

Per-Olov Löwdin and the Coulomb Hamiltonian: Implications for Definition of Atoms in Molecules

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In his later papers, Per-Olov Löwdin addressed the issue of devising a satisfactory mathematical definition of molecular structure with characteristic clarity and insight, placing earlier studies in the context of a common unifying perspective. He particularly noted the apparent impossibility of meaningful assignments of indistinguishable electrons to particular atomic nuclei in a molecular Hamiltonian, and the consequent absence of atoms, isomers, molecular spatial symmetries, and other structural aspects of a molecule on this basis. Although much has been written in this connection both before and after Per-Olov's review, mathematical definition of molecular structure is still widely regarded by many as an open problem. In this contribution we address the assignments of electrons to atoms in molecules and the meaningful definition of atomic fragment operators in the Coulomb Hamiltonian from the perspective of representation theory. Use of an orthonormal (Eisenschitz-London) outer product of atomic spectral eigenstates as a representational basis in the absence of over-all aggregate electron antisymmetry is seen to both allow meaningful assignments of electrons to particular atomic nuclei and to provide support for solutions of the Schrödinger equation. Well-defined self-adjoint atomic fragment operators within a molecular aggregate are obtained in this conditional context which have physically significant Hermitian expectation values in the spectral-product representation. The adiabatic (Born-Oppenheimer) molecular Hamiltonian matrix representative takes the form of a sum of atomic Hamiltonian matrices and a pairwise-atomic sum of interaction matrices, providing a partitioning into corresponding physically significant fragment atomic and atomic-interaction energy expectation values free from ambiguity. The adiabatic molecular energies and eigenfunctions obtained in the spectral-product representation are shown to converge in the limit of closure to the results of conventional variational calculations employing explicitly antisymmetric aggregate basis functions, insuring that total energies obtained in the representation are in accord with commonly accepted calculated values. Expectation values of physical properties, such as electronic charge density distributions, are shown to be expressible in terms of sums of atomic fragment contributions, providing a quantitative *ab initio* method for calculations of the redistribution of electronic charge from individual atoms consequent of the formation of chemical bonds. Illustrative results are provided in clarification of the formalism.

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