

7-1-1986

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

Gordon A. Gallup  
*University of Nebraska-Lincoln, ggallup1@unl.edu*

Follow this and additional works at: <http://digitalcommons.unl.edu/physicsgallup>

 Part of the [Physics Commons](#)

---

Gallup, Gordon A., "Comment on “Valence-bond theory and the evaluation of electronic energy matrix elements between nonorthogonal Slater determinants”" (1986). *Gordon Gallup Publications*. 9.  
<http://digitalcommons.unl.edu/physicsgallup/9>

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Gordon Gallup Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

## Comments

---

Comments are short papers which comment on papers of other authors previously published in the *Physical Review*. Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

---

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

G. A. Gallup

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588

(Received 29 April 1985; revised manuscript received 21 October 1985)

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<sup>1</sup> 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.<sup>2</sup> 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<sup>3</sup> to the spin-projected Slater determinants discussed by Löwdin.<sup>4</sup> 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.<sup>5</sup> 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.<sup>6,7</sup> 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.

---

<sup>1</sup>S. C. Leasure and G. G. Balint-Kurti, Phys. Rev. A 31, 2107 (1985).

<sup>2</sup>G. A. Gallup, Int. J. Quantum Chem. 6, 899 (1972).

<sup>3</sup>G. A. Gallup, Int. J. Quantum Chem. 21, 1057 (1982).

<sup>4</sup>P.-O. Löwdin, Calcul des Fonctions d'onde Moléculaire (CNRS, Paris, 1958).

<sup>5</sup>G. A. Gallup, R. L. Vance, J. R. Collins, and J. M. Norbeck, Adv. Quantum Chem. 16, 229 (1982); 16, 248 (1982) (Sec. IIE).

<sup>6</sup>M. Raimondi, W. Champion, and M. Karplus, Mol. Phys. 34, 1483 (1977).

<sup>7</sup>M. Raimondi (private communication).