

**Supplementary information of:  
Principles of isomer stability in small clusters**

Giuseppe Fisicaro\*

*Consiglio Nazionale delle Ricerche, Istituto per  
la Microelettronica e Microsistemi (CNR-IMM),  
Z.I. VIII Strada 5, I-95121 Catania, Italy*

Bastian Schaefer, Jonas A. Finkler, and Stefan Goedecker  
*Department of Physics, University of Basel,  
Klingelbergstrasse 82, CH-4056 Basel, Switzerland*

In the following we show two additional analysis concerning the redistribution of the electronic charge density for selected Na and Mg clusters together with various figures from the main publication augmented by the data used to make the figure plus selected structural and electronic properties.

---

\* Giuseppe.Fisicaro@imm.cnr.it

isovalue = 0.00032

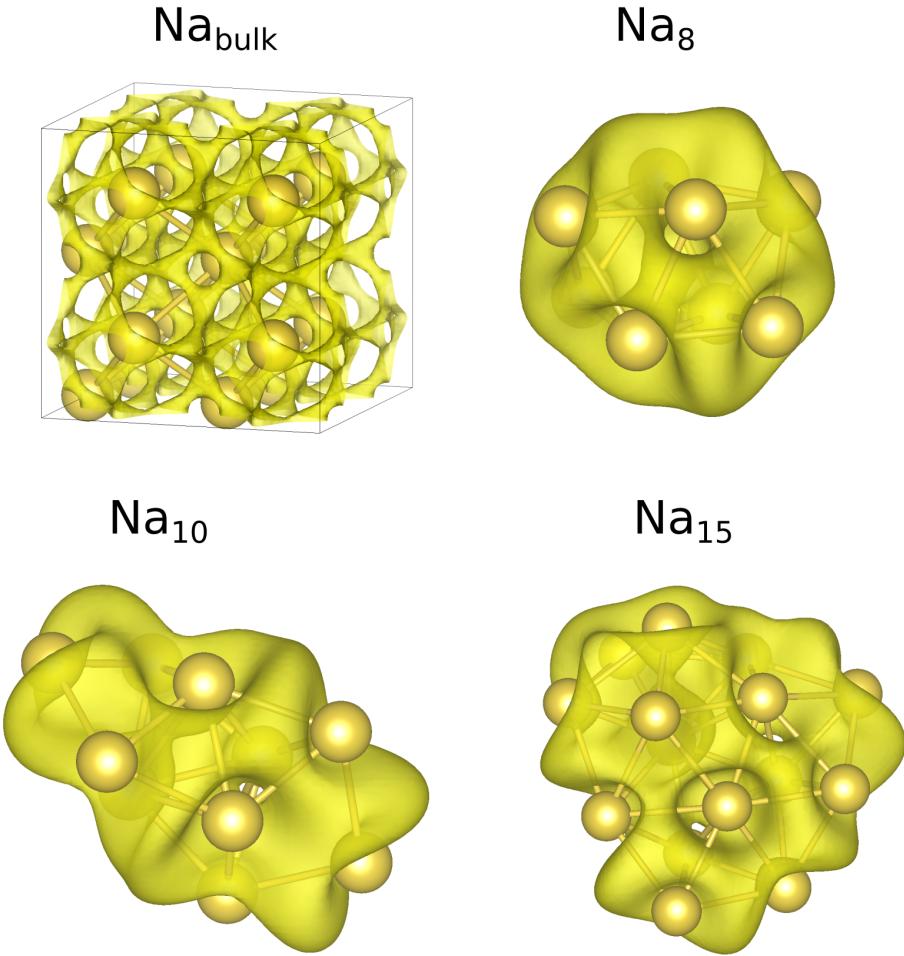


FIG. S1. Difference between the selfconsistent DFT charge density and the sum of the atomic charge densities of spherically symmetrized atoms. For each iso-value only the positive part is shown which illustrates the flow of the electronic charge density when the structure is formed out of individual atoms. All representations refer to an iso-value of 0.00032. Top row shows the charge difference for bulk Na and the global minimum of the Na<sub>8</sub> cluster. Bottom panels in the second row show the charge difference for the global minima of the Na<sub>10</sub> and Na<sub>15</sub> clusters. For large identical iso-charge values, the volume included by the iso-surface is always substantially larger in the case of the clusters compared to the solid. Since these regions of high charge densities are in between neighboring atoms, the bonds are contracted in the cluster compared to the solid.

isovalue = 0.016

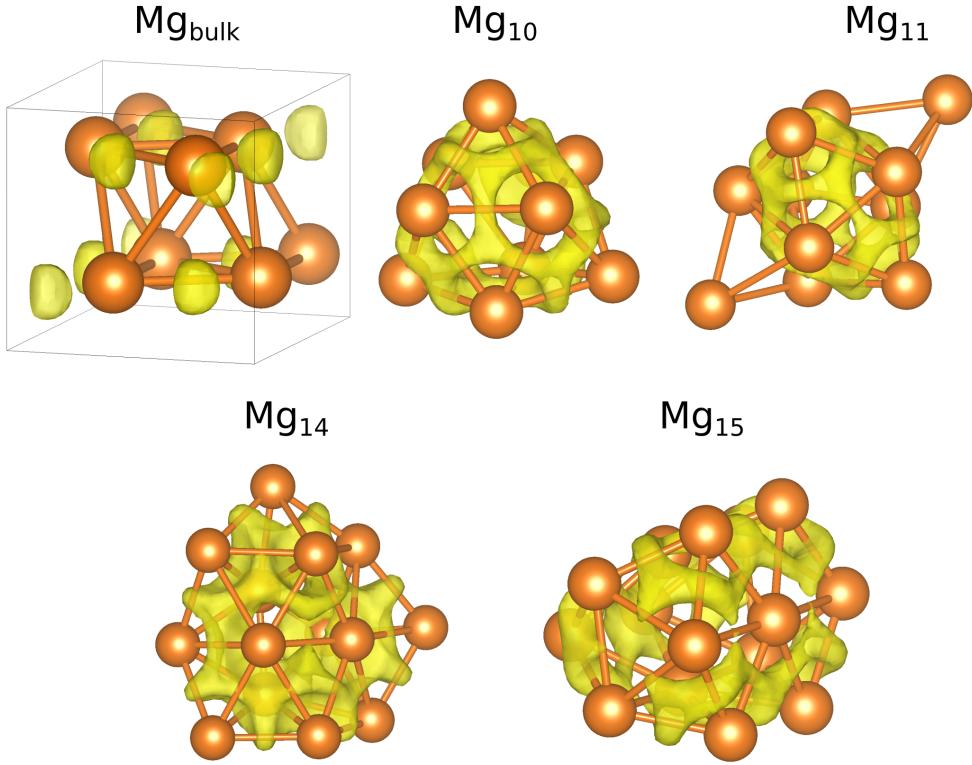


FIG. S2. Difference between the selfconsistent DFT charge density and the sum of the atomic charge densities of spherically symmetrized atoms. For each iso-value only the positive part is shown which illustrates the flow of the electronic charge density when the structure is formed out of individual atoms. All representations refer to an iso-value of 0.016. Top row shows the charge difference for bulk Mg and the global minima of the  $\text{Mg}_{10}$  and  $\text{Mg}_{11}$  clusters. Bottom panels in the second row show the charge difference for the global minima of the  $\text{Mg}_{14}$  and  $\text{Mg}_{15}$  clusters. For large identical iso-charge values, the volume included by the iso-surface is always substantially larger in the case of the clusters compared to the solid. Since these regions of high charge densities are in between neighboring atoms, the bonds are contracted in the cluster compared to the solid.

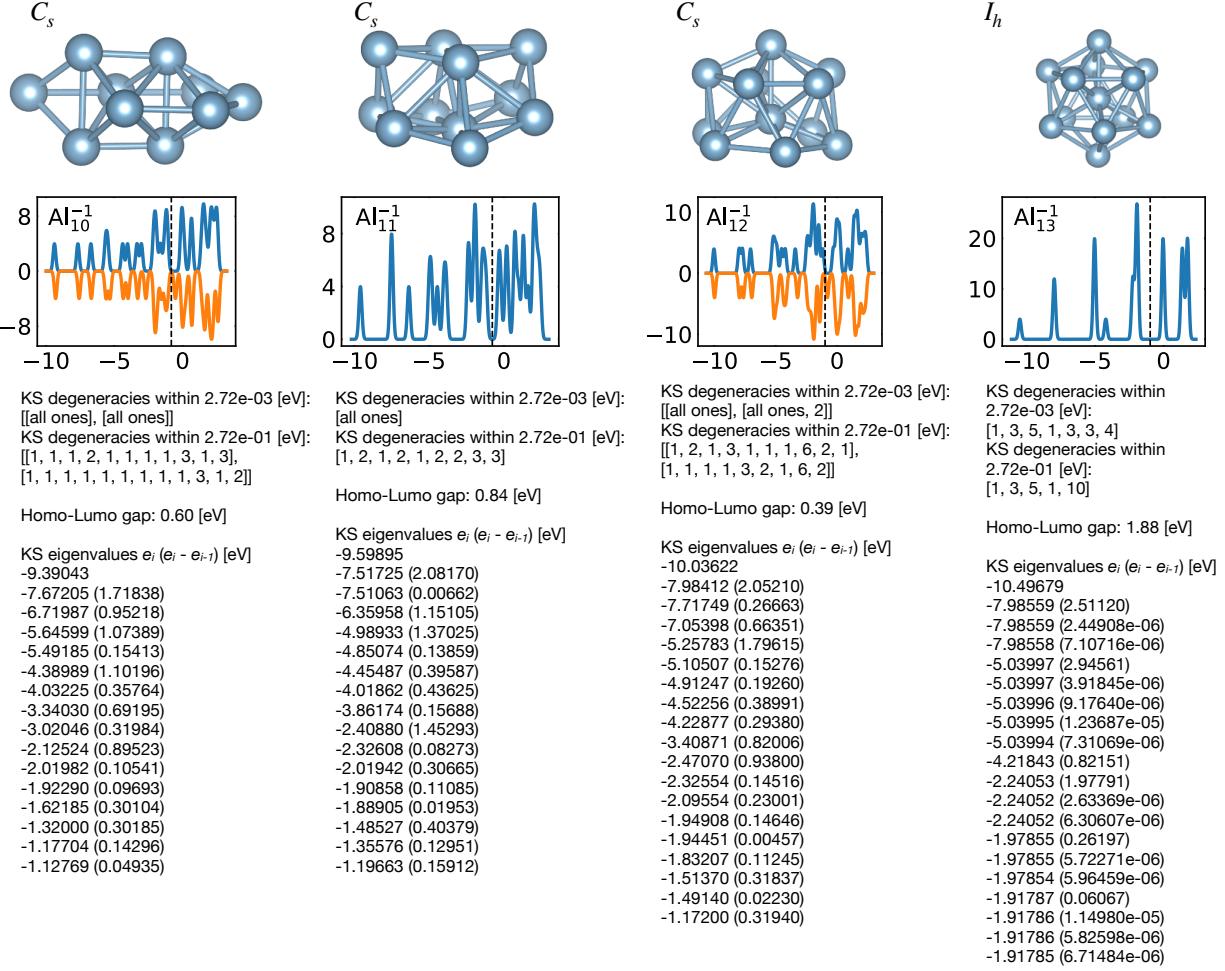


Figure continued on next page ...

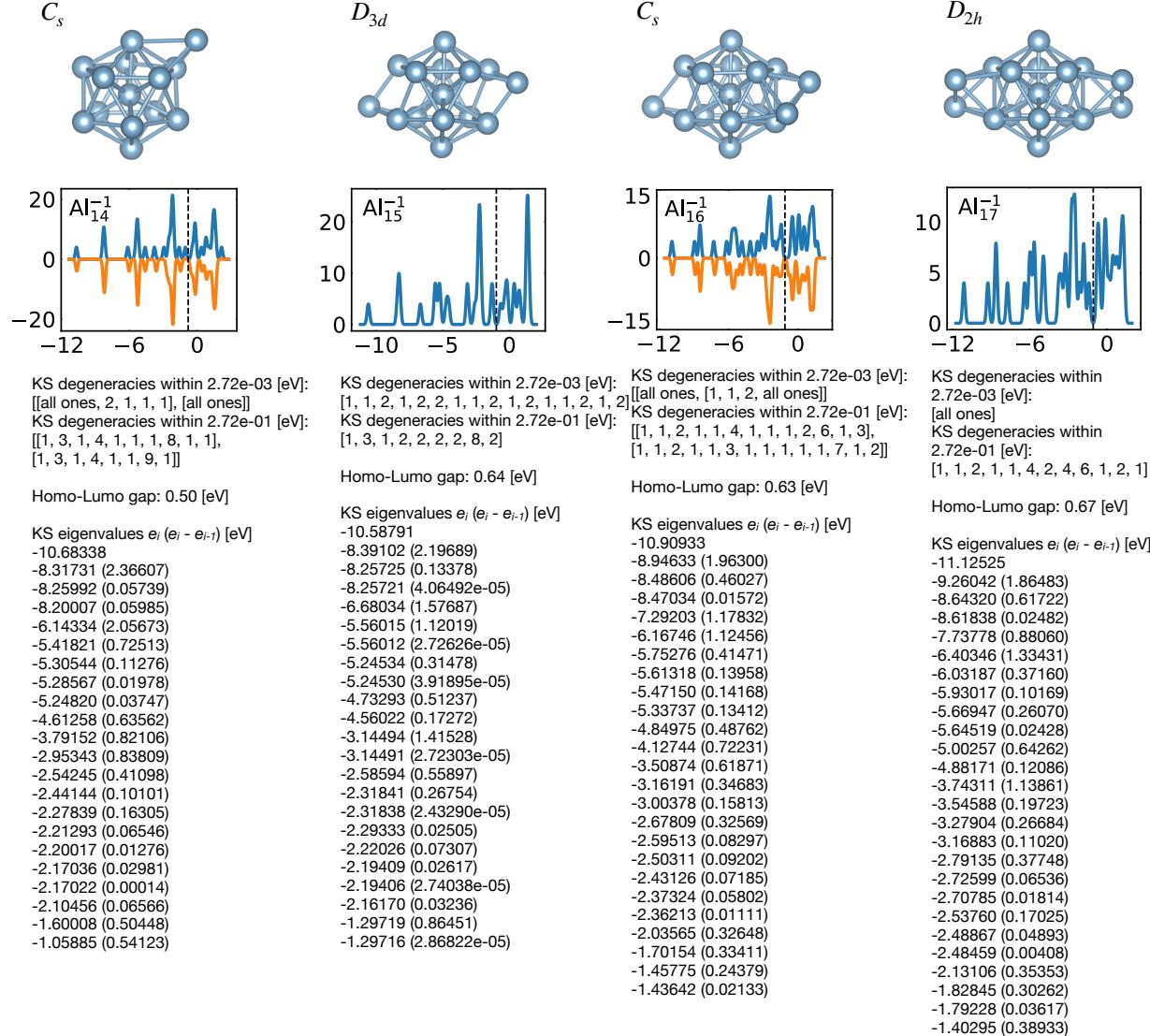


Figure continued on next page ...

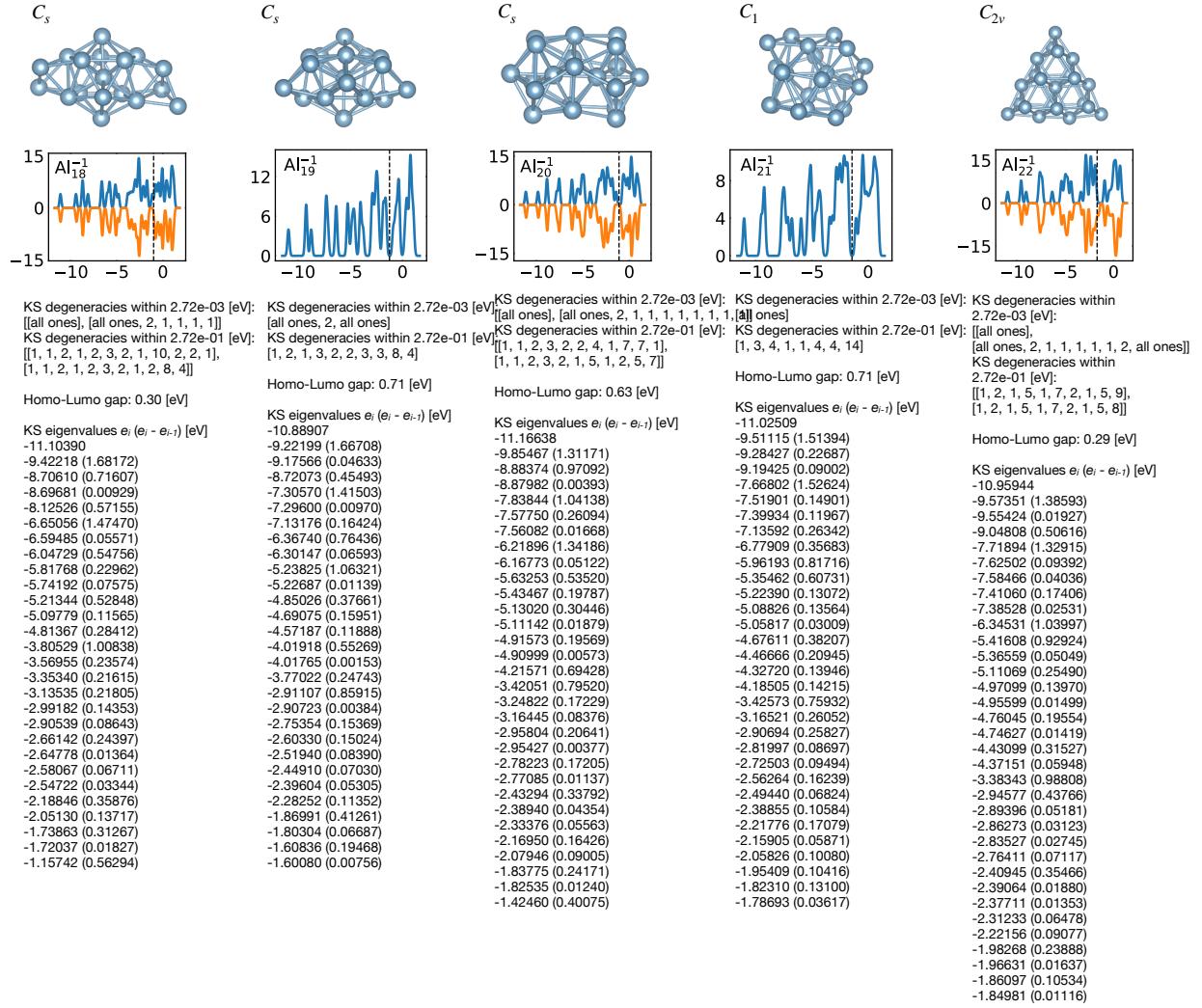
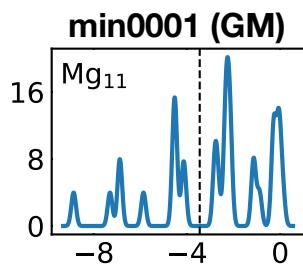
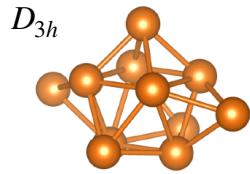


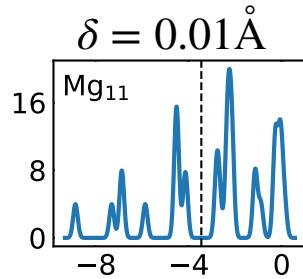
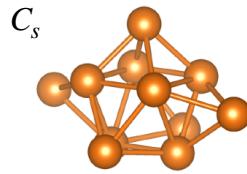
FIG. S3. Structures and degeneracies of the series of anionic Al clusters.



KS degeneracies within 2.72e-03 [eV]:  
 $[1, 1, 2, 1, 2, 2, 1, 1]$   
 KS degeneracies within 2.72e-01 [eV]:  
 $[1, 1, 2, 1, 4, 2]$

Homo-Lumo gap: 1.32 [eV]

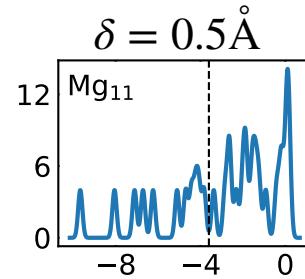
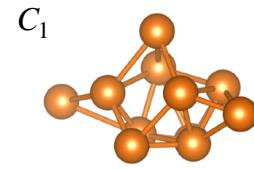
KS eigenvalues  $e_i (e_i - e_{i-1})$  [eV]  
 -8.85455  
 -7.29491 (1.55964)  
 -6.87417 (0.42074)  
 -6.87415 (1.72005e-05)  
 -5.86012 (1.01404)  
 -4.55165 (1.30847)  
 -4.55162 (2.68130e-05)  
 -4.49597 (0.05565)  
 -4.49597 (8.66982e-06)  
 -4.16104 (0.33492)  
 -4.10920 (0.05184)



KS degeneracies within 2.72e-03 [eV]:  
 $[1, 1, 1, 1, 1, 1, 1, 1, 1, 1]$   
 KS degeneracies within 2.72e-01 [eV]:  
 $[1, 1, 2, 1, 4, 2]$

Homo-Lumo gap: 1.32 [eV]

KS eigenvalues  $e_i (e_i - e_{i-1})$  [eV]  
 -8.86900  
 -7.30805 (1.56096)  
 -6.88060 (0.42745)  
 -6.87194 (0.00866)  
 -5.86827 (1.00367)  
 -4.54841 (1.31986)  
 -4.54000 (0.00841)  
 -4.50173 (0.03827)  
 -4.49340 (0.00832)  
 -4.16305 (0.33035)  
 -4.11745 (0.04560)

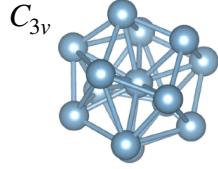


KS degeneracies within 2.72e-03 [eV]:  
 $[1, 1, 1, 1, 1, 1, 1, 1, 1, 1]$   
 KS degeneracies within 2.72e-01 [eV]:  
 $[1, 1, 1, 1, 1, 1, 5]$

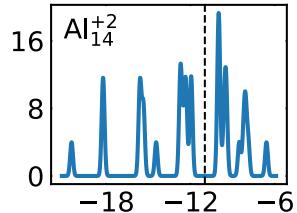
Homo-Lumo gap: 0.46 [eV]

KS eigenvalues  $e_i (e_i - e_{i-1})$  [eV]  
 -9.66752  
 -8.05320 (1.61432)  
 -7.10796 (0.94524)  
 -6.70894 (0.39902)  
 -6.23332 (0.47561)  
 -5.10134 (1.13198)  
 -4.69412 (0.40723)  
 -4.42798 (0.26614)  
 -4.23038 (0.19760)  
 -4.07493 (0.15545)  
 -3.83185 (0.24308)

Figure continued on next page ...



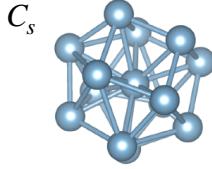
**min0001 (GM)**



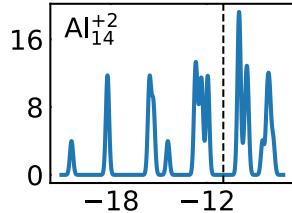
KS degeneracies within 2.72e-03 [eV]:  
 $[1, 2, 1, 2, 1, 2, 1, 1, 2, 1, 2, 1, 1, 2]$   
 KS degeneracies within 2.72e-01 [eV]:  
 $[1, 3, 5, 1, 7, 3]$

Homo-Lumo gap: 1.92 [eV]

KS eigenvalues  $e_i (e_i - e_{i-1})$  [eV]  
 -20.45841  
 -18.22946 (2.22895)  
 -18.22940 (6.60547e-05)  
 -18.17873 (0.05066)  
 -15.60630 (2.57243)  
 -15.60608 (0.00023)  
 -15.52758 (0.07850)  
 -15.33591 (0.19167)  
 -15.33561 (0.00030)  
 -14.43568 (0.89993)  
 -12.72299 (1.71269)  
 -12.70054 (0.02245)  
 -12.70036 (0.00017)  
 -12.55302 (0.14734)  
 -12.36136 (0.19166)  
 -12.36121 (0.00015)  
 -12.28822 (0.07299)  
 -11.96542 (0.32280)  
 -11.93014 (0.03528)  
 -11.92992 (0.00022)



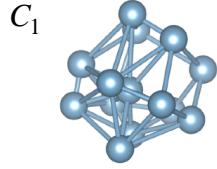
$\delta = 0.01 \text{ \AA}$



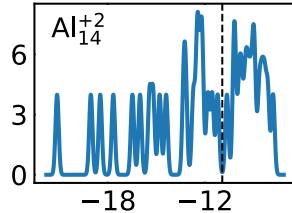
KS degeneracies within 2.72e-03 [eV]:  
 $[1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1]$   
 KS degeneracies within 2.72e-01 [eV]:  
 $[1, 3, 5, 1, 7, 3]$

Homo-Lumo gap: 1.92 [eV]

KS eigenvalues  $e_i (e_i - e_{i-1})$  [eV]  
 -20.46181  
 -18.23038 (2.23143)  
 -18.21997 (0.01041)  
 -18.18556 (0.03441)  
 -15.60806 (2.57750)  
 -15.59854 (0.00953)  
 -15.52797 (0.07056)  
 -15.34617 (0.18180)  
 -15.32921 (0.01697)  
 -14.43652 (0.89269)  
 -12.72528 (1.71123)  
 -12.70442 (0.02086)  
 -12.69129 (0.01313)  
 -12.55545 (0.13584)  
 -12.37068 (0.18476)  
 -12.35491 (0.01578)  
 -12.27920 (0.07570)  
 -11.97332 (0.30588)  
 -11.93066 (0.04266)  
 -11.92439 (0.00627)



$\delta = 0.5 \text{ \AA}$

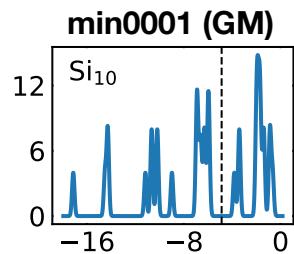
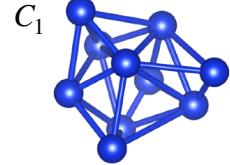
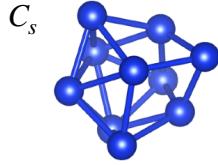
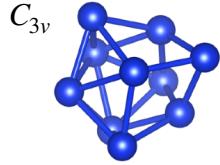


KS degeneracies within 2.72e-03 [eV]:  
 $[1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1]$   
 KS degeneracies within 2.72e-01 [eV]:  
 $[1, 1, 1, 1, 1, 2, 1, 1, 2, 5, 2, 1]$

Homo-Lumo gap: 0.57 [eV]

KS eigenvalues  $e_i (e_i - e_{i-1})$  [eV]  
 -21.12539  
 -19.04121 (2.08418)  
 -18.45860 (0.58261)  
 -17.65299 (0.80561)  
 -16.47132 (1.18167)  
 -15.99913 (0.47219)  
 -15.41084 (0.58829)  
 -15.19507 (0.21577)  
 -14.79044 (0.40464)  
 -14.38801 (0.40243)  
 -13.30152 (1.08648)  
 -13.18047 (0.12105)  
 -12.70541 (0.47506)  
 -12.47920 (0.22621)  
 -12.41180 (0.06740)  
 -12.22514 (0.18667)  
 -12.14920 (0.07594)  
 -11.80942 (0.33978)  
 -11.54083 (0.26860)  
 -11.20645 (0.33438)

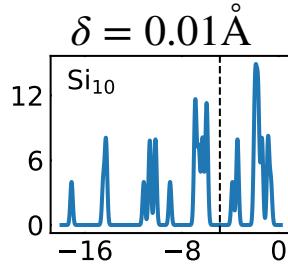
Figure continued on next page ...



KS degeneracies within 2.72e-03 [eV]:  
 $[1, 1, 2, 1, 2, 2, 1, 1, 2, 1, 1, 2, 2, 1]$   
 KS degeneracies within 2.72e-01 [eV]:  
 $[1, 3, 1, 2, 2, 1, 7, 3]$

Homo-Lumo gap: 2.09 [eV]

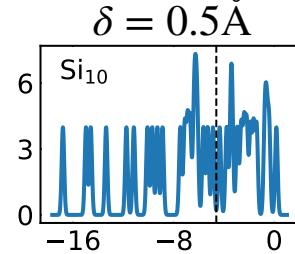
KS eigenvalues  $e_i (e_i - e_{i-1})$  [eV]  
 -17.12166  
 -14.50120 (2.62046)  
 -14.27155 (0.22965)  
 -14.27140 (0.00015)  
 -11.16173 (3.10966)  
 -10.64567 (0.51606)  
 -10.64546 (0.00021)  
 -10.18284 (0.46262)  
 -10.18276 (8.24397e-05)  
 -8.97187 (1.21088)  
 -6.94153 (2.03035)  
 -6.87553 (0.06600)  
 -6.87535 (0.00018)  
 -6.65232 (0.22303)  
 -6.56035 (0.09197)  
 -6.29172 (0.26863)  
 -6.29156 (0.00015)  
 -5.97521 (0.31636)  
 -5.97510 (0.00011)  
 -5.91293 (0.06217)



KS degeneracies within 2.72e-03 [eV]:  
 $[1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1]$   
 KS degeneracies within 2.72e-01 [eV]:  
 $[1, 3, 1, 2, 2, 1, 7, 3]$

Homo-Lumo gap: 2.08 [eV]

KS eigenvalues  $e_i (e_i - e_{i-1})$  [eV]  
 -17.10782  
 -14.49016 (2.61765)  
 -14.28971 (0.20045)  
 -14.23991 (0.04980)  
 -11.14278 (3.09713)  
 -10.66491 (0.47787)  
 -10.62589 (0.03902)  
 -10.18913 (0.43675)  
 -10.16849 (0.02064)  
 -8.97303 (1.19546)  
 -6.93467 (2.03836)  
 -6.88416 (0.05051)  
 -6.85779 (0.02637)  
 -6.65583 (0.20196)  
 -6.55913 (0.09670)  
 -6.29931 (0.25982)  
 -6.28201 (0.01729)  
 -5.98017 (0.30185)  
 -5.97339 (0.00678)  
 -5.90297 (0.07042)



KS degeneracies within 2.72e-03 [eV]:  
 $[1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1]$   
 KS degeneracies within 2.72e-01 [eV]:  
 $[1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 3, 3, 1, 1, 1, 1]$

Homo-Lumo gap: 0.54 [eV]

KS eigenvalues  $e_i (e_i - e_{i-1})$  [eV]  
 -16.79156  
 -14.95667 (1.83489)  
 -14.58116 (0.37551)  
 -13.35817 (1.22299)  
 -11.74541 (1.61276)  
 -11.15529 (0.59012)  
 -10.07269 (1.08259)  
 -9.69380 (0.37889)  
 -9.28600 (0.40780)  
 -8.87694 (0.40906)  
 -7.46001 (1.41693)  
 -7.11702 (0.34299)  
 -6.89036 (0.22666)  
 -6.68185 (0.20851)  
 -6.37897 (0.30288)  
 -6.25232 (0.12665)  
 -6.11478 (0.13753)  
 -5.62673 (0.48805)  
 -5.28749 (0.33925)  
 -4.87315 (0.41433)

FIG. S4. Lifting of the KS eigenvalue degeneracies by random atomic displacements away from the global minima. The effect for two different displacement amplitudes  $\delta$  is shown,  $\delta = 0.01$  and  $0.5 \text{ \AA}$ .

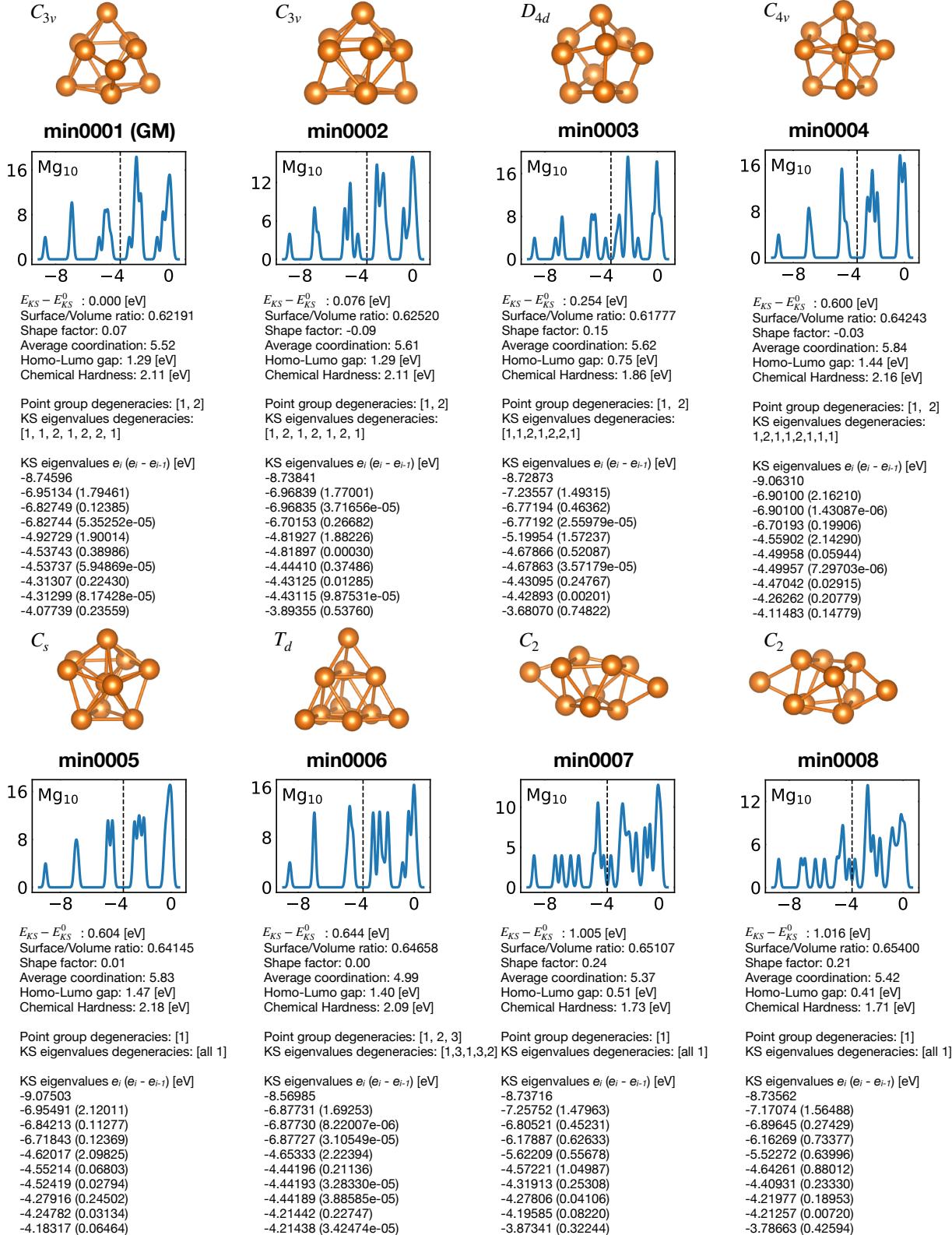


FIG. S5. Structural and electronic properties of the first eight low-lying minima for the Mg<sub>10</sub> cluster.

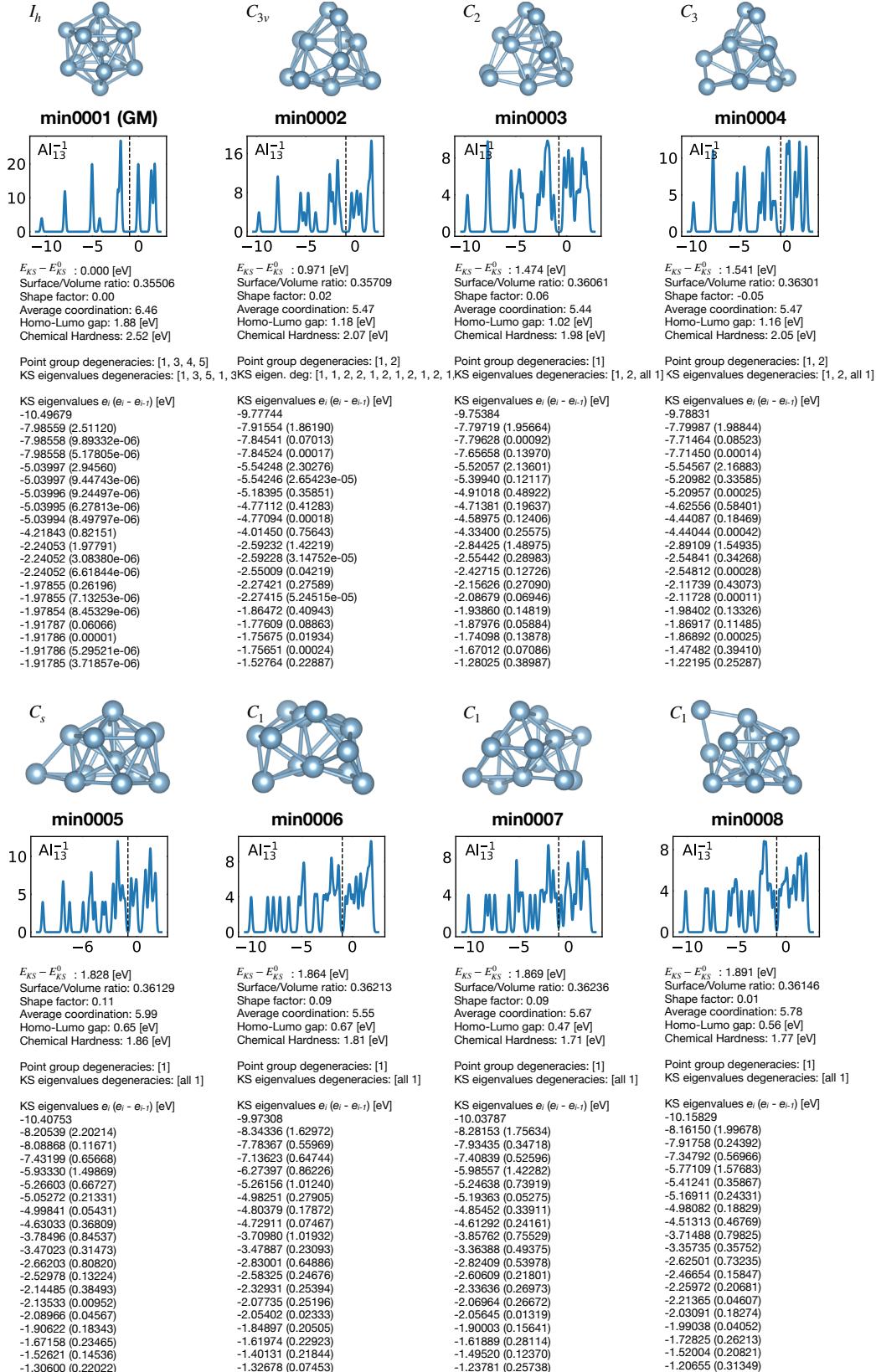
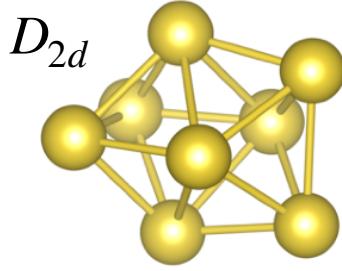
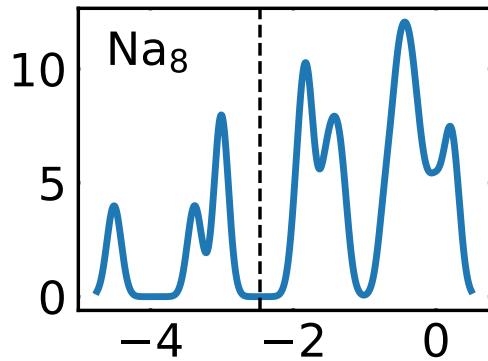


FIG. S6. Structural and electronic properties of the first eight low-lying minima for the  $\text{Al}_{13}^{+1}$  cluster.



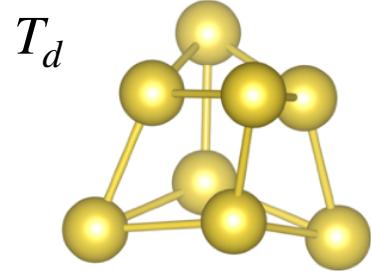
**min0001 (GM)**



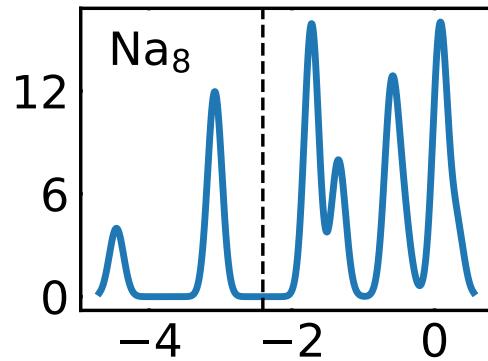
$E_{KS} - E_{KS}^0$  : 0.000 [eV]  
 Surface/Volume ratio: 0.84330  
 Shape factor: 0.23  
 Average coordination: 4.49  
 Homo-Lumo gap: 1.08 [eV]  
 Chemical Hardness: 1.84 [eV]

Point group degeneracies: [1,2]  
 KS eigenvalues degeneracies: [1, 1, 2]

KS eigenvalues  $e_i$  ( $e_i - e_{i-1}$ ) [eV]  
 -4.51033  
 -3.38137 (1.12895)  
 -3.00809 (0.37328)  
 -3.00765 (0.00044)



**min0002**



$E_{KS} - E_{KS}^0$  : 0.093 [eV]  
 Surface/Volume ratio: 0.84345  
 Shape factor: 0.00  
 Average coordination: 4.50  
 Homo-Lumo gap: 1.34 [eV]  
 Chemical Hardness: 1.91 [eV]

Point group degeneracies: [1, 2, 3]  
 KS eigenvalues degeneracies: [1, 3]

KS eigenvalues  $e_i$  ( $e_i - e_{i-1}$ ) [eV]  
 -4.45624  
 -3.07899 (1.37724)  
 -3.07825 (0.00074)  
 -3.07788 (0.00036)

FIG. S7. Structural and electronic properties of the first two low-lying minima for the Na<sub>8</sub> cluster.

The two structures are completely unrelated and the degeneracy of the KS eigenvalues in the ground state is accidental and not caused by symmetry.

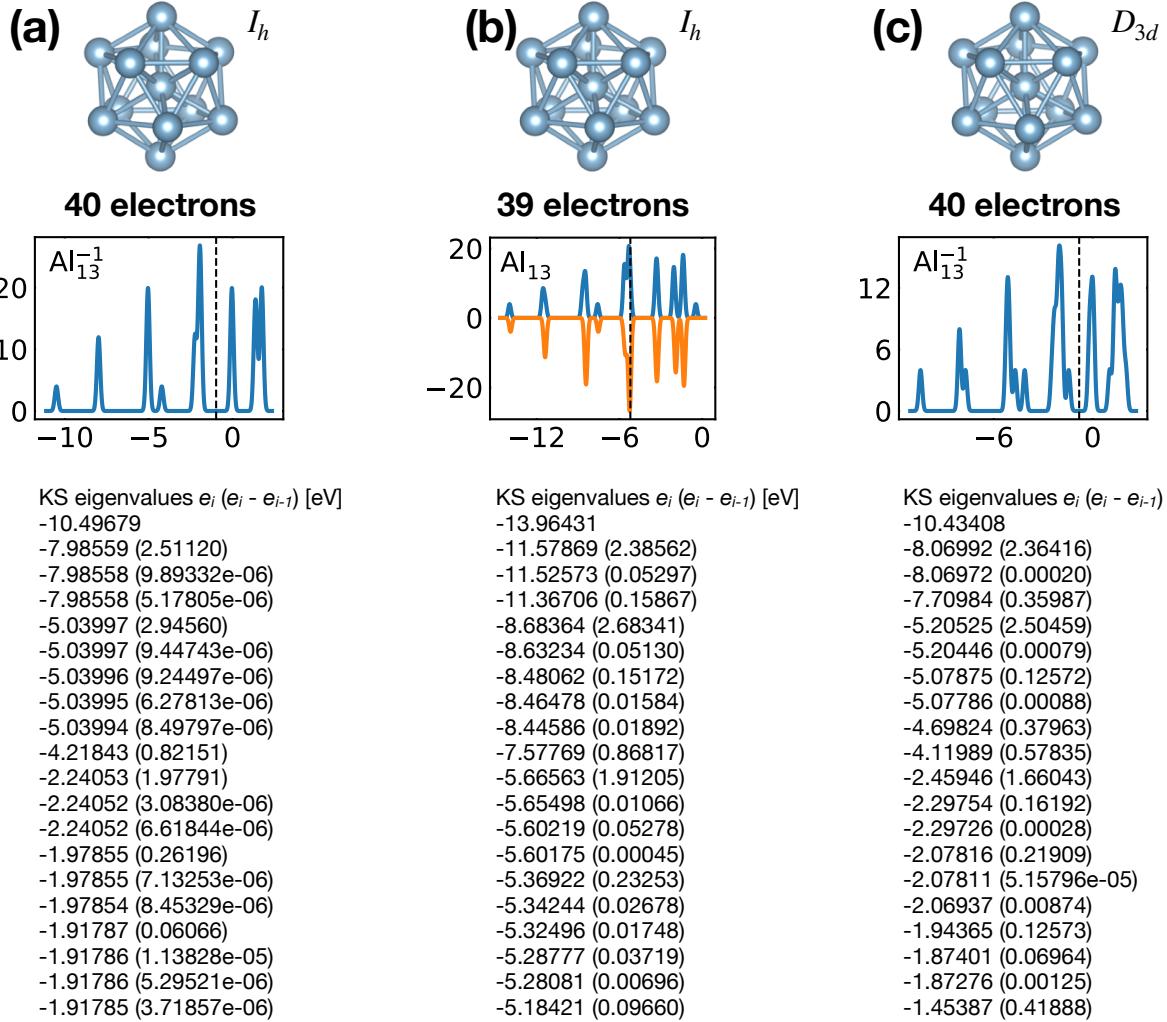


FIG. S8. Density of states of 40 (a) and 39 (b) valence electrons, distributed over a perfect icosahedron with point group  $I_h$ . This structure is the GM of  $\text{Al}_{13}^{-1}$  and has point group degeneracies [1, 3, 4, 5]. (c) shows the DoS of 40 electrons distributed over the slightly distorted icosahedron  $D_{3d}$  GM of  $\text{Al}_{13}$  which has point group degeneracies [1, 2].