**Electronic Structure: Valence Bond Theory, Molecular Orbital Theory and Hybrid Atomic Orbitals**

In Chapter 8, which was new to the second edition, we considered a selection of approximate models which included a brief discussion of how best to represent the benzene molecule and how to describe the bonding in methane. The point was made that approximate models are valuable in chemistry as simple heuristics and are used accordingly, albeit with due care and attention given to ensuring that any models employed are not applied outside of the domain in which they are applicable. In this Addendum, we will expand upon some of the discussion presented in Chapter 8 and consider in more detail, albeit at a very simple level, alternative models of electronic structure and the value of hybrid atomic orbitals based, in part, on some interesting recent discussions in the chemical literature.1

Chemistry is ultimately all about electrons and how electrons are arranged in molecules. When chemists wish to understand something about the arrangement of electrons in a molecule, the so-called electronic structure, they use the theory of quantum mechanics and specifically, the Schrödinger wave equation for that particular molecule. A solution to the Schrödinger equation provides information about the distribution of electrons throughout the molecule as well as the structure of lowest energy which can also afford an insight into how the molecule is likely to react with other molecules. At one level, this might be deemed to be sufficient but in reality, for all but the simplest of molecules (strictly, for anything other than one-electron systems), a number of approximations are required in order to solve the relevant Schrödinger equation, but even making these approximations, the solutions can be difficult and time-consuming to determine. We will not be concerned here with the various approximations (of which there are many) made in the computational processes used to solve the Schrödinger equation itself. Rather, we will consider the more general approximations that are employed to try and visualise the results of these computations in ways that help us to gain the chemical insights we desire.

There are two main theories which have been used to understand and visualise the electronic structure of molecules, specifically the bonding interactions which hold the atoms together within a given molecule. These are Valence Bond (VB) theory and Molecular Orbital (MO) theory, both of which were first developed in the early 20th century.1 The history of the development of both VB and MO theory is a fascinating topic to which we cannot do justice here, but in brief and at a very basic level, VB theory generally treats molecules as if the bonding electron pairs are localised between pairs of atoms, forming so-called two-centre, two-electron (2c,2e) or electron-pair bonds as originally articulated by G N Lewis.2 In contrast, in MO theory the electrons are considered to be delocalised over many more atoms according to rules based on molecular symmetry. It is important to stress, however, that it is not a question of which of VB theory or MO theory is right or correct. Both, as they are commonly encountered, are approximations of the deeper quantum mechanics from which they are each derived, and both have value (and are therefore used) in different contexts. This is best illustrated with some simple examples.

Consider the molecule methane, CH4. As shown in Fig. 1(a), methane is tetrahedral. Moreover, it is a regular tetrahedron in which all the hydrogens and all the C–H bonds are equivalent. If we wish to consider the arrangement of electrons in methane, we must first take account of the single electron from each of the four hydrogen atoms and the four valence electrons from the carbon, together with the corresponding atomic orbitals: the 1s orbitals on the hydrogens and the 2s and three 2p orbitals on carbon, the so-called valence orbitals. We tend to ignore the pair of electrons in the 1s orbital on carbon since these are too low in energy to be involved in bonding.3



**Figure 1**. (a) Tetrahedral methane; (b) the 2s and the three orthogonal 2p orbitals of carbon; (c) a carbon atom with four tetrahedral sp3 hybrid orbitals; (d) an individual sp3 hybrid orbital; (e) a carbon sp3 hybrid orbital overlapping with a hydrogen 1s orbital.

One of the simplest ways to describe the bonding in methane is to assume that each C–H bond is a 2c,2e bond but if we consider the orbitals on carbon, we have one 2s and three 2p as shown in Fig. 1(b) and it is not immediately obvious how these can be arranged with each of the hydrogen 1s orbitals to give four equivalent C–H bonds in a tetrahedral structure. However, an important feature of the VB approximation is that it allows for a linear combination of all four carbon atomic orbitals (2s and three 2p) into a set of four equivalent sp3 hybrid atomic orbitals which point towards the vertices of a tetrahedron as shown in Fig. 1(c).4 An individual sp3 hybrid orbital is shown in Fig. 1(d) which reveals the smaller lobe not shown in Fig. 1(c), and Fig. 1(e) shows the overlap between a single carbon sp3 hybrid and a hydrogen 1s orbital to form a C–H bonding orbital.

The value of the hybrid orbital model in organic chemistry is further illustrated by the fact that the properties of C–H bonds, such as bond length and stretching frequency, are remarkably constant for those bonds in which the carbon is sp3 hybridised and measurably different from C–H bonds involving sp2 and sp hybridised carbon which are themselves distinct and with consistent properties for a given degree of hybridisation. Reference to the increasing electronegativity of sp*n* hybrids as the s character of the hybrid increases is made in the text (Ch 2, p 34) which accounts for the observed greater acidity of alkynyl C–H bonds compared with alkenyl or alkyl C–H bonds as a result of the greater stability of the conjugate base.

In addition to the obvious simplicity of the VB approach regarding methane in terms of localised 2c,2e bonds, this model offers other advantages. Consider, for example, the methane derivative iodomethane, CH3I, undergoing an SN2 substitution reaction in which the iodide is substituted for another group X. If we wish to represent this reaction using the curly arrow formalism (so often employed to rationalise organic reaction mechanisms and considered briefly in Chapter 8) as shown in Fig. 2(a), a localised bonding picture is particularly useful. Furthermore, the orbital into which the X– lone pair is donated is simply the vacant antibonding s\* C–I orbital [Fig. 2(b)] associated with the localised C–I s bonding orbital.5



**Figure 2**. (a) An SN2 reaction between an incoming X– group and CH3I leading to CH3X and I– using curly arrows to show the movement of electron pairs and with the important lone pairs shown on both X– and I–; (b) a representation of the antibonding s\* C–I orbital.

However, despite the simplicity of the VB approach involving localised bonds and hybrid atomic orbitals, not least in terms of the curly arrow formalism, there are other features of methane that are more easily rationalised using an MO-based explanation. Consider the photoelectron spectrum of methane, for example. In a photoelectron spectrum, UV radiation of known frequency and hence energy is used to eject (ionise) valence electrons from the molecule being studied.6 The kinetic energy of the ejected electrons is then measured and the difference between the energy of the UV radiation and the kinetic energy of the ejected electron is a direct measure of the binding or ionisation energy of the electron in the molecule. If we look at the photoelectron spectrum of methane, which provides us with a direct measure of the energies of the bonding electrons, we observe that there are two sets of bonding orbitals, one lower in energy than the other. This can be rationalised in a very straightforward manner using simple MO theory. A part of the MO energy level diagram for methane is illustrated in Fig. 3(a) which shows a single bonding orbital at lower energy and a triply degenerate set of bonding orbitals at higher energy.7 All four molecular orbitals are delocalised across all five atoms, but the average summed over all atoms is one bonding pair per C–H bond so the VB and MO descriptions are complementary in that sense. Importantly, however, it is not necessary in this simple MO analysis to invoke any hybridisation at the carbon atom as is evident from the cartoons of two of the molecular orbitals shown in Fig. 3(b).8



**Figure 3**. (a) Part of the molecular orbital energy level diagram for CH4 showing the four delocalised bonding orbitals and their associated electron pairs; (b) (i) a diagram of methane, (ii) the lower energy bonding orbital involving the carbon 2s orbital, and (iii) one of the triply degenerate higher energy bonding orbitals involving a carbon 2p orbital.

Cartoons of molecular orbitals, more specifically, bonding orbitals, are often drawn as illustrated in Fig. 3(b)(ii) and (iii) which emphasises the atomic orbitals from which the molecular orbitals are derived.9 We should recognise, however, that the images obtained from computation will generally show the overlap between orbitals, or those parts of orbitals, with the same phase. The two types of representation for the H–H bond in H2 in cartoon form are shown in Fig. 4(a) and, for our purposes, these should be considered equivalent in terms of what they represent. Another important point to appreciate in this context is that one should not necessarily expect to see images from an MO calculation that resemble hybrid orbitals since the simple hybrid orbital model outlined above derives more from the VB approximation rather than the MO method. An example of a calculated molecular orbital for methane is shown in Fig. 4(b).10



(a)



(b)

**Figure 4**. (a) Two different representations of the bonding orbital in H2 derived from the overlap of the two hydrogen 1s orbitals. The image on the left illustrates the atomic orbitals from which the molecular orbital can be considered to be derived while the right-hand image better represents the resulting overlap and electron density distribution between nuclei. At a cartoon level, these representations are often used interchangeably; (b) Calculated molecular orbitals for methane corresponding to the cartoon depictions shown in Fig. 3 (b) (ii) (left) and Fig. 3 (b) (iii) (right).

As a further example, consider benzene. Benzene (and arenes generally) are often represented as shown in Fig. 5(a) with localised C–C and C=C bonds since this makes the movement of electron pairs using curly arrows much easier to manage than if we were to use the image shown in Fig. 5(b). Thus, we can and do use the picture of benzene shown in Fig. 5(a) because it helps us to understand mechanistic pathways even though we know that this cyclohexatriene rendition of the structure with alternate single and double bonds is not a very satisfactory description of the electronic structure; if we want to better represent the delocalised electronic structure, Fig. 5(b) is a more suitable depiction. It is therefore all about what we are trying to explain; both pictures/representations are approximate, but both nevertheless have value. The former derives rather more from a VB approximation with localised bonds and sp2 hybridisation at each carbon whereas the latter better illustrates the delocalisation of the p system inherent in an MO treatment. What we should be careful not to do is mix up the different models. Fig. 5(a) is not a good representation of the delocalised electronic structure of benzene, but Fig. 5(b) is of little value when it comes to representing mechanisms such as electrophilic aromatic substitution, the first step of which is shown in Fig. 5(c) and discussed in Chapter 8.



**Figure 5**. Two different representations of benzene (a) and (b), and the first step of electrophilic aromatic substitution (c).

As a final example, the paramagnetic ground state of the O2 molecule with two unpaired electrons is often cited as a triumph of MO theory over VB theory since a simple MO energy level diagram provides a ready explanation for the observed paramagnetism in which two electrons are placed one in each of the p\* orbitals according to Hund’s Rule (Ch 1, p 13). A VB model with localised bonding, as shown in Fig. 6(a) in which each oxygen obeys the octet rule, offers no obvious clue as to why O2 should be paramagnetic but it should be recognised that a more nuanced VB treatment provides a perfectly adequate account for the paramagnetic ground state structure of O2 [see ref. 1(c)] and we must resist any conclusion that one theory is right and the other wrong. Indeed, it is sometimes the case that simple VB and MO descriptions are combined as in the example of ozone, O3. Thus, the s-bonding electrons and the lone pairs on each oxygen can be considered as localised assuming sp2 hybridisation at each oxygen [Fig. 6(b)] whereas the p-bonding involving the unhybridized p orbitals on each oxygen is usually described as delocalised based on a simple MO analysis as shown in Fig. 6(c). The classical VB representation of the p-bonding in O3 is in terms of the resonance structures shown in Fig. 6(d).



**Figure 6**. (a) A simple representation of O2; (b) a representation of O3 showing the s-bonds and the lone pairs on each oxygen; (c) a simple MO energy level diagram showing the delocalised p-bonding in O3; (d) VB-type resonance structures of O3 with formal charges shown.

In summary, VB theory and MO theory are both approximations. Neither should be considered as right or wrong but merely as more or less useful according to whatever we wish to explain especially in an educational context. Thus, VB-style localised bonds derived from hybrid atomic orbitals are sometimes better for understanding many aspects of structure and reactivity whereas MO theory is generally more informative with regard to electronic structure particularly where more extensive delocalisation is important.

We’ll finish with some aphorisms regarding approximate models, the first of which was noted in Chapter 8, which stress that it is usefulness which is important rather than whether or not they are correct.

* *Chemical bonding models are not right or wrong, they are more or less useful*, Frenking, Schwerdtfeger and co-workers. *Chemical Bonding and Bonding Models in Main-Group Chemistry*. L. Zhao, S. Pan, N. Holzmann, P. Schwerdtfeger and G. Frenking, *Chem. Rev*., 2019, **119**, 8781-8845.
* *All models are wrong but some are useful*. This aphorism is generally attributed to the statistician, George Box (1979).
* *The only criterion of a model is usefulness, not its “truth”*, Michael Dewar. *Chemical Implications of s Conjugation*. M. J. S. Dewar, *J. Am. Chem. Soc*., 1984, **106**, 669-682.

***References***

1. (a) *A Conversation on VB vs MO Theory: A Never-Ending Rivalry?* R. Hoffmann, S. Shaik and P. C. Hiberty, *Acc. Chem. Res*., 2003, **36**, 750-756; (b) *Valence Bond and Molecular Orbital: Two Powerful Theories that Nicely Complement One Another*. J. Morrison Galbraith, S. Shaik, D. Danovich, B. Braïda, W. Wu, P. Hiberty, D. L. Coopwer, P. B. Karadakov and T. H. Dunning Jr., *J. Chem. Ed*., 2021, **98**, 3617-3620; (c) *Valence Bond Theory – Its Birth, Struggles with Molecular Orbital Theory, Its Present State and Future Prospects*. S. Shaik, D. Danovich and P. C. Hiberty, *Molecules*, 2021, **26**, 1624-1647.

2. Not all bonding is amenable to being considered in terms of 2c,2e bonds although the majority of organic and electron precise compounds can be represented in this way. Examples of 3c,2e and 3c,4e bonds are discussed in the main text and Pauling’s VB treatment of O2 in terms of two-centre, three electron (2c,3e) bonds is addressed in ref. 1(c).

3. We should recognise that even the 1s, 2s, 2p etc. orbitals we so commonly take for granted are themselves an approximation especially in terms of how they are illustrated pictorially.

4. Hybrid atomic orbitals such as sp, sp2 and sp3, but also including dsp3 and d2sp3, are an important feature of VB theory and are encountered in many rationalisations throughout the main text. Although arguments involving hybrids which incorporate d orbitals have now largely been superseded, even sp*n* hybrids still excite controversy in some quarters. See for example, (a) *Is it Time to Retire the Hybrid Atomic Orbital?* A. Grushow, *J. Chem. Ed*., 2011, **88**, 860-862 and (b) *In Defense of the Hybrid Atomic Orbital.* P. C. Hiberty, F. Volatron and S. Shaik, *J. Chem. Ed*., 2012, **89**, 575-577.

5. Remember that s orbitals are cylindrically symmetric.

6. This technique is often referred to as UV-PES (sometimes UPS) indicating that the incident radiation is UV radiation. The complementary technique XPS employs X-radiation which ionises core electrons and is important in surface analysis.

7. MO energy level diagrams are constructed based on the symmetries of the orbitals involved using simple Group Theory arguments.

8. More advanced VB treatments can readily account for the photoelectron spectrum of methane but at the expense of some of the simplicity inherent in the MO approximation.

9. Molecular orbitals are often constructed from atomic orbitals based on the Linear Combination of Atomic Orbitals (LCAO) approach, but this approach should be seen as a shorthand to deriving pictorial representations of orbitals from the results of MO calculations.

10. For a useful article on orbitals and their representations relevant to this level of discussion, see *Orbitals: Some Fiction and Some Facts*. J. Autschbach, *J. Chem. Ed*., 2012, **89**, 1032-1040.