

January 1973

Projected Hartree product wavefunctions. VIII. Relationship of DODS and SCF orbitals for Be

Gordon A. Gallup
UNL, ggallup1@unl.edu

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



Part of the [Physics Commons](#)

Gallup, Gordon A., "Projected Hartree product wavefunctions. VIII. Relationship of DODS and SCF orbitals for Be" (1973). *Gordon Gallup Publications*. 18.

<http://digitalcommons.unl.edu/physicsgallup/18>

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.

Projected Hartree product wavefunctions. VIII. Relationship of DODS and SCF orbitals for Be

G. A. GALLUP

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68508

(Received 15 July 1971)

Recently, several calculations of the beryllium atom, including radial correlations, have been made using the DODS scheme.¹⁻⁴ It is interesting to note the relationship of the DODS orbitals for this system with the SCF orbitals calculated by Roothaan *et al.*⁵ Following the notation in Ref. 4, the wavefunction ψ is written

$$\psi = \theta NPN \{ \gamma_1 a(1)b(2)c(3)d(4) + \gamma_2 a(1)c(2)b(3)d(4) \},$$

where a and d are $1s$ -like orbitals and b and c are $2s$ -like orbitals. The orbitals a , b , c , and d are linear combinations of a fixed basis given in Ref. 4. The energy provided by the DODS wavefunction, used here, is -14.5900 a.u. as compared with an SCF energy of -14.5730 a.u. Further details of the DODS calculations are also given in Ref. 4.

We define orbitals u' and v' as the simple, unweighted arithmetic means of $1s$ -like and $2s$ -like orbitals, respectively,

$$u' = (a+d)/2,$$

$$v' = (b+c)/2.$$

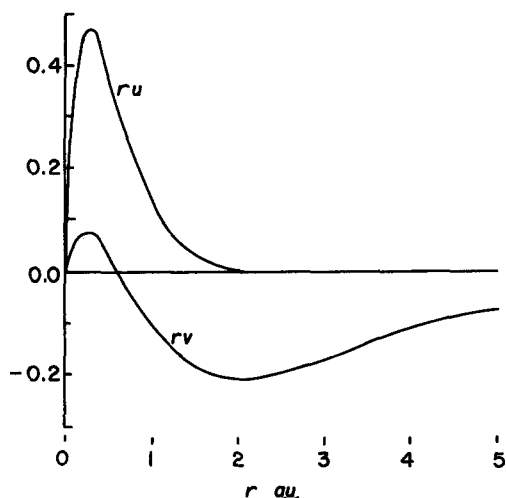


FIG. 1. Plots of average DODS orbitals and SCF orbitals for Be versus r .

Neither is normalized, nor are they orthogonal, but these conditions may be imposed, so that the functions u and v defined as

$$u = Au',$$

$$v = Bv' - Cu'$$

satisfy the relations

$$\langle u | u \rangle = \langle v | v \rangle = 1,$$

$$\langle u | v \rangle = 0.$$

Figure 1 shows the graphs of ru and rv for the orbitals given in Ref. 4. The similar quantities $r(1s)$ and $r(2s)$ (eight-member basis set) given by Roothaan are also plotted on the graph. It is seen that the functions are identical to the accuracy available on the graph.

A more sensitive test involves the trace of the product of the density matrices corresponding to the pairs of functions. This has been computed:

$$\langle u | 1s \rangle^2 + \langle u | 2s \rangle^2 + \langle v | 1s \rangle^2 + \langle v | 2s \rangle^2 = 1.99977.$$

If this were exactly 2, the subspaces of Hilbert space spanned by u , v and $1s$, $2s$ would be identical. The actual discrepancy here of 0.00023 is quite small, and may be due to the quite different bases used in the two calculations as much as to inherent differences between hypothetical "exact" solutions to the two problems. The essential equality of linear subspaces of the two calculations adds considerable weight to the arguments of Ref. 4 concerning the relative amounts of different types of excitations implicit in DODS calculations.

¹ W. A. Goddard, J. Chem. Phys. **48**, 1008 (1968).

² U. Kaldor, H. F. Schaefer, and F. E. Harris, Intern. J. Quantum Chem. **25**, 13 (1968).

³ S. Lunell, Phys. Rev. **173**, 85 (1968).

⁴ L. G. Heikes and G. A. Gallup, J. Chem. Phys. **52**, 888 (1970).

⁵ C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).