Quantum Theoretical Study on Bond Energy

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Abstract :

We have already studied the characteristic features of these bonds by idealizing the problem to the electronic structure of fictitious diatomic molecules. In this paper, we carry out the modified calculation in the case of account of the modified bonding atomic orbitals

$$\varphi_4 \rightarrow \frac{1}{\sqrt{N}}(\varphi_4+\lambda\varphi_4), \qquad \varphi_4' \rightarrow \frac{1}{\sqrt{N}}(\varphi_4+\lambda\varphi_4)$$

We conclude that in the case of $\lambda=0$ (Heitler–Londn Approximation) the adiabatic potential curve takes minimum value.

§1. Introduction

Although the relation between bond order and bond length is of great importance in the theory of carbon compounds, the quantum theoretical study for these has not yet been fully carried out.[1] Systematical and quantum theoretical investigation of the true nature of single, double and triple bonds is of great importance especially from a chemical point of view. We have already studied the characteristic features of these bonds by idealizing the problem to electronic structure of fictitious diatomic molecules.[2]

In this paper, we carry out the modified calculation in the case of account of the bonding orbitals.

§2 General formulas for electronic energy

Based on our idea, the total energy E of the fictitious molecular system is found to be given by

$$E=\frac{\Sigma\int \Phi_{pq}\ H\ \Phi_{pq}\ d\tau}{\Sigma\int \Phi_{pq}\ \Phi_{pq}\ d\tau}=\frac{\langle\int \Phi_{pq}\ H\ \Phi_{pq}\ d\tau\rangle}{\langle\int \Phi_{pq}\ \Phi_{pq}\ d\tau\rangle} \quad \cdots\cdots(1)$$

For the proof of the formula, the reader is refered to our paper.

Applying to this case, we obtain the following result:

$$E = E_o - C_o + \frac{C_b^{(1)}}{1+k} - C_s^{(1)} \quad \cdots\cdots\cdots\cdots(2)$$

wher, $Eo=\sum Hii+\sum'(ii:jj)$

$Co=3(12:12)+3(14:14)$

$Cs^{(1)}=G_{11}'+3G_{12}'+3G_{14}'$

$Cb^{(1)}=G_{44}'$

$k=S_{44}'^2$

$Gij'=(ij':ij')-Sij'^2(ii:j'j')+2Sij'Hij'-(Hii+Hjj)(Sij'^2+2Sij'\sum_{k\neq ij}(ij':kk)-Sij'^2\sum_{k\neq ij}$

$\{(ii:kk)+(jj':kk)\}$

$Hij'=\int \varphi\ (1)H(1)\varphi\ (1)d\tau.$

$$Hi=-\frac{1}{2}\Delta i-\frac{1}{r_{ci}}-\frac{1}{r_{c'i}}$$

$$\varphi_4\longrightarrow\frac{1}{\sqrt{N}}(\varphi_4+\lambda\varphi_4') \qquad N=1+\lambda^2+2\lambda S_{44}'^{\circ}$$

$$\varphi_4'\longrightarrow\frac{1}{\sqrt{N}}(\varphi_4'+\lambda\varphi_4)$$

$$H_{44}'=\frac{1}{1+\lambda^2+2\lambda S_{44}'^{\circ}}[2\lambda H_{44}^{\circ}+(1+\lambda^2)H_{44}'^{\circ}]$$

$$H_{44}=\frac{1}{1+\lambda^2+2\lambda S_{44}'^{\circ}}[(1+\lambda^2)H_{44}^{\circ}+2\lambda H_{44}'^{\circ}]$$

$$S_{44}'=\frac{1}{1+\lambda^2+2\lambda S_{44}'^{\circ}}[2\lambda+(1+\lambda^2)S_4'^{\circ}]$$

$$S_{14}'=\frac{1}{\sqrt{1+\lambda^2+2\lambda S_{14}'^{\circ}}}\lambda S_{14}'^{\circ}$$

$$S_{14}=\frac{1}{\sqrt{1+\lambda^2+2\lambda S_{44}'^{\circ}}}\lambda S_{14}'^{\circ}$$

$$(14:14)=\frac{1}{1+\lambda^2+2\lambda S_{44}'^{\circ}}[(14:14)^{\circ}+\lambda^2(14:14')^{\circ}+2\lambda(14':14)^{\circ}]$$

$$(14:14')=\frac{1}{1+\lambda^2+2\lambda S_{44}'^{\circ}}[\lambda^2(14:44)^{\circ}+(14':14')^{\circ}+2\lambda(14:14)^{\circ}]$$

$$(44:11)=\frac{1}{1+\lambda^2+2\lambda S_{44}'^{\circ}}[\lambda^2(11:4'4')^{\circ}+(11:44)^{\circ}+2\lambda(11:44')]$$

$$(44:4'4')=\frac{1}{(1+\lambda^2+2\lambda S_{44}'^2)^2}[2\lambda^2(44:44)^{\circ}+(1+\lambda^4)(44:4'4')^{\circ}+4\lambda(11\lambda^2)(44:44')^{\circ}+4\lambda^2(44':44)^{\circ}]$$

§3 Numerical Calculation :

The adiabatic potentiale between two atoms in the molecule is the eigen value of electronic energy as a function of the distance between the nuclei. In order to know explicitly the dependence on the distance, we have to evaluate the eigenvalue for various distances.

For this purpose we have to carry out the numerical calculations of molecular integals Sij; Hij; (pq : r's') etc and we calculate the total energy E variating the parameter λ between 0.1 and 0.6 (interval 0.1)

Actually we have used only ordinary desk machine of the type "Tiger".

§4 Result and Discussion :

The numerical calculations of these fornurlas are tabulated in the Tables 1 ~ 4

$$-\triangle E_0=\{2(H_{44}-H_{44}^{\circ})+(44:4'4')-(44:4'4')^{\circ}\}$$

λ / o	2.50	2.75	3.00	3.25	3.50	3.75	4.00	4.25	4.50	4.75	5.00	5.25
λ=0.1	0.09971	0.08776	0.08047	0.07611	0.07260	0.06837	0.06518	0.06021	0.05478	0.04864	0.04259	0.03473
0.2	0.17433	0.15240	0.13756	0.13114	0,12517	0.11768	0.11225	0.10380	0.09464	0.08408	0.07348	0.06269
0.3	0.22918	0.19925	0.18127	0.16758	0.16253	0.15295	0.14594	0.13556	0.12330	0.10956	0.09564	0.08140
0.4	0.26870	0.23278	0.21120	0.19850	0.18907	0.17791	0.16877	0.15753	0.14369	0.12765	0.11131	0.09446
0.5	0.29660	0.25629	0.23215	0.21799	0.20752	0.19528	0.18639	0.17307	0.15790	0.13752	0.12222	0.10348
0.6	0.31572	0.27233	0.24939	0.23121	0.22007	0.20709	0.19757	0.18364	0.16758	0.14887	0.12962	0.10958

Table 1

$S_{44}' = (2\lambda + (1+\lambda^2)S_{44}^{\circ\prime})/(1+\lambda^2+2\lambda S_{44}^{\circ\prime})$

λ / ρ	2.50	2.75	3.00	3.25	3.50	3.75	4.00	4.25	4.50	4.75	5.00	5.25
λ=0.1	0.73906	0.78390	0.81447	0.83205	0.83873	0.83539	0.82310	0.80442	0.78023	0.72199	0.72040	0.68648
λ=0.2	0.82404	0.85112	0.87286	0.88525	0.88974	0.88760	0.87895	0.86574	0.84849	0.82818	0.80522	0.78027
λ=0.3	0.89006	0.90029	0.91519	0.92362	0.92666	0.92521	0.91934	0.91032	0.89849	0.88446	0.86848	0.85096
0.4	0.92092	0.93566	0.94542	0.95093	0.95291	0.95197	0.94813	0.94224	0.93448	0.92522	0.91462	0.90094
0.5	0.95140	0.96058	0.96662	0.97002	0.97124	0.97066	0.95830	0.96469	0.95984	0.95409	0.94747	0.94013
0.6	0.97237	0.97763	0.98109	0.98303	0.98372	0.98340	0.98204	0.97996	0.97721	0.97391	0.97011	0.96588

$-3\triangle G_{14} = 3(G_{14}' - G_{14}^{\circ})$

λ=0.1	0.03651	0.03306	0.03012	0.02730	0.02499	0.02289	0.02088	0.01914	0.01758	0.01614	0.01476	0.01365
0.2	0.06564	0.05964	0.05418	0.04944	0.04500	0.04131	0.03825	0.03525	0.03285	0.03021	0.02793	0.02592
0.3	0.08832	0.08043	0.07323	0.06708	0.06708	0.05667	0.05250	0.04857	0.04512	0.04209	0.03930	0.03681
0.4	0 10542	0.09669	0.08850	0.08115	0.08115	0.07473	0.06408	0.05961	0.05574	0.05223	0.04902	0.04443
0.5	0.11835	0.10914	0.10047	0.09246	0.08553	0.08535	0.07356	0.06879	0.06453	0.06087	0.05754	0.05448
0.6	0.12810	0.11907	0.10980	0.10155	0.09402	0.09402	0.08148	0.07635	0.07194	0.06813	0.06453	0.06159

Table 2

$-3\triangle G_{14}'$

λ / ρ	2.50	2.75	3.00	3.25	3.50	3.75	4.00	4.25	4.50	4.75	5.00	5.25
λ=0.1	0.00267	0.00108	-0.00012	-0.00102	-0.00111	-0.00111	-0.00090	-0.00060	-0.00039	-0.00024	-0.00018	-0.00015
0.2	0.00582	0.00186	-0.00075	-0.00291	-0.00345	-0.00345	-0.00309	-0.00267	-0.00219	-0.00207	-0.00204	-0.00204
0.3	0.00834	0.00213	-0.00234	-0.00525	-0.00630	-0.00630	-0.00603	-0.00549	-0.00519	-0.00492	-0.00489	-0.00501
0.4	0.01044	0.00159	-0.00450	-0.00828	-0.00975	-0.00984	-0.00954	-0.00897	-0.00867	-0.00834	-0.00843	-0.00867
0.5	0.01143	0.00024	-0.00720	-0.01164	-0.0 305	-0.01365	-0.01350	-0.01287	-0.01242	-0.01215	-0.01239	-0.01269
0.6	0.01131	-0.00147	-0.01023	-0.01533	-0.01740	-0.01764	-0.01737	-0.01668	-0.01638	-0.01608	-0.01641	-0.01680

$\triangle\left(\frac{G_{44}'}{1+S_{44}^{2\prime}}\right)$

λ=0.1	0.04679	0,05112	0.05309	0.05387	0.05317	0.05069	0.04583	0.04269	0.03692	0.03043	0,02412	0.01760
0.2	0.09903	0.09873	0.09846	0.09800	0.09713	0.09260	0.08566	0.07973	0.07034	0.05978	0.04930	0.03932
0.3	0.13997	0.13785	0.13565	0.13399	0.13145	0.12495	0.11750	0.10906	0.09754	0.08421	0.07106	0.05822
0.4	0.17447	0.16797	0.16313	0.16003	0.15629	0.14905	0.14007	0.13125	0.01809	0103050	0.08807	0.07334
0.5	0.20027	0.19005	0.18306	0.17883	0.17438	0.16631	0.15733	0.14772	0.13313	..11667	0.10088	0.08446
0.6	0.21860	0.20555	0.19698	0.19182	0.18664	0.17815	0.16844	0.15834	0.14367	0.12669	0.19058	0.09848

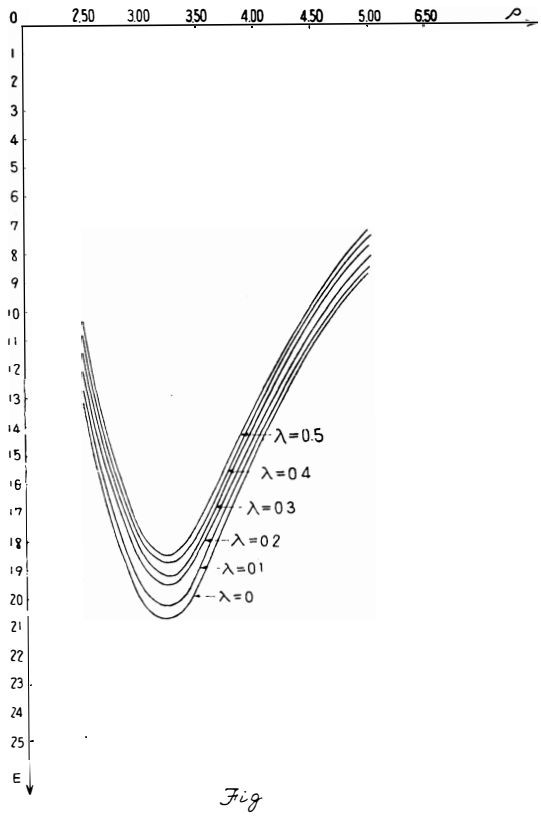
Table 3

$\triangle E = -3\triangle G_{14} - 3\triangle G_{14}' + \triangle\frac{G_{44}'}{1+k} + 2(H_{44}-H_{44}^{\circ}) + (44:4'4') - (44:4'4')^{\circ}$

λ / ρ	2.50	2.75	3.00	3.25	3.50	3.75	4.00	4.25	4.50	4.75	5.00	5.25
λ=0.1	-0.01374	-0.02050	0.00262	0.00404	0.00445	0.00410	0.00270	0.00102	-0,00067	-0.00231	-0.00389	-0.00550
λ=0.2	-0.00384	0.00783	0.01160	0.01339	0.01351	0.01278	0.01100	0.00851	0.00636	0.00384	0.00171	0.00051
λ=0.3	0.00745	0.02116	0.02527	0.02824	0.02590	0.02237	0.01930	0.01658	0.01417	0.01182	0.00983	0.00862
λ=0.4	0.02163	0.03347	0.03593	0.03440	0.03220	0.02970	0.02700	0.02436	0.02147	0.01929	0.01735	0.01570
λ=0.5	0.03345	0.04314	0.04418	0.04166	0.03916	0.03640	0.03340	0.03057	0.02734	0.02520	0.02381	0.02291
λ=0.6	0,04234	0.05082	0.05016	0.04683	0.04319	0.04030	0.03730	0.03437	0.03165	0.02930	0.02808	0.03100

Table 4

The results of evaluating the adiabatic potential according to the general formnlas given in (2) are shown in Fig



Fig

We conclude from these results that in the case of $\lambda=0$ (Heitler–London Approximation) the adiabatic energy potential curve takes minimum value,

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