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Ionicity in solids

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Abstract. We review the use of the ideas of 'ionicity' and 'covalency' in quantitative studies of the solid state. Such ideas have taken several distinct forms: a description of charge distributions of bonding, a spectroscopic classification of perfect solids, and a framework for quantitative modelling of defects in polar solids. The limits on the usefulness of ionic pictures clearly depend on which form of idea and which application is involved. Nevertheless, many misunderstandings persist through failing to recognise that unique, universal, charges cannot be assigned except in trivial cases. Further confusion arises from the temptation to ascribe almost any unexpected features of ionic crystals to covalence. We discuss in particular the use of ionicity in the quantitative modelling of polar solids. Here, it appears, the ionic picture provides a framework for defect models and theories which, properly used, covers both the traditional 'ionic' crystals and ones, like silicates, where appreciable covalency is acknowledged.

1. Introduction

Most scientists hold clear views on *ionicity* and *covalency*. If they all held the same views as their colleagues, this paper would be unnecessary. In fact, these old ideas continue to stimulate papers clarifying (e.g. Cochran 1961), disputing (e.g. Pauling 1971, Phillips 1971) and frequently (as when the word merely covers up ignorance or incomplete characterisation) obscuring the issues involved. It is because there are several distinct ideas that some of the conflicts arise. These, in turn, reflect the several ways in which the concepts of ionicity and covalency are used. The debate on ionicity is given an added topicality by the recent growth in computer modelling of solids (Catlow and Mackrodt 1982) where potential models play a central role. Ionic model potentials have been widely and successfully applied, and it is clearly important to define any limitations of these potentials.

The central idea is that there is a qualitative difference between ionic crystals, like LiF, and covalent crystals, like diamond. Cohesion in LiF, the ionic picture proposes, involves electron transfer from Li to F, giving Li^+ and F^-, two closed-shell ions which interact mainly by Coulomb forces and short-range repulsion. Cohesion in diamond, the covalent picture indicates, involves bond charge between atoms instead of charge transfer; directed hybrids and their 'chemical' interaction describe the interactions. At this stage controversy is minimal. The two extremes are straightforward, and some qualitative implications are obvious. One expects the Coulomb interactions within ionic crystals to favour close packing of cations around anions and vice versa, whereas the directed bonds of covalent crystals favour open structures. There are thus structural criteria for qualitative assessments of degree of covalency or ionicity.

Such qualitative criteria illustrate one of the several uses of these ideas: *classification*. One may use as input data crystal structure, crystal thermochemistry, molecular thermochemistry, spectroscopic information, dielectric constant data, etc, to *order* systems according to their covalency/ionicity, in the hope that other properties show useful related orderings. The optimist may even construct quantitative, if empirical, rules involving an ionicity parameter. Such cases, as Phillips has observed very aptly, parallel the use of temperature scales based on specific properties (e.g. Pt wire resistance). But whereas one can confidently accept an absolute temperature scale for all systems, absolute ionicity scales of general validity have little justification beyond pedagogical convenience†.

There are five main aspects that will concern us here. First, to what extent are covalency and ionicity essential in qualitative solid state physics? There is no doubt about the value of the ideas related to covalency, of course. But if one used the ideas of ionic crystals to describe a covalent crystal, would misrepresentation or merely complexity result? We shall show later that (in some cases at least) precisely parallel descriptions can be given from either the ionic or covalent limits. Secondly, can we obtain consistent, operationally defined, quantitative measures of ionicity? Over what range of phenomena are these defined? Thirdly, if we wish to relate an experimentally defined ionicity to a theoretical parameter (e.g. bond-structure charge density, Szigeti charge, or a shell charge) where should we expect this matching to fail? Fourth, what should one anticipate about the *transferability* of ionicity/covalency parameters? Finally, how valid are potentials based on an ionic description for different classes of heteropolar solids?

2. Scales of Ionicity

We shall limit our survey to a discussion of the thermochemical approach of Pauling, to the spectroscopic approach of Phillips, and to the ensemble of approaches which express themselves in terms of effective charges. To this summary we shall add remarks about the frames of reference within which much discussion is concentrated.

2.1. The grand unified schemes

Perhaps the hardest step is convincing oneself that such schemes could exist. They imply at least that one can assign (though possibly not measure) a one-parameter description of all species which orders them in a consistent and useful way. Consistency demands the same ordering whichever one uses of the many sources of experimental data (presumed reliable). Usefulness requires that observable properties are predicted with significant precision. Here one can reasonably demand that molecular, perfect-crystal and (where appropriate) defect properties all be categorised, without extra parameters to whittle away the meaning of the initial assumptions.

The first major scheme, due to Pauling (1932, 1939, 1971) is thermochemically based. Suppose the formation energy of a diatomic molecule XY is written E_{XY}. Then, for molecule AB, the quantity:

$$\varepsilon_{AB} = E_{AB} - [\text{mean of } E_{AA}, E_{BB}]$$

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† By 'general' we recognise, of course, that there are important problems in physics which do go beyond the special, if standard, cases of defect-free semiconductors and insulators usually discussed.

is a measure of the electronegativity difference $(X_A - X_B)$ of A and B, in so far as it corresponds to electron transfer from the less to more electronegative atom. The concept is ionic, i.e. covalent contributions are implicit only. The two working postulates giving *fractional ionic character* f_{AB} are designed to be both intuitively sensible and to satisfy the obvious constraints $f_{AB} = f_{BA}$ and $0 \leqslant f_{AB} \leqslant 1$, with $f_{AB} = 1$ the ionic extreme. In this case Pauling's algorithms are:

$$(X_A - X_B)^2 = \gamma\varepsilon_{AB}$$

where γ ensures that the dimensionless X_A and X_B change by 0.5 with each unit valence change in the first row of the periodic table:

$$f_{AB} = 1 - \exp[-\tfrac{1}{4}(X_A - X_B)^2] = 1 - \exp(-\tfrac{1}{4}\gamma\varepsilon_{AB}).$$

It is this quantity that has been used to understand a very wide range of chemical behaviour.

Phillips (1970; see also Phillips and van Vechten 1969, van Vechten 1969) chose a spectroscopic definition, defining a 'total energy gap' with two components

$$E_g^2 = E_h^2 + E_c^2.$$

The total gap is obtained from the optic dielectric constant

$$E_g = \hbar\omega_p/(\varepsilon_\infty - 1)^{1/2}$$

with $\hbar\omega_p$ the plasma frequency for the valence electrons; the covalent gap E_h is obtained from E_g for the non-polar system in the same row of the periodic table, with a correction for the interatomic spacing. The ionic part, E_c, is obtained as $(E_g^2 - E_h^2)^{1/2}$. Phillips defines an ionic character

$$f = E_c^2/(E_h^2 + E_c^2).$$

It is this parameter that has been used to classify, divide and identify trends in many solid state properties.

We can classify some features by considering again the diatomic AB molecule in a simple LCAO approximation (Pearson 1971). Suppose the diagonal matrix elements of the Hamiltonian are H_{AA}, H_{BB}, and that H_{AB} is the off-diagonal term. The (2×2) secular equation is easily solved to show the bonding and antibonding orbitals are separated in energy by E_G, where:

$$E_G^2 = (H_{AA} - H_{BB})^2 + 4H_{AB}^2.$$

The natural analogies make $H_{AA} - H_{BB}$ the ionic term (like E_c), and $2H_{AB}$ the covalent term (like E_h). When there is overlap S between the orbitals, the ionic term is multiplied by $(1 - S^2)^{-1}$ and the covalent term by $(1 + S^2)/(1 - S^2)$. Suppose we assume the orbitals on A and B do not overlap, so charges can be assigned without difficulty. Then we readily find

$$f' = (Q_A - Q_B)/(Q_A + Q_B) = (1 + 4\lambda^2)^{-1/2}$$

with $\lambda \equiv 2H_{AB}/(H_{AA} - H_{BB})$. Phillips' definition gives:

$$f = (1 + 4\lambda^2)^{-1} = (f')^2.$$

Clearly both f and f' will classify, divide, and identify trends equally well. They are, however, only representative members of a broad class of 'ionicities'.

2.2. *Ionicity from charge densities*

It is widely believed, especially by those who have just calculated approximate band structures, that 'ionicity' can be obtained from a knowledge of the charge density for the mean (static equilibrium) geometry. It is equally well known that this belief is false. As Orgel (1960) observes '. . . let us suppose . . . we could obtain electron densities with as great an accuracy as we wished. Would this settle the problem of covalency once and for all? The answer to this question is negative'.

2.2.1. Theoretical techniques. We now demonstrate the ambiguities that remain even when the exact charge density $\rho(\boldsymbol{r})$ is known. We shall see that the only case in which $\rho(\boldsymbol{r})$ uniquely implies ionic charges is the trivial case when the charge distributions do not overlap (i.e. $\int d^3\boldsymbol{r}\, \psi_A(\boldsymbol{r}) \Omega \psi_B(\boldsymbol{r})$ is zero for a variety of operators $\Omega(\boldsymbol{r})$, not just $\Omega = 1$). A convenient survey of definitions of ionic charges in molecules is given by Polák (1978). He also gives quantitaitve examples for what is, in effect, a generalised H_2^+ ion. For our purposes, we shall assume the *exact* charge density is given in the analytic form

$$\varphi = c_a \psi_A + c_b \psi_B,$$

where ψ_A and ψ_B are normalised functions centred on sites A and B; $\langle A|B\rangle = S$ is their (finite) overlap.

Among the more important divisions of charge density $\rho(r) \equiv |\varphi(r)|^2$ between the two sites are these, where we quote the electron charge associated with site A:

Mulliken definition, with the overlap charge equally divided:

$$Q_M = c_a^2 + c_a c_b S.$$

Löwdin definition 1, preserving the molecular dipole moment (Löwdin 1953):

$$Q_L = c_a^2 + c_a c_b S(1 - 2\bar{z}/RS)$$

where $(\bar{z}/R)$ is $\int d^3r\, \psi_A^*(z - z_M)\psi_B/R$, with z_M the midpoint of AB, z the axial coordinate and R the AB spacing.

Löwdin definition 2, based on orthogonalised orbitals $\tilde{\psi}_A$, $\tilde{\psi}_B$ (Löwdin 1950),

$$Q_0 = c_a^2 + c_a c_b S + (c_a^2 - c_b^2)F(S)$$

with $F(S) = \frac{1}{2}[(1 + S)^{1/2}(1 - S)^{1/2} - 1]$.

Projection definition, using the first-order density matrix to project out components associated with A and B (note $Q_{PA} + Q_{PB} \neq 1$ in general) (Roby 1974)

$$Q_{PA} = c_a^2 + 2c_a c_b S + c_b^2 S^2$$

$$Q_{PB} = 1 - c_a^2 + c_a^2 S^2.$$

2.2.2. Geometric partitioning. Here there are various definitions, e.g. charge within a given radius, or charge within the contour of minimum charge density. Analytical forms need further assumptions.

Even without numerical estimates, several points are clear. First, the definitions do not yield a unique Q_A or Q_B unless $S = 0$, $\bar{z} = 0$. Secondly, it is easy to devise still more sensible definitions. One might perhaps partition the overlap charge unequally, e.g. in the ratio of the atomic coefficients; giving Christofferson and Baker's (1971) $Q_{CB} = c_a^2 + [c_a^2/(c_a^2 + c_b^2)]2c_a c_b S$. Or one might make the change of dipole moment with R exact, giving a useful form Q'_L which involves derivatives $\mathrm{d}c_A/\mathrm{d}R$, $\mathrm{d}\bar{z}/\mathrm{d}R$ and $\mathrm{d}S/\mathrm{d}R$. Thirdly, in exasperation, one might note that it is possible to choose a complete set of functions centred on any site (A, B or elsewhere) and to write $\rho(\boldsymbol{r})$ exactly in terms of these one-centred functions. This would tempt one to associate all charge with the single centre, thus avoiding (albeit unhelpfully) the whole question of partitioning.

2.2.3. Ionicity from band structures. Charge partition is a more naive exercise in band theory than it is in small-molecule studies. The commonest definitions use the charge within a muffin-tin sphere (a case of geometric partitioning), the weights associated with Wannier functions (which correspond exactly to Q_0) or, in LCAO methods, analogues of the Mulliken approximation. We note in passing that methods based on dipole moments have to be used with caution in cluster calculations, since the boundary conditions can be deceptively inappropriate.

2.2.4. Experimental charge densities. Information on charge distribution is, of course, available from experiment. Single-crystal x-ray diffraction experiments can yield electron density maps. Studies of diamond and quartz, for instance, provide clear evidence of the enhancement of electron density between the nuclei that is the defining characteristic of the covalent model. Reviews of the technique are given by Stewart and Spackman (1981) and by Coppens (1977).

The data provided by such experiments, although of undoubted value, are of little use in defining ionicity scales. The method suffers from precisely the same deficiencies as those based on theoretically derived charge densities, i.e. the unavoidable ambiguities in the division of the total charge density into ionic components.

Valuable information is also provided by polarised neutron scattering experiments. These allow one to obtain maps of unpaired spin density, which may be related to covalency parameters (Hubbard and Marshall 1965). The method has been especially useful for covalency in transition-metal oxides and fluorides (see e.g. Tofield and Fender 1970, Jacobson *et al* 1974). However, the method is confined to studies of open-shell systems, and it yields information on spin delocalisation only for the partially filled orbitals. As such, the technique is clearly limited. We note that spin-resonance techniques (EPR and ENDOR) similarly yield information on unpaired spin distributions (see e.g. Hall *et al* 1963, Owen and Thornley 1966). Both neutron and spin-resonance methods give useful upper bounds on covalency in the nearly ionic limit. For instance, Fender *et al* (1968) put quite low bounds on the level of covalency in MnO and NiO.

2.3. *Ionic charges, effective and ineffective*

An effective charge, notes Cochran (1961), is a 'value for the ionic charge deduced from a physical measurement on the basis of an oversimplified model or theory'. This serves to illustrate three simple truths: first, the physical measurement is not itself of the ionic charge of supposed interest; secondly, the ionic charge is extracted within a chosen framework; thirdly, the theory or model used contains imprecisions or artefacts which limit its value. We have already encountered 'exact' theories in which an ionic charge is deduced from a 'known' charge distribution, without reference (or in cases without useful application) to experiment.

2.3.1. Lattice dynamics. In most theoretical lattice dynamics there are three basic assumptions: the Born–Oppenheimer approximation to separate electronic and nuclear motion so as to ensure a unique energy surface, the harmonic approximation to provide a correspondence with harmonic oscillator solutions, and the dipole approximation. The third approximation, that only the lowest-order multipole moment due to ionic displacement need be retained, leads naturally to a definition of effective charge

$$Q^{\mathrm{eff}} = \mathrm{d}\mu/\mathrm{d}x$$

where μ is the dipole moment magnitude and x the displacement. Three approximations are implied here. First, there is the assumption that the vectors $\boldsymbol{u}$ and $\boldsymbol{x}$ are parallel, so that Q^{eff} is representable as a scalar. Secondly, $\boldsymbol{x}$ is a single coordinate; the ion is *rigid*, so that there is no deformation of the ion to make ambiguous the definition of where the displaced ion is. Thirdly, only the single coordinate $\boldsymbol{x}$ enters: neither the dipole moment nor Q^{eff} must depend on the positions of neighbouring atoms. This group of working approximations and their problems provide strong reasons for using the shell model. Nevertheless, it is useful to look first at variants of Q^{eff} based on rigid-ion models.

2.3.2. Transverse, longitudinal and Szigeti charges. When planes of ions vibrate in the plane of a slab-like sample, Q^{eff} is the *transverse* charge e_{T}^* given by (Born and Goeppert-Mayer 1926, Callen 1949, Cochran and Cowley 1962, Burstein *et al* 1967)

$$e_{\mathrm{T}}^* = [(\omega_{\mathrm{LO}}^2 - \omega_{\mathrm{TO}}^2)\varepsilon_\infty(M\Omega/4\pi)]^{1/2}$$

with M the reduced mass and Ω the cell volume. If the ions vibrate normal to the plane of the slab, one has instead the *longitudinal* charge (Callen 1949)

$$e_{\mathrm{L}}^* = [(\omega_{\mathrm{LO}}^2 - \omega_{\mathrm{TO}}^2)\varepsilon_\infty^{-1}(M\Omega/4\pi)]^{1/2}.$$

Finally, depending on precisely where one puts local-field corrections, one can end with the Szigeti charge:

$$e_{\mathrm{Sz}}^* = \frac{3}{\varepsilon_\infty + 2}e_{\mathrm{T}}^* = \frac{3\varepsilon_\infty}{\varepsilon_\infty + 2}e_{\mathrm{L}}^*.$$

For $\varepsilon_\infty = 3$, typical of ionic crystals,

$$e_{\mathrm{Sz}}^* = 0.6e_{\mathrm{T}}^* = 1.8e_{\mathrm{L}}^*.$$

For $\varepsilon_\infty = 10$, typical of III–V hosts:

$$e_{\mathrm{Sz}}^* = 0.25e_{\mathrm{T}}^* = 2.5e_{\mathrm{L}}^*.$$

In general $e_{\mathrm{T}}^* \geqslant e_{\mathrm{Sz}}^* \geqslant e_{\mathrm{L}}^*$. If one insists on using a rigid-ion model, therefore, there are many choices without even resorting to experiment.

2.3.3. Cohesive energy. Whilst close relations are usually assumed between cohesion and the interatomic forces which determine lattice vibrations, this is often mere wishful thinking. In the NaCl structure, for instance, the ionic polarisability does not appear in cohesion (all ions are at sites with inversion symmetry, so dipole moments vanish) but is fundamental in lattice dynamics. Clearly it is a convenience to assume that the charge Q_{coh}, which comes from a simple model of cohesion, equals some other charge Q^{eff} from lattice dynamics. In rigid-ion models, there is no flexibility to guarantee $Q_{\mathrm{coh}} = Q^{\mathrm{eff}}$, whichever definition is used. In shell models, some flexibility remains, since Q_{coh} should equal the sum of core and shell charges ($Q^{\mathrm{eff}} \equiv Z = X + Y$). However, one is not entirely free to vary $X + Y$ arbitrarily, and the assumption that the sum is equal to Q_{coh} is an arbitrary constraint. Whether it is a strong constraint or not depends too on the short-range interactions. Whilst they give only a modest part of the cohesive energy (typically 10% in respectably ionic crystals) they can incorporate a number of short-range corrections. Thus *empirical* short-range potentials may have an extra component of flexibility over directly calculated ones (the phrase *a priori*, used in this context, often means merely that the workers found a convenient place to begin).

2.3.4. Interatomic potentials. This discussion leads us naturally into what is possibly the most 'practical' question in the debate on ionicity: how valid are the potential models for solids based on an ionic description? In general, ionic model potentials have a simple pairwise form: short-range repulsive terms (usually described by some simple analytical function) are added to the Coulomb interaction; and electronic polarisation is simulated in most modern studies by the shell model. An incentive for studies of interatomic potentials has been provided by the development of computer simulation codes for modelling the perfect and defect properties of crystals. Potentials (i.e. some simple algorithm for total energy as a function of geometry) are the basic input into these simulations, and their quality is the major factor in determining the reliability of the results. Most modern simulation codes are limited to pair potential models, although extensions are in progress to include, for example, bond–charge interactions or bond-bending terms.

Potentials may be developed by parameter fitting to observed crystal properties, including structural data, elastic and dielectric constants and phonon dispersion curves, and for a wide range of crystals, an impressive measure of agreement can be achieved between observed and fitted crystal properties; moreover such crystals include examples of compounds where a contribution from covalence might be thought to be significant. Examples of fitted and observed properties are given in table 1.

Potentials may also be developed using theoretical methods; both electron gas techniques (e.g. Gordon and Kim 1972) and Hartree–Fock methods have been applied to the study of short-range potentials. In many cases the parameters derived are similar to those obtained from the empirical fitting procedures although sometimes significant differences may occur. A compilation of both types is given by Stoneham (1979). Ionic model potentials have proved remarkably successful in computer modelling studies of defective solids. Formation and activation energies have been calculated for many oxide and halide crystals; typical results are given in table 2. The same methods have even worked well for systems like ZnSe and Li_3N. Greater details of these studies are available in the reviews of Catlow (1980) and Catlow and Mackrodt (1982).

To what extent does the success of these studies validate the model used? A danger inherent in all fitting procedures is that, if sufficient parameters are available, the fitted values may have no physical significance, being merely a parameterisation of the data used in their derivation. The ability to reproduce the parameters by theoretical methods may at least partially remove this problem. A better test, however, is provided by the successful extension of the model to the prediction of properties outside the range used in their derivation. For this reason we believe that the success of the potentials used in defect studies is of particular significance. Defect energies depend critically upon the extent of lattice relaxation around the defect. The accuracy of the defect calculation for the materials reported in table 2 suggests that for these crystals ionic model potentials describe well the response of the lattice to the extensive perturbation that is provided by a charged defect, i.e. the *displacements* which are caused by these perturbations are accurately modelled by the potentials based on the use of integral or near-integral

Table 1. (*a*) Calculated and observed crystal properties for Al_2O_3 (after Catlow *et al* (1982a, b) who give references to experimental data).

Properties		Calculated	Observed
Lattice energy (eV)		−160.21	−160.4
Elastic constants (10^{11} dyn cm^{-2})	C_{11}	42.96	49.69
	C_{12}	15.48	16.36
	C_{13}	12.72	11.09
	C_{33}	50.23	49.8
	C_{14}	−2.99	−2.35
	C_{44}	16.66	14.74
	C_{66}	13.70	$(C_{11} - C_{12})/2$
Dielectric constants	ε^0_{11}	9.38	9.34
	ε^0_{33}	11.52	11.54
	ε^∞_{11}	2.08	3.1
	ε^∞_{33}	2.02	

Table 1. (*b*) Calculated and observed crystal properties for CaF_2 (after Catlow and Norgett (1973) who give references to experimental data). Values in parentheses were used in fitting.

Properties		Experimental	Calculated value
Lattice constant (Å)	r_0	2.722	(2.722)
Second-order elastic constants (10^{11} dyn cm^{-2})	C_{11}	17.124	(16.9)
	C_{12}	4.675	(4.80)
	C_{44}	3.624	3.23
Dielectric constants at zero and high frequency	ε_0	6.47	(6.42)
	ε_∞	2.05	(2.01)
Transverse optic and Raman frequencies (cm^{-1})	ω_{TO}	270.0	(259.2)
	ω_R	330.5	310.7
Third-order elastic constants (10^{11} dyn cm^{-2})	C_{111}	−124.6	−107.8
	C_{112}	−40.0	−33.8
	C_{123}	−25.4	−17.5
	C_{144}	−12.4	−9.3
	C_{166}	−21.4	−23.2
	C_{456}	−7.5	−7.8
Lattice formation energy (eV)	H_L	−26.76	−28.06

charge. To this extent, the ionic model provides the basis of a good description of these systems.

To summarise this section, our knowledge of ionicity derives from a variety of experimental and theoretical techniques, each of which yields information on different properties of the solid. The most widely used ionicity scales are based on thermochemical and spectroscopic data. Information on charge distribution may be obtained from x-ray-polarised neutron diffraction, although the analysis of these data in terms of ionic charges is always and necessarily ambiguous when interpretation in terms of effective charges is required. Lattice properties—phonon dispersion curves, elastic and dielectric constants—yield information on the extent to which displacements and dipole moments in crystals are compatible with an ionic description. We note that applications of ionicity in the development and use of interatomic potential models are often most closely related to this last usage: it is the ionicity of § 2.3, not of § 2.1 or 2.2, that is important.

Table 2. Some defect formation and activation energies in metal halides and oxides. For references to calculated and experimental data we refer to Catlow and Mackrodt (1982).
(*a*) Formation energies

Compound	Defect	Calculated energy (eV)	Experimental energy (eV)
NaCl	Schottky pair	2.32	2.30
CaF_2	Frenkel pair	2.75	2.7
MgO	Schottky pair	7.5	5–7
ZnO	Cation Frenkel pair	2.51	—
AgCl	Cation Frenkel pair	1.4	1.45

(*b*) Activation energies

Compound	Process	Experimental energy (eV)	Calculated energy (eV)
NaCl	Cation vacancy migration	0.67	0.65–0.75
CaF_2	Anion interstitial migration	1.0	0.91
MgO	Cation vacancy migration	2.1–2.3	2.2

3. Frames of reference

Before discussing ionicity in specific systems, we turn to a number of features presumed in our last section.

3.1. Electronegativity versus covalency/ionicity

Whilst many discussions are framed as if the concepts were the same, this is clearly not so. *Electronegativity* is only the first of several concepts which decide the degree of covalency. A second is a '*propensity to bond*' parameter. This takes various forms: the homopolar gap in Phillips' (1970a, b) approach, the off-diagonal (transfer) matrix element in standard tight-binding, the density of electrons at the edge of the Wigner–Seitz cell in the theory of Miedema *et al* (1973), the bonding parameter in semi-empirical molecular orbital schemes, etc. And a third factor (though it can be built into the first two parameters) is the ratio of a typical orbital radius to interatomic spacing.

3.2. One charge per ion

A second assumption is that each ion can be represented by one charge only. This unique number has to fulfil many separate conditions, notably to represent the field at large distances and the dipole produced per unit displacement (ignoring the many, often unmeasurable, alternatives). When one goes to the *shell model*, for instance, one uses two charges, both to recognise the several criteria and to represent the interactions between short-range repulsions and polarisability. But how general is Dick and Overhauser's original idea that the shells correspond to the outer electrons, and the cores to the nucleus plus inner electrons? Sadly, the clear physical picture can lead one astray. Sometimes this is painfully apparent: shells with charges opposite in sign to electrons clearly represent other effects, e.g. overlap charge components (Bilz *et al* 1975). At other times deception is subtle. In a calculation coupling pseudopotential electronic structure and shell-model displacements, suppose one divides the interaction of a bound electron with an ion into (*a*) a point-ion contribution and (*b*) an 'ion-size correction' (Bartram *et al* 1968). Can one assume the shells experience all the ion-size forces, as one's intuition might suggest (Stoneham and Bartram 1970)? On the other hand, if one uses a self-consistent treatment, e.g. Hartree–Fock, of some small group of atoms, should one force this group to have the dipole moment given in the shell model? Or should one make sure that these atoms experience the correct electric field due to the rest of the crystal, and assume Hartree–Fock theory takes care of the rest (see Norgett *et al* 1977, Sharma and Stoneham 1970)? These questions are part of a whole range of problems, often merely ignored, in calculations of defect structure. They emerge too in the separate context of relating experiment and theory. Does a particular experiment monitor a *shell* coordinate or a *core* coordinate? This is important, since the displacements can be opposite in sign. In surface structure measurements, for instance, (see Stoneham 1981) core positions are measured in neutron scattering, LEED and EXAFS experiments, whereas low-energy rare-gas atom diffraction appears to monitor shell positions.

3.3. Is the covalent/ionic switch sudden?

If one is to limit one's vocabulary to covalent *or* ionic, there must be a minimal intermediate regime. This sharp boundary notion is implied in much 'mapping' work for crystal structures. Are there cases where sudden changes seem to appear? The situations which appear to show relatively sudden changes include Schottky barriers (Kurtin *et al* 1969, Mele and Joannopoulos 1978), organic polar semiconductor/metal systems (Metzger 1981), excited states of rare gases on metals (Cunningham *et al* 1980), and no doubt some other systems. Other situations show no sign whatsoever of a sudden change, e.g. the trends of Mn^{2+} hyperfine structure in hosts with different degrees of covalency (Simanek and Müller 1970). We note in passing that the fractional charges associated with solitons are not in any way associated with covalency. As Prange (1982) has noted, these non-integral (possibly irrational) multiples of $|e|$ occur only if there is a change in polarity on crossing the soliton, rather like a case noted for ferroelectric domain walls.

Sudden transitions presumably require a reinforcement mechanism: a cooperative interaction which drives the system away from comparable ionic and covalent contributions. Madelung terms, quadratic in suitable effective charges, help; shifts of ionisation energy and other factors with occupancy (e.g. Coulson *et al* 1962) are also involved.

4. Materials

Previous sections have stressed the diversity of meaning that may be attached to the term 'ionicity' when used in any operational sense. The present section attempts to summarise for a range of materials the present states of our knowledge of the degree of ionicity in its various senses. We shall emphasise the consequences after theoretical investigations of the materials.

4.1. *Metal halides*

Table 3 lists Phillips ionicities for a range of metal halides; Pauling electronegativities are also given. We exclude from consideration the molecular halides found by metals in higher valence states, e.g. UF_6, $PbCl_4$. The halides of the metals of groups I and IIA show high values of f, in line with our preconception that they are the most strongly ionic materials. The decline in ionicity with increased electronegativity of the metal is reflected in corresponding structural changes seen in the trend to lower coordination numbers (as in $ZnCl_2$) and the adoption of layer structures (e.g. $CdCl_2$). The inability of ionic model potentials to reproduce accurately the cohesive energies of specific halides such as AgCl might perhaps be evidence of significant deviation from ionicity in these halides.

Table 3. Phillips ionicities and Pauling (1960) electronegativities of some metal halides.

Compound	Phillips ionicity (f)	Metal electronegativity	Non-metal electronegativity
LiF	0.915	1.0	3.90
LiCl	0.903	1.0	3.15
NaF	0.946	0.9	3.90
NaCl	0.935	0.9	3.0
NaBr	0.934	0.9	2.8
KF	0.955	0.8	4.0
KBr	0.952	0.8	2.8
AgCl	0.856 [0.877†]	1.9	3.0
AgBr	0.850 [0.864†]	1.9	2.8
AgI	0.770 [0.772†]	1.9	2.5

† Pauling (1960) ionicity.

Evidence from sources other than those implied above (i.e. from thermochemical and dielectric data) is sparse, except for a small group of materials—principally the alkali halides, alkaline-earth fluorides and silver chloride. For these compounds there is detailed information on lattice dynamical properties: reviews are available from e.g. Cochran (1971) and Singh (1982). There is little indication from these data of any significant deviation from ionicity, where 'ionicity' is used in the sense of Cochran (1971) and amplified in § 2 of the present paper. Whilst measured phonon curves *are* observed to deviate from the predictions of simple shell-model ionic potentials, we should stress that for certain compounds, e.g. KCl, such deviations are small and are confined to optical branches of the dispersion curves. The deviations are greater for AgCl than for the alkali halides, but there is no clear evidence that any of these effects may be attributed to covalence. Most of the discrepancies between observed and calculated dispersion curves may be accounted for by going beyond the dipole approximation to include quadrupole terms, or by the inclusion of ion deformation terms, e.g. 'breathing' and deformable shell effects, i.e. isotropic and elliptical shell deformations—the latter being of particular importance for AgCl. There seems therfore to be no clear evidence from lattice dynamical studies for covalence in non-molecular metal halides. The ionic model potentials have enjoyed a remarkable degree of success in predicting both phonon dispersion curves and more testing properties such as defect formation energies (see Mackrodt 1982). This applies to the silver halides, for instance, as well as to the alkali halide materials. It would seem that for most 'modelling' purposes ionic model potentials are fully acceptable.

In concluding this section we should note that detailed electron density maps are available for some compounds in this class. These observed maps clearly support the assumption of ionicity, for there is no evidence for bonding electron density between the nuclei. Yet even here there is ambiguity if the density maps are used to deduce partial ionic charges: as usual, a range of values may be obtained, depending on the choice of sphere radii.

4.2. Metal oxides

A greater diversity of information is available for these compounds. In addition to thermochemical and spectroscopic data and dielectric functions, which yield Phillips ionicities, data are available from lattice dynamical studies, from magnetic measurements, including polarised neutron scattering and from theoretical calculations.

The Phillips ionicities given in table 4 demonstrate the trends to be expected from the deviations in electronegativity. However, the lattice dynamical data, as for the halides, show little evidence for covalence: figure 1 shows dispersion curves for NiO and UO_2 both of which can be reasonably reproduced by ionic, shell-model potentials. Again, deviations from the predictions of this model can generally be attributed to ion deformation effects; an example is provided by MgO, where 'breathing' effects of the O^{2-} ion appear to play an important role.

Table 4. Phillips ionicities and Pauling electronegativities for some metal oxides.

Compound	Phillips ionicity (f)	Metal electronegativity†
MgO	0.841 [0.911‡]	1.20
CaO	0.913	1.00
SrO	0.926	1.00
ZnO	0.616	1.49
CdO	0.785	1.40

† Pauling electronegativity for oxygen = 3.50.
‡ Pauling (1970) ionicity.

Polarised neutron scattering experiments have been performed on MnO, NiO and UO_2. In all three cases, the degree of transfer of unpaired electron density from the unpaired cation spin orbitals to the ligand, is small (Fender *et al* 1968). As argued in § 2, the interpretation of transferred spin density quantitatively in terms of partial charges (or called any other ionicity scale) is ambiguous. Nevertheless, there seems to be no clear evidence from polarised neutron studies for large degrees of covalence in transition-metal or actinide oxides.

The evidence from theory is confusing. Band-structure calculations are reported for a number of the divalent transition-metal oxides like TiO, MnO and NiO (Mattheiss 1972, Kunz 1981) and for UO_2. The exact interpretation of the results is difficult, although population analyses suggest significant deviation from ionicity. In contrast, detailed Hartree–Fock calculations of Colbourn and Mackrodt (1983) for MgO for small clusters of ions (surrounded by point charges) indicate a very high degree of ionicity for

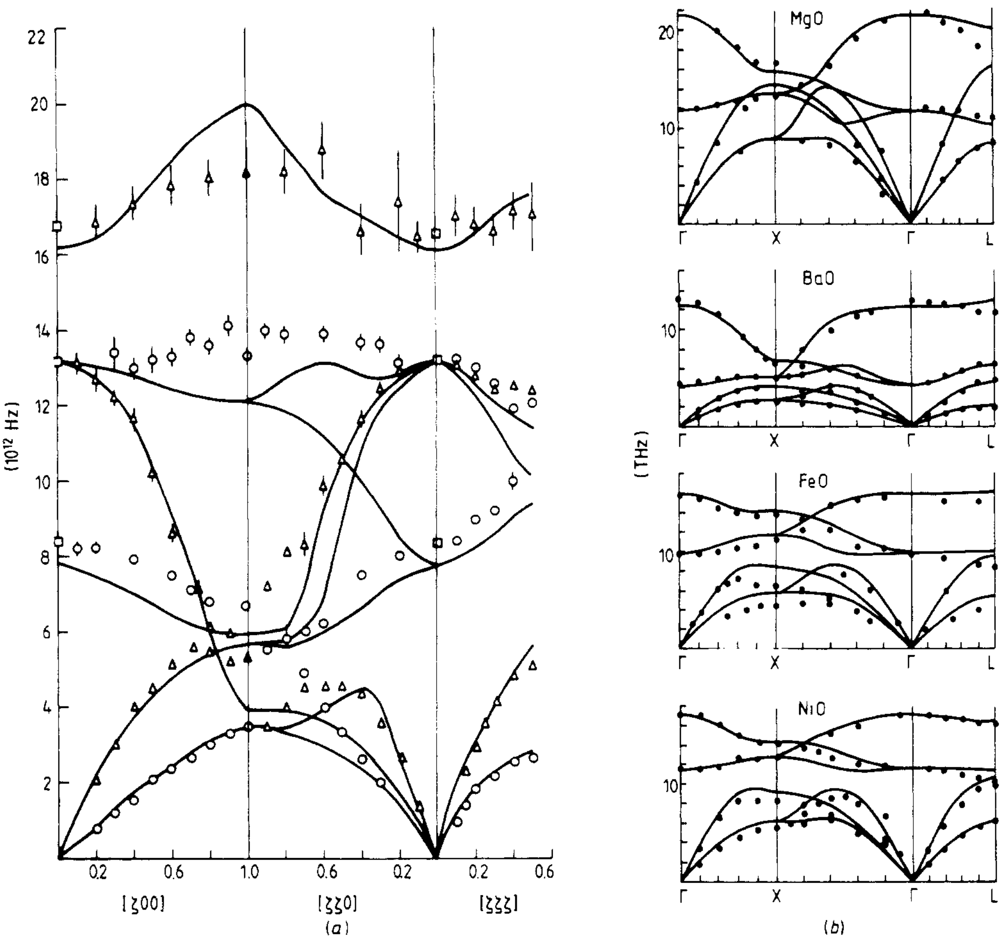

Figure 1. Phonon dispersion: predictions from ionic models compared with experiment. (*a*) Theory for UO_2 (Harding *t al* (1980), based on potentials of Catlow (1977)) and experiment of Dolling *et al* (1965). (*b*) Theory for simple oxides (Sangster and Stoneham 1980) compared with experiments of Sangster *et al* (1970) for MgO, Chang *et al* (1975) for BaO, Kugel *et al* (1977) for FeO and Reichardt *et al* (1975) for NiO.

this oxide. Mackrodt and co-workers (Mackrodt 1983) have also shown that for a large number of oxides interionic potentials derived by theoretical methods—either electron gas or Hartree–Fock—can yield remarkably good agreement with structural and dynamic properties of transition-metal and actinide oxides. Moreover, the potentials, when applied in studies of defect and surface properties, yield reliable quantitative results.

The position for the oxides therefore appear to resemble those of the halides. There is clear evidence of the inability of ionic model potentials to reproduce adequately thermochemical data in the oxides of the less electropositive metals, but there is little evidence from other sources of strong deviations from the model. We have noted before that cohesion (measured thermochemically) and interatomic forces (from elastic or dielectric data) are determined by different features on an atomic scale. The results for these less electropositive metal compounds suggest we may still use an ionic framework provided we do not try to invoke both types of feature simultaneously.

4.3. *(II/VI) and (III/V) semiconductors*

There is no question of the occurrence of extensive deviations from ionicity in these systems; this is shown by Phillips ionicities (see table 5), by electron density maps and by lattice dynamical studies (Martin 1970). The main question is whether the ionic model can ever form an acceptable approximation in studies of these systems. Some evidence here has recently been provided by Harding and Stoneham (1982) who derived ionic model potentials for ZnSe which successfully reproduced elastic and dielectric constants for these materials. The potentials were applied in a study of defect formation and charge-transfer transition energies in ZnSe.

Table 5. Phillips ionicities and Pauling electronegativities for II–VI and II–V compounds.

Compound	Phillips ionicity (f)	Metal electronegativity	Non-metal electronegativity
ZnS	0.623	1.49	2.60
ZnSe	0.630	1.49	2.55
CdSe	0.699 [0.558†]	1.40	2.55
CdTe	0.675 [0.519†]	1.40	2.30
GaP	0.327	1.95	2.15
GaAs	0.310	1.95	2.10

† Pauling (1970) ionicity.

Harding and Stoneham's discussion makes two points relevant here. First, one can start from two entirely different extremes, namely ionic (Zn^{2+}, Se^{2-}) or covalent (Zn^{2-}, Se^{2+}) and deduce qualitatively identical pictures of some simple defects. This, shown for the V^- centre (formed by removing Zn^+) was noted previously by Stoneham (1975, p 618). Secondly, certain observable properties are determined by the polarisation of the lattice. Any model that correctly quantifies polarisation will successfully predict these properties. Degrees of covalency and ionicity become important only for other properties (Stoneham and Harding 1982).

Harding and Stoneham's work suggests that the ionic model could form the basis of acceptable potentials for certain properties of some of these systems; although clearly elaborations of the model of the type that will be discussed in the next section will almost certainly be necessary for satisfactory models.

4.4. *Quartz and silicates*

These materials are generally considered as covalently bonded networks with some degree of ionicity. Such models are supported by electron density maps which for SiO_2, for instance, clearly show regions of bonding electron density (Stewart *et al* 1980, Stewart and Spackman 1981). More general support for this description is provided by the 'openness' of the structures of the polymorphs of SiO_2 and of many mineral systems.

The question of the degree of ionicity in quartz has been controversial. Pauling (1980) on the basis of electronegativity arguments proposed an ionicity of 52%. A study of x-ray photoemission favoured 58% for SiO_2 and 63% for $MgSiO_3$ (Tossell 1977). Such values are now widely accepted. Whilst lattice dynamical studies clearly reveal the inadequacy of ionic models for quartz, recent work of Catlow *et al* (1983) has shown that it is possible to reproduce the elastic and dielectric properties of SiO_2 with reasonable accuracy using a shell model plated with full ionic charges, two-body ion–ion repulsive forces, and bond-bending terms.

There is some evidence for higher ionicities in the less-condensed silicate structures, i.e. those systems based on isolated SiO_4^{4-} groups and on silicate chains and rings. X-ray diffraction studies (Sasaki *et al* 1980) suggest relatively high ionicities (of 60–70%) for $CaMg(SiO_3)_2$ (a chain-structured silicate). In addition, for these types of silicates a surprising measure of success has been enjoyed by ionic model potentials in predicting crystal structures by energy minimisation techniques (Parker 1983, Parker and Catlow 1983). Table 6 lists some of the silicates whose structures which have been reproduced within experimental error by energy minimisation using ionic model potentials. More critical tests of the validity of these potential models will be provided by calculations of dispersion curves and of phase transition energies. Such work is in progress.

Table 6. Silicate minerals investigated by energy minimisation techniques for which structures have been successfully reproduced.

Type	Name	Formula
(1) Isolated SiO_4 tetrahedra	Forsterite	Mg_2SiO_4
	Fayalite	Fe_2SiO_4
	Tephroite	Mn_2SiO_4
	Zircon	$ZrSiO_4$
	Thorite	$ThSiO_4$
	Uranite	$USiO_4$
(2) Ring structures	—	$Na_2Be_2Si_3O_9$
	α-strontium metasilicate	α-$Sr_3Si_3O_9$
	Beryl	$Al_2Be_3Si_6O_8$
(3) Chain structures	Orthoenstatite	$MgSiO_3$
	Orthoferrosilite	$FeSiO_3$
	Sodium metasilicate	Na_2SiO_3

We should note that the simpler ionic model potentials showed clear inadequacies when applied to structural studies of more condensed silicates (e.g. zeolites), although it is likely that improvements will follow when bond-bending forces of the type used in the study of quartz are incorporated.

For silicates, therefore, despite the undisputed existence of an appreciable contribution from covalence, ionic model potentials are useful approximations for at least certain classes of structure and behaviour, and it is possible that relatively simple extensions of the model would enable useful models to be constructed for the entire range of mineral systems.

4.5. Materials: summary

The brief survey we have just presented has for obvious reasons excluded certain classes of solids—mainly metals, homopolar and molecular solids. However, for the materials considered, i.e. heteropolar solids with continuous structures, we have found that the ionic model often provides useful approximations *for certain classes of application*. This is true even when thermochemical and spectroscopic data and electron density studies may suggest appreciable contributions from covalence. The use of the ionic model potentials for these systems should not be rejected on the grounds that some deviation from simple ionicity is known to occur. Ionic models of the sort described provide a framework within which the important energies can be described. Properly used, ionic potentials may still provide useful and reliable results, and should certainly not be discarded because some effective charge (perhaps irrelevant to the calculation in hand) deviates from the ionic charge adopted.

5. Conclusions: practical ionicity

This article has emphasised repeatedly that the meaning and use of the terms ionicity and covalency depend upon the physical properties that are being discussed. In which contexts are these concepts useful? There is certainly no value in debasing the words by using them to hide ill-understood complex behaviour. But, apart from such misuse, we believe that the terms now have least quantitative use in those solid state contexts closest to their original molecular applications, that is in the description of bonding and its relation to the electron density distribution. Although these areas have attractive qualitative applications, we have seen that it proves impossible to abstract unique and unambiguous ionicity parameters (e.g. partial charges) from such sources. In particular, the analysis of electron density distributions into charged spheres appears to be an exercise of little value.

The Pauling and Phillips ionicity scales fulfil a useful function in parameterising experimental data (thermochemical and spectroscopic respectively) which are clearly related to charge distribution, and the scales which emerge have unquestioned value. However, it is questionable as to the extent to which these scales do more than provide a useful summary of the data on which they are based. The most practical application of the concept of ionicity concerns the development of interatomic potentials. Here 'ionicity' is used to provide a workable framework for modelling, rather than an ordered sequence of systems. The validity of such potentials can be assessed by their performance in predicting perfect-lattice properties. More critically, tests of the model and the framework are provided by their success in predicting defect and surface properties and, where data are available, the properties of molten salts. Using these criteria, we believe it will be found that the ionic picture and ionic model potentials may be used consistently and accurately in describing a wide range of heteropolar solids.

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