

Inner shell structure of heavy atoms[†]

M P DAS and P NAYAK*[†]

Department of Physics, Sambalpur University, Jyoti Vihar, Sambalpur 768 019, India

*Department of Physics, G.M. College, Sambalpur 768 004, India

[†]Present address: Department of Physics, Sambalpur University, Sambalpur 768 019, India

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Abstract. The inner-shell structure of some heavy atoms is examined using a self-consistent relativistic local density method. Ar(*K*), Kr(*K*) and Xe (*K*, *L*₁, *L*₂ and *L*₃) binding energies and *K*_α^h (hyper-satellite) energies of Tl, Hg and Tm are calculated. The results are compared with available experimental data.

Keywords. Binding energies; density functional; SCF procedure; double hole satellites.

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1. Introduction

Using high resolution x-ray and electron spectroscopy the binding energies of electrons in atoms throughout the periodic table have been determined earlier (Bearden and Burr 1967; Siegbahn *et al* 1971). Since then relativistic atomic structure calculations have been performed for obtaining the atomic electron binding energies and the results were compared with the experimental data. A common approach for calculating binding energies is what is known as a non-local Dirac-Fock Scheme (Desclaux 1973). Another, which is not strictly an alternative to the former, is the local approach (Slater 1974) where the Dirac-Hartree-Fock exchange is approximated through one-particle density. These two methods were used to calculate the atomic orbitals and binding energies (Desclaux 1973; Lu *et al* 1971; Lindgren and Rosen 1974). However, there are some differences between the calculated and experimental values which are attributed to the further relativistic (Breit) and quantum electrodynamical (Lamb shift) corrections. A somewhat hybrid approach was used for calculating binding energies and the wave functions have been calculated by employing the local density approach (LDA) (Huang *et al* 1976). Later the calculations were extended to include the expectation values of all other energies. The exact non-local exchange energies were calculated using the wave functions due to LDA. Though this approach is much more involved than LDA it is less tedious than the non-local Dirac-Hartree-Fock scheme. The results of Huang *et al* (1976) with relativistic and quantum electrodynamical corrections agree very well with the experiments for almost all atoms.

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Many electron interactions are usually considered pair-wise for which Coulomb interaction is most commonly used. If the two electrons are relativistic (*i.e.* momenta of the electrons are comparable with the photon momentum) a contribution from the transverse photon-mediated electron pair interaction (TPE) becomes significant. In the longer wavelength limit this is known as Breit interaction, which is often used in relativistic atomic structure calculations. In the local density approach one includes this TPE through exchange-correlation in a one-particle effective potential. Das (1983a, b) carried out the relativistic atomic structure calculations in the local density approximation by including the TPE correction through a self-consistent density functional theory.

Recently Breinig *et al* (1980) have precisely determined the Ar (K), Kr(K), and Xe (L_1 , L_2 , L_3) levels by absorption spectrometry with synchrotron radiation. Within the limits of error the results of these authors are compared with existing experimental data (Bearden and Burr 1967; Siegbahn *et al* 1971) and theoretical calculations (Huang *et al* 1976). On comparison the binding energies of ESCA (Siegbahn *et al* 1971) agree well for all cases except for Kr(K) and when compared with the Bearden-Burr (1967) values, these are always systematically smaller in magnitude. It also agrees well with the hybrid calculations of Huang *et al* (1976). As mentioned earlier the calculations of Huang *et al* (1976) are based on a theory in which the exchange is calculated exactly with the wave functions due to LDA.

Unlike ordinary single K -ionisation the probability of the creation of a double K -ionisation in heavy atoms is very small. There seems to have been some measurements of double vacancies in the K -shell on Hg, Tl and Tm during nuclear processes like electron capture and internal conversion. Accordingly calculations have been performed based on Dirac-Fock-Breit theory (Chen *et al* 1982). It has been proved beyond doubt that the effect of Breit interaction gives a dominant contribution to the hypersatellite energies.

In view of these two observations, it was felt worthwhile to calculate similar quantities fully within the LDA. To our knowledge no LDA calculations have been reported for double vacancy states. We have used approximate ground state energy functional for the excited states because the latter is unknown. The results of our calculations of Ar(K), Kr(K) and Xe(K , L_1 , L_2 and L_3) binding energies and K_2^h (hypersatellite) energies of Tl, Hg and Tm are given in §2 and the results are compared with the available experimental data.

2. Results

Based on the Δ SCF procedure (Das 1983b), we calculate the total energy of an atom and the total energy of an ion with a hole in a particular state. The difference between these two total energies gives the major contribution to the binding energies of the electron in a state where there is a hole. In this procedure the binding energies obtained take into account the static relaxation of the electronic charge densities due to the creation of a hole in a certain orbital. The difference of this binding energy and the frozen Koopmans' orbital energy is known as rearrangement energy, which is governed by the relaxation of orbitals.

In table 1, we have displayed the atomic electron binding energies of Ar(K), Kr(K) and Xe(K , L_1 , L_2 , L_3). It is seen from the table that the Ar(K) binding energy is 1 eV and

2 eV lower than that of hybrid theory and experiment respectively. This discrepancy may be accounted for by correlation contributions. As the nuclear charge increases from Ar to Kr and Xe, the discrepancy of our calculation with the experiments becomes larger (see table 1). It is always found for high Z atoms that the spatial distribution of electron becomes more and more inhomogeneous as the atomic number is increased. It is well known that a local approach is suitable for a system of weakly varying density. Since charge density in an atom varies rapidly, an inhomogeneity correction is necessary. The inhomogeneity correction is a non-local one to which the discrepancies may be attributed. After the major discrepancies are explained one should worry about the further many-body aspects as mentioned in Breining *et al* (1980). The Xe_L doublet splitting is 320.7 eV in the case of experiment and 320.2 eV due to Huang *et al* (1976), while in our case it is 327 eV. This is because our K and L_1 orbitals are loosely bound as compared to those of Huang *et al* (1976), or with experiment, since the corresponding energies are smaller in magnitude. These K and L_1 shells poorly screen the L_2 and L_3 orbitals in the present calculations as a result of which the splitting is larger. Table 2 gives the results of K -hypersatellite shifts for Hg, Tl and Tm. The hypersatellite shifts are calculated from the formula (Schreckenbach *et al* 1977)

$$E_h^s(K) = [E(1s^1, 2p^3) - E(1s^0, 2p^4)] - [E(1s^1, 2p^3) - E(2s^1, 2p^4)]$$

where $2p$ stands for $2p_{3/2}$ and E 's are the total energies for the corresponding configurations (Chen *et al* 1982; Schreckenbach *et al* 1977; Desclaux *et al* 1974; Van Eijk and Wijnhorst 1977).

The hyper-satellite shifts given in table 2 are from calculations in which the Kohn-Sham non-relativistic exchange potential is used. The values are very poor when compared with the experimental ones. The shifts are calculated from the fully

Table 1. K -shell binding energies (in eV).

Levels	Theory		Experiment
	Present	Huang <i>et al</i> (1976)	Breining <i>et al</i> (1980)
Ar(K)	3204.5	3205.4	3206.3(3)
Kr(K)	14312.2	14325.7	14327.2(8)
Xe(K)	34536.3	34562.5	
(L_1)	5383.2	5458.7	5452.9(5)
(L_2)	5094.6	5106.7	5107.0(5)
(L_3)	4757.3	4786.5	4786.3(6)

Table 2. Hypersatellite energy (in eV).

System	Present			Expt.
	(Kohn-sham)	(RLDA)	DFB	
Tl	852	1028	1234 ^a	1160 ± 70
Hg	835	1006	1184 ^b	1145 ± 12
Tm	672	791	918 ^c	902 ± 9

^a Desclaux *et al* (1974); ^b Schreckenbach *et al* (1977); ^c Desclaux (1980).

relativistic exchange potential in which the transverse photon-electron contribution is included. This shows an improvement over the Khon-Sham values. But the values are smaller by about 12%, compared to the experiments while the DFB results given in table 2 are fairly satisfactory. We attribute the discrepancy of our relativistic local density calculations to (a) the neglect of non-local effects and (b) use of approximate ground state energy functionals for exchange correlation in a situation where the system is in a highly excited state.

3. Conclusion

From our study of the doubly-ionized inner-shell states it is clear that the local density scheme is inadequate whereas it has been fairly successful with many systems (Das 1983a) for the inner-shell binding of heavy atoms. In the non-local analysis it has been shown (Desclaux (1974) that the TPE interaction provides a dominant contribution to the doubly ionized inner-shell states. This has been confirmed by our local density study. In view of the discrepancy one should incorporate non-local effects and the appropriate energy functional for the excited states, which is unknown at present.

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