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Calculation of relativistic self-consistent-field wave functions with local-density approximations. Core-exchange polarization calculation for free alkali-metal atoms

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Core-exchange effects in free atoms have been examined through the determination of the spin density at the nucleus of (^2S) Li, Na, Rb, and Cs atoms. The use of relativistic corrections and of different local-spin-density approximations is evaluated in both restricted and spin-polarized self-consistent-field wave functions.

I. INTRODUCTION

Recently, an investigation on core-exchange polarization (CEP) effects in free atoms was reported in order to test the ability of the $X\alpha$ method to predict correctly the atomic hyperfine structure or the Knight shift in metals via the Fermi contact term.[1] Unrestricted Hartree-Fock-Slater (UHFS) calculations were performed for 15 elements and the results were compared to unrestricted Hartree-Fock (UHF) results, and, when available, to experimental data. It was concluded that the $X\alpha$ approximation does not reproduce well the CEP effects for each s orbital, though it gives a rather good value (indeed better than UHF) for the total CEP. (Therefore, the correctness of HF results should also be questioned.) Finally, it was suggested that the so-called local-spin-density (LSD) approximation, in which the exchange-correlation potential is given as a functional of the charge density and spin polarization should be tested, while the discrepancy observed for the heavier elements was attributed to relativistic effects.

Let us remember that the Fermi contact term is a function of the spin density at the nucleus (SDN), i.e.,

$$\rho^S(0)=\sum_{i=1}^{n}[\,|\psi_{is}^{\uparrow}(0)|^2-|\psi_{is}^{\downarrow}(0)|^2]\,, \tag{1}$$

in which the atomic orbitals $\psi_i^{\uparrow}$ or $\psi_i^{\downarrow}$ are self-consistent solutions to the one-electron equation (in a.u.):

$$\left[-\frac{1}{2}\nabla^2-\frac{Z}{r}+\int\frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,'-V_X+H_m+BH_D\right]\psi^{\uparrow}=\epsilon\psi^{\uparrow}\,, \tag{2}$$

where H_m+BH_D are relativistic corrections (mass-velocity plus Darwin terms, according to Wood and Boring[2]), and V_X is the exchange potential.

The electronic density at the nucleus (EDN) is defined similarly,

$$\rho(0)=\sum_{i}^{n}|\psi_{is}^{\uparrow}(0)|^2+|\psi_{is}^{\downarrow}(0)|^2\,, \tag{3}$$

and is directly connected to the Mössbauer isomeric shift. Equation (2) is solved numerically with the spherically averaged potential on a Herman and Skillman mesh (400 points).[3]

In this paper a large-scale comparison of different schemes to approximate the exchange correlation potential V_X is made on a limited number of elements. The following approximations are used:

(a) The original $X\alpha$ approximation[4] in which the Slater exchange potential $V_X=3[3/(4\pi)\rho(\vec{r})]^{1/3}$ is scaled by the α values, optimized by Schwarz.[5] The use of different α values is tested on the Cs atom for which additional calculations are performed with the (smaller) α value given by the Bass, Green, and Wood formula[6] and the $\alpha=0.70$ value used in many molecular HFS calculations.[7]

(b) The LSD approximation. Among the different formulas given in the literature by Gunnarson, Hedin, Lundqvist, and collaborators[8–11] we selected (arbitrarily) the formula given by Gunnarson and Lundqvist[8]

$$V_{XL}=F(\Delta\rho,V_X)V_X$$

in which $F(\Delta\rho,V_X)$ is a function of V_X and the spin density through an interpolation formula given in Ref. 8.

(c) The so-called local mass-operator approximation (LMOA) of the many-body theory, as proposed recently by Leite and co-workers[12,13]

$$V_{XM}=F(k_1,V_X)V_X$$

in which $F(k_1,V_X)$ is a function of V_X and the Thomas-Fermi wave number through a formula given in Ref. 12.

(d) The spin-dependent $X\alpha$ approximation, as proposed by Gopinathan, Whitehead, and Bogdanovic[14] who demonstrated that α values should be different for majority and minority spin and proposed

$$\alpha^{\uparrow}=C\frac{1/n_{\uparrow}+\frac{1}{2}}{(1/n_{\uparrow}+\frac{1}{3})^{2/3}}$$

in which $n_{\uparrow}$ is the number of spin up electrons and C is a constant set to 0.68 to fit Schwarz values[5] for averaged values of $\alpha_{\uparrow}$ and $\alpha_{\downarrow}$.

For each case, different calculations are performed, namely:

(i) Restricted HFS (RHFS) calculations, in which the

TABLE I. Spin densities at nucleus (SDN) for different (^2S) alkali-metal atoms. Experimental values are taken from Ref. 16. Abbreviations are defined in the text.

Element and local exchange approximation	RHFS SDN		UHFS SDN	
	Nonrelativistic	Relativistic	Nonrelativistic	Relativistic
Li (experimental, 0.2313)				
$X\alpha$	0.2129		0.2212	
LSD	0.2182		0.2325	
LMOA	0.1633		0.1833	
$X\alpha_\uparrow\alpha_\downarrow$ (0.767 88, 0.841 99)			0.2188	
HF (Ref. 16)	0.1637		0.2247	
Na (experimental, 0.7492)				
$X\alpha$	0.7725	0.7181	0.7802	0.7288
LSD	0.8310	0.7724	0.8563	0.7951
LMOA	0.5826	0.5418	0.6144	0.5713
$X\alpha_\uparrow\alpha_\downarrow$ (0.719 62, 0.723 78)			0.7706	0.7146
HF (Ref. 16)	0.5667		0.6469	
Rb (experimental, 2.3446)				
$X\alpha$	1.993	2.382	1.922	2.302
LSD	2.260	2.696	2.274	2.704
LMOA	1.427	1.712	1.440	1.720
$X\alpha_\uparrow\alpha_\downarrow$ (0.708 89, 0.709 06)			1.927	2.305
Cs (experimental, 3.9196)				
$X\alpha$, $\alpha=0.692$	2.581	4.735	2.483	4.552
$\alpha=0.700$	2.604	4.777	2.503	4.593
$\alpha=0.708$	2.628	4.823	2.526	4.634
LSD	3.006	5.492	3.012	5.482
LMOA	1.823	3.376	1.841	3.410
$X\alpha_\uparrow\alpha_\downarrow$ (0.708 03, 0.708 09)			2.526	4.632

TABLE II. Contributions of the different subshells to the SDN of a Cs atom (experimental value, 3.9196) (Refs. 1 and 17).

	$\rho^S_{1s}(0)$	$\rho^S_{2s}(0)$	$\rho^S_{3s}(0)$	$\rho^S_{4s}(0)$	$\rho^S_{5s}(0)$	$\rho^S_{6s}(0)$	$\sum_i^n \rho^S_{is}(0)$	Deviation from experiment (%)	Ratio of relativistic to nonrelativistic value
Nonrelativistic calculations									
$X\alpha$, $\alpha=0.692$	0.018	0.001	−0.001	−0.005	−0.123	2.592	2.483	−37	
$\alpha=0.700$	0.018	0.001	−0.001	−0.005	−0.125	2.615	2.503	−36	
$\alpha=0.708$	0.018	0.001	−0.001	−0.005	−0.128	2.640	2.526	−35	
$\alpha_\uparrow$ and $\alpha_\downarrow$	0.018	0.001	−0.001	−0.005	−0.127	2.640	2.526	−35	
LSD	0.018	0.001	−0.001	−0.005	−0.083	3.081	3.012	−23	
LMOA	0.018	0.001	−0.001	−0.004	−0.76	1.903	1.841	−52	
Relativistic calculations									
$X\alpha$, $\alpha=0.692$	0.015	0.003	−0.002	−0.008	−0.197	4.741	4.552	+16	1.83
$\alpha=0.700$	0.017	0.003	−0.002	−0.008	−0.201	4.784	4.593	+17	1.83
$\alpha=0.708$	0.019	0.003	−0.002	−0.008	−0.204	4.828	4.634	+18	1.83
$\alpha_\uparrow$ and $\alpha_\downarrow$	0.019	0.003	−0.002	−0.008	−0.207	4.829	4.632	+18	1.83
LSD	0.010	0.004	−0.002	−0.006	−0.136	5.612	5.482	+40	1.82
LMOA	0.028	0.004	−0.002	−0.007	−0.125	3.512	3.410	−13	1.85

CEP is constrained to depend only on the open shells; then for the ground state of most of the atoms, only the last occupied s orbital is involved and one gets

$$\rho^S(0)=|\psi^{\uparrow}_{ns}(0)|^2$$

(strictly speaking, there is no CEP in this case).

(ii) In UHFS calculations, the core electrons with spins parallel to those of unpaired electron(s) may experience stronger total exchanges forces than core electrons of opposite spin; accordingly each s shell may contribute to the CEP. The spin density at the nucleus is then given by Eq. (1).

In nonrelativistic calculations both H_m and BH_D terms of Eq. (2) are neglected. Moreover, if $V_X=V_{X\alpha}$, Eq. (2) reduces to the well-known $X\alpha$ equation which can be solved numerically by use of Herman and Skillman programs.[3]

In relativistic calculations, H_m and BH_D terms of Eq. (2) are taken into account self-consistently through Wood and Boring's algorithm.[2]

II. RESULTS AND DISCUSSION

The calculations are performed on a limited number of atoms among those for which experimental values are available, namely, four alkali-metal elements in their ^2S term (Li,Na,Rb,Cs). The results, which are gathered in Tables I and II deserve some comments.

(1) The LMOA leads always to too small values (10—50%); for heavy elements, this discrepancy is always smaller in relativistic calculations than in nonrelativistic calculations. As there is no free parameter in the formulation to fit some physical property (like the α value in the $X\alpha$ scheme), this is probably the price to pay for the use of an *ab initio* approximation.

The LSD approximation leads always to larger SDN values than $X\alpha$ schemes. For Rb and Cs atoms the experimental values are bracketed by nonrelativistic and relativistic results while the SDN of Na is overestimated in both LSD calculations.

The experimental values are also bracketed by nonrelativistic and relativistic calculations through $X\alpha$ approximations. However, the experimental value is only slightly overestimated by relativistic calculations (less than 2%), the case of Cs (which is discussed later on through this paper) excepted.

(2) Let us remember that both LSD or LMOA approximations cannot be considered only as effective $X\alpha$ calculations, because the exchange-correlation factor $F(\Delta\rho,V_x)$ or $F(k,V_x)$ is r dependent. This dependence is one of the reasons for the superiority of the LSD schemes over the $X\alpha$ approximation. An example of the variation of the $F(\Delta\rho,V_x)$ factor with r in the Hedin-Lundqvist scheme[10] is given in Ref. 18 for P atoms; it is clearly shown that this factor [called $\alpha_{\rm HL}(r)$] is smaller than Schwarz's α value for small-r values, and greater than α for r values larger than about 1 a.u.

(3) The use of spin-dependent α values could be expected to yield larger effects in light element calculations than in heavy elements, for which the $\alpha_\uparrow$ and $\alpha_\downarrow$ values tend to the same limit. The results which can be seen in Table I show clearly this trend: The deviation of the spin-dependent α results is small (from $X\alpha$ results) for the Li or Na atoms, and negligible in the case of the Cs atom. In fact, the SDN of Cs looks very sensitive to the α value itself rather than to the tiny difference between $\alpha_\uparrow$ and $\alpha_\downarrow$. This result appears very clearly in Table II in which are reported the contributions of each Cs shell to the SDN value.

(4) For heavy elements (Rb,Cs) the relativistic corrections led to an increase of the SDN, but to a decrease of the SDN of the sodium atom, a result which was unexpected. This result is independent of the exchange-correlation approximation chosen. This may be correlated to the change in the wave-function expansion at small r induced by the inclusion of the self-consistent field relativistic corrections.

For all exchange-correlation schemes, the relativistic corrections in RHFS calculations induce a constant relative change into the SDN. The ratio of the relativistic SDN value over the nonrelativistic one is thus equal to 0.93, 1.19, and 1.84 (±0.01) for Na, Rb, and Cs atoms, respectively. On the other hand, this ratio may fluctuate in UHFS calculations, according to the selected exchange-correlation potential used (see Table III).

The ratio of the UHFS SDN value over the RHFS one is rather constant between the relativistic calculation and the nonrelativistic one. This ratio may fluctuate (6%) according to the different local exchange approximations used.

In UHFS calculations the contributions of the inner shells to CEP in the SDN may be slightly different according to the various local exchange approximations, and also, for a given exchange approximation, between relativistic and nonrelativistic calculations. However, the inner-shell contribution is always a small part of the total SDN.

(5) The importance of the relativistic corrections is clearly seen in Table III where the reported ratios of relativistic values over nonrelativistic values of both SDN and EDN are given. These values are compared to the corrections to nonrelativistic values proposed by Pyykkö and Pajanne[19] for the SDN and by Shirley[15] for the EDN. Let us recall that the ratios have been found to be rather insensitive to the exchange-correlation approximation scheme used. It is worth noting that the ratios may be quite different for SDN and EDN (e.g., 1.83 for Cs SDN and 1.676 for Cs EDN). Pyykkö's prediction of Rb SDN ratios is in good agreement with our value, while his prediction of the Cs SDN ratio is clearly smaller than ours, leading in both cases to SDN values which compare fairly well to experiment. On the contrary, Pyykkö's formula is unable to give the 0.93 ratio we find for Na and which agrees well with experiment. Finally Shirley's values clearly overestimate the relativistic corrections to the EDN values.

In a recent paper,[20] Kolar and Farkas calculated the Fermi contact term in free light atoms. They used the LSD formalism through the Vosko-Wilk-Nusair LSD ap-

TABLE III. Incidence of the relativistic corrections: Ratio of the relativistic values to the nonrelativistic values.

	SDN		EDN	
Element	RHFS calculations[a,b] (this work)	Pyykkö's values[c]	RHFS calculations[a,d] (this work)	Shirley's factors[e]
Na	0.93	1.0138	0.926(770)	1.06
Rb	1.19	1.176–1.170	1.145(40 100)	1.63
Cs	1.83(1.82–1.85)	1.463–1.438	1.676 (196 900)	2.68

[a] A change in the local exchange correlation scheme does not alter the value.
[b] Values in parentheses are UHFS values bounds.
[c] Reference 19; bounds are given among 1*s*-*ns* factor values.
[d] Values in parentheses are relativistic $\rho(0)$ values (in a.u.$^{-3}$).
[e] Reference 15.

proximation[21] and their results show trends similar to our calculations. They also used the so-called self-interaction correction to LSD (Ref. 22) and they concluded that the contact term was not improved by this formalism. Finally, they investigated the incidence of a finite nuclear radius in the calculation of the contact term. Surprisingly, they found this factor to be not negligible, mainly for the lightest elements, but it led to even worse results than those obtained with the common punctual nucleus approximation.

III. CONCLUSIONS

The $X\alpha$ density functional leads to quite good estimations of the SDN if relativistic calculations are performed. In this respect, the use of local spin-density approximations, like Gunnarson and Lundqvist's approximation does not significantly improve the accuracy. Moreover, the quite good estimation of the $X\alpha$ UHFS SDN by the $X\alpha$ RHFS calculation may be pointed out. Finally the sensibility of the $X\alpha$ UHFS SDN to a somewhat slight variation of the α value is pointed out in the particular case of the Cs atom.

IV. CALCULATIONS DETAILS

All the calculations were performed by means of our MS $X\alpha$ program adapted to handle calculations on free atoms through the different options cited in the text. The calculation was reiterated until the relative difference of potential and eigenvalues do not exceed 10^{-4} and 10^{-7}, respectively, between two consecutive iterations. A use of the Latter tail[23] does not affect significantly the results. In all cases the full telescopic Herman and Skillman mesh size (320—360 or 400 points) has been used.

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