

Gillespie R J & Nyholm R S. Inorganic stereochemistry.

Quart. Rev. Chem. Soc. 11:339-80, 1957.

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It is shown that the shapes of a wide variety of inorganic molecules can be understood on the basis of the idea that the electron pairs in the valence shell of an atom keep as far apart as possible. [The SCI® indicates that this paper has been cited in over 460 publications since 1957.]

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"This paper arose out of discussions with my colleague R.S. Nyholm (later Sir Ronald Nyholm) at University College London. We were concerned about how to best give students some understanding of the shapes of inorganic molecules. At the time, molecular shapes were usually discussed in terms of Pauling's hybrid orbital theory.¹ Although this theory had led to a much improved understanding of chemical bonding and molecular structure, we had both become somewhat dissatisfied with it. We felt that in many cases it gave only an after-the-fact rationalization of molecular shape. Moreover, the basic quantum mechanical ideas were difficult for students.

"We had been intrigued by the simple relationship between the geometry of the bonds surrounding an atom and the number of electron pairs in the valence shell that had been pointed out earlier by Sidgwick and Powell.² We set out to show that their simple ideas could be used to explain the shapes of molecules from across the periodic table. We found that we could explain the shapes of essentially all molecules of the type AX_n on the basis that the electron pairs

in the valence shell of a central atom keep as far apart as possible. Moreover, by making allowance for the differences between bonding and nonbonding electron pairs, we could account for small deviations from the basic idealized shapes that had not previously been satisfactorily explained.

"In subsequent articles on the theory, I labelled it the valence-shell electron-pair repulsion (VSEPR) theory,³ and it is now widely known under this name. I published a detailed treatment of the theory, in 1972, in a book entitled *Molecular Geometry*.⁴

"A notable event in the history of the theory was its use to correctly predict, very soon after the discovery of the first noble gas compound, the shapes of many noble gas molecules which had not had their structures determined or which had not even been prepared at that time.⁵

"The success of the theory has been due, I think, to its great simplicity and its remarkable ability to predict the shapes of molecules more reliably, and in greater detail, than any other method. It is now widely used by inorganic chemists to discuss the structures of molecules, and it has gradually replaced hybrid orbital theory for this purpose. It is used in almost all chemistry textbooks at the first-year university and high school levels as a basis for the discussion of molecular shapes. The considerable influence of the theory on the teaching of chemistry and its contribution to the understanding of molecular structure were, I think, largely responsible for my receiving the American Chemical Society Award for Inorganic Chemistry in 1973 and the Canadian Institute of Chemistry Award for Chemical Education in 1976.

"It is only now, after 26 years, that direct experimental evidence for the basic assumptions of the theory concerning the distribution of electron density in molecules is being provided by very accurate X-ray crystallographic studies. Theoretical calculations of the variation of electron density in molecules are also providing similar confirmation of the basic ideas of the theory."

1. Pauling L. *The nature of the chemical bond and the structure of molecules and crystals.*

Ithaca, NY: Cornell University Press, 1960. 644 p.

2. Sidgwick N V & Powell H M. Stereochemical types and valency groups.

Proc. Roy. Soc. London Ser. A 176:153-80, 1940. (Cited 75 times since 1955.)

3. Gillespie R J. The valence-shell electron-pair repulsion (VSEPR) theory of directed valency.

J. Chem. Educ. 40:295-301, 1963. (Cited 235 times.)

4., *Molecular geometry.* London: Van Nostrand Reinhold, 1972. 228 p. (Cited 330 times.)

5., The noble-gas fluorides, oxyfluorides, and oxides. Predictions of molecular shapes and bond lengths.

(Hyman H H, ed.) *Noble-gas compounds.* Chicago: University of Chicago Press, 1963. p. 333-9.