Table IV. Pair Potential Constants Obtained by Fitting the Energies of Table II[a]

Class	A	B	C
1	225.916 1	5 754.583	0.995 6
2	1.202 519	5 299.747	0.994 1
4	135.871 4	7 977.913	1.005 7
5	94.334 28	2 969.783	0.999 9
7	38.594 89	717 127.1	1.000 4
8	4.349 975	180 192.2	1.000 0
9	3.937 161	791 789.8	1.000 7
10	3.559 070	604 114.1	0.997 7
11	21.543 43	379 813.4	0.998 5
16	430.660 8	2 763.452	1.005 8
18	9.707 054	329 446.3	0.999 7
19	84.944 96	29 013.76	1.260 8
1	1.973 512	905.527 0	1.003 2
2	15.079 57	1 014.282	1.002 7
4	0.557 081	12 012.26	1.002 0
5	1.241 310	478 766.2	0.999 2
7	12.118 16	3 715.439	1.002 4
8	94.043 25	1 116.766	0.999 3
9	29.474 20	2 258.113	0.997 1
10	203.227 5	2 658.550	1.002 1
11	367.034 4	969.035 5	1.003 3
16	7.504 153	363.941 2	0.996 1
18	2.266 371	56 711.22	0.999 9
19	1.241 310	407 886.2	0.793 0

[a] The first group of constants for the classes 1–19 refers to interactions with the oxygen of water; the second group of constants for the classes 1–19 refers to interactions with the hydrogen of water.

surface, now more feasible than previously because of the availability of our embrional "library" of potentials; (c) refinement of the analytical form of the potentials, in order to describe more faithfully the Coulombic part, retaining, however, a very simple form in order to allow for statistical thermodynamics simulations, where temperature, free energy, and entropy find their proper definitions.

Acknowledgment. One of us (G.B.) gratefully acknowledges Professor G. Nardelli of the Facoltà di Fisica, Università defli Studi di Milano, for useful discussions.

References and Notes

(1) (a) This work has been partially presented at the International Symposium of Theoretical Chemistry, Boulder, Col., June 1975, and at the VI Simposio dei Chimici Teorici di Lingua Latina, Arles, France, September 1975. (b) In partial fulfillment of the doctoral dissertation; (c) Università degli Studi di Milano; (d) Società Montedison, Istituto Ricerche "G. Donegani".

(2) E. Clementi, F. Cavallone, and R. Scordamaglia, *J. Am. Chem. Soc.*, accompanying paper in this issue.

(3) R. Scordamaglia, F. Cavallone, and E. Clementi, *J. Am. Chem. Soc.*, accompanying paper in this issue.

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(8) Note: in addition to ref 2–7, see the series of papers "Study of the Structure of Molecular Complexes", referred to in ref 2.

(9) See Montedison Technical Report DDC-767, February 1976; to secure such document written request should be made to the authors of this paper.

(10) E. Clementi, "Lecture Notes in Chemistry", Vol. II, Springer-Verlag, Heidelberg, 1976. See the bond energy analyses section in particular.

(11) See, however, the series of papers "Study of the Electron Structure of Molecules". In the paper XXII of the series (G. C. Lie and E. Clementi, *J. Chem. Phys.*, **60**, 1288 (1974)) reference to the previous papers are given.

(12) The interaction of water with an enzyme has been recently computed. See E. Clementi, G. Ranghino, and R. Scordamaglia, *Chem. Phys. Lett.*, in press.

Qualitative Molecular Orbital Theory of Molecular Electron Affinities

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Abstract: The simple notions of qualitative MO theory are systematically compared with literature values of electron affinities for molecules of types A_2, AB, AH, AH_2, AH_3, A_2H, A_3, AB_2, AB_3. The degree of agreement is high. A few cases are uncovered where theory disagrees strongly enough with literature values to suggest that the latter are incorrect. Estimates of D_0 are made for a number of diatomic cations and anions (K_2^+, Rb_2^+, Be_2^+, Mg_2^+, Ca_2^+, Sr_2^+, Al_2^+, Ga_2^+, Si_2^+, Ge_2^+, Sn_2^+, P_2^+, Na_2^-, K_2^-, Rb_2^-, B_2^-, Si_2^-, Ge_2^-, Sn_2^-, N_2^-, Sb_2^-, Se_2^-, Te_2^-). Enhancement (over prediction) of the electron affinities of NO_2 and O_3 is suggested to arise from end effects. It is anticipated that S_3 will show a similarly enhanced electron affinity.

The purpose of this paper is to draw attention to the relevance of simple qualitative molecular orbital (MO) concepts to electron affinities of small molecules. Certain of the ideas to be discussed here have been recognized for many years (and even appear in general chemistry textbooks[1]), but have not been systematically tested against experimental data nor systematically extended to polyatomic systems. Here we shall survey existing data on small-molecule electron affinities and attempt to rationalize them in terms of qualitative MO notions. Because these notions are relevant for ionization potentials as well, we will have occasion to discuss positive ions too; however, the principal concern is with electron affinities.

The main reason for the arrested development of MO theory of molecular electron affinities (EA's) has been the great difficulty in obtaining reliable and accurate experimental or theoretical data.[2-4] Indeed, it is only in recent years that good

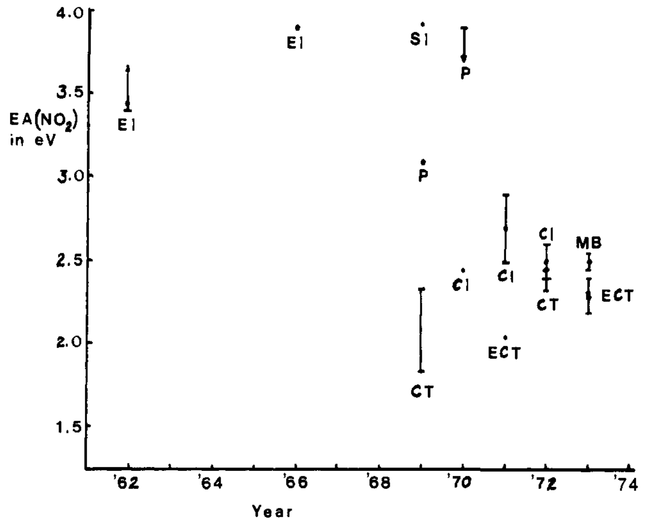

Figure 1. Measured EA(NO_2) vs. year. EI = electron impact, SI = surface ionization, CT = charge transfer, CI = chemical ionization, ECT = endothermic charge transfer, P = photodetachment, MB = molecular beam techniques. Data from ref 2.

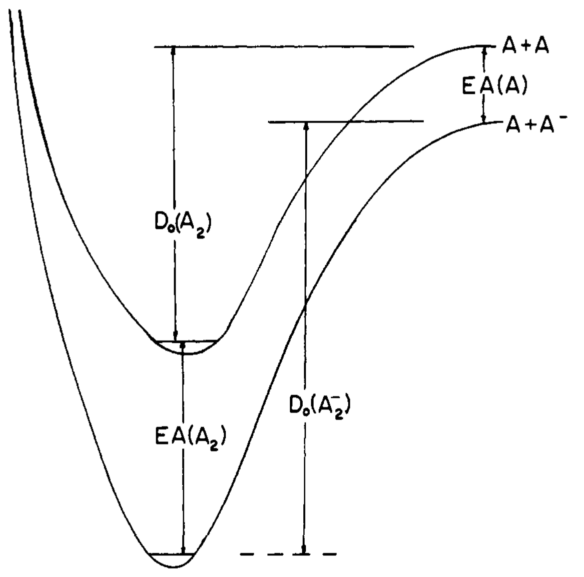

Figure 2. Total energy vs. internuclear separation for a diatomic molecule A_2 and its anion A_2^-.

values of many *atomic* EA's have become available.[4,5] Reliable EA values for many diatomic molecules are now available, but few good measurements of EA's for polyatomic systems exist. Many of the tabulated values are several years old, and, as Figure 1 indicates, the older measurements are not trustworthy. However, rapid progress is now being made, both on experimental[2] and computational fronts,[6] and this seems a reasonable juncture at which to develop a qualitative model; sufficient data exist to test it, and sufficient data are as yet unknown for it to be useful.

We begin by discussing homonuclear diatomic molecules and ions, focusing first on relations among their D_0 values and then converting to a qualitative MO model which will be applied to heteronuclear diatomic and polyatomic systems.

Homonuclear Diatomic Molecules and Ions

In Figure 2 are idealized energy curves for a homonuclear diatomic molecule and its anion. The relation between the *thermodynamic* EA of A_2 and the other quantities in the figure is

$$\mathrm{EA}(A_2) = \mathrm{EA}(A) + D_0(A_2^-) - D_0(A_2) \qquad (1)$$

A similar figure applies for ionization potential (IP) and yields the relation

$$\mathrm{IP}(A_2) = \mathrm{IP}(A) - D_0(A_2^+) + D_0(A_2) \qquad (2)$$

In this paper, we will assume EA and IP to refer to these, rather than vertical, processes.

The quantities EA(A) and $D_0(A_2)$ are fairly accurately known for many elements. In such cases, if we can guess $D_0(A_2^-)$, we can estimate EA(A_2). The advantage of this approach is that elementary ideas about the effects of bonding and antibonding electrons on bond dissociation energies can be used. Thus Mulliken[7] estimated the EA of I_2 by guessing that $D_0(I_2^-)$, with a net of one bonding electron, was half as large as $D_0(I_2)$. This approach works well for all the halogen X_2 systems.[8] Closely related methods have been used for a few other homonuclear diatomic molecules.[8,10]

Perhaps the simplest and most obvious way to estimate $D_0(A_2^+)$ or $D_0(A_2^-)$ in general is to interpolate between $D_0(A_2)$ values. How well such an approach would work is indicated in Figure 3, where are plotted all the known D_0 values[11-74] for main group A_2 molecules, anions, and cations in the first five periods of the periodic table. Lines connect the $D_0(A_2)$ points. [Some of the $D_0(A_2)$ values are not very precisely known, so some shifting of these lines could occur in the future.] Many of the points for A_2^+ and A_2^- are fairly close to the lines, indicating that interpolated D_0 values for the ions would give roughly correct EA(A_2) or IP(A_2) estimates for many systems. However, there are some rather large deviations and also some trends in deviations which deserve further comment.

Consider first the positive ions. Except for O_2^+, these all show positive (or zero) deviation. This deviation is pronounced for group 1A cases (Li_2^+, Na_2^+) and appears to increase slightly in most families as we go from period 2 (Li-Ne) to period 3, and then to stay about the same as we move to periods of 4 and 5. In the cases of Li_2^+, Na_2^+, Si_2^+, As_2^+, and Sb_2^+, the deviations are large enough to invalidate the qualitative expectation that loss of a bonding electron will decrease D_0. Li_2^+ and Na_2^+ have long been recognized as exceptions to this rule,[75] but the others appear to have escaped notice.

A likely contributor to these positive deviations of $D_0(A_2^+)$ is energy lowering due to attraction between A^+ and an induced dipole on A. This interaction would be largely absent from A_2, and its long-range character would explain the fact that R_e is larger in Li_2^+ and Na_2^+ than in Li_2 and Na_2, even though D_0 is greater for these positive ions.[76-78] Support for this as an explanation for the deviations in Li_2^+ and Na_2^+ comes from ab initio calculations[78,80] in which about 50% of D_0 results from inclusion of polarization functions in the basis set. Furthermore, if we examine the ground state atomic polarizabilities of the elements[81] (Figure 4), we find some correspondence with deviations in D_0; the polarizabilities are largest for the 1A group of the periodic table and increase down each group, the major increase coming in the jump from the second to the third period. The relatively large polarizabilities of group 2A atoms suggests (by comparison with group 1A cases and use of Figure 3) that Be_2^+, Mg_2^+, Ca_2^+, and Sr_2^+ should have D_0 values in the range of 0.5-1.3 eV. We are unaware of other experimental or theoretical estimates of D_0 for these cations, though Be_2^+ has been calculated to have a potential minimum,[82,83] and Mg_2^+ has been seen experimentally.[84]

Why does $D_0(O_2^+)$ deviate negatively? This corresponds to the ionization of O_2 requiring more energy than expected. O_2 differs from most of the other A_2 systems in having a triplet ground state. Ionization causes the population of a π_u MO to decrease from one to zero. A similar situation applies to B_2. For

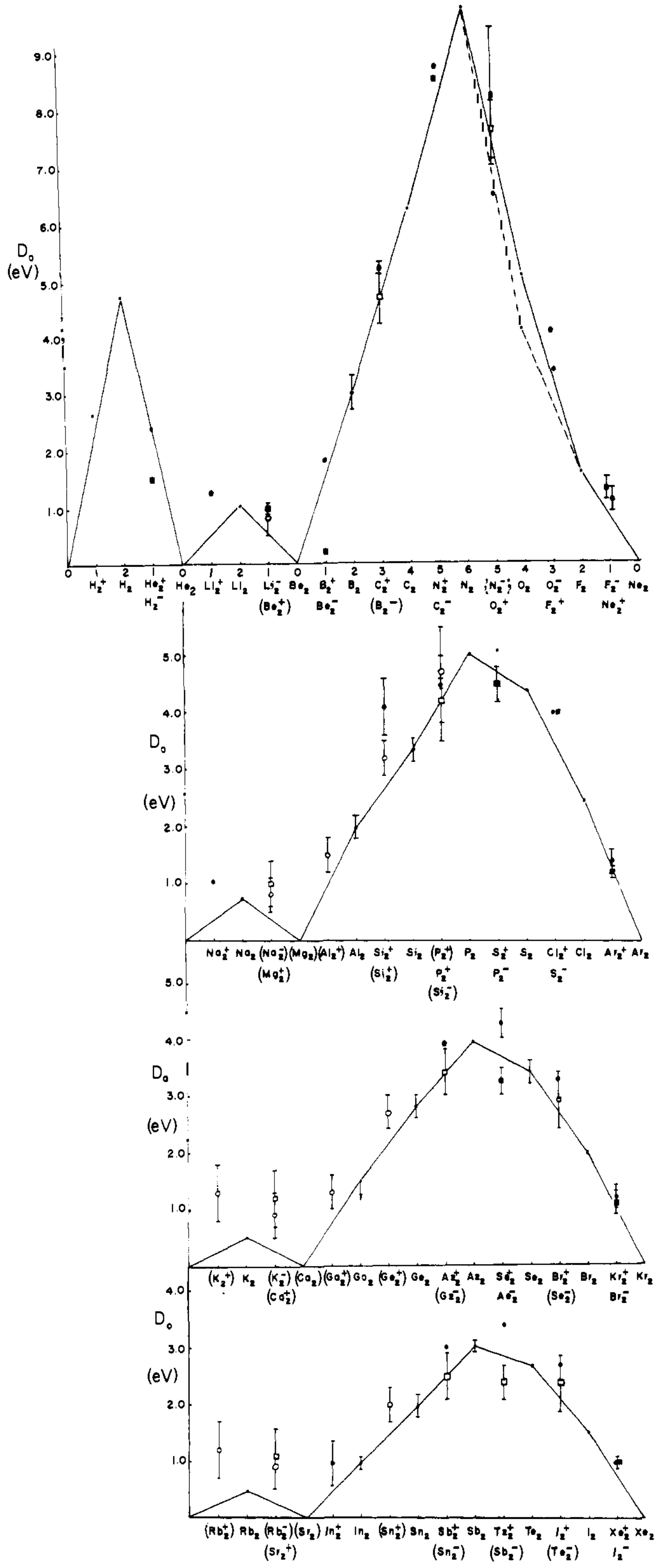

Figure 3. D_0 values of A_2, A_2^+, and A_2^- arranged in periodic table sequence. A_2^- is placed one step to the right, A_2^+ one step to the left, from A_2 to correspond to gain or loss of one electron. Data sources are given in ref 11-74. Circles refer to cations, squares to anions. Open shapes refer to estimated values, filled shapes to literature values. Parentheses around a formula also indicate an estimated quantity.

H 0.6668							He 0.205
Li 23.97	Be 5-7	B 3-5	C 1-3	N 1.13 ± 0.06	O 0.77±0.06	F 0.5-0.6	Ne 0.395
Na 24.4±0.7	Mg 10-20	Al ~5, 11.0	Si 6.8, 4.2	P ~4, 4.4	S 3.45, 3.9	Cl 2.61, 2.3	Ar 1.642
K 41.5±0.2	Ca 20-50	Ga ~5, 9.3	Ge 3.3, 7	As ~4, 5.2	Se ~4.5	Br 3.4, 3.8	Kr 2.480
Rb 43.65±0.06	Sr 25±3	In 3-6	Sn 5.6, 6.0	Sb 4.8, 5	Te ~4.1	I 3.5, 5.4	Xe 4.044

Figure 4. Static dipole polarizabilities of neutral atoms in their ground states (in Å^3). Data are from ref 81.

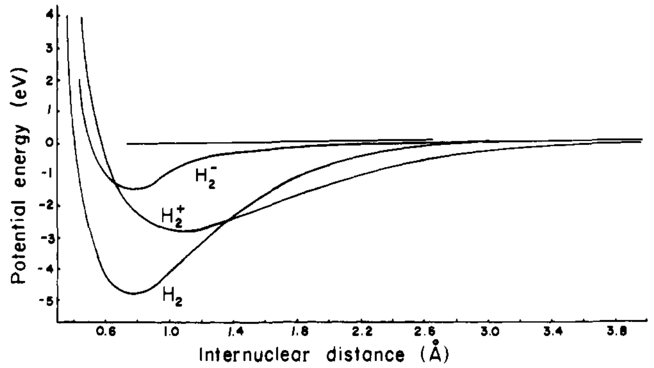

Figure 5. Total energy vs. internuclear distance for H_2^+, H_2^-, and H_2. The curves have been adjusted vertically to have a common dissociation energy. (Data from Sharp, ref 85.)

the other second period molecules, ionization is from a singlet, causing the HOMO population to decrease from two to one. The negative deviation for O_2^+ is consistent with the notion that it is easier to remove an electron from a filled MO than from a half-filled MO, which is equivalent to the observation that atoms or molecules prefer to half-fill a set of degenerate orbitals before filling any of them. In effect, two one-electron π bonds (or antibonds) give lower energy than one two-electron π bond (or antibond). To compensate for this effect, we could plot D_0 for O_2 in the $^1\Delta$ state. This is done in Figure 3 and is connected to neighboring neutral systems by dashed lines. With respect to this new basis for comparison, $D_0(O_2^+)$ shows a much smaller deviation (though it is still negative). The positive deviation of F_2^+ increases. An analogous reduction in $D_0(B_2)$ would increase the positive deviations for C_2^+ and B_2^+, increasing the similarity between trends in D_0 deviation and atomic polarizability. However, the value of D_0 for the $^1\Delta$ state of B_2 is not known. Similar changes could be made for D_0 values of S_2, Al_2, etc., but data are not available. Indeed, in many cases it is not known whether the ground state is in fact a triplet.

For A_2^- ions, the situation is more complicated. Consider H_2^- first. At large distances, we expect H to respond as readily to a negative ion (H^-) as to a positive one (H^+). However, Figure 5 shows that, by the time the internuclear distance has dropped to 4 Å, H_2^+ and H_2^- are already behaving quite differently.[85] Whereas H_2^+ shows a noticeable energy drop at 4 Å, H_2^- shows very little energy lowering until the nuclei are about 2.5 Å apart, giving H_2^- a much narrower well than H_2^+. A plausible explanation for this difference is that polarization in H,H^+ draws electronic charge into the incipient bond region (the polarization cooperates with bond formation) whereas in H,H^- the polarization effect works against bond formation, delaying its onset to shorter distances. Thus, there is reason to think that polarization contributes less to $D_0(H_2^-)$ than to $D_0(H_2^+)$.

The situation for Li_2^- is quite different. Li_2^- is calculated to have a bond as strong but longer than Li_2,[86] suggesting that stabilization due to polarization is important in Li_2^-. It may

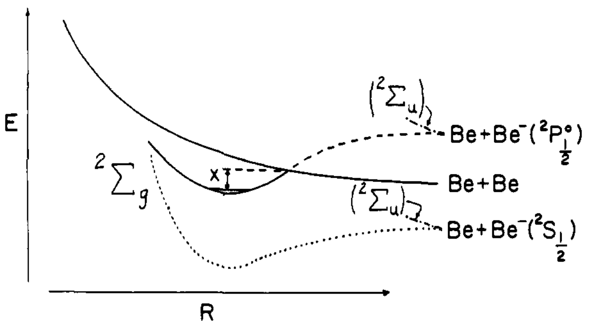

Figure 6. Energy curves vs. internuclear distance for Be_2 and Be_2^-. Solid curves calculated by Jordan and Simons (ref 82). Dashed curve shows correlation to $^2P_{1/2}{}^0$ Be^- state. Dotted curve shows correlation with $^2S_{1/2}$ Be^- state. Lack of 3s AO representation in a basis set would artificially prevent a calculation from achieving this latter correlation.

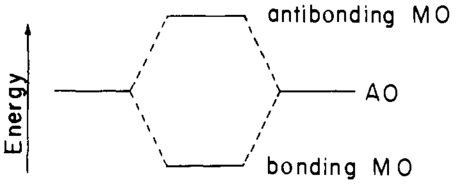

Figure 7. Idealized sketch of antibonding and bonding energy levels for MO's produced from two identical AO's.

Table I. Estimated Values of D_0, IP, and EA for Homonuclear Diatomic Systems

System	Est D_0, eV	EA or IP of A_2, eV
K_2^+	1.3 ± 0.5	3.3 ± 0.6[b]
Rb_2^+	1.2 ± 0.5	3.5 ± 0.5[b]
Be_2^+	0.8 ± 0.3	8.5 ± 0.3
Mg_2^+	0.8 ± 0.3	7.1_5 ± 0.3
Ca_2^+	0.9 ± 0.4	*a*
Sr_2^+	0.9 ± 0.4	*a*
Al_2^+	1.5 ± 0.3	6.5 ± 0.5
Ga_2^+	1.3 ± 0.3	*a*
Si_2^+	3.2 ± 0.3	8.3 ± 0.5[b]
Ge_2^+	2.7 ± 0.3	8.0 ± 0.5
Sn_2^+	2.0 ± 0.3	7.3 ± 0.5
P_2^+	4.7 ± 0.3	10.8 ± 0.3[b]
Na_2^-	1.0 ± 0.4	0.8 ± 0.4
K_2^-	1.2 ± 0.5	1.2 ± 0.5
Rb_2^-	1.1 ± 0.5	1.1 ± 0.6
B_2^-	5.0 ± 0.5	2.2 ± ~1
Si_2^-	4.2 ± 0.4	2.2 ± 0.5
Ge_2^-	3.4 ± 0.4	1.8 ± 0.5
Sn_2^-	2.5 ± 0.4	1.8 ± 0.5
N_2^-	8.1 ± 0.5	−1.8 ± 0.7[b]
Sb_2^-	2.4 ± 0.3	0.4 ± 0.4
Se_2^-	2.9 ± 0.5	1.5 ± 0.7
Te_2^-	2.4 ± 0.5	1.7 ± 0.5

[a] Insufficient data on $D_0(A_2)$ exists to make an estimate worthwhile. [b] See discussion in text.

be that energy increase resulting from repulsion of charge from the internuclear region is swamped by a much greater energy decrease due to polarization. Li is 36 times as polarizable as H.

The H_2^- and Li_2^- systems illustrate that A_2^- ions can show both positive and negative deviations and that this may be due in part to the fact that polarization and bond formation do not cooperate in these ions as they do in A_2^+. Figure 3 shows that positive and negative deviations occur for other A_2^- systems as well.

Once again, the fact that B_2, O_2, S_2, etc. have triplet ground states might be expected to affect comparisons of D_0 values. As before, this could be incorporated in Figure 3 by plotting D_0 values for the appropriate excited singlet states. In the case of O_2 (dashed lines in Figure 3), this "correction" increases the deviation of $D_0(O_2^-)$ by a factor of 2. It would appear that the change in D_0 when $^1\Delta$ O_2 goes to O_2^- is so small that the added electron is essentially nonbonding. However, R_e increases by 8-9%.[87] This might indicate additional antibonding character in O_2^-, but it is also at least partly ascribable to the swelling up of orbitals which occurs when an atom or molecule becomes negatively charged. Robinson[88] attributes a 4% shortening of bond lengths to orbital contraction in positive ion formation. At this time, further speculation about deviations by $D_0(A_2^-)$ is probably not justified since data are sparse and imprecise. Also, we have no guarantee that such deviations can ever be fully accounted for by a simple one-electron model.

Special comment should be made about Be_2^-. Extrapolation techniques suggest that Be^- in the $^2P_{1/2}{}^0$ ($1s^2\,2s^2\,2p$) state is unstable by 0.2-0.7 eV but that Be^- in the $^2S_{1/2}$ ($1s^2\,2s^2\,3s$) state may be stable by 0.4-0.7 eV.[89] Jordan and Simons[82] have performed calculations on Be_2^- and find a $^2\Sigma_g$ state which is stable with respect to electron detachment and dissociation and which crosses their calculated repulsive Be_2 energy curve[90-92] at 5.8 au (see Figure 6). [The quantity plotted for $D_0(Be_2^-)$ in Figure 3 is labeled "x" in Figure 6.] If it is indeed true that $^2S_{1/2}$ Be^- is stable, then this crossing is unlikely, for the lowest $^2\Sigma_g$ state of Be_2^- should correlate with the more stable ion state as shown by the dotted line in Figure 6. Since Jordan and Simons[82] used a basis set of functions which did not include 3s orbitals, it seemed possible that their calculated curve is artificially forced to correlate with the higher unstable $^2P_{1/2}{}^0$ ion state[93] (dashed line in Figure 6). If this is the case, inclusion of 3s AO's should strongly modify Figure 6. However, very recent (unpublished) calculations by these workers indicate that inclusion of additional s functions does not significantly affect the Be_2^- curve. Thus, the computational evidence indicates at this time that Be^- is not stable in either the $^2P_{1/2}{}^0$ or $^2S_{1/2}$ states.

The major idea we have sought to test through Figure 3 is that one can roughly estimate D_0 for ions by interpolating between D_0 values for neutrals. The data indicate that this works reasonably well in many cases. One is tempted to go even farther, and guess the position of missing points in Figure 3. We have done this, with an eye on existing trends in deviations and polarizabilities. The resulting estimated D_0 values appear in Table I along with the resulting estimate of IP or EA of A_2, and are indicated by open shapes in Figure 3. Three of the estimated values in Table I are for systems where experimental data already exist. For P_2^+ and N_2^-, the estimate is compatible with the experimental value and serves to decrease the uncertainty. However, our estimated $D_0(Si_2^+)$ does not agree with the experimental value which has been reported by more than one group,[94,95] and which seems unlikely to change much in the future. We include the estimated value to draw attention to the disparity between experiment and model in this case. We have no explanation for the remarkably large experimental value for $D_0(Si_2^+)$. Theoretical calculations[78,96,97] for K_2^+ and Rb_2^+ give D_0 values of 0.93-1.03 and 0.75-0.86 eV, respectively. These seem low for cases where the atoms are so polarizable, but are still within our rather large range of uncertainty.

We now turn to a different, but equivalent, point of view which has the advantage of being easily extendable to polyatomic molecules. In Figure 7 appears an idealized sketch of the MO energy levels resulting when a pair of identical AO's interact to produce bonding and antibonding MO's. According to Koopmans' theorem,[98] if the neutral molecule has a singlet ground state, the energy of the lowest unfilled MO (LUMO) provides an approximate measure of the vertical EA of the

Table II. $EA(A_2)$ and $IP(A_2)$ Compared with $EA(A)$ and $IP(A)$

Electron Affinities

Molecule	LUMO[a]	$EA(A_2)$[b,c]	$EA(A_2)$ expected > or < $EA(A)$	$EA(A)$[b,d]	In accord?
H_2	σ_u(a)	~−2	<	0.754	Yes
Li_2	σ_u(a)	0.58 ± 0.08	<	0.61[e]	?
Be_2	σ_g(b)	~0.2	>	<0? see text	Yes
C_2	σ_g(b)	3.54	>	1.27	Yes
N_2	π_g(a)	−1.6 ± 1.2	<	0.0 ± 0.2	Yes
O_2	π_g(a)	0.43	<	1.46	Yes
F_2	σ_u(a)	2.9	<	3.34	Yes
P_2	π_g(a)	0.2	<	0.77	Yes
S_2	π_g(a)	1.66	<	2.08	Yes
Cl_2	σ_u(a)	2.3	<	3.61	Yes
As_2	π_g(a)	0.1	<	0.8	Yes
Br_2	σ_u(a)	2.5	<	3.36	Yes
I_2	σ_u(a)	2.6	<	3.06	Yes

Ionization Potentials

Molecule	HOMO[a]	$IP(A_2)$[b,c]	$IP(A_2)$ expected > or < $IP(A)$	$IP(A)$[b,f]	In accord?
H_2	σ_g(b)	15.427	>	13.598	Yes
Li_2	σ_g(b)	5.13 ± 0.1	>	5.39	No
B_2	σ_g(b)	~9.5	>	8.3	Yes
C_2	(π_u(b)	12.3 ± 0.1	>	11.26	Yes
N_2	π_u(b)	15.58	>	14.53	Yes
O_2	π_g(a)	12.06	<	13.61	Yes
F_2	π_g(a)	15.7	<	17.42	Yes
Na_2	σ_g(b)	4.90	>	5.14	No
Si_2	π_u(b)	7.4 ± 0.3	>	8.15	No
P_2	π_u(b)	10 ± 1	>	10.48	?
S_2	π_g(a)	8.3 ± 0.2	<	10.36	Yes
Cl_2	π_g(a)	11.5 ± 0.1	<	13.01	Yes
As_2	π_u(b)	9.86	>	9.81	No
Se_2	π_g(a)	8.9 ± 0.3	<	9.75	Yes
Br_2	π_g(a)	10.53	<	11.84	Yes
In_2	σ_g(b)	5.8 ± 0.3	>	5.78	No?
Sb_2	π_u(b)	8.64	>	8.64	No
Te_2	π_g(a)	8.29	<	9.01	Yes
I_2	π_g(a)	9.3	<	10.45	Yes

[a] b = bonding, a = antibonding. [b] Energies are in electron volts. [c] Data from ref 11–74. [d] Except where otherwise noted, data are from ref 4. [e] Reference 106. [f] Reference 107.

molecule and the energy of the highest occupied MO (HOMO) is similarly related to the vertical IP of the molecule. The relations are only approximate because the changes in electron correlation energy and also changes in orbital descriptions of the system's electrons with gain or loss of an electron are ignored in the Koopmans approach. Ordinarily, these factors give errors of opposite sign for IP, so fortuitous cancellation is possible. However, discrepancies of 1 eV or more are common.[99,100] For EA, the errors will ordinarily augment in a direction such that the Koopmans theorem estimate of EA is too small. Calculations indicate that vertical EA's indeed do not agree at all well with LUMO energies for some systems.[101,102] However, it is reasonable to postulate that the *change* in MO energy upon molecule formation is similar to the *difference* in EA or IP when A is compared to A_2. [It is important to recognize that this postulate is less restrictive than is Koopmans' theorem.] This involves the implicit assumption that changes in correlation energy and in orbital energies of "underlying" electrons will be similar upon ion formation from A or A_2. [This is equivalent to assuming that the difference between EA (Koopmans) and EA (actual) will remain approximately constant as R varies. This has been found to be true over a fair distance in a few cases. See, for instance, ref 103.] It is apparent that this assumption is consistent with the one-electron model for D_0 since eq 1 rearranges to $EA(A_2) - EA(A) = D_0(A_2^-) - D_0(A_2)$ and $D_0(A_2^-)$ is taken to be larger or smaller than $D_0(A_2)$ simply by considering whether the electron gained (or lost) occupies a bonding or antibonding MO. Our qualitative rule for $EA(A_2)$, then, is *$EA(A_2)$ is > (<) $EA(A)$ if the LUMO of A is bonding (antibonding).* [An analogous rule exists for IP's.[104]] This rule is more qualitative than the estimated D_0 approach since it gives only an upper or lower bound for molecular EA's. However, even this can be useful in view of the complete absence of data for many systems. It also directs our attention to systems, such as Li_2, which violate the rule, and causes us to seek explanations for such deviant behavior. Table II compares $EA(A_2)$ and $IP(A_2)$ with our expectations based on this simple rule.[105] The data show a high degree of accord with the above rule. [Mulliken[104] has discussed corrections which should be made when applying this approach to IP's. These include corrections for molecules, such as O_2, which lack ${}^1\Sigma_g{}^+$ ground states, corrections for $A_2{}^+$ (e.g., averaging ${}^2\Pi_{3/2}$ and ${}^2\Pi_{1/2}$ states for $Cl_2{}^+$), and corrections for A to get the proper *valence state* IP. Similar kinds of corrections are appropriate for EA's, but usually the necessary information is unavailable. We have, therefore, omitted all such corrections from the IP data in Table II in order to give a fairer idea of the capabilities of the completely unrefined approach we are applying to EA's.]

Heteronuclear Diatomic Systems

When an electron is added to an atom, the AO's become

Table III. EA(AB) Compared to EA(A) and EA(B)[a]

AB	LUMO	EA(AB)[b]	Expectation	EA(A)[c]	EA(B)[c]	In accord?
		(Fairly reliable values)				
LiH	σ(a + b)	0.30	See text	0.61[d]	0.75	See text
NaH	σ(a + b)	0.36	See text	0.55	0.75	See text
BeH	σ(a + b)	0.74	See text	<0?	0.75	See text
MgH	σ(a + b)	1.08	See text	<0	0.75	See text
BeO	σ(a)	1.77	See text	<0?	1.46	See text
LiF	σ(a)	0.46	See text	0.61[d]	3.34	See text
LiCl	σ(a)	0.61	See text	0.61[d]	3.61	See text
HF	σ(a)	$\sim$0.0	$\lesssim$A	0.75	3.34	Yes
NaCl	σ(a)	0.67	$\lesssim$A	0.55	3.61	Yes
NC	σ(b)	3.8	>B	1.27	0.0 ± 0.2	Yes
BO	σ(b)	2.8 ± 0.2	>B	0.24	1.46	Yes
NO	π(a)	0.015 ± 0.1	$\lesssim$A	0.0 ± 0.2	1.46	Yes
OS	π(a)	1.1	$\lesssim$A	1.465	2.08	Yes
PO	π(a)	1.09	$\lesssim$A	0.77	1.46	?
IBr	σ(a)	2.7 ± 0.2	$\lesssim$A	3.06	3.63	Yes
		(Less reliable values)				
AlO	σ(b)	$\sim$2.6	>B	0.46	1.46	Yes
CO	π(a)	<−1.8	$\lesssim$A	1.27	1.46	Yes
CS	π(a)	$\leq$1.2	$\lesssim$A	1.27	2.08	Yes
CF	π(a)	$\gtrsim$3.3	$\lesssim$A	1.27	3.34	?
NS	π(a)	1.3 ± 0.3	$\lesssim$A	0.0 ± 0.2	2.08	?
SF	π(a)	2.5 ± 0.5	$\lesssim$A	2.08	3.34	?
SI	π(a)	2.7 ± 0.3	$\lesssim$A	2.07	3.06	?
SeF	π(a)	$\leq$2.8 ± 0.5	$\lesssim$A	2.02	3.34	?
FCl	σ(a)	1.5 ± 0.4	$\lesssim$A	3.34	3.61	Yes
ICl	σ(a)	1.43	$\lesssim$A	3.06	3.61	Yes

[a] See Table II for notes. [b] Data sources are given in ref 109–133. [c] Except where noted otherwise, atomic EA values are from ref 4. [d] See ref 106.

more diffuse as a result of increased interelectronic repulsion. When an electron is added to a homonuclear diatomic molecule A_2, the MO's become more diffuse but still must be symmetric or antisymmetric for inversion. However, when AB gains an electron, the MO's of the system can adjust more toward A or B in an effort to minimize the energy. Thus, a virtual antibonding MO for the neutral will tend to become less antibonding once it is occupied, and a bonding virtual will tend to become more bonding. This is indicated in Figure 8, in which appears a sketch of the one-electron levels resulting from interaction between nonidentical AO's. *It is assumed in what follows that the AO on atom B has lower energy.* The shading represents energy lowering due to lateral shifting of MO's if their occupancy increases upon anion formation. [Even though shifting and energy change can occur in all the MO's, we can formally represent it as a lowering of the LUMO level.] Another way of stating the case is to note that heteronuclear diatomic MO's are not divided into g, u symmetry classes, so greater opportunities exist for mixing of the LUMO with other virtual MO's upon perturbation due to adding an electron.

From Figure 8 we deduce the following rule: *If the LUMO of AB is bonding, EA(AB) should be greater than EA(B), which is the larger of the two atomic EA's. If the LUMO is antibonding, then EA(AB) may be greater than, equal to, or less than EA(A), depending on the system's capability for stabilizing the LUMO when it becomes occupied (i.e., depending on the depth of the shaded area in Figure 8).* A third possibility, that the LUMO of AB is nonbonding, will be discussed later. The data are surveyed in Table III. In the three cases where the LUMO of AB is formally bonding EA(AB) > EA(B) as expected. Details on the MO relaxations in two of these systems (CN, BO) have been reported by Griffing and Simons.[108] Most of the systems in Table III have antibonding LUMO's and therefore require consideration on a case-by-case basis.

Consider first molecules such as CO, NO, IBr, ICl, which are not expected to be very different from the homonuclear diatomics in terms of charge separation and dipole moment. For such molecules, energy lowering due to orbital polarization is not likely to be as great as in more polar molecules, so we expect EA(AB) to be less than or in the neighborhood of EA(A). Of these molecules, the interhalogens should have the least flexibility for energy lowering because they possess only one virtual MO (in a minimal basis subspace). As the molecules become more heteropolar (CF, SeF) the capabilities for stabilizing the anion increase and the EA(AB) may become significantly greater than EA(A). Although many of the EA(AB) values of Table III are as yet unreliable, these generalizations seem to be well supported.

The molecules LiH, NaH, BeH, and MgH have as LUMO a σ MO comprised of a 1s AO on H (call it $1s_H$) and s and p_σ AO's on the heavier atom. This σ MO is the second *valence* σ MO (let us call it 2σ) and, if we restricted our basis set to, say, $1s_H$ and 1s, 2s on the heavy atom, it would be $1s_H$–2s antibonding, analogous to the $1\sigma_u$ MO of H_2. Because a p_σ AO is present at somewhat higher energy than 2s, it mixes into this MO in a bonding fashion. As we move right in the periodic table, the 2s and 2p AO's drop in energy, so that $1s_H$ mixes more strongly with 2p, less strongly with 2s, and 2σ becomes more $1s_H$–$2p_\sigma$ bonding, while 1σ becomes more purely 2s nonbonding. Thus, while we cannot say how much bonding or antibonding character the LUMO's for these systems possess we do expect the LUMO's for BeH and MgH to have more bonding character than those for LiH and NaH. The EA's for these systems are consistent with these expectations. Those for LiH and NaH are less than the smaller atomic values, indicating more antibonding LUMO's; those for BeH, MgH are close to the larger atomic value. Here, then, we have a case where the data are consistent with the model, but the model offers little help in predicting the data. This problem results

Table IV. EA(AH) Compared to EA(A)[a] for Six to Nine Valence Electron AH Systems

AH	No. of valence electrons	EA(AH)[b]	EA(A)	Difference
BH	4	<0, 0.09	0.24	<−0.24, −0.15
AlH	4	~0.04	0.46	~−0.4
CH	5	1.24	1.27	−0.03
		(1.61 ± 0.2)[c]		0.3 ± 0.2
SiH	5	1.277 ± 0.009	1.38[d]	0.1
		(1.46 ± 0.2)[c]		0.1 ± 0.2
NH	6	0.381 ± 0.014	0.0 ± 0.2	0.4 ± 0.2
		(0.22 ± 0.2)[c]		0.2 ± 0.4
PH	6	1.03 ± 0.01	0.77	0.15 ± 0.2
		(0.93 ± 0.2)[c]		0.26
OH	7	1.825 ± 0.002	1.46	0.36
		(1.91 ± 0.1)[c]		0.45 ± 0.1
SH	7	2.32 ± 0.010	2.08	0.24 ± 0.010
		(2.25 ± 0.1)[c]		0.2 ± 0.1
SeH	7	2.21 ± 0.03	2.02	0.2

[a] See Table II for notes. [b] EA data sources appear in ref 144-152. [c] Cade's theoretical estimate. See ref 101. [d] See ref 147.

from the lower symmetry in AB systems, which allows for mixed bonding and antibonding character in the MO's.

We have already alluded to the fact that electron affinity can be influenced by molecular polarity. Crawford[134] has emphasized the fact that any radical or molecule having a permanent dipole moment greater than 1.625 D[134-138] possesses an infinite number of bound negative ion states whose wavefunctions are of the same symmetry as those of the molecular ground state. [This statement applies only if effects due to rotation are ignored. Vide infra.] It has also been shown[134] that such states exist also in the Hartree-Fock approximation, so they are not outside the purview of a one-electron model. [In the orbital model, the requirement that state space symmetry be preserved means that the added electron must go into a σ MO, in a diatomic system.] Thus, molecules such as LiH (μ = 5.88 D), NaH (6.89 D), LiF (6.33 D), LiCl (7.13 D), LiBr (7.27 D), NaF (8.16 D), NaCl (9.00 D), CS (1.98 D), and HF (1.82 D) must have positive EA values. Indeed, Crawford[134b] has shown that the LUMO's in such molecules must have negative energy levels, so that even a Koopmans' theorem approach would yield a positive EA here. Calculations[139-141] on LiH$^-$, NaH$^-$, BeO$^-$, LiF$^-$, and LiCl$^-$ (only the last two have been seen experimentally) indicate that the extra electron resides in a diffuse, fairly nonbonding, σ MO, located mostly in the positive region of the electric dipole field, just as would be expected for a dipole-bound state.[137b,138] Efforts to find by ab initio methods the bound negative ion state for HF were at first unsuccessful,[140] probably because the electron is only very weakly bound and in a *very* diffuse MO analogous to high Rydberg states of hydrogen. However, very recently, a calculated Born-Oppenheimer (no rotation) EA of 10^{-6} eV has been reported for HF.[142] It would be difficult to separate unambiguously dipole and valence energy contributions to EA, and we shall simply view the dipole effect as one of the factors which allows the orbital energies of Figure 8 to move down into the shaded regions (even when $\mu < 1.625$ D). The great utility of Crawford's rule[134] is that it provides us with another bound on the EA of molecules with dipole moments exceeding 1.625 D. For instance, our qualitative rule *suggests* that EA(HF) $\lesssim$ 0.75 eV. Crawford's rule *requires* EA(HF) > 0.0. *Provided that the same negative ion state is referred to in these two approaches*, such bracketing is useful. The dipole moments of HCl, HBr, and HI are all less than 1.625 D, but Crawford and Koch[143] suggest that EA(HX) > 0 for all these molecules, based on dissociative attachment studies. Accepting this as a lower limit and applying our qualitative model for the upper limit, gives 0 < EA(HX) < 0.75 eV for all these systems.

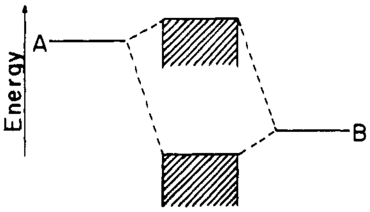

Figure 8. Idealized sketch of antibonding and bonding energy levels for MO's produced from nonidentical AO's. The shading represents energy lowering due to lateral rearrangement of MO's if they become occupied upon anion formation.

AH molecules having four to seven valence electrons have LUMO's which are nonbonding, being comprised of a p_π AO on A. This means that, to a first approximation, the energy change involved in adding an electron to this MO should be similar to that for adding it to the atom itself. [This assumes that the atom and the molecule have the same populations in the relevant p orbital, i.e., that both change from 0 to 1 or else both change from 1 to 2 upon formation of the anion.] However, there are secondary effects which should lead to some shifting of EA(AH) relative to EA(A). Upon gaining an electron, the molecule can shift charge onto the hydrogen atom through redistribution of its σ orbitals, a mode of relaxation not open to the atom. This suggests that EA(AH) should be slightly greater than EA(A) for these systems. There is support for this picture in the available data (Table IV) for six or seven valence electron systems, which show EA(AH) > EA(A) by 0.2-0.5 eV, the larger stabilization occurring for A near the top of the periodic table. The correlation-corrected SCF calculations of Cade[101] for these systems are presented for comparison. Cade's predictions are generally quite close to the current best experimental values. Cade also predicted that EA's of GeH, AsH, and SeH would be within 0.1 eV of the atomic EA's for Ge, Se, and As, respectively. The subsequently measured value for EA(SeH) comes very close to this prediction. Cade also found that R_e for AH and AH$^-$ is almost identical for these systems, in accord with qualitative MO expectations for effects of a nonbonding electron, and also with experimental measurements.[153]

The data for four or five valence electron systems indicate that EA(AH) is fairly close to EA(A), but not necessarily slightly greater. The experimental values for SiH and CH are reliable; the others are questionable. Notice that all of Cade's predictions accord with our qualitative model, even for SiH and CH, indicating that small deviations from our expectations

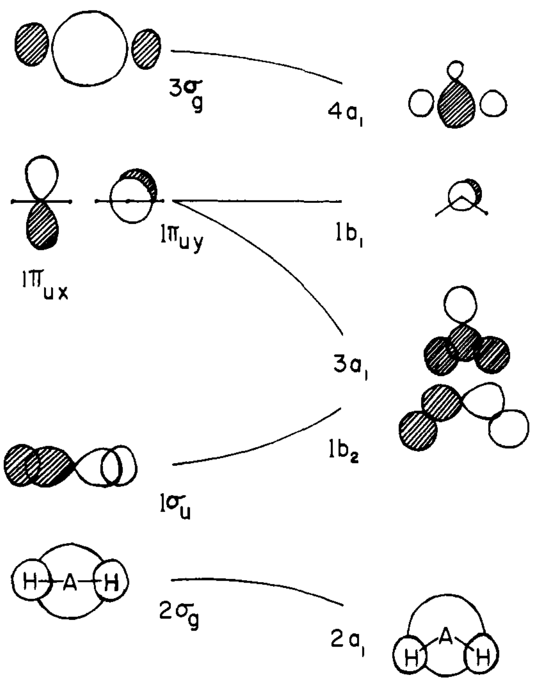

Figure 9. MO's for AH_2 molecules showing linear-bent correlations. After Gimarc (ref 158).

may be due to factors subtle enough to have been inadequately handled in Cade's careful analysis and hence beyond the scope of so simple an approach as we are using here. [An updated analysis of the SCF and correlation parts of molecular and atomic EA's by Zittel and Lineberger[154] indicate that Cade's treatment of correlation is basically correct. At least some of the discrepancy, then, is at the SCF level.] Calculations by Griffing and Simons[155] indicate that BH does not have a positive EA, whereas our qualitative model would favor an EA slightly greater than 0.24 eV. It is not clear why the formally nonbonding LUMO of BH should take on antibonding characteristics in BH^-. Overall, the data suggest that some factor operates to destabilize these molecule-ions as we move from right to left in the periodic table. More study, both experimental and computational, is needed to resolve these questions concerning group 3a and 4a hydrides.

Since the negative ions just discussed involve addition of an electron to a π MO, and furthermore, to an MO located on the more electronegative atom (in most cases), these negative ions are not in states which are significantly stabilized by molecular dipole moment. This means that a system such as OH (μ = 1.66 D)[156] should have another kind of negative ion state (in fact, an infinite number of them), with the added electron in a diffuse σ MO concentrated near the hydrogen end of the system. [This assumption ignores the fact that the real OH radical undergoes rotations which may upset the 1.625 D rule.[134,137a] For a system having a dipole so near the limiting value, this might prevent the bound negative ion from really existing. However, ab initio calculations also fail to consider these factors, so such states should be calculable by such methods, though this would be difficult since the state functions should be very diffuse.] An interesting system to consider in this context is LiN, which is similar to HN in valence electron configuration. LiN has a calculated dipole moment of about 7 D and an estimated EA of 0.40 eV for a *dipole stabilized anion with the added electron in a 5σ MO.*[157] The EA for addition of an electron to a p AO on N is not known but is probably smaller. Here, then, is a case where dipole stabilization apparently causes the extra electron to prefer an orbital other than the LUMO we would expect in a normal basis set calculation on the neutral molecule.

Table V. Electron Affinities of AH_2 and AH_3 Systems[a]

Molecule	No. of valence electrons	EA(molecule)[b]	EA(A)[c]
		AH_2	
BH_2	5	~1.4 (?)	0.24
AlH_2	5	~2.1 (?)	0.46
CH_2	6	1.06[d]	1.27
SiH_2	6	1.12	1.38
NH_2	7	0.78	0.0 ± 0.2
PH_2	7	1.27	0.77
AsH_2	7	1.27	0.80
OH_2	8	~0.9 (?)	1.46
SH_2	8	~1.1 (?)	2.08
		AH_3	
BeH_3	5	~3.8 (?)	<0.0?
CH_3	7	1.8, ~1.1 (?)	1.27
SiH_3	7	≤1.44	1.38
GeH_3	7	≤1.74	1.20

[a] All energies are in electron volts. [b] See ref 160-172 for sources of molecular EA values. [c] See Tables I-IV for atomic EA data sources. [d] This is the electron affinity of the excited $^1A_1$ state of CH_2. EA of ground state CH_2 is 0.21 eV.

Summary of Diatomic Molecule Results

We have tested simple qualitative notions against existing data and found support for the following rules for molecular EA's. (1) If the LUMO of A_2 is bonding, $EA(A_2) > EA(A)$. If antibonding, $EA(A_2) < EA(A)$. (2) If the LUMO of AB is bonding, EA(AB) > the larger atomic EA. (3) If the LUMO of AB is antibonding, EA(AB) $\lesssim$ or $\gtrsim$ the smaller atomic EA, the larger stabilization being associated with more polar AB systems. (4) If the LUMO of AH is nonbonding, EA(AH) $\gtrsim$ EA(A). [For A in group 5a or 6a, EA(AH) > EA(A) by 0.1-0.5 eV, the larger values occurring for A near the top of the periodic table. For A in group 4a, EA(AH) $\simeq$ EA(A). For A in group 3a, it appears that EA(AH) < EA(A). The reason for this is not known.]

While these rules appear to have some exceptions and certainly fail to yield reliable numerical estimates for EA's, they do provide a framework for qualitative understanding of data. Flagrant disagreement with these rules should signal either an erroneous value for EA or else the existence of a physical effect not adequately handled in the simple model. The EA value of <0 for BH is an example.

For ionization potentials of A_2 systems, we find that usually $IP(A_2) > IP(A)$ if the HOMO of A_2 is bonding, < if antibonding, as discussed long ago by Mulliken[104] and that $D_0(A_2^+)$ almost always deviates positively from the value interpolated from neutrals. This deviation tends to be largest for systems where A is most polarizable and is presumably partly due to charge-induced polarization of A by A^+. A similar uniform direction of deviation does *not* appear to occur for $D_0(A_2^-)$.

Polyatomic Systems

Data for polyatomic systems are fewer and less reliable than for diatomics. Nevertheless, there are indications that qualitative MO notions can be applied here too.

AH_2. The MO's for these molecules are sketched in Figure 9. On the basis of this figure, we expect molecules having five valence electrons to be bent and to become more bent upon adding an electron to the $3a_1$ MO.[158] (Ferguson et al.[159] have pointed out that such geometry changes may lower the cross section for electron attachment.) Our simple rules lead us to expect the EA of such molecules to be greater than the larger of the atomic values. Table V shows that the data for BH_2 and

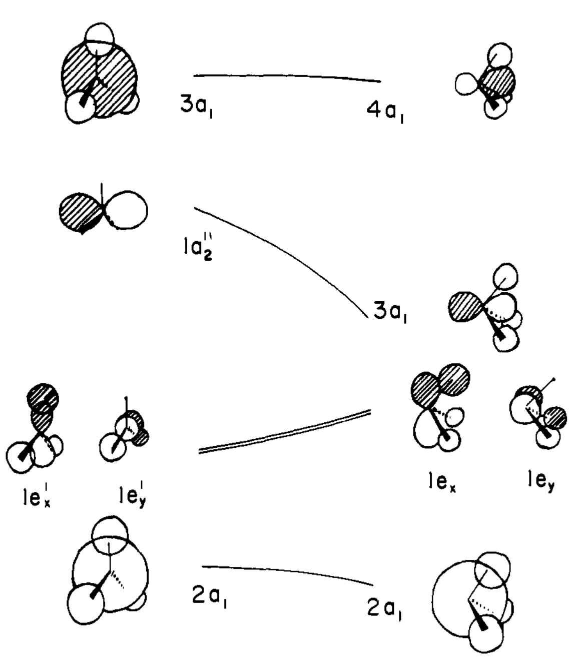

Figure 10. MO's for AH_3 molecules showing planar-pyramidal correlations. After Gimarc (ref 158).

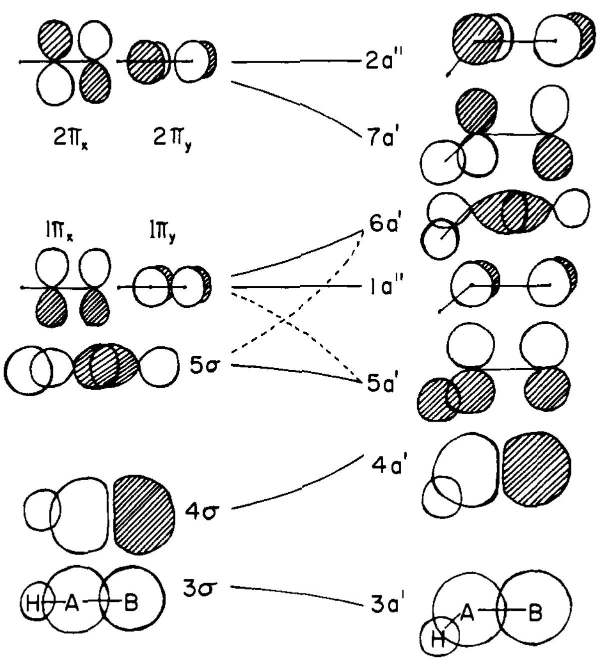

Figure 11. MO's for HA_2 systems showing linear-bent correlations. After Gimarc (ref 158).

AlH_2, though not reliable, so far conform to this expectation.

Molecules with six or seven valence electrons add an electron to the formally nonbonding $1b_1$ MO. As before, we expect the EA of these molecules to be near that of the central atom itself, with some extra anion stability coming from the ability to delocalize charge onto the hydrogens. Also, we expect rather little change in A-H bond distance or H-A-H angle upon anion formation. Structure studies indicate that this latter expectation is met in the cases of CH_2,[162] NH_2,[46] and PH_2.[122] The pattern that is emerging for the EA values (Table V) is similar to that seen for AH systems. That is, molecules containing atoms from group 5 do indeed have EA's somewhat enhanced over the atomic value, but those containing a group 4 atom have EA's which are smaller than the atomic value. The extent of stabilization or destabilization of the anion by the presence of hydrogens is roughly doubled in going from AH to AH_2 (with the possible exception of CH_2). It should be pointed out that the tabulated EA(CH_2) is for addition of an electron to the excited closed shell $(3a_1)^2\ {}^1A_1$ state of the molecule, since this permits addition of an electron to an empty p AO on carbon, which is analogous to the situation for the ground state atom.

Molecules having eight valence electrons add an electron to the antibonding $4a_1$ MO, which should make EA(AH_2) less than either EA(A) or EA(H). For H_2O, this means EA < 0.75 eV. Since water has a dipole moment of 1.85 D, we have a lower limit of zero for the EA of this molecule. The pronounced antibonding of this MO leads us to expect EA(H_2O) to be closer to zero than to 0.75 eV. H_2S is similar except that its dipole moment is too small to guarantee a stable anion. Here we again expect a rather small positive EA at best. Thus, the theory suggests that the rather old and unreliable values for H_2O and H_2S in Table V are too large.

AH_3. The MO's for these molecules appear in Figure 10. According to the one-electron approach, AH_3 molecules having five valence electrons are planar and equilateral triangular, have a bonding LUMO, and remain planar as anions. Therefore, we expect BeH_3 to have an EA greater than the larger atomic value. The value for BeH_3, while not firm, agrees with this qualitative prediction.

AH_3 systems having seven valence electrons could be planar or pyramidal, depending on the tradeoffs between energy increases and decreases in Figure 10.[158] NH_3^+, for instance, is planar,[173] whereas SiH_3 and GeH_3 may be slightly pyramidal.[171] This means that, when a six valence electron system such as BH_3 or AlH_3 gains an electron, that electron goes into an MO which is probably mostly a nonbonding 2p AO on the central atom ($1a_2''$ in Figure 10). This would ordinarily lead us to expect EA(AH_3) $\gtrsim$ EA(A) for these molecules. But our experience with nonbonding p orbitals in AH and AH_2 has indicated that hydrogen *destabilizes* anions in groups 3 and 4, so it seems likely that EA(BH_3, AlH_3) will show a similar effect.

When AH_3 molecules having seven valence electrons add an eighth, the anion is definitely pyramidal and the added electron finds itself in a bonding MO. Hence, EA(AH_3) should exceed EA(A) (which is always greater than EA(H) for this series). Data on SiH_3 and GeH_3 agree. The values on CH_3 are not reliable. The theory is not in agreement with the smaller value.

AH_3 molecules having eight valence electrons (NH_3, PH_3, etc.) are pyramidal and have an antibonding LUMO. Some dipole stabilization can occur, but it seems likely that EA's for these systems will not be greater than the smaller constituent atom value. This would mean that EA(NH_3) is almost certainly negative, while EA(PH_3, AsH_3, SbH_3) are either positive (though small) or negative. Data are not yet available for these molecules.

HA_2. MO's for these systems are produced by combining A_2 MO's with a 1s AO on hydrogen. The resulting MO's are displayed in Figure 11. Systems having nine valence electrons become linear upon acquiring a tenth electron. This electron occupies either a π bonding MO ($1\pi_x$ of Figure 11) or a σ bonding MO (5σ) depending respectively on whether $1\pi_x$ is above 5σ (as shown) or vice versa. In either event, EA(HA_2) should exceed EA(A), and the data for HC_2 and HSi_2 are in accord with this (Table VI).

Systems having 11 valence electrons (e.g., HN_2) would have bent anions, with the added electron occupying an antibonding π MO with some H-A bonding character. This implies that EA(HA_2) $\gtrsim$ EA(A_2). Therefore, HN_2 should probably have a negative EA and EA(HP_2, HAs_2) should be fairly small (somewhat greater than 0.2 and 0.1 eV, respectively).

Table VI. Electron Affinities of HA_2 Systems[a]

Molecule	No. of valence electrons	EA(molecule)[b]	EA(A)[c]	In accord?
HC_2	9	2.2	1.27	Yes
HSi_2	9	~4.08 (?)	1.24	Yes
HO_2	13	~4.06 (?)	1.46	No

[a] All energies are in electron volts. [b] See ref 174-176 for sources of molecular EA values. [c] See Tables I-IV for atomic EA data sources.

Table VII. Electron Affinities of A_3 and AB_2 Systems[a,b]

System	No. of valence electrons	EA(system)[c]	EA(A)[d]	EA(B)[d]	In accord?
C_3	12	≈2	1.27		Yes
BO_2	15	4.1 ± 0.2	0.24	1.46	Yes
N_3	15	3.5 ± 0.2, ~2.3	0.0 ± 0.2		Yes
P_3	15	~1	0.77		Yes?
As_3	15	0.8 ± 0.3	0.80		?
CO_2	16	−0.9, −0.4, −0.6	1.27	1.46	Yes
CS_2	16	0.5 ± 0.2, 1.0 ± 0.2	1.27	2.08	Yes
NO_2	17	2.3 ± 0.2	0.0 ± 0.2	1.46	? see text
O_3	18	2.14 ± 0.15	1.46		? see text
CF_2	18	≤1.3 ± 0.8	1.27	3.34	Yes
$SiCl_2$	18	>2.6	1.38	3.61	No
SO_2	18	1.1 ± 0.04	2.08	1.46	Yes
NF_2	19	1.7 ± 0.2	0.0 ± 0.2	3.34	No

[a] All energies are in electron volts. [b] AB_2 has structure BAB unless explicitly written otherwise. [c] Sources for EA's may be found in ref 180-192. [d] See Tables I-IV for atomic EA data sources.

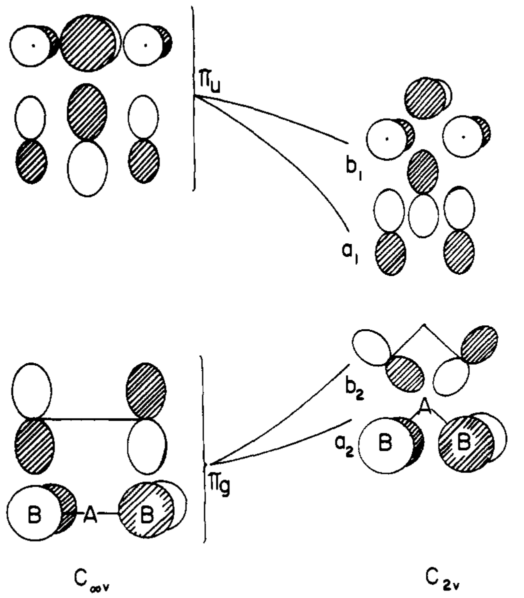

Figure 12. Some MO's for AB_2 showing linear-bent correlations.

Systems with 13 valence electrons (HO_2, HS_2, etc.) are bent and should remain so as anions. The added electron must enter an antibonding π MO. This means that $EA(HA_2) < EA(A)$. $EA(A_2)$ is probably reasonably close to $EA(HA_2)$. For HO_2, this suggests an EA of ~0.4 eV. Table VI lists a value estimated 40 years ago from Born-Haber cycle considerations.[176] This value is in strong disagreement with our predictions and is likely to be incorrect. [Similar estimates of EA(O_2, OH) made at that time were much too large.]

It is possible to apply qualitative MO reasoning to HAB systems such as HCN and HCO through Figure 11. The uncertainty in these cases is increased because of polarity in the AB moiety. Since no data are available for comparison on HAB systems, we do not pursue them here.

AB_2. The molecules A_3 or AB_2 possess a pair of nonbonding MO's which are degenerate (π_g) in the linear geometry (see Figure 12). These are the LUMO's for molecules having 12-15 valence electrons. (Such molecules and their anions are expected to be linear on the basis of correlation diagram arguments.[177,178]) These MO's are nonbonding, but are delocalized onto two centers. In this regard they differ from the nonbonding MO's previously encountered in AH, AH_2, and AH_3 systems, which are localized on atom A. As before, simple Hückel-type considerations would suggest that adding an electron to such an MO in BAB releases the same energy as adding an electron to a p AO on an isolated atom, i.e., that $EA(AB_2) \approx EA(B)$. However it seems likely that this relation will be incorrect since differences in interelectronic repulsion, core relaxation, and correlation energy change should be quite large in these two kinds of system.

When a neutral atom accepts an electron, its valence orbitals become much more diffuse to mitigate increased interelectronic repulsion. The orbital energy of the accepting atomic orbital rises when the new electron is accepted. In the extreme case of the hydrogen atom, the 1s energy level rises from −13.6 to −0.7 eV when H becomes H^-. If we imagine adding an electron in fractions to an atom, we would expect the first fractions to bind more strongly than the last ones. That is, the EA of an atom is greater for the first "half-electron" than for the second. This is a well-recognized concept in the field of chemisorption, where an atom adsorbed on a surface may have a nonintegral electron occupation.[179] When an electron adds to a nonbonding MO distributed over several atoms, we have the likelihood of an enhanced EA, since each atomic orbital is now accepting "first fractions" of electronic charge. Thus, for AB_2 molecules having 12-15 valence electrons, we expect $EA(AB_2) > EA(B)$. Reference to Table VII indicates that this rule is generally obeyed in such cases, with P_3 and As_3 being possible exceptions. [Since many of these data are unreliable,

Table VIII. Electron Affinities of AB_3 Systems[a,b]

System	No. of valence electrons	EA(system)[c]	EA(A)[d]	EA(B)[d]	In accord?
CO_3	22	2.9 ± 0.3	1.27	1.46	Yes
NO_3	23	3.5 ± 0.2	0.0 ± 0.2	1.46	Yes
SO_3	24	≤1.7 ± 0.2	2.08	1.46	Yes?
CF_3	25	2.2 ± 0.3	1.27	3.34	No
CCl_3	25	≥2.1 ± 0.4, 1.22	1.27	3.61	No
PCl_3	26	0.8 ± 0.1	0.77	3.61	?
PBr_3	26	1.6 ± 0.2	0.77	3.36	No
SF_3	27	3.0 ± 0.1	2.08	3.34	No

[a] All energies are in electron volts. [b] The structures are all assumed to have A at the apex of three AB bonds. [c] Sources for EA data are given in ref 197–204. [d] See Tables I–IV for atomic EA data sources.

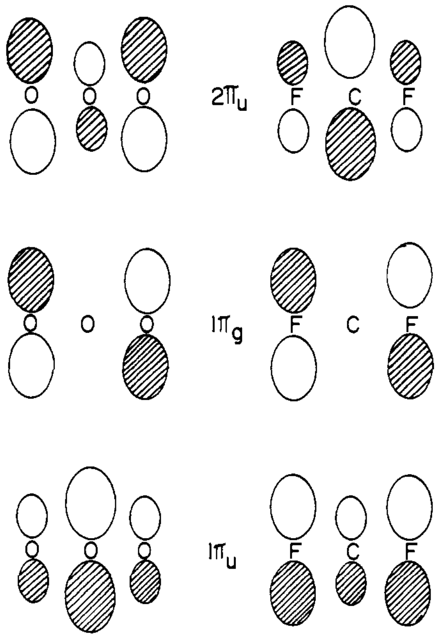

Figure 13. Sketches of one member from each degenerate pair of π MO's for linear CF_2 and O_3. The relative electronegativities of C and F act to enhance coefficients of F in the $1\pi_u$ MO and therefore decrease the coefficients of F in the $2\pi_u$ MO. In O_3, this factor is absent, so end atoms have enhanced coefficients in the $2\pi_u$ MO.

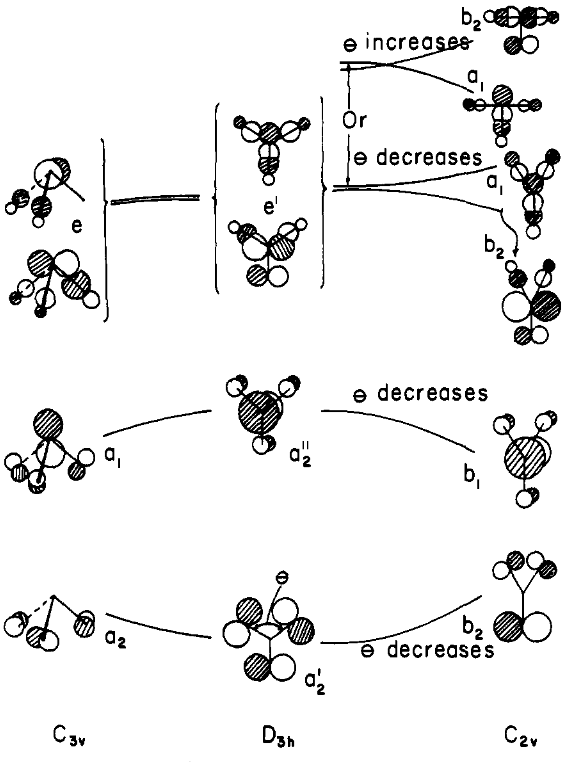

Figure 14. Some MO's for AB_3 systems in various geometries.

many of the agreements and disagreements are only tentative.]

AB_2 molecules having 16–19 valence electrons have as LUMO an antibonding MO which correlates with a degenerate pair of π_u MO's in the linear geometry (see Figure 12). The anions of these systems should be bent and, in the absence of any new effects, should have EA's smaller than or in the neighborhood of the smaller atomic value. The data in Table VII indicate that this rule does not always work. CO_2 and CS_2, which go from linear neutrals to bent but fairly open anions (O-C-O⁻ angle = 135°[193]), do obey the rule, whereas O_3 and NO_2, which go from bent molecule to very bent anion (O-N-O⁻ angle = 109°[194]), have well-characterized EA values greater than those for the *more* electronegative atom. Evidently, something is happening to offset the antibonding nature of the LUMO in these systems. A likely explanation for this is related to the fact that these MO's are end-to-end bonding. In cases where the B-A-B angle is relatively small, the B- - -B bonding aspect may be dominating the B-A antibonding aspect. [In fact, inspection of Figure 12 suggests that the B-A interaction has lost a good deal of its antibonding character in the a_1 MO.] This is most likely to happen in systems where these MO's are primarily on the B atoms, less on A. This in turn tends to happen in systems where A is not much less electronegative than B. [See Figure 13 for an explanation of this.] It is noteworthy that O_3 and NO_2 are the two compounds in Table VII for which the A,B electronegativity difference is smallest. If this explanation is the correct one, then EA(S_3) may also be enhanced enough to exceed EA(S). [For an early discussion of AB_2 MO's and their effects on molecular shape and ionization potential, see the work of Mulliken.[195]] NF_2 does not satisfy this electronegativity requirement, so the LUMO for this highly bent system should possess significant N-F antibonding character in addition to some F-F bonding character. However, the N atom is partially positive due to the electronegativity difference, and this should make this atom more attractive for an added electron. While considerations like this may provide after-the-fact rationalizations for cases such as NF_2 and $SiCl_2$, they are difficult to employ as predictors.

AB_3. CO_3 has C_{2v} symmetry with probably a fairly small (ca. 80–90°) unique O-C-O angle.[196] The LUMO for this molecule has b_2 symmetry[196,197] (see Figure 14). Occupation of this MO should open up the unique angle and make the molecule closer to D_{3h} in symmetry. This MO is nonbonding and polycentric, so we expect EA(CO_3) > EA(O), as is the case (see Table VIII). Addition of another electron makes the

D_{3h} shape most stable (NO_3^-, PO_3^-). Again, both NO_3 and PO_3 should have EA's greater than 1.46 eV. The value for PO_3 is not known. The next MO is a_2'' in D_{3h} symmetry.[196,205] Occupation of this should produce a slight tendency to fold the system into a C_{3v} pyramidal structure.[196] This MO is principally located on the central atom and is weakly antibonding. The EA values for SO_3, CF_3, and CCl_3 are consistent with this being practically a nonbonding orbital. The enhanced EA's may be attributable to the electronegativity differences between edge and central atoms which would act to make the central atoms electron deficient in the neutral molecules. A 27th or 28th valence electron should enter an e MO in C_{3v} symmetry (correlates with e′ in D_{3h}).[196] This is an antibonding MO, so EA(AB_3) should be smaller than or in the neighborhood of the smaller atomic EA. EA(PCl_3) fits this prescription but EA(PBr_3) seems a little too large. When SF_3 gains an electron we have a 28-valence electron system, isoelectronic with ClF_3, which is T shaped.[196] If SF_3^- is also T shaped, then the extra electron occupies an MO (a_1) which has some antibonding character, though less than in the e(C_{3v}) MO just discussed. Thus, we would predict an EA(SF_3) of around 2.1 eV whereas it appears to be around 3 eV. Again, since this MO is heavily concentrated on the S atom, this unexpectedly large EA may result from the electronegativity of the fluorines.

Conclusions

This comparison of MO characteristics with molecular EA values indicates that qualitative MO reasoning can be helpful in understanding molecular EA's. It appears that one can use the approach to make rough estimates of EA's for small molecules, especially those having a fair degree of symmetry. Lack of agreement between the theory and accurate data focuses attention on cases where factors operate which are not adequately handled in this simple approach. As is usually the case, these "exceptions to the rules" will probably be the most fertile for further study.

The restriction of this paper to small molecules is not meant to imply that similar MO notions cannot be applied to the electronegativities of larger molecules. Indeed, some good correlations between LUMO energies and electron affinities have already been demonstrated for certain classes of related large molecules.[206]

Acknowledgment. It is a pleasure to thank Professor B. M. Gimarc for an opportunity to make an extended research visit to the University of South Carolina. There, untrammeled by the usual responsibilities, I was able to do much of the research described in this article. I also acknowledge a helpful discussion with Dr. Oakley Crawford.

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On the Tilt and Asymmetry of Methyl Groups in Asymmetric Environments

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Abstract: An interpretation of the tilt and asymmetry of methyl groups in asymmetric environments is sought by means of ab initio calculations on a variety of geometry-optimized conformations of methylamine, nitrosomethane, methanol, and methylborine. Constraining parts of the molecules to nonequilibrium geometries and allowing the remainder to seek the minimum energy structure provides additional data beyond that available from the stable form. Localized orbitals and Mulliken population analyses are used in examination of the electronic structures. The methyl tilt can be interpreted as a combination of bond-bond repulsions between the C–H and X–H bonds and between the X–H bonds and the lone pair. Both are important, although the C–H···X–H interaction is dominant. The observed asymmetric differences in the C–H bond lengths are also discussed.

The C_{3v} symmetry of a methyl group need not be preserved in any compound in which it is attached to an asymmetric group. Relatively little experimental information exists on the extent to which such distortion occurs, but some data have become available.

As a first approximation, the methyl group may be treated as a rigid, symmetric rotor and the angle which the symmetry axis of the group makes with the C–X direction used as a structural parameter to be determined experimentally. This angle is known as the methyl tilt. Most cases that have been studied involve an atom X with one or more lone pairs of electrons, in which case the tilt has been determined to fall in the range from 2 to 4° and to be invariably directed toward the lone pair. Some compounds in which this has been observed are shown in Table I.

In some cases, the full asymmetry of the methyl group has been explored experimentally. This has been possible in some studies by microwave spectroscopy,[2] and a recent series of infrared studies[3] has indicated that the methyl C–H bond trans to a lone pair on the substituent atom X is generally longer than the other two. The differences in C–H bond distances are on the order of 0.01 Å and the angular asymmetries within the methyl group range up to 3.5°.

Several ab initio calculations on methanol,[4-6] methylamine,[6-8] methyl mercaptan,[6] and dimethylamine[9] have shown that experimentally measured methyl tilts are very well reproduced within the LCAO-MO-SCF approximation. It may at first seem surprising that such minor structural features may be predicted with high accuracy, but the major sources of error in the Hartree–Fock method, finite basis sets and neglect of electron correlation, are of minimal importance here. The difference in electron correlation produced by tilting a methyl group a few degrees is certainly insignificant. The energy optimization used in the SCF iteration weighs most heavily the electron distribution near the nuclei, so that properties such as the dipole moment which are sensitive to the charge density at large distances from the nucleus require a large basis set for accurate determination. The angular geometry of molecules, however, is most sensitive to the charge density in the bonding region near the central atom, and it appears that an extremely close approximation to the Hartree–Fock limit is not required. In spite of the several studies on methyl group tilt, few attempts have been made to analyze the behavior in terms of localized orbitals and coulomb or exchange effects as has been done, for example, with rotational barriers.[10]

The purpose of this paper is to seek a simple model which explains the methyl group asymmetries. In structural chemistry, such explanations are usually constructed by examining data on known, stable substances and seeking correlations which have predictive power. Molecular orbital calculations have introduced a powerful new tool for such purposes in that structures which are artificially constrained in some desired manner may also be examined. In effect, one may distort the molecule in a selected way and then, by energy optimization of the remaining geometrical parameters, see how the rest of the molecule responds to this distortion. The test of the "bent bond explanation" for the methyl tilt in methylamine discussed below provides a particularly straightforward illustration of this procedure.

Details of the Calculations

Several series of geometry-optimized ab initio calculations have been made on methylamine staggered, eclipsed, and in two conformations with the amine planar; nitrosomethane staggered and eclipsed; methanol staggered and eclipsed; and methylborine with the borine planar, eclipsed, and staggered. The conformations examined are sketched in Figure 1.

All calculations were made by solving the Roothaan LCAO-MO-SCF equations[11] using a basis set of Gaussian atomic orbitals. A set with 7s and 3p functions on the heavy atoms and 4s on the hydrogens was contracted to 4s and 2p on the heavy atoms and 2s on hydrogen. The exponents and contraction coefficients were those of Roos and Siegbahn[12] for carbon, oxygen, and nitrogen and Huzinaga's exponents[13] scaled with 1.25 for hydrogen. The calculations were performed with the program MOLPRO, written by Pulay and Meyer. The program uses Gaussian lobe functions to approximate the p functions. All geometries were optimized using the gradient method of Pulay[14] and the force field for methylamine found by Pulay and Török.[7] The gradient method calculates analytically the forces acting on the atoms as functions of the internal parameters and greatly facilitates the geometry optimization. Geometries were optimized until the predicted changes in the angles were less than 0.2° and the