

## An SCF-MO-CNDO Study of Equilibrium Geometries, Force Constants, and Bonding Energies: CNDO/BW.† Part II.<sup>1</sup> Diatomics

By R. J. Boyd and M. A. Whitehead,‡\* Quantum Chemistry Laboratory, Chemistry Department, McGill University, The Royal Institution for the Advancement of Learning, Montreal 110, Quebec, Canada

The CNDO/BW method is used to calculate the spectroscopic states, equilibrium geometries, bonding energies, and force constants of diatomic molecules and ions. Four parameter sets are used, based on Hinze and Jaffé, and Hartree-Fock atomic parameters and on resonance integrals,  $\beta$ , evaluated with, and without, the inclusion of valence-state ionization potentials. All parameter sets yielded better predictions of experimental results than any other current CNDO parametrization.

In the semi-empirical all-valence electron SCF-MO-CNDO theory designated CNDO/BW,<sup>1</sup> the core repulsion energy is expressed as a linear combination of the point charge and electron repulsion forms,<sup>1</sup> and the resonance integrals are evaluated with and without the inclusion of valence-state ionization potentials.<sup>1</sup>

The spectroscopic ground states of a large number of molecules have been calculated and compared with experiment. The calculated equilibrium geometries and bonding energies are compared with experiment in Tables 1 and 2 respectively. The calculated force constants for diatomic molecules are given in Table 3.

### DISCUSSION

The four parameter sets considered in CNDO/BW<sup>1</sup> predict the same spectroscopic ground states for the diatomic molecules, and the predictions agree with experiment for all molecules whose ground states have been established. Thus the ground state of  $C_2$  is calculated to be the known  $^1\Sigma_g^+$ ,<sup>2</sup> and not the erroneous  $^3\pi_u$ ,<sup>3,4</sup> whereas the ground states of some diatomic molecules are predicted incorrectly by the CNDO/2 method.<sup>5</sup> Thus  $B_2$  is found to be  $2\sigma_g^2 1\pi_u^3 2\sigma_u$  ( $3\pi_g$ ) by the CNDO/2 method,<sup>5</sup> and the experimental  $^3 2\sigma_g^2 2\sigma_u^2 1\pi_u^2$  ( $3\Sigma_g^-$ ) by CNDO/BW with all four parameter sets.<sup>1</sup> The difference arises from the ordering of the occupied MO's. The CNDO/2 method places the second  $\beta$  electron in the  $1\pi_u$  orbital, while the CNDO/BW places the second  $\beta$  electron in the  $2\sigma_u$  orbital. The configuration of NO is found to be  $3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma$  by CNDO/2 and  $3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 2\pi$  by the CNDO/BW method respectively. The CNDO/2 method places the  $6\sigma$  orbital below the  $2\pi$  orbital and predicts the wrong ground state.

The CNDO/2 ground states are also obtained with the INDO approximation,<sup>3</sup> therefore the inclusion of

one-centre exchange integrals has no effect on the ordering.

Although the values of the orbital energies associated with the occupied MO's are determined by the SCF-MO-CNDO parametrization, it has been observed in the present work that the ordering of the MO's is sensitive to the magnitude of the bonding parameters. Thus for  $B_2$ , the CNDO/2  $\beta_{AB}$  (ref. 6) is 17.0 eV, while in the CNDO/BW method the value is 7.0 eV with parameter set (III).<sup>1</sup> Increasing  $\beta_{AB}$  from 7.0 to 17.0 eV results in the CNDO/BW method giving the CNDO/2 ground state<sup>5</sup> for  $B_2$ . This behaviour is insensitive to changes in the other parameters since all four parameter sets studied give the same orbital rearrangement. If the orbital rearrangements involve doubly occupied MO's only, the prediction for the ground state is not affected.<sup>3</sup>

Most experimental trends for the equilibrium bond lengths, bonding energies, and force constants of the diatomic molecules considered are predicted correctly by the present SCF-MO-CNDO method. The agreement with experiment is good and much better than the results of other semiempirical MO theories. The effect of using different valence-state data and of including VSIP values in the evaluation of the resonance integrals<sup>1</sup> is relatively small.

For those equilibrium bond lengths which are not used to calibrate the bonding parameters, the average deviations from the experimental values are 0.022, 0.026, 0.021, and 0.026 Å with parameter sets (I)–(IV), comparing favourably with a mean deviation of 0.127 Å obtained by the CNDO/2 method.<sup>5</sup> The mean deviations for  $r_e$  are smaller with the atomic parameters evaluated from Hinze and Jaffé<sup>1,7,8</sup> than from Hartree-Fock valence states.<sup>1,9</sup>

The calculated and experimental bonding energies agree well, and the agreement is comparable to that previously obtained with CNDO/SW.<sup>10-13</sup> No particular

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‡ Present address: University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW

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TABLE 3

Force constants of diatomic molecules (mdyn Å<sup>-1</sup>)<sup>a</sup>

Molecule	Parameter set <sup>b</sup>				Expt. <sup>c</sup>
	(I)	(II)	(III)	(IV)	
H <sub>2</sub>	6.4	6.4	6.4	6.4	5.7
BH	3.7		3.7		3.0
BH <sup>+</sup>	3.3		3.0		3.2
CH	5.7	5.4	5.6	5.4	4.5
CH <sup>+</sup>	5.5	5.7	5.4	5.7	4.1
NH	7.2	7.1	6.6	6.6	6.0
NH <sup>+</sup>	5.9	7.0	5.4	6.2	
OH	9.7	10.0	9.0	9.2	7.8
OH <sup>+</sup>	7.1	8.4	6.3	7.6	4.9
FH	12.2	13.1	11.3	12.0	9.7
FH <sup>+</sup>	8.0	9.9	7.3	8.8	5.0
SiH	2.8	2.5	2.8	2.6	3.0
SiH <sup>+</sup>	2.8	2.8	2.8	2.9	
PH	3.7	3.3	3.6	3.2	3.3
PH <sup>+</sup>	3.4	3.5	3.2	3.3	1.1 <sup>d</sup>
SH	4.6	4.5	4.4	4.3	
SH <sup>+</sup>	4.1	4.4	4.0	4.2	
ClH	5.8	5.9	5.6	5.6	5.2
ClH <sup>+</sup>	4.8	5.3	4.6	5.0	4.1
BrH	4.4		4.3		4.1
BrH <sup>+</sup>	3.9		3.8		
IH	3.6		3.5		3.1
IH <sup>+</sup>	3.1		3.0		
B <sub>2</sub>	4.3		4.0		3.6
B <sub>2</sub> <sup>+</sup>	2.7		2.3		
BF	9.8		9.3		7.9
BF <sup>+</sup>	10.9		9.5		
<sup>1</sup> C <sub>2</sub>	14.2	13.8	14.8	14.1	12.2
<sup>3</sup> C <sub>2</sub>	11.1	10.9	11.0	10.8	9.5
C <sub>2</sub> <sup>+</sup>	10.5	10.5	10.3	10.1	
CN	17.3	18.0	16.6	17.4	16.3
CN <sup>+</sup>	16.7	17.5	16.2	16.7	15.7 <sup>d</sup>
CO	21.7	22.0	19.9	20.0	19.0
CO <sup>+</sup>	19.1	19.5	17.3	17.4	19.8
CS	10.4	10.2	9.7	9.4	8.5
CS <sup>+</sup>	10.3	10.3	9.0	8.7	
N <sub>2</sub>	23.0	23.6	21.7	22.2	23.0
N <sub>2</sub> <sup>+</sup>	22.3	22.7	20.5	20.9	20.1
NO	20.5	20.6	19.0	19.1	15.9
NO <sup>+</sup>	25.6	24.6	22.9	23.6	
O <sub>2</sub>	23.4	23.5	20.8	20.7	11.8
O <sub>2</sub> <sup>+</sup>	28.2	29.3	24.8	25.5	16.6
OS	12.6	12.6	11.3	11.3	7.9
OS <sup>+</sup>	15.1	13.2	13.9	13.7	
F <sub>2</sub>	14.0	14.1	12.4	12.7	4.8 <sup>e</sup>
F <sub>2</sub> <sup>+</sup>	18.9	18.9	15.6	16.0	
FCl	9.4	10.0	8.0	8.1	4.6
FCl <sup>+</sup>	10.8	12.6	8.2	8.2	
FBr	7.3		6.2		4.1
FBr <sup>+</sup>	8.3		6.7		
FI	7.0		5.6		
FI <sup>+</sup>	7.5		5.8		
S <sub>2</sub>	7.2	7.0	6.6	6.3	5.0
S <sub>2</sub> <sup>+</sup>	8.5	8.3	7.8	7.5	
Cl <sub>2</sub>	6.0	5.7	5.1	4.9	3.3
Cl <sub>2</sub> <sup>+</sup>	7.5	7.2	6.3	6.0	4.3
ClBr	5.1		4.3		2.7
ClI	4.4		3.7		2.4
ClI <sup>+</sup>	4.7		3.4		
Br <sub>2</sub>	4.2		3.4		2.6
Br <sub>2</sub> <sup>+</sup>	5.3		4.1		
BrI	4.0		3.1		2.1
I <sub>2</sub>	3.5		2.8		1.7
I <sub>2</sub> <sup>+</sup>	4.3		3.4		

<sup>a</sup> Molecules used to parametrize CNDO/BW are included in this Table since the force constant was not used in the parametrization. <sup>b</sup> Parameter sets are defined in Table 1. <sup>c</sup> Ref. 3, except where noted otherwise. <sup>d</sup> P. E. Empedocles, *J. Chem. Phys.*, 1967, **46**, 4474; *Theor. Chim. Acta*, 1968, **10**, 331. <sup>e</sup> See footnote (b) (i) to Table 2.

latter predict the formation of the experimental <sup>16</sup>Cl<sup>+</sup> while the former predict H<sup>+</sup>.

Both sets of valence-state data predict that NO<sup>+</sup> dissociates to give N<sup>+</sup>, whereas the observed dissociation products<sup>17</sup> are N and O<sup>+</sup>. Excluding these dissociations all cases are predicted correctly by both sets of atomic parameters.

The calculated force constants of the diatomic molecules reproduce the experimental trends. The simple overlap approximation for the resonance integrals, yields better force constants. The two sets of atomic parameters yield more accurate force constants for about the same number of molecules, which are in all cases, better than the CNDO/2 results<sup>5</sup> and compare well with those calculated from a semi-theoretical method by use of a distortion operator.<sup>18</sup>

Table 3 indicates that the calculated force constants of the halogen and interhalogen diatomic molecules are too large, although they reproduce all experimental trends, and the calculated equilibrium bond lengths are less than the observed values, even though the experimental values of  $r_e$  were used to calibrate bonding and core repulsion parameters between halogen atoms. This is because it was impossible to fit simultaneously the bonding energies and equilibrium bond lengths. For a given diatomic molecule, and a given value of  $\beta_{AB}$  or  $\beta_{AB}'$ , a core repulsion parameter can be found which gives the correct bond length. Then  $\beta_{AB}$  can be adjusted and a new  $\alpha_{AB}$  found and the process repeated until the parameters have been optimized to give the experimental bond length and bonding energy. The halogen and interhalogen diatomics cannot be optimized in this manner. For an AB molecule and a given value of  $\beta_{AB}$ , an  $\alpha_{AB}$  can be found, but where A and B are halogen atoms, each successive iteration increases the value of  $\beta_{AB}$  until eventually  $E_{\text{bond}}$  decreases owing to an inversion of bonding and antibonding orbitals. To obtain agreement with experiment for  $E_{\text{bond}}$ , it is necessary to calibrate  $\alpha_{AB}$  and  $\beta_{AB}$  to yield a bond length less than the observed  $r_e$ .

Similarly in O<sub>2</sub>, no orbital rearrangement occurs, and the optimization is possible, but the calculated force constants of 23.4, 23.5, 20.8, and 20.7 mdyn Å<sup>-1</sup> for parameter sets (I)–(IV) are in poor agreement with the experimental value of 11.8 mdyn Å<sup>-1</sup>. The CNDO/2 method, however, gives even less satisfactory results:  $r_e$  1.132 Å,  $E_{\text{bond}}$  17.44 eV, and  $h_e$  56.8 mdyn Å<sup>-1.5</sup>

The equilibrium bond length of F<sub>2</sub> is predicted to be 1.315 Å by an *ab initio* calculation<sup>19</sup> with a minimal basis set. The poor agreement with experiment is because a minimal basis set leads to a relatively high ratio of electrons to basis functions.<sup>19</sup> This effect has also been observed in *ab initio* calculations on molecules with fluorine bonded to oxygen.<sup>19</sup> In order to eliminate those discrepancies it has been suggested that extended basis sets would be required.<sup>19</sup>

<sup>18</sup> P. E. Empedocles, *J. Chem. Phys.*, 1967, **46**, 4474; *Theor. Chim. Acta*, 1968, **10**, 331.

<sup>19</sup> M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1970, **52**, 4064.

<sup>16</sup> F. Norling, *Z. Phys.*, 1937, **106**, 177.

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## APPENDIX

Calculation of Hartree-Fock Valence-state Energies.— Nuclear attraction plus kinetic energy per electron values<sup>20,21</sup> and Slater-Condon parameters<sup>22,23</sup> evaluated

TABLE 4  
Hartree-Fock valence-state energies (eV)

Valence state	System	Energy	System	Energy
<i>sp</i>	C <sup>+</sup>	-1007.1428	Si <sup>+</sup>	-7845.5178
<i>p</i>	C <sup>+</sup>	-997.0836	Si <sup>+</sup>	-7837.0707
<i>s<sup>2</sup>p</i>	C	-1025.1096	Si	-7859.4310
<i>sp</i>	C	-1017.0961	Si	-7853.0389
<i>sp<sup>2</sup></i>	C	-1015.1100	Si	-7851.6846
<i>s<sup>2</sup>pp</i>	C <sup>-</sup>	-1025.1200	Si <sup>-</sup>	-7859.9425
<i>sp<sup>2</sup>pp</i>	C <sup>-</sup>	-1015.5159	Si <sup>-</sup>	-7852.6108
<i>s<sup>2</sup>pp</i>	N <sup>+</sup>	-1465.7282	P <sup>+</sup>	-9260.4814
<i>spp</i>	N <sup>+</sup>	-1454.5841	P <sup>+</sup>	-9251.8242
<i>p<sup>2</sup>pp</i>	N <sup>+</sup>	-1437.7352	P <sup>+</sup>	-9239.3014
<i>s<sup>2</sup>ppp</i>	N	-1478.7973	P	-9269.9474
<i>sp<sup>2</sup>pp</i>	N	-1464.7231	P	-9259.8122
<i>s<sup>2</sup>p<sup>2</sup>pp</i>	N <sup>-</sup>	-1477.7148	P <sup>-</sup>	-9270.1459
<i>sp<sup>2</sup>p<sup>2</sup>p</i>	N <sup>-</sup>	-1464.0202	P <sup>-</sup>	-9260.3590
<i>s<sup>2</sup>ppp</i>	O <sup>+</sup>	-2021.7647	S <sup>+</sup>	-10805.9067
<i>s<sup>2</sup>p<sup>2</sup>p</i>	O <sup>+</sup>	-2018.5744	S <sup>+</sup>	-10803.9071
<i>sp<sup>2</sup>pp</i>	O <sup>+</sup>	-2003.2053	S <sup>+</sup>	-10792.9768
<i>p<sup>2</sup>p<sup>2</sup>p</i>	O <sup>+</sup>	-1981.2742	S <sup>+</sup>	-10777.7332
<i>s<sup>2</sup>p<sup>2</sup>pp</i>	O	-2035.0169	S	-10815.7280
<i>sp<sup>2</sup>p<sup>2</sup>p</i>	O	-2016.3652	S	-10803.0496
<i>s<sup>2</sup>p<sup>2</sup>p<sup>2</sup>p</i>	O <sup>-</sup>	-2035.0225	S <sup>-</sup>	-10817.0099
<i>s<sup>2</sup>p<sup>2</sup>pp</i>	F <sup>+</sup>	-2688.5095	Cl <sup>+</sup>	-12490.2899
<i>s<sup>2</sup>p<sup>2</sup>p<sup>2</sup></i>	F <sup>+</sup>	-2684.9860	Cl <sup>+</sup>	-12488.1020
<i>sp<sup>2</sup>p<sup>2</sup>p</i>	F <sup>+</sup>	-2664.8275	Cl <sup>+</sup>	-12474.7058
<i>p<sup>2</sup>p<sup>2</sup>p<sup>2</sup></i>	F <sup>+</sup>	-2637.3612	Cl <sup>+</sup>	-12456.5836
<i>s<sup>2</sup>p<sup>2</sup>p<sup>2</sup>p</i>	F	-2704.9225	Cl	-12502.4760
<i>sp<sup>2</sup>p<sup>2</sup>p<sup>2</sup></i>	F	-2681.0024	Cl	-12487.0704
<i>s<sup>2</sup>p<sup>2</sup>p<sup>2</sup>p<sup>2</sup></i>	F <sup>-</sup>	-2706.2872	Cl <sup>-</sup>	-12505.0771

from analytical Hartree-Fock wavefunctions<sup>24,25</sup> were used in this work. The valence-state energies were computed<sup>26</sup> by the method of Van Vleck<sup>27</sup> and Mulliken.<sup>28</sup>

<sup>20</sup> S. Fraga, personal communication.

<sup>21</sup> S. Fraga and G. Malli, 'Tables of One-Electron Expectation Values for Many-electron Atoms, Evaluated from Analytical Hartree-Fock Functions,' Technical Report TC 6601, Department of Chemistry, University of Alberta, 1966.

<sup>22</sup> C. Fisk and S. Fraga, *Canad. J. Phys.*, 1968, **46**, 1140.

The valence-state energies used to evaluate Hartree-Fock atomic parameters for the CNDO/BW calculations are listed in Table 4. The seven valence states (unipositive, neutral, or uninegative) included for each element are the same as those used by Sichel and Whitehead<sup>10,29</sup> to evaluate atomic parameters from the valence-state data of Hinze and Jaffé. Promotion energies defined by equations (1)–(3) are calculated from the valence-state energies in Table 4 and the corresponding ground-state energy of the atom or ion.<sup>24,25</sup> The Hartree-Fock valence-state ionization potentials in Table 4 of ref. 1 have been calculated directly as the difference of the valence-state energies of the ion and neutral atoms. This is equivalent to equation (4) if the definitions of  $I_g$ ,  $P^+$ , and  $P^0$  are substituted.

$$P^0 = E - E^0 \quad (1)$$

$$P^+ = E - E^+ \quad (2)$$

$$P^- = E - E^- \quad (3)$$

$$I_V = I_g + P^+ - P^0 \quad (4)$$

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<sup>23</sup> C. Fisk and S. Fraga, 'Tables of Slater-Condon Parameters, Evaluated from Analytical Hartree-Fock Functions,' Technical Report TC 6801, Department of Chemistry, University of Alberta, 1968.

<sup>24</sup> E. Clementi, Tables of Atomic Functions, IBM, San José, California, 1965.

<sup>25</sup> G. Malli, *Canad. J. Phys.*, 1966, **44**, 3121.

<sup>26</sup> S. Fraga provided a FORTRAN programme due to J. Thorhallsson.

<sup>27</sup> J. H. Van Vleck, *J. Chem. Phys.*, 1934, **2**, 20.

<sup>28</sup> R. S. Mulliken, *J. Chem. Phys.*, 1934, **2**, 782.

<sup>29</sup> J. M. Sichel and M. A. Whitehead, *Theor. Chim. Acta*, 1967, **7**, 32.