

Comparing Several Orbital Approaches to the Hydrogen Molecule

By Joel M Williams (text and image are © 2013)

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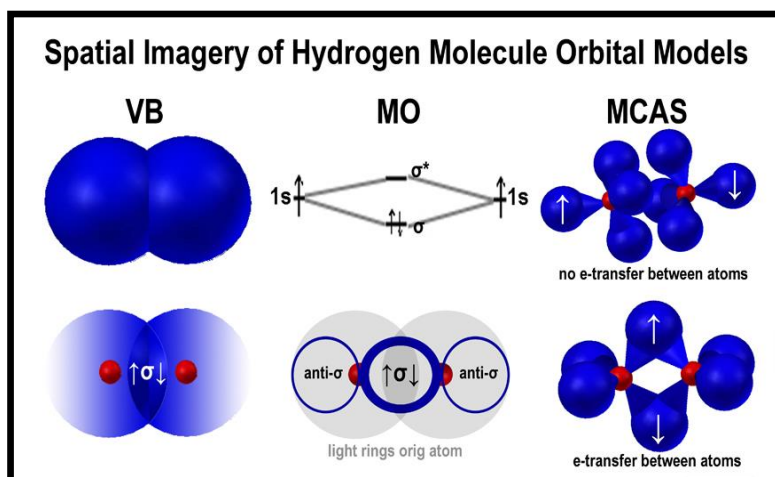
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Abstract

The current spdf and MO modeling of chemical molecules are well-established, but do so by continuing to assume that non-classical physics is operating. The MCAS electron orbital model is an alternate particulate model based on classical physics. This paper compares these models as applied to the hydrogen molecule.

The Molecular Orbital approach to the bonding of molecules is touted to be the proper one to address the bonding issue and maybe the hybrid atomic orbitals need to be archived¹. While MOs might address energy levels and presumably bond order better, they have substantial shortcomings when it comes to addressing reaction mechanisms and molecular spatial arrangements. In many ways, the tinker toy/simple VB approaches to molecules and their interactions gave and will continue to give students and practitioners a hands-on mental grasp of what might be occurring at the femto-level. It is this 3D spatial appreciation of molecules that is sacrificed in the MO effort to emphasize energy levels. This short paper takes a look at the spatial implications of the MO approach compared to those of the Valence Bond (VB) and MCAS² models.

The figure at the right presents conceptual imageries of the Valence-Bond (VB), Molecular Orbital (MO) and MCAS approaches to the hydrogen molecule. This allows the three to be compared in the simplest molecular case. The VB and MO representations are illustrated tightly as implied by having two electrons located between the nuclei. Some readers would probably prefer that the e-fields be rather wide-spread to bath the nuclei with negativity - just how this occurs given the implied proximal constraint on the electron pair requires some imagination.



The bond strength of H-H (436 KJ/mole) is almost equal to that of O=O (497 KJ/mole). Thus, the two electrons provide significant coupling. The data tell us how much; what makes it happen is a different matter.

Two MCAS possibilities are given in the figure. The "no e-transfer" version is purely electrostatic with the electrons on each atom paired in motion with that of the other. Note that there all no antibonding electrons to destabilize the bond. The "e-transfer" version has the two electrons flow through the joined M-orbitals in concerted opposition; they are thus paired. The latter would provide synchronous looping from one nucleus to the other.

¹ "Is It Time To Retire the Hybrid Atomic Orbital?," Alexander Grushow, <http://pubs.acs.org/doi/full/10.1021/ed100155c>, J. Chem. Educ., 2011, 88 (7), pp 860–862

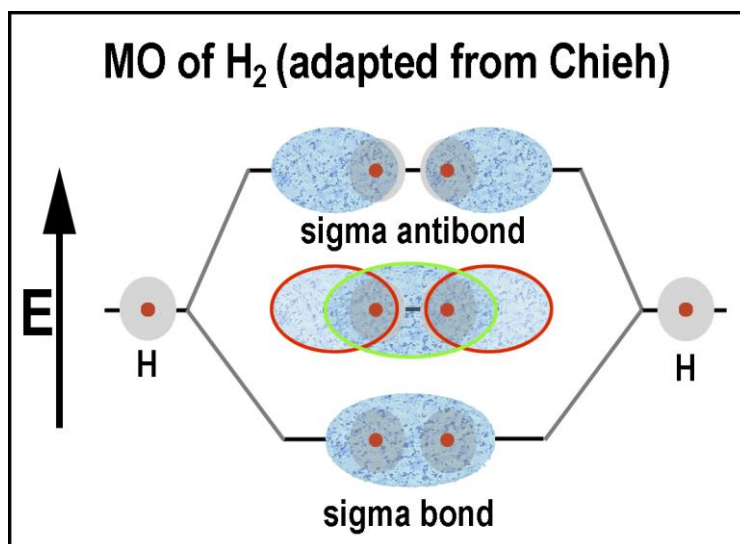
² "Modeling the MCAS Way" (<http://arxiv.org/html/physics/9902046v2>); shaper image version at <http://pages.swcp.com/~jmw-mcw/science>; "The MCAS Electron Orbital Model" - <http://vixra.org/abs/1205.0114> or http://pages.swcp.com/~jmw-mcw/MCAS/The_MCAS_Electron_Model_Booklet_for_web.pdf (booklet); all by the author

Resonance energy? Both MCAS versions provide significant negativity around both nuclei as the electrons are free flowing through the orbital quartets. Which version is correct would take more detailed analyses.

The VB and MO treatments, on the other hand, call for both electrons to be cloistered between the nuclei to effect bonding. The commonly shown VB model in the upper left of the figure is hardly an accurate portrayal of the negativity with the electrons so cloistered. If fact, what is the basis for assuming that the electron cloud has nearly the same "probability distribution" of negativity (i.e, electron presence!) when the electrons are cloistered between the nuclei as when they are not? The bottom VB illustration is probably more accurate although it probably still shows too much negativity on the axis exo to the bond. The MO model is more explicit in its bonding/antibonding orbital assignment which leaves the ends bare-naked with unfilled antibonding orbitals. Such exposure of the nuclei as indicated by the VB and MO orbital models is hardly what one would expect for a molecule as stable as diatomic hydrogen.

Of course, $O+O$ might equal ∞ (a conjunction?), but now we are talking MCAS and orbital pathways through which electron particles and their associated negativity flow while avoiding others with like attributes. As long as electrons are considered particles, it is reasonable to assume that their negativity is an inherent property that they carry with them and not something strewn in their wake. Whether they leave a persistent "charge-related" effect in the orbital space as they rapidly and repeatedly pass through is a different matter.

Serious consideration of spatial placements and e-e repulsions should raise major concerns, indeed, about the spdf-hybrid system and its MO offshoot. Some (many?) would say I have taken too narrow a view of the VB and MO models. I would counter that the VB and MO models take matters too loosely. For example, what is the mechanism for the MO sigma bond/antibonds orbitals for the hydrogen molecule covering so much space as indicated in a typical MO figure [see the figure on the right (adapted from ref 3)]. The appearance is that the electron clouds are just nebulous ovules drawn around points and squished together. If there is any probability of an electron being somewhere, there needs to be a rational reason (path) for its getting there. In fact, what are those spin-paired electrons doing while they are in the sigma bond? If there is so much force to have them concentrate on the axis between the nuclei, how can there be much extended coverage exo the bond. The image in the center gives a composite of all the components. The packaging is tidy with bands demarking some limit of probability, but it gives no indication about the machine inside nor how it works. The extent of the bonding zone should be tighter in the molecule than in the atom since the 1st ionization of the atom is 13.6 eV⁴ whereas that of the molecule is 13% higher at 15.4 eV⁵. In this particular representation, I am not trying to single out Chieh by any means, but rather critiquing the vagaries of the MO concept!



³ "Molecular Orbitals of H₂", <http://www.science.uwaterloo.ca/~cchieh/cact/fig/sigma1s.gif>;
<http://www.science.uwaterloo.ca/~cchieh/cact/c120/mo.html>

⁴ http://chemwiki.ucdavis.edu/Inorganic_Chemistry/Descriptive_Chemistry/Periodic_Table_of_the_Elements/Ionization_Energy

⁵ Walker Bleakney, Phys. Rev. 40, 496–501 (1932) Walker Bleakney, http://prola.aps.org/abstract/PR/v40/i4/p496_1;
and A. G. Khrapak, W. F. Schmidt, and K. Yoshino (published after 2003)
http://www.researchgate.net/publication/4163009_Ionization_potential_and_nature_of_charge_carriers_of_fluid_hydrogen_in_wide_pressure_interval/file/79e4150bb42806fb8f.pdf

MO imagery is much like the statement that “two is company, but three is a crowd” – why that is so requires more delving than simply making the observation. MO diagrams are like observing that stable marriages, wherein two can live together cheaper than two separately, become quite unstable and break up when an interfering third comes along – just a tabulation of the average costs of people or electrons bonding and debonding.

The MCAS model, on the other hand, provides a physical representation that does not resort to e-e non-repelling couplets and stresses coverage of the nuclei on all fronts, rears, and sides. As long as electrons are considered particles and move rapidly, they need “flyways”!

VB and MO approaches do not define how and where electrons move very well. In fact, the MO approach just treats the electrons as “blue hazes”. Somehow, body parts and the world around us seem more substantial and orderly connected than this. Considering their reproducible atomic and molecular electronic spectra, their constant physical properties, etc, etc, etc, electrons are certainly operating in well-defined manners and NOT in “blue hazes”! After a century of thinking about them, we should have a clearer notion of how these little atomic machines juggle their electrons so consistently; especially considering that scientists seem ready to claim they know all about what is happening in the nucleus which occupies orders of magnitude smaller volume. Instead of thinking fuzzier and fuzzier orbital spaces, we should be thinking more refined orbital spaces. The MCAS model is an effort in that direction.