

# Experimental Detection and Theoretical Characterization of Germanium-doped Lithium Clusters $\text{Li}_n\text{Ge}$ ( $n = 1 - 7$ )

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and Minh Tho Nguyen<sup>a,c,\*</sup>

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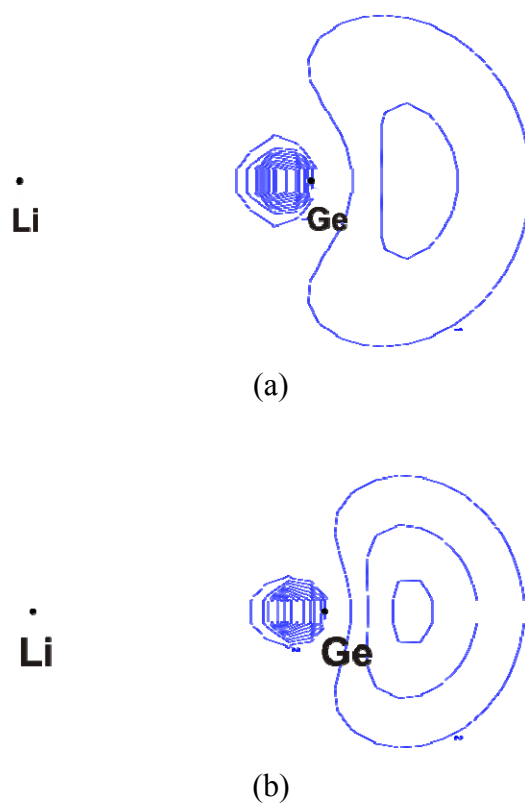
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<sup>c</sup> Institute for Nanoscale Physics and Chemistry (INPAC)

Katholieke Universiteit Leuven, B-3001 Leuven, Belgium

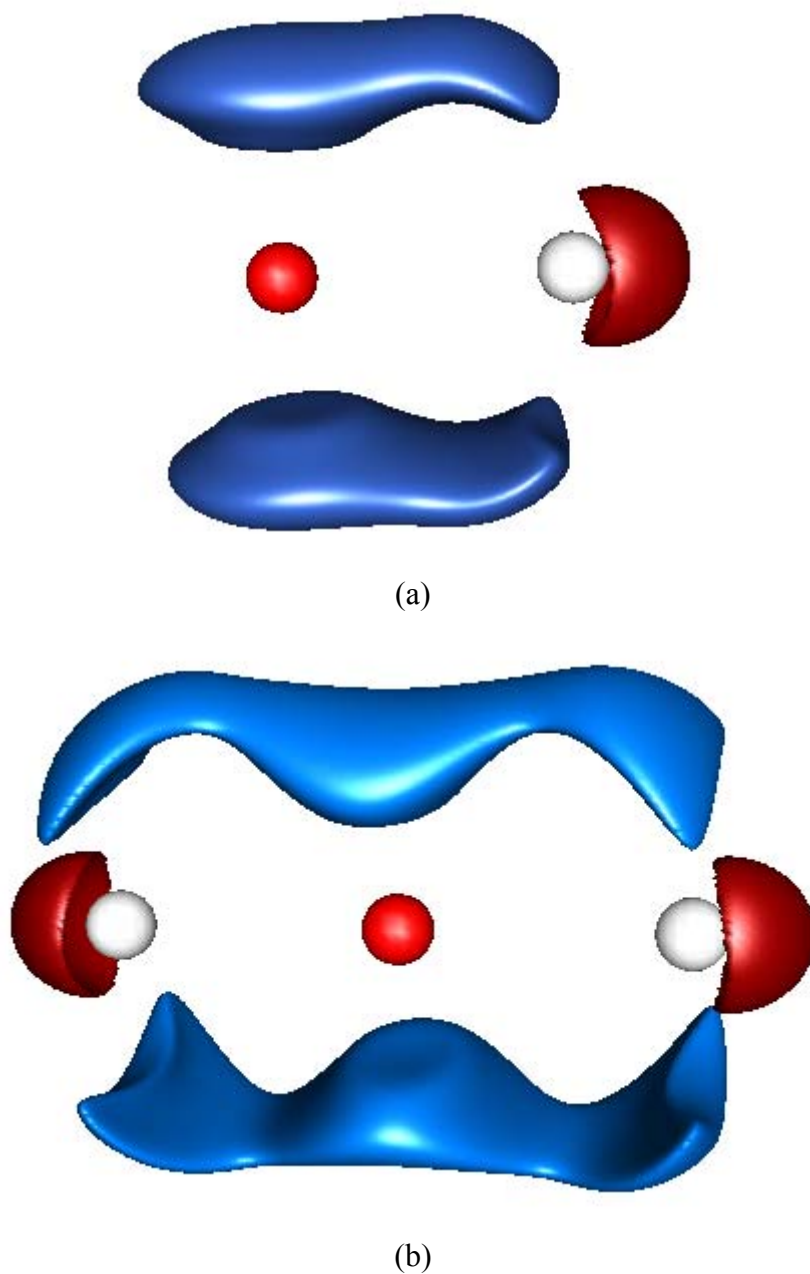
## Electronic Supporting Information

**Figure S1.** Spin density plot of the  $\text{LiGe}$  quartet state (a) and  $\text{LiGe}^+$  triplet state (b). Blue color indicates positive sign of spin density ( $\alpha$ -electron).



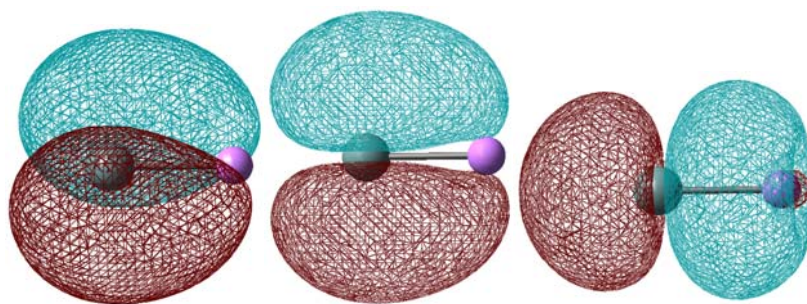
\* Email: [peter.lievens@fys.kuleuven.be](mailto:peter.lievens@fys.kuleuven.be), [minh.nguyen@chem.kuleuven.be](mailto:minh.nguyen@chem.kuleuven.be)

**Figure S2:** Isosurfaces of the  $\Delta$ ELF between: (a) quartet state of neutral LiGe and triplet state of cation  $\text{LiGe}^+$ ; (b) triplet state of neutral  $\text{Li}_2\text{Ge}$  and doublet state of cation  $\text{Li}_2\text{Ge}^+$ . The isosurfaces 0.35 represent in blue and isosurface -0.35 in red; the red ball is Ge atom, white ball is Li atom

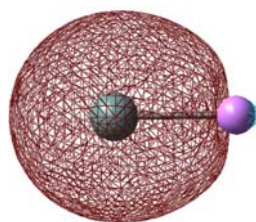


**Figure S3:** Frontier orbitals of  $\text{Li}_n\text{Ge}^{0,+}$  with isosurface value of 0.02 au

**$\text{LiGe}$  (quartet)**

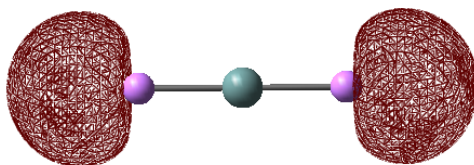


SOMO, SOMO-1, SOMO-2

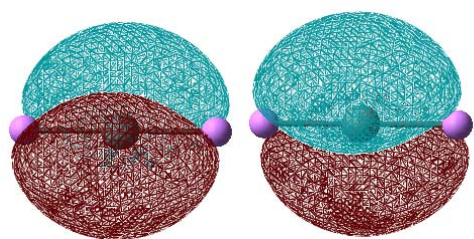


HOMO-3

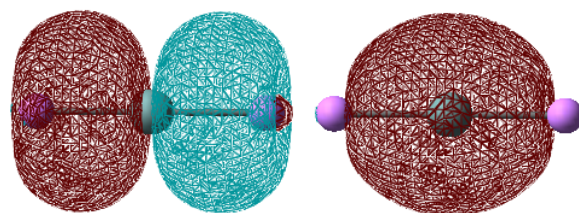
**$\text{Li}_2\text{Ge}$  (triplet)**



LUMO

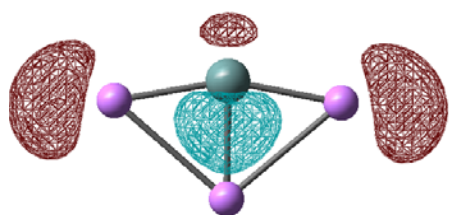


SOMO, SOMO-1

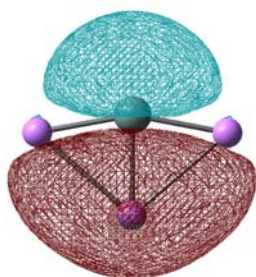


HOMO-2, HOMO-3

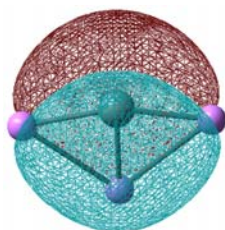
**$\text{Li}_3\text{Ge}$  (T-shape, doublet)**



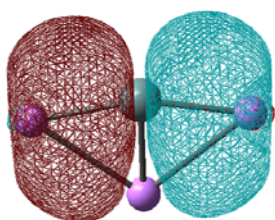
LUMO



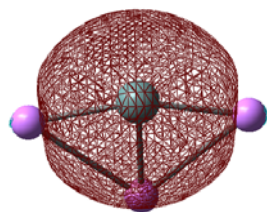
SOMO



HOMO-1

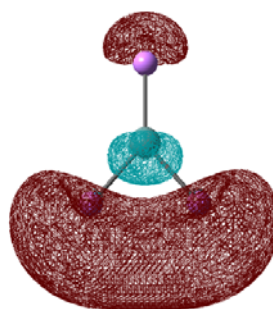


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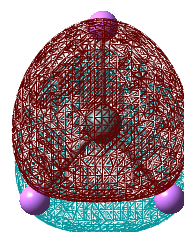


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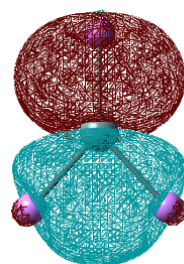
**$\text{Li}_3\text{Ge}^+$  (distorted  $D_{3h}$ , triplet)**



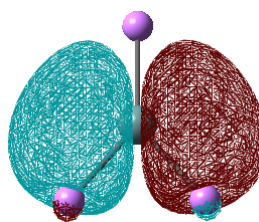
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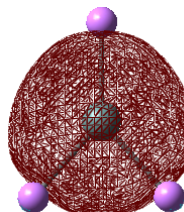
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SOMO-1



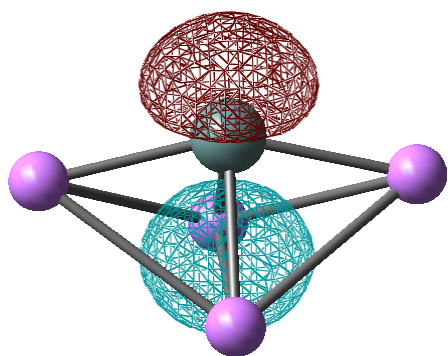
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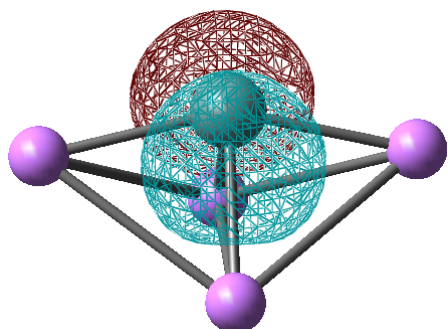
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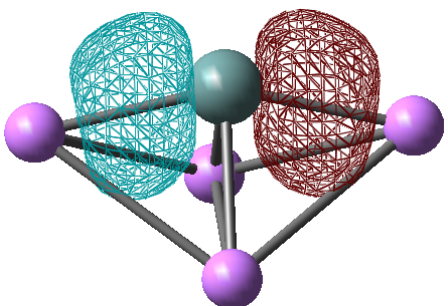
**Li<sub>4</sub>Ge**



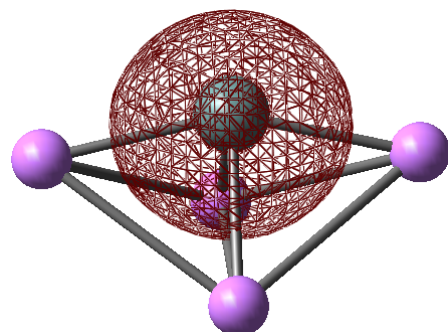
HOMO



HOMO-1

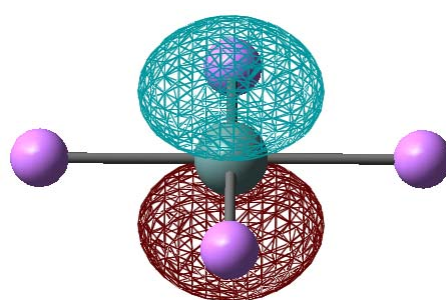


HOMO-2

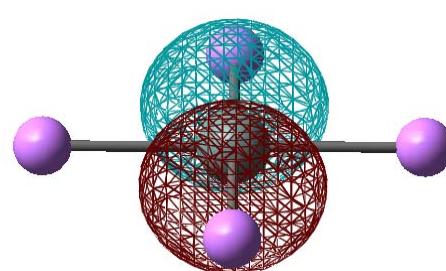


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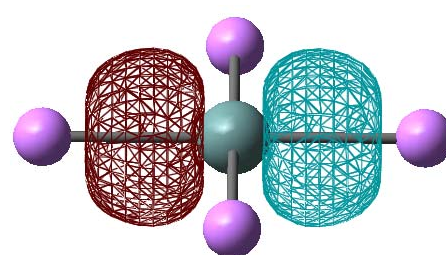
**Li<sub>4</sub>Ge<sup>+</sup>**



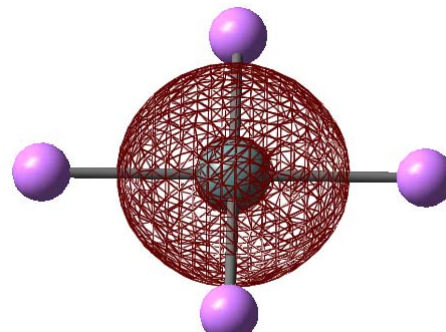
SOMO



HOMO-1

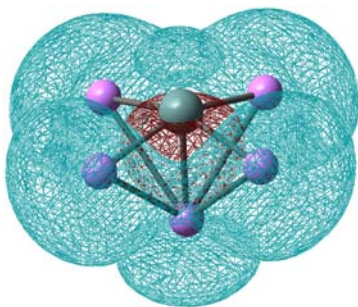


HOMO-2

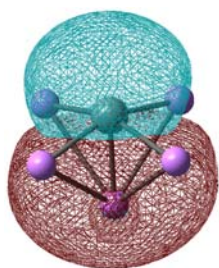


HOMO-3

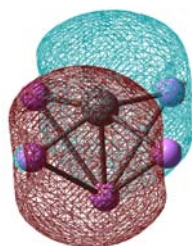
**Li<sub>5</sub>Ge**



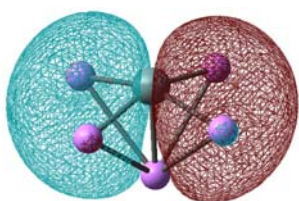
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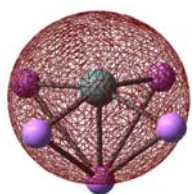
HOMO-1



HOMO-2

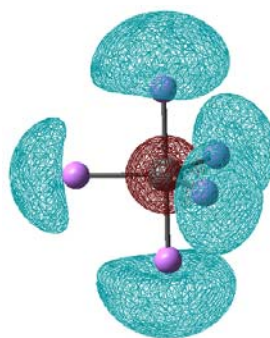


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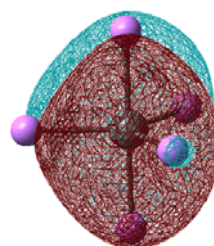


HOMO-4

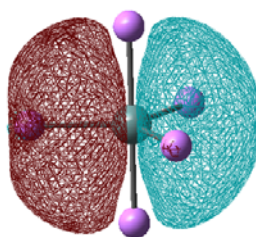
**Li<sub>5</sub>Ge<sup>+</sup>**



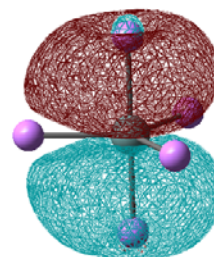
LUMO



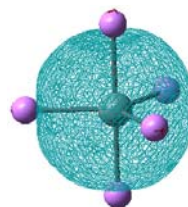
HOMO



HOMO-1

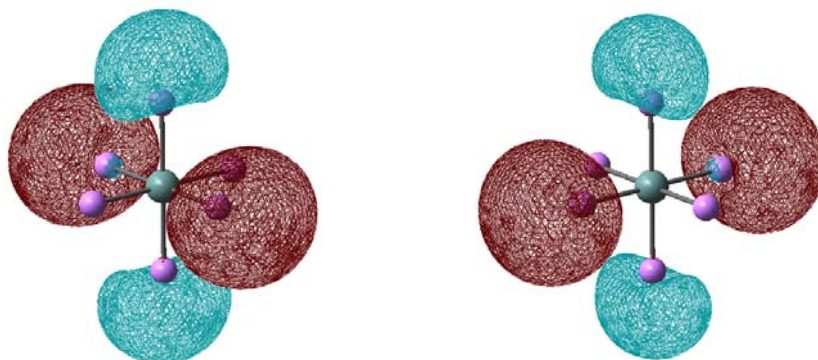


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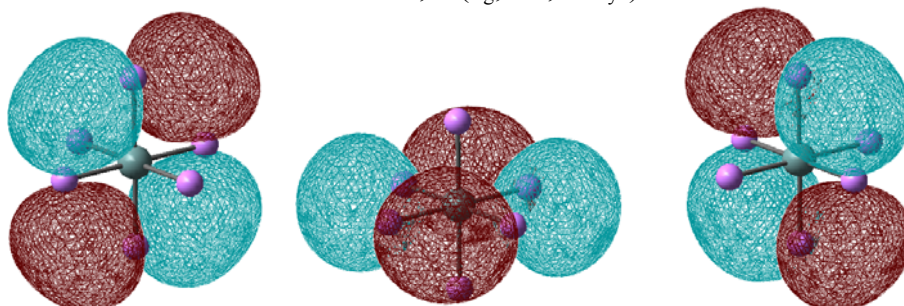


HOMO-3

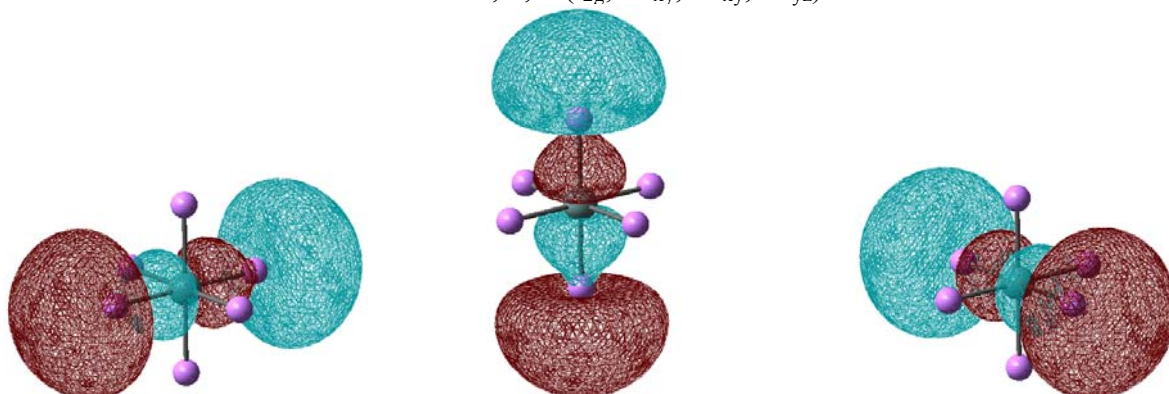
# **Li<sub>6</sub>Ge**



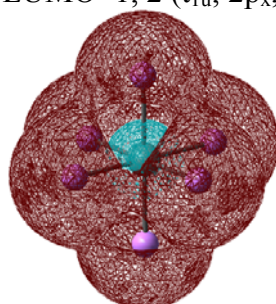
LUMO+6, 7 ( $e_g$ ;  $d_{z^2}$ ,  $d_{x^2-y^2}$ )



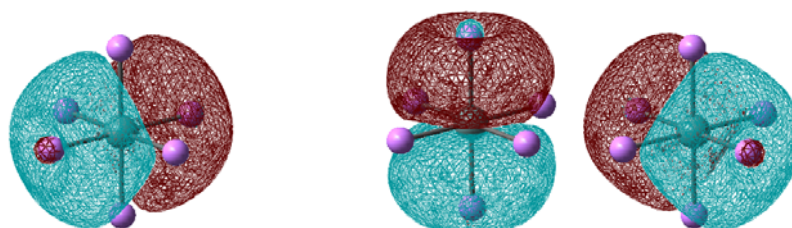
LUMO+3, 4, 5 ( $t_{2g}$ ;  $1d_{xy}$ ,  $1d_{yz}$ ,  $1d_{zx}$ )



LUMO, LUMO+1, 2 ( $t_{1u}$ ;  $2p_x$ ,  $2p_y$ ,  $2p_z$ )

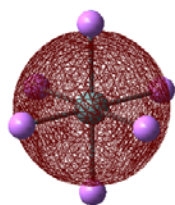


HOMO( $a_{1g}$ ;  $2s$ )



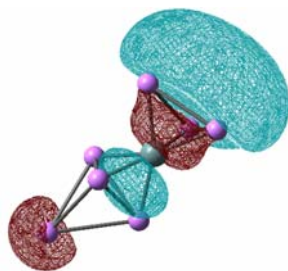
HOMO-1, 2, 3 ( $t_{1u}$ ;  $1p_x$ ,  $1p_y$ ,  $1p_z$ )



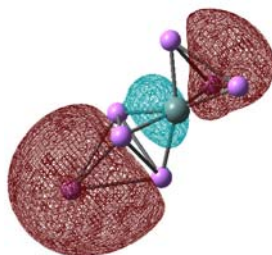


HOMO-4 ( $a_{1g}$ , 1s)

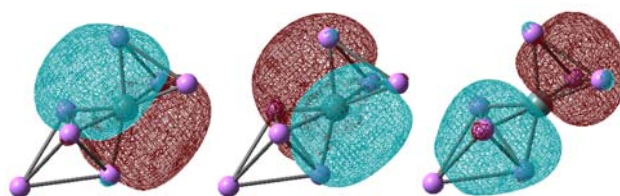
**Li<sub>7</sub>Ge**



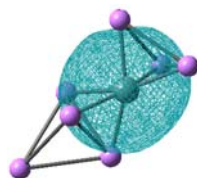
HOMO



HOMO-1



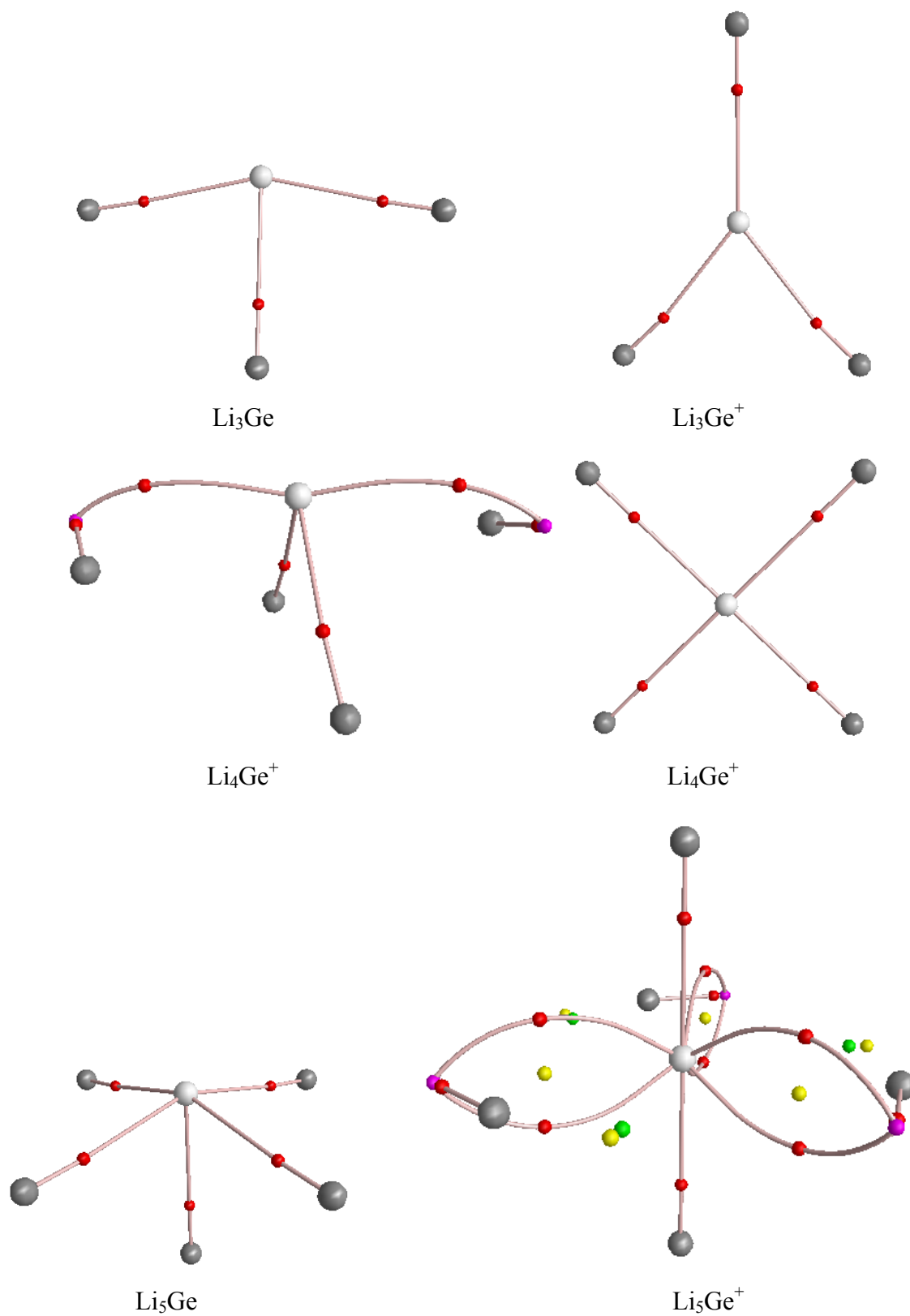
HOMO-2, 3, 4

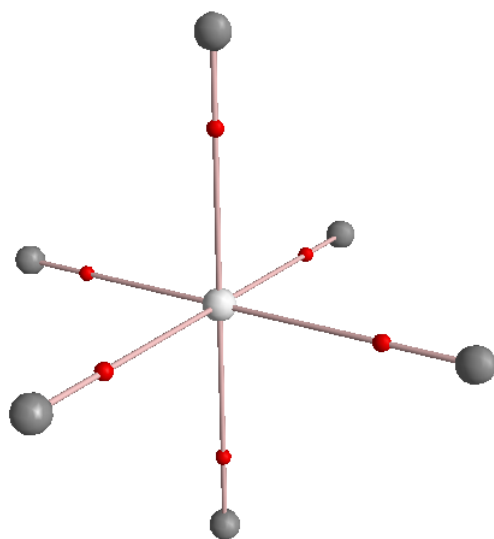


HOMO-5

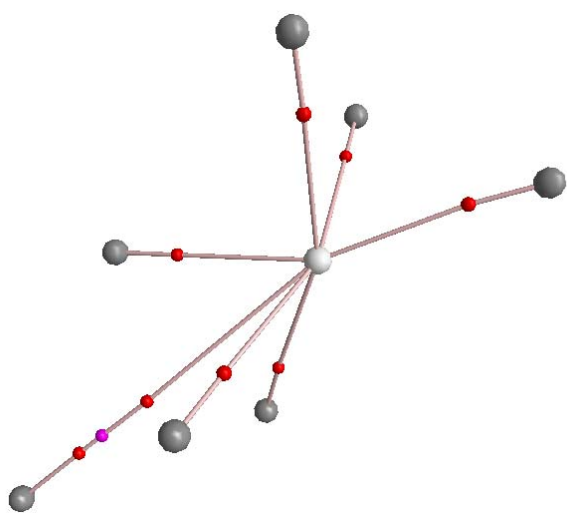


**Figure S4.** Molecular graphs of the ground states of  $\text{Li}_n\text{Ge}^{0,+}$ . Red balls are *bcps*, violet balls are pseudo atom, gray balls are lithium atoms and white balls are germanium atoms.

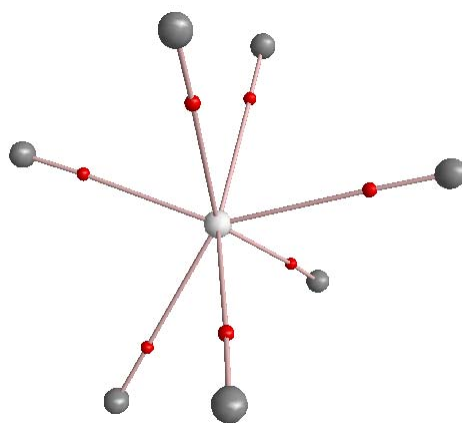




$\text{Li}_6\text{Ge}^{0,+}$



$\text{Li}_7\text{Ge}$



$\text{Li}_7\text{Ge}^+$

**Coordinates of minima.** *Optimized geometries of neutral and cationic Ge-doped lithium cluster ( $n=4-7$ ) are at the B3LYP/aug-cc-pVTZ level.*

**Note:** the label of each state include 3 parts:

- the first is label of structure (denoted by number in Figure 2)
- the second is charge state (neutral or cation)
- the last is spin state (singlet, doublet, triplet or quartet)

## 1. $\text{Li}_4\text{Ge}$

### ***Li4Ge-7-neutral-singlet***

Ge	0.000000	0.331401	0.000000
Li	-2.329354	-0.230808	-0.000001
Li	0.000000	-1.536664	1.599115
Li	2.329354	-0.230808	-0.000001
Li	0.000000	-1.536666	-1.599113

### ***Li4Ge-7-neutral-triplet***

Ge	0.000000	0.331401	0.000000
Li	-2.329354	-0.230808	-0.000001
Li	0.000000	-1.536664	1.599115
Li	2.329354	-0.230808	-0.000001
Li	0.000000	-1.536666	-1.599113

### ***Li4Ge-8-cation-doublet***

Ge	0.000000	0.000000	0.000000
Li	0.000000	2.436048	0.000000
Li	2.436048	0.000000	0.000000
Li	-2.436048	0.000000	0.000000
Li	0.000000	-2.436048	0.000000

### ***Li4Ge-9-neutral-triplet***

Ge	0.000000	0.000000	0.000000
Li	0.000000	1.574876	1.865883
Li	0.000000	-1.574876	1.865883
Li	0.000000	1.574876	-1.865883
Li	0.000000	-1.574876	-1.865883

### ***Li4Ge-10-cation-quartet***

Ge	0.264252	0.000222	-0.000002
Li	2.780333	-0.000435	0.000005
Li	-1.865726	-0.821281	-1.408211
Li	-1.867575	1.629326	-0.006523
Li	-1.865725	-0.809974	1.414747

## 2. Li<sub>5</sub>Ge

### *Li5Ge-16-neutral-doublet*

Li	-0.000004	0.000000	-2.194638
Li	1.727906	1.618725	-0.194119
Li	-1.618729	1.727911	-0.194117
Li	-1.727912	-1.618733	-0.194116
Li	1.618736	-1.727899	-0.194121
Ge	0.000000	0.000000	0.278542

### *Li5Ge-16-cation-singlet*

Li	-0.000001	0.000007	-2.308416
Li	-0.395506	-2.361056	0.175496
Li	2.361057	-0.395508	0.175384
Li	0.395502	2.361057	0.175502
Li	-2.361058	0.395499	0.175386
Ge	0.000000	0.000000	0.150623

### *Li5Ge-17-cation-singlet*

Ge	0.000000	0.000000	0.000000
Li	0.000000	0.000000	2.387152
Li	0.000000	2.415056	0.000000
Li	2.091499	-1.207528	0.000000
Li	-2.091499	-1.207528	0.000000
Li	0.000000	0.000000	-2.387152

### *Li5Ge-18-neutral-quartet*

Li	1.585174	1.198959	-1.321573
Li	1.585219	1.198918	1.321574
Li	-1.758834	1.776814	0.000011
Li	-2.557121	-0.804350	-0.000004
Li	2.109707	-1.380596	-0.000024
Ge	-0.090389	-0.186539	0.000001

### *Li5Ge-19-cation-triplet*

Ge	0.150749	-0.031743	-0.000016
Li	-1.622723	-1.853195	-0.000399
Li	-1.852425	0.787834	1.377455
Li	1.515702	2.022660	0.000064
Li	-1.852396	0.788655	-1.377010
Li	2.203853	-1.407364	0.000066



### 3. Li<sub>6</sub>Ge

#### *Li6Ge-20-neutral-singlet*

Li	1.668613	0.524484	1.674368
Li	0.276033	2.203341	-0.965169
Li	1.733106	-0.856106	-1.458122
Li	-0.276282	-2.203261	0.965110
Li	-1.733215	0.856006	1.458130
Ge	0.000022	0.000013	-0.000003
Li	-1.668486	-0.524600	-1.674285

#### *Li6Ge-20-cation-doublet*

Ge	-0.000022	-0.000026	-0.000073
Li	-0.822135	-1.965817	1.187592
Li	-1.140003	1.444277	1.601563
Li	0.822658	1.966062	-1.186816
Li	1.993794	0.014904	1.405284
Li	1.140071	-1.444235	-1.601501
Li	-1.994146	-0.014909	-1.405348

#### *Li6Ge-21-neutral-singlet*

Li	-1.565484	1.394637	-0.573279
Li	-1.019426	0.000032	1.773815
Li	-1.565491	-1.394665	-0.573233
Li	1.753727	1.630571	0.862600
Ge	0.447058	-0.000018	-0.260758
Li	-4.125833	0.000002	0.428771
Li	1.753888	-1.630379	0.862739

#### *Li6Ge-21-cation-doublet*

Li	-1.444764	1.492882	-0.779916
Li	-0.958222	-0.000001	1.850800
Li	-1.444764	-1.492881	-0.779916
Li	1.704956	1.778241	0.803363
Ge	0.411743	0.000000	-0.230265
Li	-3.954085	0.000000	0.558462
Li	1.704958	-1.778240	0.803363

#### *Li6Ge-23-neutral-triplet*

Li	2.091610	-1.120148	-0.863914
Li	-2.072050	-1.223497	0.749688
Li	1.487603	1.695054	-0.722354
Li	-1.722576	0.390285	-1.677132
Ge	0.000421	-0.142278	-0.013990
Li	1.695776	0.187425	1.729244
Li	-1.484849	1.588509	0.933695

***Li6Ge-24-cation-quartet***

Ge	0.212971	-0.000003	-0.000002
Li	-1.029290	2.232906	-0.463532
Li	-2.262911	0.299010	1.265928
Li	-2.262918	-0.299003	-1.265923
Li	2.156351	1.524241	0.430719
Li	2.156369	-1.524223	-0.430709
Li	-1.029296	-2.232903	0.463536

***Li6Ge-25-cation-quartet***

Li	-1.742011	-0.002565	1.540113
Li	-1.330622	-1.904680	-0.456550
Li	-1.330571	1.906041	-0.451442
Li	2.124916	-1.716698	0.013558
Ge	0.364178	0.000161	-0.023512
Li	-3.732829	0.000872	-0.405671
Li	2.126552	1.715319	0.010789

**4. Li<sub>7</sub>Ge*****Li7Ge-26-neutral-doublet***

Li	1.442164	1.608071	-0.125284
Li	1.654948	-0.884421	-1.334775
Li	1.630264	-0.661875	1.462823
Li	-1.634835	1.328816	1.408145
Li	-1.695128	1.152907	-1.520458
Ge	-0.296224	-0.149474	-0.000518
Li	4.301072	0.214691	0.002940
Li	-2.538765	-1.163804	0.112139

***Li7Ge-26-cation-singlet***

Ge	0.000000	0.000000	0.051273
Li	0.000000	2.446217	0.654989
Li	-1.565671	0.903941	-1.715945
Li	1.565671	0.903941	-1.715945
Li	-2.118486	-1.223109	0.654989
Li	2.118486	-1.223109	0.654989
Li	0.000000	-1.807881	-1.715945
Li	0.000000	0.000000	2.635951

***Li7Ge-27-neutral-doublet***

Li	0.955394	2.341336	0.000006
Li	-1.752405	-1.010242	1.466155
Li	-2.204453	1.364517	0.000005
Li	1.991931	-0.216294	-1.475583
Li	1.991889	-0.216300	1.475621
Ge	-0.003870	0.102523	-0.000007
Li	0.811364	-2.346340	-0.000005
Li	-1.752442	-1.010259	-1.466123

***Li7Ge-27-neutral-quartet***

Li	0.000000	1.332787	2.257747
Li	0.000000	-1.332787	2.257747
Li	-1.377526	1.900974	-0.735330
Li	1.377526	-1.900974	-0.735330
Li	1.377526	1.900974	-0.735330
Li	-1.377526	-1.900974	-0.735330
Ge	0.000000	0.000000	0.085944
Li	0.000000	0.000000	-2.490916

***Li7Ge-27-cation-singlet***

Li	0.000000	1.609820	2.046512
Li	0.000000	-1.609820	2.046512
Li	-1.689153	1.771161	-0.532827
Li	1.689153	-1.771161	-0.532827
Li	1.689153	1.771161	-0.532827
Li	-1.689153	-1.771161	-0.532827
Ge	0.000000	0.000000	0.048839
Li	0.000000	0.000000	-2.482667

***Li7Ge-27-cation-triplet***

Li	0.000000	1.536942	2.044782
Li	0.000000	0.000000	-2.507926
Li	1.924133	1.387861	-0.761800
Li	0.000000	-1.536942	2.044782
Li	-1.924133	1.387861	-0.761800
Ge	0.000000	0.000000	0.137397
Li	-1.924133	-1.387861	-0.761800
Li	1.924133	-1.387861	-0.761800

***Li7Ge-28-cation-singlet***

Li	0.000000	0.000000	2.463481
Li	0.000000	2.549862	0.000000
Li	2.425062	0.787951	0.000000
Li	1.498771	-2.062881	0.000000
Li	-1.498771	-2.062881	0.000000
Li	-2.425062	0.787951	0.000000
Li	0.000000	0.000000	-2.463481
Ge	0.000000	0.000000	0.000000

***Li7Ge-29-cation-singlet***

Ge	0.000000	0.000000	0.051273
Li	0.000000	2.446217	0.654989
Li	-1.565671	0.903941	-1.715945
Li	1.565671	0.903941	-1.715945
Li	-2.118486	-1.223109	0.654989
Li	2.118486	-1.223109	0.654989
Li	0.000000	-1.807881	-1.715945
Li	0.000000	0.000000	2.635951

***Li7Ge-30-neutral-quartet***

Ge	0.000000	0.000000	0.196828
Li	0.000000	2.477872	0.147027
Li	-1.518488	0.876699	-1.698980
Li	1.518488	0.876699	-1.698980
Li	-2.145900	-1.238936	0.147027
Li	2.145900	-1.238936	0.147027
Li	0.000000	-1.753399	-1.698980
Li	0.000000	0.000000	2.556356