

Effect of nonlocal corrections to the local-density approximation on total-energy calculations of K, Rb, and Cs

R. H. Mutlu

Department of Engineering Physics, Ankara University, Faculty of Sciences, 06100 Ankara, Turkey

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Total-energy calculations are carried out on K, Rb, and Cs for five different exchange-correlation potentials employing the linear-muffin-tin-orbital method within the atomic-sphere approximation. It is shown that inclusion of nonlocal corrections to the local-density approximation gives improvement in predicting the equilibrium lattice parameters and the stable structures of these elements correctly.

In the course of studies on the ground-state properties of alkali metals by means of electronic structure calculations based on the local-density approximation (LDA) of the density-functional theory,¹ controversial results with regard to previous calculations²⁻⁴ and experiments have been reported⁵ (Table I). Although the equilibrium space group of Li, Na, and Rb was correctly predicted, the fcc phase was found⁵ to be energetically lower than the bcc phase for K and Cs. It has already been suggested⁶ that these results may be altered by adding a nonlocal correction to the LDA exchange-correlation potential (ECP) which favors inhomogeneous charge densities. Very recently, substantial improvement has been achieved⁷ for heavy alkaline-earth metals by inclusion of such corrections and therefore we shall, in what follows, focus on K, Rb, and Cs, for which the theoretical predictions disagree⁵ with experiment. It turns out to be that not only the different band-structure calculation methods, but the use of different ECP's yield controversial results especially for the bcc-fcc energy differences.⁸ Therefore, in this paper, we present and discuss the structural properties of these elements for different ECP's used in the electronic structure calculations.

Electronic band-structure calculations are carried out self-consistently by means of the linear-muffin-tin-orbital (LMTO) method⁹ within the atomic sphere approximation (ASA) using the codes of Skriver.¹⁰ The combined

TABLE I. Summary of the previous work (lattice constant in Å and the stable structure) on the structural properties of K, Rb, and Cs.

	K	Rb	Cs
Moruzzi, Janak, and Williams ^a	5.000, bcc	5.403, bcc	
Skriver ^b	bcc	bcc	bcc
Dacorogna and Cohen ^c	5.117, bcc		
Sigalas <i>et al.</i> ^d	6.355, fcc	5.361, bcc	7.345, fcc

^aReference 2.

^bReference 3.

^cReference 4.

^dReference 5.

TABLE II. The exchange-correlation potentials (ECP's) used in the present work

ECP	Abbreviation	Reference
Barth-Hedin	BH	12
Barth-Hedin-Janak	BHJ	13
Vosko-Wilk-Nusair	VWM	14
Langreth-Perdew-Mehl	LPM	15
Ceperley-Alder	CA	16

correction terms to the ASA and the zero-point corrections¹¹ are included for the bcc and fcc structures considered. The number of k points used in the irreducible wedge of the Brillouin zone were 240 and 285 for fcc and bcc structures, respectively. The self-consistency is achieved in such a way that total-energy values between the consecutive iterations was $\pm 2 \times 10^{-6}$ Ry. To find the equilibrium volume, we have calculated the total energies at various lattice constants and determined the minimum by fitting the results to a cubic polynomial. All computations are performed using five different ECP's presented in Table II.

The calculated structural properties are summarized in Table III, IV, and V for K, Rb, and Cs, respectively. The

TABLE III. Effect of different exchange-correlation potentials (ECP's) on the equilibrium lattice constant (a) in Å, and on the total-energy difference (ΔE) in Ry, of metallic K in fcc and bcc structures.

ECP	Structure	a	$\Delta E \times 10^6$	Stable structure
BH	fcc	6.399	64	bcc
	bcc	5.080		
BHJ	fcc	6.443	59	bcc
	bcc	5.115		
VWN	fcc	6.451	64	bcc
	bcc	5.120		
LPM	fcc	6.565	68	bcc
	bcc	5.211		
CA	fcc	6.448	65	bcc
	bcc	5.117		
Experiment ^a		5.225		bcc

^aReference 21.

TABLE IV. Effect of different exchange-correlation potentials (ECP's) on the equilibrium lattice constant (a) in Å, and on the total-energy difference (ΔE) in Ry, of metallic Rb in fcc and bcc structures.

ECP	Structure	a	$\Delta E \times 10^6$	Stable structure
BH	fcc	6.869	3	?
	bcc	5.452		
BHJ	fcc	6.917	10	bcc
	bcc	5.490		
VWN	fcc	6.924	3	?
	bcc	5.497		
LPM	fcc	6.924	36	bcc
	bcc	5.496		
CA	fcc	6.923	8	bcc
	bcc	5.494		
Experiment ^a		5.585		bcc

^aReference 21.

experimental results²¹ are also given for comparison.

The equilibrium lattice constants that were calculated are almost the same for different ECP's used. Slight differences can be attributed^{13,17,18} to the different parameters used in the exchange-correlation expressions, even if the functional forms are similar. It is well known that the LDA commonly underestimates the lattice constants.^{19,20} However, inclusion of nonlocal exchange corrections to the LDA provides an improvement⁶ in this estimation and thus among the calculated lattice constants for the bcc structures, which is the experimentally verified structure for K, Rb, and Cs, the LPM potential¹⁵ yields the best values with regard to experiment.²¹ Furthermore, for the total-energy differences, only the LPM predictions are consistent with experiment especially for Cs. In fact in alkali metals the total energy does not vary significantly in different structures and the error introduced by the LDA exceeds this variation.⁸ This could be attributed to the fact that nonlocal contributions to the LDA are important in the valence states of atoms and solids rather than the inner shells,¹⁵ and since in the LMTO-ASA method the total energy of the solid is calculated in the frozen-core approximation, the LPM scheme represents a substantial improvement over all local approximations. For K, which has valence electrons not too far from the nucleus, nonlocal corrections are

TABLE V. Effect of different exchange-correlation potentials (ECP's) on the equilibrium lattice constant (a) in Å, and on the total-energy difference (ΔE) in Ry, of metallic Cs in fcc and bcc structures.

ECP	Structure	a	$\Delta E \times 10^6$	Stable structure
BH	fcc	7.493	-17	fcc
	bcc	5.943		
BHJ	fcc	7.548	-31	fcc
	bcc	5.989		
VWN	fcc	7.558	-24	fcc
	bcc	5.998		
LPM	fcc	7.494	9	bcc
	bcc	5.945		
CA	fcc	7.553	-24	fcc
	bcc	5.992		
Experiment ^a		6.079		bcc

^aReference 21.

suppressed, and all ECP's used yield almost the same energy differences (Table III). For Rb and Cs (Tables IV and V), on the other hand, valence electrons are far from the nucleus, the valence-charge densities are smaller, and thus the nonlocal exchange contributions become significant.¹⁵

It should be emphasized that these conclusions are valid in predicting the stable structure of K, Rb, and Cs, for which the structural energy differences are much smaller than that of the alkaline-earth metals,⁷ by means of the LMTO-ASA method, and it should not be the intent to generalize them for all materials and for all ECP's used in the electronic structure calculation methods.

In summary, we have performed LMTO-ASA calculations of the total energy of K, Rb, and Cs using different exchange-correlation potentials (ECP's). It is predicted that only the LPM potential, which includes nonlocal corrections to the LDA, reliably yields the stable structure of these elements as bcc. It is also emphasized that, for a given element, not only the band-structure calculation method, but also the choice of the ECP suitable for that method, should be considered to obtain reliable results.

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