

Majorana, Pauling and the chemical bond

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Abstract: Very little known results obtained by the Italian physicist Ettore Majorana in 1931 are here discussed, concerning the quantum theory of the chemical bond in homopolar molecules. The focus is on the formation of the helium molecular ion He_2^+ as well as on the accurate description of the hydrogen molecule H_2 . Group theory-inspired methods adopted by Majorana are contrasted with that more known by Pauling and their effectiveness in the explanation of the stability of the helium molecular ion is underlined. Finally, a proposal of Majorana concerning the possible existence of ionic structures in homopolar compounds is discussed.

Keywords: Homopolar compounds, Helium molecular ion, Ionic structures.

1. Introduction

The complete understanding of the nature of the chemical bond is the result of a wide number of different contributions, each one clarifying a piece of the whole picture.

The idea of valence was very early introduced into chemistry (Frankland 1866) to explain some number relationships in the combining ratios of atoms and ions, but the first attempt to incorporate the atomic structure information in a consistent – though qualitative – theoretical framework was performed by G.N. Lewis only in 1916. In his own view, the chemical bond consisted of a pair of electrons held jointly between two atoms. However, Lewis theory didn't say anything on the nature of the forces involved in the formation of the homopolar bond, and only with the advent of quantum mechanics appropriate and powerful theoretical tools became available in order to tackle the problem (Mehra, Rechenberg 1982). In principle, it became possible to write down an equation for any system of nuclei and electrons, whose solution would provide thorough predictions on the stability of the system under study, but the n-body problem revealed to be not amenable to exact analytical solutions, thus triggering the development of several approximation methods. In this scenario the key idea of *exchange forces*, introduced in molecular physics by W. Heitler and F. London (and borrowed by W. Heisenberg's theory of the helium atom (Heisenberg 1926)), grew up, as opposed to the polarization forces able to describe ionic compounds, and became the basis of the quantum theory of the homopolar chemical bond. Heitler and London (1927) succeeded to account for the stability of the hydrogen molecule and predicted,

with remarkable accuracy, the dependence of the total electronic energy on the internuclear distance.

Indeed Heitler and London's approach resulted difficult to apply to molecules more complex than the simple H_2 . So, by following the same path as in atomic physics since the times of the old quantum theory, several scientists – headed mainly by F. Hund, R.S. Mulliken, G. Herzberg and J.E. Lennard-Jones – introduced molecular spectroscopy (Herzberg 1951) as a guiding principle in developing a theory of the chemical bond. For spectroscopists, used to observe similar properties in many different molecules with the same number of electrons, it was quite natural to view a molecule as a collection of nuclei fixed in given spatial positions with an additional electron cloud surrounding them. *Molecular orbitals* occupied by each electron were introduced (Lennard-Jones 1929), whose extent stretched over the whole of the molecule, so that the chemical bond resulted from “sharing” electrons among the constituent atoms; as a consequence these lose their identity to a large extent, as opposed to the Heitler-London method.

A number of different refinements and generalizations of both approaches appeared in the subsequent literature, but quantitative calculations remained “much too complicated” to allow tests of the novel ideas in molecules other than those formed from hydrogen and helium atoms, such calculations being performed mainly within the Heitler-London approach. However, the value of the contributions developed for molecules composed of helium atoms is often underestimated. Indeed, the quantitative study of helium compounds led to relevant results that allowed to test significantly the theory of the chemical bond and to explore their potentialities. Already Heitler and London (1927) concluded that no stable He_2 could be formed, but the more intricate problem with the helium molecular ion was discussed and solved by E. Majorana and, independently, L. Pauling around 1931. The results obtained by Pauling, which we discuss in Section 2, are an extension of his previous ideas on one-electron and three-electron bonds applied to molecules different from the paradigmatic H_2 example. Vice versa, Majorana's description of the helium molecular ion, presented in Section 3, is a pure quantum mechanical theory strongly relying on the relevant symmetry properties of the system, thus complemented by group theoretical methods. A second relevant contribution on the chemical bond, also provided by Majorana in 1931, introduces the so-called “ionic structures” and is the topic of Section 4. Finally some concluding remarks will follow.

It is clear that Majorana's contributions do not exhaust the fascinating story of the theory of the chemical bond, but certainly contribute to it with important pieces that are not at all widely known, while their importance to present day research has been disclosed only in the last years (Corongiu 2007).

2. Pauling idea: one-electron and three-electron bond

The resonance phenomenon, namely the exchange interaction, brought into the theoretical picture of the chemical bond by Heitler and London (1927) applied to pairs of electrons (as in the H_2 molecule) due to their identity, but its application to molecular

compounds with one or three electrons appeared soon much more intriguing. So a question arose: how to realize a chemical (homopolar) bond in the presence of more electrons, according to the requirements imposed by Pauli exclusion principle?

Indeed, already in 1928 Pauling recognized how a one-electron bond could be physically realized in H_2^+ , and he himself got back to the problem in 1931 (Pauling 1931) by explaining that a resonance phenomenon applies also to this molecular ion, since the unperturbed system is degenerate: the two nuclei have the same charge, and thus also the same energy. More in general, he proposed the existence of a one-electron bond according to the following rule:

A stable one-electron bond can be formed only when there are two conceivable electronic states of the system with essentially the same energy, the states differing in that for one there is an unpaired electron attached to one atom, and for the other the same unpaired electron is attached to the second atom (Pauling 1931, p. 3225).

By looking at the values of the dissociation energy of several compounds, Pauling suggested also that, in addition to H_2^+ , one-electron bonds were present in H_3^+ , Li_2^+ , boron hydrides, etc., thus opening the road to the understanding of the nature of the chemical bond in more complex systems.

The problem remained for molecular compounds with three electrons,¹ such as HeH, He_2^+ , etc. By following Heitler and London, in 1930 Gentile evaluated the interaction energy between H and He, and between two helium atoms and showed that normal He and H have no tendency to form a stable molecule (Gentile 1930). Indeed, as recognized more in general one year later by Pauling (1931), resonance forces corresponding to the exchange of three electrons (with two electrons on a nucleus and one electron on the other) are mainly repulsive. This allowed him to formulate a rule for the occurrence of a three-electron bond:

A three-electron bond, involving one eigenfunction for each of two atoms and three electrons, can be formed in case the two configurations $A\cdot B$ and $A\cdot\bar{B}$ correspond to essentially the same energy (Pauling 1931, p. 3229).

Indeed, both for the one-electron and for the three-electron cases, Pauling envisaged an exchange mechanism that was a direct generalization of Heitler and London's one for molecules with identical atoms, where the resonance phenomenon involved degenerate (or nearly degenerate) electronic states. For the three-electron bond this applied – Pauling suggested – to the cases of He_2^+ , NO, NO_2 , O_2 , etc.

The problem of the formation of He_2^+ was considered only qualitatively by Pauling in the same 1931 paper, by assuming – following Weizel (1929) – that its formation was due to the bonding of a neutral helium atom with a ionized one, $He + He^+ \rightarrow He_2^+$, in full analogy with the case of the hydrogen molecular ion H_2^+ (but with three electrons instead of only one), rather than with that of the compound HeH, which

¹ As pointed out by Pauling (1931) following Heitler and London reasoning, with four electrons there is no tendency to form a strong molecular bond, since two of them are necessarily nuclear symmetric, while the remaining two are nuclear antisymmetric.

exhibits a three-electron bond. A similar process was envisaged also for the (excited) neutral helium molecule: there, an unpaired 1s electron comes into play as a result of the excitation of one atom, whose interaction with the pair of 1s electrons of the other atom eventually leading to a three-electron bond. The contribution to the chemical bond from the remaining outer electron could be neglected, so giving rise to a hydrogen-like spectrum (Pauling 1931).

More clearly, since the neutral helium molecule He_2 can be formed only from a normal (ground state) helium atom and an excited one, such a compound may undergo a dissociation into a neutral atom and a ionized one for sufficiently high energies of the excited electron, thus suggesting that the formation of the helium molecular ion occurs through the reaction above.

Pauling did not pursue further the quantitative consequences of such an assumption in his 1931 paper: we find them only about two years later (Pauling 1933). Indeed this work was carried out by Majorana in the same year 1931, about nine months before Pauling's first paper, by means of a deeper mathematical formalism (Majorana 1931a).

3. First Majorana contribution: the helium molecular ion

The issue of the formation of He_2^+ was addressed by Majorana starting from a discussion of experimental results on the band structure in the helium emission spectrum. The key idea was to consider the system He_2^+ similar to H_2^+ and then to study the chemical reaction $\text{He} + \text{He}^+ \leftrightarrow \text{He}_2^+$:

We want to study the reaction $\text{He} + \text{He}^+$ from the energy point of view and prove that such a reaction may lead to the formation of the molecular ion. [...] The method we will follow is the one that has been originally applied by Heitler and London (1927) to the study of the hydrogen molecule. We shall assume that the electronic eigenfunctions of the molecule are linear combinations of the eigenfunctions belonging to the separate atoms and we shall use them to evaluate the average value of the interaction between the two atoms. However since the two nuclei have the same charge whereas only one of the atoms is ionized, the problem as we will show is mechanically rather different from the one discussed by Heitler and London and in general from the problem that one encounters in the normal theory of the homopolar valence (Bassani *et al.* 2006, p. 49).²

Majorana built up a quantum mechanical theory for the system, whose eigenfunctions were constructed according to its symmetry properties, as already done in other papers (Drago, Esposito 2004).

Proceeding as Heitler and London, also Majorana started from the asymptotic solution of the problem for large R , the wave functions of the system being those for a neutral helium atom and its ion, and neglected the possibility that all electrons in He_2^+ be located on the same nucleus. Vice versa, when the nuclei approach each other, their

² Original article published in *Il Nuovo Cimento* (Majorana 1931a, p. 22).

reciprocal interaction has to be taken into account, and such an interaction mixes all the wave functions previously introduced. Majorana was able to select out the only two appropriate combinations satisfying general symmetry principles, by pointing out the relevance in the context of inversion symmetry: the total electronic wave function must show a definite symmetry with respect to the midpoint of the internuclear line. In particular he showed that, out of the two possible molecular states for the He_2^+ molecular ion, only one corresponds to the bonding molecular orbital of the ion: the ground state of the system is a resonance between the $\text{He}:\text{He}$ and $\text{He}:\text{He}$ configurations. His reasoning runs as follows. By denoting with Φ and φ the unperturbed eigenfunctions of the neutral or ionized atom a , and similarly Ψ and ψ those of atom b , there are six eigenfunctions of the separate atoms obtained by permutations of the electrons and exchange of the nuclei:

$$\begin{aligned} A_1 &= \varphi_1 \Psi_{23}, & A_2 &= \varphi_2 \Psi_{31}, & A_3 &= \varphi_3 \Psi_{12}, \\ B_1 &= \psi_1 \Phi_{23}, & B_2 &= \psi_2 \Phi_{31}, & B_3 &= \psi_3 \Phi_{12}. \end{aligned}$$

However, the interaction among the two atoms mixes these states “according to the symmetry characters of the electrons and according to their behavior under spatial inversion”, so that we are left with only two singlet and two doublet states, whose eigenfunctions are as follows:

$$\begin{aligned} y_1 &= A_1 + A_2 + A_3 + B_1 + B_2 + B_3, \\ y_2 &= A_1 + A_2 + A_3 - B_1 - B_2 - B_3, \\ y_3 &= A_1 - A_2 + B_1 - B_2, \\ y_4 &= A_1 - A_2 - B_1 + B_2. \end{aligned}$$

The corresponding perturbed energy eigenvalues are symbolically written down in terms of several integrals involving the above functions and, just “by taking into account the order of magnitude and the sign” of such integrals, coming from symmetry and physical considerations and without explicitly evaluate them, Majorana concluded that the solution y_3 “gives rise to repulsion whereas y_4 leads to the formation of a molecule”.

In order to produce explicit numerical predictions for the potential energy curve, equilibrium distance, energy minimum and oscillation frequency of the helium molecular ion, Majorana made recourse to variational calculations, for which explicit expressions for the helium wave functions were required. He wrote the ground state of the helium atom simply as the product of two hydrogenoid wave functions, but introduced (Esposito, Naddeo 2012) an effective nuclear charge (as a variational parameter) describing the screening effect of the nuclear charge by means of the atomic electrons. Within this simple approximation, Majorana succeeded in obtaining a good agreement with experimental data on the equilibrium internuclear distance and a quite perfect agreement with the experimentally determined value of the vibrational frequency of He_2^+ . Furthermore he estimated the dissociation energy of the molecular ion, obtaining a value $E_{\min} = -2.4$ eV (including polarization forces effects) which Majorana could not compare with experiments, due to no available data, but which is now remarkably closer to the

experimental determination of $E_{\min} = -2.4457 \pm 0.0002$ eV (Coman *et al.* 1999) than the recent theoretical prediction of $E_{\min} = -2.47$ eV (Ackermann, Hogreve 1991), obtained with much more refined mathematics than that used by Majorana.

Similar quantitative results will be obtained independently³ by Pauling two years later (Pauling 1933), by adopting approximately the same variational procedure, with similar eigenfunctions. However, it should be stressed that Pauling did not employ a group-theory inspired method that allows to pick up the relevant terms in the wave functions, by exploiting the symmetry properties of the system, so that the underlying physical meaning was not as fully transparent as in Majorana.

4. Second Majorana contribution: ionic structures in homopolar molecules

The successful description of the chemical bond of homopolar molecules did not exhaust the whole story, since further experiments produced apparently conflicting results claiming for a thorough explanation. That happened just when certain excited states of the hydrogen molecule were considered.

Such states were a subject of research by a number of authors (Pauling, Wilson 1935) but a peculiar phenomenon observed in the spectrum of H_2 molecule remained still unexplained: the decay of the excited $(2p\sigma)^2 \ ^1\Sigma_g$ (gerade) into the (ungerade) $1s\sigma \ 2p\sigma \ ^1\Sigma_u$ state in the infrared spectral region (Weizel 1930), contrarily to what happened in atomic systems, where the frequency corresponding to the transition $2p2p - 1s2p$ involving two excited optical electrons was very close to that of the transition $1s2p - 1s2s$ involving only one excited optical electron.

The theoretical justification of even the existence of the $(2p\sigma)^2 \ ^1\Sigma_g$ term, along with an explanation of its strange energy level, when compared to similar atomic systems, then required a reconsideration of the Heitler-London paradigm.

It was Majorana (1931b) who, very early in 1931, attacked the problem and, after a lucid analysis of the known results, promptly recognized the relevant difference between atomic and molecular systems:

To consider such a state as a state with two excited electrons has purely formal meaning. In reality, to designate such terms with the states of the single electrons, though it may be convenient for their numbering and for the identification of those symmetry characters that are not affected by the interaction, does not allow by itself to draw reliable conclusions on the explicit form of the eigenfunctions. The situation is very different from the one of central fields [in atomic systems] where it is generally possible to neglect the interdependence of the electron motions (polarization) without losing sight of the essentials (Bassani *et al.* 2006, p. 84).⁴

Then, in order to explain the intriguing experimental results, Majorana generalized Heitler-London theory of the hydrogen molecule, where only configurations corresponding to one

³ It seems that Pauling became aware of Majorana paper around 1935 (Pauling, Wilson 1935).

⁴ Original article published in *Rendiconti dell'Accademia dei Lincei* (Majorana 1931b, p. 58).

electron in each atom of the molecule were considered, by including different configurations where both electrons or no electron belong to a given atom. While Heitler and London considered only the chemical reaction $H + H \leftrightarrow H_2$ for the formation of the hydrogen molecule, Majorana argued that also the reaction $H^+ + H^- \leftrightarrow H_2$, involving *ionic structures*, could play a role. He was well aware of the fact that the apparent charge transfer via ionic structures has no proper physical interpretation in homopolar molecules, so he designated such a reaction between the two hydrogen atoms as “pseudopolar” rather than ionic. He concluded that, while the normal $(1s\sigma)^2 \ ^1\Sigma_g$ state mainly refers to the Heitler-London $H + H$ reaction,

the term $(2p\sigma)^2 \ ^1\Sigma_g$ [...] can be thought of as partially formed by the union $H^+ + H$. This does not mean, however, that it is a polar compound since, because of the equality of the constituents, the electric moment changes sign with a high frequency (exchange frequency) and therefore cannot be observed. It is in this sense that we speak of a pseudopolar compound (Bassani *et al.* 2006, p. 84).⁵

By limiting himself to gerade singlet states (which is the case of both the X terms and the ground state of the H_2 molecule), Majorana divided the configuration space into four regions – *aa*, *ab*, *ba*, *bb* – according to whether one or both electrons (labeled by 1, 2) are close to the nucleus *a* or *b*. When neglecting the interaction between the two electrons, the four possibilities above-mentioned are equally represented in the given state, but “the interaction increases the probability to find the system in *aa* and *bb*, whereas it decreases that of *ab* and *ba*” (Majorana 1931b).

Indeed the chemical reaction between neutral atoms, $H + H \leftrightarrow H_2$, considered by Heitler and London, corresponds to configurations *ab* and *ba*, described by an unperturbed wave function of the type

$$y_2 = \varphi_1\psi_2 + \varphi_2\psi_1,$$

while configurations *aa* and *bb* originate from the reaction $H^+ + H^- \leftrightarrow H_2$ involving hydrogen ions, and are described by a wave function (symmetrized with respect to the exchange of the two nuclei) of the form

$$y_1 = \Phi_{12} + \Psi_{12}.$$

Majorana realized that the two states y_1 and y_2 are not orthogonal, but the ground state and the X term of the H_2 molecule should result, in a first approximation, from two orthogonal combinations of them. The characteristic equation for the calculation of energy eigenvalues then followed, once an approximate expression for the wave function describing the H^- ion, Φ_{12} , was introduced semi-empirically to evaluate the corresponding energy integrals.

Majorana’s numerical results for the equilibrium internuclear distance of the molecule in the X state and for the corresponding vibrational frequency were close to the experimental observations. Nevertheless, he concluded his paper by saying that:

⁵ Original article published in *Rendiconti dell’Accademia dei Lincei* (Majorana 1931b, p. 59).

This result is even too favorable, as, with the method we followed, we could have expected a value considerably smaller than the true one. [...] A quantitative evaluation is difficult but it is plausible that such an approximation tends to produce errors compatible with the discrepancies ascertained between calculation and experiment (Bassani *et al.* 2006, p. 86).⁶

5. Conclusions

A complete understanding of the nature of the chemical (homopolar) bond was the result of a number of different contributions, each one enlightening a particular issue. Several methods of approximation able to find reliable solutions to the Schrödinger equation of the relevant molecular problem were developed, but novel ideas had to be introduced in order to gain more physical insight into the problem. The Heitler-London approach (1927), complemented by the concept of molecular orbitals introduced by Lennard-Jones, was just a seminal starting point towards such a step, allowing the thorough description of the most simple molecules, H_2^+ and H_2 , in terms of exchange interactions, together with the prediction of the non-existence of a stable helium molecule. The qualitative description of more complex molecules required the introduction of the concepts of one-electron and three-electron bonds by Pauling, as presented in Section 2. On the other hand, a generalization of the resonance phenomenon was employed in order to handle molecules with a number of valence electrons different from two. The helium molecular ion He_2^+ was a subject of intensive studies. Its full quantitative description was given in 1931 by Majorana (and, two years later, independently by Pauling), who built up a reliable quantum theory relying entirely on symmetry properties of the system under study, as explained in Section 3. A second Majorana contribution, accounted for in Section 4, deals with the introduction of ionic structures into homopolar molecular compound in order to explain some puzzling experimental results regarding excited states of the hydrogen molecule. Indeed, only in recent times ionic structures have been recognized to give rise to binding energy predictions for homopolar molecules close to the experimental values (Clementi, Corongiu 2007), while referring to *Majorana structures* as to ions that are not in the lowest ionic configuration (Corongiu 2007).

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⁶ Original article published in *Rendiconti dell'Accademia dei Lincei* (Majorana 1931b, p. 61).

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