

## Search for Simplicity: The molecular bond

The chemical bond, the force that binds atoms to molecules, has curious properties. It is a force that acts only over short distances—a few atomic radii—it is attractive but becomes repulsive at smaller distances. Furthermore, attraction occurs only between certain combinations of atoms. The study of these rules is the subject of chemistry. Before quantum mechanics, chemistry and physics were different endeavors. Quantum mechanics can explain the properties of the chemical bond. Thus physics and chemistry became one science.

We start with the hydrogen molecule  $H_2$  from which we learn the nature of the “electron-pair” bond, the most important type. Consider two hydrogen atoms. We measure their distance by the distance  $\rho$  between the two nuclei. When  $\rho$  is much larger than the Bohr radius  $a_B = \hbar/mv^2$ , there will be no force between them since they are electrically neutral. The energy  $E$  of the system will be simply the sum of the energies of the two isolated atoms:  $E = -2 \text{ Ry}$  for  $\rho \gg a_B$ , where  $\text{Ry} = -me^4/2\hbar^2$  (see the March essay). The vanishing of interaction at large  $\rho$  can be viewed as a cancellation of repulsive and attractive interactions: repulsions between the nuclei and between the electrons; attractions between each nucleus and the other atom's electron. (The attraction between the nuclei and their own electrons does not depend on  $\rho$  and is contained in  $E = -2 \text{ Ry}$ .)

What happens if  $\rho$  is no longer large compared to  $a_B$ ? Let us concentrate upon the part  $E'$  of the energy, which excludes the trivial repulsion energy  $e^2/\rho$  between the nuclei:  $E' = E - e^2/\rho$ . We know the values of  $E'$  for large  $\rho$ :

$$E' = -2 \text{ Ry} - e^2/\rho, \quad \rho \gg a_B. \quad (1)$$

But we also know  $E'$  for  $\rho = 0$ : It is the energy of two electrons attracted by a central charge  $2e$ . This is nothing else but helium! We determined that energy in the previous essay:  $E' = -5.7 \text{ Ry}$ . What happens to the repulsion of the two protons in helium? This question will be answered in the next installment.

We now make a rough approximation: We assume that (1) is valid for  $\rho > 2a_B$ . We interpolate  $E'$  between  $\rho = 0$  and  $\rho = 2a_B$  by a straight line (see Fig. 1). The actual energy  $E$  of the two hydrogen atoms is arrived at by adding  $e^2/\rho$  to  $E'$ . Obviously, this energy is  $-2 \text{ Ry}$  for  $\rho > 2a_B$ , and it has a minimum at  $\rho = \rho_0 = 1.22a_B$  as seen in Fig. 1. The minimum value is  $E(\rho_0) = -2.42 \text{ Ry}$ . For smaller  $\rho$ ,  $E$  rises strongly because of the preponderance of the repulsion between the nuclei.  $E(\rho)$  gives a good account of the chemical bond, its short range attraction and its repulsion at small distances. The position and depth of its minimum compares favorably with the actual distance  $1.43a_B$  of the nuclei in the hydrogen molecule and the actual binding energy of the H atoms, of  $0.34 \text{ Ry}$ . [The binding energy is the difference between  $E(\rho_0)$  and  $E(\infty)$  which is  $0.42 \text{ Ry}$  in our model.]

Figure 1 also shows  $E'(\rho)$  and  $E(\rho)$  as calculated exactly from the Schrödinger equation of two electrons in the field of two fixed unit charges at a distance  $\rho$ . We see that our bold linear approximation between  $\rho = 2a_B$  and  $\rho = 0$  for  $E'$  is not so bad. Compared to a smooth interpolation, it is a little too low for  $\rho \sim \rho_0$ ; this is why we get too deep a minimum and too large a binding. Furthermore the corner at  $\rho = 2a_B$  raises the energy around that distance and causes a steeper minimum and a smaller  $\rho_0$  than with the exact curve. Note that the true  $E'(\rho)$  has a horizontal tangent at

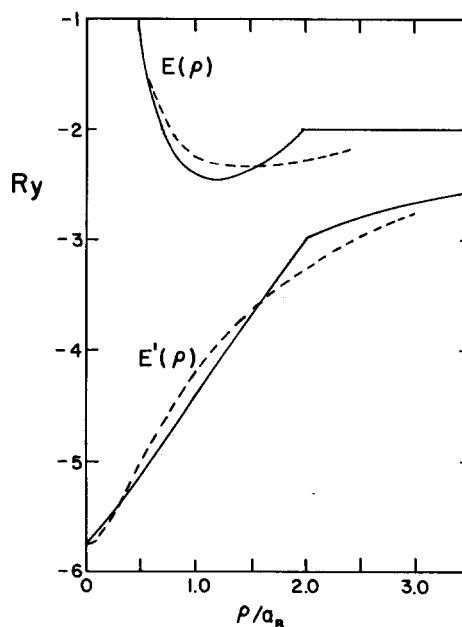


Fig. 1. Energy  $E$  of two hydrogen atoms as a function of the distance  $\rho$  between the nuclei.  $E'(\rho) = E - e^2/\rho$ . The energies are measured in Ry, the distance in units of  $a_B$ . The full curves are the approximate results, and the broken curves are the exact results.

$\rho = 0$  as expected since, at distances small compared to the Bohr radius for  $Z = 2$ ,  $(a_B/2)$ ,  $E'$  cannot differ much from the  $\rho = 0$  value.

Our conclusions are valid only if the two electrons have opposite spin. Only then does  $E'(\rho)$  go to the helium ground state for  $\rho = 0$ . If the spins are parallel, the lowest state in helium would be the triplet  $S$  state with an energy of  $-1.13 \text{ Ry}$ . Putting  $E'(0)$  equal to that value would lead to a curve of  $E'(\rho)$  which bends upwards going from  $\rho = 2a_B$  to zero. It would not give rise to values of  $E$  less than  $-2 \text{ Ry}$ ; there is no binding for parallel spins.

What is the physics that causes the minimum of  $E(\rho)$ ? When  $\rho$  becomes smaller than  $2a_B$  the electron clouds merge and the situation becomes similar to helium: either electron is attracted by the charge of both nuclei. This is counteracted by the increase in repulsion between the nuclei. The repulsion between the electrons is already considered in the value of the helium energy, where it plays an important role (see the April essay). But the double attraction wins out for values of  $\rho$  of the order of one-and-a-half  $a_B$ . The merging of the electron clouds is possible only if the electrons have different spin states. The Pauli principle would prevent the merging for parallel spin and would raise the energy because of the compression of the clouds when  $\rho < 2a_B$ .

These considerations show that the chemical bond is an electrostatic effect: The two electrons are exposed to twice as much positive charge within their clouds than in the separated atoms. This increased attraction is larger than the repulsions between the nuclei and between the electrons.

The chemical bond is often described as an “exchange effect.” I believe that such a formulation is misleading. It refers to mathematical terms appearing in the detailed calculation, in which two wave functions appear, differing by an exchange of coordinates. These terms are a consequence

of the Pauli principle requiring antisymmetric wave functions. They have no direct physical significance. Electrons are "exchanged" only in the sense that in the merged molecular quantum state it is no longer possible to assign an electron to one or the other nucleus.

The question left upon in the last essay was this. Why is  $\beta = R / r_{12}$  smaller for more peaked electron distributions  $\rho(r)$ ? Here  $R$  is an average of the distance from the center and  $r_{12}$  an average of the distance between two electrons distributed as  $\rho(r)$ . Take a given distribution  $\rho(r)$  and change it by moving a small part from a distance  $x$  to the center,

which would increase the peak. The contribution of this part to  $R$  goes from  $x$  to zero. However, the contribution to  $r_{12}$  goes from a certain value to another value larger than zero. Hence  $\beta$  would become smaller.

I use this occasion to thank Professor Herbert Bernstein of Hampshire College for most valuable discussions, and help in improving the clarity of presentation in this series.

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