QUALITATIVE MOLECULAR ORBITAL THEORY SUITED FOR THE HIGH SCHOOL STUDENT

Rasmus Persson
Department of Pedagogical, Curricular and Professional Studies, University of Gothenburg, Sweden
E-mail: rasmusp@chem.gu.se

ABSTRACT

We introduce and discuss a pedagogical approach to molecular orbital theory which, devoid of any mathematics beyond simple arithmetic on experimental data, is suitable as an introduction to chemical bonding concepts as a complement to Lewis theory in high-school chemistry. Examples are discussed that highlight the reasoning that could be imparted to students. This exercise may also give rise to discussions about scientific theories and "truth." Notably, within the realm of our qualitative theory, we conclude that HF is a double-bonded diatomic. *[African Journal of Chemical Education—AJCE 13(1), January 2023]*

INTRODUCTION

In a recent article in this Journal, Barke and Harsch [1] discuss the chemical bond within the purview of nineteenth century valence theory. Their discussion prompted the present contribution, in which we aim to approach the chemical bond using twenty-first century quantum theory, but at a level suitable for the upper-level secondary school student.

We must start this paper by recognizing that there is no rigorous definition of the chemical bond; definitions for it hitherto advanced are all arbitrary to some extent. In practice, atoms are considered chemically bonded if found that the aggregate that they form is sufficiently stable to allow isolation and characterization. Despite this inherent arbitrariness which would seem to preclude prima faciae rigorous discussion of the topic, it is a very common topic in the chemical education literature. The issue in these discussions center around what is the “right reason” for chemical bonds to form, focusing on the significance of different partial energy contributions and other terms in quantum mechanics [2-10]. Needless to say, such discussions are not likely to influence classroom teaching, whatever their conclusion.

From a pedagogical point of view, there is no point in teaching theories that are more complicated than required to explain and organize whatever chemical knowledge the student needs for future studies or work. Lewis theory [11], for instance, correctly predicts the molecular formula of water as H2O (and, with its VSEPR extension [12,13], also the bent geometry of this molecule) from solely the information contained in a minimalistic periodic table, that is, the number of valence electrons of each element. Although true that the concept of the “valence electron” needed for this prediction is not easily defined without recourse to quantum theory or experimental ionization energies, the actual number of electrons that are considered “valence” can nevertheless be inferred from the periodic table and conceptualized using, for instance, Bohr’s atomic model. This means that Lewis theory is conceptually self-contained without quantum mechanics.

Indeed, in high-school chemistry, the chemical bond is typically approached within the framework of Lewis theory (the concept of atomic orbitals introduced before that provides the necessary definition of the “valence electron”). In the introductory chemistry courses at the university level, Lewis theory still predominates, but quantum theory is usually covered as well. At this point, many textbooks purport, at least indirectly, to provide an “explanation” for Lewis theory from quantum theory, but this inevitable requires some “hand-waving.” As a case in point, we have valence-bond theory which, in the form introduced in introductory university level chemistry courses, basically amounts to nothing more than Lewis theory with the electron dot structures replaced with computer-generated imagery of hybrid orbitals. In other words, when Lewis theory predicts, for instance, carbon to be tetravalent, the textbook will state that the carbon is “sp3-hybridized”; but short of appealing to Lewis theory itself, there is no simple argument to reach this conclusion independently.

At the high-school level, the theoretical treatment of the chemical bond is arguably what separates chemistry as a discipline most clearly from physics. Indeed, whereas in high-school physics courses, students are taught that electrons repel each other vigorously on account of their identical electrical charge; in their chemistry courses, they are instead taught that electrons “pair up”.

It is hard to imagine a more perfect obstacle to knowledge transfer between these two subjects when they teach incompatible properties of the electron! When the inquiring student asks about this apparent contradiction, the high-school instructor often has no choice but to say that it is explained by quantum mechanics in university level courses and cannot provide any examples of quantum-mechanical reasoning at a level that the high-school student would grasp. While the core high-school curriculum usually includes some notions of quantum mechanics, typically atomic orbitals and the shell structure of atoms [14], this is insufficient for answering the student’s question directly and serves little purpose in high-school chemistry beyond providing a definition of “valence electrons”.

The topic of this paper is to introduce a qualitative, theoretical framework for the chemical bond that is suitable for the inquisitive high-school student and still devoid of Lewis theory. This qualitative molecular orbital theory is intended to serve as a starting point for future studies at the university level, while avoiding entrenching the student with the misconceptions [15] observed by Autschbach [16]. The prerequisite knowledge of the student is at least a superficial understanding of atomic orbitals and the corresponding Aufbau-principle covered in most high-school chemistry textbooks; the reader of this paper (in his or her capacity as the instructor) is expected to have a more complete understanding of quantum mechanics from university-level chemistry courses in order to easily follow along with the arguments in this paper and to present them (or similar ideas) to the student without undue distortion. This last point is important, as distorted views (likely detrimental to the progress of learning) of what orbitals are have been identified even for students in college courses on the topic [15].

Before we proceed, it is useful to highlight in which way our approach is novel. Qualitative discussions around molecular orbital diagrams can be found in most introductory chemistry courses at the university level. However, these invariably start out from precalculated molecular orbital diagrams. The discussion thus cannot proceed from the same basic input that Lewis theory of bonding does, viz. basic atomic structure apparent from the periodic table. This hampers the student's own inquisitive mind and thinking, as the discussion has to be scaffolded on obscure (at that point in time to the student, anyway) computer calculations.

QUALITATIVE MOLECULAR ORBITAL THEORY

All the student needs to know at this point is that an "orbital" is a mathematical function describing the motion of an electron without pinpointing its position at any given time, but rather gives (after taking the square of the modulus) the probability distribution associated with this motion. Most importantly, connected with the electron's motion is an invariant energy (which is the sum of kinetic and potential energy contributions) and so each orbital is said to have a certain energy. The energy of the atomic nuclei, in particular, their mutual electrostatic repulsion is not included.

The qualitative treatment that we shall present is based on the following principles:

1. Combining two valence atomic orbitals on different atomic centers yields two molecular orbitals, of which one lies higher (called "antibonding") and the other lies lower (called "bonding") in energy than the energy of the atomic ones. This can be understood as the motion described by the electron in the molecule being a superposition of its motion in the isolated atom [17].
2. The increase or decrease in energy of said molecular orbitals with respect to their atomic counterparts is the more pronounced the more similar in energy these latter are, and the more the orbitals overlap, that is, the more similar the spatial motions they describe are with respect to a common molecule-frame coordinate system.
3. As a corollary to the above point due to reasons of symmetry, in diatomics, the atomic orbitals are restricted in with which atomic orbitals they may combine, so that s- orbitals may combine with other s- and pz-orbitals, and p-orbitals may combine with other p-orbitals of the same type, but other types of mixing are not possible.
4. Electrons are distributed among the molecular orbitals from low to high energy in accordance with the Aufbau-principle of two electrons per orbital.

These principles can be shown mathematically in a more complete treatment (see e. g., Ref. 18). For now, the restriction that the atomic orbitals be valence orbitals in point 1 is to ensure the "correct" (at the level of approximation of atomic orbitals) limiting ground- state wavefunction be obtained at infinite atomic separation. Using other forms of the basis functions, for instance so-called "virtual orbitals" corresponding to higher principal quantum number, will lead to spurious overestimation of the atomic energies in this limit, and "bonding" orbitals formed from them will not necessarily lower the actual ground-state energy.

However, since neglecting interelectron repulsion, the atomic orbitals are all degenerate in energy for the same principal quantum number, using "virtual" orbitals in the valence shell will not lead to a large error in this limit, whereas using more than two orbitals (or other basis functions) in the linear combination leads to unnecessary complications for the student. This said, the molecular orbitals formed within this "linear combination of atomic orbitals" as the approximation is often called, should not be reified. The actual numerical solution of the Schrödinger equation needs to proceed from the Hamiltonian of the system, and cannot, in any case, be written exactly as a product of orbitals. Restricting their number to the actual number of electrons in the system does not imply that they "exist" with the same ontological status as the electrons themselves. We therefore impose no such restrictions (yet this often seems not to be the case in introductory textbooks, although not explicitly mentioned; see, for instance, the treatment in Ref. 19).

The most important reason to introduce molecular orbitals, even in the qualitative guise defined above, is that it produces a natural explanation for the special affinity observed for the electron pair. At most two electrons may follow the same spatial motions in the molecule frame. This does not mean, however, that the two electrons are always at the same place, or even close. In fact, two electrons moving according to the same orbital will tend to avoid each other because of electrostatic repulsion. The basis for the “exchange interaction” [20] that modulates this effect somewhat need probably not concern the high school student, save for the very curious one.

Last, we introduce a fifth principle that is more approximate than the ones presented this far:

5. Electrons in atomic orbitals (as opposed to those in molecular orbitals) shield the nuclear charge of their parent atom completely, and thus contribute indirectly to the energy of the chemical bond through reduction of the internuclear repulsion.

This principle will prove useful in the examples to be discussed presently, but it should be clear that it overestimates the electrostatic shielding. We are, however, not aiming for quantitative accuracy but merely qualitative explanations.

DISCUSSION OF SOME CHOSEN EXAMPLES

It is now easy to show that H_2, H_2^+ and H_2^- are stable species, on account of their having more bonding than antibonding electrons according to the principles above. Likewise, He_2 is proven not to exist because it is predicted to have equal numbers of bonding and antibonding electrons. However, one may fruitfully inquire about the heteronuclear diatomics HHe and HeF as prototype cases of helium compounds. At first glance, they would seem to be erroneously predicted as stable species according to the postulates presented.

HHe

That HHe is not predicted to be a stable species becomes clear from the above principles if we consider also the electrostatic repulsion between the atomic nuclei, which we have hitherto ignored. This hypothetical species is isoelectronic with H_2^- but has twice the internuclear repulsion (given the same bond length). Alternatively, it can be compared with the more studied H_2^+ whose bond energy is 269 kJ/mol [21] and internuclear repulsion (at 1 Å, a typical bond length) of 1386 kJ/mol. In other words, the one-electron bond of H_2^+ provides roughly 1650 kJ/mol of stabilization. The stabilization energy predicted by our qualitative model for HHe will be smaller than this value on account of principle 2 above (in total, there is only one electron contributing to the bond). However, the internuclear repulsion (at 1 Å) alone is 2770 kJ/mol (there are no shielding core electrons on either atom), far in excess of the upper limit for the stabilization energy of HHe, which indicates that this species is not stable *even before we account for interelectron repulsion* which we have neglected. (Removing an electron, yielding HHe^+ with two bonding electrons, the same arguments lead to a doubling of the upper limit for the stabilization energy of roughly 3300 kJ/mol, which exceeds the internuclear repulsion, proving the feasibility of this molecular cation.)

HeF

The case of HeF may similarly be analyzed in the same manner as HHe. The 2*s*- and 2p_z- orbitals on F combine with the 1*s*-orbital on He, yielding two bonding and two antibonding molecular orbitals, by the first principle. By principle 4, of the eleven electrons in the system, four enter the molecular bonding orbitals, two enter an antibonding orbital and the remaining ones remain in the atomic 2p_x- and 2p_z- and 1*s*-orbitals on F. By principle 5, these remaining electrons shield the nuclear charge of F, reducing its apparent value to 4+. Even so, although there is an excess of two bonding electrons with respect to antibonding ones, the remaining internuclear repulsion (at 1 Å) is roughly 11000 kJ/mol, much more than twice greater than that of HHe, which we know to be unstable for half the number of excess bonding electrons. From the experimental data for H_2^+, we know that each bonding electron provides roughly 1650 kJ/mol of stabilization, and so an excess of about seven bonding electrons would be needed for HeF to be stable.

Alkaline Earth Metals

Unlike helium, the alkaline earth metals are predicted to form dimers on account of their *p*-orbitals that can combine and form molecular orbitals, thus ensuring there are enough bonding orbitals to account for all the valence electrons on each atom. (According to our first principle, only atomic orbitals from the valence shell contribute to the bonding, and the helium atom has no valence *p*-orbitals). In fact, each alkaline earth metal dimer is predicted to have four excess bonding electrons, but this prediction overestimates the actual bond strength because it neglects the high energy of the atomic *p*-orbitals (see our second principle). The internuclear repulsion is modest because of shielding by the core electrons.

O_2 and HF

While it is easy to see from our principles that O_2 should have a net total of four binding electrons, in accordance with the Lewis picture of this bond, it is a failure of the Lewis model that the bond energy of HF is greater (if ever so slightly) than that of O_2, given that the former is taken to be a "single bond" whereas the latter is a "double bond". With the qualitative theory that we advance here, both bonds are the result of four bonding electrons [22]. This can be seen if we combine the 1*s*-orbital on the H atom twice: once with the 2*s*-orbital and once with the $2p_z$-orbital on the F atom, both of which have the appropriate symmetry. Indeed, the prediction does not change if we combine the $1s_2$-orbital on H in turn with each of the occupied orbitals on F, whether valence or core, but ignoring the core electrons contribution to the molecular orbitals is justified on account of principle 2. Moreover, it allows us, by principle 5, to treat the nuclear charge of F as an effective nuclear charge of 4+, it being shielded by the electrons not participating in the chemical bond. According to the same arguments as before, the internuclear repulsion that the bonding electrons must overcome is then roughly 5550 kJ/mol. With four bonding electrons, it is reasonable to expect a stabilization energy at most four times that found in H^+, that is, about 6600 kJ/mol if we neglect interelectron repulsion. This leads to a predicted upper limit for the bond strength of 1050 kJ/mol, whereas the actual value is around 550 kJ/mol [23]. The discrepancy is due partly to the neglect of interelectron repulsion, partly to the overestimation of the nuclear screening and partly to the better overlap and more similar energies of the orbitals in the homonuclear diatomic H_2^+ than in the heteronuclear HF.

What about Ionic Contributions?

One could be tempted to argue that the higher bond strength of HF is due to its supposedly large ionic character, compared to the nonpolar covalent bond in O_2. This is an especially appealing argument at the high-school level where students are well acquainted with the concepts of covalent and ionic bonds (and their intermediates). Indeed, the student might even reach this conclusion within the confines of the qualitative treatment presented in this paper. This type of question also illustrates the nature of theoretical explanations. What is *actually* meant by the "ionic character" of a covalent bond?

Let us briefly consider this case. A completely ionic bond would require that there be virtually no overlap between the orbitals of F and H, which is *a priori* not altogether unlikely given the strong nuclear attraction of the fluorine atom. Transferring an electron between the 1*s*-orbital on H and any "receiving" orbital on F (which then plays the role of the "molecular orbital") amounts, in the most generous estimate (neglect of interelectron repulsion), to an energy gain equal to the difference in ionization energy between the two atoms. It would be a conceptual fault, however, to then add to this energy the ionic attraction between the resulting hydrogen and fluoride ions. According to our postulates, all electronic energy except the internuclear repulsion is included in the orbital energies and adding a Coulombic attraction between the resulting ions would amount to a double counting. For a purely ionic bond to form, the energy difference between the ionization energies must hence exceed the "residual" internuclear repulsion (that part of the internuclear repulsion that remains when the shielding effect of the non-bonding electrons has been taken into account). However, it is easily verified that even the most conservative estimate (*i. e.*, all F-electrons except one are nonbonding) of the corresponding internuclear repulsion at bonding distances (to wit, roughly 1400 kJ/mol) greatly exceeds the difference in ionization energy between F and H (to wit, about 370 kJ/mol). This explanation is hence not admissible.

CONCLUDING REMARKS

Avoiding higher mathematics and computer simulations altogether (even indirectly), we have introduced five principles that build upon a typical high-school curriculum that covers atomic orbitals in an at least qualitative fashion. These principles allow us to discuss the chemical bonding, or lack thereof, in simple diatomics without invoking Lewis theory [24]. The foundations thus laid do not impede the further development of quantum mechanics in higher-level courses, while at the same time illustrating an alternative approach to the chemical bond than the Lewis one. In particular, because of the generalization of atomic to molecular orbitals, the enigmatic importance of the electron pair can be explained at least partly as a consequence of the Pauli exclusion principle, known to students from the *Aufbau* principle in atomic theory.

I stress once again that the point of this qualitative treatment of molecular orbital theory is as an introduction to the topic in upper secondary education in preparation for tertiary education on the topic. Establishing a simple, but firm, foundation devoid of misconceptions is important for progressing further into the topic in later studies. At the same time, the implications according to the theory of HF having a double bond serves to challenge categorical notions of "correct" and "incorrect" science explanations that are common among high school students.

Finally, although the use of qualitative molecular orbital diagrams has been eschewed in this text for reasons of space, they are definitely pedagogically valuable in the classroom to illustrate the points and should be used liberally.

REFERENCES

1. Barke, H.-D.; Harsch, N. Bond forces versus electron pairs: two concepts for chemical bonding. *African Journal of Chemical Education* **2021**, *11*, 15–28.
2. Bacskay, G. B.; Reimers, J. R.; Nordholm, S. The mechanism of covalent bonding. *Journal of Chemical Education* **1997**, *74*, 1494.
3. Nordholm, S. Delocalization the key concept of covalent bonding. *Journal of Chemical Education* **1988**, *65*, 581.
4. Nordholm, S.; Bäck, A.; Bacskay, G. B. The mechanism of covalent bonding: Analysis within the hückel model of electronic structure. *Journal of chemical education* **2007**, *84*, 1201.
5. Ashkenazi, G.; Kosloff, R. The uncertainty principle and covalent bonding. *The Chemical Educator* **2006**, *11*, 66–76.
6. Rioux, F. The covalent bond examined using the virial theorem. *Chem Educator* **2003**, *8*, 10–12.
7. Ogilvie, J. F. The nature of the chemical bond—1990: There are no such things as orbitals! *Journal of Chemical Education* **1990**, *67*, 280.
8. Ogilvie, J. *Conceptual trends in quantum chemistry*; Springer, 1994; pp 171–198.
9. Pauling, L. The nature of the chemical bond—1992. *Journal of Chemical Education* **1992**, *69*, 519.

10. Hoganson, C. The Mechanism of Covalent Bonding. *Journal of Chemical Education* **1999**, *76*, 318.
11. Gillespie, R. J.; Robinson, E. A. Gilbert N. Lewis and the chemical bond: The electron pair and the octet rule from 1916 to the present day. *Journal of computational chemistry* **2007**, *28*, 87–97.
12. Gillespie, R. A defense of the valence shell electron pair repulsion (VSEPR) model. *Journal of Chemical Education* **1974**, *51*, 367.
13. Erlina,; Cane, C.; Williams, D. P. Prediction! The VSEPR Game: Using cards and molecular model building to actively enhance students' understanding of molecular geometry. *Journal of Chemical Education* **2018**, *95*, 991–995.
14. The limitations of this "orbital approximation" for many-electron atoms is beyond the topic of this paper.
15. Autschbach, J. Orbitals: some fiction and some facts. *Journal of Chemical Education* **2012**, *89*, 1032–1040.
16. Some economy of language is however necessary, so that we will not adhere strictly to all of Autschbach's recommendations.
17. With respect to this principle, it is important to stress that the orbitals (atomic or molecular) being simply mathematical functions of the motion of the electrons, one and the same orbital (that is, function) can be used in many different combinations.
18. Atkins, P. W.; Friedman, R. S. *Molecular quantum mechanics*; Oxford university press, 2011.
19. Zumdahl, S. S.; DeCoste, D. J. *Chemical principles*; Nelson Education, 2012.
20. Jensen, F. *Introduction to computational chemistry*; John wiley & sons, 2017.
21. Bressanini, D.; Mella, M.; Morosi, G. Nonadiabatic wavefunctions as linear expansions of correlated exponentials. A quantum Monte Carlo application to H2+ and Ps2. *Chemical physics letters* **1997**, *272*, 370–375.
22. We are essentially arguing that HF contains a double bond, which is an important point of disagreement with Lewis theory but more in line with the experimental data of bond strength.
23. Dibeler, V. H.; Walker, J. A.; McCulloh, K. Photoionization Study of the Dissociation Energy of Fluorine and the Heat of Formation of Hydrogen Fluoride. *The Journal of Chemical Physics* **1969**, *51*, 4230–4235.
24. The existence of these diatomics does not, however, indicate that higher polyatomics may not form; whereas the nonexistence of the dimer implies that the atom is inert.