

Electronic configuration of Iron (Fe)

Fareed M. Mohammed¹, Abdul Hadi M. Ghaleb², Muataz A. Majeed³,
Mohammad N. Mohammed¹ and Nawras S. Mohammed¹

¹Department of Physics, College of Science, U. O. Tikrit, Iraq

²Department of Physics, College of Science, U. O. Kirkuk, Iraq

³Ministry of Education, Salahdeen Education Directorate, Iraq

ABSTRACT

Compton profile of Iron was calculated by adopting the Re-normalized-Free-Atom (RFA) and Free Electron models, choosing $(3d^{7-x}-4s^{1+x})$ configuration, whereas $(x=0$ to 1step 0.1). This result was compared with recent experimental values. It is seen that the RFA calculation for $(3d^{6.7}-4s^{1.3})$ configuration gives a better agreement with the experiment. This theoretical Compton profile data have been used to compute the cohesive energy of Iron for the first time and compared it with available data. Also we compute the Band structure and Density of state of Iron crystals(DFT-LDA) using code Quantum wise.

Keywords: Compton profile, Cohesive energy, Re-normalized-Free-Atom (RFA), Free Electron models, Density of state.

INTRODUCTION

Iron, one of the most important metals, has been the subject of extensive experimental and theoretical research for many years[1]. In our endeavor to extend the Compton scattering of 3d transition metals , we referred to Compton profile polycrystalline Fe[2,3,4,5]. Since new measured data were reported for Fe . It was thought to re-establish and hold new study . Irons internal electronic configuration and peculiar crystalline structure makes it to be naturally attractive to magnets, it is known to be a ferromagnetic material .Iron does not possess a singular form of crystalline structure ,but shows three different forms or allotropes .these three allotropic forms of Iron are known as delta ,gamma and alpha iron. Iron exists in these three different allotropic forms, at different temperatures, as it cools down form molten form [6]. In recent years there have been several Compton scattering studies of transition metals which have consistently revealed interesting discrepancies between experiment and theory. First experimental Compton profile for (Fe) reported by Paakkari et al [7]. 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 [8]. Within the impulse approximation, $J(p_z)$ is given by:

$$J(p_z) = \iint \rho(\vec{p}) dp_x dp_y \quad (1)$$

Where p_x and p_y are the momentum components in x and y directions while the z direction is parallel to the resultant of the incident and scattered wave vectors, $\rho(\vec{p})$ momentum density [9]. In all these studies the electron momentum, is p_z expressed in atomic units (a.u.) where $e = \hbar = m = 1, c = 137$ and 1 a.u. of momentum = 1.993×10^{-24} kg . m/s. In §2 we present the details of theoretical calculation . In §3 and 4 described the result and discussion, conclusions. Objective of the study is due to the shortage of refine calculation of electronic momentum density (Fe). In determining these areas, the contributions of (1s) electrons were taken up to 6 a.u. for Fe because beyond these values the recoil energy becomes smaller than the corresponding K-shell binding energy [16].

MATERIALS AND METHODS

2.1 Renormalized – Free-Atom (RFA) model:

The renormalized - atom approach was the firstly to be used by [10]. In the RFA model one starts with the free –atom wave function, truncates them at the Wigner-Seitz (WS) Sphere and renormalizes the wave function to one within this Sphere to preserve charge neutrality .

For bcc metals, the Compton profile for 4s electrons, can be written by as [11]:

$$J_{4s}(P_z) = 4\pi \sum_{n=0}^{\infty} |\Psi_0^c(K_n)|^2 G_n(p_z) \tag{2}$$

Where K_n is a reciprocal lattice vector and p_z the projection of electron momentum along the scattering vector direction.

$\Psi_0^c(K_n)$ is the Fourier transform of the RFA wave function $\phi_0^c(r)$.

(S-Electrons): The procedure for computing Compton profiles is already published and here we rewrite these equation for the sake of completeness. Following Berggren [12] the momentum transform of a Bloch function (for the unhybridised outermost “s” electrons) for the cubic structures is given by:

$$\Psi_{\vec{k}}^c(\vec{p}) = N\delta(\vec{p} - \vec{k}_1\vec{k}_n)\Psi_{\vec{k}}^c(\vec{p}) \tag{3}$$

Here N is the total number of atoms, \vec{k}_n is the reciprocal lattice vector and the transform $\Psi_{\vec{k}}^c(\vec{p})$ is defined as:

$$\Psi_{\vec{k}}^c(\vec{p}) = (2\pi)^{-\frac{3}{2}} \int e^{-i\vec{p}\cdot\vec{r}}\Psi_{\vec{k}}^c(\vec{r})d\vec{r} \tag{4}$$

Where the integration is over the Wigner-Seitz polyhedron .In the conventional cell approximation and the transform

$$\Psi_{\vec{k}}^c(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\Psi_{\vec{k}=0}^c(\vec{r}) \tag{5}$$

When $\vec{k}_n = \vec{P} - \vec{k}$, then $\vec{k} = 0$

$$\Psi_{\vec{k}}^c(\vec{p}) = \Psi_0^c(\vec{k}_n) \tag{6}$$

For $k_n = 0$

$$\Psi_0^c(0) = (2/\pi)^{\frac{1}{2}} \int_0^{r_0} dr r^2 \phi_0^c(r) \tag{7}$$

And for $k_n \neq 0$

$$\Psi_0^c(\vec{k}_n) = (2/\pi)^{\frac{1}{2}} k_n^{-1} \int_0^{r_0} dr r \sin(k_n r) [\phi_0^c(r) - \phi_0^c(r_0)] \tag{8}$$

The auxiliary function $G_n(p_n)$ is given as.

For $n = 0$

$$G_0(P_z) = \begin{cases} \frac{1}{2} (P_F^2 - P_z^2) P_z \leq P_F \\ 0 \text{ otherwise} \end{cases} \tag{9}$$

For $n \neq 0$

$$G_n(P_z) = \begin{cases} 0 & P_z > K_n + P_F \\ \tilde{G}_n(P_z) & P_z \in (K_n - P_F, K_n + P_F) \\ \tilde{G}_n(K_n - P_F) & P_z < K_n - P_F \end{cases} \tag{10}$$

Where

$$\tilde{G}_n(P_z) = \frac{N_n \{ (P_F^2 - K_n^2)(K_n + P_F - P_z) - \frac{1}{3} [(K_n + P_F)^3 - P_z^3] + K_n [(K_n + P_F)^2 - P_z^2] \}}{4K_n} \tag{11}$$

N_n is the number of reciprocal lattice points in the shell in the reciprocal space, as regards the wave function for 4s-electrons, the free atom Hartree -Fock wave function was taken from tables of [13]. The Compton profile was then calculated using equation (2) to (6) for several cases choosing various (3d-4s) configuration. The values of the Compton profile of 3d electrons and other inner electrons were taken from [14]. All the theoretical Compton profiles were normalized to an area of 11.14067 electrons. As usual in all 15 shortest reciprocal lattice vectors were considered electrons.

2.2. Free Electron-based model profile:

In case of an isotropic momentum distribution, eqn. (1) reduces to the well-known form:

$$J_{4s}(p_z) = 2\pi \int_{p_z}^{\infty} dp \rho(\vec{p}) p \quad (12)$$

If we consider the valence electrons in a metal as a non-interacting electron gas, then the momentum density by:

$$\rho(\vec{P}) = \text{constant} = \frac{n}{\frac{4}{3}\pi p_F^3} \quad (13)$$

Where n the number of free electrons per site and p_F is the Fermi momentum.

Substitution of $\rho(p)$ from eq.(13) to eq.(12) gives

$$J_{4s}(p_z) = \frac{3n}{4p_F^3} (p_F^2 - p_z^2) \quad \text{for } p_z \leq p_F \quad (14)$$

The free electron Compton profile is then an inverted parabola including discontinuities of the first derivative at $\pm p_F$ [6]. Using eqn.(14), we have also calculated the free electron Compton profile for 4s electron of Fe.

To get a total profile in the momentum range(0 to +6)a.u., the Compton profile for core electrons(1s² to 3d⁶) were directly taken from the tables of Biggs et al [14].

2.3. Cohesive energy:

The cohesive energy which is defined as the difference between the total ground -state energy of the solid and the energy of the individual isolated atoms can be calculated from Compton profile data [15] using following relation:

$$E_{\text{Coh}} = \int_0^{P_{\text{max}}} p_z^2 [J_s(p_z) - J_{\text{FA}}(p_z)] dp_z \quad (15)$$

Where the $J_s(p_z)$ and $J_{\text{FA}}(p_z)$ refer to solid state and free atom profiles, respectively. In our calculation, P_{max} was taken as infinite. The values of $J_s(p_z)$ were taken from the present RFA calculation which represents the solid-state phase of (Fe) and those for free atom Compton profile tables 1. the contribution of core electrons are same in the $J_s(p_z)$ and $J_{\text{FA}}(p_z)$ and hence cancel out in the difference seen in Eqn.(15).

2.4. Band structure:

The one-electron band structure energy is given by [1]:

$$E_{\text{band}} = \sum_i \left(\int_{-\infty}^{E_f} E N_i(E) dE - \sum_{\alpha} n_{i,\alpha} \epsilon_{\alpha} \right) \quad (16)$$

Here, The summation extends over all atomic sites i , $N_i(E)$ is the local electronic density of states, and E_f is the Fermi energy which is a global quantity. The reference energy of an isolated atom is expressed in terms of the energy levels ϵ_{α} and the corresponding occupation numbers $n_{i,\alpha}$ which satisfy the condition.

$$\sum_{\alpha} n_{i,\alpha} = \int_{-\infty}^{E_f} N_i(E) dE \quad (17)$$

With this definition, E_{band} is zero for both empty and full bands.

In Fig (1). We show the band structure of a Fe (bcc) crystal as obtained by the(DFT-LDA) using code Quantum wise. And it was compared with the tight-binding and the ab-initio LDA method [1]. We find that the agreement between these two calculations is very good, especially in the energy range close to the Fermi level E_F .

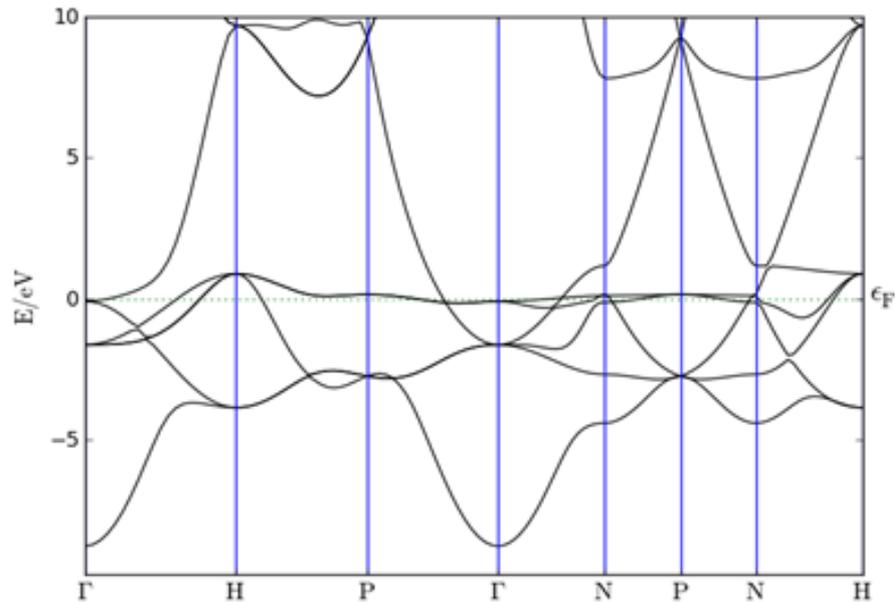


Fig.1 Band structure of Fe(bcc)obtained the(DFT-LDA) using code Quantum wise

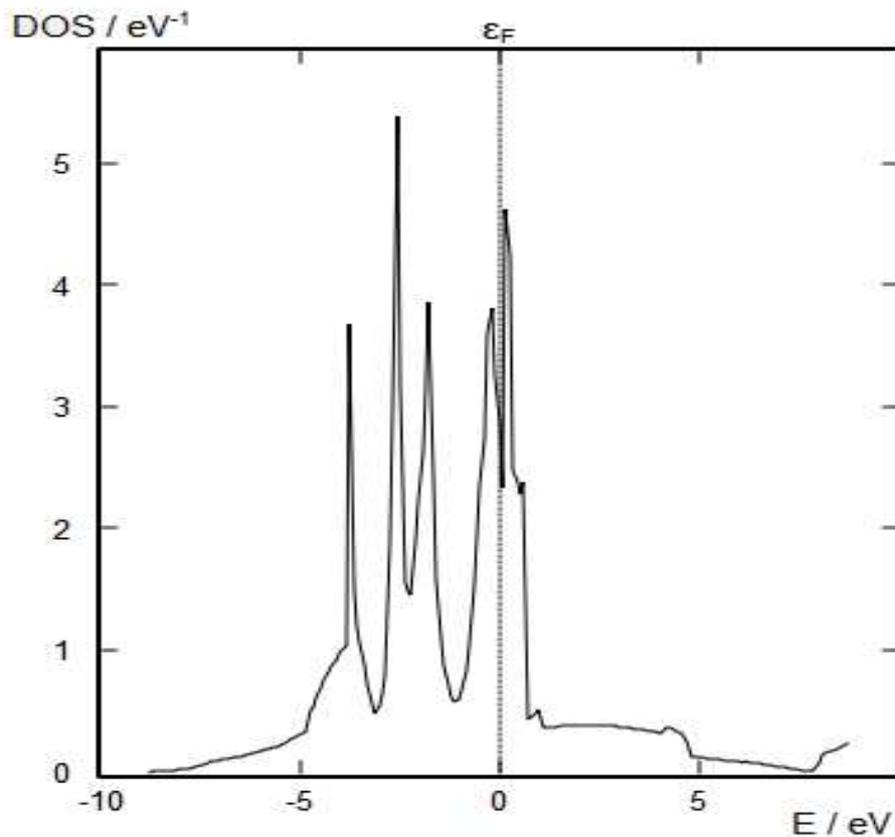


Fig.2Nonmagnetic density of states for Fe(bcc) obtained the(DFT-LDA) using code Quantum wise

2.5. Density of state:

The magnetic interaction in this system can be obtained using the Stoner-theory of itinerant ferromagnetism[1]. This theory describes the electronic structure of the magnetic system by a rigid shift of the spin-up and spin-down states as.

$$N_{\uparrow}(E) = N(E + \Delta E_{\uparrow}) \quad (18)$$

$$N_{\downarrow}(E) = N(E - \Delta E_{\downarrow}) \quad (19)$$

Here, $N_{\uparrow}(E)$ and $N_{\downarrow}(E)$ are the densities of states for spin-up and spin-down electrons corresponding to majority and minority sub bands, respectively, and $N(E)$ is the density of states for the nonmagnetic state. The energy shifts ΔE_{\uparrow} and ΔE_{\downarrow} of $N_{\uparrow}(E)$ and $N_{\downarrow}(E)$ with respect to $N(E)$ are constrained by the charge conservation.

$$\int_{E_f - \Delta E_{\downarrow}}^{E_f} N(E) = \int_{E_f}^{E_f + \Delta E_{\uparrow}} N(E) \quad (20)$$

Our results for the corresponding total electronic density of states $N(E)$ of Fe (bcc) [1] at displayed in Fig (2), again in very good agreement with each other. The density of states is dominated by a large peak near the Fermi level which is responsible for a stable ferromagnetic phase of Fe (bcc).

RESULTS AND DISCUSSION

Table 1. includes three theoretical profiles for $(3d^{6.9}-4s^{1.1}, 3d^{6.8}-4s^{1.2}, 3d^{6.7}-4s^{1.3})$ computed by RFA model using the procedure of Sec.2.A. The free atom values for $(3d^6-4s^2)$ are also included for comparison. Also given here are the Free electron profile. All the theoretical values given in this table I are obtained **after** convoluting the theory with the residual instrumental function (RIF) of 0.6 a.u. and normalized to an area of **11.14067** being the number of electrons from (0 to 6) a.u. We now compare the various theoretical and experimental Compton profiles given in this table I. Coming first to the high momentum region ($p_z > 2.0$ a.u.), it is seen that all theoretical values are nearly equal. This is easily understood because in this region only core electron contribute and for them the same model has been used in all cases. It is interesting to note that values are close to the experiment.

Coming next to the low momentum region ($p_z = 0-0.5$ a.u.), it is seen that the free atom model shows the maximum disagreement. On the whole the RFA values are considerably flatter but the free electron values are close to the experiment. In Fig 3. shows this comparison where we plot the theoretical (except free atom) and experimental results up to 5 a.u. [16]. when ($p_z > 0.5$ a.u.) it is seen that the RFA values for $(3d^{6.7}-4s^{1.3})$ are lower than $(3d^{6.9}-4s^{1.1}, 3d^{6.8}-4s^{1.2})$ results but between ($p_z > 0.8$ a.u.) a.u. the trend is reversed and the $(3d^{6.7}-4s^{1.3})$ values are higher than from $(3d^{6.9}-4s^{1.1}, 3d^{6.8}-4s^{1.2})$.

Comparison between Free electron and Free atom, it is seen in low momentum Free atom $(3d^6-4s^2)$ higher than the Free electron $(3d^6-4s^2)$ but in part between $p_z = (0.3$ and $0.8)$ the trends get reversed and the free electron values are somewhat larger than the free atom. At $p_z > 0.9$ a.u. both models values to become similar. In Fig(4) shows the difference between theoretical (after convolution) and experimental profiles in Fe. It can be seen in the low momentum that $\Delta J(3d^{6.9}-4s^{1.1}, 3d^{6.8}-4s^{1.2} - \text{Exp})$ larger than from $\Delta J(3d^{6.7}-4s^{1.3} - \text{Exp})$, as well as the $\Delta J(3d^{6.7}-4s^{1.3} - \text{Exp})$, have similar values only in low momentum different, but (Free atom - Expt.) and (Free Electron - Expt.) are nearly the same where $p_z > 1$ a.u. Also in the high momentum transfer region ($p_z > 4$ a.u.) , Experimental values are very close to corresponding theoretical data. It is known that the contribution of valence electron is very small in this region and hence, most of the contribution may be due to the inner-core electrons. These inner-core electrons are reasonably described by the free-atom values.

In order to determine the best configuration electrons, the total square deviation $\sum_0^{6 \text{ a.u.}} |\Delta J|^2$ was obtained for each cases. The values founded were (0.2859688, 0.2812289, 0.2811589) for $(3d^{6.9}-4s^{1.1}, 3d^{6.8}-4s^{1.2}, 3d^{6.7}-4s^{1.3})$ configuration respectively. Thus $(3d^{6.7}-4s^{1.3})$ seems to be the best configuration. From this we can observe by effect of convolution the theoretical values. The purpose of the computation of cohesive energy was to see the applicability of the RFA scheme in reproducing the cohesive of transition metals. The value of calculated cohesive energy (with $p_{\text{max}} = 2$ a.u.). Table II show comparison between our theoretical by RFA model, experiment [16] and another data. A choice of low value of p_{max} is justified because, to a good approximation, after this value the major contribution in the theoretical and experimental profile is expected only due to core electrons, which almost remain unaffected in formation of solids.

Table 1: Theoretical results Compton profile of Iron (Fe) compared with experimental value [16]. All the quantities in atomic units .All theoretical values have been convoluted with the residual instrumental function (RIF) of 0.6 a.u. These values have been normalized to 11.14067 electrons as discussed in the text

P_z (a.u.)	$J(p_z)(e/a.u.)$					
	Free atom ($3d^6-4s^2$)	Free electron ($3d^7-4s^1$)	Theory(RFA)			Expt. [16]
			Core +RFA $3d^{6.9}-4s^{1.1}$	Core +RFA $3d^{6.8}-4s^{1.2}$	Core +RFA $3d^{6.7}-4s^{1.3}$	
0.0	6.839	5.41	5.242	5.226	5.211	5.21
0.1	6.433	5.336	5.183	5.172	5.159	5.19
0.2	5.948	5.228	5.094	5.087	5.079	5.13
0.3	5.513	5.093	4.981	4.98	4.976	5.04
0.4	5.125	4.931	4.847	4.851	4.851	4.93
0.5	4.769	4.746	4.691	4.698	4.702	4.78
0.6	4.452	4.548	4.517	4.527	4.534	4.60
0.7	4.188	4.348	4.339	4.349	4.356	4.39
0.8	3.975	4.159	4.165	4.173	4.179	4.18
1.0	3.648	3.823	3.843	3.847	3.848	3.77
1.2	3.366	3.522	3.543	3.544	3.543	3.38
1.4	3.078	3.221	3.238	3.238	3.237	3.00
1.6	2.781	2.914	2.925	2.926	2.925	2.68
1.8	2.486	2.612	2.617	2.617	2.617	2.39
2	2.205	2.326	2.325	2.325	2.326	2.11
3	1.227	1.291	1.285	1.287	1.287	1.17
4	0.778	0.809	0.807	0.808	0.81	0.75
5	0.575	0.591	0.59	0.592	0.594	0.53

Table2: Cohesive energy of Iron.(E_{Coh} in eV)

Reference	E_{Coh} (in eV)
Our theoretical(RFA)	4.43
Experiment[1]	4.28

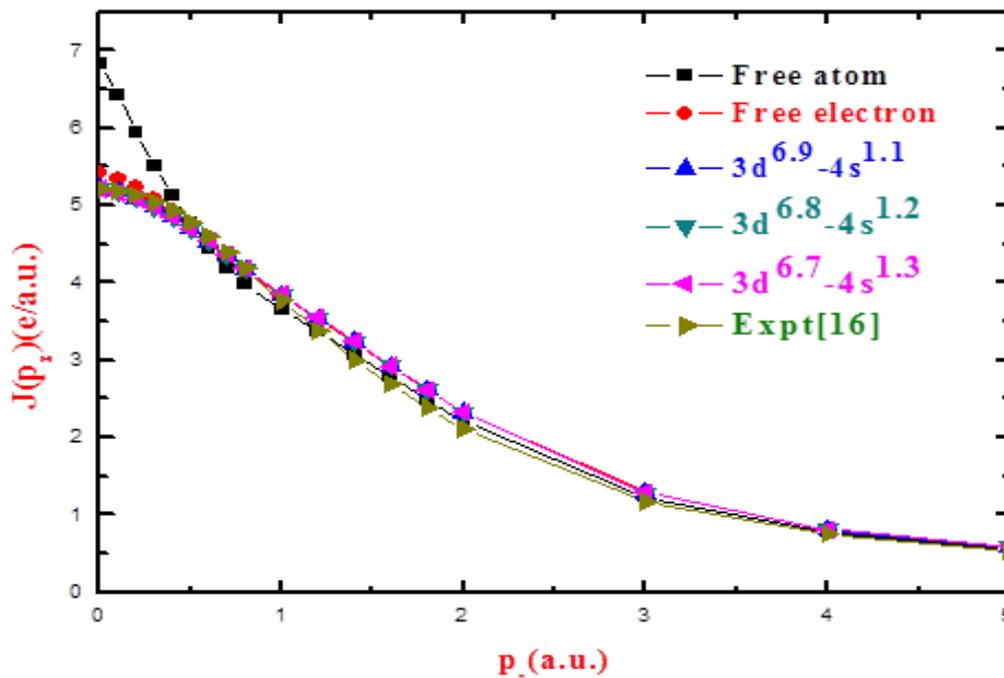


Fig.3 Comparison of theoretical results with experimental [16] Compton profiles for Fe

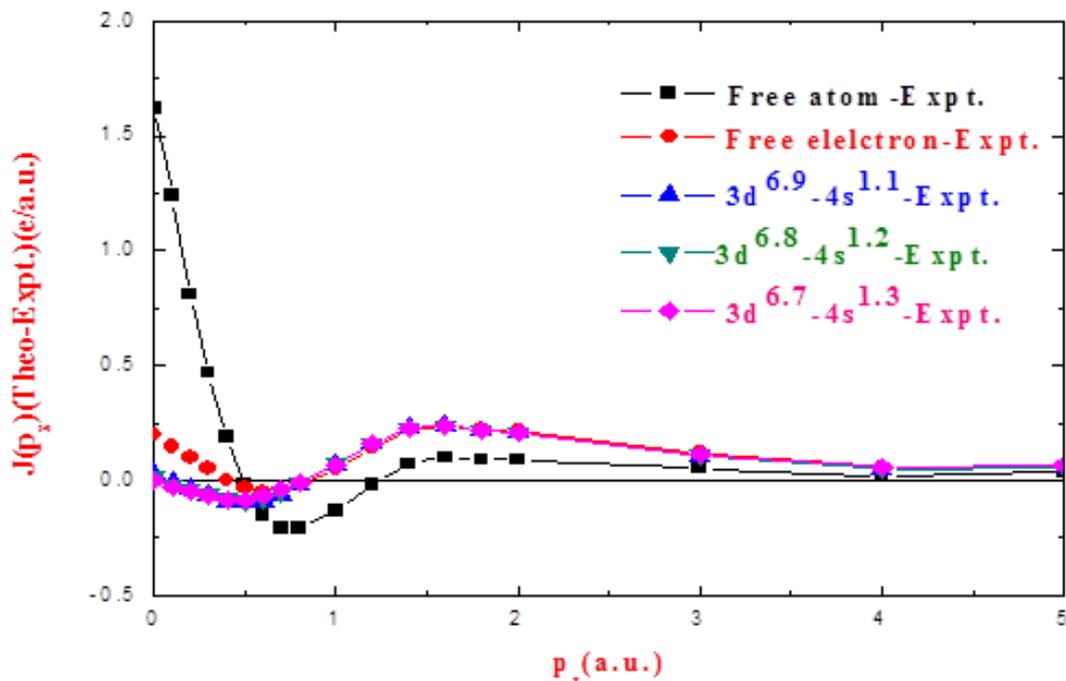


Fig.4 Difference between our theoretical and experimental [16] Compton profiles of Fe

CONCLUSION

The RFA model shows good agreement with the experiment in the ($3d^{6.7}-4s^{1.3}$) configuration, while free electron model Compton profile values are higher than experimental. Evidently, there is a need for a relativistic band structure calculation to interpret the Compton profile data. In table I illustrate the comparison between theoretical results using (RFA) model with previous works [16] in the process transfer charge of shells (s,d). The cohesive energy of Iron computed by (RFA) model and comparison with another results [1].

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