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Comments

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Comment on "Valence-bond theory and the evaluation of electronic energy matrix elements between nonorthogonal Slater determinants"

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In a recent article [Phys. Rev. A 31, 2107 (1985)] Leasure and Balint-Kurti claim to give a more efficient algorithm than any previously available for determining matrix elements of the Hamiltonian in valence-bond calculations. Actually, an algorithm of no significant difference and the same efficiency has been available since 1972 and has been applied to valence-bond calculations.

In numerical calculations it is important to have efficient algorithms. For those that operate in "polynomial time," the efficiency of algorithms is characterized by N^m, where N is a parameter determining the size of the problem being treated. In this case lower values of m present the least problem in scaling the calculation up to large systems. In a recent article[1] Leasure and Balint-Kurti demonstrate an N^4 algorithm for the evaluation of electronic energy matrix elements between nonorthogonal Slater determinants, where N is the number of electrons. They also state, "The time required for previously available methods . . . increases as N^6. . . ."

It should be pointed out that an N^4 algorithm for evaluating matrix elements of the Hamiltonian between nonorthogonal determinants has been available since 1972.[2] If the same basis is used, this earlier method, although incorporating spin somewhat differently, will produce final eigenvalues and eigenvectors equivalent to those from a calculation using the results of Ref. 1.

The algorithm in Ref. 2 is given in terms of *tableau functions.* These are completely equivalent[3] to the spin-projected Slater determinants discussed by Löwdin.[4] Thus, they are already eigenfunctions of the total spin, unlike general open-shell Slater determinants. Tableau functions are written as a short linear combination of determinantal functions that are evaluated in N^4 times.[5] These differences are not significant and, if desired, the identical method may be applied directly to Slater determinants, themselves.

Other workers, also, have been using practical, N^4 algorithms for valence-bond calculations prior to this time.[6,7] Therefore, Leasure and Balint-Kurti have not produced an algorithm that is an improvement over previous methods. Indeed, their contention is surprising since they refer to Ref. 5 (their Ref. 10), in which the N^4 nature of the algorithm is explicitly stated.

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