

of the band program. They are grateful to Dr. T. Hughbanks, Dr. L. Messerle, and Dr. S. Wijeyesekera for their comments. O.E. thanks Du Pont for a summer salary, and E.C. thanks the University of Michigan for its hospitality during the summer.

### Appendix

The exponents and parameters for iodine and chlorine were taken from Clementi and Roetti<sup>10</sup> and from Hinze and Jaffe,<sup>11</sup> respectively. The exponents and parameters of the cobalt are those of ref 12. The modified weighted Wolfsberg-Helmholtz

formula was used.<sup>13</sup> Experimental structural data were used for the polymer. In the bridge dimer, bond distances and angles at the iodine (96.2°) were kept as in the polymer.

atom	orbitals	$H_{ii}$ , eV	$\zeta$
Co	4s	-10.2	1.700
	4p	-6.11	1.050
	3d	-12.84	5.55 (0.5551)
I	5s	-18.0	1.9 (0.6461)
	5p	-12.7	2.679
Cl	3s	-24.2	2.322
	3p	-15.0	2.356

Registry No. 1, 13931-93-6; 2, 28986-75-6.

- (10) Clementi, E.; Roetti, C. *At. Data Nucl. Data Tables* 1974, 14, 177.  
 (11) Hinze, J.; Jaffe, H. H. *J. Phys. Chem.* 1963, 67, 1501.  
 (12) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* 1976, 98, 3219.

- (13) Ammeter, J. H.; Burgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* 1978, 100, 3686.

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## A New Electrostatic Model of Molecular Shapes

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Rationale and procedure are presented for a formal distribution of valence electrons that makes each ligand electrically neutral. Ligands are classified according to the number of bonding electrons thus assigned to each ligand. The valence electrons remaining on the central atom are treated as point charges with interorbital repulsions given by Coulomb's law. This approach is called the neutral-ligand electron-repulsion (NLER) model. The NLER model correctly predicts the main features of most molecular shapes, including relative energies of bond-bond, bond-lone, and lone-lone repulsions, and the tendency of the bond orbitals to remain stationary as the bonds bend. A few cases are considered where isomers are possible, and the NLER model predicts the energetically favored isomer for every case where experiment has shown a clearly favored isomer to exist.

### Introduction

Various models and theories have been proposed to enable chemists to correlate, and possibly to predict, the shapes of molecules and polyatomic ions. Approximate solutions of the Schrödinger equation give molecular shapes that are in good agreement with experiment, whether the approximation is in the valence bond (VB) or molecular orbital (MO) form.<sup>1</sup> When canonical MO's are transformed to localized MO's (LMO's), the results support the chemist's concepts of electron-pair bonds and lone pairs.<sup>2</sup> Because the computations of VB and LMO theories are difficult, there remains a need for simpler models that every chemist can use.

A currently popular approach is to follow the rules of the valence-shell-electron-pair repulsion scheme (VSEPR).<sup>3</sup> The amazing success of those rules has stimulated much work aimed at discovering their theoretical basis.<sup>4</sup> A point worthy of emphasis, however, is that those rules were derived from

experiment<sup>5</sup> and are still regarded as largely empirical.<sup>6</sup> The indiscriminate inclusion of the empirical rules under the heading of "VSEPR theory" tends to give the *theory* credit for the success of the *rules*. As a result, the theory appears to be better substantiated than it really is. However, criticism of the theory is likely to be construed as criticism of the rules, about which many chemists are justifiably defensive. In this paper, disagreement with the VSEPR theory does not extend to the empirical rules, which are fully supported by our work. Moreover, the proponents of the VSEPR theory have contributed many of the ideas incorporated in our model, and we acknowledge our indebtedness to them.

Unfortunately, there is some ambiguity as to what the VSEPR theory is. Some authors have described the VSEPR theory as an electrostatic model,<sup>4,6,7</sup> but this attribute has been repudiated.<sup>8</sup> Indeed, one account of VSEPR claimed that molecular shapes can be deduced from the Pauli exclusion principle even when electrostatic forces are neglected.<sup>9</sup> Other statements, which must not be taken literally, are recent claims that screened one-electron models have "no electron-electron repulsions"<sup>4f</sup> and that another model "omits electrostatic

- (1) Chipman, D. M.; Palke, W. E.; Kirtman, B. *J. Am. Chem. Soc.* 1980, 102, 3377-3383.  
 (2) Levine, I. N. "Quantum Chemistry", 2nd ed.; Allyn and Bacon: Boston, 1974; pp 397-405.  
 (3) Gillespie, R. J. *J. Chem. Educ.* 1970, 47, 18-23.  
 (4) (a) Bader, R. F. W.; Preston, H. J. *Can. J. Chem.* 1966, 44, 1131-1145. (b) Bartell, L. S. *J. Chem. Educ.* 1968, 45, 754-767. (c) Allen, L. C. *Theor. Chim. Acta* 1972, 24, 117-131. (d) Naleway, C. A.; Schwartz, M. E. *J. Am. Chem. Soc.* 1973, 95, 8235-8241. (e) Palke, W. E.; Kirtman, B. *Ibid.* 1978, 100, 5717-5721. (f) Hall, M. B. *Ibid.* 1978, 100, 6333-6338. (g) Schmiedekamp, A.; Cruickshank, D. W. J.; Skaarup, S.; Pulay, P.; Hargittai, I.; Boggs, J. E. *Ibid.* 1979, 101, 2002-2010.

- (5) Gillespie, R. J.; Nyholm, R. S. *Q. Rev., Chem. Soc.* 1957, 11, 339-380 (note especially the discussion of chlorine trifluoride on p 343).  
 (6) Bartell, L. S. *Inorg. Chem.* 1966, 5, 1635-1636. Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry. A Comprehensive Text", 3rd ed.; Wiley: New York, 1972; p 128; 4th ed., 1980, p 198.  
 (7) Schnuelle, G. W.; Parr, R. G. *J. Am. Chem. Soc.* 1972, 94, 8974-8983.  
 (8) Gillespie, R. J. *J. Chem. Educ.* 1974, 51, 367-370.  
 (9) Gillespie, R. J. *Can. J. Chem.* 1960, 38, 818-826.

Table I. Charges of Bonds Relative to Lone Pair = 2.00

period of central atom	ligand	ERN <sup>a</sup>	VSEPR <sup>b</sup>	CFT <sup>c</sup> and NLER
2	H	1.62 <sup>d</sup>	1.4	1.0
2	F	1.26	1.4	1.0
2	Cl	1.44	1.4	1.0
3-5	H	0.76	1.4	1.0
3-5	F-I	1.04	1.4	1.0
2-5	O, S	1.88	1.4, 2.8 <sup>e</sup>	2.0
all	N, CH	?	4.2?	3.0
all	H <sub>2</sub> O, NH <sub>3</sub>	?	1.4?	0.1

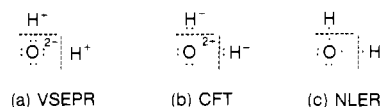
<sup>a</sup> Reference 12; doubled here. <sup>b</sup> Reference 14. <sup>c</sup> Reference 13. <sup>d</sup> LMO angles of H<sub>2</sub>O in Table III from ref 2 or 4d give an ERN of 1.1 or 1.3, respectively. <sup>e</sup> For single and double bonds, respectively.

repulsions<sup>7,10</sup> Without interelectronic repulsions the H<sub>2</sub>O molecule would be linear, and without internuclear repulsions the nuclei would coalesce.<sup>11</sup> Therefore, electrostatic repulsions, which play a negligible role in VSEPR theory, are really of primary importance.

A successful electrostatic model was developed several years ago by Searcy and Parsons.<sup>12</sup> In that model, a lone pair of electrons was arbitrarily assigned an electrostatic repulsion number (ERN) of 1.00, and each ligand was empirically assigned a relative ERN. Although Searcy gave a plausible explanation for the fact that oxygen has a higher ERN than hydrogen or a halogen,<sup>12a</sup> he obviously did not anticipate that the oxygen ERN would be *twice* the others nor did he attempt to explain why the oxygen ERN should be nearly the same as that of a lone pair. The Parsons-Searcy generalization<sup>12c</sup> that the ERN is half the bond order presupposes that oxygen is always double bonded and still fails to relate the lone-pair ERN to the bond values.

An ionic model equivalent to crystal field theory (CFT) was developed by Takahata, Schnuelle, and Parr.<sup>7,13</sup> The integral charges assigned in the CFT model are approximately twice the corresponding ERN's of Searcy's model (see below, Table I). Since the ERN's are only relative numbers, the CFT model would appear to provide a theoretical basis for the ERN's, except for one fundamental difference: The distance from the central nucleus is the same for all ERN's, while the CFT model places the bond charges at the experimental bond lengths, much farther out than the lone pairs.

In some cases, the ratio of the bond-charge/lone-pair distances has surprisingly little effect on the equilibrium bond angles. In CH<sub>2</sub> (<sup>1</sup>A<sub>1</sub>), for example, that ratio can be varied from 0.9 to 3.7 and yet span only a 5° range in bond angle. The ratio of distances *is* important, though, when the central atom has two lone pairs. In the CFT model, the lone pairs were assumed to be nonequivalent, but we found that equivalent lone pairs give a lower energy of repulsion. Because the lone pairs are so much shorter than the bond charges in the CFT model, the lone pairs become linear, and the bonds spread out in the plane perpendicular to the lone pairs. In the CFT model, the bonds of H<sub>2</sub>O end up linear, and those of ClF<sub>3</sub> form an equilateral triangle. The angle of 102° previously reported<sup>7,13</sup> for the CFT model of H<sub>2</sub>O sits on a saddle point instead of in a minimum of the potential surface. (The bent model lies at least 3.3 MJ/mol above the linear model. This difference was calculated by assuming that the charges in the p<sub>x</sub> lone pair are at most as far out as those in the other lone

Figure 1. Various assignments of the valence electrons of H<sub>2</sub>O.

pair.) Since the ERN model gives the correct structures for H<sub>2</sub>O and ClF<sub>3</sub>, the reason for the failure of the CFT model is the disparity in the distances of the charges.

The electron pairs are placed equidistant from the nucleus in the semiquantitative version of VSEPR formulated by Thompson.<sup>14</sup> However, he used an energy law of the form  $1/r^n$ , with  $n = 2-4$ , which has never been theoretically justified for electron pairs on the same atom. The references he cited<sup>15</sup> deal with crowded seven-coordinated molecules, and the authors admit to the possibility that the force law includes steric repulsions between the ligands. Also, the VSEPR theory has never established a value for the ratio of lone-lone/bond-bond repulsions. The ratio of 2/1 empirically assigned by Thompson is probably too high for verification by any theory that considers only the repulsions between pairs of electrons (see below, Table IV).

In this paper, we use simple reasoning to develop an electrostatic model that predicts most of the empirical rules of VSEPR,<sup>3</sup> that gives a fair account of the empirical ERN's,<sup>12</sup> and that eliminates the need for the empirical distances that encumber CFT.<sup>7</sup>

#### Development of the Model

The rationale of the new model is readily seen by comparing the three possible assignments of the electrons in each bond of H<sub>2</sub>O as shown in Figure 1. In (a), both electrons are assigned to the oxygen atom as a pair, as in VSEPR. This assignment leaves each H atom with a positive charge, which is ignored in VSEPR except for its effect on the width of the bond orbital. In (b), both electrons are assigned to the hydrogen atom as in CFT. Inclusion of the nuclear charge gives each hydrogen atom a single negative charge, which is farther from the oxygen nucleus than the lone pairs are. In (c), one electron is assigned to hydrogen and one to oxygen. This assignment makes each hydrogen atom neutral, so that it has no attraction or repulsion for the lone pairs or for the other bond. Because each proton is imperfectly screened by its own electron, each hydrogen atom is attracted to the other electron of its own bond on the oxygen atom.

The deliberate assignment of electrons to make each ligand neutral is the essential feature of the new model, which is called the neutral-ligand electron-repulsion model, abbreviated NLER. With the ligands neutral, the main repulsions are between the electrons assigned to the central atom. Those electrons determine an effective population of each orbital. Each lone pair L has an effective population  $n_L = 2.00$ . The effective population of a bond to a ligand is the number of electrons needed to complete the octet (for H, the duet) of the *initially neutral* ligand. Each bond toward a radical R such as hydrogen or a halogen has  $n_R = 1.00$ , as in Figure 1c. Thus in H<sub>2</sub>O and in other molecules, as well, the effective populations of NLER are the same as the charges of CFT, but in NLER all charges are at the same distance from the central nucleus.

A neutral ligand that donates a pair of electrons such as H<sub>2</sub>O or NH<sub>3</sub> is called a donor, D. Because the donor atom needs no electrons to complete its octet, to a first approximation  $n_D = 0$ . In order to take the dipole moment of the ligand into

- (10) Thompson, H. B.; Wells, M.; Weaver, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 7213-7219.  
 (11) Bills, J. L.; Snow, R. L. *J. Am. Chem. Soc.* **1975**, *97*, 6340-6342.  
 (12) (a) Searcy, A. W. *J. Chem. Phys.* **1958**, *28*, 1237-1242. (b) *Ibid.* **1959**, *31*, 1-4. (c) Parsons, A. E.; Searcy, A. W. *Ibid.* **1959**, *30*, 1635-1636.  
 (13) Takahata, Y.; Schnuelle, G. W.; Parr, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 784-785.

- (14) Thompson, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 4609-4610.  
 (15) Thompson, H. B.; Bartell, L. S. *Inorg. Chem.* **1968**, *7*, 488-491. Adams, W. J.; Thompson, H. B.; Bartell, L. S. *J. Chem. Phys.* **1970**, *53*, 4040-4046.

Table II. Comparison of Predicted and Experimental Angles (deg)

	NLER orbital angles	exptl bond angles <sup>a</sup>		NLER orbital angles	exptl bond angles <sup>a</sup>
BH <sub>2</sub>	120	131	NO <sub>2</sub>	138	134
AlH <sub>2</sub>	120	119	O <sub>3</sub>	120	117
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	102	102	SO <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	120	120
SiF <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	102	101	CH <sub>3</sub>	109	120
H <sub>2</sub> O	94	105	NH <sub>3</sub>	100	107
OF <sub>2</sub>	94	103	NF <sub>3</sub>	100	102
H <sub>2</sub> S	94	92	PH <sub>3</sub>	100	93
HCO	129	120	PF <sub>3</sub>	100	102
FNO	111	110	ClO <sub>3</sub> <sup>-</sup>	109	109
CINO	111	116	SO <sub>3</sub> <sup>2-</sup>	109	107

<sup>a</sup> Sources in ref 7.

account, the orbital on the central atom must be assigned a partial negative charge, making  $n_D > 0$ . Fortunately, the precise magnitude of  $n_D$  need not be known. For molecules containing both radical and donor ligands (see below), the same isomeric forms are predicted to be stable for all values of  $n_D < 0.425$ . In the examples discussed below, we used  $n_D = 0.100$ .

As a ligand, an oxygen or a sulfur atom needs two electrons to complete its octet. Because a single-bonded formula shows oxygen or sulfur accepting both electrons from the central atom, the ligand is called an acceptor, A. Whether the ligand is believed to be single- or double-bonded makes no difference to the NLER model, for in either case the neutral ligand leaves the central atom with two electrons in its bond orbital. The double-bonded ligands NH and CH<sub>2</sub> are also acceptors, with  $n_A = 2.00$ .

A nitrogen atom as a ligand accepts three electrons from the central atom. If a pair of electrons is considered normal, the third electron accepted by nitrogen conceivably could have been used in normal circumstances for an additional radical ligand. Since the nitrogen atom precludes a radical, it is called an antiradical. The use of this term, which also includes a triple-bonded CH group, is illustrated later.

The ERN, VSEPR, CFT, and NLER models are compared as to the relative charges of various bonds in Table I. The ERN values are empirical, as is the basic VSEPR value of 1.4. For each class of ligand, the theoretical NLER value comes close to the average ERN value. The values are not strictly comparable because the NLER values are for orbital angles and the ERN values are for bond angles. In at least one case (Table I, footnote *d*) adjustment of the ERN value to orbital angles improves its agreement with NLER.

### Orbital Angles and Repulsions

The distance of each charge from the central nucleus can be arbitrary, because only relative values are needed for the repulsions. With  $1/2$  unit for the distance from the nucleus, the distance between two charges  $n_U$  and  $n_V$  that form an angle  $\theta_{UV}$  at the nucleus is  $\sin(\theta_{UV}/2)$ . The energy of repulsion between the charges is shown in eq 1. The total interorbital

$$E_{UV} = \frac{n_U n_V}{\sin(\theta_{UV}/2)} \quad (1)$$

energy  $E_{NLER}$  is found by summing eq 1 over all pairs of orbitals. The optimum angles  $\theta_{UV}$  are those that give the minimum total energy. These angles are orbital angles rather than bond angles, but the bonds are expected to be fairly close to the orbitals. Table II compares the NLER orbital angles with experimental bond angles for a score of compounds. The agreement is generally quite good.

The VB and LMO theories give orbital angles that can be compared with those of the simpler models. A few examples are given in Table III. The agreement is satisfactory for

Table III. Orbital Angles (deg) of Various Models

	VBa <sup>a</sup>	LMO <sup>a</sup>	VSEPR <sup>b</sup>	CFT <sup>c</sup>	NLER
H <sub>2</sub> O, $\angle RR'$	95	106 (102, <sup>d</sup> 95 <sup>e</sup> )	103	180 (102 <sup>f</sup> )	94
H <sub>2</sub> O, $\angle LL'$	172	112 (120, <sup>d</sup> 122 <sup>e</sup> )	117	180	126
H <sub>2</sub> S, $\angle RR'$	90	99	103	180 (99 <sup>f</sup> )	94
H <sub>2</sub> S, $\angle LL'$	139	119	117	180	126
NH <sub>3</sub> , $\angle RR'$	111	107	106	101	100

<sup>a</sup> Reference 1. <sup>b</sup> Reference 14;  $n = 2$ . <sup>c</sup> Equivalent lone pairs (true minimum). <sup>d</sup> Reference 4d. <sup>e</sup> Reference 2. <sup>f</sup> Nonequivalent lone pairs (saddle point).

Table IV. Relative Energies of Radical and Lone-Pair Repulsions in H<sub>2</sub>O at Angles in Table III

	LMO (eq 2) <sup>a</sup>	VSEPR <sup>b</sup>	LMO (eq 3) <sup>a</sup>	CFT <sup>c</sup>	NLER
$E_{RL}/E_{RR'}$	1.07	1.30	1.74	3.83	1.82
$E_{LL'}/E_{RR'}$	1.15	1.68	3.06	13.2	3.30

<sup>a</sup> Values from ref 4d at 104.52° bond angle. <sup>b</sup> Reference 14;  $n = 2$ . <sup>c</sup> Equivalent lone pairs.

VSEPR and NLER but not for the CFT model with two lone pairs (cf. Introduction).

The tendency of bond orbitals to remain stationary rather than to follow the bending motions of ligands was investigated by Chipman, Palke, and Kirtman.<sup>1</sup> The NLER model accounts for this phenomenon very neatly. The orbital angles, which are determined by repulsions between the effective populations of the orbitals, should hardly be affected by the motions of the neutral ligands.

The LMO theory provides accurate values of repulsion energies that can be compared with the NLER values of  $E_{UV}$  and the CFT and VSEPR counterparts. We examine H<sub>2</sub>O here because it contains  $E_{LL'}$ ,  $E_{RL}$ , and  $E_{RR'}$ , all of which can be calculated from published data. For the LMO repulsions to compare with VSEPR, we used

$$E_{UV}^\circ = 4J_{UV} - 2K_{UV} \quad (2)$$

for all interactions, where  $J_{UV}$  and  $K_{UV}$  are Coulomb and exchange integrals. For the LMO repulsions to compare with CFT and NLER, we used

$$\begin{aligned} E_{LL'} &= E_{LL'}^\circ & E_{RL} &= E_{RL}^\circ + 2V_{LH} \\ E_{RR'} &= E_{RR'}^\circ + 4V_{RH'} + V_{HH'} \end{aligned} \quad (3)$$

where  $V_{LH}$  is the attraction of a lone-pair electron for a hydrogen nucleus,  $V_{RH'}$  is the attraction of a bond electron for the hydrogen nucleus of the other bond, and  $V_{HH'}$  is the repulsion between the two hydrogen nuclei. In evaluating eq 2 and 3, we used the values of Naleway and Schwartz<sup>4d</sup> at 104.52°.

The actual repulsions of VSEPR, CFT, and NLER to be compared with the above LMO values are calculated from the optimum angles of each model as given in Table III. Two ratios of the actual energies of each model are compared with the corresponding LMO values in Table IV. Only the NLER values are in agreement with their LMO reference values.

### Justification from Molecular Orbital Theory

For the background of this section, see the section under the same heading in the paper by Schnuelle and Parr.<sup>7</sup> The NLER model changes their eq 6 to

$$V_{nn} + 2 \sum_{i \neq F} V_i + 2V_F^\circ + \sum_{i,j \neq F} (2J_{ij} - K_{ij}) + J_{FF} \approx \frac{(8 - Z_B)^2}{2R_A \sin(\theta/2)} + \text{constant}$$

and the bracketed term on the far right of their eq 5 becomes

$$2V_{F'} + \sum_{i \neq F} (4J_{iF} - 2K_{iF}) \approx \frac{2(8 - Z_B)}{R_A \cos(\theta/4)} + \text{constant}$$

where  $R_A$  is the effective radius of  $A$  and  $\theta$  is the angle between the bond orbitals.

### General Use of the NLER Model

A previous section showed that the NLER model is capable of refined predictions of orbital angles and repulsions. If one is satisfied knowing the gross features of a molecule, the NLER model can be used very quickly and easily. The following discussion was written for molecules that contain a single central atom  $X$ , but the geometry about any main-group atom in a complex molecule can be predicted simply by identifying that atom as  $X$ .

**Symbols and Formula.** As explained above, the NLER model classifies ligands or orbitals as radicals, acceptors, donors, and lone pairs, using the symbols  $R$ ,  $A$ ,  $D$ , and  $L$ , respectively. The same letters in the lower case are used to represent the number of ligands or orbitals of each type. Hence, the general formula for a molecule is  $XR_nA_dD_l(L_l)$ , where  $L_l$  is in parentheses because it may not be included in the formula. In a redundant but convenient extension of these symbols, we define  $t$  as the total number of ligands and  $s = t + l$  as the number of  $\sigma$  orbitals around atom  $X$ . We also define a quantity  $e$  in terms of the group number  $g$  of the central atom (from the periodic table, with group 8 for noble gases) and the net charge  $q$  on the molecule:

$$e = g - q \quad (4)$$

By assigning the charge  $q$  to atom  $X$ , we interpret the quantity  $e$  as the number of valence electrons on the uncombined atom (or ion)  $X$ . The values of  $s$  and  $l$  can be found by drawing an electron-dot structure for the molecule<sup>7</sup> or else by using

$$s = (e + r)/2 + d \quad (5)$$

$$l = s - t \quad (6)$$

These equations can accommodate an antiradical ( $N$  or  $CH$ , see above) by counting it as  $-1$  toward  $r$ . By counting each donor as 2 toward  $r$ , we can drop the  $d$  from eq 5.

**Orbital and Molecular Geometries.** As is well-known, lone pairs are important in determining molecular shapes, but they are generally ignored in describing those shapes.<sup>3</sup> The NLER model accommodates this convention by distinguishing between the orbital geometry, which includes the lone pairs, and the molecular geometry, which does not. In the remainder of this paper, we use idealized orbital geometries, which depend only on  $s$ . These geometries can be found by assigning the same value of  $n_R$  to all  $s$  valence orbitals and then adjusting the angles between the orbitals to minimize the total energy of repulsion between all pairs of orbitals. For values of  $s$  from 2 to 7, the corresponding orbital geometries are linear, trigonal planar, tetrahedral, trigonal bipyramidal, octahedral, and pentagonal bipyramidal.

**Prediction of Isomeric Form.** For values of  $s$  less than 5, all orbital positions are equivalent regardless of how the various ligands and lone pairs are allocated among the  $\sigma$  orbitals. For these cases, only one molecular shape can result from a given combination of  $s$  and  $l$ . For example, when  $s = 4$  and  $l = 0-3$ , the molecular shapes predicted by NLER are tetrahedral, trigonal pyramidal, bent, and linear, respectively. However, when  $s = 5$  and  $l = 1-3$  or when  $s = 6$  and  $l = 2$ , the orbital positions are not all equivalent, and two or three isomers can be imagined for each case. Similar isomers are possible when  $l = 0$  if, in place of the lone pairs, the central atom has a second class of ligand or even a different ligand of the same class. The isomers of a given case are not equally likely to be observed,

Table V. Relative Energies of Isomers Containing Lone Pairs and/or Acceptor Ligands

formula <sup>a</sup>	locations of L <sup>a</sup>	$E_{NLER}$
XR <sub>4</sub> (L)	ax	18.192
	eq	18.087
	axis of square pyramid L (0), each R (111.7)	17.908
XR <sub>3</sub> (L <sub>2</sub> )	ax, ax	24.435
	ax, eq	24.744
	eq, eq	24.380
	distorted eq, eq	24.195
	L1 (117.6, 90), L2 (117.6, 270), R1 (0), R2 (77.5, 0), R3 (77.5, 180)	
XR <sub>2</sub> (L <sub>3</sub> )	ax, ax, eq	32.401
	ax, eq, eq	32.451
	eq, eq, eq	31.827
XR <sub>4</sub> (L <sub>2</sub> )	cis	34.698
	trans	34.284
	distorted cis	34.242
	L1 (53.1, 0), L2 (53.1, 180), R1 (143, 0), R2 (143, 180), R3 (99.4, 90), R4 (99.4, 270)	

<sup>a</sup> Acceptor ligands (A) may be substituted for one or more lone pairs (L).

Table VI. Relative Energies of Isomers Containing Donor Ligands

formula	locations of D	$E_{NLER}^a$
XR <sub>4</sub> D	ax	8.231
	eq	8.325
	distorted ax	7.958
	D (0), R1 (73.6, 0), R2 (73.6, 120), R3 (73.6, 240), R4 (180)	
XR <sub>3</sub> D <sub>2</sub>	ax, ax	4.323
	ax, eq	4.752
	eq, eq	4.637
XR <sub>2</sub> D <sub>3</sub>	ax, ax, eq	1.990
	ax, eq, eq	2.209
	eq, eq, eq	1.883
XR <sub>4</sub> D <sub>2</sub>	cis	9.134
	trans	8.798
	distorted R <sub>4</sub> tetrahedron	8.587
	D1 (53.3, 0), D2 (53.3, 180), R1 (127.9, 0), R2 (127.9, 180), R3 (58.4, 90), R4 (58.4, 270)	

<sup>a</sup> Using  $n_D = 0.100$  (see text).

Table VII. Relative Energies of Isomers Containing More Electronegative Radical Ligands, R'

formula	locations of R'	$E_{NLER}^a$
XR <sub>4</sub> R'	ax	12.425
	eq	12.436
	distorted ax	12.423
	R' (0), R1 (88.7, 0), R2 (88.7, 120), R3 (88.7, 240), R4 (180)	
XR <sub>3</sub> R' <sub>2</sub>	ax, ax	11.911
	ax, eq	11.925
	eq, eq	11.933
XR <sub>2</sub> R' <sub>3</sub>	ax, ax, eq	11.425
	ax, eq, eq	11.437
	eq, eq, eq	11.443
	distorted ax, ax, eq	11.423
	R'1 (0), R'2 (87.7, 0), R'3 (87.7, 180), R1 (120.4, 90), R2 (120.4, 270)	

<sup>a</sup> Using  $n_{R'} = 0.900$  (see text).

however. The energetically favored isomer is the one with the lowest total energy of repulsion between all pairs of orbitals.

The molecules used in the following examples can be viewed as substitution derivatives of either a trigonal bipyramid or an octahedron initially containing only radical ligands. The substituents are either lone pairs, acceptor ligands, donor ligands, or more electronegative radical ligands. In several cases, a lower energy was found by allowing the geometry to

distort from the regular polyhedron. The results are summarized in Tables V–VII, where the lowest energy found is printed in boldface, the lowest energy of the regular polyhedron (if different) is printed in italics, and each ligand in a distorted geometry is located by its spherical coordinates ( $\theta$ ,  $\phi$  where needed, in degrees).

**Lone Pairs and/or Acceptor Ligands.** These substituents are considered together because  $n_L = n_A$ . As seen in Table V, the energetically favored locations for lone pairs and/or acceptor ligands in the regular polyhedra are the equatorial positions in a trigonal bipyramid and the trans positions in an octahedron. If the octahedron is drawn with the substituted positions vertical, there is an apparent anomaly between the octahedron and the trigonal bipyramid: Substitution is *axial* in the octahedron but *equatorial* in the trigonal bipyramid. This peculiarity has a satisfying, semiquantitative explanation in the NLER model, which predicts the favored isomers of the regular polyhedra simply as those with the lowest energies of repulsion. The NLER model also gives a theoretical explanation for the empirical observation<sup>16</sup> that lone pairs and oxygen atoms are stereochemically equivalent.

A reviewer kindly informed us that an  $\text{XR}_4(\text{L})$  molecule has lower energy of repulsion when it is a square pyramid than when it is a trigonal bipyramid. The square pyramid can be obtained from the trigonal bipyramid by distorting the two axial and two equatorial ligands until they become equivalent. The reviewer also found the lowest energy given in Table V for  $\text{XR}_3(\text{L}_2)$ . The lowest energy we found for an  $\text{XR}_4(\text{L}_2)$  molecule has a shape that is best described as distorted cis octahedral, rather than trans, because the  $\text{LXL}$  angle is only  $106.2^\circ$ .

Table I of Searcy<sup>12b</sup> is equivalent to our Table V, except that his electrostatic energies were calculated from his empirical ERN's at a distance of 1 unit, making his energies approximately one-eighth of ours. In some of his calculations, he assumed that an axial lone pair would have a longer distance from the nucleus than an equatorial lone pair, an assumption which to us seems a bit speculative. For a trigonal bipyramid with two lone pairs, that assumption led him to estimate the energy difference between the axial, axial and the equatorial, equatorial isomers as less than 0.1%, equal to 0.003 of his units. If we were to accept his value, we would still disagree with his conclusion that this difference is completely negligible. We estimate the order of magnitude of his difference in energy to be 10 kJ/mol. If the isomerization reaction had a  $\Delta G^\circ$  value of this magnitude, the equilibrium constant would be about  $10^{-2}$ , which may be too small to detect any of the second isomer. Chemically significant energies are often only a small fraction of the total energies.

**Donor Ligands.** The energies of several isomers containing donor ligands are listed in Table VI. In trigonal bipyramids, the sites occupied by the donor ligands are predicted to switch

from axial with one or two donors present to equatorial with three donors present. This prediction differs from VSEPR, which predicts that two of the three donors will remain axial as long as the donor ligands are more electronegative than the others. The axial preference for one or two donors is shown by  $(\text{CH}_3)_3\text{SnCl}\cdot\text{C}_5\text{H}_5\text{N}$ <sup>17</sup> and  $\text{AlH}_3\cdot 2(\text{CH}_3)_3\text{N}$ ,<sup>18</sup> but as far as we know, structural data are lacking for trigonal bipyramids with three donors. Whether molecules such as  $\text{HgR}_2\text{D}_3$  or  $\text{TlR}_2\text{D}_3^+$  will confirm the predicted switch to equatorial positions remains to be seen.

In regular octahedra, the NLER model predicts that two donors will take trans positions. The trans configuration has been found, for example, in  $\text{GeCl}_4\cdot 2\text{C}_5\text{H}_5\text{N}$ .<sup>19</sup> However, some molecules with distorted cis configurations are also known, such as  $\text{SnCl}_4\cdot 2\text{Cl}_3\text{PO}$ .<sup>20</sup> Using the distorted angles,<sup>20</sup> the NLER model predicts a relative energy of 8.795, slightly less than that of the regular trans configuration. The lowest energy we found was for a distorted tetrahedron of radical ligands, with each donor ligand above one of the tetrahedral faces.

**More Electronegative Radical Ligands.** To a first approximation, the effective population of an orbital bonded to any radical ligand is 1.00. However, this value will certainly be affected by the electronegativity of the ligand. By definition, a highly electronegative ligand  $\text{R}'$  will attract more of the electron cloud in a bond than will a less electronegative ligand  $\text{R}$ . The NLER model accounts for this shift by using a smaller value of  $n_{\text{R}'}$ . The precise values of  $n_{\text{R}'}$  and  $n_{\text{R}}$  need not be known, since the same isomers are predicted to be favored within wide limits, viz.  $0.425 < (n_{\text{R}'}/n_{\text{R}}) < 1.000$ . In our calculations on trigonal bipyramids, we used  $n_{\text{R}'} = 0.900$  and  $n_{\text{R}} = 1.000$ . The results are given in Table VII. The favored isomers always have the more electronegative ligands in axial positions. This rule was discovered empirically,<sup>21</sup> but the NLER model provides a clear theoretical explanation for it. An earlier explanation in terms of VSEPR<sup>22</sup> was roughly equivalent to the present one as far as it went, but it was entirely qualitative and relied on the subjective judgement that there is "more room" in an equatorial position than in an axial site. Of course, the electronegativity rule only applies to ligands of the same class. Considering only electronegativity, one would expect the oxygen atom in  $\text{SeOCl}_3^-$  to be axial. The NLER model predicts correctly<sup>23</sup> that the oxygen atom, being an acceptor ligand, is equatorial.

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- (17) Hulme, R. *J. Chem. Soc.* **1963**, 1524–1527.  
 (18) Beattie, I. R.; Gilson, T. *J. Chem. Soc.* **1964**, 3528–3532.  
 (19) Hulme, R.; Leigh, G. J.; Beattie, I. R. *J. Chem. Soc.* **1960**, 366–371.  
 (20) Bränden, C.-I. *Acta Chem. Scand.* **1963**, *17*, 759–768.  
 (21) Muetterties, E. L.; Schunn, R. A. *Q. Rev. Chem. Soc.* **1966**, *20*, 245–299.  
 (22) Gillespie, R. J. *Inorg. Chem.* **1966**, *5*, 1634–1635.  
 (23) Paetzold, R.; Aurich, K. *Z. Anorg. Allg. Chem.* **1966**, *348*, 94–106.

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(16) Bent, H. A. *J. Chem. Educ.* **1968**, *45*, 768–778.