

# Challenges to the Structural Conception of Chemical Bonding\*

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## Abstract

While the covalent bond plays a central role in chemical predictions, interventions, and explanations, it is a difficult concept to define precisely. This paper investigates the structural conception of the covalent bond, which says that bonding is a directional, sub-molecular region of electron density located between individual atomic centers that is responsible for holding the atoms together. Several approaches to constructing molecular models are considered in order to determine which features of the structural conception of bonding, if any, are robust across these models. The paper concludes that key components of the structural conception are absent in all but the simplest quantum mechanical models of molecular structure, seriously challenging the conception's viability.

Crucial to chemical practice and discourse is the notion of the chemical bond, specifically the covalent bond. For most synthetic and analytical purposes, molecules are conceived of not just as collections of atoms, but as structural entities consisting of directionally oriented atomic centers connected, in some way or other, by

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covalent bonds. Hydrogen gas is said to be composed of two hydrogen atoms held together by a single, covalent bond; oxygen gas, two oxygen atoms and a double bond; methane, four equivalent C–H single bonds.

While the chemical bond plays a central role in chemical predictions, interventions, and explanations, it is a difficult concept to define precisely. Fundamental disagreements exist between classical and quantum mechanical conceptions of the chemical bond, and even between different quantum mechanical models. Once one moves beyond introductory textbooks to advanced treatments, one finds many theoretical approaches to bonding, but few if any definitions or direct characterizations of the bond itself. While some might attribute this lack of definitional clarity to common background knowledge shared among all chemists, I believe this reflects uncertainty or maybe even ambivalence about the status of the chemical bond itself.

This kind of ambiguity has led chemists to different conclusions. Most commonly, chemists adopt a pragmatic stance and simply demand that bonding theories be useful for making predictions and aiding in the synthesis of new molecules. The underlying ontological status of the bond holds little interest. Although useful to everyday chemical practice, this approach is deeply unsatisfying to the philosopher of chemistry because it leaves unanswered fundamental questions about the nature of the chemical bond.

Other chemists, including ones of deep realist commitment, draw a different and more skeptical conclusion from these facts. Robert Mulliken, a founder of quantum chemistry said, “I believe the chemical bond is not so simple as some people seem to think.” (Coulson, 1960) Charles Coulson, another founder wrote that the chemical bond “is a figment of our imagination.” (1952) These chemists believe that progress in quantum chemistry shows that there is something deeply flawed about the chemist’s notion of the bond. While this degree of skepticism may be warranted in the end, it is a hard thing for most chemists to accept given the ubiquity and usefulness of the bond concept.

Whatever the ultimate verdict, entertaining Coulson and Mulliken’s skepticism

raises many deep philosophical questions about the nature of chemical bonds and molecular structure. These questions include: Are chemical bonds real? If so, should we think of them as entities? If bonds are not real, is the phenomenon of bonding real? If so, how should this phenomenon be characterized? What is the relationship between molecular structure and bonding?

These issues are complex and interrelated, and philosophers of chemistry are beginning to consider them. (Woody, 1998; Needham, forthcoming; Berson, forthcoming; Stemwedel, forthcoming; Hendry, forthcoming) Approaches to answering these questions necessarily involve the combination of philosophical analysis and argumentation with a close examination of chemical theory itself. The latter has proved especially difficult because the last 80 years have seen myriad theoretical models of varying complexity developed to account for molecular structure. Much of the diversity comes from different approximations and idealizations that are made in the course of developing such models. Different models say different things about the phenomenon of covalent bonding and no single model is obviously the correct one, making the task of philosophical analysis more difficult. The problem of unclear foundations for the chemical bond is thus compounded by the diversity of models of structure and bonding.

This paper addresses one of these issues: It asks what the myriad models of molecular structure collectively say about the nature of bonding. Specifically, it asks whether models of molecular structure endorse a structural conception of covalent bonds. To cope with the multiplicity of models, I will follow a modified form of robustness analysis. (Levins, 1966; Wimsatt, 1981; Weisberg, 2006; Weisberg & Reisman, ms) As in standard robustness analysis, I will examine multiple models of molecular structure, looking for features and predictions common to models. Where this paper will differ from standard robustness analysis is that we are already in possession of an external calibration point for the predictions of each model: experimentally measurable quantities. Using this external standard, we can examine successively more predictively accurate model types, investigating the general features that these models have and which ones they lack. Approaching the problem

in this way will let us determine which bonding features of molecular models are on the surest theoretical footing, the features which ought to guide our inquiry about the foundations of covalency.

## 1 The Structural Conception of Bonding

The chemical literature often describes covalent bonds in structural terms, employing what I will call the *structural conception* of bonding. In subsequent sections, I will investigate whether this conception is robust and if not, which features of bonding are robust. In order to carry out this analysis, I will rely on a working definition for the structural conception of bonding. Characterized in purely functional terms, the structural conception of bonding says:

A covalent bond is a directional, submolecular relationship between individual atomic centers that is responsible for holding the atoms together.

As this initial definition is functional, it does not say what realizes the role of the bond. Defining the bond this way will be useful in historical studies because bonds were an important part of chemical theory before the discovery that electrons played a role in bonding.

In modern chemistry, it is completely uncontroversial to see electrons or electron density as what realizes the submolecular relationship. This leads to the following structural conception of bonding:

A covalent bond is a directional, sub-molecular region of electron density located between individual atomic centers that is responsible for holding the atoms together.

This conception tells us three important things about the nature of covalent bonds. First, it distinguishes covalent bonds from ionic bonds with the directionality restriction. Ionic bonds are omni-directional electrostatic interactions between

positively and negatively charged ions. Covalent bonds are regions of electron density that bind atoms together along particular trajectories. Second, this conception says that bonding is a *sub-molecular* phenomenon, confined to regions between the atoms. This eliminates the possibility that bonds are a molecule-wide phenomenon. Third, the region of electron density between the atomic centers has to hold these centers together, which I will interpret to mean that they are closer together than they would have been in the absence of the bond. In other words, bonds are a *stabilizing* force for the molecule, and this stabilization will manifest itself in the amount of energy required to separate the atomic centers.<sup>1</sup> The next sections ask how robustly this conception of the chemical bond is represented in models of molecular structure.

## 2 Valence Bond Models

Valence bond models are the first type of quantum mechanical treatment of molecular structure I will discuss. These models can be thought of as “bringing together complete atoms and then allowing them to interact to form bonds.” (Carroll, 1998, 24) In other words, covalent bonds are formed when two isolated atoms, each possessing a full complement of protons, neutrons, and electrons, are brought together and allowed to interact. The change in electron distribution and the resulting energetic stabilization from this change is taken to be the bond. All of this has to be unpacked in some detail, but we need to begin by considering what a quantum mechanical description of an atom looks like.

The quantum mechanical description of atoms and molecules are given as wavefunction of the form  $\psi(x, y, z, t)$ . Different molecular modeling techniques will generate somewhat different wavefunctions for the molecule in question because of the different approximations they employ. In all of the bonding models I will discuss, several simplifying assumptions will be made: First, I will only focus on the

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<sup>1</sup>For further discussion about the structural conception as well as other conception of covalent bonding, see Hendry, forthcoming.

electrons and hence on the electronic wavefunctions.<sup>2</sup> Second, I will only examine time-independent wavefunctions, taking into account the spatial properties of the electronic wavefunctions, but not how they evolve in time. Third, I will only discuss models of molecular hydrogen ( $H_2$ ), a two-proton, two-electron system. Because this system only has two electrons, it is safe to simply assume that the electrons have opposite spin. This will prevent us from having to explicitly keep track of the spin component of electronic wavefunctions, which would make the analysis more complicated.

I will begin the robustness analysis with the simplest possible valence bond model of hydrogen, one that most closely embodies the structural conception of bonding.

## 2.1 Simple Valence Bond Model

The first model of  $H_2$  is constructed by multiplying together two wavefunctions corresponding to the electrons originally associated with two individual hydrogen atoms. The electrons are still “tied” to the nuclei that they came to the bond with.

Let  $a$  and  $b$  denote electronic wavefunctions centered around two distinct hydrogen nuclei. They will each bring along an electron which we will designate as 1 and 2. This simple model keeps the first electron (1) in the vicinity of the first hydrogen nucleus ( $a$ ) and the second electron (2) being in the vicinity of the second nucleus ( $b$ ), but multiplies them together to represent the mixing of the wavefunctions upon bring the atoms together. Mathematically, this can be expressed as follows, where  $c$  is a normalization parameter:

$$\psi_1 = c a(1)b(2) \tag{1}$$

Using this wavefunction, the Hamiltonian for the molecule, and the Schrödinger equation, we can calculate the dissociation energy of the molecule described by this

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<sup>2</sup>The assumption that the nuclear and electronic wavefunctions can be computed separately is called the Born-Oppenheimer approximation. (Born & Oppenheimer, 1927)

wavefunction. The dissociation energy is the energy required to pull the atoms apart, removing the interaction between them and hence destroying the covalent bond. Using this model, the dissociation energy is calculated to be 24kJ/mol. We can also calculate the equilibrium distance between the atomic nuclei. This gives us what is usually called the *bond length*. In this model, the equilibrium bond length is calculated to be 90 pm.

We can check these predictions against experimental measurements of these properties. The simple valence bond model predicts 24 kJ/mol and 90 pm, but experimental investigation has measured the bond length to be 74.1 pm and the dissociation energy to be 458.0 kJ/mol. We are in the right ballpark, but clearly there is much room to improve our model. The first improvement will be to loosen the spatial restriction of each electron.

## 2.2 The Heitler-London Model

A substantial improvement in accuracy can be made to our simple model of the H–H bond. The model was first proposed by Heitler and London (1927). It starts from the model discussed in §2.1, but modifies it by making the following observation: The electrons are indistinguishable and hence it is arbitrary to have put electron 1 around atomic center *A* and electron 2 around atomic center *B*. The model thus considers a compound wavefunction, generated from the one discussed in §2.1 and the following:

$$\psi_2 = c a(2)b(1) \tag{2}$$

This corresponds to the electrons “swapping places.”

In quantum mechanics, complex wavefunctions can be built up by taking linear combinations of simpler wavefunctions, which are sometimes called *bases* or *basis sets*. Thus our full wavefunction will be the linear combinations of (1) and (2). These linear combinations can be written as follows:

$$\psi_{\text{BOND}} = c a(1)b(2) + c a(2)b(1) \tag{3}$$

$$\psi_{\text{ANTI}} = c a(1)b(2) - c a(2)b(1) \quad (4)$$

Since we will be confining our discussion to the ground state energies of the electrons, we will not consider (4) further, as this corresponds to an excited state, where the bond would actually be broken. Confining our attention then to (3), let's consider what the wavefunction tells us qualitatively about the distribution of electrons. If we think about them as particles, it tells us that they are free to move between the atoms, but in a coordinated fashion. They must always be near opposite atomic centers, but they still have mobility. It is impossible for a verbal description to be fully accurate, but a somewhat better description is that when we calculate the probability distribution of the electrons through space ( $\Psi\Psi^*$ ), we find that there is a buildup of electron density between the two atomic centers, with maximum electron density centered on each of the two atomic centers. The biggest difference between this model and the simpler one considered in the previous section is that the electrons have greater mobility and there is a greater distribution of density throughout the molecule.

How well does the Heitler-London model predict the measurable properties of H-H bonds? Considerably better than the simple valence bond model, it turns out. The bond distance is calculated to be 86.9 pm, which is a little better than the simple model, but the dissociation energy is calculated to be 303 kJ/mol, which now brings it to the same order of magnitude as the measured value. By allowing for electron mobility, the model is brought in to closer alignment with the experimentally measured values. This is a theme that I shall return to throughout the paper.

### 2.3 Improving Valence-Bond Models

The Heitler-London model can be improved further if we take the Heitler-London wavefunction to be a just one part of the basis for a more complex wavefunction. In other words, we add additional terms corresponding to other characteristics the



wavefunction might have. I will only discuss one example of this, but it illustrates a very general principle at the heart of modern model building in quantum chemistry.

One thing that the Heitler-London model does not do is take in to account the possibility that the molecule could have ionic character. In other words, it does not allow for the possibility that there is a greater distribution of electron density on one side of the molecule or the other, however briefly or however slightly.

We can take this possibility in to account by adding in additional terms corresponding to an ionic distribution of electron density, which at the extreme would correspond to the electrons both being on one side of the molecule or on the other side (e.g.  $a(1)b(1)$ ). At the same time, we do not want to over-compensate, adding too much ionic character. One way around this is to add an adjustable parameter  $\lambda$  to each term. The wavefunction is then optimized by setting  $\lambda$  to some value, calculating the energy of molecule, then trying another value for  $\lambda$ , and keep iterating until we find the lowest value, making the well-motivated assumption that the ground state electronic wavefunction will be the one with the lowest energy.<sup>3</sup> The new model has the following wavefunction:

$$\psi_{\text{ionic}} = c a(1)b(2) + c a(2)b(1) + \lambda c a(1)b(1) + \lambda c a(2)b(2) \quad (5)$$

Adding these ionic terms considerably improves the model, allowing us to calculate 388 kJ/mol and 74.9pm, bringing the dissociation energy of the model even closer to the experimental value.

Having looked at three successively improved valence bond models, let's consider what they have told us collectively about the structural conception of bonding. First, by letting the electrons have greater mobility, as in the Heitler-London approach, the model came closer to agreement with experimentally measured quanti-

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<sup>3</sup>Technically, we also rely on the variation theorem which tells us that this procedure will only every overestimate the energy, but not under estimate. Thus we can keep varying parameters until we get the energy minimum, without fear that we are underestimating. (Levine, 1991)

ties. When the model was made even more flexible, allowing the electrons to travel further afield and giving the model ionic character, the model came in even better agreement with experimental measurements. This trend continues with increasing electron mobility: In 1968, Kolols and Wolniewicz used a 100-term, highly flexible wavefunction, and after optimizing the parameters, they came within 0.01kJ/mol of the measured values. (Kolols & Wolniewicz, 1968) Thus the result most strongly robust among these many models of the covalent bond is that greater electron mobility leads to greater stabilization and closer agreement to experiment.

What do these valence bond models say about our three criteria for the structural conception of bonds? First, they are directional and allow us to distinguish between ionic and covalent bonds. However, as we have just seen, adding ionic character actually stabilizes many molecular models such those for H<sub>2</sub> model. Second, while the simple valence bond models start out with sub-molecular regions of electron density that we can identify as the bond, they are improved by allowing the electrons to have increased mobility, spreading some of the density throughout the molecule. Finally, the valence bond models do nothing to challenge the idea that bonds hold the molecule together.

### 3 Molecular Orbital Models

Our robustness analysis will continue with a second, distinct approach to constructing molecular models: the *molecular orbital* method. Rather than looking at bonding as what happens when we bring together two atoms and let them interact, we start off with atomic centers at equilibrium distances, then calculate electron wavefunctions for the entire molecule. The electrons are affected by a potential field generated by the nuclei collectively.

As with valence bond models, one can start with an arbitrary form for the molecular orbital wavefunction, and then improve the model by adding more terms and adding adjustable parameters on these terms. We will start with a simple trial wavefunction for H<sub>2</sub> to illustrate some of the key features of molecular orbitals. A

prudent way to begin is to use wavefunctions corresponding to linear combinations of the atomic orbitals of our two hydrogen atoms, which we will call A and B. So we have:

$$\psi_{\text{bond}} = \psi_A + \psi_B \quad (6)$$

$$\psi_{\text{anti}} = \psi_A - \psi_B \quad (7)$$

Equation 6 gives us the lower energy bonding wavefunction, while equation 7 gives us the higher energy anti-bonding wavefunction. If we want to calculate the total electronic wavefunction for the molecule, corresponding to adding the two electrons into the hydrogen molecular orbital, we take the product of the wavefunction for each orbital.

$$\psi_{\text{H}_2} = \psi_{\text{bond}(1)}\psi_{\text{bond}(2)} \quad (8)$$

Combining equation 6 with equation 8, we get the following expansions:

$$\psi_{\text{H}_2} = [\psi_{A(1)} + \psi_{B(1)}][\psi_{A(2)} + \psi_{B(2)}] \quad (9)$$

$$\psi_{\text{H}_2} = \psi_{A(1)}\psi_{A(2)} + \psi_{B(1)}\psi_{B(2)} + \psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)} \quad (10)$$

Interesting structure emerges from the terms in this equation. The third and fourth terms ( $\psi_{A(1)}\psi_{B(2)}$  and  $\psi_{A(2)}\psi_{B(1)}$ ) are exactly the same terms as those found in the Heitler-London model of the  $\text{H}_2$  molecule. This corresponds to a single electron being located in the vicinity of each nucleus. However, there are two additional terms  $\psi_{A(1)}\psi_{A(2)}$  and  $\psi_{B(1)}\psi_{B(2)}$  which correspond to the electrons simultaneously positioned near the A nucleus or the B nucleus. These ionic terms corresponding to asymmetric electronic distributions had to be added manually to the Heitler-London model. So right from the start, this model includes the possibility of ionic character in what would classically be treated as a non-polar, covalent

bond. We will come back to this point below.

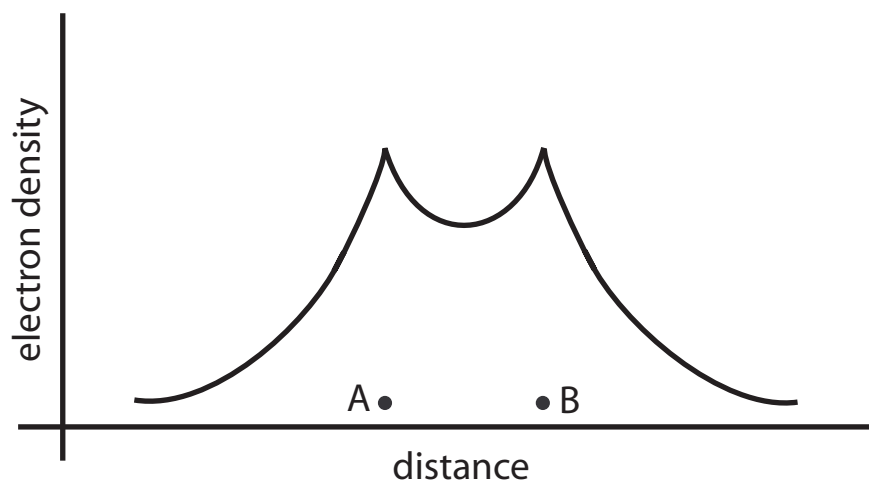
How does this simple molecular orbital model conform to experiment? If we calculate the dissociation energy and bond distance predicted by this model, we come up with  $-260\text{kJ/mol}$  and  $85\text{pm}$  respectively, values which accord reasonably well with the measured values of  $-458.0\text{kJ/mol}$  and  $74.1\text{pm}$ . These values are similar to those calculated with the Heitler-London model, but considerably better than those calculated with the simplest valence bond model.

One of the interesting things about molecular orbital models of bonding is that very little classical structure is built in from the beginning. Essentially, the nuclear centers are oriented in space, then electronic wavefunctions are constructed, relying only on the potential field generated by these atomic centers. In accurate calculations, we also search for the equilibrium distances of the atomic centers by moving them around to find the minimum total energy for the molecule. Even in this simple model, we see some interesting and non-classical structural features.

First of all, there is the importance of the aforementioned ionic terms. This suggests that there is far greater electron mobility than in a case of two isolated atoms. Further, the electronic density is at its peak in the areas immediately surrounding the nuclear centers. Figure 1 is a cross-section of the amplitude of the wavefunction of  $\text{H}_2$  calculated from our model. We can see that the highest density is just around the nuclear centers, with considerable density in between the atomic centers, but also a reasonable amount of electronic density on the far sides of the atomic centers.

There are many ways to improve this simple molecular orbital model, some of which will be discussed in the next section. But even from this very simple model and the Heitler-London model discussed in the last section, we can see the continuation of the pattern that has been emerging. Electron mobility or delocalization of electron density is a prominent feature of this model of molecular structure. The electrons are not sitting between the two atoms holding everything together; rather, they are distributed throughout the molecule. This puts pressure on the second part of the structural conception of bonds, the idea that bonds are sub-molecular

Figure 1: A cross-section of the electronic density distribution calculated from a molecular orbital model of hydrogen. This diagram is not to scale.



phenomena. Similarly, delocalization makes the bonds less directional. The nuclei are still located in particular places that minimize the total energy of the molecule; however, the bonds themselves are considerably more diffuse. As we will see in the next section, the trend continues with more complex molecular orbital models.

## 4 Modern Molecular Orbital Models

The methods considered so far were worked out for simple molecules in the first half of the twentieth century. Since that time, there has been considerable progress in developing models which can yield more accurate calculations of molecular properties. To review all of these methods here would be impossible and unnecessary; however, many modern methods can be seen as systematic improvements to molecular orbital models along two dimensions relevant to the structural conception of bonds.

The first type of improvement involves using more complex basis functions as trial wavefunctions. These basis functions are expanded by taking in to account many possibilities (with adjustable parameters), including greater delocalization of the electrons as well as occupation of higher energy electronic states. Just as ionic terms are “mixed” in to the valence bond wavefunctions, so too these spatially diffuse, delocalized, and higher energy states are mixed in to the starting molecular wavefunctions.

The second dimension on which modern methods improve upon simple molecular orbital models is in the nature of the optimization of the wavefunction, given the basis set. I have already alluded to the way calculations are typically performed using simple molecular models, a method called the Hatree-Fock method. The method works as follows:

1. Make an initial guess of the position of the nuclei.
2. Start with initial values of the parameters on all the electronic terms in the trial wavefunction.

3. Choose the terms corresponding to a single electron, then vary the parameters on those terms in order to minimize the energy.
4. Repeat the step 3 for each electron in sequence.
5. Repeat step 4, cycling through all of the electrons until the energy values no longer change, having reached self-consistency of the orbitals with the field generated by the electrons.
6. Perturb the nuclei a small distance and repeat steps 2–5, searching for an energy minimum. (Levine, 1991; Anslyn & Dougherty, 2005)

Although wavefunctions calculated with the Hartree-Fock method can yield excellent results, the method does not take in to account electron *correlation*. Recall that electronic wavefunctions are optimized from the point of view of a single electron. The method imagines that each electron is influenced by a field generated by the stationary distribution of all of the other electrons. It moves systematically through the electrons, treating them in this fashion, until self consistency is achieved. But any two electrons in the vicinity of one another will repel one another and this is not taken in to account in the Hartree-Fock method. Hence a more accurate calculation would take this electronic correlation in to account. One method for doing this is called *configuration interaction*.

Configuration interaction approximates the affect of electron correlation by constructing a new molecular wavefunction from linear combinations of the ground state and electronically excited molecular wavefunctions. Each of these terms has a coefficient that can be varied in order to minimize the total energy. The resultant wavefunction from a configuration interaction calculation will take the following form:

$$\Psi_{\text{CI}} = c_1\Psi_1 + c_2\Psi_2 + c_3\Psi_3 + \dots \quad (11)$$

A full configuration interaction calculation would take in to account all of the excited states of the molecule. In practice, only a few excited states are usually taken

in to account because of the great computational cost of these calculations.

These approximation methods and others are interesting, but take us away from the important question that is needed for robustness: What do successively better calculations that take in to account CI tell us about bonds?

We can answer this question by reflecting on why configuration interaction allows us to build very good molecular models that take into account electron correlation. Remember that correlation is the property of the electrons “avoiding” one another because of electron-electron repulsions. Conceptually, adding in these repulsions will change the shape of the molecular orbital, because the electrons may spread apart further in space. A systematic way to alter the shape of molecular orbitals is to mix in orbitals corresponding to excited states, which will have different shapes and symmetry properties from the ground state orbital. When enough of these are mixed together, we will have the flexibility to accurately describe the resultant molecular orbitals for the molecules, orbitals which correctly account for correlation as well as the nucleus-electron attractions that account for the electronic distribution. (Anslyn & Dougherty, 2005, 824)

Configuration interaction is another example of how moving electrons out of the classical bonding region stabilizes the molecular model and brings it in to closer agreement with experimentally determined values. When we allow for greater delocalization, taking in to account electrons temporarily entering higher energy states so as to avoid one another, molecular models increasingly agree with experimentally measurable quantities.

## **5 Robust Properties of Chemical Bonds**

We have now come to the conclusion of our whirlwind tour of molecular models, searching for the robust properties of chemical bonds. In this concluding section, I will review what we have discovered, examining both what is and what is not robust across models of molecular structure.

Our examination of molecular models began with the simple valence bond



model, the one that most faithfully illustrates the structural conception of bonding. In this model, electrons were associated with particular nuclei and as a result, the molecule was represented by bringing together two atoms, letting their electrons interact, and taking advantage of the stabilization created by this interaction. The electrons remained associated with a particular nucleus and could be seen as being shared between two atoms to form a bond.

This idea of electrons coming along with nuclei and being shared between two nuclei is resolutely *not* robust across bonding models. As we move in the direction of models which correspond more accurately to experimentally measurable values, this property diminishes and seems to vanish altogether in modern models.

The structural conception does not demand that electrons are shared or even fully located in the region between the atoms. Indeed it only demands that bonds can regularly be identified as directional, sub-molecular regions of electron density. So what we really need to know is whether such regions of density can be identified in molecular models. Answering this question is considerably more difficult and this paper certainly gives no definitive answer to it; however, the properties which we have found to be robust go a long way towards answering it.

Among the bonding models, several things have been shown to be robust. In the examples we have considered, the models became energetically stabilized by forming the bond. Energy is liberated when the bond is formed — conversely, it takes energy to break a bond. This means that for atoms that readily form covalent bonds, it is energetically more stable for them to be in the bonding state than separated from each other such that the electrons cannot interact. Bonding seems to fundamentally involve energetic stabilization.

The second robust feature of the models is that greater electron mobility or delocalization leads to stabilization. When we moved from the simple valence bond model to the Heitler-London model, we saw considerable stabilization. This accompanied relaxing the restriction that pinned electron 1 to nucleus A and electron 2 to nucleus B. We further improved that model by adding terms to the basis function which allowed greater flexibility to the resultant wavefunction, which has

the physical significance of allowing greater delocalization.

The same is true in the molecular orbital models. Even the simple molecular orbital models represent the electrons as delocalized across the molecule. Improvements to the molecular orbital model involved using basis functions with greater numbers of terms, which also allows more flexibility in describing the electronic distribution, a distribution which is not tied to the classical positioning of the electrons in between the nuclei.

These robust features of molecular models put considerable pressure on the structural conception of bonds, and are no doubt the sorts of results that led Coulson and Mulliken to their skepticism about the reality of bonds. To be explicit, the robust conception says that covalent bonds are directional, sub-molecular regions of electron density that hold molecules together. Throughout this paper, we have seen that delocalization—density spread beyond the sub-molecular region between the atoms—is the norm in molecular models. Further, the addition of ionic character, correlation, and the mixing of higher energy states all seem to improve the model, but make the bonds less directional and sub-molecular.

I believe that this clearly rules out any straightforward version of the structural conception of covalent bonding. However, while the features I have pointed to that improve bonding models including correlation and ionic character involve deviations from local, sub-molecular regions of electron density, they themselves describe electronic characteristics of molecules in structural terms. They may in fact be compatible with a revised structural conception of bonding. While future analysis is required to either vindicate or fully reject the structural conception of bonding, the considerations in this paper go a long way towards motivating Coulson and Mulliken's skepticism about the reality of the covalent bond.

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