Electronic supplementary information for

Geometric and electronic properties of Si-atom-doped Al clusters: Robustness of binary superatoms against charging

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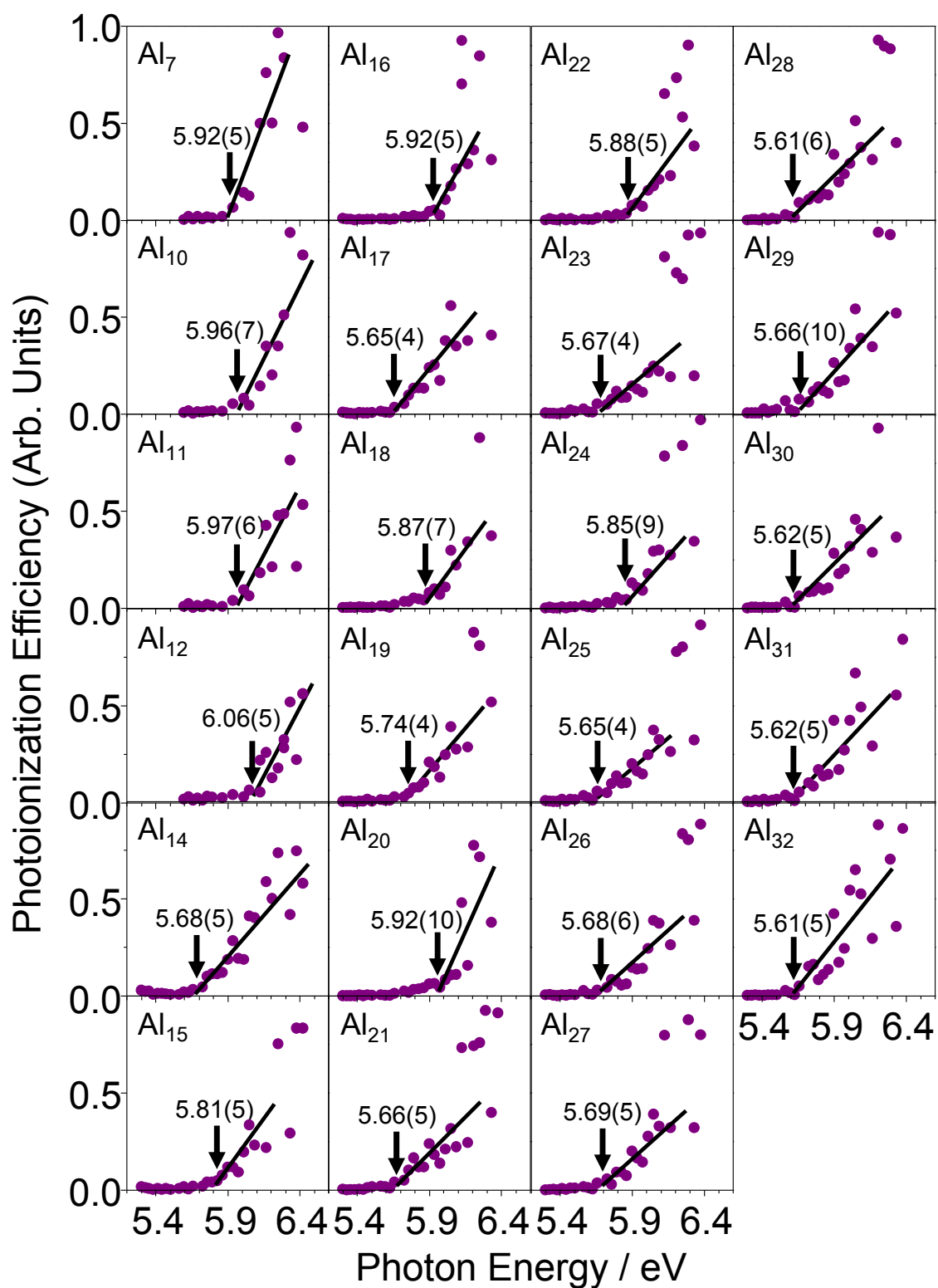
Figure S1. Photoionization efficiency plots for Al_n clusters (n = 7, 10, 11, 12, and 14–32) with ionization energy values, where uncertainties are given in parentheses in the last digit(s).
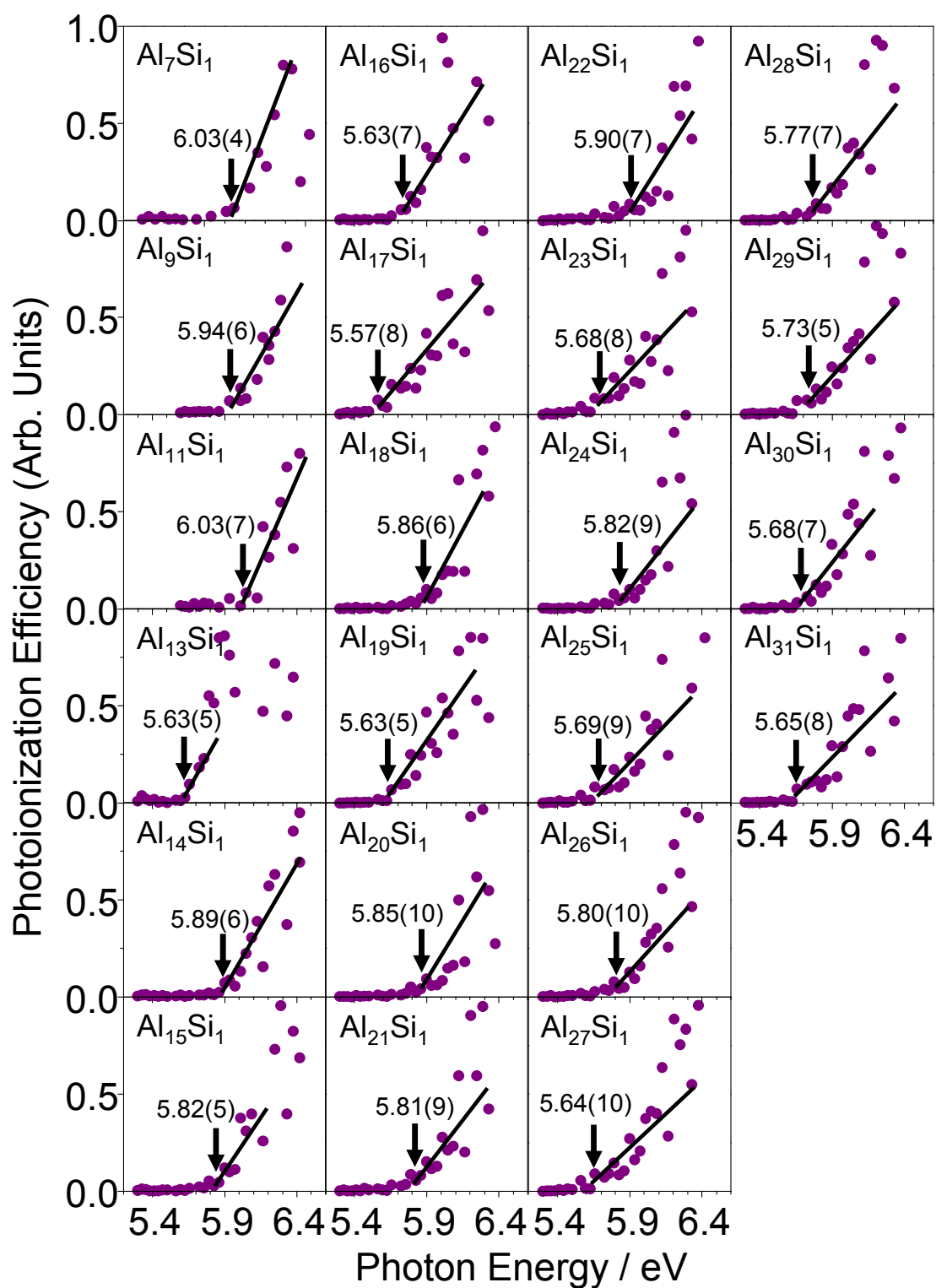
Figure S2. Photoionization efficiency plots for Al$_n$Si clusters (n = 7, 9, 11, and 13–31) with ionization energy values, where uncertainties are given in parentheses in the last digit(s).
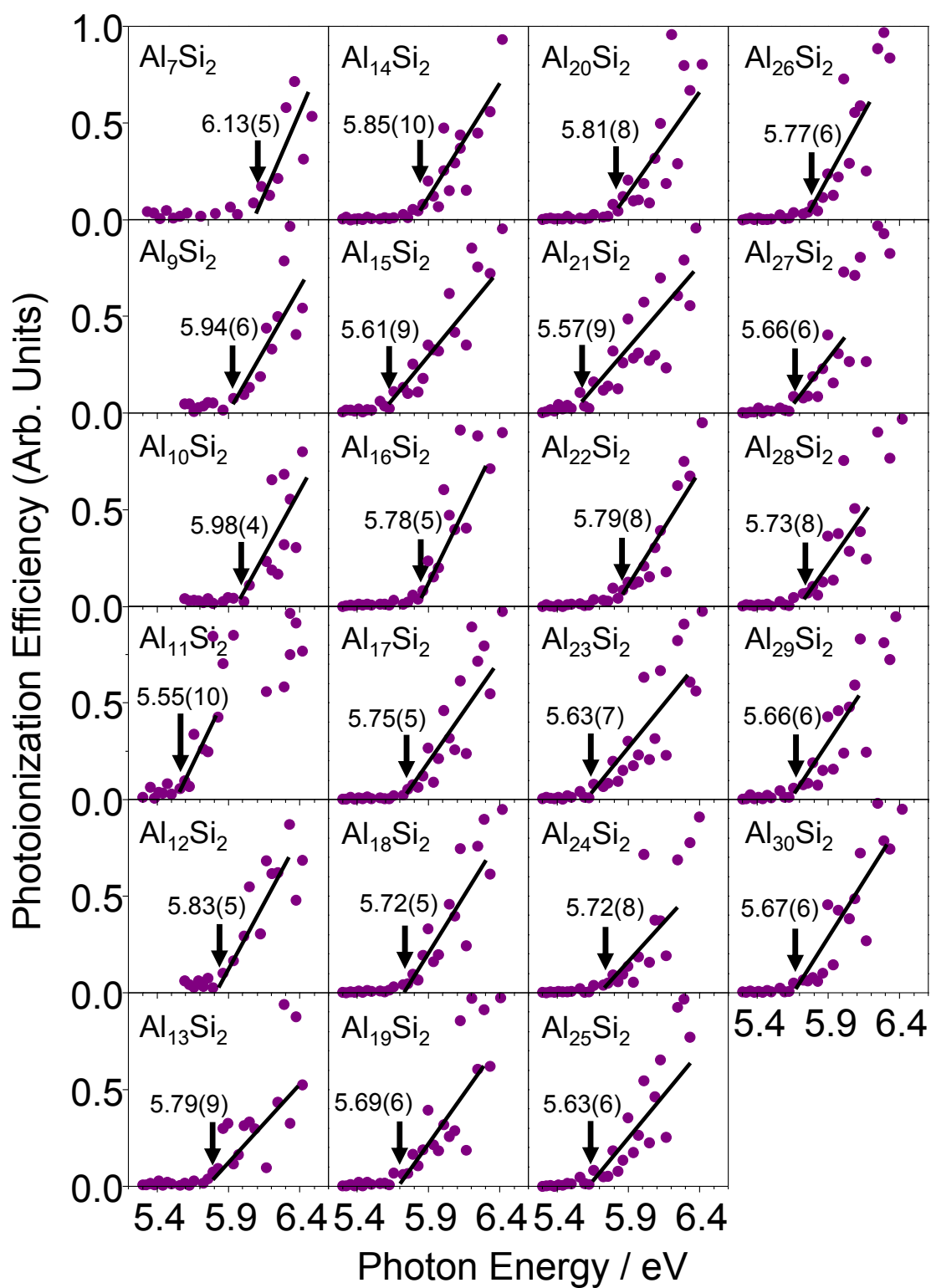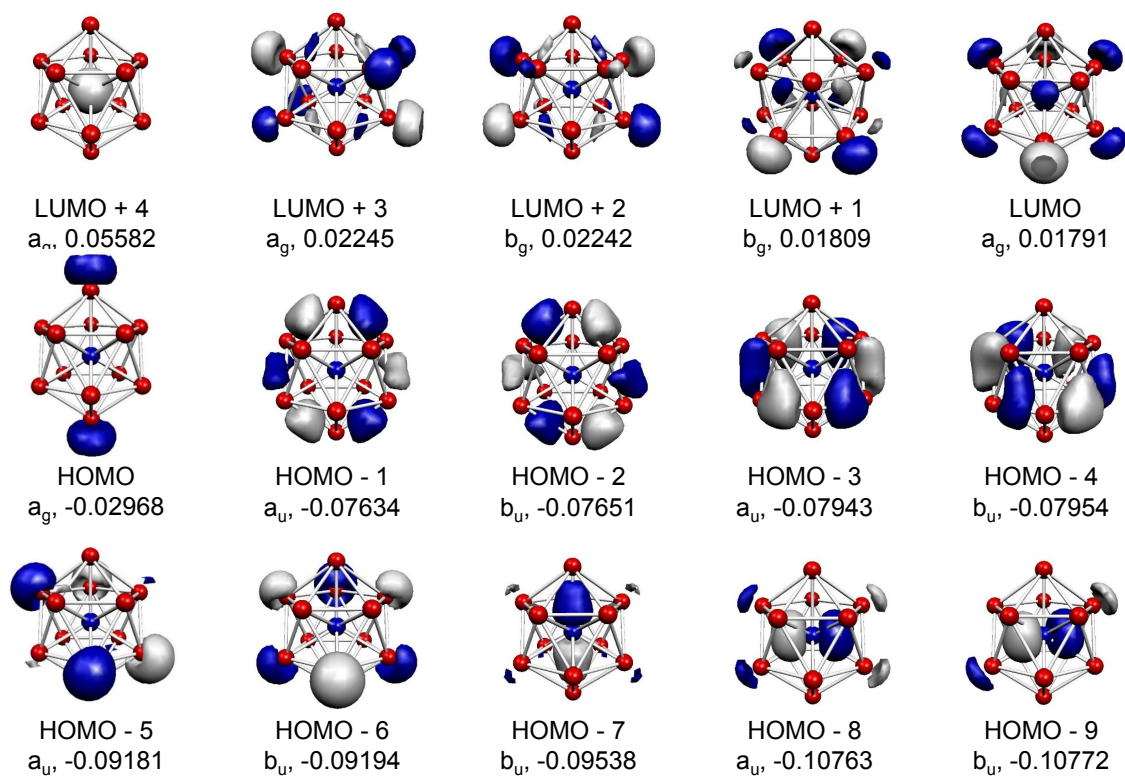
Figure S3. Photoionization efficiency plots for Al*n*Si$_2$ clusters (*n* = 7 and 9–30) with ionization energy values, where uncertainties are given in parentheses in the last digit(s).
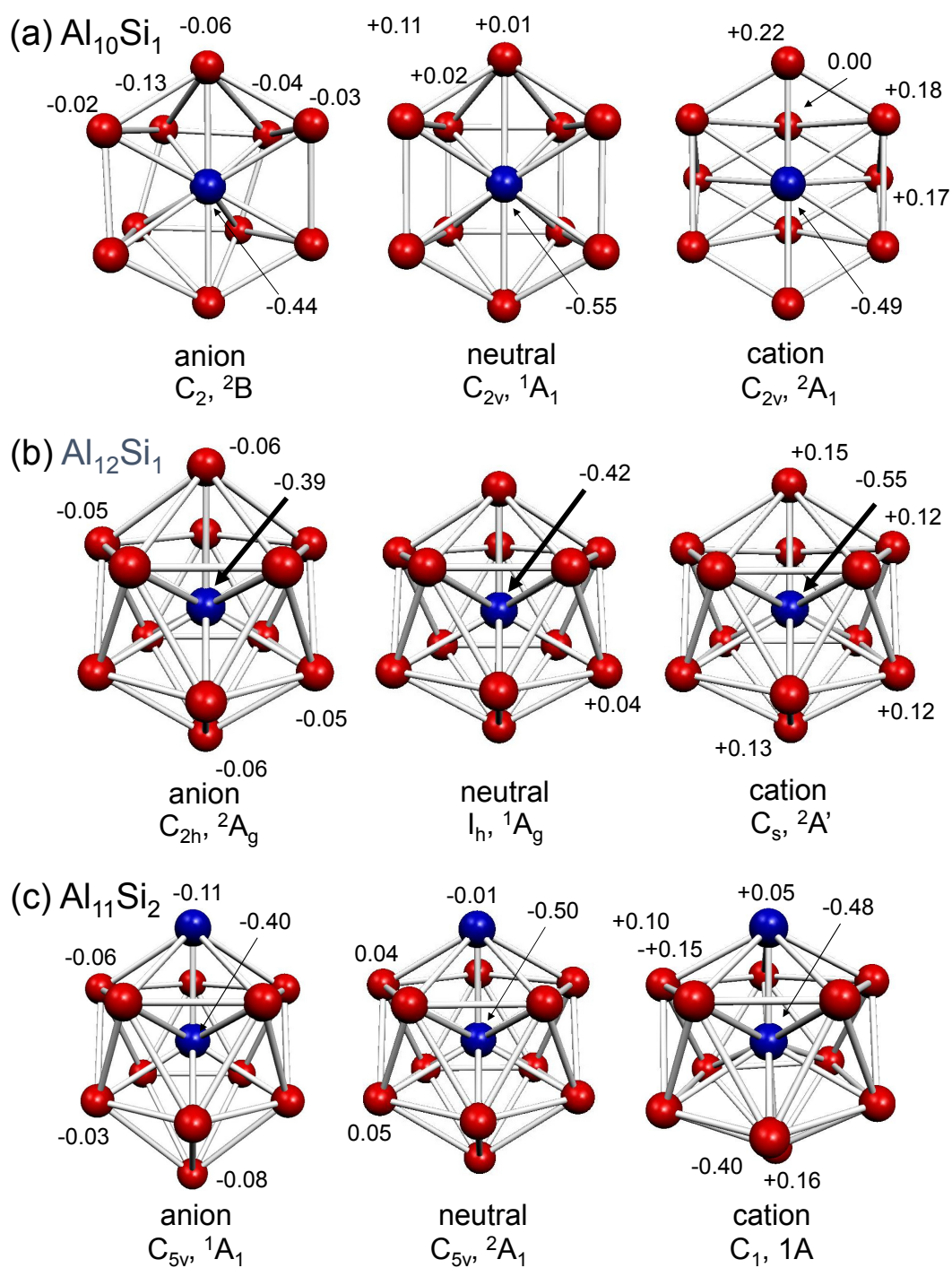
Figure S4. Optimized Geometries of (a) $Al_{10}Si^{-/0/+}$, (b) $Al_{12}Si^{-/0/+}$, and (c) $Al_{11}Si_2^{-/0/+}$ with Mulliken populations.
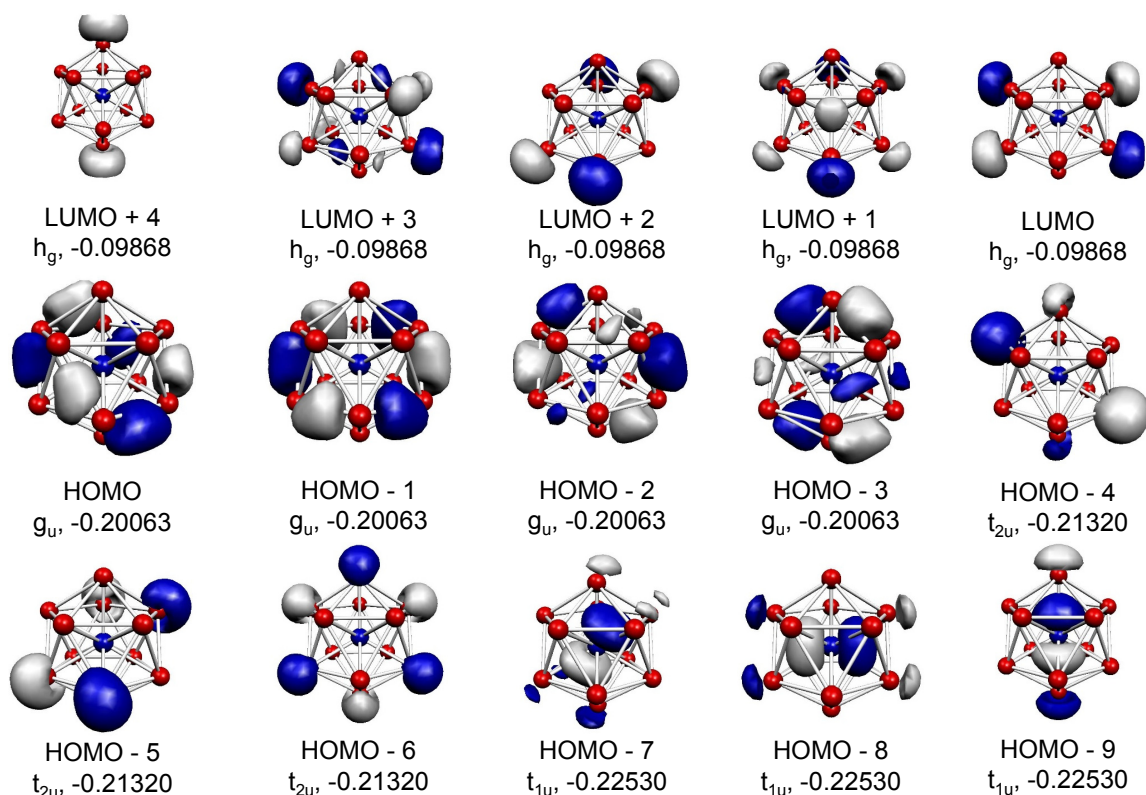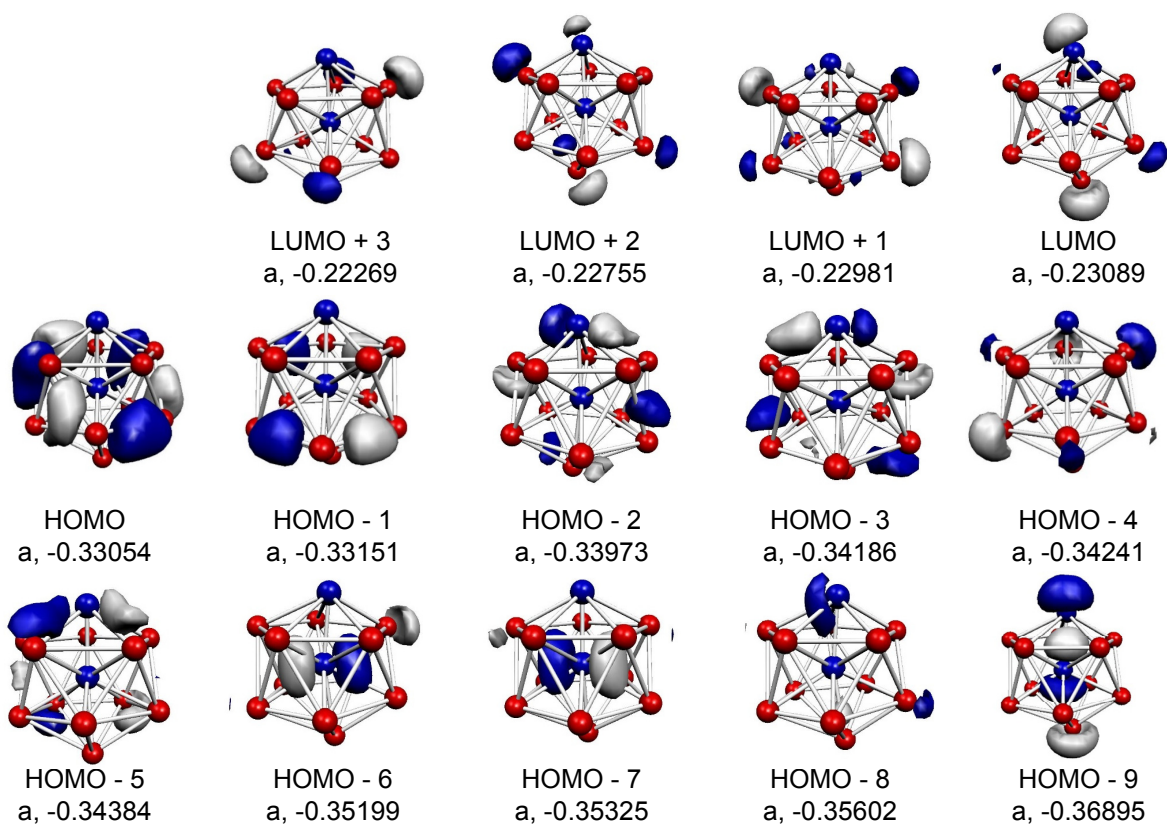
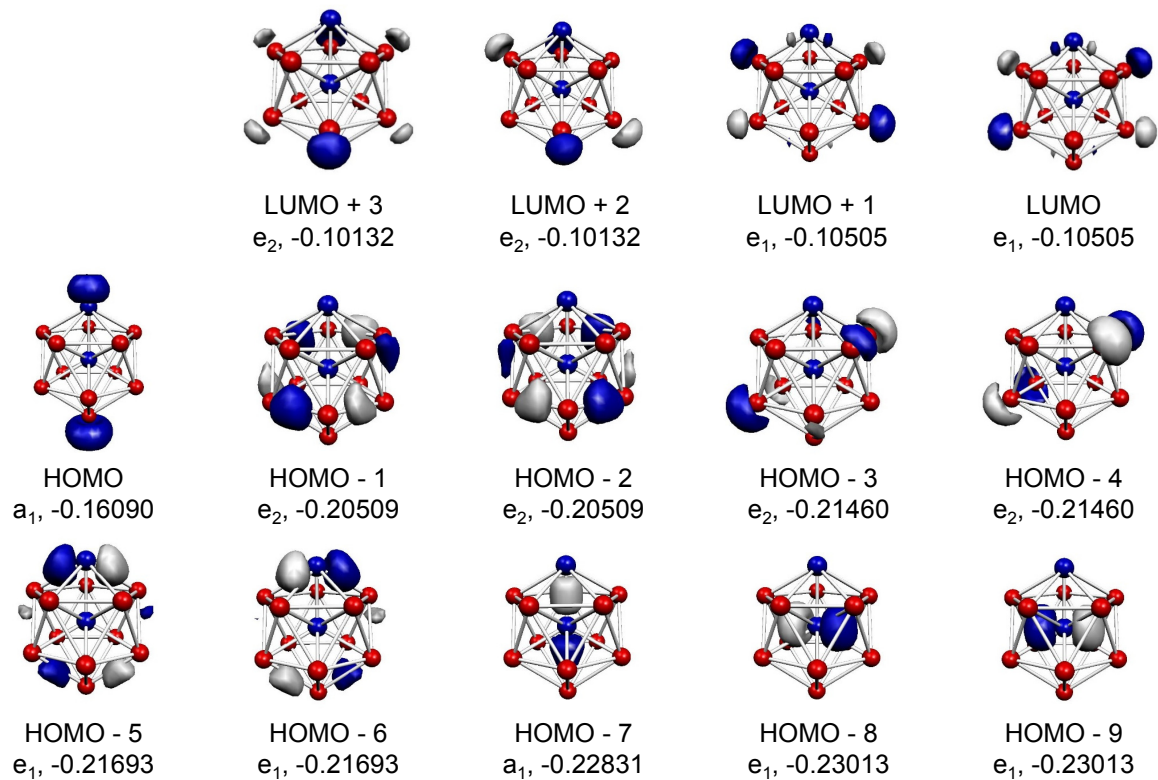**Figure S5.** Occupied and virtual frontier orbitals from HOMO – 9 to LUMO + 4 for Al$_{12}$Si.

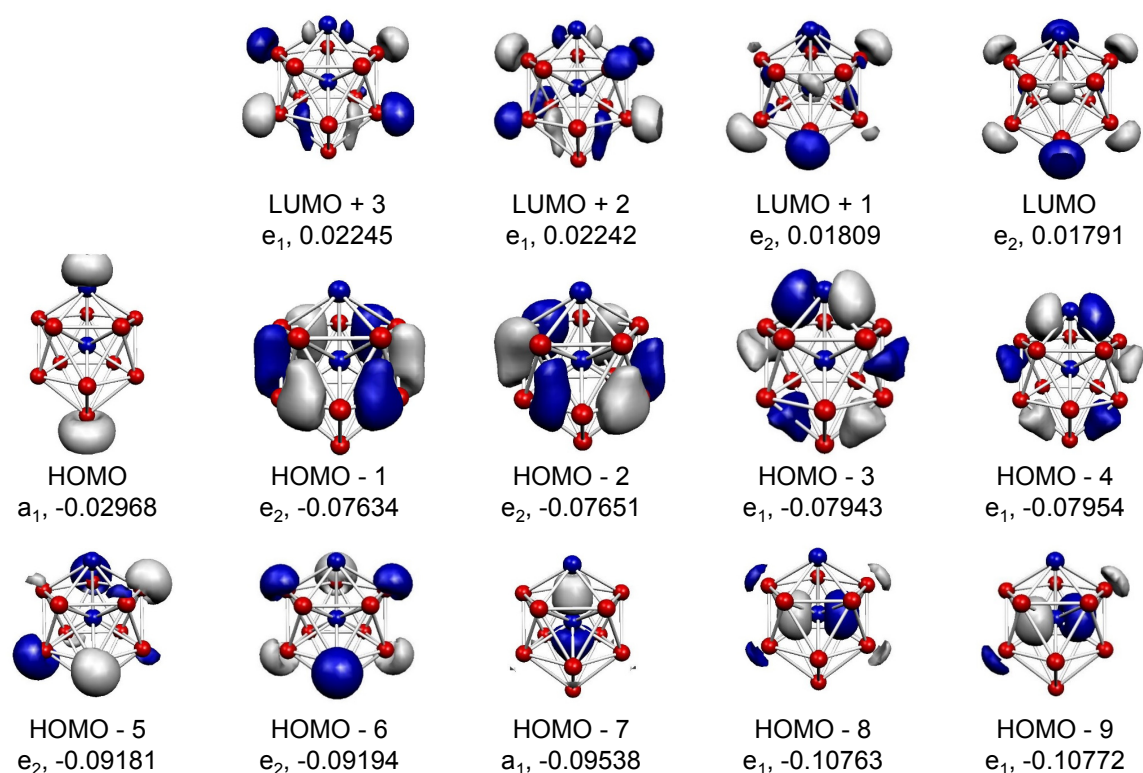**Figure S6.** Occupied and virtual frontier orbitals from HOMO – 9 to LUMO + 4 forAl$_{12}$Si$^-$.

LUMO + 3
a, -0.22269

LUMO + 2
a, -0.22755

LUMO + 1
a, -0.22981

LUMO
a, -0.23089

HOMO
a, -0.33054

HOMO - 1
a, -0.33151

HOMO - 2
a, -0.33973

HOMO - 3
a, -0.34186

HOMO - 4
a, -0.34241

HOMO - 5
a, -0.34384

HOMO - 6
a, -0.35199

HOMO - 7
a, -0.35325

HOMO - 8
a, -0.35602

HOMO - 9
a, -0.36895

Figure S7. Occupied and virtual frontier orbitals from HOMO − 9 to LUMO + 3 for$Al_{11}Si_2^+$

LUMO + 3
e_2, -0.10132

LUMO + 2
e_2, -0.10132

LUMO + 1
e_1, -0.10505

LUMO
e_1, -0.10505

HOMO
a_1, -0.16090

HOMO - 1
e_2, -0.20509

HOMO - 2
e_2, -0.20509

HOMO - 3
e_2, -0.21460

HOMO - 4
e_2, -0.21460

HOMO - 5
e_1, -0.21693

HOMO - 6
e_1, -0.21693

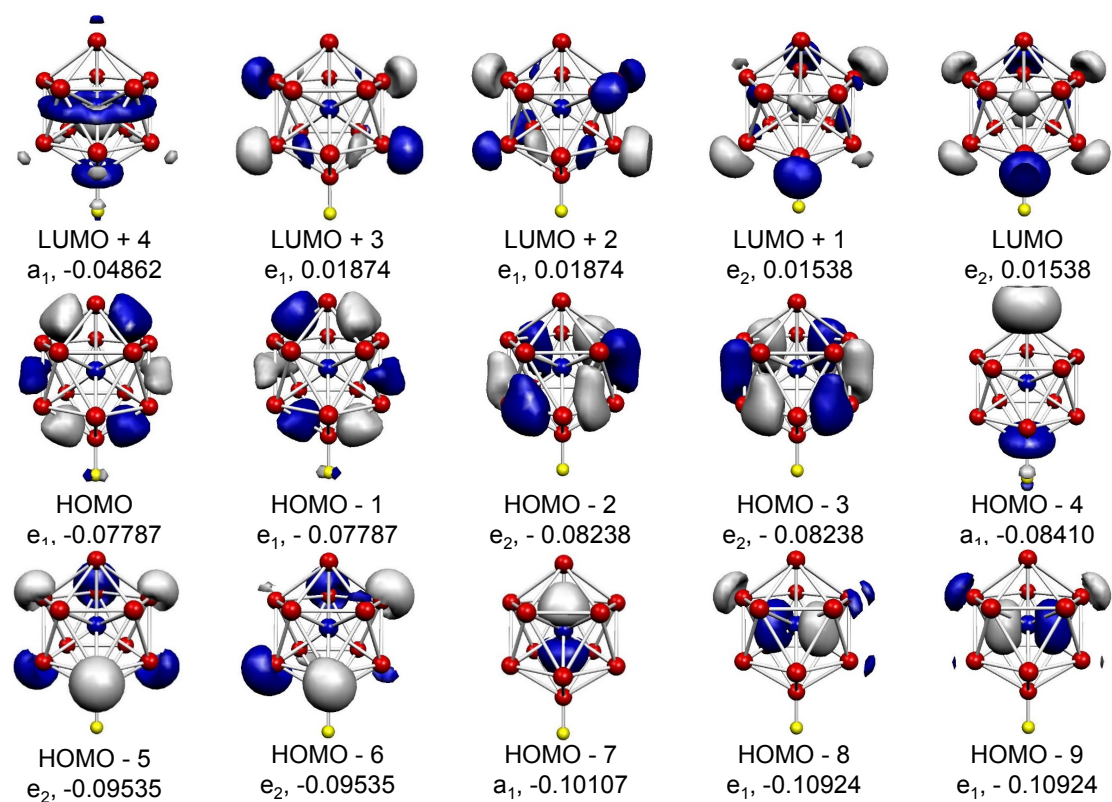HOMO - 7
a_1, -0.22831

HOMO - 8
e_1, -0.23013

HOMO - 9
e_1, -0.23013

Figure S8. Occupied and virtual frontier orbitals from HOMO − 9 to LUMO + 3 for $Al_{11}Si_2$.
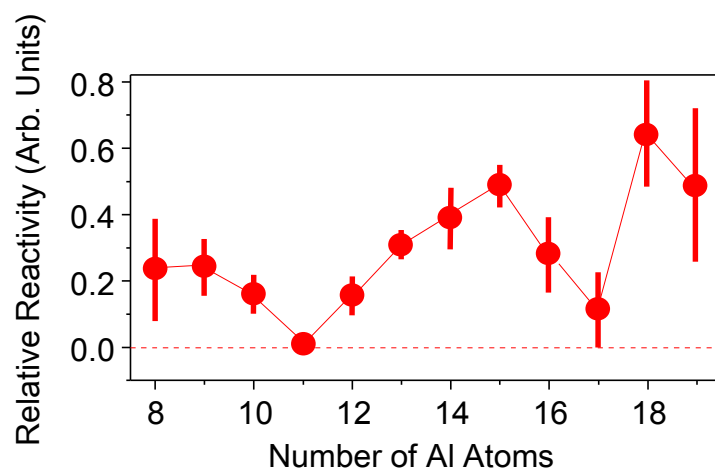
Figure S9. Occupied and virtual frontier orbitals from HOMO − 9 to LUMO + 4 for Al$_{11}$Si$_2^-$.

Figure S10. Occupied and virtual frontier orbitals from HOMO − 9 to LUMO + 4 for Al$_{12}$SiF$^-$.

Figure S11. The relative reactivity for the cationic $Al_nSi_2^+$ clusters at $n = 8-19$ against O_2 molecules. Local maxima are observed at $n = 11$ and 17. Both $Al_{11}Si_2^+$ and $Al_{17}Si_2^+$ satisfy the SAO closings of 2P (40 e) and 1G (58 e), respectively, and the low reactivities are explicable of electronic stability.
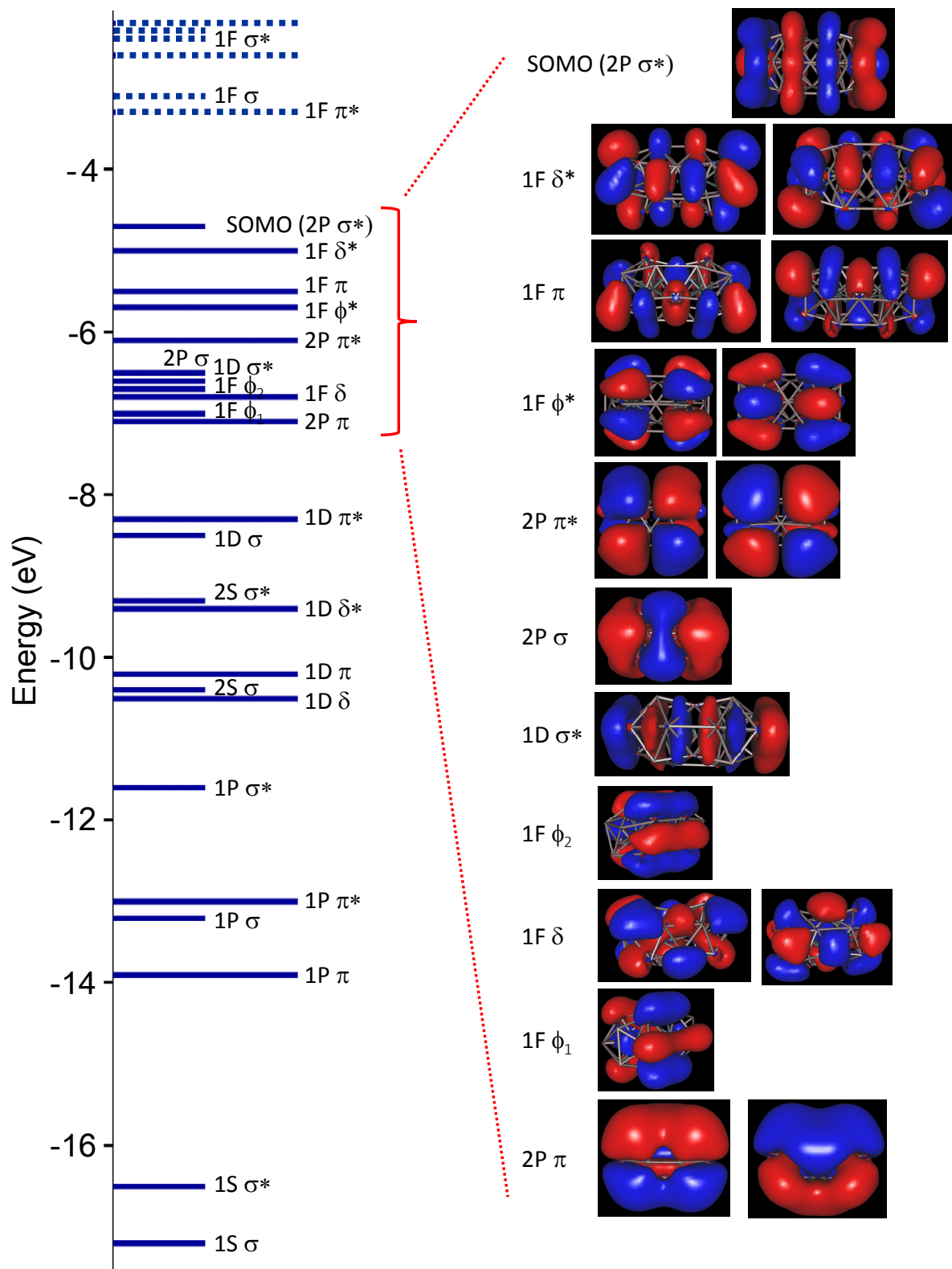
Figure S12. Calculated energy diagram and orbital shapes of LCSAO-MOs for *bi*-icosahedral Al$_{21}$Si$_2$. Solid lines show filled or half-filled states, whereas dotted lines do unoccupied states.
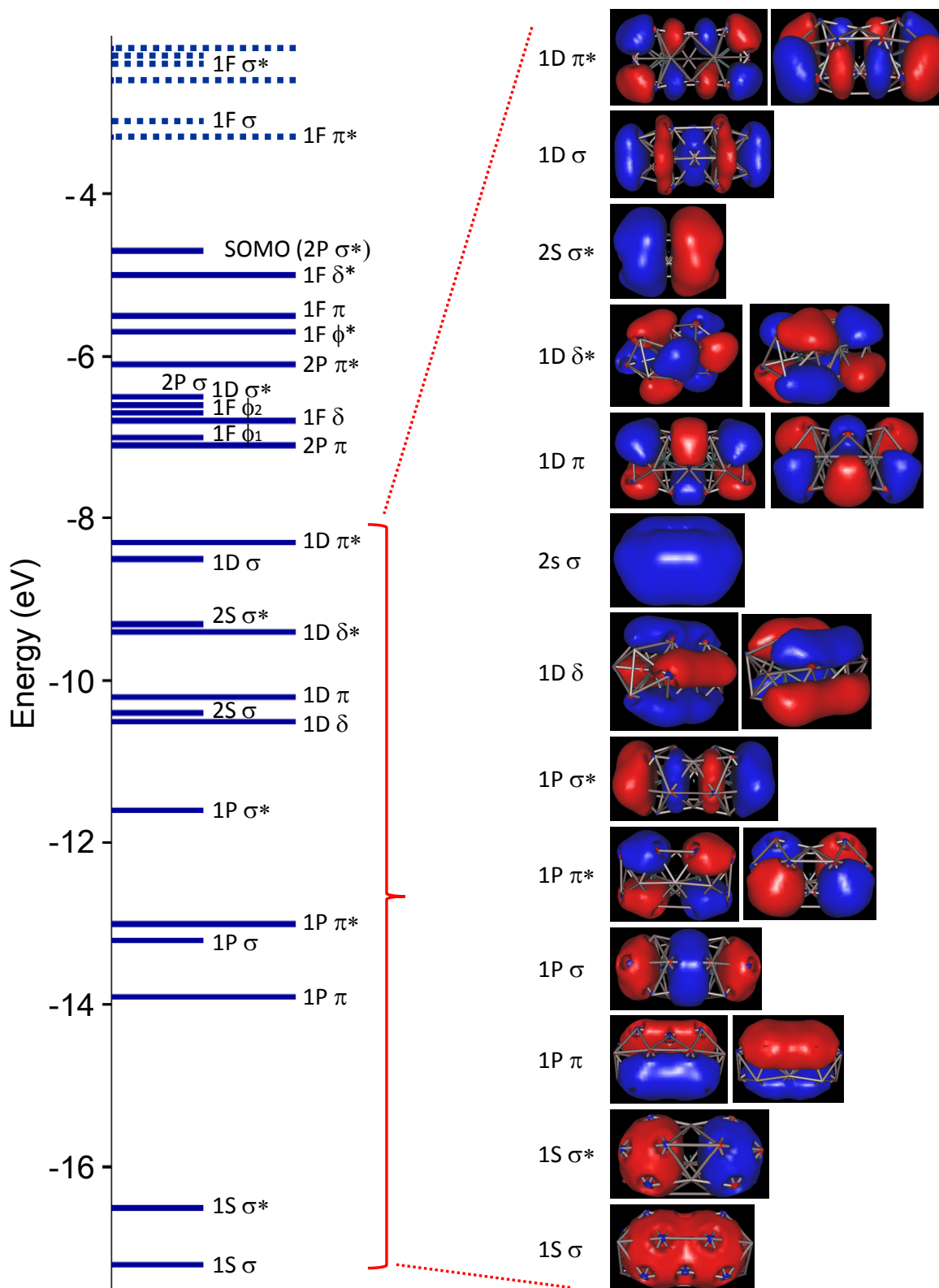
Figure S12. (continued) Calculated energy diagram and orbital shapes of LCSAO-MOs for *bi*-icosahedral Al₂₁Si₂. Solid lines show filled or half-filled states, whereas dotted lines do unoccupied states.