

Relativistically Parametrized Extended-Hückel Calculations. II. Orbital Energies of Group-IV Tetrahalides and Tetramethyls

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Abstract

Relativistically parametrized extended-Hückel (REX) calculations are reported for MX_4 ($\text{M} = \text{Ti, Zr, Hf, C, Si, Ge, Sn, Pb}$; $\text{X} = \text{Cl, Br, I}$) and for $\text{M}(\text{CH}_3)_4$ ($\text{M} = \text{Ti, C, Si, Ge, Sn, Pb}$). Satisfactory agreement is obtained with experiment and with earlier assignments both for the energy levels and for their relativistic splittings. This encourages the use of REX for assigning PES spectra. Double- ζ radial functions (REX and EHT) are given for Cl, Br, and I.

1. Introduction

Relativistic effects strongly influence the chemical properties of heavier elements [1, 2]. Perhaps the simplest method, where all the qualitatively different relativistic effects (contractions, expansions, and splittings) can still be included, is provided by the "relativistically parametrized extended Hückel method (REX)" [3-5].

This method is a noniterative one, at the low end of the quality scale. It consists of a single diagonalization of a Hamiltonian matrix, set up using $|jm_j\rangle$ basis orbitals on each atom. Thus the usual EHT basis size is doubled. The diagonal matrix elements h_{ii} are put equal to calculated Dirac-Fock or Hartree-Fock orbital energies in neutral atoms. The off-diagonal ones are obtained from the Wolfsberg-Helmholtz formula. One or more Slater orbitals are used for describing each atomic orbital. In the single-STO case the orbital exponent ζ can be obtained from the average orbital radius via

$$\zeta_i = (n + \frac{1}{2}) / \langle r \rangle_i. \quad (1)$$

This affords a systematic comparison of the relativistic and nonrelativistic cases, with both the radial and the energetic effects of relativity included. The REX program [5] contains default parameters for the elements 1-120. This parametrization is described in Ref. 4. The program requires only the molecular geometry and yields the relativistic molecular orbitals as a result of the diagonalization.

We expect that the assignment of photoelectron spectra will form one of the main applications of REX. A rather similar method, incorporating the relativistic splitting but using unsplit radial functions [6], has already been used for this purpose. Two other methods, resembling the present one, have also been proposed [7, 8]. The experimental PES groups have used simpler means, like an EHT calculation on the Cl_4 tetrahedron of MCl_4 ($\text{M} = \text{Ti, Zr, Hf}$) [9]. The purpose of this paper is to explore these possibilities for halogen and methyl compounds of group-IV metals. We then find that halogen-halogen repulsions are important and demand in some cases a double- ζ description. The necessary parameters are given in the Appendix.

2. Group IVa

Photoelectron spectra for the entire series MX_4 ($\text{M} = \text{Ti, Zr, Hf}$; $\text{X} = \text{Cl, Br, I}$) were reported by Egdell and Orchard [9]. Their results and assignments are shown as the right-most ones in Figure 1, together with the present EHT and REX ones, obtained using the single- ζ default parameters [4, 5] for the metal and the double- ζ exponents in the Appendix for the halogens. The bond lengths assumed are shown in Table I.

As seen from Figure 1, the experimental breadths of this "halogen p band" are satisfactorily reproduced. If single- ζ radial functions would be used for the halogens, the breadth for, e.g., TiBr_4 would drop from 2.61 to 1.11 eV. The order of orbitals remains unchanged.

Compared to the original assignments, our e and lower t_2 orbitals are interchanged for ZrCl_4 , TiBr_4 , ZrBr_4 , and HfBr_4 . Otherwise our labels agree with those of Egdell and Orchard [9]. The REX relativistic splittings of the t_1 HOMO also agree well with the experimental values. Reasonable agreement is found for the t_2 splittings in the iodides as well. For the upper t_2 of HfI_4 , we predict the Γ_7 to lie below the Γ_8 and not vice versa. The TiCl_4 LUMO at -10.32 eV is a $\Gamma_8(e)$ having 91% of its norm in the $3d$ of Ti.

The REX energy levels of TiMe_4 in Table II have the same order and roughly the same spread as the *ab initio* ones. The t_2 HOMO of TiMe_4 consists of 43% Ti $3d$ and 52% C $2p$. It exhibits an "inverted spin-orbit splitting" (see Ref. 20), characteristic of d AO:s. Closely under it, the a_1 MO consists of 88% C $2p$ and 8% Ti $4s$. Then follow the $\sigma(\text{C-H})$ t_1 , t_2 , and e bands.

3. Group IVb

Photoelectron spectra were reported for the various group-IVb tetrahalides in Refs. 10–13, for the tetramethyls in Refs. 13–15, and for the mixed halo-methyls in Ref. 16. Further calculations on these systems appeared in Refs. 17 and 18.

The present results for the halides are shown in Tables III and IV. REX fully supports the earlier assignments, except for SiBr_4 , GeBr_4 , and SnBr_4 where it is not quite clear that these assignments are for the e and upper t_2 . Refined ex-

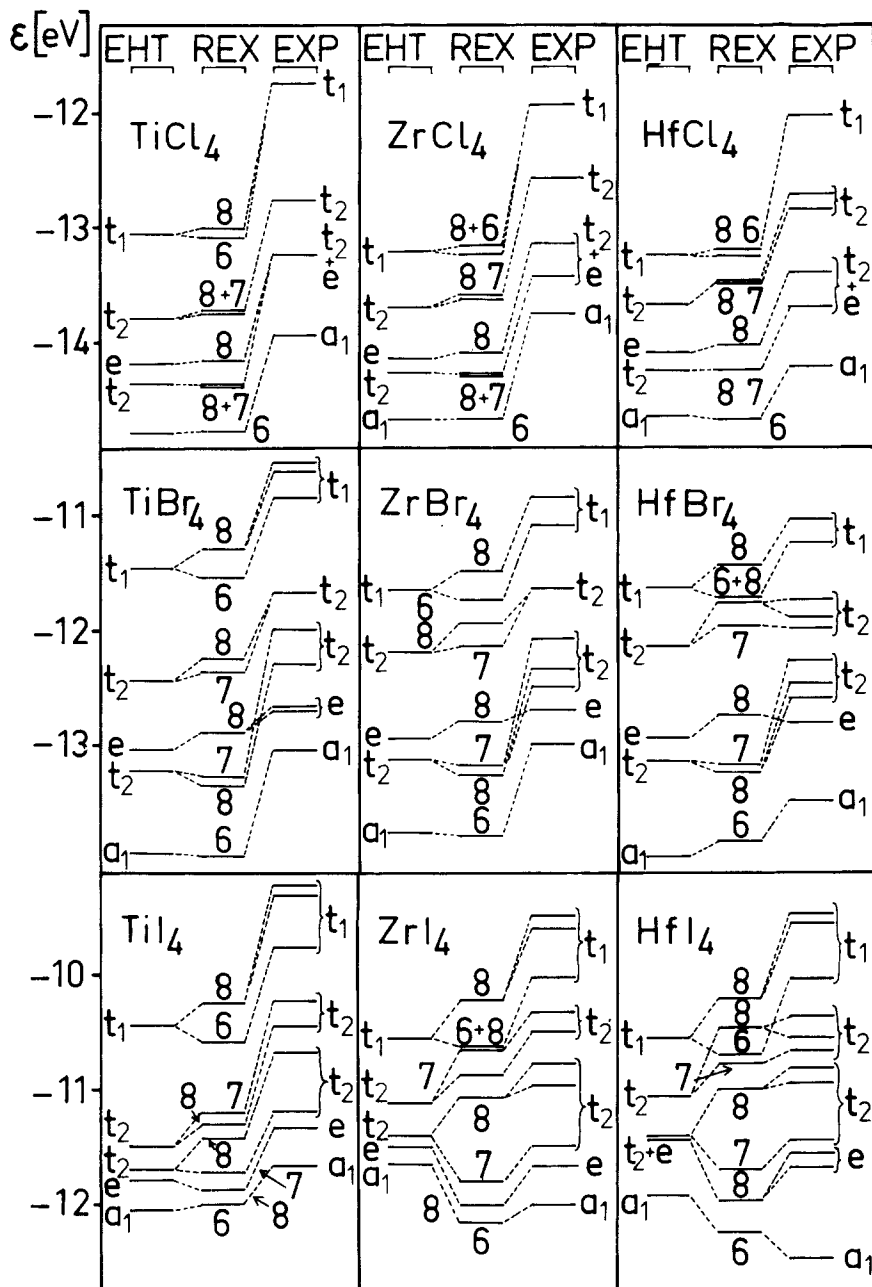


Figure 1. Calculated and experimental (PES) orbital energies [9] for group-IVa halides. For each molecule the EHT, REX, and experimental ones are given from left to right, respectively. In the molecular double-group notation $\Gamma_6 = e'$, $\Gamma_7 = e''$, and $\Gamma_8 = u'$.

TABLE I. Halogen-metal and carbon-metal bond lengths, assumed in the calculations (in pm).

M	X			
	Cl	Br	I	-CH ₃
C	176.6	194.2	212	154.1
Si	201.7	215	243	187
Ge	211.3	229	250	194.5
Sn	227.5	244	264	218
Ti	217	233.9	254.6	213
Zr	232	246.5	266	-
Hf	233	245	266.2	-

TABLE II. Orbital energies for TiMe₄ from REX and from the *ab initio* calculation [19] (in eV).

REX	Ab initio		
7	12.36	t ₂	10.78
8	12.36		
6	12.57	a ₁	11.22
8	14.61	t ₁	14.29
6	14.61		
8	15.20	t ₂	14.94
7	15.20		
8	15.35	e	15.18
Spread 2.99			4.40

periments would be desirable on these systems and also on Cl₄ and SiI₄. A particularly satisfying case are the iodides of Ge and Sn, where the original assignments were done in double-group notation. The NEVE spin-orbit splittings [18] in Table IV also are in reasonable agreement with the present ones.

TABLE III. Calculated and experimental orbital energies for CX₄, SiX₄, and GeX₄. REX energies (in eV) are labeled by the extrairreducible representations, e.g., $\delta' = \Gamma'_8 = t' = u_{3/2}$.

M	X = Cl			X = Br			X = I			
	EHT	REX	Exp.	EHT	REX	Exp.	EHT	REX	Exp.	
C	t_1	12.29	8 12.23	t_1	11.69 ^a , 11.60 ^b	t_1	10.52	8 10.35	t_1	10.39, 10.48, 10.76 ^a ;
		6 12.31					6 10.63			10.40, 10.49, 10.75 ^b ;
	t_2	13.16	8 13.10	t_2	12.44-12.78 ^a ,	t_2	11.74	8 11.55	t_2	11.07, 11.28, 11.73 ^a ,
		7 13.24			12.40-12.75 ^b		7 12.05			11.05, 11.23, 11.69 ^b ,
	e	14.11	8 14.09	e	13.37, 13.50 ^a ,	e	12.86	8 12.81	e	12.11, 12.24 ^a ,
					13.40 ^b		12.06 ^b			
Si	t_2	15.27	7 15.23	t_2	16.58 ^a , 16.60 ^b	t_2	14.28	7 14.15	t_2	15.15 ^a , 15.04 ^b
		8 15.28					8 14.36			
	a_1	17.09	6 17.07	a_1	20.0 ^a	a_1	17.24	6 17.44	a_1	19.7 ^a , 19.48 ^b
	t_1	12.86	8 12.81	t_1	12.03, 12.12 ^b	t_1	11.11	8 10.93	t_1	10.8, 10.9, 11.17 ^b
		6 12.88					8 11.18			
	t_2	13.09	8 13.04	t_2	12.85, 13.05	t_2	11.36	6 11.21	t_2	t_1+t_2 , 11.52, 11.63
Ge	e	14.01	8 13.99	e	13.35, 13.44	e	12.80	8 12.74	t_2+e'	12.05, 12.14, 12.33
	t_2	14.63	7 14.61	t_2	15.05, 15.13,	t_2	13.61	7 13.55	t_2	13.92, 14.06,
		8 14.63			15.25, 15.35		8 13.69			14.19, 14.23
	a_1	16.11	6 16.14	a_1	17.98	a_1	15.75	6 15.84	a_1	17.31
	t_1	13.00	8 12.95	t_1	12.12 ^b	t_1	11.39	8 11.21	t_1	10.75, 10.85 ^b
		6 13.02					8 11.38			
Ge	t_2	13.20	8 13.14	t_2	12.60, 12.75	t_2	11.58	6 11.50	t_1+t_2	11.11, 11.23
		7 13.26					7 11.81			
	e	13.98	8 13.96	e	13.08	e	12.76	8 12.70	t_2+e'	11.89
	t_2	14.55	7 14.53	t_2	14.7, 14.8,	t_2	13.49	7 13.43	t_2	13.63, 13.70,
		8 14.55			14.9		8 13.58			13.9, 14.0
	a_1	16.60	6 16.77	a_1	18.0	a_1	16.43	6 16.71	a_1	17.6
Ge	t_1	13.00	8 12.95	t_1	12.12 ^b	t_1	11.39	8 11.21	t_1	10.75, 10.85 ^b
		6 13.02					8 11.38			
	t_2	13.20	8 13.14	t_2	12.60, 12.75	t_2	11.58	6 11.50	t_1+t_2	11.11, 11.23
		7 13.26					7 11.81			
	e	13.98	8 13.96	e	13.08	e	12.76	8 12.70	t_2+e'	11.89
	t_2	14.55	7 14.53	t_2	14.7, 14.8,	t_2	13.49	7 13.43	t_2	13.63, 13.70,
	8 14.55			14.9		8 13.58			13.9, 14.0	
Ge	a_1	16.60	6 16.77	a_1	18.0	a_1	16.43	6 16.71	a_1	17.6
	t_1	13.00	8 12.95	t_1	12.12 ^b	t_1	11.39	8 11.21	t_1	10.75, 10.85 ^b
		6 13.02					8 11.38			
	t_2	13.20	8 13.14	t_2	12.60, 12.75	t_2	11.58	6 11.50	t_1+t_2	11.11, 11.23
		7 13.26					7 11.81			
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t_2	14.55	7 14.53	t_2	14.7, 14.8,	t_2	13.49	7 13.43	t_2	13.63, 13.70,	
	8 14.55			14.9		8 13.58			13.9, 14.0	
Ge	a_1	16.60	6 16.77	a_1	18.0	a_1	16.43	6 16.71	a_1	17.6
	t_1	13.00	8 12.95	t_1	12.12 ^b	t_1	11.39	8 11.21	t_1	10.75, 10.85 ^b
		6 13.02					8 11.38			
	t_2	13.20	8 13.14	t_2	12.60, 12.75	t_2	11.58	6 11.50	t_1+t_2	11.11, 11.23
		7 13.26					7 11.81			
	e	13.98	8 13.96	e	13.08	e	12.76	8 12.70	t_2+e'	11.89
t_2	14.55	7 14.53	t_2	14.7, 14.8,	t_2	13.49	7 13.43	t_2	13.63, 13.70,	
	8 14.55			14.9		8 13.58			13.9, 14.0	
Ge	a_1	16.60	6 16.77	a_1	18.0	a_1	16.43	6 16.71	a_1	17.6
	t_1	13.00	8 12.95	t_1	12.12 ^b	t_1	11.39	8 11.21	t_1	10.75, 10.85 ^b
		6 13.02					8 11.38			
	t_2	13.20	8 13.14	t_2	12.60, 12.75	t_2	11.58	6 11.50	t_1+t_2	11.11, 11.23
		7 13.26					7 11.81			
	e	13.98	8 13.96	e	13.08	e	12.76	8 12.70	t_2+e'	11.89
t_2	14.55	7 14.53	t_2	14.7, 14.8,	t_2	13.49	7 13.43	t_2	13.63, 13.70,	
	8 14.55			14.9		8 13.58			13.9, 14.0	
Ge	a_1	16.60	6 16.77	a_1	18.0	a_1	16.43	6 16.71	a_1	17.6
	t_1	13.00	8 12.95	t_1	12.12 ^b	t_1	11.39	8 11.21	t_1	10.75, 10.85 ^b
		6 13.02					8 11.38			
	t_2	13.20	8 13.14	t_2	12.60, 12.75	t_2	11.58	6 11.50	t_1+t_2	11.11, 11.23
		7 13.26					7 11.81			
	e	13.98	8 13.96	e	13.08	e	12.76	8 12.70	t_2+e'	11.89
t_2	14.55	7 14.53	t_2	14.7, 14.8,	t_2	13.49	7 13.43	t_2	13.63, 13.70,	
	8 14.55			14.9		8 13.58			13.9, 14.0	
Ge	a_1	16.60	6 16.77	a_1	18.0	a_1	16.43	6 16.71	a_1	17.6
	t_1	13.00	8 12.95	t_1	12.12 ^b	t_1	11.39	8 11.21	t_1	10.75, 10.85 ^b
		6 13.02					8 11.38			
	t_2	13.20	8 13.14	t_2	12.60, 12.75	t_2	11.58	6 11.50	t_1+t_2	11.11, 11.23
		7 13.26					7 11.81			
	e	13.98	8 13.96	e	13.08	e	12.76	8 12.70	t_2+e'	11.89
t_2	14.55	7 14.53	t_2	14.7, 14.8,	t_2	13.49	7 13.43	t_2	13.63, 13.70,	
	8 14.55			14.9		8 13.58			13.9, 14.0	
Ge	a_1	16.60	6 16.77	a_1	18.0	a_1	16.43	6 16.71	a_1	17.6
	t_1	13.00	8 12.95	t_1	12.12 ^b	t_1	11.39	8 11.21	t_1	10.75, 10.85 ^b
		6 13.02					8 11.38			
	t_2	13.20	8 13.14	t_2	12.60, 12.75	t_2	11.58	6 11.50	t_1+t_2	11.11, 11.23
		7 13.26					7 11.81			
	e	13.98	8 13.96	e	13.08	e	12.76	8 12.70	t_2+e'	11.89
t_2	14.55	7 14.53	t_2	14.7, 14.8,	t_2	13.49	7 13.43	t_2	13.63, 13.70,	
	8 14.55			14.9		8 13.58			13.9, 14.0	
Ge	a_1	16.60	6 16.77	a_1	18.0	a_1	16.43	6 16.71	a_1	17.6
	t_1	13.00	8 12.95	t_1	12.12 ^b	t_1	11.39	8 11.21	t_1	10.75, 10.85 ^b
		6 13.02					8 11.38			
	t_2	13.20	8 13.14	t_2	12.60, 12.75	t_2	11.58	6 11.50	t_1+t_2	11.11, 11.23
		7 13.26					7 11.81			
	e	13.98	8 13.96	e	13.08	e	12.76	8 12.70	t_2+e'	11.89
t_2	14.55	7 14.53	t_2	14.7, 14.8,	t_2	13.49	7 13.43	t_2	13.63, 13.70,	
	8 14.55			14.9		8 13.58			13.9, 14.0	
Ge	a_1	16.60	6 16.77	a_1	18.0	a_1	16.43	6 16.71	a_1	17.6
	t_1	13.00	8 12.95	t_1	12.12 ^b	t_1	11.39	8 11.21	t_1	10.75, 10.85 ^b
		6 13.02					8 11.38			
	t_2	13.20	8 13.14	t_2	12.60, 12.75	t_2	11.58	6 11.50	t_1+t_2	11.11, 11.23
		7 13.26					7 11.81			
	e	13.98	8 13.96	e	13.08	e	12.76	8 12.70	t_2+e'	11.89
t_2	14.55	7 14.53	t_2	14.7, 14.8,	t_2	13.49	7 13.43	t_2	13.63, 13.70,	
	8 14.55			14.9		8 13.58			13.9, 14.0	
Ge	a_1	16.60	6 16.77	a_1	18.0	a_1	16.43	6 16.71	a_1	17.6
	t_1	13.00	8 12.95	t_1	12.12 ^b	t_1	11.39	8 11.21	t_1	10.75, 10.85 ^b
		6 13.02					8 11.38			
	t_2	13.20	8 13.14	t_2	12.60, 12.75	t_2	11.58	6 11.50	t_1+t_2	11.11, 11.23
		7 13.26					7 11.81			
	e	13.98	8 13.96	e	13.08	e	12.76	8 12.70	t_2+e'	11.89
t_2	14.55	7 14.53	t_2	14.7, 14.8,	t_2	13.49	7 13.43	t_2	13.63, 13.70,	
	8 14.55			14.9		8 13.58			13.9, 14.0	
Ge	a_1	16.60	6 16.77	a_1	18.0	a_1	16.43	6 16.71	a_1	17.6
	t_1	13.00	8 12.95	t_1	12.12 ^b	t_1	11.39	8 11.21	t_1	

TABLE IV. Orbital energies of tin halides SnX_4 (in eV).

X	Orbital energy $-\epsilon$				Splitting			
	EHT	REX	Exp.	NEVE ^b	MO REX	Exp.	NEVE ^b	
Cl	t_1	13.18	8 13.12 8 13.16	t_1 12.10 ^a	8 11.04 6 11.10	t_1 0.04	-	0.06
	t_2	13.22	6 13.20 7 13.29	t_2 12.38, 12.50	8 11.12 7 11.23	t_2 0.09	-	0.12
	e	13.93	8 13.91	e 12.71	8 11.30			
	t_2	14.41	8 14.40 7 14.41	t_2 14.0	7 13.33 8 13.49	t_2 -0.01	-	0.16
	a_1	16.00	6 16.34	a_1 17.0	6 15.73			
	Br	t_1	11.62	8 11.39 8 11.49	t_1 11.00, 11.25 ^a	8 9.16 8 9.35	t_1 0.25	0.25
t_2		11.64	6 11.74 7 11.88	t_2+e 11.75	6 9.42 8 9.53	t_2 0.49	0.50	0.45
e		12.70	8 12.63	t_2 13.2	7 9.80			
t_2		13.33	7 13.28 8 13.42	a_1 16.7	7 11.75 8 12.03	t_2 0.14	0.28	0.29
a_1		15.60	6 16.06	$t_2?$ 18.2-19.7	6 14.39			
I		t_2	10.48	8 10.07 8 10.23	8 9.45 ^c 8 9.64	8 7.53 8 7.82	t_2 0.99	1.14
	t_1	10.54	6 10.86 8 10.98	6 10.10 8 10.29	6 8.09 8 8.14	t_1 0.63	0.65	0.56
	e	11.17	7 11.06	7 10.78	7 8.73			
	t_2	11.76	7 11.64 8 12.16	7 11.72 8 12.1	7 10.15 8 10.59	t_2 0.52	0.38	0.44
	a_1	14.18	6 14.76	6 16.1	6 12.52			

^a Green et al. [11].^b Hyde and Peel [18].^c Burroughs et al. [12].

The calculated and observed orbital energies of the tetramethyls are compared in Table V. We first note that, in agreement with the experimental assignments [13, 15], the PES spectrum can be divided into three bands, *A*: the M—C t_2 HOMO, *B*: a broad $\sigma(\text{C—H})$ band, and *C*: an M—C a_1 at the bottom of the spectrum. For PbMe_4 , the *A* band suffers a relativistic splitting of 0.91 eV [15] or 0.65 eV [13]. We find a somewhat smaller splitting of 0.46 eV, probably because the noniterative REX pulls off too much charge from Pb to the carbons, giving too little Pb $6p$ character to the t_2 HOMO. For SnMe_4 the splitting, predicted to be 0.13 eV, was not observed [13, 15]. For SnMe_4 the REX calculation predicts that band *C* merges into band *B*, providing a natural explanation that it was not experimentally seen in Ref. 15. In Ref. 13 the structure seen at 14.8 eV might correspond to this a_1 MO. The EHT band *C* for PbMe_4 would also merge into band *B* but the relativistic contraction of the $6s$ AO in REX again pulls it down.

The detailed structure of the *B* band was only experimentally resolved for neopentane. The present calculations disagree with the presumably more reliable

TABLE V. Calculated and observed orbital energies for the tetramethyls MMe_4 ($M = C, Si, Ge, Sn, \text{ and } Pb$). Symbols A-C for the bands are explained in the text and in Ref. 15.

M	Orbital energy $-\epsilon$ (eV)				
	REX	Exp.			
C	8	12.36	t_2	10.89, 11.39, 11.86^a	(A)
	7 (t_2)	12.37		10.96, 11.44^b	
	8	13.26	t_1	12.61, 12.88 , 13.14^a	(B)
	6 (t_1)	13.26		12.58	
	8	15.54	e	13.94, 14.29^a	
	7 (t_2)	15.54		13.91, 15.83^a	
8 (e)	15.92	t_2	15.21, 15.24^b		
	6 (a_1)	17.95	a_1	17.77 ^a , 17.68 - 18.34 ^b	(C)
Si	8	11.55	t_2	10.29, 10.62 , 10.9^a	(A)
	7 (t_2)	11.56		10.57	
	8	14.24	t_1	12.7, 12.9^a	(B)
	6 (t_1)	14.25		13.06 ^b	
	8	15.28	e	15.6 ^a	
	7 (t_2)	15.28			
8 (e)	15.51	t_2	13.8, 14.4^a		
	6 (a_1)	15.98	a_1	14.5 ^a , 15.58 ^b	(C)
Ge	8	11.61	t_2	9.89, 10.21 , 10.5^a	(A)
	7 (t_2)	11.68		10.23 ^b	
	8	14.37	t_1	13.0 ^a , 13.0^b	(B)
	6 (t_1)	14.38			
	8	15.24	e	15.8 ^a	
	7 (t_2)	15.24			
8 (e)	15.43	t_2	14.0 ^a , 13.85^b		
6 (a_1)	16.48	a_1	14.0 ^a , 15.9^b	(C)	
Sn	8	11.61	t_2	9.36, 9.65 , 9.85^a	(A)
	7 (t_2)	11.75		9.70	
	8	14.63	t_1	13.0 ^a , 13.4^b	(B)
	6 (t_1)	14.66			
	8	15.14	e	14.8 ^a	
	7 (t_2)	15.15			
8 (e)	15.24	t_2	13.8 ^a		
6 (a_1)	15.61	a_1	12.1 ^a	(C)	
Pb	8	11.45	t_2	9.10, 9.75^a	(A)
	7 (t_2)	11.91		8.81 - 9.86 ^b	
	8	14.70	t_1	12.96, 13.1^a	(B)
	6 (t_1)	14.71		13.3	
	8	15.12	e	15.0, 15.2^a	
	7 (t_2)	15.14			
8 (e)	15.20	t_2	13.7 ^a		
6 (a_1)	16.50	a_1	11.5 ^a , 15.3^b	(C)	

^a Jones et al. [13].^b Evans et al. [15].

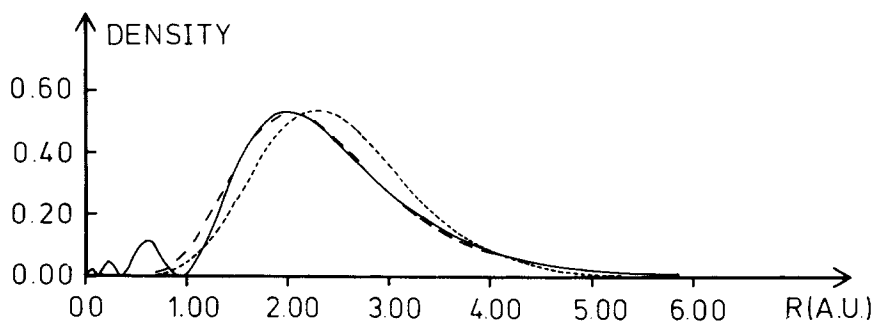
IODINE $5p^*$ ORBITAL

Figure 2. Dirac-Fock radial electron density for the $5p_{1/2}$ AO of neutral iodine (—) and a double- ζ fit to it (---). Fit to various expectation values $\langle r^n \rangle$ (see text) is also shown (-.-).

TABLE VI. Double- ζ radial functions for Cl, Br, and I.

Case	AO	c_1	ζ_1	c_2	ζ_2
Cl(n.r.)	3s	0.999682	2.25842	0.012665	2.25842
	3p	0.919820	2.05909	0.146813	0.775109
Cl(rel.)	3s	0.999697	2.26709	0.012394	2.26709
	3p*	0.919490	2.06710	0.149084	0.773385
	3p	0.918358	2.05843	0.149436	0.776501
Br(n.r.)	4s	0.984626	2.65277	0.012664	0.525888
	4p	0.836835	2.42481	0.277220	1.09979
Br(rel.)	4s	0.983296	2.70069	0.019014	0.596134
	4p*	0.840782	2.46529	0.283303	1.08780
	4p	0.831212	2.42750	0.286533	1.10022
I(n.r.)	5s	0.949378	2.72014	0.063054	1.31258
	5p	0.745168	2.54251	0.311936	1.51109
I(rel.)	5s	0.947035	2.83202	0.079050	1.27504
	5p*	0.777557	2.62109	0.293935	1.46964
	5p	0.731350	2.55534	0.331125	1.50492

CNDO/2, SCCMO, and MINDO ones in Ref. 13 by putting the t_1 , t_2 , and e levels in the order given in Table V.

4. Conclusion

The present results, both for the nonrelativistic levels and for their relativistic shifts and splittings, encourage further applications of REX on the assignment of photoelectron spectra.

Appendix: Double- ζ Functions for Cl, Br, and I

Two different ways were tried for obtaining the fit.

(1) A least-squares fit to the radial expectation values r_{\max} , $\langle r \rangle$, $\langle r^2 \rangle$, $\langle r^4 \rangle$, and $\langle r^6 \rangle$.

(2) A direct least-squares fit to the radial electron density $P^2 + Q^2$ at the tabulation points of an average-of-configuration Dirac-Fock calculation on the neutral halogen atom.

As seen from Figure 2 for the $5p_{1/2}$ AO of iodine, method 2 gives a better fit to the original density, in addition to being more stable numerically, both for Cl, Br, and I. Therefore it was chosen for the final parameters given in Table VI.

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Received February 7, 1980