

Ab Initio Investigation of the LiHe X $^2\Sigma^+$, A $^2\Pi$, and B $^2\Sigma^+$ States: A Basis Set Study

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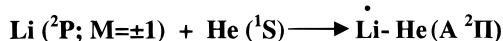
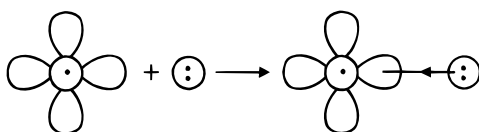
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Employing a series of correlation-consistent basis sets, we have examined the properties of the LiHe system in the X $^2\Sigma^+$, B $^2\Sigma^+$, and the A $^2\Pi$ states as a function of the basis set size. In our largest basis set, aug-(Li+He)-cc-pCV5Z, our BSSE-corrected results are in complete agreement with existing experimental findings. In the largest basis sets, we have also examined the binding properties and geometry of the triatomic species LiHe₂ proven to be quasilinear with a $\tilde{A}^2B_1 \rightarrow A^2\Pi_u$ inversion barrier of 32 cm⁻¹.

1. Introduction

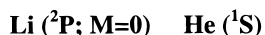
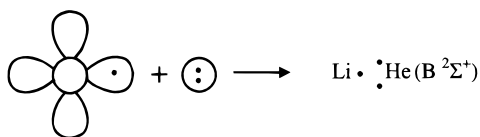
One of the simplest van der Waals diatomics is the three (active) electron system LiHe. In general, the interaction of alkali and rare-gas atoms has attracted considerable attention, both experimentally¹ and theoretically.² The basic understanding of a wide range of collision processes has been cited as the principal reason for this kind of research.¹ Among these systems, LiHe, due to its small number of electrons, can be thoroughly studied theoretically and it is exactly what the present paper is trying to achieve.

We focus at three states of the LiHe molecule, the ground X $^2\Sigma^+$ and the A $^2\Pi$ and B $^2\Sigma^+$ states. The ground X $^2\Sigma^+$ state correlating to the ground states of the Li and He atoms is obviously repulsive. The A $^2\Pi$ and B $^2\Sigma^+$ states trace their ancestry to the first excited 2P state of Li and the 1S state of the He atom. The Li–He interaction along the $^2\Pi$ potential energy curve (PEC) is clearly represented by the following valence-bond–Lewis (vbL) scheme:



anticipating an attractive interaction via a harpoon-like σ bond.

The $M = 0$ component of the Li 2P state gives rise to the B $^2\Sigma^+$ state,



clearly interacting repulsively with the ground 1S state of the He atom.

Table 1 summarizes all ab initio calculations performed so far starting as early as 1962 on the LiHe molecule concerning the A $^2\Pi$ state, as well as some recent and very accurate experimental results.¹ The most recent calculations by

Staemmler et al.,⁷ at the CEPA-2 level of theory for the A $^2\Pi$ state, are in good agreement with the experimental findings (but see below). CEPA (coupled electron pair approximation) is an improved version of the IEPA (independent electron pair approximation), or an approximate version of the CCSD ($e^{\hat{T}_1 + \hat{T}_2}$ ansatz) approach.⁸ CEPA-2 was first proposed by Meyer.⁹ Notice that CEPA is a size-extensive but not variational method.

Interestingly enough, for the ground X $^2\Sigma^+$ repulsive state of LiHe, there are experimental findings estimating a van der Waals attractive interaction of about 1.14 cm⁻¹ at 6.01 Å interatomic distance.¹⁰ CEPA-2 calculations by Staemmler¹¹ employing the same basis set as given in ref 7 predict a van der Waals interaction of 1.49 cm⁻¹ at 6.12 Å.

We decided to carry out CASSCF+1+2 [complete active space SCF + single + double replacements = MRCI (multi-reference configuration interaction)] calculations on the LiHe system as a function of basis set size and then extrapolate our findings to the complete basis set (CBS) limit. On account of the small number of electrons (3 or 5 e⁻), the LiHe molecule offers itself for an in-depth study of its spectroscopic properties and the manner with which these properties converge toward their CBS limits. We have examined the X $^2\Sigma^+$ and B $^2\Sigma^+$ repulsive states and the A $^2\Pi$ bound (with respect to Li 2P + He 1S) state. Focusing mainly on the A $^2\Pi$ state, we obtain total energies, full potential energy curves (PEC), dissociation energies (D_e), spectroscopic properties (r_e , ω_e , $\omega_e x_e$), and dipole moments (μ) for all four isotopic species, i.e., ⁶Li³He, ⁷Li³He, ⁶Li⁴He, and ⁷Li⁴He as a function of basis set size. Notice that accurate experimental results exist for the (6,3), (6,4), and (7,4) isotopic species.¹ In addition, and essentially at the same level of theory, we have examined the triatomic molecule LiHe₂ in its \tilde{A}^2B_1 bound (with respect to Li 2P + 2He 1S) state. To the best of our knowledge, no relevant experimental or theoretical results exist in the literature for the LiHe₂ system.

2. Basis Sets and Computational Details

For both atoms, the, by now well-established, correlation-consistent basis sets cc-pVnZ of Dunning¹² were used, where n is an integer $n = 2$ (D), 3 (T), 4 (Q), and 5 defining the quality of the basis set. The following six sets were employed, cc-pVnZ, aug(Li)-cc-pVnZ, aug(Li+He)-cc-pVnZ, cc-pCVnZ, aug(Li)-cc-pCVnZ, and aug(Li+He)-cc-pCVnZ, $n = D, T, Q, \text{ and } 5$. By aug(Li)- and aug(Li + He)- it is meant that diffuse functions have been grafted to the plain sets (with core, “C”, or not

TABLE 1: Energies, E , Binding Energies, D_e , and Bond Distances, r_e , of the LiHe A 2Π State of All ab Initio Results Reported So Far in the Literature with Experimental Values Given for Comparison

authors, ref	method	basis set	$-E$ (hartree)	D_e (cm $^{-1}$)	r_e (Å)
Scheel and Griffing, 1962 ³	SCF	\sim DZ-STO	10.1979		\sim 2.1
Schneiderman and Michels, 1965 ⁴	VB	elliptic-STO	10.2552	504.8	1.96
Krauss et al., 1971 ⁵	SCF	DZ+P-STO	10.22871	\sim 500	\sim 1.85
Jungen and Staemmler, 1988 ⁶	CEPA-2	91 Gaussians ^a	10.303338	868	1.81
Billig et al., 1994 ²	MRCI	6-311G+3p _{He} +3d _{Li}		894	1.82
Behnenburg et al., 1996 ⁷	CEPA-2	152 Gaussians ^b	10.312969	1005	1.79
Lee et al., 1991 ¹	experiment			1020 \pm 20	1.783 \pm 0.016

^a (19s12p6d)_{Li}/(12s3p)_{He} contracted to [13s9p6d]_{Li}/[6s3p]_{He}. ^b (20s12p8d3f)_{Li}/(13s5p3d1f)_{He} contracted to [14s11p8d3f]_{Li}/[7s5p3d1f]_{He}.

TABLE 2: Absolute Energies E (Hartree) of the Ground $2S(2s^1)$ State of the Li Atom and Energy Splittings (cm $^{-1}$) of the First Three Excited States in Different Methodologies and in Two Basis Sets, cc-pCV5Z and aug-cc-pCV5Z

method	$-E$ ($2S; 2s^1$)	$2P(2p^1) \leftarrow 2S(2s^1)$	$2S(3s^1) \leftarrow 2S(2s^1)$	$2P(3p^1) \leftarrow 2S(2s^1)$
NHF ^a	7.432727			
cc-pCV5Z				
SCF	7.432723	14 850.3	29 182.0	32 472.4
CISD	7.477305	14 907.8	29 429.6	32 682.6
CISDT	7.477350			
aug-cc-pCV5Z				
SCF	7.432723	14 849.7	27 068.2	30 655.1
CISD	7.477307	14 907.4	27 363.2	30 939.3
exact ^b	7.4780603			
exptl	7.4780604 ^c	14 903.89 ^d	27 206.12 ^d	30 925.38 ^d

^a Numerical Hartree–Fock, ref 18. ^b Nonrelativistic “exact” calculation, ref 20. ^c Nonrelativistic “experimental” estimate, ref 20. ^d Reference 19.

functions), first to the Li and then to both Li and He atoms, respectively, according to the standard rules.¹³ Due to the fact that augmented basis sets for the Li atom were not available, we empirically constructed the augmented exponents by observing that in the series of atoms B to Ne the diffuse exponents are approximately doubled for every second element. Therefore, the augmented Li exponents used are those of the B atom divided by 2. For the same reason, the analogous procedure was followed for the construction of the core functions of the Li-cc-pCV5Z basis set. Our smallest generalized contracted basis set, cc-pVDZ [(3s2p1d)_{Li}/(2s1p)_{He}] contains 19 functions, with the largest, aug(Li+He)-cc-pCV5Z [(11s10p8d6f4g2h)_{Li}/(6s5p-4d3f2g)_{He}], consisting of 261 Gaussians for the LiHe molecule. For the diatomic system CBS limits of the properties D_e , r_e , ω_e , and μ were obtained by a least means square fitting to the simple exponential formula¹⁴

$$P_n = P_\infty + A e^{-Bn}$$

where A and B are adjustable parameters and $n = 2-5$, the cardinal basis set number.

As was already mentioned, the CASSCF+1+2 = MRCI methodology was followed with our active space comprised of three valence electrons distributed to five orbitals, (s + p)_{Li} + s_{He}. For the LiHe system and for the A 2Π state, our $|\Lambda| = 1$ CASSCF space is composed of 51 configuration functions (CF) with the MRCI expansion consisting of 659 355 CFs in the largest aug(Li + He)-cc-pCV5Z basis. Upon applying the internally contracted scheme,¹⁵ this space is reduced to 187 978 CFs with, in the present case, insignificant total energy losses (vide infra).

For the LiHe₂ $\tilde{A} 2B_1$ state, the CASSCF space contains 188 CFs, while the MRCI space expansion in the aug(Li)-cc-pCV5Z basis is comprised of 6 609 061 CFs, sliced down to 546 360 CFs in the internally contracted MRCI scheme.

Basis set superposition error (BSSE) corrections following the counterpoise method of Boys and Bernardi¹⁶ were applied for all basis sets used and for every point along the potential curves X $2\Sigma^+$, B $2\Sigma^+$, and A 2Π of the LiHe diatomic system.

Interatomic distances and spectroscopic constants for the A 2Π state of LiHe were extracted via a standard Dunham analysis, by fitting always 23 energy points of the PECs and up to an interatomic distance of 5 bohr.

All calculations were performed with the MOLPRO suite of codes.¹⁷

3. Results and Discussion

3.a. Li and He Atoms. Table 2 presents total energies of the ground $2S$ state of the Li atom at the SCF, CISD, and CISDT level at the core quintuple and aug-core quintuple bases, as well as the calculated atomic energy separations for the first three excited states, one valence ($2P(2p^1)$) and two Rydberg ($2S(3s^1)$; $2P(3p^1)$) states. For comparison, the numerical Hartree–Fock energy (NHF),¹⁸ experimental energy splittings,¹⁹ and the “exact” nonrelativistic total energy of the Li $2S$ state²⁰ are also presented. We observe the, in essence, exact agreement between the NHF and our SCF energy Li result, and that the CISD/aug-cc-pCV5Z total energy is 0.000753 hartrees above the “exact” result.²⁰ This last energy difference is due to the basis set incompleteness as the energy difference between the CISD and CISDT (full CI) result reveals. The energy separation $2P(2p^1) \leftarrow 2S(2s^1)$ is in excellent agreement with the experimental findings,¹⁹ in both quintuple core basis sets, augmented or not, but of course, for the accurate prediction of the $2P(3p^1) \leftarrow 2S(2s^1)$ and $2S(3s^1) \leftarrow 2S(2s^1)$ energy splittings, the presence of the diffuse functions is essential (Table 2).

The “exact” energy of the ground $1S$ state of the He atom is -2.903724 hartrees,²¹ which should be contrasted with our CISD/aug-cc-pV5Z result of -2.903201 hartrees.

3.b. LiHe X $2\Sigma^+$ and B $2\Sigma^+$ Repulsive States. Figure 1 shows the repulsive PECs of X $2\Sigma^+$ and B $2\Sigma^+$ states correlating to Li($2S$) + He($1S$) and Li($2P$) + He($1S$), respectively. The only interesting aspect about these (repulsive) states is the very weak van der Waals interaction at very long interatomic distances and the existence of relevant experimental findings¹⁰ for the LiHe X $2\Sigma^+$ state. Table 3 lists our findings on the interaction energy ΔE and corresponding van der Waals distances, $r(\text{vdW})$ in a series of quintuple basis sets.

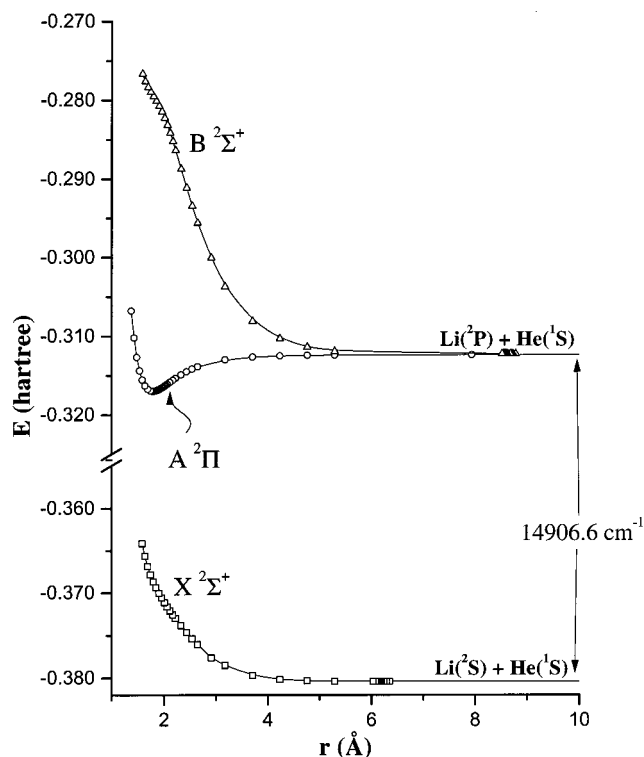


Figure 1. Potential energy curves of the LiHe $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states at the MRCI/aug(Li + He)-cc-pCV5Z level. Energies have been shifted by 10 hartrees.

TABLE 3: Total Energies E (Hartree), van der Waals Distances $r(\text{vdW})$ (Å), and Energies of Interaction ΔE and $\Delta E(\text{BSSE})$ (cm^{-1}) of the Repulsive $X^2\Sigma^+$ and $B^2\Sigma^+$ States of the LiHe Molecule at the MRCI Level and in Different Quintuple Size Basis Sets

basis set	$-E$	$r(\text{vdW})$	ΔE	$\Delta E(\text{BSSE})^d$
$X^2\Sigma^+$				
cc-pV5Z	10.3358787	6.5	-0.92	-0.37
cc-pCV5Z	10.3803409	6.5	-0.92	-0.33
aug(Li)-cc-pV5Z	10.3358809	6.4	-1.38	-0.83
aug(Li)-cc-pCV5Z	10.3803447	6.4	-1.38	-0.83
aug ² -cc-pCV5Z ^b	10.3803933	6.1	-1.50	-1.42
experiment ^c		6.010 ± 0.016	-1.14	
$B^2\Sigma^+$				
cc-pV5Z	10.2682106	9.3	-0.22	-0.20
cc-pCV5Z	10.3121971	9.3	-0.22	-0.20
aug(Li)-cc-pCV5Z	10.3122020	8.9	-0.40	-0.26
aug ² -cc-pCV5Z ^b	10.3122508	8.6	-0.52	-0.50

^a ΔE corrected with respect to BSSE. ^b aug(Li+He)-cc-pCV5Z, ^c Reference 10.

We observe the absolute necessity of the diffuse basis set functions in both atoms and the significant role of the BSSE correction if we want accurate results and the excellent agreement between theory and experiment of our largest calculation in the $X^2\Sigma^+$ state, considering the smallness of the interaction energy ΔE . Although no experimental results seem to exist for the $B^2\Sigma^+$ state, our results on the $X^2\Sigma^+$ state warrant that our final numbers $\Delta E = -0.50 \text{ cm}^{-1}$ at $r(\text{vdW}) = 8.6 \text{ \AA}$ should be close to reality.

3.c. LiHe $A^2\Pi$ State. This is the first excited state of the LiHe system bound with respect to $\text{Li}(^2\text{P}) + \text{He}(^1\text{S})$ fragments. Figure 1 shows the MRCI/aug(Li+He)-cc-pCV5Z PEC, and Table 4 condenses most of our pertinent results, i.e., total energies, E , dissociation energies, D_e , and BSSE-corrected $D_e = D_e^*$, bond distances, r_e , and BSSE-corrected $r_e = r_e^*$, harmonic, ω_e , and anharmonic, $\omega_e\chi_e$, frequencies with corre-

sponding ω_e^* and $\omega_e\chi_e^*$ values, and dipole moments, μ , in a series of basis sets. At this point, it should be stressed that the BSSE corrections were applied for every calculated point of the corresponding potential energy curve; that is, all our properties are, somehow, a priori BSSE-corrected. Complete basis set (CBS) limits for most calculated properties are also listed in Table 4. Finally, for reasons of completeness and easy comparison, some literature data have been transferred from Table 1 to Table 4.

Table 5 presents BSSE-corrected harmonic ω_e^* and anharmonic $\omega_e\chi_e^*$ frequencies and their CBS limit values of the isotopic species $^6\text{Li}^3\text{He}$, $^7\text{Li}^3\text{He}$, $^6\text{Li}^4\text{He}$, and $^7\text{Li}^4\text{He}$, as well as corresponding experimental numbers.¹

Some interesting conclusions can be drawn from Table 4. In our largest basis set, aug(Li+He)-cc-pCV5Z, all properties presented, BSSE-corrected or not, are in complete agreement with the experimental results. Our CBS limits prove the essentially complete convergence of our numbers at this level. Interestingly enough, even at this level a BSSE of 6.4 cm^{-1} still exists, reflecting the lack of completeness of the basis set. Considering the dissociation energy as the most sensitive quantity, our best CBS limit result is $D_e^* = 1011.2 \pm 2.8 \text{ cm}^{-1}$, as compared to an experimental value¹ of $1020 \pm 20 \text{ cm}^{-1}$. The best $D_e = 1005 \text{ cm}^{-1}$ value in the literature comes from CEPA-2 calculations⁷ but is BSSE uncorrected. Within the clamped nuclei approximation, the “exact” nonrelativistic energy of the LiHe $A^2\Pi$ state is given by

$$\begin{aligned}
 E_{\text{LiHe}}(A^2\Pi, \text{exact}) &= E_{\text{Li}}(^2\text{S}, \text{exact}) + \Delta E_{\text{Li}}(^2\text{P} \leftarrow ^2\text{S}) + \\
 &E_{\text{He}}(^1\text{S}, \text{exact}) - D_e^* \text{LiHe}(\text{CBS}) = \\
 &-7.478060 \text{ hartrees} + 14907.4 \text{ cm}^{-1} - \\
 &2.903724 \text{ hartrees} - 1011.2 \text{ cm}^{-1} = \\
 &-10.318468 \text{ hartrees}
 \end{aligned}$$

within no more than 10 cm^{-1} . This number should be contrasted with our best total energy value of -10.316994 hartrees being higher than the “exact” value by 323.5 cm^{-1} , or less than 1 kcal/mol, and reflecting the combined basis set incompleteness-correlation effects and internal contraction approximation. The above estimate for the exact nonrelativistic total equilibrium energy of the $A^2\Pi$ state is corroborated from the full CI (SCF+1+2+3+4+5 excitations) results on this state at the cc-pCVDZ and cc-pCVTZ level. Total equilibrium energies for the cc-pCVDZ (448 063 CFs) and cc-pCVTZ (46 698 960 CFs) cases are -10.288956 and -10.310538 hartrees, respectively, just 27 and 59 cm^{-1} lower than our corresponding MRCI results; see Table 4.

Table 4 suggests that, at least for this particular system, even the largest plain cc-pV5Z basis is inadequate for a very accurate determination for almost all calculated quantities. As it is shown, although the augmented sets on both atoms significantly improve the D_e value and lower the BSSE correction, they do not improve the interatomic distance or harmonic frequency, with the D_e^* and r_e^* values at this level (aug(Li+He)-cc-pV5Z) differing from our final (or experimental) findings by as much as 54 cm^{-1} and 0.024 \AA . The combination of core and diffuse functions gives finally the best results. In particular, the core functions bring the interatomic distance to the correct value even at the quadruple level, while the addition of diffuse on top of the core functions makes the convergence to the CBS limits much smoother.

The CBS limits of dipole moment show a rather erratic behavior, but certainly the μ value increases as a function of

TABLE 4: MRCI Results on the A 2Π State of ${}^7\text{Li}^4\text{He}$: Energies, E (Hartree), Dissociation Energies, D_e (cm^{-1}), Equilibrium Bond Distances, r_e (\AA), Harmonic, ω_e , and anharmonic, $\omega_e\chi_e$, Frequencies (cm^{-1}), and Dipole Moments, μ (D), in a Series of Basis Sets

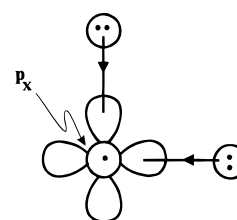
basis set ^a	$-E$	D_e	D_e^{*b}	r_e	r_e^{*b}	ω_e	ω_e^{*b}	$\omega_e\chi_e$	$\omega_e\chi_e^{*b}$	μ
exptl ^c		1020 \pm 20		1.783 \pm 0.016		356.8 \pm 1.1		33.4 \pm 0.5		
DZ	10.255361	698.1	512.0	1.955	1.972	261.7	246.9	30.3	31.2	0.007
TZ	10.268990	827.2	790.8	1.833	1.837	327.5	325.5	34.7	35.1	0.104
QZ	10.271609	915.2	903.8	1.818	1.819	337.3	337.8	34.4	35.4	0.168
5Z	10.272488	939.1	934.3	1.815	1.815	340.1	338.4	34.7	32.6	0.191
CBS ^d		986.5(36.3)	960.5(10.4)	1.815(0.001)	1.815(0.001)	340.1(0.6)	339.2(0.7)			0.231(0.021)
aug-DZ	10.255495	724.3	492.5	1.950	1.966	262.6	248.2	31.8	33.3	0.158
aug-TZ	10.269147	861.0	817.3	1.836	1.836	327.1	326.4	29.0	34.2	0.215
aug-QZ	10.271689	932.5	919.4	1.818	1.819	338.2	336.7	34.7	34.3	0.256
aug-5Z	10.272533	948.6	944.2	1.815	1.816	339.8	338.4	35.1	29.8	0.269
CBS ^d		972.3(16.2)	958.6(4.4)	1.815	1.816	340.3(0.2)	338.5(0.2)			0.296(0.019)
aug ² -DZ	10.257651	768.8	722.3	1.882	1.889	306.4	298.1	37.1	37.0	0.180
aug ² -TZ	10.269773	918.1	899.8	1.827	1.828	331.7	330.1	35.5	35.6	0.261
aug ² -QZ	10.271894	950.8	945.3	1.817	1.817	339.1	338.5	35.5	35.7	0.273
aug ² -5Z	10.272614	955.6	952.7	1.815	1.816	339.8	339.6	35.7	35.9	0.275
CBS ^d		958.1(1.3)	957.2(2.4)	1.815	1.815(0.001)	340.8(0.8)	340.5(0.6)			0.275
CDZ	10.288832	711.1	523.0	1.948	1.965	264.6	249.5	29.7	31.3	0.007
CTZ	10.310269	875.9	838.2	1.813	1.815	340.6	337.9	35.1	35.6	0.089
CQZ	10.315041	972.9	960.0	1.795	1.796	353.1	352.1	35.4	35.6	0.144
C5Z	10.316863	994.7	989.2	1.792	1.792	354.5	352.3	34.9	34.6	0.171
CBS ^d		1033.0(29.3)	1014.4(11.6)	1.792	1.792(0.001)	354.6(0.6)	353.4(1.1)			0.219(0.014)
aug-CDZ	10.289038	738.5	505.2	1.942	1.959	265.7	250.7	31.1	33.3	0.150
aug-CTZ	10.310450	910.6	863.6	1.813	1.817	342.5	339.1	34.0	33.9	0.188
aug-CQZ	10.315118	989.2	974.7	1.794	1.795	353.8	352.6	36.3	36.3	0.220
aug-C5Z	10.316909	1003.9	998.4	1.792	1.792	353.8	353.6	35.1	35.1	0.227
CBS ^d		1024.1(14.5)	1013.7(6.4)	1.791	1.791	354.6(0.8)	354.3(0.5)			0.248(0.023)
aug ² -CDZ	10.291263	803.1	739.4	1.863	1.874	311.3	302.5	36.9	37.7	0.163
aug ² -CTZ	10.311087	971.6	942.6	1.806	1.810	343.9	340.7	35.1	35.5	0.223
aug ² -CQZ	10.315309	1004.5	996.4	1.794	1.795	353.0	352.1	36.1	36.2	0.230
aug ² -C5Z	10.316994	1012.0	1005.6	1.791	1.792	354.1	353.4	35.4	35.6	0.231
CBS ^d		1013.3(0.6)	1011.2(2.8)	1.790	1.791	355.2(0.8)	354.9(1.2)			(0.231)
VB/STO ^e	10.2552	505.5		1.964		285.7		39.7		
SCF/STO ^f	10.22871	\sim 500		\sim 1.85						
CEPA-2 ^g	10.303338	868		1.81		335 ^h		37 ^h		
MRCI ⁱ		894		1.82						
CEPA-2 ^j	10.312968	1005		1.79						

^a nZ , aug- nZ , aug²- nZ , CnZ , aug- CnZ , and aug²- CnZ refers to cc-pVnZ, aug(Li)-cc-pVnZ, aug(Li+He)-cc-pVnZ, cc-pCVnZ, aug(Li)-cc-pCVnZ, and aug(Li+He)-cc-pCVnZ respectively, with $n = D, T, Q,$ and 5 . ^b BSSE-corrected values. ^c Experimental values, ref 1. ^d Complete basis set limit; see text. ^e Valence bond, Slater basis, ref 4. ^f Reference 5. ^g Coupled electron pair approximation, ref 6. ^h ω_e and $\omega_e\chi_e$ values obtained from the first two vibrational levels given in ref 6 by applying the formula $G(v) = (v + 1/2)\omega_e - (v + 1/2)^2\omega_e\chi_e$ for $v = 0, 1$. ⁱ MRCI/6-311G (3p,3d), ref 2. ^j Reference 7.

the basis set size within each different set. The diffuse functions tend to increase the dipole moment, while the opposite effect is induced by the core functions giving a final seemingly converged value of 0.23 D.

Finally, from Table 5 we observe that at the highest level of basis set size and at the CBS limit, the harmonic frequencies for the species ${}^6\text{Li}^3\text{He}$, ${}^6\text{Li}^4\text{He}$, and ${}^7\text{Li}^4\text{He}$ are in practical agreement with the corresponding experimental values, the theoretical numbers being systematically lower from the experimental ones by 2 cm^{-1} . Again, the role of core functions is instrumental for bringing the calculated values to agreement with the experimental results.

3.d. LiHe₂ \tilde{A}^2B_1 State. The triatomic LiHe₂ system is expected to conform to the shown vbL diagram, predicting a bent geometry, and indeed this is the case. Table 6 presents our results at the MRCI/cc-pV5Z, aug(Li)-cc-pV5Z, cc-pCV5Z, and aug(Li)-cc-pCV5Z levels. The $\angle\text{HeLiHe}$ angle is very close to 100° in the core basis sets with the Li-He distance being 1.800 \AA , 0.008 \AA longer than the diatomic at the same basis set level; see Table 4. However, the molecule is extremely floppy; the process bent-to-linear configuration or $\tilde{A}^2B_1 \rightarrow A^2\Pi_u$ requires only 32 cm^{-1} of energy (inversion barrier) at the

**Li (2P ; $M=\pm 1$)**

largest basis set. Therefore, the LiHe₂ molecule, although formally bent, should be characterized as a quasilinear system. The atomization energy of the process $\text{LiHe}_2({}^2B_1) \rightarrow \text{Li}({}^2P) + 2\text{He}({}^1S)$ is 1948.6 or 974.3 cm^{-1} per Li-He bond in the largest basis set used.

4. Summary and Concluding Remarks

Employing a series of correlation-consistent basis sets of increasing size, we have performed MRCI calculations for the X $2\Sigma^+$, A 2Π , and B $2\Sigma^+$ states of the LiHe molecule. The LiHe₂ molecule was also examined at the MRCI-quintuple level of theory. Our main conclusions are as follows.

TABLE 5: BSSE-Corrected Harmonic ω_e^* (cm⁻¹) and Anharmonic $\omega_e\chi_e^*$ (cm⁻¹) Frequencies of Different Isotopic Species of the A ²Π State of LiHe at the MRCI Level of Theory and in Different Quintuple Size Basis Sets

basis set	freq	⁶ Li ³ He ^a	⁷ Li ³ He ^a	⁶ Li ⁴ He ^a	⁷ Li ⁴ He ^a
cc-pV5Z	ω_e^*	381.1	371.9	348.4	338.4
	$\omega_e\chi_e^*$	41.2	39.3	34.6	32.6
CBS ^b	ω_e^*	382.0(0.8)	372.8(0.8)	349.2(0.8)	339.2(0.7)
aug(Li)-cc-pV5Z	ω_e^*	381.2	372.0	348.5	338.4
	$\omega_e\chi_e^*$	37.1	35.5	31.4	29.8
CBS ^b	ω_e^*	381.5(0.0)	372.2(0.0)	348.7(0.0)	338.5(0.2)
aug ² -cc-pV5Z ^c	ω_e^*	382.5	373.3	349.7	339.6
	$\omega_e\chi_e^*$	45.6	43.4	38.0	35.9
CBS ^b	ω_e^*	383.5(0.7)	374.3(0.7)	350.7(0.7)	340.5(0.6)
cc-pCV5Z	ω_e^*	396.9	387.3	360.1	352.3
	$\omega_e\chi_e^*$	43.8	41.8	36.1	34.6
CBS ^b	ω_e^*	398.1(1.2)	374.3(0.7)	362.1(2.5)	353.3(1.1)
aug(Li)-cc-pCV5Z	ω_e^*	398.2	388.6	364.1	353.6
	$\omega_e\chi_e^*$	43.5	41.4	36.4	35.1
CBS ^b	ω_e^*	399.0(0.7)	389.4(0.6)	364.8(0.6)	354.3(0.5)
aug ² -cc-pCV5Z ^c	ω_e^*	398.0	388.4	363.9	353.4
	$\omega_e\chi_e^*$	45.1	43.0	37.7	35.6
CBS ^b	ω_e^*	399.7(1.4)	390.1(1.3)	365.5(1.3)	354.9(1.2)
exptl ^d	ω_e	401.8 ± 1.2		367.4 ± 1.1	356.8 ± 1.1
	$\omega_e\chi_e$	42.3 ± 0.7		35.4 ± 0.6	33.4 ± 0.5

^a The following reduced masses were employed for ⁶Li³He, ⁷Li³He, ⁶Li⁴He, and ⁷Li⁴He, 2.008801, 2.109290, 2.403354, and 2.548623 g mol⁻¹, respectively. ^b Complete basis set limit; see text. ^c aug(Li+He)-cc-pV5Z and aug(Li+He)-cc-pCV5Z. ^d Reference 1.

TABLE 6: MRCI Results in Different Basis Sets on the \tilde{A} ²B₁ State of the LiHe₂ System: Absolute Energies, E (Hartree), Atomization Energies, AE (cm⁻¹), HeLi-He Bond Dissociation Energies, D_e (cm⁻¹), Bond Lengths, r_e (Å), Bond Angles, \angle HeLiHe (degrees), and Dipole Moments, μ (D)

basis set	$-E$	AE ^a	D_e^b	r_e	\angle HeLiHe	μ
cc-pV5Z	13.179493	1823.4	895.9	1.824	98.5	0.21
aug(Li)-cc-pV5Z	13.179575	1840.8	916.9	1.824	98.5	0.28
cc-pCV5Z	13.223788	1932.0	931.4	1.800	100.2	0.18
aug(Li)-cc-pCV5Z	13.223868	1948.6	939.1	1.800	100.2	0.25

^a AE refers to the process LiHe₂(\tilde{A} ²B₁) → Li(²P) + 2He(¹S). ^b D_e refers to the process LiHe₂(\tilde{A} ²B₁) → LiHe(²Π) + He(¹S).

(i) The X ²Σ⁺ and B ²Σ⁺ states are repulsive with van der Waals interactions of -1.42 and -0.50 cm⁻¹, respectively, at 6.1 and 8.6 Å.

(ii) At the highest level of theory, i.e., MRCI/aug(Li+He)-cc-pCVnZ, $n = 2-5$, the BSSE-corrected CBS limit, $D_e = 1011.2 \pm 2.8$ cm⁻¹, is in complete agreement with the experimental results of 1020 ± 20 cm⁻¹. At this level, the rest of the calculated quantities, namely, r_e , ω_e , and $\omega_e\chi_e$, are in excellent agreement with experimental findings.

(iii) For this particular system, core basis functions were found as necessary in order to achieve complete agreement with the experimental results, while diffuse functions played a role in making the convergence toward the CBS limits smoother.

(iv) Our most reliable dipole moment for the A ²Π state of LiHe is $\mu = 0.23$ D with a corresponding charge transfer of about 0.05 e⁻ from He to Li.

(v) At the \tilde{A} ²B₁ state, the triatomic molecule LiHe₂ is formally bent with a \angle HeLiHe angle of 100°, but extremely floppy having a bent-to-linear inversion barrier of 32 cm⁻¹. The molecule is bound with respect to Li(²P) + 2He(¹S) fragments with an atomization energy of 1948.6 cm⁻¹ at the MRCI/aug-(Li)-cc-pCV5Z level, practically twice that of the A ²Π state of LiHe binding energy. Its dipole moment is 0.25 D with a charge transfer of about 0.1 e⁻ from the He atoms to Li. By bending the molecule in A₁ fashion (xz plane), the repulsive B ²A₁ state is obtained.

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