

FROM FINITE TO INFINITE CRYSTALS: SOME ELECTRONIC PROPERTIES OF BCC CLUSTERS

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Using results obtained within the framework of the tight binding nearest neighbour approximation (BÍLEK O., SKÁLA L., Czech. J. Phys. B 28 (1978), 1003) the analytical formulae for the band width, binding energy per atom, charge orders and bond orders of bcc clusters having a rectangular parallelepiped geometry are given. Numerical results for the number of atoms in the cluster in the range $9 - 2 \times 10^6$ illustrate the convergence of these properties. The asymptotic form of the formulae yields further detailed information. The band width and bond orders converge more quickly than the binding energy while the charge orders are equal to unity independently of the size of the cluster.

1. INTRODUCTION

In recent years, the investigation of physical and chemical properties of clusters as a function of their size has been of increasing interest (see e.g. [1-8]). In principle, the convergence of physical properties of clusters to their bulk counterpart can be estimated by increasing the number of atoms \mathcal{N} in the cluster. Using standard quantum chemical methods as EHT, CNDO etc. \mathcal{N} is restricted by computational possibilities and in fact is too small to approach the infinite crystal. However, this restriction is removed if the eigenvalues and eigenfunctions can be obtained in closed form ("the analytical cluster model" [2]). It is of course at the cost of very crude approximations [1-8].

The aim of this paper is to present analytical and numerical results for the bcc clusters with (100) surface making use of the analytical formulae given in [1]. Analogous numerical investigations have been done by BLIZNAKOV and DELINESHEV for fcc clusters [3] and by KADURA and KÜNNE for fcc clusters [4]. In the case of bcc clusters not only eigenvalues and eigenfunctions but even the band width, binding energy and information about the distribution of electrons (charge orders and bond orders) can be obtained in closed form. The analytical formulae can also be written in asymptotically valid forms and they yield further interesting information.

2. DESCRIPTION OF CLUSTERS

The clusters taken into consideration are cut-outs of the infinite bcc crystal in the form of a rectangular parallelepiped with (100) surface (see Fig. 1). Atomic sites are

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given by triplets (l, m, n) subjected to the conditions

$$(1) \quad 1 \leq l \leq L, \quad 1 \leq m \leq M, \quad 1 \leq n \leq N, \\ l, m \text{ and } n \text{ all odd or all even.}$$

Size and shape of the cluster are specified by integers L, M and N . For the sake of simplicity we assume here that L, M and N are odd. The number of atoms in the cluster is then equal to

$$(2) \quad \mathcal{N} = \frac{(L+1)(M+1)(N+1)}{8} + \frac{(L-1)(M-1)(N-1)}{8}.$$

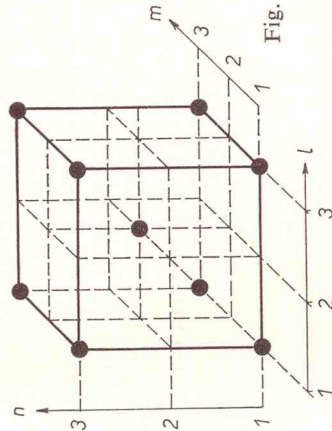


Fig. 1. Enumeration of atoms in the bcc cluster.

According to [1] the tight binding s-like quasi-band of the cluster is given by the energy levels

$$(3) \quad E_{pqr} = \alpha + 8\beta \cos \frac{p\pi}{L+1} \cos \frac{q\pi}{M+1} \cos \frac{r\pi}{N+1}.$$

Here, α is the coulomb integral and β is the resonance integral ($\beta < 0$). In the case when all numbers L, M and N are odd the list of all quantum states reads as follows [1]

$$(4a) \quad p = 1, \dots, \frac{L+1}{2}; \quad q = 1, \dots, \frac{M+1}{2}; \quad r = 1, \dots, \frac{N+1}{2},$$

$$(4b) \quad p = \frac{L+3}{2}, \dots, L; \quad q = 1, \dots, \frac{M-1}{2}; \quad r = 1, \dots, \frac{N-1}{2}.$$

If $p = \frac{1}{2}(L+1)$ or $q = \frac{1}{2}(M+1)$ or $r = \frac{1}{2}(N+1)$ we get from (3) the center of the band $E = \alpha$. This level is at least $(LM + LN + MN + 1)/4$ -fold degenerate. The other levels are symmetrical with respect to $E = \alpha$. Denoting the s-like atomic orbital located at the site (l, m, n) as $\varphi(\mathbf{r} - \mathbf{r}_{lmn})$, the normalized tight binding wave function

$$(5) \quad \psi^{par} = \sum_{l,m,n} c_{lmn}^{par} \varphi(\mathbf{r} - \mathbf{r}_{lmn})$$

determined by the coefficients

$$c_{lmm}^{par} = \sqrt{\frac{32 \int^{par}}{(L+1)(M+1)(N+1)}} \sin \frac{l p \pi}{L+1} \sin \frac{m q \pi}{M+1} \sin \frac{n r \pi}{N+1},$$

where

$$f^{par} = 1 + \delta_{2p-1, l} \delta_{2q-1, m} + \delta_{2p-1, l} \delta_{2r-1, n} + \delta_{2q-1, m} \delta_{2r-1, n},$$

$$l = 1, \dots, L; \quad m = 1, \dots, M; \quad n = 1, \dots, N,$$

l and n all odd or all even.

3. RESULTS AND DISCUSSION

In this section we present analytical formulae for the band width (*BW*), binding energy per atom (*BE*), charge order (Q_{lmm}) and bond order ($P_{lmm, l+1, m+1, n+1}$) as a function of the size and shape of the cluster specified by L , M and N . Numerical results for the clusters in the form of the cube ($L = M = N$) illustrate the convergence of these quantities to their values corresponding to $L, M, N \rightarrow \infty$.

Band width

Independently of the size and shape of the cluster the lower band edge of the s -like band (3) is determined by $p = q = r = 1$. The upper band edge is given, for instance, by $p = L, q = M$ and $r = N$ (see Eqs. (4)). Increasing the number of atoms the lower band edge decreases, the upper band edge increases, and, as a result, band width

$$BW = 16|\beta| \cos \frac{\pi}{L+1} \cos \frac{\pi}{M+1} \cos \frac{\pi}{N+1}$$

decreases. The rate of convergence of this and other quantities is discussed in sections 3.4 and 3.5 in detail.

Binding energy per atom

In order to obtain the binding energy we sum the energies of all occupied levels subtract the energy of free atoms $\mathcal{N}\alpha$ and divide the result by \mathcal{N} . In the ground state all levels given by (4a) are occupied by two electrons except for $p = \frac{1}{2}(L+1)$ ($l = \frac{1}{2}(M+1)$ or $r = \frac{1}{2}(N+1)$). The remaining electrons occupy the degenerate levels $l = 1, \dots, L$ ($m = 1, \dots, M$ or $n = 1, \dots, N$). The sums of cosines can be calculated analytically so that the formula for the binding energy has the form

$$BE = \frac{2\beta}{\mathcal{N}} \left(\operatorname{ctg} \frac{\pi}{2(L+1)} - 1 \right) \left(\operatorname{ctg} \frac{\pi}{2(M+1)} - 1 \right) \left(\operatorname{ctg} \frac{\pi}{2(N+1)} - 1 \right).$$

Increasing L, M and N to the infinity the binding energy becomes

$$BE(L \rightarrow \infty, M \rightarrow \infty, N \rightarrow \infty) = \left(\frac{4}{\pi}\right)^3 \beta.$$

The convergence of the binding energy (8) to this value is shown in Fig. 2. It is obvious that the convergence is rather slow. Even for $\sim 10^6$ atoms we get a relatively large difference with respect to the infinite crystal value.

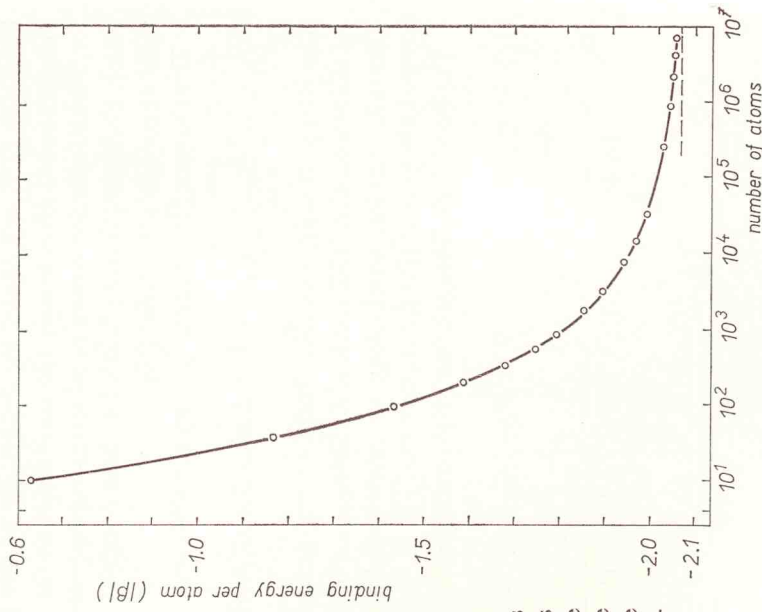


Fig. 2. Binding energy per atom *BE* as a function of the total number of atoms \mathcal{N} in the cluster. The cluster has the form of a cube ($L = M = N$). The dashed line on the right-hand side shows the binding energy of the infinite crystal.

3.3 Charge order and bond order

In contrast to the band width and binding energy the distribution of electrons is a local property. As usual we calculate the charge orders and bond orders summing products of couples of coefficients (6) belonging to the same or neighbouring atoms, respectively. At the same time, the products are multiplied by the appropriate occupation numbers (0, 1 or 2).

At this point, certain ambiguity of the usual definition of the charge order and bond order should be mentioned. The definition of the charge order

$$Q_{lmm} = \sum_{p,q,r} g_{pqr} |c_{lmm}^{par}|^2,$$

ere g_{par} is the occupation number of the energy level E_{par} , becomes ambiguous whenever the highest occupied level is at once degenerate and just partly occupied. For example, in our case $(LM + LN + MN + 1)/4$ electrons must be distributed the same number of quantum states corresponding to $E = \alpha$. However, since the number of electrons being found in each state can be equal to 0, 1 or 2, their distribution can be performed in different ways. If all of them are realized with equal probabilities the resulting charge order can be calculated as the mean value of the particular charge orders. It is easy to show, however, that when the number of electrons belonging to $E = \alpha$ equals the degeneracy of this level, the complicated procedure mentioned gives exactly the same result as the particular charge order obtained the uniform occupation of all states corresponding to $E = \alpha$ (one electron in each site). Formula (9) given below has been obtained just in this way. The same comment applies to bond order (10).

The charge order is equal to unity for all atoms

$$Q_{lmm} = 1; \quad l, m \text{ and } n \text{ all even or all odd.}$$

The charge is uniformly distributed among atoms in the cluster independently of shape and size. This result is a consequence of the bcc structure (in terms of the quantum chemical terminology we investigate here alternant clusters) and it does hold in general (for fcc clusters see [5]).

The bond order between two neighbouring atoms

$$P_{lmm, l+1 m+1 n+1} = \frac{1}{(L+1)(M+1)(N+1)} \left(\text{ctg} \frac{\pi}{2(L+1)} - (-1)^l \text{ctg} \frac{(2l+1)\pi}{2(L+1)} \right) \times \left(\text{ctg} \frac{\pi}{2(M+1)} - (-1)^m \text{ctg} \frac{(2m+1)\pi}{2(M+1)} \right) \times \left(\text{ctg} \frac{\pi}{2(N+1)} - (-1)^n \text{ctg} \frac{(2n+1)\pi}{2(N+1)} \right),$$

l, m and n all even or all odd,

ends on the size and shape of the cluster as well as on the position of the atom (l, m, n) . The convergence of the bond orders as a function of the number of atoms is shown in Fig. 3.

The bond order has the maximum value for the corner atom, probably because it interacts with one neighbour only. For other sites, where the bond capability of the atom must be distributed among a greater number of atoms, the bond orders are smaller to an adequate extent.

Increasing L, M and N to the infinity, the bond orders of the atom at the corner, middle of the edge, center of the face and in the center of the cluster become

$$\left(\frac{4}{3}\right)^3 \left(\frac{2}{\pi}\right)^3, \quad \left(\frac{4}{3}\right)^2 \left(\frac{2}{\pi}\right)^3, \quad \frac{4}{3} \left(\frac{2}{\pi}\right)^3 \quad \text{and} \quad \left(\frac{2}{\pi}\right)^3,$$

respectively. These values are indicated by dashed lines in Fig. 3.

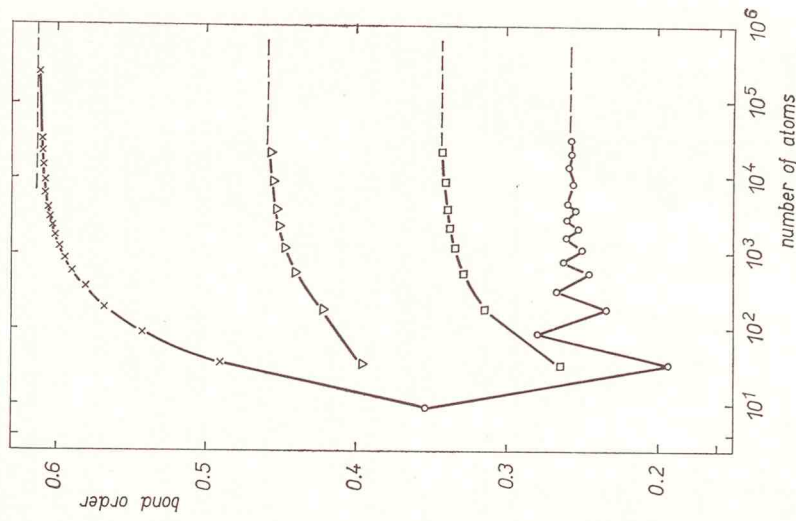


Fig. 3. Bond orders $P_{lmm, l+1 m+1 n+1}$ for different positions of the atom (l, m, n) as a function of the total number of atoms in the cluster. ○ — atom (l, m, n) in the center of the cluster ($l = m = n = (L+1)/2$),

- — center of the face ($l = m = (L+1)/2, n = 1$),
- ▽ — middle of the edge ($l = (L+1)/2, m = n = 1$),
- × — corner of the cluster ($l = m = n = 1$).

As regards the center of the face and middle of the edge, the bond orders are plotted for $L = 4k + 1$ only since for $L = 4k + 3$ there are no atoms at these sites. The cluster has the form of a cube ($L = M = N$). The dashed lines give the corresponding values for the infinite crystal.

3.4 Numerical estimation of convergence

In this section we discuss relative deviations of the quantities in question from the corresponding values for the infinite crystal. The clusters are assumed to have a cubic form ($L = M = N$). Relative deviations of the band width, binding energy and bond orders defined in the usual way

$$\Delta BW(\mathcal{N}) = \frac{BW(\infty) - BW(\mathcal{N})}{BW(\infty)} 100 [\%] \text{ etc.},$$

are given for some L in Table 1.

For instance, in order to get the band width of the infinite crystal with an error less than 10, 5 or 1 percent, it is sufficient to take the cluster with $L = 11, 17$ or 39. If we require the same accuracy for the binding energy, the cluster with $L = 21, 37$ or 175 must be taken.

Similar conclusions hold true for the bond orders. The corresponding values of L for the atom in the center of the cluster, at the center of the face, middle of the edge and corner are $L = 7, 11, 31, L = 9, 13, 33, L = 9, 13, 29$ and $L = 9, 13, 27$, respectively. We see that the rate of convergence of the considered bond orders practically does not depend on the position of the atom to which it relates.

The convergence of bond orders is the quickest one. The band width converges somewhat more slowly. In comparison with these two quantities, the convergence of the binding energy is very slow.

The convergence of the bond order corresponding to the atom in the center of the cluster has an oscillatory character (different rate of the convergence for $L = 4k + 1, k = 1, 2, \dots$ and for $L = 4k + 3, k = 0, 1, 2, \dots$ — something like "size effect"). The absolute value of the relative deviation of the bond order of the central atom from the infinite crystal value is about two times greater for $L = 4k + 1$ than for $L = 4k + 3$. It is interesting that the bond capability of the central atom can be both greater ($L = 4k + 3$) and lower ($L = 4k + 1$) than for the infinite crystal.

In all other cases investigated here the convergence of analyzed quantities is monotonic (see Table 1).

Table 1

L	\mathcal{N}	ΔBW [%]	ΔBE [%]	ΔP [%]			
				center of the cluster	center of the face	middle of the edge	corner
3	9	65	70	-37	—	—	42
5	35	35	44	25	24	22	20
7	91	21	30	-8.1	—	—	11
9	189	14	23	9.6	8.8	8.1	7.3
11	341	10	18	-3.5	—	—	5.1
13	559	7.3	15	5.0	4.6	4.2	3.8
15	855	5.7	13	-1.9	—	—	2.9
17	1241	4.5	11	3.0	2.8	2.5	2.3
19	1729	3.6	10	-1.2	—	—	1.8
21	2331	3.0	9.1	2.0	1.9	1.7	1.5
23	29449	0.59	3.7	0.39	0.36	0.33	0.30
25	33201	0.55	3.5	-0.18	—	—	0.27
27	242649	0.15	1.8	-0.049	—	—	0.074
29	257651	0.14	1.7	0.095	0.087	0.079	0.071
31	1970299	0.037	0.87	-0.012	—	—	0.019
33	2030301	0.036	0.86	0.024	0.022	0.020	0.018

3.5 Asymptotical laws of convergence

In order to better understand the laws of convergence we discuss the asymptotical behaviour of Eqs. (7), (8) and (10). We confine ourselves to the cubic clusters ($L = M = N$).

The asymptotically valid formula for the band width exact to the second power of $1/L$ reads as follows

$$BW_{\text{asym}}(L) = BW(\infty) \left(1 - \frac{3}{2} \frac{\pi^2}{L^2} \right).$$

Take notice of the $1/L^2$ convergence. It explains the relatively quick convergence of the band width discussed in the preceding section.

The relative deviation of the band width calculated according to this approximate formula from its exact value is defined as

$$\Delta BW_{\text{asym}}(L) = \frac{BW_{\text{asym}}(L) - BW(L)}{BW(L)} \cdot 100 \text{ [%]}$$

and is given for some L is Table 2.

Table 2

L	\mathcal{N}	ΔBW_{asym} [%]	ΔBE_{asym} [%]	ΔP_{asym} [%]			
				center of the cluster	center of the face	middle of the edge	corner
3	9	-280	41	13	—	—	-69
5	35	-37	16	-19	-16	-14	-12
7	91	-12	8.6	1.9	—	—	-4.3
9	189	-5.0	5.3	-2.8	-2.5	-2.3	-2.0
11	341	-2.6	3.6	0.56	—	—	-1.1
13	559	-1.5	2.6	-0.92	-0.83	-0.74	-0.65
15	855	-0.98	1.9	0.24	—	—	-0.43
17	1241	-0.66	1.5	-0.41	-0.37	-0.33	-0.29
19	1729	-0.47	1.2	0.12	—	—	-0.21
21	2331	-0.34	0.99	-0.21	-0.19	-0.17	-0.16
23	29449	-0.26	0.18	-0.017	-0.015	-0.014	-0.012
25	33201	-0.23	0.17	0.070	—	—	-0.011
27	242649	-0.0031	0.046	0.00099	—	—	-0.0015
29	257651	-0.0029	0.044	-0.00019	-0.0018	-0.0016	-0.0014

The analogous formula for the binding energy exact to the first power of $1/L$ has the form

$$BE_{\text{asym}}(L) = BE(\infty) \left(1 - 3 \left(\frac{\pi}{2} - 1 \right) / L \right).$$

The $1/L$ convergence is in agreement with the slow convergence shown in Fig. 2 and Table 1. Formula (12) is the same as for the sc cluster except for the constant before $1/L$ [6].

Let us discuss now the asymptotical behaviour of the bond orders. The formulae exact to the second power of $1/L$ are as follows

$$(13) \quad P_{\text{asym}}(L) = P(\infty) \left(1 - \frac{\pi^2}{L^2} \right), \quad L = 4k + 1 \quad \left. \begin{array}{l} \text{atom} \\ \text{center of the cube} \end{array} \right\}$$

$$P(\infty) \left(1 + \frac{\pi^2}{2L^2} \right), \quad L = 4k + 3$$

$$P(\infty) \left(1 - \frac{11\pi^2}{12L^2} \right), \quad L = 4k + 1 \quad \text{center of the face}$$

$$P(\infty) \left(1 - \frac{5\pi^2}{6L^2} \right), \quad L = 4k + 1 \quad \text{middle of the edge}$$

$$P(\infty) \left(1 - \frac{3\pi^2}{4L^2} \right) \quad \text{corner.}$$

We get again the $1/L^2$ convergence. The oscillatory behaviour of the bond order of the central atom shown in Fig. 3 can be now easily verified. The absolute value of the relative deviation of the central atom bond order from the infinite crystal value is for $L = 4k + 1$ $1/(L^2) = 2$ times greater than for $L = L - 2$.

To estimate the range of validity of the approximate formulae (11)–(13) see Table 2. In order to achieve 10, 5 or 1 percent accuracy of the asymptotical formulae for the band width, binding energy and bond orders of the atom in the center of the cube, at the center of the face, middle of the edge and corner, it is sufficient to take $L = 9, 9, 15, L = 7, 11, 21, L = 7, 7, 11, L = 9, 13, 13, L = 9, 9, 13$ and $L = 7, 7, 13$, respectively. We see that the asymptotical formulae give an error less than one percent beginning with L in the range 11–21. For greater values of L the accuracy rapidly increases (omitted terms are of the order $1/L^2, 1/L^3, \dots$ for the binding energy and of the order $1/L^3, 1/L^4, \dots$ in other cases). It is interesting that the asymptotical formulae both for the binding energy and the bond order of the central atom for $L = 4k + 3$ give for large L values even closer to those for the infinite crystal than exact ones. In these two cases the omitted higher order terms slow down the convergence.

The question which should be clarified is whether the $1/L$ convergence of the binding energy and the $1/L^2$ convergence of the band width and bond orders take place in general (some results of [6] indicate that at least for the binding energy it is true) or whether it is a property of our simple model. In the former case, asymptotical formulae may be a useful tool for the investigation of physical properties of very large clusters.

4. CONCLUDING REMARKS

The results and conclusions presented in this paper are obtained within a very simple model so that the range of their validity should be re-examined using more sophisticated methods. On the other hand, the analytical form of all main results enables us to carry out calculations for practically arbitrary large clusters and so to bridge over the gap between finite and infinite crystals. Thus, investigations performed within the framework of the analytic cluster model should be considered as preliminary results which can show the way that is to be taken in order to obtain conclusions valid in general.

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