

CHAPTER 7

MODELS AND APPROXIMATIONS IN QUANTUM CHEMISTRY

1. INTRODUCTION

Here is a familiar story about how quantum mechanics is applied to chemistry: where smaller entities are to be found among the remains of larger ones, it is reasonable to expect that good theories of the former should explain good theories of the latter. Now molecules are made of atoms, and atoms of electrons and nuclei, so when successful theories of the sub-atomic realm began to appear early last century, it was hoped that out of them would emerge deeper insights into the structure and behaviour of atoms and molecules. The equations produced by these applications of quantum theory were often insoluble, but methods for their approximate solution—based on idealised models—were made available. Long-standing philosophical expectations that reductive explanation should be a deductive affair were to be protected with the claim that the soluble approximate equations serve merely to reveal the content of the as-yet inscrutable exact ones: ‘in principle’, the approximate proxies introduced nothing new.

My aim in what follows is to examine this last thesis: can the idealised models of quantum chemistry be rationalised as approximations to exact quantum-mechanical equations for molecules? In section 2, I will consider a traditional account of how quantum mechanics is applied to atoms and molecules, drawing out its methodological consequences: the traditional account has it that to apply a theory is to construct a model that satisfies its equations. Section 3 is a brief and selective survey of some reasons to think that idealised models in quantum chemistry do not, in fact, satisfy the relevant quantum-mechanical equations, nor can they be approximate solutions to them. More poignantly, however, their ability to do the explanatory work that is required of them depends on this failure. One response here is to take a normative turn: if the models of quantum chemistry cannot be rationalised as approximations to the exact treatments, one must question their status as applications of quantum mechanics. Are they then *ad hoc*? Alternatively, one might question the methodological views—outlined in section 1—on which they are methodologically suspect: this is the subject of section 4.

2. QUANTUM CHEMISTRY IN AN IDEAL WORLD

In this section, I will very briefly outline a standard model of how general theories are applied in the explanation of particular facts or regularities. What this view entails for explanatory relations between physical theory (quantum mechanics) and chemical fact can then be drawn

out. Certain key features of Hempel's covering-law model of scientific explanation (Hempel 1966) suffuses what seems to be a standard view—or mere intuition—about how theories are applied. According to Hempel, to explain the behaviour of a real system with a general theory one draws on two kinds of statement: internal principles and bridge principles. Internal principles (like Newton's laws or the Schrödinger equation) are general statements, tied to specific cases by bridge principles, which are true statements about the systems of interest that are relevant to the system we are applying. My terminology here departs from Hempel's, who distinguished: (i) specific assumptions about the target systems couched in the language of the explanatory theory; from (ii) principles that link the explanatory theory's language to the antecedently understood language of the explanandum statement. Hempel reserved the term 'bridge principle' for the latter, but for simplicity's sake I will follow Nancy Cartwright's critical discussion of Hempel's model (Cartwright 1983) and call both kinds of assumption bridge principles. Modulo suitable bridge principles, then, the explanatory theory explains the behaviour of a kind of system if that behaviour follows deductively from its internal principles. So on the covering-law account, the equations of (say) quantum mechanics stand to the equations with which we explain the behaviour of atoms and molecules in the relation of general to specific, as Cartwright has put it (1983, 103).

How does this apply to quantum chemistry? How would we come by bridge principles in the (methodologically) ideal world of the covering-law model? Two stages are involved. At the first stage we write down the bridge principles for the system under study, yielding a set of equations that describe the target systems within the theory. Then (at the second stage) we solve these equations. In quantum chemistry, the first stage is the familiar process of enumerating the particles in a molecule, and writing down the Hamiltonian in terms of their charges, masses and any incident potentials. Textbooks of quantum chemistry typically consider only Hamiltonians containing Coulombic potential terms for interactions between particles (see for instance Atkins 1983, or Szabo and Ostlund 1982). Note that a certain amount of idealisation has already occurred, for a Hamiltonian has been written down that is known to be incorrect for any real molecule: relativistic corrections are ignored, and the Hamiltonians are usually relevant only to isolated molecules, of which there are none in the real world.

In the ideal world, the second stage would involve unfolding the consequences of the theory as applied to this idealised description—by solving the Schrödinger equation for the molecule—but further idealisations become necessary if, as is almost invariably the case, the relevant Schrödinger equation is insoluble. Useful idealisations might (for instance) falsify interactions between subsystems of a composite system. In molecular calculations, nuclear and electronic motions are almost universally separated in this way via the adiabatic approximation. The Born-Oppenheimer approximation compounds this by setting nuclei

instantaneously at rest (typically in the ‘equilibrium geometry’ that is known empirically); electrons move in the resultant nuclear potential. Structural features of the molecule are then explained by calculating the effect of changes in nuclear configuration on electronic energy. How is the electronic problem solved? Hartree-Fock methods (for atomic calculations) replace a multi-electron wavefunction $\Psi(x_1, \dots, x_n)$ with a product $\psi_1(x_1)\dots\psi_n(x_n)$ of one-electron ‘orbitals’ corresponding to a system of non-interacting electrons. The distortion involved in this idealisation can be calculated away using increasingly sophisticated mathematical devices to model electronic interactions. There are various methods for constructing molecular orbitals out of atomic orbitals: the molecule’s chemical behaviour can be investigated by determining the occupancy of its molecular orbitals, allowing calculation of charge densities, molecular geometry and so on.

A different approach is the direct quantisation, again via idealised models, of the motion of *subsystems* of the molecule. For instance, the action of carbon dioxide as an atmospheric greenhouse gas is explained by associating its infrared and microwave absorption with its rotational and vibrational energy levels. Without solving the Schrödinger equation for CO₂, we know that it is a linear triatomic molecule. By analogy with macroscopic systems of three balls attached by springs, we can imagine the types of motion that a system of this kind will exhibit. The molecule is treated as if it were a system of quantised oscillators and rigid rotators such as appear in any undergraduate quantum mechanics course: transitions between vibrational and rotational states account for the molecule’s infrared and microwave spectrum. Silverstein, Bassler and Morrill (1981) provide a graphic example of this kind of description:

The CO₂ molecule is linear and contains three atoms; therefore it has four fundamental vibrations ... The symmetrical stretching vibration is inactive in the infrared since it produces no change in the dipole moment of the molecule. The bending vibrations ... are equivalent, and are the resolved components of bending motion oriented at any angle to the internuclear axis; they have the same frequency and are said to be doubly degenerate (Silverstein, Bassler and Morrill 1981, 96.).

Finer spectroscopic structure can be saved by allowing for coupling between different motions (for details see Steinfeld 1985, Chapter 8).

The use of these models in explanations and predictions raises two closely connected issues. Firstly, to separate nuclear and electronic motions and hold the nuclei fixed, or to replace a multi-electron wavefunction with a product of one-electron wavefunctions, is to misrepresent the molecule. Secondly, modulo plausible background assumptions, quantum mechanics itself implies that: (i) nuclei do not have fixed positions; and (ii) where two systems interact, the composite system cannot be represented as a product of wavefunctions for the two separate systems. Insofar as there are exact quantum-mechanical equations which mathematical

intractability forces us to discard, and those equations yield (i) and (ii), we are not consistently applying quantum mechanics if we represent a molecule by a model in which (i) or (ii) fail.

Now the first issue raises well-known problems for the idea that laws truly apply to concrete systems: Duhem, for instance, objected that general theories should be thought of as depictions of reality only if we can apply them to true descriptions of the real systems we investigate with their help. Now this issue arises also at the first stage (for there were idealisations there too), and the topic of this chapter is the view of idealised models as proxies for exact ones, so let us turn to the second issue. The second issue might not be thought to present a problem for the covering-law account, for the following reasons. The idealised models amount to approximations that stand in for true pictures of molecules in quantum-mechanical explanations and predictions of their behaviour. Perhaps these models do not accurately represent molecules, perhaps they also do not satisfy the exact Schrödinger equations. However, if the covering-law intuitions are right, the assumption must be that when an idealised model is introduced, although it does not satisfy the exact equations, mathematical or physical arguments are—in principle—available that show that wherever we use such a model in an explanation, any of its features that figure in the explanation could be attributed also to the results of an ‘exact’ treatment. So the idealised models are proxies for solutions to the exact Schrödinger equations: whatever we can explain with the former, we could explain with the latter, if only we could handle them.

3. QUANTUM CHEMISTRY IN THE REAL WORLD

In the last section I outlined how a common view of the explanatory use of theories requires that the idealised models of quantum chemistry must be mathematical devices designed to approximate to solutions of the exact Schrödinger equations. I also noted that this view would be plausible only if it can be shown that, whenever an idealised model is used in an explanation, the exact model will share explanatorily relevant features of the idealised model. A number of commentators have, for different reasons, questioned whether this last condition holds, giving examples of differences between exact and idealised models in explanatorily relevant respects (Claverie and Diner 1980, Weininger 1984 and Woolley 1985 provide surveys of this literature). Responses to these failings are diverse. Primas (1975, 1983) has concluded that molecular structure is not possessed by molecules, but is something we read into the surface patterns of a quantum world. Woolley (1976, 1977, 1978, 1985) argues that Born-Oppenheimer wavefunctions should not be viewed as an approximations to solutions of exact Schrödinger equations: instead they should be regarded as applying to different kinds of situation. Scerri (1991) and Ogilvie (1990) find opposed methodological lessons—for Scerri,

more rigorous quantum mechanical methods should be developed, while Ogilvie has suggested that the application of quantum mechanics to large areas of chemistry might as well be abandoned.

Primas' views are set out most fully in his (1983). A succinct argument appears in his (1975), on which the following discussion will concentrate: Primas' starting point is the holism associated with quantum mechanics. Theoretical propositions in physics are typically formulated with closed systems in mind, and then applied in modified form to open systems. Even for classical mechanics, background knowledge implies that all systems interact: there *are* no closed systems apart from the universe as a whole. The effect of EPR correlations in quantum mechanics is, however, more dramatic: composite systems must be represented as single quantum systems, rather than as networks of coupled subsystems each having a well defined state. For a given system s composed of two interacting subsystems s_1 and s_2 , the state of the composite cannot in general be represented as a simple product of well defined subsystem states, no matter how weak the interactions:

$$\Phi(s) \neq \Psi(s_1) \otimes \Xi(s_2).$$

This quantum-mechanical holism has some interesting consequences. Firstly, to pick out a system for study, and then calculate its quantum state is to impose a separation of the world into system-plus-background. This process—which for Primas is central to the scientific enterprise—therefore necessitates a degree of idealisation: there are no exact quantum-mechanical equations that exactly describe real systems, or at least none that can be written down. Secondly, if there is only one real closed system, and therefore one system to which one could attribute a well-defined quantum state, 'we need an interpretation of quantum mechanics in which the notation of a world-state is conceptually well-defined' (1975, 132). The 'traditional' epistemic and operational interpretations such as the Copenhagen interpretation, or the von-Neumann-London-Bauer ensemble formulation—both 'meaningless' when applied to the universe as a whole—are to be rejected in favour of an alternative 'ontic' interpretation.

Ironically, the ontic interpretation of quantum mechanics suggests a pragmatic interpretation of that theory's particular applications. Quantum mechanics implies universal entanglement, and entanglement implies non-separability: subsystems of the Great System do not have quantum states to call their own. The central activity of quantum chemistry could not, therefore, be the calculation of correct quantum states for real molecular systems. Rather, quantum chemistry associates quantum states for model molecular systems with recognised phenomenal patterns. Neither the subsystem states nor the phenomenal patterns are given by nature: both are created, and essentially interest-dependent. Primas presents an interesting formal characterisation of this process. When we single out a system and study its quantum

state, we decompose the state space H_w for the world (or ‘universe of discourse’) into a tensor product of system and environment Hilbert spaces (H and H_e respectively):

$$H_w = H \otimes H_e.$$

For arbitrary world-state $\Phi \in H_w$, there are non-unique expansions:

$$\Phi = \sum_j \sum_k c_{jk} \Psi_j \otimes \Xi_k,$$

such that $\Psi_j \in H$ and $\Xi_k \in H_e$. Primas quotes a theorem due to Schmidt that if the coefficients c_{jk} are chosen to be diagonal, and the Ψ_j and Ξ_k are orthonormal, there is (if the c_j are non-degenerate) a unique expansion of the form:

$$\Phi = \sum_{j=0}^{\infty} c_j \Psi_j \otimes \Xi_j,$$

from which it follows that if Φ is normalised:

$$\|\Phi\|^2 = \sum_j |c_j|^2 = 1$$

and

$$\langle \Psi_j | \Phi \rangle = c_j \Xi_j,$$

$$\langle \Xi_j | \Phi \rangle = c_j \Psi_j.$$

Now if it is chosen that

$$1 \geq |c_0|^2 \geq |c_1|^2 \geq \dots \geq 0,$$

then in order to generate a model of a quantum system (a molecule, say), the world-state Φ is replaced by the particular direct product Φ_0 of system and background states (respectively, Ψ_0 and Ξ_0):

$$\Phi_0 = \Psi_0 \otimes \Xi_0.$$

Φ_0 then provides the best approximation to the real world-state that can be expressed in product form for this particular decomposition. Now it is obvious that

$$|\langle \Phi | \Phi_0 \rangle|^2 = |c_0|^2 \leq 1.$$

The entanglement of all real systems means that $|c_0|^2$ can never reach unity; Primas uses its proximity as a measure of the closeness of model world-state Φ_0 to real world-state Φ . Thus $|c_0|^2$ also provides a measure of the accuracy with which the exact world-state can be treated as a simple product state, that is, the extent to which the system under study is independent of

its environment. If $|c_0|^2 \approx 1$, Φ_0 is the *dominant Schmidt state*, and will be robust with respect to environmental perturbation. It is, however, ‘background-dependent’, in that its applicability depends on the chosen decomposition of the world-state into system and environment states. When the entangled world-state is replaced in our calculations by a separable dominant Schmidt state for a system of interest, we thereby introduce any properties we attribute to the system via the representation, with $|c_0|^2$ representing the degree to which the real system can be said to have those properties. Born-Oppenheimer methods are one example of this: Primas argues that those features of quantum-mechanical molecular models that are typically associated with molecular structures—determinate internuclear distances, moments of inertia—are artefacts of the methods, they are not inherent in the quantum-mechanical problem (1975, 143). Successful quantum chemistry is the construction of robust model states which ‘explain’ the phenomenal patterns that we read into a structureless quantum world.

Woolley and Sutcliffe (1977) are also critical of the supposition that Born-Oppenheimer procedures provide approximate solutions to exact Schrödinger equations for isolated molecules. Their argument is simple: the Born-Oppenheimer structures do not have the right symmetry properties. It can be shown that the standard electrostatic Hamiltonian of quantum chemistry commutes with translation and rotation operators \mathbf{P} and \mathbf{J} :

$$[\mathbf{H}, \mathbf{P}] = [\mathbf{H}, \mathbf{J}] = 0.$$

The Born-Oppenheimer procedure picks out a structure in which the nuclei have determinate positions and are at rest. Electrons move in quantum-mechanical molecular orbitals in the field produced by the nuclei. For the purposes of explaining the chemical behaviour of a molecule, the most useful Born-Oppenheimer structure is likely to be the most probable one: the equilibrium structure, for which the energy of the system as a whole is a minimum. It is important to realise that this structure is attributed to the molecule on the basis of empirical constraints applied within the chemical theories of molecular structure that originated in the nineteenth century. Quantum mechanics, via momentum-position uncertainty, implies that nuclear positions must be blurred, however, and adds a zero-point energy Δ_0 to the classical minimum energy E^{cl} . Thus the Born-Oppenheimer energy E^{BO} is given by:

$$E^{\text{BO}} = E^{\text{cl}} + \Delta_0$$

The zero-point energy, Δ_0 , can be visualised as an ‘uncertainty oscillation’ about the equilibrium nuclear position. According to Woolley and Sutcliffe, the Born-Oppenheimer structures are semi-classical: classical structures perturbed by quantum effects. Crucially, they are of lower symmetry than eigenstates of isolated-molecule Hamiltonians. Operations on these structures by \mathbf{P} and \mathbf{J} sweep out six-dimensional hypersurfaces of constant—albeit blurred—energy. So the Born-Oppenheimer procedure amounts to the addition of classical

molecular structure to the quantum-mechanical treatments, rather than approximations to them. One could add to this a further argument: Coulombic Hamiltonians for isolated molecules typically applied in quantum chemistry are fully symmetric. Consider a Coulombic Hamiltonian \mathbf{H} for a molecular system with eigenfunctions ψ_n and eigenvalues E_n . Thus:

$$\mathbf{H}\psi_n = E_n\psi_n$$

If \mathbf{R} is an operator which effects inversion of co-ordinates, we have

$$\mathbf{R}(\mathbf{H}\psi_n) = \mathbf{H}(\mathbf{R}\psi_n)$$

putting these two together:

$$\mathbf{H}(\mathbf{R}\psi_n) = E_n\mathbf{R}\psi_n$$

So if \mathbf{H} is symmetric, and ψ_n is one of its eigenfunctions, then so is $\mathbf{R}(\psi_n)$ with the same energy eigenvalue. If ψ_n and $\mathbf{R}(\psi_n)$ have some directional property such as a dipole moment, the associated dipoles will act in opposite directions, but the two states have the same energy. Were an arbitrary energy eigenstate of a fully symmetric Hamiltonian to be represented as a superposition of states with dipoles oriented in opposite directions like ψ_n and $\mathbf{R}(\psi_n)$, they should appear with equal weight in the expansion. Given Coulombic Hamiltonians, it seems that according to quantum mechanics molecular states with (for instance) equal dipole moments in opposite directions should be equiprobable, and the expectation value for the dipole moment of a molecule in an arbitrary eigenstate of the full molecular Hamiltonian must be zero. More generally it follows that according to quantum mechanics, no directional properties will be possessed by an isolated molecule in a general energy eigenstate. Nor is it easy to see how a large ensemble of molecules in such states could have directional properties *en masse*. Therefore to explain the directional properties of molecules, *non*-symmetric Hamiltonians must be used, and this will typically involve taking in to account the action of the molecule's environment in the form of a term for an incident potential.

In his (1976), Woolley presents a fundamental discontinuity between the behaviour of small, isolated molecules and large molecules interacting strongly with their environment. Woolley points out that non-adiabatic calculations based on isolated molecular Hamiltonians in fact are accurate for high-resolution investigations of the well-separated energy levels of atoms and small molecules in the form of rarefied gases or molecular beams. When care is taken to minimise line-broadening processes such as intermolecular collisions and Doppler effects (see Woolley 1976 and 1977), and the molecules illuminated by lasers, the spectra will be very close to those of the isolated-molecule Hamiltonian. In such calculations, the notion of molecular structure is not required, and is indeed 'no longer appropriate' (1976, 30). In contrast, when environmental interactions cannot be ignored, and for large molecules which

are not suitable for preparation in states of high rarefaction, classical molecular structure becomes 'indispensable'. In fact any explanation—of, for instance, isomerism or optical activity—that requires a semi-rigid structure to be attributed to a molecule is an explanation in which an exact isolated-molecule treatment would be unsuitable. Born-Oppenheimer structures, with classical structure built in, may provide a suitable basis for the application of quantum mechanics in these contexts. However, the models so produced could not have the status of approximations to intractable exact treatments, because features of these models that are relevant to the explanation could not—for the above reasons—be shared by solutions to the exact equations.

Woolley has interpreted these arguments in two quite different ways. The first concentrates on the different experimental contexts in which energy eigenvalues and structural properties are measured. Physical concepts such as energy and structure are well defined only for those experimental situations in which quantum systems with sharp values for the corresponding quantities have been prepared. If we cannot prepare molecules with sharp values for both energy and structural quantities, these concepts must be 'complementary in Copenhagen sense' (1976, 30). Now the formal expression of complementarity between two physical concepts is non-commutivity between the corresponding operators, but Woolley does not present a proof that the operator for some quantity necessary for the attribution of molecular structure fails to commute with the Hamiltonian. This isn't necessarily a criticism of Woolley: for Bohr, complementarity between physical quantities seems to have been a broader relation than non-commutivity, possibly explaining it (see for instance Murdoch 1987, 87). In the second interpretation with which Woolley glosses his formal arguments, he is much closer to Primas. The absence of classical structure in isolated molecules suggests it to be the effect of physical interaction between a molecule and its environment: physical properties dependent on molecular structure might therefore 'disappear abruptly' (1978, 1077) as these interactions vanish. For Woolley, the future of quantum chemistry lies in developing rigorous quantum-mechanical (for instance non-adiabatic) treatments of small molecular systems in isolated states, in which molecular structures do not figure. To complement these methods, there would be semi-classical treatments of large molecules interacting strongly with their environments, which will figure in structural explanations of chemical behaviour.

The aim of Ogilvie's rather more trenchant criticisms is to distinguish between 'what is fundamental and what is artefact' in quantum chemistry (1990, 280). His chief target is the separation of multi-electron wavefunctions into single-electron terms which is basic to the Hartree-Fock procedure. It is not the approximation itself to which he is hostile, but the use of approximate one-electron orbitals in the explanation of chemical facts. The worst such case is the usual account of chemical bonding in terms of hybridisation (the interference of atomic

orbitals to form bonding molecular orbitals): the subtitle of Ogilvie (1990) is ‘There are no such *things* as orbitals’. Ogilvie takes the quantum-chemical account of the structure of methane (CH_4) as his main example. It is often claimed in textbooks of chemistry that methane’s electronic structure explains its tetrahedral shape. Eight electrons occupy four SP^3 -hybridised molecular orbitals, resulting in increased charge density in the space between the carbon nucleus and each of the four hydrogen atoms. Mutual repulsions between these four charge centres spread out the carbon-hydrogen bonds over a sphere to give the familiar tetrahedral angle of 109° . The remaining two electrons are localised close to the carbon centre, and do not significantly contribute to bonding.

The attack on electronic orbitals has three main prongs. Firstly, just because molecular energies can be calculated successfully by constructing molecular states out of atomic orbital bases, one cannot infer that molecular orbitals are somehow formed from the interactions of atomic orbitals. The choice of basis functions in an expansion of the molecule’s state in terms of molecular orbitals (themselves constructed out of atomic orbitals) is irrelevant to the quality of the final energy value (other bases provide equally good values), and is therefore arbitrary and cannot have the physical meaning attributed to it in the hybridisation explanation of methane’s bond angle. Secondly, the ten electrons in CH_4 are ‘fundamentally identical and indistinguishable’ (1990, 283). It therefore makes no sense to distinguish qualitatively between them, as their occupancy of distinct electronic orbitals must (to be fair to the Hartree-Fock method, this artefact can be calculated away using exchange integrals). Thirdly, ‘a molecule consists of only electrons and nuclei, certainly not orbitals or even atoms’ (1990, 287). Atoms are not present in molecules as atoms—methane consists of a carbon nucleus, four protons and ten electrons, rather than a carbon atom and four hydrogen atoms—and it is a ‘category fallacy’ (1990, 287) to think otherwise. It makes no sense to explain the behaviour of a system by reference to entities which are not in fact present in that system, so explanations of molecular structure that invoke interactions between either atoms or electrons in one-electron orbitals cannot be legitimate.

Historically, Ogilvie argues, molecular structure—and the standard electrostatic accounts of chemical bonding—arose against the background of classical physics. There is no reason why these explanatory tools should be transferable into a quantum-mechanical context. On the above arguments, the quantum-theoretic explanations are essentially parasitic on the classical accounts they are supposed to supersede, because they certainly make no sense against the background of rigorous quantum mechanics. Quoting photoelectron studies of methane, Ogilvie argues that the approximate models of quantum chemistry are not even empirically adequate; the purported electronic structure is not found. Classical models of molecular structure and bonding often do no worse, and at least have the advantage of conceptual

consistency. The valence shell electron pair repulsion theory is cited by Ogilvie as an—admittedly unsatisfactory—starting point.

Scerri (1991) detects conceptual problems in standard quantum-chemical models of the electronic configuration of atoms. Any problems here would also infect the accounts of molecular structure in which they are embedded. Scerri points out that atomic models are constructed in accordance with the *aufbau* principle which, in the quantum theory of atomic structure that developed out of Bohr's atomic model of 1913, was used to build up electronic configurations for successive elements in the periodic table. Central to the building-up process was the occupation by individual electrons of stable stationary states embodied in their possession of quantum numbers. Such individual stationary states would of course be perturbed by the addition of further electrons, but the continuity of their existence was a cornerstone of the spectroscopic theory.

The retention of individual electronic stationary states during perturbations of the atom was problematic even within the old quantum theory, claims Scerri, because it relied on the adiabatic principle. This principle, which had been proven to hold for particular classes of systems by Ehrenfest, and extended by Burger, had not been shown to hold generally. In particular, the principle was not known to hold in aperiodic systems, a class that sadly includes multi-electron atoms. Now to be fair to Ehrenfest he, following Einstein, called the principle a 'hypothesis' (1917, 80). Bohr called it the *Principle of Mechanical Transformability*, and was similarly aware of its status as an idealisation, stressing the 'limits of its applicability' (1918, 102). In the context of quantum mechanics, however, Scerri notes that one-electron angular momentum operators for individual electrons do not commute with the full Hamiltonian, from which it follows that electrons in atoms described by eigenstates of the full Hamiltonian cannot also be in stationary states characterised by the usual quantum numbers. For among the usual quantum numbers are some which correspond to eigenstates of one-electron angular-momentum operators, and non-commuting operators cannot share eigenfunctions. Scerri concludes: 'Standard quantum mechanics thus shows that giving electrons individual quantum numbers, or putting them into boxes or orbitals is incorrect', and 'only the atomic system as a whole possesses stationary states' (1991, 317). The 'orbital approximation', however, is a useful device for classifying spectroscopic terms, and as a zero-order starting point for more accurate calculations. Scerri concludes by arguing that the approximate orbital models, although indispensable in practice, are 'floating' models in the sense of Post (1974): lacking either theoretical justification or empirical support. The orbital approximation does, however, represent the 'only practical approach', but 'its proponents might benefit by moderating their claims to success' (1991, 321).

To summarise this section: when tractable quantum-mechanical methods are applied to complex molecules, it seems that the semi-classical nature of the molecule is presupposed.

According to Woolley, for instance, the Born-Oppenheimer approximation represents the molecule as a quantum-mechanical system draped on a (classical) rigid structure. Even in the case of the adiabatic approximation, nuclear configurations are averaged over in an iterated process which hopefully approaches a quantum-mechanical limit. Anywhere short of that limit, however, and the adiabatic models disentangle the states of the molecules' subsystems in a way that would be, according to Primas, foreign to quantum mechanics. Ogilvie and Scerri object to a further separation: of the state of the system of electrons into products of one-electron states corresponding to atomic or molecular 'orbitals'. All of these methods, and the molecular models on which they are based, are closer to the old quantum theory—in their haphazard quantisation of the motion of subsystems of the molecule—than to coherent applications of quantum mechanics proper. If we think of these methods as introducing models that are approximations to exact quantum-mechanical treatments, then some features of the models that play crucial explanatory roles are artefacts of the approximations.

We can usefully distinguish two kinds of response to these arguments: (i) metaphysical and (ii) methodological. (i) Molecular structure is either not a real feature of molecules (Primas) or is complementary (in the Copenhagen sense) to other features that quantum mechanics attributes to molecules (Woolley). (ii) Quantum-mechanical molecular models are suspect as applications of quantum mechanics, so we should either develop theoretically rigorous models (Scerri) or give up on the application of quantum mechanics in this area (Ogilvie). There is also a methodological aspect to Woolley's response: although his argument is not that there is anything wrong with the Born-Oppenheimer models as quantum-mechanical descriptions of situations in which molecular structure is important, models for the situations in which molecular structure is less important are worthy of independent study, and the independence of Born-Oppenheimer structures from the exact quantum mechanics of isolated molecules calls for a broader investigation of how molecular structure does arise (Woolley 1991).

4. APPROXIMATION AND IDEALISED MODELS

To rehearse a commonplace of modern philosophy of science, physical theories of any breadth of application do not provide detailed descriptions of the behaviour of interesting systems on their own. Rather, they must be supplemented with the particular facts of the system to be studied that are of interest to the theory in question. In the covering-law model, to convey background information (relative to theory) is the job of the bridge principles. Together, theory and background determine a model, and theory is to model as general is to specific. On this view, idealised models must—where legitimate—be approximations to some absent or intractable exact treatment. The force of the previous section, however, is that

modelling in quantum chemistry fails to fit this picture: explanations do not seem to take the form of deductions from the Schrödinger equation modulo truths about the molecules in question. Idealised molecular models that in fact are used cannot be rationalised as approximations to exact treatments, for we have seen plausible arguments that such features of the models as are invoked in explanations are not shared by the exact treatments. Of course we don't have direct access to the results of the exact treatments, but we can discern some of their gross features, for instance via symmetry arguments.

What of the responses we have seen—metaphysical and methodological—to these conflicts? Let us take them in reverse order. If the methodological critiques are accepted, it would seem that the methods presently pursued in large parts of quantum chemistry must be either emended or abandoned. But the relationship between theory and evidence being what it is, the moderate prescription for more rigorous methods—is a less stable response than Ogilvie's extreme view. If the models of quantum chemistry are vitiated as legitimate applications of quantum mechanics, we surely lose most of our reasons for thinking that quantum mechanics has anything useful to say about atoms and molecules. A theory lives through its applications, and any support it does enjoy, it enjoys through their success. Quantum mechanics, though, is applied mostly through the idealised models whose legitimacy is at issue here: if they are not true applications of quantum mechanics, their success cannot accrue to it. There are few alternative methods—available and tractable ones, that is—whose success would give us an argument that quantum mechanics covers molecules. So we cannot both question the legitimacy of our models and expect (with any good empirical reason) that more rigorous methods would do better, for the applicability of the very theory with respect to which the projected methods would be more rigorous is called into question along with the legitimacy of the idealised models as applications of quantum mechanics. Nor would it be plausible to generalise from the success of the (very few) exact treatments—like the hydrogen atom—that do happen to be tractable: the old quantum theory was tractable and successful in many of the same cases, yet it failed for more complex systems. To get beyond the very simple systems in quantum mechanics, the kinds of 'approximation' whose legitimacy is at issue here need to be used. So if the covering-law view of application is applied, the idealised models become suspect, and the only coherent way to address these suspicions once raised seems to be the wholesale suspension of quantum-mechanical model building. The loss of large parts of post-war quantum chemistry is an unattractive consequence: the alternative is to suspect the methodological view—the covering law template—which made the idealised models of quantum chemistry seem methodologically suspicious. The same facts of theory and evidence present problems for the metaphysical response: Primas' discussion begins with the explicit assumption that quantum mechanics is universally applicable, from which he then derives an instrumental interpretation of its particular applications. This attitude also seems to get things the wrong way round. Why should we think that quantum mechanics is universally

applicable? Presumably because its applications are successful, but it is hard to see how wide-ranging metaphysical conclusions can coherently be founded on the success of applications that are interpreted instrumentally.

Sometimes the idealised models are presented as conflicting with background information (i.e. that the problem is one of idealisation), sometimes with quantum mechanics. Of course both views are right, for the conflict is with background information presented via quantum mechanics, as embodied in the exact treatments. But this is naive: we have not compared the approximate molecular models with what quantum mechanics says about molecules simpliciter, only with what quantum mechanics says about molecules if we pretend they are isolated systems of point-mass nuclei and electrons that are subject only to Coulomb interactions. This description is itself an idealised one: there are no isolated molecules; electrons and nuclei experience interactions that are non-Coulombic; nuclei are not without internal structure; and the Hamiltonian should be relativistic. That the idealised models falsify some details of real molecules and therefore seem to ‘conflict’ with quantum mechanics cannot itself be a good reason not to use them. If it is responded that the molecular models constitute worse falsifications than the (more) exact treatments, two important questions are begged. (i) Are idealisations so ordered that phrases like ‘more exact’ are applicable? Different models might capture different features of the same molecule for the purposes of different investigations. It doesn’t make sense to ask whether Hückel methods are ‘more approximate’ than treatments in which functional groups are treated as harmonic oscillators. Different functional groups that may cohabit in a molecule feature in quantum-chemical explanations of, for instance, IR and UV spectra. Any such group may be the subject of a model that ignores other functional groups. An emphasis on accuracy for one aspect or feature may well preclude an accurate account of another. (ii) Why should we think that the ‘more exact’ treatment will yield better results? We have already seen that the *ur*-model for isolated molecules seems to have the wrong symmetry to play a role in explanations of molecular geometry. Meanwhile, the broken symmetry that is an ‘artefact’ of the Born-Oppenheimer approximation allows Born-Oppenheimer models to play important explanatory roles. Anyone who wishes to explain molecular geometry, it seems, should prefer the less exact Born-Oppenheimer models.

What is required, then, is an approach to the methodology of model-construction that appraises a model independently of its mathematical relationship to some exact treatment. In what remains of this piece, I will make a few local points about appraising models in quantum chemistry. Cartwright (1983, Chapter 7) has observed that, in giving a theoretical account of a system’s behaviour, we don’t just write down a literal description of the system and apply the formalism to the result: there are two distinct stages of theory entry. First imagine a list of everything we know about the system: we cannot go from this to an equation, for the

description has to be prepared for entry into theory. Preparation is more than just deciding what is relevant, for we must pick a description *for which the theory has an equation*. Now equations can be tailored to some extent, and the list of tractable applied equations that is associated with any living theory is always growing, but it is important to see that they are ‘off the peg’ rather than bespoke: we fit the facts to the equations, rather than vice-versa. How we go from an unprepared description to a prepared one is not dictated by the theory we are applying, but there are nevertheless good and bad prepared descriptions. The criteria for assessment are ‘rules of thumb, good sense, and, ultimately, the requirement that the equation we end up with must do the job’ (1983, 133). Cartwright’s account fits the use of the quantum-mechanical harmonic oscillators in spectroscopy nicely: we start with the insight that some absorption bands in the infrared region are due to vibrations of some part of the molecule. But we do not start with an exact treatment and work downwards; rather, we start with the equations we have for vibrations—the textbook harmonic oscillator—and tailor them to the situation.

When is a molecular model a good one? A good model will at least provide good predictions, and some understanding of the behaviour of the target system. But the usual standards for prediction don’t apply: we cannot expect predictions based on false assumptions to be true. Laymon (1983, 1987) has presented a diachronic criterion of appraisal for theories applied to counterfactual initial conditions: monotonic piecemeal improvability. The reasoning is as follows: although we cannot expect predictions that are precisely true, if our model is a good one, we will have some idea of how the distortions we have made will affect its predictions, and some idea of how to *de-idealise* it. In particular, if we improve our models (that is, make them more realistic) we can expect that the predictions of a good theory will also improve. Although it can only be a *ceteris paribus* criterion—because errors sometimes cancel—Laymon’s criterion is *prima facie* reasonable, resonating as it does with Lakatos’ requirement of empirical progressiveness. However, Laymon presents his criterion as one of theory confirmation, mainly because he assumes that the motivation for de-idealising moves must come from overarching theory. Motivation comes in because a theory is supported if theoretical improvements are matched by increased accuracy in prediction, but what counts as a theoretical improvement is a matter of motivation (Ramsey 1992 provides a helpful examination of Laymon’s criterion and the role of motivation). Now Laymon applies the criterion in his defence of realism about theories against Cartwright’s critique (Laymon 1989), but that defence will work only in so far as the de-idealising moves that lead to increased predictive accuracy are inspired by theory, by the information that the theory gives us about how the idealised treatments differ from the exact one. If the motivation of the de-idealising moves is local to a particular model, it is hard to see why credit should go to the theory. Quantum mechanics, for instance, is not the source of the moves (cited in the first section) to take into account coupling between rotational and vibrational molecular motions:

in that case, the empirical support that Laymon's criterion encodes should accrue to the molecular model, and could reach the (various) theories that are used in its construction only secondarily. Change the object of appraisal, and Laymon's becomes: we have a good model when well motivated de-idealising moves improve the predictions.

Similar points can be made about motivation and explanation: Redhead (1980) distinguishes approximation and idealisation: in approximation we include a factor in the model, and then neglect it in the equations; in idealisation we leave it out of the model itself. The distinction is not a principled one from a mathematical point of view, for Redhead points out that there is an approximate solution to an exact equation (an approximation in Redhead's terminology), for every approximate equation which can be solved exactly (i.e. idealisation). However, the difference is important from a heuristic point of view: idealisations sometimes come with ready-made physical interpretations (e.g. switching off inter-electronic interactions to get a wavefunction that is a product of one-electron wavefunctions); others are only mathematical, amounting only to the neglect of higher terms in an expansion, perhaps. The physically motivated approximation will (by assumption) depart from reality in ways that are understood physically, and therefore might allow causal differences between real systems to be understood. In addition, where a physical factor is neglected we might have some idea about the physical situations to which the model will fail to apply without emendation: just those situations where the neglected factor makes itself felt most strongly in the system's behaviour. The moral is clear: a physically interpreted idealisation might contribute to the understanding.

Del Re (1974) observes that some approximate models are more amenable than others to this kind of interpretation. The much-maligned models in which molecular orbitals are constructed from linear combinations of atomic orbitals are a good vehicle for chemical explanation—notwithstanding what he calls the 'basis problem' (raised also by Ogilvie)—just because they are readily interpretable in terms of the 'bonds, atoms and simple orbitals' (Del Re 1974, 95) in which chemical explanations deal. He also provides (1974, 97) a very nice example: the explanation of conjugation. On the classical theory of valence, covalent bonds within molecules are formed by atoms sharing pairs of electrons, so a useful way to cut a molecular wavefunction at its joints is to divide it into two-electron orbitals. These can be bonding, non-bonding or anti-bonding orbitals, depending on the contribution their occupation makes to the energy of the molecule. Now suppose we replace a many-electron wavefunction for an organic molecule with a product of such bond-pair-orbitals (two electrons per orbital). Bonds, and therefore bonding orbitals, can be divided into σ -bonds (that form the skeleton of an organic molecule), and π -bonds. If the electrons did not interact, the electronic energy would be the sum of the pair-bond energies. Now non-bonding orbitals are concentrated around nuclear centres, and there will be little interaction (or overlap)

between them. Similarly for the σ -bonds: they are concentrated, and therefore interact but little. π -bonds, in contrast, are diffuse, and interactions between adjacent π -bonds are strong. Obviously, molecules in which π -bonds are close together will deviate further from the sum-energy than molecules in which they are further apart, because the π -orbital electrons will interact more strongly, and should be treated as a separate electronic system. Hence the centrality of π -bond interactions to the standard story of the (in)famous resonance energy of benzene. Del Re's is a nice example because we can see that knowing how the equations fit on to the structure of a known target system (and also how they falsify it) is key information when new models for different—but related—cases are constructed. We can also see how an idealised model can help us to understand the differences between related molecules (like benzene and 1,3 cyclohexadiene). Ogilvie singled out this type of explanation for special disapproval, but what is the alternative? Insoluble equations contribute little to understanding.

In conclusion, understanding the motivation of the equations that are the mathematical manifestation of idealised models is the key to seeing how they perform their main duties: the enjoyment of evidential support, and the provision of understanding. If, as I have argued, motivation is often local, then so too are confirmation and explanatory power. To echo a point once made by Hilary Putnam (1974, section 13), philosophical accounts of how theories are applied often mistake means for ends. Accurate models (or true initial conditions) are not sought as means to theoretical ends; rather, they are ends in themselves. Models have their own value, for they are the vehicle of whatever understanding we have of how the different parts of molecules work together to produce their complex behaviour.

REFERENCES

- Atkins, P.W. 1983 *Molecular Quantum Mechanics* Second Edition Oxford: Oxford University Press
- Bohr, N. 1918 'On the quantum theory of line spectra' Page references are to the reprint in B.L. van der Waerden (ed.) *Sources of Quantum Mechanics* Amsterdam: North-Holland, 1967, 95-137
- Cartwright, Nancy 1983 *How the Laws of Physics Lie* Oxford: Clarendon Press
- Claverie, P. and S. Diner 1980 'The concept of molecular structure in quantum theory: interpretation problems' *Israel Journal of Chemistry* 19, 54-81

- Del Re, G. 1974 'Current problems and perspectives in the MO-LCAO theory of molecules' in Per-Olov Löwdin (ed.) *Advances in Quantum Chemistry* 8 New York: Academic Press, 95-136
- Ehrenfest, Paul 1917 'Adiabatic invariants and the theory of quanta', *Philosophical Magazine* 33, 500-13. Page references are to the reprint in B.L. van der Waerden (ed.) *Sources of Quantum Mechanics* Amsterdam: North-Holland, 1967, 79-93
- Hempel, Carl 1966 *Philosophy of Natural Science* Englewood Cliffs: Prentice Hall
- Laymon, Ronald 1983 'Newton's demonstration of universal gravitation and philosophical theories of confirmation' in John Earman (ed.) *Minnesota Studies in the Philosophy of Science X* Minneapolis: University of Minnesota Press, 179-99
- Laymon, Ronald 1987 'Using Scott domains to explicate the notions of approximate and idealised data' *Philosophy of Science* 54, 194-221
- Laymon, R. 1989 'Cartwright and the lying laws of physics' *Journal of Philosophy* 86, 353-72
- Murdoch, Dugald 1987 *Niels Bohr's Philosophy of Physics* Cambridge: Cambridge University Press
- Ogilvie, J. 1990 'The nature of the chemical bond—1990' *Journal of Chemical Education* 67, 280-9
- Post, Heinz 1974 'Against ideologies', Inaugural Lecture, Chelsea College, University of London
- Primas, Hans 1975 'Pattern recognition in molecular quantum mechanics', *Theoretica Chimica Acta* 39, 127-48
- Primas, Hans 1983 *Chemistry, Quantum Mechanics and Reductionism*, Second Edition Berlin: Springer-Verlag
- Putnam, Hilary 1974 'The "corroboration" of theories' in P.A. Schilpp (ed.) *The Philosophy of Karl Popper* Volume I La Salle, IL: Open Court, 221-40
- Ramsey, J. 1992. 'Towards an expanded epistemology for approximations' in D. Hull, M. Forbes and K. Okruhlik (eds.) *PSA 1992* Volume 1 East Lansing, MI: Philosophy of Science Association, 154-64

- Redhead, M.L.G. 1980 'Models in physics' *British Journal for the Philosophy of Science* 31, 145-63
- Scerri, Eric 1991 'The electronic configuration model, quantum mechanics and reduction' *British Journal for the Philosophy of Science* 42, 309-25
- Silverstein, R.M., Bassler, G.C., and Morrill, T.C. 1981 *Spectrometric Identification of Organic Compounds*, Fourth Edition New York: Wiley
- Steinfeld, J. 1985 *Molecules and Radiation*, Second Edition Cambridge, MA: M.I.T. Press
- Szabo, A. and N. Ostlund 1982 *Modern Quantum Chemistry* New York: Macmillan
- Weininger, Steven J. 1984 'The molecular structure conundrum: can classical chemistry be reduced to quantum chemistry' *Journal of Chemical Education* 61, 939-44
- Woolley, R.G. 1976 'Quantum theory and molecular structure' *Advances in Physics* 25, 27-52
- Woolley, R.G. 1977 'Must a molecule have a shape?' *Chemical Physics Letters* 55, 443-6
- Woolley, R.G. 1978 'Must a molecule have a shape?' *Journal of the American Chemical Society* 100, 1073-8
- Woolley, R.G. 1985 'The molecular structure conundrum' *Journal of Chemical Education* 62, 1082-4
- Woolley, R.G. 1991 'Quantum chemistry beyond the Born-Oppenheimer approximation' *Journal of Molecular Structure (Theochem)* 230, 17-46
- Woolley, R.G. and Brian Sutcliffe 1977 'Molecular structure and the Born-Oppenheimer approximation' *Chemical Physics Letters* 45, 393-8