

Hinze J & Jaffé H H. Electronegativity. I. Orbital electronegativity of neutral atoms. *J. Amer. Chem. Soc.* 84:540-6, 1962.

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The electronegativity concept is discussed on the basis of Mulliken's definition, $\chi = (E_v + I_v)/2$.¹ Here the ionization potential, I_v , and the electron affinity, E_v , to be used are not those of an atom in its ground state, but those of an atom in a particular valence state the atom assumes as part of a molecule. Using atomic spectroscopic data, the valence state promotion energies, the I_v 's, E_v 's and χ 's were calculated for various valence states of the atoms H through Cl. As different electronegativity values are obtained for the σ and π orbitals of an atom, electronegativity becomes an orbital and not an atomic property. [The *SCI*® indicates that this paper has been cited in over 1,030 publications since 1962.]

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In the fall of 1960, I went from the University of Stuttgart, Federal Republic of Germany, where I had done my undergraduate work, to the University of Cincinnati for postgraduate work. Above all, the excellent guidance of H.H. Jaffé, who became my research adviser, and who had suggested electronegativity as a research topic, permitted me to make rapid progress. Due to his intellectually challenging stimulation, I adjusted rapidly to the new, initially strange environment, learned the, for me, new languages, English and computerese, as well as the physics and mathematics required for the theoretical chemistry research. My background had been much more laboratory oriented in the old classical German chemistry tradition. I remember mentioning to Jaffé my desire to also measure the electronegativity values we calculated, not knowing then that this cannot be done directly.

Given many nights spent with the computer, an IBM 650, and several long and forceful discussions with Jaffé, the research proceeded rapidly. Because some preliminary work and computer programs had been

completed already by I. Goldfarb and V.T. Zung, former graduate students with Jaffé, I could compute the Slater-Condon parameters and valence state promotion energies of the atoms rather quickly. In less than one year, the valence state promotion energies, ionization potentials, and electron affinities, and, from these, the orbital electronegativities were calculated. We were aware then that the promotion energies and I_v and E_v values obtained would be useful also as parameters in semi-empirical molecular orbital theories and had insisted on tabulating them together with the electronegativity values. More than half the citations to our article justify now our insistence then.

At that time, I was not sure whether I wanted to stay for an extended period in the US, so I sent an expanded version of the preprint to the University of Stuttgart, asking whether it would be acceptable as a *Diplom* (master's) thesis. The negative answer I received, because the work contained no experimental part, illuminates the state of chemistry in Germany at the time. For me this was fortunate. I became a theoretical chemist and stayed in the US until 1975. Initially, I extended the electronegativity work in the elements up to iodine into a PhD thesis in Cincinnati.

Gradually, after long hours in the library, I began to understand what electronegativity meant or could mean. We coined the term "orbital electronegativity" and defined it as $\chi_i = \alpha E \eta_i$,² the partial derivative of the energy of an atom with respect to the orbital occupation number η_i . This permitted the definition of electronegativity not only for singly occupied valence orbitals, identical with Mulliken's definition, but also for lone pairs and virtual, empty orbitals. In addition, with this definition, the concept of electronegativity equalization^{3,4} could be justified, and group electronegativities became calculable. I realized only recently,⁵ after these ideas had been dormant with me for more than 20 years, how these concepts can be used effectively to calculate group electronegativities and charge distributions in molecules easily. These ideas may also yield a useful parameter to characterize the softness or hardness of acids and bases, nucleophiles, and electrophiles.

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3. Sanderson R T. An interpretation of bond lengths and a classification of bonds. *Science* 114:670-2, 1951. (Cited 60 times since 1955.)
4. -----, *Chemical periodicity*. New York: Reinhold, 1960. 330 p.
5. Hinze J. *Chemische Gesellschaft Zürich. Chimia* 36:465-7, 1982.