

# The genesis of the quantum theory of the chemical bond

## Key ideas

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*Abstract:* A brief historical overview is given of the key ideas that allowed the genesis of the quantum theory of the chemical bond, starting from the appearance of the new quantum mechanics and following later developments till approximately 1931. The focus is on the novel concepts introduced by the Heitler-London theory, which are here complemented by those underlying the method of molecular orbitals. Further improvements in the understanding of the nature of the chemical bond are also discussed.

*Keywords:* Quantum resonance, Molecular orbitals, Homopolar chemical bond.

### 1. Introduction

The prominence of molecular spectroscopy in the early investigations about the nature of the chemical bond, which paralleled the analogous atomic framework, persisted for some time in the first decades of the 20th century, also when the new quantum mechanics entered into the game. The basic idea to ascribe all the known phenomenology to either the rotation or the vibration motion of the nuclear component of the molecules, faced with the appearance of a fine structure in the molecular spectra that originated from electronic motion, and strongly influenced the observed band spectra. The main theoretical problem was, thus, to explain the relationship between the electronic motion and the band spectrum and, in this respect, the key contributions by F. Hund and (many) others, deduced from spectroscopic data, played a seminal role, though still within an effective old quantum theory framework (Hund 1926, 1927).

With the advent of quantum mechanics, however, appropriate and powerful theoretical tools became available in order to tackle the problem (Mehra, Rechenberg 1982), and it became possible – in principle – to write down an equation for any system of nuclei and electrons, whose solution would have provided thorough predictions on the stability of the molecular system. Nevertheless, the  $n$ -body problem revealed to be not amenable to exact analytical solutions, thus triggering the development of several approximation methods, even for simple molecular systems such as the hydrogen molecular ion and molecule. The general task of an approximate separation of variables in the Schrödinger equation was, finally, realized by M. Born and J.R. Oppenheimer

(Born, Oppenheimer 1927), who showed that, at a first approximation, the motion of the nuclei in the molecules could be neglected, and a well-defined hierarchy exists between electronic, vibrational and rotational states.

However, the development of a quantum theory of the chemical bond, especially for homopolar molecules, required the introduction of novel ideas in order both to understand the nature of the bond and to make reliable quantitative predictions.

As happened already in atomic physics, spectroscopy again contributed as a key tool towards the elaboration of such a theory, and several scientists, including Hund, R.S. Mulliken, G. Herzberg and J.E. Lennard-Jones, appealed to molecular spectroscopy in order to introduce the concept of molecular orbital. Although the initial intent was not to provide a true theory of the chemical bond, it finally led to a picture featuring the electrons in a molecule as each occupying an orbital stretching over the whole molecule: atoms lose their identity while starting to share electrons and, in this sense, a chemical bond arises. A different approach was, instead, envisaged by W. Heitler and F. London, who introduced the key idea of exchange forces (or quantum resonance), as borrowed by W. Heisenberg's theory of the helium atom (Heisenberg 1926).

A number of different refinements and generalizations of both approaches later appeared in the subsequent literature, but quantitative calculations remained much too complicated to allow tests of the novel ideas in molecules other than diatomic ones, such as those formed from hydrogen and helium atoms. Some additional light upon the intricate problem came also from the application of the powerful tools of group theory, although only few authors exploited it appropriately to get some insight into the mathematical form of the wave function, as deduced from the symmetry properties of the molecular system it describes.

The transmission of the achievements gained by the quantum theory of the chemical bond to people more accustomed to a chemistry-based language produced, remarkably, also a non-negligible result in the understanding of several points of the theory itself. L. Pauling and J.H. van Vleck, indeed, in addition to their own original contributions to the subject, wrote some review papers that served to clarify substantially the physical meaning of the novel concepts introduced, and thus helped to digest the corresponding mathematical results, both to chemists and physicists.

In the present contribution the key contributions that allowed the genesis of a quantitative quantum theory of the chemical bond are analyzed. The method of molecular orbitals and that of Heitler-London are discussed in Sections 2 and 3, respectively, together with a further inspection about the nature of the valence bond. Final remarks are then summarized in our concluding section.

## 2. Molecular orbitals

The relationship between the spectral terms of the component atoms and those of the molecule formed was the focus of early theoretical interpretations of spectroscopic data, with or without the proper aid of group theory. The result of this search was a classification of all the possible molecular terms, but without any explanation about

their stability. The first step towards the understanding of such a point was performed already by Hund (Hund 1928, 1930), who, by extending previous ideas, assigned to each electron within a molecule a definite and unique series of quantum numbers, coming out from the fact that each electron has a given angular momentum quantized along the molecular axis and from the same atomic quantum numbers which it would have if the component atoms were pushed together to form a “united atom”.

Just along the lines followed by Hund, in 1928 Mulliken provided a general spectroscopic interpretation of the band spectrum (Mulliken 1928) aimed at assigning appropriate “molecular” quantum numbers to the electrons in (non rotating) diatomic molecules.

Hund’s work enables us to understand how a continuous transition can exist between ionic and atomic binding. Briefly, the molecule may be said to be latent in the separated atoms; in a certain sense, the molecular quantum numbers already exist before the atoms come together, but take on practical importance, at the expense of the atomic quantum numbers, only on the approach of the atoms to molecular distances. This of course does not exclude the possibility that in some cases a quantum jump in the usual sense may be needed to reach the most stable state of the molecule (Mulliken 1928, p. 189).

The Pauli principle was recognized to hold in molecules as well, and its application allowed to classify the possible molecular states corresponding to a given electron configuration. Indeed, Mulliken’s idea was to study the group theory properties of spectral terms, but without the use of group theory.

The relative energies of the different electronic levels, which can be obtained – in the limiting case of zero internuclear distance – when molecular states collapse on atomic states, were deduced theoretically by Hund (Hund 1928, 1930), but, in the more involved case of intermediate internuclear distances, no simple limit exists, and the energy levels were obtained by interpolation and then fitted to the experimental data, in order to produce a smooth transition between the two extreme limiting cases (zero or infinity internuclear distance). Both Hund and Mulliken realized as well that the table of energy levels had to be supplemented by certain empirical rules, but while Hund tried to limit the intersections of the possible transitions from a given state of the separated atoms to the corresponding states of the united atom, Mulliken adopted the hypothesis of a constant number of  $\sigma$ ,  $\pi$ , ... electrons during such transitions.

In order to improve the results obtained, Mulliken tried to determine and classify the electronic states of the atomic products (i.e. one excited atom or ion) resulting from the dissociation of unexcited molecules when increasing the vibrational quantum number of the corresponding states. In Mulliken’s own words, the basic assumption of his theory was that

Molecular stability is primarily a matter of promotion energy, rather than of valence bonds in the sense of Lewis or London (Mulliken 1929, p. 730).

He thus looked at a molecule as at a collection of nuclei fixed in given spatial locations and surrounded by an electron cloud (Mulliken 1932), and it was soon easy to take the next step and thus embed each electron into a “molecular orbital” which spreads over the whole molecule: as the atoms approach each other, they lose their identity and share electrons, giving rise to the chemical bond.

In 1929, Lennard-Jones (1929) further developed Mulliken’s ideas, and introduced a clear distinction between atomic levels and molecular levels within a molecule: molecular levels give rise to binding while atomic ones produce repulsion due to an asymmetry of the corresponding. He then set up an *Aufbau* method for molecules analogous to that for atoms:

We suppose a molecule built up in the following way. We add one charge at a time to each nucleus and then, supposing the nuclei held fixed, add to the system two electrons successively. The system is then allowed to take up its equilibrium value adiabatically. Next, we add the components of the angular momenta about the nuclear axis [...]. Then, as in atoms, we add the electron spins to determine the multiplicity (Lennard-Jones 1929, p. 672).

The effect of core electrons was supposed to produce only an imperfect screening of the charge of the nucleus, depending on the configuration of the outer electron, and the effective charge had to be adjusted in order to give rise to the observed energy level for the atomic states. Vibrational and rotational effects were, instead, assumed to be small perturbations on the electronic configuration, and thus negligible. Of course, that didn’t apply to the light molecule  $\text{He}_2$ , so that Lennard-Jones’ work was mainly devoted to describe the ground levels or excited states of heavier molecules. In particular, he explicitly built up the electronic structures of the series of diatomic molecules and molecular ions from  $\text{Li}_2$  to  $\text{F}_2$  (but also applied his method to H and He molecular compounds).

Hund’s and Mulliken’s original ideas about molecular orbitals were mainly qualitative in nature, aimed to deal with spectroscopic data in the “style” of the old quantum theory, and the implementation of the molecular orbital concept into a mathematical formulation suitable for application to quantum mechanics took some time to be performed. However, the method of molecular orbitals originally devised by Hund, Mulliken and Lennard-Jones, was eventually translated into a method for the writing of appropriate molecular wave functions to be used in suitable approximations to be adopted in order to solve the relevant Schrödinger equation.

An especially clear formulation was provided later (in 1935) by van Vleck (van Vleck, Sherman 1935, p. 169), from whom we quote:

A *molecular orbital* is defined as a wave function which is a function of the coordinates of only one electron, and which is, at least hypothetically, a solution of a dynamical problem involving only one electron. The method of molecular orbitals seeks to approximate the wave function of a molecule containing  $n$  electrons as the product of  $n$  molecular orbitals, so that

$$\Psi = \psi_1(x_1, y_1, z_1) \psi_2(x_2, y_2, z_2) \dots \psi_n(x_n, y_n, z_n).$$

For a diatomic molecule this becomes:

$$\Psi = a^2 \psi_A(1) \psi_A(2) + b^2 \psi_B(1) \psi_B(2) + ab [\psi_A(1) \psi_B(2) + \psi_A(2) \psi_B(1)],$$

where  $\psi_A$  and  $\psi_B$  are atomic orbitals for atoms *A* and *B*. It is evident that terms such as  $\psi_A(1)\psi_A(2)$  and  $\psi_B(1)\psi_B(2)$  imply that electrons 1 and 2 are both on the atom *A* or on the atom *B*, so that they represent ionic terms while the remaining terms  $\psi_A(1)\psi_B(2)$  and  $\psi_A(2)\psi_B(1)$  are characterized by one electron on each atom, and then feature exchange terms.

### 3. Heitler-London theory

The Heitler-London theory (Heitler, London 1927; Heitler 1928) of homopolar molecules, indeed, was primarily based on symmetry properties of the wave functions as required by the Pauli exclusion principle, but the key novel idea was to extend Heisenberg's idea of resonance (Heisenberg 1926) by introducing purely quantum-mechanical exchange forces, as opposed to polarization forces. The rationale of their work was just the quest for a theoretical understanding of the interaction between neutral atoms (of which homopolar molecules are composed of), which led them to take into account the possibility of a non-polar binding.

Heitler and London investigated this issue by making explicit reference to the simplest examples of  $H_2$  and  $He_2$ . The first problem they considered was the determination of the change in energy as experienced by two neutral hydrogen atoms in their ground states, when approaching each other up to a fixed distance *R* (taken as the distance between the two nuclei). The corresponding Schrödinger equation for the system of two nuclei *a* and *b* and two electrons 1 and 2, had to be solved, and, to this end, Heitler and London adopted a simple perturbation theory to be applied to unperturbed wave functions built up from the well-known eigenfunctions  $\psi_i$ ,  $\varphi_i$  of the hydrogen atom for the *i*-electron (*i* = 1, 2) present on nucleus *a*, *b*. As unperturbed eigenfunctions they chose those characterized by one electron on the first nucleus and the other electron on the other nucleus, but since a two-fold degeneracy is present, the two following linear combinations were considered:

$$\begin{cases} \alpha = \frac{1}{\sqrt{2+2S}} (\psi_1\varphi_2 + \psi_2\varphi_1), \\ \beta = \frac{1}{\sqrt{2+2S}} (\psi_1\varphi_2 - \psi_2\varphi_1), \end{cases}$$

with normalization factors expressed in terms of the integral  $S = \int \psi_1\varphi_1\psi_2\varphi_2 d\tau_1 d\tau_2$ . From the expression above, it is clear that the two combinations  $\alpha$  and  $\beta$  are symmetric and antisymmetric in the exchange of the two electrons 1 and 2 (or the two nuclei), respectively. The perturbation theory was applied, yielding the two perturbed energies corresponding to the above two states:

$$\begin{cases} E_{\alpha} = E_{11} - \frac{E_{11}S - E_{12}}{1 + S}, \\ E_{\beta} = E_{11} + \frac{E_{11}S - E_{12}}{1 - S}, \end{cases}$$

where  $E_{11}$  and  $E_{12}$  are the so-called Coulomb and exchange integrals. Here, the key result was the lifting of the initial degeneracy, and since the eigenfunction of atom a does not vanish in the spatial position occupied by atom b and vice versa, Heitler and London deduced that a finite probability exists for the electron of atom a to belong to b. A resonance phenomenon *à la* Heisenberg (1926) took place,  $[h(E_{\beta} - E_{\alpha})]^{-1}$  being the frequency of the average exchange between electrons.

While in classical mechanics it is possible to label the electrons (we put each electron in a sufficiently steep potential well and do not allow energy addition), something similar is impossible in quantum mechanics: when at one moment in time one is certain to know one electron in the potential well, one can never be certain that in the next moment it does not exchange with another (Hettema 2000, p. 145 note 7).<sup>1</sup>

Heitler and London realized that the solution  $\alpha$  doesn't have any node while the antisymmetric one  $\beta$  always has one node, so that  $E_{\beta} > E_{\alpha}$ . However, they also proceeded to give a quantitative estimate of such energies, starting from the calculation of  $E_{11}$  and  $E_{12}$ , but, while  $E_{11}$  was clearly interpreted as due to the pure Coulomb interaction of the charge distributions present in the molecule, the meaning of  $E_{12}$  was not so transparent. But they carried out the full calculation only for  $E_{11}$ , while obtaining simply an estimate for  $E_{12}$ . The exact evaluation of  $E_{12}$  was instead carried out some months later by Sugiura (1927), thus allowing the explicit evaluation of the moment of inertia and the oscillation frequency (and then the dissociation energy) of the hydrogen molecule, and, in the appropriate limit, also the ionization energy of the helium atom.

However (and correctly), here the focus was not on numerical predictions for the hydrogen molecule, but rather on the physical interpretation of the two solutions  $\alpha$ ,  $\beta$  obtained so far. Heitler and London interpreted the antisymmetric solution with energy  $E_{\beta}$  as representing the van der Waals repulsion between the two hydrogen atoms ("elastic reflection"), while that corresponding to the attractive potential  $E_{\alpha}$  was identified with the formation of a stable homopolar molecule, the minimum of  $E_{\alpha}$  representing the equilibrium configuration. They thus concluded that "the non-polar attraction is a characteristic quantum-mechanical effect" (Heitler, London 1927), driven just by their exchange interaction.

The interaction between two helium atoms was dealt with as well by the same authors. Here the basic units are the eigenfunctions  $\psi$  and  $\varphi$  for the two nuclei a and b, each one corresponding to two electrons, six combinations of their products being, in general, possible:  $\psi_{12}\varphi_{34}$ ,  $\psi_{34}\varphi_{12}$ ,  $\psi_{13}\varphi_{42}$ ,  $\psi_{42}\varphi_{13}$ ,  $\psi_{14}\varphi_{23}$ ,  $\psi_{23}\varphi_{14}$ . Heitler and London, however, realized that two of them,  $\psi_{13}\varphi_{42}$  and  $\psi_{42}\varphi_{13}$ , were forbidden by the Pauli principle, so that they introduced only the following linear combinations:

<sup>1</sup> Original article published in *Zeitschrift für Physik* (Heitler, London 1927).

$$\begin{aligned}\Psi_1 &= \psi_{12}\phi_{34} + \psi_{34}\phi_{12}, & \Phi_1 &= \psi_{12}\phi_{34} - \psi_{34}\phi_{12}, \\ \Psi_2 &= \psi_{14}\phi_{23} + \psi_{23}\phi_{14}, & \Phi_2 &= \psi_{14}\phi_{23} - \psi_{23}\phi_{14},\end{aligned}$$

and, within the same reasoning as for the  $H_2$  molecule, the appropriate unperturbed wave functions resulted to be:

$$\begin{aligned}\alpha &= \Psi_1 + \Psi_2 = \psi_{12}\phi_{34} + \psi_{34}\phi_{12} + \psi_{14}\phi_{23} + \psi_{23}\phi_{14} \\ \beta &= \Psi_1 - \Psi_2 = \psi_{12}\phi_{34} + \psi_{34}\phi_{12} - \psi_{14}\phi_{23} - \psi_{23}\phi_{14} \\ \gamma &= \Phi_1 = \psi_{12}\phi_{34} - \psi_{34}\phi_{12} \\ \delta &= \Phi_2 = \psi_{14}\phi_{23} - \psi_{23}\phi_{14}\end{aligned}$$

They also found that  $\gamma$  and  $\delta$  were two-fold degenerate in energy ( $E_\gamma = E_\delta$ ), and then had to be discarded, thus remaining with the non-degenerate wave functions  $\alpha$  and  $\beta$  ( $E_\alpha \neq E_\beta$ ). As for the hydrogen molecule problem, also here  $E_\alpha$  was identified with the lowest energy eigenvalue, so that the state  $\alpha$  would represent (at zeroth order) the formation of a stable molecule, while  $\beta$  the elastic repulsion between the two helium atoms. Nevertheless, Heitler and London realized that  $\alpha$  did not satisfy the requirements of the Pauli principle, since two He atoms (and, in general, two noble gas atoms) cannot be distinguished with respect to their spin, contrary to what happens for hydrogen (and for all atoms with open shells). For  $He_2$ , the only allowed solution would correspond to  $\beta$ , but since this describes an unstable configuration, the molecule formation was predicted to be forbidden.

Of course, a linear combination of the solutions  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  could be alternatively introduced but, likewise, it could not lead to the formation of a stable molecule because, as recognized by Heitler and London, that would correspond to four electrons in a K-shell, i.e. a configuration again forbidden by the Pauli principle. A solution could, then, be found only with excited helium atoms, and the conclusion was that, on the basis of the new quantum mechanics, no stable  $He_2$  molecule could form. In Pauling's words:

It is of particular significance that the straightforward application of the quantum mechanics results in the unambiguous conclusion that two hydrogen atoms will form a molecule but that two helium atoms will not; for this distinction is characteristically chemical, and its clarification marks the genesis of the science of sub-atomic theoretical chemistry (Pauling 1928, p. 174).

London and Heitler further investigated the issue of the formation of the homopolar chemical bond in a subsequent series of papers (London 1928a,b; Heitler 1930), and – especially London – pointed out the crucial role played by group theory. Valence numbers of homopolar molecules were interpreted in the framework of quantum mechanics as group theory properties of the given problem, and coming out directly from the symmetry properties of the eigenfunctions of the component atoms.

The valence number is therefore given by the number of ones in the decomposition of the electronic number of an atom, which represents the symmetry character of the atomic state considered (Hettema 2000, p. 164).<sup>2</sup>

Valence was, thus, determined from the symmetries of the unperturbed atoms in the molecule, i.e., showed up already in zeroth order eigenfunctions (and first order energies), the different modes of the homopolar binding being related to the “lifting of the exchange degeneracy”. Higher order terms describe only effects concerning the molecule already formed, such as condensation, crystallization or van der Waals attraction.

The (qualitative) extension to molecules more complex than  $H_2$  and  $He_2$  was, indeed, considered, and the main findings were that: a) inert gases cannot exhibit valences; b) halogens may have the valences 1, 3, 5, 7 except that the valence of fluorine may only assume the value 1; c) in the oxygen group, S, Se and Te may have valences 0, 2, 4, 6 but O only values 0 and 2; d) in the nitrogen group, P, As, Sb, Bi may have 1, 3, 5 but N only 1 and 3; e) in the carbon group, C, Si, Ge may have 0, 2, 4.

Instead, a generalization to atoms of the first and second column of the periodic table was provided by Pauling (1928). He argued that the interaction between two alkali metal atoms is similar to that between two hydrogen atoms: while the closed shells of the ions experience van der Waals-like forces typical of noble gases, the two valence electrons are shared between the two ions as in the original Heitler-London theory, and a molecule sets up in close agreement with band spectra observations. Conversely, two atoms with two valence electrons, such as Hg, interact as two helium atoms, thus giving rise only to very small attractive forces.

The guidance of group theory was especially required in the quantum mechanical study of non simple molecules, since the mathematical complexities of the corresponding  $n$  body problem prevented the integration of the relevant Schrödinger equation with a suitable accuracy, as instead happened for  $H_2$ . After some “metabolization”, the two competing methods of molecular orbitals and of Heitler-London were finally regarded as different approximations within which the unperturbed wave functions of the molecular system could be chosen.

#### 4. Conclusions

At the end of his review paper, in 1929 van Vleck hopefully asked:

Is it too optimistic to hazard the opinion that this is perhaps the beginning of a science of “mathematical chemistry” in which chemical heats of reaction are calculated by quantum mechanics just as are the spectroscopic frequencies of the physicist? Of course the mathematics will be laborious and involved, and the results always successive approximations. The theoretical computer of molecular energy levels must have a technique comparable with that of a mathematical astronomer (van Vleck 1929, p. 506).

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<sup>2</sup> Original article published in *Zeitschrift für Physik* (London 1928a).



What discussed here has shown that the quantum explanation of the nature of the chemical bond in molecules was (unfortunately) not at all only a matter of laborious and involved mathematical calculations, but its story has been rather intricate, when compared to that of the analogous quantum-mechanical description of atoms.

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