Relativistic effects in physics and chemistry of element 105. IV. Their influence on the electronic structure and related properties

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Results of relativistic (Dirac–Slater and Dirac–Fock) and nonrelativistic (Hartree–Fock–Slater) atomic and molecular calculations have been compared for the group 5 elements Nb, Ta, and Ha and their compounds MCl_5 to elucidate the influence of relativistic effects on their properties especially in going from the $5d$ element Ta to the $6d$ element Ha. The analysis of the radial distribution of the valence electrons of the metals for electronic configurations obtained as a result of the molecular calculations and their overlap with ligands show opposite trends in behavior for $ns_{1/2}$, $np_{1/2}$, and $(n-1)d_{5/2}$ orbitals for Ta and Ha in the relativistic and nonrelativistic cases. Relativistic contraction and energetic stabilization of the $ns_{1/2}$ and $np_{1/2}$ wave functions and expansion and destabilization of the $(n-1)d_{5/2}$ orbitals make hahnium pentahalide more covalent than tantalum pentahalide and increase the bond strength. The nonrelativistic treatment of the wave functions results in an increase in ionicity of the MCl_5 molecules in going from Nb to Ha making element Ha an analog of V. Different trends for the relativistic and nonrelativistic cases are also found for ionization potentials, electronic affinities, and energies of charge-transfer transitions as well as the stability of the maximum oxidation state.

I. INTRODUCTION

The influence of relativistic effects on the electronic structure of elements within the Periodic Table and on their chemical properties has been discussed in quite a number of publications. Original works were based on atomic Dirac–Slater (DS),[1] Dirac–Fock (DF),[2] and on molecular calculations within different approximations.[3,4] There are several reviews[5] trying to comprehend this extensive area and a large bibliography.[6]

In these publications along with general trends in the Periodic Table (e.g., similarity between the $4d$ and $5d$ elements and difference in their electronic configurations), some peculiarities in properties and anomalous behavior (e.g., extrastability of the Hg^{2+} ion, the yellow color, and nobility of gold, and some other interesting phenomena) have been explained as a result of relativistic effects. The role of relativistic effects in the *trans*-actinide compounds on the basis of molecular calculations have been, however, analyzed in very few publications. In Refs. 5(f) and 7 model systems, hydrides of elements 104 and 106 have been investigated using the one-center expansion DF method. Some publications are devoted to the properties of the superheavy elements.[8]

In a strict treatment, relativistic Hamiltonians should be already used in the case of H_2^+ and H_2, but the effects are very small. For the heavier elements, the importance of relativistic effects becomes more pronounced since the relativistic energy contributions increase proportionally to Z^2. An essential difference in properties in the relativistic and nonrelativistic treatments is already seen in the cases of Ag and Au.

Since we have been interested in the physicochemical properties of heavy systems such as halides and oxyhalides of elements 104 and 105 (Refs. 9 and 10), we wanted to learn to which extent the properties of these compounds depend on the relativistic effects, or to which extent the relativistic treatment is a necessity.

The importance of relativistic effects in the chemistry of heavy systems has been already determined in early investigations[1] based on atomic DS calculations. As mentioned above, the results of the DF one-center expansion molecular calculations[7] of 104 H_4 vs analogs ZrH_4 and HfH_4, and $106H_6$ vs analogs MoH_6 and WH_6 were used to analyze the influence of relativistic effects on the bond distances and the bond strengths. In this investigation, equal bond lengths for $4d$ and $5d$ compounds were explained as a consequence of the relativistic bond contraction for the $6d$ elements. The bond lengths in the hydrides of elements 104 and 106 were found to be 0.03 and 0.06 Å larger in comparison with Hf and W, respectively. The hydride of element 104 was shown to have a weaker bond in comparison with HfH_4, while $106H_6$ should have a stronger bond in comparison with WH_6.

In the present work, we will analyze the influence of relativistic effects on the physicochemical properties of the pentachlorides (real compounds) MCl_5 of elements Nb, Ta, and Ha to see where the inclusion of relativistic effects is necessary and how they modify the properties of the related *trans*-actinide compounds. With this aim in mind, we have performed in addition to our previous molecular DS calculations[10(a)] a series of nonrelativistic ones for the MCl_5 molecules. A number of DS calculations of atoms and ions with electronic configurations obtained from the corresponding molecular calculations have also been performed to simulate the behavior of the wave functions in the molecules (and/or to give a pictorial representation for the better understanding of the process of involvement of these orbitals in bonding).

Thus in Sec. II the behavior of the valence orbitals in neutral Nb, Ta, and Ha is analyzed in relativistic and nonrelativistic cases. Section III contains some remarks

about the DS method. In Sec. IV, some physicochemical properties of MCl_5 are discussed as a comparison of relativistic and nonrelativistic results of the molecular calculations. A resume is given in Sec. V.

II. INFLUENCE OF THE RELATIVISTIC EFFECTS ON ATOMIC CHARACTERISTICS OF Nb, Ta, AND Ha

A. Atomic wave functions

The influence of the relativistic effects on electronic shells is threefold: (1) a relativistic radial contraction of the s and $p_{1/2}$ shells and their energetic stabilization; (2) the well-known spin–orbit splitting; (3) a secondary relativistic effect—the radial expansion and energetic destabilization of the d and f shells. All the three effects increase proportionally to Z^2.

Since the relativistic Bohr radius of the $1s$ electron is related to the nonrelativistic one as

$$a_0^{rel}/a_0^{nr} = m_0/m \qquad (1)$$

with

$$m_0/m = \sqrt{1 - v/c}, \qquad (2)$$

where $v/c = Z\alpha$ and $\alpha = 1/137$ (m_0 is the rest mass and v is the speed of the electron), the relativistic contractions for the $1s$ orbital of Nb, Ta, and Ha will be 16%, 32%, and 52%, respectively. The outer ns orbitals will experience a similar contraction due to their orthogonality to the inner ones. Figure 1 presents the radial distribution of the valence ns orbitals of Nb, Ta, and Ha for electronic configurations d^4s, d^3s^2, and d^3s^2, respectively. According to the present DS results, the relativistic shifts of the main maximum are 3%, 9.11%, and 20.5%. The DF calculations[11] give 3.72% and 10.02% for Nb and Ta, respectively. The ratios between relativistic and nonrelativistic DS values of the main maximum of the radial density (R_{max}) for outer valence orbitals are given in Table I. For comparison, we give the values from the DF calculations[11] for Nb and Ta, respectively—0.9627 and 0.8998 for $5s$ and $6s$, 1.0061 and 1.0052 for $4d_{3/2}$ and $5d_{3/2}$, and 1.0167 and 1.0389 for $4d_{5/2}$ and $5d_{5/2}$ orbitals. From Table I, one can see that the relativistic contraction of the ns orbitals of Ha relative to Ta is 50% more than that of Ta relative to Nb.

It is interesting to note here that the nonrelativistic R_{max} of $(6s)$Ta is smaller than R_{max} of $(5s)$Nb, which is obviously a result of the lanthanoid contraction. In Ref. 7, however, the nonrelativistic radial ns functions in MH_6 molecules for Mo and W show the other relation $R_{max}(Mo) < R_{max}(W)$ and relativistic effects shift the main maximum of W close to that of Mo. According to our calculations, this is not the case for Nb and Ta. On the contrary, relativistic effects enlarge this difference (see Fig. 1). The nonrelativistic R_{max} of $7s$(Ha) is larger than R_{max} of $6s$(Ta) due to the orbital effect (expansion), while relativistic contraction moves its maximum much closer to the core, making the difference $R_{max}(6s) - R_{max}(7s)$ negative. So one can clearly see that the orbital and relativistic effects act in opposite directions, which is especially pro-
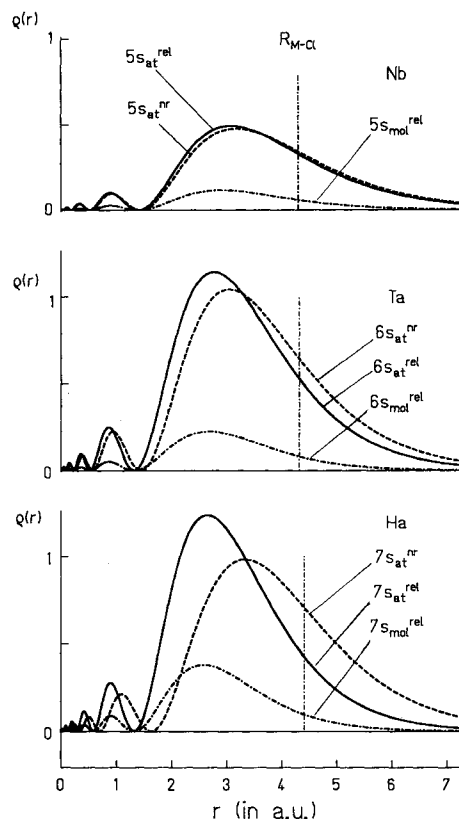

FIG. 1. Radial distribution of the ns electrons in Nb, Ta, and Ha as a result of the atomic (at) DS relativistic (full line) and nonrelativistic (dashed line) calculations. The dashed–dotted lines (mol) are relativistic calculations of the metal ions for the electronic configurations obtained in the calculations of MCl_5. $R_{max}^{nr}(Ta) - R_{max}^{nr}(Nb) = -0.1241$ (at) and -0.0486 (mol); $R_{max}^{rel}(Ta) - R_{max}^{rel}(Nb) = -0.3067$ (at) and -0.2208 (mol); $R_{max}^{nr}(Ha) - R_{max}^{nr}(Ta) = 0.2867$ (at) and 0.2645 (mol); $R_{max}^{rel}(Ha) - R_{max}^{rel}(Ta) = -0.1207$ (at) and -0.1021 (mol). The vertical line gives the bond distance.

nounced in the case of the $6d$ elements (Ha). As a result, the nonrelativistic treatment of the $7s$ function of Ha would result in a reverse trend in the bonding caused by involvement of the ns orbitals along the group 5 in comparison with the relativistic case.

The valence $np_{1/2}$ orbital contraction is also more pronounced in going from Ta to Ha than in going from Nb to Ta. The ratio of the relativistic to the nonrelativistic values of R_{max} for $p_{3/2}$ orbitals is nearly equal to unity for all the

TABLE I. Ratio of the relativistic (DS) to the nonrelativistic (HFS) R_{max} and eigenvalues (E) for valence electrons of Nb, Ta, and Ha.

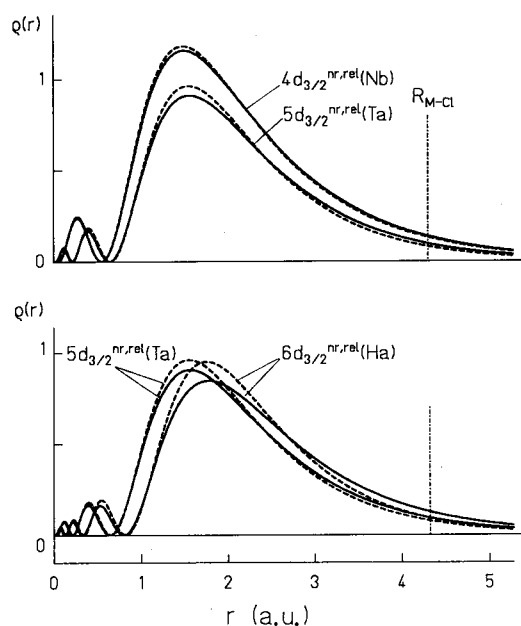| Atom	ns	$np_{1/2}$	$np_{3/2}$	$(n-1)d_{3/2}$	$(n-1)d_{5/2}$
		$R_{max}^{rel}/R_{max}^{nr}$			
Nb(d^4s)	0.9702	0.9660	0.9989	1.0080	1.0186
Ta(d^3s^2)	0.9089	0.9080	1.0191	1.0081	1.0453
Ha(d^3s^2)	0.7945	0.7870	1.0596	1.0127	1.0962
		E^{rel}/E^{nr}			
Nb(d^4s)	1.0715	1.0879	0.9695	0.9341	0.8762
Ta(d^3s^2)	1.1833	1.1458	0.7521	0.7543	0.6164
Ha(d^3s^2)	1.5245	1.4612	0.4480	0.5514	0.3264

FIG. 2. Radial distribution of the $(n-1)d_{3/2}$ electrons in atoms $Nb(d^4s)$, $Ta(d^3s^2)$, and $Ha(d^3s^2)$. Full lines are relativistic and dashed lines are nonrelativistic calculations. For the $(n-1)d_{3/2}$ functions, $R^{nr}_{max}(Ta) - R^{nr}_{max}(Nb) = 0.0665$ (at) and 0.0857 (mol), $R^{rel}_{max}(Ta) - R^{rel}_{max}(Nb) = 0.0661$ (at) and 0.0791 (mol); $R^{nr}_{max}(Ha) - R^{nr}_{max}(Ta) = 0.2045$ (at) and 0.2040 (mol), $R^{rel}_{max}(Ha) - R^{rel}_{max}(Ta) = 0.2142$ (at) and 0.1977 (mol).
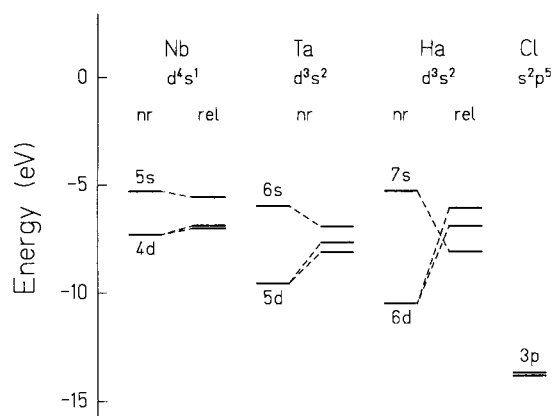

FIG. 3. Binding energies of Nb, Ta, and Ha as a result of the DF relativistic and HF nonrelativistic calculations (Ref. 11). The nonrelativistic energies for Ha are obtained from the relativistic data (Ref. 11) taking into account the $R^{rel}_{max}/R^{nr}_{max}$ from present DS results.

group 5 elements. (In our DS calculations of R_{max} of the $p_{3/2}$ orbitals of the metals for electronic configurations of a neutral state, this ratio is slightly larger than unity since these orbitals are not occupied. For the real electronic configuration with occupied $np_{3/2}$ orbitals, this ratio is less than unity, which will be shown later.) The ratio $R^{rel}_{max}/R^{nr}_{max}$ for the occupied $d_{3/2}$ orbitals is nearly the same for Nb and Ta. In Fig. 2, one can see the equal positions of R_{max} of the nonrelativistic and relativistic $d_{3/2}$ functions for Nb and Ta. There is no difference between radial distributions of the $4d_{3/2}$ electrons of Nb and $5d_{3/2}$ electrons of Ta due to the shell-structure effect (lanthanoid contraction). In the lower part of the graph, one can see that the difference between the $5d_{3/2}$ functions of Ta and the $6d_{3/2}$ functions of Ha is also nearly fully the shell-structure effect. The $(n-1)d_{5/2}$ electrons, on the contrary, show the increasing expansion due to the relativistic effect with increasing Z in the group, even if it is not so large in going from Nb to Ta (see Table I). For them, relativistic and orbital effects act in the same direction increasing the difference between the elements. The relativistic expansion of the $d_{5/2}$ wave function in going from Nb to Ha will make them more available for chemical bonding in Ha compounds.

The spin–orbit splitting of $(n-1)d$ orbitals increases for Nb, Ta, and Ha from 0.14 to 0.48 and to 0.80 eV, and for p orbitals from 0.16 to 0.68 and to 1.74 eV, respectively. This finally decreases the energy transitions between electronic configuration and facilitates the stability of the maximum oxidation state in this direction.

The relativistic stabilization of the ns and destabilization of $(n-1)d$ electron energies is demonstrated in Fig. 3, showing the binding energies in the nonrelativistic (HF) and relativistic (DF) approximations. In Table I, the ratios of the relativistic (DS) to the nonrelativistic (HF) eigenvalues are presented. For comparison, the DF values[11] for Nb and Ta are 1.0541 and 1.1560 eV for ns orbitals, 0.9622 and 0.8488 eV for $(n-1)d_{3/2}$, and 0.9426 and 0.7985 eV for $(n-1)d_{5/2}$ ones, respectively.

The values in Table I and Fig. 3 show a drastic increase (more negative) in energy for the relativistic $7s$ orbital of Ha in comparison with the nonrelativistic value. The $7p_{1/2}$ orbitals are stabilized nearly to the same degree. The energies of the (unoccupied) $np_{3/2}$ orbitals are about the same in the relativistic and nonrelativistic cases. Both $d_{3/2}$ and $d_{5/2}$ electrons show increasing destabilization from Nb to Ha. Thus, the analysis of the atomic functions shows that the properties of Nb and Ta should be close in both relativistic and nonrelativistic schemes, while Ha should behave differently due to relativistic effects, but to the opposite direction than in the nonrelativistic case.

B. Atomic properties

The relativistic change of the electron functions results in the change in the atomic properties, such as electronic configurations, ionization potentials (I.P.s), electron affinities (E.A.s), energies of electron transitions, etc.

1. Electronic configurations

The influence of relativistic effects on the electronic configurations is seen in the stabilization of the s^2 pair in Ta having the electronic configuration d^3s^2 in comparison with Nb having the d^4s^1 one. Further relativistic stabilization of the s orbitals with increasing Z makes the d^3s^2 configuration of Ha more stable. The relativistic stabilization of the $p_{1/2}$ orbital with increasing Z, resulting for Lr and element 104 in the ground state electronic configurations $7s^27p_{1/2}$ and $7s^27p_{1/2}6d$, respectively, is dominated for element 105 by the shell-structure stabilization of the $6d$ orbitals. The pronounced relativistic stabilization of the $7s$

TABLE II. Some ionization potentials for Nb, Ta, and Ha.[a]

Element	Transition	Calc. (eV)[b]	Exp. (eV)[c]
Nb→Nb$^+$	d^4s→d^4	$\cdots$	6.77
Ta→Ta$^+$	d^3s^2→d^3s	6.82	7.89
Ha→Ha$^+$	d^3s^2→d^2s^2	6.10	(6.89)
Nb$^+$→Nb^{2+}	d^4→d^3	13.09	14.32
Ta$^+$→Ta^{2+}	d^3s→d^3	14.11	(15.40)
Ha$^+$→Ha^{2+}	d^2s^2→d^3	14.82	(16.03)
Nb^{2+}→Nb^{3+}	d^3→d^2	24.20	(25.04)
Ta^{2+}→Ta^{3+}	d^3→d^2	23.06	(23.84)
Ha^{2+}→Ha^{3+}	d^3→d^2	23.77	(24.65)
Nb→Nb^{5+}	d^4s→(core)	$\cdots$	135.05
Ta→Ta^{5+}	d^3s^2→(core)	126.14	(132.03)
Ha→Ha^{5+}	d^3s^2→(core)	121.00	(126.38)

[a]Values in brackets are normalized and extrapolated to the experimental ones.
[b]Reference 12.
[c]Reference 13.

orbital of Ha (a s^2 pair) is particularly seen for the $+1$ ionized state with d^4, d^3s, and d^2s^2 configurations for Nb$^+$, Ta$^+$, and Ha$^+$, respectively.[12]

It is interesting to note here that the difference between the elements will be more pronounced for the lower oxidation states, where relativistic effects make the electronic configurations different. This is the case of MCl$_5$ molecules having effective charges $\simeq +1$ [see Ref. 10(a)]. For the higher oxidation states (M^{2+} and higher), all the elements have the same electronic configurations.

The relativistic stabilization of the $7p_{1/2}$ orbital in Ha is more pronounced for the first excited-state electronic configuration. Thus, the first excited-state electronic configurations of Nb and Ta are d^3s^2 and d^4s, respectively,[13] while for Ha, the MCDF calculations[14] give $\Delta E(d^3sp - d^3s^2) = 1.9(\pm0.4)$ eV and $\Delta E(d^4s - d^3s^2) = 2.0(\pm0.4)$ V. The availability of the $7p_{1/2}$ state in the first excited-state electronic configuration of Ha would increase, e.g., ΔH_{subl} of metal.[14]

2. Ionization potentials

In Table II, the excitation process is shown for the $(0) \rightarrow (+5)$ ionization and corresponding I.P.s are taken from Ref. 12. In calculating the I.P., initial and final states for an excitation should be taken into consideration. Since relativistic effects in Ha destabilize 6d atomic orbitals (AOs) and split them by the spin–orbit interaction, the first I.P. of Ha is lower than that of Ta. In comparison with the nonrelativistic values, the potentials (III, IV, and V) are also decreased. The decrease of the $(0) - (+5)$ I.P.s through the destabilization of the d shells and their increased spin–orbit splitting makes it easier for Ha to reach the $+5$ oxidation state (see Table II).

The expected stability of the $+3$ oxidation state of Ha due to the stability of the "inert" $7s^2$ pair is not pronounced in Ha due to the relatively small energy gap between the 7s and 6d levels. (The energy difference between 7s and 6$d_{3/2}$ levels is of the order of the $6d_{3/2}$–$6d_{5/2}$ separation). The MCDF calculations[12] show no decrease in the $(0) - (3+)$ I.P.s in going from Nb to Ha. The estimates of

the redox potentials[10(d)] $E^0(\text{IV})/E^0(\text{III})$ and $E^0(\text{III})/E^0(0)$ show the following change in the stability of the three-valent state in the group: V > Nb > Ta > Ha. The situation might be of course more complex if the local geometry and type of compound are taken into consideration.

3. Atomic/ionic radii

It has been shown[5(f),7] that relativistic effects make the bond lengths in ZrH$_4$ and HfH$_4$, MoH$_6$ and WH$_6$, and, correspondingly, the covalent ionic radii of Zr and Hf, and Mo and W equal. The relativistic shrinkage of the radii is $\sim 3\%$ in the 5d elements bringing them to the size of the 4d ones.

The relativistic contraction of the bond length can be expressed as

$$C(\%) = c_Z Z^2, \tag{3}$$

where c_Z depends on the group. For the hydrides,[7] the following equation holds

$$c_Z = [10(3)] \times 10^{-4}. \tag{4}$$

Using this expression and taking into account the dependence on the group [see Fig. 3 in Ref. 5(f)], we assumed $c_Z \simeq 6 \times 10^{-4}$ for group 5, resulting in a contraction of 1.0%, 3.0%, and 6.5% for Nb, Ta, and Ha, respectively.

MCDF calculations[12] of the ionic radii (extrapolated and normalized to the experimental values) give the values of 0.64, 0.64, and 0.74 Å for the $+5$ state of Nb, Ta, and Ha, respectively. Thus, if Ta has the same ionic radius as Nb due to the relativistic bond contraction (similar to those of Zr/Hf and Mo/W), the shell-structure expansion of the outer 6p orbitals (the outer orbitals for the $+5$ ionized state) of Ha is not dominated by the relativistic contraction, so that the ionic radius of Ha is larger than those of Nb and Ta. The nonrelativistic value would be 0.79 Å according to Eq. (3).

III. THE DIRAC–SLATER DISCRETE VARIATIONAL METHOD (DS-DVM)

The advantage of the presently used[10(a)] DS-DV method is the possibility to do both relativistic and nonrelativistic calculations within the same scheme just setting in the latter case $c = \infty$ in all Dirac–Slater equations.

Having the numerical accuracy of a fraction of an electron volt for one-electron or total energies, this method offers the possibility of a quantitative comparison of relativistic with nonrelativistic values—energy levels, I.P.s, E.A.s, ionization energies (photoelectron spectra), electronic transition energies, charge-density distribution, and bonding. All these electronic-structure characteristics will be analyzed in the next section in terms of the relativistic/ nonrelativistic comparison for the pentahalides MCl$_5$ (M =Nb, Ta, and Ha) as good representatives of the group 5 element compounds.

TABLE III. Input bond lengths for relativistic and nonrelativistic calculations of MCl$_5$.

	Case	Nb	Ta	Ha
$R_{M-Cl_{ax}}$ (Å)	exp	2.338	2.369	2.42[a]
$R_{M-Cl_{eq}}$ (Å)	(rel)	2.241	2.227	2.28[a]
$R_{M-Cl_{ax}}$ (Å)	est	2.362	2.447	2.59
$R_{M-Cl_{eq}}$ (Å)	(nr)	2.264	2.300	2.44

[a]Estimated values.

IV. MOLECULAR PROPERTIES

A. Bond contraction

Since the application of the DS DV method precludes calculations of the potential energy curves, we have estimated the nonrelativistic bond distances which are larger than the relativistic (experimental) ones knowing the latter values for NbCl$_5$ and TaCl$_5$ and using Eq. (3) with $c_z \simeq 6 \times 10^{-4}$. Relativistic and nonrelativistic distances used in the calculations are given in Table III. Thus, we have performed the calculations for three cases: (1) relativistic calculations for experimental (relativistic) bond lengths; (2) nonrelativistic calculations for the experimental bond lengths; and (3) nonrelativistic calculations for the estimated nonrelativistic bond lengths. These three sets of the data obtained will be analyzed in the following chapters.

B. Orbital energies

The energy levels shown in Figs. 4(a) and 4(b) reflect all the relativistic effects—the stabilization and contraction of the ns and $np_{1/2}$ orbitals (increasing in the direction to Ha) destabilization and expansion of the $(n-1)d$ orbitals, and their spin–orbit splitting.

From Fig. 4(a), one can see that the relativistic treatment of the wave functions drastically decreases the energy of the highest unoccupied MO of an $[(n-1)d+ns]$-character in HaCl$_5$, for which the $7s$ contribution is large. This will result in different trends for the energies of the highest electronic d–d transitions, so that in the nonrelativistic case, the energies would be $E(\text{Nb}) < E(\text{Ta}) < E(\text{Ha})$, while in the relativistic case, $E(\text{Nb}) < E(\text{Ta}) > E(\text{Ha})$.

In the nonrelativistic case [Fig. 4(b)], the trends in the group for the energies of the highest occupied MOs (HOMO) and lowest unoccupied MOs (LUMO) are changed in comparison with the relativistic MOs. This results in the lower values of the energy gap (ΔE) between occupied and unoccupied levels (see Table IV), leading to the diminishing (for the molecules with nonrelativistic distances) the charge-transfer electronic transitions in HaCl$_5$ compared to TaCl$_5$ and even to NbCl$_5$. This would finally decrease the stability of the HaCl$_5$ system.

In all the molecules under consideration, relativistic effects increase ΔE (Table IV). This increase of the ΔE enhances finally the stability of the systems, which is much more pronounced for HaCl$_5$. The difference $\Delta E(\text{Ta}) > \Delta E(\text{Nb})$ can be seen already in the nonrelativistic case, while the relativistic effects increase this difference even
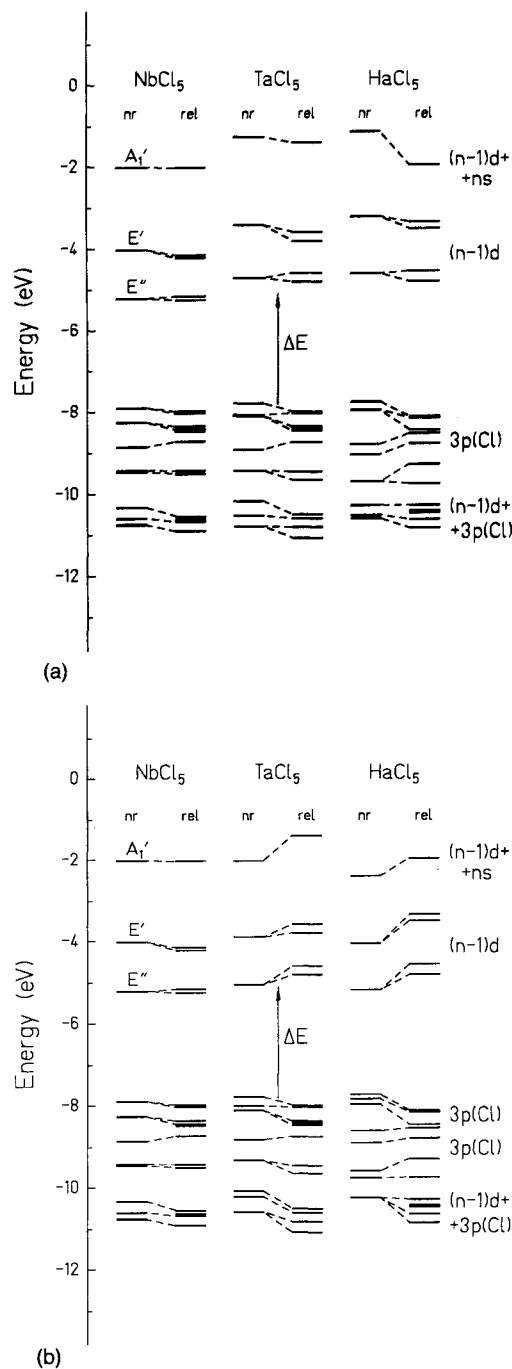

(a)

(b)

FIG. 4. Energy level diagrams for NbCl$_5$, TaCl$_5$, and HaCl$_5$ (a) as a result of the nonrelativistic (nr) and relativistic (rel) calculations both with experimental bond lengths; (b) as a result of the nonrelativistic (nr) calculations with nonrelativistic bond lengths and of the relativistic (rel) calculations with experimental bond lengths.

more. The nonrelativistic ΔE for Ta and Ha are similar [Fig. 4(a)] or $\Delta E(\text{Ha}) < \Delta E(\text{Ta})$ [Fig. 4(b)], so that the increase in ΔE of the Ha compound is a purely relativistic effect.

Relativistic effects generally increase I.P.s (Table IV), particularly for the Ha compound. Without relativity, E.A. of HaCl$_5$ would be higher than that of Nb and Ta pentachlorides.

The spin–orbital splitting increases in the direction Nb→Ta→Ha (see Fig. 4).

TABLE IV. Orbital energies (E), energy gaps (ΔE), energies of the lowest charge-transfer transitions $(E_{\pi-d})$, ionization potentials (I.P.s), and electron affinities (E.A.s) for MCl$_5$ as a result of relativistic and nonrelativistic calculations.[a]

Parameter	NbCl$_5$	TaCl$_5$	HaCl$_5$
HOMO[b]			
$E^{nr}(1)$	7.91	7.78	7.75
$E^{nr}(2)$	7.90	7.76	7.72
E^{rel}	7.93	7.90	8.04
LUMO[b]			
$E^{nr}(1)$	5.21	4.71	4.50
$E^{nr}(2)$	5.31	5.03	5.17
E^{rel}	5.23	4.78	4.60
$\Delta E^{nr}(1)$	2.69	3.08	3.15
$\Delta E^{nr}(2)$	2.60	2.73	2.55
ΔE^{rel}	2.70	3.10	3.36
$E^{nr}_{\pi-d}(1)$	2.98	3.43	3.48
$E^{nr}_{\pi-d}(2)$	2.89	3.11	2.83
$E^{rel}_{\pi-d}$	2.98	3.41	3.70
I.P.$^{nr}(1)$	10.75	10.62	10.54
I.P.$^{nr}(2)$	10.75	10.60	10.50
I.P.^{rel}	10.77	10.73	10.83
E.A.$^{nr}(1)$	2.02	1.48	1.39
E.A.$^{nr}(2)$	2.12	1.78	2.06
E.A.^{rel}	2.04	1.53	1.49

[a]Nonrelativistic results are shown for two cases (1) with experimental bond lengths; (2) for the estimated nonrelativistic bond lengths.
[b]HOMO—highest occupied MO; LUMO—lowest unoccupied MO.

TABLE V. Effective charges on atoms (Q_M) and atomic orbital populations (q_l) for MCl$_5$ as a result of relativistic and nonrelativistic calculations.[a]

Molecule	$R_{M-Cl_{ax}}$ (Å) / $R_{M-Cl_{eq}}$ (Å)	Q_M	q_s	q_p	q_d
NbCl$_5^{nr}$(1)	2.338 / 2.241	0.97	0.16	0.21	3.67
TaCl$_5^{nr}$(1)	2.369 / 2.227	1.12	0.19	0.30	3.39
HaCl$_5^{nr}$(1)	2.42 / 2.28	1.19	0.14	0.25	3.43
NbCl$_5^{nr}$(2)	2.362 / 2.264	0.96	0.17	0.22	3.65
TaCl$_5^{nr}$(2)	2.447 / 2.300	1.08	0.24	0.33	3.35
HaCl$_5^{nr}$(2)	2.59 / 2.44	1.13	0.20	0.29	3.38
NbCl$_5^{rel}$	2.338 / 2.241	0.93	0.20	0.22	3.65
TaCl$_5^{rel}$	2.369 / 2.227	0.95	0.35	0.33	3.37
HaCl$_5^{rel}$	2.42 / 2.28	0.81	0.55	0.33	3.32

[a]The first set (1) of the nonrelativistic data is for the molecules with experimental bond lengths; the second set (2) is for the estimated nonrelativistic distances.

C. Electron configurations and charge distribution

The charge-density distribution is different in the relativistic and nonrelativistic cases due to the electron reorganization at a given interatomic distance and due to the relativistic change of it. In Table V, effective atomic charges and occupancies of the valence orbitals are given for the three cases under consideration. The most striking difference between the relativistic and nonrelativistic results is the trend of the effective charges within the group. Without relativity, the value of Q_M increases down the group, which means an increase in ionicity in this direction. Relativistic effects cancel the difference in Q_M between Ta and Nb making their values nearly equal, and further down in Ha, they diminish drastically the effective charge making Ha halide highly covalent in comparison with the preceding analogs.

A drastic decrease in Q_M for Ha compared to the analogs comes at the expense of a large relativistic stabilization (and contraction) of the 7s and $7p_{1/2}$ orbitals, as one can see from Table VI. In going from Nb to Ta, the populations of these two orbitals increase for both relativistic and nonrelativistic calculations, while in going from Ta to Ha, these populations decrease for the nonrelativistic case and increase for the relativistic one. The populations of the nonrelativistic and relativistic $np_{3/2}$ orbitals behave similarly along the group. What concerns d orbitals is the basic difference in the behavior of the $(n-1)d_{5/2}$ ones, where in the relativistic case, $q_{d_{5/2}}$ decreases down the group, while

in the nonrelativistic case, this value increases from Ta to Ha. Finally, the trends are different for total d orbital populations in the group (Table V).

Thus, if the nonrelativistic results show the right trend in the properties in going from Nb to Ta, and relativity gives only quantitatively correct values, the nonrelativistic treatment of the systems would result in completely different qualitative trends in going from Ta to Ha.

TABLE VI. Atomic spin–orbit populations (q_j) for MCl$_5$ as a result of relativistic and nonrelativistic calculations.[a]

Molecule	$R_{M-Cl_{ax}}$ (Å) / $R_{M-Cl_{eq}}$ (Å)	$q_{s_{1/2}}$	$q_{p_{1/2}}$	$q_{p_{3/2}}$	$q_{d_{3/2}}$	$q_{d_{5/2}}$
NbCl$_5^{nr}$(1)	2.338 / 2.241	0.16	0.07	0.14	1.47	2.20
TaCl$_5^{nr}$(1)	2.369 / 2.227	0.19	0.10	0.20	1.36	2.04
HaCl$_5^{nr}$(1)	2.42 / 2.28	0.14	0.08	0.17	1.37	2.06
NbCl$_5^{nr}$(2)	2.362 / 2.264	0.17	0.07	0.15	1.46	2.19
TaCl$_5^{nr}$(2)	2.447 / 2.300	0.24	0.11	0.22	1.34	2.01
HaCl$_5^{nr}$(2)	2.59 / 2.44	0.20	0.10	0.19	1.35	2.02
NbCl$_5^{rel}$	2.338 / 2.241	0.20	0.08	0.14	1.51	2.14
TaCl$_5^{rel}$	2.369 / 2.227	0.35	0.15	0.18	1.45	1.92
HaCl$_5^{rel}$	2.42 / 2.28	0.55	0.22	0.11	1.54	1.78

[a]The first set (1) of the nonrelativistic data is for the molecules with experimental bond lengths; the second set (2) is for the estimated nonrelativistic distances.
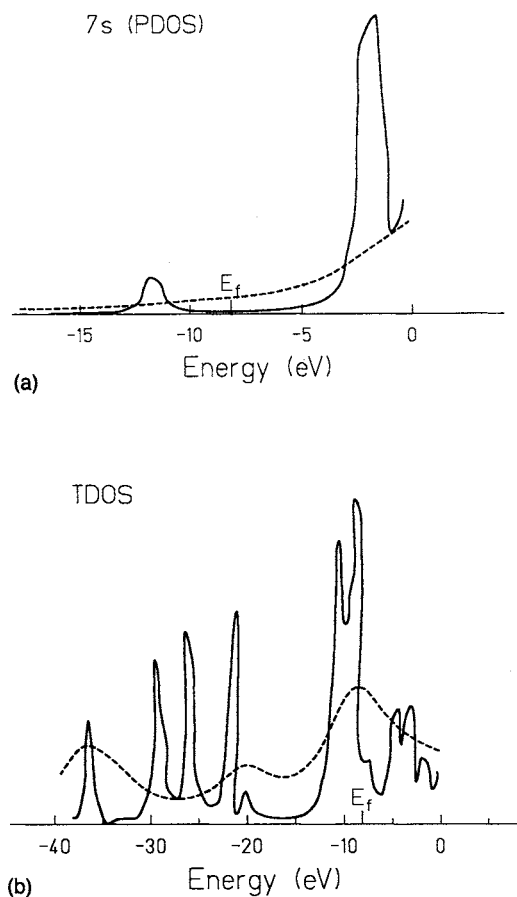
7s (PDOS)

E_f

−15   −10   −5   0

(a)   Energy (eV)

TDOS

E_f

−40   −30   −20   −10   0

(b)   Energy (eV)

FIG. 5. (a) Partial $(7s)$ and (b) total densities of states (TDOS) in HaCl$_5$ from the relativistic (full line) and nonrelativistic (dashed line) calculations.

D. Bonding

The contribution of the atomic orbitals (AOs) into molecular orbitals (MOs) also changes along the group in a different way for the relativistic and nonrelativistic calculations. (In the former case, the contribution of ns and $np_{1/2}$ AOs increases, while in the latter case, it decreases from Ta to Ha.) The redistribution of atomic $7s$ character over the binding energy spectra of HaCl$_5$ from relativistic and nonrelativistic calculations is seen from the partial density of states (PDOS) shown in Fig. 5(a). The total DOS [Fig. 5(b)] shows bonding components of all the valence orbitals resulting from covalent mixing of metal orbitals with $3p$(Cl) ones for the relativistic and nonrelativistic cases. In the relativistic case, the density of states has a more pronounced structure with higher density. Besides, the structures are shifted to higher binding energies.

To elucidate the process of involvement of the valence orbitals in bonding, we have performed DS and HFS calculations of the metal ions for electronic configuration, obtained as a result of the corresponding molecular ones. Figure 1 shows the radial charge density of the ns functions in the molecules. The difference in R_{max} between $5s$(Nb) and $6s$(Ta) becomes smaller in the molecules than in the free atoms, while the differences in R_{max} between $6s$(Ta) and $7s$(Ha) are nearly the same in the atoms and in the molecules. Relativity shifts the $np_{1/2}$ and $np_{3/2}$ functions of Ta closer to those of Nb and functions of Ha closer to those of Ta (Figs. 6 and 7). Relativity is responsible for the difference in the radial distribution of the $d_{5/2}$ functions between Ta and Ha (Fig. 8).

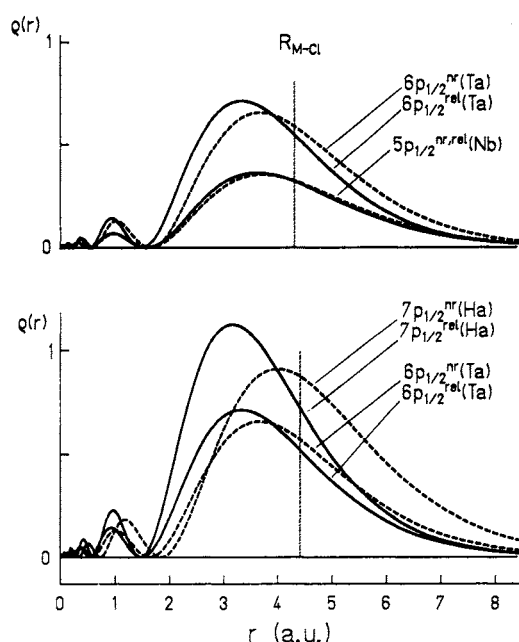The ratios of the relativistic to the nonrelativistic val-

$\varrho(r)$

R_{M-Cl}

$6p_{1/2}$^{nr}(Ta)
$6p_{1/2}$^{rel}(Ta)
$5p_{1/2}$^{nr,rel}(Nb)

$\varrho(r)$

$7p_{1/2}$^{nr}(Ha)
$7p_{1/2}$^{rel}(Ha)
$6p_{1/2}$^{nr}(Ta)
$6p_{1/2}$^{rel}(Ta)

0   1   2   3   4   5   6   7   8
r (a.u.)

FIG. 6. The radial density of the relativistic (full lines) and nonrelativistic (dashed lines) $np_{1/2}$ electrons in the molecules MCl$_5$ (mol). R_{max}^{nr}(Ta) − R_{max}^{nr}(Nb) = −0.3392 (at) and −0.0441 (mol), R_{max}^{rel}(Ta) − R_{max}^{rel}(Nb) = −0.5639 (at) and −0.2806 (mol), R_{max}^{nr}(Ha) − R_{max}^{nr}(Ta) = 0.3007 (at) and 0.3394 (mol), and R_{max}^{rel}(Ha) − R_{max}^{rel}(Ta) = −0.2563 (at) and −0.1630 (mol). The vertical line gives the bond length.

$\varrho(r)$

R_{M-Cl}

$6p_{3/2}$^{nr}(Ta)
$6p_{3/2}$^{rel}(Ta)
$5p_{3/2}$^{nr,rel}(Nb)

$\varrho(r)$

$6p_{3/2}$^{nr}(Ta)
$6p_{3/2}$^{rel}(Ta)
$7p_{3/2}$^{nr}(Ha)
$7p_{3/2}$^{rel}(Ha)

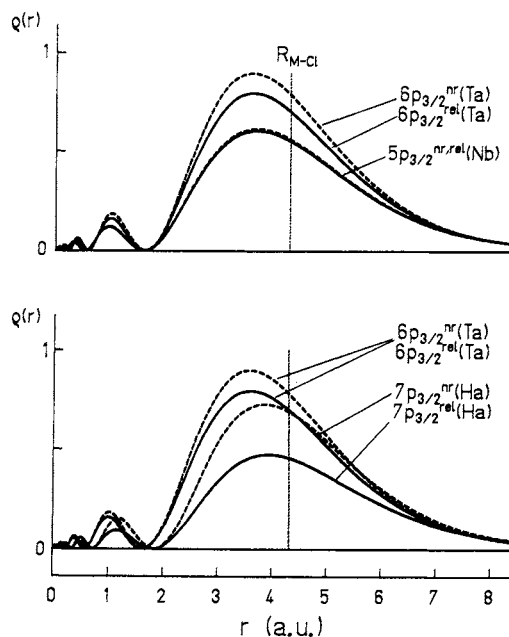0   1   2   3   4   5   6   7   8
r (a.u.)

FIG. 7. The radial distribution of the relativistic (full lines) and nonrelativistic (dashed lines) $np_{3/2}$ electrons in the molecules MCl$_5$ (mol). R_{max}^{nr}(Ta) − R_{max}^{nr}(Nb) = −0.3392 (at) and −0.0831 (mol), R_{max}^{rel}(Ta) − R_{max}^{rel}(Nb) = −0.2567 (at) and −0.0702 (mol), R_{max}^{nr}(Ha) − R_{max}^{nr}(Ta) = 0.3007 (at) and 0.2724 (mol), R_{max}^{rel}(Ha) − R_{max}^{rel}(Ta) = 0.4835 (at) and 0.3200 (mol).

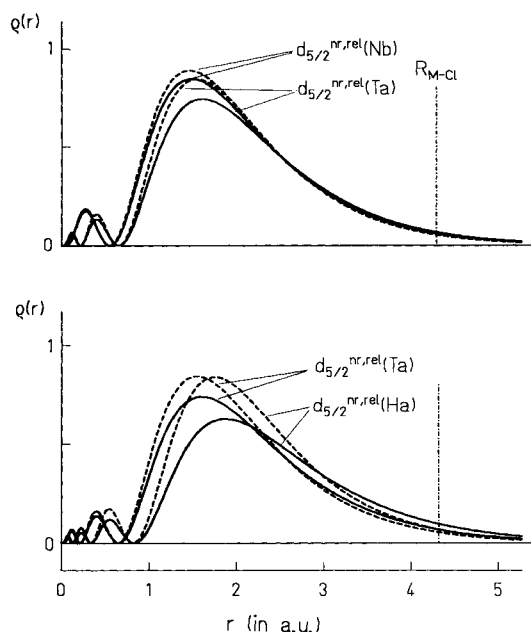FIG. 8. The radial distribution of the relativistic (full lines) and nonrelativistic (dashed lines) of the $(n-1)d_{5/2}$ electrons in the molecules MCl_5 (mol). For the $(n-1)d_{5/2}$ functions $R^{nr}_{max}(Ta) - R^{nr}_{max}(Nb) = 0.0665$ (at) and 0.0857 (mol), $R^{rel}_{max}(Ta) - R^{rel}_{max}(Nb) = 0.1080$ (at) and 0.1184 (mol), $R^{nr}_{max}(Ha) - R^{nr}_{max}(Ta) = 0.2045$ (at) and 0.2040 (mol), $R^{rel}_{max}(Ha) - R^{rel}_{max}(Ta) = 0.3030$ (at) and 0.2712 (mol).

ues of R_{max} for Nb, Ta, and Ha with electronic configurations as in the molecules are given in Table VII.

The quantitative comparison of the involvement of the valence orbitals in bonding for relativistic and nonrelativistic cases is done in terms of overlap population (OP) data, the counterpart of the covalent binding energy. From Table VIII, one can see that relativistic ns functions give increasing overlap with Cl functions in going from Nb to Ha, while the nonrelativistic shell-structure expansion of them (see Fig. 1) induces a lower $7s(Ha)$–Cl overlap, even smaller than that of $5s(Nb)$–Cl.

The relativistic contraction of the $np_{1/2}$ orbitals down the group also results in a higher $7p_{1/2}$–Cl for Ha in comparison with the analogs, while in the nonrelativistic case this overlap is in between those of $5p_{1/2}(Nb)$–Cl and $6p_{1/2}(Ta)$–Cl. This can be easily understood by looking at Fig. 6. The nonrelativistic difference in R_{max} of $np_{1/2}$ func-

tions between Nb and Ta in MCl_5 is very small. The relativistic effects make this difference larger. The relativistic difference in R_{max} of these functions between Ha and Ta is negative (-0.1630 a.u.), which means a larger contraction of the $7p_{1/2}$ function of Ha giving a higher overlap. In the nonrelativistic case, the $7p_{1/2}$ orbital of Ha is more expanded [the difference between $7p_{1/2}(Ha)$ and $6p_{1/2}(Ta)$ is $+0.33941$, resulting in the lower overlap with Cl, shown in Table VIII. Thus, for the $np_{1/2}$ orbitals as for the ns ones, the orbital and relativistic effects act in opposite directions resulting in the different overlap with the wave functions of the ligands.

The trends in overlap for $np_{3/2}$ orbitals are similar both for the relativistic and nonrelativistic cases (Table VIII). As one can see from Fig. 7, there is a very small (nonrelativistic and relativistic) contraction of the $np_{3/2}$ functions in going from Nb to Ta and expansion in going from Ta to Ha, which is a shell-structure effect.

Figure 8 reflects the radial expansion of the relativistic and nonrelativistic $(n-1)d_{5/2}$ functions in the molecule. In both relativistic and nonrelativistic cases, the $d_{3/2}$ and $d_{5/2}$ functions of Nb and Ta are very similar [see the upper part of Fig. 8(a)]. The difference in R_{max} of the $(n-1)d_{3/2}$ functions between Ha and Ta is mainly an orbital effect (Fig. 2), while for the $(n-1)d_{5/2}$ functions, relativistic effects increase the nonrelativistic difference by 0.07 a.u. ($\sim 35\%$). Relativistic and orbital effects act in the same direction for the d functions. This results in the increase of the $d_{5/2}$ (M)–Cl overlap from Ta to Ha. [As one can see from Table VIII, in the case of the molecules with nonrelativistic distances the overlap $(n-1)d_{3/2}$–(Cl) and $(n-1)d_{5/2}$–(Cl) decreases from Nb to Ha.]

The different trends in the overlap of the ns, $np_{1/2}$, and $(n-1)d_{5/2}$ functions with Cl orbitals in the group for the relativistic and nonrelativistic cases result in completely different trends in bonding, which is expressed in terms of the total OP (Table IX). First, in the relativistic case all the molecules under consideration are more covalent. Second, and more important is that the relativistic description of the wave functions gives rise to an increase in covalent bonding from Ta to Ha, while in the nonrelativistic case $HaCl_5$ would be less covalently bound than even $NbCl_5$. Thus, relativistic effects steadily increase the covalency of the halide compounds of the group 5 elements with in-

TABLE VII. Ratio of the relativistic (DS) to the nonrelativistic (HFS) R_{max} and eigenvalues (E) for valence electrons of Nb, Ta, and Ha in the electronic configurations obtained from corresponding relativistic molecular calculations of MCl_5.

Atom	ns	$np_{1/2}$	$np_{3/2}$	$(n-1)d_{3/2}$	$(n-1)d_{5/2}$
			$R^{rel}_{max}/R^{nr}_{max}$		
$Nb(s^{0.20}p^{0.22}d^{3.65})$	0.9736	0.9729	0.9977	1.0060	1.0157
$Ta(s^{0.35}p^{0.33}d^{3.37})$	0.9095	0.9079	0.9898	1.0009	1.0354
$Ha(s^{0.55}p^{0.33}d^{3.32})$	0.7965	0.7902	0.9858	0.9977	1.0701
			E^{rel}/E^{nr}		
$Nb(s^{0.20}p^{0.22}d^{3.65})$	1.0401	1.0321	1.0013	0.9866	0.9679
$Ta(s^{0.35}p^{0.33}d^{3.37})$	1.1515	1.1256	1.0064	0.9742	0.9119
$Ha(s^{0.55}p^{0.33}d^{3.32})$	1.4192	1.3441	0.9735	0.9225	0.7908

TABLE VIII. Partial overlap populations of the metal valence orbitals with all chlorine ones for MCl_5 as a result of relativistic and nonrelativistic calculations.[a]

Molecule	$R_{M-Cl_{ax}}$ (Å) $R_{M-Cl_{eq}}$ (Å)	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	p_{tot}	$d_{3/2}$	$d_{5/2}$	d_{tot}
$NbCl_5^{nr}(1)$	2.338 2.241	0.23	0.12	0.24	0.36	0.83	1.25	2.08
$TaCl_5^{nr}(1)$	2.369 2.227	0.27	0.16	0.33	0.49	0.83	1.25	2.08
$HaCl_5^{nr}(1)$	2.42 2.28	0.21	0.14	0.28	0.42	0.84	1.26	2.10
$NbCl_5^{nr}(2)$	2.362 2.264	0.24	0.12	0.25	0.37	0.82	1.23	2.05
$TaCl_5^{nr}(2)$	2.447 2.300	0.31	0.17	0.35	0.52	0.80	1.19	1.99
$HaCl_5^{nr}(2)$	2.59 2.44	0.27	0.15	0.31	0.46	0.77	1.16	1.93
$NbCl_5^{rel}$	2.338 2.241	0.28	0.14	0.24	0.38	0.83	1.25	2.08
$TaCl_5^{rel}$	2.369 2.227	0.41	0.22	0.30	0.52	0.84	1.28	2.12
$HaCl_5^{rel}$	2.42 2.28	0.48	0.29	0.20	0.49	0.87	1.33	2.19

[a]The first set (1) of the nonrelativistic data is for the molecules with experimental bond lengths; the second set (2) is for the estimated nonrelativistic distances.

creasing Z. Without relativity Ha would be rather similar to V.

E. Stability of the maximum oxidation state

As one sees from Fig. 4 and Table IV, in the relativistic treatment, the energy gap (ΔE) increases from Nb to Ta and to Ha, while in the nonrelativistic case, this trend is broken. The same is correspondingly valid for the energies of the lowest electron charge-transfer transitions (Table IV). In Ref. 10(a), it was shown that the correlation of the relativistic charge-transfer transitions with the known re- dox potentials for V, Nb, and Ta results in the potential E^0(V–IV) for Ha equal to -1.0 V, showing the maximum stability of the $+5$ oxidation state for Ha in group 5. A similar correlation for the nonrelativistic values of the π–d transitions would result in the E^0(V–IV) = -0.02 V, thus changing completely the trend in the stability of the $+5$ oxidation state within the group, which in this case would have been Ha < Nb < Ta.

TABLE IX. Effective charges on atoms (Q_M) and total overlap popula- tions (OPs) for MCl_5 as a result of relativistic and nonrelativistic calcu- lations.[a]

Molecule	Effective charges			Overlap populations		
	$Q_M^{nr}(1)$	$Q_M^{nr}(2)$	Q_M^{rel}	$OP^{nr}(1)$	$OP^{nr}(2)$	OP^{rel}
VCl_5	1.12	1.12	1.12	1.70	1.70	1.70
$NbCl_5$	0.97	0.96	0.93	1.92	1.97	2.04
$TaCl_5$	1.12	1.08	0.95	2.09	2.24	2.49
$HaCl_5$	1.19	1.13	0.81	1.82	2.08	2.60

[a]The first set (1) of the nonrelativistic data is for the molecules with experimental bond lengths; the second set (2) is for the estimated non- relativistic distances.

V. CONCLUSIONS

A comparison of the results for atomic and molecular relativistic and nonrelativistic calculations of group 5 ele- ments and their compounds (MCl_5) have shown that rel- ativistic effects change completely trends in the group.

The principally different behavior of the relativistic ns, $np_{1/2}$, and $(n-1)d_{5/2}$ orbitals in the group compared to the nonrelativistic ones results in diametrically opposite trends in I.P.s, E.A.s, energies of the electron transitions, ionicity, bonding, and stability of the oxidation states.

The relativistic treatment of the electron wave func- tions and relativity generally steadily increase covalency in going from V to Ta and further to Ha, the thermodynamic stability of the systems and bonding, stability of the max- imum oxidation state. Without relativity, there would have been an increase in ionicity in going from the $5d$ element Ta to the $6d$ element Ha, a decrease in stability, and the trends of all the other properties would have been reversed compared to the relativistic case.

Finally, if the nonrelativistic treatment of Nb and Ta gives qualitatively the right trend in properties and relativ- istic effects only shift the properties of Ta closer to those of Nb, the relativistic treatment of hahnium compounds is absolutely indispensible since it results in the principally different trends compared to the nonrelativistic case.

ACKNOWLEDGMENTS

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