Population analysis of plane-wave electronic structure calculations of bulk materials

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Ab initio plane-wave electronic structure calculations are widely used in the study of bulk materials. A technique for the projection of plane-wave states onto a localized basis set is used to calculate atomic charges and bond populations by means of Mulliken analysis. We analyze a number of simple bulk crystals and find correlations of overlap population with covalency of bonding and bond strength, and effective valence charge with ionicity of bonding. Thus, we show that the techniques described in this paper may be usefully applied in the field of solid state physics. [S0163-1829(96)07847-2]

I. INTRODUCTION

First-principles density-functional theory (DFT) calculations are common tools used for the study of bulk materials. Recent advances[1] in numerical methods and computer technology have allowed systems of practical interest to be investigated in this way. Many of these techniques have used a plane-wave (PW) basis set expansion of the electronic states as this provides a natural representation for a periodic system. This approach offers a number of advantages. Results may be systematically converged with respect to basis set by variation of a single parameter, the cutoff energy. In addition the use of a PW basis set allows efficient calculation of atomic forces, enabling relaxation of atomic structure and dynamical simulation. Although a PW basis set can be very large, the use of optimized pseudopotentials[2,3] significantly reduces the number of plane waves needed to accurately represent the electronic states. PW calculations may only be applied to systems with periodic boundary conditions. However, an aperiodic system, e.g., a defect, may be modeled using a supercell, provided careful consideration is given to Brillouin zone sampling[4] and electrostatics.[5]

One remaining limitation of the use of a PW basis set is that the extended basis states do not provide a natural way of quantifying local atomic properties. Sanchez-Portal *et al.* describe a technique for the projection of PW states onto a linear combination of atomic orbitals (LCAO) basis set and show that this may be used to perform population analysis in bulk systems.[6,7] In a previous paper we have applied these techniques to the analysis of molecular systems.[8] We use the formalism due to Mulliken[9] in order to perform the population analysis. These techniques are widely used in the analysis of calculations performed using localized basis sets, particularly in the field of quantum chemistry. However, they have not been routinely applied to PW calculations of bulk systems. It is widely accepted that the absolute magnitude of the atomic charges have little physical meaning as they display an extreme sensitivity to the atomic basis set with which they are calculated.[10,8] In this paper we demonstrate that consideration of relative values of Mulliken populations, in contrast to the absolute magnitudes, can yield useful information.

We have carried out electronic structure calculations using the[1] CASTEP and[11] CETEP codes within the local-density approximation (LDA). Section II presents results for several simple bulk crystals. Previous work by Garcia and Cohen[12,13] considered the link between total valence charge density and measures of ionicity and electronegativity. We discuss the use of Mulliken bond populations and valence charges in this context. Finally, Sec. III summarizes our conclusions.

II. BONDING IN BULK CRYSTALS

We have analyzed electronic structure calculations of several simple bulk crystals using the techniques described in Refs. 6 and 8. In each case the LCAO basis set used was the atomic pseudo-orbitals corresponding to the shell containing the valence electrons. The spilling parameter and atomic charges resulting from these calculations are presented in Table I. It was found that the spilling parameters for these systems were very low, indicating a good representation of the electronic bands using the LCAO basis set. A spilling parameter in the region of 10^{-3} indicates that only approximately 0.1% of the valence charge has been missed in the projection. As an example of the sensitivity to basis set, the omission of the Si d orbitals from the LCAO basis set used in the analysis of SiC gives rise to a charge transfer of 1.25 rather than 0.66. The spilling parameter when the Si d orbit-

TABLE I. Spilling parameters, atomic Mulliken charges and valence charges calculated from PW electronic structure calculations.

Material	Spilling parameter	Anion charge ($|e|$)	Cation charge ($|e|$)	Effective valence ($|e|$)
NaF	1×10^{-3}	-0.59	0.59	0.41
NaCl	4×10^{-4}	-0.42	0.42	0.58
TiO_2	1×10^{-3}	-0.73	1.45	2.55
NaI	1×10^{-3}	-0.42	0.42	0.58
MgO	1×10^{-3}	-0.76	0.76	1.24
TiC	4×10^{-3}	-0.23	0.23	1.77
MgS	6×10^{-4}	-0.50	0.50	1.50
GaAs	4×10^{-3}	-0.29	0.29	2.71
SiC	2×10^{-3}	-0.66	0.66	3.44
Si	2×10^{-3}	N/A	N/A	4.00

TABLE II. Mulliken overlap populations calculated from PW pseudopotential calculations, Mulliken and Pauling electronegativity differences and bulk moduli.

Material	Structure	Overlap population ($|e|$)	X_M (Ref. 15) (eV)	X_P (Ref. 16)	K (Ref. 17) (10^{10} Pa)
NaF	NaCl	0.18	7.56	3.1	4.83
NaCl	NaCl	0.22	5.45	2.1	2.4
TiO$_2$	Rutile	0.35, 0.43[a]	4.09	1.9	21.1
NaI	NaCl	0.19	3.93	1.5	1.6
MgO	NaCl	0.34	3.82	2.3	15.9
TiC	NaCl	0.52	2.84	0.9	24.2
MgS	NaCl	0.40	2.47	1.3	8.9[b]
GaAs	Zinc blende	0.65	2.1	0.4	7.54
SiC	Zinc blende	0.83	1.5	0.7	9.7
Si	Diamond	0.87	0	0	9.8

[a]There are two Ti-O bond lengths in bulk rutile.
[b]Calculated using a LDA-corrected Hartree-Fock technique (Ref. 18).

als are absent is only 9×10^{-3}, indicating that this change is not due to an underrepresentation of the electronic bands. The discrepancy in the Mulliken charges is explained by the change in the number of basis states associated with the Si atoms used in the representation of the charge distribution. Table I also lists the effective ionic valences for each of the crystals. This is defined to be the difference between the formal ionic charge and the Mulliken charge on the anion species in the crystal. This is also used as a measure of ionicity; a value of zero implies an ideal ionic bond while values greater than zero indicate increasing levels of covalency.

Table II shows the overlap populations for nearest neighbors in the crystal. Positive and negative values indicate bonding and antibonding states, respectively. A value for the overlap population close to zero indicates that there is no significant interaction between the electronic populations of the two atoms. For example, in GaAs the overlap population between next-nearest neighbors was found to be -0.11 while in NaCl this population is -0.03. This indicates that the antibonding interaction between atoms in the second coordination shell is stronger in GaAs than in NaCl. A high overlap indicates a high degree of covalency in the bond. Also shown in Table II is the difference in Mulliken and Pauling electronegativities of the species in each crystal. The Mulliken electronegativity of a species is defined as

$$X_M = \frac{A+I}{2}, \qquad (1)$$

where A is the electron affinity of an atom of the species and I is the ionization energy of the atom. The Pauling electronegativity X_P is defined empirically from the bond energies of diatomic molecules containing the species.[14] The difference in electronegativities between two species is used as a guide to the ionicity of the interaction between two such atoms, a high value indicating high ionicity. Pauling suggests that the degree of ionicity is given by $1 - e^{-a(\Delta X)^2}$, where a is a

constant. It is notable that using this method the two electronegativity scales disagree even on the ordering of the ionicity of the crystals studied.

Our calculations provide us with overlap population and effective valence charge as measures of ionicity. These may be compared with those derived from electronegativities. Figures 1 and 2 show graphs of the overlap populations against the Mulliken and Pauling electronegativity differences. Figure 1 indicates that there is a correlation between the overlap population of nearest neighbors and the covalency of the bonds within the crystal as measured by the Mulliken electronegativity. Also shown in Fig. 1 is a fit of the data to a function of the form

$$\text{overlap population} = a e^{-b(\Delta X)^2} + c, \qquad (2)$$

where a, b, and c are constants. The standard error in this fit is 0.08. This demonstrates that our measure of covalency in
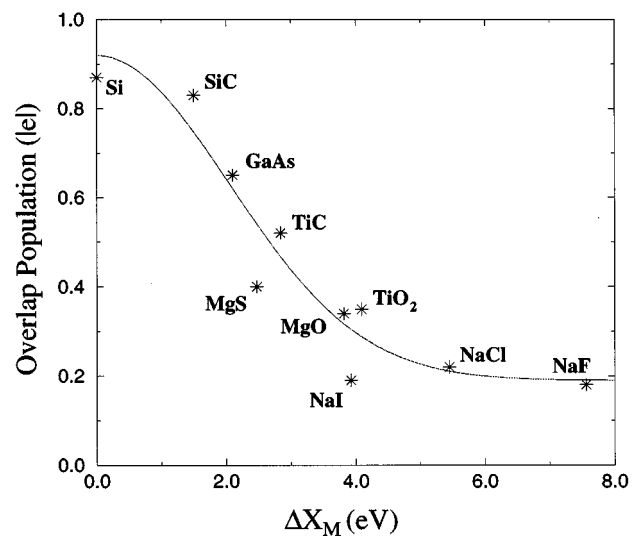

FIG. 1. Graph of overlap population against Mulliken electronegativity difference. The best fit function $0.73 e^{-0.12(\Delta X)^2} + 0.19$ is plotted for comparison.
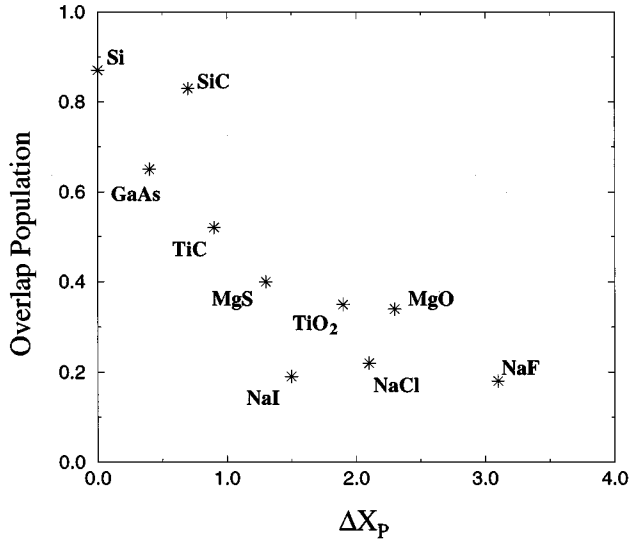
FIG. 2. Graph of overlap population against Pauling electronegativity difference.

terms of overlap population is proportional to that of Pauling. However, we find a constant offset indicating that a completely ionic bond is not possible within our definition. The agreement between the overlap populations and Pauling electronegativities as shown in Fig. 2 is not as good. This may be due to the fact that the Pauling electronegativity scale is derived from the energetics of diatomic molecules and therefore may not be suitable for application to bulk materials. A graph of the effective valence charge against the difference in Mulliken electronegativities, Fig. 3, again shows a correlation between these values. The notable exception is TiO_2, which has a higher effective valence charge than predicted by the electronegativity difference between Ti and O. However, this is due to the fact that there are two O
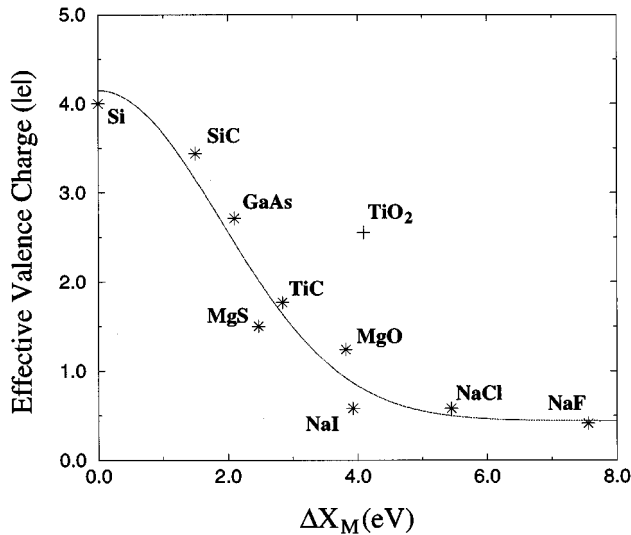

FIG. 3. Graph of effective valence charge against Mulliken electronegativity difference. Note that TiO_2 is a special case (see text). The best fit function $3.71e^{-0.14(\Delta X)^2} + 0.44$ is plotted for comparison.
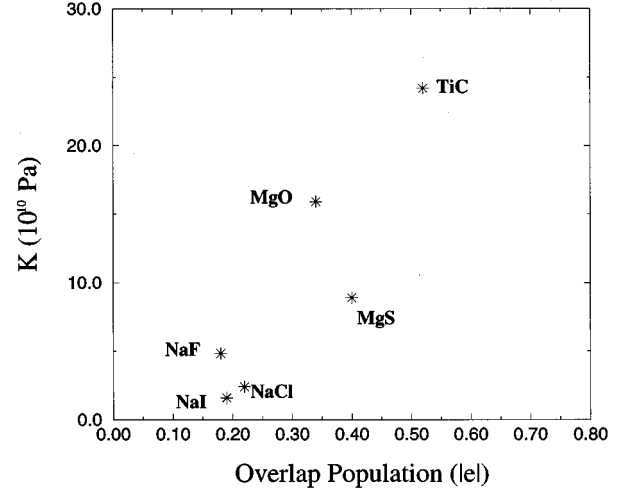

FIG. 4. Graph of bulk modulus against Mulliken overlap population for crystals with the NaCl structure.

atoms for every Ti atom. This result indicates that the effective valence charge is also a good measure of ionicity although it must be used with care. A fit has also been performed to a function of the form shown in Eq. (2). The standard error of such a fit is 0.11. This demonstrates that this measure is similar to that provided by the overlap population and electronegativities.

Finally, Fig. 4 shows a graph of bulk modulus against overlap population for the crystals in Table II with a NaCl structure. This suggests a correlation between the overlap populations of the bonds within the crystal and the bulk modulus of the crystal. If we take the bulk modulus as a measure of the strength of the interatomic bonds, this result indicates that the bond strength increases with overlap population.

III. CONCLUSION

Calculation of local atomic quantities from plane-wave pseudopotential calculations gives useful information on the properties of bulk materials. In particular the technique offers information on the nature of the bonds formed in the system. We have shown that the overlap population and effective charge may be used as a measure of the covalency of the system. These results have been compared to those derived from electronegativities. The methods we have demonstrated have also been applied to systems of practical interest, in particular showing the redistribution of charge and bonds in the neighborhood of a grain boundary in rutile.[19]

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