

tural properties. For instance the extensions of “wood,” “wool,” and “silk” might be picked out by causal origin rather than microstructure, allowing for a microstructural duplicate of silk (artificial silk) that is not silk. This need not undermine microstructuralism about *chemical* substances, however, because usage and classificatory interests may well vary. To take a well-known example, the term “jade” applies to two microstructurally distinct substances, jadeite, and nephrite. But even if jewelers count both jadeite and nephrite as jade, chemists will attend to the difference between them.

Chemistry and physics

The central issue in discussing the relationship between chemistry and physics is *reduction*. Although chemistry is distinct from physics from the point of view of its practice and history, the relationship has often been viewed as the clearest example of a true interdisciplinary reduction. Ernest Nagel contended: “The reduction of various parts of chemistry to the quantum theory of atomic structure now seems to be making slow if steady headway” (1961: 365). Oppenheim and Putnam (1958: 417–18) fitted chemistry into the hierarchical structure of science just above atomic physics, and they interpreted the twentieth-century unification of chemical and physical theories of molecular reality accordingly as a micro-reduction. Now chemistry studies both macroscopic and microscopic kinds, so there are two layers to the reduction issue: between macroscopic substances and their characteristic microscopic species, and between chemical microspecies like molecules and their physical bases. One may also address these candidate reductions in quite different ways, emphasizing either *inter-theoretic* or *ontological* relationships. I address these in turn.

Intertheoretic reduction

Quantum chemistry is the interdisciplinary field that uses quantum mechanics to explain the structure and bonding of atoms and molecules. For any isolated atom or molecule, its non-relativistic Schrödinger equation is determined by enumerating the electrons and nuclei in the system, and the forces by which they interact. Of the 4 fundamental physical forces, 3 (gravitational, weak, and strong nuclear) can be neglected in calculating the quantum-mechanical states governing molecular structure. Intertheoretic reduction, then, requires a derivation of the properties of atoms and molecules from the quantum mechanics of systems of electrons and nuclei interacting via electrostatic forces, by solving relevant Schrödinger equations. There is an exact analytical solution to the non-relativistic Schrödinger equation for the hydrogen atom and other one-electron systems, but these cases are special owing to their simplicity and symmetry properties. Caution is required in drawing any consequences for how quantum mechanics applies to chemical systems more generally. The Schrödinger equation for the next simplest atom, helium, cannot be solved analytically, and to solve the Schrödinger equations for more complex atoms, or for any molecule, quantum chemists apply a battery of approximate methods and models which have become very accurate with the development of powerful digital computing.

Whether they address the electronic structure of atoms or the structure and bonding of molecules, many explanatory models are calibrated by an array of theoretical assumptions drawn from chemistry itself. Commentators therefore argue that explanations in quantum chemistry do not meet the strict demands of classical reduction, because the models of molecules they employ bear only a loose relationship to exact atomic and molecular Schrödinger equations (for references see the suggested readings). In the case of atomic calculations, quantum-mechanical calculations assign electrons to one-electron orbitals that, to a first approximation, ignore interactions between electrons. Scerri (2007: Chs 8 and 9) argues that although the orbitals are artefacts of an approximation scheme, they seem to play an important role in explaining the structure of atomic electron shells, and the order in which they are filled is determined by chemical information rather than fundamental theory. In the case of molecular calculations, the nuclei are constrained within empirically calibrated semi-classical structures, with the electrons moving in the resultant field. Only the electrons are assumed to move quantum-mechanically, and the molecular structure is *imposed* rather than explained.

Reductionists can make two responses here. The first is that the models are just ad hoc, but since these models provide much of the evidence for the explanatory success of quantum mechanics in chemistry, the response would seem to undermine the motivation for reductionism. The second response is that inexact models are common in computationally complex parts of physics, and do not signal any deep explanatory failure. There is something of worth in this response, but it requires that atomic and molecular models that are used in explanations are justifiable as approximations to solutions of exact Schrödinger equations, and stand in for them in explanations of molecular properties (hence call this the “proxy defense” of inexact models). This is a more stringent condition than it may sound, requiring that the inexact models attribute no explanatorily relevant features to atoms or molecules that cannot be justified in the exact treatments. The Born–Oppenheimer, or “clamped nucleus,” approximation seems to offer a justification for the assumed semi-classical molecular structures because the masses of atomic nuclei are thousands of times greater than those of electrons, and so move much more slowly. Fixing the positions of the nuclei makes little difference to the calculated energy, so in calculating the electronic motions the nuclei may be considered to be approximately at rest.

However, chemical physicist R. G. Woolley argues that Born–Oppenheimer clamping of nuclei cannot be regarded as an approximation to exact quantum mechanics in this way. One problem concerns isomerism. As noted previously, ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and dimethyl ether (CH_3OCH_3) are different compounds with distinct molecular structures, but contain the same nuclei and electrons. If the Schrödinger equation is determined only by the nuclei and electrons present, then the alcohol and the ether share the same Schrödinger equation, and it is difficult to see how their structures could be recovered from it (see Woolley 1998). Symmetry properties pose a deeper problem. Arbitrary solutions to exact Coulombic Schrödinger equations should be spherically symmetrical, but the Born–Oppenheimer models simply replace this higher symmetry with structures of lower symmetry (see Woolley and Sutcliffe

2005). Therefore the Born–Oppenheimer clamping of nuclei cannot be regarded as an approximation, because although it makes only a small difference to the calculated energy of a molecule, it makes a big difference to its symmetry properties.

To give an example, chirality is a form of molecular asymmetry in which, for instance, a carbon atom is bonded to four different groups of atoms arranged at the corners of a tetrahedron, and is not superimposable on its mirror image. Hence chirality gives rise to a form of isomerism (the different forms are called “enantiomers”), and it has been known since the nineteenth century that in some cases the two enantiomers will rotate plane-polarized light in opposite directions, but by the same angle. Within the Born–Oppenheimer approximation, in which nuclear positions are fixed, it is possible to calculate the observed optical rotation angles. Exact solutions to the isolated molecule Hamiltonian, in contrast, ought to yield an optical rotation angle of zero. The symmetry problem is not specific to optical activity: asymmetries in molecular structures are essential to all kinds of explanation at the molecular level. Hence the “proxy defense” of the Born–Oppenheimer models seems to fail, because they do seem to attribute explanatorily relevant features to molecules that cannot be justified by exact quantum mechanics.

It is worth emphasizing that Woolley’s symmetry problem has nothing to do with either the insolubility of Schrödinger equations for molecules or the computational complexity of numerical methods for solving them. The problem is not that molecular structure is difficult to recover from the exact quantum mechanics, but that it is not there to begin with. It arises from the mathematical properties of electrostatic Schrödinger equations for isolated molecules, suggesting that molecular structure might ultimately be explained through (i) non-electrostatic forces or (ii) a molecule’s interactions with its environment. On the latter option, molecular structure would turn out to be an oddly relational feature of molecules. In advance of further investigation of those options, however, molecular structure seems to be an unexplained explainer in quantum chemistry.

Ontological reducibility

The confidence of classical reductionists like Nagel, Oppenheim, and Putnam was far from naive. They were aware that massive computational complexity blocked simple deductive relationships between physical and chemical theories. They were aware also that the explanatory relationship between chemistry and physics is a function of the available theories (see for instance Nagel 1961: 365). Even if reduction fails at one point in the development of science, the situation may well change, either because physics provides new theories that are more successful in this respect or because chemistry eliminates the explanatory concepts that resisted reduction, providing alternative explanations for the phenomena those concepts were used to explain. One can, however, distinguish two broad kinds of reason why chemistry might be *permanently* irreducible to physics.

The first kind of reason arises from the ways in which chemists and physicists represent, or think about, their subject matters. There might, for instance, be concepts or explanatory practices that do not fit on to or match those of physics,

yet are ineliminable from chemistry, for instance because they are constitutive of ways of thinking that characterize the science. By analogy with Davidson's account of the mental, this invites a *non-realist* interpretation of the non-reducible chemical concepts, although it is a further question whether there is one *global* ontology, and whether it is physical. According to Primas (1983: Ch. 5), molecular structure is something that chemistry reads into the surface patterns of a fundamentally quantum-mechanical world. On the other hand van Brakel is ontologically pluralistic (2000: Ch. 8), seeing physics and chemistry as only two among many different levels of discourse, none of which is ontologically privileged.

The second kind of reason for the irreducibility of the chemical is more congenial to scientific realism, and concerns the ontological relationship between the subject matters of the two sciences, that is, their entities, properties, and laws. Assuming a clear distinction between a theory and its subject matter, one might describe the issue as follows: whether or not the chemically important properties of molecules are deducible from current or future physical theory, is chemistry's subject matter *nothing but* that of physics? *A's being nothing but B* is here understood to be an ontological relationship, quite distinct from any explanatory relationships that might exist between theories about *A* and *B*. Let us pursue the issue of ontological reducibility directly.

Chemical entities like molecules and substances are clearly composed of more basic physical entities. If the microstructural account of chemical kinds is broadly correct, chemical-kind membership must also supervene on micro-physical properties: there can be no change in chemical-kind membership without micro-physical change. Neither composition nor supervenience amounts to reducibility, however. Composition establishes only a weak ontological dependence that is compatible with non-reducibility. Supervenience is not an ontological relationship, being just modally robust property co-variance, and is also compatible with both reducibility and emergence (see, e.g., Kim 1998: Ch. 1). Robin Le Poidevin (2005) distinguishes intertheoretic (or as he calls it, "epistemological") reduction from ontological reducibility, arguing, rightly, that the unfeasibility of intertheoretic reduction does not settle the issue of ontological reducibility. He attempts to identify just what could count as an argument for ontological reducibility of the chemical to the physical: chemical properties, he argues, are more than merely correlated with microphysical properties; they are *exhausted* by them. All *possible* instances of chemical properties are constituted by combinations of discretely varying physical properties. It is just not possible that there is an element between (say) helium and lithium. There are two lines of objection to an argument of the kind Le Poidevin envisages (see Hendry and Needham 2007). Firstly, it applies only to properties that vary discretely, like the elements. The elements do not exhaust the whole of chemistry, however, because as we have seen, isomers are distinct substances that are identical in respect of their elemental composition, yet differ in respect of their molecular structure. Furthermore molecular structure is not discrete but defined in terms of continuously varying quantities like bond lengths and bond angles. Secondly, it is not clear just why the exhaustion of chemical properties by combinations of physical properties would establish the ontological reducibility of

the chemical. Here's why not. In recent philosophy of mind, ontological reducibility has been understood in terms of causal powers: *A* is ontologically reducible to *B* just in case the causal powers conferred by possession of *A*-properties are exhausted by those conferred by possession of *B*-properties (see Kim 1998: Ch. 4). On this formulation neither Le Poidevin's combinatorial determination nor micro-structuralist supervenience is sufficient for ontological reduction, for the *A*-properties may confer *additional* causal powers. If, for each cluster of *B*-properties corresponding to an *A*-property, there is a *sui generis* law of nature conferring distinct causal powers that are not conferred by more fundamental laws governing the *B*-properties, then the *A*-properties are irreducible to the *B*-properties in a robustly ontological sense.

Is this more than a mere logical possibility? The symmetry problem discussed earlier would seem to indicate that it is. For over a century, chemical explanations of the causal powers of molecules, and of the substances they compose, have appealed to molecular structures attributed on the basis of chemical and physical evidence. Yet the existence of such structures does not seem to have an explanation in exact quantum mechanics. To be an ontological reductionist is to think that molecular structures are determined by more fundamental laws, and that the required explanation must in some sense exist, even if it is unfinished business for physics. The *emergentist* interpretation of the situation is that for each molecular structure there is a *sui generis* law of nature that can be expressed in the language of quantum mechanics, but is an instance of no deeper physical law. The issue of ontological reduction is not settled by the existence of quantum-mechanical explanations of molecular structure and bonding. Both reductionism and emergence are compatible with there being such explanations, differing over their structure and the degree to which the laws that appear in them are unified. To address the issue of the ontological reduction of chemistry is to assess the relative plausibility of those two interpretations (see McLaughlin 1992 and Hendry 2008: Chs 9 and 10 for differing views).

Apart from physics itself, chemistry is unique in the way that detailed applications of fundamental physical theories have deepened and extended its explanations. This is significant beyond the philosophy of chemistry: in philosophy of mind, arguments for the causal exclusion of the mental assume that there is evidence from science itself that the physical is causally closed, yet only rarely is the science considered in any detail. Quantum chemistry is a unique source of such evidence.

Although it is a central issue, reduction is not the only foundational problem involved in quantum chemistry. Nineteenth-century chemists attributed detailed structures to organic molecules on chemical evidence alone, decades before there was any detailed interaction with physics. Many such structures continue to play important explanatory roles in modern chemistry: with its allied notion of the chemical bond, molecular structure seems here to stay in modern science. Yet as we have seen, it is far from clear how either molecular structure or the chemical bond are realized in quantum-mechanical states.

See also Essentialism and natural kinds; Explanation; Laws of nature; Models; Philosophy of language; Physics; Reduction.

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Further reading

Two journals are devoted to the philosophy of chemistry, *Foundations of Chemistry* and *Hyle*. Two recent collections of articles covering a range of issues in the philosophy of chemistry are: N. Bhushan and S. Rosenfeld (eds) *Of Minds and Molecules: New Philosophical Perspectives on Chemistry* (Oxford: Oxford University Press, 2000) and D. Baird, E. Scerri, and L. McIntyre (eds) *Philosophy of Chemistry: Synthesis of a New Discipline* (Dordrecht: Springer, 2006). For the historical background to the identification of the elements in terms of nuclear charge, see Helge Kragh, "Conceptual Changes in Chemistry: The Notion of a Chemical Element, ca. 1900–1925," *Studies in History and Philosophy of Modern Physics* 31B (2000): 435–50. On the question of whether it was discovered that water is H₂O, see Joseph LaPorte, *Natural Kinds and Conceptual Change* (Cambridge: Cambridge University Press, 2004) and Paul Needham, "The Discovery that Water Is H₂O," *International Studies in the Philosophy of Science* 16 (2002): 205–26. On reductionism and models see: Paul Bogaard "The Limitations of Physics as a Chemical Reducing Agent," in *PSA 1978* (East Lansing, MI: Philosophy of Science Association, 1981), Volume 2, pp. 345–56; Mario Bunge "Is Chemistry a Branch of Physics?" *Zeitschrift für Allgemeine Wissenschaftstheorie* 13 (1982): 209–23; and James Hofmann "How the Models of Chemistry Vie," in *PSA 1990* (East Lansing, MI: Philosophy of Science Association, 1990), Volume 1, pp. 405–19. On the status of molecular structure in quantum mechanics, see Jeffry Ramsey, "Realism, Essentialism and Intrinsic Properties: The Case of Molecular Shape," in Bhushan and Rosenfeld (eds) *Of Minds and Molecules*, pp. 118–28.

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