

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U.S. Patent Office. © Copyright, 1977, by the American Chemical Society

VOLUME 99, NUMBER 19

SEPTEMBER 14, 1977

Molecular Orbital Theory of the Electronic Structure of Molecules. 34. Structures and Energies of Small Compounds Containing Lithium or Beryllium. Ionic, Multicenter, and Coordinate Bonding

James D. Dill,^{1a,b} Paul v. R. Schleyer,^{*1c} J. Stephen Binkley,^{1d} and John A. Pople^{*1d}

Contribution from the Departments of Chemistry, Princeton University, Princeton, New Jersey 08540, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213, the Institute of Organic Chemistry, University of Erlangen-Nuremberg, 8520 Erlangen, West Germany, and Physicalisch Chemisches Institut der Universität Basel, 2056 Basel, Switzerland. Received August 31, 1976

Abstract: A systematic set of 33 neutral molecules and molecular complexes is examined, each containing lithium or beryllium and one other heavy atom. These include singly bonded MX (M = Li, BeH) for all X of the first short period (Li to F), doubly bonded BeY (Y = Be, BH, CH₂, NH, O), hydrogen-bridged metal complexes MH...M'H (M' = Li, BeH, BH₂), and coordinate donor-acceptor complexes HM...D (D = NH₃, OH₂, FH). Geometries are optimized at the STO-3G level followed by single 6-31G* calculations. Single bonds in MX molecules with lone pair X are predicted to be too short at STO-3G due to exaggerated MX π bonding. Bonds in MM' and MCH₃ species are long and relatively weak; the lengths of these appear to be well reproduced by the theory. Structures of MX compounds reflect optimum arrangements for π bonding (NH₂ planar, OH linear). Lowest energy geometries of metal hydrides may be bound through two or three bridging hydrogen atoms. Three are favored in LiBH₄ and BeBH₅ and two in Li₂H₂, LiBeH₃, and Be₂H₄.

In previous papers of this series,²⁻⁵ a major aim has been to develop a systematic and extensive "model chemistry" in which varieties of molecules are examined theoretically at a uniform level of approximation. In studying series of compounds, we do not require molecular descriptions which are accurate in an absolute sense but may employ reasonably inexpensive levels of theory to examine relationships among structures and energies. Early applications of this model have dealt largely with molecules well characterized experimentally and have served to calibrate the predictive ability of the theory. At this point, we may proceed with confidence into experimentally inaccessible or unexplored areas to model further structural and energetic trends.

The study of small compounds involving lithium and beryllium is a natural extension of previous work. While many of the structures in the present paper have not been observed experimentally as monomeric species, it is nevertheless worthwhile to examine these small compounds for comparison with those studied at the same level elsewhere.^{4,5} In fact, the present contribution fills one of the last major gaps in a complete model chemistry involving bonds between first-row elements. The set of molecules comprising this complete system is well defined and includes only neutral one- and two-heavy-atom species, specifically the two hydrides LiH and BeH₂, the

singly bonded molecules combining Li or HBe with any of the first-row radicals (Li, BeH, BH₂, CH₃, NH₂, OH, F), the molecular complexes combining LiH or BeH₂ with first-row hydrides (LiH, BeH₂, BH₃, CH₄, NH₃, OH₂, FH), and the formally doubly bonded combinations of Be with Be, BH, CH₂, NH, and O. For the formally doubly-bonded Be systems, both singlet and triplet states are considered.

Known compounds of lithium and beryllium span a wide range of structural types.⁶⁻⁹ Electron deficiency in these species is manifested in high degrees of association and solvation, while electronegativity differences lead to high degrees of ionic character in LiX and BeX bonds. Structures of lithium and beryllium compounds thus involve multicenter electron-deficient, coordinate, ionic, and covalent bonding. Depending on the surrounding medium, the organometallic system R-M (M = Li or BeR) may be accurately represented as oligomeric (R-M)_n, base-coordinated R-M(:B)_n, or ionic R⁻M⁺. Gas-phase structures are usually associated, consisting of small polyhedra of metal atoms bridged by organic radicals. However, in studying lithium and beryllium chemistry systematically, we begin with small (two-heavy-atom) systems in order to understand the nature of the various bond types, the corresponding bond strengths, and the factors which lead to molecular association.

Table I. Theoretical Energies of Lithium and Beryllium Compounds

No.	Formula	Structure ^a	Energy, STO-3G		Energy, 6-31G*	
			Total ^b	Rel ^c	Total ^b	Rel ^c
Lithium Compounds						
1	LiH	LiH	-7.863 38		-7.978 74	
2	Li ₂	LiLi	-14.638 75		-14.866 56	
3	Li ₂ H ₂	Li-(H) ₂ -Li	-15.796 81	0	-16.031 99	0
4		LiH-LiH	-15.765 11	19.89	-15.999 33	20.48
5	LiBeH	Li-BeH	-22.297 19		-22.607 72	
6	LiBeH ₃	Li-(H) ₂ -BeH	-23.481 86	0	-23.808 33	0
7		Li-(H) ₃ -Be	-23.458 04	14.95	-23.785 78	14.09
8		LiH-BeH ₂	-23.442 47	24.72	-23.773 26	21.95
9		HLi-HBeH	-23.440 42	26.00	-23.757 15	32.06
10	LiBH ₂	LiBH ₂	-32.776 71		-33.208 03	
11	LiBH ₄	Li-(H) ₃ -BH	-34.002 47	0	-34.447 11	0
12		Li-(H) ₂ -BH ₂	-33.992 07	6.53	-34.438 55	5.37
13		LiH-BH ₃	-33.950 83	32.41	-34.404 18	26.94
14		HLi-(H) ₂ -BH	-33.945 69	35.63	-34.374 31	45.68
15		HLi-HBH ₂	-33.943 65	36.91	-34.372 89	46.58
16	LiCH ₃	LiCH ₃	-46.421 59		-47.015 33	
17	LiCH ₅	HLi-(H) ₂ -CH ₂	-47.599 64		-48.177 55	
18	LiNH ₂	LiNH ₂	-62.206 51		-63.037 37	
19	LiNH ₄	HLi-NH ₃	-63.397 96		-64.201 03	
20	LiOH	LiOH	-81.768 57		-82.890 73	
21	LiOH ₃	HLi-OH ₂	-82.914 28		-84.020 25	
22	LiF	LiF	-105.373 09		-106.923 57	
23	LiFH ₂	HLi-FH	-106.515 56		-108.000 82	
Beryllium Compounds						
24	BeH ₂	HBeH	-15.561 35		-15.764 74	
25	Be ₂ H ₂	HBeBeH	-29.981 56		-30.376 70	
26	Be ₂ H ₄	HBe-(H) ₂ -BeH	-31.154 00		-31.568 46	
27	BeBH(¹ A')	BeBH	-39.125 91		-39.691 67	
28	BeBH(³ Π)	BeBH	-39.216 27 ^f		-39.757 98 ^f	
29	BeBH ₃	HBeBH ₂	-40.484 89		-40.995 39	
30	BeBH ₅	HBe-(H) ₃ -BH	-41.669 88	0	-42.203 78	0
31		HBe-(H) ₂ -BH ₂	-41.667 59	1.44	-42.198 71	3.19
32	BeCH ₂ (¹ A ₁)	BeCH ₂	-52.799 86		-53.490 46	
33	BeCH ₂ (³ B ₁)	BeCH ₂	-52.897 59 ^f		-57.577 887 ^f	
34	BeCH ₄	HBeCH ₃	-54.153 21		-54.815 26	
35	BeNH(¹ Σ ⁺)	BeNH	-68.638 44		-69.542 06	
36	BeNH(³ Π)	BeNH	-68.684 87 ^f		-69.594 81 ^f	
37	BeNH ₃	HBeNH ₂	-69.942 64		-70.847 00	
38	BeNH ₅	H ₂ Be-NH ₃ cis ^d	-71.091 11	0	-71.980 33	0
39		H ₂ Be-NH ₃ perp ^e	-71.091 07	0.03	-71.980 27	0.04
40	BeO(¹ Σ ⁺)	BeO	-88.187 71		-89.408 26	
41	BeO(³ Π)	BeO	-88.240 48 ^f		-89.452 93 ^f	
42	BeOH ₂	HBeOH	-89.495 81		-90.697 58	
43	BeOH ₄	H ₂ Be-OH ₂ planar ^d	-90.609 97	0	-91.797 13	0
44		H ₂ Be-OH ₂ perp ^e	-90.598 06	7.47	-91.788 57	5.37
45	BeFH	HBeF	-113.121 60		-114.722 76	
46	BeFH ₃	H ₂ Be-FH planar ^d	-114.202 96	0	-115.772 62	0
47		H ₂ Be-FH perp ^e	-114.196 19	4.25	-115.766 78	3.66

^a The notation "-(H)_n- " indicates *n* equivalent bridging hydrogens. A "-." indicates a bond containing formally fewer than two electrons. See text. ^b In hartrees, at STO-3G optimized geometry. Unless stated otherwise, energies refer to singlet state. ^c Energy (kcal mol⁻¹, where 1 hartree = 627.53 kcal mol⁻¹) relative to lowest energy isomer. ^d H-A-B-H coplanar. ^e H-A-B-H dihedral angle = 90°. ^f Energy obtained by the UHF procedure of Pople and Nesbet (ref 16).

Methods

Two levels of *ab initio* single-determinant molecular orbital theory were employed as in previous studies.²⁻⁴ First, the minimal STO-3G basis set,¹⁰ which includes a full set of p functions on Li and Be, was used together with standard molecular scaling factors for geometry optimizations. For each of the 47 structures listed in Table I, all independent geometrical parameters were varied until the energy was minimized. Minimum STO-3G energies are given in Table I, the corresponding geometries in Tables II and III. Also given are the final symmetry point groups assumed during each optimization, although in most cases a lower symmetry than that

specified was assumed at the outset. However, individual structures were not studied with respect to stability to all displacements, so that some may not represent the local potential minima. Not given in the tables are several metal hydride dimers calculated with partial geometry optimization. These are discussed below under the appropriate headings. In these systems, it was found after some variation of the most critical geometrical parameters that the dimer energy did not fall below the sum of monomer energies, and further study was deemed unnecessary.

Following STO-3G geometry optimizations, single calculations were carried out at the 6-31G* level using the STO-3G

Table II. STO-3G Geometries of Structures without Bridging Hydrogens

No. ^a	H _n A-BH _m	Symmetry	Geometrical parameters ^b
1	Li-H	C _{∞v}	A-H = 1.510
2	Li-Li	D _{∞h}	A-B = 2.696
5	Li-BeH	C _{∞v}	A-B = 2.384; B-H = 1.300
10	Li-BH ₂	C _{2v}	A-B = 2.194; B-H = 1.164; ∠HBH = 112.4
16	Li-CH ₃	C _{3v}	A-B = 2.009; B-H = 1.083; θ ₄ = 112.6
18	Li-NH ₂	C _{2v}	A-B = 1.635; B-H = 1.026; ∠HBH = 102.3
19	HLi- -NH ₃	C _{3v}	A-B = 1.944; A-H = 1.514; B-H = 1.028; θ ₄ = 113.0
20	Li-OH	C _{∞v}	A-B = 1.432; B-H = 0.971
21	HLi- -OH ₂	C _s	A-B = 1.765; A-H ₃ = 1.513; B-H ₅ = 0.977; θ ₃ = 167.9; θ ₅ = 144.3
22	Li-F	C _{∞v}	A-B = 1.407
23	HLi- -FH	C _s	A-B = 1.627; A-H ₂ = 1.512; B-H ₄ = 0.937; θ ₂ = 168.9; θ ₄ = 149.0
24	HBe-H	D _{∞h}	A-H = 1.291
25	HBe-BeH	D _{∞h}	A-B = 2.062; A-H = 1.295
27	Be= BH (¹ A')	C _s	A-B = 1.966; B-H ₄ = 1.186; θ ₄ = 120.5
28	Be= BH (³ Π)	C _{∞v}	A-B = 1.744; B-H ₄ = 1.162
29	HBe-BH ₂	C _{2v}	A-B = 1.860; A-H = 1.292; B-H = 1.163; ∠HBH = 114.9
32	Be=CH ₂ (¹ A ₁)	C _{2v}	A-B = 1.472; B-H = 1.083; ∠HBH = 111.2
33	Be=CH ₂ (³ B ₁)	C _{2v}	A-B = 1.652; B-H = 1.086; ∠HBH = 111.1
34	HBe-CH ₃	C _{3v}	A-B = 1.691; A-H = 1.291; B-H = 1.085; θ ₄ = 111.8
35	Be=NH(¹ Σ ⁺)	C _{∞v}	A-B = 1.288; B-H = 1.021
36	Be=NH(³ Π)	C _{∞v}	A-B = 1.438; B-H = 1.027
37	HBe-NH ₂	C _{2v}	A-B = 1.457; A-H = 1.287; B-H = 1.020; ∠HBH = 108.4
38	H ₂ Be- -NH ₃ cis	C _s	A-B = 1.747; A-H ₂ = 1.296; A-H ₃ = 1.296; B-H ₄ = 1.029; B-H ₅ = 1.030; θ ₂ = 112.9; θ ₃ = 111.3; θ ₄ = 113.6; θ ₅ = 126.4; ∠HBH = 106.2
39	H ₂ Be- -NH ₃ perp	C _s	A-B = 1.747; A-H ₁ = 1.296; B-H ₄ = 1.030; B-H ₅ = 1.030; θ ₁ = 178.8; ∠HAH = 135.8; θ ₄ = 111.0; θ ₅ = 130.2; ∠HBH = 107.7
40	Be=O(¹ Σ ⁺)	C _{∞v}	A-B = 1.269
41	Be=O(³ Π)	C _{∞v}	A-B = 1.435
42	HBe-OH	C _{∞v}	A-B = 1.301; A-H = 1.285; B-H = 0.961
43	H ₂ Be- -OH ₂ planar	C _{2v}	A-B = 1.582; A-H = 1.296; B-H = 0.975; ∠HAH = 138.1; ∠HBH = 109.3
44	H ₂ Be- -OH ₂ perp	C _s	A-B = 1.674; A-H ₂ = 1.294; A-H ₃ = 1.298; B-H ₅ = 0.982; θ ₂ = 112.8; θ ₃ = 110.0; θ ₅ = 126.1; ∠HBH = 103.7°
45	HBe-F	C _{∞v}	A-B = 1.299; A-H = 1.285
46	H ₂ Be- -FH planar	C _s	A-B = 1.588; A-H ₂ = 1.297; A-H ₃ = 1.292; B-H ₄ = 0.945; θ ₂ = 108.0; θ ₃ = 110.3; θ ₄ = 114.5
47	H ₂ Be- -FH perp	C _s	A-B = 1.621; A-H ₁ = 1.294; B-H ₄ = 0.946; θ ₁ = 174.6; ∠HAH = 140.8; θ ₄ = 114.7

^a Corresponding to the numbering in Table I. ^b Distances in ångströms, angles in degrees. For positions of numbered hydrogens and angles (H_n, θ_n) refer to Figure 1. No numbering is given when symmetry eliminates ambiguity.

geometries. In the 6-31G* basis set,¹¹ d-type polarization functions on heavy atoms supplement an extended split-valence basis set (6-31G), which has recently been developed for Li, Be, and B,^{12a,b} and is specified elsewhere for C, N, O, and F.¹³ In the calculations involving beryllium compounds that are reported here, the new 6-31G* basis, derived from energy optimization of the beryllium ³P excited state, has been used.^{12b} Standard d exponents were used (Li = 0.2, Be = 0.4, B = 0.6, C-F = 0.8). Calculated 6-31G* energies are given in Table I.

The calculations reported in this paper were carried out with the "GAUSSIAN 70" series of programs and modifications to it.^{11,14} Singlet states were computed using standard single-determinant spin-restricted Hartree-Fock theory (RHF).¹⁵ Open-shell states were calculated using the spin-unrestricted Hartree-Fock (UHF) formalism of Pople and Nesbet.¹⁶

Results

Geometries. Specifying structures of the types included in this paper, it is convenient to employ dashed lines to indicate a bond containing formally fewer than two electrons. Thus if M is a metal atom (Li-B), D a lone-pair donor (N-F), and H hydrogen, then "M- -D" represents a coordinate bond (Lewis acid-base interaction), "MH- -M" a single hydrogen bridge between metal atoms, and "M- -(H)_n- -M" a bridge of *n* (equivalent) hydrogens. In this notation, diborane is designated H₂B- -(H)₂- -BH₂ and the hydrogen-bonded dimer of water as HOH- -OH₂. Throughout this paper, structures are iden-

tified using this notation as well as by the numbers assigned in Table I.

In order to specify detailed geometries, we separate the complete list of molecules into two categories distinguishing those without bridging hydrogens (Table II) from those with (Table III). The former group is described with reference to the geometrical fragments in Figure 1. In order to visualize a particular structure, the right-hand fragment of Figure 1 is joined, without rotation from the plane of the paper, to one of the left-hand fragments (the numbered hydrogens in Table II specify which one). The assembled picture then has five hydrogens, some subset of which corresponds to the actual structure. The structure is determined from the specified symmetry, the molecular formula, and the correspondence between hydrogen numbers in Figure 1 and Table II.

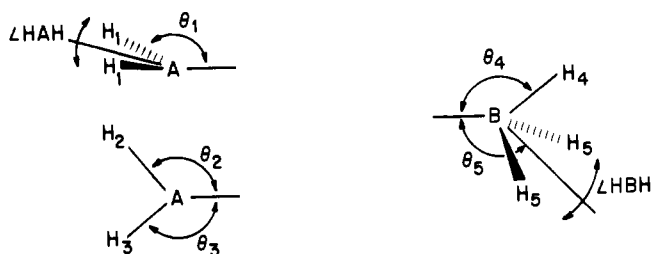
Each hydrogen-bridged structure is described by one of the diagrams in Figure 2. In the figure, five general shapes are depicted, each having one to three equivalent bridging hydrogens H_{br}. In order to specify a bridged structure fully, the general shape (1-5) is given along with letters (a, b, b') indicating which of the terminal hydrogens drawn in the figure is present in the structure. All bridging hydrogens in the figure are present in each case. The digit-letter combination gives the structure type and is listed in Table III along with the symmetry. Also given are the bond lengths and terminal (HMH) angles, specified with reference to the labels in Figure 2. We now discuss the structures individually.

Lithium Compounds. (1) LiH. Lithium hydride, having only

Table III. Geometries of Bound Dimers of LiH or BeH₂ with LiH, BeH₂, BH₃, and CH₄

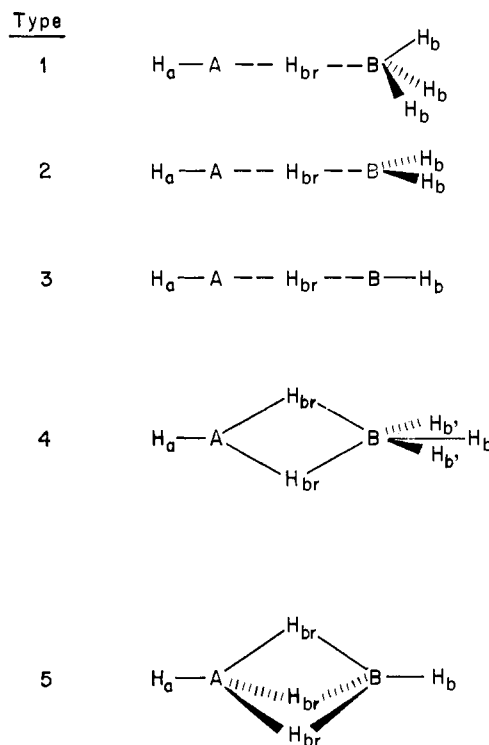
No. ^a	Structure ^b	Type ^c	Symmetry	Geometrical parameters ^d					Ref	
				H _a -A	A-H _{br}	A-B	H _{br} -B	B-H _b		∠H _b -B-H _b ^e
STO-3G Geometries										
3	Li-(H) ₂ -Li	4	<i>D</i> _{2h}		1.701	2.222	1.701			
4	LiH-LiH	3b	<i>C</i> _{∞v}		1.565	3.332	1.767	1.512		
6	Li-(H) ₂ -BeH	4b	<i>C</i> _{2v}		1.694	2.158	1.440	1.286		
7	Li-(H) ₃ -Be	5	<i>C</i> _{3v}		1.907	1.843	1.358			
8	LiH-BeH ₂	2b	<i>C</i> _{2v}		1.553	3.121	1.568	1.292	138.6	
9	HLi-HBeH	3ab	<i>C</i> _{∞v}	1.510	1.865	3.183	1.317	1.290		
11	Li-(H) ₃ -BH	5b	<i>C</i> _{3v}		1.788	1.877	1.231	1.149		
12	Li-(H) ₂ -BH ₂	4b'	<i>C</i> _{2v}		1.662	2.084	1.271	1.156	115.9	
13	LiH-BH ₃	1b	<i>C</i> _{3v}		1.534	2.924	1.391	1.159	115.2	
14	HLi-(H) ₂ -BH	4ab	<i>C</i> _{2v}	1.509	2.188	2.516	1.178	1.158		
15	HLi-HBH ₂	2ab	<i>C</i> _{2v}	1.510	1.915	3.098	1.184	1.159	123.0	
17	HLi-(H) ₂ -CH ₂	4ab'	<i>C</i> _{2v}	1.509	2.093	2.486	1.094	1.083	110.6	
26	HBe-(H) ₂ -BeH	4ab	<i>D</i> _{2h}	1.285	1.464	1.991	1.464	1.285		
30	HBe-(H) ₃ -BH	5ab	<i>C</i> _{3v}	1.284	1.599	1.687	1.241	1.146		
31	HBe-(H) ₂ -BH ₂	4ab'	<i>C</i> _{2v}	1.286	1.469	1.876	1.297	1.154	120.4	
Other Theoretical Geometries										
3	Li-(H) ₂ -Li	4	<i>D</i> _{2h}		1.81	2.36	1.81			43
		4	<i>D</i> _{2h}		1.75	2.26	1.75			26
4	LiH-LiH	3b	<i>C</i> _{∞v}		1.62	3.45	1.83	1.67		43
26	HBe-(H) ₂ -BeH	4ab	<i>D</i> _{2h}	1.3	1.5	2.1	1.5	1.3		100
30	HBe-(H) ₃ -BH	5ab	<i>C</i> _{3v}	1.32	1.60	1.69	1.26	1.19		105a
31	HBe-(H) ₂ -BH ₂	4ab'	<i>C</i> _{2v}	1.32	1.48	1.90	1.32	1.19	120.0	105a

^a Corresponding to the numbering in Table I. ^b As in Table I. ^c The digit corresponds to one of the dimer shapes in Figure 2. The letter indicates which of the terminal hydrogens illustrated is present in the structure. ^d Bond lengths in ångströms. Hydrogen labels refer to Figure 2. ^e Angles given in degrees.

**Figure 1.** Molecular fragments defining geometrical parameters.

four electrons, has been a favorite among theoreticians as a test case for new quantum mechanical methods. Recent bibliographies of *ab initio* calculations^{17,18} list over 120 entries for LiH through 1973. These include the extensive study of first-row hydrides by Cade and Huo,¹⁹ in which the ground state Hartree-Fock limit of LiH is determined (-7.987 31 hartrees) and the systematic configuration-interaction (CI) studies on diatomics by Fraga and Ransil,²⁰ Bender and Davidson,²¹ and recently Meyer and Rosmus.²² All of these include reviews of previous work. Excited states of LiH have been investigated,^{23,24} and recent high-quality CI^{25,26} and valence bond^{27,28} calculations have appeared. The lowest energy obtained to date appears to be that of Boys and Handy,²⁹ who present a "transcorrelated" wave equation, obtaining $E = -8.063$ hartrees compared to the experimental estimate¹⁹ of -8.070.

Lithium hydride is known as an ionic NaCl-like solid³⁰ and as a polar gas-phase monomer. The bond length in the latter ($r_e = 1.595$ Å)³¹ is somewhat larger than the STO-3G value of 1.510 Å (Table II). On the other hand, the bond length calculated at 5-21G³² is too long (1.637 Å) as is that obtained from optimization at the Hartree-Fock limit (1.605 Å).¹⁹ This behavior is opposite that of hydrides of more electronegative atoms (CH₄ through FH), where STO-3G generally overestimates³ while 4-31G³ and higher basis sets³³ underestimate A-H distances. We find a regular trend along the first row:

**Figure 2.** Prototype molecules defining hydrogen positions.

STO-3G gives bond lengths too short (by 5.3%) for LiH, improving until fairly precise for CH₄, and then becoming too long (by 4.1%) for FH. With the split valence bases, LiH is too long by 2.6%, FH too short by 0.5%.

The electronic properties of LiH have been determined with precision.³⁴ The experimental dipole moment is $\mu_e = 5.828$ D,^{34b} in the direction Li⁺H⁻. Our calculated values of 4.84 (STO-3G) and 5.74 (6-31G*) agree satisfactorily. It is ap-

appropriate to mention that Mulliken population analysis³⁵ of the STO-3G wave function indicates total atomic charges of -0.017 on Li, $+0.017$ on H, *opposite* the polarity implied by the dipole moment. This is to some extent an artifact of the population scheme, but it serves as an indication that the minimal basis set is unbalanced with regard to lithium. p functions on lithium resemble polarization functions, providing a degree of flexibility not available to heavier atoms; in the population analysis, these orbitals are assigned an unrealistically high degree of electron density. Opposite problems are experienced in describing fluorine compounds at the minimal basis set level.³⁶

(2) **Li₂**. The lithium molecule (dilithium) is a simple homonuclear diatomic species which has also been popular among theoreticians.^{20,37-41} A thorough analysis of bonding in the first row X₂ systems⁴¹ demonstrates Li₂ to have little interatomic p overlap, resulting in a long weak σ bond. The experimental bond length³¹ is 2.672 \AA , in good agreement with STO-3G (2.696), and represents the longest known (or calculated) single bond between first-row atoms in a two-heavy-atom species.

(3, 4) **Li₂H₂**. Although there has been no experimental observation of a dimer of LiH, there is reason to believe that such a structure is stable. The evidence stems from previous theoretical studies of Li₂H₂^{26,42,43} and from inference based on the gas-phase behavior of alkali halides.^{44,45} In the first category, Tyndall and Companion⁴² applied the semiempirical diatomics-in-molecules (DIM) method to the Li₂H₂ potential surface, finding the *D*_{2h} dimer (3) to be less favorable than a nonplanar *C*_{2v} form resulting from perpendicular interaction of Li₂ with H₂. However, linear Li₂H₂ arrangements were found to decrease in stability LiLiHH > LiHHLi > LiHLiH (=4) > HLiLiH, the first of these being more stable than either separated Li₂ + H₂ or the *D*_{2h} dimer (3). These results appear contradictory to our own, but the accuracy of the DIM method is difficult to assess.

More recently, Kollman et al.⁴³ have applied ab initio and CI methods to both dimers 3 and 4. Using a large basis of s and p functions, they obtain $r = 1.633 \text{ \AA}$ and $E = -7.98262 \text{ au}$ for LiH itself. This bond length is close to that found at 4-31G (5-21G)³² but the energy is slightly lower than 6-31G*. The geometries of 3 and 4 obtained by Kollman et al. are given in Table III along with STO-3G results. Their larger basis gives *all* bonds longer than STO-3G values and provides an interpretation of the linear dimer (4) which differs somewhat from ours, as discussed below.

The *D*_{2h} dimer has also been studied by Ahlrichs^{100b} using a large basis set and the CEPA correlation method. The CEPA structure (Table III) is intermediate between the STO-3G geometry and that of Kollman et al.⁴³

Our results suggest that the *D*_{2h} dimer (3) is the most stable form. In this, two LiH molecules are bound together in such a way that the Li-Li distance (2.22 \AA) is smaller than in Li₂ (2.70 \AA). Thus the three-center two-electron Li(H)Li bond is shorter than the two-center two-electron Li-Li bond. Also upon dimerization the Li-H monomer distances increase by 13% to 1.70 \AA in the dimer. There is precedent for these changes in the dimerization of BH₃ to B₂H₆, in which bridging B-H distances are significantly longer than terminal B-H lengths, and the B-B distance is similar to that calculated for planar H₂B-BH₂.⁴

The linear LiH dimer (4) is bound by what is conceptually similar to a hydrogen bond but with opposite electronic properties. The principal binding force is the interaction of LiH dipoles which might be schematically represented as Li₁→H₁(δ^-)...(δ^+)Li₂→H₂, the hydrogen in the LiH monomers being negatively charged (unlike the hydrogens in the dimer of hydrogen fluoride which are positively charged). This type of binding can also be termed a "lithium bond"⁴⁶ with the positive lithium taking the role of the electron-deficient species.

As the population analysis shows (see below), there is a net transfer of electrons from Li₁-H₁ to Li₂-H₂, leaving the Li-H₁ unit slightly deficient in electrons and causing a lengthening in the Li-H₁ bond to 1.56 \AA (at STO-3G) compared to 1.51 in LiH itself. An opposite effect is found in the study of Kollman et al.,⁴³ where additional s and p functions on H₁ lead to an apparent charge *buildup* at that center according to a Mulliken population analysis, and LiH₂ becomes longer while LiH₁ remains constant. However, this discrepancy between their results and ours is evidently minor, since the two calculated dimerization energies agree closely (see discussion below). It is gratifying to note that the monomer-monomer separation (H₁-Li₂) is in reasonable agreement between the two studies (Kollman 1.83 \AA , STO-3G 1.77). In contrast, the corresponding distance in hydrogen-bonded systems is highly basis set dependent. For example, the O-O distance in H₂O-HOH changes from STO-3G to 4-31G to 6-31G* as $2.73 \rightarrow 2.87 \rightarrow 2.99 \text{ \AA}$ (exptl = 2.98).⁴⁷

Other linear arrangements were investigated with variation of all bond distances. These were HLi- -LiH and LiH- -HLi, neither of which became bound relative to 2 LiH. In addition, the Li₁-H₁- -Li₂ angle of 4 was varied and found to give an energy minimum at 180° .

The geometry of the bridged dimer 3 may be compared with known structures of alkali halide dimers.^{45,48-50} In the vapor phase, LiF (for example) exists primarily as planar cyclic Li₂F₂,⁵⁰ which is approximately 62 kcal mol^{-1} more stable than separated LiF monomers at 100°C .⁴⁵ Calculation of Li₂F₂ at the STO-3G level⁵¹ gives a dimerization energy of $43.6 \text{ kcal mol}^{-1}$ and a geometry of Li-F = 1.596 \AA , F-F = 2.325 \AA , $\angle\text{F-Li-F} = 93.5^\circ$, and $\angle\text{Li-F-Li} = 86.5^\circ$. Like our calculated Li₂H₂ structure, this indicates that the lithiums lie within single-bonding distance of each other and demonstrates an increased Li-F distance (from 1.56 \AA in the monomer⁵²) upon dimerization. Similarly, an electron-diffraction structure of gaseous Li₂Cl₂ (Li-Li = 2.64 \AA ; Cl-Cl = 3.61 \AA ; Li-Cl = 2.23 \AA)⁴⁸ shows the Li-Cl distance to be longer than that of monomeric LiCl (2.02 \AA) but shorter than the Li-Cl distance in the crystalline state (2.57 \AA).⁴⁸ In this sense our STO-3G structure for (LiH)₂ is reasonable in giving LiH = 1.701 \AA , and between the known values of 1.595 for the LiH monomer³¹ and 2.043 for the crystal.⁵³

(5) **LiBeH**. Like the Li-Li single bond, a bond between Li and BeH is expected to be long and weak. We find a linear structure with $r_{\text{Li-Be}} = 2.394 \text{ \AA}$. In support of this is the ab initio study of Kaufman and Sachs on BeLi₂,⁵⁴ in which the Be-Li distance is found to be 2.56 \AA and the structure to be linear.

(6-9) **LiBeH₃**. Mixed polymers containing lithium and beryllium are not unknown. The following stoichiometries have been reported: LiBeR₃⁵⁶ (R = Ph,⁵⁵ OAlk, OSiMe₃), Li₂BeH₄,⁵⁷ Li₂BeMe₄,⁵⁸ LiR₂BeH.⁵⁹ Available x-ray data^{8a,58} on such systems indicate dibridged Be- -(R)₂-Li to be a common structural unit. Our findings concur, the structure Li- -(H)₂- -BeH (6) being the best of the five geometries considered. In-plane dimerization of LiH and BeH₂ is similar to Li₂H₂ or B₂H₆ formation. In the *C*_{2v} form (Li- -(H)₂- -BeH) bonds to the bridging hydrogens from Li and Be are considerably longer than those in monomeric LiH or BeH₂, while the Li-Be distance is shorter than that in LiBeH. The terminal Be-H distance is unchanged upon dimerization.

At somewhat higher energy is a *C*_{3v} structure, Li- -(H)₃- -Be (7), having three equivalent bridging hydrogens. Here, bridge Li-H and Be-H distances are larger than in the doubly bridged form (6), while the Li-Be distance is smaller.

Two linear forms (single bridges) were optimized. In these cases, in addition to the "lithium bond" in HLi- -HBeH (9), we have a "beryllium bond" in LiH- -BeH₂ (8), the latter being slightly stronger. Geometry variations upon dimerization

leading to **8** and **9** are analogous to those leading to linear $(\text{LiH})_2$. The LiH bond increases upon formation of $\text{LiH} \cdot \text{BeH}_2$ but is unchanged in $\text{HLi} \cdot \text{HBeH}$. The Be-H length increases in the bridging position of $\text{HLi} \cdot \text{HBeH}$ but is unchanged in the terminal position and in $\text{LiH} \cdot \text{BeH}_2$. Li-Be distances are roughly the same in both structures, 32% longer than the single bond distance in $\text{Li} \cdot \text{BeH}$. $\text{LiH} \cdot \text{BeH}_2$ (structure **8**) is of C_{2v} symmetry and has a terminal H-Be-H angle of 139° , indicating a tendency toward sp^2 hybridization at beryllium, which obtains charge from the interaction with LiH. The same H-Be-H bending occurs upon coordinate bond formation leading to donor $\rightarrow \text{BeH}_2$ complexes, as discussed below.

(10) LiBH_2 . Lithioborane is an unknown derivative of BH_3 . Its calculated structure is planar (C_{2v}). The effect of substituting BH_3 with a strong σ donor is to reduce the HBH angle from its ideal 120° value, so that the following trend is found along the series of substituted boranes $\text{X} \cdot \text{BH}_2$:⁴ HBH = 112.6° (X = Li), 114.9° (BeH, see below), 117.2° (BH_2 perpendicular), 118.5° (CH_3), 120.0° (H), 121.1° (NH_2), 121.0° (OH), 121.0° (F). The Li-B single bond is fairly long (2.19 \AA) and not very strong.

(11-15) LiBH_4 . Lithium borohydride is a common reducing agent, the crystal structure of which indicates tetrahedral BH_4^- units surrounded by lithium ions with $r_{\text{Li-B}} = 2.47\text{-}2.56 \text{ \AA}$.⁶⁰ The more recent structure of $\text{LiB}(\text{CH}_3)_4$ is analogous⁶¹ and involves both dibridged Li-(Me)₂-B and monobridged Li-(Me)-B units but is apparently poorly described in terms of triple Li-(Me)₃-B bridges.

The $\text{LiH} \cdot \text{BH}_3$ potential surface we calculate is similar to that of $\text{LiH} \cdot \text{BeH}_2$ but with some important differences. The calculated order of decreasing stability is triply bridged Li-(H)₃-BH (**11**) > doubly bridged Li-(H)₂-BH₂ (**12**) > B-bonded Li-H-BH₃ (**13**) > doubly bridged HLi-(H)₂-BH (**14**) > Li-bonded HLi-HBH₂ (**15**). A triple hydrogen bridge is favored, unlike the beryllium systems, where Li-(H)₂-BeH was preferred over Li-(H)₃-Be. Furthermore, doubly bridged HLi-(H)₂-BH is bound relative to $\text{HLi} + \text{BH}_3$, while the corresponding beryllium system (HLi-(H)₂-Be) was not. These preferences will be discussed below along with the dimerization energies.

Detailed geometries of structures **11-15** are as expected by extrapolation from other systems and may be summarized in two general statements. First, metal-metal distances in species having double or triple (but not single) bridging hydrogens are shorter than in covalent molecules having direct metal-metal bonds. Thus, for example, Li-B distances increase as Li-(H)₃-BH < Li-(H)₂-BH₂ < LiBH_2 < $\text{LiH} \cdot \text{BH}_3$. Second, metal-hydrogen distances increase upon dimerization (relative to monomer values) for those hydrogens which become bridging but remain unchanged for terminal hydrogens.

(16) LiCH_3 . It is well established that methyl lithium exists as a tetramer under standard conditions.⁷ The x-ray structure⁶² reveals a tetrahedral array of lithium atoms ($r_{\text{Li-Li}} = 2.56 \text{ \AA}$) above each face of which is centered a methyl group ($r_{\text{C-Li}} = 2.28 \text{ \AA}$). However, at low temperature in an argon matrix, CH_3Li has been observed as a monomer.⁶³ The resulting infrared analysis yielded little structural information apart from the force constant for asymmetric deformation of the methyl group and a very rough estimate of the dipole moment ($\mu = 6 \text{ D}$, assuming $r_{\text{C-Li}} = 2.10 \text{ \AA}$).

Theoretical studies, both semiempirical⁶⁴⁻⁶⁶ and ab initio,⁶⁶⁻⁶⁹ have provided more detailed geometries for methyl lithium and its aggregates, but only one of these studies⁷⁰ included full geometry optimization. In most previous work, the methyl group in LiCH_3 has been assumed to be strictly tetrahedral. We find at STO-3G that the methyl group, while not far from tetrahedral, is more pyramidal than that of any other X-CH₃ system for first-row X. Thus, STO-3G op-

timized values^{4,5} of the average HCH angle vary as 106.2° (LiCH_3), 107.0° (HBeCH_3), 107.7° (H_2BCH_3 perpendicular form),⁴ 108.2° (H_3CCH_3), 108.2° (H_2NCH_3), 108.1° (HOCH_3), 108.3° (FCH_3), where unspecified conformations have staggered hydrogens.

Full STO-3G optimization of LiCH_3 gives a C-Li distance of 2.009 \AA . In an interesting study at STO-2G and STO-3G, Baird et al.⁶⁷ find $r_{\text{C-Li}} = 2.05 \text{ \AA}$, but when $p\pi$ orbitals on Li are removed the value becomes 2.09 \AA . Fitzpatrick⁶⁸ deduces considerable ionic character in the C-Li bond since his calculated $r_{\text{C-Li}} = 2.03 \text{ \AA}$ is smaller than the value of 2.12 \AA obtained from the sum of covalent radii $\frac{1}{2}r_{\text{LiLi}}(\text{Li}_2) + \frac{1}{2}r_{\text{C-C}}(\text{C}_2\text{H}_6)$. All of these minimal-basis estimates are shorter than the 2.10 \AA proposed by Andrews⁶³ on the basis of extrapolations of force constants and other data from known Li-X monomers. However, an estimate of the CH_3Li dipole moment (6 D) made in the same way⁶³ agrees well with that obtained at $6\text{-}31\text{G}^*$ (5.71 D). The structure of methyl lithium has been fully optimized at the $4\text{-}31\text{G}/5\text{-}21\text{G}$ level;^{69e} the C-Li bond actually shortens slightly, to 1.989 \AA and C-H = 1.092 \AA , while the HCH angle increases from 106.2° to 107.3° . This differs somewhat from the recent results of Streitwieser et al.,⁷⁰ who employ three basis sets (STO-4G, split valence, and split valence + polarization) in a thorough examination of methyl lithium. They find the C-Li distance to increase in going from minimal to split-valence levels. Their best basis, which includes d orbitals on carbon but not on lithium, gives $r_{\text{C-Li}} = 2.021 \text{ \AA}$, $r_{\text{C-H}} = 1.089 \text{ \AA}$, and $\angle\text{HCH} = 105.8^\circ$. Altogether these comparisons suggest that the STO-3G structure for CH_3Li is reasonably accurate.

Streitwieser et al. stress that there is very little covalent C-Li bonding in methyl lithium, but an opposite conclusion has been reached by Guest, Hillier, and Saunders. Much depends on how "ionic" or "covalent" character is defined. While we plan to study the problem of the natural bonding in lithium compounds in more detail, we have already emphasized that the peculiar structures adopted by poly lithium compounds^{69a-d} are better understood in terms of multicenter covalent bonding rather than "ion pair" character.

(17) LiCH_5 . The small degree of charge polarization in C-H bonds of methane is sufficient to produce a weak interaction with LiH, giving $\text{H}_2\text{C} \cdot (\text{H})_2 \cdot \text{LiH}$ (**17**). The same C-H charge separation is responsible for the weak $\text{CH}_4 \cdot \text{D}$ hydrogen bonds calculated to exist when D = NH_3 , OH_2 , and FH .^{5,71} For $\text{LiH} \cdot \text{CH}_4$, three conformations other than **17** were examined and found to lead to no binding between LiH and CH_4 ; they were $\text{HC} \cdot (\text{H})_3 \cdot \text{LiH}$, $\text{H}_3\text{CH} \cdot \text{LiH}$, and $\text{H}_3\text{CH} \cdot \text{HLi}$. Note that the $\text{CH}_4 \cdot \text{LiH}$ system thus differs from the isoelectronic $\text{BH}_3 \cdot \text{BeH}_2$, which is not only bound as $\text{HB} \cdot (\text{H})_3 \cdot \text{BeH}$ but slightly favors that configuration over $\text{H}_2\text{B} \cdot (\text{H})_2 \cdot \text{BeH}$ (see below).

There is little change in geometry of either CH_4 ($r = 1.083 \text{ \AA}$ at STO-3G) or LiH (1.510 \AA) upon complexation to form **17**, $\text{HLi} \cdot (\text{H})_2 \cdot \text{CH}_2'$. CH' distances are 1.083 \AA , C-H = 1.094 \AA , LiH = 1.509 \AA , and the H'CH' angle widens slightly to 113.1° . The Li-C distance is 2.486 \AA , only 20% larger than the single bond distance in methyl lithium. In contrast, the CO distance in the methane-water complex ($\text{H}_3\text{CH} \cdot \text{OH}_2$) is 130% larger than that in methanol at STO-3G.⁵

(18) LiNH_2 . This compound is strongly basic, generating the amide ion (NH_2^-) in liquid ammonia, and is thus named lithium amide rather than lithioamine.⁶ A recent crystal structure⁷² gives Li-N distances of $2.059\text{-}2.213 \text{ \AA}$ in the rather complicated packing arrangement. Though monomeric Li-NR₂ units have not been reported, dimers exist as bridged $\text{R}_2\text{N} \cdot (\text{Li})_2 \cdot \text{NR}_2$ systems with bulky R groups such as SiMe_3 .⁷³

The STO-3G structure of LiNH_2 is planar, with $\angle\text{HNH} = 102.3^\circ$ and Li-N = 1.635 \AA . A recent ab initio optimization⁷⁴

gave $\angle\text{HNH} = 110^\circ$, $\text{Li-N} = 1.782 \text{ \AA}$ with a large polarized basis set. The discrepancy in HNH angle between STO-3G and the higher level is similar to many other cases, in which STO-3G generally underestimates while higher levels overestimate HXH angles.⁷⁵ The discrepancy in bond lengths may be another manifestation of imbalance in the STO-3G basis due to the presence of p functions on lithium.

LiNH_2 has the same number of valence electrons as ammonia, which is pyramidal. When lithium is a ligand, however, its 2s orbital is high in energy, diffuse, and mixes less effectively; at the same time its vacant π orbitals may benefit by π conjugation with (sp^2) nitrogen. In this case, the result is planar LiNH_2 , which seems reasonable considering the planarity of HBeNH_2 (discussed below) and H_2BNH_2 .⁴ This result is implicit in the Walsh rule that H_2AB molecules are planar with fewer than 13 valence electrons.^{76,77}

(19) LiNH_4 . The interaction between LiH and NH_3 represents a coordinate donor-acceptor bond similar to that in the more familiar NH_3BH_3 .⁴ Alkyl lithium compounds are generally chelated by two or more amine groups, with Li-N distances ranging from 2.03 to 2.10 \AA in the crystal.⁷⁸ We find HLi-NH_3 (19) to have trigonal C_{3v} symmetry, with $\text{Li-N} = 1.944 \text{ \AA}$. Neither LiH nor NH_3 geometries are greatly perturbed by the coordinate interaction: for NH_3 , STO-3G gives $\angle\text{HNH} = 104.2^\circ$, $\text{N-H} = 1.033 \text{ \AA}$,⁵ while the corresponding values in LiNH_4 are $\angle\text{HNH} = 105.7^\circ$, $\text{N-H} = 1.028 \text{ \AA}$; the LiH distance changes only 0.004 \AA on complexation.

(20) LiOH . Lithium hydroxide and a dimer assumed to have a C_{2h} structure ($\text{HO-(Li)}_2\text{-OH}$) are known to exist in the gas phase^{79,80} but structural data are lacking. A reasonable estimate of the gaseous monomer structure based on rotational data is⁸⁰ linear with $\text{Li-O} = 1.582 \text{ \AA}$ and O-H assumed equal to the bond length in H_2O (0.97 \AA). The STO-3G structure is linear and has a considerably shorter Li-O bond of 1.432 \AA with $\text{O-H} = 0.971 \text{ \AA}$. An early theoretical study employing a double- ζ basis⁸¹ gave $r_{\text{O-Li}} = 1.60 \text{ \AA}$. In that study, the effects of removing p functions from lithium were examined, but only with regard to the angular orientation, not on bond lengths. The molecule was found to be linear in agreement with the STO-3G structure. A more recent theoretical study^{82a} assumed a value of $r_{\text{Li-O}} = 3.02 \text{ au}$ but mistakenly reported the value as 5.71 au (3.02 \AA).^{82b}

The better established experimental Li-O distance in gaseous lithium oxide, Li_2O , may be cited for comparison. This molecule is linear^{49,83,84} with $\text{Li-O} = 1.55^{83}\text{-}1.59 \text{ \AA}$.⁸⁴ The evidence seems to indicate that STO-3G gives an Li-O bond length which is considerably too short, in line with the similar results for LiH and LiNH_2 .

Both Li_2O and LiOH have the same number of valence electrons as H_2O which is bent. This is in agreement with Walsh's prediction that AB_2 systems with not more than 16 valence electrons and ABH systems containing 10 or fewer valence electrons should be linear, while HAH systems with more than 4 valence electrons should be bent. These Walsh rules are based on the participation of p functions in π bonding in the linear forms. Another factor influencing the structure of alkali metal oxides is that charge separation leads to a large contribution from resonance forms such as $\text{Li}^+\text{O}^{2-}\text{Li}^+$ in which repulsion between the positive ions favors a linear geometry.⁸¹ On the other hand, the polarization of the O^{2-} ion by the positive charges favors a bent structure. This is because such charges (treated as points) lead to a nonvanishing electric field at the center of O^{2-} only if the molecule is bent. That competing factors are present is suggested by experimental observations that Na_2O and Cs_2O are nonlinear.^{85,86}

(21) LiOH_3 . In the STO-3G structure of HLi-OH_2 , the Li-O axis forms an angle of 144° with the plane of the water molecule. Additionally, the H-Li-O angle is 168° , so that the overall shape is cisoid (Figure 3). We find the Li-O distance

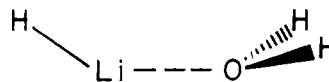


Figure 3. Cisoid HLiOH_2 .

to be 1.765 \AA , considerably shorter than the intermolecular distance in HLi-NH_3 (1.944 \AA). A similar decrease is found⁴ in going from H_3BNH_3 to H_3BOH_2 . This cisoid structure is the only minimum found on the intermolecular potential surface. Rigid rotation by 180° about the Li-O line, giving a transoid structure, increases the energy 0.8 kcal mol^{-1} . The lower energy of the cisoid form may be interpreted in terms of the interaction of dipole components perpendicular to the Li-O line.

For comparison we mention a recent study of $\text{LiF-H}_2\text{O}$ by Clementi et al.⁸⁷ using a very high quality basis set and presenting a detailed picture of the three-body potential surface of Li^+ , F^- , and H_2O . A total of 250 geometrical arrangements were examined, but none in which F^- was allowed to move out of the plane of the water molecule, such as would correspond to the STO-3G optimized geometry for LiOH_3 . The lowest energy arrangement among those studied was a C_{2v} configuration, FLi-OH_2 , having $r_{\text{O-Li}} = 1.89 \text{ \AA}$. The structure of a related aqueous solution ($\text{LiCl-H}_2\text{O}$) has been investigated by an elegant x-ray and neutron-diffraction study.⁸⁸

(22) LiF . Monomeric LiF is very precisely characterized experimentally, having $r = 1.5639 \text{ \AA}$,⁵² $\mu = 6.2841 \text{ D}$.⁸⁹ Large basis sets give optimized values of r_{LiF} as 1.581⁸⁷ to 1.528 \AA at the Hartree-Fock limit⁹⁰ to 1.5637 \AA with extensive CI.⁹¹ However, STO-3G fares poorly, giving $r = 1.407 \text{ \AA}$, $\mu = 3.12 \text{ D}$, which again indicates that the minimal basis is not sufficiently balanced to describe LiX bonds adequately for electronegative X. In a previous comparison between STO-3G and experimental results on 69 bond lengths involving H, C, N, O, and F,⁵ the mean absolute deviation found was only 0.03 \AA . Poorest results were seen for cations, excited states, and single bonds between the heaviest atoms (O, F), the worst such example (F_2) having an STO-3G bond length 0.103 \AA shorter than the experimental. Now we find the deviation for LiF (0.157 \AA) to be even greater. A combination of factors is responsible for this, among them the extensive flexibility at Li along with the lack of flexibility at F, both atoms having five orbitals to accommodate 3 vs. 9 electrons, and the use of averaged molecular scaling factors, a concept which does not allow strongly polarized bonds to be modelled accurately. These factors become less important with larger basis sets; at 6-31G* the calculated dipole moment (5.57 D) indicates a much more accurate representation.

(23) LiFH_2 . Like LiOH_3 (21), the coordinately bound HLi-FH system is nonlinear and thus parallels hydrogen-bonded systems such as the HF dimer.^{5,47} The H-Li-F and Li-F-H angles are calculated to be 168.9 and 149.0° , with bonds in a cis arrangement. The intermolecular separation $r_{\text{Li-F}} = 1.627 \text{ \AA}$ is shorter than in the HLi-OH_2 coordinate bond. A theoretical study of the related systems HF-LiF , Li-F-LiF , and LiF-H_2 has been reported by Kollman et al.⁴⁶ They found a cyclic structure for HFLiF although the linear form FH-LiF was most stable. The $(\text{LiF})_2$ dimer was most stable in cyclic form.^{26b,43b,46}

Beryllium Compounds. (24) BeH_2 . Beryllium hydride has four valence electrons and is predicted by Walsh's rules^{76,77} to be linear, with sp hybridization at beryllium. This has been confirmed theoretically,⁹² although gaseous BeH_2 has not been observed and in the solid state the arrangement of hydrogens about Be is nearly tetrahedral.³⁰ The Hartree-Fock limit for BeH_2 is estimated⁹³ to be -15.7730 au ; correlation estimates are given in several recent studies⁹²⁻⁹⁵ the best of which⁹⁵ gives a Be-H bond length of 1.334 \AA (with CI) and includes a review

of earlier studies. The STO-3G bond length is 1.291 Å. At 4-31G/5-21G the value is 1.369 Å.³²

Be₂. The ground state of the Be atom (¹S) has the closed shell configuration (1s)² (2s)², so that there is no tendency for bond formation between two beryllium atoms. This has been examined theoretically elsewhere^{20,41,96,97} and by us at STO-3G; the minimum energy obtained for Be₂ was -28.70438 hartrees at $r = 3.542$ Å. This is only 0.39 kcal mol⁻¹ below the STO-3G energy of two ¹S Be atoms calculated with standard molecular scale factors.⁹⁸ This is apparently an artifact of the limited STO-3G basis as this small binding energy disappears when larger basis sets are used.⁹⁹

(25) Be₂H₂. This molecule bears the same relation to BeH₂ as mercurous derivatives do to mercuric. It represents the simplest system with a Be-Be single bond, as yet an unknown entity. The bond is characterized by features found in Li₂: little interatomic overlap and a large bond length (2.062 Å at STO-3G). The structure is predicted to be linear, in accord with Walsh's rules.

(26) Be₂H₄. Three topologies were investigated but only one significantly bound dimer was located on the BeH₂-BeH₂ potential surface. This dimer **26** has a doubly bridged HBe-(H)₂-BeH structure, as might be expected considering the stability of the analogues Li-(H)₂-Li and H₂B-(H)₂-BH₂.⁴ This structure has been proposed on qualitative grounds by Pearson. A similar geometry obtained by Ahlrichs¹⁰⁰ using a near-Hartree-Fock basis is given in Table III.

The trend noted previously in lithium hydrides appears to be a general one. In dimerization of BeH₂, the Be atoms approach each other to 1.991 Å, within the single bond distance in HBe-BeH, while bridged Be-H bonds become considerably longer (1.464 Å) than in BeH₂. Terminal Be-H bonds change little upon dimerization.

Also examined for Be₂H₄ were a C_{2v} "beryllium bonded" structure HBeH-BeH₂ and an unsymmetrical triply bridged form HBe-(H)₃-Be. The latter species was found to be unbound (with respect to two BeH₂ moieties) after a partial optimization. The C_{2v} species, however, was found to be slightly bound by ~0.4 kcal mol⁻¹ after partial optimization, holding rigid BeH₂ subunits, resulting in a Be-Be distance of 4.214 Å. This small stabilization can be rationalized in terms of a quadrupole-quadrupole interaction. There is some experimental support for the D_{2h} form; a similar geometry has been suggested for dimeric Be₂Cl₄, observed at 500 °C to be the predominant oligomer of BeCl₂ present in the gas phase.¹⁰² Also, x-ray structures of alkali metal dialkylberyllium hydrides^{59,103} indicate the presence of R₂Be-(H)₂-BeR₂ units, isolectronic with diborane-type structures R₂B-(H)₂-BR₂.

(27, 28) BeBH. For BeBH, two electronic states, ³Π and ¹A', were studied. Formally, this species represents a Be=B double bond. In the singlet state, however, bonding is relatively weak; the calculated bond length is long (1.966 Å) and the species is nonlinear with an H-B-Be angle of 120.5°. The singlet binding energy (relative to Be(¹S)^{12b,98} and BH(¹Σ⁺)⁴) is only 13.2 and 4.1 kcal·mol⁻¹ with the STO-3G and 6-31G* bases, respectively.

The geometry of the triplet state is found to be linear, with a substantially shorter Be-B bond length (1.744 Å). At the STO-3G level, this state lies 56.7 kcal mol⁻¹ below the ¹A' state and is bound by 69.9 kcal mol⁻¹. At the 6-31G* level, the triplet state is 41.6 kcal mol⁻¹ below the singlet species and is bound by 45.7 kcal mol⁻¹. It is therefore quite likely that the ground state is a triplet. It is interesting to note that the ³Π state obtained has only one π electron. A ³Σ⁻ state, with two π electrons, was obtained at the STO-3G level but was found to lie some 39 kcal mol⁻¹ above the ³Π state at the ³Π equilibrium geometry. This state was not studied further.

(29) BeBH₃. HBeBH₂, "beryllioborane", has been mentioned above in connection with the bond angle series in XBH₂

systems. The structure is calculated to be planar, C_{2v}. Beryllium-boron single bonding appears to be unreported elsewhere.

(30, 31) BeBH₅. We find at both the STO-3G and 6-31G* levels that triply bridged HB-(H)₃-BeH (**30**) is very slightly favored over the doubly bridged form H₂B-(H)₂-BeH (**31**). This agrees with calculations by Ahlrichs.^{105a} The energy difference is sufficiently small (4.6 kcal mol⁻¹ at 6-31G*) that the two forms should be experimentally difficult to distinguish, as appears to be the case in several related systems. For example, recent electron diffraction data are unable to distinguish between doubly bridged B-(H)₂-Be or triply bridged B-(H)₃-Be units in cyclopentadienyl-BeBH₄¹⁰⁴ or BeB₂H₈.¹⁰⁵ However, a methyl derivative of **30**, CH₃BeBH₄, appears to involve only double hydrogen bridges.¹⁰⁶

In addition to **30** and **31**, four other BeBH₅ structures were investigated. None was found to be significantly bound relative to BH₃ and BeH₂. Two are singly bridged species, HBeH-BH₃ (C_{3v}) and H₂BH-BeH₂ (C_{2v}, with BeH₂ and BH₃ planes perpendicular). The third is the doubly bridged (C_{2v}) form H₂Be-(H)₂-BH, and finally the (C_s) triply bridged Be-(H)₃-BH₂, in which one of the three bridging hydrogens is distinct from the others. Partial geometry optimization was performed in each case.

(32, 33) BeCH₂. As with the other beryllium systems containing formal double bonds, we have considered two electronic states (³B₁ and ¹A₁) for Be=CH₂. The 6-31G* basis predicts a strongly bound (56.1 kcal mol⁻¹) ³B₁ ground state and a slightly bound ¹A₁ state (relative to CH₂(³B₁) + Be(¹S)) that lies 54.9 kcal mol⁻¹ above the triplet. These results are consistent with the findings of Lamanna and Maestro¹⁰⁷ who, based on a study using a moderate Gaussian sp basis, found CH₂Be dissociation energies of 56.1 and 3.2 kcal mol⁻¹ for the triplet and singlet states, respectively. Further, they concluded that the ¹A₁ state is very likely unbound relative to CH₂(³B₁) and Be(¹S) when zero-point vibrational corrections are taken into account. However, the question of carbon-beryllium binding in CH₂Be has been further pursued in a recent theoretical study¹⁰⁸ with correlation corrections. This indicates substantial carbon-beryllium binding in both triplet and singlet states.

Both the singlet and triplet states are predicted to be of C_{2v} symmetry at the STO-3G level. The STO-3G Be-C bond length increases from 1.472 to 1.652 Å on going from ¹A₁ to ³B₁. Similar lengths of 1.498 and 1.651 Å were reported by Lamanna and Maestro. The singlet Be=C bond length falls in line with bond lengths calculated for other X=CH₂ systems. Calculated singlet double bond lengths^{4,5} decrease as X goes from boron to oxygen: 1.472 Å (Be=CH₂), 1.339 Å (HB=CH₂), 1.306 Å (H₂C=CH₂), 1.273 Å (HN=CH₂), 1.217 Å (H₂C=O).

(34) BeCH₄. Methylberyllium hydride, HBeCH₃, is not known as a monomer but exists only as a coordinated dimer, (S)MeBe-(H)₂-BeMe(S), where (S) is NMe₃, OEt₂, or other lone-pair donor complexed to beryllium.^{8a} Structural data are available, however, concerning the disubstituted analogue, Me₂Be, which has been observed by electron diffraction as a gas-phase monomer.¹⁰⁹ The following geometry was reported for D_{3h} Me₂Be (with STO-3G values for C_{3v} HBeCH₃ in parentheses): $r_{\text{Be-C}} = 1.698$ Å (1.691 Å), $\angle \text{Be-C-H} \approx 113.9^\circ$ (111.8°), $r_{\text{C-H}} = 1.127$ Å (1.085 Å). The agreement is good. In previous theoretical studies of HBeCH₃⁶⁷ and Be(CH₃)₂^{64,66,68} strict tetrahedral geometry at CH₃ was assumed but calculated Be-C distances were close to the STO-3G value. One of these studies⁶⁷ found dimerization to be slightly unfavorable, two HBeCH₃ molecules being preferred by 4 kcal mol⁻¹ over HBe-(Me)₂-BeH. A fully optimized 4-31G/5-21G structure of CH₃BH is now available:^{69c} $r_{\text{Be-C}} = 1.698$ Å, $r_{\text{Be-H}} = 1.335$ Å, $r_{\text{C-H}} = 1.089$ Å, $\angle \text{Be-C-H} =$

111.8°, $E = -54.75469$ hartrees.

BeCH₆. Several geometries were examined in an attempt to find a stable complex of methane and beryllium hydride analogous to LiH-CH₄ (17). However, none of the following was bound with respect to BeH₂ plus CH₄, after partial optimization: (C_{2v}) H₂Be-(H)₂-CH₄, isostructural and isoelectronic with B₂H₆; triply bridged (C_s) H₂Be-(H)₃-CH; triply bridged (C_s) HBe-(H)₃-CH₂; beryllium bonded (C_s) H₂Be-HCH₃.

(35, 36) **BeNH.** Beryllium imide, BeNH, is formed upon pyrolysis of beryllium amide (Be(NH₂)₂),¹¹⁰ but no structural parameters have been reported. For this molecule, the ³Π state was studied in addition to the ¹Σ⁺ state. Both are found to be linear. The singlet has a sufficiently small Be-N distance (1.288 Å) that it seems to involve a genuine multiple bond. The triplet state (³Π), also of $C_{\infty v}$ symmetry, has a somewhat longer Be-N bond distance of 1.438 Å. Here, there are only three π electrons (compared to the four in the ¹Σ⁺ state). Thus the lengthening of the B-N bond may, in part, be attributed to the promotion of one of the (1π) orbital electrons to the (5σ) orbital thereby weakening one of the π bonds. The triplet state is found to lie 29.1 and 33.1 kcal mol⁻¹ below the singlet state with STO-3G and 6-31G* bases, respectively. However, it is unclear at this time which state is the ground state; comparison of UHF triplets vs. RHF singlets can be misleading due to the preferential stabilization of triplets relative to singlets in the UHF formalism.

(37) **BeNH₃.** Although monomeric beryllium monoamides are apparently not known, diameric beryllium have been reported.^{8a} For example, gaseous (SiMe₃)₂N-Be-N(SiMe₃)₂ has been found¹¹¹ to have Be-N distances of 1.566 Å in an allene-shaped framework. We find HBeNH₂ to have a planar C_{2v} structure with $r_{\text{Be-N}} = 1.457$ Å, shorter than both the 1.53 Å found by Baird et al.⁶⁷ (at STO-2G) and the 1.566 Å in the Be(N(SiMe₃)₂)₂ structure. Of course, this experimental value may be abnormally long due to steric crowding of the trimethylsilyl groups. It is noteworthy that HBeNH₂ has a structure similar to that of the isoelectronic classical vinyl cation.^{5,112,113}

(38, 39) **BeNH₅.** Amine beryllium complexes are well known,^{8a} but structural data are generally lacking for 1:1 adducts. A Be-N coordinate bond length of 1.91 Å has been found by x-ray diffraction for the bis quinuclidine adduct of BeMe₂[Me₂Be(NC₇H₁₃)₂],¹¹⁴ but unfortunately the structure of the simpler known adduct Me₂Be-NMe₃ has not been reported. We have calculated two rotamers of H₂Be-NH₃: "cis", having a coplanar H-Be-N-H arrangement (38), and "perpendicular" (39), rotated by 90° from cis and reoptimized. The cis form is very slightly preferred over the perpendicular at both levels of calculation. The calculated Be-N distance (1.747 Å) is longer than the corresponding calculated distance in the boron analogue H₃B-NH₃ (1.657 Å staggered⁴) but considerably shorter than HLi-NH₃ and the x-ray value cited above. In forming the amine beryllium complex, the geometry of NH₃ is changed only slightly and the HBeH angle bends from 180 to 136°. These structures are analogous to those of the isoelectronic ethyl cation.⁵

(40, 41) **BeO.** Beryllium oxide has been the subject of several previous theoretical studies¹¹⁵⁻¹¹⁸ and the determination of the ground state has caused some difficulty. We have considered only two electronic states, ³Π and ¹Σ⁺, in this study. The ¹Σ⁺ state is known experimentally¹¹⁹ to be the lowest singlet state (although Huo et al.¹¹⁷ report that the ¹Π state is below the ¹Σ⁺ state when studied near the Hartree-Fock limit). The ³Π state appears to be the lowest triplet state but has to our knowledge never been observed experimentally. Based on theoretical considerations, Schaefer¹¹⁸ has concluded that the BeO ground state is ¹Σ⁺. It is interesting to note that C₂, isoelectronic with BeO, is experimentally known¹²⁰ to have a ¹Σ_g⁺ ground state and first excited state of ³Π_u. For BeO, both the

STO-3G and 6-31G* bases incorrectly predict that the ground state is ³Π, presumably due to lack of correlation corrections.

The bond length for the ¹Σ⁺ state has been determined as 1.331 Å (exptl),³¹ 1.313 Å (first order wave function CI),¹¹⁸ 1.290 Å (near Hartree-Fock),¹¹⁵ and 1.269 Å (STO-3G). In the ³Π state, no experimental value is available. The theoretical bond lengths are 1.463 Å (first order wave function CI),¹¹⁸ 1.447 Å (near Hartree-Fock),¹¹⁵ and 1.435 Å (STO-3G). As has been observed in other polar molecules, the STO-3G bond length is too short. The triplet state is found to be 28 kcal mol⁻¹ below the singlet state at the 6-31G* level. (Some caution must be exercised in interpreting singlet-triplet splittings derived solely from Hartree-Fock theory, as correlation corrections are likely to be important.) As has been noted elsewhere,²⁰ convergence difficulties were encountered in obtaining the 6-31G* wave function for the ¹Σ⁺ state. This problem was solved through use of special programs due to Seeger.^{20c}

(42) **BeOH₂.** Hydroxyberyllium hydride is not known experimentally. Crystal data are, however, available for an ROBeR' tetramer, [Me₃SiOBeCH₃]₄,¹²¹ it has Be and O atoms at alternate corners of a distorted cube, with $r_{\text{Be-O}} = 1.73$ Å. We calculate the HBeOH monomer to have a linear structure with a short Be-O bond (1.301 Å). This is similar to the isoelectronic molecules HBNH⁴ and HCCH.

(43, 44) **BeOH₄.** Beryllium-oxygen coordinate bonds are generally weaker than beryllium-nitrogen,¹²² and we calculate them to be shorter as well. The water-BeH₂ system is isoelectronic with aminoborane⁴ and shows similar rotational behavior; in both cases, a planar C_{2v} form (43) is preferred over the 90°-rotated C_s form (44). The 6-31G* rotational barrier is 4.8 kcal mol⁻¹. The Be-O bond distance in the planar form is the smaller (1.582 Å vs. 1.674 Å rotated), reflecting additional π bonding.

(45) **HBeF.** Alkaline earth halides have not been as extensively studied as alkali halides. In BeF₂, the experimental structure is linear with $r_{\text{Be-F}} = 1.430$ Å,¹²³ a value well reproduced by a near-Hartree-Fock calculation.¹²⁴ Our structure for HBeF is linear with a B-F distance (1.299 Å) which is considerably shorter than in BeF₂. Recently, a study of CH₃BeF has been published¹²⁵ giving a Be-F length of 1.40 Å. It is possible that some extra shortening in HBeF is due to additional π bonding between Be and F since the beryllium atom does not accept any π electrons from the other substituent in this case.

(46, 47) **BeFH₃.** The BeH₂-FH complex falls in line with others. The Be-F distance (1.588 Å planar, 1.621 Å rotated by 90°) is shorter than corresponding values in H₂Be-OH₂ or H₂Be-NH₃ but longer than in H₃B-FH;⁴ the rotational behavior is as expected from the isoelectronic H₂BOH,⁴ the planar form permitting π-electron delocalization and thus being strongly favored. Beryllium-fluorine coordinate bonds have not been discussed elsewhere.

Standard Geometrical Models

We have often employed a set of standard bond lengths and angles when calculating large systems having well-defined structures. A standard set of lengths has been given previously for bonds between the atoms C to F¹²⁶ and those involving B,⁴ and we now extend this to include Li-X and Be-X bonds.

A set of standard bond lengths is given in Table IV. These were obtained from STO-3G structures as well as the experimental and other theoretical data cited above. These lengths represent average distances regardless of hybridization at X. The single bond lengths apply only to monocoordinate lithium and dicoordinate beryllium, the latter having a standard X-Be-Y angle of 180°. The values for Li-C, Be-H, and Be-C have appeared previously.¹²⁷

Table IV. Standard Bond Lengths for Li-X and Be-X^a Bonds

Bond	Length, Å	Bond	Length, Å
Single Bonds			
Li-H	1.59	Be-H	1.29
Li-Li	2.68	Be-Be	2.10
Li-Be	2.50	Be-B	1.90
Li-B	2.30	Be-C	1.69
Li-C	2.01	Be-N	1.50
Li-N	1.70	Be-O	1.41
Li-O	1.58	Be-F	1.40
Li-F	1.56		
Double Bonds ^b			
Be=C	1.48	Be=O	1.33
Be=N	1.36		

^a Standard X-Be-Y angle = 180°. ^b Standard values here refer to singlet states.

Discussion

To facilitate discussion, it is convenient to subdivide the list of molecules according to bond type. In one category are the singly bonded Li-X and HBe-X and doubly bonded Be=X systems involving covalent and ionic bonding. Dimers of LiH and BeH₂ with Lewis acid hydrides (LiH, BeH₂, BH₃, and CH₄) form a second category involving three-center two-electron bonding. Finally, coordinate complexes of LiH and BeH₂ with NH₃, OH₂, and FH represent a third bond type. In each of these categories, we shall discuss electron distributions and the nature of bonding.

We shall examine the electron distribution by Mulliken population analysis.³⁵ This method has its drawbacks, especially in attempting to describe highly polar bonds. In LiX, for

example (with electronegative X), the large, diffuse lithium orbitals overlap with smaller X orbitals in a region of space near the X nucleus, yet the Mulliken scheme assigns half the electrons in this overlap region to each atom. The result is an artificially large number of electrons assigned to lithium, making the Li-X bond seem less polar, or more homogeneous, than is realistic. This problem is especially acute at the minimal STO-3G basis set level, particularly when p functions are included on lithium. Nevertheless the STO-3G populations do give some comparative information about electron displacements and they will be used unless otherwise indicated.

Single Bonds. Some Mulliken STO-3G overlap populations for Li-X and HBe-X molecules are given in Table V. The π -overlap population is the sum of the p_x - p_x and p_y - p_y overlap populations where the heavy atoms lie on the z axis. The σ -overlap population is defined to be the sum of all overlap populations between the two heavy atoms involving 1s, 2s, and 2p_z atomic functions.

In general, σ overlap is reduced as the substituent X becomes more electronegative, and this is compensated by an increase in π overlap. For both Li-X and HBe-X maximum π overlap occurs when X is OH, and clearly it is to assure this that the OH group adopts a linear conformation. π overlap is also high if X is NH₂ or F, and the fact that values are nearly equal for these groups demonstrates the single lone pair on N to be roughly twice as effective as each of the two on F at providing π electrons.

Also given in Table V are total electron populations on Li and HBe and total electron transfer to Li and HBe for these singly bonded molecules. The total electron population on M is further subdivided into σ and π components. The π component gives the total electron population residing in the p_x and p_y orbitals at M. The electron population in the remaining orbitals of the lithium or beryllium, plus the hydrogen orbital

Table V. Population Data and Dipole Moments for Li-X, LiBe-X, and Be=X Molecules

No. ^a	M-X ^b	Overlap population ^c (STO-3G)		Total electron popu- lation on M ^c (STO-3G)		Total electron ^{c,d} transfer to M	Dipole moment ^e (6-31G*)
		σ	π	σ	π		
1	Li-H	0.78	0	3.02	0	+0.02	5.74 ^f
2	Li-Li	0.71	0	3.0	0	0	0
5	Li-BeH	0.78	0	3.11	0	+0.11	4.86
10	Li-BH ₂	0.67	0.01	3.06	0.02	+0.08	5.19
16	Li-CH ₃	0.58	0.05	2.78	0.06	-0.16	5.70 ^g
18	Li-NH ₂	0.48	0.29	2.34	0.44	-0.22	4.21
20	Li-OH	0.29	0.45	2.18	0.64	-0.18	3.67
22	Li-F	0.15	0.37	2.17	0.61	-0.23	5.57 ^h
24	HBe-H	0.82	0	4.95	0	-0.05	0
5	HBe-Li	0.78	0	4.89	0	-0.11	4.86
25	HBe-BeH	0.83	0	5.00	0	0	0
29	HBe-BH ₂	0.78	0.02	5.00	0.02	+0.02	0.21
34	HBe-CH ₃	0.72	0.06	4.78	0.07	-0.15	0.34
37	HBe-NH ₂	0.62	0.28	4.49	0.34	-0.17	1.59
42	HBe-OH	0.45	0.46	4.32	0.54	-0.14	1.95
45	HBe-F	0.28	0.37	4.33	0.48	-0.19	0.66
27	Be=BH(¹ A')	0.43	0.06	4.01	0.11	+0.11	0.66
28	Be=BH(³ Π)	0.78	0.15	3.86	0.23	+0.09	0.96
32	Be=CH ₂ (¹ A ₁)	0.76	0.48	2.86	0.99	-0.16	4.19
33	Be=CH ₂ (³ B ₁)	0.71	0.13	3.73	0.16	-0.11	0.56
35	Be=NH(¹ Σ ⁺)	0.60	0.83	2.47	1.27	-0.26	4.13
36	Be=NH(³ Π)	0.52	0.36	3.41	0.42	-0.17	1.32
40	Be=O(¹ Σ ⁺)	0.35	0.72	2.47	1.26	-0.27	6.87
41	Be=O(³ Π)	0.33	0.28	3.44	0.37	-0.19	1.30

^a Numbering corresponds to scheme in Table I. ^b M is defined as Li in the case of lithium compounds, HBe in the case of singly bonded beryllium compounds, and Be in the case of doubly bonded beryllium compounds; see text. ^c From Mulliken population analysis. π includes both π_x and π_y with z axis along M-X. ^d Positive value indicates electron transfer from X to M. ^e Debyes. ^f Experimental value 5.83 D (ref 34b). ^g Experimental value 6 D (ref 63). ^h Experimental value 6.28 D (ref 89).

Table VI. Calculated Heats of Hydrogenation ΔH_{hyd} for LiX, HBeX, and Be=X Molecules (kcal mol⁻¹)

Molecule	$\Delta H_{\text{hyd}}^{a,b}$	Molecule	$\Delta H_{\text{hyd}}^{a,b}$
Li-Li	22.4 (19.8)	HBe-BeH	-16.4
Li-BeH	-5.8	HBe-BH ₂	-19.8
Li-BH ₂	-20.6	HBe-CH ₃	-11.3
Li-CH ₃	-20.1	HBe-NH ₂	16.9
Li-NH ₂	2.1	HBe-OH	33.1
Li-OH	20.0 (30.5)	HBe-F	52.7
Li-F	44.4 (49.6)	Be=BH(¹ A')	-131.0
		Be=BH(³ Π)	-89.3
		Be=CH ₂ (¹ A ₁)	-135.7
		Be=CH ₂ (³ B ₁)	-80.9
		Be=NH(¹ Σ ⁺)	-95.0
		Be=NH(³ Π)	-61.9
		Be=O(¹ Σ ⁺)	-69.0 (-64.3)
		Be=O(³ Π)	-41.0

^a Experimental values in parentheses (0 K), corrected for zero-point vibration, from data in ref 128. ^b 6-31G* energies of nonmetal hydrides from ref 129, BH₃ from ref 4.

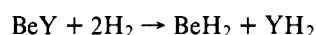
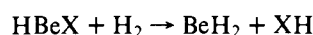
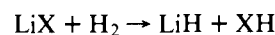
in the case M = HBe, gives rise to the σ total electron population at M. The total electron transfer to M represents the fractional number of electrons transferred to M. Thus, in the case of HBe-F, the value -0.19 indicates that 0.19 electron has been transferred away from the HBe unit.

Some caution must be exercised in interpreting the results listed in Table V because the $p\pi$ orbitals on lithium and beryllium are assigned excessive amounts of electron population in the STO-3G analysis. This effect is highly basis set dependent. In Li-F, for example, the STO-3G analysis indicates that the $p\pi$ orbitals on the lithium have an electron population of 0.61. The corresponding value at the 6-31G* level is only 0.28. As a result of this exaggerated π population, the gross STO-3G population suggests too small a polarity for these bonds. The total σ populations, on the other hand, are less dependent on the basis set and indicate that electrons move toward X in the σ system with some back-donation in the π system. In general, net electron transfer is toward X and leads to substantial dipole moments as shown in the last column of Table V.

Double Bonds Be=X. Population data on the four doubly bonded beryllium systems (both singlet and triplet states) are also given in Table V. This group of doubly bonded molecules can be logically subdivided into a group of ten-electron molecules (singlet and triplet Be=BH) and a group of twelve-electron molecules (the remaining doubly bonded systems, both singlet and triplet states). Further, it is useful to note that although varying point groups are represented (C_s , C_{2v} , and $C_{\infty v}$), it is possible to define π -type orbitals as those having a node in the molecular plane and σ -type orbitals as those lacking such a node (in all cases, the heavy atoms lie on the z axis, and if nonlinear, the hydrogens lie in the xz plane). For Be=BH, the 10-electron case, the low π population for the singlet is readily explained by noting that the molecule has C_s symmetry, and there are no occupied a'' orbitals in the singlet configuration (the nonzero π population arises from the fact that there are a' orbitals having p_x character). The linear triplet, however, is formed by occupying one of the a'' orbitals (becoming a π orbital in the linear molecule), and consequently additional π overlap is acquired. The 10-electron systems are further characterized by the electron-acceptor nature of the beryllium atom at the STO-3G level. This effect is somewhat basis dependent, and at the 6-31G* level, total electron transfer is away from the beryllium in the singlet (total electron transfer +0.04) and to the beryllium in the triplet (total electron transfer -0.05). Both singlet and triplet Be=BH have moderate dipole moments, as might be expected by the small electron transfer values at the 6-31G* level. For the 12-electron systems, the trends are largely reversed. The singlets are characterized by

having large π -overlap populations. There is, in each molecule, a significant reduction in π overlap in going from the singlet to the triplet because in each case there is a reduction from four to three π -type orbitals. In all these 12-electron systems, the total electron transfer is away from the beryllium. Further, the singlets are characterized by very large dipole moments, the triplets having only moderate dipole moments. In the singlet state of Be=CH₂, π overlap is similar to that in ethylene (0.40 at STO-3G), and the total electron π population indicates that the two Be=CH₂ π electrons are almost equally shared between Be and C. π overlap in Be=NH and Be=O indicates nearly triple bonding. In these, π electrons are polarized toward Be with strong σ donation in the opposite direction.

Heats of Hydrogenation. In previous studies,¹² the Hartree-Fock method with the 6-31G* basis has been found to give good values for hydrogenation energies. In Table VI we list the theoretical energies for the hydrogenation reactions



The limited experimental data¹²⁸ available are also given.

Variations in hydrogenation energies reflect strengths of Li-X and Be-X bonds relative to H-X. In general, negative hydrogenation energies indicate metal-metal single bonds to be weak, a result of high s character and little π bonding. With lone-pair substituents, π bonding leads to increased bond strengths, especially when two lone pairs are available (X = OH or F). A full study of bond dissociation energies in two-heavy-atom molecules will be presented in a future publication.

Multicenter Bonds. We now turn to the metal hydride dimers. Table VII gives the total atomic charges (from Mulliken STO-3G gross populations) for the structures we have considered. Atomic charges in LiH, BeH₂, and BH₃ are also given in the table for comparison. The table is arranged with similar structures grouped together and in some cases entries are duplicated in order to permit easy comparisons.

Consider the charge reorganization in formation of a linear three-center two-electron bond, such as in dimerization of LiH to Li¹⁻-H_{br}-Li²⁻-H². The charge distributions in Table VII show Li¹ to become highly positive in the dimer, while Li² becomes negative. There is a slight accumulation of negative charge at the bridging hydrogen as well. Overall, charge shifts toward B in the AH-B arrangement, just opposite the direction of polarization in hydrogen bonding.⁴⁷ As the electron acceptor (Li²H²) changes to BeH₂ or BH₃, more charge is

Table VII. Total Atomic Charges in Hydrogen-Bridged Dimers Containing LiH or BeH₂

No. ^a	H _a -A- -H _{br} - -B-H _b ^{a,b}	Atomic charge				
		H _a	A	H _{br}	B	H _b
1	HLi			+0.017	-0.017	
24	HBeH			-0.046	+0.091	-0.046
	HBH ₂			-0.061	+0.183	-0.061
4	LiH- -LiH		+0.305	-0.038	-0.268	+0.002
8	LiH- -BeH ₂		+0.371	-0.072	-0.106	-0.097
13	LiH- -BH ₃		+0.439	-0.096	+0.009	-0.117
4	HLi- -HLi	+0.002	-0.268	-0.038	+0.305	
9	HLi- -HBeH	+0.013	-0.153	-0.075	+0.233	-0.018
15	HLi- -HBH ₂	+0.015	-0.109	-0.081	+0.237	-0.031
3	Li- -(H) ₂ - -Li		+0.043	-0.043	+0.043	
6	Li- -(H) ₂ - -BeH		+0.214	-0.076	+0.002	-0.064
12	Li- -(H) ₂ - -BH ₂		+0.352	-0.084	-0.017	-0.083
6	HBe- -(H) ₂ - -Li	-0.064	+0.002	-0.076	+0.214	
26	HBe- -(H) ₂ - -BeH	-0.028	+0.096	-0.068	+0.096	-0.028
31	HBe- -(H) ₂ - -BH ₂	-0.020	+0.181	-0.042	+0.002	-0.040
14	HLi- -(H) ₂ - -BH	+0.016	-0.135	-0.033	+0.206	-0.021
17	HLi- -(H) ₂ - -CH ₂	+0.017	-0.093	+0.073	-0.268	+0.099
7	Li- -(H) ₃ - -Be		+0.266	-0.057	-0.094	
11	Li- -(H) ₃ - -BH		+0.318	-0.068	-0.042	-0.071
30	HBe- -(H) ₃ - -BH	-0.017	+0.153	-0.021	-0.057	-0.015

^a Corresponding to Table I numbering and notation. ^b Hydrogen labels refer to Figure 2.

Table VIII. Binding Energies of Hydrogen-Bridged Dimers Containing LiH or BeH₂

No. ^a	Structure	Binding energy, kcal mol ⁻¹ ^b	
		STO-3G	6-31G*
4	LiH- -LiH	24.1	26.3
8	LiH- -BeH ₂	11.1	18.7
13	LiH- -BH ₃	10.5	23.0
4	HLi- -HLi	24.1	26.3
9	HLi- -HBeH	9.8	8.6
15	HLi- -HBH ₂	6.0	3.4
3	Li- -(H) ₂ - -Li	44.0	46.8
6	Li- -(H) ₂ - -BeH	35.8	40.7
12	Li- -(H) ₂ - -BH ₂	36.4	44.6
6	HBe- -(H) ₂ - -Li	35.8	40.7
26	HBe- -(H) ₂ - -BeH	19.6	24.5
31	HBe- -(H) ₂ - -BH ₂	22.3	28.4
14	HLi- -(H) ₂ - -BH	7.3	4.3
17	HLi- -(H) ₂ - -CH ₂	5.9	2.3
7	Li- -(H) ₃ - -Be	20.9	26.5
11	Li- -(H) ₃ - -BH	42.9	49.9
30	HBe- -(H) ₃ - -BH	23.7	31.5

^a Numbering and notation as in Table I. ^b Energy relative to appropriate sum of LiH, BeH₂ (Table I), BH₃ (ref 4), or CH₄ (ref 3 and 129) energies.

transferred from Li¹ via H_{br} and is ultimately transmitted to terminal hydrogens. Similar charge shifts are seen in other singly hydrogen bridged dimers.

In structures having more than one bridging hydrogen, it is difficult to generalize the charge distributions in Table VII. Often hydrogens in bridging positions are more negative than in monomers, but this is not always true, particularly when neither of the heavy atoms is lithium. In unsymmetrical dimers, the more electropositive heavy atom generally provides charge to the other. Thus in Li- -(H)₂- -AH or Li- -(H)₃- -A (A = Be or BH), lithium becomes positive while A and bridging hydrogens become negative.

Dimerization Energies. Table VIII gives the energies of hydrogen-bridged structures relative to the appropriate sums of monomer (LiH, BeH₂, BH₃, CH₄) energies. A few general comments are in order concerning the ability of theory to reproduce binding energies of this type. A well-studied related

dimer known experimentally is diborane, H₂B- -(H)₂- -BH₂, for which the STO-3G dimerization energy of BH₃ is 15.5 kcal mol⁻¹, in reasonable agreement with the 6-31G* value (20.5) and other theoretical determinations.⁴ However, the experimental value³⁰ is around 36. These and other calculations^{26a,131} are consistent with a large correlation energy change in comparing two BH₃ moieties with B₂H₆. Similar conclusions have been reached for BH₃ + BeH₂. Using an extensive sp basis and the IEPA method of determining correlation energies, Ahlrichs^{105a} finds the following binding energies: for HBe- -(H)₃- -BH (30), 25.4 kcal mol⁻¹ increasing to 39.9 kcal mol⁻¹ with correlation (cf. 23.7 at STO-3G, 32.2 at 6-31G*); for HBe- -(H)₂- -BH₂ (31), 22.5 or 33.0 with correlation (STO-3G gives 22.3, 6-31G* gives 27.6). Thus correlation differences seem to be important for hydrogen-bridged structures, but the inclusion of d functions is also clearly important.

Table IX. Charge Reorganization upon Acid (LiH, BeH₂)-Base (NH₃, OH₂, FH) Complexation^a

No. ^b	H _n A-BH _m	$\Delta q^{c,d}$		Charge transfer ^e	$\Delta q^{c,d}$	
		H _a	A		B	H _b
19	HLi-NH ₃	-0.012	-0.208	0.221	0.062	0.159
21	HLi-OH ₂	-0.008	-0.206	0.214	0.103	0.110
23	HLi-FH	-0.004	-0.197	0.201	0.108	0.093
38	H ₂ Be-NH ₃	-0.130	-0.159	0.289	0.068	0.221
43	H ₂ Be-OH ₂	-0.130	-0.166	0.296	0.112	0.184
46	H ₂ Be-FH	-0.106	-0.153	0.259	0.145	0.113

^a From STO-3G Mulliken population analysis. ^b From numbering scheme in Table I. Only lowest energy conformations of Be complexes are given. ^c Difference between total atomic charge q in complex and in monomer: $\Delta q = q(\text{cx}) - q(\text{mon})$. Monomer values are $q = -0.017, +0.091, -0.486, -0.406, -0.228$, where A is the heavy atom in LiH, BeH₂, NH₃, OH₂, FH (from Table VII and W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 2191 (1970)). ^d Hydrogen values for BeH₂, NH₃, and OH₂ are summed over all H's. ^e Total excess charge on LiH or BeH₂.

Table X. Complexation Energies of Lone-Pair Bases with LiH and BeH₂ (kcal mol⁻¹)

No.	Complex	Complexation energy ^{a,b}	
		STO-3G	6-31G*
19	HLi-NH ₃	49.7	25.4
21	HLi-OH ₂	53.3	21.8
23	HLi-FH	49.8	13.4
38	H ₂ Be-NH ₃	46.6	21.1
43	H ₂ Be-OH ₂	51.9	16.1
46	H ₂ Be-FH	43.2	4.5

^a Energy of the reaction H_nA + BH_m → H_nA-BH_m. ^b Energies of NH₃, OH₂, and FH from ref 3 and 129.

In contrast to the dimers involving boron, it has been found that the LiH dimer Li-(H)₂-Li (3) is adequately described without correlation. Kollman et al.⁴³ find the binding energy to be 47.2 kcal mol⁻¹ with a near-Hartree-Fock basis, slightly decreasing (to 46.8 kcal mol⁻¹) with inclusion of CI. The values obtained by Ahlrichs^{26a} are more reliable: 47.3 kcal mol⁻¹ (Hartree-Fock with large basis) and 48.3 kcal mol⁻¹ (correlation corrections introduced with CEPA). Our values are similar, 44.0 and 46.8 kcal mol⁻¹ at STO-3G and 6-31G*, respectively. In Kollman's study,⁴³ the dimerization energy for linear (LiH)₂ was found to be 26.0 kcal mol⁻¹, in excellent agreement with our 6-31G* value of 26.3 kcal mol⁻¹. Apparently the lithium representation is sufficiently flexible without d functions, and correlation is less important for three-center bonds involving lithium than boron.

Finally, the effect of correlation has been studied¹⁰⁰ on the BeH₂ dimerization leading to HBe-(H)₂-BeH (26). Using SCF only, the dimerization energy increases from 9.8 to 21.6 kcal mol⁻¹ with basis set expansion (compared to 19.6 at STO-3G and 24.5 at 6-31G*). Inclusion of correlation gives 27.9 kcal mol⁻¹ and a final estimate of 31 ± 6 kcal mol⁻¹ is made when all data are considered. Thus Be₂H₄, predictably, is intermediate between Li₂H₂ and B₂H₆ with regard to correlation and d-function importance.

Table VIII shows the strongest linear MH-M' bond to be that in LiH-LiH, 26.3 kcal mol⁻¹. Other linear systems involve LiH and BeH₂ or BH₃ in one of two configurations, LiH-M or MH-Li; the first of these is favored in both cases. Thus LiH-BeH₂ (binding energy = 18.7 kcal mol⁻¹) is more stable than HLi-HBeH (8.6 kcal mol⁻¹), and LiH-BH₃ is better than HLi-HBH₂ (23.0 vs. 3.4 kcal mol⁻¹). Apparently LiH is a better hydride donor than acceptor.

Similar patterns are seen in the di- and tribridged species. The highest binding energies are those involving lithium as "hydride donor", i.e., in the [Li-(H)_n-] configuration rather

than [HLi-(H)_n-]. Beryllium and boron, on the other hand, prefer configurations in which they have terminal hydrogens. In beryllium systems, HBe-(H)₂-Li is preferred by 14 kcal mol⁻¹ (6-31G*) over Be-(H)₃-Li and Be-(H)₂-LiH is not bound at all. The situation among boron analogues is different: HB-(H)₃-Li is strongly bound and is 5 kcal better (6-31G*) than H₂B-(H)₂-Li, HB-(H)₂-LiH is weakly bound, and there are no bound states involving boron without terminal hydrogens. In general it seems that boron gives more stable bridged dimers than beryllium, based on the binding energy orders H₂B-(H)₂-Li > HBe-(H)₂-Li, H₂B-(H)₂-BeH > HBe-(H)₂-BeH, and HB-(H)₃-Li > Be-(H)₃-Li.

Coordinate Bonds

Charge Distributions. In Table IX are given STO-3G values indicating the extent to which charge is reorganized upon complex formation, H_nM + DH_m → H_nM-DH_m. If total atomic charges did not change in this process, "Δq" values (Table IX) would be zero. Instead, complex formation results in a transfer of electron density from the donor molecule NH₃, OH₂, or FH to the acceptor LiH or BeH₂. As the table shows, all atoms of the donor become more positive as all atoms of the acceptor become more negative, especially the metal atom. The total amount of charge transferred from donor to acceptor molecules is listed in Table IX; understandably, it decreases as the electronegativity of the donor increases, but changing the acceptor from BeH₂ to LiH results in a decrease in charge transfer. Apparently the additional hydrogen on BeH₂ allows distribution of greater negative charge.

Complexation Energies. The energies of complex formation are given in Table X. As noted elsewhere⁴ (for complexes of electron donors with BH₃), the STO-3G basis gives poor complexation energies, as do extended basis sets without polarization functions. The effect of correlation has not been investigated, nor has any possible geometry change at higher levels of theory; it might well be that the intermolecular donor-acceptor distance is too short at STO-3G and that distances and binding energies would significantly increase with 6-31G* geometry optimization.

Although we cannot fully assess the reliability of the 6-31G* binding energies, certain trends are clear from Table X. LiH is a better Lewis acid than BeH₂ or BH₃ (6-31G* binding energies between BH₃ and NH₃, OH₂, and FH are 21.3, 5.5, and -7.7 kcal mol⁻¹, the last not bound at the STO-3G geometry⁴), while NH₃ is a better base than OH₂ or FH. It seems probable on the basis of the 6-31G* binding energies that the amine-LiH or amine-BeH₂ systems would be stable and observable in the gas phase, as amine boranes are. However, further theoretical study is required in order to establish firmly

the geometries and binding energies of such coordinately bound species.

Conclusions

This study of lithium and beryllium compounds has led to a better understanding of bond types involving these electro-positive atoms and has demonstrated some limitations of the theoretical model. The following general conclusions have been reached:

(1) Single metal-metal bonds are long and relatively weak. Bonds to lone-pair atoms are strong and short due to π bonding, the magnitude of which is somewhat exaggerated at STO-3G leading to discrepancies between experimental and theoretical bond distances. In order to maximize π bonding, NH_2 adopts a planar conformation in LiNH_2 and HBeNH_2 , while LiOH and HBeOH are linear.

(2) All systems containing formal $\text{Be}=\text{X}$ double bonds with the exception of Be_2 are found to be bound both in singlet and triplet states.

(3) Doubly and triply bridged dimers of metal hydrides are generally more favorable than singly bridged forms. The fragments Li^- , HBe^- , and H_2B^- seem more apt to bridge than others with different numbers of terminal hydrogens.

(4) Coordinate bonds require d functions for proper description and may also require geometries better than STO-3G.

Acknowledgments. This research was supported by the National Science Foundation, Grants CHE75-09808 (Carnegie-Mellon University) and GP-29078X (Princeton University) and by the Fonds der Chemischen Industrie (Erlangen). Computer time was in part provided by Princeton and Carnegie-Mellon Universities. Mr. E. D. Jemmis is gratefully acknowledged for carrying out some of the computations in Munich, with the assistance of the Leibniz Rechenzentrum and the support of an award by the von Humboldt Foundation (to P.v.R.S.). Dr. Rolf Seeger assisted with the BeO and LiFH_2 calculations, and additional input was provided by R. White-side, Y. Apeloig, J. B. Collins, and D. Poppinger. We thank a referee for constructive criticisms and useful suggestions.

References and Notes

- (1) (a) Ph.D. Thesis, Princeton University, 1976; (b) University of Basel; (c) University of Erlangen-Nuremberg; (d) Carnegie-Mellon University.
- (2) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 808 (1971).
- (3) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971).
- (4) J. D. Dill, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 3402 (1975); see also *ibid.*, **98**, 2371 (1976).
- (5) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).
- (6) General surveys of lithium and beryllium chemistry are found in: (a) A. F. Trotman-Dickenson, Ed., "Comprehensive Inorganic Chemistry", Vol. 1, Pergamon Press, Oxford, 1973; (b) M. F. Lappert, Ed., *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, **1**, (1972); (c) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds", 3rd ed, Vol. 1, Methuen, London, 1967; (d) "Gmelin Handbuch der Anorganischen Chemie": No. 20, Verlag-Chemie, Weinheim, 1960, and No. 26, Verlag-Chemie, Berlin, 1930.
- (7) Reviews of organolithium chemistry: (a) B. J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon Press, Oxford, 1974; (b) P. West, *MTP Int. Rev. of Sci.: Inorg. Chem., Ser. One*, **4**, 1 (1972); (c) L. D. McKeever, "Ions and Ion Pairs in Organic Reactions", Vol. 1, M. Swarc, Ed., Wiley, New York, N.Y., 1972, Chapter 6; (d) T. L. Brown, *Pure Appl. Chem.*, **23**, 447 (1970); (e) T. L. Brown, *Acc. Chem. Res.*, **1**, 23 (1968); (f) T. L. Brown, *Adv. Organomet. Chem.*, **3**, 365 (1965).
- (8) Reviews of organoberyllium chemistry: (a) G. E. Coates and G. L. Morgan, *Adv. Organomet. Chem.*, **9**, 195 (1970); (b) N. R. Fetter, *Organomet. Chem. Rev., Sect. A*, **3**, 1 (1968); (c) D. A. Everest, "The Chemistry of Beryllium", Elsevier, Amsterdam, 1964.
- (9) For periodic summaries of lithium and beryllium research, see: (a) W. H. Glaze, *J. Organomet. Chem.*, **48**, 1 (1973); **68**, 1 (1974); D. W. Slocum, *ibid.*, **95**, 1 (1975); E. M. Kaiser, *ibid.*, **98**, 1 (1975); (b) D. Seyferth, *ibid.*, **62**, 19 (1973); **75**, 1 (1974); **98**, 117 (1975); (c) B. C. Crosse, "Organometallic Chemistry", Vol. 1, The Chemical Society, London, 1971; J. L. Wardell, *ibid.*, Vol. 2, 1973; J. L. Wardell, *ibid.*, Vol. 3, 1975.
- (10) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969). Revised Li and Be scaling factors used here are given by W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **52**, 2769 (1970).
- (11) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973).
- (12) (a) J. D. Dill and J. A. Pople, *J. Chem. Phys.*, **62**, 2921 (1975); (b) J. S. Binkley and J. A. Pople, *ibid.*, **66**, 879 (1977).
- (13) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).
- (14) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, GAUSSIAN 70, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind. 47401. During the course of this work, an omission in the initial guess section of GAUSSIAN 70 was brought to our attention by Dr. R. Seeger. The initial guess parameters for beryllium are missing from routines GESMIN and GESEXT. The following statements should be added to both routines: ENEG(4, 2) = -0.660; ENEG(4, 3) = -0.240.
- (15) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
- (16) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).
- (17) (a) A. Hammett, P. A. Cox, and A. F. Orchard, "Electronic Structure and Magnetism of Inorganic Compounds", Vol. 1, The Chemical Society, London, 1972; (b) A. Hammett, *ibid.* Vol. 2, 1973; (c) A. Hammett and A. F. Orchard, *ibid.* Vol. 3, 1974.
- (18) (a) W. G. Richards, T. E. H. Walker, and R. K. Hinkley, "A Bibliography of Ab Initio Molecular Wave Functions", Clarendon Press, Oxford, 1971; (b) W. G. Richards, T. E. H. Walker, C. Farnell, and P. R. Scott, "Bibliography of Ab Initio Molecular Wave Functions. Supplement for 1970-1973", Clarendon Press, Oxford, 1974.
- (19) P. E. Cade and W. M. Huo, *J. Chem. Phys.*, **47**, 614 (1967).
- (20) (a) S. Fraja and B. J. Ransil, *J. Chem. Phys.*, **36**, 1127 (1962); (b) B. J. Ransil, *Rev. Mod. Phys.*, **32**, 239, 245 (1960); (c) R. Seeger and J. A. Pople, *J. Chem. Phys.*, **65**, 265 (1976).
- (21) C. F. Bender and E. R. Davidson, *Phys. Rev.*, **183**, 23 (1969); (b) *J. Phys. Chem.*, **70**, 2675 (1966).
- (22) W. Meyer and P. Rosmus, *J. Chem. Phys.*, **63**, 2356 (1975).
- (23) C. F. Melius and W. A. Goddard III, *J. Chem. Phys.*, **56**, 3348 (1972).
- (24) K. K. Docken and J. Hinze, *J. Chem. Phys.*, **57**, 4928, 4936 (1972).
- (25) (a) A. K. Q. Siu and E. F. Hayes, *J. Chem. Phys.*, **61**, 37 (1974); (b) R. J. Bartlett and D. M. Silver, *Int. J. Quantum Chem., Symp.*, **No. 8**, 271 (1974).
- (26) (a) R. Ahlrichs, *Theor. Chim. Acta*, **35**, 59 (1974); (b) M. Rupp and R. Ahlrichs, private communication.
- (27) J. M. Norbeck and G. A. Gallup, *Int. J. Quantum Chem., Symp.*, **No. 7**, 161 (1973).
- (28) M. Raimondi, G. F. Tantardini, and M. Simonetta, *Int. J. Quantum Chem., Symp.*, **No. 8**, 285 (1974).
- (29) S. F. Boys and N. C. Handy, *Proc. R. Soc. London, Ser. A*, **311**, 309 (1969).
- (30) E. Wiberg and E. Amberger, "Hydrides of the Elements of Main Groups I-IV", Elsevier, Amsterdam, 1971.
- (31) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules", 2nd ed, Van Nostrand, Princeton, N.J., 1950.
- (32) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, J. A. Pople, and L. Radom, *J. Am. Chem. Soc.*, **98**, 3436 (1976); 5-21G on Li and Be is equivalent to 4-31G on B-F (see ref 13).
- (33) P. C. Hariharan and J. A. Pople, *Mol. Phys.*, **27**, 209 (1974).
- (34) (a) L. Wharton, L. P. Gold, and W. Klemperer, *J. Chem. Phys.*, **33**, 1255 (1960); (b) E. Rothstein, *ibid.*, **50**, 1899 (1969); (c) K. K. Docken and R. R. Freeman, *ibid.*, **61**, 4217 (1974).
- (35) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).
- (36) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 2191 (1970).
- (37) (a) A. C. Wahl, P. J. Bertocini, G. Das, and T. L. Gilbert, *Int. J. Quantum Chem., Symp.*, **No. 1**, 123 (1967); (b) G. Das and A. C. Wahl, *J. Chem. Phys.*, **44**, 87 (1966).
- (38) P. Sutton, P. Bertocini, G. Das, T. L. Gilbert, and A. C. Wahl, *Int. J. Quantum Chem., Symp.*, **No. 3**, 479 (1970).
- (39) (a) W. Kutzelnigg, V. Staemmler, and M. Gélus, *Chem. Phys. Lett.*, **13**, 496 (1972); (b) W. Kutzelnigg and M. Gélus, *ibid.*, **7**, 296 (1970).
- (40) R. Sundar and A. K. Chandra, *Indian J. Chem.*, **12**, 145 (1974).
- (41) R. F. W. Bader, W. H. Henneker, and P. E. Cade, *J. Chem. Phys.*, **46**, 3341 (1967).
- (42) J. R. Tyndall and A. L. Companion, *J. Chem. Phys.*, **52**, 2036 (1970).
- (43) (a) P. Kollman, C. F. Bender, and S. Rothenberg, *J. Am. Chem. Soc.*, **94**, 8016 (1972); (b) C. P. Baskin, C. F. Bender, and P. A. Kollman, *ibid.*, **95**, 5868 (1973).
- (44) J. Berkowitz and W. A. Chupka, *J. Chem. Phys.*, **29**, 653 (1958).
- (45) S. H. Bauer and R. F. Porter, "Molten Salt Chemistry", M. Blander, Ed., Wiley-Interscience, New York, N.Y., 1964, pp 607-680.
- (46) P. A. Kollman, J. F. Liebman, and L. C. Allen, *J. Am. Chem. Soc.*, **92**, 1142 (1970).
- (47) J. D. Dill, L. C. Allen, W. C. Topp, and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 7220 (1975).
- (48) S. H. Bauer, T. Ino, and R. F. Porter, *J. Chem. Phys.*, **33**, 685 (1960). For more recent references to LiCl monomer, see ref 83.
- (49) A. Büchler, J. L. Stauffer, and W. Klemperer, *J. Am. Chem. Soc.*, **86**, 4544 (1964).
- (50) A. Snelson, *J. Chem. Phys.*, **46**, 3652 (1967).
- (51) M. B. Krogh-Jespersen, unpublished results. Other higher level studies of Li_2F_2 give dimerization entropies of 65-66 kcal/mol^{26b} and 66-67 kcal/mol.^{43b}
- (52) S. E. Veazey and W. Gordy, *Phys. Rev.*, **183**, 1303 (1965).
- (53) "Tables of Interatomic Distances", *Chem. Soc. Spec. Publ.*, **No. 11** (1958).
- (54) J. J. Kaufman and L. M. Sachs, *J. Chem. Phys.*, **52**, 638 (1970).
- (55) G. Wittig, F. J. Meyer, and G. Lange, *Justus Liebigs Ann. Chem.*, **571**, 167 (1951).
- (56) R. A. Anderson and G. E. Coates, *J. Chem. Soc., Dalton Trans.*, 1729 (1974).

- (57) N. A. Bell and G. E. Coates, *J. Chem. Soc. A*, 628 (1968).
 (58) E. Weiss and R. Wolfrum, *J. Organomet. Chem.*, **12**, 257 (1968).
 (59) G. E. Coates and R. E. Pendlebury, *J. Chem. Soc. A*, 156 (1970).
 (60) R. M. Adams and A. R. Siedle, "Boron, Metallo-Boron Compounds and Boranes", R. M. Adams, Ed., Wiley-Interscience, New York, N.Y., 1964, Chapter 6.
 (61) D. Groves, W. E. Rhine, and G. D. Stucky, *J. Am. Chem. Soc.*, **93**, 1553 (1971); W. E. Rhine, G. D. Stucky, and S. W. Peterson, *ibid.*, **97**, 6401 (1975).
 (62) E. Weiss and E. A. C. Lucken, *J. Organomet. Chem.*, **2**, 197 (1964); E. Weiss and G. Hencken, *J. Organomet. Chem.*, **21**, 265 (1970).
 (63) L. Andrews, *J. Chem. Phys.*, **47**, 4834 (1967).
 (64) A. H. Cowley and W. D. White, *J. Am. Chem. Soc.*, **91**, 34 (1969).
 (65) G. R. Peyton and W. H. Glaze, *Theor. Chim. Acta*, **13**, 259 (1969).
 (66) M. F. Guest, I. I. Hillier, and V. R. Saunders, *J. Organomet. Chem.*, **44**, 59 (1972).
 (67) N. C. Baird, R. F. Barr, and R. K. Datta, *J. Organomet. Chem.*, **59**, 65 (1973).
 (68) N. J. Fitzpatrick, *Inorg. Nucl. Chem. Lett.*, **10**, 263 (1974).
 (69) (a) J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 5419 (1976); (b) Y. Apeloig, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *ibid.*, **98**, 4332 (1976); (c) Y. Apeloig, P. v. R. Schleyer, J. S. Binkley, J. A. Pople, and W. L. Jorgensen, *Tetrahedron Lett.*, 3923 (1976); (d) E. D. Jemmis, D. Popinger, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, in press; (e) E. D. Jemmis and G. Wenke, unpublished calculations.
 (70) A. Streitwieser, Jr., J. E. Williams, Jr., S. Alexandratos, and J. M. McKelvey, *J. Am. Chem. Soc.*, **98**, 4778 (1976).
 (71) S. R. Ungemach and H. F. Schaefer III, *J. Am. Chem. Soc.*, **96**, 7898 (1974).
 (72) H. Jacobs and R. Juza, *Z. Anorg. Allg. Chem.*, **391**, 271 (1972).
 (73) U. Wannagat and H. Niederprum, *Chem. Ber.*, **94**, 1540 (1961).
 (74) A. Hinchcliffe and J. C. Dobson, *Theor. Chim. Acta*, **39**, 17 (1975).
 (75) J. A. Pople, *Tetrahedron*, **30**, 1605 (1974).
 (76) A. D. Walsh, *J. Chem. Soc.*, 2260, 2266, 2288, 2296, 2301, 2306, 2318, 2321, 2325, 2330 (1953).
 (77) R. Buenker and S. Peyerimhoff, *Chem. Rev.*, **74**, 127 (1974).
 (78) G. Stucky, *Adv. Chem. Ser.*, **No. 130** (1972).
 (79) J. Berkowitz, D. J. Meschl, and W. A. Chupka, *J. Chem. Phys.*, **33**, 533 (1960).
 (80) M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud, and L. C. Walker, *J. Phys. Chem. Ref. Data*, **3**, 311 (1974).
 (81) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **45**, 3682 (1966).
 (82) (a) G. H. F. Diercksen and W. P. Kramer, *Theor. Chim. Acta*, **23**, 387 (1972); (b) G. H. F. Diercksen, private communication.
 (83) A. Büchler, J. L. Stauffer, W. Klemperer, and L. Wharton, *J. Chem. Phys.*, **39**, 2299 (1963).
 (84) D. White, K. S. Seshadri, D. F. Dever, D. E. Mann, and M. J. Linevsky, *J. Chem. Phys.*, **39**, 2463 (1963).
 (85) J. F. Liebman, *J. Chem. Educ.*, **49**, 415 (1972).
 (86) A. Büchler, J. L. Stauffer, and W. Klemperer, *J. Chem. Phys.*, **46**, 605 (1967).
 (87) J. W. Cress, E. Clementi, J. J. Kozak, and M. E. Schwartz, *J. Chem. Phys.*, **63**, 3907 (1975).
 (88) A. H. Narten, F. Vaslow, and H. A. Levy, *J. Chem. Phys.*, **58**, 5017 (1973).
 (89) A. J. Hebert, F. J. Lovas, C. A. Melendres, C. D. Hollowell, T. L. Story, Jr., and K. Street, Jr., *J. Chem. Phys.*, **48**, 2824 (1968).
 (90) A. D. McLean, *J. Chem. Phys.*, **39**, 2653 (1963).
 (91) L. R. Kahn, P. J. Hay, and I. Shavitt, *J. Chem. Phys.*, **61**, 3530 (1974).
 (92) J. J. Kaufman, L. M. Sachs, and M. Geller, *J. Chem. Phys.*, **49**, 4369 (1968).
 (93) (a) M. C. Goldberg and J. R. Riter, Jr., *J. Phys. Chem.*, **71**, 3111 (1967); (b) R. C. C. Lao and J. R. Riter, Jr., *ibid.*, **71**, 2737 (1967).
 (94) G. A. Gallup and J. M. Norbeck, *Chem. Phys.*, **2**, 19 (1973).
 (95) R. P. Hosteny and S. A. Hagstrom, *J. Chem. Phys.*, **58**, 4396 (1973).
 (96) C. F. Bender and E. R. Davidson, *J. Chem. Phys.*, **47**, 4972 (1967).
 (97) W. von Niessen, *Theor. Chim. Acta*, **31**, 111 (1973).
 (98) UHF/STO-3G energies with standard molecular scaling factors (ref 10) are in hartrees: Li(²S) -7.315 526, Be(¹S) -14.351 881.
 (99) R. A. Whiteside, unpublished results.
 (100) R. Ahlrichs, *Theor. Chim. Acta*, **17**, 348 (1970).
 (101) R. G. Pearson, *J. Chem. Phys.*, **52**, 2167 (1974).
 (102) A. Büchler and W. Klemperer, *J. Chem. Phys.*, **29**, 121 (1958).
 (103) G. W. Adamson and H. M. M. Shearer, *Chem. Commun.*, 240 (1965).
 (104) D. A. Drew, G. Gunderson, and A. Haaland, *Acta Chem. Scand.*, **26**, 2147 (1972).
 (105) (a) R. Ahlrichs, *Chem. Phys. Lett.*, **19**, 174 (1973); (b) G. Gunderson, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **59**, 3777 (1973); (c) H. Beall and C. H. Bushweller, *Chem. Rev.*, **73**, 465 (1973).
 (106) T. H. Cook and G. L. Morgan, *J. Am. Chem. Soc.*, **92**, 6487 (1970).
 (107) U. Lamanna and M. Maestro, *Theor. Chim. Acta*, **36**, 103 (1974).
 (108) J. S. Binkley, R. Seeger, J. A. Pople, J. D. Dill, and P. v. R. Schleyer, *Theor. Chim. Acta*, in press.
 (109) A. Almenningen, A. Haaland, G. L. Morgan, *Acta Chem. Scand.*, **23**, 2921 (1969).
 (110) H. Jacobs and R. Juza, *Z. Anorg. Allg. Chem.*, **370**, 248 (1969).
 (111) A. H. Clark and A. Haaland, *Chem. Commun.*, 912 (1969).
 (112) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972).
 (113) J. Weber and A. D. McLean, *J. Am. Chem. Soc.*, **98**, 875 (1976).
 (114) C. D. Whitt and J. L. Atwood, *J. Organomet. Chem.*, **32**, 17 (1971).
 (115) M. Yoshimine, *J. Chem. Phys.*, **40**, 2970 (1964).
 (116) G. Verhaegen and W. G. Richards, *J. Chem. Phys.*, **45**, 1828 (1966).
 (117) W. M. Huo, K. F. Freed, and W. Klemperer, *J. Chem. Phys.*, **46**, 3556 (1967).
 (118) (a) S. V. O'Neil, P. K. Pearson, and H. F. Schaefer III, *Chem. Phys. Lett.*, **10**, 404 (1971); (b) H. F. Schaefer III, *J. Chem. Phys.*, **55**, 176 (1971); (c) P. K. Pearson, S. V. O'Neil, and H. F. Schaefer III, *ibid.*, **56**, 3938 (1972).
 (119) (a) W. A. Chupka, J. Berkowitz, and C. F. Grieser, *J. Chem. Phys.*, **30**, 827 (1959); (b) A. Lagerqvist, *Ark. Fys.*, **7**, 473 (1954); (c) B. A. Thrush, *Proc. Chem. Soc.*, 339 (1960); (d) A. Lagerqvist, *Ark. Mat. Astron. Fys.*, **34B** (1947); (e) A. Lagerqvist and R. Westov, *ibid.*, **32A** (1945).
 (120) E. A. Ballik and D. A. Ramsay, *Astrophys. J.*, **137**, 84 (1963).
 (121) D. Mootz, A. Zinnius, and B. Böttcher, *Angew. Chem.*, **81**, 398 (1969).
 (122) (a) G. E. Coates and N. D. Huck, *J. Chem. Soc.*, 4502 (1952), and accompanying papers; (b) F. Bertin and G. Thomas, *Bull. Soc. Chim. Fr.*, 3951 (1971).
 (123) P. A. Akishin and V. P. Spiridonov, *Sov. Phys.-Crystallogr. (Engl. Transl.)*, **2**, 472 (1957).
 (124) J. L. Gole, *J. Chem. Phys.*, **58**, 869 (1973).
 (125) C. P. Baskin, C. F. Bender, R. R. Lucchese, C. W. Bauschlicher, Jr., and H. F. Schaefer III, *J. Mol. Struct.*, **32**, 125 (1976).
 (126) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
 (127) J. D. Dill, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 1663 (1976).
 (128) (a) *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 37** (1971); (b) 1974 Supplement, ref 80; (c) 1975 supplement, M. W. Chase, J. L. Curnutt, H. Prophet, R. A. McDonald, and A. N. Syverud, *J. Phys. Chem. Ref. Data*, **4**, 1 (1975).
 (129) 6-31G* total energies at STO-3G geometries (previously unpublished) are -40.195 171 (CH₄), -56.181 887 (NH₃), -76.006 702 (OH₂), -100.000 659 (FH), and -1.126 58 (H₂). STO-3G geometries are from ref 3.
 (130) T. P. Fehlner and G. W. Mappes, *J. Phys. Chem.*, **73**, 873 (1969).
 (131) M. Gélus, R. Ahlrichs, V. Staemmler, and W. Kutzelnigg, *Chem. Phys. Lett.*, **7**, 503 (1970).