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### RAPID COMMUNICATIONS

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#### Spin-dependent pseudopotentials

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Near degeneracies and strong spin polarization are characteristics of transition metals that offer challenges to the pseudopotential approximation. Here we investigate the spin dependence of pseudopotentials generated from atomic, all-electron density-functional calculations. Different spins are found to require different pseudopotentials for any spin-polarized atom. Ignoring this leads to significant errors in the representation of all but the nonmagnetic configurations. Including a correction that is linear in the local spin polarization results in a spin-dependent expression, which dramatically improves the transferability of the atomic pseudopotential beyond previous nonlinear core corrections. [S0163-1829(98)50544-9]

The use of pseudopotentials to effectively describe the combined potentials of the nucleus and core electrons on the valence electrons, predates many electronic structure techniques.<sup>1,2</sup> Modern computers allow all-electron (AE) calculations to be performed for the full periodic table. Pseudopotentials can be derived from these AE results that give “exact” agreement in the valence eigenvalues between the atom and pseudoatom.<sup>3-5</sup> The phenomenal success<sup>6</sup> of pseudopotentials within the local-density approximation (LDA) to density-functional theory (DFT) has led to blasé use. The current work investigates the applicability of spin-averaged pseudopotentials (currently used almost exclusively) in describing strongly-spin-polarized atomic configurations. We find that there are significant errors introduced by spin averaging, and that an additional potential, linear in the local spin polarization, makes a dramatic improvement.

The construction of *ab initio* pseudopotentials is invariably performed by following the same “recipe.” For a given reference atom, the all-electron radial wave function [ $R(r)$ ] of each valence spin ( $\sigma$ ) and angular momentum ( $l$ ) channel is replaced by a pseudo-wave function [ $\bar{R}(r)$ ]. The pseudo-wave function is identical to the true wave function beyond a chosen “core” radius, and is a smooth function that maintains normalization within. It is the freedom in the generation of this smooth function that has produced the diversity of techniques.

Within density-functional theory,<sup>7</sup> a screened potential, which contains both valence and core electron contributions,

is obtained by inverting the radial Schrödinger equation:

$$\text{scr}\bar{V}_l^\sigma(r) = \epsilon_l^\sigma - \frac{l(l+1)}{2r^2} + \frac{1}{2r\bar{R}_l^\sigma(r)} \frac{d^2}{dr^2} [r\bar{R}_l^\sigma(r)]. \quad (1)$$

The ionic pseudopotential is obtained by removing the valence Hartree ( $\bar{V}_{\text{Har}}$ ) and exchange-correlation ( $\bar{V}_{\text{XC}}^\sigma$ ) potentials:

$$\text{ion}\bar{V}_l^\sigma(r) = \text{scr}\bar{V}_l^\sigma(r) - \bar{V}_{\text{Har}}(r) - \bar{V}_{\text{XC}}^\sigma(r). \quad (2)$$

The spin dependence will manifest itself through two fundamental properties. For any spin-polarized atom, the valence electron eigenvalues ( $\epsilon_l^\sigma$ ) will have different energies for different spins ( $\epsilon_l^\uparrow \neq \epsilon_l^\downarrow$ ), and the pseudo-wave functions will have different radial dependences ( $\bar{R}_l^\uparrow(r) \neq \bar{R}_l^\downarrow(r)$ ). This will affect all three terms in the right-hand side of Eq. (2), resulting in an ionic pseudopotential that differs between spin channels in a manner that is dependent on the spin state of the reference system. The valence Hartree potential exactly cancels itself from the screened potential implicitly, offering no net spin dependence. The exchange-correlation potential is nonlinear and does not produce such a cancellation.

Calculations in the current work are performed within the local-spin-density approximation (LSDA) to DFT, as parametrized by Perdew and Zunger.<sup>8</sup> The exchange-correlation energy is a local functional of the valence spin density ( $\bar{\rho}_v = \bar{\rho}_v^\uparrow + \bar{\rho}_v^\downarrow$ ):

$$E_{XC} = \int d\mathbf{r} \bar{\rho}_v(\mathbf{r}) \epsilon_{XC}[\bar{\rho}_v^\uparrow(\mathbf{r}); \bar{\rho}_v^\downarrow(\mathbf{r})], \quad (3)$$

$$V_{XC}^\sigma(\mathbf{r}) = V_{XC}^\sigma[\bar{\rho}_v^\uparrow(\mathbf{r}); \bar{\rho}_v^\downarrow(\mathbf{r})],$$

$$= \frac{\partial \{ \bar{\rho}_v(\mathbf{r}) \epsilon_{XC}[\bar{\rho}_v^\uparrow(\mathbf{r}); \bar{\rho}_v^\downarrow(\mathbf{r})] \}}{\partial \bar{\rho}_v^\sigma(\mathbf{r})}. \quad (4)$$

The nonlinear core correction (NLCC) to the LSDA (Refs. 9 and 10) has been seen to improve transferability within standard DFT. The addition of a partial core charge within the calculation of the valence exchange-correlation (XC) potential includes much of its nonlinearity:

$$V_{XC,NLCC}^\sigma(\mathbf{r}) = \frac{\partial \left\{ (\bar{\rho}_v(\mathbf{r}) + \bar{\rho}_c(\mathbf{r})) \epsilon_{XC} \left[ \bar{\rho}_v^\uparrow(\mathbf{r}) + \frac{1}{2} \bar{\rho}_c(\mathbf{r}); \bar{\rho}_v^\downarrow(\mathbf{r}) + \frac{1}{2} \bar{\rho}_c(\mathbf{r}) \right] \right\}}{\partial \bar{\rho}_v^\sigma(\mathbf{r})}. \quad (5)$$

All pseudopotentials in this work were generated numerically using the *ab initio* method of Troullier and Martins.<sup>5</sup> The cutoffs used were chosen to be 90% of the radius of the outermost maximum in the radial wave function, values that have been shown previously to produce reliable pseudopotentials.<sup>11</sup>

Figure 1 demonstrates the magnitude of the spin dependence, in the total energy of the  $4s^n 3d^{6-n}$  chromium atom. The deviation from the AE energy is compared first using spin-averaged pseudopotentials  $V[r]$  calculated using the nonmagnetic  $4s\{\frac{1}{2}\uparrow, \frac{1}{2}\downarrow\} 3d\{\frac{5}{2}\uparrow, \frac{5}{2}\downarrow\}$  configuration.

Calculations were also performed using spin-averaged pseudopotentials generated from spin-polarized configurations, weighting by occupation:<sup>5</sup>

$$V_{ion} = \frac{N_e^\uparrow}{N_e} V_l^\uparrow + \frac{N_e^\downarrow}{N_e} V_l^\downarrow. \quad (6)$$

Use of either the nonmagnetic or fully-spin-polarized reference configuration for the generation of the spin-averaged pseudopotential was found to have little effect on the spin dependence, merely producing a chemically insignificant shift in the energy.<sup>6</sup> We therefore follow tradition, and use the nonmagnetic reference system to generate the spin-averaged pseudopotentials throughout.

One can see that the spin-averaged pseudopotentials give significant deviations from the AE results. The relative energies of the different states of Cr are in error by as much as 50%. Including nonlinear core effects improves the energies, but does not fully capture the spin dependence.

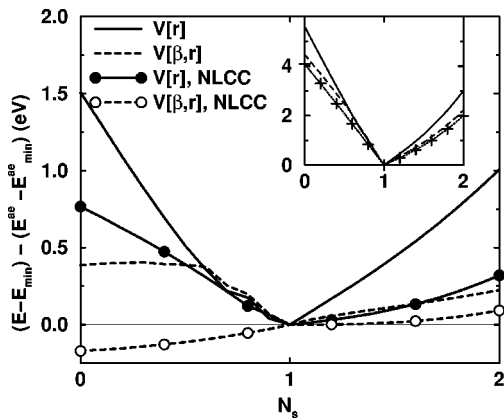


FIG. 1. The deviation from the LSDA all-electron energy for high-spin chromium  $s^n d^{6-n}$  with varying number of  $s$  electrons  $N_s$ . Spin-averaged ( $V[r]$ ) and spin-dependent ( $V[\beta, r]$ ) pseudopotentials are used, without and with the nonlinear core correction. Inset: the spin-averaged, spin-dependent, and all-electron ( $\cdot \cdot \cdot$ ) absolute energies, relative to the  $s^1 d^5$  ground state. Energies are in eV.

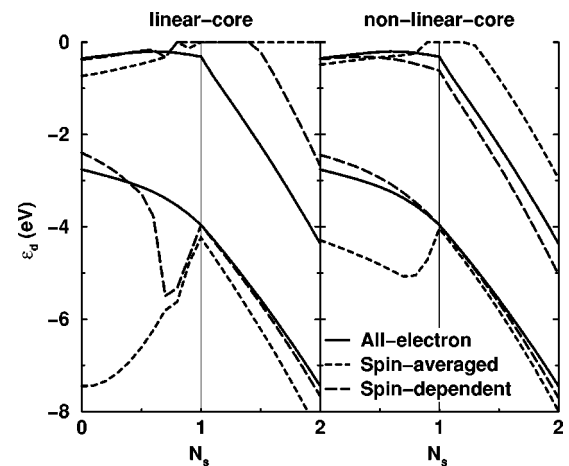


FIG. 2. The variation of the  $d$  atomic eigenvalues with number of  $s$  electrons  $N_s$ , for the high-spin chromium configuration  $s^n d^{6-n}$ . Results using the nonlinear core correction are to the right. The upper curves are the minority spin, the lower curves, the majority spin. Unbound orbitals are indicated by an eigenvalue greater than zero.

This failure of the spin-averaged pseudopotential is illustrated even more dramatically in the eigenvalues. Figure 2 shows the  $3d$  eigenvalues for the same high-spin states of chromium as Fig 1. For all states  $N_s \geq 1$ , the  $3d$  minority-spin orbitals (upper curves) are unoccupied (and as far as DFT is concerned, irrelevant<sup>6</sup>). However, for  $N_s < 1$  the minority-spin orbitals are partially occupied. Many of these states have a minority  $3d$  orbital that is not fully bound (indicated by a non-negative eigenvalue). The occupation of these partially-bound states leads to considerable problems in the self-consistent potentials, and significant errors in the eigenvalues and energies.

It is clear that, in order to accurately reproduce even atomic energies, for partially (or fully) polarized spin configurations, a spin dependence should somehow be incorporated into the pseudopotential. A potential, explicitly dependent upon atomic configuration<sup>12,13</sup> is not desirable, however, as this would require some arbitrary assignment of an atomic configuration in nonatomic environments.

Within the LSDA, the symmetry of the spin requires that, for nonrelativistic methods, the potential for a majority spin should be the same, regardless of whether that spin is up or down. This means that the pseudopotential is not so much spin-dependent as spin-polarization-dependent (unlike Ref. 14, which is explicitly spin-dependent). The method proposed here for the incorporation of this spin-polarization dependence is via an additional potential that is some function of the spin polarization (in a similar manner to the local-spin-density approximation LSDA). For the present work a simple linear correction is investigated.

The ionic pseudopotential is partitioned into up and down ‘‘potentials’’ that apply to the up and down electron density, respectively. The ion-electron interaction energy for the spherically symmetric atom is given by

$$E^{I-e} = \int 4\pi r^2 dr [\mathcal{V}^\uparrow(r)\rho^\uparrow(r) + \mathcal{V}^\downarrow(r)\rho^\downarrow(r)], \quad (7)$$

where

$$\mathcal{V}^\uparrow(r) = V_0(r) + F[\beta(r)]V_1(r), \quad (8)$$

$$\mathcal{V}^\downarrow(r) = V_0(r) + F[-\beta(r)]V_1(r), \quad (9)$$

have a functional dependence (through  $F[\beta]$ ) on the local spin polarization:

$$\beta(r) = \frac{\rho^\uparrow(r) - \rho^\downarrow(r)}{\rho^\uparrow(r) + \rho^\downarrow(r)}. \quad (10)$$

For the current work, we shall investigate the linear functional  $F[\beta] = \beta$ .

The potentials resulting from the energy expression are no longer trivial:

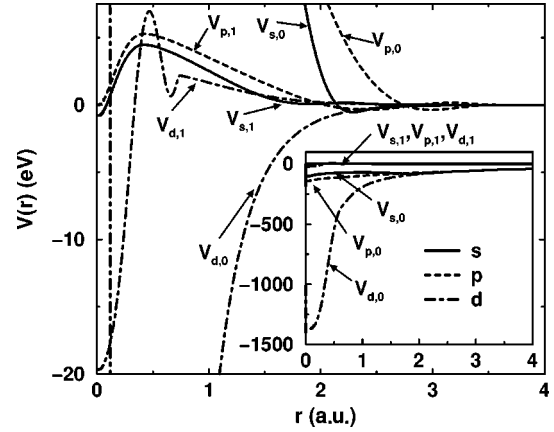


FIG. 3. The magnitude of the spin-dependent term  $V_{l,1}$ , compared to the non-Coulombic contribution to the spin-independent pseudopotential,  $V_{l,0} + Z/r$  for chromium without the NLCC ( $Z = 6$  for the chromium pseudo-atom). The pseudopotential with Coulombic contributions is shown in the inset.

$$\begin{aligned} \frac{\delta E^{I-e}}{\delta \rho^\uparrow(r)} &= V^\uparrow(r) = V_0(r) \\ &+ V_1(r) \left( F[\beta(r)] + \rho^\uparrow(r) \frac{\delta F[\beta(r)]}{\delta \rho^\uparrow(r)} \right) \\ &+ \rho^\downarrow(r) \frac{\delta F[-\beta(r)]}{\delta \rho^\uparrow(r)} \\ &= V_0(r) + \beta(r)(2 - \beta(r))V_1(r), \end{aligned} \quad (11)$$

$$\frac{\delta E^{I-e}}{\delta \rho^\downarrow(r)} = V^\downarrow(r) = V_0(r) - \beta(r)(2 + \beta(r))V_1(r). \quad (12)$$

For nonlocal pseudopotentials, each angular momentum component experiences a different spin dependence, the potentials becoming  $l$ -dependent ( $V_0 \rightarrow V_{l,0}$  and  $V_1 \rightarrow V_{l,1}$ ). The evaluation of the radial potentials  $V_{l,0}(r)$  and  $V_{l,1}(r)$  involves the calculation of the unscreened ionic potentials for two different pseudoatom spin configurations. For a nonmagnetic, nonrelativistic pseudo-atom ( $\rho^\uparrow(r) = \rho^\downarrow(r)$ ;  $\beta(r) = 0$ ),  $V_{l,0}(r)$  is obtained directly from Eqs. (11) and (12) ( $V_{l,0}(r) = V_l^\uparrow(r) = V_l^\downarrow(r)$  evaluated via Eq. (2)).  $V_{l,1}(r)$  is more ambiguous.

In the current work,  $V_{l,1}(r)$  is obtained from the potential affecting the majority spin of a fully-polarized pseudo-atom. For example, the chromium  $4s^1 d^5$  nonmagnetic configuration ( $4s\{\frac{1}{2}\uparrow, \frac{1}{2}\downarrow\}3d\{\frac{5}{2}\uparrow, \frac{5}{2}\downarrow\}$ ) gives  $V_{l,0}(r)$  directly. Then  $V_l^\uparrow(r)$  is obtained, by Eq. (2), from the fully-spin-polarized configuration ( $4s\{1\uparrow, 0\downarrow\}3d\{5\uparrow, 0\downarrow\}$ ). These results, along with the fully-polarized spin polarization  $\beta(r)$ , will give us  $V_{l,1}(r)$  from Eq. (11).

The spin-dependent potential  $V_{l,1}(r)$  is not currently constructed to reproduce the fully-polarized limit for the minority spin, only the majority-spin potential. Doing so, using the local spin polarization, would require a nonlinear, asymmetric functional  $F[\beta(r)]$  in Eqs. (8) and (9),<sup>15</sup> which could be derived from a series of all-electron results (using the projector augmented wave method,<sup>16</sup> for example). However,

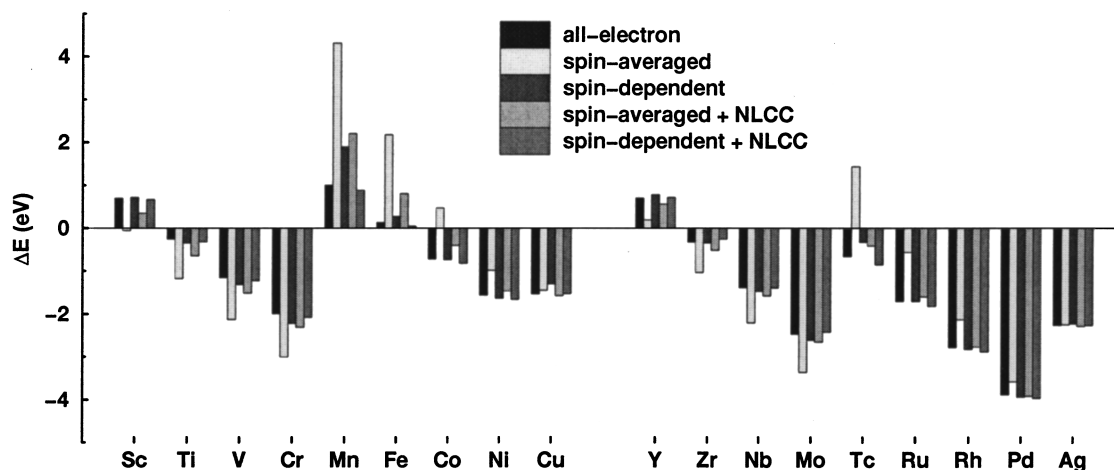


FIG. 4. The atomic state splitting energy  $E[s^1d^{n-1}] - E[s^2d^{n-2}]$  for the first- and second-row transition metals (except Zn and Cd). A positive value indicates  $s^1d^{n-1}$  is the more stable configuration, a negative value that it is  $s^2d^{n-2}$ .

for the cases studied here (all first- and second-row transition metal atoms) the results for this energy expression are already seen to be a dramatic improvement over the corresponding spin-averaged pseudopotential.

In order to maintain a consistent, and unbiased approach, the pseudo-core density of the nonmagnetic  $s^1d^{n-1}$  reference state is used in all expressions involving the nonlinear core correction. In particular, it is used when descreening the ionic potential [Eqs. (2) and (5)] for the fully-polarized reference state.

The magnitude of the spin-dependent term  $V_{l,1}(r)$  is shown in Fig. 3. In all instances it is at least an order of magnitude smaller (see inset) than the corresponding spin-independent term  $V_{l,0}(r)$ . The Coulombic nature of the pseudopotential is fully captured in the spin-independent term. Thus, the range of  $V_{l,1}(r)$  is short, very similar to that of the core electron density, falling quickly to zero as one moves away from the atomic center.

Figures 1 and 2 include results generated using the spin-dependent pseudopotential, with and without the NLCC. In all instances these pseudopotentials give relative energies and eigenvalues in much better agreement with the all-electron results, than do the spin-averaged pseudopotentials. With a linear core, there are still problems in describing the minority-spin orbitals of some states, leading to some large nonlinear errors (see the inset of Fig. 1). However, including the NLCC leads to fully bound minority-spin orbitals for all states, and much improved energies and eigenvalues.

The atomic state splitting energy  $E[s^1d^{n-1}] - E[s^2d^{n-2}]$  provides a strong test of the ability of a pseudopotential to describe the spin properties of the transition metal atoms. Figure 4 shows the splitting energy for the first- and second-row transition metal atoms. The all-electron results are compared with several pseudopotential methods. The spin-averaged pseudopotential is used with and without the nonlinear core correction. The spin-dependent pseudopotential, also with and without the NLCC, is generated as prescribed earlier.

The spin-averaged pseudopotential does consistently poorly at reproducing the all-electron energy gaps. It gives

an energy too negative for the first half of the transition row, and too positive for the second half. This trend is seen in both rows, and is bad enough to predict the wrong relative stabilities more than once. Including the NLCC improves these results. This confirms again the need for such a correction in standard transition metal simulations.<sup>9,17-19</sup>

Including spin dependence (without the NLCC) improves the energies over the spin-averaged results in all instances. It never fails to reproduce the relative stabilities of the two configurations. It is also an improvement over the conventional spin-averaged NLCC in most cases, including the NLCC in the spin-dependent potential gives almost perfect agreement with the all-electron results.

In conclusion, we have shown that pseudopotentials generated from nonmagnetic reference systems—in common use today—lack the transferability properly required to describe various electronic and spin configurations. Further, spin averaging the LSDA-generated pseudopotentials, à la Eq. (6), offers no improvement, merely producing a shift in the total energy relative to the pure LDA pseudopotential. Introducing a spin-dependent correction, calculated within the LSDA, gives much better agreement with all-electron results for all states examined. Greater accuracy for electronic and spin configurations for which the pseudopotential was not constructed, goes to the very heart of the issue of transferability. This improvement can be credited to an incorporation [Eqs. (8) and (9)] of the explicit spin-state dependence of the pseudopotential [in Eq. (2)]. Use of the nonlinear core correction reduces the spin dependence due to the valence exchange-correlation potential. The remaining spin-dependent term in the ionic pseudopotential is associated with the combined effect of the nucleus and core electrons. Use of the new spin-dependent pseudopotential captures the spin-state dependence of the core effects, providing an *implicit* means of going beyond the frozen-core approximation.

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