

An Ab Initio Study of Hydrogen, Lithium & Sodium Bonding on the Basis of Atomic Charges, Valencies, Bond Orders & Overlap Populations

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Received 19 February 1987; revised and accepted 10 April 1987

A comparative study of H-, Li- and Na-bonding in the $X \cdots M-Y$ ($X = H_2O, NH_3$; $M = H, Li, Na$; $Y = F, Cl$) complexes has been made on the basis of atomic charges, valencies, bond orders and overlap populations calculated from the Mulliken and Löwdin density matrices using the STO-3G basis set. The complex formation is found to be accompanied by decrease in the charge and valency of bridging H and increase in the charge and valency of Li and Na, and in total valency. The overlap population and the bond order of the intermolecular $X \cdots M$ ($X = N, O$; $M = H, Li, Na$) bonds bear a linear relationship. For a given electron donor these quantities increase in the order, H-bond < Na-bond < Li-bond. The contribution of Li and Na *p*-orbitals to the valence interaction between the monomers is highly exaggerated, which may be attributed to the deficiency of a minimal basis set. The Löwdin analysis overwhelmingly underestimates the bond ionicities and yields quite unrealistic charge distribution in Li-bonded complexes.

Of the numerous theoretical models proposed for population analysis in molecules, those of Mulliken^{1,2} and Löwdin³ have been widely used and these refer to standard nonorthogonal and symmetrically orthogonalised basis sets respectively. These population analysis schemes have also been employed⁴⁻¹⁰ to define bond order and valency of molecules. Baker¹¹ has recently compared the performance of the definitions based on Mulliken and Löwdin schemes and concluded that the later scheme is preferable. We, however, feel that further studies are needed to substantiate or invalidate his conclusion. With this objective in mind, we have made an ab initio comparative study of the nature of bonding in some H-, Li- and Na-bonded complexes of the general formula $X \cdots M-Y$ ($X = H_2O, NH_3$; $M = H, Li, Na$; $Y = F$ and Cl) using the minimal basis set (STO-3G)¹². We are aware of the limitations¹³⁻¹⁵ of this basis set in the case of lithium compounds. Still we have used it because the fully optimised geometries of all the complexes and pertinent monomers considered herein are available¹⁶ to date only for the STO-3G basis set.

Method of Calculation

For the nonorthogonal basis set bond orders (B_{AB}) and valencies (V_A) are defined⁹ by Eqs (1) and (2), respectively.

$$B_{AB} = \sum_a^A \sum_b^B (PS)_{ab} (PS)_{ba} \quad \dots (1)$$

$$V_A = \sum_{B \neq A} B_{AB} \quad \dots (2)$$

where *S* is the overlap matrix and

$$P = \sum_i^{OCC} C_i C_i^\dagger,$$

C_i being the column matrix of the AO coefficients corresponding to the *i*th occupied MO. Equations (1) and (2) are valid for closed-shell systems. For the symmetrically orthogonalised basis set¹⁰,

$$B_{AB} = \sum_a^A \sum_b^B (S^{1/2} P S^{1/2})_{ab}^2 \quad \dots (3)$$

and V_A has the same form as given by Eq. (2). The overlap population (OP) is given by Eq. (4)

$$(OP)_{AB} = \sum_a^A \sum_b^B P_{ab} S_{ba} \quad \dots (4)$$

All calculations have been performed at the theoretical geometry¹⁶ of the molecules concerned.

Results and Discussion

(A) Bond orders, valencies and atomic charges

Calculated values of bond orders, valencies and atomic charges for all the complexes and pertinent monomers based on Mulliken and Löwdin density matrices are given in Table 1. We shall refer to them by Mulliken and Löwdin values respectively.

In the case of H-bonded complexes the Löwdin values for valencies and bond orders are only slightly higher than the Mulliken values. Thus there is no particular reason for preferring one to the other. Both sets of calculations predict a decrease in the valency of bridging H and an increase in N and O valencies upon complex formation. Some of the charge transferred from X to HY is utilised in the formation of the O/N—H bond. However, a major part of this charge is localised on Y (halogens are strong σ -acceptors and π -donors) which weakens the HY bond and decreases its bond order. The fact that the H-bond is strongest in $H_3H \cdots HCl$ is reflected from the bond order of the $N \cdots H$ bond which may be taken roughly as a measure of the valence interaction leading to the complex formation. Atomic charges in all cases show an alternating pattern implying that the dipoles are favourably oriented. The Löwdin atomic charges are, however, considerably lower (in the absolute sense) than the corresponding Mulliken values.

In the case of LiF and LiCl back donation of π electrons takes place from the halogens to the vacant P_π -orbitals of lithium. Unusually high values for Li valency and LiY bond order indicate that π -bonding in LiY is exaggerated. The back donating tendency of Y is somewhat reduced in the complexes since M has already accepted some charge from X. This causes a decrease in the LiY bond order. Valencies of Li, N and O increase upon complex formation due to the formation O/N---Li σ -bond. These bond orders are substantially higher than those of O/N \cdots H and O/N \cdots Na bonds, in conformity with the highest complexation energy¹⁶ of the Li-bonded systems. The contribution of Li p-orbitals to the O/N \cdots Li bond order is about 60-70%. As in H-bonded complexes Löwdin valencies and bond orders of constituent atoms and bonds involved in three-centre interaction, O/N \cdots Li-Y are higher than the corresponding Mulliken values and the two sets of values differ by a much wider margin. Atomic charges predicted by the Löwdin analysis for Li-bonded complexes do not follow an alternating pattern implying an unfavourable orientation of the interacting dipoles. A more disturbing fact is that Li is predicted to carry more negative charge than halogens which appears quite absurd. The noted absurdity is due to the fact that the ionicity of LiF and LiCl bonds is overwhelmingly underestimated in the Löwdin analysis.

In the case of Na-bonded complexes the discrepancy between the Mulliken and Löwdin values for valencies, bond orders and atomic charges is not as pronounced as in the case of Li-bonded complexes. Both sets of calculations predict an increase in the

Table 1—Bond Orders, Valencies and Atomic Charges of Some H-, Li and Na-Bonded Complexes and the Constituent Monomers^a

System	Bond	Bond ^b order	Atom ^c	Valency	Atomic change	
H_3N	H—N	0.96	H	0.98	+0.15	
		0.99	N	2.88	-0.45	
					2.97	-0.30
H_2O	H—O	0.96	H	0.97	+0.17	
		0.99	O	0.99	+0.12	
					1.93	-0.34
					1.97	-0.24
HF	H—F	0.96	H	0.96	+0.19	
		0.98		0.98	+0.14	
$H_3N \cdots HF$	H—N	0.95	H_d	0.97	+0.17	
		0.99		0.99	+0.11	
	N \cdots H	0.07	N	3.00	-0.45	
		0.07		3.08	-0.28	
	H—F	0.88	H_a	0.95	+0.22	
		0.90		0.97	+0.16	
			F	0.92	-0.28	
				0.95	-0.21	
$H_2O \cdots HF$	H—O	0.95	H_d	0.96	+0.19	
		0.98		0.98	+0.14	
	O \cdots H	0.07	O	2.02	-0.33	
		0.08		2.09	-0.21	
	H—F	0.88	H_a	0.95	+0.21	
		0.90		0.98	+0.16	
			F	0.93	-0.26	
				0.95	-0.23	
HCl	H—Cl	0.97	H	0.97	+0.17	
		0.99		0.99	+0.11	
$H_3N \cdots HCl$	H—N	0.94	H_d	0.95	+0.21	
		0.98		0.98	+0.15	
	N \cdots H	0.28	N	3.18	-0.43	
		0.27		3.34	-0.22	
	H—Cl	0.67	H_a	0.93	+0.26	
		0.69		0.96	+0.19	
			Cl	0.78	-0.46	
				0.83	-0.42	
$H_2O \cdots HCl$	H—O	0.93	H_d	0.94	+0.24	
		0.97		0.97	+0.18	
	O \cdots H	0.22	O	2.18	-0.30	
		0.23		2.28	-0.16	
	H—Cl	0.72	H_a	0.94	+0.24	
		0.74		0.97	+0.17	
			Cl	0.83	-0.42	
				0.87	-0.37	
LiF	Li—F	1.34 (1.21)	Li	1.34	+0.23	
		1.59 (1.40)		1.59	+0.06	
$H_3N \cdots LiF$	H—N	0.94	H	0.96	+0.21	
		0.96		0.97	+0.16	
	N \cdots Li	0.39 (0.20)	N	3.21	-0.41	
		0.57 (0.33)		3.47	-0.12	
	Li—F	1.31 (1.16)	Li	1.70	+0.02	
		1.55 (1.34)		2.15	-0.28	
			F	1.32	-0.24	
				1.57	-0.08	

(Contd)

Table 1—Bond Orders, Valencies and Atomic Charges of Some H-, Li and Na-Bonded Complexes and the Constituent Monomers^a—Cont

System	Bond	Bond ^b order	Atom ^c	Valency	Atomic change
H ₂ O...LiF	H—O	0.92	H	0.94	+0.24
		0.94		0.96	+0.20
	O...Li	0.35 (0.21)	O	2.21	-0.29
		0.56 (0.36)		2.47	-0.06
	Li—F	1.31 (1.21)	Li	1.67	+0.04
		1.54 (1.32)		2.12	-0.27
		F	1.32	-0.23	
			1.56	-0.07	
LiCl	Li—Cl	1.11 (0.85)	Li	1.11	+0.38
		1.48 (1.13)		1.48	+0.10
H ₃ N...LiCl	H—N	0.94	H	0.95	+0.22
		0.96		0.97	+0.17
	N...Li	0.40 (0.24)	N	3.22	-0.42
		0.59 (0.36)		3.47	-0.12
	Li—Cl	1.04 (0.78)	Li	1.45	+0.19
		1.39 (1.04)		2.02	-0.23
		Cl	1.04	-0.43	
			1.41	-0.16	
H ₂ O...LiCl	H—O	0.92	H	0.94	+0.25
		0.94		0.95	+0.21
	O...Li	0.38 (0.26)	O	2.23	-0.29
		0.60 (0.41)		2.49	-0.06
	Li—Cl	1.04 (0.77)	Li	1.43	+0.20
		1.39 (1.03)		2.02	-0.22
		Cl	1.05	-0.41	
			1.41	-0.14	
NaF	Na—F	0.72 (0.33)	Na	0.72	+0.58
		0.79 (0.39)		0.79	+0.53
H ₃ N...NaF	H—N	0.95	H	0.95	+0.18
		0.98		0.98	+0.13
	N...Na	0.14 (0.11)	N	2.99	-0.47
		0.22 (0.13)		3.17	-0.26
	Na—F	0.69 (0.34)	Na	0.84	+0.52
		0.75 (0.39)		0.98	+0.43
		F	0.69	-0.59	
			0.75	-0.56	
H ₂ O...NaF	H—O	0.94	H	0.95	+0.21
		0.97		0.98	+0.16
	O...Na	0.16 (0.09)	O	2.05	-0.34
		0.23 (0.14)		2.18	-0.19
	Na—F	0.70 (0.27)	Na	0.86	+0.51
		0.76 (0.39)		1.00	+0.42
		F	0.70	-0.59	
			0.76	-0.55	
NaCl	Na—Cl	0.39 (0.16)	Na	0.39	+0.79
		0.52 (0.29)		0.52	+0.71
H ₃ N...NaClH—N	H—N	0.95	H	0.96	+0.19
		0.98		0.98	+0.13
	N...Na	0.17 (0.10)	N	3.01	-0.48
		0.25 (0.14)		3.19	-0.26
	Na—Cl	0.35 (0.16)	Na	0.52	+0.72
		0.48 (0.27)		0.74	+0.59
		Cl	0.52	-0.81	
			0.74	-0.72	

 Table 1—Bond Orders, Valencies and Atomic Charges of Some H-, Li and Na-Bonded Complexes and the Constituent Monomers^a—Cont

System	Bond	Bond ^b order	Atom ^c	Valency	Atomic change
H ₂ O...NaClH—O	H—O	0.94	H	0.95	+0.22
		0.97		0.97	+0.16
	O...Na	0.18 (0.10)	O	2.06	-0.34
		0.26 (0.16)		2.22	-0.19
	Na—Cl	0.36 (0.17)	Na	0.55	+0.70
		0.49 (0.26)		0.47	+0.58
		Cl	0.36	-0.80	
			0.49	-0.71	

(a) Of the two values for each quantity the first one corresponds to the Mulliken analysis and the second one to the Löwdin analysis.

(b) The quantities in the parentheses denote the Li/Na *p*-orbital contributions.

(c) In H_d and H_a, d and a stand respectively for donor and acceptor.

valency of Na, N and O, and a decrease in MY bond order upon complex formation. Now NaY π -bonding is almost negligible (although not shown in Table 1, we have verified it by partitioning the total bond order into σ and π components), and the valency of Na and NaY bond order are less than unity. The bond orders of the O/N...Na bonds generally lie between those of O/N...H (HCl complexes are exceptions) and O/N...Li in conformity with the intermediate complexation energy¹⁶ of the Na-bonded complexes. The contribution of Na *p*-orbitals to these bond orders is less ($\approx 50\%$) than that of the Li *p*-orbitals in the case of O/N...Li bonds. This difference can be understood from the fact that the 3*s*-3*p* energy gap (2.1 eV) in Na is slightly higher than the 2*s*-2*p* energy gap (1.8 eV) in Li¹⁷. Atomic charges predicted by both Löwdin and Mulliken analyses follow an alternating pattern. As usual, the former calculations underestimate the bond ionicity and the atomic charges, although to a much lesser extent than in Li-bonded complexes.

(B) Overlap populations and other quantities

Since the overlap population (OP) is zero for an orthogonal basis, it has been calculated only from the Mulliken density matrices. In Table 2 are given the calculated values of complexation energy (ΔE)¹⁶, the OP of O/N...M bonds, the change in total valency

$$\left(\Delta V = \sum_A V_A(\text{complex}) - \sum_{A'} V_{A'}(X) - \sum_A V_A(MY) \right),$$

the amount of charge transfer (Δq) and the change in dipole moment ($\Delta \mu$). As in the case of bond or-

Table 2—Complexation Energy (ΔE), Change in Dipole Moment ($\Delta\mu$), Overlap Population (OP) of O/N...M Bonds, Total Valency Change (ΔV) and Amount of Charge Transfer (Δq) of Some H-, Li- and Na-Bonded Complexes^a

System	$-\Delta E$ (kcal/mol)	$\Delta\mu$ (Debye)	OP ^b	ΔV	Δq
H ₃ N...HF	8.30	0.94	0.02	0.04 0.07	0.05 0.06
H ₂ O...HF	7.51	0.30	0.02	0.02 0.04	0.06 0.07
H ₃ N...HCl	18.42	3.38	0.09	0.02 0.15	0.21 0.23
H ₂ O...HCl	15.70	2.01	0.07	0.03 0.11	0.18 0.19
H ₃ N...LiF	46.29	1.53	0.16 (0.09)	0.62 0.98	0.22 0.36
H ₂ O...LiF	48.56	0.96	0.14 (0.09)	0.53 0.91	0.20 0.34
H ₃ N...LiCl	51.87	1.79	0.17 (0.11)	0.54 0.91	0.23 0.38
H ₂ O...LiCl	55.48	1.10	0.15 (0.11)	0.48 0.89	0.22 0.37
H ₃ N...NaF	23.54	0.90	0.05 (0.04)	0.16 0.33	0.08 0.12
H ₂ O...NaF	23.33	0.14	0.06 (0.03)	0.20 0.34	0.09 0.13
H ₃ N...NaCl	28.95	1.04	0.06 (0.04)	0.19 0.37	0.09 0.13
H ₂ O...NaCl	28.04	0.22	0.06 (0.04)	0.22 0.10	0.10 0.14

(a) Of the two values for ΔV and Δq , the first one corresponds to the Mulliken analysis and the second to the Löwdin analysis.

(b) The quantities in the parentheses denote the Li/Na *p*-orbital contributions.

ders the overlap population of O/N - M bonds generally increase (again O/N...H in HCl complexes are exceptions) in the order, H < Na < Li for a given electron donor. Mayer¹⁸ was the first to observe a linear relationship between bond order and overlap population of the NO bond in several nitrogen oxides and ions. A similar relationship is found (Fig. 1) to hold good in the case of N/O...M bonds. The contribution of Li and Na *p*-orbitals to the OP of these bonds is quite significant. The Löwdin values of ΔV and Δq are in general considerably higher than the corresponding Mulliken values. No correlation seems to exist between ΔE and other quantities although higher complexation energy is generally associated with higher ΔV , Δq and OP values. The $\Delta\mu$ values do not follow any trend.

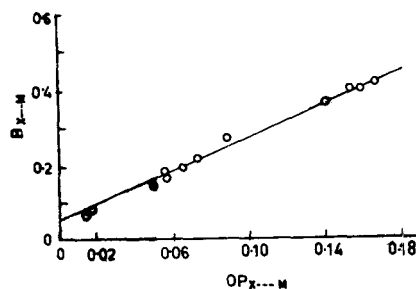


Fig. 1—Plot of bond order (B) of the intermolecular X...M (X = N or O) bonds versus the corresponding overlap population (OP).

(C) CNDO/2 calculations

The results of the ab initio calculations reported in the two subsections (A) and (B) indicate that Li and Na *p*-orbitals make a large contribution to the valence interaction between the monomers. Now the question remains: Are the valence *p*-orbitals of Li and Na essential for the description of Li- and Na-bonding? In order to provide a direct answer to this question we have carried out two sets of CNDO/2 calculations¹⁹, namely, CNDO/2 (s) and CNDO/2 (sp) on the Li- and Na-bonded complexes. In the former set of calculations *p*-orbitals of Li and Na are excluded from the basis set. In order to save space we have not tabulated these results and shall outline only the important points.

The bond orders of LiF, LiCl, NaF and NaCl are (0.51, 1.06), (0.68, 1.39), (0.37, 0.80) and (0.52, 1.16), respectively where two sets of values refer to CNDO/2 (s) and CNDO/2 (sp) calculations respectively. The corresponding atomic charges on Li and Na are (0.70, 0.41), (0.57, 0.18), (0.80, 0.57) and (0.89, 0.34), in these compounds, respectively. In view of the highly ionic character²⁰ of alkali halides, the CNDO/2 (s) values seem to be more realistic. As in the ab initio case, both sets of CNDO/2 calculations predict an increase in the charge and valency of Li and Na and a slight decrease in the MY bond order upon complex formation. The CNDO/2 (s) calculations, however, predict negative ΔV values in all the cases and quite low values of O/N...M bond order (≈ 0.1) implying that valence interaction between the monomers is underestimated when *p*-orbitals are not included in the basis set. In the CNDO/2 (sp) calculations, higher values of valency and bond order are obtained due to the presence of Li and Na *p*-orbitals. However, as in the Löwdin analysis, the atomic charges predicted for the Li-bonded complexes are quite unreliable.

(D) Concluding remarks

One of the main conclusions of the present study

is that at the STO-3G level the role of Li and Na *p*-orbitals is exaggerated especially in the case of Li-bonds. Since the polarity of the MY bond increases only marginally during complex formation the H-, Li- and Na-bonded complexes considered herein are essentially of molecular type²¹. In the case of Li-bonded complexes and the pertinent monomers the Löwdin population analysis yields quite unrealistic charge distribution in contrast to the observation made by Baker¹¹. Unusually high values of bond order and valency obtained from the Löwdin density matrices is attributed⁹ to spurious global effects. In brief, the Mulliken analysis performs far more satisfactorily in the case of ionic molecules treated at the minimal basis set level.

Acknowledgement

The time and service made available by the Regional Computer Centre, Calcutta were essential to this study, and are gratefully acknowledged.

References

- 1 Mulliken R S, *J chem Phys*, **23** (1955) 1833, 1841, 2338, 2343.
- 2 Mulliken R S & Ermler W C, *Diatomc molecules, results of ab initio calculations* (Academic Press, New York) 1977.
- 3 Löwdin P O, *Phys Rev*, **97** (1955) 1474.
- 4 Wiberg K A, *Tetrahedron*, **14** (1968) 1083.
- 5 Armstrong D R, Perkins P G & Stewart J J, *J chem soc Dalton Trans*, (1973) 833.
- 6 Cohen I, *J chem Phys*, **57** (1972) 5076.
- 7 Borisova N P & Semenov S G, *Vestn Leningrad Univ*, **16** (1973) 119.
- 8 Gopinathan M S & Jug K, *Theoret chim Acta*, **63** (1983) 497, 511.
- 9 Mayer I, *Chem Phys Lett*, **97** (1983) 270; 110 (1984) 440.
- 10 Natiello M A & Medrano J A, *Chem Phys Lett*, **105** (1984) 180; 110 (1984) 445.
- 11 Baker J, *Theoret chim Acta*, **68** (1985) 221.
- 12 Hehre W J, Stewart R F & Pople J A, *J chem Phys*, **51** (1969) 2657.
- 13 Dill J D, Schleyer P V R, Binkley J S & Pople J A, *J Am chem Soc*, **99** (1977) 6159.
- 14 Collins J B & Streitwieser A, *J comp Chem*, **81** (1980) 1.
- 15 Reed A E, Weinstock R B & Weinhold F, *J chem Phys*, **83** (1985) 735.
- 16 Kulkarni G V & Rao C N R, *J molec struc*, **100** (1983) 531.
- 17 Hinze J & Jaffe H H, *J Am chem Soc*, **84** (1962) 540.
- 18 Mayer I, *Intern J Quantum Chem*, **26** (1984) 151.
- 19 Pople J A & Beveridge D L, *Approximate molecular orbital theory* (McGraw-Hill, New York) 1970.
- 20 Pauling L, *The nature of the chemical bond* (Cornell University Press, Ithaca) 1960.
- 21 Szczesniak M M, Latajka Z, Piccuch P, Ratajczak H, Orville-Thomas W J & Rao C N R, *Chem Phys*, **94** (1985) 55.