Keith S. TABER
University of Cambridge, Faculty of Education

COMPOUNDING QUANTA: PROBING THE FRONTIERS OF STUDENT UNDERSTANDING OF MOLECULAR ORBITALS

ABSTRACT: College level students are expected to be able to make sense of, and explain, aspects of chemical bonding and structure in terms of molecular orbital concepts. The present paper derives from in-depth research into the thinking of a small sample of college chemistry students. This study in one UK college revealed the ways in which students found the orbital concept problematic. A previous paper ("Conceptualizing quanta: illuminating the ground state of student understanding of atomic orbitals") reports how these students struggled to make sense of atomic structure in orbital terms. The present paper considers the students' understanding of the molecular orbital concept. It is suggested that when learners are introduced to ideas about molecular orbitals before they have mastered ideas about atomic systems, then their learning difficulties may be 'compounded' in the more complex context. For example, it was found that students often identified the orbitals involved in two-centre bonds as atomic orbitals. Representations of delocalised bonds invoked various alternative interpretations: but were seldom conceptualised as implying poly-centred molecular orbitals. These findings suggest that students are not given sufficient time to construct acceptable models of atoms and molecules as 'quanticles'. [Chem. Educ. Res. Pract. Eur.: 2002, 3, 159-173]

KEY WORDS: *students' conceptions; quanta; orbitals; bond formation; molecular structure; molecular orbitals*

INTRODUCTION - THE SIGNIFICANCE OF MOLECULAR ORBITALS

The quantization of energy and angular momentum are key principles in understanding modern models of atomic and molecular structure. The notion of the orbital is a central explanatory device used to help conceptualise chemical structures at the molecular level, and aspects of orbital theory are now taught in University entrance level courses (Taber 1997; 2002a).

This is the second of two papers exploring how college level students (i.e. 16-18 year olds between secondary and university levels) make sense of orbitals and related concepts. The first paper concentrated on how the students attempted to make sense of *atomic* structure in terms of orbitals (Taber, 2002a). This sequel considers how the same group of students made sense of *molecular* structure in orbital terms. It was reported in the previous paper that students found applying orbital ideas to atoms was problematic, and so it is to be expected that these difficulties might be compounded when they are asked to consider more complex (molecular) systems.

Understanding molecular structure is important as chemists explain the properties of substances largely in terms of molecular level models. These enable us to explain everyday

properties of substances in terms of the *distinct* properties of the molecules. Yet it is known that students find such explanations problematic (Lijnse, et al., 1990; Taber 2001a, 2002b).

Students' tend to find it difficult to develop these types of explanations even when the molecular level properties are familiar from macroscopic scale phenomena (e.g. the same electrostatic forces that allow a comb to attract small pieces of tissue also act at the molecular level). Yet many of the important features of the behaviour of matter at the scale of molecules, ions and electrons are *not* familiar from experience of the macroscopic world. These features might be classed as 'quantum properties'.

It is not surprising that the 'weirdness' of quantum behaviour - what one Nobel prize winning physicist has called "the crazy ideas of quantum mechanics" (Feynman, 1985, p.1) - proves to be an additional barrier to students learning to use the chemists' models of matter. The quantization of energy, angular momentum etc., and the wave-particle nature of entities such as electrons, are alien to students. For example, the 'spin' of electrons ($m_s=\pm^1/_2$) is intrinsic, and does not mean the electron is spinning. Electron spin is sometimes referred to as *quantum-mechanical* spin to emphasise that the term spin is here used by analogy with the everyday meaning.

This paper, and its prequel (Taber 2002a), are concerned with learning about the properties of matter at scales where these quantum effects *do* become significant, where particles might be labelled 'quanticles'. The particle model (or kinetic theory) of matter is a quantum theory: i.e. it claims that matter is not continuous but composed of myriad minute particles. The term quanticle is used to refer to the quanta of substances: i.e. the constituent particles such as *molecules* of water, *ions* in sodium chloride, *cations and electrons* in copper. Quanticle is intended as a generic term to stand for molecules, ions, atoms etc., to distinguish them from macroscopic particles (e.g. grains of sand), and to emphasise the distinct 'quantum behaviour' of particles at this scale (Taber, 2002a). The term *quantactions* has been suggested for the interactions (sometimes labelled 'fruitful collisions') that occur between quanticles which lead to substances *reacting* (Taber, 2001b, 2002a).

The quanticle nature of these systems is of utmost importance in the most basic areas of the chemistry curriculum. In particular the concept of *the orbital* is fundamental to modern chemistry. For example, a chemical bond may be conceptualised in terms of the overlap of atomic orbitals to form molecular orbitals (Pauling, 1960), and reactivity and reaction path may be related to the characteristics of the interacting orbitals on the quanticles of the reactants (Fleming, 1976).

The quantization of properties such as energy, angular momentum, charge etc. is a key feature of the universe at the quanticle level, and - for example - leads to the consequences of the Pauli exclusion principle (so that electrons occupy shells with limited capacity). One of the particular features of quanticles is that they have properties of both particles and waves ('wave-particle duality'), and the wave nature of electrons has been well demonstrated, for example in terms of electron diffraction. By analogy with stationary waves in macroscopic physical systems (which are only possible at those frequencies where constructive interference occurs) an electron (considered as a wave) is restricted to specific stable states.

One way of describing the single electron in a hydrogen atom is by using the mathematical formalism of Schrödinger's wave equation (which tends to be used in preference to Heisenberg's alternative, and equivalent, matrix approach). The solutions to the Schrödinger equation may be interpreted as a set of atomic orbitals. At the college level it is common for the set of orbitals derived from the hydrogen case to be used as a basis for describing more complex atoms with several or many electrons, which are in turn used as the starting points for considering molecular orbitals.

University level courses often present orbital ideas at a much greater level of sophistication. Molecular orbitals are generally labelled as bonding, non-bonding and anti-bonding depending on whether they are at lower, similar or higher energy than the atomic orbitals they are considered to derive from (Murrell et al., 1978). Overall bond order is determined by the relative occupancy of the bonding and antibonding orbitals to derive from the overlap. Aromaticity and anti-aromaticity extends these ideas to polynuclear systems of molecular orbitals, i.e. delocalised systems (Pauling, 1960). Organic reaction mechanisms have been studied in terms of the HOMOs and LUMOs (highest occupied and lowest unoccupied molecular orbitals) on the quantacting species (Fleming, 1976). There have also been attempts to rationalise the study of inorganic and organic mechanisms using orbital concepts (Leach, 1999).

These ideas are *not* considered in *school* level chemistry, where molecules are usually described in terms of overlapping atomic electron *shells*, as if this is an unproblematic notion. It is at the next stage of chemistry learning, often at around 16 years or so of age, that quantum theory is first *explicitly* met (although students will already be tacitly aware of the quantization of charge, and will have learnt about the particle model of matter), for it is at this level that the concept of the orbital and related ideas (energy levels, quantum-mechanical spin, quantum numbers and associated rules) are first introduced.

When students first meet orbital concepts at college level they are usually presented with visual representations of ground state atomic orbitals (strictly based on the single-electron case of the hydrogen atom - Scerri, 1993), and are likely to be given relatively qualitative explanations of the way the electron density from overlapping atomic orbitals combines to give molecular orbitals. Orbital hybridisation is introduced to explain how *the maximum number of half occupied atomic orbitals best arranged for overlap with other atoms' orbitals* may be produced.

Previous research acknowledges that learning about orbital ideas is problematic both at college level and in the university (Cervellati and Perugini, 1981; Cros et al., 1986, 1988; Jones, 1991; Mashhadi, 1994; Shiland, 1997; Tsaparlis, 1997.) This was echoed in the present study (Taber, 1997, 2002a).

THE CONTEXT OF THE PRESENT STUDY

The data reported in this paper derive from an interview-based study with UK college students (c.16-18 years of age), designed to explore their developing understanding of ideas related to the chemical bond. These students were enrolled on two-year 'A level' courses (i.e. the General Certificate of Education Advanced Level), including the study of chemistry as one of their chosen subjects. The teaching team were chemistry graduates and experienced at teaching at this level. Typically, students taking this course were intending to proceed to university, and the A-level course was the standard means of bridging between school and university level study. Orbital ideas were presented during the students' first chemistry lesson at their college, and were regularly used in the teaching throughout the course.

The interviews were all undertaken by the author, who was one of the lecturers on the course, and therefore knew the students as a teacher as well as a researcher. The data presented are from a selection of in-depth interviews with a sample of students, who volunteered to be interviewed. Fifteen students were interviewed for the study (Taber, 1997, p.395-400). The students are referred to by assumed names. The material forms part of a larger study where grounded theory approaches were used to move from detailed exploration of the ideas of individual learners to the development of general models of wider application (Taber, 1997, 2000a). This approach led to the reporting of a model of student progression in understanding aspects of chemistry which involved moving from a common alternative

conceptual framework (the octet framework) to an increasing reliance on electrostatic *and orbital* ideas (Taber, 1999).

It is important to point out that the learning difficulties considered here are largely discussed in terms of the comments of a small number of learners in one college in one country. Clearly the findings can not be *assumed* to be generalised to all students studying chemistry at this level. Such accounts may be considered to be *illustrative* of the types of thinking, and sorts of learning difficulties that students at this level may present, but should not be taken to be representative of the extent or specifics of such thinking in the wider population of college level students.

The extent to which orbital ideas were elicited from the colearners varied considerably, and specific data from interviews with twelve of the fifteen students are presented in this paper and its prequel (Taber, 2002a). The theoretical approach used in this research, grounded theory, is primarily a qualitative approach. Grounded theory can produce models which are suitable for forming the basis of quantitative surveys, and the categories of student difficulties presented in this study could be used in this way (Taber, 2000a). However, in the present papers no attempt is made to quantify the frequency with which the particular difficulties were observed, as the methodology (i.e. sampling and data collection) would not justify such an approach.

Verbatim comments from individual learners may seen idiosyncratic when they can not be claimed to be representative of the wider population, but this approach is part of a developing research programme of exploring aspects of science learning by detailed case studies (e.g. Harrison and Treagust, 2000; Johnson, 1998; Petri & Niedderer, 1998; Scott, 1992; Taber, 1995, 2000b, 2001c). The value of the data discussed is in providing authentic cases of how students may struggle to make sense of these scientific ideas. These cases should be seen as *examples* which *indicate* the nature and range of learning problems: each reader needs to consider the extent to which conclusions could be transferred to her own teaching context - a process labelled reader generalization (Kvale, 1996).

FINDINGS FROM THE STUDY

The interviews with the college students suggested that they were mentally groping to make sense of new concepts such as orbital, energy level, quantum number, and so forth. The previous paper (Taber 2002a) describes how students would adopt the term 'orbital' but apply it to their pre-existing notion of an electron shell. As further ideas are met (sub-shells, energy levels, probability envelopes, electron density diagrams, electronic transitions) students are provided with more distinct, yet inter-related, concepts to confuse and conflate. Unsurprisingly perhaps in these circumstances, the labelling of atomic orbitals and electronic configurations, and the order of filling of atomic orbitals seems to be an ordeal of rote memory for many students. The spin of electrons is commonly interpreted in the form of the physical rotation or circular motion of an electron - which is viewed as a classical particle rather than as a quanticle with very different properties (Taber, 2002a).

The present paper considers what sense students - often still struggling to assimilate and accommodate ideas about ground state *atomic* orbitals - were able to make of the notion of *molecular* orbitals. The first part of this findings section considers the case of 2-centre-2-electron bonds. This is an important category, as most bonds in many simple compounds may be considered, *to a first approximation*, to be of this type. The students were expected to be able to appreciate something of hybridisation (in terms of maximising bond number and orbital overlap), and to be able to classify molecular orbitals as either σ (sigma) or π (pi) depending on the distribution of the electron density.

The second part of this findings section of the paper considers how students responded to focal diagrams representing resonance in systems which could not be effectively represented in terms of two-centre-two-electron bonds. Benzene, for example, is presented at this level as having a σ bond skeleton of localised C-C and C-H bonds, and a π system of six electrons derived from the overlap of six atomic orbitals to give volumes of electron density above and below the ring of carbon atomic centres.
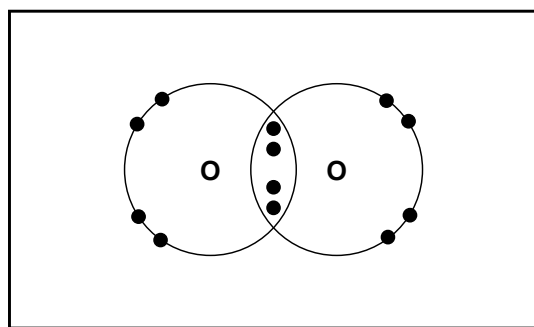
Understanding molecular orbitals

FIGURE Σφάλμα! Άγνωστη παράμετρος αλλαγής.: *Representing a molecule in terms Of overlap of shells.*

When students are operating with a model of molecules based on overlapping shells (e.g., see Figure 1) then they may suggest that the bonding electrons are *more restricted* than the non-bonding (i.e. 'lone pair') electron. The circles representing shells are often seen as orbits (Taber, 2002a). Annie explained that this allows the electrons to "move around" their shells, except for the bonding electrons, "the ones that are involved in [bonding], they can't really move around, like all the way around the shell". The electrons shown in the area of overlap were thought to be limited to this region, where other electrons were considered to be free to move around a complete shell. (It is interesting to note that Annie's deductions seem to match, at least superficially, the electron domain model which would consider the four non-bonding electrons not to occupy two orbitals, but a single 'nonbonding domain' - Gillespie & Matta, 2001, p.78.)

Even by the end of her two year course Annie did not appear to have a clear conception of how to describe a covalent bond in terms of a molecular orbital,

> "each atom contributes an electron, well the electrons are shared equally between the atoms involved, so you haven't got dominance from one atom with the electrons...the electrons are sort of held in *circuits, orbitals*, because when they sort of combine together, they're sort of *going around freely*, so you've got all the forces, sort of just like they're being pulled in by the nucleus. Electrons are being pulled in, so you've got sort of the nucleus pulling in the electrons from the other atom. So it helps them stay together"

Students readily became confused between atomic and molecular orbitals. Near the end of one year's study Lovesh suggested that in molecular hydrogen the electrons would be in orbitals that would "would be sphere" shaped. Then he decided that "they form molecular orbitals", before suggesting that "it would be linear orbital", presumably a reference to the 'linear combination of atomic orbitals' model.

Pi-bonds

π-bonding provided an additional challenge to the students. Unlike many σ-bonds, π-bonds are usually considered to be formed from unhybridised atomic orbitals, and lead to two distinct regions of high electron density. Carol described the π-bond in oxygen as "π-hybridisation", and although she referred to "overlapping of p-orbitals", she also suggested

that "you have to hybridise them otherwise they don't overlap fully", not realising that this particular bond was formed by the overlap of *unhybridised* atomic orbitals.

The geometrical properties of π-molecular orbitals was an another source of confusion. Paminder struggled to explain what a π-bond was,

> "when you have something with a double bond, like say for example, ... suppose you have carbon-carbon double bond, like an alkene. Like this is all *to do with orbitals and thing*s, like, suppose we have ethene, which is C double bond C, H, H, H, H, and like, this, *we're talking about orbitals now right*, when the double bond is formed it's like an actual π-bond is formed, *it's not like a σ-bond*, a σ-bond is like just simple overlap of like the orbitals. A π-bond is *slightly different*, it's like, it's like a hamburger you could say. You know, this π-bond, if you look at the molecule three dimensionally, there's a π-bond on top, π-bond cloud there, π-bond cloud there, that's the kind of thing."

The presence of two distinct concentrations of electron density in the π-bond may lead to students identifying two separate orbitals or bonds. Shortly before the end of his course, Lovesh described how in benzene "each carbon atom has got an unhybridised p-orbital with an electron in it and that forms...*two π-bonds*, and that's where the electrons can move around, in a π-bond". These 'two' separate bonds were "above the ring and below the ring...one above and one below, the ring".

Hybridisation

Another complication for students is the status of hybridised atomic orbitals. Although some of the molecular orbitals students met were considered to be formed by the overlap of ground state atomic orbitals, most were considered to involve the use of hybridised orbitals. The schemes that students met therefore often involved three stages. The starting point would be the ground state configurations of the atoms concerned. Students would then be expected to consider how a different set of atomic orbitals would be more suitable for overlap (i.e. hybridisation), before considering the formation of molecular orbitals. The description of the electronic structure of even a simple molecule *could* include electrons in ground state atomic orbitals, hybridised atomic orbitals, molecular orbitals formed by overlap of ground state atomic orbitals, molecular orbitals formed by overlap of hybridised atomic orbitals, and molecular orbitals formed by the overlap of a ground state orbital on one atom with a hybrid orbital on another (e.g. consider methanal).

Confusing atomic and molecular orbitals

A common error made by students was to locate bonding electrons in atomic orbitals, (or at least to label the bonding orbitals *as* atomic orbitals). Lovesh made the comment that "*molecular orbitals are hybrids*", and Paminder suggested that in a tetrachloromethane *molecule* the electrons in one bond were in a chlorine "3p" orbital, and a carbon "2p" orbital. She thought that the four carbon bonding electrons were in the $2p_x$, $2p_y$ and 2s orbitals, and indeed that *two* of the bonding electrons, i.e. in two different bonds, were in "*the* 2s" orbital. A number of other students made similar errors (see Table 1).

It is considered significant that students were sometimes making these errors *despite* apparently appreciating orbital hybridisation and even the orbital overlap approach to explaining bonding. So Edward was able to explain "hybridisation, where you put energy into the system, in the hope that you'll get a more stable resultant structure", and argued that

TABLE Σφάλμα! Άγνωστη παράμετρος αλλαγής.: *Assignment of electrons in molecules to atomic orbitals.*

molecule/structure	assignment of orbitals	student
hydrogen	1s	Kabul
hydrogen	s orbital	Paminder
diamond	sp^3	Kabul
graphite	unpaired p-orbitals	Lovesh
methane	sp^3	Kabul
tetrachloromethane	3p (Cl), 2p + 2s (C)	Paminder
tetrachloromethane	sp^3 hybrids	Lovesh
benzene	1s (H), sp^2 hybrids + p (C)	Lovesh
benzene	hybrid molecular orbitals	Debra

the energy of an sp^3 hybrid would "be slightly less than the p, but greater than the s". The energy level of the sp^3 hybrid orbital had "got to be nearer to the p" as "more p[orbital]s are contributing towards the ... average energy", so as sp^3 hybrid orbital would consequently have "seventy five percent p quality". Despite mastering this abstract scheme, he explained the bonding in tetrachloromethane in terms of the electrons from chlorine having "left their orbitals, to obtain a more stable structure" and entered the carbon sp^3 "hybridised orbitals".

A similar pattern was observed with Kabul. Again, this is a student who seems capable of appreciating the abstract nature of orbital ideas. Kabul knew that a (ground state) carbon atom also had two unpaired electrons which would suggest it could form "two [bonds], but we can form more if we want" by "hybridising it [because the] 2s orbital has got two electrons, so when hybridising it, it can let one of its electrons go into $2p_z$ orbital, and then you have got four". Kabul knew that when an atom

> "undergoes hybridisation...the s and p orbitals combine together to form...orbitals of the equal energy level...2p orbitals are at a higher energy level compared to 2s orbitals, when you combine them the energy level...is less than energy level of the p, but it is greater than s".

He explained that, unlike phosphorus, nitrogen only formed one chloride as "it [nitrogen] has no low lying d-orbitals, to promote electrons during hybridisation". Kabul thought that for forming ammonia there would need to be "sp^3" hybridisation which he thought would provide "three equal bonds with hydrogen".

Despite this sophisticated appreciation, Kabul (like Edward) did not seem able to appreciate the 'next step' in the conceptual scheme, i.e. the formation of molecular orbitals. He believed that in methane carbon produced four "similar" sp^3 hybrids to "form four equal bonds with hydrogen", but in ammonia where there were also "four" orbitals formed in sp^3 hybridisation, he suggested that "three" of them were similar, where the "fourth one ... goes to the lone pair of electrons", and was "not that similar" to the others. Kabul appeared was comparing the nitrogen *atomic hybrid* containing the lone pair, with the *molecular orbitals* formed from the overlap of the other hybrids with the hydrogen atomic orbitals.

Taking this evidence alone might suggest that Kabul did not appreciate the model of molecular orbitals formed through orbital overlap. Yet he referred to the "overlap" of atomic orbitals (in the bonding of carbon dioxide), and even explained the purpose of hybridisation in terms of improving orbital overlap,

> "if you look at the electronic configuration of nitrogen, that's $1s^2$, $2s^2$, $2p^3$, it's got three unpaired electrons, in its p-orbitals you know, and in order to get good overlap, they hybridise it, and they form sp^3 hybridisation".

Kabul thought that in a hydrogen molecule there would be "s orbitals, 1s orbitals...just 1s orbitals". However, when it was put to him that there would be a molecular orbital present he agreed, and explained that this was "made up of, for example, two atomic orbitals, when they form a bond, the orbitals, you know, combine together to form a molecular orbital". In this particular case the molecular orbital was made up from "the two 1s orbitals", and the 1s atomic orbitals were no longer present in the molecule. So it seems Kabul 'knew' that atomic orbitals overlapped to give molecular orbitals, and that hybridisation sometimes occurred to give better overlap between atomic orbitals: yet when he was asked about the orbitals present in a molecule he responded in terms of atomic orbitals and *did not bring to mind* the molecular orbitals.
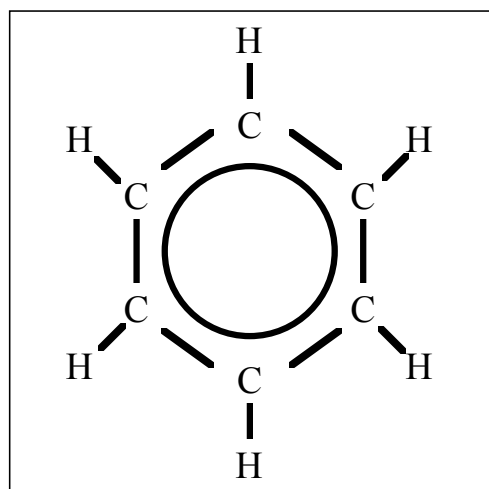
Resonance

FIGURE Σφάλμα! Άγνωστη παράμετρος αλλαγής.**:** *A representation of the structure of a benzene molecule.*

In the study there was evidence of learners having difficulty conceptualising resonance. A particularly important system that student meet at this level of study is the aromatic ring, with benzene as the archetype.

A range of interpretations of the bonding in benzene was elicited from colearners, although three themes may be identified from the comments made. The first theme is that of the interpretation of the circle used to represent aromaticity (Figure 2), which was seen by some colearners as indicating some type of *electron reservoir inside the ring*. A second theme concerns the use of the term *delocalisation*, but in the absence of a molecular orbital interpretation that makes the notion vague, and even

unrelated to the bonding. Thirdly, although learners use the term resonance, they may mean an *alternation* between single and double bonds, albeit perhaps one which occurs very rapidly. One of the students, Annie, moved between these different approaches during her course.

After the first term of her course Annie thought that the circle used to represent the aromatic character of benzene "shows where the electrons are, because it's electron rich" and so the electrons were "denser in the circle". By the end of her first year Annie showed an awareness of *delocalisation* (although this did not appear to be related to any concept of molecular orbitals). Her interpretation was that the electrons "go around in the ring, so they sort of charge around and...they're not fixed anyway, they don't belong to anything in particular, so they're free-flowing". By the end of her course Annie demonstrated some notion of the *resonance*, but in terms of single and double bonds that move around the ring,

"If you've got the benzene ring with the double bond and the single bond and then, I don't know somehow, a simplistic way of looking at it, and the bond moves"

Annie had acquired some of the language used to talk about aromatic systems: describing benzene as "an unsaturated, aromatic or something", although she thought *aromatic* simply meant "that it smells". She even developed some awareness that the various

diagrams used to depict the benzene structure were limited representations, but she was unable to appreciate the nature of the bonding in terms of molecular orbitals extending over the ring,

> "you've got delocalised electrons in a benzene molecule, the electrons they're sort of distributing throughout the complex...because you've got such a structure with benzene whereby you haven't got single bonds all the way around, you've got to have three double bonds out of six, they sort of delocalise so that everything's sort of, equal in the end...It's a...conjugated bond system, or something...you can draw like canonical forms of benzene...[and] it just shows where the bonds could lie, but they don't really exist, it's sort of something that [a] scientist has in their minds to show, to explain something. So three out of the six could be in one position or they could be in the sort of reverse, although, in nature, they don't actually perform that way"

The 'electron' reservoir notion was also found among other students, at different levels of sophistication. For Carol the circle in the benzene symbol represented "six *spare electrons* in the middle" which were "just spinning around". According to Carol, as each carbon centre was only bonded to three other atoms "it's got to have one [electron] still whizzing round itself", that is these electrons were seen as localised and "attracted to their own nucleus". These 'spare' electrons would be "left in the middle" and "you show that by the circle". Debra also thought there were "spare electrons", which were "*within* the carbons, *within* the ring...Or *in the middle*" but that these were "free to move...in between carbons".

Kabul demonstrated a more sophisticated interpretation of the circle symbol, that it represented "the electron density, of carbon atoms", which was high inside the benzene ring "because ... the outermost electrons [from "just the carbon atoms"] are equally attracted by the whole ring of atoms, not just one atom". Brian went one stage further by the end of his first year of the course and was able to justify the delocalisation occurring *inside* the ring in terms of electron overlap. He thought that p-orbitals "of the ring overlap, and the electrons can pass from orbital to orbital, to become delocalised", but he thought that the p-orbitals used to overlap to give the delocalised system were in "the plane of the" of the ring. Had this been the case, then the circle would realistically have represented the area of orbital overlap.

Brian's understanding at this point had progressed from his original attempt to make sense of the notion of benzene as "a delocalised system" which simply meant that "the double bonds aren't in any set place...they're not in specific places on every benzene...molecule". Carol's first attempts to make sense of the notion of delocalisation had her identify the delocalised electrons as *unrelated* to the π-electron clouds: in benzene there was,

> "kind of like a ring [with] like electron thing underneath it, and electron thing on the top...the electron density below and above it...because they're π-bonds...*and* then you've got delocalised electrons in the middle, but I don't know what they look like."

This is an interesting example of a student not connecting fragments of knowledge that were intended to be seen as related. Carol had an image of the two regions of electron density due to the π-bonds (i.e. the system of six electrons occupying the three bonding molecular orbitals encompassing the six carbon atoms). She also knew that there were delocalised electrons, represented by the circle, but she located those separately and did not appreciate that it was those electrons which produced "the electron density below and above" the ring.

Resonance as alternation

Figure 2 shows one way that the bonding in benzene is commonly represented, but students at this level are commonly introduced to the Kekulé structures (see Figure 3) as well.
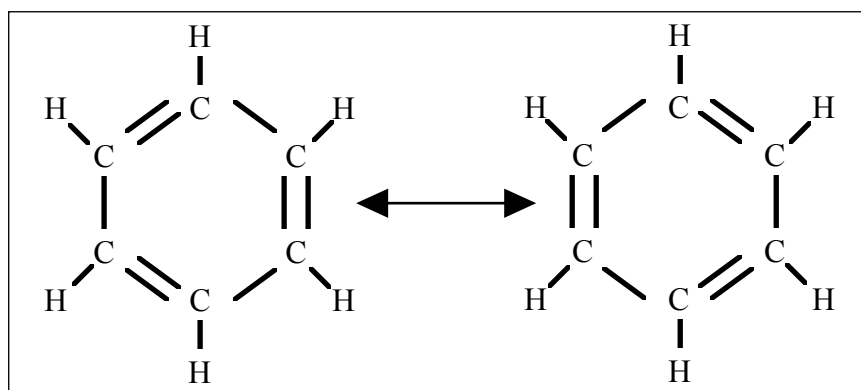

FIGURE Σφάλμα! Άγνωστη παράμετρος αλλαγής.**:** *Canonical Kekulé structures for the benzene molecule.*

Brian's reference to how "the double bonds aren't...in specific places on every benzene...molecule" was one of several descriptions of resonance as an alternation between double and single bonds. Quorat referred to "resonance structures" and "canonical forms" but construed these notions as a device *for overcoming ignorance* about which bonds were double and which were single, "since the actual positions are not known, it is better shown as a delocalised system". Carol described how

"it will be double bond, single bond, double bond, single bond, double bond, single...and, to make the resonance, you draw a little two way arrow, and where there was a double bond in one diagram there would be a single bond in the other one...[the circle] shows that you can either have a double bond, or a single bond, and it happens so quickly that you might as well just have a single bond...[the bond was] sometimes single, sometimes double"

Similar notions of resonance were found when students discussed other examples. So when Debra considered a diagram of canonical forms of the ethanoate ion (Figure 4) she suggested that the arrow between the two structures "represents that it can change from one to the other", when "the electrons that are in that double bond, move over to the other carbon and the oxygen, and form a double bond there". Brian also thought that this species "alters between the two states", so that at any one moment an oxygen "could be minus, or it could have no charge".

Brian made a similar interpretation when presented with a representation of the polar bonding in boron trifluoride in terms of a resonance between forms with ionic and covalent bonds (Figure 5) rather than single and double bonds. In this example the resonance is meant to imply that the electron density reflects a polar bond (something between ionic and covalent) rather than - as in the benzene and ethanoate examples - a bond with fractional bond order. He describes how the diagram is meant to imply "an alternation between the states of boron fluoride" where "the majority of the time [a particular bond] is covalent, but occasionally it is ionic". Kabul described how in this case,

"sometimes, one of these fluoride ions is negative, so sometimes this fluoride, another fluoride ion can be negative: it shows like resonance...it's bonded covalently with two and ionically with one"
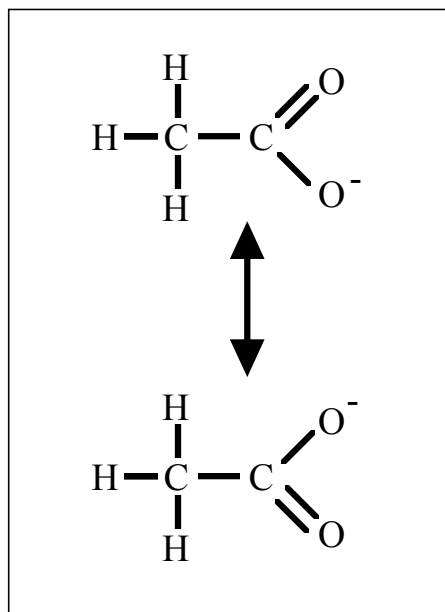
FIGURE Σφάλμα! Άγνωστη παράμετρος αλλαγής.: *Canonical forms representing the resonance in the ethanoate ion.*
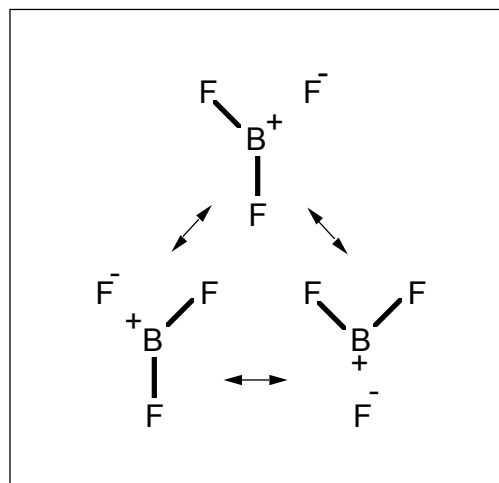
FIGURE Σφάλμα! Άγνωστη παράμετρος αλλαγής.: *Resonance as a way of representing bond polarity.*

For Kabul, changing between the different forms required the "atom" to "just flick around". These students found the notion of alternation (between single and double bonds or between covalent and ionic bonds) a more acceptable interpretation of canonical forms than the intended interpretation that the electron density pattern suggested an intermediate electronic structure somewhere between the structures that could be represented in several simple valence bond type representations.

DISCUSSION

Given that the interviewed students appeared to struggle to develop the scientific concept of *atomic* orbitals (Taber, 2002a), it is unsurprising that they did not readily develop the accepted models of chemical systems involving molecular orbitals. As an appreciation of molecular orbitals is built upon an understanding of the atomic case, it is to be expected that attempting to teach the more complex examples whilst students have limited conceptualisations of the simpler case may only compound their difficulties.

Yet there is much cause for optimism in the work reported here. For one thing, in order to explore students' learning difficulties, this paper (and its prequel) have focused on the *limitations* of student learning. Many examples of students' appropriate responses about orbital ideas have been passed over, while a selection was made of evidence of student ideas *not* matching the scientific models. Consequently, the examples presented should not be considered as fully representative of student comments relating to orbital concepts during the research. Rather, they are presented as illustrative of the ways in which students attempt to make sense of these ideas. Most of the students cited made some progress towards acquiring scientifically acceptable versions of these ideas during their two year course (Taber, 1997): something that is hinted at, but not presented in any detail, in these reports of the findings. In other aspects of their understanding of chemistry these same students made considerable

progress (e.g. Taber, 1995, 2001c). Nevertheless, progress in developing scientifically acceptable models of atomic and molecular structure in terms of orbitals tended to be more limited (Taber, 1997, 1999). The orbital concept *was* a particular area of conceptual difficulty for these students.

The main reason I find this study a cause for optimism is that despite the relative failings of students' conceptualisations, there is plenty of evidence of students *engaging* with the ideas met in their course, and actively attempting to *make personal sense* of these very abstract concepts such as quantum-mechanical spin, hybridisation, electron density clouds and delocalisation. The detail possible in a study of this type - focusing on a small group of learners, but in depth - allows the voices of the students to emerge from the study. What those voices had to say often seemed confused, was sometimes inconsistent, and would frequently be considered technically 'wrong': yet it provides plentiful indications of the students actively processing the ideas and trying to form meaningful interpretations of the concepts.

The constructivist perspective on learning recognises that knowledge construction is personal (as well as inter-personal), idiosyncratic and highly dependent upon the learner's existing conceptual frameworks (Taber, 2000c, 2002b). The acquisition of complex scientific ideas is therefore likely to be a slow process, as learners' ideas develop through conceptual trajectories that (hopefully) lead to a close match with accepted scientific models (e.g. Petri & Niedderer, 1998; Taber, 2001c). The starting point for these trajectories will depend upon the way the teacher's presentation is interpreted through prior knowledge.

In the present study much of the existing knowledge that students used as the substrate for making sense of orbital ideas derived from prior chemistry teaching. This is of course as it should be, and *much* of that prior learning helped facilitate new learning. As an example, that could be multiplied many times, when the students first saw the unfamiliar structure shown in Figure 2, they were able to make sense of it as representing a molecule of a hydrocarbon compound.

However, the students' prior learning could *also* act as a barrier as well as a portal to new learning. So, for example, knowledge of an atomic model consisting of electrons orbiting nuclei in concentric shells made it difficult for students to build a new model where electrons are quanticles which are not well described by 'orbits', and which occupy orbitals that do not have sharp boundaries and are often not spherical (Taber, 2002a). Indeed the presence of the 'electron shell' concept often delayed students acquiring an orbital concept that went beyond re-labelling shells as orbitals.

In the present paper it was found that student familiarity with valence bond structures (which satisfactorily represent 2-centre-2-electron bonds) actually impeded students from appreciating formalisms designed to represent delocalised bonds. Students tended to interpret structural diagrams more literally than intended and infer electron reservoirs (Figure 2) or rapidly alternating bonds (Figures 3-5). Previous success in interpreting unproblematic structural diagrams led to students seeing resonance in terms of *re-location* of bonds rather than *de-localisation* of bonds.

This type of situation, where prior learning actually interferes with new teaching has been labelled as a *pedagogic* learning impediment (Taber, 2001d). This often occurs when teaching models are used which are incomplete or inadequate compared with the scientific versions (Justi & Gilbert, 2000). In principle such impediments, once detected, may be avoided by revising the teaching of the prerequisite knowledge so that it forms a better foundation for the new learning. However, teachers *also* have to simplify subject matter so that it is sensible to students. Matching these two requirements asks for fine professional judgement (Taber, 2000d), and in the present topic it may well be that the models of atomic and molecular structure taught in school science are already making high cognitive demands upon learners. Perhaps the present research suggests that it is unrealistic to expect students to

develop meaningful and valid models of the quantum nature of the molecular world prior to university study (cf. Gillespie, 1996).

This tentative conclusion, i.e. that we may have unrealistic expectations of what students can be expected to grasp in a college level course (e.g. at the 16-18 year level), is supported by evidence of the problems students had appreciating the nature of molecular orbitals in compounds. I would suggest that it is significant that students often label molecular orbitals as if they are atomic orbitals, and particularly that clearly capable individuals such as Edward and Kabul were able to discuss abstract ideas about hybridisation, and even orbital overlap, yet still fail to identify molecular orbitals. Learners need time to assimilate and accommodate new ideas before they can use them effectively as a foundation for further learning. The conceptual scheme that moves from the new abstract ideas about ground state atomic orbitals, to notions of hybridisation, to consideration of the overlap of atomic orbitals, to the formation of molecular orbitals, seems to overload even the most conscientious and motivated learner. There are just too many steps, and too many abstract ideas, for students to master them all in a few months (cf. Taber, 1999, 2001c).

One of the key findings discussed in these two papers is how learners confuse concepts that are related but distinct: sub-shells and shells; orbitals and energy levels; photoemission and thermionic emission; hybridised atomic orbitals with molecular orbitals. Students also fail to identify different representations of the same basic idea: so the benzene molecule may be said to have both pi-bonds *and* delocalised electrons.

These problems are surely related to the abstract nature of the concepts concerned: which can not be shown to students, which are often formally defined mathematically, and which are commonly modelled qualitatively for students with various approximations (Scerri, 1993). Yet this study does show just how much of these formalisms students *are* able to absorb, and this suggests that the learning problems discussed could be overcome given *more time* for learners to familiarise with and practice application of each of the concepts *before* they are required to relate them to yet another abstraction.

I would even go so far as to mischievously suggest that college students' ideas about the quantum aspects of chemical structure may be subject to an uncertainty principle:

$$\Delta E \times \Delta t \geq \hbar$$

where

ΔE is the *error*, or deviation of student ideas from the model taught in the curriculum;

Δt is time interval for introducing new concepts; and

$\hbar$ is a constant called the haste coefficient.

This may seem a flippant and irreverent suggestion (and I am not seriously suggesting that ΔE could be quantified), but the humour stands in place of a serious point: we may need to apply the adage 'less haste, more speed' to our teaching if we wish our students to master the abstract conceptual schemes that explain the structure of quanticles.

CORRESPONDENCE: *Keith S. TABER, University of Cambridge Faculty of Education, Homerton site, Hills Road, Cambridge, CB2 2PH, U.K.; kst24@cam.ac.uk, keith.taber@physics.org http://www.educ.cam.ac.uk/staff/taber.html*

REFERENCES

Cervellati, R. & Perugini, D. (1981). The understanding of the atomic orbital concept by Italian high school students. *Journal of Chemical Education*, *58*, 568-569.

Cros, D., Amouroux, R., Chastrette, M., Fayol, M., Leber, J. and Maurin, M. (1986). Conceptions of first year university students of the constitution of matter and the notions of acids and bases, *European Journal of Science Education*, *8*, 305-313.

Cros, D., Chastrette, M. and Fayol, M. (1988). Conceptions of second year university students of some fundamental notions in chemistry. *International Journal of Science Education*, *10*, 331-336.

Feynman, R. P. (1985). *QED: The strange theory of light and matter*. Princeton: Princeton University Press.

Fleming, I. (1976). *Frontier orbitals and organic chemical reactions*. Chichester: John Wiley.

Gillespie, R. J. (1996). Bonding without orbitals, *Education in Chemistry*, July 1996, 103-106.

Gillespie, R. J. & Matta, C. F. (2001). Teaching the VSEPR model and electron densities, *Chemistry Education: Research and Practice in Europe*, *2*, 73-90.

Harrison, A.G. & Treagust, D.F. (2000). Learning about atoms, molecules, and chemical bonds: A case study of multiple-model use in grade 11 chemistry. *Science Education*, *84*, 352-381.

Johnson, P. (1998). Progression in children's understanding of a 'basic' particle theory: A longitudinal study. *International Journal of Science Education*, *20*, 393-412.

Jones, D. G. C. (1991). Teaching modern physics - Misconceptions of the photon that can damage understanding. *Physics Education*, *26* (2) 92-98.

Justi, R. & Gilbert, J. (2000). History and philosophy of science through models: Some challenges in the case of 'the atom'. *International Journal of Science Education*, *22*, 993-1009.

Kvale, S. (1996). *InterViews: An introduction to qualitative research interviewing*, Thousand Oaks, California: SAGE Publications.

Leach, M. R. (1999). *Lewis acid/base reaction chemistry*. Brighton: Meta-Synthesis.com

Lijnse, P. L., Licht, P., de Vos, W., & Waarlo, A. J. (1990). *Relating macroscopic phenomena to microscopic particles: A central problem in secondary science education*. Utrecht: Centre for Science and Mathematics Education, University of Utrecht: CD-β Press.

Mashhadi, A. (1994). Advanced level physics students' understanding of quantum physics. Paper presented to the *British Educational Research Association* Annual Conference, Oxford, September 1994.

Murrell, J. N., Kettle, S. F. A. & Tedder, J. M. (1978). *The Chemical bond*. Chichester: John Wiley.

Pauling, L. (1960). *The nature of the chemical bond and the structure of molecules and crystals: An introduction to modern structural chemistry (3rd edition)*. Ithaca, New York: Cornell University Press.

Petri, J. & Niedderer, H. (1998). A learning pathway in high-school level quantum atomic physics, *International Journal of Science Education*, *20*, 1075-1088.

Scerri, E. (1993). Is chemistry a reduced science? *Education in Chemistry*, *30* (4), p.112.

Scott, P. H. (1992). Pathways in learning science: a case study of the development of one student's ideas relating to the structure of matter. In Duit, R., Goldberg, F. & Niedderer, H., (Eds.) *Research in physics learning: Theoretical issues and empirical studies*, pp.203-224. Kiel: I.P.N. (Institut für die Pädagogik der Naturwissenschraften).

Shiland, T. W. (1997). Quantum mechanics and conceptual change in high school chemistry textbooks. *Journal of Research in Science Education*, *34*, 535-545.

Taber, K. S. (1995). Development of Student Understanding: A Case Study of Stability and Lability in Cognitive Structure, *Research in Science & Technological Education*, *13*, 87-97.

Taber, K. S. (1997). Understanding chemical bonding - the development of A level students' understanding of the concept of chemical bonding, Ph.D. thesis, University of Surrey.

Taber, K. S. (1999). An explanatory model for conceptual development during A-level chemistry. Paper presented at the annual meeting of the *British Educational Research Association*, September 1999, University of Sussex. [Available via Educati*on-line*, at http://www.leeds.ac.uk/educol]

Taber, K. S. (2000a). Case studies and generalisability - Grounded theory and research in science education. *International Journal of Science Education*, *22*, 469-487.

Taber, K. S. (2000b). Multiple frameworks?: Evidence of manifold conceptions in individual cognitive structure. *International Journal of Science Education*, *22*, 399-417.

Taber, K. S. (2000c). Chemistry lessons for universities?: a review of constructivist ideas, *University Chemistry Education*, *4* (2), pp.26-35. [Available at http://www.rsc.org/uchemed/uchemed.htm]

Taber, K. S. (2000d). Finding the optimum level of simplification: The case of teaching about heat and temperature. *Physics Education*, *35,* 320-325.

Taber, K. S. (2001a). Building the structural concepts of chemistry: Some considerations from educational research. *Chemistry Education: Research and Practice in Europe, 2*, 123-158. [Available at http://www.uoi.gr/conf_sem/cerapie]

Taber, K. S. (2001b). The campaign to stop molecules reacting. *Education in Chemistry*, *38* (1), 28.

Taber, K. S. (2001c). Shifting sands: A case study of conceptual development as competition between alternative conceptions. *International Journal of Science Education*, *23*, 731-753.

Taber, K. S. (2001d). The mismatch between assumed prior knowledge and the learner's conceptions: a typology of learning impediments. *Educational Studies*, *27* (2), 159-171.

Taber, K. S. (2002a). Conceptualizing quanta - illuminating the ground state of student understanding of atomic orbitals, *Chemical Education: Research and Practice in Europe, 3*, 145-158. [Available at http://www.uoi.gr/conf_sem/cerapie]

Taber, K. S. (2002b). *Chemical misconceptions: Prevention, diagnosis and cure*. London: Royal Society of Chemistry.

Tsaparlis, G. (1997). Atomic orbitals, molecular orbitals and related concepts: conceptual difficulties among chemistry students. *Research in Science Education, 27,* 271-287.