Inverse Hydrogen-Bonded Complexes

Isabel Rozas,* Ibon Alkorta, and José Elguero

Instituto de Química Médica (C.S.I.C.), c/ Juan de la Cierva 3, 28006-Madrid, Spain

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A theoretical study of the linear and multiple approximation in a series of complexes formed by molecules with electron-rich hydrogen atoms has been carried out. The interaction energy (taking into account the zero-point energy and the basis set superposition error), the atomic charges, and the electron density of the monomers and complexes have been evaluated at the MP2/6-311++G** level. The linear complexes, which show a strong similarity to the standard hydrogen bonds except for the reverse direction of the electron transfer, could be defined as inverse hydrogen bonds.

Introduction

Inter- and intramolecular weak interactions play an important role in different chemical and biological systems. Among these weak interactions the hydrogen bonds (HBs) are the most important. Their abundance in crystals and biological molecules, ease of formation and dissociation, and directionality makes them very distinctive and explains why they have been the object of many theoretical studies.[1]

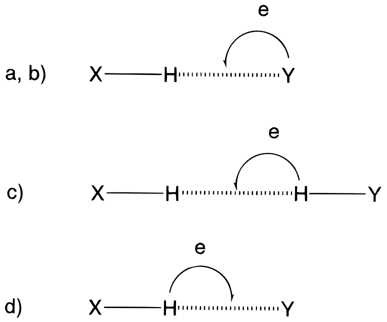
Most published works of HBs are of the type O−H···B or N−H···B in which the HB acceptor "B" posseses O or N lone pairs responsible for the HB formation. These classical HBs have been generalized in other directions such as (a) HBs with unconventional H donors such as C−H,[2] (b) HBs with unconventional H acceptors as π-bonded functional groups,[3] halogens[4] or C atoms,[5] and (c) dihydrogen bonds X−H···H−Y.[6−9]

In the HBs aforementioned, the H atom plays the role of electron acceptor, except for type c (dihydrogen bonds), where one of the H atoms accepts the electrons while the other provides them. Following this sequence, we propose the study of a new class of unconventional HBs (type d) where the H atom will provide electrons and another non-hydrogen atom will accept them (see Scheme 1).

In order to obtain these "inverse" HBs, we should consider a particular set of molecules formed by "donors" and "acceptors" of electrons as shown in Table 1. On one hand, the lithium monohydride, the beryllium dihydride, and the boron tetrahydride anion (in which the heavy atoms are very electron-deficient atoms) will be electron donors ("e-donors"). Thus, the H atoms would be electronically rich enough to provide these electrons in the formation of a HB. On the other hand, electron acceptors ("e-acceptors") will be, in principle, the Li or Be hydrides because these alkaline atoms would accept the electrons easily and without any steric restriction. Besides, other Li and Be derivatives with methyl or fluoride groups, which are electron-withdrawing groups, have been included in the e-acceptors set to make the alkaline atoms more electronically poor.

With regard to the complexes studied in this work, they can be classified in two groups depending on the spatial approximation: (I) "linear approximation", complexes formed by linear interaction between a Li, Be, or B hydride (e-donors) and a Li derivative (e-acceptors) where the Li atom will be the one accepting the electrons donated by the H atom of the e-donor (see Figure 1); (II) "multiple approximation", complexes formed by multiple interactions between Li and Be hydrides and fluorides where the metal, hydrogen, and/or fluorine atoms form a larger number of linkages than their corresponding valence (see Figure 2). This group has been studied only for comparative purposes because the interactions involved cannot be considered as HBs.

SCHEME 1



Many of the structures in the present paper, both monomers and complexes, have not been observed, but those compounds of Li, Be, and B that are experimentally known span a wide range of structural types. For example, LiH exists as an ionic NaCl-like solid[10] and as a polar gas-phase monomer with a bond length of 1.595 Å,[11] but there is no experimental evidence of a $(LiH)_2$ dimer. In addition, it is accepted that the solid state structure of BeH_2 is formed by chains in which the arrangement of H atoms around Be is nearly tetrahedral.[10] However, in the gas phase BeH_2 occurs in the form of linear H−Be−H molecules, and IR studies support the existence of a dimer with bridging H atoms.[12] Further, the molecule of LiF has shown a bond distance of 1.564 Å,[11] and the experimental structural data of BeF_2 have been previously published[13] (see Table 1). Finally, the X-ray structure of $LiCH_3$ reveals a tetrahedral array of Li atoms with a methyl group above each face.[14]

Some of these complexes were previously calculated.[15] However, in the particular case of the linear $(LiH)_2$ dimer, some authors first considered that it was "... bound by what is conceptually similar to a hydrogen bond but with opposite properties..." but later concluded that "...(the) principal binding force is the dipole−dipole interaction..." that they then term as "..."lithium bond"...".[15a] Other authors considered these aggregates as bounded binary complexes, and they never suggested these interactions to be inverse HBs.[15b]

In order to define an interaction as a HB, several conditions should be fulfilled: (i) a bond distance d(H···Y) shorter than the sum of the atomic van der Waals radii of H and Y but longer

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* Author to whom correspondence should be addressed. FAX: 34-1-564-4853. E-mail: rozas@pinar1.csic.es.

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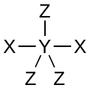
TABLE 1: Calculated Bond Distances (Å) and Angles (deg) of All the Monomers Studied at the MP2/6-311++G Level of Calculation; Some Experimental Data is Also Provided**



	symmetry group	MP2/6-311++G*				experimental	
		d(X−Y)	d(Y−Z)	a(X−Y−Z)	a(Z−Y−Z)	d(X−Y)	a(X−Y−Z)
Li−H	$C_{\infty v}$	1.599	–	–	–	1.595[a]	–
H−Be−H	$D_{\infty v}$	1.329				–	–
$H-B^{-}-(H)_3$	T_d	1.236	1.236	109.5	109.5	1.257[b]	113.0[b]
						1.278[b]	111.0[b]
						1.272[b]	110.8[b]
Li−F	$C_{\infty v}$	1.599	–	–	–	1.564[a]	–
F−Be−F	$D_{\infty v}$	1.392	–	–	–	1.384[c]	–
$Li-CH_3$	C_{3v}	1.990	1.100	112.5	106.2	2.10[d]	–
						(C−H = 1.12)[d]	

[a] Microwave data from ref 11. [b] Microwave data from ref 25. [c] Gas-phase electron diffraction data from ref 23. [d] Estimated from IR spectroscopy from: Andrews, L. *J. Chem. Phys.* **1967**, *47*, 4834.

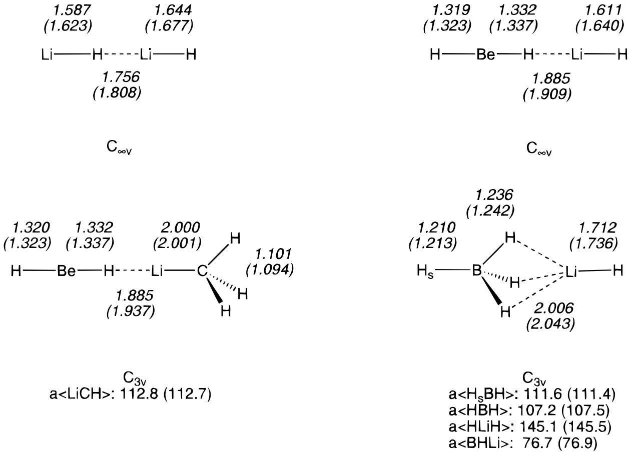


Figure 1. Calculated atomic distances (Å) and angles (deg) of all the dimers formed by linear approximation (nondeformed structures) studied at the MP2/6-311++G** level (the HF/6-31G** results appear in parentheses).

than the corresponding H−Y covalent bond; (ii) an almost linear bond angle a(X−H···Y); (iii) a transfer of electrons among these three atoms; and (iv) a small stabilization energy generally between 2 and 15 kcal/mol.[1d] In this paper, we will provide geometric, electronic, and energy proofs of the existence of inverse HBs in the linear complexes.

Computational Methods

All the *ab initio* optimizations and frequency calculations have been performed using the Gaussian 92 package of programs.[16] The monomers were optimized first at the Hartree−Fock level (HF) using the standard 6-31G** basis set including polarization functions,[17] and these geometries were used to generate the corresponding complexes. Both sets of complexes, formed by linear or multiple approximation, were also optimized using the 6-31G** basis set.

Following a similar scheme and using as starting geometries those optimized at the 6-31G** level, both the monomers and the two sets of complexes were optimized at the second-order Moller−Plesset perturbation theory level (MP2)[18] using the split valence 6-311++G** basis set, which contains diffuse and polarization functions.[19] These calculations are denoted MP2/6-311++G**. The inclusion of electronic correlation (by means of the MP2 theory) and diffuse functions was done to better describe the hydrogen bonds.[1d]

All stationary structures (monomers and both sets of complexes) obtained were characterized as minima by frequency calculations (all the frequencies were positive).

The electronic densities and their Laplacian at the bond critical points, and the atomic charges (within the frame of the theory of atoms in molecules—AIM—proposed by Bader[20]) have been computed using the appropriated keywords with the Gaussian 94[21] package of programs at the MP2/6-311++G** level of calculation and with the AIMPAC set of programs.[20]

The zero-point vibrational energy (ZPE) has been calculated for all the complexes studied, and the interaction energies have been evaluated with and without this ZPE correction.

Because the computed interaction energies will be affected by the basis set superposition error (BSSE), the latter has been estimated using the full counterpoise method[22] and the following equation:

$$\mathrm{BSSE(A-B)} = E(\mathrm{A})_{\mathrm{A}} - E(\mathrm{A})_{\mathrm{AB}} + E(\mathrm{B})_{\mathrm{B}} - E(\mathrm{B})_{\mathrm{AB}} \qquad (1)$$

where $E(\mathrm{A})_{\mathrm{AB}}$ represents the energy of the monomer A calculated using its geometry within the dimer and the complete set of basis functions used to describe the dimer, and $E(\mathrm{A})_{\mathrm{A}}$ is the energy of the same molecule, but using only the basis functions centered on it.

Results and Discussion

Before discussing the results in terms of geometry, electron distribution, and energy, several comments should be made on other attempted complexes where no minima were found.

(i) BH_4^- was never involved as an e-donor in multiple approximations either with Li or Be derivatives (B and H atoms from the tetrahydroborate interacting, simultaneously, with Li, H, and/or Be atoms from the alkali hydrides) since calculations on these systems always yielded aggregates that had negative frequencies. This was also the case of the linear $H_3B-H\cdots Li-(H)(Me)$ complexes.

(ii) Fluoride derivatives were never involved in linear approximations as e-acceptors.

In addition, other complexes were not studied for logical reasons:

(iii) BH_4^- was never used as an e-acceptor in linear or multiple approximations because of steric hindrance.

(iv) Methyllithium could only behave as an e-acceptor in linear approximations due to its structure. That is, only the Li atom is sufficiently electron deficient.

Geometrical Features. The optimized bond distances obtained for the monomers and all the complexes (in both linear and multiple approximations) are shown in Table 1 and Figures 1 and 2, respectively. All the monomers have been the object of previous *ab initio* calculations at very different levels of

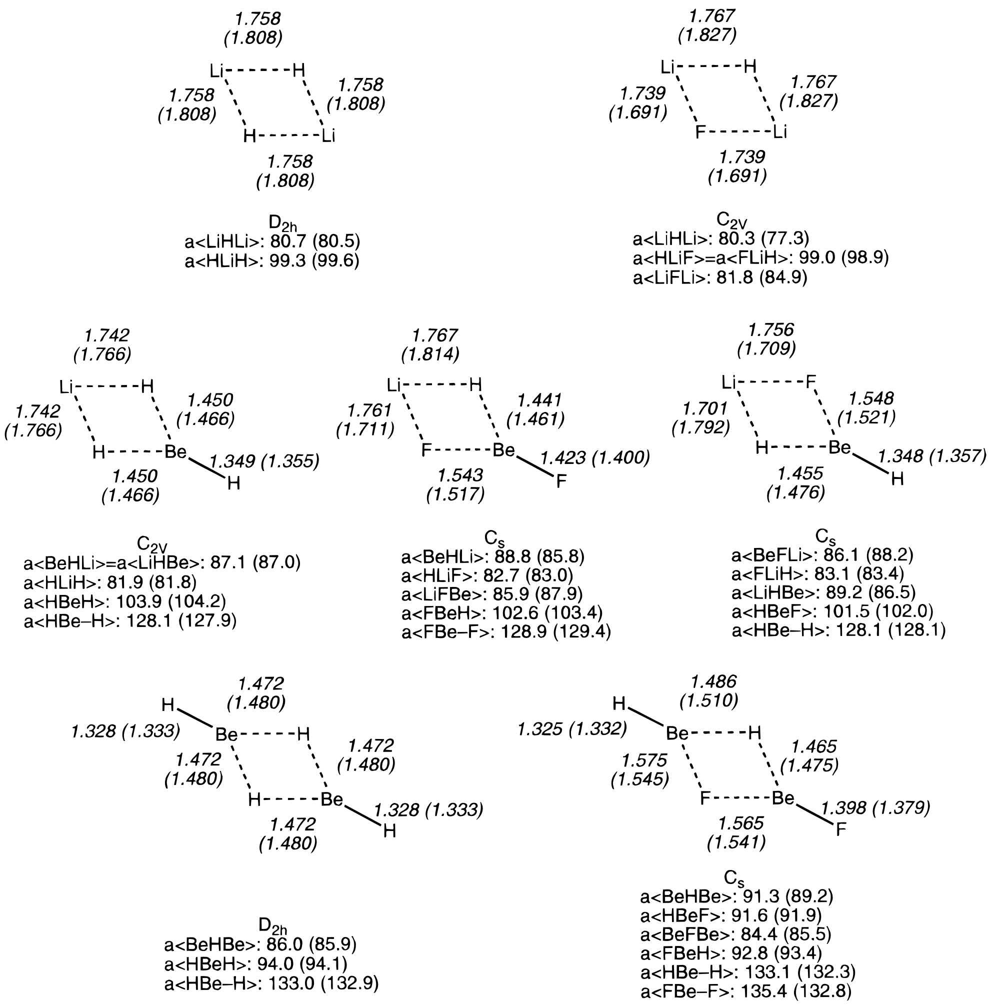


Figure 2. Calculated atomic distances (Å) and angles (deg) of all the dimers formed by multiple approximations (deformed structures) studied at the MP2/6-311++G** level (the HF/6-31G** results appear in parentheses).

computation,[15] and some experimental data have already been reported (see Table 1). We will now turn to the discussion of the complexes.

(I) Complexes Formed by Linear Approximation (See Figure 1). (i) Li–H···Li–H ($C_{\infty v}$). The bond distance Li–H of the molecule with the H atom involved in the HB slightly decreases (~0.01 Å) with respect to that of the isolated monomer, whereas in the other molecule it increases around 0.05 Å. This result does not correspond with that obtained by Dill *et al.*,[15a] who found that the charge transfer causes a lengthening in the bond of the e-donor compared to the isolated monomer, but it is more in accordance with that found by Kollman *et al.*,[23] who observed that the e-acceptor increases its bond while that of the e-donor remains constant. We found that the H···Li distance is larger than the bond distance of the Li–H isolated monomer but smaller than the sum of the Li and H van der Waals radii[24] ($1.12 + 1.17 = 2.29$ Å) and, therefore, in consonance with the formation of an inverse HB.

(ii) H–Be–H···Li–H ($C_{\infty v}$) and (iii) H–Be–H···Li–CH_3 (C_{3v}). The bond distances and angles of the molecules of beryllium hydride are not altered by the interaction with both lithium derivatives, while the Li–H distance increases very slightly and the bond distances of the methyllithium remain very similar to those of the monomer. In these complexes, the H···Li distances are larger than in the previous complex (i), but they still correspond to the formation of an inverse HB.

(iv) H_s–$B^-(H)_3$···Li–H (C_{3v}). The interaction between the tetrahydroborate and the lithium hydride was considered linear and not a multiple approximation primarily because their structures were not as deformed by the interaction (see the following discussion). Further, the H atoms of the boron anion interact only with the Li atom from the LiH molecule (the e-acceptor). We find that the bond distances remain as in the monomer for the three B–H bonds corresponding to the interacting H atoms. The fourth B–H bond becomes slightly shorter, and the Li–H bond becomes much longer, increasing 0.11 Å. Besides, the tetrahedral structure of BH_4^- changes to a pyramidal one ($a(H_sBH)$: from 109.5 to 111.6°). A similar situation is found in the gas phase of alkali metal tetrahydroborates where the metal (Li or Na) atom is bonded to the BH_4 group through three bridged H atoms.[25]

(II) Complexes Formed by Multiple Approximations (See Figure 2). (i) Li···$(H)_2$···Li (D_{2h}) and (ii) Li···(H,F)···Li (C_{2v}). In both cases the Li–H and Li–F molecules have totally lost their identity as monomers, and the complexes have Li···H bonds of the size of the inverse HB formed in the linear $(LiH)_2$ dimer. The Li···F distances are shorter that the Li···H ones but longer than the Li–F distance in the monomer. In case i both H atoms are shared by the Li atoms simultaneously, forming a double bridge between them. The complex is not a square but a regular rhomboid. In case ii not only the H atom but also F are shared by both Li atoms at the same time, forming a planar deformed rhomboid. The existence of this kind of F bridge has been reported before in the literature,[26] and, moreover, the existence of Li bonds has been previously proposed[27] for the $(LiH)_2$ cyclic dimer. This kind of Li bridge

could exist, in the present study, not only for this LiH dimer i but also for the fluoride complex (ii).

(iii) Li⋯(H)$_2$⋯Be−H (C_{2v}), (iv) Li⋯(H,F)⋯Be−F (C_s), and (v) Li⋯(F,H)⋯Be−H (C_s). The situation is very similar between these three complexes and related to both i and ii. In iii two H atoms are binding both the Li and the Be atoms, forming a regular rhomboid. In iv and v H and F atoms interact simultaneously with Li and Be atoms, forming a deformed rhomboid. The H⋯Li distances are similar to that of the linear $(LiH)_2$ dimer, and the H⋯Be distances are larger than those of the isolated monomer but much shorter (by ∼0.3 Å) than the H⋯Li ones. In the three complexes both the BeH_2 (cases iii and v) and BeF_2 (case iv) molecules witness the bending of the HBeH angle from 180.0° to 128.0° and the FBeF angle from 180.0° to 129.0°. The H or F atom not involved in the interactions is oriented outside and along one of the diagonals of the rhomboid (see Figure 2). As in the previous cyclic complexes, systems iv and v show interactions through H atoms, F bridges, and Li bonds. Following the idea of these Li bonds, we could propose the existence of Be bonds in these complexes, since they are acting as bridges between other atoms. Available X-ray data of LiR_2BeH systems indicate structure iii to be a common structural unit.[28]

(vi) H−Be⋯(H)$_2$⋯Be−H (D_{2h}) and (vii) H−Be⋯(H,F)⋯Be−F (C_s). Similar to the previous five cases, in both vi and vii systems the Be, H, and F atoms interact, forming a regular and a deformed rhomboid, respectively. The cyclic dimer of BeH_2 is totally symmetric, and the two H atoms not involved in the interactions are oriented outside and along one of the symmetry axes of the rhomboid. In case vii, the H and the F atoms not involved in the bonding are also oriented outside the ring formed by the interacting atoms. The H⋯Be and F⋯Be distances are a little longer than those of the previous three cases, possibly because Be is less electronegative than Li. The HBeH and FBeF angles become slightly less bent than when they interact with LiH and LiF, changing from 180.0° to 133.0° and from 180.0° to 135.4°, respectively. This may be due to the longer bond distances resulting in less steric hindrance. As a similar geometry has been suggested for dimeric $BeCl_2$ in the gas phase and X-ray structures of alkali metal dialkylberyllium hydrides[29] indicate the presence of $R_2Be⋯(H)_2⋯BeR_2$ units, there is some experimental support for the D_{2h} form of the BeH_2 dimer.

Linear complexes i, ii, and iv and multiple interaction systems i, iii, and vi were previously calculated by other authors[15] with similar results. The LiH, LiF, BeH_2, and BeF_2 cyclic dimers have also been previously studied at high levels of calculation, the cyclic D_{2h} isomers being the most stable ones.[15,26,27]

In the typical HBs the distances d(Y−H) and d(A−X) between the atoms involved in the bonding (Y−H⋯A−X) increase with respect to the systems not bonded due to the transfer of electrons. In the present study, and in the case of the complexes formed by linear interactions, it has been found that the distance d[Li−(H)(C)] [=d(A−X)] increases in the four systems (0.01 to 0.11 Å compared to the isolated monomer). This is consistent with the hypothesis that these are possible HB interactions. In the case of the BH_4^-⋯LiH complex, this is more evident because the Li atom is receiving the electronic contribution of three H atoms, and then the d(Li−H) distance becomes the largest of the three systems (see Figure 1) with a total increment of 0.11 Å. In the case of the multiple approximation complexes, the geometry of both e-donors and e-acceptors is totally modified and all the distances between interacting atoms become longer than in the isolated monomers. The Be−H and Be−F bonds not involved in the multiple linkages become longer than those of the isolated monomers, which is somewhat similar to the A−X distance in the linear H-bonded complexes.

TABLE 2: Electronic Density at the Bond Critical Points (ρ_c) and Its Laplacian ($\nabla^2\rho_c$) at MP2/6-311++G Level for All the Monomers Studied**

	ρ_c	$\nabla^2\rho_c$
$Li\underset{a}{-}H$	(a) 0.039	0.166
$H\underset{a}{-}Be\underset{a}{-}H$	(a) 0.096	0.186
$H\underset{a}{-}B^-\underset{a}{-}(H)_3$	(a) 0.144	−0.004
$Li\underset{a}{-}F$	(a) 0.066	0.644
$F\underset{a}{-}Be\underset{a}{-}F$	(a) 0.130	1.208
$Li\underset{a}{-}C\underset{b}{-}(H)_3$	(a) 0.041	0.206
	(b) 0.256	−0.792

Electronic Distribution. Results obtained for the charge density at the bond critical points (ρ_c) and their Laplacians ($\nabla^2\rho_c$) are gathered in Tables 2 and 3 for monomers and complexes, respectively.

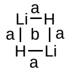
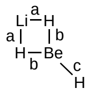
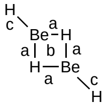
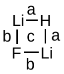
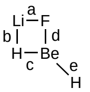
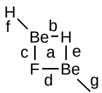
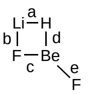
In the case of the Li monomers, small density values at the bond critical points are observed (see Table 2), which agrees with the previously posited hypothesis stating that Li gives electrons to the bonded atom (H, F, or C atom in the complexes studied here), henceforth resulting in electronically poor bonds.[30] Taking into account the closed-shell interactions as defined by Bader,[30] the bonds of these molecules can be considered as ionic bonds showing positive Laplacian and small density values (see Table 2). The case of the Be monomers is very similar, and even though the bond density values are larger than those of the Li monomers, the Laplacians are positive as well. Thus, these derivatives should be also classified among the compounds with closed-shell interactions and ionic bonds. Nonetheless, the BH_4^- molecule is different (see Table 2). The four B−H bonds show a negative and almost null value for the Laplacian and large density values, indicating that those bonds are in an intermediate situation between covalent and ionic.

The ρ_c and $\nabla^2\rho_c$ values obtained at the electron density critical points for all the complexes studied are shown in Table 3. In the linear approximation complexes, the ρ_c and $\nabla^2\rho_c$ values obtained (for the critical points of the bonds in the molecules interacting) are very similar to those obtained for the monomers. Besides, the ρ_c and $\nabla^2\rho_c$ values obtained for the bonds that interact are similar to those expected for a HB as defined by Bader: low densities and positive Laplacians (see Table 3). As an example of these particular closed-shell interactions, the plot for the density and the Laplacian obtained for the $(LiH)_2$ linear dimer, studied at the MP2 level, is shown in Figure 3. Regarding the complex formed by BH_4^-, the H−B bond not participating in the interaction with the LiH molecule is the only one that remains with high density and negative Laplacian values, as would be expected for a covalent bond. The other three B−H bonds become closed-shell interaction type with positive Laplacians but high density values (see the corresponding plots at the MP2 level in Figure 4). Concerning the linear complex with $LiCH_3$, the results show a closed-shell type interaction for the Li−C bond, confirming the noncovalent character in that bond, as was proposed by Streitwieser *et al.*[31]

In classical HB charge flows in the direction opposite that of the proton.[32] However, in the formation of the HBs proposed in the present work, charge and proton should flow in the same direction, since the H atom provides the electrons for the

TABLE 3: Electronic Density at the Critical Points (ρ_c) and Its Laplacian ($\nabla^2\rho_c$) at MP2/6-311++G Level for All the Dimers Studied**

linear approximation nondeformed	ρ_c	$\nabla^2\rho_c$
$\mathrm{Li\underset{a}{-}H\bullet\underset{b}{:}\bullet Li\underset{c}{-}H}$	(a) 0.038	0.172
	(b) 0.022	0.100
	(c) 0.035	0.141
$\mathrm{H\underset{a}{-}Be\underset{b}{-}H\bullet\underset{c}{:}\bullet Li\underset{d}{-}H}$	(a) 0.099	0.188
	(b) 0.090	0.208
	(c) 0.013	0.064
	(d) 0.038	0.158
$\mathrm{H\underset{a}{-}Be\underset{b}{-}H\bullet\underset{c}{:}\bullet Li\underset{d}{-}C\underset{e}{-}(H)_3}$	(a) 0.099	0.188
	(b) 0.090	0.207
	(c) 0.013	0.063
	(d) 0.041	0.198
	(e) 0.255	−0.786
$\mathrm{H\underset{a}{-}B^{-}\underset{b}{-}(H)_3\bullet\underset{c}{:}\bullet Li\underset{d}{-}H}$	(a) 0.157	−0.058
	(b) 0.145	0.027
	(c) 0.022	0.123
	(d) 0.030	0.116

multiple approximation deformed	ρ_c	$\nabla^2\rho_c$
	(a) 0.028	0.117
	(b) 0.017	0.171
	(a) 0.029	0.142
	(b) 0.064	0.206
	(c) 0.088	0.210
	(a) 0.064	0.215
	(b) 0.059	−0.004
	(c) 0.095	0.215
	(a) 0.027	0.115
	(b) 0.044	0.379
	(c) 0.019	0.031
	(a) 0.041	0.359
	(b) 0.028	0.138
	(c) 0.065	0.201
	(d) 0.076	0.669
	(e) 0.089	0.212
	(a) 0.053	0.080
	(b) 0.060	0.216
	(c) 0.070	0.596
	(d) 0.073	0.617
	(e) 0.064	0.232
	(f) 0.096	0.212
	(g) 0.127	1.198
	(a) 0.027	0.134
	(b) 0.041	0.352
	(c) 0.078	0.679
	(d) 0.067	0.206
	(e) 0.115	1.084

bonding. Thus, the atomic charges of the linear complexes were evaluated within the AIM frame at the MP2/6-311++G** level of calculation and were compared to those of the monomers (see Figure 5). In fact, there is an electron transfer from fragments defined as e-donors to the e-acceptors in all the complexes studied. In the Li−H···Li−H dimer there is a 0.031 electron transfer and 0.014 electron in the case of the H−Be−H···Li−H complex. Regarding the atomic charges in the last complex, it is significant that the H atom not involved in the HB formation acts as a "reservoir" of electrons, increasing its charge in 0.010 electron (this effect has been observed before[33]). This also occurs in the H−Be−H···Li−CH$_3$ complex with the transfer of 0.013 electron and the gain of 0.010 electron by the "reservoir" H atom. The same trend is observed for the linear complex formed between BH$_4^-$ and LiH where electrons (0.037 e) and H atoms flow in the same direction and all the H atoms act as "reservoirs" of electrons (see Figure 5).

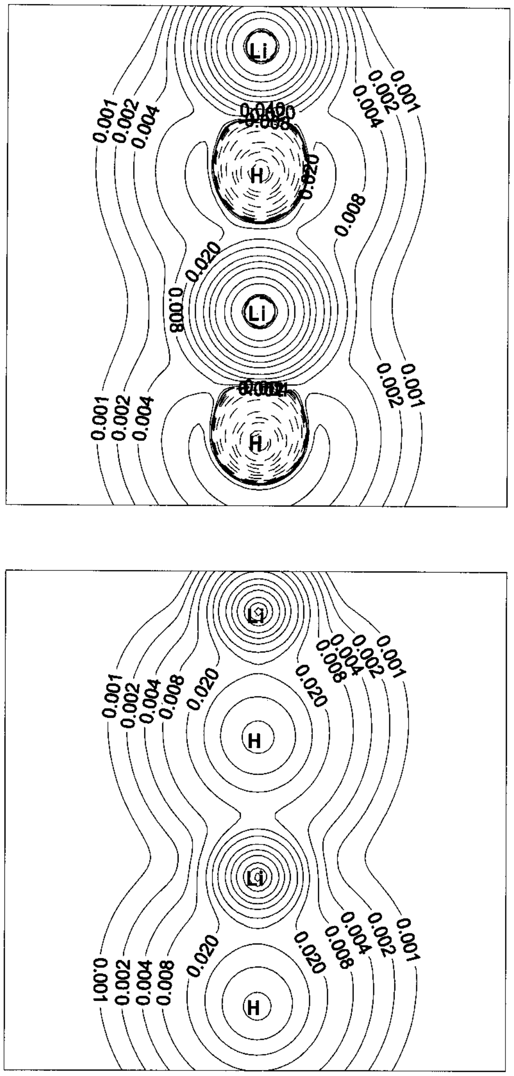


Figure 3. (Lower plot) the electron density (e/a_0^3) and (upper plot) the Laplacian of the electron density (e/a_0^5) of the LiH···LiH dimer in the molecular plane, calculated at the MP2/6-311++G** level.

In the case of the complexes formed by multiple approximation, only those Be−H or Be−F bonds that are not involved in the intermolecular interactions remain with ρ_c and $\nabla^2\rho_c$ values similar to those in the isolated monomers. These two parameters only diminish in absolute value for the rest of the found critical points (bond and ring type). Therefore, the inter- and intramolecular interactions can also be considered as closed-shell interactions (see Table 3). In these complexes the H atoms simultaneously interact with both alkaline atoms (Li and/or Be), completely changing the geometry of the original isolated monomers. An example of this is shown in Figure 6, where the plots of the ρ_c and $\nabla^2\rho_c$ of the (LiH)$_2$ cyclic dimer are represented. In the case that a F atom is involved in the interaction, the situation is exactly the same, with a double bridge to both alkaline atoms. Moreover, in most of these cyclic complexes ring critical points have been found and the density and Laplacian characteristics are those of a closed-shell interaction (see Table 3).

Some studies on the (LiH)$_2$ cyclic dimer following the energy decomposition scheme[15,34] showed that multicenter covalent bonding was important in these complexes. However, our results using the AIM approach have shown that the ring critical

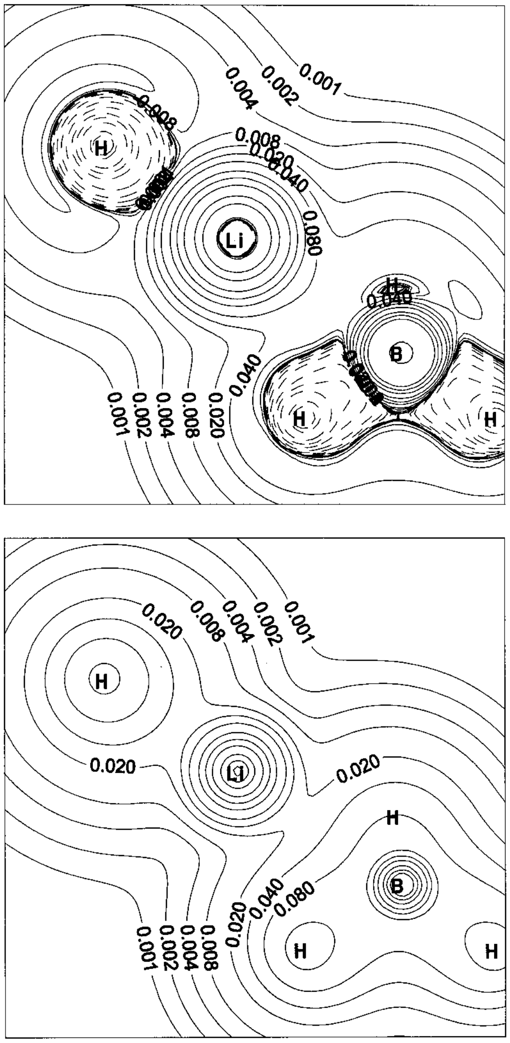


Figure 4. (Lower plot) the electron density (e/a_0^3) and (upper plot) the Laplacian of the electron density (e/a_0^5) of the HB(H)$_3$···LiH complex in the plane formed by the B atom, two of the H bonded to the B atom, and the LiH molecule, calculated at the MP2/6-311++G** level.

point observed within this cyclic dimer has a low ρ_c and positive $\nabla^2\rho_c$, which corresponds to a closed-shell, not a covalent interaction.

Nevertheless, the nature of these cyclic interactions cannot be considered a HB but another kind of linkage such as, for example, the Li bond, as previously proposed.[27]

Energy Results. The interaction energies of all the complexes studied (at HF/6-31G** and MP2/6-311++G** levels) were calculated as the difference between the total energy of the complex and the total energy of the isolated monomers ($E_I = E_{AB} - \{E_A + E_B\}$) and they are gathered in Table 4. The zero-point vibrational energies (ZPE) of these complexes were also evaluated, and they were quite large, especially for the BeH$_2$···LiCH$_3$ and BH$_4^-$···LiH linear complexes (~31 and 26 kcal/mol, respectively). Thus, even though the evaluation of ZPEs requires frequency calculations, which are computationally demanding, their incorporation into the interaction energies is desirable given their magnitude. When the ZPE correction was considered, the interaction energy was evaluated as follows: $E_{I+ZPE} = (E_{AB} + ZPE_{AB}) - \{(E_A + ZPE_A) + (E_B + ZPE_B)\}$, and the results are shown in Table 4.

All the complexes were minima on their potential energy surfaces at both levels of computation, except for the linear (LiH)$_2$ dimer, which presented one negative frequency at the MP2/6-311++G** level. The E_I obtained at the HF level for the linear and cyclic (LiH)$_2$ dimers and the LiHBeH$_2$ and (BeH$_2$)$_2$ complexes are equal to those previously reported.[15]

For the linear complexes, the inclusion of correlation (by means of the MP2 correction) and larger basis sets does not largely affect the final E_I's obtained, yielding differences between 2.90 and 0.04 kcal/mol when compared to the HF calculations. Contrarily, in the case of the cyclic complexes, the effect of the change in the basis set on the E_I depends on the nature of the monomers involved. When the molecules are hydrides, the differences in E_I are between 7.95 and 2.99 kcal/mol, being more negative in the MP2/6-311++G** calculations. When one of the monomers involved is LiF, the differences in energy are smaller (~3.4 kcal/mol), and the most negative energies are obtained at the HF level. However, when BeF$_2$ is involved, both levels of calculation provide very similar results with differences in E_I of 0.41 and 0.28 kcal/mol (see Table 4).

However, when the ZPE correction is considered, the influence of the basis set and correlation inclusion becomes slightly larger for most of the linear complexes (except for that of the BH$_4^-$) with differences in E_{I+ZPE} between 1.17 and 0.27 kcal/mol. In the case of multiple approximation hydride complexes, the differences in E_{I+ZPE} are similar to those of E_I (from 5.70 to 2.81 kcal/mol). These differences are smaller for the LiF dimers (from 0.84 to 0.70 kcal/mol) and for the BeF$_2$ complexes (from 0.41 to 0.28 kcal/mol). In all the cases but the cyclic hydride complexes and the linear (LiH)$_2$ dimer the E_{I+ZPE} values are more negative at the HF level than with the MP2 method (see Table 4).

The importance of considering the BSSE contribution to the interaction energy especially when using perturbation methods (as MP2) is known. Thus, this contribution has been evaluated for all the complexes (*cf.* eq 1) and has been added to the interaction energy corrected with the ZPE error at the MP2/6-311++G** level. The final interaction energy ($E_{I+ZPE+BSSE}$) and the BSSE contribution for each complex (in kcal/mol) are shown in Table 4. In the linear complexes, the BSSE contribution is not very large, but still significant with values between 0.6 and 2.0 kcal/mol. In the multiple interactions complexes this contribution becomes very significant (between 1.8 and 6.0 kcal/mol), where the F and Be derivatives have the larger values. This is probably due to the big deformation that the monomers suffer in these kinds of cyclic complexes. Thus, the evaluation of this BSSE contribution is very important for a correct estimation of the total interaction energy.

In previous work, it was found that the linear form of the (LiH)$_2$ dimer was around 22 kcal/mol less stable than the cyclic form.[15a,b,23,35] A similar result has been found in the present work, with a difference of 20.8 kcal/mol in the $E_{I+ZPE+BSSE}$ values. This difference is even larger between the linear and cyclic BeH$_2$···LiH dimers, where the cyclic one is 34.44 kcal/mol more stable than the linear.

Some correlations between the E_I, E_{I+ZPE}, and $E_{I+ZPE+BSSE}$ and the ρ_c and H···X distance of the linear complexes studied have been tested but to no avail. In general, the interaction energies obtained for the linear complexes agree with the stabilization provided by a HB (~2−15 kcal/mol). However, for the linear (LiH)$_2$ dimer and the BH$_4^-$···LiH complex, the corrected energies are still larger than expected (~23 and 45 kcal/mol). Only the large strength of the interaction in the first case can account for the value obtained. The result achieved for the second complex could be explained because there are three H atoms involved in the interaction with the Li atom, so the stabilization attained is larger than with one H atom. For

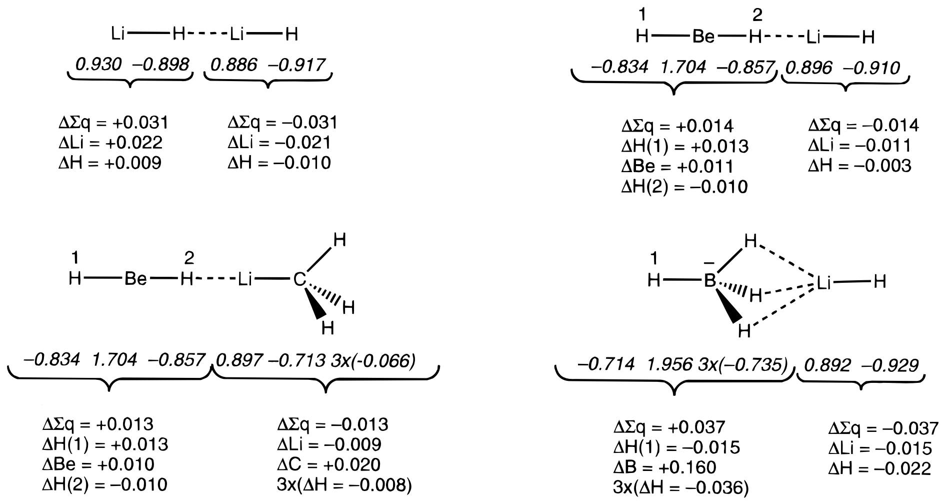


Figure 5. Calculated atomic charges of all the dimers formed by linear approximation (nondeformed structures) studied at the MP2/6-311++G** level by means of the AIM theory.

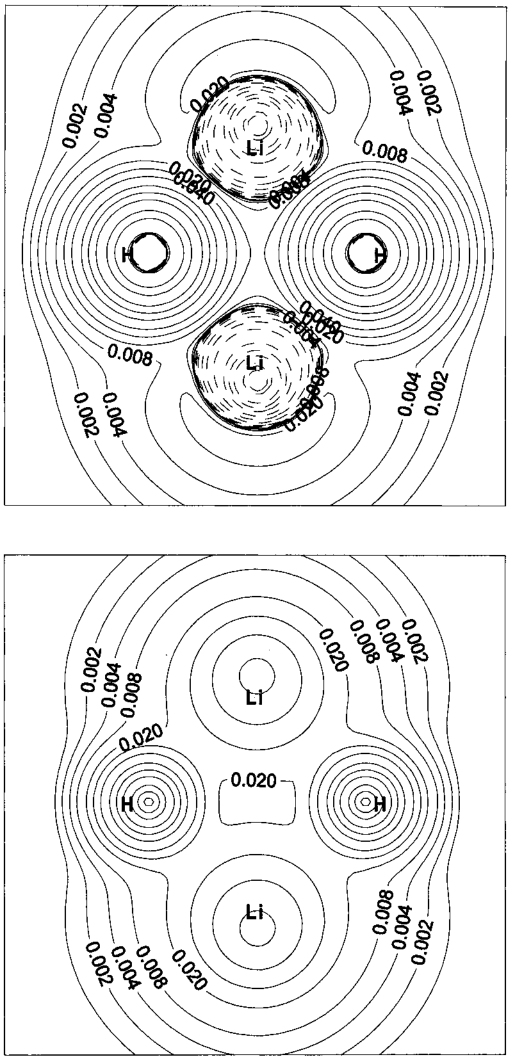


Figure 6. (Lower plot) the electron density (e/a_0^3) and (upper plot) the Laplacian of the electron density (e/a_0^5) of the $(LiH)_2$ cyclic dimer in the molecular plane, calculated at the MP2/6-311++G** level.

the cyclic complexes, all the interaction energies are larger than those expected for a HB.

One of the main differences observed between the linear and the multiple approximation complexes is the large distortion suffered by the monomers involved in the multiple approximation systems. This distortion could be quantified by computing the energy of deformation (E_D) as follows:

$$E_D(A_{AB}) = E(A)_A - E(A_{AB})_A \qquad (2)$$

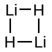
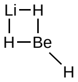
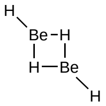
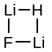
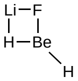
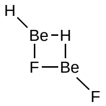
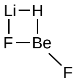
where $E(A)_A$ is the total energy of the isolated monomer in its geometrical minimum and $E(A_{AB})_A$ is the total energy of the monomer as it is within the AB complex in both cases calculated with the basis set of the monomer. The formation of a HB may imply some rotation or some distortion of the molecules involved in the bonding, but the barrier to such a deformation is always small. Then, E_D will quantify the energy needed to deform the monomers from their geometry as minima to their situation within the complexes. In other words, it will quantify the "barrier" to the distortion in the formation of the HB. The results obtained for this energy at the MP2/6-311++G** level are gathered in Table 4. The linear HB complexes show small E_D values since the monomers within the complexes are not distorted as should be expected of a weak interaction in binary HB complexes. The systems formed by multiple interactions exhibit larger values of E_D (from 3 to 35 kcal/mol). The complexes formed by Be derivatives, which are the molecules that suffer the largest deformations, show the largest E_D (H−Be···(H)$_2$···Be−H, 28.4; H−Be···(H)$_2$···Be−F, 34.6 kcal/mol).

Conclusions and Final Remarks

Given the basically accepted definition of a HB, a bond distance d(H···A) shorter than the sum of the atomic van der Waals radii of H and A, a bond angle a(D−H···A) almost linear, a certain transfer of charge among these three atoms, and an energy around 2−15 kcal/mol, our study suggests that linear complexes fulfill all the conditions and, therefore, should be considered as a new type of inverse HB. The computation of the atomic charges of the linear complexes showed that contrary to classical HBs, the charge and H atom flow in the same direction from the acid to the basic fragment. This fact makes these inverse HBs unique.

On the other hand, the systems formed by multiple interactions do not fulfill most of the conditions: the bond angles are between 80.3° and 91.3°; there is no directionality in the linkage and, therefore, the flow of H atoms and electrons is not clear; and the interaction energies are too large. Moreover, HB are considered weak interactions that do not affect, to a large extent, the geometry (bonds and angles) of the isolated monomers. However, the interactions involved in the formation of the cyclic complexes are of such a nature that deeply deforms the geometry

TABLE 4: Interaction Energies (E_I, kcal/mol) with and without Considering the ZPE and the BSSE (kcal/mol) Corrections, and the BSSE Contribution for the Complexes at HF/6-31G and MP2/6-311++G** Levels of Calculation; The Deformation Energy (E_D As Defined in the Text, kcal/mol) Is Also Included for the Calculations with the MP2 Method**

	HF/6-31G**		MP2/6-311++G**				
	E_I	E_{I+ZPE}	E_I	E_{I+ZPE}	BSSE	$E_{I+ZPE+BSSE}$	E_D
Linear Approximation, Nondeformed							
$Li-H\cdots Li-H$	−25.76	−23.78	−25.80	−24.05	0.99	−23.06	0.16
$H-Be-H\cdots Li-H$	−8.16	−6.91	−7.83	−5.83	0.57	−5.26	0.03
$H-Be-H\cdots Li-CH_3$	−7.53	−6.72	−7.59	−5.70	0.65	−5.05	0.03
$H-B^{-}-(H)_3\cdots Li-H$	−51.45	−48.73	−48.55	−47.56	1.98	−45.58	1.25
Multiple Approximation, Deformed							
	−46.19	−42.89	−49.18	−45.70	1.84	−43.86	3.23
	−40.40	−36.52	−46.93	−41.80	2.10	−39.70	17.43
	−24.31	−20.35	−32.26	−26.05	2.23	−23.82	28.37
	−59.79	−57.10	−56.40	−53.61	2.91	−50.70	4.41
	−53.28	−50.72	−49.88	−46.08	4.61	−41.47	18.21
	−32.02	−28.28	−32.43	−27.58	6.02	−21.55	34.58
	−56.21	−51.82	−55.93	−51.68	4.41	−47.26	24.52

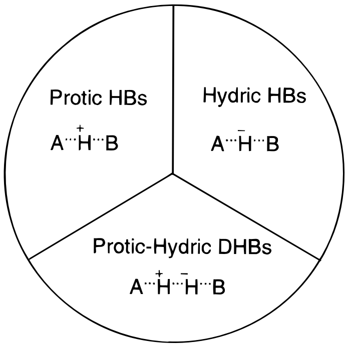
of the original monomers. Therefore, interactions in cyclic complexes cannot be considered as HBs.

Several authors[33,36] proposed that a typical HB is that where the H atom is covalently bonded (high ρ_c and positive $\nabla^2\rho_c$) to an acid fragment and ionically (low ρ_c and negative $\nabla^2\rho_c$) to a base. This is true when the starting monomers are bonded by covalent interactions. Nevertheless, in the present study, all the monomers but the BH_4^- are bonded by ionic interactions. Thus, regarding the electronic distribution in the case of linear complexes, these inverse HBs can be defined as those in which a hydrogen atom is bound to both the e-donor and the e-acceptor by closed-shell interactions, both of which are interacting fragments bonded in closed-shell. The bond critical points obtained in these interactions reflect all the characteristics associated with HBs: low ρ_c values and $\nabla^2\rho_c > 0$. More specifically, and following the definition given by Platts and Laidig,[33] these inverse HBs are "neutral" HBs since they have ρ_c values around 10^{-2}. Other remarkable exceptions to that proposed "HB definition" are, on one hand, the case of the symmetrical complex $[F\cdots H\cdots F]^-$, which is considered to represent one of the strongest HBs (55 kcal/mol)[37] and, on the other, the HBs with π-systems where the e-donor is not an atom but a delocalized π-electron system.[3b]

In the case of complexes formed by multiple approximation both H and F atoms form equal double bridges with two alkaline atoms, and the identity of the former molecules is completely lost. Even though these are clearly closed-shell interactions (low ρ_c and positive $\nabla^2\rho_c$), they should not be considered HBs but ionic bonds.

The energy results obtained show that the inclusion of correlation effect, diffuse functions, and ZPE and BSSE corrections is significant in the description of these particular hydrogen-bonded complexes. The energies obtained for the linear complexes let us classify the nature of the HB present in the systems following Platts and Laidig's definitions.[33] Thus, even though all of them should be considered "neutral" HBs according to the density values obtained (~10^{-2}), only the linear complexes of BeH_2 show energies within 5−10 kcal/mol (see Table 4), which correspond to "neutral" HBs.[32] The LiH dimer and the BH_4^- complex exhibit energies around 25−50 kcal/mol (see Table 4), which is more related to the formation of "ionic" HBs.[33]

SCHEME 2



The evaluation of the deformation energy of the monomers within the complexes has verified that the interactions present in the linear complexes are HBs (small E_D values), whereas those linkages present in the multiple interaction complexes are stronger than HBs since the E_D values obtained are very large, suggesting that the monomers become deformed by the interaction with the other molecule. Finally, these inverse HBs should exist between hydrides in which an atom (Li, Be, B, etc.) has provided enough electrons to its bonded H atom and another molecule with an electronically poor enough atom (Li, Be, etc.). The nature of these interactions has been verified to be that of a HB given their geometric, electronic, and energy features.

In conclusion, the present work provides, for the first time, an integrated view of hydrogen bonds. Besides the two cases already known, standard "protic" hydrogen bonds and "protic-hydric" dihydrogen bonds,[9] the new class of "hydric" inverse hydrogen bonds was described. The simple picture, seen in Scheme 2, represents the situation of hydrogen-bonded complexes today. Obviously, if the area were proportional to the importance (or the number of references), then "protic" HBs will cover more than 99.9% of the pie surface. We expect that this situation will become more balanced in the future.

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