

What is the Metallic Bond?

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Numerous textbooks, both at the freshman and junior inorganic levels, state that bonding in metals is specifically different from covalent bonding. Against this frequently held view, Anderson, Burdett, and Czech (ABC)¹ have presented an illuminating analysis of metallic bonding which concludes that the term "metallic bond" should be dropped from the vernacular because it is fully encompassed by molecular orbital and band theory and the broader concept of covalent bonding. We amplify their finding in this communication.

ABC give a systematic treatment of bonding concepts in molecules and solids starting with the question of localized versus delocalized bonds and showing that metals are those structures possessing partially filled energy bands without the option of a transformation to a localized (Wannier) representation. They next carry out extended Hückel tight binding calculations to determine the magnitude of the driving forces which lead to Fermi surface instabilities (Peierls distortions) and create insulators or semiconductors. A one-dimensional chain is compared with a pseudo-dimer structure where nearest neighbor interatomic separations are alternatively decreased and increased by 10%. Results for first-row atoms, Li through F, yield an undistorted Li chain favored by a small energy followed by a continuous change to F where the distorted structure is favored by a large energy. ABC then show that the pattern of their computational results is reproduced by corresponding left to right movement along the base of a van Arkel–Ketelaar triangle^{2,3} (Figure 1) whose left vertex is the M (metallic) end of a periodic table row, with right vertex C (covalent), and top vertex I (ionic). For binary compounds, A_nB_m , the horizontal axis coordinate is $(CE_A + CE_B)/2$ and the vertical axis coordinate, $CE_A - CE_B$, where CE_A is the configuration energy of A. (CE_A is the average ionization energy of A's valence electrons and has been shown to define an electronegativity scale that matches those of Pauling and Allred and Rochow and upgrades their accuracy.⁴) CE_A can be identified with the diagonal matrix element in extended Hückel theory, and therefore the van Arkel–Ketelaar horizontal coordinate, $(CE_A + CE_B)/2$, is proportional to the off-diagonal matrix element that constitutes the driving force for distortion in ABC's calculations.^{1,3} The success of CE in quantifying van Arkel–Ketelaar triangles and in characterizing the continuous change in bonding from metallic, M, to covalent, C, is also intimately dependent on the strong correlation between CE and atomic energy level spacings.^{2,5} CE embodies both the concept of "attracting" electrons that we usually identify with electronegativity plus this

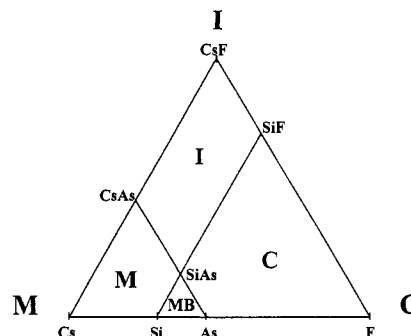


Figure 1.

additional property, thus making CE the appropriate index for quantifying the M, I, and C bonding that composes the van Arkel–Ketelaar triangles and is inherent to the periodic table itself.^{2,6,7} Therefore, the CE extended periodic table as well as its binary compound adjunct, van Arkel–Ketelaar triangles, immediately suggests the redundancy implicit in attempting to separately define a "metallic bond".

In their model computations, ABC only considered species along the M–C base line of the van Arkel–Ketelaar triangles, and to complete the analysis we must consider the ionic region above the base. Because of changes in stoichiometry and related technical difficulties it is not feasible to make additional calculations along horizontal lines in the triangles. However, we advance three arguments which together show that ABC's baseline computations are all that is required to make their claim. (1) Traditional definitions of electronegativity have always been employed to establish polar covalent bonding as a single, continuous bonding type varying from the ionic extreme to the pure homonuclear covalent bond. (2) The horizontal covalent coordinate, $(CE_A + CE_B)/2$, is orthogonal to (i.e., independent of) the ionic coordinate, $(CE_A - CE_B)/2$. (3) Vertical lines through the M region extending into I encounter binary solids of high symmetry, therefore undistorted. For example, a vertical line at 11.00 eV (to the left of Si = 11.33 eV) passes through MgSe (NaCl structure), CaBr₂ (CaCl₂ structure), NaCl, GaSb (zinc blende), and BeTe (zinc blende). A vertical line arising from Sn (10.79 eV) passes through InSb (zinc blende), MgI₂ (CdI₂), and CaS (NaCl).

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(6) CE adds a third, energy dimension to the periodic table. This hypothesis is supported by its quantification of two other longstanding puzzles: the origin and position of the metal–nonmetal dividing line and the striking increase in metalization which occurs as p-block groups are descended.^{2,5}

(7) Further substantiation of CE comes from a recent article by Prof. Gordon D. Sproul (*J. Phys. Chem.* **1994**, *98*, 6699), who found 310 binary compounds in A. F. Wells's classic text, *Structural Inorganic Chemistry* (5th ed., Oxford U. Press, 1984) that Wells was able to classify as metallic, ionic, and covalent. Except for 10 compounds whose classification is in dispute, all others were correctly placed by the dividing lines shown in Figure 1. It may be noted that CE values are obtained from multiplet averaged high resolution spectroscopic data on free atoms, and they may be regarded as the parameters required to characterize spherically symmetric, generic one-electron effective potentials from which approximate molecular and solid-state wave functions can be constructed. To more accurately reflect the detailed environment of a specific solid or molecule, CE may be replaced by an *in situ* electronegativity defined by the energy index, EI, given in the following reference: Allen, L. C.; Egolf, D. A.; Knight, E. T.; Liang, C. *J. Phys. Chem.* **1990**, *94*, 5602.

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(3) Allen, L. C.; Capitani, J. F.; Kolks, G. A.; Sproul, G. D. *J. Mol. Struct.* **1993**, *300*, 647.

(4) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003.