Effective potentials for 6-coordinated Boron: structural geometry approach

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Abstract. – We have built a database of ab-initio total energies for elemental Boron in over 60 hypothetical crystal structures of varying coordination Z, such that every atom is equivalent. Fitting to each subset with a particular Z, we extract a classical effective potential, written as a sum over coordination shells and dominated by three-atom (bond angle dependent) terms. In the case Z = 6 (lowest in energy and most relevant), the classical potential has a typical error of 0.1 eV/atom, and favours the “inverted-umbrellas” environment seen in real Boron.

Introduction. – Boron stands out among the elements for the complexity and polymorphous variety of its structures \[\text{1}\]. The structures are networks built from icosahedrally symmetric clusters, and the typical “inverted-umbrella” coordination shell is asymmetrical, containing five neighbors on one side and one on the other. The stable phase (\(\beta\)-B) is currently modeled with 320 atoms/unit cell. Of the metastable allotropes \[\text{1}\], only \(\alpha_{12}\) and \(T_{50}\) have solved structures \[\text{3}\], the latter of which is stabilized by 4% N atoms \[\text{3}\]. The simplest phase \(\alpha_{12}\) contains 3-centered bonds both within and between icosahedra \[\text{1}\]. It was thought that bonding within icosahedra is metallic and weaker, while inter-icosahedral bonds are covalent and strong \[\text{1,3}\]; however, recent experiments have questioned this behavior \[\text{1,3}\].

Boron is the only plausible candidate for a single-element or covalent quasicrystal, which can be speculatively modeled \[\text{3,4}\] on either \(\alpha_{12}\)-B or \(\beta\)-B. This idea inspired the discovery of a new Boron phase \[\text{1}\], as well as the prediction of Boron nanotubes \[\text{12}\].

Our motivation is to compare the energies of alternate Boron structures. Selected crystal structures \[\text{4,5}\], finite icosahedral clusters \[\text{6}\], micrometeorite segments, or sheet fragments \[\text{12}\] were compared by direct ab-initio calculations. Such computations, however, are limited to \(O(10^2)\) atoms whereas real Boron has more atoms per unit cell, and quasicrystal models require \(\sim 10^5\) atoms. Furthermore Monte Carlo and/or molecular dynamics simulations are desirable, especially for the liquid \[\text{4}\].

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A tractable approximation is required of the ab-initio total energy as a function of atomic positions, such as a classical (many-atom) potential. This potential must reasonably represent the energy not only for the ground-state structure with slight distortions, but also for relatively high-energy local environments, such as occur in defects or sometimes in complex ground states. We know no previous attempts at such a potential. (The closest precursor of our work is Lee’s study of a few Boron structures [15], comparing atomic-orbital total energies with a simpler geometrical function of the closed circuits in the Boron network.)

We start from a general form of potential into which all Silicon potentials [16, 17, 18, 19] could be cast, a sum $E_{\text{total}} = \sum_i E_i$ over interactions local to each coordination shell: The site energy $E_i$ of atom $i$ with coordination number $Z_i$ is broken into terms depending on one, two, etc. of its neighbors $j, k, \ldots$:

$$E_i = \sum_j f_{Z_i}(r_{ij}) + \sum_{j \neq k} G_{Z_i}(r_{ij}, r_{ik}, \theta_{jk}^{(i)}) + \ldots$$

(1)

where $r_{ij}$ is the distance from atom $i$ to $j$, and $\theta_{jk}^{(i)}$ the angle formed by two neighbours $j, k$ and center $i$. (We shall assume later that $j, k$ are restricted to “nearest” neighbours of site $i$.)

Those Si potentials mostly attempted to capture the role of $Z$ and the radial dependences. The dependence on bond angles (with fixed coordination and bond radius) is not so assured, even for Si. Three-body terms may be implicit, as each bond’s effective $Z$ depends on the surrounding atoms [17, 18]. Bazant et al [19] critiqued the angle dependence of prior potentials, but they too addressed it indirectly, by assuming various angular forms and checking which of these gave the most transferable radial behaviours.

In this letter, we develop the opposite approach: we isolate the angular dependence without a priori assumptions of analytic form, by fitting to a large database in which non-angular variables are held fixed. We have no hopes that a potential should be transferable to a structures with very different local order; thus our database must be a large family of structures, among which bond angles and coordination numbers vary independently. (1) This is not the case for previous databases of periodic structures. The reason is, in part, that at Boron’s typical coordination $Z = 6$, a much greater variety of coordination shells is plausible than at ordinary covalent ($Z = 3-4$) or metallic ($Z \approx 12$) coordinations.

Consider a database of structures in which all bond lengths are $R$, all coordination numbers are $Z$, and non-pair interactions are limited to nearest neighbors. Then eq. (1) reduces to

$$E_i = \sum_{j \neq i} f_{Z_i}(r_{ij}) + \sum_{j \neq k} G_{Z_i}(R, \theta_{jk}^{(i)}) + h_Z(i)$$

(2)

where $G_Z(R, \theta) \equiv G_Z(R, R, \theta)$, and $h_Z$ gathers all interactions beyond the three-body (or rather two-neighbor) terms. It is not obvious a priori what form $h_Z$ should have; we found empirically (see below) that four-body (three-neighbor) terms are not needed, but a $Z$-neighbor term $h_Z(i) \equiv c_Z(R)\xi(i)$ is needed. It is proportional to the “asymmetry” $\xi(i)$ of coordination shell $i$ (originally introduced to characterize dangling bonds [18]):

$$\xi(i) = \frac{|\sum_j r_{ij}|}{(1/Z) \sum_j |r_{ij}|}$$

(3)

where $r_{ij}$ is the vector from atom $i$ to its neighbour $j$. (The denominator is the mean nearest-neighbour distance.)

(1) We can quantify how well our database samples the space of possible coordination shells, by use of a metric which defines a distance in this space [20].
Fig. 1. – Some less familiar Z6 structures. Bravais lattice vertices are indicated by ∗. For layered structures, atoms • are nearer to the viewer than ◦. (a) Kagome, (b) i-dodec, (c) Pµ, (d) Pσ, (e) two layers in T-lattice (the full cubic structure is an ABC stacking of Kagome layers) (f) two layers in SC-co (full structure is • • ◦ stacking), (g) SC-ico, (h) tube-σ: the σ-lattice at top is rolled into tubes (identifying the points connected by the dashed curve) which are seen end-on at bottom.

Now, restrict the database further so that every structure is “uniform” i.e. all sites are crystallographically equivalent and have the same local environment; We investigate those uniform structures in which all nearest neighbour distances are made equal (or nearly so), the better to separate the R-dependence from the angular effects.

Then $E_i$ must be equated with the total energy per atom, as found from an LDA calculation. Now assume that, within the database, only a discrete set of inter-neighbor angles is possible, $\theta_a \quad (a = 1, 2, \ldots)$; we realize this approximately by simply dividing the range of $\theta$ into several bins. Then – if the structures sufficiently outnumber the angular bins – one obtains $G_Z(R, \theta_a)$ for each angle by a simple linear fit. For each value of the scale $R$, the coefficients $\{G_Z(R, \theta_a)\}$ and $c_Z(R)$ satisfy a set of linear equations:

$$E_m(R) - Zf_Z(R) = \sum_a N_m(\theta_a)G_Z(R, \theta_a) + c_Z(R)\xi_m$$

(4)

Here $m$ runs over the structures of the same $Z$, and $N_m(\theta_a)$ is the number times angle $\theta_a$ occurs in the coordination shell of structure $m$. The whole procedure can be repeated for each $Z$.

Structural database. – For our database, we adopted or invented over 60 uniform structures [20], spanning coordination numbers $Z$ from 3 to 12, and exhibiting a variety of angular patterns for each $Z$; We shall present details only for 6-coordinated ($Z6$) structures, which are relevant to the real phases: 80% of the sites in $\beta$-B, and 50% in $\alpha_{12}$($B$), have $Z = 6$. The same procedure was carried out for $Z = 4, 5$ and 7. [20]

Our Z6 structures, of course, include the simple cubic (SC) and the triangular (tri) lattices (parentheses give codes to be used henceforth). We systematically constructed more Z6 structures by stacking Z4 planar lattices, such as the 3.4.6.4 pattern of inter-penetrating dodecagons (i-dodec) or the 3.6.3.6 lattice (Kagome), see Figure [a,b]. We also stacked Z5 planar lattices such as 32.4.3.4 (called $\sigma$) or the 33.4.4 (called $\mu$), puckering alternate layers so that each vertex gained one more neighbour from the layer above or below: this produced the
Table I. – Local environments of Z\textsubscript{6} structures.

| Structure   | \(N_2\) | \(N_3\) | 60° | 90° | 108° | 120° | 135° | 150° | 180° |
|-------------|---------|---------|-----|-----|------|------|------|------|------|
| SC          | 12      | 8       | 0   | 12  | 0    | 0    | 0    | 3    | 0    |
| tri         | 0       | 6       | 6   | 0   | 0    | 6    | 0    | 3    | 0    |
| SC-co       | 7       | 6       | 2   | 7   | 0    | 2    | 4    | 0    | 0.586|
| T-lattice   | 0       | 12      | 6   | 0   | 0    | 6    | 0    | 3    | 0    |
| i-dodec     | 10      | 6       | 1   | 10  | 0    | 1    | 0    | 2    | 1    |
| Kagome      | 8       | 4       | 2   | 8   | 0    | 2    | 0    | 3    | 0    |
| SC-ico      | 1       | 10      | 5   | 1   | 7    | 0    | 2    | 0    | 1.854|
| \(P_\sigma\) | 4\textsuperscript{b} | 12\textsuperscript{c} | 3   | 3\textsuperscript{d} | 4\textsuperscript{d} | 1\textsuperscript{d} | 2\textsuperscript{d} | 2\textsuperscript{d} | 0    | 0.263|
| \(P_\mu\)   | 5\textsuperscript{b} | 10\textsuperscript{c} | 3   | 4   | 3\textsuperscript{d} | 2    | 2\textsuperscript{d} | 0    | 1    | 0.771|
| tube-tri    | 0       | 6\textsuperscript{a} | 6   | 0   | 0    | 6\textsuperscript{b} | 1    | 0    | 2\textsuperscript{d} | 1.163|
| tube-\(\sigma\)\textsuperscript{a} | 5\textsuperscript{b} | 7\textsuperscript{c} | 3   | 5\textsuperscript{b} | 2\textsuperscript{b} | 2    | 0    | 3\textsuperscript{b} | 0    | 0.936|

Z\textsubscript{6} puckered (\(P_\sigma\)) and (\(P_\mu\)) structures, respectively as in Figure 1(c,d). As far as possible, the inter- and intra-unit bond lengths in our packings and stackings were made equal.

Figure 1(e,f,g) show inherently three-dimensional networks: a simple cubic array of cuboctahedra (SC-co); the (T-lattice) – also called “pyrochlore lattice” – consisting of a diamond lattice’s bond midpoints; and icosahedra placed on a simple cubic lattice (SC-ico). We also rolled a triangular lattice into a single infinite nanotube  with a circumference of 8 edges (tube-tri, not illustrated). Finally, we rolled the Z\textsubscript{5} 3\^2-3.4.4 (\(\sigma\)) lattice into a tube whose circumference is the dotted arc in Figure 1(h), and packing such tubes in a square array. This made the “tube-\(\sigma\)” structure, in which one neighbor of each atom belongs to an adjacent tube.

Table I summarizes geometric data on the coordination environments of these Z\textsubscript{6} structures.

LDA Results. – We performed an \textit{ab initio} total energy calculation for each structure in our database, in the local density approximation with extended norm and hardness conserving pseudo-potentials. We used all planewaves with kinetic energy up to 54.5 Ry. The Brillouin zone is sampled with a k-point density of at least \((16\cdot3\cdot3\cdot3)\). Band structure energies are converged to within \(10^{-6}\) Ry in each calculation. The convergence with respect to k-point density shows a precision of 0.03 eV for energy comparison among different structures.

We varied the lattice constant of each structure (a uniform scale factor, without any relaxation of positions). Figure 3(a) collects the cohesive energy (per atom) of each Z\textsubscript{6} structure as a function of the nearest neighbour distance \(R\). The inset shows the single-well-like shape for \(R\) up to 5 Å for three representative structures, SC, tri, and SC-ico; beyond \(R = 3\) Å, the curves for all structures converge, approaching the non-bonding limit. The main figure

\(\textsuperscript{2}\) SC-ico was introduced in Ref. 15, but misidentified there as “primitive orthorhombic.”

\(\textsuperscript{3}\) In the table, footnote \(a\) means nearest (\(\sim R\)) neighbours are not at identical distances; \(b\) means \(N_2\) has a tolerance of 0.14\(R\) in distance; \(c\) means neighbors at various distances between \(\sqrt{2}R\) and \(\sqrt{3}R\) are binned in \(N_3\); \(d\) means \(\theta_a\) has a tolerance of 6° in angle, and the “180°” bin in tube-tri is actually at 169°.
Fig. 2. – (a). Cohesive energy $E_i(R)$ for $Z_6$ structures. In the inset, the three representative structures are SC (line), tri (dotted), and SC-ico (long-dash). The region showing the energy wells is magnified in the main figure. The structures are, in order of lowest to highest energy at $R = 1.8\text{Å}$, ideal-$\alpha_{12}$ (line), SC-ico (long-dash), SC-co ($\Box$), tube-$\sigma$ ($\circ$), T-lattice (line), P-$\mu$ (long-dash), tri (short-dash), P-$\sigma$ ($\times$), tube-tri (line), SC (line), i-dodec ($\diamond$), and Kagome ($\times$). (b). Angular and asymmetry potentials. The fitted $G(R, \theta)$ is plotted with symbols {$\ast$, $\circ$, $\times$, $+$, $\ast$}, corresponding to $R = \{1.6, 1.7, 1.8, 1.9, 2.0\}$ Å; the first and last sets are connected by solid and dashed lines, respectively. The coefficient $c(R)$ (see eqs. (2) and (3) is shown by the same symbols, on the same scale, in the “Asym” column.

enlarges the physically relevant range $R \in [1.6, 2.0] \text{Å}$, to highlight the differences among the structures. The lowest energy curve shown is the “ideal-$\alpha_{12}$” phase, topologically same as $\alpha_{12}$ but with all nearest neighbour distances set equal. (This was omitted from our $Z_6$ database because it has two kinds of sites, of which one has $Z = 7$.) The $Z_6$ uniform structure of lowest energy is SC-ico, another way of connecting $\text{B}_{12}$ icosahedra so each atom has one inter-icosahedral bond. Slightly higher is SC-co, which can be viewed analogously as a packing of $\text{B}_{12}$ cuboctahedra in place of icosahedra, with each atom having two inter-cluster bonds.

**Fitting of an effective potential.** – The simplest effective potential would be a single-well two-body potential of typical shape, so the nearest-neighbour radius lies close to the minimum of the well, while further neighbours contribute at the tail of the well. Then structures of the same coordination would have similar energies (from the near-neighbor terms) with small differences due to the farther neighbors. This will not work in general and failed badly for our energy curves. Basically, one is asking the tail of $f_Z(r)$ in (2) to account for both the total energy when $R \to \sqrt{2}R$ or $\sqrt{3}R$ – a sizeable fraction of the well depth – as well as the dependence on $N_2$ and $N_3$ (see Table I) among structures of the same $Z$ – which is smaller, as seen in Figure 2. We conclude that the two-body potential must be essentially truncated after the nearest-neighbor distance. It follows that the first term in (2) reduces to $Zf(R)$; the energy differences among structures of the same coordination $Z$ must be attributed to higher-order potentials. For each $Z$, we must choose a reference structure for which the higher-order terms are set to zero (thereby defining $Zf_{Z}(R)$ to be its energy curve); for $Z_6$ we chose the simple cubic (SC) structure.

Thus we are fitting the $E_m(R)$ from Figure (a) to the linear equations (4), in which
Table 6 (minus columns $N_2$ and $N_3$) constitutes the 11 \times 8 matrix of coefficients. Eqs. (1) are overdetermined (by three degrees of freedom); hence for each $R$, we can solve for $G_0(R, \theta, \alpha)$ and $c_0(R)$ in a least-squares sense, without assuming any functional forms. The resulting fit (Figure 2) shows the angular potential $G_0(R, \theta)$ increases monotonically with $\theta$. Both $c_0(R)$ and $G_0(R, \theta)$ show rapid decay as a function of $R$. Qualitatively similar $(R, \theta)$ dependences are found for $Z = 4, 5$, and 7 structures [24], except that for $Z = 4$ the sign of $G_4$ is reversed. The monotonicity of the fitted $G_Z(R, \theta)$, for all four values of $Z$, argues for the physical validity of the result: a spurious fit should produce random fluctuations as a function of $\theta$.

Discussion. – The first check on our potentials is that, among the 11 structures in our $Z6$ database, the total energies are in the right order (apart from exchange of certain close ones), with an average error of 0.14 eV/atom (for $R$ in the bonding range). Furthermore the “inverted-umbrella” coordination shell of real Boron – which was not used in our database – was correctly found lower (by $\sim 1$ eV) than any of the $Z6$ shells that were used. We also performed a Monte Carlo search of random $Z6$ environments, at the valid $R = 1.7\,\text{Å}$ and found the inverted-umbrella was the second-lowest in energy. Finally, our $G_6$ disfavouring $\theta = 180^\circ$ (see Fig. 3) correctly predicts that Boron in triangular sheets buckles, as found by ab-initio calculations [2].

Empirical tight-binding calculations are the successful intermediate between a fully ab-initio and our classical-potential approach [22]. It would be worthwhile to fit our database in this fashion, especially if longer-range, metallic interactions are found within the clusters, tubes, and sheets. Tight-binding (atomic orbital) total energies can also be expanded in moments related to circuits of three or four atoms. Structure selection and bond angles was studied in this way by Lee et al [13] for selected packings of $\text{B}_{12}$ icosahedra. It would be interesting to analytically relate the above-mentioned circuits to the form of classical potentials found by us.

Can our potentials, limited to fixed $Z$ and $R$, be extended to arbitrary Boron structures? First note that our results (Fig. 3) are well fit by a separable form $G_Z(R, R, \theta) = g_Z(R)^2 A_Z(\theta)$. Provided the results are physically reasonable, it is straightforward to interpolate $g_Z$ and $A_Z$ with respect to $R$ and $\theta$, respectively, and (less easily) with respect to $Z$. Then one just needs to replace the $Z$ definition used in this paper by one of the well-known formulas that depends smoothly on the coordinates, e.g. $(\sum_j r_{ij}^{-5})^2 / (\sum_j r_{ij}^{-10})$. So finally we would set $G_Z(r_i, r_j, \theta) = g_Z(r_i) g_Z(r_j) A_Z(\theta).$ in eq. (1), well-defined for general structures (provided $4 \leq Z \leq 7$ for all atoms); this would reduce to our present results (2) within each family of $Z$-coordinated uniform structures.

An attractive application of classical potentials would be in the liquid phase. Here ab initio molecular dynamics studies (on a 48 atom system) found detailed results for bond-angle distributions and other correlation functions [4], in good agreement with experiment [23]. Those authors also note [4] that $Z = 6$ but the icosahedra are broken up (the inverted-umbrella coordination shell is no longer found), contrary to earlier thought. Potentials would offer a chance to model the structure of amorphous $a$-B, in which few details are known but (from radial distribution functions) the $B_{12}$ icosahedron is believed to be the motif [24]. It would be interesting to explore more ordered (e.g. micro-quasicrystalline) or less ordered (like the liquid) variants of this picture. Finally, if our method were extended to extract a classical potential from Si and B/Si structures, this could be applied to the icosahedral [25] or cuboctahedral [26] $B_{12}$ clusters which are believed to precipitate in B-doped Si.

(4) The uninverted umbrella was lowest in energy, but there exists no extended structure in which all atoms have this coordination shell.
To conclude, we have presented a novel approach to generating a database for potential fitting which includes so many structures that the angular potential may be fitted rather than assumed. We obtain a reasonable description using potential terms that are local to the coordination shell of each atom, and which could be extended to general Boron structures. Modeling of the speculative or poorly-known quasicrystal, amorphous, unsolved crystal, liquid, and Si inclusion forms of Boron would profit from such a potential.

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