

Breakdown of the pseudopotential approximation for magnetic systems: Predicting magnetic quenching at the V(001) surface with spin-dependent pseudopotentials

Vincent Cocula and Emily A. Carter*

Department of Chemistry and Biochemistry, Box 951569, University of California, Los Angeles, California 90095-1569, USA

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Both experimentally [R.L. Fink *et al.*, Phys. Rev. B **41**, 10 175 (1990)] and using all-electron density-functional theory (DFT) methods, the V(001) surface exhibits little or no magnetization. Very recently, independent pseudopotential DFT calculations demonstrated the breakdown of the pseudopotential approximation, showing large magnetic moments at the surface of a V(001) slab. Here we demonstrate that use of spin-dependent pseudopotentials systematically corrects the inaccuracies of conventional spin-neutral pseudopotentials, producing results consistent with all-electron ones. We also show how the use of the spin-dependent pseudopotentials allows one to achieve a high level of accuracy without the numerical difficulties and cost associated with accurate spin-neutral pseudopotentials.

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The first-principles pseudopotential approximation is a reliable and successful method for the study of the electronic properties of a wide variety of physical systems, ranging from molecules to solids. For the latter, pseudopotential-based methods have and will contribute a great deal to fundamental materials research, both for the study of their properties and the design of new materials. However, the reliability of the pseudopotential approximation for transition metals is still very much an open question, and for this reason, it has been used sparingly for the study of open-shell transition metal-based materials. Specifically, the results given by the method often differ from the all-electron ones, and more disturbingly, pseudopotential calculations sometimes disagree with each other. While the former demonstrates that transition elements present a challenging case for the pseudopotential approximation, the latter clearly shows the lack of a systematic and reliable way to generate such potentials for those elements.

In those cases, the breakdown of the pseudopotential approximation is physically rather well understood: the presence of nearly degenerate low-lying states, the overlap between valence and core electrons (and thus their densities) and their open-shell nature present many potential pitfalls for the approximation itself. Moreover, the construction, and often parametrization, of so-called *ab initio* pseudopotentials is somewhat cumbersome due to the number of parameters to fiddle with: cutoff radii for each angular momentum channel, use of a nonlinear core correction (NLCC), use of the semicore states as valence states, etc. For all these reasons, different pseudopotentials may very well give quite different results, calling into question not only the transferability of the pseudopotential, but also the appellation *ab initio*.

A dramatic illustration of those difficulties is provided in the case of the surface magnetization of V(001). Vanadium is a paramagnetic metal, and a great deal of work has been done recently in assessing the presence, or not, of ferromagnetic ordering at the surface of a thin V(001) film, posing at the same time the question of whether the pseudopotential approximation is able, or not, to correctly predict its electronic structure. Using pseudopotential-based density-functional theory (DFT), Bryk, Bylander, and Kleinman¹

(BBK) reported that V(001) is magnetic within the generalized gradient approximation (GGA), although it was found to be nonmagnetic experimentally. With a Vanderbilt-type norm-conserving pseudopotential,² they obtained a surface magnetization of $1.70\mu_b$ for a bulk-truncated 7-layer film, which decreased to $1.45\mu_b$ after inward relaxation of the outermost layer by $\Delta_{12}=6.25\%$, a value chosen because of its consistency with the reported experimental value of $\Delta_{12}=6.7\pm 1.5\%$. Using an all-electron DFT method (FLAPW-GGA), Bihlmayer, Asada, and Blügel³ (BAB) found that upon relaxation, the contraction between the surface and the subsurface layers was $\sim 10\text{--}11\%$, with no surface magnetization predicted. In light of those results, Batyrev, Cho, and Kleinman⁴ (BCK) reinvestigated the question by comparing their own GGA-FLAPW results with another pseudopotential. While their all-electron DFT calculations produced essentially the same results as those of BAB, the pseudopotential DFT predicted a large magnetization of the surface layer for a 9-layer V(001) film ($1.77\mu_b$). After relaxation, the surface layer moved inward by $\Delta_{12}=12.5\%$, and its magnetization decreased to $0.75\mu_b$. Independently, using a pseudopotential linear combination of atomic orbitals DFT method, Robles, Izquierdo, Vega, and Balbas⁵ (RIVB) obtained similar GGA results to the pseudopotential ones of BCK. However, RIVB found that by explicitly treating the semicore *p* states as valence electrons, the surface magnetization of a 15-layer film vanished, though a large value remained for the 7-layer case.⁶

In an attempt to understand the reasons why the pseudopotential approximation consistently disagreed with all-electron results, Kresse, Bergermayer, and Podloucky⁷ (KBP) generated several pseudopotentials, norm conserving and ultrasoft, all differing by the value of the cutoff radius r_c used for the wave functions. For large cutoff radii, both norm-conserving and ultrasoft potentials reproduced the results obtained by BCK, but with small radii they were able to obtain results consistent with the all-electron ones. However, as the authors state, this cannot be a satisfactory answer, because BCK also used a small cutoff radius and still obtained large magnetizations. They concluded that the results of a pseudopotential calculation depend sensitively on the details of the pseudopotential generation, both for the norm-

conserving and ultrasoft schemes. In their paper, the authors raise many important and interesting points that we discuss later.

The case of V(001) thus clearly calls into question the reliability of the pseudopotential approximation for transition elements, in that the approximation yields a wide range of results highly dependent on the choice of pseudization parameters, often in disagreement with all-electron results. Thus V(001) showcases the difficulty of accurately generating pseudopotentials, and reaffirms the need for a consistent *ab initio* pseudopotential theory for transition elements. Moreover, fitting a pseudopotential by calibrating against arbitrary benchmarking tests does not at all ensure good performances in all other chemical environments; indeed, such fitting procedures may even make the pseudopotential worse. Very recently,^{8–10} we have taken a radically different approach to address the transferability issue of the pseudopotential approximation for transition elements, using the so-called spin-dependent pseudopotentials (SD-PsP). Using a perturbationlike theory, the SD-PsP's aim to systematically correct the commonly used spin-neutral pseudopotential (SN-PsP) by explicitly accounting for the different spin states adopted by the atom. The ionic potential acting on the valence electrons is allowed to self-consistently fluctuate between the spin-neutral and the fully-polarized configurations through a functional F of the local spin-polarization β , where β is defined as the usual

$$\beta(r) = \frac{n^\uparrow(r) - n^\downarrow(r)}{n^\uparrow(r) + n^\downarrow(r)}, \quad (1)$$

where $n(r)$ is the electron density. The total ionic potential for solving the one-electron Kohn-Sham equations then becomes spin dependent

$$\begin{aligned} v^\uparrow(r) &= v^0(r) + F[\beta(r)]\delta v(r), \\ v^\downarrow(r) &= v^0(r) + F[-\beta(r)]\delta v(r), \end{aligned} \quad (2)$$

where v^0 is the reference spin-neutral potential, and δv is the difference between the pseudopotential affecting the majority spin of the fully polarized atom and the spin-neutral reference v^0 . This reference potential is generated using the usual set of parameters (radial cutoffs), keeping the *ab initio* idea in mind, with any subsequent correction provided by the inclusion of the spin dependence. The SD-PsP's have been shown to improve the transferability of the commonly used SN-PsP's for a wide range of transition elements for both their atomic and bulk environment. In light of the troubles experienced by the SN-PsP's to correctly predict the electronic and magnetic structures of V(001), we decided to confront our new method with this more challenging problem and see if the inclusion of the spin dependence might solve the transferability problem encountered by others.

All our calculations were performed using the plane-wave DFT code CASTEP.^{11,12} For the generation of both our spin-neutral and fully-polarized pseudopotentials, the same parameters were employed, following the scheme described in Ref. 10: we constructed norm-conserving Troullier-Martins¹³ pseudopotentials for the $3d^4 4s^1$ electronic configuration of

TABLE I. Magnetic moments (in μ_B) for a 7-layer film of V(001), as predicted by DFT-GGA(PBE) calculations using different pseudopotentials: norm-conserving (NC), norm-conserving including semicore states (NC+SC), and ultrasoft (US). The relaxed surfaces were simulated by moving inward the surface layer by $\Delta_{12} = -6.25\%$. m_i is the magnetic moment at the surface layer.

	Relaxed	Type	m_i	m_{i-1}	m_{i-2}	m_{i-3}
BBK ^a	no	NC	1.71	-0.88	-0.22	-0.19
RIVB ^b	no	NC	1.77	-0.74	-0.20	0.04
RIVB2 ^c	no	NC+SC	1.16	-0.40	-0.14	-0.01
SN-PsP	no	NC	1.70	-0.84	-0.32	-0.01
USPP	no	US	1.38	-0.62	-0.18	-0.02
SD-PsP	no	NC	1.12	-0.49	-0.23	-0.05
BBK ^a	yes	NC	1.45	-0.70	-0.33	-0.15
RIVB ^b	yes	NC	1.48	-0.59	-0.26	0.18
RIVB2 ^c	yes	NC+SC	0.94	-0.29	-0.13	0.08
SN-PsP	yes	NC	1.47	-0.65	-0.37	0.15
USPP	yes	US	0.74	-0.34	-0.14	-0.02
SD-PsP	yes	NC	0.63	-0.25	-0.16	-0.01

^aReference 1. The GGA(PW91) was used here.

^bReference 5.

^cReference 6.

the V atom; the cutoff radius for the construction of the d pseudowave function was set to $r_d = 1.1 \text{ \AA}$, while it was left at the outermost maximum of the AE wave function for the s and p channels. A NLCC was employed for which the partial core density was set to match the exact one after a radius of $r_c^{\text{NLCC}} = 1.0 \text{ \AA}$. The exchange-correlation potential used is the GGA-PBE.¹⁴ We also performed calculations using an ultrasoft pseudopotential provided with the code. It includes a NLCC, and a very short cutoff radius for the wave functions of about 0.7 \AA . The slabs were constructed using the experimental lattice constant (3.03 \AA ; our SN-PsP yields a value of 3.05 \AA) for the nonmagnetic bulk bcc V. We used a k -point density of 0.04 \AA^{-3} for the sampling of the first Brillouin zone. We used a very fine Fourier grid, including plane waves with kinetic energy up to 1000 eV ; this converges the total energy to 1 meV/atom , beyond what is really required. A Fermi surface smearing width of 0.1 eV was also employed. We have performed single-point energy calculations (all ions fixed) similar to those previously reported, first to test our spin-neutral potential against the ones employed by others and second to determine the transferability improvements provided by the use of SD-PsP's.

The results for a 7-layer film are reported in Table I. The table collects the previous results obtained by BBK and RIVB for both the bulk truncated surface and the relaxed surface with $\Delta_{12} = -6.25\%$. We also report our results using our spin-neutral (SN-PsP), the spin-dependent (SD-PsP), and the ultrasoft (USPP) pseudopotentials. Our SN-PsP reproduces quite well the magnetic moments per layer previously obtained by BBK and RIVB, even though those calculations were performed using different pseudopotentials, and even a different basis type in the case of RIVB. The magnetization at the surface for both bulk-truncated or relaxed structures are dramatically overestimated. When the SD-PsP is em-

TABLE II. Magnetic moments (in μ_b) for a 9-layer film of V(001), as predicted by DFT-GGA(PBE) calculations using different pseudopotentials. The relaxed surfaces were obtained with interplanar relaxations of $\Delta_{12} = -12.5\%$, $\Delta_{23} = 0.9\%$, and $\Delta_{34} = 2.5\%$ (as in Ref. 4).

	Relaxed	Type	m_i	m_{i-1}	m_{i-2}	m_{i-3}	m_{i-4}
BCK ^a	no	NC	1.77	-0.61	-0.23	-0.10	-0.13
SN-PsP	no	NC	1.72	-0.77	-0.22	-0.09	-0.12
USPP	no	US	0.87	-0.37	-0.18	-0.07	-0.04
SD-PsP	no	NC	1.08	-0.44	-0.17	-0.07	-0.07
BCK ^a	yes	NC	0.75	-0.26	-0.27	-1.10	-0.09
SN-PsP	yes	NC	0.95	-0.43	-0.32	-0.08	-0.11
USPP	yes	US	0.06	-0.03	-0.02	0.00	0.00
SD-PsP	yes	NC	0.10	-0.06	-0.03	-0.01	-0.01

^aReference 4.

ployed, this surface magnetization is significantly reduced. Upon structural relaxation, the magnetic moment of the top layer is reduced by more than 50%, dropping from $\sim 1.47\mu_b$ to $0.63\mu_b$. Thus, our SD-PsP seems to favor a stabilization of the system towards vanishing magnetism. Most interestingly, our predictions show the same degree of accuracy as the calculations of RIVB2, which included semicore p states as valence states, but our calculations are not burdened by the overhead of such an approach (at least in the case of plane-wave basis expansions). It also gives slightly better results than the expected high accuracy of the USPP.

Another set of calculations was performed for a 9-layer film. Table II reports the results for the pseudopotential used by BCK, as well as our SN-PsP and SD-PsP. Once again, the results using our SN-PsP for both the bulk-truncated and relaxed surfaces are very similar to those reported earlier by BCK, essentially showing the same trend as the results for the 7-layer film.¹⁵ When the SD-PsP is employed, the correction over the SN-PsP is dramatic, even converging to an almost nonmagnetic solution for the relaxed surface, consistent with all-electron predictions, and of comparable quality to the USPP ones.

Lastly, we have performed geometry optimizations for the 9-layer slab, allowing interplanar relaxations of the first two layers. Our results, as well as those given by other methods, are reported in Table III. First, the improvement due to the spin-dependence over the SN-PsP is again stark here. For the relaxed surface, it gives a nonmagnetic solution in agreement with all-electron results, while the SN-PsP still predicts a fairly high surface magnetization. The SD-PsP also gives a much better structural description, with our $\Delta_{12} = -13.6\%$ in good agreement with previously reported all-electron PAW calculations.⁷ We have also reported in Table III results given by other pseudopotential calculations (norm conserving as well as ultrasoft), along with some information about the parameters used to generate the potential: the cutoff radius r_c^d used for the pseudization of the d wave function and the cutoff radius of the partial core density, r_c^{NLCC} (unfortunately, we do not know the value of the r_c^{NLCC} used by BCK or for the generation of the USPP). These two parameters are of critical importance for two reasons. First, they essentially govern the quality of the pseudopotential. Second, they both need to be handled with care when a plane-wave basis set is

employed. Not surprisingly, when those two parameters are varied, one obtains very different results, once again reaffirming the difficulty in defining them without bias. As mentioned by Kresse *et al.*, one should carefully choose those parameters and test the resulting pseudopotential before its widespread use. This method, essentially a fitting of the potential, is again unsatisfactory for an *ab initio* method, and does not guarantee perfect or even good transferability. Not surprisingly, and as we discussed previously,¹⁰ the results given by a norm-conserving (NC) or an ultrasoft (US) pseudopotential are very similar for a given set of parameters, clearly showing that ultrasoft potentials do not enhance transferability. Rather, they allow the use of sensibly smaller basis sets, at the price of a much more complex formalism.

Because it is difficult to capture the very sharp and localized d wave function character of transition elements when a plane-wave basis set is used, one is usually forced to move outwards the cutoff r_c beyond which the atomic all-electron and pseudowave functions match, resulting in a softer pseudowave function suitable for plane-wave methods, but also in a penalty in the transferability of the resulting potential. As mentioned by KBP, this procedure results in a poor description of the region in space where core and valence atomic densities are of the same magnitude, and thus in a poor description of the magnetic properties. KBP clearly showed that the smaller the r_c , the better the accuracy, and

TABLE III. Surface magnetization of the bulk-truncated (μ_{bt}) and the relaxed (μ_r) slab (in μ_b) for a 9-layer film of V(001), as predicted by DFT-GGA(PBE) calculations using different pseudopotentials (r_c 's in Å, Δ_{12} in %).

	Type	r_c^d	r_c^{NLCC}	μ_{bt}	μ_r	Δ_{12}	Ref.
KBP	NC	1.35	0.95	1.80	1.44	-8.5	[7]
KBP	US	1.35	0.95	1.89	1.48	-8.5	[7]
BCK	NC	1.10		1.77	0.75	-12.5	[4]
SN-PsP	NC	1.10	1.00	1.72	1.02	-11.7	
SD-PsP	NC	1.10	1.00	1.08	0.06	-13.2	
KBP	NC	1.05	0.35	1.26	0.12	-13.9	[7]
KBP	US	1.05	0.35	1.29	0.02	-14.3	[7]
USPP	US	0.70		0.87	0.00	-13.9	
KBP	US	0.60	0.35	0.47	0.00	-14.0	[7]

KBP are forced to conclude that only in the limit of very small r_c 's one can expect results to somewhat match the all-electron ones. But as mentioned earlier, and as correctly outlined by KBP, this poses serious problems. In the case of NC pseudopotentials, too short of a radius often results in a hard potential unbearable for a plane-wave basis expansion. Because of the computational advantages of the US pseudopotentials, reducing the value of r_c becomes more practical, but then it is rather difficult to accurately describe the resulting augmentation functions. We agree with KBP that this does not constitute a satisfactory answer either, and often one is left with additional fitting of the potential, playing off computational expense and transferability. The PAW method¹⁶ is indeed one way around those difficulties.

As for the NLCC, aside from the arbitrariness of its definition,^{9,10} the results show that the value of r_c^{NLCC} is also of importance. For example, KBP found it surprising that for similar values of r_c , they found rather different results than those of BCK. Our results with similar r_c agree with BCK, however we used a $r_c^{\text{NLCC}}=1.00$ Å, while KBP used a $r_c^{\text{NLCC}}=0.35$ Å. Our guess is that BCK must have used a NLCC cutoff similar to ours, certainly explaining the discrepancy in the results. But again, using the full core density in the NLCC is undesirable and reducing the value of the cutoff to very small values often results in numerical difficulties in describing the partial core function on the uniform

Fourier grid. We agree with KBP that the inclusion of a NLCC is important, but is by far not sufficient to insure good transferability.

Our results for the SD-PsP's show that they substantially enhance the transferability over the conventional spin-neutral pseudopotential for a given small set of generation parameters. They are also more *ab initio* like and rely more on the self-adaptation of the ionic potential due to its local chemical environment rather than on the parameters used for its definition. Our results also show that we are able to achieve approximately a comparable level of accuracy as the one given by a potential employing very short values of r_c and r_c^{NLCC} , while instead using reasonable values of those cutoffs (within the same pseudopotential generation scheme). For these reasons, we believe that the new method may provide a reliable and accurate scheme to generate transferable pseudopotentials for transition elements, without the overhead cost and complications usually required for comparable accuracy.

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*Corresponding Author. Email address: eac@chem.ucla.edu

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