

Electronic structure of hafnium: A Compton profile study

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Abstract. In this paper, we report the first-ever isotropic Compton profile of hafnium measured at an intermediate resolution, with 661.65 keV γ -radiation. To compare our experimental data, the theoretical computations have also been carried out within the framework of pseudopotential using CRYSTAL03 code and the renormalized-free-atom (RFA) model. It is found that the present experimental profile is in better agreement with the RFA calculations if the outer electronic configuration is chosen as $5d^{3.2}6s^{0.8}$. The cohesive energy of Hf is also deduced from the experimental data and is compared with the available data.

Keywords. Compton scattering; electron momentum density; pseudopotential calculations.

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1. Introduction

It is known that the Compton profile, $J(p_z)$, can provide information about the projection of electronic momentum distribution on the scattering wave vector [1]. Within the impulse approximation, $J(p_z)$ is given by

$$J(p_z) = \int \int n(p) dp_x dp_y, \quad (1)$$

where p_x and p_y are the momentum components in the x and y Cartesian directions and the z direction is parallel to the resultant of the incident and scattered wave vectors. Recently, high-energy γ -ray sources (like ^{137}Cs) have been used to extend the applicability of Compton profile measurements to materials of high atomic number Z (see, for example, refs [2–5]). Besides higher resolution (Gaussian FWHM of 0.38 a.u. in comparison to 0.60 a.u. from conventional ^{241}Am source), additional

advantage of high γ -ray energy arises from the impulse approximation which dictates that the energy transfer to the electron must be large when compared to the electron binding energy. The energy transfer ($\omega_1 - \omega_2$) at 160° scattering angle in ^{137}Cs spectrometer is 473.2 keV which is nearly ten times the K-electron binding energy in the lanthanides. At room temperature and ambient pressure, the titanium group of metals, namely, Ti, Zr and Hf adopt an hcp crystal structure. The electronic structure of Hf has been the subject of numerous experimental and theoretical investigations [6–18]. With the present paper we intend to continue our systematic Compton study of 5d transition metals using a high-energy ^{137}Cs Compton spectrometer. Unlike Ta [19], the decision to undertake the first measurement on a polycrystalline sample of Hf rather than on single crystals was based on the difficulty in growing large size (say about 13 mm diameter by 5 mm length) single crystals required in γ -ray Compton measurements.

To compare experimental momentum densities, we have also computed the Compton profiles using pseudopotential (PP) with Hartree–Fock (HF) and density functional (DF) approaches incorporated in CRYSTAL03 code and a simple renormalized-free-atom (RFA) model.

In this paper, all quantities are given in atomic units (a.u.) where $e = m = \hbar = 1$, $c = 137.036$ and 1 a.u. of momentum is 1.99289×10^{-24} kg m s $^{-1}$.

2. Experiment

A high-energy (661.65 keV) γ -ray Compton spectrometer with a 20 Ci ^{137}Cs source was used to measure the Compton profile of Hf. Details of experimental set-up have been given elsewhere [19,20]. The above spectrometer has already been used successfully in determining the momentum density of several rare earths and 5d transition metals (see, for example, refs [3–5]). The incident γ -rays were allowed to fall normally on the polycrystalline sample (purity 99.9%, dimension $25 \times 25 \times 1$ mm 3) and energy spectrum of radiation scattered from the sample was measured with a high-purity Ge detector (Canberra, GLP0210) at a large scattering angle of $160^\circ \pm 0.6^\circ$. The sample was procured from M/s Sigma-Aldrich Chemical Co., USA. Along with the measured raw Compton profile, the fluorescence lines of Hf were seen which confirmed the sample as Hf. The overall momentum resolution was 0.38 a.u. The raw data were accumulated for about 350 h resulting in an integrated Compton intensity of 2.6×10^7 photons in the Compton profile region.

To extract the true Compton profile from the raw data, the raw data were corrected for several systematic corrections like background, detector efficiency, sample absorption, Compton cross-section, instrumental resolution (stripping off the low energy tail), multiple scattering, etc. by using the data reduction program of Warwick group [1,21,22]. For the present sample and experimental conditions, the contribution of multiple scattering was found to be 11.9% in the momentum region -10 to $+10$ a.u.

Finally the duly corrected Compton profile was normalized to 26.66 electrons, which is the free-atom profile [23] area from 0 to 7 a.u.

3. Theory

To compare our experimental data, we have employed the PP and RFA methods. A brief description of both the models is given below.

3.1 Pseudopotential (PP) calculations

The isotropic Compton profiles of Hf have been calculated using PP with HF and DF approaches of CRYSTAL03 code [24]. In the PP approach, the core shells of the element are replaced by pseudopotential and the valence electrons are described by nodeless pseudo-orbitals. The advantage is the incorporation of relativistic effects for core electrons and savior of the computational time. Thus the one-electron Hamiltonian operator in PP–HF approach involves the kinetic, Coulomb, exchange and the effective core pseudopotential (ECP) operators. PP–HF approach begins with Hartree–Fock orbitals (ϕ_l) from which smooth nodeless pseudoorbitals ($\tilde{\phi}_l$) are generated in a manner so that $\tilde{\phi}_l$ behaves as closely as possible to ϕ_l in the outer (valence) region of the atom. In PP–DF calculations, the exchange operator is replaced by Kohn–Sham exchange–correlation potential operator. The PP–DF calculations are undertaken within local density and generalized gradient approximations (LDA and GGA, respectively).

The calculations were done for the hexagonal (P6₃/mmc) structure of Hf with lattice parameters $a = 3.195 \text{ \AA}$ and $c = 5.051 \text{ \AA}$. ECP's have been taken from [25] and the valence basis sets for 5d and 6s electrons have been used after reoptimization. It may be mentioned that due to the non-availability of all electron basis sets for Hf, only valence electron calculations have been performed. In the case of LDA, we have used the Dirac–Slater exchange and Perdew–Zunger correlation functionals while for GGA, the exchange functional of Becke and the correlation functional of Perdew–Wang have been used [24].

In the present work the self-consistent-field (SCF) calculations have been performed at 133 points in the irreducible Brillouin zone with default tolerances [24]. The wave functions generated from the SCF calculations can be used to generate the electron momentum density (EMD) after Fourier transformation and hence the Compton profile. The directional Compton profile $J_{(hkl)}(p)$ along \vec{p} is obtained by a 2D integration of the EMD (eq. (1)) over a plane perpendicular to the \vec{p} direction. To compare our polycrystalline data, we have taken the spherical average of the directional profiles.

3.2 RFA calculations

In the computation of isotropic Compton profiles, the RFA model [26] makes a reasonable compromise between a proper band structure calculation and a free atom description. This model has been applied successfully in our earlier Compton scattering investigation on some rare earth metals and few 5d transition metals (see, for example, refs [3–5]). In the present model profiles, we have used the free atom wave functions from the tables of Fischer [27]. It was found that only 34%

Table 1. The theoretical (unconvoluted) and experimental Compton profile of hafnium. In order to compare the theoretical profile with the experimental profile, the theoretical profile has to be convoluted with the energy resolution function of the spectrometer. Statistical error ($\pm\sigma$) is given at few points.

p_z	$J(p_z)$ (e/a.u.)						Expt.
	RFA			Pseudopotential			
	$5d^{3.2}6s^{0.8}$	$5d^36s^1$	$5d^26s^2$	HF	DF-LDA	DF-GGA	
0.0	9.441	9.498	9.724	10.012	9.780	9.781	9.214 ± 0.021
0.1	9.361	9.418	9.644	9.952	9.731	9.731	9.139
0.2	9.250	9.308	9.533	9.808	9.619	9.619	9.088
0.3	9.011	9.071	9.299	9.558	9.374	9.374	8.943
0.4	8.737	8.800	9.036	9.236	9.025	9.026	8.758
0.5	8.275	8.344	8.596	8.816	8.657	8.658	8.517
0.6	8.007	7.952	8.165	8.334	8.256	8.259	8.123
0.7	7.738	7.690	7.495	7.808	7.832	7.837	7.706
0.8	7.439	7.398	7.191	7.291	7.424	7.431	7.411
1.0	6.789	6.760	6.612	6.418	6.598	6.605	6.765 ± 0.017
1.2	6.147	6.128	6.029	5.777	5.864	5.870	6.139
1.4	5.562	5.549	5.487	5.288	5.324	5.329	5.488
1.6	5.079	5.070	5.029	4.900	4.928	4.932	4.984
1.8	4.698	4.691	4.661	4.590	4.615	4.619	4.706
2.0	4.399	4.394	4.369	4.334	4.352	4.356	4.371 ± 0.012
3.0	3.534	3.533	3.531	3.521	3.521	3.523	3.580 ± 0.011
4.0	2.821	2.820	2.818	2.812	2.834	2.812	2.788 ± 0.009
5.0	2.160	2.160	2.159	2.157	2.156	2.157	2.186 ± 0.007
6.0	1.650	1.650	1.650	1.649	1.648	1.649	1.647 ± 0.006
7.0	1.300	1.300	1.300	1.299	1.298	1.299	1.311 ± 0.005

of the atomic 6s wave function was inside the WS sphere while for 5d electrons this number was about 87%. $J_{6s}(p_z)$ was calculated using 25 shortest reciprocal lattice vectors (K_n values) for several $5d^{2+x}6s^{2-x}$ (where x lies between 0 and 2) configurations. For core and 5d electrons the $J(p_z)$ values were taken directly from the tables of Biggs *et al* [23]. To obtain the total theoretical profile, contribution due to core and 5d electrons were suitably added and the final profiles were normalized to 26.66 electrons.

4. Results and discussion

The duly corrected experimental data are presented in table 1. Also included in this table are the unconvoluted theoretical Compton data computed from pseudopotential and RFA models. Out of RFA calculation for several configurations ($[\text{Xe}]4f^{14}5d^{2+x}6s^{2-x}$ where x lies between 0 and 2), only three representative configurations are incorporated in table 1. The basis of reporting RFA values

Table 2. Charge occupancies in Hf.

Reference	Q_{6s}	Q_{6p}	Q_{5d}
Papaconstantopoulos [29]	0.86	0.45	2.69
Davenport <i>et al</i> [7]	0.82–0.89	0.67–0.92	2.51–2.19
Present work (RFA model)	0.8	–	3.2

for a fractional configuration $5d^{3.2}6s^{0.8}$ was the best χ^2 fitting among RFA profiles and the experiment. The inset of figure 1 depicts total experimental profile along with convoluted core profile of Hf. It can be seen from this figure that after $p_z > 2.0$ a.u., the major contribution in experimental data comes from the core electrons. In figure 1, to examine the agreement between theory and experiment, we plot the difference profile (ΔJ), i.e. the difference between the convoluted theory and the experiment. Since ΔJ corresponding to LDA and GGA within DF were almost the same, we have shown only ΔJ corresponding to DF–GGA. Figure 1 shows that all the theoretical profiles overestimate the momentum density near $p_z = 0$. It is seen from this figure that amongst all theoretical calculations, PP–HF shows the poorest agreement with the experiment whereas the RFA model with $[\text{Xe}]4f^{14}5d^{3.2}6s^{0.8}$ configuration shows the best agreement. In comparison to PP calculations, even the RFA model for outer configuration as $5d^26s^2$ is found to be in a better agreement with the experiment.

The poor agreement between the pseudopotential calculations and the experiment shows that these calculations may not be applicable for heavy metals like Hf and that there is an improper inclusion of the correlation effects in the Kohn–Sham equation in DF calculation. Further, there may be a possibility of improvement in the quality of basis sets which governs the momentum density. The poorest agreement shown by PP–HF calculation is understandable in terms of non-inclusion of the correlation effects, which are expected to be significant in 5d transition metals. Surprisingly, the RFA model which includes the crystalline effects in a cruder way has shown an overall better agreement with the experiment. Such trend was also seen in our earlier work on a 4d transition metal, namely, yttrium [28].

Now we discuss the band occupancies of Hf. In table 2 we have compiled the charge occupancies in 6s, 6p and 5d bands inferred from the present RFA investigations and other available band structure calculations [7,29]. Our RFA-based data show a good agreement for 6s band occupancy with both the band structure calculations. Some improvement can be expected if one treats the 6p electrons within the RFA scheme and also uses relativistic wave function for 6s electrons of Hf.

Very recently, the use of Compton profiles to infer cohesive energy of several rare earths has aroused considerable interest [3–5]. The cohesive energy can be calculated using the relation

$$E_{\text{coh}} = \int_0^{p_{\text{max}}} p_z^2 [J_s(p_z) - J_{\text{fa}}(p_z)] dp_z, \quad (2)$$

where J_s and J_{fa} refer to the Compton profiles for the two states, namely solid and free atom for which the energy of transformation is E_{coh} . For the calculation of

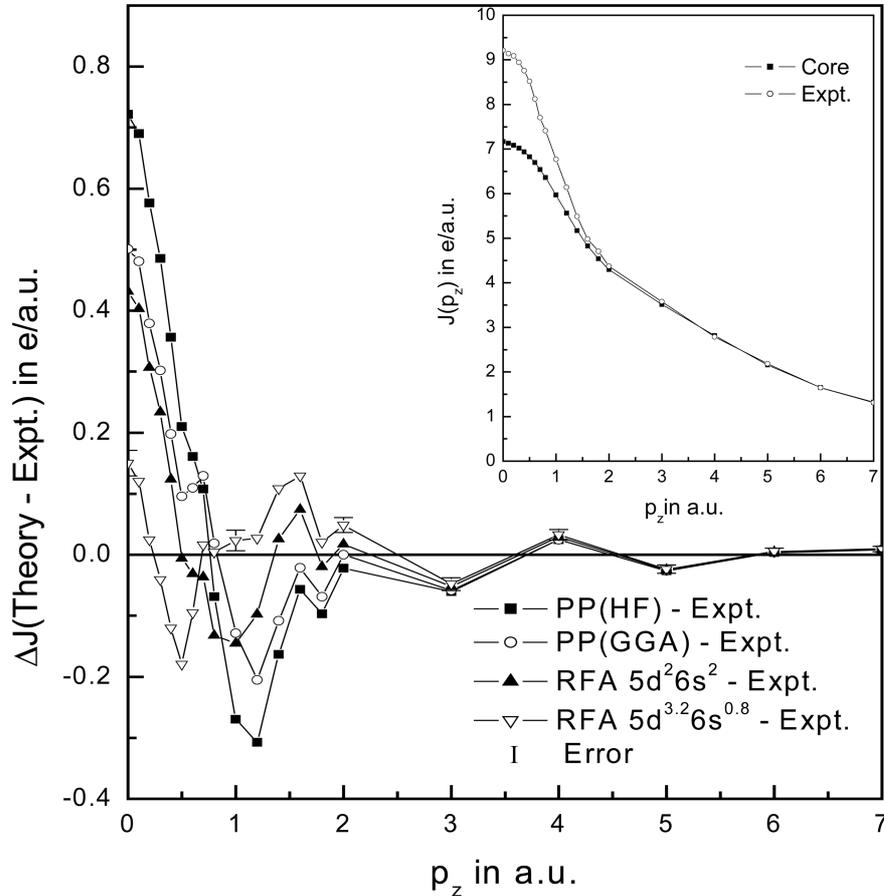


Figure 1. Difference between the theoretical convoluted and isotropic experimental Compton profiles of Hf. PP (HF) stands for pseudopotential with Hartree–Fock while PP (DF–GGA) is used for pseudopotential with density functional scheme within GGA. The RFA theoretical values are shown only for two configurations. In the inset absolute experimental and theoretical free-atom core profiles of Hf are shown. The core part corresponds to [Xe] 4f¹⁴ and has been convoluted with a Gaussian of FWHM 0.38 a.u. In the inset, the experimental error is within the size of the symbol.

cohesive energy from the experimental data, the problem related to p^2 weighting in high momentum has been highlighted earlier (see, for example, refs [3–5]). To avoid such problems in the present computation of cohesive energy from the experimental data, we have taken $p_{\max} = 2.0$ a.u. which is the valence contribution region as justified by the inset of figure 1. The numerical value of E_{coh} calculated from our experimental data comes out to be 6.96 (± 0.79) eV. Within the error bar the experimental data are not in contradiction with the values quoted earlier (6.45 eV in ref. [30] and 6.31 eV in ref. [7]).

5. Conclusion

The experimental isotropic Compton profile of Hf has been interpreted in terms of pseudopotential and the renormalized free atom models. The experimental data are in better agreement with the simple renormalized free atom calculations for $[\text{Xe}]4f^{14}5d^{3.2}6s^{0.8}$ configuration. Further, to check the applicability of HF and density functional theories, all electron Gaussian basis sets of Hf are required. Evidently, there is a need for a relativistic band structure calculation to interpret the Compton data of Hf, and then measurement on single crystals would be worthwhile. The cohesive energy of Hf computed from the present experimental data is close to the available band structure data. The 6s band occupancy inferred from the data is in better agreement with the band structure calculations by Davenport *et al* and Papaconstantopoulos.

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