Diatomic Molecules Containing Electropositive Atoms Favor High-Spin States

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The equilibrium geometries and harmonic vibrational frequencies of the low lying electronic states of LiSi, BeSi, BSi, NaSi, MgSi and AlSi were calculated at the SCF/6-31G*, MP2(full)/6-31G*, MP2(full)/6-311+G* levels of theory. For each of these species, the ground states were also studied at the QCISD(T)/6-311+G(2df) level to obtain more accurate data. The bonding in these species is found to involve high-spin ground electronic states (${}^{4}\Sigma^{-}$ for LiSi, ${}^{3}\Sigma^{-}$ for BeSi, ${}^{4}\Sigma^{-}$ for BSi, ${}^{4}\Sigma^{-}$ for NaSi, ${}^{3}\Sigma^{-}$ for MgSi and ${}^{4}\Sigma^{-}$ for AlSi) in which two electrons occupy bonding π orbitals. In each case, the number of unpaired electrons is larger than that anticipated based on straightforward covalent Si-X σ -bond formation with no further rearrangement of electronic configuration. We suggest that π^{2} configurations are favored over π^{1} because of the relatively low σ -to- π promotion energies particular to these species and the low Coulomb and favorable exchange energies of the π^{2} situation, and over π^{3} and π^{4} configurations because the latter correlate with excited states of Si and have high Coulomb energies. The π^{2} character is then the source of the high-spin nature of the ground states. Bond dissociation energies were also computed and found to be 41.5 kcal/mol (LiSi), 28.8 kcal/mol (BeSi), 71.5 kcal/mol (BSi), 33.3 kcal/mol (NaSi), 21.7 kcal/mol (MgSi) and 56.0 kcal/mol (AlSi), with all data referring to the QCISD-(T)/6-311+G(2df)+ZPE level, within which the calculated bond lengths are 2.383 Å (LiSi), 2.137 Å (BeSi), 1.905 Å (BSi), 2.697 Å (NaSi), 2.561 Å (MgSi) and 2.430 Å (AlSi).

I. Introduction

A. The Orbital Occupancy Nature of High- and Low-Spin States. In 1980 Nemukhin et al¹ found that the LiB molecule has a ³II ground electronic state with valence orbital occupancy $1\sigma^2 2\sigma^1 1\pi^1$ instead of the expected $(1\sigma^2 2\sigma^2)$ ¹ Σ^+ state, which is the ground state of the analogous molecule BH.² Moreover, Mavridis and Harrison³ found high-spin $(1\sigma^2 2\sigma^1 1\pi^2)$ ⁴ Σ^- ground states for LiC and LiSi instead of the expected $(1\sigma^2 2\sigma^2 1\pi^2)$ ⁴ Σ^- ground state, which is the ground state for CH and SiH.² Why are lower-spin states favored for BH, CH, and SiH whereas high-spin states are favored for LiB, LiC, and LiSi?

The anticipated low-spin states for the above B, C, or Si containing species describe the valence electronic structure in terms of a *doubly* occupied bonding σ orbital, a doubly occupied non-bonding or somewhat antibonding σ orbital on B, C, or Si (i.e., derived from the 2s² orbital of B or C or the 3s² Si orbital or a related sp-like hybrid directed away from the Li atom), with the remaining electrons residing in π orbitals (π^0 for LiB, π^1 for LiC, and π^1 for LiSi). Such a picture, as illustrated in Figure 1a for the LiSi case, leads to low-spin ${}^{1}\Sigma^{+}$ (for LiB), ${}^{2}\Pi$ (for LiC and LiSi) ground electronic states with one full σ bond.

However, the observed facts reported above are consistent with $\sigma^2 \sigma^1 \pi^1$ (for LiB) or $\sigma^2 \sigma^1 \pi^2$ (for LiC and LiSi, as illustrated in Figure 1b) configurations in which the singly occupied σ orbital is non-bonding or slightly antibonding and the bonding σ orbital is doubly occupied. We need to understand why additional occupancy of the π orbital and reduced occupancy in the σ -orbital framework may be favored when electropositive atoms are involved but not otherwise.

B. The Strategy of This Study. In the present work, we chose to examine the relative energies of high- and low-spin electronic states of several Si–X diatomics, where X is a group I, II, or III element. Other Si–X compounds with X from groups IV-VI such as SiC,⁴⁻⁹ SiN,¹⁰⁻¹⁶ SiO,¹⁷⁻²³ as well as Si₂,^{2,24-30} SiP,² and SiS^{2,31-34} have been studied experimentally and theoretically. In contrast, only one diatomic LiSi³ from the class examined here has yet been studied and only theoretically. For the group IV-VI Si–X diatomics, low-spin ground electronic states (³II for



Figure 1. (a, top) $\sigma^2 \sigma^2 \pi^1$ bonding configuration anticipated for LiSi. The doubly occupied bonding σ orbitals is formed from the Li 2s orbital on the left and the Si 3s-3p hybrid orbital on the right; the other σ orbital consists of a 3s-3p hybrid on Si directed away from the Li atom. (b, bottom) description of the $\sigma^2 \sigma^1 \pi^2$ bonding configuration actually found in the ground state of LiSi; here the bonding σ orbital is only singly occupied, but the degenerate π bonding orbitals have two electrons in them as does the non-bonding σ orbital.

SiC, ${}^{2}\Sigma^{-}$ for SiN, ${}^{1}\Sigma^{+}$ for SiO, ${}^{3}\Sigma_{g}^{-}$ for Si₂, ${}^{2}\Sigma^{-}$ for SiP and ${}^{1}\Sigma^{+}$ for SiS) have been observed.

Clearly, it seems that for Si-X compounds, when the electronegativity of X is large enough and/or the number of π electrons on the X atom is larger, the low-spin state becomes lower in energy, while the high-spin state is favored for electropositive and/or electron poor X species. As part of this work, we wanted to determine the "border" of electronegativity at which Si-X compounds change from low- to high-spin ground states, and to analyze what orbital occupancy characteristics make the high-spin electronic states more stable when they are. We chose to focus our attention, in this initial examination of these questions, on compounds of Si (because its valence state can vary from 2 to 4) and Li, Be, B, Na, Mg, and Al (to span groups I-III and to involve atoms both from Si's period and from the first period).

II. Computational Details

The geometries of low-energy electronic states of LiSi, BeSi, BSi, NaSi, MgSi and AlSi were preliminarily optimized employing analytical SCF gradients³⁵ with a polarized split-valence basis set (results at this level are denoted SCF/6-31G*^{36,37}) and

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TABLE I: Calculated Molecular Properties of the Lowest LiSi States

LiSi	LiSi $(4\Sigma^{-})$		
$1\sigma^2 1\pi^3 2\sigma^0$	$1\sigma^2 2\sigma^2 1\pi^1$	$1\sigma^2 1\pi^2 2\sigma^1$	
SCF/6-31G*	SCF/6-31G*	SCF/6-31G*	
$E_{SCF} = -296.21483$	$E_{SCF} = -296.27152$	$E_{SCF} = -296.30882$	
R(Li-Si) = 2.305 Å	R(Li-Si) = 2.670 Å	R(Li-Si) = 2.416 Å	
$\omega_{\rm e} = 433 \ \rm cm^{-1}$	$\omega_{\rm e} = 218 \ {\rm cm}^{-1}$	$\omega_{\rm c} = 440 \ {\rm cm}^{-1}$	
$\langle \hat{S}^2 \rangle = 0.800$	$(S^2) = 0.948$	$\langle S^2 \rangle = 3.752$	
MP2(full)/6-31G*	MP2(full)/6-31G*	MP2(full)/6-31G*	
$E_{MP2} = -296.28895$	$E_{MP2} = -296.34402$	$E_{MP2} = -296.37416$	
R(Li-Si) = 2.241 Å	R(Li-Si) = 2.546 Å	R(Li-Si) = 2.384 Å	
$\omega_{e} = 597 \text{ cm}^{-1}$	$\omega_{\rm e} = 550 \ \rm cm^{-1}$	$\omega_{\rm c} = 463 {\rm cm}^{-1}$	
$\langle \hat{S}^2 \rangle = 0.787$	$(S^2) = 0.793$	$(S^2) = 3.752$	
MP2(full)/6-311+G*	MP2(full)/6-311+G*	$MP2(full)/6-311+G^*$	
$E_{MP2} = -296.44150$	$E_{MP2} = -296.49391$	$E_{MP2} = -296.52406$	
R(Li-Si) = 2.200 Å	R(Li-Si) = 2.545 Å	R(Li-Si) = 2.355 Å	
$\omega_{\rm e} = 599 {\rm cm}^{-1}$	$\omega_{\rm e} = 464 \ {\rm cm}^{-1}$	$\omega_{\rm c} = 472 \ {\rm cm}^{-1}$	
$\langle \hat{S}^2 \rangle = 0.787$	$(S^2) = 0.773$	$\langle \hat{\mathbf{S}}^2 \rangle = 3.752$	
MP4SDTQ/6-311+G(2df)	MP4SDTQ/6-311+G(2df)	OCISD(T)/6-311+G(2df)	
//MP2(full)6-311+G*	//MP2(full)/6-311+G*	//OCISD(T)6-311+G(2df)	
R(Li-Si) = 2.200 Å	$\hat{R}(Li-Si) = 2.545 \text{ Å}$	R(Li-Si) = 2.383 Å	
$E_{PUSCF} = -296.24371$	$E_{PUSCF} = -296.29747$	$E_{PUSCF} = -296.33143$	
$E_{PMP2} = -296.32859$	$E_{PMP2} = -296.37879$	$E_{PMP2} = -296.40608$	
$E_{PMP3} = -296.34669$	$E_{PMP3} = -296.39651$	$E_{PMP3} = -296.42131$	
$E_{PMP4} = -296.35440$	$E_{PMP4} = -296.40329$	$E_{PMP4} = -296.42602$	
	$E_{OCISD} = -296.40130$	$E_{OCISD} = -296.42239$	
	$E_{OCISD(T)} = -296.40597$	$E_{OCISD(T)} = -296.42677$	
$T_{ePMP4} = 44.9 \text{ kcal/mol}$	$T_{ePMP4} = 14.3 \text{ kcal/mol}$	$T_{ePMP4} = 0.0 \text{ kcal/mol}$	

TABLE II:	Calculat	ed Molecul	ar Proj	perties o	f the	Lowest	BeSi States
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BeSi $(^{1}\Sigma^{+})$	BeSi	(³ Π)	BeSi $(^{3}\Sigma^{-})$	BeSi $(5\Sigma^{-})$
$1\sigma^2 1\pi^4 2\sigma^0$	$1\sigma^2 1\pi^3 2\sigma^1$	$1\sigma^2 2\sigma^2 1\pi^1 3\sigma^1$	$1\sigma^2 2\sigma^2 1\pi^2$	$1\sigma^2 2\sigma^1 1\pi^2 3\sigma^1$
SCF/6-31G*	SCF/6-31G*	SCF/6-31G*	SCF/6-31G*	SCF/6-31G*
$E_{SCF} = -303.22489$	$E_{SCF} = -303.34877$	$E_{SCF} = -303.42033$	$E_{SCF} = -303.41718$	$E_{SCF} = -303.42889$
R(Be-Si) = 1.806 Å	R(Be-Si) = 1.937 Å	R(Be-Si) = 2.286 Å	R(Be-Si) = 2.176 Å	R(Be-Si) = 2.118 Å
$\omega_{\rm e} = 952 \rm cm^{-1}$	$\omega_{\rm e}=791~{\rm cm}^{-1}$	$\omega_{\rm e}=499~{\rm cm}^{-1}$	$\omega_{\rm e} = 435 \ \rm cm^{-1}$	$\omega_{\rm e} = 630 \ \rm cm^{-1}$
	$\langle S^2 \rangle = 2.302$	$\langle S^2 \rangle = 2.014$	$\langle \hat{S}^2 \rangle = 2.021$	$\langle \hat{S}^2 \rangle = 6.001$
MP2(full)/6-31G*	MP2(full)/6-31G*	MP2(full)/6-31G*	MP2(full)/6-31G*	MP2(full)/6-31G*
$E_{MP2} = -303.35739$	$E_{MP2} = -303.44595$	$E_{MP2} = -303.50381$	$E_{MP2} = -303.52269$	$E_{MP2} = -303.50409$
R(Be-Si) = 1.836 Å	R(Be-Si) = 1.839 Å	R(Be-Si) = 2.257 Å	R(Be-Si) = 2.097 Å	R(Be-Si) = 2.089 Å
$\omega_{\rm e} = 878 \ \rm cm^{-1}$	$\omega_{\rm e} = 997 {\rm cm}^{-1}$	$\omega_{\rm e} = 416 \ \rm cm^{-1}$	$\omega_{\rm e} = 650 \ {\rm cm}^{-1}$	$\omega_{\rm e}=649~{\rm cm}^{-1}$
	$\langle S^2 \rangle = 2.133$	$\langle S^2 \rangle = 2.012$	$\langle S^2 \rangle = 2.018$	$\langle \hat{S}^2 \rangle = 6.001$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
$E_{MP2} = -303.51106$	$E_{MP2} = -303.59892$	$E_{MP2} = -303.65634$	$E_{MP2} = -303.67451$	$E_{MP2} = -303.65475$
R(Be-Si) = 1.836 Å	R(Be-Si) = 1.848 Å	R(Be-Si) = 2.264 Å	R(Be-Si) = 2.069 Å	R(Be-Si) = 2.089 Å
$\omega_e = 866 \text{ cm}^{-1}$	$\omega_{\rm e} = 1001 {\rm cm}^{-1}$	$\omega_{\rm e} = 415 \rm cm^{-1}$	$\omega_{\rm e} = 561 \rm cm^{-1}$	$\omega_{\rm e} = 641 \ \rm cm^{-1}$
	$\langle S^2 \rangle = 2.143$	$\langle S^2 \rangle = 2.014$	$\langle S^2 \rangle = 2.018$	$\langle S^2 \rangle = 6.001$
MP4SDTQ/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)//
//MP2(full)6-311+G*	//MP2(full/6-311+G*	//MP2(full)/6-311+G*	//QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)
R(Be-Si) = 1.836 Å	R(Be-Si) = 1.848 Å	R(Be-Si) = 2.264 Å	R(Be-Si) = 2.137 Å	R(Be-Si) = 2.108 Å
$E_{SCF} = -303.25040$	$E_{PUSCF} = -303.37580$	$E_{PUSCF} = -303.44774$	$E_{PUSCF} = -303.44436$	$E_{PUSCF} = -303.45143$
$E_{MP2} = -303.39693$	$E_{PMP2} = -303.48487$	$E_{PMP2} = -303.53727$	$E_{PMP2} = -303.55663$	$E_{PMP2} = -303.53288$
$E_{MP3} = -303.41621$	$E_{PMP3} = -303.50268$	$E_{PMP3} = -303.55737$	$E_{PMP3} = -303.57724$	$E_{PMP3} = -303.54884$
$E_{MP4} = -303.43429$	$E_{PMP4} = -303.51189$	$E_{PMP4} = -303.56530$	$E_{PMP4} = -303.58799$	$E_{PMP4} = -303.55470$
	$E_{QCISD} = -303.50747$	$E_{QICSD} = -303.56421$	$E_{QCISD} = -303.58173$	$E_{QCISD} = -303.55182$
	$E_{QCISD(T)} = -303.51660$	$E_{QCISD(T)} = -303.56964$	$E_{QCISD(T)} = -303.59191$	$E_{QCISD(T)} = -303.55745$
$T_{ePMP4} = 96.5 \text{ kcal/mol}$	$T_{ePMP4} = 47.8 \text{ kcal/mol}$	$T_{ePMP4} = 14.2 \text{ kcal/mol}$	$T_{ePMP4} = 0.0 \text{ kcal/mol}$	$T_{ePMP4} = 20.9 \text{ kcal/mol}$
	$T_{eQCISD(T)} = 47.3 \text{ kcal/mol}$	$T_{eQCISD(T)} = 14.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 0.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 21.6 \text{ kcal/mol}$

subsequently at the correlated MP2(full) level (denoted MP2-(full)/6-31G*). Even more accurate geometries were obtained by performing MP2(full) calculations with $6-311+G^*$ basis sets³⁸⁻⁴¹ for which the fundamental vibrational frequencies, normal coordinates, and zero point energies (ZPE) were calculated by standard FG matrix methods. Finally, our most accurately correlated total energies were evaluated in the full fourth-order frozen-core approximation both by Møller-Plesset perturbation theory⁴² (MP4) and the quadratic configuration interaction including singles and doubles with approximate triples QCISD-(T)⁴³ method using standard 6-311+G(2df) basis sets.

Then, for the ground electronic states only, the geometry was reoptimized at the QCISD(T)/6-311+G(2df) level. For all openshell species, the USCF wave functions were projected to produce pure spectroscopic states (whose results, in turn, are labeled PUSCF, PMP2, PMP3 and PMP4).⁴⁴ The Gaussian 90 program suite⁴⁵ was used to perform all of the results discussed here. The results of our calculations are presented in Tables I–VII and summarized in the following Section.

III. Results and Discussion

A. LiSi and NaSi. As detailed in the Introduction, for these species, one anticipates a valence orbital occupancy in which two valence electrons occupy a bonding σ orbital (the Li– or Na–Si σ bond), two electrons occups a non-bonding or antibonding σ orbital, and one electron occupies a 1π orbital. A ²II state would thus be expected to be the ground state. If, in contrast, one of the σ orbitals were singly occupied and the degenerate 1π orbital were doubly occupied with the two electrons in different 1π orbitals, the high-spin ⁴ Σ ⁻ state would be the ground state.

Among all states with π^1 , π^2 , or π^3 occupancies, we found the following states to lie lowest for both LiSi and NaSi:

TABLE III. Calculated	Holecular Tropercies of the	e Doniest DOI Dailes		
$\frac{1}{1\sigma^2 1\pi^4 2\sigma^1}$	$\frac{\mathbf{BSi} (^{2}\Pi)}{1\sigma^{2}2\sigma^{2}1\pi^{3}}$	$\frac{\text{BSi} (^{4}\Sigma^{-})}{1\sigma^{2}2\sigma^{3}3\sigma^{1}1\pi^{2}}$	$\frac{\text{BSi}({}^{4}\Pi)}{1\sigma^{2}2\sigma^{1}3\sigma^{1}1\pi^{3}}$	$\frac{BSi\ (^{6}\Sigma^{-})}{1\sigma^{2}2\sigma^{1}3\sigma^{1}1\pi^{2}4\sigma^{1}}$
HF/6-31G*	HF/6-31G*	HF/6-31G*	HF/6-31G*	HF/6-31G*
$E_{\rm HF} = -313.25604$	$E_{HF} = -313.38541$	$E_{\rm HF} = -313.44035$	$E_{HF} = -313.35368$	no minimum
R(B-Si) = 1.665 Å	R(B-Si) = 1.846 A	R(B-Si) = 1.868 A	R(B-Si) = 1.797 A	
$\omega_{\rm e} = 1189 \ {\rm cm}^{-1}$	$\omega_{\rm e} = 793 {\rm cm}^{-1}$	$\omega_{\rm e} = 867 {\rm cm}^{-1}$	$\omega_{\rm e} = 839 {\rm cm}^{-1}$	
$\langle S^2 \rangle = 0.807$	$\langle S^2 \rangle = 1.912$	$\langle S^2 \rangle = 3.756$	$(S^2) = 4.132$	
MP2(full)/6-31G*	MP2(full)/6-31G*	MP2(full)/6-31G*	MP2(full)/6-31G*	MP2(full)/6-31G*
$E_{MP2} = -313.42148$	$E_{MP2} = -313.50143$	$E_{MP2} = -313.55957$	$E_{MP2} = -313.46689$	no minimum
R(B-Si) = 1.719 Å	R(B-Si) = 1.816 Å $\omega_e = 1000 \text{ cm}^{-1}$	R(B-Si) = 1.902 Å $\omega_e = 781 \text{ cm}^{-1}$	R(B-Si) = 1.730 Å $\omega_e = 1099 \text{ cm}^{-1}$	
$(S^2) = 0.804$	$\langle \hat{S}^2 \rangle = 1.896$	$(S^2) = 3.756$	$(S^2) = 4.011$	
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
$E_{MP2} = -313.57940$	$E_{MP2} = -313.65890$	$E_{MP2} = -313.71779$	$E_{MP2} = -313.37664$	$E_{MP2} = -313.58881$
R(B-Si) = 1.722 Å	R(B-Si) = 1.819 Å	R(B-Si) = 1.905 Å	R(B-Si) = 1.726 Å	R(B-Si) = 1.941 Å
	$\omega_{\rm e} = 995 {\rm cm}^{-1}$	$\omega_{\rm e} = 772 {\rm cm}^{-1}$	$\omega_{\rm e} = 1150 {\rm cm}^{-1}$	$\omega_{\rm e} = 751 {\rm cm}^{-1}$
$(S^2) = 0.804$	$\langle S^2 \rangle = 1.892$	$\langle \hat{S}^2 \rangle = 3.757$	$\langle \hat{S}^2 \rangle = 3.992$	$\langle \hat{S}^2 \rangle = 8.753$
MP4SDTO/6-311+G(2df)	OCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311G(2df)//
//MP2/(full)6-311+G*	//MP2(full)/6-311+G*	//MP2(full)/6-311+G*	//MP2(full)/6-311+G*	MP2(full)/6-311+G*
R(B-Si) = 1.722 Å	$\hat{R}(B-Si) = 1.819 \text{ Å}$	R(B-Si) = 1.905 Å	R(B-Si) = 1.726 Å	R(B-Si) = 1.941 Å
$E_{PUHF} = -313.28957$	$E_{PUHF} = -313.42962$	$E_{PUHF} = -313.47096$	$E_{PUHF} = -313.24004$	$E_{PUHF} = -313.37772$
$E_{PMP2} = -313.47008$	$E_{PMP2} = -313.55459$	$E_{PMP2} = -313.60127$	$E_{PMP2} = -313.36126$	$E_{PMP2} = -313.46910$
$E_{PMP3} = -313.48247$	$E_{PMP3} = -313.57491$	$E_{PMP3} = -313.62421$	$E_{PMP3} = -313.38217$	$E_{PMP3} = -313.48637$
$E_{PMP4} = -313.50376$	$E_{PMP4} = -313.58838$	$E_{PMP4} = -313.63428$	$E_{PMP4} = -313.39432$	$E_{PMP4} = -313.49325$
•		$E_{OCISD} = -313.62987$		$E_{OICSD} = -313.49198$
		$E_{OCISD(T)} = -313.63980$		$E_{OCISD(T)} = -313.49788$
$T_{ePMP4} = 81.9 \text{ kcal/mol}$	$T_{ePMP4} = 22.5 \text{ kcal/mol}$	$T_{ePMP4} = 0.0 \text{ kcal/mol}$	$T_{ePMP4} = 150.6 \text{ kcal/mol}$	$T_{ePMP4} = 88.5 \text{ kcal/mol}$

TABLE IV:	Calculated	Mo	lecular	Propert	ties of	the	Lowest	NaSi	States	
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NaSi	NaSi (4Σ⁻)	
$1\sigma^2 1\pi^3 2\sigma^0$	$1\sigma^2 2\sigma^2 1\pi^1$	$1\sigma^2 1\pi^2 2\sigma^1$
 SCF/6-31G*	SCF/6-31G*	SCF/6-31G*
$E_{SCF} = -450.61794$	$E_{SCF} = -450.66854$	$E_{SCF} = -450.70749$
R(Na-Si) = 2.614 Å	R(Na-Si) = 2.977 Å	R(Na-Si) = 2.739 Å
$\omega_{\rm e} = 263 \ {\rm cm}^{-1}$	$\omega_{\rm e} = 160 \ \rm cm^{-1}$	$\omega_{\rm e}=258~{\rm cm}^{-1}$
$\langle S^2 \rangle = 0.786$	$(S^2) = 1.071$	$\langle S^2 \rangle = 3.753$
MP2(full)/6-31G*	MP2(full)/6-31G*	MP2(full)/6-31G*
$E_{MP2} = -450.69015$	$E_{MP2} = -450.74000$	$E_{MP2} = -450.77282$
R(Na-Si) = 2.564 Å	R(Na-Si) = 2.881 Å	R(Na-Si) = 2.705 Å
$\omega_{\rm e} = 340 \ {\rm cm}^{-1}$	$\omega_{\rm c}=214~{\rm cm^{-1}}$	$\omega_{\rm e}=274~{\rm cm}^{-1}$
$(S^2) = 0.781$	$(S^2) = 1.280$	$(S^2) = 3.753$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
$E_{MP2} = -450.95933$	$E_{MP2} = -451.00906$	$E_{MP2} = -451.04155$
R(Na-Si) = 2.569 Å	R(Na-Si) = 2.858 Å	R(Na-Si) = 2.697 Å
$\omega_{\rm e} = 334 \ {\rm cm}^{-1}$		$\omega_{\rm e} = 271 \ {\rm cm}^{-1}$
$\langle \hat{S}^2 \rangle = 0.776$	$(S^2) = 1.250$	$(S^2) = 3.753$
MP4SDTQ/6-311+G(2df)	MP4SDTQ/6-311+G(2df)	QCISD(T)/6-311+G(2df)
//MP2(full)6-311+G*	//MP2(full)/6-311+G*	//MP2(full)/6-311+G*
R(Na-Si) = 2.569 Å	R(Na-Si) = 2.858 Å	R(Na-Si) = 2.697 Å
$E_{PUSCF} = -450.64904$	$E_{PUSCF} = -450.70578$	$E_{PUSCF} = -450.73269$
$E_{PMP2} = -450.73129$	$E_{PMP2} = -450.77773$	$E_{PMP2} = -450.80663$
$E_{PMP3} = -450.74917$	$E_{PMP3} = -450.79393$	$E_{PMP3} = -450.82177$
$E_{PMP4} = -450.75638$	$E_{PMP4} = -450.80144$	$E_{PMP4} = -450.82640$
	$E_{OCISD} = -450.80199$	$E_{OCISD} = -450.82284$
	$E_{OCISD(T)} = -450.80692$	$E_{OCISD(T)} = -450.82710$
$T_{ePMP4} = 43.9 \text{ kcal/mol}$	$T_{ePMP4} = 15.9 \text{ kcal/mol}$	$T_{ePMP4} = 0.0 \text{ kcal/mol}$
•	•	•

 ${}^{4}\Sigma^{-}(1\sigma^{2}1\pi^{2}2\sigma^{1}), {}^{2}\Pi(1\sigma^{2}1\pi^{3}), {}^{2}\Pi(1\sigma^{2}2\sigma^{2}1\pi^{1}), {}^{4}\Pi(1\sigma^{2}2\sigma^{1}1\pi^{1}3\sigma^{1})$ and ${}^{6}\Sigma^{-}(1\sigma^{1}2\sigma^{1}1\pi^{2}3\sigma^{1})$. The energies and properties of the lowest three of these states appear in Tables I and IV, respectively.

Note that a high-spin ${}^{4}\Sigma^{-}$ electronic state having $1\sigma^{2}1\pi^{2}2\sigma^{1}$ valence orbital occupancy was found to be the ground states for both molecules. For LiSi this result agrees with the previous ab initio data by Mavridis and Harrison.³ However our bond length (2.383 Å vs 2.468 Å³), vibrational frequency (472 cm⁻¹ vs 429 cm^{-1,3}), and dissociation energy (41.5 kcal/mol vs 34.6 kcal/mol³) are quite different than given in Ref. 3. These differences are probably due to the larger basis sets and more sophisticated correlation methods used in our work.

Of the two ${}^{2}\Pi$ states, that having the $1\sigma^{2}2\sigma^{2}1\pi^{1}$ valence orbital occupancy lies lowest for both molecules. The other ${}^{2}\Pi$ state (with $1\sigma^{2}1\pi^{3}$ occupancy) is higher lying. The ${}^{4}\Pi$ and ${}^{6}\Sigma^{-}$ states do not have minima on their potential energy curves for either molecule, but both ${}^{2}\Pi$ states are bound for both molecules. The vertical excitation energies (at the ground state's equilibrium bond length) for the $4\Sigma^- \rightarrow 4\Pi$ and $4\Sigma^- \rightarrow 6\Sigma^-$ processes are 48.2 and 133.7 kcal/mol, respectively for LiSi. Small spin contamination was found for the $4\Sigma^-$ and 2Π states of both molecules.

The ${}^{4}\Sigma^{-}$ and ${}^{2}\Pi$ states differ markedly in their bonding character (recall Figures 1a and 1b). For example, in the case of LiSi, the Mulliken charge on Si is -0.34 in the ${}^{4}\Sigma^{-}$ state, while in the latter state it is -0.06; thus the ${}^{4}\Sigma^{-}$ state involves a significant amount of charge transfer from Li to Si and has substantial Li⁺Sicharacter. Moreover, the Li⁺Si⁻ character would involve the ${}^{4}S$ ground state of Si⁻ which has $3s^{2}3p_{x}{}^{1}3p_{y}{}^{1}3p_{z}{}^{1}$ orbital occupancy. Both the ${}^{4}\Sigma^{-}$ and ${}^{2}\Pi$ states have two electrons in the bonding 1σ orbital, which is polarized strongly toward the Si atom and has an orbital energy of -0.60 Hartrees in the ${}^{4}\Sigma^{-}$ state and -0.55 H in the ${}^{2}\Pi$ state. However, the ${}^{4}\Sigma^{-}$ state has only one electron in the 2σ orbital (that is concentrated on the Si but has significant Li contributions also) whose energy is -0.284 Hartrees; this state

TABLE V:	Calculated	Molecular	Properties o	f the 🛛	Lowest]	MgSi States
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MgSi ($^{1}\Sigma^{+}$)	MgS	i (¹ Π)	MgSi $(^{3}\Sigma^{-})$	MgSi (⁵ Σ ⁻)	
$1\sigma^2 1\pi^4 2\sigma^0$	$1\sigma^2 1\pi^3 2\sigma^1$	$1\sigma^2 2\sigma^2 1\pi^1 3\sigma^1$	$1\sigma^2 2\sigma^2 1\pi^2$	$1\sigma^2 2\sigma^1 1\pi^2 3\sigma^1$	
SCF/6-31G*	SCF/6-31G*	SCF/6-31G*	SCF/6-31G*	SCF/6-31G*	
$E_{SCF} = -488.22917$	$E_{SCF} = -488.35295$	$E_{SCF} = -488.42575$	$E_{SCF} = -488.45433$	$E_{SCF} = -488.43715$	
R(Mg-Si) = 2.185 Å	R(Mg-Si) = 2.403 Å	R(Mg-Si) = 2.986 Å	R(Mg-Si) = 2.604 Å	R(Mg-Si) = 2.552 Å	
$\omega_{\rm e} = 537 \ \rm cm^{-1}$	$\omega_{\rm e} = 336 \ \rm cm^{-1}$	$\omega_{\rm c} = 102 \ \rm cm^{-1}$	$\omega_{\rm e} = 304 \ \rm cm^{-1}$	$\omega_{\rm e} = 347 \ {\rm cm}^{-1}$	
	$\langle S^2 \rangle = 2.072$	$\langle S^2 \rangle = 2.094$	$\langle S^2 \rangle = 2.721$	$\langle S^2 \rangle = 6.001$	
MP2(full)/6-31G*	MP2(full)/6-31G*	MP2(full)/6-31G*	MP2(full)/6-31G*	MP2(full)/6-31G*	
$E_{MP2} = -488.34946$	$E_{MP2} = -488.44886$	$E_{MP2} = -488.50956$	$E_{MP2} = -488.53414$	$E_{MP2} = -488.51135$	
R(Mg-Si) = 2.222 Å	R(Mg-Si) = 2.321 Å	R(Mg-Si) = 2.806 Å	R(Mg-Si) = 2.558 Å	R(Mg-Si) = 2.521 Å	
$\omega_e = 496 \text{ cm}^{-1}$	$\omega_{\rm e} = 468 \ {\rm cm}^{-1}$		$\omega_{\rm e} = 322 \ \rm cm^{-1}$	$\omega_{\rm e}=362~{\rm cm}^{-1}$	
	$\langle S^2 \rangle = 2.051$	$\langle S^2 \rangle = 2.064$	$\langle S^2 \rangle = 2.727$	$\langle S^2 \rangle = 6.001$	
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	
$E_{MP2} = -488.61714$	$E_{MP2} = -488.71656$	$E_{MP2} = -488.77754$	$E_{MP2} = -488.80117$	$E_{MP2} = -488.77805$	
R(Mg-Si) = 2.220 Å	R(Mg-Si) = 2.326 Å	R(Mg-Si) = 2.815 Å	R(Mg-Si) = 2.566 Å	R(Mg-Si) = 2.527 Å	
$\omega_{\rm e} = 493 \ {\rm cm}^{-1}$	$\omega_{\rm e} = 463 \ {\rm cm}^{-1}$		$\omega_{\rm c} = 316 \ \rm cm^{-1}$	$\omega_{\rm e} = 493 \ \rm cm^{-1}$	
	$\langle S^2 \rangle = 2.047$	$\langle S^2 \rangle = 2.066$	$(S^2) = 2.727$	$\langle S^2 \rangle = 6.001$	
MP4SDTQ/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)//	QCISD(T)/6-311+G(2df)//	
//MP2(full)6-311+G*	//MP2(full)/6-311+G*	//MP2(full)/6-311+G*	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	
R(Mg-Si) = 2.220 Å	R(Mg-Si) = 2.326 Å	R(Mg-Si) = 2.815 Å	R(Mg-Si) = 2.561 Å	R(Mg-Si) = 2.545 Å	
$E_{SCF} = -488.26365$	E _{PUSCF} – –488.39040	$E_{PUSCF} = -488.46961$	E _{PUSCF} = -488.49022	$E_{PUSCF} = -488.46872$	
$E_{SCF} = -488.39548$	$E_{PMP2} = -488.49185$	$E_{PMP2} = 488.56419$	$E_{PMP2} = -488.57430$	$E_{PMP2} = -488.54711$	
$E_{MP3} = -488.41594$	$E_{PMP3} = -488.51024$	$E_{PMP3} = -488.58427$	$E_{PMP3} = -488.59125$	$E_{PMP3} = -488.56285$	
$E_{MP4} = -488.43134$	$E_{PMP4} = -488.51962$	$E_{PMP4} = -488.59336$	$E_{PMP4} = -488.59770$	$E_{PMP4} = -488.56808$	
	$E_{QCISD} = -488.51600$		$E_{QCISD} = -488.59554$	$E_{QCISD} = -488.56467$	
	$E_{QCISD(T)} = -488.52687$		$E_{QCISD(T)} = -488.60298$	$E_{QCISD(T)} = -488.56970$	
$T_{ePMP4} = 104.4 \text{ kcal/mol}$	$T_{ePMP4} = 49.0 \text{ kcal/mol}$	$T_{ePMP4} = 2.7 \text{ kcal/mol}$	$T_{ePMP4} = 0.0 \text{ kcal/mol}$	$T_{ePMP4} = 18.6 \text{ kcal/mol}$	
	$T_{eQCISD(T)} = 47.8 \text{ kcal/mol}$		$T_{eQCISD(T)} = 0.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 20.9 \text{ kcal/mol}$	

TABLE VI: Calculated Molecular Properties of the Lowest AlSi States

AlSi $(^{2}\Sigma^{+})$ $1\sigma^{2}1\pi^{4}2\sigma^{1}$	AlSi (² Π) 1σ ² 2σ ² 1π ³	AlSi $(4\Sigma^{-})$ $1\sigma^{2}2\sigma^{2}1\pi^{2}3\sigma^{4}$	AlSi (${}^{4}\Pi$) 1 $\sigma^{2}2\sigma^{1}1\pi^{3}3\sigma^{1}$	AlSi ($^{\circ}\Sigma^{-}$) 1 $\sigma^{2}2\sigma^{1}3\sigma^{1}1\pi^{2}4\sigma^{1}$
SCF/6-31G*	SCF/6-31G*	SCF/6-31G*	SCF/6-31G*	SCF/6-31G*
no minimum	R(AI-Si) = 2.377 Å $\omega_c = 341 \text{ cm}^{-1}$	R(AI-Si) = 2.493 Å $\omega_c = 346 \text{ cm}^{-1}$	R(AI-Si) = 2.244 Å	no minimum
	$\langle S^2 \rangle = 2.072$	$\langle S^2 \rangle = 3.768$	$\langle S^2 \rangle = 4.204$	
MP2(full)/6-31G*	MP2(full)/6-31G*	MP2(full)/6-31G*	MP2(full)/6-31G*	MP2(full)/6-31G*
$E_{MP2} = -530.68893$	$E_{MP2} = -530.80108$	$E_{MP2} = -530.85945$	$E_{MP2} = -530.75402$	$E_{MP2} = -530.63143$
R(AI-Si) = 2.081 A	R(AI-Si) = 2.287 A	R(AI-Si) = 2.409 A	R(AI-Si) = 2.092 Å	R(Al-Si) = 2.560 Å
$\omega_{\rm c} = 576 {\rm cm}^{-1}$	$\omega_{\rm c} = 373 {\rm cm}^{-1}$	$\omega_{\rm c} = 392 {\rm cm}^{-1}$	$\omega_{\rm e} = 735 {\rm cm}^{-1}$	$\omega_{\rm e} = 318 \ {\rm cm}^{-1}$
$\langle S^2 \rangle = 1.610$	$\langle S^2 \rangle = 2.044$	$\langle S^2 \rangle = 3.767$	$(S^2) = 3.835$	$(S^2) = 8.753$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
$E_{MP2} = -530.95599$	$E_{MP2} = -531.06781$	$E_{MP2} = -531.12668$	$E_{MP2} = -531.02123$	$E_{MP2} = -530.90110$
R(AI-Si) = 2.069 A	R(AI-Si) = 2.285 A	R(AI-Si) = 2.409 Å	R(AI-Si) = 2.089 Å	R(Al-Si) = 2.484 Å
	$\omega_{\rm c} = 369 {\rm cm}^{-1}$	$\omega_{\rm c} = 383 {\rm cm}^{-1}$		$\omega_e = 351 \text{ cm}^{-1}$
$\langle S^2 \rangle = 1.582$	$\langle S^2 \rangle = 2.043$	$\langle S^2 \rangle = 3.768$	$\langle S^2 \rangle = 3.829$	$(S^2) = 8.754$
MP4SDTQ/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)//	QCISD(T)/6-311+G(2df)//
//MP2(full)6-311+G*	//MP2(full)/6-311+G*	//QCISD(T)/6-311+G(2df)	MP2(full)/6-311+G*	MP2(full)/6-311+G*
R(AI-Si) = 2.069 A	R(AI-Si) = 2.285 A	R(AI-Si) = 2.430 A	R(AI-Si) = 2.089 A	R(AI-Si) = 2.484 A
$E_{PUSCF} = -530.62741$	$E_{PUSCF} = -530.75162$	$E_{PUSCF} = -530.78822$	$E_{PUSCF} = -530.69132$	$E_{PUSCF} = -530.58656$
$E_{PMP2} = -530.75012$	$E_{PMP2} = -530.85951$	$E_{PMP2} = -530.90765$	$E_{PMP2} = -530.80323$	$E_{PMP2} = -530.68241$
$E_{PMP3} = -530.77087$	$E_{PMP3} = -530.87927$	$E_{PMP3} = -530.93080$	$E_{PMP3} = -530.82319$	$E_{PMP3} = -530.69955$
$E_{PMP4} = -530.78551$	$E_{PMP4} = -530.89010$	$E_{PMP4} = -530.93998$	$E_{PMP4} = -530.83319$	$E_{PMP4} = -530.70750$
		$E_{QCISD} = -530.93438$	$E_{QCISD} = -530.82935$	$E_{QC1SD} = -530.70453$
		$E_{QCISD(T)} = -530.94308$	$E_{QCISD(T)} = -530.83992$	$E_{QCISD(T)} = -530.71295$
$T_{cPMP4} = 96.9 \text{ kcal/mol}$	$T_{ePMP4} = 31.3 \text{ kcal/mol}$	$\Gamma_{ePMP4} = 0.0 \text{ kcal/mol}$	$1_{cPMP4} = 67.0 \text{ kcal/mol}$	$T_{ePMP4} = 145.9 \text{ kcal/mol}$
		$T_{eQCISD(T)} = 0.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 64.7 \text{ kcal/mol}$	$T_{eQCISD(T)} = 144 \text{ kcal/mol}$

TABLE VII: Calculated Ground-State Dissociation Energies with 6-311+G(2df) Basis Set

reaction	PUSCF	PMP2	PMP3	PMP4	QCISD(T)	QCISD(T)+ZPE
LiSi $({}^{4}\Sigma^{-}) \rightarrow Li ({}^{2}S) + Si ({}^{3}P)$	+28.6	+41.4	+42.5	+42.5	+42.2	+41.5
BeSi $({}^{3}\Sigma^{-}) \rightarrow$ Be $({}^{1}S) +$ Si $({}^{3}P)$	+11.7	+30.7	+29.4	+30.6	+29.6	+28.8
BSi $({}^{4}\Sigma^{-}) \rightarrow B ({}^{3}P) + Si ({}^{3}P)$	+52.5	+73.5	+71.7	+71.9	+72.6	+71.5
NaSi $({}^{4}\Sigma^{-}) \rightarrow Na$ $({}^{2}S) + Si$ $({}^{3}P)$	+20.6	+33.1	+34.0	+34.0	+33.7	+33.3
$MgSi (^{3}\Sigma^{-}) \rightarrow Mg (^{1}S) + Si (^{3}P)$	+18.7	+23.0	+21.2	+20.9	+22.2	+21.7
AlSi $({}^{4}\Sigma^{-}) \rightarrow Al ({}^{2}P) + Si ({}^{3}P)$	+36.5	+55.8	+56.2	+56.2	+56.5	+56.0

has two electrons in the Si-localized 1π orbital (whose energy is -0.250 Hartrees). The ²II state has two electrons in the 2σ orbital (-0.234 H) and one in the 1π orbital (-0.248 H), and thus has far less ionic character.

For both LiSi and NaSi, the equilibrium bond length and harmonic vibrational frequency of the $4\Sigma^-$ state are shorter and higher, respectively, than those of the 2Π state. All of this data is consistent with the lower- energy $4\Sigma^-$ state having stronger

bonding than the ²II state (because the former has one fewer non-bonding or antibonding σ electron and one more weakly bonding π electron). However, the near degeneracy of the 2σ and 1π orbitals causes the energies and bonding strengths of these two states to be competitive.

As shown in Tables I and IV for LiSi and NaSi, the other ${}^{2}\Pi$ state (the one with $1\sigma^{2}2\sigma^{0}1\pi^{3}$ occupancy) has even shorter bond lengths and higher vibrational frequencies that either of the *lower*-

energy ${}^{4}\Sigma^{-}$ or ${}^{2}\Pi$ states. This clearly suggests that the bonding strength of the 1π orbital exceeds that of the 2σ orbital. The fact that the total energy of this $1\sigma^{2}2\sigma^{0}1\pi^{3}$ state is higher than those of the $1\sigma^{2}2\sigma^{1}1\pi^{2}$ and $1\sigma^{2}2\sigma^{2}1\pi^{1}$ states relates to the fact that the $1\sigma^{2}2\sigma^{0}1\pi^{3}$ configuration derives from an excited state of Li⁺Siin which the Coulomb repulsions among 3p electrons in Si⁻ are large. The $1\sigma^{2}$ pair correlates to the $3s^{2}$ pair of Si, and the $1\pi^{3}$ occupancy correlates to $3p_{x}{}^{2}3p_{y}{}^{1}$ Si⁻; the ground state of Si⁻ has $3s^{2}3p_{x}{}^{1}3p_{y}{}^{1}3p_{z}{}^{1}$ occupancy. So, even though the $1\sigma^{2}2\sigma^{0}1\pi^{3}{}^{2}\Pi$ state has higher total energy, it displays strong bonding character in its bond length and vibrational frequency. Similar trends are observed for the remaining Si-X compounds discussed later in this work.

B. BeSi and MgSi. Given a total of six valence electrons $(2s^2 \text{ or } 3s^2 \text{ from Be or Mg and } 3s^23p^2 \text{ from Si})$, the most likely candidates for low-energy configurations involve $1\sigma^22\sigma^21\pi^2$, $1\sigma^22\sigma^11\pi^3$, $1\sigma^21\pi^4$, or $1\sigma^22\sigma^11\pi^23\sigma^1$ occupancies. We therefore studied, for each of these two molecules, the following six low lying electronic states: ${}^{3}\Sigma^{-}(1\sigma^22\sigma^21\pi^2)$, ${}^{3}\Pi(1\sigma^21\pi^32\sigma^1)$, ${}^{5}\Sigma^{+}(1\sigma^22\sigma^11\pi^23\sigma^1)$ and ${}^{7}\Pi^{-}(1\sigma^12\sigma^11\pi^23\sigma^14\sigma^1)$. The results of our calculations appear in Tables II and V.

We find the ${}^{3}\Sigma^{-}(1\sigma^{2}\sigma^{2}1\pi^{2})$ state to be the ground state and the ${}^{3}\Pi(1\sigma^{2}\sigma^{2}1\pi^{1}3\sigma^{1})$ state to be the lowest lying excited state for both molecules. In these states, the 1σ orbital (-0.64 H and -0.63 H, in the ${}^{3}\Sigma^{-}$ and ${}^{3}\Pi$ states, respectively) is essentially a Si- polarized bonding orbital, 2σ is a Be-polarized antibonding orbital (-0.33 H and -0.37 H, respectively), 3σ is a rather covalent 2p-3p bonding orbital (-0.27 H), and 1π is a bonding orbital (-0.28 H and -0.30 H, respectively) localized more on Si. The 1σ bonding, 2σ antibonding and 1π bonding orbitals are more covalent than in the LiSi and NaSi cases, as a result of which the Mulliken charges on Si are 0.03 and 0.14 for the ${}^{3}\Sigma^{-}$ and ${}^{3}\Pi$ states. All of the high-spin states ${}^{3}\Pi$, ${}^{3}\Sigma^{-}$ and ${}^{5}\Sigma^{-}$ (but not ${}^{7}\Pi$) states are lower in energy than the low-spin ${}^{1}\Sigma^{+}$ state. The dissociation energies computed for the ground states are 28.8 kcal/mol and 21.7 kcal/mol for BeSi and MgSi, respectively.

The electronic state with the highest spin $(^7\Pi)$ is found to possess no minimum on its potential curve, but to have a vertical excitation energy from the ground state $X^{3}\Sigma^{-} \rightarrow {}^{7}\Pi$ of 200.8 kcal/mol for BeSi and 191.6 kcal/mol for MgSi. The excitation energies for the $X^{3}\Sigma^{-} \rightarrow {}^{5}\Sigma^{-}$ and $X^{3}\Sigma^{-} \rightarrow {}^{3}\Pi$ transitions are not very large for BeSi (20.9 and 14.2 kcal/mol, respectively) or for MgSi (18.6 and 2.7 kcal/mol, respectively; all at the PMP4SDTQ/6-311+G(2df)level), but the low-spin singlet state Σ^+ of both molecules lies much higher (96.5 and 104.4 kcal/mol for BeSi and MgSi, respectively). Although the $5\Sigma^{-}$ and $3\Pi^{-}$ $(1\sigma^2 2\sigma^2 1\pi^1 3\sigma^1)$ states are weakly bound for both BeSi and MgSi, all other excited states lie above the energy of the two atoms in their ground states. This ³II state of MgSi lies only 2.7 kcal/mol above the ${}^{3}\Sigma^{-}$ ground state, much as in the isoelectronic Al₂ species. Because this energy difference is very small, we are not certain that the ${}^{3}\Sigma^{-}$ state is actually the ground state.

Small spin contaminations were observed for the ${}^{3}\Pi$ and ${}^{5}\Sigma^{-}$ states of both BeSi and MgSi; these states were therefore treated using the projection methods outlined above. However, for the ${}^{3}\Sigma^{-}$ state of MgSi, the spin contamination was very large, so our data for this state should be viewed as not very reliable.

For both BeSi and MgSi, the equilibrium bond length and harmonic vibrational frequency of the $\sigma^4 \pi^{2} \, {}^{3}\Sigma^{-}$ ground state are shorter and higher, respectively, than those of the $\sigma^5 \pi^{1} \, {}^{3}\Pi$ state, which is consistent with the lower- energy ${}^{3}\Sigma^{-}$ state having stronger bonding than the ${}^{3}\Pi$ state. This indicates that the bonding strength of the 1π orbital exceed that of the 3σ orbital. However, the $1\sigma^{2}2\sigma^{1}1\pi^{2}3\sigma^{1}({}^{5}\Sigma^{-}), 1\sigma^{2}1\pi^{3}2\sigma^{1}({}^{3}\Pi)$, and $1\sigma^{2}1\pi^{4}({}^{1}\Sigma^{+})$ states all have even shorter bond lengths and higher vibrational frequencies (see Tables II and V). Clearly, the near degeneracy of the bonding $2\sigma, 3\sigma$, and 1π orbitals causes the energies and bonding strengths



Figure 2. Energies of ground and low-lying excited states of Si-X species for X ranging across the first row.

of all these states to be competitive. The higher total energies of states with π^3 and π^4 occupancies is caused by the fact that these states do not correlate with ground state Si (which has no doubly occupied 3p orbital) but to excited states in which the Coulomb repulsion is high due to the occurrence of doubly occupied 3p orbitals.

C. BiSi and AlSi. With seven valence electrons, and reflecting on the fact that π^2 , π^1 , and π^3 occupancies produced the lowestenergy states for the Li, Na, Be, and Mg containing species, the following configurations seem most favorable: $1\sigma^22\sigma^21\pi^23\sigma^1$, $1\sigma^22\sigma^21\pi^3$, $1\sigma^21\pi^42\sigma^1$, and $1\sigma^22\sigma^21\pi^13\sigma^2$. The following electronic states derived from these configurations: ${}^{2}\Sigma^{+}(1\sigma^21\pi^42\sigma^1)$, ${}^{2}\Pi(1\sigma^22\sigma^21\pi^3)$, ${}^{4}\Sigma^{-}(1\sigma^22\sigma^23\sigma^11\pi^2)$, ${}^{4}\Pi(1\sigma^22\sigma^21\pi^13\sigma^14\sigma^1)$, ${}^{2}\Pi(1\sigma^22\sigma^21\pi^13\sigma^2)$ and ${}^{6}\Sigma^{-}(1\sigma^22\sigma^13\sigma^11\pi^24\sigma^1)$ were probed for BSi and AlSi.

With the more electronegative B and Al atoms bonded to Si, the nature of the σ orbitals changes somewhat compared to the Li, Na, Be, and Mg cases. For the ground electronic state of BSi, the Mulliken charge on Si in this state is positive (0.30). The 1σ orbital (-0.76 H in the ground state) is the (rather covalent) B-Si (or Al-Si) bond, $2\sigma(-0.50$ H) is the corresponding antibonding orbital, 3σ (-0.35 H) is a p- orbital based σ bonding orbital (2p-3p for B-Si and 3p-3p for Al-Si), and the 1π orbital (-0.33 H) is delocalized over the B (or Al) and Si atoms.

As shown in Tables III and VI, for both of these molecules, a high-spin $4\Sigma^{-}(1\sigma^2 2\sigma^2 3\sigma^1 1\pi^2)$ ground state is predicted to be bound with dissociation energies of 71.5 kcal/mol (BSi) and 56.0 kcal/mol (AlSi; both at the QCISD(T)/6-311+G(2df)+ZPE level). For both species, the $(1\sigma^2 2\sigma^2 1\pi^3)^2\Pi$ is the lowest excited state. Again, the near degeneracy of two orbitals, here the 1π and the 3σ , causes two states to be close in energy.

The $(1\sigma^2 2\sigma^1 3\sigma^1 1\pi^3)^4 \Pi$, $(1\sigma^2 2\sigma^1 3\sigma^1 1\pi^2 4\sigma^1)^6 \Sigma^-$, and $(1\sigma^2 1\pi^4 2\sigma^1)^2 \Sigma^+$, exited states all lie above the isolated atoms in their ground electronic states. Only the $(1\sigma^2 2\sigma^2 1\pi^3)^2 \Pi$ excited state of each species lies below the ground-state separated atoms. The $^6\Sigma^-$ electronic state has no minimum at the SCF/6-31G* level for both species, and, for BSi, this state has no minimum even at the MP2(full)/6-31G* level. The $^2\Pi$ and $^2\Sigma^+$ states of BSi and AlSi were found to have heavy spin contaminations, so our results on these states should be treated as suspect.

Again, the bond lengths and vibrational frequencies decrease and increase, respectively, as the number of π electrons increase as shown in Tables III and VI. The total energies of π^3 and π^4 states are higher than π^2 states because states with three or four π electrons correlate with excited states of Si in which the Coulomb repulsions are high because doubly occupied 3p orbitals appear.

IV. Overview

As summarized in Figures 2 and 3, along the period from LiSi to OSi as well as from NaSi to SSi, a high-spin electronic state is the XSi ground state when X is an electropositive electron-poor

One feature characterizing the ground states of all the species studied here is their π^2 orbital occupancy. These π^2 states derive from the 3s²3p² ground-state configuration of Si. Contributions to the wavefunction of X+Si-character are also appreciable, which also favors a π^2 orbital occupancy since this occpancy correlates with the 4S ground state of Si⁻. Low-lying excited states arise primarily from π^1 or π^3 configurations; states with π^4 character lie somewhat higher in energy.

The π^3 and π^4 states are higher lying because they correlate with excited states of Si or Si⁻ in which Coulomb repulsions are high due to the occurrence of doubly occupied 3p orbitals. States with π^1 occupancy are close in energy to the π^2 ground states because of a σ - and π - orbital near degeneracy that occurs in each of the species considered here. We believe that π^1 states lie slightly above the corresponding π^2 states because the former place too much electron density in the already electron-rich σ orbital framework and thus increase Coulomb repulsions. The alternative placement of an electron in a vacant π orbital produces less Coulomb repulsion. For X-Si species in which X is a more electronegative element, the near degeneracy of the σ - and 1π orbitals is less likely to occur, hence the delicate "balance" between "crowding" (i.e, Coulomb repulsion) in the σ - and π -orbital frameworks is unlikely to dictate the state ordering.

For all of the species studied, the equilibrium bond lengths and harmonic vibrational frequencies tend to decrease and increase, respectively, as the electronic configurations vary from $\sigma^{n+1}\pi^1$ to $\sigma^n \pi^2$, $\sigma^{n-1} \pi^3$ and $\sigma^{n-2} \pi^4$ even though the total energy of the $\sigma^n \pi^2$ states are the lowest. These data indicate that the 1π orbital is bonding (which can be seen also in this orbital's LCAO-MO coefficients).

The diatomics CSi and Si₂ form the border between high-spin and low-spin ground electronic states. CSi has a triplet $X^3\Pi$ ground electronic state, but its singlet $a^{1}\Sigma^{+}$ state is only 12.5 kcal/mol higher. Similarly, the C_2 diatomic has a singlet $X^1\Sigma^+$ ground electronic state, and its $^{3}\Pi$ triplet state is only 2.05 kcal/ mol higher.² For Si₂, the triplet ${}^{3}\Sigma_{g}^{-}(\pi_{u}{}^{2}\sigma_{g}{}^{2})$ is the ground state, but the ${}^{3}\Pi_{u}(\pi_{u}{}^{3}\sigma_{g}{}^{1})$ state is nearly isoenergetic, and other singlet states ${}^{1}\Delta_{g}(\pi_{u}{}^{2}\sigma_{g}{}^{2}), {}^{1}\Pi_{u}(\pi_{u}{}^{3}\sigma_{g}{}^{1})$ and ${}^{1}\Sigma_{g}{}^{+}(\pi_{u}{}^{4})$ are only 11.1, 12.7 and 16.1 kcal/mol higher in energy.⁴

V. Summary and Conclusions

Our primary findings can be summarized as follows:

LiSi, BeSi, BSi, NaSi, MgSi and AlSi all have high-spin ground electronic states of ${}^{4}\Sigma^{-}$, ${}^{3}\Sigma^{-}$, ${}^{4}\Sigma^{-}$, ${}^{3}\Sigma^{-}$ and ${}^{4}\Sigma^{-}$ symmetry, respectively, and all of these states have two electrons in the 1π orbital.

Other low-lying states arise from π^2 configurations (with different σ - orbital occupancies), π^1 , and π^3 configurations; states derived from π^4 occupancy are higher lying.

The π^1 and π^2 ground states derive from the $3s^23p^2$ ground state of Si, whereas states with π^3 and π^4 parentage correlate with excited states of Si or Si-, and are higher lying because of greater Coulomb repulsions in states containing doubly occupied 3p orbitals.

Near degeneracy of a σ orbital and the 1π orbital cause states with $1\pi^1$ occupancy to be close to but higher in energy than those with $1\pi^2$ occupancy. Greater Coulomb repulsion in the σ -orbital framework for the $1\pi^1$ states and less Coulomb repulsion in the $1\pi^2$ states tip the energy balance in favor of the $1\pi^2$ states. For X-Si compounds with more electronegative X, this near degeneracy (and its consequences) is less likely to occur.

The equilibrium bond lengths and harmonic vibrational frequencies tend to decrease and increase, respectively, as the electronic configurations vary from $\sigma^{n+1}\pi^1$ to $\sigma^n\pi^2$, $\sigma^{n-1}\pi^3$ and $\sigma^{n-2}\pi^4$ even though the total energy of the $\sigma^n\pi^2$ states are the lowest.



Figure 3. Energies of ground and low-lying excited states of Si-X species for X ranging across the second row.

The ground states of LiSi, NaSi, BeSi, MgSi, BSi and AlSi are thermodynamically very stable with respect to dissociation, but their low-spin states are not thermodynamically bound.

Electropositive elements such as Li, Na, Be, Mg, B, and Al favor high- spin states; N, P, O, and S favor low-spin states.

CSi and Si₂ seem to form the "border" dividing high- and low-spin state preference.

Upon completion of this work, our colleague, Prof. Michael Morse, informed us that he and his co-workers have determined⁴⁶ that the ground states of BSi and AlSi are indeed of ${}^{4}\Sigma^{-}$ symmetry as we predict here.

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References and Notes

(1) Nemukhin, A. V.; Almlöf, J.; Heiberg, A. Chem. Phys. Lett. 1980, 76.601.

(2) Huber, K. P.; Herzberg, G. Molecular Spectra and Molecular Structure Constants of Diatomic Molecules; van Nostrand Reinhold: New York, 1979.

- (3) Mavridis, A.; Harrison, J. F. J. Phys. Chem. 1982, 86, 1979.
- (4) Bruna, P. J.; Peyrimhoff, S. D.; Buenker, R. J. J. Chem. Phys. 1980, 72. 5437.

(5) Bauschlicher, C. W.; Langhoff, S. R. J. Chem. Phys. 1987, 87, 2919. (6) Bernath, P. F.; Rogers, S. A.; O'Brien, L. C.; Brazier, C. R.; McLean, A. D. Phys. Rev. Lett. 1988, 60, 197.

- (7) Cernicharo, J.; Gottlieb, C. A.; Guelin, M.; Thaddeus, P.; Vrtilek, J. M. Astrophys. J. Lett. 1989, 341, L25.
- (8) Brazier, C. R.; O'Brien, L. C.; Bernath, P. F. J. Chem. Phys. 1989, 91. 7384.
- (9) Martin, J. M. L.; Francois, J. P.; Gijbels, R. J. Chem. Phys. 1990, 92. 6655.
- (10) Bredohl, H.; Dubois, I.; Houbrechts, Y.; Singh, M. Can. J. Phys. 1976, 54, 680.
 - (11) Saito, S.; Endo, Y.; Hirota, E. J. Chem. Phys. 1983, 78, 6447.
- (12) Bruna, P. J.; Dohmann, H.; Peyerimhoff, S. D. Can. J. Phys. 1984, 62.1508
 - (13) Foster, S. C. J. Mol. Spectrosc. 1984, 106, 369.
 - (14) Foster, S. C.; Lubic, K. G.; Amano, T. J. Chem. Phys. 1985, 82, 709. (15) Yamada, C.; Hirota, E. J. Chem. Phys. 1985, 82, 2547
- (16) Yamada, C.; Hirota, E.; Yamamoto, S.; Saito, S. J. Chem. Phys. 1988, 88, 46.
 - (17) Torring, E. Z. Naturforsch. Teil A23, 1968, 777.

 - (18) Anderson, J. S.; Pgden, J. S. J. Chem. Phys. 1969, 51, 4189.
 (19) Manson, E. L., Jr.; Clark, W. W.; De Lucia, F. C.; Gordy, W. Phys.

Rev. 1977. A15. 223 (20) Lovas, F. J.; Maki, A. G.; Olson, W. B. J. Mol. Spectrsc. 1981, 87,

- 449 (21) Khana, R. K.; Stranz, D. D.; Donn, B. J. Chem. Phys. 1981, 74, 2108.
 - (22) Botschwina, P.; Rosmus, P. J. Chem. Phys. 1985, 82, 1420.
 - (23) Lagerquist, A.; Malmberg, C. Phys. Scr. 1970, 2, 45.
 - (24) Dubois, I.; Leclercq, Can. J. Phys. 1971, 49, 3053.
- (25) Burger, H.; Eujen, R. Low-Valent Silicon in Topics in Current
- Chemistry; Springer-Verlag: Berlin, 1974; Vol. 50, p 1. (26) Bruna, P. J.; Peyrimhoff, S. D.; Buenker, R. J. J. Chem. Phys. 1980, 72, 5437.
- (27) Nimlos, M. R.; Harding, L. B.; Ellison, G. B. J. Chem. Phys. 1987, 87, 5116.
- (28) Kitsoupoulos, T. N.; Chick, C. J.; Weaver, A.; Neumark, D. M. J. Chem. Phys. 1991, 95, 1441.

- (29) Curtiss, L. A.; Raghavachari, K.; Deutsch, P. W.; Pople, J. A. J. Chem. Phys. 1991, 95, 2433.
- (30) Curtiss, L. A.; Deutsch, P. W.; Raghavachari, K. J. Chem. Phys. 1992, 96, 6868.
- (31) Morris, M. Astrophys. J. 1975, 197, 603. Morris, M. Ibid 1980, 236, 823. (32) Grasshoff, M.; Tiemann, E.; Henkel, C. Astron. Astrophys. 1981,
- 101, 238. (33) Olafsson, H.; Johannsson, L. E. B.; Hjalmarson, A.; Rieu, N. Q.
- Astron. Astrophys. 1982, 107, 128. (34) Henkel, C.; Matthews, H. E.; Morris, M. Astrophys. J. 1983, 267,
- 184.
- (35) Schlegel, H. B. J. Comput. Chem. 1982, 3, 214.
 (36) Hariharan, P. C.; Pople, J. A. Theor. Chim. Acta 1973, 28, 213.
- (37) Frisch, M. J.; Pople, J. A.; Binkley, J. S. J. Chem. Phys. 1984, 80, 3265.
- (38) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. J. Chem. Phys. 1980, 72, 650.

- (39) McLean, A. D.; Chandler, G. S. J. Chem. Phys. 1980, 72, 5639.
- (40) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R., J. Comput. Chem. 1983, 4, 294.
- (41) Frisch, M. J.; Pople, J. A.; Binkley, J. S., J. Chem. Phys. 1984, 80, 3265.
 - (42) Krishnan, R.; Pople, J. A. Int. J. Quant. Chem. 1978, 14, 91.
- (43) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. J. Chem. Phys. 1987, 87, 5958.
 - (44) Schlegel, H. B. J. Chem. Phys. 1984, 84, 4530.
- (45) Gaussian 90; Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.;
 Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley,
 J. S.; Gonzales, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.;
 Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol,
 S.; Pople, J. A. Gaussian Inc.: Pittsburgh, PA, 1990.
- (46) Arrington, C. A.; Morse, M. D.; Knight, L. B., Jr., private communication.