

# The Origin of the Sigma, Pi, Delta Notation for Chemical Bonds

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**ABSTRACT:** This piece traces the origins of the sigma, pi, delta bond notation used in molecular orbital theory and its analogy with the s, p, d atomic orbital notation.

**KEYWORDS:** First-Year Undergraduate/General, Upper-Division Undergraduate, Graduate Education/Research, History/Philosophy, Physical Chemistry, Textbooks/Reference Books, Atomic Spectroscopy, Covalent Bonding, MO Theory, Nomenclature/Units/Symbols

Having successfully used the new quantum mechanics to rationalize the line spectra of discrete atoms and monatomic ions, physicists began, starting in the 1920s and early 1930s, to apply these ideas to the study and systemization of the band spectra of diatomic molecules and molecular ions in the hope of achieving similar success. Among these pioneers was Robert Sanderson Mulliken, who, along with the German physicist, Friedrich Hund, and the British physicist, John Lennard-Jones, is widely regarded as one of the founding fathers of modern molecular orbital theory.

Not unexpectedly, in attempting to extend the study of atomic line spectra to the study of molecular band spectra, these early workers also attempted to apply those concepts that had proved so successful in the study of the former to the study of the latter, including the concepts of orbits or orbitals, and the assignment of both term symbols for electronic states and quantum numbers for individual electrons. Also, not unexpectedly for a newly developing field, there was initially a great diversity in the symbolism and terminology used by these pioneers.

## ■ THE UNITED ATOM APPROACH

Mulliken exploited the atom–molecule analogy more rigorously than many others active in the field via his so-called “united atom” approach, which postulated that the molecular orbitals of the diatomic molecule smoothly transformed into a set of corresponding atomic orbitals for a hypothetical atom created by uniting or fusing together the two atoms of the diatomic. By 1926, he was assigning atomic term symbols, such as  ${}^2S$ ,  ${}^1P$  or  ${}^3D$ , and individual “electron quantum numbers”, such as s, p, and d, to diatomics based on those of the corresponding hypothetical united atom.<sup>1</sup> By 1928, he had further refined his symbolism for the molecular quantum numbers of individual electrons and was talking instead of  $(1s^s)^2$ ,  $(2s^p)^1$  configurations, and so forth, where  $(2s^p)^1$ , for example, referred to an electron in the diatomic corresponding to an electron in the united atom with the quantum numbers  $n = 2$ ,  $l = 1$  or p and  $m_l = 0$  or s.<sup>2</sup>

Shortly after this, Mulliken seems to have hit on the simple expedient of using the corresponding Greek letters for molecular states and quantum numbers while retaining the original Latin letters for the atomic states and quantum numbers. Thus, the  ${}^2S$ ,  ${}^1P$  and  ${}^3D$  term symbols of the united

atom became instead the  ${}^2\Sigma$ ,  ${}^1\Pi$ ,  ${}^3\Delta$  term symbols of the diatomic, and the  $(1s^s)^2$  and  $(2p^p)^1$  configurations of the united atom became the  $1s\sigma^2$  and  $2p\pi^1$  configurations of the diatomic, and so forth, where 1s and 2p now referred to the atomic orbitals of the isolated atoms used to create the  $\sigma$  and  $\pi$  MOs rather than to the atomic orbitals formed by collapsing the MOs into the corresponding atomic orbitals of the united atom. If the nature of the component atomic orbitals was well-known, it was further suggested that the molecular electron quantum numbers could simply be written as  $\sigma^2$ ,  $\pi^1$ , and so on.

## ■ STANDARDIZING MOLECULAR SPECTROSCOPY

Feeling that the time had come to finally standardize the symbolism used in molecular spectroscopy, Mulliken circulated these ideas for discussion and modification among his fellow spectroscopists in the form of a printed flyer. Though it is unclear from his published accounts how much of the final consensus was based on Mulliken’s original suggestions and how much on the suggestions of others, the final result was, in any case, submitted for presentation at a meeting of the Faraday Society on Molecular Spectra and Molecular Structure held at the University of Bristol in September of 1929.<sup>3,4</sup> Because Mulliken was unable to attend in person, his nomenclature proposals were presented instead by O. W. Richardson<sup>5</sup> of the University of London, along with some written comments from Mulliken himself,<sup>6</sup> and Mulliken also summarized them early the next year for American physicists in a report written for the *Physical Review*.<sup>7</sup> Still later the order of writing the atomic components versus the resulting MO would be inverted from  $1s\sigma^2$  to  $(\sigma 1s)^2$  and then eventually subscripted as  $(\sigma_{1s})^2$ .

It was, however, not until 1931 that Mulliken attempted to connect these purely spectroscopic considerations with the theory of valence and chemical bonding. The resulting publication introduced the asterisk notation for distinguishing between antibonding and bonding electrons, and eventually led to the transference of the symbols  $\sigma$ ,  $\pi$ , and  $\delta$  from the electrons to the resulting bonds.<sup>8</sup> This was followed, in turn, by the practice of applying these labels to single and multiple bonds in molecules other than the diatomics, thereby further dissociating them from their original connection with the net symmetry of the overall molecule. It was not until 1965 that the

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first experimental ground-state  $\delta$ -bond was reported by F. A. Cotton for the  $[\text{Re}_2\text{Cl}_8]^{2-}$  anion.<sup>9</sup>

### ■ SEEING THE ANALOGY

The best way of seeing the analogy between the  $\sigma$ ,  $\pi$ , and  $\delta$  molecular orbitals and the s, p, and d atomic orbitals, which are the ultimate origin of this nomenclature system,<sup>10</sup> is to take a cross section of the bond MO perpendicular to the bond axis. That for a  $\sigma$ -bond will resemble the cross section of an s-orbital, that for a  $\pi$ -bond will resemble the cross section of a p-orbital, and that for a  $\delta$ -bond will resemble the cross section of a d-orbital. As stated, this is merely an analogy based on a similarity in the shapes of the orbital cross sections and is not intended to imply that these two varieties of orbitals are equivalent.

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#### Notes

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