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On the Electronic Structure of Clusters Convergence to the Solid State Properties

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The relation of the electronic structure of clusters and solids, the consequences of the surface relaxation, and the conclusions following from the analytic cluster model and numerical calculations are investigated. It is shown that the electronic properties of clusters converge with increasing number of atoms at least as quickly as $1/N^{1/d}$ to zero, N being the total number of atoms and d the number of dimensions of the cluster ($d = 1, 2, 3$). The binding energy is characterized by $1/N^{1/d}$ convergence while the bandwidth, the lower band edge, and the bond order converge as the second power of this parameter.

Обсуждаются соотношения электронной структуры кластеров и твердых тел, следствия релаксации поверхности и результаты аналитических моделей и численных вычислений. В работе показывается что электронные свойства кластеров стремятся к свойствам твердых тел по крайней мере так быстро как $1/N^{1/d}$ к нулю. Здесь N число атомов и d число размеров кластера ($d = 1, 2, 3$). Энергия связи может быть характеризована $1/N^{1/d}$ сходимостью по сравнению с шириной зоны, нижней границей зоны и порядком связи которые сходятся как вторая степень этого параметра.

1. Introduction

The physics of clusters, as a bridge between the molecular and solid state physics, must include these two branches as a special case. Clusters are usually too large to investigate them by the theoretical methods of quantum chemistry and too small to use the assumption of the translational symmetry which reduces the order of the problem in the solid state theory. It is obvious that increasing the number of atoms in a cluster its electronic structure must converge to that of the solid. Convergence of different properties can be investigated, however, the density of states is obviously one of the most important ones. It appears that using general arguments the maximum differences of the density of states and other properties of the cluster and crystal can be given. The most important results of this approach are summarized in Section 2. Another problem is the influence of the relaxation of the surface where the potential and lattice constant can have other values than inside the cluster. This leads to changes of the density of states and further properties which can be estimated similarly as in the preceding case. Some general results are summarized in Section 3. The problem of the convergence of the cluster properties to those of the solid can be elucidated within the so-called analytic cluster model [1 to 9]. It is a model simple enough to yield the analytic solution of the Schrödinger equation and calculate at least some properties analytically. Till now, the analytic solutions for the clusters with s.c., f.c.c., b.c.c., and diamond lattice have been found [1 to 7]. The asymptotical laws of convergence (Section 4) obtained from the analytic cluster model interpolate

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cluster properties in the direction towards those of the solid. The form of these results together with their agreement with numerical calculations confirm the conclusions of the preceding sections.

2. Clusters and Infinite Crystals

The electronic structure of clusters and corresponding infinite crystals can be compared in the following way [4]. We cut out from the crystal a number of identical clusters in such a way that they do not mutually interact (see Fig. 1). In this way, only clusters with unrelaxed surface can be obtained. The relaxation of the surface can be taken into account in the following step (see Section 3). This idea means in the LCAO method the blocking of the corresponding Hamiltonian in the matrix form

$$H_{mn} = \int \varphi_m^* H \varphi_n \, d\tau, \quad (1)$$

where $\varphi_m(\mathbf{r})$ are basis functions of atomic-like character localized at the atoms of the cluster. If the matrix elements corresponding to the interaction among clusters are equal to zero the infinite crystal decomposes into a system of identical noninteracting clusters. It follows from the Ledermann theorem that the greater the clusters the smaller the difference of the density of states of a system of noninteracting clusters and the crystal.

This argument can be formulated more precisely by using the negative eigenvalue theorem from which the Ledermann theorem follows as a special case. It appears [4] that the integrated density of states normalized in such a way that $I(-\infty) = 0$, $\rho(\infty) = 1$ fulfils the following relation:

$$|I_{\text{unrel}}(E) - I_{\text{bulk}}(E)| \leq P. \quad (2)$$

Here, I_{unrel} and I_{bulk} is the integrated density of states of the cluster with the unrelaxed surface and the infinite crystal, respectively. P is an energy independent upper bound to their difference;

$$P = \lim_{n_{\text{bulk}} \rightarrow \infty} \frac{n_{\text{int}}}{n_{\text{bulk}}}, \quad (3)$$

where n_{int} is the number of the basis functions $\varphi_m(\mathbf{r})$ in the region of the interaction of the clusters and n_{bulk} the total number of the basis functions in the crystal. As an example, we consider the cluster in the form of the cube with the s.c. lattice and with the nearest-neighbour interaction. It can be shown that for large I [4]

$$P = \frac{3I^2 + 3I + 1}{I^3 + 3I^2 + 3I + 1} \doteq \frac{3}{I}, \quad (4)$$

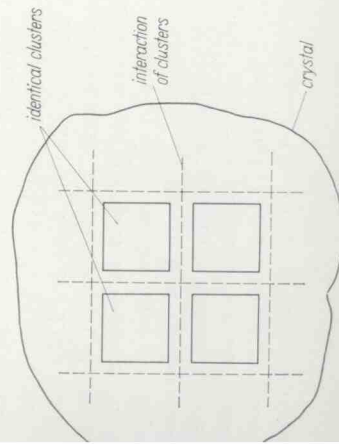


Fig. 1. Decomposition of a crystal into a number of identical clusters

where I is the number of atoms at the edge of the cube. The example of a thin film with the interaction to the r -th neighbouring layer where

$$P = \frac{r}{I + r} \quad (5)$$

(I is the total number of layers) shows that the validity of (2) is not restricted to systems finite in all three dimensions.

n_{int} is the number of atoms among surfaces of the clusters so that it increases as I while $n_{\text{bulk}} \sim I^3$. The geometrical quantity P behaves therefore as $1/I$, I being the number of atoms in one dimension. The results of the following sections indicate the importance of this parameter.

Formulae for the moments of the differential density of states $g(E)$,

$$J_k = \int_{E_1}^{E_2} E^k g(E) \, dE; \quad k = 1, 2, \dots, \quad (6)$$

can be obtained in an analogous way [4],

$$|J_k^{\text{unrel}} - J_k^{\text{bulk}}| \leq 2(|E_1|^k + |E_2|^k) P. \quad (7)$$

As a special case the estimate for the binding energy

$$E_b = 2 \int_{-\infty}^{E_F} E g(E) \, dE \quad (8)$$

can be obtained. In all cases, the quantity P multiplied by a constant plays the role of the upper bound in the corresponding estimates.

3. Relaxation of the Surface

The relaxation of the surface can be taken into account similarly as in Section 2 (see Fig. 2). Using analogous arguments it can be shown that [4]

$$|I_{\text{unrel}} - I_{\text{rel}}| \leq Q, \quad (9)$$

where unrel and rel denote the cluster with the unrelaxed and relaxed surface, respectively. Q has a similar meaning as P and equals

$$Q = \frac{n_{\text{surf}}}{n_{\text{total}}}, \quad (10)$$

where n denotes the number of atoms in the corresponding region.

Using the example of a thin film with s relaxed surface layers (near both surfaces) we have

$$Q = \frac{s}{I}. \quad (11)$$

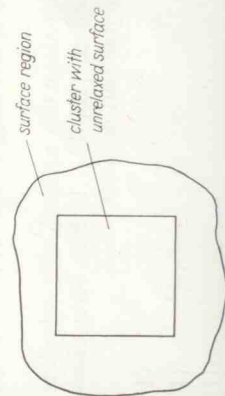


Fig. 2. A cluster with relaxed surface decomposed into a cluster with unrelaxed surface and the surface region

The integrated density of states of the cluster with the relaxed surface and of the infinite crystal can be compared in the following way:

$$|\bar{I}_{\text{rel}} - \bar{I}_{\text{bulk}}| \leq |\bar{I}_{\text{unrel}} - \bar{I}_{\text{bulk}}| + |\bar{I}_{\text{unrel}} - \bar{I}_{\text{rel}}| \leq P + Q. \quad (12)$$

As $Q \sim 1/I$ our remark regarding the one-dimensional character of the convergence is valid for the clusters with the relaxed surface, too.

The relaxation of the surface can be accompanied by the appearance of the surface states. We do not discuss this point in detail here. We note only that the conditions for the existence of surface or localized states can be in general found by using the partitioning technique leading to the effective Hamiltonian [8, 9]. The negative eigenvalue theorem then gives the conditions for the existence of surface states lying above or below the band of volume states. It appears [8, 9] that the effective Hamiltonian and the conditions for the existence of the localized states in various linear chains depend on the number of unrelaxed atoms by means of the parameters $1/(I+1)$ or $I/(I+1) = 1 - 1/(I+1)$. Therefore, the conditions for the existence of surface states seem to depend on the number of atoms in the same way as P and Q .

4. Asymptotical Laws of Convergence

The calculations based on the negative eigenvalue theorem (Sections 2 and 3) show that many important properties of the clusters converge at least as quickly as $1/I$, I having the meaning of the number of atoms in one dimension. This means that the asymptotical form of the formulae giving the behaviour of these properties for very large clusters must begin with the first or higher power of $1/I$.

The analytic cluster model can be very useful in this respect. As this model gives analytic expressions for some properties it is possible to expand them in terms of $1/I$ and obtain more detailed information about the convergence.

As an example, let us consider the binding energy of the linear chain, square, and cube with s.c. lattice [4]. The asymptotical formula for the binding energy of very large clusters has the form

$$E_b(I) = E_b(\infty) (1 - \text{const } I^{-1}), \quad (13)$$

where $E_b(\infty)$ is the binding energy for $I \rightarrow \infty$, I the number of atoms at the edge of the cluster, and the constant equals 0.571, 0.467, and 0.53 for the linear chain, square, and cube, respectively.

In case of the b.c.c. clusters more properties have been calculated analytically [3]. Similarly as in the case of the s.c. clusters, the binding energy behaves according to

$$E_b(N) = E_b(\infty) (1 - 1.079N^{-1/3}), \quad (14)$$

N being the total number of atoms in the cluster. The bandwidth, however, converges more quickly,

$$\text{BW}(N) = \text{BW}(\infty) (1 - 5.875N^{-2/3}). \quad (15)$$

The same applies to the bond orders between the neighbouring atoms which converge as $1/N^{2/3}$, too.

The possibility of using these formulae to interpolate the numerically calculated properties of the Li clusters has been investigated in [10, 11]. It has been shown that in case of the b.c.c. clusters the following formulae can be used:

$$E_b(N) = E_b(\infty) (1 - 0.735 N^{-1/3}), \quad (16)$$

$$\text{BW}(N) = \text{BW}(\infty) (1 - 2.576N^{-2/3}), \quad (17)$$

$$E(N) = E(\infty) (1 - 1.664N^{-2/3}). \quad (18)$$

The most close fit to the numerically calculated values gives the formulae for the energy of the lowest occupied molecular orbital, i.e. for the lower band edge.

The binding energies of the linear chain and the clusters with the s.c., f.c.c., and b.c.c. lattice fulfil the relation

$$E_b(N) = E_b(\infty) (1 - \text{const } N^{-1/d}), \quad (19)$$

d being the number of dimensions of the system ($d = 1$ for the linear chain, $d = 3$ for the s.c., f.c.c., and b.c.c. clusters) and $\text{const} = 1.221, 0.790, 0.735$, and 0.739 in the corresponding cases. The LOMO energies are given by

$$E_{\text{LOMO}}(N) = E_{\text{LOMO}}(\infty) (1 - \text{const } N^{-2/d}), \quad (20)$$

where $\text{const} = 1.020, 1.603, 1.664$, and 1.880 for the linear chain and the cluster with the s.c., f.c.c., and b.c.c. lattice, respectively.

We note at the end of this section that except for a numerical factor the parameter $1/N^{1/d}$ is identical with $1/I$ from Sections 2 and 3. Therefore, the form of the formulae given here agrees with general arguments of the preceding sections.

5. Conclusion

General arguments, results of simple models, and agreement with the numerical calculations show that the convergence of one-electron properties of clusters to those of the solid can be interpolated by formulae of the form similar to (13) to (20). In all these formulae, the total number of atoms in the cluster appears by means of the parameter $1/N^{1/d}$. All investigated properties converge to those of the solid at least as quickly as $1/N^{1/d}$. This parameter has a purely geometrical meaning and from the point of view of the graph theory it can serve as a measure of the compactness of the system. From this point of view, its appearance is not accidental.

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