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

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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, β, evaluated with, and without, the inclusion of valencestate 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 evaulated 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 bondong 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  ${}^{1}\Sigma_{g}{}^{+}$ , and not the erroneous  ${}^{3}\pi_{u}$ ,  ${}^{3,4}$  whereas the ground states of some diatomic molecules are predicted incorrectly by the CNDO/2 method.<sup>5</sup> Thus B<sub>2</sub> is found to be  $2\sigma_q^2 \ 1\pi_u^3 \ 2\sigma_u \ (3\pi_q)$ 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  $1\pi_{\mu}$  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

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<sup>3</sup> G. Herzberg, 'Spectra of Diatomic Molecules,' Van Nostrand, Princeton, New Jersey, 1950.
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<sup>5</sup> J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

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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<sub>2</sub>, 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 oribtal 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.1,9

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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parameter set is consistently superior to the others, although sets (I) and (IV) lead to closer agreement with experiment in more cases than sets (II) and (III). The CNDO/2 predictions for the bonding energies of

## TABLE 1

Equilibrium geometries (Å) a

For a few positive ions, the two sets of valencestate data lead to opposing predictions for the dissociation products. In NH+, the Hinze and Jaffé

#### TABLE 2

## Bonding energies (eV)

Mala			Parame	ter set <sup>b</sup>					Parame	ter set "		
cule	(IVC)	(I)	(II)	(III)	(IV)	Expt.	Molecule	(I)	(II)	(III)	(IV)	Expt. b
BH	Rpm	1.205	( )	1.212	( )	1.233	BH	4.191	· · /	4.493	· · /	3.577
BH+	RBH	1.193		1.211		1.215	BH+ (B+) ¢	2.335		$2 \cdot 166$		$2.15^{d}$
CH	Row	1.097	1.106	1.108	1.113	1.120	CH	4.594	4.647	4.882	5.102	3.649
CH+	Rou	1.104	1.095	1.113	1.100	1.131	$CH^+$ ( $C^+$ )	4.730	4.543	4.937	4.923	4.26 d
NH	RNH	1.014	1.006	1.006	1.008	1.038	NH ` ´	4.336	4.345	4.139	4.176	3.97 d
NH+	RNH	1.045	1.014	1.038	1.016	1.084	NH+ (H+)	4.924	4.604	4.622	4.287	4.46 d
OH	ROH	0.960	0.956	0.952	0.952	0.971	( <i>'</i>		(N+)		(N+)	
OH+	Rom	1.006	0.981	1.001	0.979	1.029	OH	5.118	5.076	5.025	<b>4</b> ∙989	4.627
$FH^+$	$R_{\rm FH}$	0.974	0.956	0.976	0.958		OH+ (H+)	4.321	5.784	4.031	5.425	4·83 ª
SiH	R <sub>siff</sub>	1.487	1.517	1.493	1.508	1.520	$FH^+$ $(H^+)$	3.851	5.241	3.620	4.881	3·87 ª
SiH+	R <sub>sin</sub>	1.484	1.473	1.484	1.463		SiH	3.514	3.630	3.762	4.113	3.32 d
$\mathbf{PH}$	RPH	1.414	1.416	1.416	1.423	1.433	$SiH^+$ (Si <sup>+</sup> )	3.513	3.610	3.760	<b>4</b> ·0 <b>99</b>	3.4 d
$PH^+$	$R_{\rm PH}$	1.436	1.399	1.438	1.402	1.425	PH	3.489	3.476	3.481	$3 \cdot 440$	3.45
SH	Ren	1.328	1.327	1.329	1.330	1.350	PH+ (P+)	3.795	$3 \cdot 403$	3.714	3.341	3.2 d
SH+	R <sub>SH</sub>	1.351	1.333	1.350	1.333		SH	3.942	3.944	3.930	3.920	3.85
ClH+	$R_{\rm CHH}$	1.312	1.300	1.312	1.297	1.315	SH+ (S+)	4.225	4.019	4.159	3.934	
$BrH^+$	RBH	1.442		1.441		1.448	$CIH^+(H^+)$	5.009	5.069	4.934	4.962	4.87 d
$IH^+$	$R_{1H}$	1.640		1.640			· · ·		(Cl+)		(CI+)	
$B_{2}^{+}$	$R_{BB}$	1.726		1.762			$BrH^+$ ( $Br^+$ )	4.258	. ,	4.204	. ,	4.22
$\mathbf{B}\mathbf{\tilde{F}}^+$	$R_{BF}^{DD}$	1.238		1.243			IH+ (I+)	3.735		3.680		3.25
<sup>1</sup> C <sub>2</sub>	$R_{CC}$	1.232	1.251	1.210	1.225	1.242	$B_2^+$	2.517		$2 \cdot 248$		
۶C	$R_{CC}$	1.318	1.337	1.313	1.330	1.312	BF+ (B+)	4.194		3.824		
C,Ŧ	$R_{CC}$	1.300	1.320	1.290	1.307		<sup>1</sup> C <sub>2</sub>	6.595	6.350	7.500	7.343	6·36 °
CÑ	$R_{\rm CN}$	1.155	1.155	1.150	1.150	1.172	<sup>3</sup> C <sub>2</sub>	5.699	5.485	6.512	6.435	
CN+	$R_{\rm CN}$	1.140	1.140	1.131	1.132		C <sub>2</sub> <sup>+</sup>	5.457	5.212	5.739	5.522	5.6 d
CO+	$R_{co}$	1.127	1.127	1.126	1.127	1.115	CÑ	8·709	8.859	9.073	9.204	8.44
CS+	$R_{\rm CS}$	1.503	1.502	1.510	1.508		CN+ (C+)	7.160	7.545	7.106	7.295	5.7 d
$N_{2}^{+}$	$R_{\rm NN}$	1.085	1.086	1.085	1.086	1.116	$CO^+$ (C+)	8.657	8.771	8.075	8.112	8·471 d
NÕ+	$R_{\rm NO}$	1.114	1.113	1.110	1.108	1.062	$CS^+$ (C <sup>+</sup> )	6.941	6.788	6.403	6.161	6.3 d
$O_2^+$	$R_{00}$	1.162	1.161	1.159	1.159	1.123	$N_2^+$	9.415	9.407	8.925	8.892	8·846 d
OŠ+	Ros	1.431	1.429	1.424	1.423		NO+ (N+)	8.014	<b>8</b> ·014	8.147	8.149	11·0 ď
$F_{2}^{+}$	$R_{\rm FF}$	1.212	1.202	1.218	1.217		0 <sub>2</sub> +	8.091	8.145	7.905	7.922	6·77 ª
FCl	$R_{\rm FCl}*$	1.570	1.570	1.570	1.570	1.628	OS+ (S+)	6.381	6.601	6.443	6.659	
FCl+	$R_{\rm FCl}$	1.516	1.507	1.527	1.525		$F_2$	1.388	1.389	1.390	1.390	1.391
FBr	$R_{\rm FBr}^*$	1.700		1.700		1.756	$F_{2}^{+}$	3.273	3.268	2.832	2.879	$2 \cdot 8 \ d$
$FBr^+$	$R_{\rm FBr}$	1.648		1.652			FCl	2.669	2.668	2.668	2.667	2.668
$\mathbf{FI}$	$R_{\rm FI}^*$	1.800		1.800			$FCI^+$ (Cl <sup>+</sup> )	3.000	3.376	2.855	3.024	
FI+	$R_{\rm FI}$	1.746		1.754			FBr	2.682		2.682		2.682
$S_{2}^{+}$	$R_{88}$	1.825	1.823	1.819	1.817		$FBr^{+}$ (Br <sup>+</sup> )	2.749		2.667		
$Cl_2$	$R_{\text{CICI}}*$	1.950	1.950	1.950	1.950	1.988	FI	2.911		2.910		2.910
$Cl_2^+$	$R_{ m ClCl}$	1.873	1.871	1.872	1.871	1.891	$FI^{+}(I^{+})$	2.758		2.736		
ClBr	$R_{\text{ClBr}}^*$	2.070		2.070		2.138	$S_2^+$	6.387	6.374	6.386	6.323	
ClI	$R_{CII}*$	$2 \cdot 220$		$2 \cdot 220$		2.321	Cl <sub>2</sub>	2.508	2.509	2.510	2.510	2.510
ClI+	$R_{\rm CH}$	2.143		$2 \cdot 165$			$Cl_2^+$	4.130	4.107	3.908	3.849	4.046
$Br_2$	$R_{\rm BrBr}^{*}$	2.270		2.270		2.284	ClBr	2.334		2.334		2.334
$Br_{2}^{+}$	$R_{BrBr}$	2.182		2.183			CH	2.189		2.190		2.190
BrI	$R_{BrI}*$	2.390		2.390			$ClI^+$ (I <sup>+</sup> )	$2 \cdot 951 \cdot$		2.833		
12	$R_{II}^*$	2.520		2.520		2.662	$Br_2$	1.992		1.991		1.991
$I_{2}^{+}$	$R_{II}$	$2 \cdot 427$		2.425			$Br_2^+$	3.451		3.116		3·28 ª
۹ Th	e molecul	es used t	o parame	etrize CN	DO/BW	were H.	BrI	1.930		1.928		1.928
HE HOI HER UI B BE CO CS N MO O OS S $-3$						$I_2$	1.556		1.555		1.556	

 $I_2$  $I_2^+$ 

2.961

<sup>a</sup> The molecules used to parametrize CNDO/BW were  $H_2$ , HF, HCl, HBr, HI,  $B_2$ , BF, CO, CS,  $N_2$ , NO,  $O_2$ , OS,  $S_2$  and those molecules marked with an asterisk, which are shown because the bond lengths calculated for them do not fit the experimental result. <sup>b</sup> Parameter sets: (I) resonance integrals from equation (12) with Hinze and Jaffé atomic parameters; (II) equation (12) with Hartree-Fock atomic parameters; (III) resonance integrals from equation (11) with Hinze and Jaffé parameters; (IV) equation (11) with Hartree-Fock atomic parameters, all from ref. 1. <sup>e</sup> Except where noted, from ref. 3 (1950 edn.) and Chem. Soc. Special Publ., No. 12, 1958 and No. 18, 1965.

diatomic molecules are always several electron volts too high.5

<sup>14</sup> C. E. Moore, 'Atomic Energy Levels,' Nat. Bur. Stands. Circular 467, Washington, 1958.

<sup>15</sup> M. W. Feast, Astrophys. J., 1951, 114, 344.

phys. J., 1963, **138**, 778. • G. Herzberg, personal communication: recent experiments on  $C_2$  suggest 6.25 eV for  $D_0^{\circ}$ . <sup>1</sup> V. H. Dibeler, J. A. Walker, and K. E. McCulloch, J. Chem. Phys., 1969, **51**, 4230. valence-state data predict dissociation to H<sup>+</sup>, the experimental result,<sup>14,15</sup> whereas Hartree-Fock valence states predict dissociation to N<sup>+</sup>, while for HCl<sup>+</sup> the

2.693

" Parameter sets as in Table 1. " Calculated, except where noted, from data given in (i) JANAF Thermochemical Tables,

Dow Chemical Co., Midland, Michigan, 1965 and (ii) Selected Values of Chemical Thermodynamical Properties, Nat. Bur. Standards Circular 500, U.S. Government Printing Office, Washington, 1952. <sup>e</sup> Dissociation products given in paren-theses after formula of molecule. <sup>d</sup> P. G. Wilkinson, AstroParameter set &

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

		1 aranne	ici set		
Molecule	(I)	(11)	(III)	(IV)	Expt.
$H_2$	6.4	$6 \cdot 4$	6·4	$6 \cdot 4$	5.7
BH	3.7		3.7		3.0
	3.3	5.4	3.0	<b>E</b> 4	3.2
CH+	5.5	5.7	5.4	0.4 5.7	4.5
NH	7.2	7.1	6.6	6.6	4·1 6.0
NH <sup>+</sup>	5.9	7.0	5.4	6.2	00
OH	9.7	10.0	9·0	$9.\overline{2}$	7.8
$OH^+$	$7 \cdot 1$	8.4	6.3	7.6	4.9
$\mathbf{FH}$	12.2	13.1	11.3	12.0	9.7
FH+	8.0	9.9	$7 \cdot 3$	8.8	5.0
SiH	2.8	$2 \cdot 5$	2.8	2.6	$3 \cdot 0$
	2.8	2.8	2.8	2.9	
PH+	3.4	3.5	3.9	3.2 2.2	3°3 1.1 d
SH	4.6	4.5	4.4	4.3	1.1
SH+	$4 \cdot 1$	4.4	$\hat{4}\cdot\hat{0}$	4.2	
ClH	5.8	5.9	5.6	5.6	$5 \cdot 2$
ClH+	4.8	$5 \cdot 3$	<b>4</b> ·6	$5 \cdot 0$	4.1
BrH	4.4		$4 \cdot 3$		$4 \cdot 1$
BrH <sup>+</sup>	3.9		3.8		
	3.6		3.5		$3 \cdot 1$
IП' В	3.1		3.0		2.6
$B_2^2$	2.7		2.3		3.0
$\mathbf{BF}^{2}$	9.8		9.3		7.9
BF+	10.9		9.5		
<sup>1</sup> C <sub>2</sub>	14.2	13.8	14.8	14.1	$12 \cdot 2$
${}^{3}C_{2}^{-}$	$11 \cdot 1$	10.9	11.0	10.8	9.5
$C_2^+$	10.5	10.5	10.3	10.1	
CN	17.3	18.0	16.6	17.4	16.3
CN+	16.7	17.5	16.2	16.7	15.7 4
CO+	21.7	22.0	19.9	20.0	19.0
CS	10.4	19.0	9.7	0.4	19.0
ČS+	10.3	10.3	9.0	8.7	00
$N_2$	23.0	23.6	21.7	$22 \cdot 2$	23.0
$\tilde{N_2^+}$	$22 \cdot 3$	22.7	20.5	20.9	20.1
NŌ	20.5	20.6	<b>19</b> ·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
02	28·2	29.3	24.8	25.5	16.0
05+	12.0	12.0	13.0	11.9	1.9
F.	14.0	14.1	12.4	13.7 12.7	4.8 .
<b>F</b> ,+	18.9	18.9	15.6	16.0	- •
FC1	<b>9·4</b>	10.0	8.0	8.1	<b>4</b> ·6
FCl+	10.8	12.6	$8 \cdot 2$	$8 \cdot 2$	
FBr	7.3		$6 \cdot 2$		<b>4</b> ·1
FBr <sup>+</sup>	8.3		6.7		
F1 F1+	7.0		5.0		
F1. S	7.9	7.0	0.0 8.8	6.3	5.0
$S_{1}^{2}$	8.5	8.3	7.8	7.5	00
Čĺ.	6.0	5.7	$5 \cdot 1$	4.9	3.3
$Cl_2^+$	7.5	$7 \cdot 2$	6.3	6.0	$4 \cdot 3$
ClBr	$5 \cdot 1$		$4 \cdot 3$		2.7
CII	4.4		3.7		$2 \cdot 4$
CII+ D-	4.7		3.4		0.0
$Br_2$	4·2		3.4		2.0
BrI	J-3 4.0		3.1		2.1
I.	3.5		2.8		1.7
$\tilde{I}_{2}^{2}$ +	4.3		$\mathbf{\tilde{3}} \cdot 4$		

<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>4</sup> P. E. Empedocles, J. Chem. Phys., 1967, **46**, 4474; Theor. Chim. Acta, 1968, **10**, 331. • 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 O2, 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  $k_e 56.8$  mdyn Å<sup>-1.5</sup>

The equilibrium bond length of  $F_2$  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.19

<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>&</sup>lt;sup>16</sup> F. Norling, Z. Phys., 1937, 106, 177.

<sup>&</sup>lt;sup>17</sup> P. Brix and G. Herzberg, Canad. J. Phys., 1954, 32, 110.

#### APPENDIX

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

## TABLE 4

Hartree-Fock valence-state energies (eV)

valence				
state	System	Energy	System	Energy
spp	C+	$-1007 \cdot 1428$	Si+	$-7845 \cdot 5178$
ρ́ρ́ρ	C+	-997.0836	Si+	$-7837 \cdot 0707$
$s^2 p p$	С	$-1025 \cdot 1096$	Si	$-7859 \cdot 4310$
sppp	С	-1017.0961	Si	$-7853 \cdot 0389$
$s\dot{p}^{2}\dot{p}$	С	$-1015 \cdot 1100$	Si	$-7851 \cdot 6846$
$s^2 p p p$	C-	$-1025 \cdot 1200$	Si-	$-7859 \cdot 9425$
sp2pp	C-	$-1015 \cdot 5159$	Si-	$-7852 \cdot 6108$
s <sup>2</sup> D D	$N^+$	$-1465 \cdot 7282$	$\mathbf{P}^+$	$-9260 \cdot 4814$
sppp	$N^+$	$-1454 \cdot 5841$	<u>P+</u>	$-9251 \cdot 8242$
$p^2 p p$	$N^+$	$-1437 \cdot 7352$	$\mathbf{P}$ +	$-9239 \cdot 3014$
s <sup>2</sup> p p p	N	$-1478 \cdot 7973$	$\mathbf{P}$	$-9269 \cdot 9474$
sp2pp	N	$-1464 \cdot 7231$	$\mathbf{P}$	$-9259 \cdot 8122$
$s^2 p^2 \bar{p} p$	N-	$-1477 \cdot 7148$	P	$-2970 \cdot 1459$
$s \dot{p}^2 \dot{p}^2 \dot{p}$	N-	$-1464 \cdot 0202$	P-	$-9260 \cdot 3590$
s <sup>2</sup> p p p	O+	$-2021 \cdot 7647$	$S^+$	$-10805 \cdot 9067$
$s^2 p^2 p$	O+	$-2018 \cdot 5744$	$S^+$	10803·9071
sp2pp	O+	$-2003 \cdot 2053$	$S^+$	$-10792 \cdot 9768$
$\hat{p}^2 \hat{p}^2 \hat{p}$	O+	$-1981 \cdot 2742$	$S^+$	-10777.7332
$s^2 p^2 p p$	0	$-2035 \cdot 0169$	S	$-10815 \cdot 7280$
$s p^2 p^2 p$	0	$-2016 \cdot 3652$	S	$-10803 \cdot 0496$
$s^2 p^2 p^2 p$	O-	$-2035 \cdot 0225$	S-	$-10817 \cdot 0099$
$s^2 p^2 p p$	$F^+$	$-2688 \cdot 5095$	Cl+	$-12490 \cdot 2899$
$s^2 p^2 p^2$	F+	$-2684 \cdot 9860$	Cl+	$-12488 \cdot 1020$
$s\bar{p}^2\bar{p}^2p$	$\mathbf{F}^+$	$-2664 \cdot 8275$	Cl+	$-12474 \cdot 7058$
$\dot{p}^2 \dot{p}^2 \dot{p}^2$	$F^+$	$-2637 \cdot 3612$	Cl+	$-12456 \cdot 5836$
$s^2 p^2 p^2 p$	F	$-2704 \cdot 9225$	Cl	$-12502 \cdot 4760$
$s \bar{p}^2 \bar{p}^2 \bar{p}^2$	F	-2681.0024	Cl	-12487.0704
$s^{2}p^{2}p^{2}p^{2}p^{2}$	F-	$-2706 \cdot 2872$	Cl-	$-12505 \cdot 0771$

from analytical Hartree-Fock wavefunctions 24, 25 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 Whithead 10, 29 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.24,25 The Hartree-Fock valencestate 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  $I_q$ ,  $P^+$ , and  $P^0$  are substituted.

$$P^{\mathbf{0}} = E - E^{\mathbf{0}} \tag{1}$$

$$P^+ = E - E^+ \tag{2}$$

$$P^- = E - E^- \tag{3}$$

$$I_{V} = I_{g} + P^{+} - P^{0} \tag{4}$$

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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.

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