This Week's Citation Classic®

An interpretation of quantum mechanics in terms of reduced density matrices of value in calculating the expectation values of various physical quantities is given. The eigenfunctions to the first-order density matrix or natural spin-orbitals have the property that, in the method of configurational interaction for calculating wave functions, they give the most rapid convergence. [The *SCI®* indicates that this paper has been cited in over 770 publications.]

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This paper was written in the spring of 1954 when I was a visiting professor at the Massachusetts Institute of Technology working in John C. Slater's Atomic, Molecular, and Solid-State Theory (AMSST) Group. I was aware of the fact that density matrices were a valuable tool in statistical mechanics and general quantum theory, but no one believed that they would be of any value in pure quantum mechanics, where the fundamental concept was the wave function. A little study revealed, however, that even in pure quantum mechanics reduced density matrices would be of value in the following: in calculating the expectation value of the energy and other physical quantities; in the Hartree-Fock Scheme, an approach that had been used earlier by P.A.M. Dirac; and in the general theory by K. Husimi, whose work I learned about at a much later stage.

In the early 1950s the method of configurational interaction (CI) for calculating many-electron wave functions had become popular thanks to the development of the new electronic computers. In 1953 Slater[1] had pointed out the problem of finding the one-electron basis that would lead to the most rapid convergence of such expansions and had even formulated some equations that they would have to satisfy. My little study showed that the natural spin-orbitals that diagonalize the reduced first-order density matrix would immediately provide a solution to this problem. The first applications of this approach to simple atoms were made in the AMSST Group, using hydrogenic-like functions as a starting point; however, since the programs we had available had neglected the continuum, our calculations converged to the wrong results, and Slater quickly lost all interest in this approach. The first successful applications were instead carried out in Uppsala by Harrison Shull and me,[2] and the method proved rather powerful. One would hence have expected that all CI-calculations should be expressed in terms of natural orbitals, but except for a few successful applications the development was very slow, until finally E.R. Davidson's book[3] provided a turning point among the numerical practitioners.

The reduced second-order density matrix is a key quantity in calculating the energy, and the study of its properties has led to the famous "representability problem,"[4] which is still of great international interest. The pair-functions (or geminals) that diagonalize this matrix are of essential importance in many problems in theoretical physics and chemistry, and the occurrence of anomalously large eigenvalues for certain systems may correspond to the phenomena of superconductivity and superfluidity. Going from pure quantum mechanics to the more general quantum statistic of the type developed by J. von Neumann, one can still utilize many of the properties of the reduced density matrices of the first and second order, and one can, for example, construct molecular orbitals that depend on such macroscopic parameters as temperature and pressure and take fundamental quantum-mechanical concepts into the general theory.[5,6]

1. Slater J C. A generalized self-consistent field method. *Phys. Rev.* 91:528-30, 1953. (Cited 70 times since 1955.)
2. Löwdin P-O & Shull H. Natural orbitals in the quantum theory of two-electron systems. *Phys. Rev.* 101:1730-9, 1956. (Cited 240 times.)
3. Davidson E R. *Reduced density matrices in quantum chemistry.* New York: Academic Press, 1976. 135 p. (Cited 100 times.)
4. Löwdin P-O. Some aspects on the development of the theory of reduced density matrices and the representability problem. (Smith V H & Erdahl R, eds.) *Proceedings of the Kingston Symposium, August. 1985.* Dordrecht. The Netherlands: Reidel, 1986.
5. ————. Quantum theory as a trace algebra. *Int. J. Quantum Chem.* 12(Suppl. 1):197-266, 1978.
6. ————. On the axioms of quantum theory formulated as a trace algebra. *Int. J. Quantum Chem.* 21:275-353, 1982.