

A note on Michael Weisberg's: Challenges to the Structural Conception of Chemical Bonding

Hinne Hetteema

Department of Philosophy, The University of Auckland

October 15 2007

Abstract. Weisberg's 2007 recent paper on the chemical bond makes the claim that the chemical notion of the covalent bond is in trouble. This note casts doubts on that claim.

Keywords: Chemical bond, Models, Quantum Chemistry

In a recent proceedings paper, Michael Weisberg (2007) discusses some quantum chemical theories of the chemical bond to argue that the structural model of the covalent bond is in trouble. To do so, he focuses on two competing descriptions of the chemical bond, the Heitler-London description and the Hund-Mulliken description.

This note will argue that Weisberg's description of both the chemical bond and its quantum chemical underpinning is seriously flawed, and that for that reason his main conclusion has to be doubted.

I have to admit that I am to a significant degree dismayed by the level of ignorance displayed by Weisberg in the discussion of this particular topic. The source of my dismay is primarily that in my view philosophy of chemistry is a relatively new, highly interesting topic, which has the potential to add significant new material to philosophy of science proper. For that to succeed, philosophers of chemistry have to get their facts on chemistry straight, or at least err in interesting ways. In my view, Weisberg's paper fails in a more fundamental way and is detrimental to this undertaking.

This paper being a note, I wish to be brief with references to the literature, and mainly rely on some reasonably well-known and accessible sources. I am well aware of the fact that the use of for instance McWeeny (1979) especially for historical information in this area can be highly problematic, but the explanations offered here are simple and accessible also to the non-specialist. I have decided that for the purposes of the present paper this feature overrides the drawbacks of historical accuracy.

1. What is a covalent bond?

Weisberg formulates a minimal functional characterisation of the chemical bond as follows (page 4):

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

© 2007 Kluwer Academic Publishers. Printed in the Netherlands.

He then proceeds to realise this functional characterisation as a structural concept of bonding (page 4)

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 description seems a bit contrived, and its use here is surprising the sense that it does not fit with the explanatory aim of the two wavefunction constructions that are discussed subsequently: the Heitler-London and Hund-Mulliken wavefunctions. This might not be a problem *per se*: after all, both types of wavefunctions do make specific claims regarding the chemical bond, and an investigation into whether these descriptions do fit a particular notion of the chemical bond is not an *a priori* pointless undertaking.

Further on it does seem to become pointless, however. The problem is in my view that overall, Weisberg's characterisation of the covalent bond is a better fit with the structural view of chemistry as advanced by Pauling, but a more specific discussion of Pauling's contributions to this area is not part of Weisberg's paper. It probably should be.

The explanatory aim of the Heitler and London (1927) wavefunction was two-fold: to provide a quantum theoretical underpinning of the bonding between neutral atoms (ionic bonding being understood primarily in electrostatic terms at the time), and specifically, to provide an explanation for the existence of bonding between two H-atoms and the absence of such bonding between two He-atoms. Eventually, the explanation is given in terms of 'resonance' and the Pauli exclusion principle. The existence of electron density between the two atomic centres is a consequence of the Heitler-London approach, not a starting point.

The term 'resonance' in this context would go on to play an important role in further theorising on the chemical bond, again especially by Pauling, even though it seems to have been eventually discarded by the quantum chemistry community.

The explanatory aim of the Hund-Mulliken (see for instance Hund (1927)) approach was in the first instance the *qualitative* explanation of molecular spectra. As a result, the Hund-Mulliken approach developed its approach from the study of atomic spectra and focused primarily on the symmetry of individual molecular orbitals, which spanned the entire extension of the molecule.

In the 1930s these two approaches were thought to be radically different, and the fact that both could be extended to yield equivalent results was only gradually understood. For instance, in McWeeny (1979) we find a historical note stating that in earlier editions of Coulson's *Valence* the conflict between these two approaches was apparent but that it was resolved during the 1940s (this note is found in McWeeny (1979) on page 126).

It thus seems that Weisberg's primary concept of the chemical bond does not quite fit with the stated explanatory aims of the two approaches he subsequently discusses.

This is an important point, since the primary quantum chemical method that claims to match Weisberg's description of the covalent bond is the concept of *hybridisation*; a concept that is both deeply problematic within the principled explanatory framework of quantum chemistry¹ but that provides the directional component that is needed in Weisberg's concept of the covalent bond. That is, Pauling's structural notion of the chemical bond would have been a much better candidate to start the sort of discussion Weisberg wants to have.

All of this would not be so bad if Weisberg did not make directionality one of the key distinguishing features in the difference between the covalent and the ionic bond on page 4-5:

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.

The Heitler-London approach does not include directionality as such²; the Hund-Mulliken approach does this only with the inclusion of the notion of hybridisation. Thus there seems to be a mismatch between Weisberg's key definitional aspects of the covalent bond and the quantum chemical models he claims provide an explanation of this chemical bond.

The main problem in my view is the lack of a definite notion of directionality in the models of the chemical bond Weisberg chooses to discuss. A discussion of the hydrogen bond is not able to capture directionality in full because the molecule is linear; at a minimum Weisberg's discussion would have to focus on molecules with more than two atoms³ such as NH_3 or CH_4 . At this point at least, Weisberg's discussion becomes selective and already contains his conclusion.

2. Wavefunction Construction

We next turn to the description of the quantum chemical wavefunctions that make up an important part of his paper. Weisberg makes a significant number

¹ There is ample literature discussing this fact, see for instance the summarising table and references in (van Brakel, 2000) on page 137 for an example.

² A small 'directional' modification of it is the Coulson-Fischer wavefunction which Weisberg does not discuss; this approach is discussed in McWeeny (1979) on page 130.

³ It should be noted that a discussion of hybridisation is possible for two-atomic molecules.

of typographical and real errors in the basic formulas and fails to recognise the importance of the rather simple manipulations that prove the equivalence of refined versions of both the Valence Bond (VB) and Linear Combination of Atomic Orbitals (LCAO) or Molecular Orbital (MO) approaches. The basic manipulations can be found in many places in the literature (see for instance McWeeny, McWeeny (1989, 1979)).

In his discussion of the Heitler-London approach Weisberg seems to entirely neglect the discussion of antisymmetry and electron spin in his wavefunction constructions. These are fairly serious omissions. Since electrons are fermions, the overall wavefunction has to be antisymmetric under permutation of the electrons.

It is unfortunately not clear from the context whether Weisberg wants to have a primarily *historical* orientation or whether he wants to treat the modern equivalent of the VB wavefunction. If it is the former, Weisberg's starting equations correspond to those of Heitler and London. In that case a discussion of paragraph 4 of Heitler and London's paper, dealing with the Pauli exclusion principle would have been in order. If it is a modern version he is after, then the spin functions should have been included.

In the remainder I will assume that it is the modern formulation he is after, since the VB wavefunction is ultimately contrasted with the molecular orbital (MO) and Configuration Interaction (CI) wavefunctions.

The overall wavefunction consists of a spatial part and a spin part, and the VB wavefunction for the hydrogen molecule is given in (McWeeny, 1989) as follows (where we have neglected normalisation factors and written electronic coordinates as (1) rather than as r_1, s_1 etc. to simplify the notations):

$$\Psi_g(1, 2) = [a(1)b(2) + b(1)a(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (1)$$

$$\Psi_u(1, 2) = [a(1)b(2) - b(1)a(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)] \quad (2)$$

This equation is structurally similar to Weisberg's equations (3) and (4), but they correspond to different spin states—the first one is the lowest singlet state and the second one the lowest triplet state. Ignoring spin entirely, Weisberg misses out on one of the key explanatory features (and possibly one of the key philosophical issues) of the Heitler-London paper. The chemical bond is a result of the Pauli principle. Heitler and London discuss this in section 4 of their paper. The g and u in the subscripts stand for 'gerade' and 'ungerade' which translates into 'even' and 'odd' rather than, as Weisberg would have it, BOND and ANTI.

The latter two terms stem from the construction of molecular orbitals by Hund and Mulliken, which Weisberg discusses subsequently. Oddly enough, in this section all electronic spatial coordinates of the orbitals (which Weisberg also writes as (1) rather than as r_1) end up as subscripts in this section. It is hard to make out whether this is a typo or something deeper—it happens in all subsequent expressions.

There are some further issues with Weisberg's description of wave function construction, which I will briefly discuss here.

Weisberg's remark on basis sets while he discusses wave function construction in the Heitler-London method on page 7

In quantum mechanics, complex wave functions can be built up by taking linear combinations of simpler wavefunctions, which are sometimes called bases or basis sets.

displays considerable ignorance of the methods of quantum mechanics. Basis sets do play a role in quantum chemistry, but not quite at this stage. Wave function construction in this particular instance deals with atomic orbitals, and Heitler and London actually use the exact solutions for the hydrogen atom and do not refer to basis sets at all as Weisberg seems to suggest.

When Weisberg subsequently discusses the calculation of Kolos and Wolniewicz he fails to mention that these calculations are based on explicitly correlated (modified Hylleraas type) wave functions, an approach that is very different from the two approaches he has so far described, even though they share some surface similarity to the methods he has discussed. His conclusion with regard to this calculation

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.

is entirely misguided. It seems to be based on the idea that having more terms and flexibility in the wave function leads to a greater degree of electron mobility, a conclusion that is not borne out by the actual calculation he is referencing. At various instances, Weisberg also seems to confuse electron 'mobility' with 'delocalisation'.

The next section on 'modern molecular orbital methods' is very confusing and I cannot offer much in the way of a detailed critique. It would seem to me that Weisberg gets his description of the procedural components of a Hartree-Fock calculations wrong. The HF process depends on a simultaneous optimisation of coefficients, and the necessary and sufficient condition for a HF wavefunction is the Brillouin theorem. A key feature of this situation (and one pertinent to Weisberg's claim) is that the exact shape of the orbitals is underdetermined by the HF equations, and that there exist 'localisation' procedures for HF orbitals which would seem to merit at least some discussion in this particular context (see for instance (McWeeny, 1989) for a discussion of this).

Similarly, Weisberg offers a confusing discussion of the configuration interaction approach, an approach that is actually very simple in terms of the simplified wave functions that he focuses on, and that has been explicitly described by McWeeny (1979) and related to the Valence Bond approach. McWeeny (1979) is worth quoting here (page 126):

There is thus no real conflict between MO and VB theories; they offer somewhat different first approximations to molecular wavefunctions but converge to the same results as they are systematically refined. The importance of this conclusion can hardly be overemphasized.

This statement alone goes a fair way to answering Weisberg's main question on page 16 of his paper

What do successively better calculations that take in to account CI tell us about bonds?

Weisberg's subsequent characterisation of configuration interaction is plain wrong:

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.

In fact, in the case of the CI wavefunctions one can well argue that they do the opposite. It should have been obvious even from Weisberg's flawed mathematical expressions that the 'ionic' states are 'overweight' in the LCAO method, and this 'excess of delocalisation', if you must, is a key contributing factor to problem that this method does not correctly describe the dissociation energy of molecules. The CI method corrects this deficiency, by putting additional weight on VB type structures, thus strengthening the structural picture of the chemical bond.

3. Stability analysis

Weisberg concludes that the 'myriad' of models that purport to explain bonding are not robust across models, in the sense that more refined models cannot, in fact, support the notion of the covalent bond'. In the light of the foregoing critique, I believe this conclusion needs to be discarded or at a minimum significantly revised.

Weisberg identifies the 'robust' features of his models as (i) energetic stabilisation, and (ii) the fact that greater 'electron mobility' leads to stabilisation.

We have already seen that Weisberg does not properly distinguish between adding additional variational terms to the wavefunction and the separate issue of these terms leading to potentially greater delocalisation of the electron in the bond. It is a fairly common feature of variational methods that an increase in variational parameters (even badly chosen ones in many cases) will lead to a minimisation of the variational property. This is not unlike the situation where adding 'fudge factors' to an equation will lead to that equation being better able to match experimental data.

These additional variational factors, however, do not automatically lead to additional delocalisation of the electron, as our previous discussion of the CI method pointed out.

I have already hinted that Weisberg's failure to discuss the concept of *hybridisation* is a key drawback for the ensuing discussion of directionality. It is therefore surprising that Weisberg's main conclusion reads

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.

It is striking that the 'robust conception' happens to match Weisberg's characterisation from the beginning of his paper almost word for word and does not really relate to the two features of the robust models identified earlier.

In my view, Weisberg's considerations are too basic to make any claims about directionality of the bond and his claim that 'delocalisation-density spread beyond the sub-molecular region between the atoms' is the norm in molecular models is wrong.

I conclude that Weisberg's final conclusions are dangerously limited by the lack of understanding of fundamental mathematics in general and quantum chemistry in particular that he displays in his paper. To conclude, it would be good to keep in mind a comment by Linus Pauling on structural chemistry:

I do not think that quantum mechanical calculations of molecular structure or crystal structure will ever make the sort of chemical arguments in my book [his 1939 *The Nature of the Chemical Bond*] obsolete⁴.

References

- Walther Heitler and Fritz London. Wechselwirkung neutraler Atome und homöopolare Bindung nach der Quantenmechanik. *Zeitschrift für Physik*, 44:455–472, 1927.
- Friedrich Hund. Zur Deutung der Molekelspektren I. *Zeitschrift für Physik*, 40:742, 1927.
- Roy McWeeny. *Methods of Molecular Quantum Mechanics*. Academic Press, 1989.
- Roy McWeeny. *Coulson's Valence*. Oxford University Press, 1979.
- Jaap van Brakel. *Philosophy of Chemistry*. Leuven University Press, Leuven, 2000.
- Michael Weisberg. *Challenges to the Structural Conception of Chemical Bonding*. Philosophy of Science Assoc. 20th Biennial Mtg (Vancouver): PSA 2006 Symposia., 2006.

⁴ Pauling as cited in van Brakel (2000).

