

Local ionicity - an alternative definition for *ab initio* calculations

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 2429

(<http://iopscience.iop.org/0953-8984/12/11/309>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.218

The article was downloaded on 15/05/2010 at 20:29

Please note that [terms and conditions apply](#).

Local ionicity—an alternative definition for *ab initio* calculations

S Mankefors and P O Nilsson

Department of Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

Received 10 December 1999

Abstract. Alternative general definitions of ionicity and ionic radii based on the charge density null-flux concept are introduced. This method is local in nature and possible to adapt to any atom in any physical system including surfaces, interfaces, defects and alloys. These and other explicit advantages, as compared to the standard approaches, are discussed in detail. The current approach is especially suitable for density functional methods, and is applied to a number of III–V semiconductors, alkali halides and a few alkaline earth compounds. Good agreement with traditional results is found.

1. Introduction

With the rapid development of available computing power both semi-empirical and *ab initio* methods have been increasingly applied to a vast number of different solid state systems. Consequently most of the different III–V semiconductor bulk properties were thoroughly investigated during the late 1970s and the 1980s and extensive tables were compiled, see for instance [1]. More ionic substances like NaCl, MgO etc have turned out to be more difficult to calculate *ab initio*, but during the 1990s there have been a number of investigations also in this area [2–4].

Despite this situation, the ionicity of *any* substance, is still very much a matter of discussion. The reason for this lies mainly in the *definition* of ionicity. It has even been argued that the concept of ionicity is somewhat qualitative [5] and thus not quantitative enough for modern physics. Given the number of alternative definitions of ionicity/polarity, see e.g. [6–8], which in some cases lead to as large differences as 30% or more in absolute values [9], this objection might seem to have its grounds. However, we still strongly believe that general concepts and ideas, such as ionicity, ion radii and charge transfers between individual atoms, have a very important role in solid state physics both conceptually and quantitatively. Knowing the approximate ion charges allows for easy and relatively reliable estimates of electrostatic multipole moments, core level shifts and the Madelung energy of any given system. Electrostatic considerations based on the ionicity may also in a first approximation give valuable information on the stability of surfaces, the tendency for reconstructions etc.

In this article we provide an alternative definition of ionicity based on spherical zero flux of the total charge. A similar definition has earlier been used for the computation of so called atomic surfaces, see e.g. [10]. This approach can be used locally on the atomic level in all systems, including bulk, surfaces, interfaces, defects etc. Since it is based on the ion radius instead of e.g. the ‘bond charge’ [8], it also becomes more transparent and more transferable than many other alternative definitions since the ion radius is relatively straightforward to

determine theoretically, see below. To test these ideas we have performed *ab initio* calculations on a large number of different bulk systems, ranging from III–V semiconductors to alkali halides. Good agreement is found with earlier values and established trends, while our approach in addition offers information on the individual atoms.

2. Definitions

2.1. Ionicity

In order to establish a new unambiguous definition of ionicity we have chosen to use the local charge distribution instead of any bulk property, such as the dielectric constant [7]. This in itself is not new in any way. Harrison [8] used the concept ‘bond charge’ to calculate polarity which is directly connected to ionicity. Our approach differs substantially, however, and instead of the equilibrium charge distribution [8] we let the ionic radius R_i directly define the ionicity of any substance in any environment. Given the local R_i , we simply integrate the total valence charge inside the sphere centred at the atom with radius R_i . Doing so we avoid all reference values of ‘charge density floor’ in between the atoms or similar, see e.g. [1], [8]. This is also a very intuitively clear picture: given the size of the ion, we know the total charge within it and thus any shortage or surplus of charge as compared to the neutral atom. We have the following definition of the ionic charge

$$\delta_i \equiv \int_0^{R_i} \int_0^\pi \int_0^{2\pi} n(\mathbf{r}) r^2 \sin(\theta) d\phi d\theta dr - C_v^{atom} \quad (1)$$

where C_v^{atom} is the valence charge of the neutral atom (an integer) and $n(\mathbf{r})$ is the charge density associated with the partly filled valence orbitals of the ion. This is an extremely elementary definition, but thus also a very clear one. The problem of deciding the ionicity hence reduces to finding the ion radius and then performing a simple integration, something that can be done very straightforwardly and allows for relatively small errors, see below. Furthermore, the definition is local in nature, i.e. it can be used not only for bulk systems, but also at defects, surfaces, interfaces, in alloys etc, something that turns out impossible with e.g. Harrison’s definition. The reason is that there strictly speaking is neither any constant charge density background, nor necessarily any complete bonds present in these situations. The current approach on the other hand has successfully been applied to the charge redistribution of III–V(110) surfaces [11], and can easily be adopted to other situations.

It should be noted though that in areas of charge depletion (charge accumulation) the definition in equation (1) could return negative (positive) values for *both* anions *and* cations which conceptually is not very gratifying. This might be the case for instance at interfaces or in the vicinity of defects. Still, the total charge of the ions directly reflects the ionicity. In a NaCl crystal a Cl ion will continue to have considerably more charge, relatively speaking, than a Na ion also at a defect or in a charge depleted area. Hence the ratio between the ion charges is much more relevant to use than the exact charges themselves in non-bulk-like situations. We therefore introduce the polarity ratio, defined by

$$\begin{aligned} P_{ratio} &\equiv \frac{C_{anion}^f}{C_{cation}^f} \equiv \left(\int_0^{R_1} n_1(r) \times 4\pi r^2 dr \right) \left(\int_0^{R_2} n_2(r) \times 4\pi r^2 dr \right)^{-1} \\ &\equiv \frac{\delta_{anion} + C_v^{an.atom}}{\delta_{cation} + C_v^{cat.atom}} \end{aligned} \quad (2)$$

where P_{ratio} simply equals the ratio between the total integrated charges of the anion (C_{anion}^f) and cation (C_{cation}^f) respectively. Furthermore we intuitively expect charge balance between

the ions, which for heteropolar systems implies

$$-N_{\text{cation}}\delta_{\text{cation}} = +N_{\text{anion}}\delta_{\text{anion}} \quad (3)$$

where $\text{cation}_{N_{\text{cation}}}$ $\text{anion}_{N_{\text{anion}}}$ is the chemical composition (e.g. Al_2O_3). For more complex systems the total negative ion charge should equal the total cation charge.

In practice the charge distribution in solid state systems is not confined to the ionic spheres, but is also distributed over the interstitial volumes in the crystal. For semiconductors the ionicity is relatively low and most of the charge is contained in the covalent bonds which gives a low amount of interstitial charge. In fact in most cases the balance is quite good already before normalization, see below. For a highly ionic substance like NaCl though, where the Cl ion has a nearly filled eight electron outer shell, the total charge of the negative ion will never be found within the ion radius unless it is large enough to include most of the system's volume. This reflects the shortcoming of the simple 'billiard ball' picture—electrons are indeed concentrated upon the anions in all salts, but leak out into the rest of the crystal too.

Hence the ion charge of the cation tells us more about the local ionicity than the total charge of the anion. If the cation has a valence charge of only 0.1 electrons, the substance clearly is very much ionic even if the total charge of the anion within its ion radius is less than 7.9 electrons. The reason is that any interstitial electrons almost certainly must be taken from the anion and not the cation. This situation is well handled if we use the polarity ratio (equation (2)) instead of equation (1).

For heteropolar substances it is now very straightforward to renormalize the ionic charge and define the local ionicity using equation (3):

$$\text{Ionicity value} \equiv \delta^i = \frac{P_{\text{ratio}} C_v^{\text{cat.atom}} - C_v^{\text{an.atom}}}{P_{\text{ratio}} + N_{\text{cation}}/N_{\text{anion}}} \quad (4)$$

Apart from defining the ionicity, δ^i also equals the normalized charge taken from the cation, while the renormalized ionic charge of the anion corresponds to $(N_{\text{cation}}/N_{\text{anion}})\delta^i + C_v^{\text{an.atom}}$. The above equations directly imply that the interstitial charge is *linearly* divided between the cation and anion. That is, the more charge an ion has, the larger part of the interstitial charge it receives. More specifically we have that

$$\text{Renormalized cation charge} = C_v^{\text{cat.atom}} - \delta^i = C_{\text{cation}}^f + \frac{\text{interstitial charge} \times C_{\text{cation}}^f}{C_{\text{cation}}^f + C_{\text{anion}}^f} \quad (5)$$

where the interstitial charge is defined as the difference between the combined valence charge of the neutral anion and cation species and the integrated ionic total charge $C_{\text{cation}}^f + C_{\text{anion}}^f$. The renormalized charge of the anion is found in a similar way. Because of the often great differences in anion and cation charge, a linear division is much more attractive than just splitting the interstitial charge between the ions. Knowing nothing else, it is natural to assume that the Cl ion is responsible for most of the interstitial charge in NaCl as pointed out above, and not the Na ion. This division and the renormalization hence effectively substitute the real ionic system with 'charged billiard balls' where no extra charge is to be found outside the ion radii. For non-bulk-like situations, however, the ionicity does *not* correspond directly to the physical charge, but rather to the polarity ratio which suggest that the physical charge should be presented together with the ionicity in these cases. This set of three or four numbers—the two ionic radii, the ionicity and possibly the physical cation charge—defines any local electrostatic properties surprisingly well without knowing the exact charge distribution. Listing such values together with e.g. atomic positions hence not only gives a good idea of the changes in the character of the bonds and possible electrostatic forces, but also clearly indicates the strength of e.g. any surface dipoles [12].

For other systems, like alloys, this definition is easily expanded making use of the charge balance and relative ionicity between different species of atoms.

2.2. Ionic radii

In order to make the definition in equation (4) work and become reliable and easy to use, the ionic radii of the atoms must be straightforward to calculate. In this context, the definition of the ‘atomic surface’ (see e.g. [10]) is not only a practical, but also a common choice defined by

$$S_{atom} \equiv \{\mathbf{r} : \nabla n(\mathbf{r}) \cdot \hat{\mathbf{n}}_s = 0\}. \quad (6)$$

The position \mathbf{r} is chosen to be the outermost vector fulfilling $\nabla n(\mathbf{r}) \cdot \hat{\mathbf{n}}_s = 0$ where $\hat{\mathbf{n}}_s$ is the surface normal. This is also what one expects intuitively—the outermost peak in the total wave function marks the end of the atom. The most general approach to find the atomic surface S_{atom} is by different variational methods assuming an initial set of surface types. In our case we limit the possible types to spherical only since this lies at the heart of the idea of ionic radii; speaking of a radius for a non-spherical (or possibly ellipsoid) surface is meaningless. Hence employing only spherical surfaces, equation (6) transforms into

$$\text{sphere}_{atom} \equiv \{\text{outermost } r : \nabla n(\mathbf{r}) \cdot \hat{\mathbf{r}}_s = 0\} \quad (7)$$

which directly corresponds to

$$\text{sphere}_{atom} \equiv \left\{ \text{outermost } r : \frac{\partial n(\mathbf{r})}{\partial r} = 0 \right\}. \quad (8)$$

It should be noted though that this definition demands that the condition is fulfilled simultaneously over the entire sphere of radius r , something that in general may only happen in full spherical symmetry. Still, in a highly coordinated surrounding, or alternatively, if the ions have a relatively atomic-like electronic configuration, the deviations from a perfect spherical atomic surface are quite small. To reach an unambiguous definition we therefore integrate $n(\mathbf{r})$ over θ and φ inside equation (8), which results in

$$\text{sphere}_{atom} \equiv \left\{ \text{outermost } r : \frac{\partial}{\partial r} \left(\int_0^\pi \int_0^{2\pi} n(\mathbf{r}) \sin(\theta) \, d\varphi \, d\theta \right) = 0 \right\}. \quad (9)$$

If the difference between the ‘true’ atomic surface and the spherical one on the other hand is somewhat larger, equation (9) will in some cases result in a double extreme point, i.e. two possible radii close to each other in value. This is not very surprising since the absolute value of the charge density may vary over the non-spherical atomic surface due to e.g. directional bonds. Two (or more) single charge density maxima (or minima) in different directions *and* at different distances from the origin will by superposition result in two (or more) nearby extreme points when spherically averaged. In order to produce a sphere that approximates the ‘true’ atomic surface in a good way, we therefore choose to use the weighted average radius $R_{ave.double}$ of the double value,

$$R_{ave.double} \equiv \left(\int_{R_1}^{R_2} r n(r) 4\pi r^2 \, dr \right) \left(\int_{R_1}^{R_2} n(r) 4\pi r^2 \, dr \right)^{-1} \quad (10)$$

where R_1 and R_2 are the two radii determined by the double extreme point and $n(r)$ is the radial charge distribution (the double integral in equation (9)). In the case of more than two possible radii, the integrals go from the smallest to the largest respectively. It should be noted

that this situation is very rare though, see section 4. The combination of equations (9) and (10) thus completely determines the ionic radius and results in the following definition:

$$\text{ionic radius} \equiv \left\{ (\text{averaged}) \text{ outermost } r : \frac{\partial}{\partial r} \left(\int_0^\pi \int_0^{2\pi} n(\mathbf{r}) \sin(\theta) \, d\varphi \, d\theta \right) = 0 \right\}. \quad (11)$$

The condition in (11) is very straightforward to apply and returns very well defined ionic radii. In the case of double extreme points, different methods of averaging influences the results with less than 1% of the total radius, see below. For single extreme points, the numerical uncertainty of the values of the ionic radii is even lower, see section 3.

There is, however, one remaining problem. For a single atom, the outermost extreme point in the charge density distribution $n(r)$ is well defined. In a solid on the other hand the charge density is not only increased, but also disturbed by surrounding ions which induce fast varying changes in $n(r)$. Consequently the number of extreme points increases and continues at least up to the nearest neighbouring ion core. Hence one cannot any longer just choose the outermost extreme point, but has to include other fundamental physical aspects. For e.g. NaCl the Cl ion must have a charge greater than 7, but fewer than eight electrons, and the radius has to be less than the distance to the centre of the neighbouring Na atom. Including such fundamental physical considerations when determining the radii results in completely unambiguous ion radii for any ionic solid.

3. Computational details

All wave functions and energy eigenvalues were calculated *ab initio* within density functional theory [13, 14] (DFT) using the local density approximation (LDA) as implemented by Ceperley and Alder [15] and Perdew and Zunger [16]. For the electron-ion interaction, fully separable, non-local pseudo-potentials (PP) were used [17, 18], based on self-consistent solutions of the relativistic Dirac equation for free atoms [19–21]. The calculations were performed using the plane-wave band structure code fhi94md.cth [22], which is a heavily modified version of fhi93cp [23] concerning the computational methods. The geometries were described by the slab supercell method, using the theoretical lattice constants, see table 1. All calculations employed 19 special Monkhorst–Pack k -points in the irreducible Brillouin zone (IBZ), corresponding to 125 points in the full zone. A plane-wave cut-off of 16, 32 and 48 Ryd was used depending on the specific substances, see table 1.

Table 1. The plane-wave energy cut-off and lattice constants for the investigated substances.

Substance	Cut-off (Ryd)	Theoretical lattice const. (Å)	Exp. lattice const. (Å)
AlAs	16	5.61	5.66
GaAs	16	5.56	5.63
GaP	16	5.38	5.45
InAs	16	6.06	6.06
InP	16	5.87	5.87
KCl	48	6.37	6.28
KI	32	7.07	7.05
MgO	48	4.11	4.20
MgS	48	5.14	5.20
NaCl	48	5.64	5.64
NaF	48	4.53	4.62
NaI	32	6.46	6.47

Table 2. The ionicity and ionic radius for the bulk together with the polarity ratio (in parentheses) and total charge. Radii in Å and charge and ionicity in electrons, the numerical uncertainty is ± 0.01 Å and $< 5\%$ respectively. Ionicity δ_i based on the definition in equation (4), radii after the definition in equation (11).

Compound	δ_i (P_{ratio})	Cation R_i	Anion R_i	Cation charge	Anion charge
AlAs	0.28 (1.94)	1.47	1.56	2.76	5.36
GaAs	0.32 (1.98)	1.43	1.58	2.67	5.30
GaP	0.36 (2.03)	1.40	1.50	2.64	5.36
InAs	0.41 (2.09)	1.56	1.67	2.58	5.40
InP	0.47 (2.16)	1.52	1.62	2.48	5.35
KCl	0.89 (69.4)	1.41	2.02	0.11	7.63
KI	0.81 (41.2)	1.56	2.16	0.18	7.41
MgO	1.74 (53.58)	0.91	1.31	0.24	7.15
MgS	0.98 (6.83)	1.33	1.46	0.91	6.22
NaCl	0.87 (58.6)	1.18	1.78	0.13	7.44
NaF	0.90 (75.6)	1.17	1.32	0.10	7.42
NaI	0.73 (24.5)	1.47	1.98	0.30	7.24

In order to obtain the electronic charge of the atoms as functions of the radius we extracted each wavefunction $\phi_{k,\varepsilon}(\mathbf{r})$ for a certain eigenvalue ε_i in the specified k -point from the total wavefunction. By projecting the plane-wave representation of $\phi_{k,\varepsilon}(\mathbf{r})$ onto atomic orbitals, the s, p and d contributions from each atom was subsequently found. For every case the atomic orbitals were cut off at $|\mathbf{r}| = r_0$ to ensure that the projection only took place inside the spheres centred at each atom with radius r_0 . The charge of the individual atoms was taken as the sum of the s, p and d electronic charges. By repeating the calculations for different r_0 , starting at $r = 0.025$ Å and increasing the radius stepwise by 0.1 Å, we were able to interpolate smooth results with very high accuracy for the dependency of the valence charge C_v . The resulting numerical uncertainty is estimated to be less than 5% of the absolute value of $C_v(r)$.

The radial charge $n(r)$ is straightforwardly found by inverting the integration according to

$$n(r) = \frac{1}{4\pi r_0^2} \frac{\partial C_v(r_0)}{\partial r_0} = \frac{1}{4\pi r_0^2} \frac{\partial}{\partial r_0} \int_0^{r_0} \int_0^\pi \int_0^{2\pi} n(\mathbf{r}) r'^2 \sin(\theta) d\phi d\theta dr' \quad (12)$$

where the derivative in practice is taken on the locally interpolated five degree polynomial describing C_v . Since the local extreme points directly determine the ionic radii, see equation (11), the high accuracy in the total valence charge induces a numerical uncertainty well below 5% for the ionic radii. To further eliminate any errors due to this method, the exact valence charge C_v was re-calculated for each resulting ionic radius to ensure that the interpolated charge agreed with the actual one. In all cases the deviations were found to be considerably less than the numerical error.

It should be pointed out though that the pseudo-potential method in itself risks giving rise to additional non-numerical errors. Any systematical errors due to this choice of method should be especially large inside the core region. However, the ‘hard’ potentials used here with relatively small core radius ensures that the wave functions and potentials in the region of the ionic radii (see table 2) really are the physical ones. Because of this and the norm conserving property, we strongly believe there is no reason to expect any significant errors in the results due to the choice of the numerical method.

4. Results and discussion

The theoretical lattice constants of the investigated compounds coincide with the experimental ones within approximately 0.1 Å, a typical error of the DFT-LDA, see table 1. Due to the plane-wave method and the use of relatively hard pseudo potentials with small core radii, the cut-off necessary is as high as 48 Ryd for the most ionic substances, while already 16 Ryd gives good results for the III-V semiconductors.

Turning to the ionicity and ionic radii we find that all substances exhibit very well defined ionic radii according to the definition in equation (11). It should be noticed, however, that because of the spherical averaging process, the sum of the ionic radii, see table 2, will not exactly correspond to the inter-atomic distance between the cation and anion in general. In [4] for instance, the ionic radii are defined by the local extreme point in between the anion and cation along their joint axis of symmetry which thus will give the correct inter-atomic distance, but does not ensure any spherical atomic surface (see the discussion in section 2.2). Consequently this is a very dubious method since there are a number of other choices of directions possible which would alter the 'radii' 20% or more, see the figures and discussion in [4].

The radii found in this investigation do show a remarkable stability when compared to the lattice constant, however, see figure 1. This is easily understood if one views the anion and cation as a single unit. The NaCl systems as well as the III-V compounds exhibit a face centred cubic (fcc) geometry with the anion and cation as a basis pair. In a perfect, single based, fcc lattice consisting of hard spheres only, the volume occupied by each sphere is 18.5% of the volume of the entire cubic unit cell and the radius is 35.4% of the lattice constant. A two atom base will not give rise to any perfect spheres, but rather a peanut-shaped rotational body in a simplified picture. Still, if the two contributions from each species to the 'hard sphere volume' are of the same size, the radius for the individual spheres would become 28.1% of the lattice constant, and the sum 56.1%. This agrees remarkably well with our findings where the average sum of the cation and anion corresponds to 54% of the lattice constant. In the same way the

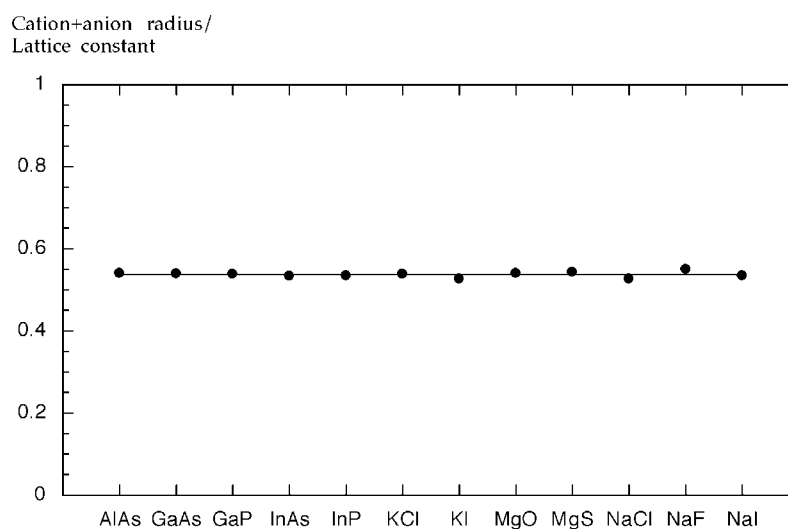


Figure 1. The sum of the cation and anion radii divided by the theoretical lattice constant for each substance.

volume of the found ionic spheres corresponds on average to 17% of the cubic unit cell, not including the overlap between the ions. Hence our definition in (11) really returns a close packed system of ‘hard spheres’ as it should in some sense. This correspondence is lacking in [4] where the ions as defined by the ionic radii are considerably more loosely packed.

It should be stressed though, that there is no ‘correct’ way to produce ionic radii. Even experimentally the measured quantity is the lattice constant and core radii rather than the valence radii since in many cases the cation more or less is completely stripped of its valence electrons, see table 2. What is to be expected by any definition though is internal self-consistency and a linear dependence of the sum of the ionic radii on the lattice constant. Our definitions and findings clearly fulfil this condition.

Since the renormalized ionicity in equation (4) only takes the charge found *within* the ionic radii into account, absolute charge balance will not be achieved since the ‘hard sphere’ system only makes up 74% of the total volume (see above and section 2.1). The exception is for strongly covalent compounds where most electrons are found in the bonds between the atoms and the ionicity may be considered as only a minor perturbation to the system. This is the case with the III–V semiconductors, where charge balance is achieved within 0.1 electrons, see table 2. These systems also agree remarkably well with the Phillips values, see [9] for instance.

The more ionic compounds i.e. non-semiconductors differ somewhat more compared to earlier findings [2–4]. It must be noted though that while we do not include the interstitial charge, see section 2.1, the wavefunction based methods used in [2]–[4] do include the entire space despite the quite small volume of the ionic spheres in [4]. The general trends in ionicity and charges for the alkali halides agree well with the results in [4], but we generally find a stronger polarization when looking at the cation charges, see table 2. We believe this to be only partly due to the differences in how the interstitial charge is treated, but mainly to the theoretical model used, i.e. cluster calculations versus DFT–LDA. Certain unphysical deviations in the charge contour maps in [4] are also noticed which indicate the use of too small clusters to enable any exact comparisons.

In contrast to the alkali halides, the exact details of the electronic structure of the alkali earth oxides and similar compounds (e.g. MgS) are not very well known [2, 3, 24]. It has, however, not been the object of this paper to advance the understanding of these materials, but rather ‘only’ to test our definition of ionicity thoroughly. Since MgO and MgS traditionally have been thought to be only partly ionized, they make a good compliment to the highly ionic alkali halides, and the weakly ionic III–V semiconductors from the point of testing.

The relatively high degree of ionization found for MgO, see table 2, agrees well with the findings in [3], even if the results there are highly dependent on the exact choice of the atomic sphere parameter. The traditional Phillips value [25] is considerably lower though, but recent cluster model calculations [2] indicate an almost total ionization of ± 2 electrons. We believe this to be an artifact from the heavily charged cluster model $(\text{metalO}_6)^{-10}$ used there, however, since this actually describes an over-oxidized ion complex rather than the bulk. It is also reasonable to expect the MgO to be somewhat less ionic relatively speaking than such alkali halides as e.g. NaF and KCl.

Finally we notice that MgS displays the largest amount of interstitial charge of all compounds investigated. Naively one might expect MgS to be similar to MgO, but less ionic. Sulphur does not, however, strive for a closed shell configuration in the same way as oxygen does, compare e.g. the S_8 and O_2 molecules and the solid state phase of sulphur. On the other hand, the covalent character of the MgS is largely undeveloped—relatively small amounts of charge are found in directional bonds when we investigate the three-dimensional charge distribution. Combined this makes MgS a relatively poor ionic material, but still not

covalent, where the remaining charge instead is lost to the interstitial volumes making up a background charge for the system.

5. Summary

We have successfully introduced an alternative definition of ionicity, local in nature and based on the integration of all charge within the given ion radii. The zero-flux condition for the spherically averaged charge density distribution is used to determine the ion radius in each case. There are a number of advantages of these new definitions, the locality being the greatest, which enables investigations of the ionicity on surfaces, in alloys, around defects etc. We have furthermore performed a number of *ab initio* calculations on the bulk systems of III–V semiconductors, alkali halides and MgS and MgO to test the current approach against more traditional methods. Our results agree well with established results and trends for all substances. MgS is found to be neither dominated by ionic nor covalent bonding, but instead loses some of the bonding charges to the interstitial volumes.

Acknowledgment

The Swedish Natural Science Research Council supported this work.

References

- [1] Cohen M L and Chelikowsky J R 1989 *Electronic Structure and Optical Properties of Semiconductors* 2nd edn (Berlin: Springer)
- [2] Pacchioni G, Sousa C, Illas F, Parmigiani F and Bagus P S 1993 *Phys. Rev. B* **48** 11 573
- [3] Lobatch V A, Kulyabin B E, Zhukov V P and Medvedeva N I 1990 *Phys. Status Solidi b* **158** 239
- [4] Adachi H 1993 *J. Phys. Soc. Japan* **62** 3965
- [5] Yu P Y and Cardona M 1996 *Fundamentals of Semiconductors: Physics and Materials Properties* (Berlin: Springer)
- [6] Pauling L 1960 *The Nature of the Chemical Bond* (Ithaca, NY: Cornell University Press)
- [7] Phillips J C 1973 *Bonds and Bands in Semiconductors* (New York: Academic)
- [8] Harrison W A 1980 *Electronic Structure and the Properties of Solids: the Physics of the Chemical Bond* (San Francisco: Freeman)
- [9] Bechstedt F and Enderlein R 1988 *Semiconductor Surfaces and Interfaces* (Akademie)
- [10] Stefanov B B and Cioslowski J 1995 *J. Comput. Chem.* **16** 1394
- [11] Mankefors S and Nilsson P O submitted
- [12] Mankefors S, Nilsson P O and Kanski J 1999 *Surf. Sci. Lett.* **443** L1049
- [13] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
- [14] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
- [15] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
- [16] Perdew J P and Zunger A 1981 *Phys. Rev. B* **23** 5048
- [17] Hamann B 1989 *Phys. Rev. B* **40** 2980
- [18] Gonze X, Käckell P and Scheffler M 1990 *Phys. Rev. B* **41** 12 264
- [19] Hamann D R, Schlüter M and Chiang C 1979 *Phys. Rev. Lett.* **43** 1494
- [20] Bachelet G B, Hamann D R and Schlüter M 1982 *Phys. Rev. B* **26** 4199
- [21] Kleinmann L and Bylander D M 1982 *Phys. Rev. Lett.* **48** 1425
- [22] fhi94md.cth is based on fhi93cp, purchased from the *Computational Physics Communications* library in 1995. While the basic computational physics is the same, the changes of computational nature are extensive.
- [23] Stumpf R and Scheffler M 1994 *Comput. Phys. Commun.* **79** 447
- [24] Souda R, Yamamoto K, Hayami W, Aizawa T and Ishizawa Y 1994 *Phys. Rev. B* **50** 4733
- [25] Phillips J C 1970 *Phys. Today* **23** 23