Core electron binding energies in heavy atoms

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Abstract. Inner shell binding of electrons in heavy atoms is studied through the relativistic density functional theory in which many electron interactions are treated in a local density approximation. By using this theory and the Δ SCF procedure binding energies of several core electrons of mercury atom are calculated in the frozen and relaxed configurations. The results are compared with those carried out by the non-local Dirac-Fock Scheme. K-shell binding energies of several closed shell atoms are calculated by using the Kohn-Sham and the relativistic exchange potentials. The results are discussed and the discrepancies in our local density results, when compared with experimental values, may be attributed to the non-locality and to the many-body effects.

Keywords. Atomic structure; binding energy; relaxed orbitals; density functional; Breit interaction.

1. Introduction

Calculations on the electronic structure of heavy atoms based on the relativistic theory, such as multi-configurational Dirac-Fock (MCDF) method (Desclaux 1980) are in reasonably good agreement with experimental findings. This theory employs one-electron Dirac Hamiltonian that contains the kinematics of the electrons and their interactions with the classical nuclear field. The electron-electron interaction is then added in two parts. The first part is treated in the Hartree-Fock sense by applying variational principle to a many-electron wavefunction as an antisymmetric product of one-electron orbitals. The second part is a quantum electrodynamical correction known as Breit interaction treated in the lowest order of the fine structure constant and is due to exchange of a transverse photon in two-electron interactions. The Breit term is treated as a first-order perturbation to the unperturbed Dirac Hamiltonian that includes the aforesaid first part of electron interaction. We shall refer to this as the MCDFB approach.

In nonrelativistic theory the orbital angular momentum (L) and the spin (S) are separately good quantum numbers. But in the relativistic theory parity and the total angular momentum (J) are constants of motion. We have to consider several (JJ) configurations for a system where LS coupling scheme is appropriate which is true even at the Hartree-Fock level. This aspect has given rise to a multi-configurational Dirac-Fock scheme that rests on a very involved analysis. The use of MCDFB approach particularly for a large and complex system like a molecule or a solid is a formidable task. Therefore there is a need for a theory based on a local approximation like Slater's X-α method (Slater 1974; Connolly 1977) or more correctly a

relativistic density functional theory (MacDonald and Vosko 1979; Rajagopal 1980; Das *et al* 1980) based on the Hohenberg-Kohn theorem. The basic aim of this approach is to obtain an effective one-body density-dependent potential which should be a reasonable representation for a many-particle interacting system, particularly in the ground state. One distinct advantage of this local density approach over the MCDFB scheme is that the exchange-correlation interaction can be treated in a self-consistent manner instead of a perturbative approach as in the MCDFB case.

In a relativistic situation a quantum electrodynamical correction due to transverse photon-electron interaction (TPE) is important. When two Dirac electrons interact through a transverse photon, the exchange force between the electrons becomes repulsive unlike ordinary Coulomb exchange. The physics of the TPE interaction has been extensively discussed in the literature in the context of high density matter (Salpeter 1961; Jancovici 1962). Recently the present author (Das 1980) calculated the TPE energy in the local density approximation (LDA) for several closed shell atoms. It is worthwhile to point out that when one makes a further approximation to the TPE interaction by neglecting the energy of the exchanged photon in the denominator of the expression of the TPE term (Brown and Ravenhall 1951, Jancovici 1962) one obtains the Breit interaction. In relativistic atomic physics the Breit interaction has been amply used (Mann and Johnson 1971). It contains two parts, one is known as the Gaunt interaction derived from two Dirac currents and the second part is known as retardation derived from the Hamiltonian of Darwin. More recently Grant and Mackenzie (1980) incorporated full transverse interaction in their non-local atomic structure calculations.

In the local density approximation we have calculated both the transverse and the Breit potentials (figure 1). It is found that the Breit potential is deeper than the TPE presumably because we have ignored the exchanged-transverse photon energy in the energy denominator which has made the Breit energy larger than that of the TPE (Das 1982). Since the potential is obtained as the density derivative of energy the Breit potential is deeper than the TPE one. In the non-local analysis the difference between the Breit and the TPE energies is quite small (Grant and Mackenzie 1980)
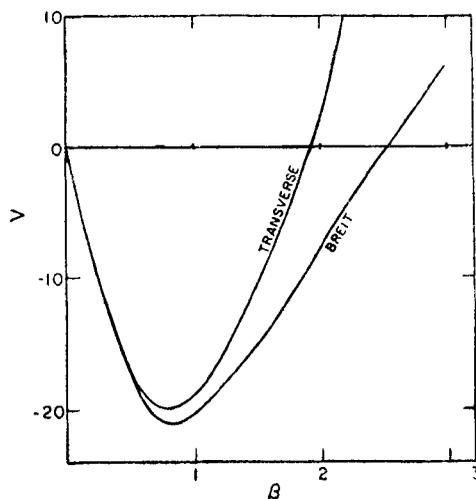

Figure 1. Breit potential and transverse potential shown as a function of β, the ratio of momenta of electron and photon.

contrary to our LDA results. This may be due to certain non-local effects which need further investigation.

As regards correlation contribution, this is considered to be the left-out part of the interactions beyond the mean Hartree-Dirac field. Several theoretical methods are available to calculate correlation energies involving heavy computational efforts. Such methods are non-local and are known as the configuration interaction scheme. Considerable simplification is attained if one adopts an LDA of the electron gas model as in the case of exchange. Considerable literature is available on the calculation of correlation energies in the non-relativistic cases (see for example, Kohn and Vashishta 1982, Singwi and Tosi 1982). It is well known that in the LDA the correlation contribution is over-estimated. Cowan (1981) has an improved interpolation scheme over his earlier one for high densities in the non-relativistic framework. Using his formula the correlation energy for Yb atom is -3.04 Hartree atomic units and the correlation contribution to the K-shell binding is -0.09 a.u. (Mann and Waber 1973). From table 2 of Mann and Waber it seems clear that the correlation contribution is negligible for inner shells whereas it is not so for outer shells. We have considered a relativistic electron gas model and have estimated the correlation energy by incorporating transverse photon contribution (Das 1981b). For Hg atom we obtain the correlation energy to be -3.5 a.u., a contribution of 10^{-4} to the total energy. In view of the above any significant effect of correlation on the inner shells may be ruled out. We shall come back later to this point in the context of Δ SCF.

2. Outline of the theory

In the present paper we adopt the self-consistent local density functional formalism (SCRDF) (Das *et al* 1980). In the past, Huang *et al* (1976) carried out relaxed orbital binding energy calculations. Their method is hybrid in which they calculate wavefunctions in the relativistic local density approximation but by using Kohn-Sham exchange potential. They then calculated energies exactly using these wavefunctions and included the Breit term and Lamb shift as perturbative corrections. In our SCRDF method the TPE included exchange potential is very different from the nonrelativistic Kohn-Sham or X-α type exchange potentials (Das 1981a). In the deep interior of an atom where the electron density is very high, the TPE contribution makes the exchange potential positive. In figure 2 we display the relativistic and Kohn-Sham non-relativistic exchange potentials for Hg atom where the above distinction can be seen.

In order to obtain the ground-state energy or binding energies in an atom one has to solve the following equations in a self-consistent manner.

$$H\psi_i \equiv [c\alpha \cdot p + \beta c^2 + V_{\text{eff}} [n(\vec{r}), \vec{r}]] \psi_i = \epsilon_i \psi_i, \tag{1}$$

$$V_{\text{eff}} [n(\vec{r})] = -\frac{Z}{r} + \int \frac{n(\vec{r}') \, d\vec{r}'}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{xc} [n(\vec{r})]}{\delta n(\vec{r})}, \tag{2}$$

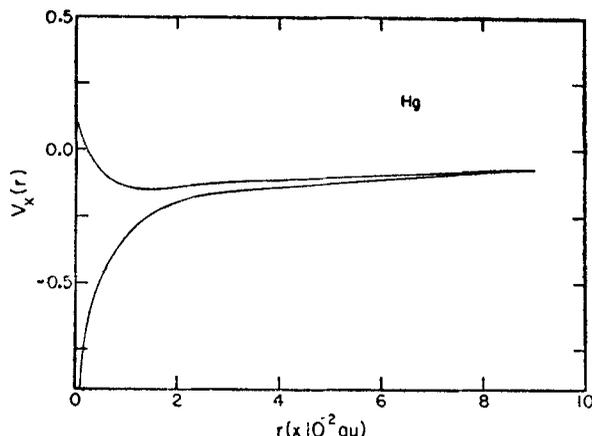and $$n(\vec{r}) = \sum_i^{\text{occ}} |\psi_i(\vec{r})|^2. \tag{3}$$

Figure 2. The self-consistent exchange potential for mercury. The lower curve is for the non-relativistic $X-\alpha$ potential while the upper is for the relativistic one (Hartree atomic units used).

Quantities in (1) to (3) have their usual meanings (Das *et al* 1980). E_x in (2) is the exchange-correlation (in the present case exchange only) energy given by

$$E_x\left[n\left(\vec{r}\right)\right] = E_x^{NR}\left[n\left(\vec{r}\right)\right] \left\{1 - \frac{3}{2}\left(\frac{\beta\left(\beta^2+1\right)^{1/2} - \sin h^{-1}\beta}{\beta^2}\right)^2\right\} \tag{4}$$

where $\beta = (3\pi^2 n)^{1/3}/c$, c being the velocity of light and E_x^{NR} is the nonrelativistic exchange energy. Note that we use Hartree a.u.

This formalism has been employed to calculate the total energies of several closed shell atoms (Das 1980) and the results are compared with non-local Dirac-Fock calculations giving reasonable agreements. The eigenvalues obtained from the above self-consistent equation (1) are somewhat fictitious and do not represent physical energies (Kohn and Vashishta 1982) as one obtains through Hartree-Fock or Dirac-Fock method in conjunction with Koopmans' theorem. Therefore binding energies are often calculated by the Δ SCF method (Rosen and Lindgren 1968). In this method the total energy of a neutral atom is calculated by incorporating the effective potential of the groundstate density. The total energy of an ion with a hole in a particular orbital is then calculated following the same prescription (Rosen and Lindgren 1968). In the latter situation the ion with a hole is considered to be in a quasi-stationary state, therefore the density functional theory is approximately used. The difference of these two energies gives the binding energy of the electron in the orbital in which there was a hole. It is important to note that while calculating the energy of the ion, the hole is not frozen but it relaxes so that the electron density adjusts to the presence of the hole. This procedure is also known as the relaxed orbital method (Huang *et al* 1976).

3. Results and discussion

3.1 *Core-electron binding in mercury atom*

We have calculated binding energies of several core electrons in Hg atom. Hg is a closed shell atom for which LDA is suitable. There exist nonlocal Dirac-Fock

calculations (McGilp and Weightman 1980) for binding energies. Besides, the gas phase data for Hg are also avilable from the high resolution ESCA measurements (Siegbahn *et al* 1967).

In table 1 we present the core electron binding energies for Hg. The values of relaxed orbital binding energies with Kohn-Sham potential only are tabulated together with the TPE contributions in both the frozen and the relaxed configurations. We also give the calculated relaxed orbital binding energies due to McGilp and Weightman (1980) which include only the Breit corrections. These values are given in order to compare similar physical quantities (electric and Breit or transverse). McGilp and Weightman (1980) showed that their DFB results are in excellent agreement with the Dirac-Slater-Breit results of Huang *et al* (1976). Both these approaches are self-consistent at the non-relativistic level so far as exchange is concerned and the Breit term is treated as a perturbation. In our approach the TPE term which is more general than the Breit term is included in the self-consistent potential. The Lamb shift corrections available for some inner shell orbitals are also given in table 1. After adding the Lamb shift corrections to the corresponding quantities the contribution to the binding energies could be compared with the experimental values (table 1). It is found that in most cases our binding energies in the frozen configurations are closer to the DFB results when compared with the relaxed ones. The difference between the energies in these two configurations is known as the rearrangement energy. For 1*s* and 2*s* orbitals the rearrangement energies are 101 and 60 eV respctively. The next correction considered is the Lamb shift (Desiderio and Johnson 1971). It constitutes two parts: (i) vacuum polarization correction, essentially due to nuclear Coulomb field and is calculated as an expansion in (αZ), (ii) self-energy correction, arising out of emission and reabsorption of photons by a moving electron. Cheng and Johnson (1976) obtained this correction numerically for the *K* shell binding energies for several heavy atoms. On adding these McGilp and Weightman (1980) obtained excellent agreement with the experimental values.

Table 1. Relaxed orbital energies for mercury (in eV).

Levels	Kohn-Sham (relaxed)	Present (frozen)	Present (relaxed)	DF + Breit (McGilp and Weightman 1980)	Lamb-Shift	Expt.
	($-$)	($-$)	($-$)	($-$)	($+$)	($-$)
1*s*	83598	83235	83134	83254	155	83108
2*s*	14804	14790	14730	14883	24	14844
2*p*	14248	14245	14180	14215	2	14214
2$\bar{p}$	12277	12294	12233	12292		12289
3*s*	3517	3535	3501	3583		3567
3*p*	3252	3274	3239	3292		3284
3$\bar{p}$	2817	2842	2809	2860		2852
3*d*	2380	2413	2376	2398		2390
3$\bar{d}$	2287	2319	2283	2303		2300

The Lamb-shift contribution for 1*s*, 2*s* and 2*p* are obtained from Huang *et al* (1976) which are to be added to the corresponding binding energies in the present calculations and also to that of McGilp and Weightman (1980).

3.2 *K-shell binding*

Two sets of Δ SCF calculations were performed for the K shell binding of almost all the closed shell atoms. The first is the SCRDF calculations with Kohn-Sham exchange potential and the second is another SCRDF calculation with relativistic exchange potential (equation (4)). In figure 3 we have presented the results. The quantities along the y-axis $\% \, E_K$ show the percentage of departure of calculated values of K shell binding energy from that of experiments. The latter are used from the tables of Bearden and Burr (1967) and Porter and Freedman (1978). These are very high precision data available from x-ray and internal conversion spectroscopies. The straight line connecting small dots is for the non-relativistic Hartree-Fock calculations of Froese-Fischer (1977) and the line connecting the crosses is the Dirac-Fock results of Desclaux (1973). In general one believes that the conventional Hartree (Dirac)-Fock eigenvalues in conjunction with Koopmans' theorem represent the orbital binding energies. Therefore we have used these calculated data from the tables of Froese-Fischer (1977) and Desclaux (1973).   But from the work of Fricke *et al* (1972) it is well known that the Δ SCF binding energy takes into account the rearrangement or relaxation arising due to creation of a hole in a particular orbital.   In the Δ SCF procedure only static or monopole type of relaxation is included.   There are further many-body effects like dynamical relaxation arising out of virtual Auger processes (Wendin 1979).   To our knowledge there are Δ SCF Dirac-Fock calculations for some atoms (Fricke *et al* 1972, McGilp and Weightman 1980; Grant and Mackenzie 1980), though the method
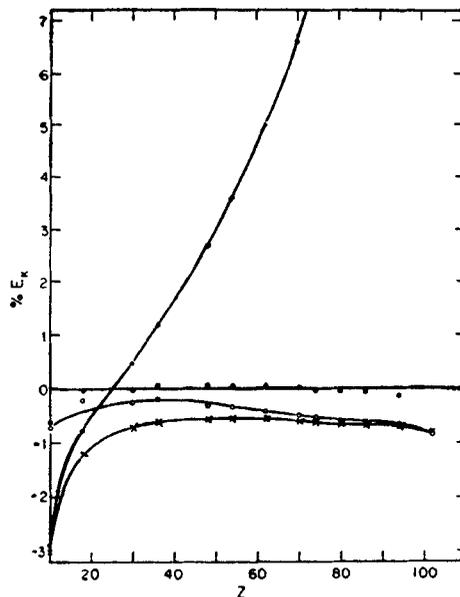
Figure 3. $\% \, E_K$ is the percentage of departure of calculated K shell binding energy from experiments, i.e. $(E^K_{exp} - E^K_{th}) \, / \, E^K_{exp} \times 100$.

The departure of various calculations are shown as a function of atomic number Z. .—.—. non relativistic, x—x—x DFB, O–O–O SCRDF Kohn-Sham, ●●● SCRDF relativistic.   Experimental data for *Rn* and after, are used from Porter and Freedmann (1978) while all others are used from Bearden and Burr (1967).

and the program are readily available. If the rearrangement energy is added to the Dirac-Fock binding energies the departure as shown in figure 3 will be substantially reduced. The non-relativistic results of Froese-Fischer (1977) show reasonable departure from experiment for atoms having $Z<20$. In this range the departure is essentially due to correlation whose importance is well understood in non-relativistic atomic physics (Cowan 1981; Froese-Fischer 1977). Of course one should not use non-relativistic theory for high Z atoms.

Our first set of calculations of SCRDF with Kohn-Sham potential is shown by open circles in figure 3. These results are closer to the experiment than the Dirac-Fock results (see also Fricke and Soff 1977). The second set of calculations of SCRDF with the relativistic exchange potential is shown by heavy dots. As mentioned before this potential includes the TPE contributions unlike Kohn-Sham potential. In DF results of Desclaux (1973) shown by crosses the magnetic part of the Breit term is included. Figure 3 shows that the SCRDF and DFB results differ nearly by a constant. If the relaxation and Lamb shift corrections are added to the DFB results it should yield a better agreement compared to ours as can be seen from Zn, Cd, Hg and Fm atoms (Das 1981a, 1982).

There are discrepancies in our calculated values when compared with experimental values. One knows that DFB method is a more accurate method but it involves an order of magnitude more computer time. This difficulty is substantially reduced by resorting to the LDA. Therefore in our view the discrepancies may be attributed to the non-locality and further many-body effects (like dynamical relaxation etc.).

References

Bearden J A and Burr A F 1967 *Rev. Mod. Phys.* **39** 125
Brown G E and Ravenhall D G 1951 *Proc. R. Soc. (London)* **A208** 552
Cheng K T and Johnson W R 1976 *Phys. Rev.* **A14** 1943
Connolly J W D 1977 in *Semiempirical methods of electronic structure calculations* Part-A (ed.) G A Segal (New York: Plenum) 105
Cowan R D 1981 *Theory of atomic structure and spectra* (Berkeley: Univ. of California Press)
Das M P 1980 *Int. J. Quantum Chem.* **S14** 66
Das M P 1981a *Phys. Rev.* **A23** 391
Das M P 1981b Sanibel Quantum Chem. Symposium (unpublished)
Das M P 1982 *Int. J. Quantum Chem.* **21** 845
Das M P, Ramana M V and Rajagopal A K 1980 *Phys. Rev.* **A22** 9
Desclaux J P 1973 *Atomic Data and Nuclear Data* **12** 311
Desclaux J P 1980 *Phys. Scr.* **21** 436
Desiderio A M and Johnson W R 1971 *Phys. Rev.* **A3** 1267
Fricke B, Desclaux J P and Waber J T 1972 *Phys. Rev. Lett.* **28** 714
Fricke B and Soff G 1977 *Atomic Data and Nuclear Data* **19** 83
Froese-Fischer C 1977 *The Hartree-Fock method for atoms* (New York: Wiley)
Grant I P and Mackenzie B J 1980 *J. Phys.* **B13** 2671
Huang K N, Aoyagi M, Chen M H and Craseman B 1976 *Atomic Data and Nuclear Data* **18** 243
Jancovici B 1962 *Nuovo Cimento* **25** 429
Kohn W and Vashishta P 1982 in *Theory of inhomogeneous electron gas* (eds) S Lundqvist and N H March (New York: Plenum)
MacDonald A K and Vosko S H 1979 *J. Phys.* **C12** 2977
Mann J B and Johnson W R 1971 *Phys. Rev.* **A4** 41
Mann J B and Waber J T 1973 *Atomic Data* **5** 201
McGilp J F and Weightman P 1980 *J. Phys.* **B13** 1953

Porter F T and Freedman M S 1978 *Phys. Chem. Ref. Data* **7** 1267
Rajagopal A K 1980 *Adv. Chem. Phys.* **41** 59
Rosen A and Lindgren I 1968 *Phys. Rev.* **176** 114
Salpeter E E 1961 *Ap. J.* **134** 669
Siegbahn K *et al* 1967 ESCA Almqvist and Wiksells, Uppsala, Sweden
Singwi K S and Tosi M P 1982 in *Solid State Physics* (eds.) H Ehrenreich, F Seitz and D Turnbull
      (New York: Academic Press)
Slater J C 1974 *The Self-consistent field for molecules and solids* (New York: McGraw Hill) Vol. 4
Wendin G 1979 *Int. J. Quantum Chem.* **S13** 659