

On Molecular Screening Constants

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ABSTRACT.

Assuming that in a diatomic molecule with two electrons, the inner one screens the charge on each nucleus by $\frac{1}{2}e$, the term values and the heat of dissociation of the molecules occurring in the following table are calculated by Hylleraas's method.

| | LiH. | BeH. | Li ₂ . |
|--|------|------|-------------------|
| Heat of Dissoc ⁿ . (Calc.) (in electron volts.) ... | 2.30 | 2.30 | 1.08 |
| Heat of Dissoc ⁿ . (Obs.) (in electron volts.) ... | 2.56 | 2.21 | 1.14 |

| | 1s2p ¹ Σ. | 1s2s ³ Σ. | $\frac{1}{2}\{1s2p(1\pi + 3\pi)\}$. | 1s1s ¹ Σ. |
|--|----------------------|----------------------|--------------------------------------|----------------------|
| Term value of H ₂ (Calc.) (in Rydberg unit) ... | -1.490 | -1.416 | -1.442 | -2.33 |
| Term value of H ₂ (Obs.) (in Rydberg unit) ... | -1.499 | -1.469 | -1.439 | -2.33 |

The Ritz method of finding the characteristic energy values of atoms very often yields a useful collateral result, *viz.*, the value of the screening constant of the atomic nucleus. By a combination of the Ritz method and the method of

separation of variables Hylleraas¹ has almost exactly calculated the term values of the H_2 -molecule in the lowest few states. The advantage he has had over his predecessors appears to lie in the fact that as a first approximation he regards the outer electron as moving in a field due to half the actual charge of each nucleus. It will be shown in the present paper that if the idea of nuclear screening to the extent of $\frac{1}{2}e$ is applied to slightly more complex molecules, that leads to a fair agreement between the observed and calculated values of the electronic terms and the heat of dissociation, the calculation being extremely simplified by the fact that certain tables prepared by Hylleraas can be directly made use of.

Let the two nuclei in the molecule be denoted by a and b , and the electrons by the numbers 1 and 2; then r_{1a} stands for the distance between the nucleus a and the electron 1; similar meanings attach to r_{2b} , r_{1b} , etc. The potential energy of the electrons in Hylleraas's units is

$$V = -4 \left(\frac{1}{r_{1a}} + \frac{1}{r_{1b}} + \frac{1}{r_{2a}} + \frac{1}{r_{2b}} - \frac{1}{r_{12}} \right),$$

and the energy operator of the system is $H = \Delta_1 + \Delta_2 + \nu$, where Δ_1 , Δ_2 are Laplacian operators with a constant factor. Then the total energy is

$$\text{where} \quad \int \bar{\psi} H \psi d\tau / \int \bar{\psi} \psi d\tau,$$

where

$$\psi = \psi_1 \psi_2$$

and

$$d\tau = d\tau_1 d\tau_2,$$

ψ_1 being the wave function of the electron 1, ψ_2 being that of 2.

Now if we write

$$E' = \int \bar{\psi} \left(\Delta_1 - \frac{4}{r_{1a}} - \frac{4}{r_{1b}} \right) \psi d\tau / \int \bar{\psi} \psi d\tau, \quad \dots (1)$$

¹ Hylleraas, *Zs. f. Phys.* 71, 789, (1931).

$$E = \int \bar{\psi} \left(\Delta_2 - \frac{2}{r_{2a}} - \frac{2}{r_{2b}} \right) \psi d\tau / \int \bar{\psi} \psi d\tau, \quad \dots (2)$$

and

$$E_s = 4 \int \bar{\psi} \left(-\frac{1}{2r_{2a}} - \frac{1}{2r_{2b}} + \frac{1}{r_{12}} \right) \psi d\tau / \int \bar{\psi} \psi d\tau \quad \dots (3)$$

the total energy is $E' + E + E_s$.

It is evident from (1) and (2) that E' is the total energy of an electron in a field of two nuclei each of charge unity, while E (without prime) is the energy in a field of half the charge; E_s is a perturbation term involving exchange integrals of the Sugiura types which Hylleraas evaluates numerically. The notion of screening is thus implicit in a treatment where E_s is regarded as mere perturbation energy.

The energy values E , E' of the individual electrons are found by Hylleraas by the use of elliptic coordinates. If $2R$ be the internuclear distance and Z_a , Z_b be the respective nuclear charges, the potential of an electron in terms of the elliptic coordinates

$$\xi = (r_a + r_b) / 2R$$

and

$$\eta = (r_a - r_b) / 2R$$

is easily seen to be

$$V = -\frac{2}{R} \frac{\xi(Z_a + Z_b) + \eta(Z_a - Z_b)}{\xi^2 - \eta^2}.$$

When the variables have been separated in the resulting wave equation, the equation involving the variable ξ is found to be

$$\frac{\partial}{\partial \xi} \left\{ (\xi^2 - 1) \frac{\partial X}{\partial \xi} \right\} - \frac{m^2 X}{\xi^2 - 1} + \left[-C\xi^2 + B\xi - A \right] X = 0 \quad \dots (4)$$

where

$$B = R(Z_a + Z_b), \quad C = -\frac{1}{4} ER^2 \quad \dots (5)$$

and A is another eigen value parameter determined by the corresponding equation in η . E is the energy parameter.

Before proceeding further we explain that in Hylleraas's notation E_{nlm} stands for the energy of an electron with quantum numbers n, l, m . For instance, an electron in the $2p$ state with quantum numbers 2, 1, 0 has energy E'_{210} , under full nuclear charge.

In the case of hydrogen $Z_a = Z_b = 1$, and Hylleraas solves the equation (4) for the $1s$ -state of the electron and tabulates the value of E'_{100} for different R values which is reproduced here :—

TABLE I.

| | | | | | | | | | | |
|------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| E'_{100} | -3.470 | -2.905 | -2.683 | -2.498 | -2.311 | -2.205 | -2.080 | -1.988 | -1.899 | -1.832 |
| R | 0.5 | 1 | 1.25 | 1.5 | 1.75 | 2 | 2.25 | 2.5 | 2.75 | 3 |

Table No 2 of his paper gives the values of E_{200} , the energy of a $2s$ -electron in a nuclear field $Z_a = Z_b = \frac{1}{2}$. This is our table II.

TABLE II.

| | | | | | | | | | |
|-----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| E_{200} | -0.250 | -0.233 | -0.227 | -0.222 | -0.216 | -0.211 | -0.207 | -0.202 | -0.194 |
| R | 0 | 1 | 1.25 | 1.5 | 1.75 | 2 | 2.25 | 2.5 | 3 |

We shall presently describe a method whereby the energy value E for any value Z_a, Z_b can be readily calculated by the use of the foregoing tables.

The equation corresponding to (4) for an electron on nuclei of charges Z'_a, Z'_b and at a distance $2R'$ apart is

$$\frac{\partial}{\partial \xi} \left\{ (\xi^2 - 1) \frac{\partial X'}{\partial \xi} \right\} - \frac{m^2 X'}{\xi^2 - 1} + \left[-C'\xi^2 + B'\xi - A' \right] X' = 0 \quad \dots (6)$$

where

$$B' = R'(Z'_a + Z'_b), C' = -\frac{1}{4} E'R'^2 \quad \dots (7)$$

Then (4) and (6) would constitute the same eigen value problem, if $A' = A$, which means that $Z_a - Z_b = Z'_a - Z'_b$ and $B' = B, C' = C$, which give from (5) and (7)

$$E(R) = \left(\frac{Z_a + Z_b}{Z'_a + Z'_b} \right)^2 E' \left(R \frac{Z_a + Z_b}{Z'_a + Z'_b} \right) \quad \dots (8)$$

Hence if a table of values of $E(R)$ be given we can construct a table for $E'(R)$ and *vice versa*, graphically by means of the formula (8).

We first take up the LiH molecule. We assume, as Hutchisson and Muskat² have done, that the Li-nucleus along with its K-electrons constitutes a simple nucleus of charge unity. The problem is to find the energy of a 1s-electron and a 2s-electron in the field of two nuclei, each of unit charge. The energy E'_{100} of the 1s-electron is already given in table I. This electron screens the nuclei to the extent of half the charge, so that the energy E_{200} of the 2s-electron is to be read from table II. Table III below gives the values of $E_{LiH} = E'_{100} + E_{200} + 2/R$ which represents the total energy of the molecule LiH.

Table III

| | | | | | | |
|-----------|--------|--------|--------|--------|--------|--------|
| E_{LiH} | -1.137 | -1.386 | -1.414 | -1.417 | -1.407 | -1.390 |
| R | 1 | 1.5 | 1.75 | 2 | 2.25 | 2.5 |

From a graph of E against R we find the minimum value of E_{LiH} to be -1.42 Rydberg units roughly. When this hypothetical molecule dissociates, the products are a hydrogen-like

² Hutchisson and Muskat, *Phys. Rev.*, 40, 340 (1932).

atom in the 1s-state and another in the 2s-state, the total energy of which is -1.25 units. Hence the heat of dissociation of the LiH molecule is -0.17 units = 2.3 electron-volts, which is the same as Hutchisson and Muskat's calculated value. The experimental value³ is 2.56 volts.

In finding the heat of dissociation of the more complex BeH molecule Ireland⁴ assumes that the Be nucleus along with its two K-electrons constitutes a simple nucleus of charge 2, so that the problem of the BeH molecule is that of two electrons, of which either both are in the 2s-state or one is in the 2s-state and the other in the 2p-state, and a third electron in the 1s-state in a field of two nuclei of charges 1 and 2 units. He shows that there is a $^2\Sigma$ state and a $^2\pi$ state in which E as a function of R has a minimum and the heats of dissociation calculated by him are 3.5 and 1.5 volts respectively while the experimental values are 2.22 and 2.21 volts. Admittedly the agreement is poor; but if we take a simplified model of the BeH molecule, in which the Be nucleus with its K-electrons and the third electron in the 2s-state is regarded as a simple nucleus of charge 1, then BeH and LiH present identical problems; then the heat of dissociation of BeH also is 2.3 volts which is in better accord with the observed value than Ireland's.

We next consider the Li_2 molecule. Effectively it has two electrons each in the 2s-state in a field of two nuclei each of unit charge. The energy E'_{200} of a 2s-electron in a field $Z'_a = Z'_b = 1$ has not been given by Hylleraas; but we can apply the formula (8) and utilise the table II for E_{200} in finding E'_{200} . We get the following values:—

| | | | | |
|------------|----|--------|--------|--------|
| E'_{200} | -1 | -0.930 | -0.846 | -0.777 |
| R | 0 | 0.5 | 1 | 1.5 |

³ Nakamura, *Zs., f. Phys.*, 59, 218 (1930).

⁴ Ireland, *Phys. Rev.*, 43, 331 (1933).

By graphical extrapolation we extend the table further :—

| | | | | | |
|------------|-------|-------|-------|-------|-------|
| E'_{200} | -0.70 | -0.62 | -0.55 | -0.47 | -0.40 |
| R | 2 | 2.5 | 3 | 3.5 | 4 |

We assume that the 2s-electron of one Li atom effectively reduces the nuclear charges by $\frac{1}{2}e$; then the energy of the 2s-electron of the second atom must be E_{200} of table II. Then the total energy of the molecule is $E_{Li_2} = E'_{200} + E_{200} + 2R$. The values of E_{Li_2} are given below :—

| | | | | | | | | |
|------------|------|------|------|------|-------|-------|-------|-------|
| E_{Li_2} | 2.82 | 0.92 | 0.33 | 0.09 | -0.02 | -0.07 | -0.08 | -0.07 |
| R | 5 | 1 | 1.5 | 2 | 2.5 | 3 | 3.5 | 4 |

E_{Li_2} has thus a minimum value -0.08 units, which is the same as Furry⁵ and Bartlett's. A Morse formula fits into the above table easily. If in the formula $E = D e^{-2a(R-R_0)} - 2D e^{-a(R-R_0)}$, we put $D = 0.08$, $R_0 = 3.5$ and $a = 0.59$, we get the following table of values :—

| | | | | | | | |
|--------------------|------|------|-------|--------|--------|--------|--------|
| E_{Li_2} (Morse) | 0.92 | 0.33 | 0.083 | -0.028 | -0.070 | -0.080 | -0.075 |
| R | 1 | 1.5 | 2 | 2.5 | 3 | 3.5 | 4 |

The heat of dissociation $D = 0.08 \times 13.53 = 1.08$ volts as against the observed value 1.14 volts.

We finally consider the hydrogen terms. If one electron be in the 1s-state while the other is in the 2p-state with quantum numbers (2, 1, 0) the resulting molecular terms are $1s2p \ ^1\Sigma$. Hylleraas's table No. 3 gives the value E_{210} of a (2, 1, 0) electron in a field of half the nuclear charges. Adding E_{210} , E'_{100} and $2/R$ we get the energy in the $1s2p \ \Sigma$ state,

⁵ Furry and Bartlett, Phys. Rev., 38, 1615 (1931).

and the minimum value is found to be -1.490 against the observed value -1.4989 of the $1s2p^1\Sigma$ term.

If the second electron is in the $(2, 0, 0)$ state, the molecular term are $1s2s^1\Sigma$, and the energy value $E_{200} + E'_{100} + 2/R$ has a minimum -1.416 as against the observed value -1.4645 of the $1s2s^3\Sigma$ term. The difference is a little marked here, showing that the amount of screening is not exactly half on the $2s$ -electron because of its penetrative character.

If the second electron is in the $(2, 1, 1)$ state the molecular terms are $1s2p^1\Sigma$, and the calculated value has a minimum -1.442 . The observed mean value

$$(1s2p^1\pi + 1s2p^3\pi)/2 \text{ is } -(1.4176 + 1.4600)/2 = -1.4388$$

which nearly agrees with the calculated term.

If both the electrons are in the $1s$ -state, the molecular term is $1s1s^1\Sigma$, but in this case the amount of screening is found to be about $\frac{3}{8}$ and not $\frac{1}{2}$. Thus putting $Z_a = Z_b = \frac{5}{8}$ and $Z'_a = Z'_b = 1$, we get from (8)

$$E_{100}(R) = \left(\frac{5}{8}\right)^2 E'_{100}\left(\frac{5R}{8}\right) \quad (9)$$

The value of the total energy

$$E_{100} + E'_{100} + \frac{2}{R} = E_{H_2}$$

is calculated with the help of (9) and tabulated below:—

| | | | | | | | |
|-----------|----------|---------|----------|---------|---------|---------|---------|
| E_{H_2} | ∞ | -0.90 | -2.205 | -2.31 | -2.32 | -2.30 | -2.25 |
| R | 0 | 0.5 | 1 | 1.25 | 1.5 | 1.75 | 2 |

The experimental value of E_{H_2} is -2.3262 , and $R_0 = 1.42$. From the foregoing table we get $E_{H_2} = -2.32$ and $R_0 = 1.5$.

It is obvious that all the labour involved in the numerical computation made by the writers referred to, when the atomic wave functions are used and the exchange integrals have to be evaluated, is reduced to a minimum here, principally because the use of elliptic co-ordinates gives a nearly exact eigen value, and secondly because of the consideration of the proper amount of screening.
