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Studies on Rydberg Orbitals. III. Calculation of the 4*s*, 4*p*, and 4*d* Orbitals of Carbon Atom

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Many different approaches to the calculation of Rydberg orbitals of small[2)] atoms and molecules have been undertaken.[3–7)] Apart from its mathematical interest, the information from these studies is useful not only for interpreting the Rydberg spectra but also for estimating, by perturbation calculations, the contribution of Rydberg orbitals of states in several problems such as electronic spectra of charge-transfer complexes and reaction mechanisms.[8)]

The author calculated the 3*s*, 3*p*, and 3*d* orbital wavefunctions and energies of Li(I)-F(I) and their isoelectronic series in their unhybridized Rydberg valence states with the lowest energy,[3)] *e.g.*, for

$$\mathrm{C(I)}\ \ 1s^2 2s^2 2p3l,\ V_2\ \ (l=s,\ p,\ d) \tag{1}$$

In this paper the least-STO-basis wavefunctions and orbital energies of carbon 4*s*, 4*p*, and 4*d* orbitals of the valence state

$$\mathrm{C(I)}\ \ 1s^2 2s^2 2p4l,\ V_2\ \ (l=s,\ p,\ d) \tag{2}$$

will be reported.

Since the calculation is an extension of the 3 *l* orbitals, only a brief account is given. The radial part of the least-STO-basis wavefunction 4 *l*, R_{4l}, has $2(4-l)$ parameters to be optimized (four C_{nl}'s and four μ_{nl}'s).

$$R_{4l}=\sum_{n=l+1}^{4} C_{nl} S(n,\ \mu_{nl}) \tag{3}$$

where $S(n,\mu_{nl})$ is a normalized Slater type orbital

$$S(n,\ \mu_{nl})=(2\mu_{nl})^{n+1/2}\{(2n)\,!\}^{-1/2} r^{n-1} \exp\left(-\mu_{nl} r\right).$$

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2) By "small" we mean "relatively small but with more than two electrons."

3) H. Hosoya, *J. Chem. Phys.*, **48**, 1380 (1968). Part II of the present series of papers. Most attempts in this problem before 1967 are referred to in this paper.

4) A. U. Hazi and S. A. Rice, *ibid.*, **45**, 3004 (1966); *ibid.*, **48**, 495 (1968).

5) M. B. Robin, R. R. Hart, and N. A. Kuebler, *ibid.*, **44**, 1803 (1966) and related papers.

6) Y. Harada and J. N. Murrell, *Mol. Phys.*, **14**, 153 (1968).

7) T. F. Lin and A. B. F. Duncan, *J. Chem. Phys.*, **48**, 866 (1968); *ibid.*, **51**, 360 (1969).

8) H. Hosoya, "Study on trans-Addition Reaction in Terms of Molecular Orbital Deformation," presented at the "Symposium on Molecular Structures," Sendai, Japan (1963); H. Hosoya and S. Nagakura, This Bulletin, **37**, 249 (1964).

The function R_{4l} should be orthogonal to all the inner orbitals $R_{nl}(n=l+1,\cdots,3;\ 3-l$ conditions). The orbital exponents of the inner loops μ_{nl}'s$(n=l+1,\cdots,3;\ 3-l$ constants) were fixed as in the $3\,l$ calculation. Then by using the normalization condition we are left a single parameter μ_{4l}, which can be determined by optimization process as adopted in the $3\,l$ calculation. The wavefunctions of the $1s$, $2s$, and $2p$ orbitals forming the fixed core potential were taken from the table by Clementi[9] for the ion

$$\mathrm{C(II)}\ 1s^2 2s^2 2p,\ V_1\ (={}^2\mathrm{P}) \qquad (4)$$

TABLE 1. LEAST-STO-BASIS RYDBERG ORBITALS[a] of C(I) $1s^2\,2s^2\,2p\ Nl,\ V_2\ (N=3,4)$

Orbital *Nl*	C_{nl}	n	μ_{nl}	–Orbital energy (cm^{-1}) (Quantum defect) Calcd	Obsd
$4s$	−0.032215	1	5.7	12884	12694
	0.128426	2	1.8	(1.08)	(1.06)
	−0.692823	3	0.550		
	1.209454	4	0.328		
$4p$	0.111538	2	1.8	9672	10009
	−0.788364	3	0.465	(0.63)	(0.69)
	1.269707	4	0.297		
$4d$	−0.880863	3	0.340	6909	7031
	1.332636	4	0.230	(0.01)	(0.05)
$3s$[b]	0.055648	1	5.7	29644	30281
	−0.219630	2	1.8	(1.08)	(1.10)
	1.018750	3	0.550		
$3p$[b]	−0.167880	2	1.8	19900	20254
	1.007695	3	0.465	(0.65)	(0.67)
$3d$[b]	1.000000	3	0.340	12281	12402
				(0.01)	(0.03)

a) See Eq. (3). b) Ref. 3.

With these analytical expressions and potential the orbital energy of $4\,l$ electron in the valence state can be calculated for a given μ_{4l} value. Since in this case interaction between the Rydberg electron and core electrons is negligibly small compared to the orbital energy of the Rydberg electron, the orbital R_{4l} giving the lowest orbital energy is close enough to what would be obtained by the Hartree-Fock method. Table 1 gives the wavefunctions, orbital energies and quantum defects of the $4\,l$ orbitals obtained by this optimization procedure and also contains, for the sake of comparison, the least-STO-basis $3\,l$ orbitals.[3]

The observed energy values in Table 1 were obtained by taking the weighted means of all the term values in the Moore table.[10] Although the calculated energy of the $4s$ orbital surpasses the observed value due to several approximations taken, all the results are very close to the observed values. Accuracy of the calculation of Rydberg sates can be better checked with the quantum defects than with the absolute values of the orbital energies. Differences between the observed and calculated values for the $4\,l$ orbitals are as large as those for the $3\,l$ orbitals. As the quantum number of the Ryberg orbital increases, the error due to penetration into the core orbitals will decrease, although the consecutive orthogonalization procedure will pile up the error of the lower members to some extent. Thus this type of calculation of the Rydberg orbitals may be expected to be equally applied to the higher members and also to other systems.

All the calculations were performed in 1967 by using a Facom 202 computer at the Institute for Solid State Physics of the University of Tokyo. Thanks are due to Professor Saburo Nagakura for his interest and criticism.

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[9] E. Clementi, "Tables of Atomic Functions," IBM Co., San Jose, Calif. (1965).

[10] C. E. Moore, "Atomic Energy Levels," U. S. Department of Commerce, Natl. Bur. Stand., Washington, D. C. (1949).