can trump accuracy. In early computational organic chemistry, it turned out that while ab initio computations were not always the most accurate, especially in the early attempts to compute activation energies of the Diels-Alder reaction and the Cope rearrangement, they were *controllable* because they more consistently generated results suggesting that the reaction mechanism proceeds in a single kinetic step via a cyclical, symmetric transition state. Furthermore, DFT approaches tend to reproduce this mechanism. Semiempirical methods tended to be less controllable (it at times generated some notable inconsistencies), and so became considered less *applicable* to studies of, for example, the Diels-Alder reaction and other pericyclic reactions like the Cope rearrangement.

4. Diagnostics and simulations.

Modularization of computational tools and procedures in computational organic chemistry is one way in which epistemic access to grey-boxed computational models is facilitated and enhanced because pluralism promotes a culture of comparative assessment central to the determination of the diagnostic controllability of the modular computational procedures. There are distinctive methods, tools and choices in computational chemistry: to what extent the choice of basis sets will impact on results, how best to approximate electron correlations, what choice of theoretical model to make, to what extent parameters drawn from experiment will contribute to the correction of error and whether the methodological choices involved in parameterization are justified. While much of this is distinctive of computational chemistry, there is much that relates to the existing literature in philosophy of science on computational models more broadly and I would like, in closing, to connect to some recent literature on simulations. One motivation for connecting with the literature on simulations is that for some chemists, for example Michael Dewar and co-workers, computers were “chemical instruments” just as important to chemistry as, say, infrared and NMR spectroscopy but used in a new kind of “experimental” chemistry (Bingham et al 1975, p. 1285). Computational chemistry of organic reactions began because transition structures were inaccessible experimentally and so data was scarce. Furthermore, computers were not just used to crunch numbers. The results or “data” produced by these models were deployed in model-based inferences about reaction mechanisms and hence chemical dynamics. And what counts as “data” is often derived from model chemistries comprising very accurate computations with large basis sets for relatively small molecules which is used to benchmark modular computational tools deployed in exploring the dynamics of larger chemical systems.

Whether or not simulated data possesses epistemic parity with experimental data is not an issue I can explore here. But I would like to briefly explore some other connections to the simulation literature. Eric Winsberg (2010) argues that the “sanctioning” of computational models where data is scarce depends on possessing model-building principles whose projectability across depends not on the truth of these principles (they are often fictions) but rather their reliability. Diagnostics in computational organic chemistry can be thought of as part of this sanctioning process for computational models in chemistry focusing more on the applicability of procedures given the contextual goals of model users. For example, much of the dispute over ab initio and semiempirical computational methods in the study of the Diels-Alder reaction was whether these methods were applicable to their target system (like the Diels-Alder reaction) and determinations of applicability ultimately closely align to demonstrations of the reliability of computational models.

In any case, applicability is cognitively prior to determining the *accuracy* of computational methods. Here it is useful to draw on a distinction Margaret Morrison (2015) adopts from the simulation literature between “verification” and “validation”. Verification concerns whether the equations are correctly solved and is a predominantly mathematical issue whereas validation concerns how well they computational models represent physical systems. In computational chemistry, and much in line with Morrison's claims, until one has a grip on verification one cannot proceed with validation. A computational chemical "verification" process is at least in part achieved by diagnostics aimed at the identification and quantification of errors and ultimately at determining the applicability of modular computational procedures for the study of classes of target systems. Until applicability is demonstrated, presumably validation cannot be achieved.[2] "Verification" would also include procedural justifications of methods: whether computations are executed in line with model-building goals like top-down ab initio computations or by parameterization from experiment, which are then offered as reasons to support the veracity of computational models.

But there is also something distinctive about diagnostics in computational chemistry in the sense that it might go beyond immediate methodological goals associated with verification. Diagnostics can play an epistemological function in relation to more foundational conceptual issues in chemistry. For example, DFT is known to suffer difficulties in studying non-bonded interactions between molecules. But diagnostic studies of DFT computations of excitation levels in these systems suggest that errors are *unsystematic* because accurate results are possible with some molecules but not others (Peach et al 2008)[3]. In this case diagnostics might reveal aleatory uncertainties associated with errors due to indeterminancy in the physical system.[4] In this case, the uncontrollability of approximations need not reflect poorly on the method. But in the case at

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[2] Diagnostics can therefore perform an exploratory function in the sense that demonstrations of applicability are what Axel Gelfert calls a "proof of principle demonstration" in the sense that "a certain type of approach or methodology is able to generate potential representations of the phenomena" (Gelfert 2015 p. 85).

[3] The molecular systems tested include dipeptide, various acenes, H_2CO, HCl, N_2, and CO.

[4] On the distinction between aleatory and epistemic uncertainties, see Morrison (2015, p. 256).

hand, the problem concerns charge transfer excitations in a wide range of molecules, which has prompted researchers to probe the viability of existing conceptions of a chemical phenomenon whose properties they are attempting to describe. This suggests that while diagnostics can correct and change computational procedures, it can also be used to challenge existing descriptions and conceptualizations of the target systems practitioners ultimately aim to represent in the validation stage. Investigations of diagnostic controllability can form a context for the criticism of existing theoretical models and background theoretical assumptions and so is sometimes used to probe the conceptual basis upon which the success of representations are characterized in chemistry. In other words, diagnostics can enter into both "verification" and "validation" in computational chemistry.

5. Conclusion.

Computational organic chemistry has arisen to address the problem of electron correlations in the study of organic reactions such as the Diels-Alder reaction. I have argued that computational differences arising from the use of semiempirical and ab initio procedures has promoted practices aimed at the deconstruction of computational models. This deconstruction is characterized by diagnostics, which focuses on identifying errors arising from plural modular computational procedures (approximations, idealizations, and theoretical models) used in computational modeling. Although accuracy is a desideratum in computational chemistry, a considerable focus of research is diagnostic controllability of modular computational procedures: their applicability and reliability to classes of target systems. This practice, as well as the idea that computers are used to perform experiments, suggests connections to the philosophical literature on simulations where distinctions between verification and validation seem appropriate but that diagnostic might perform a function in both.

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