Relativistic effects in physics and chemistry of element 105. I. Periodicities in properties of group 5 elements. Electronic structure of the pentachlorides

V. Pershina, W.-D. Sepp, and B. Fricke

Theoretical Physics Department, University of Kassel, 3500 Kassel, Germany

A. Rosén

Chalmers University of Technology and University of Göteborg, S-41296 Göteborg, Sweden

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A detailed study of the electronic structure and bonding of the pentahalides of group 5 elements V, Nb, Ta, and element 105, hahnium (and Pa) has been carried out using relativistic molecular cluster Dirac–Slater discrete-variational method. A number of calculations have been performed for different geometries and molecular bond distances. The character of the bonding has been analyzed using the Mulliken population analysis of the molecular orbitals. It is shown that hahnium is a typical group 5 element. In a great number of properties it continues trends in the group. Some peculiarities in the electronic structure of HaCl₅ result from relativistic effects.

I. INTRODUCTION

It is known that near the end of the periodic table relativistic effects play an important role in determining atomic characteristics such as binding energies, atomic (ionic) radii, etc. This finally influences the physics and chemistry of the heavy and superheavy elements leading to peculiarities in their chemical behavior.

Early relativistic calculations for atoms and ions¹² have already shown that there is a strong relativistic stabilization of $s_{1/2}$ and $p_{1/2}$ orbitals as function of atomic number and, as a secondary effect, destabilization of $d$ orbitals and their spatial expansion. Multiconfiguration Dirac–Fock (MCDF) calculations³,⁴,⁵ have shown that change of the spatial extension of orbitals in a relativistic treatment compared to a non-relativistic one leads to different ground state electronic configurations for Lr and element 104 than those which would be expected on the basis of a straightforward extrapolation of the periodic system. Lr turned out to have a $7s^27p_{1/2}$ ground state electronic configuration instead of the expected $7s^26d$ one and 104 to have $7s^27p_{1/2}6d$ instead of $7s^26d^2$. First excited configurations of Lr ($7s^26d$) and of element 104 ($6d^27d^2$) are by 0.19 and 0.24 eV, respectively, higher.

A number of chemical experiments⁶,⁷ were carefully planned to provide some evidence for the ground state electronic configurations of these elements and to observe the periodicities in their properties as a consequence of relativistic effects. Thus, e.g., the experiments⁸ of the volatility of element 103 as a possible analog of $p$-element Tl failed to confirm this idea and it was not possible to reduce the trivalent Lr to the monovalent state.⁷ This reduction was expected owing to strong "inert pair" effect of the $7s^2$ electrons.

The other two groups of experiments which studied volatility of the elements 103, 104, and 105 and their halides using the gas chromatography technique⁹,¹⁰ and the solution chemistry experiments which investigated the process of complex formation by the exchange solvent extraction¹¹,¹²,¹³ have given strong evidence that the actinide series ends at Lr and that a new series begins with element 104. Element 104 was found to be an analog of the group 4 elements and 105 an analog of the group 5 elements and their chemical behavior was characteristic of the elements of these groups.

These experiments however revealed that the properties within the groups are not changing smoothly and that there is a break in periodicity and, as it was supposed in Ref. 13, even a reversal, as in the case of solvent extraction of the element 105 complexes. In the experiments on the gas phase chemistry of elements 104 and 105 halides, it has been found that the 104 chloride and bromide are more volatile than their analogs MCl₄ and MB₃ (M = Zr, Hf)⁹(b),⁹(d),¹⁰(a) while the 105 chloride and bromide are substantially less volatile compared to MCl₄ and MB₃ (M = Nb, Ta)¹⁰(a),¹⁰(e),¹⁰(f). These interesting experimental results need to be given some theoretical interpretation and the general analogy between the transition elements within the groups is worth being considered independently.

Chemical properties of the transition elements of the first, second, and third row in general resemble each other while the members of the last two rows are different from the elements of the first row by a number of characteristics. These are atomic, ionic, and metallic radii; oxidation states (oxidation potentials); stereochemistry of ions in solutions or solid state; crystal-field, spin-orbital effects and magnetic properties. Thus to talk about analogy within the groups one should consider first these characteristics taking into account the fact that with increasing relativistic effects down columns of the periodic table some simple extrapolations of chemical properties may no longer be a reliable approach.¹⁴
Subtle, individual effects, configuration mixing can play an important role leading to changes in the periodicities.

In order to discuss the chemistry of element 105 we start with a summary of what is known from relativistic atomic calculations for V, Nb, Ta, and Ha. (This review is presented in Sec. II.) The chemical bonding in group 5 elements compounds (and Pa for comparison) has been studied by us for the pentachlorides MCl5, with M = V, Nb, Ta, Ha, and Pa. A number of relativistic molecular cluster calculations have been performed for different geometries and molecule bond distances. Section III gives a brief introduction in the Dirac–Slater discrete-variational method with self-consistent charge approximation (SCC-DS-DVM) and computational details of the molecular calculations. The results of the calculations are presented in Sec. IV where the character of the bonding is analyzed by the Mulliken population analysis of the molecular orbitals. The possibility of Ha forming a pentachloride in \( C_{ab} \) geometrical configuration is discussed in Sec. V. General conclusions about trends in group 5 are presented in Sec. VI.

II. RELATIVISTIC ATOMIC CALCULATIONS AS A BASIS FOR PREDICTING THE CHEMICAL PROPERTIES

From relativistic self-consistent field (SCF) atomic calculations some predictions can be made about chemical properties of the heavy elements and their analogs. Results of the atomic calculations together with available experimental data for the group 5 elements are given in Table I. From this table one can see that a dominating ground state electronic configuration in group 5 is \( d^3s^2 \) with the exception of Nb. For element 105 the MCDF calculations\(^{5(c)}\) prove the ground state electronic configuration to be \( 6d^77s^2 \) (with 87.1\% configuration weight). So the MCDF calculations have confirmed the ground state electronic configuration of Ha which was predicted in the earlier calculations.\(^{1,2} \) Thus element 105 is expected to be a \( d \) element with properties being determined mainly by valence \( 7s \) and \( 6d \) orbitals.

Both Dirac–Slater\(^1\) and recent MCDF calculations\(^{5(c)}\) have shown that there is an increase in atomic and ionic radii from Ta to 105. For the pentavalent state of V, Nb, Ta, and 105 the \( R_{\text{max}} \) data as a result of calculations\(^{5(c)}\) are given in Table I. These values have been normalized and extrapolated to the experimental ionic radii. Ionization potentials \((0 - (5 +)) \) decrease in going from V to Ha (see Table I). Thus because of the probably larger ionic and covalent radii and the small ionization energy element 105 will readily reach its maximum oxidation state. In this oxidation state it should therefore be a quite hard Lewis acid with low polarizability. It should be only a little bit softer than the \( 5d \)-elements in the same oxidation state.

Atomic electronic structure data (atomic, ionic radii, ionization potentials, maxima of radial charge densities) change smoothly from Nb to Ta and to element 105. So the chemical properties of element 105 should resemble the properties of its analogs Nb and Ta with peculiarities determined by the type of compound involved.

The strength of chemical bonding is determined by energies of the atomic shells and their spatial distribution. The spatial distribution of the valence \( ns \) and \((n - 1)d \) orbitals change within the group in different ways. Because of the relativistic contraction of the \( ns \) orbitals the maximum in the radial charge density function decreases from Nb to 105. Thus for the neutral V, Nb, Ta, and 105 these values are 1.54, 1.68, 1.53, and 1.45 Å. The \((n - 1)d \) functions on the contrary become more expanded in going from Nb to 105 (e.g., 0.456, 0.745, 0.804, and 0.908 Å for the three positively charged V, Nb, Ta, and Ha). The two diametrically opposed behavior of the valence \( ns \) and \( np_{3/2} \) orbitals on the one hand and \((n - 1)d \) and \( np_{3/2} \) orbitals on the other hand could result in local effects giving rise to strengthening or weakening the chemical bond in a particular case depending whether the energy of the \((n - 1)d \) orbital is above or below those of the other valence orbitals.

Energy eigenvalues of the valence \( ns \) and \((n - 1)d \) orbitals

### Table I. Some physicochemical data for group 5 elements V, Nb, Ta, Ha, and for Pa.

<table>
<thead>
<tr>
<th>Property</th>
<th>V</th>
<th>Nb</th>
<th>Ta</th>
<th>Ha</th>
<th>Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground state configuration</td>
<td>( 3d^4s^2 )</td>
<td>( 4d^4s^2 )</td>
<td>( 5d^4s^2 )</td>
<td>( 6d^4s^2 )</td>
<td>( 5f^66d^7s^2 )</td>
</tr>
<tr>
<td>First excited configuration</td>
<td>( 3d^4s )</td>
<td>( 4d^4s^2 )</td>
<td>( 5d^4s^6 )</td>
<td>( \cdots )</td>
<td>( 5f^66d^7s^2 )</td>
</tr>
<tr>
<td>Excitation energy (eV)</td>
<td>0.26</td>
<td>0.14</td>
<td>1.21</td>
<td>( \cdots )</td>
<td>0.25 (^{b})</td>
</tr>
<tr>
<td>( R_{\text{max}} ) (M(^{5+})) (Å)</td>
<td>0.435</td>
<td>0.586</td>
<td>0.604</td>
<td>0.685</td>
<td>0.865</td>
</tr>
<tr>
<td>Ionic radius (M(^{5+})) (Å)</td>
<td>0.54</td>
<td>0.64</td>
<td>0.64</td>
<td>0.74 (^{b})</td>
<td>0.78</td>
</tr>
<tr>
<td>Experimental ionization potential (0 - 5(+)) (eV)</td>
<td>162.64</td>
<td>135.05</td>
<td>132.03 (^{b})</td>
<td>126.38 (^{b})</td>
<td>( \cdots )</td>
</tr>
<tr>
<td>Calculated ionization potential (0 - 5(+)) (eV)</td>
<td>158.43</td>
<td>129.55</td>
<td>126.14</td>
<td>121.00</td>
<td>110.14 (^{b})</td>
</tr>
</tbody>
</table>

\(^{a}\) Reference \(^5(c)\).  
\(^{b}\) Reference 16.  
\(^{c}\) Normalized and extrapolated [Ref. \(^5(c)\)] to the experimental values.  
\(^{d}\) Reference 18.

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atomic orbitals (AOs) as a result of DF calculations\(^{19}\) are shown in Fig. 1. From this figure one can see that there is relativistic stabilization of \(ns\) AOs and destabilization of \((n-1)d\) ones as a secondary effect in going from V to Ha. Spin–orbital splitting of \((n-1)d\) AOs increases as well in this direction. Haehnium having \(7s\) and \(6d\) AOs in nearly the same energy region as \(ns\) and \((n-1)d\) orbitals of Nb and Ta will have different contributions to bonding of these orbitals compared to those of Nb and Ta. Protactinium has less stabilized \(7s\) and \(6d\) orbitals compared to haehnium with \(5f\) AOs being also in the valence region and taking part in chemical bonding. Taking into consideration the important information from the relativistic atomic calculations molecular relativistic quantum-chemical calculations can nevertheless provide a basis for better understanding the nature of chemical bonding in particular cases.

III. METHOD AND COMPUTATIONAL DETAILS OF THE
MOLECULAR CALCULATIONS

A. SCC-DS-DV method

Dirac–Slater calculations of the molecular electronic structure of the group 5 halides have been performed using the relativistic DVM with SCC approximation as developed by Rosen and Ellis.\(^{20}\)

The four-component basis functions \(\Phi_j\) are symmetry orbitals which are determined through a linear-combination-of-atomic-orbitals (LCAO) expansion, i.e.,

\[
\Phi_j = \sum_q W_q \left[ \frac{P_{nk}(r)}{r} Y_{km}(r,\xi) \right],
\]

where \(P_{nk}(r)\) and \(Q_{nk}(r)\) are the big and small components of numerical relativistic atomic (DS) wave functions; \(Y_{km}(r,\xi)\) are vector-coupled spin harmonics; \(W_q\) represents the expansion of the symmetry orbitals.

The quantum number \(k\) is defined as
\[
k = -(l + 1) \quad \text{when} \quad j = (l + 1/2)
\]
and
\[
k = l \quad \text{for} \quad j = (l - 1/2).
\]

The molecular integrals between the basis functions are calculated in a numerical three-dimensional grid. The Hamiltonian matrix elements are given by

\[
h_{ij} = \sum_k w_k \Phi_k^*(r_k) h_D \Phi_j(r_k),
\]

where \(w_k\) is the weight factor for grid point \(r_k\) and \(h_D\) is the Dirac Hamiltonian

\[
h_D = c\alpha p + (\beta - 1)c^2 + V.
\]

The potential \(V\) is the sum of three parts,

\[
V = V_n + V_C + V_s,
\]

with \(V_n\) being the nuclear, \(V_C\) the Coulomb, and \(V_s = -3\alpha(3p/8\pi)^{1/3}\) the exchange potentials. The diagonalization of

\[
(h - \epsilon_S)e_i = 0
\]
gives the molecular orbitals (MOs)

\[
\Psi_i = \sum_j c_j \Phi_j;
\]

The symmetry molecular orbitals for double point groups were constructed using the projection operator method\(^2\) implemented into the program.\(^2\) The program includes time reversal invariance resulting in additional selection rules in the nonrelativistic limit. The calculations have been done both within the all-electron and the frozen core approximations in which symmetry orbitals are constructed for the core and valence regions. The symmetry orbitals for the valence region are then orthogonalized to the core orbitals in the first iteration and kept frozen in the following iterations.

The basis set has been varied to investigate its influence on the electronic structure data. Minimal as well as ionized basis sets were used to test the change of the eigenvalues. The extended basis set including valence \(nP_{1/2}\) and \(np_{3/2}\) orbitals was used to examine the influence of these orbitals on the chemical bond formation. The results on the charge density distribution presented in the paper are for the neutral basis set. The trends in these values within the group are the same for the ionized basis. Numerical integration was done using 9000 integration points.

During the SCC procedure charge density functionals are generated via orbital occupations found by the Mulliken charge analysis of the occupied molecular orbitals.

Mulliken population analysis has been used to analyze the charge density distribution data.\(^3\) In a single determinant N-electron wave function built up from orthogonal molecular orbitals, the charge density in terms of symmetry orbitals is given as

\[
\rho(r) = \sum_{jk} \Phi_j^*(r) \Phi_k(r) f_{jk},
\]

where
Following Mulliken the total number of electrons $N$ is

$$N = \int \rho(r) d\tau = \sum_{j,k} S_{jk} t_{jk},$$

where $S_{jk} = \int \Phi_j^* \Phi_k d\tau$ is the symmetry orbital overlap matrix.

To analyze the chemical bonding it is important to break up the molecular electron density according to Mulliken into the following constituents. The net atomic population of an orbital $j$ on center $r$ contributing to molecular orbital $i$ is defined as

$$n(i,j_r) = N(i) c_{ij_r},$$

where $c_{ij}$ are MO coefficients for atomic orbital $j$ on center $r$ and $N(i)$ is the occupation of the $i$th MO. Then summation over all MOs gives

$$n(j_r) = \sum_i n(i,j_r),$$

and summation over all orbitals in atom $r$ gives

$$n(r) = \sum_{j_r} n(j_r).$$

Here $c_{ij}$ are MO coefficients obtained in the solution of the secular Eq. (4).

Gross atomic population of orbital $j_r$, contributing to molecular orbital $i$, is expressed as

$$N(i,j_r) = N(i) c_{ij_r} \left( c_{ij_r} + \sum_{k_s} c_{ik_s} S_{jk_s} \right).$$

Summation over all MOs gives gross atomic orbital populations

$$N(j_r) = \sum_i N(i,j_r),$$

and finally the effective charge of any AO (or in other words AO population)

$$q(j_r) = N_0(j_r) - N(j_r),$$

where $N_0(j_r)$ is the number of electrons in the AO $\Phi_j$.

The different partial overlap populations are

$$n(i,j_r,k_s) = 2N(i) c_{ij_r} c_{ik_s} S_{jk_s},$$

$$n(j_r,k_s) = \sum_i n(i,j_r,k_s),$$

$$n(i) = \sum_{j_r,k_s} n(i,j_r,k_s),$$

between orbitals $j$ and $k$ on the centers $r$ and $s$. The total overlap population is

$$n = \sum_r n(i) = \sum_{r,s} n(r,s) = \sum_{j_r,k_s} n(j_r,k_s).$$

These different overlap populations have been widely used to analyze the chemical bonding taking into account the fact that the overlap population is a counterpart of the covalent bond energy. We recite here the Mulliken expression of the MO energy via the overlap population parameter

$$\Delta E_{ij} = \int \Phi_i^* \Phi_j d\tau - 2 \int \Phi_i^* \Phi_k d\tau + \int \Phi_k^* \Phi_j d\tau,$$

where $\Phi_i$ and $\Phi_j$ are the molecular orbitals of $i$-th and $j$-th atom, respectively.

### B. Input parameters for MCl$_5$ (M = V, Nb, Ta, Ha, and Pa)

It is known that Nb and Ta form rather volatile pentachlorides existing in the gas phase as monomers. Electron diffraction study have shown that they have geometrical configuration of a trigonal bipyramid possessing $D_{3h}$ symmetry according to Fig. 2(a) with the interatomic distances listed in Table II.

Protactinium pentahalides have also been calculated because Pa is often included in the experiments as a possible analog whose properties sometimes resemble the properties of the group 5 elements. Unfortunately no data are available in the literature about structures of the protactinium penthalides in the gas phase. It is however known that Pa in most cases forms solid state compounds typical of the early actinides and especially uranium. The solid state structure of PeCl$_5$ for example is similar to that of UCl$_5$. Such a similarity in structures between UCl$_5$ and PaCl$_5$ should be expected also in the gas phase. In an earlier work (Ref. 25) we analyzed electronic structure of the gas phase UF$_5$ as a square pyramid of $C_{4v}$ symmetry with uranium atom above the planar square. This geometry and not a $D_{3h}$ one has been predicted for gaseous UF$_5$ in Ref. 26 by the analysis of the infrared spectrum. By analogy we have investigated the structures for PaCl$_5$ of $C_{4v}$ symmetry [see Fig. 2(b)], with

![Fig. 2. Geometrical structure of MCl$_5$ molecules.](image)
the $D_{3h}$ symmetry being also included in the calculations for comparison. For element 105 we considered two possible structures, $D_{3h}$ symmetry according to the $d^23p^6$ hybridization and $C_{4v}$ symmetry according to the $d^23p^2$ one. The bond lengths for PaCl$_4^-$ were estimated on the basis of the solid-state structural data. The internuclear distances for the 105 halides were varied in a range from 2.30 to 2.55 Å.

Results for 105 chlorides are mainly presented for $R_{ax}/R_{eq}$ equal to 2.45/2.31 and 2.42/2.28 Å. The first distances were estimated taking into account the differences in the ionic radii between element 105 and analogs obtained from MCDF calculations and the second ones from an assumption of the relativistic contraction of the bond length owing to a strong contribution of the 7s-orbitals to the chemical bonding (see Sec. IV). (In the latter case the increases in the bond lengths in HaCl, compared to TaCl$_6$ were taken as an average between those values for 104H$_4$ and 106H$_6$ compared to HfH$_4$ and WH$_6$ obtained in Ref. 28.)

IV. RESULTS AND DISCUSSION

A. Protactinium pentahalides

Despite the fact that Pa in many of its compounds exists in a pentavalent state and easily forms the double bond with oxygen in compounds as PaO$_2^-$, it can hardly be considered as an analog of the group 5 elements. Protactinium is a member of the $f$-element series with the $5f^26d^{17}7s^2$ ground state electronic configuration. Its properties are determined by the $f$, $d$, and $s$ electrons and by hybridization of these orbitals. As was mentioned before, the $D_{3h}$ hybridization is not typical for the $f$-elements and UF$_4$ does not exist in the gas phase in this form.

Our calculations of the electronic structure of PaCl$_4^-$ in $D_{3h}$ symmetry with bond distances equal to 2.44 Å have shown that this geometry is not the proper one. The total overlap population for PaCl$_4^-$ in this geometry is negative which means that the molecule in this shape is not stable due to the repulsion between the atoms. While interaction of the central atom with two axial ligands gives bonding with overlap population between them equal to 0.23 the three equatorial ligands interact in a repulsive way with the metal atom giving negative overlap population of 1.31. So the resulting total overlap between central atom and ligands is negative ($-1.08$). This unreal distribution of the electron density within the molecule gives meaningless values of the effective charges and atomic occupancies. The results on PaCl$_4^-$, symmetry on the contrary show quite reasonable values which will be discussed later with total overlap population being equal to 1.96.

B. Pentachlorides of the group 5d-elements

The detailed analysis of the electronic structure of HaCl$_4^-$ and comparison with the analogs NbCl$_5$, TaCl$_5$ have mainly been done in $D_{3h}$ symmetry. For comparison the hypothetic molecule VCl$_5$ has also been included in the calculations. The possible $C_{4v}$ symmetry for HaCl$_4^-$ will be discussed in Sec. V.

1. Overview of the molecular eigenvalues

In Fig. 3 the general splitting of the orbitals in the ligand fields of $D_{3h}$ and $C_{4v}$ symmetries is shown (without a scale) in relativistic and nonrelativistic representations.

The energy level diagram for the pentachlorides of V, Nb, Ta, Ha, and Pa is shown in Fig. 4(a). The relative ordering of the molecular levels depends on relative level positions for the constituent atoms, the crystal-field splitting, and covalency effect. The results show that all the $d$-elements pentachlorides have similar energy level structure. The set of bonding levels ends with levels of predominantly $3p$-character of Cl and separated from them by the energy gap are vacant $d$ levels of the metal. The energy gap $\Delta E$ increases in going from VCl$_5$ to HaCl$_4^-$ [see Fig. 4(b)] owing to the relative destabilization of the $d$ orbitals. The crystal-field splitting of $d$ orbitals increases as well along the series.

2. Analysis of the bonding character of the molecular levels

The molecular orbital eigenvalues of Nb, Ta, Ha, and Pa are given in Table III. MO bond orders and compositions are given elsewhere. The occupied orbitals of the NbCl$_5$, TaCl$_5$, and HaCl$_4^-$ can be divided into several groups. The six highest ones are essentially nonbonding halogen $p$-type orbitals. Below them are three orbitals responsible for rather weak interaction between valence $np$ metal orbitals and $3p$ chlorine ones. From MO composition it is interesting to see that from Nb to Ta and to Ha the $np_{1/2}$ orbital contribution decreases while the $np_{3/2}$ one increases. The orbital (20D7) contributing to the $(ns)$metal–ligand bonding in NbCl$_5$ is above the five $(n-1)d$-ligand (18D7–15D9) bonding orbitals while in TaCl$_5$ and HaCl$_4^-$ this orbital

![FIG. 3. General splitting of s, p, d, and f orbitals in ligand fields of $D_{3h}$ and $C_{4v}$ symmetries.](image-url)
TABLE III. Molecular orbital eigenvalues for MCIs.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Energy (eV)</th>
<th>Orbital</th>
<th>Energy (eV)</th>
<th>Orbital</th>
<th>Energy (eV)</th>
<th>Orbital</th>
<th>Energy (eV)</th>
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<tbody>
<tr>
<td>NbCl5</td>
<td>24D7</td>
<td>30D7</td>
<td>36D7</td>
<td>53D6</td>
<td>4.03</td>
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<td>TaCl5</td>
<td>24D8</td>
<td>29D8</td>
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<td>HaCl5</td>
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<td>28D7</td>
<td>40D7</td>
<td>9.74</td>
<td>36D7</td>
<td>9.74</td>
</tr>
<tr>
<td></td>
<td>19D8</td>
<td>24D8</td>
<td>29D8</td>
<td>40D7</td>
<td>9.74</td>
<td>36D7</td>
<td>9.74</td>
</tr>
<tr>
<td></td>
<td>18D8</td>
<td>23D8</td>
<td>28D8</td>
<td>40D7</td>
<td>9.74</td>
<td>36D7</td>
<td>9.74</td>
</tr>
<tr>
<td></td>
<td>17D7</td>
<td>23D7</td>
<td>28D7</td>
<td>40D7</td>
<td>9.74</td>
<td>36D7</td>
<td>9.74</td>
</tr>
</tbody>
</table>

*For R = 2.45/2.32 Å.

The diffusity and destabilization of 6d orbitals of Ha are the reason of their more complicated involvement into bonding with the final result being shown in the tables of partial and total overlap populations. Below these levels are MOs of predominantly 3s(Cl) character with slight admixture of nd(metal) orbitals. The lower lying levels are nearly pure metal orbitals not participating in bonding.

An interesting behavior however show the vacant orbitals of d character [see Fig. 4(b)]. Besides the fact that the general scheme of d orbital splitting in the crystal field of $D_{3h}$ symmetry is preserved for all the molecules under consideration the increase in the d orbital splitting from NbCl₅ to TaCl₅ is broken by the drastic decrease in energy of 36D7 MO in case of HaCl₅. The reason is that in fact 36D7 MO is no more an orbital of d character. The drastic increase in the 7s AO content of this highest MO from 3.8% to 4.4% and to 57.6% in going from NbCl₅ to TaCl₅ and to HaCl₅ (see Ref. 29) owing to the relativistic stabilization of the 7s AO results in the stabilization of this MO. This will finally influence some physicochemical properties, e.g., energies of highest electron charge-transfer transitions. Supposing that the same effect is presented for hahnium compounds with partially filled 6d shell the energies of the highest electronic d-d transitions will be lower in HaCl₅ compared to TaCl₅.

Total and partial density of states (PDOS) diagrams [see Figs. 5(a) and 5(b)] can be also used to establish the redistribution of atomic character over the binding energy spectra. The PDOS corresponding to a particular atomic

FIG. 4. (a) Energy level structure for MCl₅ molecules. (b) Highest occupied and lowest vacant energy levels.

(24D7 and 30D7, respectively) is below the five bonding MOs (19D9-26D7 for TaCl₅ and 24D9-25D9 for HaCl₅) between $(n-1)d$ metal orbitals and the chlorine ones. These five MOs are mainly responsible for the bonding between metal atom and ligands (see Ref. 29). The diffusity and destabilization of 6d orbitals of Ha are the reason of their more complicated involvement into bonding with the final result being shown in the tables of partial and total overlap populations. Below these levels are MOs of predominantly 3s(Cl) character with slight admixture of nd(metal) orbitals. The lower lying levels are nearly pure metal orbitals not participating in bonding.

An interesting behavior however show the vacant orbitals of d character [see Fig. 4(b)]. Besides the fact that the general scheme of d orbital splitting in the crystal field of $D_{3h}$ symmetry is preserved for all the molecules under consideration the increase in the d orbital splitting from NbCl₅ to TaCl₅ is broken by the drastic decrease in energy of 36D7 MO in case of HaCl₅. The reason is that in fact 36D7 MO is no more an orbital of d character. The drastic increase in the 7s AO content of this highest MO from 3.8% to 4.4% and to 57.6% in going from NbCl₅ to TaCl₅ and to HaCl₅ (see Ref. 29) owing to the relativistic stabilization of the 7s AO results in the stabilization of this MO. This will finally influence some physicochemical properties, e.g., energies of highest electron charge-transfer transitions. Supposing that the same effect is presented for hahnium compounds with partially filled 6d shell the energies of the highest electronic d-d transitions will be lower in HaCl₅ compared to TaCl₅.

Total and partial density of states (PDOS) diagrams [see Figs. 5(a) and 5(b)] can be also used to establish the redistribution of atomic character over the binding energy spectra. The PDOS corresponding to a particular atomic
orbital can be obtained by weighting MO energy levels by the Mulliken orbital population $q$ for each state. Then the discrete level structure of the cluster is broadened by introducing a Lorentzian linewidth to obtain a pictorial representation.

The nature of chemical bonding is different in PaCl$_5$ [see Table III, Ref. 29, and Fig. 4]. The set of bonding MOs is separated from vacant orbitals of 5f character by the energy gap $\Delta E$ which is more narrow than that of the d-element pentahalides. The crystal field splitting of the 5f orbitals is less than that of the d-elements due to lower spatial distribution of 5f orbitals compared to the d ones.

The last occupied MO is purely nonbonding 100% (Cl). The chemical bonding is mainly done by nearly equal participation of 5f and 6d orbitals of protactinium. It is also substantially influenced by the 6p orbital participation. Because of the strong spin–orbital splitting of the 6p orbital into $6p_{3/2}$ and $6p_{1/2}$ components the latter acts in an antibonding way destabilizing rather high 38D7 and 49D6 MOs. (The $6p_{3/2}$ orbital contributes to a great extent to 31D7 and 42D6 MOs giving the negative overlap metal–ligand.)

### 3. Analysis of the atomic populations

The effective atomic charges and occupancies of the valence $s$, $p$, $d$, and $f$ orbitals as a result of calculations are shown in Table IV. Here we show first $nl$ contributions. From this table one can see that the changes in the bond distances do not give any significant change in the charge density distribution data (as in the case of HaCl$_5$). Thus some conclusions about chemical bonding can be done without knowing the equilibrium bond distance.

The effective atomic charges within the group do not change smoothly from one element to another. There is a general decrease in values of effective atomic charges with a break on Ta. The atomic orbital populations change rather smoothly from NbCl$_5$ to HaCl$_5$: $q_s$ and $q_d$ increase while $q_p$ decreases. The $q_j$ values for the relativistic atomic orbitals (Table V) show that the behavior of the orbitals is basically in agreement with the contraction of $s$ and $p_{3/2}$ functions and an expansion of $d_{3/2}$ and $d$ functions for heavier elements as was shown by the earlier discussion of atomic (ionic) radii, etc. Nevertheless the changes in the stabilization or destabilization of some of $nlf$ orbitals are not a smooth function of atomic number. Thus gradual relativistic stabilization of $np_{1/2}$ valence orbitals in going from Nb pentachloride to Ha

![Diagram](attachment:image.png)

**FIG. 5.** (a) Total and (b) partial densities of states in MCl$_5$ (M = Nb, Ta, and Ha).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$q$</th>
<th>$q_s$</th>
<th>$q_p$</th>
<th>$q_d$</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCl$_5$</td>
<td>2.21</td>
<td>1.12</td>
<td>0.24</td>
<td>0.36</td>
<td>3.27</td>
</tr>
<tr>
<td>NbCl$_5$</td>
<td>2.338</td>
<td>0.93</td>
<td>0.20</td>
<td>0.22</td>
<td>3.65</td>
</tr>
<tr>
<td>TaCl$_5$</td>
<td>2.369</td>
<td>0.95</td>
<td>0.35</td>
<td>0.33</td>
<td>3.37</td>
</tr>
<tr>
<td>HaCl$_5$</td>
<td>2.42</td>
<td>0.81</td>
<td>0.55</td>
<td>0.33</td>
<td>3.32</td>
</tr>
<tr>
<td>PaCl$_5$</td>
<td>2.45</td>
<td>0.80</td>
<td>0.58</td>
<td>0.34</td>
<td>3.29</td>
</tr>
<tr>
<td>UCl$_5$</td>
<td>2.47</td>
<td>0.79</td>
<td>0.60</td>
<td>0.35</td>
<td>3.27</td>
</tr>
<tr>
<td>ThCl$_5$</td>
<td>2.32</td>
<td>0.98</td>
<td>0.13</td>
<td>0.13</td>
<td>2.09</td>
</tr>
</tbody>
</table>

*For comparison molecule VCl$_5$ is also included in Table IV.*
2.42/2.28 and 2.42/2.28 a.s a relativistic effect should have resulted in diminishing the overlap population between these orbitals and the orbitals of ligands, but in reality the strong space expansion of these orbitals (as it was shown with R max) results in the increase in their contribution to bonding. Nevertheless the relative contribution of d orbitals to bonding decreases from Nb to Ha as can be seen from Table VII. Thus all these complicated processes give rise to redistribution of the electron density in going from NbCl₅ to HaCl₅ so that s₁/₂ and p₁/₂ orbitals contribute relatively more to bonding while the contribution of d orbitals decreases (Table VII).

In the case of PaCl₅ one can see that the valence orbitals overlap in a different way compared to the d-element pentachlorides and HaCl₅ in particular. Having the same principal quantum number as Ha the valence orbitals of protactinium contribute differently to bonding. The 7s(Pa) orbital is not so strongly overlapping with ligands as the 7s orbital of hahnium, which is also the case for 7p orbitals. The 6d orbitals overlap rather well with the chlorines as well as 5f ones. Nevertheless the total metal-ligand overlap is much lower than that in the d-element chlorides because of the strong negative overlap of the 6p orbitals of Pa with orbitals of chlorines [n(6p₁/₂ – Cl) = 0.25] and n(6p₃/₂ – Cl) = -0.89].

This different behavior of different valence AOs as a function of atomic number explains the nongradual diminishing of the values of the effective charges from Nb to Ta and further to Ha. In going from Nb to Ta the increase in electron density on the metal atom gained by relativistic stabilization of s and p₁/₂ orbitals is compensated by the decrease in density on p₁/₂ and d orbitals owing to their destabilization. As a result the value of Q in Ta and Nb is nearly equal. Then in Ha halide 6d orbitals are only a little bit more destabilized than in Ta in contrast with their high destabilization in Ta compared to Nb. This little destabilization is highly covered by strong stabilization of 7s AO in Ha and its contributions to the bonding even to a lesser extent than the 5p₃/₂ orbital of Nb. This process leads finally to the total overlap population of 7p₁/₂ and 7p₃/₂ AOs being intermediate between those of Nb and Ta.

**4. Analysis of the orbital overlap**

The different behavior of the metal valence orbitals brings some peculiarities into their bonding with valence orbitals of ligands. The data on partial overlap populations of these orbitals with all chlorine orbitals are presented in Table VI.

From Table VI one can see that the valence orbitals contribute to the chemical bonding in a different way and the contribution of some of them is not a smooth function of atomic number. Thus relativistic stabilization of ns₁/₂ orbitals with increasing atomic number results in a bond strengthening owing to increase in (ns₁/₂)metal-ligand overlap which is especially pronounced in the case of Ha. Valence np₁/₂ orbitals have the same effect and it is worth noticing that the contribution of 7p₁/₂ orbitals of Ha in the total overlap is ~9.4% and is twice that of 5p₁/₂ orbitals in the case of Nb.

The behavior of np₁/₂ orbitals is the most interesting one. From NbCl₅ to TaCl₅ this orbital contributes more to bonding. In case of HaCl₅ it is highly destabilized and contributes to the bonding even to a lesser extent than the 5p₃/₂ orbital of Nb. This process leads finally to the total overlap population of 7p₁/₂ and 7p₃/₂ AOs being intermediate between those of Nb and Ta.

**TABLE V. Relativistic atomic orbital populations (q₁) for MCl₅.**

<table>
<thead>
<tr>
<th>Orbital</th>
<th>NbCl₅</th>
<th>TaCl₅</th>
<th>HaCl₅</th>
<th>PaCl₅*</th>
</tr>
</thead>
<tbody>
<tr>
<td>s₁/₂</td>
<td>0.20</td>
<td>0.35</td>
<td>0.58</td>
<td>0.55</td>
</tr>
<tr>
<td>p₁/₂</td>
<td>0.08</td>
<td>0.15</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>p₃/₂</td>
<td>0.14</td>
<td>0.18</td>
<td>0.12</td>
<td>0.11</td>
</tr>
<tr>
<td>d₁/₂</td>
<td>1.51</td>
<td>1.45</td>
<td>1.53</td>
<td>1.54</td>
</tr>
<tr>
<td>d₃/₂</td>
<td>2.14</td>
<td>1.92</td>
<td>1.76</td>
<td>1.78</td>
</tr>
</tbody>
</table>

*For PaCl₅, q(5f₁/₂) = 0.83 and q(5f₃/₂) = 0.86.

**TABLE VI. Partial overlap populations of the valence metal orbitals with all chlorine orbitals for MCl₅.**

<table>
<thead>
<tr>
<th>Orbital</th>
<th>NbCl₅</th>
<th>TaCl₅</th>
<th>HaCl₅</th>
<th>PaCl₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>s₁/₂</td>
<td>0.28</td>
<td>0.41</td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>p₁/₂</td>
<td>0.14</td>
<td>0.22</td>
<td>0.30</td>
<td>0.29</td>
</tr>
<tr>
<td>p₃/₂</td>
<td>0.24</td>
<td>0.30</td>
<td>0.21</td>
<td>0.20</td>
</tr>
<tr>
<td>p(tot)</td>
<td>0.38</td>
<td>0.52</td>
<td>0.50</td>
<td>0.49</td>
</tr>
<tr>
<td>d₁/₂</td>
<td>0.83</td>
<td>0.84</td>
<td>0.85</td>
<td>0.87</td>
</tr>
<tr>
<td>d₃/₂</td>
<td>1.25</td>
<td>1.28</td>
<td>1.30</td>
<td>1.33</td>
</tr>
<tr>
<td>d(tot)</td>
<td>2.08</td>
<td>2.12</td>
<td>2.16</td>
<td>2.19</td>
</tr>
<tr>
<td>The sum</td>
<td>2.74</td>
<td>3.05</td>
<td>3.14</td>
<td>3.16</td>
</tr>
</tbody>
</table>

*In case of PaCl₅, n(5f₁/₂ – Cl) = 0.44 and n(5f₃/₂ – Cl) = 0.57; 6p orbitals give negative overlap population of 1.15 so that the total value for overlap metal-ligand is 0.30.

**TABLE VII. Relative contributions of the valence metal orbitals (in %) in covalent bonding for MCl₅.**

<table>
<thead>
<tr>
<th>Orbital</th>
<th>NbCl₅</th>
<th>TaCl₅</th>
<th>HaCl₅</th>
<th>PaCl₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>s₁/₂</td>
<td>10.1</td>
<td>13.5</td>
<td>15.4</td>
<td>15.1</td>
</tr>
<tr>
<td>p₁/₂</td>
<td>5.0</td>
<td>7.3</td>
<td>9.4</td>
<td>9.2</td>
</tr>
<tr>
<td>p₃/₂</td>
<td>8.9</td>
<td>9.9</td>
<td>6.6</td>
<td>6.3</td>
</tr>
<tr>
<td>p(tot)</td>
<td>13.9</td>
<td>17.2</td>
<td>16.0</td>
<td>15.6</td>
</tr>
<tr>
<td>d₁/₂</td>
<td>30.3</td>
<td>27.5</td>
<td>27.2</td>
<td>27.4</td>
</tr>
<tr>
<td>d₃/₂</td>
<td>45.8</td>
<td>41.9</td>
<td>41.5</td>
<td>41.9</td>
</tr>
<tr>
<td>d(tot)</td>
<td>76.1</td>
<td>69.4</td>
<td>68.7</td>
<td>69.4</td>
</tr>
</tbody>
</table>

*In case of PaCl₅, the relative contributions of f₁/₂ and f₃/₂ orbitals in the total overlap are 13.0% and 16.5%, respectively.
TABLE VIII. Contributions to the binding energy for MCI, a

<table>
<thead>
<tr>
<th>MCI</th>
<th>$Q$</th>
<th>$\rho_i$</th>
<th>$E_i$ (eV)</th>
<th>$n_c$</th>
<th>$E_c$ (eV)</th>
<th>ion (%)</th>
<th>$\Delta H_{\text{diss}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>0.93</td>
<td>0.19</td>
<td>5.22</td>
<td>2.04</td>
<td>12.58</td>
<td>29.32</td>
<td>17.80</td>
</tr>
<tr>
<td>Ta</td>
<td>0.95</td>
<td>0.20</td>
<td>5.54</td>
<td>2.49</td>
<td>13.71</td>
<td>28.78</td>
<td>19.25</td>
</tr>
<tr>
<td>Pa</td>
<td>0.98</td>
<td>0.22</td>
<td>5.71</td>
<td>1.97</td>
<td>12.30</td>
<td>29.33</td>
<td>19.47</td>
</tr>
<tr>
<td>Ha</td>
<td>0.81</td>
<td>0.14</td>
<td>3.83</td>
<td>2.60</td>
<td>13.94</td>
<td>21.55</td>
<td>17.76</td>
</tr>
</tbody>
</table>

$Q$ is the effective charge on an atom; $\rho_i$ is the ionic bond order equal to $\Sigma - Q(k)Q(l)\langle a_{kl}/R \rangle$; $E_i$ is the ionic contribution to binding (dissociation) energy equal to $-ne_i^2Q_iQ_j/R_{MM-L}$ (eV); $n_c$ is the ionic order; $E_c$ is the covalent (overlap) energy; $\%$ is ionicity in %.

aData for $R = 2.45/2.31$ Å.

bCalculated from Born-Haber cycle.

cEstimated from present MO calculations.

dEstimated from present MO calculations.

5. Estimation of the chemical bond strength

The total Mulliken population analysis data (effective charges, ionic, and covalent bond orders) are presented in Table VIII.

From these data one can see how the character of the chemical bond is changing along the series. The compounds are predominantly covalent what is in line with earlier conclusions based on experimental data. Nevertheless covalency changes not smoothly from Nb to Ta and further to Ha. There is pronounced increase from Nb to Ta while HaCl$_5$ is only a little bit more covalent than TaCl$_5$. The ionicity on the contrary is nearly equal for NbCl$_5$ and TaCl$_5$, while HaCl$_5$ is obviously less ionic. PaCl$_5$ has much lower covalent contribution to binding compared to the $d$-element pentachlorides.

Data of Table VIII can be used to evaluate the chemical bond strength for HaCl$_5$. Here effective charges $Q$, ionic bond orders $\rho_i$, ionic contributions to binding energy $E_i$, and covalent bond orders $n_c$ have been obtained from the present MO calculations. Dissociation energies $\Delta H_{\text{diss}}$ for NbCl$_5$, TaCl$_5$, and PaCl$_5$ were estimated from the Born–Haber cycle (Fig. 6) using experimental data$^{30,31}$ for $\Delta H_{\text{subl}}$ of molecules MCI$_5$, $\Delta H_{\text{form}}$ for solid MCI$_5$ and $\Delta H_{\text{diss}}$ for Cl$_2$. (The data for PaCl$_5$ are not consistent.)$^{27,32}$ The atomization energy $D = - \Delta H_{\text{diss}}$ is the sum of covalent (overlap) energy, ionic bonding energy, and energy of ionic-covalent resonance. Using $\Delta H_{\text{diss}}$ for NbCl$_5$ and TaCl$_5$ and the ionic part of the dissociation energy ($E_i$), the covalent part was estimated ($E_c$). Then taking into account the fact that overlap population is a direct counterpart of the covalent energy the correlation between these two values was used (Fig. 7) to estimate $E_c$ for HaCl$_5$. Together with the ionic part it gives the enthalpy of dissociation for HaCl$_5$ equal to 17.76 eV.

6. Ionization potentials, electron affinities, and energies of electron transitions

Some other characteristics of electronic structure such as ionization potentials, electron affinity, and electron charge-transfer transitions have also been calculated using transition state procedure.$^{33}$ The results are shown in Table IX.

Transition-state calculations show that the energy gap increases in going from NbCl$_5$ to HaCl$_5$. This finally will result in an increase in the energies of electronic charge-transfer transitions from occupied MO of Cl-type to the vacant orbitals of metal character. (With increasing interatomic distances in HaCl$_5$ this value decreases.) Electron affinity decreases from NbCl$_5$ to HaCl$_5$ (in case of the short bond length for HaCl$_5$). Obviously stability of MCI$_5$ towards the process of reduction increases in direction to Ha chloride provided short bond lengths are realized in the hahnium pentachloride. Correlation between oxidation potentials $E^{0}(\text{V} - \text{IV})^{34}$ and the energies of lowest charge-transfer transitions for V, Nb, Ta, and Ha (see Fig. 8) gives the value $E^{0}(\text{V} - \text{IV})$ for hahnium between $-1.00$ and $-1.15$ V, depending on the interatomic distances in HaCl$_5$. 

---

FIG. 6. Born-Haber cycle for MCI$_5$ formation.
TABLE IX. Ionization potentials (IP), electron affinities (EA), and energies of electron charge-transfer transitions \( E_{1\pi-d} \) for MCl\(_3\) (eV).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NbCl(_3)</th>
<th>TaCl(_3)</th>
<th>HaCl(_3)</th>
<th>HaCl(_3)</th>
<th>HaCl(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>7.93</td>
<td>7.90</td>
<td>8.04</td>
<td>8.02</td>
<td>8.02</td>
</tr>
<tr>
<td>IP</td>
<td>10.77</td>
<td>10.73</td>
<td>10.83</td>
<td>10.75</td>
<td>10.71</td>
</tr>
<tr>
<td>LUMO*</td>
<td>23.97</td>
<td>29.97</td>
<td>35.97</td>
<td>35.97</td>
<td>35.97</td>
</tr>
<tr>
<td>Energy</td>
<td>5.23</td>
<td>4.78</td>
<td>4.60</td>
<td>4.77</td>
<td>4.84</td>
</tr>
<tr>
<td>EA</td>
<td>2.04</td>
<td>1.53</td>
<td>1.49</td>
<td>1.62</td>
<td>1.71</td>
</tr>
<tr>
<td>Transition</td>
<td>18D9 → 23D7</td>
<td>23D9 → 29D7</td>
<td>28D9 → 35D7</td>
<td>28D9 → 35D7</td>
<td>28D9 → 35D7</td>
</tr>
<tr>
<td>( E_{1\pi-d} ) as an energy difference</td>
<td>2.70</td>
<td>3.10</td>
<td>3.36</td>
<td>3.25</td>
<td>3.18</td>
</tr>
<tr>
<td>transition state</td>
<td>2.98</td>
<td>3.41</td>
<td>3.70</td>
<td>3.50</td>
<td>3.43</td>
</tr>
</tbody>
</table>

*HOMO is the highest occupied molecular orbital; LUMO is the lowest unoccupied molecular orbital.

V. OTHER POSSIBLE GEOMETRICAL STRUCTURES FOR HaCl\(_3\)

Notwithstanding the fact that analogs of HaCl\(_3\)—NbCl\(_3\) and TaCl\(_3\)—exist in the gas phase in the form of a trigonal pyramid \( (D_{3h}) \) alternative geometrical configurations of HaCl\(_3\) as a square pyramid with the central atom in the planar square and above it [see Fig. 2(b)] have also been considered. The \( C_{4v} \) symmetry could possibly be realized due to \( d^2sp^2 \) hybridization of the valence orbitals. The results of our calculations show that for the same average bond distances (of 2.37 Å) the charge density distribution in HaCl\(_3\) \( (C_{4v}) \) is nearly the same as in HaCl\(_3\) \( (D_{3h}) \) with \( Q \) effective equal to 0.81 and \( q_{6s}, q_{7s}, \) and \( q_{7p} \) equal to 3.27, 0.59, and 0.34, respectively. This can be compared with the values of \( Q \) and \( q_i \) for HaCl\(_3\) in \( D_{3h} \) symmetry (Table IV). In both cases the electron density distribution is close to pure \( d^{3}sp \) hybridization. The energy gap between occupied and vacant levels of metal character which in a way is a measure of stability of a compound is somewhat bigger in the case of HaCl\(_3\) \( (D_{3h}) \) \( (\Delta E = 3.25 \text{ eV}) \) than in HaCl\(_3\) \( (C_{4v}) \) \( (\Delta E = 3.12 \text{ eV}) \). The total overlap population for the \( D_{3h} \) case is 2.60 and for \( C_{4v} \) is 2.40 what indicates that \( D_{3h} \) hybridization is more favorable for covalent bonding. The dissociation energy calculations using the "counterpoise" scheme (with minimal ionized basis set) have shown close values of 14.51 and 15.60 eV, respectively for \( D_{3h} \) and \( C_{4v} \) cases. But taking into account still insufficient accuracy of the DVH method for the total energy values one should not rely much on the values of the dissociation energies while the other characteristics of the electronic structure indicate that the \( D_{3h} \) symmetry probably is more advantageous for HaCl\(_3\) than the \( C_{4v} \) one.

One way to prove experimentally the presence of one or the other structure could be feasible provided x-ray spectra of the short-lived molecules of hahnium were measured. The different geometrical \( (D_{3h} \) or \( C_{4v} \) \) configurations of the five chlorines would give significantly different structure of their \( ns \) lines in x-ray spectra. The calculated \( 2s(\text{Cl}) \) lines for these two cases are shown in Fig. 9.

![FIG. 8. Correlation between redox potentials \( E^\prime(V - IV) \) and energies of the lowest charge transfer transitions in MCl\(_3\) (M = V, Nb, Ta, and Ha). (Data \( E^\prime(V - IV) \) for V, Nb, and Ta are from Ref. 34.) \( E^\prime(V - IV) \) for Ha equal to \( -1.15 \text{ V} \) for \( R_{\text{eff}}/R_{\text{nl}} = 2.42/2.28 \text{ Å} \) in HaCl\(_3\).](image)

![FIG. 9. Theoretical x-ray spectra for HaCl\(_3\) [2s(Cl) lines].](image)
VI. CONCLUSIONS

Results of the atomic MCDF calculations as well as most data of the present molecular calculations confirm the idea of hahnium being a typical member of the group 5 elements with its properties being determined by the valence 6d and 7s orbitals. In a number of physicochemical properties Ha continues the tendencies found for the lighter elements in the group. Thus there is a steady increase in atomic and ionic radii (with exception of Ta), gradual change in $R_{\text{max}}$ of the valence orbitals, increase in ionization potentials (0) — (5 +), indicating the increasing stability of the pentavalent state down the group.

Molecular orbital calculations also confirm this fact. There is an increase in molecular ionization potentials, increase in energies of the first electronic charge-transfer transitions, and decrease in electron affinity provided relativistic bond contraction takes place.

Relativistic effects such as expansion (contraction) of the orbitals and their energetic stabilization (destabilization) introduce some peculiarities into charge-density distribution but the net result is the steady increase in covalency of the pentahalides and decrease in effective charges in going from Nb to Ta pentachlorides. The slight differences in the atomic electronic structure of element 105 compared to its analogs such as the availability of many closely spaced electronic configurations will hardly influence molecular properties due to the strong crystal field effect of the five chlorines. The value of the splitting of the d orbitals in the crystal field of the chlorines steadily increases in the group with HaCl$_3$ as a special case owing to strong relativistic contribution of 7s orbitals into bonding. This will result in the lower energies of the highest charge-transfer transitions in Ha compounds compared to Ta ones.

The electronic structure data confirm the specific position of Ta in the group. Ta obviously occupies such a position in the group where some effects are compensated by the others. Thus relativistic effects could be a reason for Ta having the same ionic radius (or bond length) as Nb, as it was in case of Zr, Hf, and Mo, when relativistic contraction contributes to the dominating shell-structure effect of lanthanoid contraction. In case of effective charges the relativistic stabilization of the valence $s$ and $p_{3/2}$ orbitals is compensated by destabilization of $d$ orbitals resulting in the values of effective charges being nearly equal for Nb and Ta. This specific electronic structure of Ta seems to be a reason of its chemical similarity to Nb while Ha should have some differences in its chemistry but in many aspects in line with the trends in the group.

The chemical bonding in tantalum pentachloride is probably stronger than in the other molecules under consideration because of both ionic and covalent contributions. The development of more precise relativistic methods may possibly allow exact values of the dissociation energies to be calculated.

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See AIP document No. PAPS JCPSA-96-8367-8 for 8 pages of molecular orbitals for NbCl₅, TaCl₅, HaCl₅, and PaCl₅. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is $1.50 for each microfiche (60 pages) or $5.00 for photocopies of up to 30 pages, and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.


