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Theoretical
Chemistry Accounts

Perspective

Perspective on "Wechselwirkung neutraler Atome und homöopolare Bindung nach der Quantenmechanik"

Heitler W, London F (1927) Z Phys 44: 455–472

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Abstract. The paper of Heitler and London was the first quantum theoretical study which explains the nature of the covalent bond. It also contains the noncrossing rule.

Key words: Covalent bond – Hydrogen molecule – Helium atom – Noncrossing rule

One of the greatest puzzles in natural sciences before the paper of Heitler and London (HL) was published in 1927 was the nature of the strong attractive interactions between neutral atoms which lead to the formation of a covalent chemical bond. It was clear that only electrostatic forces could be responsible for the interatomic attraction, but the application of classical laws of electrostatic interactions gave bond energies which were much too low. The explanation of a chemical bond in terms of classical electrostatic forces also violated the law of Earnshaw, which states that a static system held together by charge attractions should not be stable.

HL showed that strong attractive interactions between two hydrogen atoms in H_2 are predicted for certain interatomic distances when the then newly developed quantum theory of Schrödinger and Heisenberg is applied to a molecule in a similar way as was previously done only for atoms. The crucial point was that first the wavefunctions of the two atoms should be used to construct the wavefunction of the molecule which then gives the energy and charge distribution of H_2, rather than using the atomic charges in order to build up the charge distribution of the hydrogen molecule. The formation of the chemical bond was shown to be a typical quantum phenomenon and, thus, could not be understood before quantum theory was developed. The paper of HL is the birth of quantum chemistry.

The mathematical part of the paper belongs now to the introductory parts of many textbooks of quantum chemistry and is easy to read. More interesting are the comments and arguments which are given by the authors. The paper is divided into a short introduction and five chapters. The authors say in the introduction that the interaction between neutral atoms has been a difficult subject for theoretical treatments, and that the developement of quantum mechanics opens new avenues to deal with the problem. Two aspects would be new: the e^{-r} behaviour of the charge distribution, which introduces a different interplay of forces between the atoms, and more importantly, "a characteristic quantum mechanical resonance phenomenon that is closely related to the resonance vibrations that were found by Heisenberg." HL consider not only the H—H interactions in H_2 but also the forces between two helium atoms. They anticipate in the introduction that there will be two solutions for the interaction energy between two hydrogen atoms. One solution gives attractive interactions at medium interatomic distances, which is suited for the formation of covalent bonds ("homeopolar molecules"). This solution would not be allowed for two helium atoms because of the Pauli principle. The second solution is allowed for hydrogen and helium, and it gives repulsive forces at all distances.

Chapter 1 describes the ansatz, which is now known as the valence bond method, for the interactions between two hydrogen atoms. The Schrödinger equation for the hydrogen molecule is given, and the eigenfunction for H_2 is given as the product of the eigenfunctions, ψ and φ , of the hydrogen atoms. The authors point out that there are two equivalent molecular eigenfunctions, $\psi_1\varphi_2$ and $\psi_2\varphi_1$, which have the same energy, and that all pairs of orthogonalized and normalized linear combinations

$$\alpha = a\psi_1\varphi_2 + b\psi_2\varphi_1 \tag{1a}$$

$$\beta = c\psi_1\varphi_2 + d\psi_2\varphi_1 \tag{1b}$$

can be considered as undisturbed eigenfunctions of H_2. The correct linear combinations, for which the proof would be given later, would be

$$\alpha = 1/(2+2S)^{0.5}(\psi_1\varphi_2 + \psi_2\varphi_1) \tag{2a}$$

$$\beta = 1/(2-2S)^{0.5}(\psi_1\varphi_2 - \psi_2\varphi_1) \ . \tag{2b}$$

The disturbed eigenfunctions are then given by

$$\chi_\alpha = \alpha + v_\alpha \tag{3a}$$

$$\chi_\beta = \beta + v_\beta \tag{3b}$$

The ansatz (Eq. 3) for the disturbed wavefunctions is then used in the Schrödinger equation for H_2, which leads in a straightforward way to the energies of the perturbation

$$E_\alpha = E_{11} - (E_{11}S - E_{12})/(1 + S) \tag{4a}$$

$$E_\beta = E_{11} + (E_{11}S - E_{12})/(1 - S) \ , \tag{4b}$$

where E_{11} gives the Coulombic interactions and E_{12} is now known as the resonance integral, but the latter term is not used in the paper. It is only said that the E_{12} terms are not easy to interpret.

Chapter 2 discusses the results (Eq. 4). The integrals for E_{11} can be solved analytically, but for E_{12} only an upper limit can be given because it involves an integral over $1/r_{12}$ which cannot be solved exactly. Using the upper-limit expression for E_{12} leads to the curves for E_α and E_β that are shown in Fig. 1, which also shows the energy curve given by the pure Coulombic interactions E_{11}.

The authors say: "The observed nonpolar attraction appears as a characteristical quantum mechanical effect. It arises already without considering perturbation by polarization. It is also remarkable that the repulsion E_β is visibly a quantum mechanical effect, too, which is not based on Coulombic interactions (E_{11})." It is interesting that the authors, while saying that Fig. 1 gives approximate values for the dissociation energy and equilibrium distance, do not give numbers, although these can be estimated from the scale that is used in the figure. They say that it is not their goal to calculate as accurate values as possible, but rather to give insight into the nature of the covalent ("homeopolar") bond. The calculated values for the equilibrium distance (~1.5 a.u.) and the binding energy (~2.5 eV) are remarkably close to the exact values (1.401 a.u. and 4.7466 eV) considering the crude approximation.

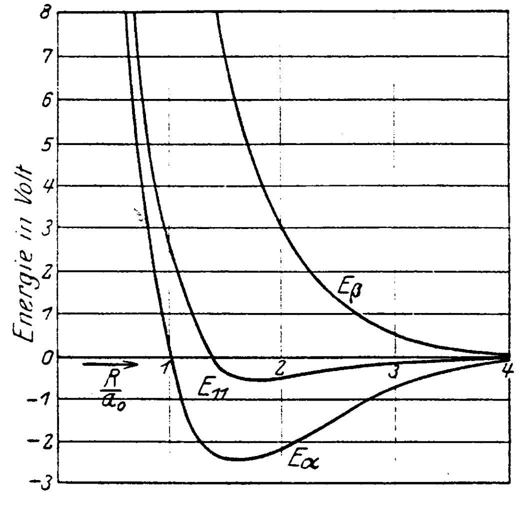

Fig. 1. Translation of the original figure caption: Potential of two neutral H atoms. (E_α = homeopolar attraction, E_β = elastic reflection.)

Chapter 3 is devoted to the interaction of two helium atoms. Again, the Schrödinger equation for He_2 is given first, and the solution of the fourth-order secular equations leads to three eigenvalues (one of them doubly degenerate) and four zeroth-order wavefunctions

$$\alpha = \psi_{12}\varphi_{34} + \psi_{34}\varphi_{12} + \psi_{14}\varphi_{23} + \psi_{23}\varphi_{14} \tag{5a}$$

$$\beta = \psi_{12}\varphi_{34} + \psi_{34}\varphi_{12} - \psi_{14}\varphi_{23} - \psi_{23}\varphi_{14} \tag{5b}$$

$$\gamma = \psi_{12}\varphi_{34} - \psi_{34}\varphi_{12} \tag{5c}$$

$$\delta = \psi_{14}\varphi_{23} - \psi_{23}\varphi_{14} \ , \tag{5d}$$

where ψ_{ab} and φ_{cd} are atomic two-electron functions.

Chapter 4 is entitled "Pauli principle and molecule formation". HL expand the Pauli principle, which was hitherto applied only to atoms, to systems with two interacting atoms. Because the Pauli principle demands that the sign of the eigenfunction changes when two electrons become exchanged, it follows that only Eq. (5b) (β) is a possible solution for He_2. This leads to the high-energy eigenvalue $E_\beta = H_{11} - H_{12}$. The authors do not give mathematical expressions for the energy terms and say that, in analogy to the H_2 case, one should expect the same curve for He_2 as for E_β (H_2) shown in Fig. 1.

The final part of this chapter is a discussion about the principal difference between systems which can form chemical bonds and those which cannot. The authors try to generalize their results for H_2 and He_2. HL point out that two helium atoms in their ground state cannot have different electron spins, while two hydrogen atoms can. The authors conclude that this is a general condition for two interacting systems to form a covalent bond, and that only repulsive forces yielding energy curves like E_β

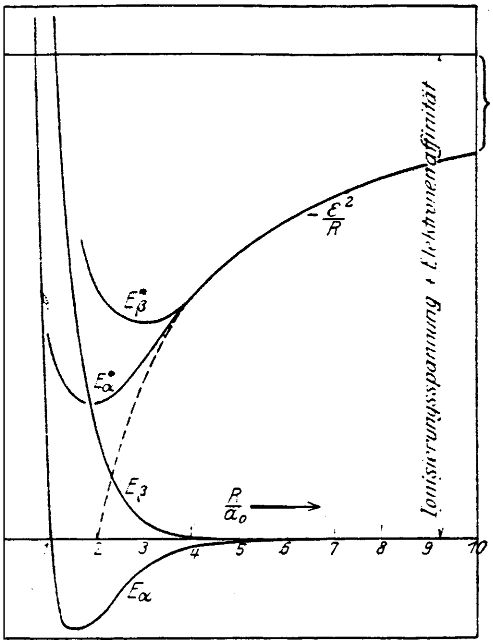

Fig. 2. Translation of the original figure caption: Ion potential (E_α^*, E_β^*), compared with the potential of neutral atoms (E_α, E_β)

in Fig. 1 will be found when one of the two systems has a closed-shell configuration like H_2 + H, He + H, H_2 + H_2, etc.

The final chapter discusses the case when H_2 dissociates into H^+ and H^-, i.e. the next higher-lying dissociation limit of H_2. The undisturbed eigenfunction for the two-electron system (H^-) is now ψ_{12} or, equivalently, φ_{12}. HL discuss qualitatively the energy curves of the eigenvalues E_α^* and E_β^* which belong to the zeroth-order eigenfunctions

$$\alpha^* = \psi_{12} + \varphi_{12} \tag{6a}$$

$$\beta^* = \psi_{12} - \varphi_{12} \ . \tag{6b}$$

Figure 2 is a reproduction of the original figure. Note that there is no scale for the energy values. The most important result from this section, which may surprise the reader, is that HL concluded that the energy curves of E_α and E_α^* cannot cross; likewise, the curves for E_β and E_β^* do not cross. Thus, the paper of HL is not only the first quantum chemical study which explains the nature of the covalent bond; it also contains the non-crossing rule. The authors clearly say that the two solutions α and α* (likewise β and β*) can be combined linearly; however, the exact form of the combination would not be predictable without further investigation.