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Relationes

Approximate Natural Orbitals for Carbon ^1S *

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A convenient method of comparison of approximate wavefunctions of electronic systems is by means of the natural analysis of Löwdin [*5*]. Detailed calculations have been made for two-electron systems** and four-electron systems [*1*] which have proved to provide much necessary information for their understanding as well as for that of the role of the density matrix in quantum mechanics (n-representability problem) [*3*].

The present note presents natural spin orbitals (NSO) and occupation numbers for the lowest ^1S state of (six-electron) Carbon for an approximate wavefunction of Boys [*2*]***, (the best available in the literature) and for the exact wavefunction in the limit of infinite nuclear charge ($Z \to \infty$).

The method of calculation is straight-forward from the definition of the natural spin orbitals ϕ_i and occupation numbers ν_i as the eigenfunctions and eigenvalues respectively of the one particle density matrix

$$\gamma_\psi(1,1') = n \int \psi(1, 2, \ldots n)\, \psi^*(1', 2, \ldots n)\, d\tau_2\, d\tau_3 \ldots d\tau_n \tag{1}$$

or expanded in terms of its eigenfunctions:

$$\gamma_\psi(1,1') = \sum_i \nu_i\, \phi_i(1)\, \phi_i^*(1') \,. \tag{2}$$

Thus one must calculate $\gamma\,(1,1')$ for the wavefunction under consideration in some basis and then diagonalize its coefficient matrix. Since the wavefunctions under consideration are given as a sum of determinants of orthonormal orbitals, the coefficient matrix for $\gamma(1,1')$ expanded over this orbital basis may be constructed by the formalism of Löwdin [*5*] or an alternative formulation of Kutzelnigg and Smith [*8*].

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** For a list of references, see Ref. [*1*].

*** A preliminary calculation for this wavefunction was made by Shull and Linderberg [*11*].

Table 1. BOYS' *wavefunction for the lowest* ^1S *of Carbon*[a]

Configuration	Coefficient[b]
$(sA)^2\,(sB)^2\,(pA)^2$	0.92521556
$(sAsC)\,(sB)^2\,(pA)^2$	$0.00588803 \times \sqrt{2}$
$(sC)^2\,(sB)^2\,(pA)^2$	−0.01452600
$(pC)^2\,(sB)^2\,(pA)^2$	0.01489597
$(sA)^2\,(pA)^4$	−0.23047119
$(sA)^2\,(sBsC)\,(pA)^2$	$0.00955170 \times \sqrt{2}$
$(sA)^2\,(sBsD)\,(pA)^2$	$-0.05933831 \times \sqrt{2}$
$(sA)^2\,(sB)^2\,(pApB)$	$0.09054491 \times \sqrt{2}$
$(sA)^2\,(sB)^2\,(pApD)$	$0.15642548 \times \sqrt{2}$
$(sA)^2\,(sBsC)\,(pApB)$	0.03210498
$(sA)^2\,(sBsD)\,(pApB)$	−0.05791850
$(sA)^2\,(sB)^2\,(pB)^2$	−0.07216681
$(sA)^2\,(sB)^2\,(dA)^2$	0.09057860

[a] S. F. BOYS [*2*].

[b] BOYS' coefficients were given to only four significant figures and have been taken to be exact and renormalized more accurately [*11*]. Note that in these configurations, the symbol ( ) indicates that the pair is singlet-coupled.

The treatment of the configurations $(1s)^2\,(2s)^2\,(2p)^2$ and $(1s)^2\,(2p)^4$ requires some care. Since these are composed of determinants

$$\begin{aligned}(1s)^2\,(2s)^2\,(2p)^2 = (3)^{-1/2}\,\{&\det\,[(1s)^2\,(2s)^2\,(2p_0)^2] - \\ &- \det\,[(1s)^2\,(2s)^2\,2p_+\alpha\,2p_-\beta] - \\ &- \det\,[(1s)^2\,(2s)^2\,2p_-\alpha\,2p_+\beta]\} \\ (1s)^2\,(2p)^4 = (3)^{-1/2}\,\{&\det\,[(1s)^2\,2p_+\alpha\,2p_-\alpha\,2p_+\beta\,2p_-\beta] - \\ &- \det\,[(1s)^2\,2p_0\alpha\,2p_-\alpha\,2p_+\beta\,2p_0\beta] - \\ &- \det\,[(1s)^2\,2p_+\alpha\,2p_0\alpha\,2p_0\beta\,2p_-\beta]\,,\end{aligned}$$

it is best to consider the $2p$ orbital members of the basis; $2p_0$, $2p_+$, and $2p_-$

Table 2. *Natural orbitals for the Boys function*

	ϕ_1	ϕ_3	ϕ_{17}	ϕ_{35}
sA	0.99998557	−0.00020144	−0.00291585	−0.00450764
sB	0.00013349	0.99787935	−0.06045417	0.02412630
sC	0.00537062	0.01251181	0.54189995	0.84033271
sD	0.00001616	−0.06387657	−0.83826084	0.54151505

	ϕ_5	ϕ_{11}	ϕ_{29}	ϕ_{37}
pA	0.98647124	−0.12566227	−0.10527819	0.00000000
pB	0.08055548	0.93088817	−0.35631172	0.00000000
pC	0.00000000	0.00000000	0.00000000	1.00000000
pD	0.14277716	0.34301052	0.92841718	0.00000000

	ϕ_{19}
dA	1.00000000

Table 3. *Occupation numbers for ^1S Carbon wavefunctions*

Number	Type	Boys	True ($Z \to \infty$)
1, 2	s	0.99956127	1.00000000
3, 4	s	0.94507540	0.95978474
5—10	p	0.34413502	0.34673842
11 –16	p	0.00329535	—
17, 18	s	0.00182818	
19—28	d	0.00164089	
29—34	p	0.00087393	
35, 36	s	0.00019632	
37—42	p	0.00007396	
	α	1.340171	1.337677
	β	0.223362	0.222945
	τ	2.844913	2.773907
	$\varkappa$	1.504742	1.436230

separately in the analysis. Configurations of this type are present in both wavefunctions. In the true wavefunction ($Z \to \infty$), these are the only two with coefficients squared of 0.95978474 and 0.04021526 respectively. The presence of these two configurations is due to the degeneracy between hydrogenic $2s$ and $2p$ orbitals [*4*]. The coefficient matrix is diagonal in the hydrogenic basis $1s\alpha$, $1s\beta$, $2s\alpha$, $2s\beta$, $2p_0\alpha$, $2p_0\beta$, $2p_+\alpha$, $2p_+\beta$, $2p_-\alpha$, $2p_-\beta$. Thus these spin orbitals are the NSO with occupation numbers given in Tab. 3, and reveals that even in the limit ($Z \to \infty$) for this state $\gamma(1,1')$ is not idempotent. The eigenvalues for the s orbitals are doubly degenerate while those for the $2p$ orbitals are six-fold degenerate i.e. $2(2l+1)$ fold.

The results for these wavefunctions are interesting. As expected for a ^1S state, the eigenvalues are doubly degenerate with the two degenerate eigenfunctions, pure spin state functions i.e. the same spatial factor multiplied by α and β respectively. The behaviour of the eigenvalues with Z is as expected [*7*]: those occupied in the limiting case decrease as Z decreases, the unoccupied ones increase.

In contrast to the reported results for the two- and four-electron systems, where the eigenvalue distribution could be divided into two groups: the strongly-occupied ones ($\nu_i \sim 1$) and the weakly occupied ones ($\nu_i \sim 0$), the Carbon eigenvalues divide into strongly-occupied, weakly-occupied and an intermediate category represented by ν_6 through ν_{10}.

The n^{th} and $(n+1)^{\text{st}}$ eigenvalues are equal, in fact $\nu_6 = \nu_7 = \nu_5 = \nu_8 = \nu_9 = \nu_{10}$. There is therefore no unique construction of a single Slater determinant from the first n NSO i.e. the best-density determinant [*6, 8, 9*]. This has an important implication for the classification of a state as of open or closed shell type [*10*] and leads to the classification of C(^1S) as of "open-shell" type [*10*].

Tab. 3 is completed by the values of the measure of "almost idempotency" of the one-particle density matrix [*5, 8, 9*]

$$\varkappa = \operatorname{tr}(\gamma_\Psi - \gamma_\Psi^2) = n - \sum_{i=1}^{\infty} \nu_i^2$$

and three measures of goodness of an idempotent approximation γ_ϕ (ϕ: single Slater determinent) to γ_Ψ [*8, 9*] given by

$$\alpha = n - 2 \sum_{i=1}^{n} \nu_i + \sum_{i=1}^{\infty} \nu_i^2$$

$$\beta = \alpha/n$$

$$\tau = 2(n - \sum_{i=1}^{n} \nu_i)\,.$$

These concepts are discussed in more detail in [*8*, *9*].

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References

[*1*] BARNETT, G. P., J. LINDERBERG, and H. SHULL: J. chem. Physics **43**, S80 (1965).
[*2*] BOYS, S. F.: Proc. Roy. Soc. **A217**, 235 (1953).
[*3*] COLEMAN, A. J.: Rev. mod. Physics **35**, 668 (1963).
[*4*] LINDERBERG, J., and H. SHULL: J. molecular Spectroscopy **5**, 1 (1960).
[*5*] LÖWDIN, P. O.: Physic. Rev. **97**, 1474 (1955).
[*6*] KUTZELNIGG, W., and V. H. SMITH, Jr.: J. chem. Physics **41**, 897 (1964).
[*7*] — — J. chem. Physics **42**, 2791 (1965).
[*8*] — — Technical Note 130, Quantum Chemistry Group. Uppsala University 1964.
[*9*] — — Technical Note 138, Quantum Chemistry Group. Uppsala University 1964.
[*10*] — — To be published.
[*11*] SHULL, H., and J. LINDERBERG: Private communication.

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