

## Electronic Structure and Chemical Bonding

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A firm underlying tenet for research in solid-state chemistry, condensed matter physics, and materials science is the fundamental relationship among atomic structure, chemical composition, and materials properties, which include electrical, magnetic, thermal, chemical, and mechanical characteristics. Structure, composition, and properties are interrelated by a substance's *electronic structure*, which describes the nature of the chemical bonds forming the solid and can be calculated by a solution of Schrödinger's equation as well as studied experimentally. This unit examines different chemical bonding types and methods for calculating and analyzing electronic structure.

READING: J.K. Burdett, *Chemical Bonding in Solids*, Chapters 1-3

H.F. Franzen, *Physical Chemistry of Solids*, Chapters 4-5

**(1) Qualitative Bonding Notions:** The chemical bond is the force holding atoms together. An effective way to describe a bond is via the energy profile for a pair of atoms **A** and **B** as a function of the distance between them. At very long distances, **A** and **B** are separate gaseous atoms. As the distance between **A** and **B** decreases, the energy of the pair gradually decreases until it reaches a minimum. Further shortening of the **A–B** distance quickly increases the energy, which even rises above the energy value of the separated atoms. The attraction between **A** and **B** can be described as electrostatic and is enhanced by effective overlap of their atomic orbitals. The short distance repulsions derive primarily from Pauli exclusion forces and the electrostatic repulsion between nuclei. In the energy profile, the separate atoms **A(g)** and **B(g)** form the reference state and three important characteristics of the chemical bond emerge: (a) the dissociation energy, which is the energy difference between the minimum value and the reference state; (b) the bond distance, which is the separation between atoms **A** and **B** at the energy profile minimum; and (c) the vibrational force constant, which is related to the curvature of the energy profile near the energy minimum and describes the bond stiffness. In general, strong bonds show short interatomic distances and exhibit large force constants.

The energy profile for a solid-state compound is typically plotted as a function of volume, but the overall shape resembles the bond-energy curve for an isolated chemical bond. The characteristics now become (a) the cohesive energy, which is the energy  $U_0$  needed to form the gaseous atoms from the solid:  $\mathbf{AB}(s) \xrightarrow{U_0} \mathbf{A}(g) + \mathbf{B}(g)$ ; (b) the equilibrium volume  $V_0$ , which is volume of the solid for the minimum energy:  $U_0 = U(V_0)$ ; and (c) the bulk modulus, which is a measure of the resistance of a substance to volume compression:  $B = V_0 \left( \frac{d^2U}{dV^2} \right)_{V_0, T}$ . This expression indicates the relationship between the bulk modulus and the curvature of the  $U(V)$  profile near the equilibrium volume.

Unlike molecules, solids display various bond types that are distinguished by various features:

- **Ionic bonds:** electrostatic attraction between cations and anions. In any ionic solid, these overall short-ranged attractions will be counteracted by somewhat longer-ranged anion-anion and cation-cation repulsions. The energy profile for the cohesive energy of an ionic bond differs from the standard definition of cohesive energy because the product gaseous

cations and anions have a higher energy than the corresponding neutral atoms by ionization potentials of the cations and electron affinities of the anions.

- (Polar) covalent bonds: electrostatic attraction between atoms by sharing electron pairs via overlapping atomic orbitals. If the two atoms forming the bond are the same, then the bond type is purely covalent, but becomes polar for two different atoms. The strengths of polar-covalent and ionic bonds are similar.
- Metallic bonds: electrostatic attraction between atoms arising from cationic centers dispersed in an electron “gas”. From an orbital perspective, metallic bonding arises from multi-centered interactions. These bonds are generally somewhat weaker than individual (polar) covalent bonds but involve similar interatomic distances.<sup>1</sup>
- van der Waals bonds: also known as dispersion forces, they arise via induced dipole interactions between closed shell species. These interactions are weak for individual pairwise connections and are important for distances longer than ionic or covalent bonds, but their sheer number in a solid-state compound can be influential.
- Hydrogen bonds: weak intermolecular forces involving asymmetrically bridging hydrogen atoms between molecules. These connections typically involve nitrogen, oxygen, or fluorine atoms.

(2) Determination of electronic structure and analysis of chemical bonding features in a solid can be obtained by experimental and theoretical, i.e., computational means. On the experimental side, measurements of electrical conductivity (or, rather, resistivity), magnetic susceptibility and heat capacities down to low temperature give information about electronic states near the highest occupied and lowest unoccupied states. Determining cohesive energies provides assessment of chemical bonding strengths in the solid. Spectroscopic techniques such as XPS or UPS can give profiles of the occupied electronic states below the highest occupied level; inverse photoelectron spectroscopies give profiles of low-lying unoccupied states of surface. Since both spectroscopic profiles include absorption cross sections, the experimental profiles are generally somewhat distorted from computed profiles. Subtle effects of electronic structure can also be elucidated from any solid-solid phase transitions that may occur or by obtaining accurate electron densities from diffraction experiments.

From the theoretical (computational) perspective, electronic structure is typically represented by an electronic *density of states* (“DOS”) curve, which is often broken down into various atomic or orbital components. Population analysis of DOS curves can yield information about two-center interactions and electron partitioning in structures. Calculation of all occupied states provides a theoretical determination of electron density in a structure, a profile that could be confirmed by thorough X-ray diffraction experiments. Translational symmetry leads to a quasi-continuous set of quantum numbers, called wavevectors or  $\mathbf{k}$ -points, so that electronic energies can be plotted as a function of  $\mathbf{k}$  in a *band structure* diagram. Additional computational modelling strategies include examining total energies with volume changes to determine *equations of state* as well as performing *molecular dynamics*-style calculations to elucidate phase transitions and models for crystallization.

(3) *van Arkel-Ketelaar Triangle*: Summarizing the types of solid-state compounds based on their electronic structures is nicely accomplished by the van Arkel-Ketelaar diagram, which is an example of a *compound map*. Compounds on this diagram are given a point  $(x, y)$ , for which the

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<sup>1</sup> W.B. Jensen, *J. Chem. Educ.* **2009**, 86, 278.

$x$ -coordinate is the average electronegativity ( $EN$ ) of the atoms and the  $y$ -coordinate is the electronegativity difference between the atoms. This assignment creates a triangle. The lower base,  $y = \Delta EN = 0$ , is the sequence of elements from the least electronegative cesium Cs to the most electronegative fluorine F. The upper apex identifies cesium fluoride CsF, the compound with the highest  $EN$  difference and its average  $EN$  value exactly in the middle between Cs and F.

The scales on this diagram do not have to be linear. Furthermore, there are several definitions of electronegativity, which is an important chemical concept defined by Linus Pauling to be *the power of an atom in a compound to attract electrons to itself*. Pauling developed an electronegativity scale ranging from  $\sim 0.8$  for Cs to  $\sim 4$  for F and based on bond dissociation energies. Mulliken proposed using the average of an atom's first ionization energy and electron affinity. In fact, there are various electronegativity scales. In the early 1990's L.C. Allen proposed a quantitative assessment of electronegativity using *configuration energies*,<sup>2,3</sup> and resurrected van Arkel-Ketelaar diagrams, although they had been known already for several decades.<sup>4</sup> Regardless of the electronegativity scale, van Arkel-Ketelaar maps can differentiate solids by their bonding characteristics:

- *Metallic* compounds involve electropositive elements with shallow atomic potentials for their valence electrons, low valence electron-to-orbital ratio and small electronegativity differences between atomic components, all of which lead to broad energy bands and valence electrons *delocalized* throughout the solid. Furthermore, metallic structures tend to be close packed with each atom having an essentially isotropic coordination environment.
- *Covalent* compounds are typically molecular solids formed by elements with deep atomic potentials for the valence electrons, high valence electron-to-orbital ratios, and also small electronegativity differences, which create narrow energy bands and electrons *localized* in covalent bonds between atoms. As a result, the atoms in covalent structures have low coordination numbers and their structures are rather anisotropic arising from repulsions between electron pairs.
- *Ionic* compounds arise from significant charge transfer from the electropositive to the electronegative components creating cations and anions. As a result, valence electrons are *localized* on anions. Since electrostatic interactions depend inversely on interionic distances, ionic structures, "salts", are close packed with ions having isotropic environments.

Another significant outcome of constructing this compound map is recognition of trends between different types of compounds. For example, proceeding from a vertex to the opposite edge of the triangle yields three different scenarios:

- CsF (Ionic) Vertex  $\rightarrow$  Cs–F (Metallic-Covalent) Edge: *decreasing* electron transfer.
- Cs (Metallic) Vertex  $\rightarrow$  F–CsF (Covalent-Ionic) Edge: *decreasing* electron delocalization.
- F (Covalent) Vertex  $\rightarrow$  Cs–CsF (Metallic-Ionic) Edge: *decreasing* structural anisotropy.

<sup>2</sup> L.C. Allen, *J. Am. Chem. Soc.* **1989**, *111*, 9003-9014; *J. Am. Chem. Soc.* **1992**, *114*, 1510-1511.

<sup>3</sup> J.B. Mann, T.L. Meek, L.C. Allen, *J. Am. Chem. Soc.* **2000**, *122*, 2780-2783; J.B. Mann et al. *J. Am. Chem. Soc.* **2000**, *122*, 5132-5137.

<sup>4</sup> W.B. Jensen, *Bull. Hist. Chem.* **1992**, *13/14*, 47-59.

(4) These distinctions in chemical bonding are *simplifications*. Nevertheless, such compounds are also identified by their general physical properties:

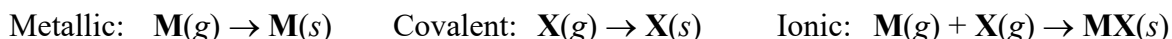
Property Type	Metallic	Covalent	Ionic
Electrical	Conducting	Insulating	Insulating; Conducting as liquids due to ions
Magnetic	Paramagnetic or itinerant moments	Diamagnetic or localized moments	Diamagnetic or localized moments
Mechanical	Malleable or ductile	Volatile – low boiling points	Brittle
Optical	Reflective	Transparent	Transparent

(5) An interesting aspect of the van Arkel-Ketelaar diagram is the proposed continuous evolution among different bonding types. As a result, compounds with mixed or intermediate bonding types emerge:

- Between *metals* and *covalent* compounds are the *metalloids*, whose complex network structures can be explained by covalent bonding arguments such as valence electron counting. Metalloids are semiconductors or semimetals, mostly diamagnetic, relatively brittle, or even hard, and generally opaque, i.e., non-reflective.
- Between *covalent* and *ionic* are polymeric *polar-covalent* compounds, which include silicates, phosphates, and various transition metal halides and oxides. Although their structures do not reveal distinct ions, the chemical or physical behavior of the electropositive components can be rationalized by considering them as either electron deficient or as formal cations. Polar-covalent compounds are generally semiconducting, diamagnetic, brittle, and transparent.
- Between *metallic* and *ionic* compounds exists the regime of so-called *Zintl phases*, formed by different metals and semimetals. Every Zintl phase generally consists of an electronegative element that accepts valence electrons from an electropositive component and adopts a structure that conforms to simple valence electron counting rules like the octet rule. Thus, the electropositive component is a formal cation. Most Zintl phases are semiconducting or semimetallic, diamagnetic, and brittle, but they can vary from opaque to transparent.

In my opinion, much research interest focuses on these intermediate regions of the van Arkel-Ketelaar triangle because emerging or interesting physical and chemical properties can arise from these *hybrid* materials. More information on various forms of van Arkel-Ketelaar triangle and related maps is available at the website *The Chemogenesis Web Book*.<sup>5</sup>

To understand these different modes of chemical bonding, consider the formation of each compound type from its atoms, processes that involve the following simplest transformations:



Simple qualitative pictures of the electronic structures of ionic salts, covalent solids, and metals can be derived from the atomic orbitals of the constituent atoms.

(6) For *ionic solids* like NaCl, charge transfer from Na atoms to Cl atoms raises the 3p orbital energy of the Cl anion relative to the Cl atom and lowers the 3s orbital energy of the Na cation relative to the Na atom. However, this process is energetically unfavorable in the gas phase by 1.52 eV, which is the ionization energy of Na minus the electron affinity of Cl. However, when

<sup>5</sup> M.R. Leach, *The Chemogenesis Web Book*, Sections 2.4 and 2.5: <https://www.meta-synthesis.com/webbook.php>.

these ions condense into an extended solid with Na cations surrounded octahedrally by Cl anions and vice versa, the chloride  $3p$  orbitals become greatly stabilized by the electrostatic Madelung potential; likewise, the valence  $3s$  orbitals of Na cations are destabilized. Via polarization and weak orbital overlap with other anions, the chloride  $3p$  orbitals form a narrow, occupied energy band called the *valence band* and the sodium  $3s$  orbitals form a broader, unoccupied *conduction band*. The energy gap between the top of the occupied valence band and bottom of the unoccupied conduction band is larger than 3 eV, which gives a maximum wavelength of 400 nm. Therefore, visible light will not be absorbed by most ionic salts. The energy gaps for alkali metal halides exceed 7 eV and, for a given anion, tend to decrease with increasing size of the alkali metal cation. Whereas this trend is distinctive for the fluorides, the band gaps for the chlorides and bromides of sodium-cesium are nearly constant. To account for this observation, some electronic structure calculations suggest that the bottom of the conduction band in chloride, bromide, and iodide salts may not be cation-centered wavefunctions but arise from excited state orbitals of the anion.

(7) *Covalent solids* are considered held together by robust bonds, which are usually two-center, two-electron bonds. As a result, bonds fall along certain directions that are influenced by the repulsions between electron pairs. A prototypical covalent solid is silicon, in which each Si atom is tetrahedrally coordinated. To account for four structurally equivalent Si–Si bonds, the valence  $s$  and  $p$  atomic orbitals form four spatially orthogonal  $sp^3$  hybrid orbitals, which overlap to give occupied bonding and empty antibonding orbitals. The hybrid orbitals are not eigenfunctions of the Hamiltonian because they do not conform to a single irreducible representation of the tetrahedral symmetry.<sup>6</sup> As a result, these hybrid orbitals are not orthogonal in energy, and the corresponding bonding and antibonding orbitals broaden into bands. The occupied bonding band is the valence band; the corresponding unoccupied antibonding band is the conduction band. Due to energetic relationships between inter-atomic ( $\beta_2$ ) and intra-atomic ( $\beta_1$ ) hybrid orbital overlap, an energy gap, called a *hybridization gap*, arises between these two bands. These gaps are generally smaller than those observed for ionic solids, i.e., they are less than 3 eV, so that electrical resistivity decreases with increasing temperature, and they are semiconducting. Among the four diamond-type elements C, Si, Ge, and Sn, the energy gaps decrease down the group. The heats of vaporization provide an estimate of the inter-atomic overlap strength ( $\beta_2$ ).

(8) In *metals*, the valence atomic orbitals are broadened into bands. Using the Aufbau principle, wavefunctions are occupied by electron pairs until the highest energy level is reached; this energy value is the *Fermi level*. In fact, the energy difference between adjacent wavefunctions in metals is much smaller than  $kT$ . Therefore, thermal excitation of electrons from occupied states at or just below the Fermi level into unoccupied states just above the Fermi level allows metals to show low electrical resistivities when an external potential is applied. In normal metals, electrical resistivity increases as temperature increases. For main group metals like Na, the conduction band arises from the valence  $3s$  and  $3p$  atomic orbitals. For transition metals like Nb, the broad  $sp$ -conduction band overlays a much narrower valence  $4d$  band and the Fermi level falls within the narrower  $d$ -band.

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<sup>6</sup> Photoelectron spectra of  $\text{SiH}_4$  reveal this energetic inequivalence. However, the validity of applying  $sp^3$  hybrids to questions of structure and bonding is due to the collective electron nature of that question. See J.K. Burdett, *Chemical Bonds: A Dialog*, John Wiley & Sons, Chichester, 1997, pp. 21-31.