Full potential linearized-augmented-plane-wave calculations for 5d transition metals using the relativistic generalized gradient approximation

R. N. Schmid, E. Engel, and R. M. Dreizler

Institut für Theoretische Physik, Universität Frankfurt, Robert-Mayer-Str. 8-10, D-60054 Frankfurt/Main, Germany

P. Blaha and K. Schwarz

Institut für Technische Elektrochemie, Technische Universität Wien, Getreidemarkt 9/158, A-1060 Wien, Austria

Abstract

The importance of relativistic exchange-correlation effects for the description of $5d$ transition metals is examined by application of a relativistic extension of the Perdew-Wang generalized gradient approximation to Pt and Au, using a full potential linearized-augmented-plane-wave approach. It is found that the relativistic corrections to exchange affect both the band structure and the cohesive properties on the 1% level, while the relativistic corrections to correlation can be safely neglected.

I. Introduction and Summary of Results

Establishing fully relativistic methods for *ab-initio* electronic structure calculations in atomic, molecular and solid state physics has been as a major activity during recent years. As density functional theory (DFT) has proven to be rather successful in nonrelativistic applications [1–3], its relativistic version [4–8] is a promising tool for the investigation of systems with heavy elements. The crucial quantity of the DFT formalism is the exchange-correlation (xc) energy functional $E_{xc}[n]$, which, together with the corresponding single particle xc-potential $v_{xc}(\boldsymbol{r}) = \delta E_{xc}[n]/\delta n(\boldsymbol{r})$, provides the DFT description of xc-effects.

A considerable amount of work has been devoted to the development of suitable approximations for $E_{xc}[n]$, which are efficient and at the same time reliable

and sufficiently accurate. For a long time, the nonrelativistic local density approximation (LDA), based on the homogeneous electron gas (HEG), has been the standard for $E_{xc}[n]$ in both nonrelativistic and relativistic calculations. During the last years, gradient corrections to the LDA have attracted widespread interest. Nonrelativistic generalized gradient approximations (GGAs) [9,10] have improved the quality of DFT results for a variety of systems, most notably for the structural properties of small molecules [11,12] and metallic iron [13]. However, it has become clear by now that for solids GGA functionals are not systematically superior to the LDA [14–20]. In particular, while GGA functionals are remarkably successful for $3d$ transition metals [13,14], they overcorrect the LDA's errors for $5d$ transition metals [17,18,20]. This even worsens the agreement with experiment for some systems, with Gold being the prime example.

On the other hand, Gold shows large relativistic effects (the *Gold maximum* — see eg. [21]). In fact, it has been explicitly demonstrated that for Au relativistic and xc-effects are nonadditive [22]. This is most obvious for its electron affinity: While a nonrelativistic CI-calculation [23] gives a value of 1.02 eV and a fully relativistic Coupled-Cluster calculation [22] yields 2.28 eV, the corresponding nonrelativistic and relativistic Hartree-Fock values are 0.10 eV [22] and 0.67 eV, respectively. Thus immediately the question arises to which extent the GGA's failure for metallic Au is due to the neglect of relativistic xc-contributions in $E_{xc}[n]$.

In the atomic context the need for relativistic corrections to $E_{xc}[n]$ is obvious and has led to the development of the relativistic LDA (RLDA) [5,6,24]. On the basis of RLDA calculations for metallic Au and Pt, MacDonald et al. [25,26] have concluded that in solids relativistic contributions to $E_{xc}[n]$ can produce small but significant modifications of measurable quantities, as eg. the Fermi surface area. On the other hand, it has been shown [7] that the RLDA suffers from several shortcomings, eg. from a drastic overestimation of transverse exchange contributions, thus making the RLDA a less reliable tool than its nonrelativistic counterpart. As relativistic corrections are clearly misrepresented by the RLDA, it seems worthwhile to reinvestigate the role of relativistic xc-effects in solids on the basis of a more accurate form for $E_{xc}[n]$.

For this purpose, the generalization of the GGA approach to the relativistic domain (RGGA) [27,28] offers itself. An x-only form of the RGGA [27], based on the Becke GGA [9], has been shown to correct the RLDA's failure for the description of transverse exchange, thus leading to rather accurate results for atomic systems. Recently, also a relativistic extension of the Perdew-Wang GGA (PW91) [10] has been derived [28], including a relativistic form of the correlation energy functional. The latter RGGA thus provides an ideal starting point for the study of the importance of relativistic xc-effects in solids.

In this contribution we present a comparative analysis of (R)LDA and (R)GGA results for both the band structure and the cohesive properties of metallic Au and Pt, as examples for systems for which relativistic xc-effects are expected to be prominent. We find that the relativistic corrections resulting from the RGGA are smaller than those produced by the RLDA. Nevertheless, the corrections are still visible in the band structure, the changes of the valence levels being of the order of 1%. On the other hand, the predictions for lattice constants are only marginally affected when going from the nonrelativistic to the relativistic form of a given type of xc-functional, in contrast to the well-known lattice expansion due to the inclusion of gradient corrections. Cohesive energies experience somewhat larger shifts, i.e. they are reduced by about 1% for both Au and Pt. These relativistic modifications are not only too small in their absolute magnitude in order to close the gap between nonrelativistic GGA results and experiment [17,18,20], but even go into the wrong direction. The results are in agreement with a recent, weakly relativistic study of diatomic molecules involving Au, which has led to the conclusion that relativistic corrections to $E_{xc}[n]$ have only a very limited impact on the structural properties of molecules [29].

The inclusion of relativistic corrections in the GGA thus does not resolve the problems of the GGA with the $5d$ transition metals, suggesting that the nonlocal contributions to $E_{xc}[n]$ beyond the first density gradient are important in these systems. In addition, the spin-orbit coupling of the valence electrons, neglected in this work, could be partially responsible for this discrepancy [25,30].

II. Theoretical background

An extensive review of relativistic DFT has recently been given in [8]. For this reason we restrict ourselves to presenting only the relevant details of the xc-functionals used in this work. Among the various xc-functionals proposed for DFT calculations the nonrelativistic LDA,

$$E_{xc}^{LDA} = \int d^3r \; e_{xc}^{HEG}(n) \;\; , \tag{1}$$

plays a central role as it is the most simple approximation and also serves as basis for the construction of most nonlocal functionals. While the exchange contribution of the HEG can be calculated exactly, the correlation energy of the HEG is only known from Monte-Carlo studies [31,32], for which a number of slightly different parametrizations have been suggested [31–34]. As nonrelativistic LDA correlation functional we here use the Vosko-Wilk-Nusair (VWN) parametrization [33].

The RLDA is obtained from the relativistic HEG [5,6,24] and can be written as

$$\begin{aligned} E_{xc}^{RLDA}[n] &= \int d^3r \; e_{xc}^{RHEG}(n) \\ &= \int d^3r \; \left[e_x^{HEG}(n)\Phi_{x,0}(\beta) + e_c^{HEG}(n)\Phi_{c,0}(\beta) \right] \; , \end{aligned} \tag{2}$$

where β is defined by

$$\beta = \frac{(3\pi^2 n)^{1/3}}{mc} \; , \tag{3}$$

and both the exchange and correlation energy densities of the relativistic HEG have been decomposed into their respective nonrelativistic limits and relativistic corrections factors $\Phi_{x/c,0}(\beta)$. While $\Phi_{x,0}$ has been known for quite some time [35],

$$\Phi_{x,0}(\beta) = 1 - \frac{3}{2}\left[\frac{\sqrt{1+\beta^2}}{\beta} - \frac{\mathrm{Arsh}(\beta)}{\beta^2} \right] , \tag{4}$$

$\Phi_{c,0}$ has only been evaluated within the RPA [24,7]. We have parametrized the resulting correction factor as

$$\Phi_{c,0}^{RPA}(\beta) = \frac{1 + a_1\beta^3\ln(\beta) + a_2\beta^4 + a_3(1+\beta^2)^2\beta^4}{1 + b_1\beta^3\ln(\beta) + b_2\beta^4 + b_3[A\ln(\beta)+B]\beta^7} \; , \tag{5}$$

utilizing the known high-density limits of both the relativistic RPA (RRPA) [36] as well as its nonrelativistic counterpart,

$$e_c^{RRPA}/n \underset{n\to\infty}{\longrightarrow} -0.197464 \; \frac{(1+\beta^2)^2}{\beta^3} \tag{6}$$

$$e_c^{RPA}/n \underset{n\to\infty}{\longrightarrow} -[A\ln(\beta)+B] \; . \tag{7}$$

With the parameters given in Table 1 the numerical data for $\Phi_{c,0}^{RPA}$ are reproduced with an accuracy better than 10^{-3}. Note that for small β the numerical results clearly allow the extraction of a $\beta^3\ln(\beta)$-dependence of the lowest order weakly relativistic contribution, rather than a β^2-dependence which one might have expected. To further check the accuracy of the parametrization (5) we have applied both (5) and a direct spline interpolation of the numerical data to atoms, finding differences for eigenvalues to be on the $0.1 mRy$-level. The form (5) is thus sufficiently accurate for the present purpose. Lacking the full density dependence of all contributions to e_c^{RHEG} beyond the RPA we have used $\Phi_{c,0}^{RPA}$ with the complete nonrelativistic e_c^{HEG} for the RLDA, utilizing the VWN-parametrization for e_c^{HEG} [33].

In the x-only limit the general form of the RGGA is [27]

$$E_x^{RGGA} = \int d^3r \; e_x^{HEG}(n) \; [\Phi_{x,0}(\beta) + g(\xi)\Phi_{x,2}(\beta)] \; , \tag{8}$$

Parameter	Exchange		Correlation	
	$\Phi^L_{x,2}$	$\Phi^T_{x,2}$	$\Phi^{RPA}_{c,0}$	Φ^{GGA}_c
a_1	2.2156	3.5122	−2.44968	1.9407
a_2	0.66967	0.62525	1.91853	0.14435
a_3	—	—	0.0718854	—
b_1	1.3267	1.3313	−1.59583	0.28142
b_2	0.79420	0.10066	1.29176	0.004723
b_3	—	—	0.364044	—

Table 1: Parameter sets for the relativistic correction factors (5,9,10).

with $\xi = [\nabla n/(2(3\pi^2 n)^{1/3} n)]^2$ and $g(\xi)$ being the gradient part of the corresponding nonrelativistic GGA. In [27] the longitudinal (L) and transverse (T) contributions to the x-only energy (compare [7,8]) have been separated, leading to a corresponding decomposition of $\Phi_{x,2} = \Phi^L_{x,2} + \Phi^T_{x,2}$. For both $\Phi^L_{x,2}$ and $\Phi^T_{x,2}$ sufficiently flexible Padé approximants have been used,

$$\Phi^L_{x,2} = \frac{1 + a^L_1\beta^2 + a^L_2\beta^4}{1 + b^L_1\beta^2 + b^L_2\beta^4} \quad ; \quad \Phi^T_{x,2} = \frac{a^T_1\beta^2 + a^T_2\beta^4}{1 + b^T_1\beta^2 + b^T_2\beta^4}\,. \tag{9}$$

The coefficients have been determined by a least squares fit to the exact relativistic x-only energies of a number of closed subshell atoms keeping the form of $g(\xi)$ fixed. For the PW91 GGA this procedure leads to the parameters listed in Table 1 [28]. As has been demonstrated in [28] the resulting RGGA produces much more accurate atomic results than both the RLDA and the corresponding nonrelativistic GGA.

The correlation energy requires a slightly different scheme, as on the one hand $\Phi_{c,0}$ is not known completely, and, on the other hand, some GGAs for correlation [37] are not even based on the LDA. Therefore only one overall correction factor for the complete GGA has been used in [28],

$$E^{RGGA}_c[n] = \int d^3r\ e^{GGA}_c(n, (\nabla n)^2, ...)\ \Phi^{GGA}_c(\beta)\ , \tag{10}$$

keeping the nonrelativistic form $e^{GGA}_c(n, (\nabla n)^2, ...)$ fixed. In view of the fact that the relativistic corrections to atomic E_c are much smaller than those to atomic E_x this less sophisticated approach should be sufficient (compare Section IV). Using again a Padé approximant of the form (9) as ansatz for Φ^{GGA}_c and fitting its coefficients to the most systematic set of atomic relativistic correlation energies available to date (second order perturbation theory results for the Ne isoelectronic series on the basis of the Dirac-Coulomb-Breit

Hamiltonian [38]) one finds the parameters of Table 1 for the PW91 correlation GGA [28]. Again, compared with the RLDA or the nonrelativistic GGA atomic correlation energies are clearly improved by this RGGA.

Eqs.(8-10) with the PW91 parameters of Table 1 define the RGGA used in this work (the longitudinal and transverse components of the x-only GGA have always been combined).

III. Computational details

The calculations for solids have been performed using a full potential linearized augmented plane wave (LAPW) code (WIEN95 [39]). For an extensive discussion of the LAPW method the reader is referred to [40,41]. We only comment on the handling of the Kohn-Sham kinetic energy of the electrons. In the calculations a fully relativistic core is used, whereas the valence electrons are treated in a scalar relativistic approximation (see [42] for details) inside the muffin tins and completely nonrelativistically in the interstitial regime. As for Pt spin-orbit coupling has been shown to be important near high-symmetry lines in the Brillouin-zone [25] this neglect of spin-orbit coupling for the valence electrons may not be justified. However, one would expect the small relativistic xc-contributions studied in this work to be additive to the spin-orbit effects. Thus, while eg. the bands will change when including spin-orbit coupling, our conclusions concerning the size of the relativistic xc-corrections should be unaffected.

For transition elements like Pt and Au the linear orbital extension to the LAPW method [43] has been used. We have employed the procedure proposed in [20], in which the $5p$-states for Au and Pt are included in the core for total energy calculations, but corresponding local orbitals are also included in the basis for the valence states in order to allow the basis functions for the actual valence electrons to orthogonalize to the extended core states.

The convergence of the calculations has been carefully checked by varying the plane wave cutoff and the number of $\boldsymbol{k}$-points used for the Brillouin-zone integration. Employing $(RK)_{min} = 10$ our results were converged to mRy-accuracy. The $\boldsymbol{k}$-integration has been performed using 165 $\boldsymbol{k}$-points in the irreducible Brillouin-zone. Adding further $\boldsymbol{k}$-points affected the total energy by less than $0.1 mRy$. All xc-functionals have been treated identically, so that the differences between the results obtained with the various functionals should be even more accurate than the corresponding absolute values. For the calculation of the cohesive energy of Pt the required atomic ground state energy has been obtained by solving the fully relativistic Kohn-Sham equations for the occupation $[Xe]4f^{14}5d^{9}6s$, using a spherical average for the density. The equilibrium lattice constant has been derived via the standard fitting procedure

Level	Functionals				
	x: LDA	x:RLDA	x: GGA	x:RGGA	x:RGGA
	c: LDA	c:RLDA	c: GGA	c: GGA	c:RGGA
1s1/2	5923.193	5885.536	5928.439	5901.832	5902.042
2s1/2	1044.186	1038.687	1045.009	1040.946	1040.999
2p1/2	1001.487	996.678	1001.983	997.494	997.553
2p3/2	866.695	863.557	867.011	863.952	863.999
3s1/2	246.250	245.104	246.479	245.656	245.670
3p1/2	227.035	226.109	227.162	226.304	226.318
3p3/2	197.296	196.702	197.378	196.799	196.810
3d3/2	165.328	165.043	165.356	165.051	165.061
3d5/2	158.932	158.686	158.956	158.690	158.699
4s1/2	53.238	52.980	53.348	53.172	53.175
4p1/2	45.049	44.860	45.113	44.940	44.943
4p3/2	37.899	37.786	37.969	37.860	37.863
4d3/2	24.486	24.457	24.511	24.478	24.479
4d5/2	23.155	23.133	23.181	23.155	23.157
4f5/2	5.933	5.959	5.924	5.947	5.947
4f7/2	5.652	5.679	5.644	5.667	5.667
5s1/2	7.767	7.724	7.763	7.737	7.737
5p1/2	5.099	5.074	5.093	5.070	5.070
5p3/2	3.869	3.857	3.875	3.864	3.864

Table 2: Core levels ($-\epsilon_{nlj}$) of solid Au relative to the Fermi level for various xc-functionals (in Ry).

to the Murnaghan equation of state [44]. The speed of light has been set to $\alpha = 137.0359895$ and point nuclei have been employed.

IV. Results

We start with a discussion of the role of relativistic xc-contributions for the band structure of Au and Pt on the basis of the RGGA, thus repeating the analysis of MacDonald et al. [25,26] with a more appropriate form for $E_{xc}[n]$. As relativistic effects are most important near the atomic nucleus, first the core levels are analyzed (on the basis of the Kohn-Sham eigenvalues, as usual). Table 2 shows the core levels of Au (relative to the Fermi level) for several xc-functionals, i.e. the nonrelativistic LDA, the RLDA, the nonrelativistic GGA, the RGGA for both exchange and correlation as well as a combination of the

Level	Functionals					Ref. [29]
	x: LDA	x:RLDA	x: GGA	x:RGGA	x:RGGA	x: LDA
	c: LDA	c:RLDA	c: GGA	c: GGA	c:RGGA	c: LDA
1s1/2	5923.389	5885.733	5928.619	5902.013	5902.223	5893.484
2s1/2	1044.379	1038.880	1045.185	1041.122	1041.175	1040.889
2p1/2	1001.679	996.870	1002.160	997.670	997.729	905.731
2p3/2	866.887	863.750	867.187	864.128	864.176	
3s1/2	246.449	245.303	246.662	245.839	245.853	245.782
3p1/2	227.234	226.308	227.345	226.486	226.500	206.230
3p3/2	197.495	196.901	197.560	196.981	196.993	
3d3/2	165.526	165.241	165.538	165.232	165.243	161.632
3d5/2	159.130	158.884	159.138	158.871	158.881	
4s1/2	53.441	53.182	53.533	53.357	53.360	53.314
4p1/2	45.251	45.062	45.299	45.126	45.129	40.233
4p3/2	38.101	37.989	38.155	38.046	38.049	
4d3/2	24.688	24.659	24.697	24.663	24.665	23.901
4d5/2	23.357	23.335	23.367	23.340	23.342	
4f5/2	6.135	6.162	6.110	6.133	6.133	5.953
4f7/2	5.855	5.881	5.830	5.853	5.853	
5s1/2	7.976	7.933	7.954	7.927	7.928	7.952
5p1/2	5.310	5.285	5.286	5.264	5.264	4.442
5p3/2	4.084	4.072	4.073	4.061	4.061	
5d5/2	0.594	0.596	0.580	0.581	0.581	0.511
5d7/2	0.481	0.483	0.468	0.470	0.470	
6s1/2	0.448	0.445	0.430	0.428	0.428	0.442

Table 3: Single-particle levels ($-\epsilon_{nlj}$) of atomic Au for various xc-functionals (in Ry). Also given are the j-averaged weakly relativistic LCGTO results of [29].

RGGA for exchange and the GGA for correlation. All these calculations have been performed for the experimental lattice constant. A comparison with the corresponding single-particle energies of the free Au atom, listed in Table 3, demonstrates immediately that the atomic eigenvalue shifts by relativistic xc-corrections are essentially transferred to the solid without any modification: This is not only true for the innermost levels, but also for the relative stabilization of the $4f$-eigenvalues with respect to the $5p$-levels. Consequently also the overestimation of relativistic effects by the RLDA can be observed: Eg. for the $5s_{1/2}$-level the RLDA shift of $43mRy$ with respect to the nonrelativistic LDA

is almost twice as large as the $26mRy$ difference between the RGGA and the GGA eigenvalues. Comparing the results obtained with the full RGGA with those from the combination of the x-only RGGA with the correlation GGA demonstrates that at least on the present level of sophistication relativistic corrections to the correlation energy functional can be neglected. Even for the innermost levels the corresponding shifts are rather small.

On the other hand, the shift induced by inclusion of relativistic corrections in the x-only GGA is larger than that resulting from the addition of gradient corrections to the LDA: Even for the $5p_{3/2}$-level the eigenvalue difference of $11mRy$ between RGGA and GGA is larger than the $6mRy$ difference between GGA and LDA (for solid Au). The eigenvalues for Pt, which are not explicitly given here, show a similar picture. In view of the fact that in the x-only limit the atomic RGGA eigenvalues are much closer to the exact Kohn-Sham single particle energies [27] than the GGA eigenvalues these substantial core level shifts indicate that an accurate microscopic description of solids requires relativistic contributions to $E_x[n]$.

A similar analysis of the relative importance of gradient and relativistic contributions has been presented by Mayer et al. [29] on the basis of weakly relativistic LCGTO results. The various relative atomic eigenvalue shifts given in [29] are consistent with those extracted from Table 3. The absolute size of the eigenvalues of Ref. [29], on the other hand, allows to estimate the importance of higher order $1/c$-corrections to the kinetic energy. In Table 3 we thus also list the j-averaged LCGTO eigenvalues for the nonrelativistic LDA, which is the only functional used in both [29] and this study. For all core levels the differences between the weakly relativistic LCGTO data and the fully relativistic eigenvalues are of the same order of magnitude as the contributions of the relativistic xc-corrections. On the other hand, for the valence levels the higher order $1/c$-corrections to the kinetic energy lead to roughly 3-5 times larger shifts than the relativistic xc-corrections.

The valence levels for Au obtained with the various xc-functionals for a number of selected $\boldsymbol{k}$-points in the Brillouin-zone are given in Table 4 (all results for the experimental lattice constant). In contrast to the substantial modifications of the core levels, only small effects of the relativistic xc-corrections on the valence levels are found. For instance, at the Γ-point the d-bands are lowered with respect to the s-band by about $2.5mRy$ when going from the GGA to the RGGA. On the other hand, the nonrelativistic gradient corrections, which set the scale for judging the importance of this shift, lower the d-bands with respect to the s-band by about $8mRy$ (see Tables 4a,4c). While the eigenvalue shifts are different at other $\boldsymbol{k}$-points, the relative impact of relativistic and gradient corrections is roughly the same. Although the importance of the latter becomes larger if the lattice constant is relaxed, i.e. if the bands

$\boldsymbol{k}$	$\epsilon_{n,\boldsymbol{k}} - \epsilon_F$					
	a) x: LDA, c: LDA					
W	−454	−393	−393	−253	−123	344
L	−558	−360	−360	−148	−148	−84
Γ	−750	−357	−357	−357	−240	−240
X	−538	−514	−150	−123	−123	63
K	−492	−444	−293	−218	−158	277
	b) x: RLDA, c: RLDA					
W	−456	−395	−395	−255	−125	349
L	−559	−362	−362	−150	−150	−83
Γ	−748	−360	−360	−360	−242	−242
X	−540	−517	−153	−125	−125	64
K	−494	−446	−295	−220	−160	281
	c) x: GGA, c: GGA					
W	−456	−395	−395	−256	−127	349
L	−557	−363	−363	−152	−152	−80
Γ	−745	−360	−360	−360	−244	−244
X	−539	−516	−155	−127	−127	68
K	−493	−446	−294	−222	−162	282
	d) x: RGGA, c: GGA					
W	−457	−396	−396	−258	−129	352
L	−559	−364	−364	−154	−154	−79
Γ	−744	−362	−362	−362	−246	−246
X	−541	−518	−157	−129	−129	68
K	−495	−447	−296	−224	−164	285
	e) x: RGGA, c: RGGA					
W	−457	−396	−396	−258	−129	352
L	−559	−364	−364	−154	−154	−79
Γ	−744	−362	−362	−362	−246	−246
X	−541	−518	−157	−129	−129	68
K	−495	−447	−296	−224	−164	285

Table 4: Valence levels of Au at selected $\boldsymbol{k}$-points relative to the Fermi level for various xc-functionals (in mRy).

corresponding to the lattice constants which give the minimum total energy for the functional of interest are compared, this nevertheless indicates that relativistic xc-corrections are not completely negligible even for valence levels.

Similar to the core levels, the relativistic corrections to eigenvalues calcu-

Functionals		a_0	$-E_{coh}$	$-E_0$(solid)	$-E_0$(atom)
x	c	$[bohr]$	$[eV]$	$[Ry]$	$[Ry]$
LDA	LDA	7.68	4.12	38075.445	38075.132
RLDA	RLDA	7.68	4.09	37997.970	37997.669
GGA	GGA	7.87	2.91	38100.029	38099.815
RGGA	GGA	7.88	2.89	38048.438	38048.225
RGGA	RGGA	7.88	2.89	38049.253	38049.040
expt		7.67	3.78		

Table 5: Lattice constants and cohesive energies of Au obtained from LAPW calculations with various xc-functionals in comparison to experiment [45,20].

Functionals		a_0	$-E_{coh}$	$-E_0$(solid)	$-E_0$(atom)
x	c	$[bohr]$	$[eV]$	$[Ry]$	$[Ry]$
LDA	LDA	7.36	6.76	36873.465	36872.968
RLDA	RLDA	7.37	6.73	36799.369	36798.875
GGA	GGA	7.51	5.34	36897.502	36897.109
RGGA	GGA	7.52	5.30	36848.219	36847.829
RGGA	RGGA	7.52	5.30	36849.005	36848.616
expt		7.40	5.85		

Table 6: Lattice constants and cohesive energies of Pt obtained from LAPW calculations with various xc-functionals in comparison to experiment [45,20].

lated with the RLDA are too large by a factor of 1.5 to 2. Moreover, the inclusion of relativistic corrections in the correlation energy functional has almost no impact on the valence states as can be seen from a comparison of Tables 4d,4e. This then *a posteriori* justifies the rather crude treatment of these contributions in both the RLDA and RGGA.

The situation is somewhat different for Pt, for which the relativistic xc-corrections only affect the s-band in the interior of the Brillouin-zone: Its bottom is shifted upwards by $3mRy$. The absolute and relative positions of the d-bands remain more or less unchanged.

The limited importance of relativistic xc-potentials for the cohesive properties of Au and Pt is demonstrated in Tables 5,6: Lattice constants remain nearly unchanged when one replaces the LDA by the RLDA or the GGA by the RGGA. Also, only a small reduction is observed for the corresponding cohesive energy E_{coh} (evaluated at the lattice constant corresponding to the

energy minimum for the functional of interest). While the total ground state energies change by almost 50 Ry, the energy difference between the solid state and the free atom experiences only a $1 mRy$ shift, which represents roughly 1% of the total cohesive energy. This percentage correction is on the same level as the shifts observed for the valence bands and for the dissociation energy of the Au-dimer [29].

Like its nonrelativistic counterpart, the RGGA predicts lattice constants which are too large by 0.21 *bohr* for Au and 0.12 *bohr* for Pt. The corresponding RGGA cohesive energies are roughly 25% too small for Au and 10% below the experimental value for Pt. Thus the reduction of E_{coh}, which is always found when going from the LDA to the GGA, by far overcorrects the LDA's error, in particular in the case of Au for which the LDA result is fortuitiously close to the experimental energy. In fact, the inclusion of relativistic corrections in the GGA even worsens the agreement with experiment, although only marginally. The nonadditivity of relativistic and xc-effects [22] is thus not responsible for the GGA's failure for some $5d$ transition elements.

In summary, there can be little doubt that for the cohesive properties of solids the relativistic contributions to $E_{xc}[n]$ are much less important than the 'nonlocal' contributions to $E_{xc}[n]$ not contained in the LDA. It should be pointed out, however, that the RGGA is as efficiently applied as the GGA, so that there seems to be no reason to rely on error cancellation in the calculation of E_{coh}. Moreover, at least for some systems (as Au) the relativistic xc-corrections are visible in the band structure, indicating that a complete description of these systems requires a relativistic form for $E_{xc}[n]$. Finally, if relativistic xc-corrections are to be included at all this should be done on the GGA- rather than the LDA-level.

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