

This Week's Citation Classic

Edmiston C & Ruedenberg K. Localized atomic and molecular orbitals. *Rev. Mod. Phys.* **35**:457-65, 1963.
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Energy-localized-molecular-orbitals (LMOs) bring the molecule (SCF wavefunction) as closely as is possible to a highly visualizable electrostatic model, with minimal coulombic and exchange repulsions between the MOs. A two-by-two MO transformation iteration process is proposed for obtaining these LMOs, which are unique generalizations of equivalent orbitals. [The SCF® indicates that this paper has been cited over 410 times since 1963.]

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"Chemists have long been interested in describing molecules in terms of nearly-transferable bonds, lone-electron-pairs, and atomic-inner-shells, to which these LMOs correspond. Lennard-Jones and Pople¹ had earlier suggested the minimum-exchange-energy property of equivalent orbitals, but gave no method for obtaining LMOs in general. I mentioned this suggestion to Klaus Ruedenberg, and we were able to quickly work out the simple 2x2 MO-transformation. He had hopes that one could work out, analytically, higher-dimensioned transformations, but that was abandoned. Simultaneously, I set about testing a succession of the 2x2-'rotations,' as I had recently been studying the analogous Jacobi method for matrix diagonalization. A few iterations on a simple tetrahedral-hybridization case indicated rapid convergence, and I was delighted! At this time we were applying Klaus' incisive analysis of chemical binding energies, and I hoped the LMOs would be useful for this.

"Other workers came to appreciate the value of these LMOs, which, by first-order perturbation theory, are least sensitive to changes in each other. Unfortunately, in

large molecules they have turned out to be more difficult to calculate than are some

other types of LMOs. In our own work, this led to the development of an 'N⁵ transformation technique' for electron repulsion integrals.² Earlier published methods were proportional to N⁶, in difficulty, where N is the number of orbitals (MOs) involved. However, LMOs have contributed towards a rigorous quantum-mechanical definition of the 'chemical bond' in polyatomics, and to simplifying calculations on large molecules using LMOs from similar small ones. I had very great hopes that comparisons of LMOs would allow unique and useful definitions of several 'chemical effects' like 'conjugation,' 'hyperconjugation,' 'delocalization (resonance) energies,' 'bond energies,' etc. LMOs have allowed a disproof of the very popular 'valence-shell-electron-pairs-repulsion model' of molecular geometries, presented in nearly every elementary chemistry text. By using the LMOs of BH₃ for B₂H₆, the electron delocalization (resonance) energy, stabilizing the latter molecule, was calculated.³ My later thinking on pseudo (pair)-natural-orbitals⁴⁻⁶ for electron correlation was a direct result of the LMO ideas, and the separated-electron-pairs theory.

"It would be a 'dream come true' if we could use a simple (perhaps semiempirical) perturbation theory to predict the changes in an LMO (and its associated PNOs) between chemically similar molecules. Chemistry might then become as much a theoretical science as an experimental one. This 'dream' helps to explain the popularity of LMOs. *Understanding* chemistry involves understanding what electrons are really doing, and thankfully real progress is being made by many quantum chemists. My mentors Ruedenberg and Robert Parr and their mentor Robert Mulliken have striven for *quantitative* confirmation of the qualitative chemical concepts of bonding and structure. The road may be long and difficult, but, in the end, nature will reward us for the correct and detailed understanding of her secrets."

1. Lennard-Jones J & Pople J. The molecular orbital theory of valency IV. The significance of equivalent orbitals. *Proc. Roy. Soc. (London)* **A202**: 166-80, 1950.
2. Tang K & Edmiston C. More efficient method for the basis transformation of electron interaction integrals. *J. Chem. Phys.* **52**:997-8, 1970.
3. Edmiston C & Lindner P. On the dimerization of BH₃ and the associated delocalization (resonance) energy. *Int. J. Quantum Chem.* **7**:309-18, 1973.
4. Edmiston C & Krauss M. Pseudonatural orbitals as a basis for the superposition of configurations. I. He₂+J. *J. Chem. Phys.* **45**:1833-9, 1966.
5. Configuration-interaction calculation of H₃ and H₂-J. *J. Chem. Phys.* **42**:1119-20, 1965.
6. Pseudonatural orbitals as a basis for the superposition of configurations. II. Energy surface for linear H₃. *J. Chem. Phys.* **49**:192-205, 1968.