The Normal State of the Hydrogen Molecule

Takao KUDOU

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Synopsis

Recently W. Kolos and C.C.J. Roothaan have discussed the electron correlation of hydrogen molecule on the ground state of energy level by use of 40 terms wave function of James and Coolidge certifying the narrow applicability only on the state of hydrogen molecule.

The use of modified Berencz wave function on the LCAO approximation used in common, may be of wide application which interprets the effect of correlation of electron on the energy level intuitively.

I. Introduction

The chemisorption of atomic hydrogen, carbon, nitrogen, oxygen and fluorine on the graphite was discussed, using the semi-empirical molecular orbital theory by Bennett et al., recently. No good results were obtained by use of the EHT calculation in which the effects of correlation between electrons were not considered, while the CNDO approximation under consideration of the effects of the electron-electron force and the core-core force gave reasonable results.

Though an evident importance of the electron-electron correlation on the orbital of molecule was already shown, the experimental results are not so enough to ascertain the theory. So theoretical consideration on the treatment of electron-electron correlation is desirable to advance the theory of adsorption of gas molecule on the surface of solids.

In this paper the mathematical treatment of the effect of electron correlation on the orbital of hydrogen molecule by the LCAO approximation was discussed.

II. Wave Function for Hydrogen Molecule

The wave function for molecular orbital calculation of hydrogen molecule was shown by Hund and Mulliken as

\[ \Phi_a = [a(1)b(2) + b(1)a(2)] + [a(1)a(2) + b(1)b(2)]^* \]  

* Let \( a \) represent a hydrogen ls wave function about atom a, and \( b \) a hydrogen ls wave function about atom b.
from the point of view of an ionic character of hydrogen molecule. This is not so
enough to describe the system fully, as the overestimation of ionic character at the
far distance between the atoms was made. And also no correction of the wave function
came from the effect of electron-electron force was made.

The wave function of Weinbaum\(^3\) is

\[ \Phi_2 = [a(1)b(2) + b(1)a(2)] + c [a(1)a(2) + b(1)b(2)] \]

where \(c\) is variation parameter having the value of zero at infinite distance of hydrogen
atoms and 0.256 at equilibrium point \((\sigma r)\). Some successful advance was achieved by
Weinbaum, but failed in the consideration of the detailed effect of electronic repulsion
terms.

Berencz\(^4\) calculated the binding energy 4.14 ev for hydrogen molecule and 1.338 a.u.
for equilibrium point \(\sigma r\) of hydrogen molecule by use of the wave function of

\[ \Phi_2 = [(a(1)b(2) + b(1)a(2)) + c (a(1)a(2) + b(1)b(2))] \chi(r_{12}) \]

derived from Hylleraas’ correlation function\(^5\).

\[ \chi(r_{12}) = 1 + pr_{12} \]

It is more reasonable to use the modified Berencz wave function by the form of

\[ \Phi_2 = [a(1)b(2) + b(1)a(2)] \chi_1(r_{12}) + [a(1)a(2) + b(1)b(2)] \chi_2(r_{12}) \]

adding the terms of different contribution of atomic character and ionic character of
hydrogen atoms to Berencz function.

### III. Results and Discussions

The computations are carried out by programming the set of recurring formulae
which are given in Kotani’s reference.

And the results of the present computations are given in **Table 1**.

<table>
<thead>
<tr>
<th>wave function</th>
<th>B.E. (e.v.)</th>
<th>(\sigma r) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. Weinbaum</td>
<td>[a(1)b(2) + b(1)a(2)] + c[a(1)a(2) + b(1)b(2)]] (c=0.256, a=1.193^*)</td>
<td>4.024</td>
</tr>
<tr>
<td>F. Berencz</td>
<td>[(a(1)b(2) + b(1)a(2)) + c(a(1)a(2) + b(1)b(2))] (1 + pr_{12})] (c=0.356, p=0.073, a=1.248)</td>
<td>4.14</td>
</tr>
<tr>
<td>T. Kudou</td>
<td>[a(1)b(2) + b(1)a(2)] (1 + c_1 r_{12}) + [a(1)a(2) + b(1)b(2)] (c_2 + c_3 r_{12})] (c_1=0.0000, c_2=0.2002, c_3=0.2950, a=1.310)</td>
<td>4.535</td>
</tr>
<tr>
<td>observed</td>
<td>(4.746)</td>
<td>1.4008</td>
</tr>
</tbody>
</table>

* \(a\); screening constant.

The value of binding energy 4.535 ev is differ from F. Berencz’s value 4.14 ev and
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shows more reasonable values to the experimental value of 4.746 ev.

The value of 4.535 ev is calculated from equation (4), where electron correlation in molecule is treated differently from that of the Berencz wave function.

So the modified wave function of the form

\[ \Phi_s = [a(1)b(2) + b(1)a(2)] \chi_1(r_{12}) + [a(1)a(2) + b(1)b(2)] \chi_2(r_{12}) \]

is more desirable for the calculation of the ground state of hydrogen molecule.

Acknowledgement

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And the author is indebted to Mr. Furuyama, Mr. Moriya, and Mr. Hiura the staffs of the computer center of college of humanities and sciences of Nihon University for this work.

Reference

3) S. Weinbaum: Journal of Chemical Physics, 1 (1933) 593.
8) M. Kotani et al.: Table of Molecular Integrals, Maruzen Co. Ltd. Tokyo 1955.

Appendix (INTEGRALS)

The integrals used here all computed with exception of integrals listed in Slater's reference. The symbols also are cited from Kotani's reference.

\[ w = aR \]

\[ [aa]_{12} [bb] = \int \alpha_1(1) \alpha_2(2) r_{12} b_1(2) b_2(1) d \tau_1 d \tau_2 \text{ etc.} \]

\[ [aa]_{12} [bb] = \frac{1}{a^2 w} \left( 2 + w^2 \right) - e^{-2 w} \left( 2 + \frac{29}{16} w + \frac{5}{8} w^2 + \frac{1}{12} w^3 \right) \]

\[ [ab]_{12} [ab] = \frac{w^2}{4 \pi} \left[ - \frac{2}{45} W_0^0(0, 0) + \frac{7}{15} W_0^0(2, 0) - W_0^0(2, 2) - \frac{1}{3} W_0^0(4, 0) + W_0^0(4, 2) \right. \]

\[ - \frac{3}{25} W_1^0(1, 1) + \frac{2}{5} W_1^0(3, 1) - \frac{1}{3} W_1^0(3, 3) + \frac{1}{75} W_1^0(0, 0) - \frac{2}{15} W_1^0(2, 0) \]

\[ - 21 - \]
\[
\begin{align*}
\frac{1}{3} W_1^2(2, 2) - \frac{4}{315} W_2^2(0, 0) - \frac{4}{175} W_4^2(1, 1) + \frac{4}{1, 575} W_3^4(0, 0) \\
[aa]\left| r_{12}\right| ab = \frac{1}{\alpha w}\left[ e^{-w}\left( \frac{7}{32} + \frac{29}{16} w + \frac{5}{2} w^2 + \frac{2}{3} w^3 + \frac{1}{6} w^4 \right) - e^{-3w}\left( \frac{7}{32} + \frac{w}{16} \right) \right] \\
[aa]\left| r_{12}^2\right| bb = \frac{1}{\alpha^2} (6 + w^2) \\
\frac{1}{\alpha w} e^{-2w}\left( 1 + w + \frac{w^2}{3} \right) (6 + 6w + \frac{5}{2} w^2 + \frac{1}{2} w^3 + \frac{1}{30} w^4) \\
\frac{1}{\alpha^2} e^{-w}\left( 6 + 6w + \frac{5}{2} w^2 + \frac{1}{2} w^3 + \frac{1}{10} w^4 \right) \\
\frac{3}{\alpha w} + 2w - e^{-2w}\left( \frac{3}{\alpha w} + \frac{9}{4} + \frac{1}{2} w \right) \\
\frac{1}{\alpha w}\left[ e^{-w}\left( \frac{1}{8} + \frac{7}{2} w + 4w^2 + \frac{4}{3} w^3 + \frac{1}{3} w^4 \right) - \frac{1}{8} e^{-3w} \right] \\
\frac{1}{\alpha w}\left[ e^{-w}\left( \frac{35}{8} - e^{-2w}(5 + 4w + 2w^2) + \frac{1}{8} e^{-4w}(5 + 2w) \right) \right] \\
\frac{16}{45} W_2^6(1, 0) - \frac{5}{3} W_2^6(2, 1) - \frac{1}{3} W_2^6(3, 0) + W_2^6(3, 2) + W_2^6(4, 1) \\
+ \frac{2}{5} W_2^6(2, 1) - \frac{2}{3} W_2^6(3, 2) - \frac{2}{15} W_1^3(1, 0) + \frac{2}{3} W_1^3(2, 1) \\
- \frac{4}{45} W_2^6(1, 0) \right] \\
\frac{1}{\alpha w}\left[ \frac{7}{15} W_2^6(1, 0) - 2W_2^6(2, 1) - \frac{1}{3} W_2^6(3, 0) + W_2^6(3, 2) + W_2^6(4, 1) \right] G_3^6(0) \\
- 2W_2^6(3, 2) G_2^2(1) + \left[ W_2^6(2, 1) - \frac{1}{3} W_2^6(1, 0) \right] G_2^6(2) \\
+ \frac{6}{5} W_2^6(2, 1) G_2^6(1) + \left[ -\frac{16}{21} W_2^6(1, 0) - \frac{2}{3} W_2^6(3, 0) \right] G_2^6(0) \\
- \frac{2}{3} W_2^6(1, 0) G_2^6(2) + \frac{4}{5} W_2^6(3, 1) G_2^6(1) - \frac{8}{35} W_3^6(1, 0) G_2^6(0) \\
+ W_2^2(2, 1) G_2^6(0) - \frac{1}{5} W_1^3(1, 0) G_1^3(0) - \frac{1}{45} W_3^3(1, 0) G_2^6(0) \right] \\
\frac{1}{\alpha w}\left[ \frac{2}{\alpha w} + \frac{2}{\alpha w}\right] \left( 4w \right) + e^{-w}\left( \frac{1}{4w} + \frac{7}{2} + 4w + 2w^2 \right) + e^{-3w}\left( \frac{1}{4w} + \frac{1}{2} \right) + 8w_2^6(1, w) \\
- 4w \sum_{k=0} \left( -1 \right)^k (2k + 1) f_k(1, 2w) G_k(0, w) \right] \\
\frac{1}{\alpha w}\left( \frac{2}{\alpha w} - \frac{2}{\alpha w}\right) [bb] = \frac{1}{\alpha w} (9 + 2w^2) \\
\frac{2}{\alpha w}\left[ \frac{2}{\alpha w} - \frac{2}{\alpha w}\right] [bb] = \left[ \frac{8 + 2w^2 - e^{-2w}(8 + 7w)}{\alpha w} \right]
\end{align*}
\]
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\[ [aa] \frac{2}{r_{1a}^2} \cdot [ab] = \frac{1}{a} e^{-\frac{1}{2} \left( 9 + 9w + 2w^3 + \frac{w^4}{5} \right)} \]

\[ [aa] \frac{2}{r_{1b}^2} \cdot [aa] = \frac{1}{aw} \left[ 12 - e^{-2w}(12 + 15w + 5w^2 + 2w^3) \right] \]

\[ [aa] \frac{2}{r_{1b}^2} \cdot [ab] = \frac{1}{aw} \left[ e^{-w} \left( 10 + 10w + \frac{13}{3} w^2 + \frac{w^4}{3} \right) - e^{-2w} \left( 10 + 21w + \frac{52}{3} w^2 + \frac{23}{3} w^3 \right) \right] \]

\[ + \frac{28}{15} \left( \frac{w^4}{5} + \frac{w^3}{3} \right) \]

\[ [bb] \frac{2}{r_{1a}^2} + \frac{2}{r_{1b}^2} \cdot [ab] = \frac{1}{a} e^{-w} \left( 18 + 36w + \frac{82}{3} w^2 + \frac{32}{3} w^3 + \frac{98}{45} w^4 + \frac{8}{45} w^5 \right) \]

\[ [bb] \frac{2}{r_{1a}^2} \cdot [bb] = \frac{2}{a} e^{-w} \left( 9 + 9w + \frac{5}{3} w^2 + \frac{2}{3} w^3 \right) \]

\[ [bb] \frac{(r_{1a} r_{1b} r_{1a} r_{1b})}{[bb]} = \frac{1}{w} \left( 1 - e^{-2w} \left( 1 + \frac{11}{8} w + \frac{3}{4} w^2 + \frac{23}{6} w^3 \right) \right) \]

\[ [bb] \frac{(r_{1a} r_{1b} r_{1a} r_{1b})}{[bb]} = \frac{1}{w} \left[ e^{-w} \left( \frac{5}{16} + \frac{1}{8} w + \frac{1}{16} w^2 \right) - e^{-3w} \left( \frac{5}{16} + \frac{1}{8} w \right) \right] \]

\[ [bb] \frac{(r_{1a} r_{1b} r_{1a} r_{1b})}{[bb]} = \frac{1}{64w} \left[ e^{-w} (9 + 32w + 6w^2 + \frac{64}{5} w^3) - e^{-3w} (35 + 32w + 8w^2) \right] \]

\[ - \frac{w^6}{16} \left[ \frac{4}{3} W^6(2, 1) G^6(0) + W^6(3, 1) G^6(1) - W^6(1, 0) G^6(2) - W^6(1, 1) G^6(3) \right] \]

\[ - 2 [W^6(2, 0) G^6(0) + W^6(3, 0) G^6(1) - W^6(0, 0) G^6(2) - W^6(1, 0) G^6(3)] \]

\[ + 2 [W^6(2, 2) G^6(0) + W^6(3, 2) G^6(1) - W^6(2, 0) G^6(2) - W^6(2, 1) G^6(3)] \]

\[ - \frac{4}{3} [W^6(2, 1) G^6(0) + W^6(3, 1) G^6(1) - W^6(1, 0) G^6(2) - W^6(1, 1) G^6(3)] \]

\[ - W^6(2, 1) G^6(1) + W^6(1, 0) G^6(2) + \frac{1}{9} W^6(2, 0) G^6(0) \]

\[ - \frac{1}{9} W^6(0, 0) G^6(2) \]

\[ [bb] \frac{(r_{1a} r_{1b} r_{1a} r_{1b})}{[bb]} = \frac{1}{64w} \left[ e^{-w} (-33 + 104w + 8w^2 + \frac{128}{3} w^3) + e^{-3w} (33 + 12w) \right] \]

\[ - \frac{w^6}{16} \left[ \frac{4}{3} [W^6(2, 1) G^6(0) - W^6(3, 1) G^6(1) - W^6(1, 0) G^6(2)] \right. \]

\[ + W^6(1, 1) G^6(3) \]

\[ - 2 [W^6(2, 0) G^6(0) + W^6(3, 0) G^6(1) + W^6(0, 0) G^6(2) - W^6(1, 0) G^6(3)] \]

\[ - W^6(1, 0) G^6(3) \]

\[ + 2 [W^6(2, 2) G^6(0) + W^6(3, 2) G^6(1) + W^6(2, 0) G^6(2) - W^6(2, 1) G^6(3)] \]

\[ - \frac{4}{3} [W^6(2, 1) G^6(0) + W^6(3, 1) G^6(1) - W^6(1, 0) G^6(2) - W^6(1, 1) G^6(3)] \]

\[ - W^6(2, 1) G^6(1) + W^6(1, 0) G^6(2) + \frac{1}{9} W^6(2, 0) G^6(0) \]

\[ - \frac{1}{9} W^6(0, 0) G^6(2) \]
\[-W_1^g(2,1)G_1^g(3)] \\
\[-\frac{4}{3}[W_2^g(2,1)G_2^g(0) - W_3^g(3,1)G_2^g(1) - W_4^g(1,0)G_2^g(2)] \\
+ W_5^g(1,1)G_5^g(3)] \\
-W_1^l(2,1)G_1^l(0) + W_1^l(1,0)G_1^l(2) - \frac{1}{9}W_2^l(2,0)G_2^l(0) \\
+ \frac{1}{9}W_3^l(0,0)G_3^l(2)\}

\[\begin{align*}
[aa | \langle \rho_1 a_1 e | \rho_1 a_1 e \rangle | r_{12} | bb] &= \frac{3}{2\pi} \\
[ab | \langle \rho_1 a_1 e | \rho_1 a_1 e \rangle | r_{12} | ab] &= \frac{3}{2\pi} e^{-2w} (1 + w + \frac{1}{3} w^2)^2 \\
[aa | \langle \rho_1 a_1 e | \rho_1 a_1 e \rangle | r_{12} | ab] &= \frac{3}{2\pi} e^{-w} (1 + w + \frac{1}{3} w^2) \\
[aa | \langle \rho_1 a_1 e | \rho_1 a_1 e \rangle | r_{12} | aa] &= \frac{1}{6\pi} e^{-w} (9 + 9w + 4w^2 + w^3) \\
[ab | \langle \rho_1 a_1 e | \rho_1 a_1 e \rangle | r_{12} | bb] &= \frac{1}{6\pi} e^{-w} (9 + 9w + 2w^2 - w^3)
\end{align*}\]