

Accurate construction of transition metal pseudopotentials for oxides

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Abstract. We generate a series of Zr pseudopotentials and use them to calculate the properties of PbZrO_3 , in order to examine the relationship between pseudo-atomic properties and solid-state oxide results. We find that lattice constants and bond lengths within the oxide unit cell are quite sensitive to pseudopotential construction errors, and clear correlations emerge. These trends motivate our identification of two criteria for accurate transition metal pseudopotentials for use in oxide calculations, which are similar to the criteria for metal use. We find that both the preservation of all-electron tail norm and the preservation of all-electron ionization energy are necessary to give good lattice constants for oxides.

INTRODUCTION

Perovskites (oxides with chemical formula ABO_3) are an important class of materials; many common minerals are perovskites, and ferroelectric perovskites such as $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) have many industrial applications including sonar. The phase diagram of PZT has been extensively studied experimentally and theoretically. Recently a virtual crystal method was used to predict theoretically a compositional phase transition in this material [1]. The changes in structure between the tetragonal and rhombohedral phases of PZT are subtle and are sensitive to temperature, composition and pressure. This makes it a good industrial material, but also presents challenging problems in modeling this material theoretically.

Density functional theory [2,3] (DFT) calculations have been widely used to study PZT and other perovskites with both the local density approximation (LDA) and generalized gradient approximation (GGA) for the exchange-correlation functional. Within DFT, one has a choice of using either all-electron or pseudopotential (PSP) methods. While the former are more accurate, they are much more computationally expensive; therefore many DFT studies of perovskites in recent years have been done using PSPs.

The absence of core electrons in the calculation and the reduced-cutoff plane-wave expansion of the PSP greatly reduce the computational cost of the solid-state calculation as compared those employing all-electron potentials. Modern PSP construction methods insure that the PSP agrees with the all-electron potential outside a specified core radius (r_c) for a given reference configuration. A perfect PSP would be completely transferable, i.e. it would mimic the behavior of the all-electron nucleus and core potential in various local chemical environments, producing solid-state results identical to those of an all-electron calculation. In practice, the transformation of a real, physical all-electron system into an artificial one consisting of PSPs and valence electrons will often introduce errors in the calculation. This can be due to either inaccuracies in the wave function and PSP in the valence region in atomic configurations other than reference or to the omission of the wave function oscillations in the core region. Methods capable of generating transferable PSPs with small plane-wave cutoffs have been developed over the course of the past twenty years [4–10].

PSP DFT calculations involving transition metal elements have become widespread. Nevertheless, some fundamental questions regarding PSP transferability remain unresolved. While it is axiomatic that a PSP must preserve certain all-electron properties to be considered transferable, it is unclear which all-electron properties are crucial. Various criteria for comparing to all-electron results have been proposed, such as agreement between all-electron and PSP eigenvalues along with total energy differences, norm-conservation at the reference configuration and preservation of logarithmic derivatives at r_c [4], and the correct chemical hardness matrix [11]. The agreement between all-electron and PSP eigenvalues and total energy differences are the criteria which are most often used and are generally considered when determining if a given PSP is transferable. However, no clear correlation has been firmly established between these criteria and solid-state results.

Recently, we have discovered that solid-state transition metal lattice constants and bulk moduli are very sensitive to PSP error, with variations in the solid-state DFT results directly correlated to errors in the atomic properties of the PSP [12]. Extending the norm conservation concept of Hamann, Schlüter and Chiang [4], we have shown that errors in the norm of the wave function beyond r_c in configurations other than the reference as well as total energy difference and eigenvalue errors affect solid-state results. Therefore, both the energy differences and wave function norms must be preserved for configurations other than reference in order to obtain correct solid-state properties.

In this work we will examine PbZrO_3 (PZ), as a test case to determine the relationship between solid-state results and PSP error for perovskite oxides.

METHODOLOGY

A PSP-DFT calculation of PZ structure involves three PSPs—lead, zirconium and oxygen. The PSPs for lead and oxygen are very accurate and are able to respond to perturbations away from the reference configuration, perhaps due to the presence of semicore-like $5d$ electrons in lead and $2s$ electrons in oxygen. The last $5s$ radial node in Zr is so far from the nucleus that one shell of semi-core states ($4s, 4p$) must be included as valence. In the standard nonlocal PSP formalism [5], the use of three non-local channels (s, p, d) for five valence states ($4s, 4p, 5s, 4d$ and $5p$) can introduce a large error in the $5s$ and $5p$ states, even in the reference configuration. While $5p$ error is unimportant ($5p$ states are not populated even in neutral Zr), the $5s$ state is populated in the neutral Zr and loses electrons to oxygen in the perovskite solid. As a result, the zirconium PSP will generally contain much more transferability error than the lead or oxygen PSPs. Since the BO_6 octahedral complex plays a crucial role in determining the characteristics of the perovskite unit cell, and since we expect the Zr PSP to provide most of the PSP error, we focus our investigation on the Zr PSP.

The designed nonlocal (DNL) PSP construction approach of Ramer and Rappe [7] allows us to adjust the amount of norm and total energy difference error in various PSP configurations, while leaving the reference configuration unchanged. We can, therefore, systematically introduce variations in Zr $5s$ norm and total energy differences to gauge the consequences of variations of atomic PSP properties for solid-state calculations.

To understand how norm-conservation and total energy difference agreement affect solid-state results, we examine five different Zr PSPs. All calculations are done using the Perdew-Zunger parameterization of the Ceperley-Alder LDA [13] exchange-correlation functional. We pick the $4s^2 4p^6 5s^0 5p^0 4d^0$ state as the reference atomic configuration. Zirconium has an oxidation number of +4 in PbZrO_3 , and this atomic configuration will therefore be important in the solid state. Since the Zr–O bond is ionic, the ionization energy of Zr going from neutral to +4 configurations will be crucial.

All PSPs were created from a +4 ionized $4s^2 4p^6 5s^0 5p^0 4d^0$ reference configuration with varying depths and placements of the DNL augmentation operator, \tilde{A} . Since the +4 state is the reference configuration, norm is conserved for the $4s$, $4p$ and $4d$ states, but it is not conserved for the $5s$ state. The $5s$ wave function tail norm can be adjusted, whereas the other norms are exact in the reference configuration and are not affected by the DNL operator. We therefore focus on the $5s$ norm. For all five PSPs we compute the PSP +4 ionization energy and the $5s$ norm in the valence region ($r \geq 1.7$ Bohr) in the +4 ionized state. For each Zr PSP we carry out DFT calculations to determine the equilibrium lattice constants a and c and the equilibrium volume for the tetragonal phase of PZ. While this phase is not found experimentally, the trends observed in our calculations will be relevant for other phases of PZ and for other perovskites. Therefore, tetragonal PZ is a valid test case for studying PSP effects and it is more tractable than the 40-atom ground

TABLE 1. Pseudopotential (PSP) results for Zr atom. Ionization energy to +4 state (I) and norm of the tail region of the +4 5s state (N_s) are given for an all-electron atom (AE) and for the PSPs described in the text. All energies are in Ry and all lengths in Å. Lattice constants a and c and volume V are given for solid-state calculations of tetragonal PbZrO_3 using the specified Zr PSP.

	I	N_s	a	c	V
AE	5.7330	0.8976			
PSP A	5.7612	0.8762	4.0738	4.2222	70.0711
PSP B	5.7443	0.8909	4.0858	4.2378	70.7451
PSP C	5.7344	0.8992	4.0924	4.2458	71.1076
PSP D	5.7274	0.8920	4.1091	4.2719	72.1301
PSP E	5.7202	0.8973	4.1113	4.2745	72.2489

state structure. The results for the five PSPs are found in Table 1.

RESULTS

From the results in Table 1, it is clear that the Zr ionization energy is correlated with the volume of the PZ unit cell. Ionization energy decreases from PSP A to PSP E by about 0.04 Ry and the lattice constants a and c increase by about 1%, increasing the unit cell volume by about 3%. However, the changes in the lattice constants and volume do not depend on ionization energy alone. This can be seen by comparing the results for PSP C, PSP D and PSP E. While the ionization energy decreases by approximately 0.007 Ry from PSP C to PSP D and from PSP D to PSP E, the volume change from PSP C to PSP D is 8.6 times larger than the volume change from PSP D to PSP E. Upon examining the tail norms of the three PSPs, the reason for this dramatic difference becomes clear. The changes in norm of the 5s state are approximately equal but opposite in sign going from PSP C to PSP D, and from PSP D to PSP E. Thus in going from PSP C to PSP D, the norm and the ionization energy effects cooperate, significantly increasing the volume of the unit cell. From PSP D to PSP E, the two effects largely cancel, leading to a small increase in volume.

The correlations between atomic properties and solid-state results can be quantified by fitting the DFT calculated PZ volumes to a function of the form

TABLE 2. Fit of PbZrO_3 volume dependence on atomic properties. All volumes are in \AA^3 / primitive cell. δV_{DFT} is the difference between the equilibrium volume obtained by solid-state calculations using a given pseudopotential (PSP) and the equilibrium volume using PSP A. δV_{Fit} is the difference between equilibrium volume obtained through Eq. 2 using I and N_s values for a given PSP and PSP A. The final column is the percent difference between fitted and DFT δV values.

	δV_{DFT}	δV_{Fit}	% error
PSP A	0.000	0.000	0.0
PSP B	0.674	0.630	-6.9
PSP C	1.037	0.999	-3.8
PSP D	2.059	1.937	-6.3
PSP E	2.178	2.240	2.8

$$V_{\text{PZ}} = aI + bN_s + c \quad (1)$$

where I is the +4 ionization energy, N_s is the norm of the 5s state in the +4 configuration and a , b and c are constants. Fitting to calculated DFT PZ volumes we get:

$$V_{\text{PZ}} = -80.637I - 50.493N_s + 528.9125. \quad (2)$$

We check the quality of the fit by comparing the volume differences obtained with Eq. 2 with computed DFT volume differences. As shown in Table 2, volume differences are predicted within 7%. We have examined fitting the volume to other atomic variables such as +3 ionization energy and the norm of 4d states and 5s states in other ionized configurations. All combinations showed a simple linear correlation between ionization energy, tail norm and volume, but the choice of +4 ionization energy and +4 ionized 5s norm gave a slightly more accurate fit.

The dependence of PZ volume on atomic properties can be understood by viewing the zirconium-oxygen bond character as a mixture of covalent and ionic bonding. Covalent bonding relies on direct overlap of atomic wave functions, favoring shorter bond lengths and smaller volumes. Ionic bond lengths result from a balance of Coulomb attraction and Pauli repulsion; this balance generally leads to longer

bond lengths and larger volume. The proportion of covalent and ionic character in the zirconium-oxygen bond is affected by the size of the tail norms and ionization energies. Decreasing the +4 ionization energy of zirconium decreases the energetic cost of charge transfer from Zr to O, making the bond more ionic. This increases the volume. More diffuse Zr 5s wave functions will result in a larger overlap with oxygen atomic orbitals, increasing the hopping element. This favors covalent bonding and leads to shorter bond lengths and smaller volumes.

CONCLUSION

In this study, we have examined the relationship between pseudopotential properties on the atomic level and the results of solid-state DFT calculations in perovskites, taking tetragonal PbZrO_3 as a test case. We constructed a family of Zr pseudopotentials with varied total energy difference and norm conservation properties. We then calculated the equilibrium lattice constants and volumes of PbZrO_3 to gauge how the variations in atomic-level properties correlate with the results of the solid-state calculations. We find that the volume of the unit cell is sensitive to small changes in ionization energy and norm of the valence states, with variations of 3% in unit cell volume depending on the pseudopotential. Therefore, both of these properties must be enforced in pseudopotential construction in order to reduce pseudopotential error at the solid-state level. We also find that the changes in volume are linear in changes of the two atomic properties, demonstrating that errors in solid-state volume are a predictable consequence of pseudopotential errors.

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