Are Covalent Bonds really Directed?

I. David Brown

Brockhouse Institute for Materials Research, McMaster University, Hamilton, ON, Canada L8S 4M1.

idbrown@mcmaster.ca

Abstract

The flux theory of the chemical bond, which provides a physical description of chemical structure based on classical electrostatic theory, correctly predicts the angles between bonds, to the extent that they depend on the intrinsic properties of the bonded atoms. It is based on the justifiable assumption that the charge density around the nucleus of an atom retains most of its spherical symmetry even when bonded. A knowledge of these intrinsic bond angles permits the measurement and analysis of the steric angular strains that result from the mapping of the bond network into three dimensional space. The work ends by pointing out that there are better ways of characterizing bonds than describing them as covalent or ionic.

Keywords

Bond angles

Flux bonding theory

Directed bonds

Introduction

It is often said that 'covalent bonds are directed but ionic bonds are not'. This is presented as if it were a profound observation about the nature of chemical bonding, but it

depends on the questionable assumption that bonds can be neatly divided into two clearly distinguishable classes, covalent and ionic, even though it is widely accepted that bonds lie on a single continuum and such a distinction is difficult to make.

The purpose of this paper is to examine to what extent bonds can be said to be directed. Using the flux theory of the chemical bond, more fully described by Brown (2014a), it argues that bond directions are determined by the spherical symmetry of the atoms and no distinction needs to be made between bonds of different character. The flux theory is first briefly reviewed as it involves few if any of the concepts commonly used to describe chemical bonding.

The flux theory of the chemical bond

For many years it has been fashionable to discuss chemical bonding as a quantum phenomenon, but the idea of a chemical bond predates quantum mechanics by half a century; its properties are rooted in classical physics, yet in our search for a quantum explanation of bonding we have failed to appreciate the extent to which classical electrostatic theory gives a physically correct description of the chemical structures formed by the quantum atom. While there is no doubt that quantum mechanics is essential for understanding atomic spectra, chemical structure generally involves only the ground state of the atom so that the greater part of structure theory is readily derived using only classical electrostatics. The key is to recognize that the chemical bond and the electrostatic flux have the same properties. Both depend only on the amount of charge (the valence) that is used to form the bond and neither depends on where that charge is located. This contrasts with quantum mechanical descriptions, which supply exactly the information that the bond theory does not require. Quantum mechanics accurately describes the location of the charge between the atoms, but is unable to identify how much charge is used to

form a given bond. Quantum mechanics cannot be entirely ignored in such a classical approach, but in most cases the essential constraints that it describes can easily be introduced via a few plausible ad hoc rules and a small number of empirically determined atomic and bond parameters. This is not to say that quantum calculations do not properly describe chemical bonding, only that the flux picture provides a complementary, simpler, yet physically accurate picture that has many advantages in predicting structure and geometry. This section describes the features of the flux model that are necessary to understand how the flux can be used to determined bond angles. It is a particularly simple theory because it uses only concepts that are introduced early into the physics curriculum at about the same time that the chemical curriculum introduces the concept of the chemical bond.

An important heuristic that underlies the flux theory of the chemical bond is the principle of maximum symmetry which states that:

> A system in stable static equilibrium adopts the highest symmetry that is consistent with the constraints acting on it (Brown 2009). (1)

The justification for this principle is that the presence of a symmetry element in such a system is necessarily an energy minimum with respect to any deformation of the system that breaks this symmetry. By definition, a system in stable static equilibrium is at an energy minimum, and displacing an atom in such a system from a mirror plane (for example) in either direction must result in an increase in the energy. An equilibrium system with mirror symmetry has a lower energy than the same system in which this mirror plane is lost, unless there is some physical constraint that prevents the system from adopting the mirror symmetry. A corollary of this principle is:

If a system lacks a potential symmetry element, a constraint that breaks that symmetry must be present. (2)

The electrostatic flux that lies at the heart of the theory is the same as the number of Faraday lines of electric field that link two equal and opposite charges. It is scaled so that the flux is equal in magnitude to each of these charges, and if each line of field represents one unit of charge, the flux is equal to the total number of lines linking the charges. The unit in which the charge and flux are measured in this theory is the valence unit (vu) which is equal to the charge of one electron. The valence of an atom is defined as the amount of charge the atom uses for bonding.

An atom consists of a nucleus surrounded by a cloud of negative charge whose density can be calculated from quantum mechanics. Although the charge surrounding the nucleus is often described as being composed of discrete electrons, individual electrons can be neither identified nor located in the atom; the electron as an entity disappears as soon as it enters the atom, but it bequeaths its charge, spin and mass to the charge cloud of the atom. For this reason the term 'charge density' is preferred to the more usual term 'electron density'.

Because the flux does not depend on the location of the charge, details of the radial distribution of the charge density are irrelevant in the flux theory. However, for the calculation of angles it is important that the flux have spherical symmetry. For the free atom spherical symmetry follows from the principle of maximum symmetry, but the strong central force of the nucleus ensures that the charge density remains essentially spherical even when the atom is bonded . Although on bond formation the charge density relaxes in important ways, the density typically changes by only a few percent. While this results in significant changes to the energy,

the difference it makes to the flux description of the bond is small and unimportant. The assumption of spherical symmetry, and a consideration of where this spherical symmetry might be violated, is central to the prediction of bond angles.

<Figure 1 >

For atoms with atomic numbers less than 18 (argon) the ionization energies identify a shell of charge (known as the valence shell) that is bound sufficiently weakly to be available to form chemical bonds. This shell carries a negative charge which is linked to the positively charged core by an electrostatic flux equal to the amount of charge in the valence shell. Fig. 1 shows a schematic picture of two bonded atoms. The valence shell (gray) of each atom is shown as separated from its respective core (light gray) so as to leave room to display the flux lines (arrows) that link the valence shell to the core. This schematic separation is permitted, because although in the physical atom the core and valence shell overlap, the flux does not depend on where the charges are physically located.

When two atoms form a bond, their valences shells overlap as shown conceptually by the black region in Fig. 1, each atom retaining spherical symmetry and contributing equal amounts of charge to the bond. The flux that forms the bond is shown by the solid arrows linking the core of each atom to the valence charge that each atom contributes to the bond.

The overlap between the two valence shells occurs at some point along the line joining the two nuclei, but since the flux does not depend on where this point occurs we are free to imagine the overlapping bonding charge lying at any convenient point. We can assume that it lies at the center of the bond, or if it proves more useful, we can assume that all the bonding charge lies within the boundary of either of the two bonded atoms. Whichever choice we make,

the flux is the same, but the different choices lead to different bond models. If we assume that the overlap occurs in the middle of the bond we have the *neutral atom model* in which we assign each portion of the bonding charge to its own atom. This is the situation shown in Fig. 1.[1] Alternatively, if we assign all the bonding charge to the atom that we call the anion, we have created the *ionic model* in which the flux lines run from the cations to the anions. Restricting bonds to those with integral valence leads to the VSEPR model discussed in Section 6 as well as the ball-and-stick model of organic chemistry. Because the flux is independent of the actual location of the charge, all these models can be used to describe any bond, regardless of where the bonding charge might physically be located, subject only to any assumptions that restrict the scope of the model. For example, the ionic model can be used to describe covalent structures such as the acetate ion (Brown 1980), subject only to the topological restriction that every bond must have an atom labelled 'anion' at one end and an atom labelled 'cation' at the other; the ionic model cannot be used to describe cation-cation or anion-anion bonds. This restriction is mathematical not chemical, so the anion electronegativity need not be larger than that of the cation. The neutral atom model can be used to describe any localized bond, but the ionic model leads to more useful theorems.

The closer two atoms are brought together, the greater the amount of charge in the bond overlap region and the greater the flux forming the bond. The length of the bond thus correlates with the amount of flux in the bond, but it also depends on the sizes of the atoms. The size does require a knowledge of the radial distribution of the charge of each atom and can only be

[1] Fig. 1 shows only one bonded atom. In crystals each atom is surrounded by other atoms so all the valence shell charge is used for bonding. However, the presence of non-bonding charge (lone pairs) in the valence shell prevents the formation of bonds in some directions resulting in the creation of molecules (see Sections 6 and 7).

calculated using quantum mechanics, so in the flux theory the correlation between the length, R_{ij}, and the flux, φ_{ij} (or valence,[2] s_{ij}) of the bond between atoms i and j is determined empirically from crystal structure determinations. This correlation can be described for most bond types by the simple expression given in eqn (3), whose two empirical parameters, R_0 and b, are tabulated for many bond types (Brown 2014b) and are robustly transferable among all bonds between the same pair of atoms.

$$s_{ij} = \exp((R_0 - R_{ij})/b) \quad (3)$$

Since the valence of an atom is the total amount of charge it uses to form all its bonds, it follows that the sum of the fluxes, φ_{ij} (or valences, s_{ij}) of all the bonds formed by atom i must be equal to its atomic valence, V_i. The valence sum rule, eqn (4), is the central rule of the flux theory.

$$V_i = \sum_j \varphi_{ij} = \sum_j s_{ij} \quad (4)$$

In the ionic version of the flux theory a chemical bond is an electric capacitor since it consists of two equal and opposite charges (on the cation and the anion) linked by electrostatic flux. A bond network is therefore a capacitive electrical circuit. It can be solved using the two Kirchhoff equations provided the capacitance of each bond is known. The bond capacitance cannot be calculated from first principles, but in the absence of any constraint that might destroy the intrinsic equivalence of all the bonds, the principle of maximum symmetry implies that all bonds should have the same capacitance. If the capacitances are all the same they cancel from

[2] The bond flux and bond valence are two different names for the same concept. The term 'bond flux', φ, is normally used for the theoretically determined flux, 'bond valence', s, is used for the same quantity when determined experimentally. The distinction is convenient when comparing theoretically predicted values with the experimentally determined values which are subject to experimental uncertainty.

the Kirchhoff equations, yielding the set of network equations (5) and (6) from which the bond fluxes can be predicted (Brown 2002).

$$V_i = \sum_j \varphi_{ij} \quad (5)$$

$$0 = \sum_{\text{loop}} \varphi_{ij} \quad (6)$$

Once the fluxes are known, bond lengths can be predicted using eqn (3) with φ substituted for *s*. In the absence of any constraint arising from electronic anisotropies (Sections 7 and 8) or steric stresses (discussed in Section 9), the bond lengths predicted this way agree with experiment to within a few hundredths of an Ångström (Preiser et al. 1999). These predictions of bond lengths can be made from a knowledge of only the bond topology; it is not necessary to know the spatial arrangement of the atoms in three-dimensions.

The ion, i, can be characterized by its bonding strength, S_i, which is defined by eqn (7), where $\langle N \rangle_i$ is a typical coordination number for atom i, conveniently taken as the average coordination number formed with oxygen (Brown, 1988).

$$S_i = V_i / \langle N \rangle_i \quad (7)$$

The bonding strengths given by Brown (2014a) are a measure of the flux of a typical bond formed by the atom. It is convenient to distinguish between the bonding strength of a cation, S_A (A for Lewis acid) and the bonding strength of an anion, S_B, (B for Lewis base), S_A often being shown with a plus sign and S_B with a minus sign. For example, the bonding strength, S_A, of the magnesium ion is +2/6 = +0.33 valence units (vu), while that for the sulfur ion is +6/4 = +1.50 vu. S_B for oxygen is −2/4 = −0.50 vu. Since the bonding strength is an estimate of the flux of a typical bond formed by an atom, one expects stable bonds to be formed only between atoms with similar bonding strengths. The condition for bond formation is given by eqn (8), known as the

valence matching rule.

$$0.5 < |S_A/S_B| < 2 \quad (8)$$

In many cases eqn (8) is sufficient to determine the bond network from which bond lengths can be predicted. This summary provides the essential background needed to understand how the flux theory can be used to determine the bond angles.

Using the flux theory to predict bond directions

The following assumption is central to the use of the flux theory in the prediction of bond angles.

Atoms are spherically symmetric even when they are bonded to other atoms. (9)

The justification for this assumption is given in Section 2. If the negative charge of an atom is distributed around the nucleus with spherical symmetry, the flux linking the core and the valence shell must also be spherically symmetric as shown in Fig. 1. Although the flux of a bond does not depend on the radial distribution of the charge around the atom, its direction does depend on its angular distribution. It follows from the assumption (9) that the solid angle subtended by a bond at the nucleus of a spherical atom is proportional to its flux as given by eqn (10):

$$\Omega_{ij} = 4\pi(\varphi_{ij}/V_i) = 4\pi(s_{ij}/V_i) \quad (10)$$

where Ω_{ij} is the solid angle in steradians at atom *i* subtended by the bond of flux, φ_{ij}, (or valence, s_{ij}). 4π is the solid angle of the whole sphere. This is the relation that determines the bond angles.

Converting the solid angle subtended by a bond into the angle between two bonds is, however, not straightforward. Complications arise on two accounts. The geometric problem of converting solid angles into bond angles, and the presence of additional constraints, either

electronic or steric, that lower the symmetry in the coordination sphere of the central atom. Each of these problems is addressed below.

High symmetry structures

The simplest cases are easy to deal with. If all the bonds formed by an atom have the same bond flux, the principle of maximum symmetry implies that, if possible, all these bonds will be related by symmetry. Two bonds will be collinear, three will point to the corners of a triangle, four to the corners of a tetrahedron and six to the corners of an octahedron. There is no reasonable coordination geometry in which five or seven bonds can all be related by symmetry. This explains the frequency with which tetrahedral and octahedral coordination are found while five and seven coordination are adopted only when constraints make four or six coordination impossible. The high symmetry coordination spheres that make the bonds equivalent automatically determine the bond angles. The principle of maximum symmetry, eqn (1), accounts for most of the observed coordination geometries without the need to distinguish between covalent and ionic bonds. The hybrid orbitals that are often presumed to determine covalent bond directions merely reflect the possible high symmetry point groups with two, three and four-fold symmetry, but for light atoms, hybrid orbitals are unable to account for the six-fold coordination found around the cations in, e.g., Al_2O_3, PF_6^- and SF_6.[3] The problem of hypervalency that arises in orbital models does not exist in the flux theory.

Lowering the symmetry, the influence of the bond network

In some compounds the presence of additional constraints results in the breaking of the

[3] There are many other problems with the hybridized orbital model. The spherical harmonics used to describe the orbitals are not wave functions, just a mathematical tool rather than a physical concept. A filled set of s-p orbitals in any hybridized form has, by definition, perfect spherical symmetry, favoring no particular directions.

high symmetries described in Section 4. Three constraints can be identified. A lower symmetry may be imposed either by the bond network (Section 5), the electronic structure of the atom (Sections 6-8), or by three dimensional space (Section 9).

If the bonded neighbors of an atom have different environments in the bond network they may have different fluxes, in which case the solid angles subtended by the bonds will not be equal. Eqn (10) still applies: stronger bonds will subtend larger angles. Consequently we expect the bond angles formed between stronger bonds to be larger than those between weaker bonds. The difficulty arises in converting the solid angles into angles between the bonds. A couple of techniques are available for making these predictions quantitative as illustrated by the following examples.

The X_2O_7 complexes (most of them anions), where X = Si^{4+}, P^{5+}, S^{6+} and Cl^{7+}, consist of two tetrahedra sharing a common bridging oxygen atom, O_b. The remaining six oxygen atoms within the complex are terminal, O_t, but if the complex is an anion the terminal oxygen atoms will also form weak bonds to external cations. The angles of interest are the O_t-X-O_t and O_t-X-O_b angles within the tetrahedron, and the X-O_b-X angle at the bridging oxygen that links the two tetrahedra. The latter angle is of particular interest in the mineralogy of silicate minerals as they link the SiO_4 tetrahedra into chain-, sheet- and framework-minerals (Gibbs et al. 1972) . These X-O_b-X angles are discussed in Section 7.

Since the behavior of the O-X-O angles of all these complexes is the same, the discussion here is limited to the case where X is S^{6+}. The bond fluxes can be predicted using the network equations (5) and (6), but in the case where the S-O_t bonds are all equivalent the fluxes can be assigned by inspections. Since the valence sums at S and O_b must equal the atomic valence, the

flux of each of the two S-O_b bonds is 1.00 vu, hence that of the S-O_t bonds is 1.67 vu. From eqn (10) it is clear that the O_t-S-O_t angle must be greater than 109° and that the O_t-S-O_b angle must be correspondingly smaller. These estimates can be made quantitative in two different ways, the difficulty lies in how to convert the solid angles, which can cover the sphere in different ways, into the angles between bonds.

<Table 1 here>

The first approach to calculating these angles was proposed by Murray-Rust et al. (1975) and Brown (1980b). A correlation between the bond angle and the average valence of the two bonds that defines the angle is found by interpolating between two limiting configurations in which the angles are defined by symmetry. In the present case one of these is the regular SO_4 tetrahedron in which the four S-O bonds each have a flux of 1.50 vu and the angle between them is 109°. The other limiting configuration is the planar SO_3 triangle that would be obtained by removing the bridging oxygen, O_b, to infinity. In the latter case the bond fluxes are 2.00 vu for the three S-O_t bonds and 0 vu for the S-O_b bond, with an O_t-S-O_t angle of 120° and an O_t-S-O_b angle of 90°. A second order fit (eqn (11)) between the average fluxes of the bond pairs, *s*, and these three angles, θ, yields the predictions shown in column 2 of Table 1.

$$\theta = 46(\varphi-1) - 16(\varphi-1)^2 + 90^\circ \qquad (11)$$

An alternative approach, proposed independently by Harvey et al. (2006) and Zachara, (2007), makes use of the bond valence vector, $\boldsymbol{s_{ij}}$: a vector parallel to the bond with a magnitude equal to the bond flux. Harvey et al. and Zachara proposed that as long as an atom is expected to lie at the center of its coordination polyhedron, the sum of the bond valence vectors, $\boldsymbol{\Delta s_i}$ in eqn (12), should be zero.

$$\Delta s_i = \sum_j s_{ij} \quad (12)$$

In coordination spheres with sufficiently high symmetry such as a trigonally distorted tetrahedron, eqn (12) provides sufficient constraints to determine both the O_t-S-O_t and O_t-S-O_b angles. These are shown in the third column of Table 1. The fourth column in Table 1 shows the observed angles in $K_2S_2O_7$. As the disulfate ion always shows a small additional (as yet unexplained) systematic distortion that breaks the trigonal symmetry (Brown 1980b), the angles shown in Table 1 have been averaged to give trigonal symmetry; the reported O_t-S-O_t angles range from 112.9 to 115.7° and the O_t-S-O_b angles from 101.3 to 105.9°. In this example the differences between the two predictions and the observed angles is comparable to the experimental uncertainty of one or two degrees. Like the prediction of bond lengths using eqns (5) and (6), the prediction of angles using eqn (11) or (12) does not depend on knowing the positions of the atoms in space, only on the way in which they are linked by bonds.

When Δs_i is found by experiment to deviate from zero, it provides a direct measure of the deviation from the higher symmetry environment. Using eqn (3) it is easily shown that Δs_i points along the direction in which an atom is displaced from the center of its coordination sphere, a result that can be useful in analysing the nature of a distorting constraint, for example when predicting the S-O_b-S angle discussed in Section 7. Before pursuing this calculation it is necessary to review the application of the flux theory to atoms with lone pairs.

The flux theory of lone pairs (non-bonding valence-shell charge)

The assumption that the charge in the valence shell is spherically symmetric still applies to atoms with non-bonding charge (lone pairs)[4] in its valence shell. Even though the valence

[4] All non-bonding charge in the valence shell is referred to here as 'lone pairs' as this terminology is simple and familiar. It is not intended to imply that this charge consist of

shell retains its spherical symmetry, the bonding or non-bonding function of the charge in the valence shell can be distributed in different ways that do not necessarily observe this symmetry. In some compounds both the bonding charge and lone pairs are arranged within the valence shell with spherical symmetry allowing the bond angles to be calculated in the same way as for the high symmetry coordination environments described in Sections 4 and 5. In this case the lone pair is said to be inactive. In other compounds the bonding and non-bonding charge may appear on opposite sides of the valence shell, with the result that the bonding is asymmetric; one side of the atom forms one or more strong (primary) bonds and the other side forms only weak (secondary) bonds or no bonds at all. In this case the lone pair is said to be stereoactive. The bonding around the oxygen atoms in the sulfate ion is an example of this asymmetric bonding. In the sulfate ion the lone pair is said to be stereoactive, but this distortion is not an intrinsic property of the oxygen atom; it is driven by the environment in which the atom finds itself; an atom with lone pairs is able to form bonds that are much stronger than is permitted by the valence matching rule (eqn (8)) by concentrating its bonding charge in the portion of the valence shell used to form the primary bond(s). In order to preserve the spherical symmetry of the valence shell charge, the non-bonding lone pairs must be moved away from the bond region. The result is the separation of the bonding and lone pair charge into separate sections of the valence shell.

Since all anions have lone pairs, whether they are stereoactive or not, it is convenient focus this discussion on anions, specifically on oxygen which forms the bridging bond in the X_2O_7 complexes. The arguments, suitably adapted, apply to other anions besides oxygen, as

---

identifiable pairs of electrons. The integral charge associated with the non-bonding charge is a consequence of the requirement that atomic valences must be integers.

well as to cations containing lone pairs. When the bonding around the anion is regular as found around the oxygen atom in MgO which has the NaCl structure, the bonding and non-bonding functions of the valence shell of oxygen are both spherically distributed, but in the presence of a cation such as S^{6+} that has a bonding strength (+1.5 vu) that is larger than that of the anion (−0.5 vu), the bonding and non-bonding functions of oxygen are rearranged so as to ensure that the bonding region of the valence shell contains sufficient bonding charge to match that of the sulfur.

Most anions adopt an intermediate configuration between the extremes of having full spherical symmetry, and full stereoactivity with all the bonds appearing on one side of the atom. The Principle of Maximum Symmetry (eqn (1)) implies that the default configuration is the symmetric environment observed when the lone pair is not stereoactive. This arrangement is found when the bonding strength, S_A, of the cation is less than that of the anion, S_B. When S_A is larger than S_B this symmetry is broken, but breaking the symmetry implies the presence of an additional constraint (eqn (2)), namely the need to place more bonding charge (and less of the lone pair charge) in the region of the primary bond. In MgO, where in eqn (8) the ratio $|S_A/S_B|$ 0.33/0.50 = 0.67) is less than 1.0, oxygen adopts regular octahedral coordination, but in the sulfate ion, SO_4^{2-}, where $|S_A/S_B|$ (1.50/0.50 = 3.0) is greater than 1.0, the S-O bond can only be formed if three quarters of the oxygen bonding charge (1.50 vu) resides in the region of the bond. The remaining one quarter (0.5 vu) then shares the rest of the valence shell with the lone pairs, and the secondary bonds formed by the oxygen atom must have bond valences (fluxes) of less than 0.5 vu.

<Table 2 here>

The influence of the lone pair on the geometry can be made quantitative by considering the relative bonding strengths of the cation and anion, as illustrated by the oxides of the cations from the third row of the Periodic Table shown in Table 2. The fifth column of this table shows the ratio, $|S_A/S_B|$, between the bonding strength of the cation and the bonding strength, −0.50 vu, of oxygen. The valence matching rule (eqn (8)) is not obeyed by Na_2O which is why Na_2O is unstable, but it is obeyed by Mg^{2+}, Al^{3+} and Si^{4+} all of whose oxides are stable. The remaining elements, P^{5+}, S^{6+} and Cl^{7+} do not satisfy the valence matching rule, but they can form a stable bond with oxygen if the oxygen lone pairs become stereoactive. These cations use as much of the valence-shell charge of the oxygen as needed to form the primary bond by matching the bonding strength of the cation (S_A in column 4 of Table 2). The rest of the valence shell of the oxygen atom comprises most of the non-bonding lone-pair charge together with the remaining bonding charge which is sufficient to form only weak secondary bonds. The number of primary and secondary bonds is shown in column 7.

The degree to which the lone pair can be described as stereoactive increases as the bonding strength of the cation increases. No stereoactivity is seen as long as the cation bonding strength is less than that of oxygen, but once that boundary has been passed, the anion moves off-center in its coordination sphere, producing progressively stronger primary bonds and weaker secondary bonds. The oxygen atom in Al_2O_3 (corundum) is four coordinate, but since the bonding strength of aluminum is 0.57 vu, two primary bonds are formed with bond fluxes of 0.57 vu (1.86 Å) leaving the two secondary bonds with only 0.43 vu of flux (1.97 Å). The degree of stereoactivity increases as the bonding strength of the cation increases. Once the ratio of the bonding strengths exceeds 2.0 the oxides become unstable and oxyanions are formed

instead. In all cases the lone pair is not fully stereoactive and some weak (secondary) bonds are formed in the region primarily occupied by the lone pairs.

Where the lone pairs are fully stereoactive no secondary bonds are formed and in cases where there is only one primary bond the anion necessarily terminates the bond network leading to the formation of molecules such as CO_2 and CF_4. Molecules are therefore associated with strong bonds, often regarded as covalent, while crystals are associated with weaker bonds, usually described as ionic.

The popular Valence Shell Electron Pair Repulsion (VSEPR) model described by Gillespie and Hargittai, (1991) can be derived by replacing the flux with the corresponding number of valence-shell electron-pairs. By defining bonds in terms of electron pairs the VSEPR model restricts its scope to molecules in which the lone pairs are fully stereoactive, though the model also works for partially stereoactive lone pairs if one ignores the secondary bonds. The flux theory is, however, more general, allowing the degree of stereoactivity to be explored and in many cases predicted as described in Section 7.

Predicting bond angles around atoms with lone pairs

The angles around atoms with lone pairs depend on several factors, namely: the bonding strength of the primary ligands, the atomic valence of the ligand and the steric constraints imposed by the surrounding structure. The degree of stereoactivity can be determined from the value of $\mathbf{\Delta s_i}$ in eqn (12). If the valence shell is spherically symmetric and the lone pairs are fully stereoactive, the vector sum of the fluxes linking the core to the lone pairs should be equal and opposite to the sum of the valence vectors of the bonds, $-\mathbf{\Delta s_i}$. In the case of a single lone pair this would be 2.00 vu, but both Harvey et al. (2006) and Zachara (2007) found that $\mathbf{\Delta s_i}$ was

typically somewhat less, indicating that the lone pairs were only partially stereoactive. Bickmore et al. (2013) have shown that the principal determinant of the degree of stereoactivity is the bonding strength of the primary bonds, approximated in Fig. 2 (taken from their paper) by the bond valence of the strongest bond plotted along the horizontal axis. This shows that as long as the valence of the primary bond is less than the bonding strength of oxygen (−0.50 vu), the lone pair is not stereoactive, but if it is larger than this, the lone pair becomes increasingly stereoactive with $\mathbf{\Delta s_i}$, plotted along the vertical axis, following eqn (13), reaching a value of 2.0 vu when the cation bonding strength is equal to 2.0 vu.

$$|\mathbf{\Delta s_i}| = 0 \qquad \text{for } S_A<0.5 \text{ vu}$$

$$|\mathbf{\Delta s_i}| = 1.33(S_A-0.5) \qquad \text{for } S_A>0.5 \text{ vu} \qquad (13)$$

Eqn (13) places restrictions on the possible bond angles but it is not always possible to predict individual angles exactly. When the lone pairs on oxygen are not stereoactive, the coordination is symmetric and the angles can be derived from the symmetry, but when the lone pairs are stereoactive, the number and directions of the secondary bonds are determined in large measure by the bonding strengths and packing requirements of the remaining atoms in the structure. Fig. 2 shows that when the primary bond has a flux greater than 1.0 vu, eqn (13) gives a reasonable prediction of $\mathbf{\Delta s_i}$. In this region only one primary bond is possible and the bond angles will depend on how the secondary bonds are disposed. If the primary bond has a flux between 0.5 and 1.0 vu, there may be more than one primary bond, and we expect the bond angle between them to be determined by their relative bond fluxes. However, the solid line in Fig. 2 shows that while eqn (13) is approximately followed in this region there is a wide scatter which suggest that the bond flux is not the only determinant of the bond angle.

<Table 3 here>

The nature of these other factors can be seen by examining the X-O_b-X angles in the X_2O_7 complexes with X = Si^{4+}, P^{5+}, S^{6+} or Cl^{7+}. Since the fluxes of the X-O_b bonds are all the same in these complexes (1.00 vu), the variations in the bridging bond angles ranging from 114° to 180° (column 5 in Table 3) cannot be explained by the variation in the strength of the primary bond. The X-O-X angle is found to vary systematically with X, suggesting that the valence of the bonded atom, X, is also responsible for determining the degree of lone pair stereoactivity on the bridging oxygen.

Because O_b forms only two bonds, each with a flux of 1.00 vu, there is a simple relationship between the X-O-X bond angle, θ, and the magnitude of the bond valence vector sum, $\Delta \boldsymbol{s_O}$, around O_b given by eqn (14).

$$|\Delta \boldsymbol{s_O}| = 2s_{xo}\cos(\theta/2) \qquad (14)$$

Since s_{xo} = 1.00 vu, if θ is known $\Delta \boldsymbol{s_i}$ can be calculated and vice versa. Fig. 2 shows that when s_{xo} = 1.0 vu, $\Delta \boldsymbol{s_i}$ has a range that extends from zero to 1.0 vu corresponding to θ varying from 180° to 120° which, as expected, covers the range of bridging angles shown by the X_2O_7 complexes in Table 3.

The most obvious factor that correlates with these angles is the valence of the X atom which measures the total charge in the valence shell of X, and hence determines the density of the flux around X. Even though the X-O bond flux does not change, increasing the valence of X concentrates this flux into a smaller solid angle at X, and since the flux lines linking the X and O atoms are continuous, the solid angle of the X-O bond at O must also be reduced. Increasing the density of the bonding charge in the valence shell of O can only be achieved by displacing more

of the non-bonding charge from the bond region by making the lone pairs more stereoactive. Silicon has a valence of 4.0 vu so a bond of valence 1.0 vu subtends a solid angle of $4\pi/4 = 3.14$ steradians at the silicon nucleus, where 4π is the solid angle of the whole sphere. Chlorine on the other hand has a valence of 7.0 vu so a bond of 1.0 vu occupies a solid angle of just $4\pi/7 = 1.79$ steradians at the chlorine nucleus. The smaller the angle at X, the greater the density of the flux in the bond and the smaller the angle at O. Increasing the valence of X thus increases the density of the bonding flux at O leaving less space for the lone pair in the bond region; the lone pair is forced to become more stereoactive and the X-O_b-X angle becomes smaller. If the degree of stereoactivity is given by $|\mathbf{\Delta s_i}|/\sqrt{2}$, where the denominator is the value of $|\mathbf{\Delta s_i}|$ when the two lone pairs are fully stereoactive, then the degree of stereoactivity shown by the complexes in Table 3 ranges from zero to 77%.

This can be made semi-quantitative (Brown 2014a). The bond flux occupies a volume that can be approximated by two outward pointing cones sharing a common base of area A, one with its apex at the X atom subtending an angle Ω_X , the other with its apex at O subtending an angle Ω_O. Since the base area of a cone with height r and apical solid angle Ω is given approximately by eqn (15):

$$A = r^2\Omega \qquad (15)$$

and since the area A is common to both cones, we can write:

$$r_X^2\Omega_X = r_O^2\Omega_O$$

where r_X and r_O are the distances from X and O respectively to the common area A,

or $$\Omega_O = \Omega_X (r_X/r_O)^2 \qquad (16)$$

From eqn (10)

$$\Omega_X = 4\pi\varphi/V_X$$

and since φ, the flux of the X-O bond, is 1.0 vu it follows that:

$$\Omega_O = 4\pi(r_X/r_O)^2/V_X \quad (17)$$

The ratio $(r_X/r_O)^2$ is not known, but if the common base of the cones lies at the point where the space occupied by the bond is widest, the ratio is likely to be of the order of 1.0. The value of 2.0 gives reasonable agreement with the observed angles. If this value is assumed, the angle subtended by the X-O bond at the oxygen atom is given by eqn (18).

$$\Omega_O = 4\pi(2.0/V_X) \quad (18)$$

The relationship between θ and the solid angle, Ω, requires a calibration that can be fixed by three high symmetry points; the two extreme cases where the lone pairs are inactive and fully active, and one intermediate point. If the lone pairs are inactive, θ = 180°, $\Omega_O = 4\pi\times0.5$ steradians. If the lone pair is fully stereoactive the bond flux of 1.0 vu occupies 1/6 of the total oxygen valence shell and the oxygen atom's six valence units will be arranged at the corners of an octahedron, in this case θ = 90°, $\Omega_O = 4\pi\times0.17$ steradians. The intermediate case has triangular symmetry: a lone pair flux of 2 vu points to one corner of the triangle and a combination of 1.0 vu of bonding and 1.0 vu of non-bonding (lone pair) flux each point to the other two corners. For this case θ = 120° and Ω_O is $4\pi\times0.33$ steradians. The correlation between θ (in degrees) and V_X, eqn (19), is found by converting Ω_O to V_X using eqn (18).

$$\theta = 90 - 90/V_X + 540/V_X^2 \quad (19)$$

The angles, θ, predicted by eqn (19) are compared with the observed ranges in the last two columns of Table 3. These angles are used to calculate the values of Δs_i shown in columns 2 and 3 using eqn (14). Given the assumptions made in the above analysis, the agreement

between the predicted and observed angles is sufficient to suggest that the difference in flux density is the cause of the narrowing of the X-O_b-X angles in going between X = Si^{4+} and Cl^{7+}.

The wide range of observed angles for a given X, up to 40° in the case of $Si_2O_7^{6-}$, suggests that the angles are affected by other non-intrinsic factors, factors that depend on the context in which the complex is found. These include the steric and packing requirement and must be analyzed separately for each compound. The range of observed bridging angles is largest for the disilicate ion for several reasons, the angle is particularly sensitive to the choice of $(r_X/r_O)^2$ in deriving eqn (19), the flux has a lower density making the bond soft, and the disilicate group, being more tightly bonded to the external structure, is more responsive to the external stresses. As V_X increases, the angles become stiffer and the linkages to the rest of the structure weaker.

The above discussion shows that three separate effects affect the angles between the primary bonds formed by atoms with lone pairs. The first is the size of the flux of the X-O bond, the second is the density of this flux and the third is the stress induced by the structure of adjacent atoms.

Bond angles in transition metal complexes

As the concept of a valence shell is not well defined in the transition metals, we must define the valence shell as containing just the bonding charge, relegating any non-bonding charge to the core, even though the core and valence shell may have similar energies.

As most transition metals are either four- or six-coordinate, their bond angles can be derived from their tetrahedral or octahedral geometries in the same way as main group cations. There are, however, a few exceptions in which intrinsic electronic instabilities result in bonding geometries in which the expected high symmetry is broken.

The largest of these distortions is found around early transition metals in their d^0 and d^1 states. When they are in an environment with a center of symmetry they are unstable. Tetrahedral coordination is unaffected as it has no center of symmetry, but when these atoms are six-coordinated, they show a tendency to move away from the center of their coordination sphere, a distortion that becomes larger as one moves across the Periodic Table. It is absent for Sc^{3+}; small displacements are found in some compounds of Ti^{4+} as for example in $BaTiO_3$, but it may also appear as a disordered displacement in compounds where the titanium atom nominally occupies a site with a crystallographic center of symmetry as in $SrTiO_3$ (Abramov et al. 1995). Around V^{5+} the distortion is much larger and is always present, while six-coordinated Cr^{6+} is unknown, even though the chromium atom could easily surround itself with six oxygen atoms at the expected bond distance. The environment of V^{5+} in V_2O_5 provides a useful case study. The vanadium atom is displaced towards one of the six ligands, giving it a tetragonally distorted octahedral environment of oxygen atoms with the two axial bonds having lengths of 1.59 Å (1.80 vu) and 2.80 Å (0.06 vu) and four equatorial bonds of length 1.89 Å (0.80 vu). The large flux of the short bond causes the equatorial bonds to be bent by 14° towards the longer axial bond (Shklover et al. 1996). One can describe this distortion as a displacement of the vanadium atom away from the center of a rigid octahedron of oxygen atoms, but as the discussion in Section 5 points out, displacing the atom in a rigid octahedron of ligands will always result in a non-zero valence vector sum pointing in the direction of the displacement. Bending the equatorial bonds away from the shortest bond helps to reduce this sum, but it is not sufficient to keep the sum at zero. Any distortion shown by d^0 and d^1 transition metal cations moving off-center in an octahedral environment implies a polarization of the charge in the valence shell in the direction

of the displacement of the vanadium atom. In V_2O_5 the bond valence vector sum is 0.97 vu, indicating a significant polarization, but this appears to be compensated by a corresponding opposite polarization of the core so as to retain a total charge density that is as close as possible to spherical (Gillespie et al. 1996). One could consider the polarization of the valence shell to be an artifact of the way the valence shell has been defined, since a definition that included the polarized non-bonding charge would be closer to maintaining spherical symmetry. Kunz and Brown (1995) were able to predict the variation in the bond lengths in d^0 transition metals by assigning specific capacitances to the bonds in the network equations (eqns (5) and (6)) but so far there has been no attempt to explore either the bond angles or the properties of $\mathbf{\Delta s_i}$ in these complexes.

A centrosymmetric tetragonal distortion of octahedral coordination is found around Cu^{2+} and Mn^{3+}, with both axial bonds becoming longer and the equatorial bonds shorter. This is usually called the 'Jahn-Teller' distortion, though the Jahn-Teller theorem is more general, stating that any system will distort if such a distortion can remove a degeneracy in the ground state (Dunitz and Orgel 1960). Since this distortion is centrosymmetric, all the bond angles are fixed at 90° by symmetry. A similar distortion is found around Ni^{2+} and Pt^{2+} where it is sufficiently large that the axial bonds have disappeared and only the four equatorial bonds remain.

The late transition metals show a number of unusual bonding features associated with Pearson (1973) softness, but though unusual environments are sometimes found, the bond angles generally remain close to those expected for high symmetry coordination.

Steric strains

The prediction of bond lengths and angles in the flux theory depends only on a knowledge of the bond topology — that is, a knowledge of the way in which the atoms are linked by bonds. There is no guarantee that this geometry can be sustained when the atoms are mapped into three-dimensional space. Some bonds may need to be stretched and others compressed and the bond angles may also have to be strained. Table 3 shows that the Si-O_b-Si angles can be strained by as much as 20 or 30°. Such strains depend on the way in which all the atoms in the structure are packed, making it impossible to predict how the angles will change without a detailed knowledge of the crystal structure. However, the predictions of the bond lengths and angles using the flux theory constitute a reference geometry from which the size of the steric strain can be measured, and a knowledge of this strain allows one to analyse the stresses that occur within a given crystal structure. Further study is needed to reveal how much steric strain the angles can absorb before the structure becomes unstable.

Implications

The electrostatic flux theory provides a physically correct explanation of the bonding that occurs between two atoms with overlapping valence shells. Both the electrostatic flux and the chemical bond depend on the size of the valence charge that forms the bond, but neither of them depends on how that charge is distributed. The result is a physical theory of the bond that is as simple and intuitive as the empirical chemical bond model, while avoiding the traditional language of chemistry that is often more confusing than enlightening. 'Resonance' is made redundant by the principle of maximum symmetry (eqn (1)), the distinction between 'covalent' and 'ionic' bonds vanishes before an electrostatic flux that treats all localized bonds equally, and 'orbitals' used for calculating charge densities become irrelevant since the flux does not depend

on the distribution of the charge.

If one knows the chemical formula of a compound, the valence matching rule, eqn (8), is often sufficient to propose a reasonable bond network that can be used with eqns (5) and (6) to predict the lengths of the bonds, and with eqn (11) or (12) to predict the angles between them. In this way one can determine the ideal chemical geometry of the compound from a knowledge of just its formula. The difficult part is mapping this network into three-dimensional space while preserving the ideal geometry. If the network has a high enough symmetry, there are ways in which a matching crystal space group can be found (Brown, 2002), but preserving the chemical geometry during this mapping may not be possible, in which case the bond lengths and angles will be strained. Knowing this strain helps us to understand the stresses involved in the mapping, and may suggest ways in which the strain might be relaxed, for example by lowering the symmetry of the crystal or redistributing the valence among the cations (charge transfer). This can lead to a fuller understanding of the phase diagram and such unusual physical properties as ferroelectricity, colossal magnetoresistance and superconductivity.

While the use of the bond valence model in the prediction and analysis of bond lengths is well established, the prediction of bond angles is a new application only now being explored. In this paper I have presented a number of examples to show the potential of the flux theory. It shows promise to extend the VSEPR model to the prediction of the bond angles formed by atoms with lone pairs, even though predicting bond angles around electronically distorted transition metals may prove to be more of a challenge.

This study shows that bond angles are determined by the angular distribution of charge densities that remain essentially spherical even when atoms are bonded. The spherical symmetry

of the electrostatic field around each atom is responsible for directing all bonds. The presence of lone pairs allows anions to form bonds that are stronger than would otherwise be expected, by concentrating their bonding flux in the region of the strong bonds, leaving other parts of the valence shell with higher concentrations of non-bonding flux. The result is an asymmetric bonding environment. Spherical symmetry around an anion is found only when the bonds ae weak. Despite this difference in geometry, all bonds have the same flux character, though this underlying unity is obscured when it is asserted that bonds in asymmetric environments are directed *because* they are covalent and those in symmetric environments are not directed *because* they are ionic. The statement that 'covalent bonds are directed and ionic bonds are not' might more appropriately be inverted to read 'the bonds we call 'covalent' are the strong primary bonds that are arranged asymmetrically around the anions, while those we call 'ionic' are weak and often arranged symmetrically. Directionality has nothing to do with covalency or ionicity; it is more correct and informative to talk of 'strong' and 'weak' bonds according to the size of their flux, and to describe their coordination as 'asymmetric' or 'symmetric' rather than 'directed' or 'not directed'.

Acknowledgements

I wish to thank Barry Bickmore for stimulating discussions of the problems discussed in this paper and Matthew Wander for helpful comments on this manuscript

References

Abramov, Yu.A., Zavodnik, V.E., Ivanov, S.A., Brown, I.D., and Tsirelson, V.G. (1995) The Chemical Bond and Atomic Displacements in $SrTiO_3$ from X-ray Diffraction Analysis. Acta Crystallographica B51, 942-951.

Bickmore, B.R., Wander, M.C.F., Edwards, J., Maurer, J., Shepherd, D., Meyer, E., Johansen E.J., Frank, R.A., Andros, C., and Davis, M. (2013) Electronic structure effects in the vectorial bond-valence model. American Mineralogist, 98, 340-349.

Brown, I.D. (1980a) A Structural Model for Lewis Acids and Bases. An Analysis of the Structural Chemistry of the Acetate and Trifluoroacetate Ions. Journal of the Chemical Society, Dalton Transactions 1980, 1118-1123.

Brown, I.D. (2008b) On the Prediction of Angles in Tetrahedral Complexes and Pseudotetrahedral Complexes with Stereoactive Lone Pairs. Journal of the American Chemical Society, 102, 2112-2113.

Brown, I.D. (1988) What Factors Determine Cation Coordination Numbers. Acta Crystallographica B44, 545-553.

Brown, I.D. (2002) The Chemical Bond in Inorganic Chemistry: the Bond Valence Model, Oxford, Oxford University Press.

Brown, I.D. (2009) Recent developments in the methods and applications of the bond valence model. Chemical Reviews 109, 6858-6919.

Brown I.D. (2014a) Bond valence theory. In Bond Valences, Brown I.D. and Poeppelmeier, K.R. Eds, Structure and Bonding 158, 11-58

Brown, I.D. (2014b) A comprehensive updated listing of bond valence parameters can be found at www.iucr.org/resources/data/datasets/bond-valence-parameters

Dunitz, J.D., and Orgel, L.E. (1960) Stereochemistry of inorganic solids. Advances in Inorganic Chemistry and Radiochemistry, 2, 1-160.

Gibbs, G.V., Hamil, M.M., Louisnathan, S.J., and Bartell, L.S. and Yow, H. (1972) Correlation

between Si-O bond lenggth, Si-O-Si angle and bond overlap populations calculated using extended Huckel molecular orbital theory. American Mineralogist 57, 1578-1613.

Gillespie, R.J., and Hargittai, I. (1991) The VSEPR Model of Molecular Geometry. New York, Prentice Hall.

Gillespie, R.J., Bytheway I., Tang, T-H., and Bader, R.F.W. (1996) Geometry of the fluorides, oxyfuorides and methanides of vanadium(V), chromium(VI) and molybdenum(VI): understanding the geometry of non-VSEPR molecules in terms of core distortion. Inorganic Chemistry 35, 3954-3963.

Harvey, M.A., Baggio, S, and Baggio, R. (2006) A new simplifying approach to molecular geometry description: the vectorial bond-valence model. Acta Crystallographica B62, 1038–1042.

Kunz, M., and Brown, I.D. (1995) Out-of-center distortions around octahedrally coordinated d^0 transition metals. Journal of Solid State Chemistry. 115, 395-406.

Lynton, H., and 'Truter, M.R.. (1960) An accurate determination of the crystal structure of potassium pyrosulphate. Journal of the Chemical Society 1960, 5112-5118.

Murray-Rust, P., Burgi, H-B., and Dunitz, J.D. (1975) Chemical reaction paths. V. The SN1 tetrahedral reaction of molecules. Journal of the American Chemical Society 97, 921-923.

Pearson, R.G. (1973) Hard and soft acid and bases. Stroudberg PA USA: Dowden, Hutchinson and Ross.

Shklover, V., Haibach, T., Ried, F., Nesper, R., and Novak, P. (1996) Crystal structure of the product of Mg^{2+} insertion into V_2O_5 single crystals. Journal of Solid State Chemistry 123, 317-323.

Zachara, J. (2007) Novel approach to the concept of bond-valence vectors. Inorganic Chemistry 46, 9760–9767.

Captions

Figure 1 The valence shells (gray) overlap (black) in the bonding region. The flux is shown by the arrows linking the cores (light gray) to the valence shell. The bond is formed by the flux (solid arrows) linking the cores to the overlapping bonding region.

Figure 2 The relation between the bond valence vector sum shown along the vertical axis labelled $||S_O||$, and the valence of the strongest primary bond, shown along the horizontal axis labelled S_{max}, for oxygen atoms. The solid line follows eqn (13). (Reproduced with permission of the American Mineralogical Society from Bickmore et al. 2013).

Tables

Table 1 Angles in degrees in the $S_2O_7^{2-}$ ion.

	Predicted by eqn (11)	Predicted by eqn (12)	Observed (average)
O_t-S-O_t	115.2	116.1	114.1
O_t-S-O_b	103.5	101.5	104.3

Notes The observed angles are the trigonally averaged angles found in $K_2S_2O_7$ (Lynton & Truter. 1960).

Table 2 Oxides of third row elements

Compound	V_A	$\langle N_A \rangle$	S_A vu	$\lvert S_A/S_O \rvert$	Stability	N_O[a]	Oxygen environment
Na_2O	+1	6.4	+0.16	0.32	deliquescent	8	cubic (CaF_2)
MgO	+2	3.98	+0.33	0.66	stable	6	octahedron (NaCl)
Al_2O_3	+3	5.27	+0.57	1.14	stable	2+2	distorted tetrahedron
SiO_2	+4	4.02	+1	2	stable	2+0	lone pair active
PO_4^{3-}	+5	4.01	+1.25	2.5	oxyanion	1+*n*	lone pair active
SO_4^{2-}	+6	4	+1.5	3	oxyanion	1+*n*	lone pair active
ClO_4^-	+7	4	+1.75	3.5	oxyanion	1+*n*	lone pair active

Notes

a. Where two values are shown the first refers to the strong primary, the second to the weak secondary bonds. The value of *n* depends on the nature of the counterion.

Col. 2: V_A is the valence of the cation,

Col. 3: $<N_A>$ is the average observed coordination number of the cation (Brown 1988)

Col 4: S_A is the cation bonding strength (Brown 2014a).

Col 7: N_0 is the coordination number of the oxygen.

Table 3. Bridging bond angle in X_2O_7 complexes

	Δs_i predicted from angle (vu)	Δs_i observed (vu)	X-O-X Predicted Eqn 17 (degrees)	X-O-X observed (degrees)
$Si_2O_7^{4-}$	0.00	0.00-0.68	180	140-180
$P_2O_7^{3-}$	0.68	0.42-0.97	140	122-156
$S_2O_7^{2-}$	1.00	0.98-1.09	120	114-121
$Cl_2O_7^{-}$	1.17	1.07	108	115

Figure 1

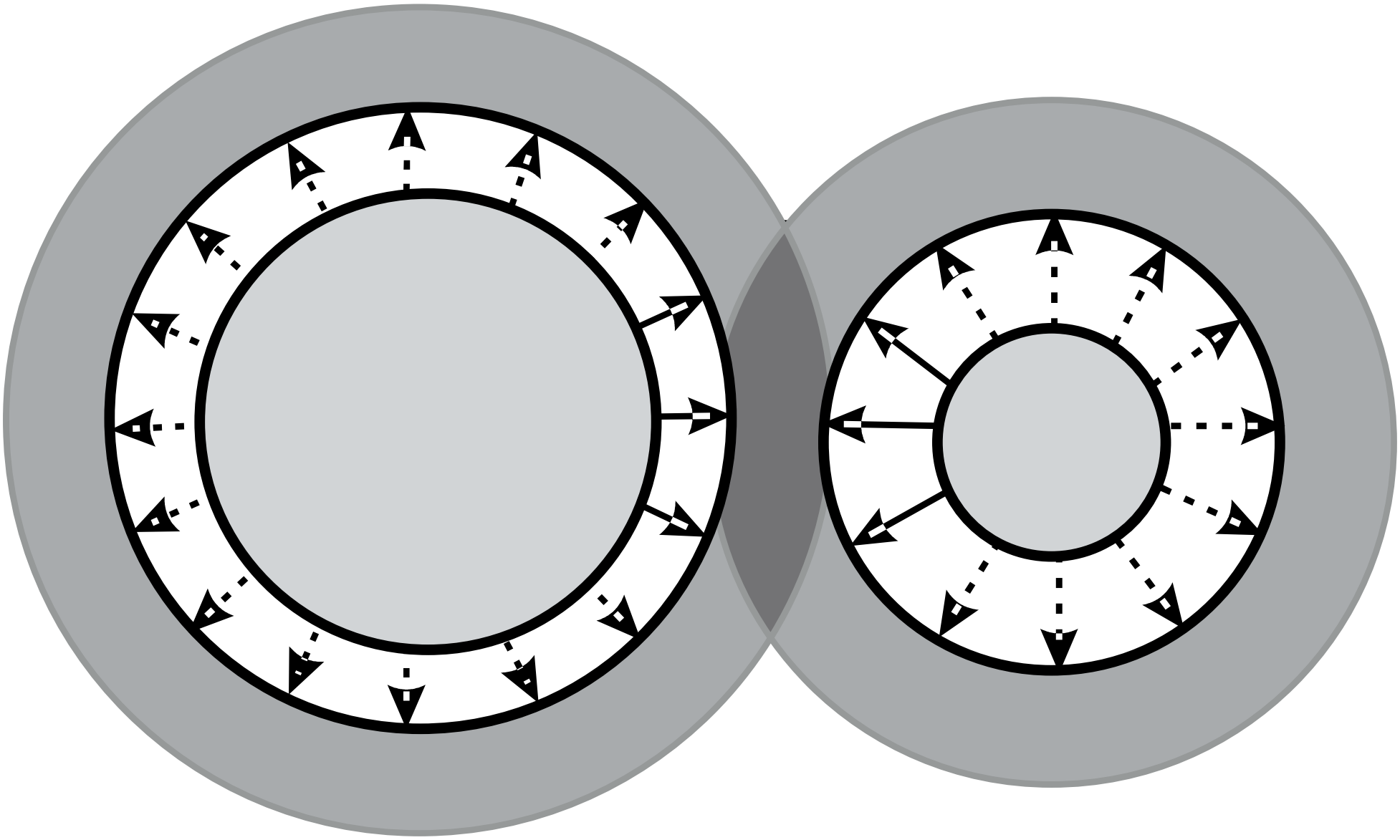

Figure 2