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Abstract

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THE SPLITTING ENERGY OF THE TERMS OF THE HYDROGEN MOLECULE

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The energies of the electronic terms of the hydrogen molecule are usually calculated in the Heitler—London scheme, in which the symmetrized and antisymmetrized combinations of the wave functions of electrons in neutral atoms are chosen as the initial wave functions. In the present note we wish to show that this approximation is incorrect even at large distances between the atoms. Below we shall calculate the asymptotic value of the splitting energy of the singlet and triplet terms of the hydrogen molecule. The singlet term corresponds to the symmetric coordinate wave function $\Psi_S(\mathbf{r}_1, \mathbf{r}_2)$, and the triplet term to the antisymmetric coordinate wave function $\Psi_A\{\mathbf{r}_1, \mathbf{r}_2\}$. The Schrödinger equation, in atomic units, has the form

$$\left\{-\frac{\Delta_1}{2} - \frac{\Delta_2}{2} - \sum_i \frac{1}{R_{1i}} - \sum_i \frac{1}{R_{2i}} + \frac{1}{r_{12}} + \frac{1}{2a}\right\} \Psi_{S,A} = E_{S,A} \Psi_{S,A}, \quad (1)$$

where R_{1i}, R_{2i} are the distances of the i-th electron from the first or the second nucleus, which we place on the x-axis at the points $\pm a$.

In the Heitler—London theory the splitting energy is expressed in terms of integrals over the overlap region of the product of the wave functions $\Psi_a(\mathbf{r}_1)\Psi_{-a}(\mathbf{r}_1)\Psi_a(\mathbf{r}_2)\Psi_{-a}(\mathbf{r}_2)$, where $\Psi_{\pm a}(\mathbf{r})$ are the Bohr functions of the hydrogen atom $\exp\{-|\mathbf{r} \pm \mathbf{a}|\}$. It is easy to see where the essential region is located in such integrals. Indeed, if one expands

$$|\mathbf{r} \pm \mathbf{a}| \simeq |x \pm a| + \frac{\rho^2}{2|x \pm a|}$$

in the product of the functions

$$\Psi_a(\mathbf{r})\Psi_{-a}(\mathbf{r}) \simeq \exp\left\{-2a + \frac{\rho^2}{2(x+a)} + \frac{\rho^2}{2(x-a)}\right\},$$

where ρ is the distance to the x-axis, then it follows at once that the essential region is a cylindrical region: x is of order a, whereas $\rho \sim \sqrt{a} \ll x$. In this region the distances and the energy of the interaction of the electrons with one another and of an electron with the foreign nucleus are of the same order as the energy of its Coulomb interaction with the nucleus on which it is assumed to be localized. It is therefore illegitimate to treat these terms by perturbation theory, as is done in the Heitler–London theory. Instead, it is necessary to solve the Schrödinger equation anew, in order to determine sufficiently accurately the electron wave functions in the region of the potential barrier. This circumstance, as applied to the problem of the molecular ion of hydrogen, was first pointed out in 1961 by L. D. Landau (1)*.

The splitting of the terms of the molecule $E_S - E_A$ is exponentially small at large distances between the atoms: $E_S - E_A \sim e^{-4a}$. Meanwhile, as is known, two neutral atoms interact with one another by van der Waals forces, i.e., in a power-law manner according to the law $\sim a^{-6}$. It is therefore very important to obtain a formula for the term splitting that would have the exponential accuracy needed by us. For this purpose we draw in the 6-dimensional space $\{\mathbf{r}_1, \mathbf{r}_2\}$ the hyperplane S $(x_1 = x_2)$, which divides it into two parts. Let us now consider the integrals $\iint_\Omega \Psi_A E_S \Psi_S \, dr_1 dr_2$ and $\iint_\Omega \Psi_S E_A \Psi_A \, dr_1 dr_2$, in which the integration is carried out over the region "to the left" of the hyperplane S $(x_1 = x_2)$ (this region is schematically shown in Fig. 1). With the aid of the Schrödinger equation (1) we obtain

$$(E_S - E_A) \iint_\Omega \Psi_A \Psi_S \, dr_1 dr_2 = \frac{1}{2} \iint_\Omega \{\Psi_S(\Delta_1 + \Delta_2)\Psi_A - \Psi_A(\Delta_1 + \Delta_2)\Psi_S\} \, dr_1 dr_2$$

$$= \iint_\Omega \nabla_1(\Psi_S \nabla_1 \Psi_A - \Psi_A \nabla_1 \Psi_S) \, dr_1 dr_2 = \iint_S (\Psi_S \nabla_1 \Psi_A - \Psi_A \nabla_1 \Psi_S) \, dS.$$

Introduce the combinations of functions $\Psi_1 = \frac{1}{2}(\Psi_S + \Psi_A)$, $\Psi_2 = \frac{1}{2}(\Psi_S - \Psi_A)$, which correspond to states in which each electron, for large $a \gg 1$, is localized mainly on its own atom. We choose Ψ_1 and Ψ_2 so that:

$$\Psi_1(r_1, r_2) \simeq \frac{1}{\pi} \exp[-|r_1 + a| - |r_2 - a|] \qquad (r_1 \to -a;\ r_2 \to a),$$

$$\Psi_2(r_1, r_2) \simeq \frac{1}{\pi} \exp[-|r_1 - a| - |r_2 + a|] \qquad (r_1 \to a;\ r_2 \to -a), \tag{2}$$

i.e. under the indicated conditions they would pass into the product of normalized Bohr functions of the hydrogen atoms.

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* A criticism of the Heitler–London model and a calculation of the molecular ion of hydrogen are also contained in the recently published work of Herring (2).

Fig. 1

Figure 1: Fig. 1

In the integral

$$\iint_{\Omega} \Psi_A \Psi_S \, dr_1 dr_2 = \iint_{\Omega} (\Psi_1^2 - \Psi_2^2) \, dr_1 dr_2$$

the integration with respect to r_1 proceeds mainly in the neighborhood of $-a$, and with respect to r_2—near a. To within small van der Waals corrections, in this region the functions Ψ_1, Ψ_2 are determined by (2). Owing to this, with the indicated accuracy,

$$\iint_{\Omega} \Psi_A \Psi_S \, dr_1 dr_2 = 1.$$

As a result we obtain:

$$E_S - E_A = 2 \iint_{S} (\Psi_2 \nabla_1 \Psi_1 - \Psi_1 \nabla \Psi_2) \, dS. \tag{3}$$

Fig. 1

Thus, $E_S - E_A$ is expressed in terms of the integral of the product $\Psi_2 \Psi_1$ over the hypersurface S $(x_1 = x_2)$. From (3) it is immediately clear that $E_S - E_A \sim e^{-4a}$. The essential region of integration here, as is not difficult to estimate with the aid of (2), is $x_1 = x_2 \sim a$; $\rho_1, \rho_2 \sim \sqrt{a}$. We now turn to the determination of Ψ_1 and Ψ_2 in this region.

Let us first note that for $a \gg 1$ one may neglect the van der Waals interaction in the energies E_S and E_A, i.e. $E_S \simeq E_A \simeq -1$. We shall seek Ψ_1 and Ψ_2 in the form

$$\Psi_1(r_1, r_2) = \frac{\chi_1(r_1, r_2)}{\pi} \exp[-|r_1 + a| - |r_2 - a|],$$

$$\Psi_2(r_1, r_2) = \frac{\chi_2(r_1, r_2)}{\pi} \exp[-|r_1 - a| - |r_2 + a|]. \tag{4}$$

In the region of interest to us, $x_1, x_2 \sim a$, $\rho_1, \rho_2 \sim \sqrt{a}$, the functions $\chi_{1,2}(r_1, r_2)$ vary slowly in comparison with the exponentials:

$$\exp\{-|r_1 + a| - |r_2 - a|\} \simeq \exp\left\{-2a - x_1 + x_2 + \frac{\rho_1^2}{2(x_1 + a)} + \frac{\rho_2^2}{2(x_2 - a)}\right\}.$$

Substituting (4) into (1) and retaining, upon differentiation, only the principal terms, we obtain the equation for χ_1:

$$\left\{\frac{\partial}{\partial x_1} - \frac{\partial}{\partial x_2} + \frac{1}{2a} - \frac{1}{a - x_1} - \frac{1}{a + x_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right\}\chi_1 = 0. \tag{5}$$

Introducing $x_1 = \xi + \eta/2,\ x_2 = \xi - \eta/2$, we rewrite it in a more convenient form:

$$\left\{\frac{\partial}{\partial \eta} - \frac{1}{2(a-\xi)-\eta} - \frac{1}{2(a+\xi)-\eta} + \frac{1}{2\sqrt{\eta^2 + \rho_{12}^2}} + \frac{1}{4a}\right\}\chi_1 = 0$$

The solution of the last equation is

$$\chi_1 = \frac{C(\xi, \rho_{12})\left[\sqrt{\eta^2 + \rho_{12}^2} - \eta\right]^{1/2}}{[2(a-\xi)-\eta][2(a+\xi)-\eta]}e^{-\eta/4a},$$

where $C(\xi, \rho_{12})$ is an arbitrary function of the variables ξ and ρ_{12}.

To determine it we shall use the obvious condition that χ_1 tends to unity when either $x_1 \to -a$ or $x_2 \to a$. Indeed, suppose, for example, $x_1 \to -a$ (x_2 arbitrary). In this case the charge of the electron compensates the charge of the ion at the point $-a$, and the motion of the second electron takes place only in the field of the ion at the point $+a$. This circumstance is also seen directly from (5). After simple calculations we obtain:

$$\Psi_1(\mathbf{r}_1, \mathbf{r}_2) = \frac{2a\exp\left[-2a + x_2 - x_1 + \frac{\rho_1^2}{2(x_1+a)} + \frac{\rho_2^2}{2(x_2-a)}\right]}{\pi(a-x_1)(a+x_2)}\times$$
$$\times\begin{cases} (2a + x_1 + x_2)\exp\left[-\dfrac{a+x_1}{2a}\right]\left[\dfrac{\sqrt{(x_1-x_2)^2+\rho_{12}^2}+x_2-x_1}{\sqrt{(2a+x_1+x_2)^2+\rho_{12}^2}+x_1+x_2+2a}\right]^{1/2} \\ \qquad (x_1+x_2<0); \\ (2a - x_1 - x_2)\exp\left[-\dfrac{a-x_2}{2a}\right]\left[\dfrac{\sqrt{(x_1-x_2)^2+\rho_{12}^2}+x_2-x_1}{\sqrt{(x_1+x_2-2a)^2+\rho_{12}^2}+2a-x_1-x_2}\right]^{1/2} \\ \qquad (x_1+x_2>0). \end{cases} \tag{6}$$

The function $\Psi_2(\mathbf{r}_1, \mathbf{r}_2)$ is obtained from (6) by the replacement $1 \leftrightarrow 2$.

Let us now return to formula (3). Substituting (4) into it and differentiating only the exponential, we transform it to the form:

$$E_S - E_A = -8\int_0^a dx\, d^2\rho_1\, d^2\rho_2\, [\Psi_2\Psi_1]_{\substack{x_1+x_2>0\\ x_1=x_2}}$$

(here $[\Psi_2\Psi_1]_{\substack{x_1+x_2>0\\ x_1=x_2}}$ means that the functions (6) are taken as $x_1 \to x_2$, but $x_1 + x_2 > 0$).

As a result of the calculations we obtain:

$$E_S - E_A = -\frac{4}{e}\sqrt{\pi}\,(2a)^{5/2}e^{-4a}\int_0^1 \frac{e^x\,dx}{x+1}. \tag{7}$$

If $R = 2a$ is the distance between the nuclei in atomic units, then it is convenient to rewrite (7) in the form

$$E_S - E_A = -2.94\,R^{5/2}e^{-2R}. \tag{8}$$

The result obtained by the Heitler–London scheme (3):

$$E_S - E_A = -e^{-2R}\frac{4}{15}R^3(\ln R - 4.34). \tag{9}$$

Both expressions differ by pre-exponential factors. Note, however, that in contrast to (9), expression (8) is asymptotically exact for $R \gg 1$. The relative accuracy with which (8) has been calculated is determined by the one-dimensional approximation made in equation (5) and is of order R^{-1}.

In conclusion, let us emphasize once more that as $R \to \infty$ the term-splitting energy is exponentially small in comparison with the power-law character of the decrease of the van der Waals interaction energy: $E_{\text{v.–W.}} \simeq -6.5R^{-6}$. Comparison of this quantity with (8) shows, however, that the two energies become of the same order for rather large $R \sim 5$. For smaller R, the exchange part of the interaction energy of the atoms predominates.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.

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