

Periodicity of Two-Dimensional Bonding of Main Group Elements

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In the periodic table the position of each atom follows the 'aufbau' principle of the individual electron shells. The resulting intrinsic periodicity of atomic properties determines the overall behavior of atoms in two-dimensional (2D) bonding and structure formation. Insight into the type and strength of bonding is the key in the discovery of innovative 2D materials. The primary features of 2D bonding and the ensuing monolayer structures of the main-group II–VI elements result from the

The cohesive energy or binding energy per atom in -eV/atom, studied for the elements of main groups II–VI highlighted in Figure 1, describes the energy difference between the free atom and the atom bonded in the 2D network. The bond length is a sensitive measure of the strength of individual chemical bonds. While accurate values are available for the length of bonds information on the bond dissociation energy of single bonds is rare. To investigate the bonding–structure relation, the cohesive energy and bond length are correlated with the individual periods (rows) and columns (groups) of the periodic table.

This study concentrates on the cohesive energy and bond length of monolayers of the main-group elements. Currently, most results obtained by density functional theory (DFT) use the generalized gradient approximation (GGA) with Perdew– Burke–Ernzerhof (PBE) functionals.^[1,2] First-principles calculations have not only predicted the existence of new 2D materials but also helped to find possible routes of synthesis.^[1,3] Besides the main-group elements theory already covers a large number of their binary and isoelectronic compounds.^[4] Only limited information on structural properties and mechanical behavior comes from the few synthesized free-standing monolayers and the steadily increasing number of adsorbed monolayers grown on stabilizing surfaces.

Table 1 presents a selection of published cohesive energies and bond lengths (lattice constants) of the group-II monolayers of Be, Mg, Ca, Sr, and Ba,^[5,6] named beryllene, magnesene, calcene, strontene, and barene in analogy with previous

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number of valence electrons and the change of atom size, which determine the type of hybridization. The results reveal the tight connection between strength of bonding and bond length in 2D networks. The predictive power of the periodic table reveals general rules of bonding, the bonding-structure relationship, and allows an assessment of published data of 2D materials.

Η																	He
Li	Be											B	С	Ν	0	F	Ne
Na	Mg											Al	Si	Р	S	Cl	Ar
Κ	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	Ι	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn						

Figure 1. Periodic table highlighting the main group elements studied in this work.

nomenclature, the group III monolayers borophene,^[7–9] aluminene,^[10–12] gallenene,^[13–14] indiene,^[15,16] and thalliene,^[5,6] the group IV monolayers graphene,^[17–20] silicene,^[17–20] germanene,^[17–20] stanene,^[17–20] and plumbene,^[18,20,21] the group V monolayers nitrogene,^[22–24] phosphorene,^[23,25–27] arsenene,^[23,25–27] ant bismuthene,^[23,26,27] and the group VI monolayers selenene,^[28–30] tellurene,^[30–32] and poloniumene.^[33]

Figure 2 displays the cohesive energies of the monolayers of the five main group elements, plotted versus the period number. Thus, the graph reveals in the x direction the change of binding energies within the diverse columns. The diagram presents the cohesive energies of the (most) stable structures of group II: Be–Ba planar honeycomb, group III: B planar, Al–TI buckled or puckered, group IV: C planar, Si–Pb buckled, group V: N–Bi puckered or buckled, and group VI: Se rhombic, Te rhombic, Po square. Note the comparable cohesive energies of several allotropes (see Table 1).

The characteristic inverse dependence of the cohesive energies of the group members on the period number derives primarily from the increase of atom size within each column with increasing atomic number. Importantly, the atom size determines the efficiency of orbital overlap and thus the strength of interaction that finally controls the length of individual chemical bonds, namely perfect covalent bonds in homonuclear 2D structures. Tight-binding theory predicts an inverse dependence of bond length 'd' on orbital overlap 'V' according to the fundamental relation V $\sim 1/d^2$.^[26] Irrespective of

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Figure 2. Plot of cohesive energy versus period number of the periodic table.

the type of orbitals and their principal quantum numbers, the relationship describes the covalent interaction of the valence shells of all neighboring orbitals.

The tabulated van der Waals radii deliver reasonable estimates of the size of atoms for all elements.^[34,35] The recommended crystallographic van der Waals radii^[34] increase within each group and for many elements the suggested values are larger than those of subsequently published van der Waals radii, which are characterized as consistent for all main-group elements.^[35] The larger atom size of B than that of Al in this work is not supported by the cohesive energies. The dependences in Figure 2 reflect the strong increase of the van der Waals diameter between periods two and three, compared with a smaller change between the higher periods. This enlargement of atom size induces an alteration of hybridization from planar sp² to buckled sp²-sp³ hybrids from graphene to its higher homologues (see Figure 3). Owing to the reduced orbital overlap, mixed sp²-sp³ hybrids become more stable for silicene



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Figure 3. Schematic presentation of hybrids of main group elements of the periodic table.

and with increasing sp³ contribution corrugation increases and binding energy decreases for the higher homologues.

Note that measurements of the thickness of planar monolayers by atomic force microscopy (AFM) are in good agreement with tabulated van der Waals diameters.^[36] The exceptionally small atom radius given for Be^[35] implies much stronger bonding of Be than the larger crystallographic value, consistent with calculated cohesive energies. The almost constant cohesive energies of the higher homologues of Be, despite strong increase of atom size, point to weaker metallic bonding.

A plot of bond lengths of group II–VI monolayers versus period number shows the expected significant elongation of bonds between periods two and three, followed by an asymptotic behavior, qualitatively reflecting the increase of the van der Waals diameters (see Figure 4). Different from the mean cohesive energy the individual bond energies and bond lengths may vary in corrugated structures. In the case of different bond lengths, the plot displays the shortest one. In total, the bond length increases by a factor of about three from graphene with



Figure 4. Plot of the bond length versus period number of the periodic table.



Table 1. A selection of cohesive e	energies and bond lengths of group-II–VI mone	olayers (ML).	
ML	Structure, space group	Cohesive energy [eVatom ⁻¹]	Bond length, d ₁ , d ₂ (lattice const.) [nm]
bondlong	hovegonal six noighbors	2 01 ^[5]	0.215 ^[5]
beryliene	nlanar honovcomb	-2.91 ⁶	(0.213) ^[6]
magnosono	hovegonal six noighbors	- 5.00 0.01 ^[5]	0.207 ^[5]
Inagriesene	nlanar hanaycamh	-0.9 ^[6]	(0.206)[6]
calcono	planal noneycomb	1.00 ^[5]	0.200
calcene	nexagonal six neighbors	- 1.09 ^{co}	(0.283 ¹⁶
strantona	planar honeycomb	- 1.18	(0.387)
strontene	nexagonal six neighbors	-0.85	(0.427)[6]
havena	planar noneycomb	-0.97	(0.425)(-)
barene	nexagonal six neighbors	- 1.04 ⁽⁶⁾	0.448 ⁽⁻⁾
	planar honeycomb	-1.20	(0.447)
borophene	planar B ₁₂ , Pmm2 ^[7]	-6.15 ^[7] , -5.71 ^[8]	0.165-0.170 ^[9]
	planar γ_{2} , Cmmm ^[7]	$-6.16^{[7]}, -5.72^{[8]}$	0.160-0.171 ^[9]
aluminene	planar, P6/mmm ^[10]	$-1.96^{[10]}, -2.32^{[11]}$	0.259 ^[10] , 0.257 ^[11]
	buckled, P-3m1	-3.27 ^[11]	0.265, 0.275 ^[12]
gallenene	planar, a ₁₀₀ -Ga, Pbam ^[13]		0.266, 0.267 ^[13]
5	puckered, base-Ga	-2.32 ^[14]	0.271, 0.273 ^[14]
indiene	planar, <i>P6/mmm</i> ^[16]	$-1.81^{[15]}$, $-2.08^{[16]}$	$0.286^{[15]}, 0.282^{[16]}$
indicite	buckled P3m1 ^[16]	$-1.83^{[15]} -2.13^{[16]}$	$0.289^{[15]} 0.302^{[16]}$
thalliene	hexagonal six neighbors	$-1.67^{[5]}$	0.331 ^[5]
liancie	planar honeycomb	-1.65 ^[6]	(0.332) ^[6]
	. ,		
graphene	planar, <i>P</i> 6/mmm ^[20]	-7.85 ^[17] , -7.82 ^[18]	0.142 ^[17] , 0.142 ^[18,19]
silicene	low buckled, P-3m1 ^[20]	-3.91 ^[17] , -3.86 ^[18]	0.228 ^[17] , 0.227 ^[18,19]
germanene	low buckled, P-3m1 ^[20]	-3.24 ^[17] , -3.19 ^[18]	0.244 ^[17] , 0.242 ^[18,19]
stanene	high buckled, P-3m1 ^[20]	-2.73 ^[17] , -2.65 ^[18]	0.284 ^[17] , 0.283 ^[18,19]
plumbene	high buckled, P-3m1 ^[20]	-2.28 ^[18]	0.302 ^[21] , 0.300 ^[18]
nitrogono	buckled bb 0.2 ml	6 01[22] 2 67[23]	0 1 40[23] 0 1 50[23,24]
ntrogene	buckled, hb, P-5 mi	-0.81° , -3.07°	0.149° , 0.150°
phosphorene	buckered, sw, Prind ²	$-5.59^{-1}, -5.10^{-1}$	$0.222, 0.220^{-1}$
	buckled, hb, P-3/11	$-5.55^{\circ}, -5.14^{\circ}$	0.220 0.248 ^[26]
arsenene	puckered, sw, Pmnd ²¹	$-3.13^{(-7)}, -2.85^{(-7)}$	$0.250, 0.248^{-1}$
	buckled, nd, $P-3m$ [27]	$-3.14^{(-3)}, -2.89^{(-3)}, $	0.251,,0.245,,
antimonene	puckered, aw, $PmnZ_1^{(2)}$	$-1.77^{\circ}, -2.56^{\circ}$	$0.290, 0.284^{\circ}$
1.2	buckled, hb, $P-3m I^{(27)}$	$-1.96^{(20)}, -2.57^{(27)}$	0.287(20), 0.287(25)
bismuthene	puckered, aw, $PmnZ_1^{(27)}$	$-1.38^{(20)}, -2.42^{(27)}$	$0.306, 0.298^{(20)}$
	buckled, nb, $P-3m1^{2/3}$	$-1.44^{(23)}, -2.41^{(23)}$	0.301,203, 0.307,223
selenene	tetragonal	$-2.71^{[28]}, -2.77^{[29]}$	0.265-0.338 ^[29]
	rhombic, P-3m1	$-2.56^{[28]}, -2.72^{[29]}$	0.266 ^[29]
	monoclinic, Cm ^[30]	-2.65 ^[30]	0.240, 0.271 ^[30]
tellurene	tetrag., P2/m, P2,/m ^[32]	-2.56 ^[31]	0.275, 0.302 ^[31]
	rhombic, <i>P</i> -3 <i>m</i> 1 ^[32]	-2.62 ^[31]	0.302 ^[31]
	monoclinic. Cm ^[30]	-2.51 ^[30]	0.287. 0.305 ^[30]
poloniumene	square lattice structure	-2 58[33]	0.318 ^[33]
poloniamene	hexagonal six neighbors	-2 35[33]	0.334 ^[33]
	honeycomb structure	-2 33 ^[33]	0.312 ^[33]
	noncycomo structure	2.33	0.012

the shortest bond of 0.142 nm,^[17] to Ba with the longest bond of 0.448 nm,^[5] while the corresponding cohesive energy changes by a factor of about eight from -7.85 eV/atom,^[17] to -1.04 eV/atom,^[5] respectively. Within the errors involved in such first-principles calculations this enormous decrease of the cohesive energy supports the theoretically predicted invers quadratic dependence predicted by tight-binding theory.^[26]

Figure 5 shows the calculated cohesive energies of maingroup elements versus column number. The plot reveals again the pronounced change of binding energies between the second and third period. From the second to the fifth period, in the dependences of the individual periods, the group-IV monolayers exhibit the maximum bonding strength. This demonstrates that the four valence electrons form the most stable 2D bonds with their noble gas configuration ('octet rule'). Along each period the effect of the varying number of valence electrons dominates bonding over minor contributions from the varying atom size. The regular pattern of cohesive 2D interaction observed for the five periods is a consequence of the 'aufbau' principle of electron shells in the periodic table.

The deficiency of valence electrons in group II–III compounds causes a drastic decrease of cohesive energy (see Figure 5). Boron, for example, with its three valence electrons can form 2D networks, however, the available bonding orbitals are partially empty. According to tight-binding theory, based on the linear combination of atomic orbitals (LCAO) and the hybridization concept, not all three valence electrons are in bonding orbitals and therefore, the uniform trivalent network is not stable.^[37] Note that the experimentally synthesized planar monolayers of boron, included in Table 1, contain a mixture of



Figure 5. Plot of cohesive energy versus column number of the periodic table.

triangular and hexagonal motifs. A change in the type of bonding to weaker metallic interaction leads to an even larger reduction of the cohesive energies in group-II monolayers. Metallic bonding usually prefers a large coordination with six nearest neighbors (see Figure 3), which in group-II monolayers has a comparable low binding energy as the planar honeycomb configuration (see Table 1).

A surplus of valence electrons in groups V-VI has a much smaller effect on the binding energy. In pnictogens, with five valence electrons, tetrahedral-like hybrids with a backbone consisting of three $\boldsymbol{\sigma}$ bonds and a lone-electron pair lead to dynamically stable puckered and buckled structures with an equilibrium configuration controlled by the repulsion of the lone-electron pairs (see Figure 3). Interestingly, the binding energies of the two allotropes often are comparable and may lead to the synthesis of their mixtures (see Table 1). While a three-dimensional solid of N does not seem to be stable, 2D buckled nitrogene is thermodynamically and dynamically stable.^[22-24] Owing to the multivalency of chalcogenides with oxidation states -2 and +6, the group-VI elements exist in diverse hybrids and form low-symmetry structures that no longer exhibit hexagonal symmetry such as trigonal, tetragonal, rhombic, monoclinic, and square phases. The transition to metallic-type bonding in this column from Se to Po seems to be the main reason for comparable bonding strengths and small deviations from the regular dependence of the heavy compounds (see Figure 5). As an example, Figure 3 shows the rare square lattice with tetra-coordination of metallic poloniumene, specified in Table 1.

Figure 6 displays the variation of bond length (for group II also lattice constants) with the column number. The minima of the group-IV bond lengths are consistent with the maxima of the cohesive energies in Figure 5. On the side of deficiency of valence electrons with respect to group-IV monolayers, a strong increase of bond length and enormous weakening of bonding occurs, whereas the bond length increases only slightly on the



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Figure 6. Plot of the bond length versus column number of the periodic table.

side with a surplus of valence electrons and agrees for silicene and phosphorene. The diagrams reveal different consequences of electron deficiency and a surplus of valence electrons on bonding. The deficiency of valence electrons leads to only partially filled bonding orbitals with an essential loss of bonding power, e.g., in the delocalized three-centered bonds of boron. One of the three electrons even occupies an in-plane antibonding orbital.^[37] Conversely, when the valence shells contain additional electrons, it is possible to fill the bonding orbitals completely. However, the surplus of electrons may reduce the binding energy and extend bond lengths slightly, e.g., by the repulsion effect of lone-electron pairs.

In summary, both, σ and π bonds react flexible on the restriction to 2D space, the variation of atom size, and deviations of the number of valence electrons from the octet rule. The diversity of corrugated atomic monolayers demonstrates variable covalent and metallic-like bonding with novel types of hybridization and coordination, surpassing by far the number of perfect planar structures. Detailed understanding of the bonding behavior of elemental monolayers allows a useful prediction of bonding in the large family of their binary, e.g., SiC, and isoelectronic compounds, e.g., h-BN, by taking the mean values of binding energies and bond lengths of the two constituents.⁴

The diagrams of the cohesive energy and bond length versus period number and column number reveal the two main factors controlling type and strength of 2D bonding and structure of main-group II–VI monolayers. Covalent 2D bonding depends on the inherent periodicity of atom size of the columns, mostly following the tabulated van der Waals diameter. Furthermore, the periodic variation of the number of valence electrons along the periods describes the performance of the groups with a deficiency or a surplus of valence electrons in comparison with octet stability. The atomic orbital-hybridization concept offers a simple explanation of these fundamental findings. The 2D bonding-structure relation is consistent with an inverse quadratic relationship between covalent



bonding and bond length. Weaker metallic-type interaction appears for group-II and group-VI monolayers, as well as period-VI monolayers, with large separation from the graphene position in the periodic table. This position may be identified as the center of perfect covalent bonding. Hence, the predictive power of the periodic table gives access to general guidelines of 2D bonding and structure formation and allows an assessment of published data.

Notes

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Conflict of Interest

There are no conflicts of interest to declare.

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