

# Studies in Halogen-Halogen Bonding

## I. The $p$ - $\sigma$ Model

G. H. CHEESMAN, A. J. T. FINNEY, and I. K. SNOOK

Chemistry Department, University of Tasmania

Received May 19, 1969

The VESCF-MO method is used to investigate the  $p$ - $\sigma$  bonding model of halogen-halogen bonding. Procedures for estimating values of the core resonance integral,  $\beta$ , are discussed. It is found that if a semi-empirical procedure is used for estimating this integral, the model adequately predicts equilibrium bond-lengths for halogen-halogen molecules, but does not give an accurate description of the molecular wavefunction. The implicit assumptions of the semi-empirical approach are examined in some detail.

Mit Hilfe der VESCF-MO-Methode wird das  $p$ - $\sigma$ -Bindungsmodell der Halogen-Halogen-Bindung untersucht. Verschiedene Verfahren für die Abschätzung des Kernresonanzintegrals  $\beta$  werden diskutiert. Legt man ein semi-empirisches Verfahren für die Abschätzung dieses Integrals zugrunde, so zeigt sich, daß das Modell die Gleichgewichtsbindungsabstände in Halogen-Halogen-Molekülen in guter Übereinstimmung mit dem experimentellen Befund wiedergibt. Für die Wellenfunktionen der Moleküle erhält man dagegen keine besonders genaue Beschreibung. Die implizierten Annahmen dieser semi-empirischen Näherung werden im Detail geprüft.

La méthode VESCF MO est utilisée pour étudier le modèle de liaison  $p$ - $\sigma$  pour la liaison halogène-halogène. Des procédés pour estimer les valeurs de l'intégrale de résonance de coeur  $\beta$  sont discutés. On trouve que si cette intégrale est évaluée par un procédé semi-empirique, le modèle prédit correctement les longueurs de liaison pour les molécules halogènes-halogène, mais ne fournit pas une description précise de la fonction d'onde moléculaire. Les hypothèses implicites dans l'approche semi-empirique sont examinées au détail.

A number of theoretical studies of halogen-halogen bonding in interhalogens and polyhalides has been made; these include studies based on simple electrostatic models [1–5], calculations and discussions using the valence-bond approach [6–9], inert pair theory [10], non-paired spatial orbitals [11], the method of maximum overlap [12] and Murrell's best-hybrid-orbital treatment [13]. Various molecular orbital treatments have been made ranging in complexity from the free electron approximation [14], through Hückel and extended Hückel calculations [2, 3, 8, 15–18], semi-empirical selfconsistent field (SCF) treatments [19, 20] to all-valence-electron SCF calculations [23, 24, 61–64]. Treatments employing Bloch orbitals have also been applied to both  $I_2$  and  $I_3^-$  in the solid state [25–28].

Most of the molecular orbital studies appear to indicate that  $d$ -orbitals are not involved to any extent in the bonding of these compounds, and in fact an adequate model of the bonding in the interhalogens can be developed by considering only the  $p\sigma$ -orbitals of the valence shell as originally suggested by Pimentel [29] and subsequently discussed by others [17, 30, 31]. This bonding

model assumes that the only significant contribution to the interhalogen bond is made by the  $p\sigma$ -electrons, the other electrons in the valence shell remaining non-bonding. This hypothesis appears to be supported by experimental data, notably the results of studies of nuclear quadrupole resonance [32–35], Raman and infra-red spectra [36–38]. However, for ionic species, in particular polyiodides, it has been shown theoretically [19–21] that this simple  $p\sigma$ -electron bonding model must be modified to take into account the electrostatic perturbation due to the ionic environment. That this perturbation affects the properties of polyhalide ions is demonstrated by a variety of experimental data [39]: for example the dependence of nuclear quadrupole resonance frequencies of similar ions upon their crystalline environment. In fact, these ions, by virtue of their weak bonding and sensitivity to external fields, provide convenient tools for the exploration of environmental effects in the solid and perhaps the liquid state.

In view of this potential usefulness, this preliminary study was initiated in order to test the validity of the  $p\sigma$ -bonding model. The ground state properties of diatomic halogen and interhalogen molecules were calculated by the VESCF method, and as we shall demonstrate, the  $p\sigma$ -bonding model predicts the correct internuclear distances in the isolated molecules. Therefore, if the effect of the environment can be accurately included in the calculations, then the  $p\sigma$ -model allows quite accurate investigations of the effect of environment on molecular geometry to be made. However, it turns out that the model has only limited power to predict those properties which depend upon charge distribution. This inadequacy in the model points to the fact that interactions between the non-bonding valence electrons of the bonded atoms cannot be neglected.

### Method

The  $p\sigma$ -electron bonding model can be formulated in a manner analogous to the typical semi-empirical SCF  $\pi$ -electron theory as currently applied to investigations of the electronic properties of planar unsaturated aromatic compounds. It is assumed that only one  $p$ -orbital per atom contributes to the  $\sigma$ -bonding molecular orbital set, the remaining occupied atomic orbitals forming an electronic core around each nucleus. The basic assumption is that of zero differential overlap (ZDO) [40]; this assumption in the case of diatomic interhalogen molecules reduces the problem to that of a two-electron system involving relatively simple integrals [40, 52]. In this study the calculations have been carried out using the variable electronegativity SCF procedure (VESCF method) [45–49], as this allows some optimization of orbital exponents to be made which improves the values calculated for some molecular properties [49].

In the calculations reported here, the one-centre electron repulsion integral,  $\gamma_{pp}$  has been derived from a formula of the Paoloni type [19, 41]. The two-centre repulsion integral,  $\gamma_{pq}$ , was calculated from the Mataga-Nishimoto formula [42]; the approximation represented by the relation (1) has been suggested [20] as a more reliable one for  $p\sigma$ -electrons on the grounds that in this case the Mataga-Nishimoto formula underestimates the value of this integral when compared with values calculated using Slater orbitals:

$$\gamma_{pq} \approx 1/r_{pq} \quad (1)$$

(where the subscripts  $p, q$  label orbitals). However, electron correlation studies [43, 44] indicate that this integral should be reduced from the value obtained using a Slater basis set. The low values of the integral calculated from the Mataga-Nishimoto formula make some semi-empirical allowance for electron correlation as the Paoloni formula does in  $\gamma_{pp}$  and  $\gamma_{qq}$ . For this reason the Mataga-Nishimoto approximation has been preferred to (1) which makes no such allowance and in fact overestimates the integral.

There are two main strategies which may be adopted for the selection of the core resonance integral  $\beta_{pq}$ , which in this treatment is assumed (as is usual) to be a bond property:

- (i)  $\beta_{pq}$  may be calculated in some theoretical fashion, or
- (ii) a semi-empirical approach may be used to derive a value of  $\beta_{pq}$  from some readily observed molecular property, *e.g.* electronic spectra.

These two strategies were compared by calculating potential energy curves for homonuclear halogen diatomic molecules, using the comparison between calculated and observed internuclear separation as a criterion of success. As the integrals for the fluorine molecule vary most sharply with internuclear separation, this molecule provides the most stringent test of the approximations used. The total valence electron energy at a given  $r_{pq}$  was calculated from the relationship [19]

$$E_{\text{total}} = \frac{1}{2} \sum_{p,q} P_{pq}(H_{pq} + F_{pq}) + \frac{1}{2} \sum_{p,q} \frac{14.40}{r_{pq}} X_p X_q \quad (2)$$

where  $E_{\text{total}}$  is the total valence electron energy, the first summation represents the electronic energy due to the bonding electrons and the last summation the core-core repulsion energy, with the cores being treated as point charges<sup>1</sup>.

For a diatomic molecule,  $\beta_{pq}$  may be expressed as

$$\beta_{pq} = (p | -\frac{1}{2} \Delta | q) - X_p(p | 1/r_p | q) - X_q(p | 1/r_q | q). \quad (3)$$

Several theoretical methods were used to calculate  $\beta_{pq}$ ; these were

- (a) Slater orbital representation with the approximation [50]

$$(p | 1/r_p | q) = (p | 1/r_q | q) = \frac{1}{2} S_{pq} \gamma_{pq};$$

- (b) the Wolfsburg-Helmholtz-Mulliken approximation [54]

$$\beta_{pq} = \frac{1}{2} S_{pq}(H_{pp} + H_{qq});$$

- (c) the Cusach approximation [55]

$$\beta_{pq} = \frac{1}{2} S_{pq}(2 - |S_{pq}|)(H_{pp} + H_{qq});$$

- (d) the Ohno approximation [56]

$$\beta_{pq} = \frac{1}{2} S_{pq}(X_p + X_q)(\gamma_{pq} - 2.0 C/r_{pq})$$

(where  $C$  was taken as 0.85).

All approximations except (b) were also tried with orthogonality corrections [50], *i.e.*

$$\beta_{pq(\text{orthogonal})} = \beta_{pq} - \frac{1}{2} S_{pq}(H_{pp} + H_{qq}).$$

<sup>1</sup> The factor 14.40 appears in this equation to give  $E_{\text{total}}$  in electron volts when  $r_{pq}$  is measured in Ångstrom units.

Table 1. *Halogen molecules*

Molecule	$r_e$ (calc) Å	$R_e$ (obs) Å
F <sub>2</sub>	0.71	1.42
Cl <sub>2</sub>	1.34	1.98
Br <sub>2</sub>	1.72	2.28
I <sub>2</sub>	2.34	2.66

Table 2. *Fluorine molecule*

	$r_e$ calc (without orthog.)	$r_e$ calc (with orthog.)
W.M.H.	1.0	— <sup>a</sup>
Cusach	0.85	1.1
Ohno	< 1.0	> 1.7

<sup>a</sup> The orthogonality correction exactly cancels the approximation for  $\beta_{pq}$ .

The equilibrium internuclear separation,  $r_e$ , for the halogen molecules calculated using approximation (a) are presented in Table 1, and for the fluorine molecule calculated using approximations (b)–(d) in Table 2. These results show that the calculated separations are seriously in error; we conclude that the discrepancy must be due to inadequacies in the  $p\sigma$ -model itself, i.e. an inadequate representation of the core electrons and their interactions.

This same difficulty was experienced by Pohl, Rein, and Appel [52] in calculations of the ground-state properties of the hydrogen-halide molecules using a  $p\sigma$ -model. To overcome this difficulty the core penetrations and interactions with non-bonding electrons in the halogen valence shell were represented by the Hartree-Fock potentials tabulated by Hermann and Skillman [53], that is

$$E_{\text{core-core}} = E_{\text{electrostatic}} + E_{\text{penetration}} \quad (4)$$

where  $E_{\text{core-core}}$  is the total core interaction energy,  $E_{\text{electrostatic}}$  is the total Coulomb repulsion between the charged cores and  $E_{\text{penetration}}$  the total core penetration energy [52].

Although this remedy allowed Pohl *et al.* to calculate reasonable ground state properties for the hydrogen halides, it cannot be readily applied to calculations on diatomic halogen molecules [60], for in this case  $E_{\text{penetration}}$  cannot be simply represented in terms of Hermann and Skillman's potentials. Further, the use of these potentials involves the implicit assumption that the charge distribution of all non-bonding electrons in the bonded atom is the same as that in the isolated atom. The measure of agreement between calculated and observed halogen halide [52] and interhalogen [60] bond lengths and dipole moments shows that this assumption is not entirely adequate.

#### *The Core Resonance Integral – The Semi-Empirical Approach*

The most successful application of this  $p\sigma$ -model of the interhalogen bond using a value of  $\beta_{pq}$  derived from experimental data is that of Brown and Nunn [19]. In the following section we investigate the assumptions implicit in their

derivation. The derivation underlying their procedure is based on the Born-Oppenheimer approximation [40]

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{nuclear}}. \quad (5)$$

This may be written

$$E_{\text{total}} = E_{\text{valence electron}} + E_{\text{core electron}} + E_{\text{electrostatic}} + E_{\text{penetration}} \quad (6)$$

where  $E_{\text{valence electron}}$  is the energy of the valency electrons,  $E_{\text{core electron}}$  is the electronic energy of the core electrons, and  $E_{\text{electronic}}$  and  $E_{\text{penetration}}$  have the same meaning as in Eq. (4). For a diatomic molecule with pure *p* $\sigma$ -bonding, the terms on the right hand side of Eq. (6) can be written:

$$E_{\text{valence electron}} = \frac{1}{2} \sum_{p,q=1}^2 P_{pq}(H_{pq} + F_{pq}), \quad (7)$$

$$E_{\text{electrostatic}} = X_1 X_2 14.4/r_{12}, \quad (8)$$

$$E_{\text{total}} = \frac{1}{2} \sum_{p,q=1}^2 P_{pq}(H_{pq} + F_{pq}) + X_1 X_2 14.4/r_{12} + E_{\text{core electron}} + E_{\text{penetration}}. \quad (9)$$

As  $r_{12}$  tends to infinity, from Eqs. (6–9) we have

$$\begin{aligned} E_{\text{total}} &\rightarrow -P_{11}I_1 + P_{11}^2\gamma_{11} - P_{22}I_2 + P_{22}^2\gamma_{22} + E_{\text{core electron}}, \\ E_{\text{total}}(r) - E_{\text{total}}(\infty) &= -\{P_{11} - 1\}I_1 - \{P_{22} - 1\}I_2 \\ &\quad - P_{22}X_1\gamma_{12} - P_{11}X_2\gamma_{12} + \frac{1}{4}\{P_{11}^2 - 1\}\gamma_{11} \\ &\quad + \frac{1}{4}\{P_{22}^2 - 1\}\gamma_{22} + \frac{1}{2}P_{11}P_{12}\gamma_{12} + \frac{1}{2}P_{22}P_{12}\gamma_{12} \\ &\quad - \frac{1}{2}P_{12}\gamma_{12} + 2P_{12}\beta_{12} + 14.4/r_{12} + E_{\text{penetration}} \end{aligned}$$

for which the following assumptions have been made:

- (i)  $E_{\text{core electron}}(r) = E_{\text{core electron}}(\infty)$ .
- (ii)  $I_1, I_2, \gamma_{11}, \gamma_{22}$  have the same value in the atoms as in the molecule.
- (iii)  $P_{11}(\infty) = P_{22}(\infty) = 1$ .
- (iv)  $X_1 = X_2 = 1$ .

The further assumption made by Brown and Nunn was

- (v)  $P_{11} = P_{22} = P_{12} = P_{21} = 1$

thus

$$\begin{aligned} \beta &= \left( \beta_{12} + \frac{1}{2P_{12}} E_{\text{penetration}} \right) \\ &= \left( \frac{1}{2P_{12}} \right) (E(r) - E(\infty)) + \frac{(P_{11} - 1)}{2P_{12}} I_1 + \frac{(P_{22} - 1)}{2P_{12}} I_2 \\ &\quad + \frac{P_{22}}{2P_{12}} \gamma_{12} + \frac{P_{11}}{2P_{12}} \gamma_{12} - \frac{(P_{11}^2 - 1)}{4P_{12}} \gamma_{11} - \frac{(P_{21}^2 - 1)}{4P_{12}} \gamma_{22} \\ &\quad - \frac{1}{4} P_{11}\gamma_{12} - \frac{1}{4} P_{22}\gamma_{12} + \frac{1}{4} P_{12}\gamma_{12} - \frac{7.1995}{P_{12}\gamma_{12}}. \end{aligned} \quad (10)$$

It follows therefore, with assumption (v) that

$$\beta_{12} = \{E(r) - E(\infty)\} + \frac{3}{4}\gamma_{12} - 7.2/r_{12} - \frac{1}{2}E_{\text{penetration}} \quad (11a)$$

or

$$\beta = (\beta_{12} + E_{\text{penetration}}) = \frac{1}{2}\{E(r) - E(\infty)\} + \frac{3}{4}\gamma_{12} - 7.2/r_{12}. \quad (11b)$$

That is, the  $\beta$  used in their calculations includes contributions from the core-core interactions. Although the inclusion of  $E_{\text{penetration}}$  terms in  $\beta$  is not formally justified, their good results for calculated internuclear separations in the triiodide ion show that this is a workable method for including core-core interactions. This method also allows for problems related to orthogonality, in that Eq. (10) is derived from (9) using the ZDO approximation, that is, assuming an orthogonal basis set.

We performed calculations using Eq. (11b) for the homonuclear diatomic halogens in order to test assumptions (i) to (iii) since assumption (iv) holds for homonuclear molecules. The term  $\frac{1}{2}\{E(r) - E(\infty)\}$  was calculated from Morse functions. Brown and Nunn [19] estimated the term  $(E(\infty) - E(r))$  from the iodine dissociation curve; but as the corresponding curves are not as well defined for the other halogen and interhalogen diatomic molecules, Morse functions were used to estimate this term in the present study. This procedure would lead to false values of dissociation energies because the "experimental" curves do not coincide with those calculated from the MO model; but since in the present study (as in Brown and Nunn's study) it is only sought to determine the equilibrium interatomic separation, it is only required to locate the position of the minimum of the energy curve, and not its absolute value. It is therefore legitimate to use this modification of Brown and Nunn's procedure for estimating  $\beta$  and thence the interatomic distance.

The results are shown in Fig. 1, and the correct internuclear distances were predicted in all cases. This shows that assumptions (i) and (iii) hold; to test the validity of assumption (v), calculations were performed on the heteronuclear halogen diatomic molecules using both Eqs. (10) and (11). The results are presented in Fig. 2; once again the correct internuclear distances were predicted in all cases. It should be noted that although the calculated magnitude of the total energy depends upon whether Eq. (10) or (11) was used to estimate  $\beta$ , both equations give the same internuclear separation, as is shown in Fig. 3 for ICl. Further, the charge distributions, but not the bond order, depend upon which equation is used for the estimation of the core resonance integral. From the calculated charge distributions at the observed internuclear separations, the molecular dipole moments were calculated. These results are presented in Table 3, together with the calculated charge distribution. We draw attention to the result for IBr where in both cases the charge distribution is the reverse of that expected on the basis of the chemical behaviour of this compound [59]. It may be seen that the agreement with experimental is not outstandingly good, a point which further supports the conclusion that more than the  $p\sigma$ -electrons must be included in calculations of the electronic structure of these molecules.

The fact that Brown and Nunn's [19] calculations would lead to incorrect values for the dissociation energy is not a serious criticism since the object was

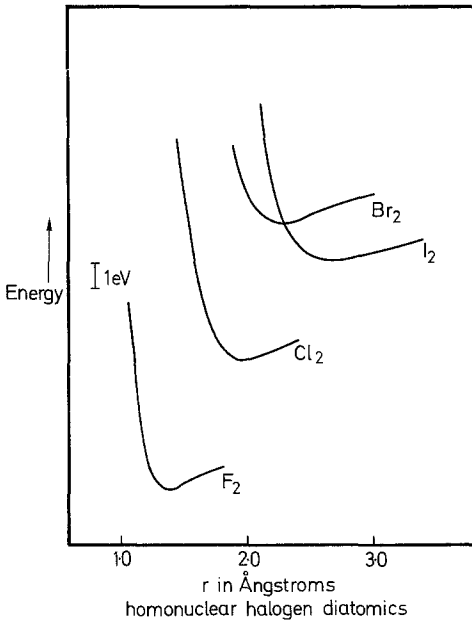


Fig. 1

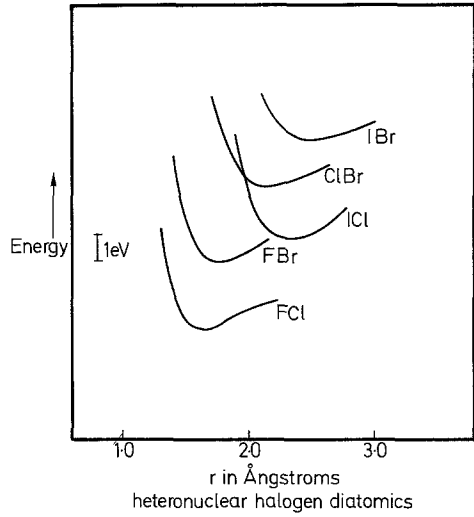


Fig. 2

Fig. 1. Total molecular energy curves for the homonuclear halogen diatomics

Fig. 2. Total molecular energy curves for the heteronuclear halogen diatomics

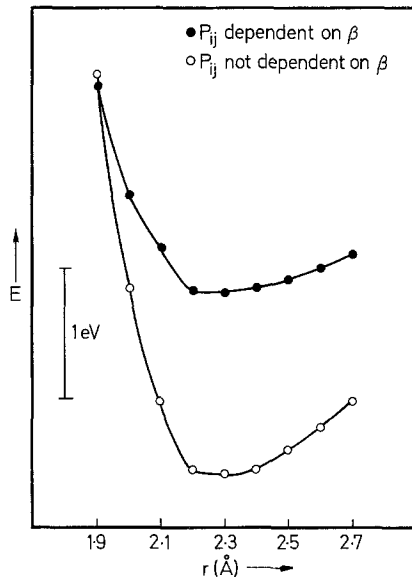


Fig. 3. Total molecular energy curves for the ICl molecule for the two cases,  $\beta$  dependent on  $P_{ij}$  (filled circles) and  $\beta$  not dependent on  $P_{ij}$  (unfilled circles)

Table 3. *Properties of interhalogens*

Molecule	Calculated charge on most electronegative atom		Calculated dipole moment (debye)		Observed dipole moment (debye)
	$\beta$ not dependent	$\beta$ dependent	$\beta$ not dependent	$\beta$ dependent	
	on $P_{pq}$	on $P_{pq}$	on $P_{pq}$	on $P_{pq}$	
FCl	-0.066	-0.071	0.505	0.535	0.88
FBr	-0.157	-0.178	1.285	1.450	1.29
BrCl	-0.113	-0.123	1.140	1.240	—
ICl	-0.106	-0.117	1.170	1.290	0.63
IBr	+0.103	0.110	1.235	1.320	1.26 (in solution)

The bond order was in all cases approximately 0.99.

primarily to predict the geometry of polyhalide ions. We conclude from the comparisons of our results with experimental values that their method can give correct geometries (*i.e.* the results were not fortuitous) but that it does not lead to very satisfactory estimates for the charge distribution in these cases.

A limited application of the same method was made by Migchelsen and Vos who derived their value of  $\beta$  from electronic spectra, that is, assuming a fixed nuclear framework, a method commonly used in semi-empirical  $\pi$ -electron theory. As they imply, this does not include contributions from electrons other than those directly involved in the bonding. In this context Migchelsen and Vos only discuss explicitly contributions from inner shells; our study would indicate that non-bonding valency electrons make a most significant contribution. If  $\beta$  estimated in this way is used in any study which involves variation of the internuclear distance, the problem of including or estimating  $E_{\text{penetration}}$  would remain unsolved. The validity of using an integral calculated from an excited state for the investigation of groundstate properties is also questionable.

### Conclusion

In the absence of an adequate theoretical method for estimating the contribution of the core overlap energy to the total energy, the semi-empirical approach was explored. We conclude that the VESCF  $p\sigma$ -model using a value for the core resonance integral estimated in the manner of Brown and Nunn is satisfactory for predicting internuclear distances, and is therefore suitable for investigating the effect of lattice environment on the geometry of polyhalide ions. On the other hand the usefulness of the method for calculating charge distributions and properties derived from charge distributions is strictly limited and gives little insight into the electronic structure of the halogen-halogen bond. We are engaged in evaluating the usefulness of all electron models for this family of compounds and hope to present the results of these calculations in subsequent papers.



## References

1. van Arkel, E., de Boer, T. H.: *Reçueil Trav. chim.* **47**, 593 (1928).
2. Havinga, E. E.: Ph. D. Thesis, Groningen, 1957.
3. —, Weibenga, E. H.: *Reçueil Trav. chim.* **78**, 724 (1959).
4. Davies, M., Gwynne, E.: *J. Amer. chem. Soc.* **74**, 2748 (1952).
5. Meyerstein, D., Treinin, A.: *Trans. Farad. Soc.* **59**, 1114 (1963).
6. Pauling, L.: *Nature of the chemical bond*, 3rd ed. New York: Cornell University Press 1960.
7. Kimbal, G. E.: *J. chem. Physics* **8**, 188 (1940).
8. Havinga, E. E., Wiebenga, E. H., Boswijk, K. H.: *Advances inorg. Chem. Radiochem.* **3**, 133 (1961).
9. van Vleck, J. H., Sherman, A.: *Rev. mod. Physics* **7**, 167 (1935).
10. Sidgwick, N. V.: *Annual Reports of the Chemical Society (London)* **30**, 26 (1933).
11. Linnett, J. W.: *Electronic structure of molecules*, Methuen edition. New York: Wiley 1964.
12. Volkov, V. M., Dyatkina, M. E.: *Zh. Strukt. Khim.* **4**, 610 (1963).
13. Ali, M. A.: Unpublished work, quoted by Manne, R. (see Ref. [24]).
14. Müller, H.: *Theoret. chim. Acta (Berl.)* **6**, 445 (1966).
15. Rundle, R. E.: *Acta crystallogr.* **14**, 585 (1961).
16. Christie, K. O., Guertin, J. P.: *Inorg. Chem.* **4**, 905 (1965).
17. Coulson, C. A.: *J. chem. Soc. (London)* 1442 (1964).
18. Oakland, R. L., Duffy, G. H.: *J. chem. Physics* **46**, 19 (1967).
19. Brown, R. D., Nunn, E. K.: *Austral. J. Chem.* **19**, 1567 (1966).
20. Migchelsen, T., Vos, A.: *Acta crystallogr.* **23**, 796 (1967).
21. Mooney-Slater, R. C. L.: *Acta crystallogr.* **12**, 187 (1959).
22. Slater, J. C.: *Acta Crystallogr.* **12**, 197 (1959).
23. Santry, D. P., Segal, G. A.: *J. chem. Physics* **47**, 158 (1967).
24. Manne, R.: *Theoret. chim. Acta (Berl.)* **6**, 312 (1966).
25. Boersohn, R.: *J. chem. Physics* **36**, 3445 (1962).
26. Rosenberg, J. L.: *J. chem. Physics* **40**, 1707 (1964).
27. Yamasaki, R. S.: *J. physic. Soc. Japan* **17**, 1202 (1962).
28. Robin, M. B.: *J. chem. Physics* **40**, 3369 (1964).
29. Pimentel, G. C.: *J. chem. Physics* **19**, 446 (1951).
30. Hack, R. J., Rundle, R. E.: *J. Amer. chem. Soc.* **73**, 4321 (1951).
31. Pimentel, G. C., Spratley, R. D.: *J. Amer. chem. Soc.* **85**, 826 (1963).
32. Cornwell, C. D., Yamasaki, R. S.: *J. chem. Physics* **27**, 1060 (1957).
33. — — *J. chem. Physics* **30**, 1265 (1959).
34. Kurita, Y., Nakamura, D., Hayakawa, N.: *J. chem. Soc. Japan, Pure Chemistry Section* **79**, 1093 (1958).
35. Evans, J. C., Lo, G. Y. S.: *J. physic. Chem.* **71**, 2730 (1967).
36. Stammreich, H.: *J. chem. Physics* **35**, 908 (1961).
37. Maki, A. G., Forneris, R.: *Spectrochim. Acta* **23A**, 867 (1967).
38. Christie, K. O., Sawodny, W.: *Inorg. Chem.* **6**, 313 (1967).
39. Snook, I. K.: *Hons. Thesis, University of Tasmania*, 1967.
40. Parr, R. G.: *Quantum theory of molecular electronic structure*, 1st ed. New York: Benjamin 1964.
41. Paoloni, L.: *Nuovo Cimento* **4**, 410 (1956).
42. Mataga, N., Nishimoto, K.: *Z. physik. Chem. NF*, **13**, 140 (1957).
43. Sinanoglu, O.: *Adv. Chem. Physics* **6**, 384 (1964).
44. Parr, R. G.: *Reference* 40, page 51.
45. Brown, R. D., Heffernan, M. L.: *Trans. Farad. Soc.* **54**, 757 (1958).
47. — — *Austral. J. Chem.* **12**, 543 (1959).
48. — — *Harcourt, R. D.: Austral. J. Chem.* **16**, 737 (1963).
49. — — *Coller, B. A. W.: Theoret. chim. Acta (Berl.)* **7**, 259 (1967).
50. Tanaka, M., Nagakura, S.: *Theoret. chim. Acta (Berl.)* **6**, 320 (1966).
51. Fischer-Hjalmars, I.: *Ark. Fysik.* **21**, 123 (1962).
52. Pohl, H. A., Rein, R., Appel, K.: *J. chem. Physics* **41**, 3385 (1964).
53. Hermann, F., Skillman, S.: *Atomic structure calculations*, 1st ed. New Jersey: Prentice Hall 1963.
54. Ballhausen, C. J., Gray, H. B.: *Molecular orbital theory*, 1st ed. New York: Benjamin 1965.

55. Cusachs, L. C., Cusachs, B. B.: J. physic. Chem. **71**, 1060 (1967).
56. Ohno, K.: Theoret. chim Acta (Berl.) **2**, 219 (1964).
57. Moffitt, W.: Proc. Roy. Soc. (London) A **210**, 224 (1951).
58. Pariser, R.: J. chem. Physics **21**, 568 (1953).
59. Cremer, H. W., Duncan, D. R.: J. chem. Soc. (London) 181 (1933).
60. Pohl, H. A., Raff, L. M.: Int. J. Quantum Chem. **1**, 577 (1967).
61. Sichel, J. A., Whitehead, M. A.: Theoret. chim. Acta (Berl.) **11**, 220 (1968).
62. — — Theoret. chim. Acta (Berl.) **11**, 239 (1968).
63. — — Theoret. chim. Acta (Berl.) **11**, 254 (1968).
64. — — Theoret. chim. Acta (Berl.) **11**, 263 (1968).

Dr. G. H. Cheesman  
Chemistry Department  
University of Tasmania  
Box 252 C, G.P.O., Hobart, Australia, 7001