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Valence-Only Correlation in LiH and BeH^{+} *

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The pseudonatural orbital procedure has been applied to the calculation of the potential energy curve of LiH and the dissociation energy of BeH^+. Only the two-electron bonding pair is correlated and estimates of σ and π type correlation are obtained. The results for LiH are in good agreement with the most accurate previously published calculations. Comparison with experimental results for LiH indicates that the calculated dissociation energies are accurate to about 0.15 to 0.2 eV.

Key Words: BeH^+, correlation energy, dissociation energy, LiH, molecular orbital, potential energy curve.

1. Introduction

The calculation of accurate potential energy curves of small molecules cannot be achieved within the framework of the Hartree-Fock one-electron model. Consideration of the correlation is necessary to insure both the correct asymptotic dependence and the depth and shape of the curve near the equilibrium separation. In order to simplify the problem correlation considerations should be limited to only those electrons intimately involved in the binding process, i.e., the valence electrons. This permits the utilization of localization techniques which limit the number of relevant electrons that must be correlated. Prior to the introduction of localization techniques it is necessary to show that, as expected, only the valence electrons need be considered. Evidence for the validity of this concept has been accumulated by extended Hartree-Fock (H. F.) calculations [1][1] on the molecules H_2 and Li_2, for which the bonding valence electrons are a simple pair. Additional work has been done on systems for which intershell pairs are significant [2]. However, such complicated systems fall beyond the range of the present investigation, which is to add to the evidence for the accuracy of potential curves calculated by correlating only the two-electron valence shell.

The simplest case beyond H_2 is the isoelectronic LiH sequence. Numerous calculations [3] of this molecule have appeared over the years but the relative simplicity of the model has enticed all the investigators to do as complete a calculation as possible within their model. Those studies which consider correlation therefore apply a correlated trial function to both the Li *K* shell and the bonding shell. Although the probability of success for a valence-shell-only treatment is predictably high, we feel that such a calculation is required as a basis for future work in this area.

The calculation in this paper is equivalent to the extended H. F. calculation with a frozen 1σ(*K* shell) H. F. molecular orbital. The actual procedure follows the pseudonatural orbital (PNO) procedure previously applied to the three-electron system [2]. In effect the virtual H. F. orbitals are transformed into approximate natural orbitals [4] which span the same region of space as the occupied H. F. valence orbitals. Such orbitals provide for rapid convergence in the superposition of configurations (SOC) calculation. A number of points of the LiH curve were calculated in this way. The results are compared in particular to the natural orbital based calculation of Bender and Davidson [3f] which is the most accurate calculation for LiH. We can anticipate our conclusion by noting that the outer-shell correlation energies for the two calculations are quite comparable.

The isoelectronic system BeH^+ is also considered only at the equilibrium internuclear separation. Since the electronic distributions in the H. F. solution for LiH and BeH^+ are quite different, the correlation

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[1] Figures in brackets indicate the literature references at the end of this paper.

results shed light on different bonding cases ranging from the ionic or strongly polarized through the covalent. For the LiH and BeH^+ molecules the techniques utilized have proved convenient and quantitative.

2. Pseudonatural Orbitals and Basis Functions

All calculations are based on trial functions of the form

$$\psi(1,2,3,4) = A\psi_1(1)\psi_1(2)\psi(3,4)$$

where ψ_1 is an accurate approximation to the 1σ H. F. molecular orbital, φ is a two-electron pair function including a singlet spin function, and A is the antisymmetrizer. The pair function is held strongly orthogonal to the ψ_1 orbital. The overall symmetry is $^1\Sigma^+$ and the wave function would agree with the result of an extended H. F. calculation if the ψ_1 orbital were permitted to relax in the field of the pair function.

The $\varphi(3,4)$ is determined here in two steps. Using the σ virtual H. F. solutions, a superposition of all configurations formed by all single and double excitations from the valence shell molecular orbital is diagonalized. Similarly, an arbitrarily orthonormalized set of π orbitals is diagonalized. The first-order density matrices for both the σ and π substituted wave functions are diagonalized by determining the equivalent transformation which diagonalized the coefficient matrix for the SOC expansion. The approximate or pseudonatural orbitals are now available for a complete SOC involving both σ and π excitations. Only diagonal excitations are now considered and the final SOC requires a limited number of interaction integrals in the new basis, thereby simplifying the calculation.

The use of pseudonatural orbitals is most convenient when intershell pairs are significant. Extended H. F. procedures would actually be better in the present case, since only one pair is being correlated. However, the results are essentially equivalent and are obtained with comparable effort.

The basis set is built around the best atom Gaussian-type function (GTF) H. F. solutions of Huzinaga [5]. As is widely known [6], the natural orbitals are localized in the same region of space as the respective H. F. orbitals. Except for polarization orbitals of new symmetry type the H. F. basis should suffice. Polarization orbitals were added by scaling GTF fits to $p\sigma$ and $p\pi$ functions and varying the scale factor to determine the best energy. The variations were by no means exhaustive and improvements are possible. The variations were done only for LiH at 3.0 a.u. and the same basis was used for the entire curve (or appropriately scaled for the BeH^+ case).

Small exponent s and p GTF are centered on the Li atom. They are intended to account for the polarization of the charge distribution toward the H atom. Whether the LiH charge density can be represented by an ionic model is somewhat debatable [7] with the present evidence leaning toward the polarization of a diffuse Li $2s$ function. The large set on the Li actually contributes to the wavefunction near H with the heavy weight to the small exponent functions.

The accuracy of the basis is best judged in this light by comparison with the results using significantly different bases. The BeH^+ charge density has even less resemblance to an ionic model and the basis should be adequate.

The basis sets are defined in table 1 and the PNO coefficients are given in table 2. The first two orbitals are exactly the undisturbed $1s_{Li}$ H. F. molecular orbital and the bonding PNO which is very similar to the second occupied H.F. molecular orbital. This orbital has been referred to as a $1s_{H^-}$ orbital because of the ionicity of the LiH bond [8]. However, the $2s_{Li}$ and $2p_{Li}$ densities are far from insignificant. From our results and those of Bender and Davidson on the partitioning of the correlation into σ and π type terms, the identification of this orbital as a $1s_{H^-}$ is obviously oversimplified. The basis set that was chosen to represent both the H. F. and correlation may, however, underestimate the need for polarization of the H centered density.

TABLE 1. *Parameters for basis orbitals,* f(x, y, z) *exp*($-$ al^{-2})

(a) LiH	Atomic orbital basis		
Orbital No.	Type	Center	Exponent
1	P_σ	Li	1.34829
2	P_σ	Li	.31932
3	P_σ	Li	.098736
4	P_σ	H	.75
5	S	Li	.028643
6	S	Li	.076663
7	S	Li	.44462
8	S	Li	1.15685
9	S	Li	3.15789
10	S	Li	9.35328
11	S	Li	31.9415
12	S	Li	138.73
13	S	Li	921.271
14	S	H	0.101309
15	S	H	.321144
16	S	H	1.1468
17	S	H	5.05796
18	S	H	33.6444
19	P_π	Li	2.9353
20	P_π	Li	0.696844
21	P_π	Li	.222852
22	P_π	Li	.08074
23	P_π	H	.557104
24	P_π	H	.129568
(b) BeH^+	Atomic orbital basis		
1	P_σ	Be	1.483
2	P_σ	Be	.351
3	P_σ	Be	.109
4	P_σ	H	.75
5	S	Be	.0583
6	S	Be	.1806
7	S	Be	.8589
8	S	Be	2.1847
9	S	Be	5.9326
10	S	Be	17.6239
11	S	Be	60.3255
12	S	Be	262.139
13	S	Be	1741.38
14	S	H	0.1013
15	S	H	.3211
16	S	H	1.1468
17	S	H	5.0579
18	S	H	33.6444
19	P_π	Be	3.22883
20	P_π	Be	0.766528
21	P_π	Be	.245137
22	P_π	Be	.088814
23	P_π	H	.557104
24	P_π	H	.129568

TABLE 2. *Expansion coefficients for the Hartree-Fock and pseudo-natural orbitals*

1 a.u. (length) = 0.529172 Å

(a) PNO Coefficients, LiH $R = 2.0$

Orbital No.	1σ H. F.	2σ H. F.	2σ	3σ	4σ	5σ
1	0.004407	0.033912	0.034077	0.008329	−0.032827	−0.017292
2	.007878	.091818	.088182	−.068465	−.477243	−.012876
3	−.002017	.117561	.114025	−.231170	−.554928	.367876
4	.004964	−.021768	−.021483	−.072883	.484559	.234911
5	−.000002	−.073225	−.099539	.252490	−.225179	−.323240
6	.002588	−.172702	−.174916	.317555	1.704137	−.693758
7	.167498	.097015	.095932	−.069496	.568379	−.050188
8	.424381	.118228	.118447	.015033	−.533391	−.122566
9	.341843	.066803	.067831	.003539	.002012	−.007132
10	.160068	.029541	.029685	.003243	−.069599	−.017212
11	.049580	.008663	.008762	.000617	−.007569	−.002056
12	.010380	.001814	.001826	.000175	−.003246	−.000788
13	.001360	.000235	.000237	.000018	−.000279	−.000069
14	−.001627	−.317569	−.310838	.625276	−1.598575	.257708
15	.010437	−.360808	−.346714	−.794154	−.378740	1.736012
16	.009115	−.164161	−.173403	−.447228	.012201	−1.266605
17	.002351	−.038021	−.038413	−.054958	−.010818	−0.165061
18	.000373	−.005348	−.005422	−.008110	.000229	−.010251
	1π	2π				
19	0.006254	0.017242				
20	.010794	.047861				
21	.103205	.130557				
22	−.049588	−.026074				
23	.499923	−1.089518				
24	.591811	.934826				

(b) PNO Coefficients, LiH $R = 2.6$

Orbital No.	1σ H. F.	2σ H. F.	2σ	3σ	4σ	5σ
1	0.006374	0.022623	0.022271	0.006199	−0.028556	−0.014421
2	.005588	.078845	.077196	.059848	−.398499	−.111385
3	−.001458	.107365	.102291	.254043	−.428187	.458737
4	.001660	−.018462	−.017715	.052101	.447592	.198343
5	−.000365	−.076565	−.100904	−.249082	−.231610	−.327268
6	.002908	−.196271	−.203380	−.484031	1.190100	−.833528
7	.171372	.053235	.051759	.101569	.385691	.224806
8	.423021	.097091	.099854	.048487	−.376673	−.134147
9	.343919	.048569	.049199	.027676	−.011197	.009049
10	.160316	.022722	.023160	.011783	−.050662	−.015508
11	.049759	.006484	.006589	.003410	−.006656	−.000927
12	.010401	.001382	.001406	.000710	−.002475	−.000667
13	.001364	.000177	.000180	.000091	−.000229	−.000045
14	−.000849	−.342670	−.328782	−.458568	−1.339842	.595913
15	.004437	−.334963	−.325985	.829587	−.000825	1.280689
16	.002763	−.147001	−.155785	.383794	.033370	−1.174829
17	.000597	−.035569	−.035967	.053933	−.007512	−0.127366
18	.000109	−.004919	−.005002	.007591	.000534	−.010907
	1π	2π				
19	0.005296	−0.009818				
20	.005507	−.002790				
21	.154002	−.187711				
22	−.011169	−.115084				
23	.449336	1.057181				
24	.599113	−0.739935				

1 a.u. (length) = 0.529172 Å

(c) PNO Coefficients, LiH $R = 3.0$

Orbital No.	1σ H. F.	2σ H. F.	2σ	3σ	4σ	5σ
1	0.006264	0.016858	0.016266	0.011714	−0.007152	−0.000853
2	.005319	.069495	.068472	.067528	−.380256	.174121
3	−.001506	.107464	.102147	.276211	−.378214	−.434746
4	.000962	−.016321	−.014973	.018269	.443654	−.231176
5	−.000437	−.085497	−.109990	−.249975	−.280662	.370475
6	.002998	−.207120	−.220749	−.576710	.996402	.728993
7	.170797	.042737	.042031	.092888	.323136	−.289679
8	.423435	.086114	.089866	.083038	−.326297	.143809
9	.344369	.039994	.040816	.040843	.003043	−.030252
10	.160459	.019650	.020300	.018641	−.041905	.012447
11	.049808	.005456	.005598	.005257	−.004722	−.000831
12	.010409	.001184	.001220	.001118	−.001997	.000431
13	.001366	.000150	.000154	.000143	−.000174	.000005
14	−.000747	−.364782	−.342419	−.303882	−1.304840	−.654657
15	.002781	−.318529	−.313586	.814402	0.245100	−1.045312
16	.001290	−.140493	−.149304	.338235	.060241	1.112123
17	.000281	−.034264	−.034721	.052848	.003527	0.105760
18	.000050	−.004698	−.004787	.007121	.001194	.011175
	1π	2π				
19	0.005663	−0.007912				
20	−.005169	.005612				
21	.161447	−.209146				
22	.022901	−.193739				
23	.413339	1.031171				
24	.622294	−0.630077				

(d) PNO Coefficients, LiH $R = 3.4$

Orbital No.	1σ H. F.	2σ H. F.	2σ	3σ	4σ	5σ
1	0.005777	0.012993	0.012383	−0.012011	0.015253	0.018591
2	.005095	.058102	.057180	−.067785	−.353559	−.198672
3	−.001441	.110553	.104984	−.285139	−.378649	.347227
4	.000646	−.014262	−.012337	.004920	.447394	.291657
5	−.000436	−.097410	−.123429	.255716	−.340258	−.422054
6	.002847	−.213738	−.235591	.615901	.903941	−.562947
7	.170049	.040677	.041490	−.088486	.236146	.272905
8	.423967	.075020	.079468	−.100022	−.268000	−.129519
9	.344544	.034459	.035914	−.046361	.014584	.047560
10	.160571	.017156	.018024	−.022163	−.034262	−.008843
11	.049833	.004721	.004935	−.006135	−.002916	.002546
12	.010415	.001030	.001080	−.001324	−.001572	−.000172
13	.001366	.000130	.000136	−.000168	−.000123	.000036
14	−.000574	−.388998	−.356436	.184030	−1.297227	.650819
15	.001807	−.302829	−.302215	−.768513	0.438748	.853499
16	.000598	−.136544	−.145546	−.296663	.073463	−1.058826
17	.000151	−.033149	−.033677	−.050383	.014132	−0.088454
18	.000023	−.004542	−.004638	−.006625	.001653	−.011337
	1π	2π				
19	0.005932	0.007031				
20	−.012050	−.009586				
21	.149304	.216540				
22	.063263	.263758				
23	.382200	−1.000147				
24	.646210	0.545015				

TABLE 2. *Expansion coefficients for the Hartree-Fock and pseudo-natural orbitals*—Continued

1 a.u. (length) = 0.529172 Å

(e) PNO Coefficients, LiH $R=4.0$

Orbital No.	1σ H. F.	2σ H. F.	2σ	3σ	4σ	5σ
1	0.004917	0.009900	0.009271	−0.010910	0.026950	0.031569
2	.004625	.039332	.038823	−.048059	−.251935	−.134434
3	−.001250	.116407	.108802	−.276563	−.471289	.122146
4	.000359	−.010693	−.007997	.015361	.455548	.370528
5	−.000404	−.119925	−.151321	.282965	−.429119	−.503933
6	.002553	−.215459	−.251724	.606841	.890824	−.275745
7	.169221	.042781	.046063	−.096618	.044140	.117570
8	.424585	.060143	.066555	−.097040	−.137987	−.028820
9	.344632	.029858	.032587	−.050435	.003492	.042146
10	.160685	.014223	.015584	−.022909	−.020659	.001788
11	.049852	.004007	.004378	−.006559	−.002060	.003494
12	.010420	.000861	.000942	−.001388	−.000976	.000312
13	.001367	.000109	.000120	−.000178	−.000081	.000075
14	−.000350	−.426049	−.375174	.082667	−1.273220	.631880
15	.000985	−.281052	−.288216	−.693330	0.596246	.572505
16	.000153	−.134137	−.143327	−.248696	.082459	−.966482
17	.000070	−.031798	−.032398	−.046355	.025582	−.071228
18	.000008	−.004401	−.004500	−.005993	.001990	−.014196

	1π	2π
19	0.005310	0.006601
20	−.012126	−.013210
21	.108804	.203931
22	.123893	.363187
23	.347961	−.950778
24	.677194	.458483

(f) PNO Coefficients, LiH $R=6.0$

1	0.002703	−0.006172	−0.004003	0.005354	0.025793	−0.013727
2	.002877	−.004471	−.006218	.003205	−.152044	.095237
3	−.000616	−.111914	−.072472	.121849	.740686	−.312469
4	−.000011	.005416	.001766	−.005371	−.553481	.274310
5	−.000319	.218056	.289034	−.418685	.450527	−.430933
6	.001914	.179907	.298790	−.467353	−.695251	.060749
7	.168348	−.039456	−.058646	.090123	.253192	−.100854
8	.425325	−.041442	−.060795	.085498	−.114445	.115331
9	.344690	−.023180	−.033747	.048901	.054881	−.006532
10	.160819	−.010249	−.014897	.021093	−.007640	.016090
11	.049869	−.003010	−.004373	.006273	.003538	.001180
12	.010426	−.000629	−.000913	.001298	−.000057	.000733
13	.001367	−.000081	−.000118	.000169	.000059	.000054
14	−.000004	.520188	.361914	.104801	.898639	.897501
15	.000089	.240391	.292588	.496591	−.550843	−.220667
16	.000033	.136112	.142144	.168076	−.130697	−.646153
17	.000009	.029438	.030877	.037554	−.029655	−.052456
18	.000001	.004280	.004301	.004759	−.002595	−.009329

	1π
19	0.000790
20	.007953
21	−.010902
22	.197279
23	.326293
24	.739552

1 a.u. (length) = 0.529172 Å

(g) PNO Coefficients, LiH $R=8.0$

Orbital No.	1σ H. F.	2σ H. F.	2σ	3
1	−0.001449	0.004125	0.000824	−0.000916
2	−.001564	−.006912	.000074	.000871
3	.000283	.084680	.016580	−.019912
4	−.000001	−.003467	−.000248	.000412
5	−.000307	.306383	.365248	−.415246
6	.001755	.147139	.355322	−.414143
7	.168259	−.036650	−.069391	.080760
8	.425437	−.041815	−.071124	.081196
9	.344690	−.022221	−.039241	.045218
10	.160840	−.010078	−.017341	.019845
11	.049870	−.002912	−.005082	.005839
12	.010429	−.000615	−.001062	.001217
13	.001366	−.000078	−.000137	.000158
14	−.000006	.571740	.296693	.227271
15	.000055	.219115	.329643	.398485
16	−.000002	.140310	.142635	.150219
17	.000003	.028597	.031340	.033858
18	.000000	.004308	.004262	.004430

	1π
19	−0.000368
20	.009481
21	−.028502
22	.134216
23	.349310
24	.755300

(h) PNO Coefficients, BeH^{+} $R=2.48$

Orbital No.	1σ H. F.	2σ H. F.	2σ	3σ	4σ	5σ
1	0.007213	0.047173	0.045504	−0.015329	−0.113542	0.061338
2	−.000225	.147334	.137219	−.176527	−.470720	.249390
3	.000239	.085880	.074154	−.131239	.149033	−.043572
4	.000591	−.033569	−.031121	−.093298	.466382	.058923
5	.000557	.103897	.107463	−.182799	.339832	−.338659
6	−.002563	.434705	.447353	−.912291	−.332627	−.369361
7	−.161356	−.044723	−.042953	.070612	−.384425	.136442
8	−.425490	−.120599	−.124988	.148209	.319595	−.044554
9	−.351194	−.056745	−.057854	.065945	−.009526	.018136
10	−.158475	−.025758	−.026487	.030270	.037430	.000387
11	−.047991	−.007002	−.007162	.008003	.003327	.001269
12	−.009950	−.001494	−.001533	.001724	.001667	.000106
13	−.001302	−.000189	−.000194	.000216	.000133	.000024
14	−.000128	.103976	.102979	−.068896	.506348	.175235
15	−.000943	.341322	.335900	.760629	−.008797	1.146932
16	−.000627	.142022	.150177	.385022	−.105262	−1.170663
17	−.000144	.034818	.035313	.049967	.016663	−0.117906
18	−.000023	.004820	.004899	.007649	−.002056	−.011233

	1π	2π
19	0.015553	0.011738
20	.115097	.138439
21	.500244	.582119
22	−.067143	−.002065
23	.439962	−.958014
24	.304166	.204944

The final wavefunctions are obtained with a trial function based on the PNO. The square of the coefficients are listed in table 3. Since only one pair of electrons is excited the C^2 are equivalent to the occupation number for the natural spin orbital. Only configurations with $C^2 > 0.0001$ are included.

3. Analysis of the Correlation

The initially occupied 1σ and 2σ H. F. orbitals are listed in table 2. Comparison of the 2σ H. F. orbitals with the 2σ NO shows no appreciable difference until R exceeds 6 a.u. The first NO and the Hartree-Fock orbital are very similar at the equilibrium configuration [9].

The asymptotic behavior of the 2σ and 3σ PNO results in the correct atom products, the H. F. ground states of H and Li. No other σPNO contributes to the correlation as R approaches infinity. Of the π orbitals only the 1π PNO still contributes significantly at 8 a.u.

The 3σ PNO in the neighborhood of the equilibrium separation acts mostly as an in-out type of correlation on the H^- bonding distribution. Bender and Davidson note that their 3σ orbital resembles a $2s$ hydrogen atom orbital orthogonalized to the $1s$ Li orbital. In our case the Li portion of the 3σ orbital resembles that part of the 2σ which serves as a hybridized $2s$ Li orbital. However, the left-right type of correlation required to assure proper asymptotic dependence is also present. As R increases this type dominates and accounts for the rapid rise in the σ correlation energy.

TABLE 3. *Square of the SOC expansion coefficient for a.* LiH *as a function of the internuclear distance and b.* BeH^+ *at* $R=2.48$ *a.u.*

(a) LiH Wave Function

Configuration	$C^2(R)$						
	$R=2.0$	2.6	3.0	3.4	4.0	6.0	8.0
$2\sigma^2$	0.97166	0.97175	0.96989	0.96640	0.95723	0.85232	0.64815
$3\sigma^2$	.01398	.01396	.01609	.02032	.03119	.14324	.35131
$4\sigma^2$	.00208	.00303	.00329	.00309	.00238	.00052	.00004
$5\sigma^2$	.00016	.00017	.00018	.00019	.00020	.00021	.00003
$1\pi^2$	.01176	.01070	.01014	.00959	.00861	.00355	.00045
$2\pi^2$	.00025	.00026	.00026	.00026	.00024	.00007	.00000

(b) BeH^+ Wave Function

	$R=2.48$
$2\sigma^2$	0.97320
$3\sigma^2$	.01428
$4\sigma^2$	.00263
$5\sigma^2$	.00017
$1\pi^2$	.00930
$2\pi^2$	.00031

The $p\sigma$ contribution is significant in the 4σ PNO but without plots of the orbitals it becomes increasingly difficult to ascertain the dominant correlating effects. This orbital tends to shift charge along the bond toward the Li.

The only other correlating orbital with a simple effect is the 1π PNO, which dominates the angular correlation. As R increases and charge transfers back toward the Li, the angular correlation also becomes more diffuse and eventually goes to zero. The dependence of the σ and π type correlation as a function of R is shown in table 4 along with the total and correlation energy.

The σ and π type correlation are determined by considering the σ and π SOC independently. As a result these estimates do not add up to the total correlation which is the difference between the total energy, for the combined σ and π SOC, and the H. F. energy. Such estimates are always found to exceed the true value as do the C^2 coefficients. Comparison with Bender and Davidson's breakdown of the correlation is encouraging. The σ and π results are essentially identical. As Bender and Davidson note, this correlation breakdown does not correspond to that expected for H^-.

The dissociation energy relative to the Hartree-Fock products is 2.36 eV. This is within 0.15 eV of the experimental value of 2.51 eV [10]. The neglect of intershell and δ-type correlations cannot account for such an error. The error is also not in the convergence properties of the NO expansion for this basis. The results quoted in table 4 are for the entire basis. The PNO listed in table 2 subsume all but about 0.05 eV of the energy contributions from this basis. The basis set is poor and will require further experimentation if an improvement is to be had.

TABLE 4. *Hartree-Fock, total, and correlation energies for* LiH *and* BeH^+

1 a.u. (energy) = 27.20976 eV.

LiH

R	$-E$(H. F.)	$-E$(tot.)	$-E\sigma$	$-E\pi$	$-E$(corr.)
2.0	7.911640	7.946792	0.02125	0.01668	0.03515
2.6	7.977167	8.010911	.02138	.01507	.03374
3.0	7.985388	8.018806	.02213	.01408	.03342
3.4	7.981539	8.015129	.02333	.01324	.03359
4.0	7.966088	8.000858	.02598	.01220	.03473
6.0	7.904227	7.951813	.04407	.01004	.04759
8.0	7.859542	7.934728	.07470	.00925	.07518
∞	[a] 7.932088				

BeH^+

R	$-E$(H. F.)	$-E$(tot.)	$-E\sigma$	$-E\pi$	$-E$(corr.)
2.48	14.85108	14.88497	0.02357	0.01510	0.03489

[a] This result is the approximate Hartree-Fock energies of the atoms for the Gaussian basis used; the accurate sum of H. F. atom energies is −7.9327257 a.u. (See E. Clementi, Tables of Atomic Functions, Supplement to IBM Journal of Research and Development **9**, 2 (1965).)

BeH^+ at the equilibrium configuration presents results comparable to that for equilibrium LiH. The correlation breakdown in terms of σ and π contributions are essentially the same and nearly independent of the bonding characteristics of the respective Hartree-Fock molecules. The dissociation energy is 2.93 eV and on the basis of the LiH calculation should be good to about 0.2 eV.

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