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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

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

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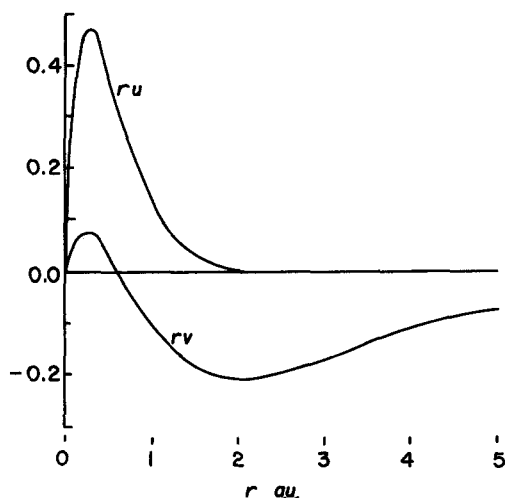
$$u' = (a+d)/2,$$

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

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

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

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

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:

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

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.

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

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