

Kitaura K & Morokuma K. A new energy decomposition scheme for molecular interactions within the Hartree-Fock approximation. *Int. J. Quantum Chem.* 10:325-40, 1976.

[Department of Chemistry, University of Rochester, NY]

A new method is proposed for the analysis of components of molecular interaction energy within the Hartree-Fock approximation. This method allows the evaluation of electrostatic, polarization, exchange repulsion, and charge transfer terms separately and on equal footing and is easily applicable. [The SC7® indicates that this paper has been cited in over 255 publications.]

Keiji Morokuma
 Institute for Molecular Science
 Myodaiji, Okazaki 444
 and
 Kazuo Kitaura
 Department of Chemistry
 Osaka City University
 Sugimotocho, Sumiyoshi,
 Osaka 558
 Japan

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When this paper was written, Kazuo Kitaura was a special graduate student at the University of Rochester. He was on leave from Osaka City University and was spending a year with Keiji Morokuma. It had been only six years since the first *ab initio* calculation of water dimer by Morokuma and L. Pedersen had been published.¹ A microwave experiment by T.R. Dyke and J.S. Muenter at Rochester in 1973 had just confirmed that the theoretical prediction of linear dimer geometry had been correct. Many more papers were appearing on molecular orbital studies of hydrogen bonding. A major concern then was to learn from *ab initio* calculations what causes such an interaction. Morokuma had in 1971 already proposed a method, based on various forms of the total Hartree-Fock wave function, for extracting the electrostatic, exchange repulsion, and polarization contributions from the total interaction energy.² What was leftover was tentatively called the "charge transfer energy," though it certainly contained mixing terms between various components. Kitaura was to find a simple way of separating charge transfer from mixing terms.

Several months passed without success, Kitaura working vigorously with the many-body technique and both of us having discussions and exchanging notes. We both felt that an analysis based on individual molecular orbitals rather than on the total wave function might be more promising. One morning in February 1975, each of us had similar equations that seemed workable. In a few weeks we polished up the procedure, did a few test calculations, and wrote up this paper. With this procedure, we were able to separate the charge transfer energy from the mixing terms and discuss its contribution on the same footing as the other energy terms. Soon afterward, we applied the method to elucidate the origin of various intermolecular interactions, such as hydrogen bonding,³ proton affinity, electron donor-acceptor interaction,⁴ and transition-metal donative and back-donative interaction.⁵

Why has this method been quoted many times? One reason is obviously timeliness. Molecular orbital studies of molecular interaction were becoming very popular, and many people used our method for the analysis of their results. The clarity of the method is probably another important reason. The method defines and calculates all the essential energy components—electrostatic, polarization, exchange, and charge transfer—separately. Earlier methods could calculate only the sum of some terms. It is a variational approach, more easily applicable than a perturbation approach to varieties of intermolecular interactions, and can be executed with little additional computer time with minor modifications of a standard Hartree-Fock program. Very importantly, each energy term defined has a clear physical meaning in accord with the intuitive viewpoint. Recently, some groups have used quite different definitions of these terms. They should be using different names for their terms. Their conclusions are anti-intuitive.

As a further development of the present idea, Kitaura has recently developed a new functional form representing intermolecular interaction in terms of the molecular orbital overlap and has found it to be superior to the popular multipole expansion.⁶

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