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Accurate optimized-potential-model solutions for spherical spin-polarized atoms: Evidence for limitations of the exchange-only local spin-density and generalized-gradient approximations

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We present accurate optimized-potential-model (OPM) results for spherical spin-polarized atoms emphasizing the precise construction of the OPM exchange potential from the numerical solution of the OPM integral equation, especially for large r. The results are used to discuss the quality of the local spin-density approximation (LSDA) and a generalized-gradient expansion (GGA) [A. D. Becke, Phys. Rev. A **38**, 3098 (1988)] for describing these atoms. It is shown that the LSDA can produce substantial errors (beyond what is known from unpolarized atoms) for quantities which are directly related to the spin polarization of these systems. In particular, the LSDA overestimates the magnetization density in the interior of Cu by a factor of 2. While the GGA improves integral quantities like total ground-state and exchange energies, remarkably it is less successful for energy differences like $E_{x\uparrow} - E_{x\downarrow}$. Most important, however, it is not able to reduce the LSDA's errors for local quantities like the difference between spin-up and spin-down exchange potentials and magnetization densities significantly nor does it reverse the LSDA's incorrect ordering of the two highest occupied majority-spin eigenvalues of Cr and Cu.

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I. INTRODUCTION

Recently it has become clear that the so-called optimized potential model (OPM) [1, 2] represents the most advantageous approach to define the exchange part $E_x[n]$ (often referred to as exchange-only) of the exchange-correlation functional $E_{xc}[n]$ of density-functional theory (DFT) (see, e.g., [3, 4]). Although not always utilized, a substantial amount of recent work concerned with the properties of $E_x[n]$ [5–12] is based on this definition. It has, for example, the advantage that its gradient expansion exists [13] in contrast to that of $E_x^{\mathrm{DFT-HF}}[n] \equiv E_{\mathrm{tot}}^{\mathrm{HF}}[n]-T_s[n]-E_{\mathrm{ext}}[n]-E_H[n]$ (where $E_{\mathrm{tot}}^{\mathrm{HF}}[n]$ represents the total Hartree Fock (HF) energy, $T_s[n]$ is the kinetic energy obtained by insertion of the HF density into the noninteracting kinetic-energy functional, and $E_{\mathrm{ext}}[n]$ and $E_H[n]$ are the external and Hartree energy, respectively) [14]. Furthermore, the exchange potential corresponding to $E_x^{\mathrm{DFT-HF}}[n]$ is only known for a few atoms [15, 16] due to the complicated scheme required for its construction. In contrast to this older approach the $E_x[n]$ based on the OPM provides direct information about both total exchange energies and the corresponding local exchange potential $v_x(\mathbf{r})$. In addition, this $E_x[n]$ has a simple scaling behavior [17, 18] which leads to a useful and easily interpretable relation between $v_x(\mathbf{r})$ and $E_x[n]$.

The explicit numerical application of the OPM approach to physical systems, however, is rather involved due to the fact that it requires the simultaneous self-consistent solution of both a Kohn-Sham-like equation for the single-particle orbitals and an integral equation defining $v_x(\mathbf{r})$. Consequently, at present only a limited number of results for atoms has been presented [19, 20, 6, 9, 11, 12]. To obtain a rough estimate of their accuracy it is instructive to analyze the data for sodium given by Talman [20]. Comparing the kinetic energy of 161.799 hartree with the total ground state energy of 161.857 hartree one observes an error in the standard virial relation $2T = -V$ of 58 mhartree. The corresponding HF solution [21], on the other hand, shows an error of less than 10^{-2} mhartree. Two more refined criteria to estimate the accuracy of OPM solutions have been used: Wang *et al.* [6] applied the virial relation introduced by Ghosh and Parr [17] and Levy and Perdew [18] (which will be referred to as the exchange virial relation here). For the atoms considered they found the error given by the exchange virial relation to be of the order of 1–100 mhartree depending on the size of the atoms. Li *et al.* [9] analyzed a relation [7] for the eigenvalue of the highest occupied orbital finding errors of the order of 2 mhartree. Krieger, Li, and Iafrate [11] were able to improve their OPM results with respect to this relation. Their highest occupied eigenvalues satisfy this criterion with an accuracy of better than 0.8 mhartree with the noble gases and the alkali metals being the worst cases. As for the exchange virial relation, some room for improvements seems to be left for the highest occupied eigenvalues. Also, for technical reasons (see Appendix) these two criteria are to some extent competing with each other, i.e., improving one of them reduces the quality of the other one. As the OPM is going to serve as a new standard for the properties of $E_x[n]$ it is desirable to have highly accurate solutions available. One purpose of this paper is to provide such a standard for spherical atoms. Our solutions reduce the error in the exchange virial relation by more than two orders of magnitude and that in the relation for the highest occupied eigenvalue by one order of magnitude. In particular, by expanding and utilizing Talman and Shadwick's discussion [2] of the asymptotic behavior of $v_x(\mathbf{r})$ beyond the leading $-1/r$ term more precise values for the highest occupied eigenvalues are obtained (details are given in the Appendix).

While for unpolarized atoms the OPM exchange potential has been used to some extent [6, 11, 12] there has been less attention to spin-polarized systems [22]. The analysis of such systems has the potential to give some insight into the source of the failure of the local spin-density approximation (LSDA) and gradient based corrections to the LSDA [23–28] [often called generalized gradient approximations (GGA's)] for the magnetic properties of solids (see, e.g., [29–33]). GGA's have shown some promising features both for atoms and molecules [34–39] as well as for condensed-matter systems [39–44]. These studies, however, always combined the exchange and the correlation part of the total $E_{xc}[n]$ and used experimental data as the standard. The OPM, on the other hand, sets an unambigous standard for exchange-only allowing for much more detailed and definitive analysis of $E_x[n]$ for "model systems" such as spherical atoms than experimental data of much more complex real systems. Moreover, these studies have focused on quantities like E_x's, but did not examine the local $v_x(\mathbf{r})$ produced by the approximate $E_x[n]$.

By examining Cu, Cr, Mn, As, and Eu in some detail we show that while the quality of the LSDA and Becke's GGA [27] (which is representative for most of the widely used GGA's for $E_x[n]$) for global quantities such as total ground-state and exchange energies of polarized systems is similar to that for unpolarized atoms, quantities related to spin polarization turn out to be much more sensitive. The error in the spin splitting of the exchange energy $E_{x\uparrow} - E_{x\downarrow}$ is considerably larger than that for total E_x's. Also, we find that the eigenvalues of the highest occupied orbitals can be significantly more in error when spin polarization is present and eigenvalues may even be incorrectly ordered. Most important, the splitting in the OPM exchange potential $v_{x\uparrow}(r) - v_{x\downarrow}(r)$ is not reproduced by either the LSDA or the GGA. This is corroborated by an analysis of the magnetization densities of these atoms. While for Cr, Mn, and As the LSDA and the GGA reproduce the exact magnetization density rather well, they have some difficulties with Eu. The magnetization density in the interior of Cu, on the other hand, is overestimated almost by a factor of 2. Again the GGA is not able to improve on the LSDA. Quite generally the GGA's improvement on the LSDA for integral quantities is not transferred to local quantities which are sensitive to the differences between spin-up and spin-down potentials.

The paper is organized as follows. Section II discusses the accuracy of our OPM results on the basis of the exchange and the conventional virial relation as well as the relation of Krieger, Li, and Iafrate [7]. In section III our OPM results for spherical spin-polarized atoms are compared with those of spin-unrestricted HF (SUHF), LSDA, and GGA calculations. In Sec. IV we analyze Cu, Cr, Mn, As, and Eu in more detail. Finally, in the Appendix we give an outline of the OPM equations (for spherical systems) emphasizing the accurate construction of $v_x(r)$ from the numerical solution of the OPM integral equation which is relevant for obtaining improved eigenvalues.

We use atomic units throughout this paper.

II. ACCURACY OF RESULTS

As has been shown by Ghosh and Parr [17] and Levy and Perdew [18] the $E_x[n]$ based on the OPM satisfies a simple virial relation. First of all, from the definition of $E_x^\sigma[n_\sigma]$,

$$E_x^\sigma[n_\sigma] = -\frac{1}{2}\int d^3r \int d^3r' \, \frac{\rho_\sigma(\mathbf{r},\mathbf{r}')\rho_\sigma(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}, \tag{1}$$

$$\rho_\sigma(\mathbf{r},\mathbf{r}') = \sum_i \Theta(\varepsilon_F - \varepsilon_i^\sigma)\, \phi_{i,\sigma}^*(\mathbf{r}')\, \phi_{i,\sigma}(\mathbf{r}) \, , \tag{2}$$

$$n_\sigma(\mathbf{r}) = \rho_\sigma(\mathbf{r},\mathbf{r}), \tag{3}$$

where the $\phi_{i,\sigma}(\mathbf{r})$ and ε_i^σ are the OPM single-particle orbitals and eigenvalues for given spin σ, it is clear that the basic scaling relation

$$E_x^\sigma[\lambda^3 n_\sigma(\lambda\mathbf{r})] = \lambda E_x^\sigma[n_\sigma(\mathbf{r})]. \tag{4}$$

holds for either spin. Differentiation with respect to λ then directly leads to

$$E_x^\sigma[n(\mathbf{r})] = \int d^3r \; v_{x\sigma}(\mathbf{r})[3n_\sigma(\mathbf{r}) + \mathbf{r}\cdot\nabla n_\sigma(\mathbf{r})]. \tag{5}$$

Thus the factor $[3n_\sigma(\mathbf{r}) + \mathbf{r}\cdot\nabla n_\sigma(\mathbf{r})]$ provides a natural connection between $v_{x\sigma}(\mathbf{r})$ and the total exchange energy.

Equation (5) is a very useful tool for checking the accuracy of any calculation even for systems where the conventional virial theorem $2T = -V$ does not hold. This is of particular interest for OPM calculations as here $v_{x\sigma}(\mathbf{r})$ results from a rather involved procedure (details are given in the Appendix). Wang *et al.* [6] used this criterion and found their OPM calculations satisfy Eq. (5) within 1–100 mhartree increasing monotonically with the size of the system. The differences between total exchange energies as evaluated by Eq.(1) and the right-hand side of (5) of our results are given in Tables I and II [for completeness we also list the total ground-state energies $E_{\rm tot}$, E_x's, and eigenvalues of the highest occupied orbitals (ϵ_{mk}) of spherical unpolarized atoms in Table I extending the results of Ref. [11] to Pd, Ba, Yb, Pt, and Rn]. As is obvious from Table I our errors are more than two orders of magnitude smaller than those of Wang *et al.* [6]. Although these errors are still about one order of magnitude larger than those of HF results [21] they lead

TABLE I. Total ground-state energies E_{tot}, total exchange energies E_x, eigenvalues of highest occupied orbitals ε_{mk} (in hartrees), and differences between E_x's as obtained from Eq. (1) and the right-hand side of the exchange virial relation, Eq. (5), for spherical unpolarized atoms (in mhartrees).

Atom	E_{tot} (hartrees)	E_x (hartrees)	$-\varepsilon_{mk}$ (hartrees)	Error (mhartrees)
He	2.8617	1.0258	0.9180	0.005
Be	14.5724	2.6658	0.3092	0.010
Ne	128.5455	12.1050	0.8507	0.024
Mg	199.6116	15.9884	0.2530	0.023
Ar	526.8123	30.1748	0.5908	0.006
Ca	676.7520	35.1991	0.1956	−0.021
Zn	1 777.8345	69.6189	0.2928	0.016
Kr	2 752.0431	93.8331	0.5234	0.039
Sr	3 131.5336	101.9264	0.1786	0.008
Pd	4 937.9062	139.1136	0.3350	0.038
Cd	5 465.1146	148.8798	0.2655	0.010
Xe	7 232.1213	179.0638	0.4564	−0.091
Ba	7 883.5268	189.0666	0.1577	−0.182
Yb	13 391.4166	276.1469	0.1822	0.399
Pt	17 331.0935	331.3390	0.3416	0.828
Hg	18 408.9609	345.2455	0.2620	0.899
Rn	21 866.7461	387.4527	0.4271	0.949

to an accuracy of better than 1 mhartree for all components of the energy even for very large atoms like Rn.

As a further check on the accuracy of OPM results Li *et al.* [9] introduced the relation [7]

$$\varepsilon_{mk}^{\sigma} = \overline{\varepsilon}_{mk}^{\sigma,\text{HF}} , \qquad (6)$$

where $\varepsilon_{mk}^{\sigma}$ and $\overline{\varepsilon}_{mk}^{\sigma,\text{HF}}$ are the exact highest occupied OPM eigenvalue of spin σ and the HF single-particle expectation value for the corresponding exact OPM orbital, respectively. For any numerical OPM solution Eq. (6) will not be satisfied exactly. Thus it can be used as a criterion for the quality of the solutions obtained. Note that due to the variational character of the OPM equations $\overline{\varepsilon}_{mk}^{\sigma,\text{HF}}$ is much more stable against numerical errors than $\varepsilon_{mk}^{\sigma}$ as already discussed by Krieger, Li, and Iafrate [11]. Consequently, $\overline{\varepsilon}_{mk}^{\sigma,\text{HF}}$ gives a much better approximation to the exact highest occupied eigenvalue than the direct eigenvalue obtained from the OPM solution. In fact, variation of the point where the constant in the numerically obtained solution of the OPM integral equation is determined (for details see Appendix) did not change $\overline{\varepsilon}_{mk}^{\sigma,\text{HF}}$ on the 0.01-mhartree level. The maximum difference between the left- and right-hand sides in Eq. (6) of our results for unpolarized atoms, on the other hand, is smaller than 0.05 mhartree (compared to 0.8 mhartree for the results of Ref.[11]) so that we do not list $\overline{\varepsilon}_{mk}^{\sigma,\text{HF}}$ separately.

TABLE II. Difference between E_x as obtained from Eq. (1) and the right-hand side of the exchange virial relation, Eq. (5), for the individual spins of spherical spin-polarized atoms and errors in the conventional virial relation $T = -E_{\text{tot}}$ (all energies in mhartrees).

Atom	Spin-up	Spin-down	$-T - E_{\text{tot}}$
Li	−0.014	0.004	0.006
N	0.009	0.009	0.017
Na	0.008	0.013	0.024
P	0.007	0.010	0.018
K	−0.014	−0.003	−0.008
Cr	−0.001	−0.016	−0.016
Mn	0.005	−0.022	−0.013
Cu	−0.002	0.008	0.007
As	0.016	0.037	0.055
Rb	−0.023	0.015	0.025
Mo	0.006	−0.008	0.001
Tc	0.010	−0.015	−0.002
Ag	0.005	0.013	0.021
Sb	−0.027	−0.010	−0.034
Cs	−0.100	−0.065	−0.136
Eu	0.142	−0.098	0.052
Re	0.342	0.333	0.682
Au	0.438	0.449	0.894
Bi	0.478	0.488	0.975

Table II gives the corresponding errors for spin-polarized atoms separated into their spin components (spin-up has always been chosen as majority-spin component). On average the errors for both spins are about the same. The sum of spin-up and spin-down errors for a given atom is comparable to the error for an unpolarized atom of similar size. It is obvious from Tables I and II that while these errors are somewhat random for smaller atoms and can have different signs for the individual spins in a polarized atom they start to show a systematic dependence on the step size of the grid for larger systems. Furthermore, in Table II we also list the corresponding errors in the conventional virial relation $E_{\text{tot}} + T = 0$. In particular for large atoms these errors turn out to be more or less identical to the sum of spin-up and spin-down errors from Eq. (5). This leads to the conclusion that, while the Kohn-Sham-like radial equations for given $v_x(r)$ are solved as accurately as in any LSDA or HF calculation, the source of the remaining errors for these large systems is in the construction of $v_x(r)$ from the OPM integral equation.

For almost all the spin-polarized atoms Eq. (6) is satisfied to better than 0.07 mhartree, the only exceptions being the spin-up components of Cu (the correct eigenvalues are less attractive by about 0.2 mhartree), Cr (the correct eigenvalues are more attractive by about 1 mhartree), and Mo (the correct eigenvalues are more attractive by about 1.2 mhartree). Clearly, the construction of $v_{x\sigma}(r)$ from the solution of the OPM integral equation is particularly complicated for these atoms where the two outermost eigenvalues differ by only 0.064 mhartree (Cu), 0.019 mhartree (Cr), and 0.038 mhartree (Mo) (see discussion in Appendix).

This accuracy has been achieved by a careful numerical preparation of the kernel and the inhomogeneity of the OPM integral equation in combination with utilizing the analytic form of the asymptotic $v_{x\sigma}(r)$ beyond the leading $-1/r$ term (as discussed in the Appendix) as well as increasing the grid to 800 points.

TABLE III. Total ground-state energies ($-E_{\text{tot}}$) of spherical spin-polarized atoms for spin-unrestricted HF (SUHF), OPM, exchange-only LSDA, and the GGA of Ref. [27] (in hartrees).

Atom	SUHF	OPM	LSDA	Ref. [27]
Li	7.4328	7.4325	7.1934	7.4288
N	54.4045	54.4034	53.7093	54.4009
Na	161.8590	161.8567	160.6443	161.8834
P	340.7193	340.7151	338.8885	340.7107
K	599.1649	599.1592	596.7115	599.1483
Cr	1043.3568	1043.3458	1040.2732	1043.4917
Mn	1149.8698	1149.8601	1146.5831	1149.9671
Cu	1638.9642	1638.9524	1635.2392	1639.2804
As	2234.2399	2234.2283	2229.6475	2234.3657
Rb	2938.3576	2938.3456	2932.9835	2938.3909
Mo	3975.5530	3975.5373	3969.3323	3975.6140
Tc	4204.7949	4204.7795	4198.3724	4204.8362
Ag	5197.6989	5197.6817	5190.5783	5197.7652
Sb	6313.4870	6313.4699	6305.5658	6313.4799
Cs	7553.9338	7553.9168	7545.2828	7553.9246
Eu	10423.5506	10423.5236	10413.8251	10423.9367
Re	15784.5441	15784.5129	15772.6624	15785.0273
Au	17865.4006	17865.3706	17852.5601	17865.6923
Bi	20095.5886	20095.5611	20081.7926	20095.6989

III. RESULTS FOR SPIN-POLARIZED ATOMS

In this section we summarize our results for spin-polarized spherical atoms and compare them to SUHF and LSDA data as well as to the GGA of Ref. [27].

In Table III we list the total ground-state energies (whose absolute value is identical to T_s) for spin-polarized spherical atoms with $Z \leq 83$ comparing SUHF, OPM, LSDA, and Ref. [27] results. Quite generally, SUHF and OPM results are nearly equal, the biggest difference of 31 mhartree occurring for Re. The LSDA, on the other hand, deviates by about 12 hartree for Re. These differences are very similar to those observed for unpolarized atoms [11]. The GGA is able to remove most of the error in the LSDA (for Re its error is about 0.5 hartree), although at the price that it can give lower ground-state energies than the OPM [which is mainly due to the fact that the GGA overestimates the exchange energy in comparison to the exact functional, i.e., Eq. (1)].

Table IV shows the corresponding total exchange energies. Again the differences between SUHF and OPM results are very small. The LSDA, on the other hand, leads to errors of 4–15%. In particular, one notes that the error only depends on the size of the atom but not on the specific electronic configuration, i.e., the type of the half-filled (outermost) shell. It decreases monotonically with the electron number as one expects from the LSDA's statistical nature, in complete analogy to unpolarized atoms. Becke's GGA reproduces the OPM exchange energies extremely well, the error being of the order of the differences between the OPM and SUHF energies.

Table V gives the differences $E_{x\uparrow} - E_{x\downarrow}$ for spin-polarized atoms. These differences are a global measure for the ability of an approximate $E_x[n]$ to reproduce spin-polarization. The errors of the LSDA range from 35% for Au to 0.4% for Eu. In particular, one notes the relation between the error and the type of the half-filled shell: While the minimum error is obtained for an open f shell, Cr and Mo (open d and s shells) lead to about 1.7% error and Mn, Tc, and Re (open d shell) show about 2.3% error. The series of atoms with half-filled p shells produces errors between 5.4% (N) and 2.3% (Bi) with a clear ten-

TABLE IV. Total exchange energies ($-E_x$) of spherical spin-polarized atoms for SUHF, OPM, LSDA, and the GGA of Ref. [27] (in hartrees).

Atom	SUHF	OPM	LSDA (error in %)	Ref. [27] (error in %)
Li	1.7812	1.7808	1.5054 (15.46)	1.7681 (0.71)
N	6.6067	6.6044	5.8368 (11.62)	6.5687 (0.54)
Na	14.0176	14.0131	12.7024 (9.35)	13.9933 (0.14)
P	22.6423	22.6342	20.7104 (8.50)	22.5925 (0.18)
K	32.6781	32.6669	30.1269 (7.78)	32.6290 (0.12)
Cr	47.7724	47.7555	44.4674 (6.89)	47.7577 (0.00)
Mn	51.0001	50.9833	47.5219 (6.79)	50.9788 (0.01)
Cu	65.7934	65.7749	61.7578 (6.11)	65.8765 (-0.15)
As	81.5177	81.4961	76.7132 (5.87)	81.5139 (-0.02)
Rb	97.8936	97.8704	92.3499 (5.64)	97.8417 (0.03)
Mo	119.9238	119.8943	113.4771 (5.35)	119.8517 (0.04)
Tc	124.4063	124.3769	117.7772 (5.31)	124.3345 (0.03)
Ag	144.0357	144.0035	136.6482 (5.11)	143.9345 (0.05)
Sb	163.8444	163.8115	155.7290 (4.93)	163.7425 (0.04)
Cs	184.0930	184.0595	175.2889 (4.77)	184.0292 (0.02)
Eu	230.5581	230.5102	220.4942 (4.35)	230.7098 (-0.09)
Re	310.2161	310.1581	297.9542 (3.93)	310.4318 (-0.09)
Au	338.3630	338.3059	325.1358 (3.89)	338.3840 (-0.02)
Bi	366.3158	366.2627	352.2296 (3.83)	366.2521 (0.00)

TABLE V. Exchange energy differences $E_{x\downarrow} - E_{x\uparrow}$ for spherical spin-polarized atoms from spin-unrestricted OPM, exchange-only LSDA, and the GGA of Ref. [27] (in hartrees).

Atom	OPM	LSDA (error in %)	Ref. [27] (error in %)
Li	0.1346	0.1194 (−11.3)	0.1362 (1.2)
Na	0.1230	0.1174 (−4.6)	0.1291 (5.0)
K	0.1005	0.1029 (2.4)	0.1100 (9.5)
Rb	0.0945	0.1003 (6.1)	0.1058 (12.0)
Cs	0.0856	0.0929 (8.5)	0.0972 (13.6)
Cu	0.1044	0.0990 (−5.2)	0.1085 (3.9)
Ag	0.1243	0.1579 (27.0)	0.1605 (29.1)
Au	0.1318	0.1777 (34.8)	0.1784 (35.4)
N	1.7016	1.6096 (−5.4)	1.6821 (−1.1)
P	1.1525	1.0918 (−5.3)	1.1331 (−1.7)
As	1.0748	1.0330 (−3.9)	1.0546 (−1.9)
Sb	0.9630	0.9350 (−2.9)	0.9452 (−1.8)
Bi	0.9241	0.9031 (−2.3)	0.9080 (−1.7)
Mn	4.9568	4.8454 (−2.2)	4.9196 (−0.8)
Tc	3.7461	3.6544 (−2.4)	3.7092 (−1.0)
Re	3.4921	3.4110 (−2.3)	3.4329 (−1.7)
Cr	4.2336	4.1580 (−1.8)	4.2310 (−0.1)
Mo	3.2743	3.2182 (−1.7)	3.2722 (−0.1)
Eu	11.8870	11.8391 (−0.4)	11.9138 (0.2)

dency to decrease with the size of the atoms. The most pronounced errors are found for atoms with half-filled s shells: The series Li to Cs (noble-gas configuration plus half-filled s shell) gives errors between 2.4% and 11.3%. Finally, for the noble metals Cu, Ag, and Au the LSDA shows substantial discrepancies. It is obvious that these spin-difference exchange energies are much more sensitive to the quality of the exchange potential than total E_x's. Also, $E_{x\uparrow} - E_{x\downarrow}$ depends much more strongly on the specific atomic configuration (compare Table IV).

The error pattern is similar for the GGA. In particular, the GGA increases the spin splitting in E_x for all atoms considered. This leads to smaller errors than for the LSDA for atoms with half-filled f, d, and p shells, i.e., for systems where the LSDA underestimates $E_{x\downarrow} - E_{x\uparrow}$. However, this improvement is much less dramatic than that observed for total ground-state and total exchange energies. No systematic improvement, on the other hand, is found for atoms with half-filled s shells where already the LSDA often overestimates $E_{x\downarrow} - E_{x\uparrow}$. The effect that GGA's increase the magnetic energy is also found for metals [31, 32]. While this is desirable for Fe where it stabilizes the ferromagnetic bcc ground state, it is less helpful for systems such as Ni and Fe_3Ni.

TABLE VI. Eigenvalues $-\varepsilon^{\uparrow}_{mk}$ of highest occupied spin-up orbitals of spherical spin-polarized atoms from SUHF, OPM, LSDA, and the GGA of Ref. [27] (in hartrees). Note that for Cu and Cr the 4s is not the most weakly bound orbital for the LSDA and GGA which is indicated by an asterisk.

Atom	SUHF	OPM	LSDA	Ref. [27]
Li (2s)	0.1964	0.1963	0.1004	0.1092
N (2p)	0.5709	0.5712	0.2763	0.2846
Na (3s)	0.1822	0.1821	0.0967	0.1025
P (3p)	0.3921	0.3916	0.2033	0.2100
K (4s)	0.1477	0.1477	0.0805	0.0842
Cr (4s)	0.2220	0.2231	0.1511*	0.1536*
Mn (4s)	0.2735	0.2745	0.1793	0.1819
Cu (4s)	0.2396	0.2407	0.1588*	0.1625*
As (4p)	0.3702	0.3691	0.1929	0.1975
Rb (5s)	0.1381	0.1383	0.0764	0.0794
Mo (5s)	0.2230	0.2246	0.1495	0.1500
Tc (5s)	0.2659	0.2677	0.1760	0.1767
Ag (5s)	0.2210	0.2221	0.1416	0.1431
Sb (5p)	0.3357	0.3347	0.1785	0.1819
Cs (6s)	0.1239	0.1241	0.0694	0.0719
Eu (6s)	0.1745	0.1742	0.1043	0.1072
Re (6s)	0.2692	0.2714	0.1807	0.1814
Au (6s)	0.2220	0.2234	0.1447	0.1459
Bi (6p)	0.3214	0.3204	0.1721	0.1748

In Tables VI and VII we list the eigenvalues of the highest occupied orbitals for spin-up and -down, respectively. As for the total energies the highest occupied eigenvalues of SUHF and OPM are very close, the differences being smaller than 4 mhartrees (Cr, Cu, spin-down) for all atoms considered (note that there is no rigorous reason for the highest occupied eigenvalues of SUHF and OPM to be equal). The LSDA, on the other hand, shows the well-known deficiency of underestimating these eigenvalues by almost 50% which is directly related to its incorrect asymptotic behavior for finite systems. The most severe cases in this respect are the minority-spin eigenvalues for Cu, Ag, and Au. As already observed for unpolarized atoms [12] the GGA produces highest occupied eigenvalues which are only marginally larger than those of the LSDA. Moreover, the LSDA and GGA can pro-

TABLE VII. Eigenvalues $-\varepsilon^{\downarrow}_{mk}$ of highest occupied spin-down orbitals of spherical spin-polarized atoms from SUHF, OPM, LSDA, and the GGA of Ref. [27] (in hartrees).

Atom	SUHF	OPM	LSDA	Ref. [27]
Li (1s)	2.4687	2.4688	1.8046	1.8693
N (2s)	0.7258	0.7257	0.4820	0.5036
Na (2p)	1.5170	1.5177	0.9970	1.0111
P (3s)	0.5562	0.5561	0.3840	0.3921
K (3p)	0.9535	0.9534	0.6405	0.6509
Cr (3p)	1.8399	1.8361	1.4738	1.4877
Mn (4s)	0.2260	0.2257	0.1280	0.1341
Cu (3d)	0.4933	0.4893	0.1512	0.1558
As (4s)	0.5560	0.5561	0.4106	0.4145
Rb (4p)	0.8092	0.8086	0.5421	0.5489
Mo (4p)	1.5730	1.5716	1.2546	1.2596
Tc (5s)	0.2031	0.2028	0.1174	0.1220
Ag (4d)	0.5364	0.5341	0.2460	0.2507
Sb (5s)	0.4689	0.4692	0.3478	0.3491
Cs (5p)	0.6827	0.6820	0.4581	0.4629
Eu (6s)	0.1676	0.1679	0.0963	0.0994
Re (6s)	0.1994	0.1991	0.1176	0.1219
Au (5d)	0.5193	0.5164	0.2523	0.2558
Bi (6s)	0.4456	0.4461	0.3346	0.3349

TABLE VIII. Eigenvalues $-\varepsilon_{nl}^{\sigma}$ of Cu obtained from SUHF, OPM, LSDA, and GGA calculations (in hartrees). Note the accuracy of the OPM spin-up component: The exact eigenvalues are less attractive by about 0.2 mhartree.

Atom	SUHF	OPM	LSDA	Ref. [27]
$1s\uparrow$	328.7940	321.5110	320.7080	321.4929
$2s\uparrow$	40.8187	38.2781	38.0830	38.1898
$2p\uparrow$	35.6168	33.5337	33.4214	33.4859
$3s\uparrow$	5.0124	4.2331	4.0054	4.0360
$3p\uparrow$	3.3222	2.7537	2.5577	2.5751
$3d\uparrow$	0.4891	0.3048	0.1575	0.1616
$4s\uparrow$	0.2396	0.2407	0.1588	0.1625
$1s\downarrow$	328.7921	321.7164	320.7069	321.4919
$2s\downarrow$	40.8195	38.4734	38.0860	38.1925
$2p\downarrow$	35.6193	33.7274	33.4235	33.4877
$3s\downarrow$	5.0116	4.4213	4.0093	4.0399
$3p\downarrow$	3.3274	2.9410	2.5609	2.5782
$3d\downarrow$	0.4933	0.4893	0.1512	0.1558

duce incorrect ordering of eigenvalues (see Table VI and Sec. IV).

IV. DETAILS FOR Cu, As, Mn, Cr, AND Eu

In this section we discuss Cu, As, Mn, Cr, and Eu in some more detail. These atoms characterize the spectrum of spherical spin-polarized atoms: The half-filled shells are 4*s* for Cu, 4*p* for As, 3*d* for Mn, 4*s* and 3*d* for Cr, and 4*f* for Eu.

We start by listing the complete series of SUHF and Kohn-Sham eigenvalues for these systems in Tables VIII–XII. While the highest occupied eigenvalues of the OPM for all atoms are very close to the corresponding SUHF values, the remaining eigenvalues differ appreciably illustrating the auxiliary nature of all but the highest occupied eigenvalues of DFT calculations. More interesting for our purposes, however, is the comparison of the LSDA with the OPM. It becomes most obvious from Tables VIII–XII that while for the minority-spin the LSDA underestimates only the highest occupied eigenvalue by roughly a factor of 2, in complete analogy to unpolarized atoms [11, 12], for the majority-spin the eigenvalues of the two outermost orbitals are seriously in error. In most cases the next to the highest occupied eigenvalues are also underestimated by 50%. Among the atoms considered here the only exception is As where the 4*s*-eigenvalue still is 25% too small. For the alkali metals this error is reduced to 10-15%. Nevertheless, for sensitive systems like Cr and Cu where the two outermost OPM eigenvalues are nearby this deficiency of the LSDA can produce an incorrect ordering of eigenvalues: While the OPM (and SUHF) in both cases leads to a more weakly bound 4*s* orbital compared to the competing 3*d* orbital the LSDA inverts this order (although the difference between the two eigenvalues is small for Cu). As already mentioned in the preceding section the GGA is not able to improve the quality of the highest occupied

TABLE IX. Eigenvalues $-\varepsilon_{nl}^{\sigma}$ of As obtained from SUHF, OPM, LSDA, and GGA calculations (in hartrees).

Atom	SUHF	OPM	LSDA	Ref. [27]
$1s\uparrow$	432.5903	424.2583	423.2352	424.1324
$2s\uparrow$	56.3114	53.3354	53.0131	53.1342
$2p\uparrow$	50.1580	47.6762	47.4468	47.5207
$3s\uparrow$	8.0366	7.0145	6.6620	6.6998
$3p\uparrow$	5.8907	5.0933	4.7839	4.8058
$3d\uparrow$	2.1174	1.7298	1.4790	1.4845
$4s\uparrow$	0.8156	0.6874	0.5145	0.5192
$4p\uparrow$	0.3702	0.3691	0.1929	0.1975
$1s\downarrow$	432.5820	424.2419	423.2308	424.1284
$2s\downarrow$	56.3083	53.3343	53.0111	53.1328
$2p\downarrow$	50.1495	47.6679	47.4433	47.5174
$3s\downarrow$	8.0224	7.0049	6.6561	6.6945
$3p\downarrow$	5.8704	5.0829	4.7769	4.7995
$3d\downarrow$	2.1076	1.7167	1.4669	1.4738
$4s\downarrow$	0.5560	0.5561	0.4106	0.4145

TABLE X. Eigenvalues $-\varepsilon_{nl}^{\sigma}$ of Mn obtained from SUHF, OPM, LSDA, and GGA calculations (in hartrees).

Atom	SUHF	OPM	LSDA	Ref. [27]
$1s\uparrow$	240.5339	234.2981	233.5752	234.2461
$2s\uparrow$	29.1762	27.0325	26.8084	26.8954
$2p\uparrow$	24.8773	23.1428	22.9961	23.0464
$3s\uparrow$	4.0215	3.3300	3.0930	3.1187
$3p\uparrow$	2.7276	2.2184	2.0077	2.0226
$3d\uparrow$	0.6409	0.4513	0.2819	0.2857
$4s\uparrow$	0.2735	0.2745	0.1793	0.1819
$1s\downarrow$	240.5350	234.3523	233.5748	234.2464
$2s\downarrow$	29.0435	27.0012	26.7173	26.8117
$2p\downarrow$	24.7488	23.1346	22.9268	22.9837
$3s\downarrow$	3.6123	2.9694	2.8831	2.9091
$3p\downarrow$	2.2319	1.8635	1.8012	1.8160
$4s\downarrow$	0.2260	0.2257	0.1280	0.1341

TABLE XI. Eigenvalues $-\varepsilon_{nl}^{\sigma}$ of Cr obtained from SUHF, OPM, LSDA, and GGA calculations (in hartrees). Note the limited numerical accuracy of the OPM spin-up eigenvalues: The exact eigenvalues are more attractive by about 1 mhartree.

Atom	SUHF	OPM	LSDA	Ref. [27]
$1s\uparrow$	220.3856	214.4066	213.7569	214.3996
$2s\uparrow$	26.2596	24.2156	24.0469	24.1304
$2p\uparrow$	22.1876	20.5456	20.4499	20.4979
$3s\uparrow$	3.4588	2.8260	2.6470	2.6704
$3p\uparrow$	2.2614	1.8100	1.6526	1.6658
$3d\uparrow$	0.3737	0.2423	0.1200	0.1230
$4s\uparrow$	0.2220	0.2231	0.1511	0.1536
$1s\downarrow$	220.3868	214.8073	213.7565	214.3997
$2s\downarrow$	26.1593	24.5554	23.9771	24.0666
$2p\downarrow$	22.0919	20.9004	20.3966	20.4498
$3s\downarrow$	3.1111	2.8507	2.4680	2.4919
$3p\downarrow$	1.8399	1.8361	1.4738	1.4877

TABLE XII. Eigenvalues $-\varepsilon_{nl}^{\sigma}$ of Eu obtained from SUHF, OPM, LSDA, and GGA calculations (in hartrees).

Atom	SUHF	OPM	LSDA	Ref. [27]
$1s\uparrow$	1690.6972	1673.9234	1672.1718	1673.9138
$2s\uparrow$	272.3188	265.4045	265.0836	265.3372
$2p\uparrow$	258.3645	252.2050	252.0583	252.2206
$3s\uparrow$	61.4053	58.2094	58.0157	58.0859
$3p\uparrow$	55.1714	52.3618	52.2244	52.2681
$3d\uparrow$	43.7013	41.4870	41.3936	41.4193
$4s\uparrow$	12.9598	11.5693	11.2837	11.3239
$4p\uparrow$	10.4848	9.2996	9.0418	9.0703
$4d\uparrow$	6.0917	5.2694	5.0496	5.0648
$5s\uparrow$	1.8857	1.5211	1.4406	1.4451
$5p\uparrow$	1.1220	0.9158	0.8435	0.8468
$4f\uparrow$	0.7146	0.4108	0.2483	0.2516
$6s\uparrow$	0.1745	0.1742	0.1043	0.1072
$1s\downarrow$	1690.6973	1673.9251	1672.1718	1673.9137
$2s\downarrow$	272.3143	265.4151	265.0787	265.3344
$2p\downarrow$	258.3625	252.2123	252.0554	252.2191
$3s\downarrow$	61.2202	58.0454	57.9002	57.9746
$3p\downarrow$	54.9780	52.2139	52.1185	52.1665
$3d\downarrow$	43.5059	41.3880	41.3153	41.3459
$4s\downarrow$	12.5309	11.1027	11.0543	11.0946
$4p\downarrow$	10.0086	8.8339	8.8132	8.8413
$4d\downarrow$	5.4691	4.8098	4.8236	4.8369
$5s\downarrow$	1.7486	1.3724	1.3276	1.3331
$5p\downarrow$	1.0117	0.8098	0.7540	0.7596
$6s\downarrow$	0.1676	0.1679	0.0963	0.0994

eigenvalues and consequently also suffers from this ordering problem. It does, however, improve the lowest eigenvalues, i.e., the $1s$, $2s$, and $2p$.

These observations give some insight into the source of the failure of the LSDA (and GGA's) to reproduce experimental s-d promotion energies [45, 46, 35, 47, 38, 44]. In particular, these results might explain why the LSDA's s-d promotion energies are somewhat closer to experimental values for $4d$ and $5d$ transition metals than for $3d$ as for Mo, Ag, and Au, at least the ordering problem disappears.

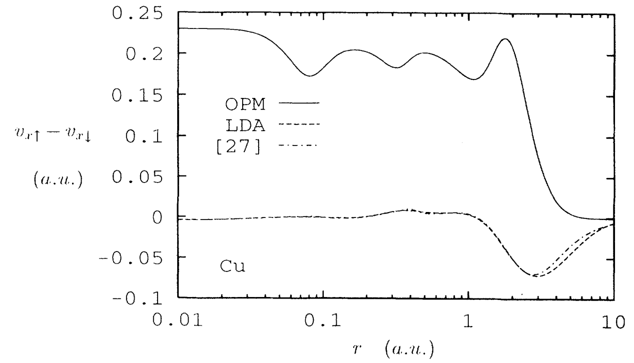

FIG. 1. Difference between spin-up and spin-down exchange potentials, $v_{x\uparrow}(r)-v_{x\downarrow}(r)$, for Cu from the OPM (solid line), LSDA (dashed line), and the GGA of Ref. [27] (dotted line) (in hartrees).

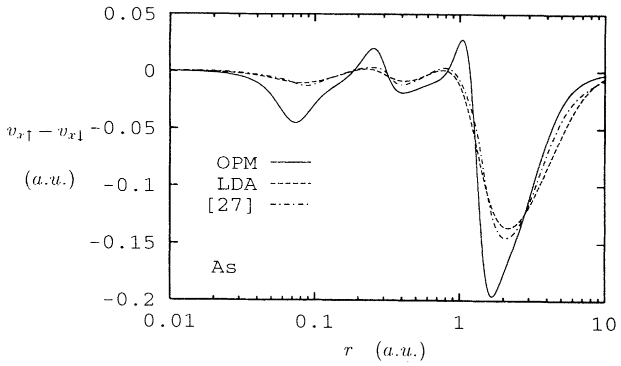

FIG. 2. Same as Fig. 1 for As.

As is clear from this discussion the LSDA does not just underestimate the eigenvalues of all orbitals by some common constant, but rather does not reproduce eigenvalue differences for given spin. Analyzing the eigenvalue differences between the outermost orbitals of the two spin components the same feature shows up. Again the error is roughly a factor of 2. Finally, the spin splitting of the eigenvalues for a given orbital cannot be reproduced much better: While $\varepsilon_{nl}^{\uparrow}-\varepsilon_{nl}^{\downarrow}$ is roughly correct for Mn (4s: OPM, 49 mhartree; LSDA, 51 mhartree) and Eu (6s: OPM, 6 mhartree; LSDA, 8 mhartree), the error amounts to 21% for As (4s: OPM, 131 mhartree; LSDA, 104 mhartree) and even the sign is wrong for Cr (3p: OPM, −25 mhartree; LSDA, 179 mhartree) and Cu (3d: OPM, −186 mhartree; LSDA, 6 mhartree). Again the GGA is not doing any better.

In Figs.1–5 we plot $v_{x\uparrow}(r)-v_{x\downarrow}(r)$, which is a measure for the tendency of the atom to favor spin polarization. In all cases the differences between the OPM, on one hand, and the LSDA and the GGA, on the other hand, are striking. For Cu one essentially observes a huge constant shift between $v_{x\uparrow}(r)$ and $v_{x\downarrow}(r)$ which only vanishes in the extreme asymptotic regime where both $v_{x\uparrow}(r)$ and $v_{x\downarrow}(r)$ approach $-1/r$. This shift is not reproduced at all by the LSDA or the GGA. The situation is similar for Cr where the outermost orbital again is of s type. Here, however, the shift is convoluted with additional structures originating from the $3d$ electrons. The comparison looks

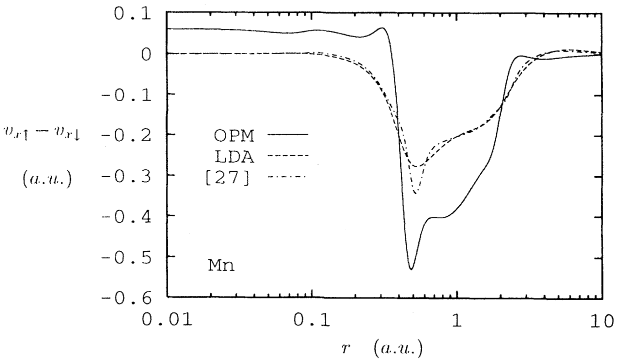

FIG. 3. Same as Fig. 1 for Mn.

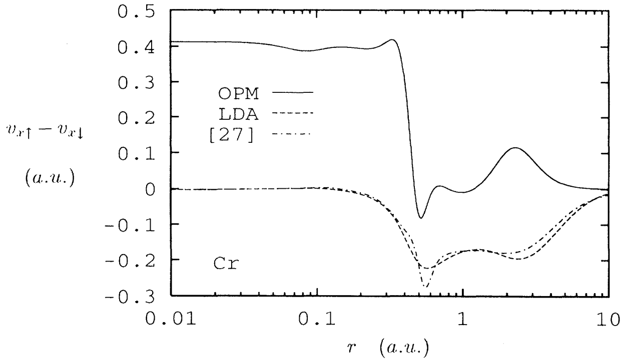

FIG. 4. Same as Fig. 1 for Cr.

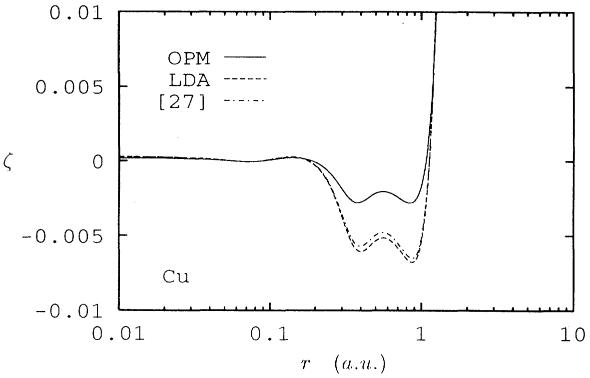

FIG. 6. Magnetization density $\zeta = (n_\uparrow - n_\downarrow)/(n_\uparrow + n_\downarrow)$ for Cu from the OPM (solid line), LSDA (dashed line), and the GGA of Ref. [27] (dotted line).

more favorable for the LSDA and the GGA for As, Mn, and Eu where these approximations at least make some attempt to follow the OPM. Still, they underestimate all structures in the OPM spin splitting considerably. While the GGA overall tends to correct the LSDA in the right direction its quantitative success is only marginal.

As to be expected from the fact that $n_\uparrow(r)$ and $n_\downarrow(r)$ are determined by the total spin-up and spin-down potentials, respectively,

$$v^{\sigma}_{\rm tot}(r) = v_{\rm ext}(r) + v_H(r) + \frac{1}{2}[v_{x\uparrow}(r) + v_{x\downarrow}(r)] + \frac{1}{2}\mathrm{sgn}(\sigma)[v_{x\uparrow}(r) - v_{x\downarrow}(r)],$$

where the error in $v_{x\uparrow}(r) - v_{x\downarrow}(r)$ represents only a minor component, the spin magnetization

$$\zeta(r) = \frac{n_\uparrow(r) - n_\downarrow(r)}{n_\uparrow(r) + n_\downarrow(r)}$$

is considerably less sensitive to the quality of an approximate $E^{\sigma}_x[n]$ than $v_{x\uparrow}(r) - v_{x\downarrow}(r)$. In particular, the position and shape of ζ are more or less determined by the quantum numbers of the polarized orbital as it and thus the total magnetization are fixed for these atomic calculations. In fact, ζ is reproduced much better by the LSDA and the GGA (which are more or less indistinguishable) than $v_{x\uparrow}(r) - v_{x\downarrow}(r)$ as can be seen from Figs. 6–10. While for As, Cr, and Mn the LSDA and GGA can follow the OPM rather accurately there are some differences for Eu. The spin polarization in the interior of Cu, on the other hand, for which already $v_{x\uparrow}(r) - v_{x\downarrow}(r)$ showed the biggest discrepancy, is overestimated by more than a factor of 2. We only mention that the same effect occurs for Ag and Au, although there it is not as pronounced as in Cu. It thus becomes obvious that the LSDA can lead to erroneous magnetization densities even for atoms and the GGA does not improve on the LSDA. Given the even greater importance of $v_{x\sigma}$ for the total potential in Kohn-Sham calculations for solids and the fact that in this case the total magnetization is not *a priori* fixed but rather determined self-consistently, it is not difficult to imagine that many of the failures of the LSDA and GGA for condensed-matter systems could be traced back to their insufficient reproduction of the spin splitting in v_x.

It should be emphasized that the differences between the spin densities of the LSDA-GGA and the OPM are not the source of the huge errors in the self-consistent $v_{x\uparrow}(r) - v_{x\downarrow}(r)$ shown in Figs. 1–5. This is immediately clear for As, Mn, and Cr where the spin densities are

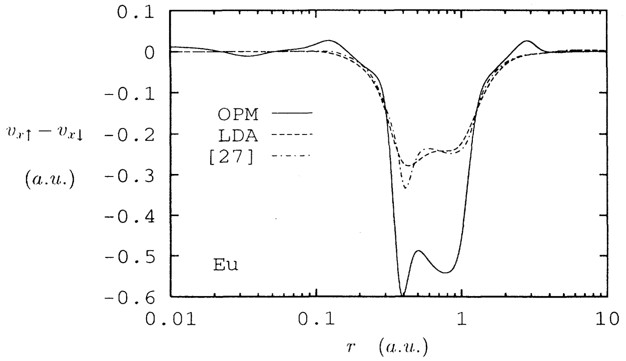

FIG. 5. Same as Fig. 1 for Eu.

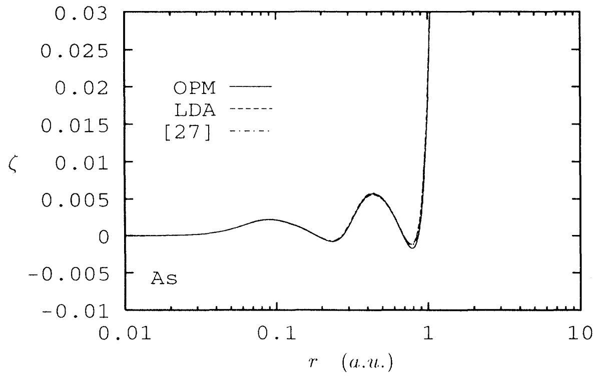

FIG. 7. Same as Fig. 6 for As.

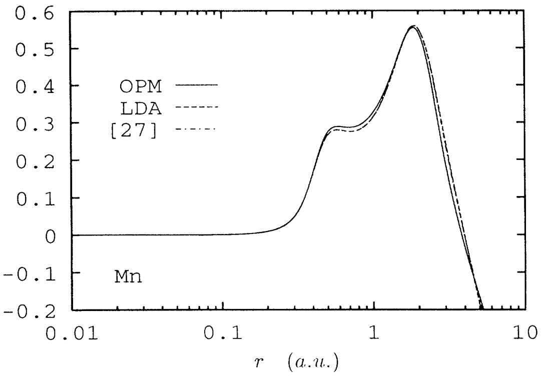

FIG. 8. Same as Fig. 6 for Mn.

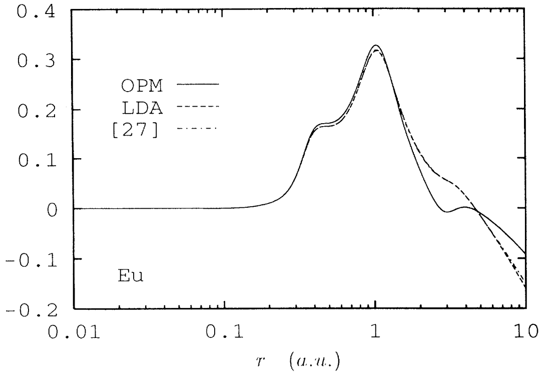

FIG. 10. Same as Fig. 6 for Eu.

rather similar, but also holds for Cu as the absolute value of ζ and consequently also $(n_\sigma^{\text{OPM}} - n_\sigma^{\text{LSDA}})/n_\sigma^{\text{OPM}}$ are rather small. Most obvious, however, is the localization of the error in ζ: This confinement contrasts with the extended error in $v_{x\uparrow}(r) - v_{x\downarrow}(r)$.

V. CONCLUDING REMARKS

In this paper we have presented accurate OPM results for all spherical atoms (both unpolarized and spin-polarized ones) with $Z \leq 86$ discussing in some detail the technical questions which have to be addressed to achieve this accuracy (in the Appendix). These results allowed a detailed study of the magnetization properties of spin-polarized atoms. In particular, we have used them to check the quality of the LSDA and a widely used GGA [27] to reproduce spin-dependent quantities like the spin splitting in the exchange energy and the exchange potential, i.e., $E_{x\uparrow} - E_{x\downarrow}$ and $v_{x\uparrow}(r) - v_{x\downarrow}(r)$, and the magnetization density. Our analysis shows that, while the GGA removes most of the error in the LSDA for global quantities such as ground-state and total exchange energies, it is less successful for $E_{x\uparrow} - E_{x\downarrow}$ and it does not improve $v_{x\uparrow}(r) - v_{x\downarrow}(r)$ and the magnetization density. Thus its quality for E_{tot}'s and E_x's can be somewhat misleading and most likely results from cancellation of local errors. Furthermore, it is found that for Cr and Cu, where the eigenvalues of the two outermost orbitals of the majority-spin component are nearby in the OPM, the LSDA and GGA produce incorrect orders of eigenvalues due to the fact that for the majority spin not only the highest occupied but also the next eigenvalue is seriously in error. In view of these results it is not surprising that the LSDA and GGA produce unphysical magnetic phases in a number of metals [29, 32, 33].

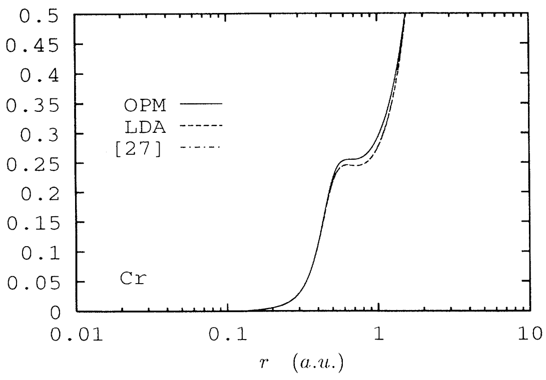

FIG. 9. Same as Fig. 6 for Cr.

It seems to us that as for the asymptotic properties of GGA's [12] the source of the failure of the GGA to improve local spin-dependent quantities over the LSDA is its limited nonlocality. The exact $E_x[n]$ contains at least one ingredient which is much more nonlocal than that which could be reproduced by the GGA's simple quasilocal functional dependence on the density, i.e., the self-interaction correction part. Though one could hope that this ingredient of $E_x[n]$ is less important for the description of condensed matter systems it appears necessary to study the capability of inherently more nonlocal schemes to reproduce $v_{x\uparrow}(r) - v_{x\downarrow}(r)$ and $\zeta(r)$.

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APPENDIX: ON THE ACCURATE CONSTRUCTION OF $V_X(R)$ FROM THE OPM INTEGRAL EQUATION

In this appendix we briefly review the OPM approach in order to provide the details required for the discussion of the asymptotic form of the OPM exchange potential. The analytic asymptotic form is used to accurately obtain $v_x(r)$ from the OPM integral equation.

For spherical systems the spin-unrestricted OPM equations [2] consist of a radial Kohn-Sham equation for each spin,

$$\left\{\partial_r^2 - \frac{l(l+1)}{r^2} + 2[\epsilon^\sigma_{nl} - v^\sigma_{\text{tot}}(r)]\right\}P^\sigma_{nl}(r) = 0 \ , \tag{A1}$$

where

$$v^\sigma_{\text{tot}}(r) = v_{\text{ext}}(r) + v_H(r) + v_{x\sigma}(r) \ , \tag{A2}$$

$$v_{\text{ext}}(r) = -\frac{Z}{r} \ , \tag{A3}$$

$$v_H(r) = 4\pi\left\{\frac{1}{r}\int_0^r x^2dx\ n(x) + \int_r^\infty xdx\ n(x)\right\} \ , \tag{A4}$$

$$n(r) = n_\uparrow(r) + n_\downarrow(r) \ , \tag{A5}$$

$$n_\sigma(r) = \sum_{n,l}\Theta(\varepsilon_F - \varepsilon^\sigma_{nl})\frac{2l+1}{4\pi r^2}[P^\sigma_{nl}(r)]^2 \ , \tag{A6}$$

and $v_{x\sigma}(r)$ being the exchange potential constructed from the solution of the OPM integral equation for given spin,

$$\int_0^\infty dr' K^\sigma(r,r')v_{x\sigma}(r') = I^\sigma(r) \ . \tag{A7}$$

The kernel K^σ and the inhomogeneity I^σ of this Fredholm equation of first kind are given in terms of the solutions P^σ_{nl} and the corresponding complementary solutions Q^σ_{nl} of Eq. (A1),

$$1 = P^\sigma_{nl}(r)\ \partial_r Q^\sigma_{nl}(r) - Q^\sigma_{nl}(r)\ \partial_r P^\sigma_{nl}(r) \ . \tag{A8}$$

Using the Green's function

$$\begin{aligned} G^\sigma_{nl}(r,r') = 2\Bigg\{ & \Theta(r-r')\ P^\sigma_{nl}(r)\ Q^\sigma_{nl}(r') + \Theta(r'-r)\ Q^\sigma_{nl}(r)\ P^\sigma_{nl}(r') \\ & -P^\sigma_{nl}(r)\left[P^\sigma_{nl}(r')\int_0^{r'} dxP^\sigma_{nl}(x)Q^\sigma_{nl}(x) + Q^\sigma_{nl}(r')\int_{r'}^\infty dx[P^\sigma_{nl}(x)]^2\right] \\ & -P^\sigma_{nl}(r')\left[P^\sigma_{nl}(r)\int_0^{r} dxP^\sigma_{nl}(x)Q^\sigma_{nl}(x) + Q^\sigma_{nl}(r)\int_{r}^\infty dx[P^\sigma_{nl}(x)]^2\right] \\ & +2P^\sigma_{nl}(r)P^\sigma_{nl}(r')\int_0^\infty dx\int_0^x dy[P^\sigma_{nl}(x)]^2P^\sigma_{nl}(y)Q^\sigma_{nl}(y)\Bigg\} \ , \end{aligned} \tag{A9}$$

which satisfies

$$\left\{\partial_r^2 - \frac{l(l+1)}{r^2} + 2[\epsilon^\sigma_{nl} - v^\sigma_{\text{tot}}(r)]\right\}G^\sigma_{nl}(r,r') = 2\{P^\sigma_{nl}(r)P^\sigma_{nl}(r') - \delta(r-r')\} \ , \tag{A10}$$

one finds

$$K^\sigma(r,r') = \sum_{n,l}\Theta(\varepsilon_F - \varepsilon^\sigma_{nl})(2l+1)P^\sigma_{nl}(r)G^\sigma_{nl}(r,r')P^\sigma_{nl}(r') \ , \tag{A11}$$

$$\begin{aligned} I^\sigma(r) = -\sum_{n,l}\Theta(\varepsilon_F - \varepsilon^\sigma_{nl})(2l+1)\sum_{n',l'}\Theta(\varepsilon_F - \varepsilon^\sigma_{n'l'})(2l'+1) \\ \times P^\sigma_{nl}(r)\int_0^\infty dxG^\sigma_{nl}(r,x)P^\sigma_{n'l'}(x)\int_0^\infty dy\sum_{L=|l-l'|}^{l+l'} c_{ll'L}\frac{r_<^L}{r_>^{L+1}}P^\sigma_{nl}(y)P^\sigma_{n'l'}(y) \ , \end{aligned} \tag{A12}$$

where $r_<$ is the smaller of x, y and $r_>$ the larger, and $c_{ll'L}$ is given by

$$c_{ll'L} = \left[\frac{(l'+L-l)!(L+l-l')!(l+l'-L)!}{(l+l'+L+1)!}\right]\left[\frac{(\frac{l+l'+L}{2})!}{(\frac{l'+L-l}{2})!(\frac{L+l-l'}{2})!(\frac{l+l'-L}{2})!}\right]^2$$

if $l+l'+L$ is even and is 0 otherwise. K^σ has the obvious properties

$$K^\sigma(r,r') = K^\sigma(r',r) \ , \tag{A13}$$

$$\int_0^\infty dr\ K^\sigma(r,r') = 0 \ . \tag{A14}$$

Consequently Eq. (A7) defines $v_{x\sigma}(r)$ only up to a constant. This constant is fixed by the physical requirement

$$\lim_{r\to\infty} v_{x\sigma}(r) = 0 \ . \tag{A15}$$

Any discretization of Eq. (A7) necessary for practical calculations, however, no longer satisfies (A14) but rather has a unique solution. Apart from numerical inaccuracies this solution differs from the exact $v_{x\sigma}(r)$ by some unknown constant, i.e., it does not satisfy Eq. (A15). This constant has to be subtracted out of the solution in order to construct $v_{x\sigma}(r)$. The only regime where one knows $v_{x\sigma}(r)$ analytically and thus is able to define the constant is the asymptotic regime. Talman has shown [2] that $v_{x\sigma}(r)$ asymptotically approaches $-1/r$. The r values where $v_{x\sigma}(r)$ actually starts to follow $-1/r$, however, are rather large [12]. Thus fixing the constant becomes more accurate the larger the r value is at which $v_{x\sigma}(r)$ is determined. The numerical evaluation of (A7), on the other hand, is becoming increasingly difficult where the kernel and the inhomogeneity decay exponentially. Also, the accuracy of the numerical solution of Eq. (A7) as characterized by the exchange virial relation is mainly determined by the step size of the grid used and thus decreases with increasing size of the r range where $v_{x\sigma}(r)$ has to be evaluated numerically. This procedure is even more critical for spin-polarized systems where the spin-up and -down potentials have to be fixed at different r values with that for the minority spin component being rather small as the corresponding kernel and inhomogeneity are decaying faster. The difference $v_{x\uparrow}(r) - v_{x\downarrow}(r)$, however, is crucial for the spin polarization the atom displays.

In their paper Talman and Shadwick [2] noted that for large r the sum over all occupied orbitals in Eq. (A11) reduces to just the term corresponding to the most slowly decaying orbital $P^{\sigma}_{mk}(r)$. In fact, the remaining terms are suppressed relative to this leading one by

$$\left(\frac{P^{\sigma}_{nl}(r)}{P^{\sigma}_{mk}(r)}\right)^2 , \quad n,l \neq m,k \, .$$

Apart from atoms where the eigenvalues of the two outermost orbitals are extremely close this ratio turns out to be very small as can be checked with any solution. Even for the exceptional cases Cr and Mo it still is reasonably small. The same arguments apply to $I^{\sigma}(r)$ such that asymptotically one obtains the integral equation [2]

$$\int_0^{\infty} dr' G^{\sigma}_{mk}(r,r') P^{\sigma}_{mk}(r') v_{x\sigma}(r') = \int_0^{\infty} dr' G^{\sigma}_{mk}(r,r') F^{\sigma}(r')$$

with

$$F^{\sigma}(r') = -\sum_{n,l} \Theta(\varepsilon_F - \varepsilon^{\sigma}_{nl})(2l+1) P^{\sigma}_{nl}(r') \times \int_0^{\infty} dy \sum_{L=|k-l|}^{k+l} c_{klL} \frac{r_<^L}{r_>^{L+1}} P^{\sigma}_{mk}(y) P^{\sigma}_{nl}(y) \, .$$

Applying (A10) one ends up with

$$v_{x\sigma}(r) \underset{r>>1}{\longrightarrow} \frac{F^{\sigma}(r)}{P^{\sigma}_{mk}(r)} \, . \tag{A16}$$

As already emphasized by Talman and Shadwick [2] the leading term in this expression is $-1/r$. The next correction to $-1/r$ depends on the quantum numbers of the two outermost orbitals. It is most pronounced if $k \neq 0$,

$$v_{x\sigma}(r) \underset{r>>1}{\longrightarrow} -\frac{1}{r} - \frac{(2k+1)c_{kk2}}{r^3} \int_0^{\infty} x^2 dx [P^{\sigma}_{mk}(x)]^2 \, .$$

For the spin-up component of Bi, for example, this $1/r^3$ term contributes -4.3 mhartree at $r = 10$ a.u. Note also that our 2p eigenvalue for the spin-down component of Na satisfies the relation of Krieger, Li, and Iafrate [7] much better than the result of Krieger, Li, and Iafrate (compare Table VIII of Ref. [11]). At 8 a.u., e.g., the above correction contributes -0.64 mhartree to $v_{x\sigma}(r)$, which is transferred to the eigenvalues.

However, not only power-law corrections can be of significant size, also terms which decay exponentially with respect to the leading one can contribute if the eigenvalues of the two outermost orbitals are very close together. This occurs, e.g., for the spin-up component of Cr where the highest occupied eigenvalue ($4s$) is -0.2231 hartree while the next ($3d$) is obtained as -0.2423 hartree. In this case the first exponentially smaller correction contributes 0.53 mhartree at 10 a.u.

We consequently use Eq. (A16) without any further approximation to define the constant present in any numerical solution of (A7). This leads to eigenvalues whose accuracy is on the 0.1 mhartree level without reducing the overall accuracy of $v_{x\sigma}(r)$ as it allows using r values for defining the constant which are not excessively large. The only exceptions from this level of accuracy are those atoms where already the first approximation, i.e., reducing the sum in $K^{\sigma}(r,r')$, Eq. (A11), to a single term introduces a small error. This, however, is only the case if the two outermost eigenvalues are extremely close together as occurs for the spin-up orbitals of Cr and Mo and to a limited extent for Cu. Even for Cr and Mo the accuracy achieved is about 1 mhartree as can be seen from a comparison of $\varepsilon^{\sigma}_{mk}$ and $\bar{\varepsilon}^{\sigma,\mathrm{HF}}_{mk}$ on the basis of the relation (6).

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