

# Global Molecular Identification from Graphs. Neutral and Ionized Main-Group Diatomic Molecules

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Received May 14, 2001

Diophantine equations and inequalities are presented for main-group closed-shell diatomic molecules. Specifying various bond types (covalent, dative, ionic, van der Waals) and multiplicities, it becomes possible to identify all possible molecules. While many of the identified species are probably unstable under normal conditions, they are interesting and present a challenge for computational or experimental analysis. Ionized molecules with net charges of  $-1$ ,  $1$ , and  $2$  are also identified. The analysis applies to molecules with atoms from periods 2 and 3 but can be generalized by substituting isovalent atoms. When closed-shell neutral diatomics are positioned in the chemical space (with axes enumerating the numbers of valence electrons of the free atoms), it is seen that they lie on a few parallel isoelectronic series.

## 1. INTRODUCTION

Since closed-shell molecules are of such importance in organic chemistry, in large part because of their stabilities, it seems possible that a method of determining all possible closed-shell species would be useful. The method, consisting of a simple algebraic formulation, is explored here for the simplest possible molecules, i.e., diatomic molecules. The formulation assigns eight electrons to each main-group atom, the lone-pair electrons plus the valence electrons contributed by the atom itself and by those of the neighboring atom by means of covalent, ionic, and coordinate-covalent bonding. The equations guaranteeing full valence shells, together with appropriate constraints, form a system of first degree Diophantine equations and inequalities (integer variables and coefficients) whose solution set consists of all such possible molecules. There is no reference to molecular-orbital or valence-bond theory except in limiting the bond order to three or less.

The equations lead to the determination of familiar molecules and also of interesting species which may have short lifetimes, may exist only under very unusual conditions, or may be only resonances. The stabilities of the identified species are not discussed. The distributions of properties of diatomic molecules in their periodic system have been described extensively elsewhere.<sup>1–3</sup>

Various bond types are considered in succession, for both neutral and ionized species. Inequalities and equations applicable in all cases are presented first, in Section 2; those that are specific to ionic bonds are presented in Sections 7 and 8. The appearance of the equations in terms of the matrix elements of Ugi et al.<sup>4</sup> is presented in Section 9. The differences and the sums of the primary pairs of equations given for each of the various cases are discussed in Section 10. They lead to an understanding of where the closed-shell

molecules lie in chemical space (a subspace of the diatomic-molecular periodic system<sup>5,6</sup>) and of the extent to which these locations are the same as those of the most stable molecules.

## 2. DEFINITIONS AND UNIVERSAL INEQUALITIES

Diatomic molecules are located in their periodic system with coordinates  $(R_1, C_1, R_2, C_2)$ . Two of these coordinates, the period numbers  $R_1$  and  $R_2$ , do not appear in the formulation as they have been fixed at 2, except in a portion of Table 2, where they are 3; however, they may be changed at will by substituting isovalent atoms. Thus,  $F_2$  could be  $ClF$  or  $BrAt$  or even  $118F$ . Also, the molecular symbols in this paper may be reversed;  $BrAt$  and  $AtBr$  are of course the same molecule. The other two coordinates, the column numbers  $C_1$  and  $C_2$ , are enumerated as in older periodic tables of the elements (before the IUPAC convention was adopted) as

$$0 \leq C_i \leq 8 \quad (1)$$

for both atoms  $i$ . Helium has  $C_i = 0$  when considered as a row-2 element, a device employed by Kong.<sup>7</sup>  $C_i$  also has significance, for neutral molecules, as the number of electrons in the valence shell of the isolated atom  $i$ . The molecular formulas are always (except for one column of a table) presented in the order

$$C_1 \leq C_2 \quad (2)$$

It is assumed that atoms retain their identities within molecules and that  $s$  and  $p$  atoms will achieve the imperative closed-shell status of having  $S_i$  valence-shell electrons, i.e.,

$$S_1, S_2 \in \{2, 8\} \quad (3)$$

The requisite number of electrons is drawn from each free atom's own inventory plus from the bond with the other atom. For covalent bonds,  $v_{ij}$  will represent the number of

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**Table 1.** Closed-Shell Neutral Diatomic Molecules Having Covalent and Dative Bonds and Closed-Shell Ions Having Covalent Bonds

molecule	atoms, ions	bonding	rule(s)	$\nu_{12}$	$C_1$	$C_2$	molecule	analogue
neutral	p and p	covalent	8	0	8	8	Ne Ne <sup>a</sup>	
				1	7	7	F-F	
				2	6	6	O=O	
				3	5	5	N≡N	
	s and s	covalent	2 and 8	2	4	6	C=O <sup>b</sup>	
				0	2	2	Be Be <sup>a</sup>	
	s and p	covalent	2 and 8	1	1	1	Li-Li	
				0	2	8	Be Ne <sup>a</sup>	
	p and p	dative, one electron pair from atom 1	8	1	1	7	Li-F	
				0	6	8	O<Ne	Ne Ne <sup>a</sup>
				1	5	7	N<-F	F-F
				2	4	6	C<=O	O=O
				0	4	8	C<<Ne	Ne Ne
				1	3	7	B<<-F	F-F
				0	2	8	B<<<Ne	Ne Ne <sup>a</sup>
				0	0	2	He<Be	Be Be <sup>a</sup>
				0	2	6	Be>O	Be Ne <sup>a</sup>
				0	8	0	Ne>He	Ne Be <sup>a,c</sup>
				0	7	8	(F <sup>-</sup> Ne)	Ne Ne <sup>a</sup>
anion	p <sup>-</sup> and p	covalent	8	1	6	7	(O <sup>-</sup> -F)	F-F
				2	5	6	(N <sup>-</sup> =O)	O=O
				3	4	5	(C <sup>-</sup> ≡N)	N≡N
				0	8	9	(Ne Na <sup>+</sup> )	Ne Ne <sup>a</sup>
				1	7	8	(F-Ne <sup>+</sup> )	F-F
				2	6	7	(O=F <sup>+</sup> )	O=O
				3	5	6	(N≡O <sup>+</sup> )	N≡N
				0	9	9	(Na <sup>+</sup> Na <sup>+</sup> )	Ne Ne <sup>a</sup>
				1	7	9	(Ne <sup>+</sup> -Ne <sup>+</sup> )	F-F
				2	7	7	(F <sup>+</sup> =F <sup>+</sup> )	O=O
				3	6	6	(O <sup>+</sup> ≡O <sup>+</sup> )	N≡N
	p and p <sup>++</sup>	covalent	8	0	8	10	(Ne Mg <sup>++</sup> )	Ne Ne <sup>a</sup>
				1	7	9	(F-Na <sup>++</sup> )	F-F
				2	6	8	(O=Ne <sup>++</sup> )	O=O
				3	5	7	(N≡F <sup>++</sup> )	N≡N
anion	s <sup>-</sup> and s	covalent	2	0	1	2	(Li <sup>-</sup> Be)	Be Be <sup>a</sup>
				1	0	1	(He <sup>-</sup> -Li)	Li-Li
cation	s <sup>+</sup> and s	covalent	2	0	3	2	(B <sup>+</sup> Be)	Be Be <sup>a</sup>
				1	2	1	(Be <sup>+</sup> -Li)	Li-Li
	s <sup>+</sup> and s <sup>+</sup>	covalent	2	0	3	3	(B <sup>+</sup> B <sup>+</sup> )	Be Be <sup>a</sup>
				1	2	2	(Be <sup>+</sup> -Be <sup>+</sup> )	Li-Li
	s <sup>++</sup> and s	covalent	2	0	4	2	(C <sup>++</sup> Be)	Be Be <sup>a</sup>
anion	s <sup>-</sup> and p	covalent	2 and 8	1	3	1	(B <sup>++</sup> -Li)	Li-Li
				0	1	8	(Li <sup>-</sup> Ne)	Be Ne <sup>a</sup>
				1	0	7	(He <sup>-</sup> -F)	Li-F
cation	s and p <sup>-</sup>	covalent	2 and 8	0	2	7	(Be F <sup>-</sup> )	Be Ne <sup>a</sup>
				1	1	6	(Li-O <sup>-</sup> )	Li-F
	s <sup>+</sup> and p	covalent	2 and 8	0	3	8	(B <sup>+</sup> Ne)	Be Ne <sup>a</sup>
				1	2	7	(Be <sup>+</sup> -F)	Li-F
	s and p <sup>+</sup>	covalent	2 and 8	0	2	9	(Be Na <sup>+</sup> )	Be Ne <sup>a</sup>
				1	1	8	(Li-Ne <sup>+</sup> )	Li-F
	s <sup>+</sup> and p <sup>+</sup>	covalent	2 and 8	0	3	9	(B <sup>+</sup> Na <sup>+</sup> )	Be Ne <sup>a</sup>
				1	2	8	(Be <sup>+</sup> -Ne <sup>+</sup> )	Li-F
	s <sup>++</sup> and p	covalent	2 and 8	0	4	8	(C <sup>++</sup> Ne)	Be Ne <sup>a</sup>
				1	3	7	(B <sup>++</sup> -F)	Li-F
	s and p <sup>++</sup>	covalent	2 and 8	0	2	10	(Be Mg <sup>++</sup> )	Be Ne <sup>a</sup>
				1	1	9	(Li-Na <sup>++</sup> )	Li-F

<sup>a</sup> van der Waals bonded. <sup>b</sup> C is not an octet. <sup>c</sup> C<sub>2</sub> < C<sub>1</sub>.

electrons contributed by atom  $j$  to atom  $i$  (or, equivalently, it represents the bond order). From this definition,

$$\nu_{12} = \nu_{21} \quad (4)$$

Given eq 4,  $\nu_{12}$  will be used to stand for either term unless the more general notation  $\nu_{ij}$  is required. For dative bonds,  $d_{ij}$  will mean that atom  $j$  delegates one lone pair to form a bond (or *additional* bond) to atom  $i$ . The outer-shell electron inventory of atom  $j$  remains unchanged but that of atom  $i$  is

increased by 2. A dative bond may exist in one direction only. The combined bond orders are constrained by

$$0 \leq (\nu_{ij} + d_{ij}) \leq 3 \quad (5)$$

The covalent bond order may be zero, indicating a van der Waals molecule, and there may be no dative bond. For other than van der Waals molecules, each atom must have some bond, so

$$\nu_{12} = \nu_{21} \neq 0 \vee d_{12} \neq 0 \vee d_{21} \neq 0 \quad (6)$$

**Table 2.** Closed-Shell Ionized Diatomic Molecules, Transition States, or Resonances Having Covalent and Coordinate-Covalent Bonds

dative bond(s)	atoms and charges	prototype									
		two period-2 p atoms				one period-3 s atom and one period-3 p atom				two period-3 s atoms	
		covalent <sup>a</sup>			van der Waals <sup>a</sup> Ne Ne	covalent <sup>a</sup>		van der Waals <sup>a</sup>		covalent <sup>a</sup> Na – Na	van der Waals <sup>a</sup> Mg Mg
		N≡N	O = O	F – F		Na – Cl	Cl – Na	Mg Ar	Ar Mg		
none	X <sup>-</sup> and X	C <sup>-</sup> ≡N	N <sup>-</sup> = O	O <sup>-</sup> – F	F <sup>-</sup> Ne	Ne <sup>-</sup> – Cl	S <sup>-</sup> – Na	Na <sup>-</sup> Ar	Cl <sup>-</sup> Mg	Ne <sup>-</sup> – Na	Na <sup>-</sup> Mg
	X and X <sup>-</sup>	N≡C <sup>-</sup>	O = N <sup>-</sup>	F – O <sup>-</sup>	Ne F <sup>-</sup>	Na – S <sup>-</sup>	Cl – Ar <sup>-</sup>	Mg Cl <sup>-</sup>	Ar Na <sup>-</sup>	Na – Ar <sup>-</sup>	Mg Na <sup>-</sup>
	X <sup>+</sup> and X	O <sup>+</sup> ≡N	F <sup>+</sup> = O	Ne <sup>+</sup> – F	Na <sup>+</sup> Ne	Mg <sup>+</sup> – Cl	Ar <sup>+</sup> – Na	Al <sup>+</sup> Ar	K <sup>+</sup> Mg	Mg <sup>+</sup> – Na	Al <sup>+</sup> Mg
	X and X <sup>+</sup>	N≡O <sup>+</sup>	O = F <sup>+</sup>	F – Ne <sup>+</sup>	Ne Na <sup>+</sup>	Na – Ar <sup>+</sup>	Cl – Mg <sup>+</sup>	Mg K <sup>+</sup>	Ar Al <sup>+</sup>	Na – Mg <sup>+</sup>	Mg Al <sup>+</sup>
	X <sup>++</sup> and X	F <sup>++</sup> ≡N	Ne <sup>++</sup> = O	Na <sup>++</sup> – F	Mg <sup>++</sup> Ne	Al <sup>++</sup> – Cl	K <sup>++</sup> – Na	Si <sup>++</sup> Ar	Ca <sup>++</sup> Mg	Al <sup>++</sup> – Na	Si <sup>++</sup> Mg
	X and X <sup>++</sup>	N≡F <sup>++</sup>	O = Ne <sup>++</sup>	F – Na <sup>++</sup>	Ne Mg <sup>++</sup>	Na – K <sup>++</sup>	Cl – Al <sup>++</sup>	Mg Ca <sup>++</sup>	Ar Si <sup>++</sup>	Na – Al <sup>++</sup>	Mg Si <sup>++</sup>
	X <sup>+</sup> and X <sup>+</sup>	O <sup>+</sup> ≡O <sup>+</sup>	F <sup>+</sup> = F <sup>+</sup>	Ne <sup>+</sup> – Ne <sup>+</sup>	Na <sup>+</sup> Na <sup>+</sup>	Mg <sup>+</sup> – Ar <sup>+</sup>	Ar <sup>+</sup> – Mg <sup>+</sup>	Al <sup>+</sup> K <sup>+</sup>	K <sup>+</sup> Al <sup>+</sup>	Mg <sup>+</sup> – Mg <sup>+</sup>	Al <sup>+</sup> Al <sup>+</sup>
one	X <sup>-</sup> and X		B <sup>-</sup> <= O	C <sup>-</sup> <- F	N <sup>-</sup> < Ne	O <sup>-</sup> <- Cl	Si <sup>-</sup> <- Na	F <sup>-</sup> < Ar	P <sup>-</sup> < Mg	O <sup>-</sup> <- Na	F <sup>-</sup> < Mg
	X and X <sup>-</sup>		C <= N <sup>-</sup>	N <- O <sup>-</sup>	O < F <sup>-</sup>	F <- S <sup>-</sup>	P <- Ar <sup>-</sup>	Ne < Cl <sup>-</sup>	S < Na <sup>-</sup>	F <- Ar <sup>-</sup>	Ar < Na <sup>-</sup>
	X <sup>+</sup> and X		N <sup>+</sup> <= O	O <sup>+</sup> <- F	F <sup>+</sup> < Ne	Ne <sup>+</sup> <- Cl	S <sup>+</sup> <- Na	Na <sup>+</sup> < Ar	Cl <sup>+</sup> < Mg	Ne <sup>+</sup> <- Na	Na <sup>+</sup> < Mg
	X and X <sup>+</sup>		C <= F <sup>+</sup>	N <- Ne <sup>+</sup>	O < Na <sup>+</sup>	F <- Ar <sup>+</sup>	P <- Mg <sup>+</sup>	Ne < K <sup>+</sup>	S < Al <sup>+</sup>	F <- Mg <sup>+</sup>	Ar < Al <sup>+</sup>
	X <sup>++</sup> and X		O <sup>++</sup> <= O	F <sup>++</sup> <- F	Ne <sup>++</sup> < Ne	Na <sup>++</sup> <- Cl	Cl <sup>++</sup> <- Na	Mg <sup>++</sup> < Ar	Ar <sup>++</sup> < Mg	Na <sup>++</sup> <- Na	Mg <sup>++</sup> < Mg
	X and X <sup>++</sup>		C <= Ne <sup>++</sup>	N <- Na <sup>++</sup>	O < Mg <sup>++</sup>	F <- K <sup>++</sup>	P <- Al <sup>++</sup>	Ne < Mg <sup>++</sup>	S < Si <sup>++</sup>	F <- Al <sup>++</sup>	Ar < Si <sup>++</sup>
	X <sup>+</sup> and X <sup>+</sup>		N <sup>+</sup> <= F <sup>+</sup>	O <sup>+</sup> <- Ne <sup>+</sup>	F <sup>+</sup> < Na <sup>+</sup>	Ne <sup>+</sup> <- Ar <sup>+</sup>	S <sup>+</sup> <- Mg <sup>+</sup>	Na <sup>+</sup> < K <sup>+</sup>	Cl <sup>+</sup> < Al <sup>+</sup>	Na <sup>+</sup> <- Mg <sup>+</sup>	Na <sup>+</sup> < Al <sup>+</sup>
two	X <sup>-</sup> and X			Be <sup>-</sup> <<- F	B <sup>-</sup> << Ne	C <sup>-</sup> <<- Cl	Mg <sup>-</sup> <<- Na	N <sup>-</sup> << Ar	Al <sup>-</sup> << Mg	C <sup>-</sup> <<- Na	N <sup>-</sup> << Mg
	X and X <sup>-</sup>			B <<- O <sup>-</sup>	C << F <sup>-</sup>	N <<- S <sup>-</sup>	Al <<- Ar <sup>-</sup>	O << Cl <sup>-</sup>	Si << Na <sup>-</sup>	N <<- Ar <sup>-</sup>	O << Na <sup>-</sup>
	X <sup>+</sup> and X			C <sup>+</sup> <<- F	N <sup>+</sup> << Ne	O <sup>+</sup> <<- Cl	Si <sup>+</sup> <<- Na	F <sup>+</sup> << Ar	P <sup>+</sup> << Mg	O <sup>+</sup> <<- Na	F <sup>+</sup> << Mg
	X and X <sup>+</sup>			B <<- Ne <sup>+</sup>	C << Na <sup>+</sup>	N <<- Ar <sup>+</sup>	Al <<- Mg <sup>+</sup>	O << K <sup>+</sup>	Si << Al <sup>+</sup>	N <<- Mg <sup>+</sup>	O << Al <sup>+</sup>
	X <sup>++</sup> and X			N <sup>++</sup> <<- F	O <sup>++</sup> << Ne	F <sup>++</sup> <<- Cl	P <sup>++</sup> <<- Na	Ne <sup>++</sup> << Ar	S <sup>++</sup> << Mg	F <sup>++</sup> <<- Na	Si <sup>++</sup> << Mg
	X and X <sup>++</sup>			B <<- Na <sup>++</sup>	C << Mg <sup>++</sup>	N <<- K <sup>++</sup>	Al <<- Al <sup>++</sup>	O << Mg <sup>++</sup>	Si << Si <sup>++</sup>	N <<- Al <sup>++</sup>	O << Si <sup>++</sup>
	X <sup>+</sup> and X <sup>+</sup>			C <sup>+</sup> <<- Ne <sup>+</sup>	N <sup>+</sup> << Na <sup>+</sup>	O <sup>+</sup> <<- Ar <sup>+</sup>	Si <sup>+</sup> <<- Mg <sup>+</sup>	F <sup>+</sup> << K <sup>+</sup>	P <sup>+</sup> << Al <sup>+</sup>	F <sup>+</sup> <<- Mg <sup>+</sup>	F <sup>+</sup> << Al <sup>+</sup>
three	X <sup>-</sup> and X				Li <sup>-</sup> <<< Ne			B <sup>-</sup> <<< Ar	Na <sup>-</sup> <<< Mg		B <sup>-</sup> <<< Mg
	X and X <sup>-</sup>				Be <<< F <sup>-</sup>			C <<< Cl <sup>-</sup>	Mg <<< Na <sup>-</sup>		C <<< Na <sup>-</sup>
	X <sup>+</sup> and X				B <sup>+</sup> <<< Ne			N <sup>+</sup> <<< Ar	Al <sup>+</sup> <<< Mg		N <sup>+</sup> <<< Mg
	X and X <sup>+</sup>				Be <<< Na <sup>+</sup>			C <<< K <sup>+</sup>	Mg <<< Al <sup>+</sup>		C <<< Al <sup>+</sup>
	X <sup>++</sup> and X				C <sup>++</sup> <<< Ne			O <sup>++</sup> <<< Ar	Si <sup>++</sup> <<< Mg		S <sup>++</sup> <<< Mg
	X and X <sup>++</sup>				Be <<< Mg <sup>++</sup>			C <<< Mg <sup>++</sup>	Mg <<< Si <sup>++</sup>		C <<< Si <sup>++</sup>
	X <sup>+</sup> and X <sup>+</sup>				B <sup>+</sup> <<< Na <sup>+</sup>			O <sup>+</sup> <<< K <sup>+</sup>	Al <sup>+</sup> <<< Al <sup>+</sup>		N <sup>+</sup> <<< Al <sup>+</sup>

<sup>a</sup> Initial bonding type.

## 3. NEUTRAL DIATOMICS WITH COVALENT AND VAN DER WAALS BONDS

For this simple case, the equations to solve are

$$C_1 + v_{12} = S_1 \quad (7)$$

$$v_{21} + C_2 = S_2 \quad (8)$$

With eqs 4–6, these expressions result in identifying the molecules Li<sub>2</sub>, LiF, Ne<sub>2</sub>, F<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>. (The closed-shell form of O<sub>2</sub> appears, not its triplet state.)

It will be of importance to Section 5 to subtract eqs 7 and 8 to obtain

$$C_1 - C_2 = S_1 - S_2 \quad (9)$$

This reduced “difference” equation is interesting because it includes only the  $C_i$  and not the covalent bond order. Of course eq 9 ignores the various inequalities and hence it allows for many molecules that are not solutions of eqs 4–8. Also pertinent to Section 5 is the sum of eqs 7 and 8:

$$C_1 + C_2 + 2v_{12} = S_1 + S_2 \quad (10)$$

The first section (containing three subsections) of Table 1 shows the molecules identified as a result of this formalism. Also included, to illustrate the sort of spurious solutions that can be obtained by using eq 10 alone, is CO, the most stable diatomic molecules known (at least on the basis of spectroscopic data).

## 4. NEUTRALS WITH COVALENT, DATIVE, AND VAN DER WAALS BONDS

The algebraic equalities are

$$C_1 + v_{12} + 2d_{12} = S_1 \quad (11)$$

$$v_{21} + 2d_{21} + C_2 = S_2 \quad (12)$$

As stated in Section 2, only of the  $d_{ij}$  may exist, and the factor of 2 is because the beneficiary atom adds two electrons to its valence-shell count. The first subsection under the first heavy bar of Table 1 shows the molecules that result from solving these equations under all the constraints given above. They are O < Ne, N < -F, and C < =O, with atom 2 donating one lone pair to make a dative bond (indicated by <) in addition to the null, single, and double covalent bonds. It is recalled that CO was used as an example of an inadmissible solution to the purely covalent bonding equations. The last three subsections show one molecule with two  $s$  atoms and two molecules with one  $s$  and one  $p$  atom. In the latter, it is striking how different the molecules are when the dative bond is reversed. It should be noted that molecules containing rare-gas atom are common in the spectroscopy of gases and that properties for many have been tabulated.<sup>8–10</sup>

**Inference 1.** Molecules containing one inert-gas atom may satisfy the requirement of having both atoms possessing closed shells by means of coordinate-covalent bonding.

**Inference 2.** The effect of a new dative bond from atom 1 is to reduce the value of  $C_2$  by 2. As examples, O < Ne, N < -F, and C < =O have the same electron inventories

as Ne Ne, F–F, and O=O. These analogue molecules are shown in the last column of the table.

**Inference 3.** An  $s$  atom may act as a  $p$  atom in obeying the rule of 8. An example is BeNe; more such molecules will be encountered in the next Section.

**Inference 4.** It is seen that the more electronegative atom delegates electron pairs to serve as dative bonds, rather than the less electronegative atom. However, these more electronegative atoms do not actually lose valence-shell electrons but merely reposition them. Also, the discourse has been limited to row-2 atoms. The less (or equally) electronegative atom does delegate the lone pair in several molecules isovalent to FN, i.e., CIN, BrN, IN, and AtN, and in several molecules isovalent to OC, i.e., SC, SeC, TeC, and PoC. (Pauling electronegativities are used.)

The difference equation is

$$(C_1 - C_2) \pm 2d_{ij} = S_1 - S_2 \quad (13)$$

The presence of the  $2d_{ij}$  term is because either, but not both, of  $d_{12}$  and  $2d_{21}$  may exist. The sum equality is

$$C_1 + C_2 + 2(v_{12} + 2d_{ij}) = S_1 + S_2 \quad (14)$$

where  $d_{ij}$  is either  $d_{12}$  or  $d_{21}$ .

## 5. DIATOMIC IONS WITH COVALENT AND VAN DER WAALS BONDS

If either atom is once positively or negatively charged, then its valence-shell electron inventory in eqs 6 or 7 is replaced by  $C_i \pm 1$ . If an atom has a positive charge of two, then the replacement is  $C_i + 2$ . If both atoms carry unipositive charge, which is always the case when the atoms are the same, then both  $C_i$  are replaced by  $C_i + 1$ . The excess number of *electrons* on atom  $i$  (excess negative charge) is  $q_i$ , which appears from experiment to be limited such that

$$q_1, q_2, (q_1 + q_2) \in \{-1, 0, 1, 2\} \quad (15)$$

More extreme stages of ionization may be encountered, and if they are then generalization is trivial. The relevant equations are

$$(C_1 + q_1) + v_{12} = S_1 \quad (16)$$

$$v_{12} + (C_2 + q_2) = S_2 \quad (17)$$

Table 1, in sections three and four, shows the solution set for  $p$  atoms. Notation such as “ $p^-$  and  $p$ ” means that the first  $p$  atom of the molecular-ion formula in the next to last column holds the added electron [e.g., the fluorine in (FNe)<sup>−</sup>]. The closed-shell structures of these ions are the same as those of the analogous (or prototype) neutral molecules shown in the last column. (Those with no apparent bond are van der Waals molecules.)

**Inference 5.** Row-3  $s$  atoms such as Na and Mg may appear with positive ionizations to serve the role of row-2  $p$  atoms (cf. Inference 3).

The next two sections of Table 1 show ionized covalent-bonded molecules with two “ $s$ ” atoms, using the rule of 2. The notation “ $s$ ” is due to the appearance of  $p$  atoms playing the role of  $s$  atoms, as in (B<sup>+</sup>Be).

**Inference 6.** All the ions have the same numbers of valence-shell electrons as Ne<sub>2</sub>, F<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> (for ions with two *p* atoms), Li<sub>2</sub> and Be<sub>2</sub> (two “*s*” atoms), or LiF and BeNe (one “*s*” and one *p* atom). As a check, all of the determined molecular ions can be retrieved by replacing the neutral atoms in these eight molecules with positively or negatively charged atoms.

The difference equation is

$$(C_1 - C_2) + (q_1 - q_2) = S_1 - S_2 \quad (18)$$

and the sum equation is

$$(C_1 + C_2) + (q_1 + q_2) + 2v_{12} = S_1 + S_2 \quad (19)$$

Some additional comments about the material of this section are germane. (1) For some heteronuclear cations with one atom doubly ionized, the more electronegative atom appears to lose the two electrons (N≡F<sup>2+</sup>, B<sup>2+</sup>-Li, and C<sup>2+</sup>-Be). The appearance is deceptive, however, because the comparisons are to be made to N<sub>2</sub>, O<sub>2</sub>, and F<sub>2</sub> and not to FN, BLi, and CBe. (2) Inspection of tables giving first and second ionization potentials shows that of all of the cases with one atom doubly ionized, only NeMg<sup>2+</sup> requires more energy to form from the neutral molecule (is more “stable”) than if the one positive charges were placed on each atom. (3) Of the cases where each atom has one positive charge, only the molecules Ne<sup>+</sup>-Ne<sup>+</sup>, Be<sup>+</sup>-Ne<sup>+</sup>, and Be<sup>+</sup>-Be<sup>+</sup> would be more “stable” if both positive charges were on one of the atoms. Of course, many of these species are not stable at all: they may exist only as momentary collision states.

## 6. IONS WITH COVALENT, DATIVE, AND VAN DER WAALS BONDS

Without further definitions or inequalities it is possible to write

$$(C_1 + q_1) + v_{12} + 2d_{12} = S_1 \quad (20)$$

$$v_{21} + 2d_{21} + (C_2 + q_2) = S_2 \quad (21)$$

The process of finding hits by using eqs 20 and 21 with the appropriate inequalities is tedious, so another approach is desirable. This other approach is suggested by Table 1, where nearly 50 molecular ions were shown to be related to six analogous neutral molecules. Why not begin with these analogues and use them as prototypes of coordinate-covalent bonded ions? This approach would imply using the equations for neutral atoms ( $q_1 = q_2 = 0$ ) and taking  $C_i$  as the valence-shell electron count of atom *i* (but no longer the position of atom *i* in the chart of the elements). Thus,  $C_i = 6$  would represent any of N<sup>-</sup>, O, F<sup>+</sup>, and Ne<sup>2+</sup>.

The results are shown in Table 2. The dative bonds are shown as contributed by atom 2 to atom 1, although the opposite would be equally valid. The top section of the table contains the ions presented in Table 1, in differently organized fashion, plus the ions with prototypes Ne Be and BeHe. Vacant areas in the columns 3–5 and 7, 8, and 11 are due to the rejection of quadruple bonds.

**Inference 7.** A consequence of Inference 2 is that the atom benefitting from the dative bond may have to be found in a

**Table 3.** Closed-Shell Neutral and Ionized Ionically bonded Diatomics, Using the Rule of 2 for the *s* Atom

electrons added to atom		8-sum = (C <sub>1</sub> +C <sub>2</sub> )	molecule	alternative form	analogue
q <sub>1</sub>	q <sub>2</sub>				
0	0	8	He Ne		
-1	+1	8	[Li] <sup>+</sup> [F] <sup>-</sup>		
-2	+2	8	[Be] <sup>++</sup> [O] <sup>--</sup>		
-3	+3	8	[B] <sup>+++</sup> [N] <sup>---</sup>		
+1	0	7	[He] <sup>-</sup> [F] <sup>-</sup>	He F <sup>-</sup>	[Li] <sup>+</sup> [F] <sup>-</sup>
0	+1	7	[Li] <sup>+</sup> [O] <sup>-</sup>		[Li] <sup>+</sup> [F] <sup>-</sup>
0	-1	9	[Li] <sup>+</sup> [Ne] <sup>+</sup>	Li <sup>+</sup> Ne	[Li] <sup>+</sup> [F] <sup>-</sup>
-1	0	9	[Be] <sup>+</sup> [F] <sup>-</sup>		[Li] <sup>+</sup> [F] <sup>-</sup>
-2	0	10	[B] <sup>++</sup> [F] <sup>-</sup>		[Li] <sup>+</sup> [F] <sup>-</sup>
-1	-1	10	[Be] <sup>+</sup> [Ne] <sup>+</sup>	Be <sup>++</sup> Ne	[Li] <sup>+</sup> [F] <sup>-</sup>
0	-2	10	[Li] <sup>+</sup> [Na] <sup>++</sup>		[Li] <sup>+</sup> [F] <sup>-</sup>

previous period of the chart of the elements. The first instance is F<sup>-</sup><Ar, derived from Mg Ar, in column 9 of Table 2 (cf. inferences 3 and 5).

The last four columns of Table 2 contain entries based on prototypes having period-3 (instead of period-2) atoms in order to avoid large empty spaces or the use of awkward notations.

The difference and sum equations are

$$(C_1 - C_2) + (q_1 - q_2) \pm 2d_{ij} = S_1 - S_2 \quad (22)$$

$$(C_1 + C_2) + (q_1 + q_2) + 2(v_{12} + d_{ij}) = S_1 + S_2 \quad (23)$$

## 7. NEUTRAL DIATOMICS WITH IONIC BONDS

If the *s* atom is labeled 1, then the equations become

$$(C_1 - n) = 0 \quad (24)$$

$$(C_2 + n) = S_2 \quad (25)$$

where *n* is the number of electrons transferred, which experiments appear to limit to

$$0 \leq n \leq 3 \quad (26)$$

The difference and sum equations are

$$(C_1 - C_2) - 2n = -S_2 \quad (27)$$

$$(C_1 + C_2) = S_2 \quad (28)$$

The value 0 in eq 24 indicates that there are no valence-shell electrons left; for row-2 atoms this means that the atom is helium. The top portion of Table 3 shows that these equations result in identifying HeNe, [Li]<sup>+</sup>[F]<sup>-</sup>, [Be]<sup>+</sup>[O]<sup>-</sup>, and [B]<sup>3+</sup>[N]<sup>3-</sup> [*n* = 0 (van der Waals bond) to *n* = 3, respectively].

**Inference 8.** The constituents of [Li]<sup>+</sup>[F]<sup>-</sup> can also be obtained by solving the eqs 7 and 8 with rules of 2 and 8 and with  $v_{12} = 1$ .

## 8. IONICALLY BONDED IONS

Equations 4 and 25 become

$$(C_1 + q_1) - n = 0 \quad (29)$$

$$(C_2 + q_2) + n = S_2 \quad (30)$$

where *n* is again the equal and opposite charge associated



with the bond but in this case appears from experiment to be limited to

$$n = 1 \quad (31)$$

For example,  $[\text{Li}]^+[\text{O}^-]$  has  $n = 1$  and  $q_2 = 1$ . The second portion of Table 3 shows all the ionically bonded ions. If the limit on  $n$  is exceeded by experiment, then the resulting structures may be determined without difficulty.

The difference and sum equations are

$$(C_1 - C_2) + (q_1 - q_2) - 2n = -S_2 \quad (32)$$

$$(C_1 + C_2) + (q_1 + q_2) = S_2 \quad (33)$$

## 9. ANOTHER FORMULATION OF THE EQUATIONS

Ugi and his colleagues<sup>4</sup> also created an algebraic formulation to describe molecular structure, although it was used in a study of reactions rather than as a predictive tool. Bond and electron matrices **B** are defined such that the  $i$ th row and column pertain to atom  $i$ . The diagonal entry  $b_{ii}$  is the number of free (nonbonded) electrons in the valence shell, and each off-diagonal entry  $b_{ij}$  is the bond order of the covalent bond between atoms  $i$  and  $j$ . For instance, the bond and electron matrix for HCN is

$$\mathbf{B} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 3 \\ 0 & 3 & 2 \end{pmatrix} \quad (34)$$

In terms of these matrix elements, it is possible to rewrite eqs 7 and 8, for example, as

$$b_{11} + 2b_{12} = 8 \quad (35)$$

$$2b_{12} + b_{22} = 8 \quad (36)$$

The factors of 2 come about because

$$C_i = b_{ii} + b_{ij} \quad (37)$$

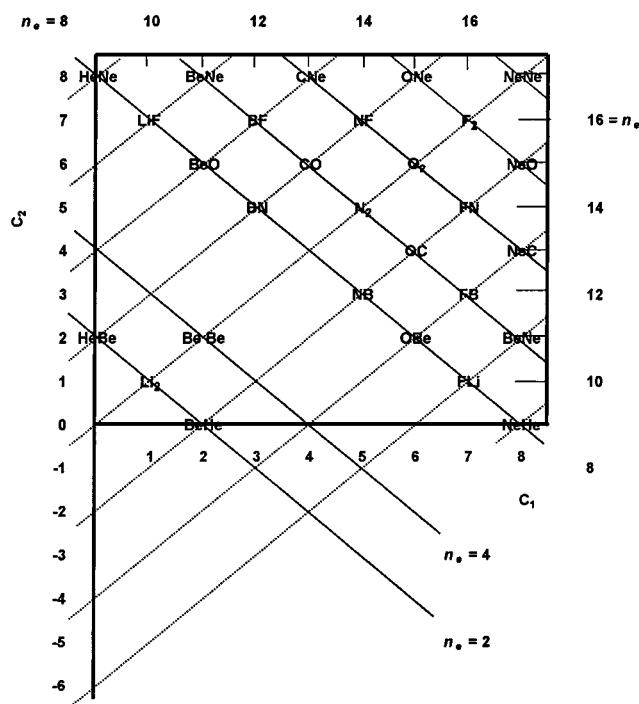
Equations 5 and 36 could be used for predictive purposes just as could eqs 7 and 8, in both cases with the limitations expressed as inequalities. However, an added step, using eq 37, would be necessary in order to find  $C_i$  and hence to identify the atoms.

## 10. GEOMETRICAL SIGNIFICANCE

Figure 1 shows the space with  $C_1, C_2$  axes and all permitted closed-shell neutral diatomic molecules. A series of parallel lines, one of them the line for homonuclear species [eq 3 and other difference equations], pass through them:

$$C_2 = C_1 \pm b \quad (38)$$

where  $b$ , the intercept, is 0 (covalent bonding for  $pp$  and  $ss$  molecules), or is  $\pm 2$  (dative bonding with one lone pair delegated to add a bond to the other atom),  $\pm 4$  (dative bonding with two lone pairs delegated), and  $\pm 6$  (dative bonding with three lone pairs delegated). Alternatively,  $b$  is  $\pm 6$  for ionic bonding with one electron transferred,  $\pm 4$  for ionic bonding with two electrons transferred, and  $\pm 2$  for ionic bonding with three electron transferred.



**Figure 1.** The space pertaining to closed-shell neutral diatomic molecules formed of period-2  $s$  and  $p$  atoms.  $C_2$  is absent because it would have a quadruple bond. Any of the molecules may be replaced by an isovalent species (CO with CS or SiO, etc.). The parallel solid lines are isoelectronic sequences with 2, 4, and 8 to 16 valence electrons, from lower left to upper right; the bond orders are 1, 0, (ionic), 3, 2, 1, and 0, respectively. Molecules lying on (the central portions of) these sequences have much more similar gas-phase properties than molecules chosen at random. For example, the most stable diatomic molecules, CO and  $\text{N}_2$ , are in the central part of the 10-electron isoelectronic series. The parallel dotted lines, perpendicular to the solid lines, are all parallel to the line on which homonuclear molecules lie. The ordinate is extended downward to show intercepts. Beginning with the line of homonuclear molecules and moving toward the top left or bottom right, the numbers of dative bonds are 0, 1, 2, and 3 and the sums of the absolute values of the formal charges are 0, 2, 4, and 6 (in both cases, omitting the ionically bound molecules LiF, BeO, and BN).  $\text{Ne}_2$ , HeNe, Be<sub>2</sub>, and HeBe are van der Waals bonded.

The molecules also lie on the parallel lines represented by eqs 10, 14, 19, and 23 as

$$C_2 + C_1 = n_e \quad (39)$$

$n_e$  being the number of valence-shell electrons equal to 2, 4 and 8 to 16 for neutral molecules. On these parallel lines lie isoelectronic molecules. In the four-dimensional chemical space constituting the periodic system of diatomic molecules, these same closed-shell molecules lie on parallel hyperplanes. Additional research<sup>11</sup> indicates that these lines are preferable to the lines of eq 22 even for other reasons than their isoelectronic significance.

The sets of lines defined by eqs 28 and 29 are, of course, perpendicular. If all the molecules in any isoelectronic sequence [eq 29] were to be collapsed perpendicularly onto the line  $C_1 = C_2$  [eq 28], they would all fall to the position of one of the prototype molecules in Tables 1 and 2.

One can also place ionized molecules in Figure 1 by using the lists in the tables. It is found that the ions are scattered in areas surrounding the prototype neutral species.

## 11. DISCUSSION

It appears that the pursuit of closed-shell diatomics is a useful tool for characterizing the distribution of the stabilities of the molecules in their periodic system. For example, the most stable molecules (including CO and N<sub>2</sub>) are found on the line  $n_e = 10$  in Figure 1, and the least stable species are found around the edges of the figure.<sup>1-3</sup> For other values of  $R_1$  and  $R_2$ , the same line contains SiO, PN, or other isovalent species, and again the van der Waals molecules are on the edges.

The algebraic approach defined in Sections 3 and 4 (diatomic molecules with covalent, van der Waals, and dative bonding) has been used to identify all possible neutral, linear and cyclic, triatomic species<sup>11</sup> and is currently being employed to find all possible neutral four-atomic molecules with various structures.

## ACKNOWLEDGMENT

The authors express their gratitude to Sergio Aragon (San Francisco State), Carl Wulfman (University of the Pacific), Fan-Ao Kong (Academia Sinica, Beijing), Dragutin Svrtan (University of Zagreb), and especially Danail Bonchev (Exxon contractor) for their valued assistance.

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CI010047J