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1. Introduction

In order to discuss the question of the reduction of chemistry it will be necessary to begin with a brief review of what philosophers mean by reduction in science. I follow most authors on this subject by starting with the writings of Nagel (Nagel 1961). As is well known, Nagel stipulates that two formal conditions, namely connectability and derivability should be fulfilled in order to say that reduction of theory T_2 to theory T_1 has occurred. In addition he stipulates a non formal condition, that the primary or reducing science should be supported by experimental evidence.

Furthermore Nagel considers that reductions occur in two main varieties which he calls homogeneous and heterogeneous respectively. In homogeneous reduction the terms used by the reducing theory are also common to the theory to be reduced. For example Galileo's science of freely falling bodies was conceived of as separate from the mechanics of celestial bodies. Nagel claims that Newton's theory of mechanics absorbed or reduced both of these theories. The reduction in question is considered to be homogeneous since no new concepts are needed to describe motion in the Newtonian theory than were used in the older forms of mechanics. In heterogeneous reduction the distinctive traits of some subject matter are assimilated into those of a set of quite different traits. Nagel sees this type of reduction as problematical and worthy of further analysis unlike homogeneous reduction.

We may note in passing that the question of the reduction of chemistry would presumably fall into the heterogeneous category according to Nagel's scheme since, as many authors have pointed out, some typically chemical terms cannot be found in quantum mechanical language. For example Primas has written,

Many calculations have been extremely sophisticated, designed by some of the foremost researchers in this field to extract a maximum of insight from quantum theory. For simple molecules, outstanding agreement between calculated and measured data has been obtained. Yet, the concept of a chemical bond could not be found anywhere in these calculations. We can calculate bonding energies without ever knowing what a bond is! (Primas, 1983, 5)

A number of criticisms of Nagel have appeared, which aim to sharpen the criteria for reduction. Some of these have been described as falling under the label of indirect reduction. For example Kemeny & Oppenheim claim that T_2 is not obtained in terms of T_1 as in Nagel's form of reduction. Instead one obtains identical observable evidence from T_2 and T_1 although T_1 can may predict more. (Kemeny & Oppenheim 1956)

Other authors deny that reduction of theories takes place at all. Popper would presumably argue that if a theory is refuted it can hardly be said to correspond to, or be derived from the reducing theory. In Popper's own words,

Newton's theory unifies Galileo's and Kepler's. But far from being a mere conjunction of these two theories...it corrects them while explaining them. The original explanatory task was the deduction of the earlier results. It is solved not by deducing them but by deducing something better in their place. (Popper 1957, 33)

Then there are the radical critics of reduction. The early Kuhn holds that two competing theories cannot be compared because the terms used in each theory are incommensurable (Kuhn 1962). Also, for Kuhn all significant reductions are replacement reductions, where the reduced theory is replaced by the theory to which it reduces and not retained as a correct theory.

Meanwhile, in characteristic fashion, Feyerabend attacks both of Nagel's formal conditions for reduction (Feyerabend 1962). For example, Nagel considers that Galileo's laws of mechanics are reduced to Newton's laws in the sense that both conditions (connectability and derivability) are fulfilled.

With regards to connectability, Feyerabend claims that this feature often does not exist between successive theories. For example, in classical mechanics length is a relation that is independent of signal velocity, gravitational fields and motion of the observer. This meaning of length differs from the meaning of length in relativity theory in which it is dependent on all three of the above factors. Classical and relativistic length he says are incommensurable concepts. On the question of derivability, Feyerabend points out that in Galileo's laws of mechanics the acceleration of a freely falling body is constant whereas in Newton's mechanics, acceleration increases with decreasing distance from the earth. The two systems of mechanics are thus incompatible according to Feyerabend. His conclusion is that either (i) approximate reduction is possible but we must forego derivability as a condition for reduction, or (ii) reduction fails. Feyerabend eventually decides on the second option whereby reduction fails altogether.

The early Putnam has criticized Feyerabend on the question of derivability claiming that Nagel's requirement can be maintained provided that we accept approximations.

It is perfectly clear what it means to say that a theory is approximately true, as it is clear what it means to say that an equation is approximately correct: it means that the relationships postulated by the theory hold not exactly, but with a certain specifiable degree of error. (Putnam 1965, 206-207)

I believe that Putnam's statement can be used to give a working definition of what constitutes approximate reduction and I will return to this statement in a later part of this article.

For the intervening sections however I wish to adopt an approach which I will call pragmatic reduction. I will attempt to examine the extent to which chemistry has

been reduced in the terms used by physicists and chemists themselves. The most overt attempts at reduction in chemistry have been made through the use of Schrödinger's time independent equation. In the purest or *ab initio* approach the aim is to calculate the properties of atoms and molecules entirely from first principles, without recourse to any experimental input whatsoever.¹ Another part of current theoretical chemistry is concerned with semi-empirical approaches in which some experimental data is introduced into calculations. However the present survey will not consider such semi-empirical work.

The following two quotations may serve to give the essence of the *ab initio* approach. Firstly there is a little known remark made by Langmuir in the course of a popular lecture in 1921, before the advent of quantum mechanics.

These things mark the beginning, I believe, of a new chemistry, a deductive chemistry, one in which we can reason out chemical relationships without falling back on chemical intuition....I think that within a few years we will be able to deduce 90 percent of everything that is in every textbook on chemistry, deduce it as you need it, from simple ordinary principles, knowing definite facts in regard to the structure of the atoms. (Langmuir 1921)

Secondly, the much quoted passage from one of the founders of quantum mechanics, Dirac, who put the case for *ab initio* calculations somewhat optimistically,

The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations which are too complicated to be soluble. (Dirac 1929)

2. Quantum Chemistry

The time-independent Schrödinger equation may be expressed in its most compact form as,

$$H\psi = E\psi$$

where H is the Hamiltonian operator concerning the kinetic and potential energy of the system, ψ is the wavefunction, which is a function of the coordinates of all the particles in the system and E is the observable energy of the system.

For a hydrogenic atom, that is a one-electron system such as the hydrogen atom, the He^{+1} ion or the Li^{+2} ion, the equation takes the form,

$$(-\hbar^2/2\mu\nabla^2 - Ze^2/r)\psi = E\psi$$

where \hbar is Planck's constant divided by 2π and μ is the reduced mass of system. In the case of the hydrogen atom $\mu = m_n \cdot m_e / m_n + m_e$, ∇^2 or $(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)$ is the operator for the kinetic energy, Z is the nuclear charge, e the electronic charge and r the distance between the nucleus and the electron.

The solution to this one-electron equation is exact and characterized by three integers n , ℓ and m , the quantum numbers (Pauling, Wilson 1935).

$$\Psi_{n,\ell,m}(r,\theta,\varphi) = R_{n,\ell}(r) \cdot \Theta_{\ell,m}(\theta) \cdot \Phi_m(\varphi)$$

The ground state wavefunction, that is the solution corresponding to $n = 1$, $\ell = 0$ and $m = 0$, is found to be,

$$\psi_1 = 1/\pi^{1/2} (Z/a_0)^{3/2} e^{-\rho/2}, \text{ where } \rho = (2Z/na_0)r, \text{ and } a_0 = h^2/4\pi^2\mu e^2.$$

Another solution includes the case where $n = 2$, $\ell = 1$, $m = -1$,

$$\psi_{2p(-1)} = 1/4(2\pi)^{1/2} (Z/a_0)^{5/2} r e^{-Zr/2a_0} \sin\theta e^{-i\phi}$$

These so called ‘orbitals’ are related to electron clouds encountered in elementary chemistry courses. The energies permitted for a hydrogenic atom are found to be,

$$E = -\mu Z^2 e^4 / 2\hbar^2 n^2 = -Z^2/n^2. W_H$$

where W_H is the energy for the ground state of the hydrogen atom or 13.60 eV.

The time-independent Schrödinger equation for atomic, ionic or molecular systems containing two or more electrons does not yield exact solutions and approximation methods must be employed. To consider the simplest such atomic case, the helium atom, the time-independent Schrödinger equation for the system is,

$$(-\hbar^2/2m_e \nabla_1^2 - \hbar^2/2m_e \nabla_2^2 - Ze^2/r_1 - Ze^2/r_2 + e^2/r_{12}) \psi = E \psi$$

This differential equation cannot be solved by the method of separation of variables because of the presence of the term e^2/r_{12} which represents the inter-electronic distance. A good approximation method consists in the variation approach in which a trial function ϕ is chosen which contains variable parameters. It can be shown that the energy corresponding to this trial function E , is larger or equal to the exact ground state energy for the system E_0 (Pauling, Wilson, 1935).

$$E = \int \phi * H \phi \, d\tau \geq E_0$$

where H represents the true Hamiltonian for the system.

For example, an approximate wavefunction for the helium atom can be taken to be,

$$\phi = \phi_1 \phi_2 = (Z'^3/\pi) e^{-Z'r_1} e^{-Z'r_2}$$

that is the product of two one-electron functions, each containing a variable parameter Z' . Evaluation of these integrals and minimization with respect to Z' gives the energy for the ground state of the helium atom as -77.45 e.V. This result represents an error of approximately 2%.

Perhaps the most commonly used approximation in quantum chemistry is the Hartree-Fock method in which the wavefunction consists of an anti-symmetric product of one-electron functions, to take account of the permutation of electrons as dictated by the Pauli exclusion principle. It is assumed that each electron moves in the average field due to the nucleus and all the other electrons in the system. For the helium atom the required wavefunction takes the form of the determinant of a 2 x 2 matrix,

$$\psi = 1s(1)\alpha(1)1s(2)\beta(2) - 1s(2)\alpha(2)1s(1)\beta(1)$$

The so called Hartree-Fock equations represent a pseudo-eigenvalue problem which requires an iterative approach and for which the use of computers is ideally suited. The total energy of the helium atom calculated in this way shows an error of approximately 1.5% as compared with the experimental value.

The atomic energies calculated by the Hartree-Fock method typically show errors of approximately 1% when compared with experimental atomic energies. Such relative errors of 1% may not appear to be very significant, but since the energy of a typical atom in its ground state is about 1000 e.V., the absolute error represents about 10 e.V. This is of the same order of magnitude as a typical chemical bond. The Hartree-Fock method can therefore fail to predict chemical bonding and it becomes necessary to resort to more accurate methods of approximation in order to obtain chemically meaningful predictions. Nevertheless, the Hartree-Fock wavefunction serves as a point of departure in more elaborate approximation methods.

In the so called Configuration Interaction method more than a single determinant is used to represent the wavefunction of the system. The wavefunction for the helium atom, for example, is now represented by a linear combination of determinants,

$$\psi = c_1 D_1 + c_2 D_2 + \dots$$

and the computational procedure consists in minimising the energy by variation of the mixing coefficients or c_i 's. The additional determinants are formally excited states of the helium atom. Whereas in the helium atom the ground state configuration is $1s^2$, two excited configurations might be $1s^1 2s^1$ and $1s^1 2p^1$.

Other methods which go beyond the Hartree-Fock level of approximation include Cluster Methods and Many-Body Perturbation Theory (Wilson 1984). These approaches involve the introduction of repulsion effects due to simultaneous interactions between three, four, and even more electrons in the expansion of the wavefunction. One important drawback of cluster methods and many-body perturbation theory is that they are not variational. That is to say, the calculated energies no longer represent upper bounds and it is possible to obtain predictions in excess of 100% of the experimental values. Nevertheless, their use is capable of reducing the error in the calculation of the energy of the helium atom to something of the order of 10^{-3} %.

We might just pause at this point in order to take stock of the progress made in the light of the original question as to how successfully chemistry has been reduced to quantum mechanics. It has to be said that the calculation of the ground-state energy of an atom carried out completely from first principles and to an accuracy of 10^{-3} % does seem to provide an argument in favour of the reduction of atomic chemistry, at least with regards to the reduction of a physically measurable quantity. However, I believe that it is necessary to adopt a more critical attitude to such claims especially in view of the computational approaches which are used and which are examined further in the following section.

3. Convergence and Error Bounds

Provided that increasingly larger linear combinations of atomic orbitals are taken, the experimental energy of the atom may be approached ever more closely. This is not surprising due to completeness property of series expansions (Pauling, Wilson 1935). Authors in modern theoretical chemistry often make a virtue of being able to guess the correct procedure by a mixture of intuition and past experience. The usual means of proceeding with a calculation appear to be somewhat ad hoc in this sense.

The common approach used in all these approximations is one of expansion of the wavefunction for the system as an infinite series of one-electron functions. In using such a procedure it is essential that the series used in the expansion should converge to the function which it is meant to represent. It is often assumed that with a sufficiently flexible trial function the results will eventually converge to the exact solution. Otherwise convergence is checked, up to a point, by examining the results of successive approximations.

However, there is no guarantee that, although the experimental value is being approached, the next level of accuracy might not show a sudden divergence. Such occurrences are not unknown in mathematical physics. Ideally, a general proof of convergence is required, which is independent of the data arising from any particular approximation in any particular case. The present lack of such convergence proofs in quantum chemistry must be recognized to mar any claim in favour of strict reduction.

From a pragmatic point of view however, it must be admitted that the convergence problem is no longer so pressing, since most modern computer packages such as the Gaussian series contain built-in convergence checking procedures.

The second problem which I wish to point out is more serious. Although a variational calculation gives an upper bound to the exact solution it does not tell us how close we are to the true value. As is well known, error limits are demanded of experimental results as a matter of course. As Weinhold writes, perhaps one should also ask for a corresponding standard of reliability from the theoretical side (Weinhold, 1972).

A general method of improving the situation would consist in finding a way to calculate both upper and lower bounds to the energy of any particular system under consideration. If this form of 'bracketing' were possible, it would endow quantum mechanics with a genuine power of prediction. The problem has been that whereas variation methods provide an upper bound to the energy as can readily be proved, sufficiently general and tractable method for determining lower bounds in cases applicable to atomic systems are not available. To sum up, what is needed in theoretical chemistry, is an independent non-empirical method of assessing the accuracy of the calculations².

4. The case of the CH₂ molecule

Although the early predictions made in quantum chemistry were generally unreliable, it has been forcefully argued that since 1970 quantum chemistry has "come of age" (Goddard, 1985). This arose from theoretical predictions on the geometry of the methylene molecule CH₂. This short lived and highly reactive molecule is unusual in having two unpaired electrons around the carbon atom as compared with the better known methane molecule in which all four of the outer electrons are said to be shared with electrons from four hydrogen atoms.

Various calculations carried out for methylene suggested that the molecule should be bent³. The molecule was first observed spectroscopically by Hertzberg who contrary to the theoretical predictions found it to have a linear shape. A more accurate treatment the following year by Bender and Schaefer put the angle in methylene at 135.1° (Bender, Schaefer, 1970). Three new experiments by independent groups finally confirmed (pace Popper) a bent geometry in methylene.

In 1971 Hertzberg re-examined his data and was forced to concede that he had previously been wrong and that his own experiment was also in keeping with a bent geometry. This change of mind on the part of Hertzberg has been frequently been ex-

ploited by Schaefer, who concludes that his own work represented a successful challenge against the findings of the world's leading spectroscopist.

I now turn to the claimed landmark paper of Bender and Schaefer. Firstly, to take up a general objection which was raised earlier, Bender and Schaefer do not produce any proof of convergence but merely examine convergence up to a certain point. In fact the authors applied computational methods developed earlier by Bender and Davidson but a key passage in this earlier paper betrays a rather serious drawback;

The main difficulty in the selection of configurations...was of course the enormous number of possible configurations. In a typical calculation there are billions of configurations which can be formed with the correct symmetry. For an unfortunate choice...all of these might be equally important, but for a good initial guess only a few will really contribute to the wavefunction. (Bender, Davidson 1966, 2676).

Any procedure which relies on initial guesses must surely be judged to be essentially ad hoc and this raises doubts as to the extent to which chemical phenomena are being reduced in such supposedly ab initio calculations. Schaefer and co-workers also claim in a later paper that they set out to attempt to place error bars on the theoretical prediction of the bond angle. (McLaughlin, Bender, Schaefer, 1972). By employing an even larger basis set than the previous calculation, the authors estimate a bond angle of $134 \pm 2^\circ$. However, a detailed examination of the original source reveals a somewhat different picture for this claimed determination of error bars. To quote the authors:

To aid our evaluation of the expected reliability of this 134° CH_2 angle, we point to the comparable first order calculations on the ground and excited states of NH_2 , which yielded bond angles differing by 0.6 and 0.7 degrees from experiment values. In the light of these results and the H_2O results discussed above we estimate our theoretical bond angle of 134° is accurate to within 2° . (McLaughlin et al. 1972, 356-7)

Clearly, this approach represents an extrapolation from the application of the method from one molecule to that of another, and not a rigorous determination of error bars for the CH_2 molecule itself. In fact these calculations on CH_2 represent a perfect example of what Davidson has described as calibrated ab initio, as opposed to true ab initio work (Davidson 1984, 8-9)

5. The Si_2C story

In 1964 the molecule of Si_2C was first observed by infra-red spectroscopy (Veltner, McLeod, 1964). About twenty years later the fundamental Si-C symmetric stretching frequency was identified at 658 cm^{-1} (Kafafi et al. 1983). Shortly afterwards the molecule was studied theoretically and a value of 823 cm^{-1} was obtained for the symmetric stretching frequency (25% error). The authors did not however presume to challenge the assignment of the 658 cm^{-1} line (Grev, Schaefer 1985).

More recently another experimental group has identified the symmetric Si-C stretching mode with a new line at 840 cm^{-1} contrary to the earlier experiments (Presilla-Marquez, Graham 1991). In 1992 Schaefer and colleagues returned to the calculation to determine which line, the one at 658 cm^{-1} or at 840 cm^{-1} , is the true symmetric stretching mode. This provides an example of a state-of-the-art quantum chemistry calculation by one of the leading practitioners. The results obtained using various levels of approximation are tabulated below;

	$[\omega_1 - \nu_1/\nu_1] \times 100$.	$[\omega_3 - \nu_3/\nu_3] \times 100$	Energy (eV)
TZ+ 2P SCF	1.4 %	17.9 %	- 615.64079
TZ + 2P CISD	2.4 %	9.2 %	
TZ + 2P CCSD	0.9 %	5.2 %	
TZ + 2P CCSD (T)	-2.6 %	1.2 %	
TZ + 2P + f SCF	-4.3 %	21.3 %	- 615.64462
TZ + 2P + f CISD	5.2 %	9.4 %	
EXT + 2P SCF	1.0 %	17.9 %	- 615.65611
EXT + 2P + f SCF	-2.9 %	20.4 %	- 615.65925

Table 1. Percentage errors in the calculation of the spectroscopic mode in question ω_1 as well as another fundamental mode ω_3 .

TZ...	Triple Zeta.
2P...	Double Polarization.
SCF....	Self Consistent Field.
CISD...	Configuration Interaction. Single and Double Excitation.
CCSD...	Coupled Cluster. Single and Double Excitation.
(T)...	Triple Excitations included perturbatively.
+ f...	Also includes f functions on Si and C atoms.
EXT....	Extended Basis Set.

Several features of these results are significant.

- (i) The addition of f orbitals on the silicon and carbon atoms, which usually improves agreement with experiment in these types of calculations, produces a worsening in the frequency error in three separate methods (SCF, CI and EXT SCF), although the energy shows improvement.
- (ii) None of the above methods emerges as the clear winner in calculating fundamental modes from first principles. The outcome seems to depend on which particular mode is being considered.
- (iii) Overall, the error in ω_1 strays considerably from one method to the next and even on going to more extended sets within the same method.

None of this suggests that we have a reliable method which can be applied systematically to a new molecule and finally, no error bars are computed in order to lend reliability to the calculated values. However, there is worse to come! A week or so after the Schaefer and Grev paper was published, Handy, another leading quantum chemist, presented some new results on the same molecule⁴. This author used an alternative approach called the density functional method which does not depend on solving the Schrödinger equation directly and which is becoming increasingly common in theoretical chemistry (Parr, Yang 1989). Handy announced the following results on the Si₂C molecule.

- (i) At low levels of approximation the results are consistent with those of Schaefer and Grev above.
- (ii) A more extended calculation causes the computed value of ω_1 to change to a lower value.

- (iii) On addition of f functions to the Si and C basis sets, the value of ω_1 goes to 620 cm^{-1} , i.e., close to the discredited observation of 658 cm^{-1} !

This represents a flat contradiction of Schaefer and Grev results, all of whose methods attribute ω_1 to around 840 cm^{-1} . Once again this raises the question of which of the two observed lines should be assigned to the symmetric stretching mode. It should be recalled that this was precisely the question which had motivated the work of Schaefer and Grev. In more general terms, these findings on Si_2C do not say much for the reliability of current quantum chemistry, the claim that “quantum chemistry has come of age” or indeed the claim that chemistry has been reduced to quantum mechanics.

6. Conclusion

To return to the introduction, it will be recalled that the hope of any strict or exact reduction in the special sciences seems to have been abandoned and that all that remains is the possibility of approximate reduction. However, criteria for approximate reduction have not been put forward and the notion remains vague. The proposal here is that we should make use of an early Putnamian characterization of approximation in the context of theories. That is to say, an approximation is such that the relationships postulated by the theory hold not exactly, but with a certain specifiable degree of error.

As I have argued, errors are seldom computed by independent *ab initio* criteria in any of the calculations in theoretical chemistry which I discuss. Only the Self-Consistent Field calculations provide an upper bound whereas Many-Body Perturbation Theory and Coupled Cluster methods do not. More importantly perhaps, none of these methods computes a lower bound. As was remarked earlier the calculation of the ground state energies of atoms has been achieved to a remarkable degree of accuracy and similarly calculations on small or even medium sized molecules have given encouraging results. However, whether one can draw the conclusion that chemistry has been reduced rather depends on one's criteria of reduction. If we are to define approximate reduction as has been suggested in this paper then it must be concluded that *chemistry is not even approximately reduced to quantum mechanics*. The point I wish to emphasize is that we should not be misled by the apparent quantitative successes achieved and should appreciate the full nature of the approximation procedures employed.

Notes

¹It should be mentioned that in the *ab initio* approach the values of experimentally determined fundamental constants such as Planck's constant, the velocity of light and the electronic charge are introduced. However, no experimental information on the particular system under investigation is permitted.

²Ramsey has made a similar plea in discussing approximations in general (Ramsey, PSA, 1990). I believe that the calculation of upper and lower bounds would provide the criteria which Ramsey seeks.

³For a detailed account of all the calculations on the methylene molecule as well as experimental results see Scerri, E.R., 1993, in 'Correspondence, Heuristics and Invariance, Essays in honour of Heinz Post', pp 45-61, eds, S. French, H. Kamminga, Boston Studies in Philosophy of Science, 148, Kluwer, Dordrecht.

⁴Lecture delivered by N.C. Handy, 'New Applications of Quantum Chemistry', Royal Society of Chemistry Symposium, Cambridge, 3rd December, 1992.

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