Density Functional Theory, Self-Consistent Prediction of Electronic Properties of Sodium Oxide (Na_2O)

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Abstract

This poster presents the findings of ab-initio calculations of electronic and structural properties of cubic crystalline sodium oxide (Na_2O). These results were obtained using density functional theory (DFT), specifically a local density approximation (LDA) potential, and the linear combination of Gaussian orbitals (LCGO) formalism. Our implementation of LCGO followed the Bagayoko, Zhao, and Williams method as enhanced by the work of Ekuma and Franklin (BZW-EF). Our results include predicted values for:

1) The electronic band structure and associated band gaps,
2) The total and partial density of states (DOS and pDos),
3) The equilibrium lattice constant of Na_2O, and
4) The bulk modulus.

Introduction and Method

Despite its potential for applications, Na_2O has not attracted much attention for experimental studies after 1940. The room temperature lattice constant and band gap have been measured in 1934[1] and 1940[2], respectively. A handful of calculations, mainly using DFT potentials, reported band gaps over a range of 1.8 to 4.9 eV[3]. Previous success of our computational method motivated us to attempt to resolve the discrepancy between previous theoretical findings. Several past predictions with the BZW-EF method have been confirmed by experimental measurements, i.e., for cubic Si_3N_4 and InN.[4]

Our method utilizes a local density approximation (LDA) potential and the The linear combination of Gaussian orbitals (LCGO). These two features of our work are similar to those of previous calculations. The distinctive feature of our calculations is our implementation of the BZW-EF method that adheres the conditions of validity of DFT. Calculations have to (1) keep the total number of particle constant, (2) attain the absolute minima of the occupied energies, and (3) avoid excessively large basis sets that destroy the physical content of the lowest unoccupied energies. Successively augmented basis sets are used by the method in calculations of electronic energies up to the attainment of the absolute minima of the occupied energies. [4]

Results

Table 1 shows the various basis sets for which the band structure of Na_2O was calculated, with a room temperature lattice constant of 5.56 Å[1]. The direct band gap values at the Γ point are shown in the last column, in eV. The absolute minima of the occupied energies are reached with Calculation 2.

Calc. #	Na^{1+} Orbitals	O^{2-} Orbitals	# of Functionals	Γ-Γ Band Gap (eV)
1	$2s^2\ 2p^6\ 3s^0$	$2s^2\ 2p^6$	28	2.38
2	$2s^2\ 2p^6\ 3s^0\ 3p^0$	$2s^2\ 2p^6$	40	2.22
3	$2s^2\ 2p^6\ 3s^0\ 3p^0\ 4p^0$	$2s^2\ 2p^6$	52	2.24
4	$2s^2\ 2p^6\ 3s^0\ 3p^0\ 4p^0\ 4s^0$	$2s^2\ 2p^6$	56	2.24

Results Cont.

Figure 2 below shows the band structure from Calc. #1 (solid line) and #2 (dotted) with a lattice constant of 5.560Å[1]. Some occupied energies for Calc. #2 are lower than corresponding energies in Calc. #1.

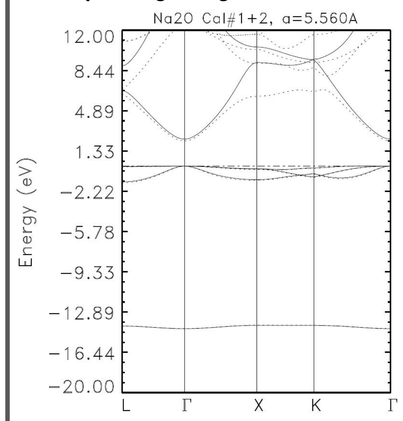
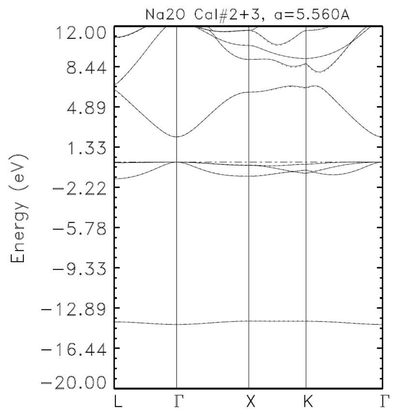


Figure 3 below shows the band structure from Calc. #2 (solid line) and #3 (dotted). The occupied energies for the two calculations are notably the same.



Calc. #3 and #4 shared the same occupied energies as Calc. #2 which tells us that Calc. #2 is the first basis set for which an absolute minimum occupied energy is reached. We therefore call the basis set for Calc. #2 the "optimal basis" set. We use this optimal basis set to calculate all other properties of Na_2O.

Figure 4 below shows the density of states of Na_2O calculated using the bands from Calc. #2.

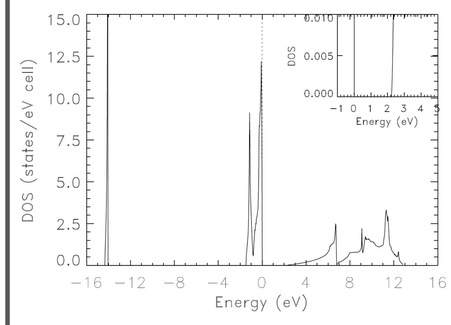
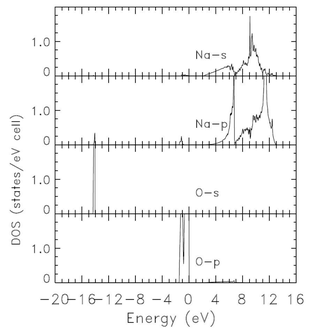


Figure 5 below shows the partial density of states calculated using the bands from Calc. #2 .



From these figures we can see that the lower valence bands are due to the Oxygen-S and the upper valence band is from the Oxygen-P. The higher energy unoccupied bands are due to a hybridization of Sodium S and P.

Results Cont.

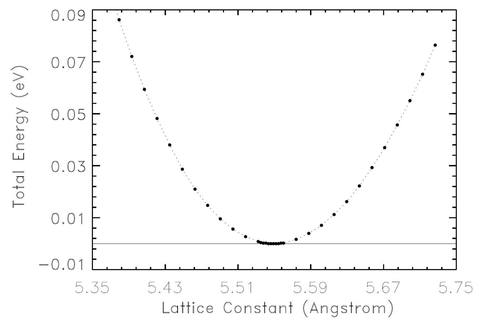


Figure 6 to the left shows the plot of the total energy versus the lattice constant.

From this plot we determined the lattice constant corresponding to the minimum of the total energy. This is the equilibrium lattice constant for Na_2O, equal to, 5.55 Å with an estimated uncertainty of ±0.01 Å.

The curvature around the minimum of the total energy was used to calculate the bulk modulus. We calculated a bulk modulus for Na_2O of 61.67 GPa.

Conclusions

- We calculated a direct band gap of 2.22 eV for Na_2O. This result is larger than but qualitatively similar to some other LDA predictions which is expected as many other LDA calculations tend to underestimate band gaps. There is only one experimental value for an Na_2O band gap calculated in 1940. This experimental value is 4.41eV[2]. Additional experimental data would be useful in this case.
- We determined the density of states and partial density of states for Na_2O. The plots we found were again qualitatively similar to other theoretical predictions. However in this case we were unable to find any experimental data.
- We determined an equilibrium lattice constant of 5.55Å. This is slightly lower than the room temperature one of 5.56 Å[1] – as expected with the relatively large bulk modulus.
- We calculated a bulk modulus for Na_2O of 61.67 GPa. This is a value similar to several other theoretical findings. No experimental value could be found at this time.
- We expect future experimental measurements to confirm our results not only for the band structure and gap, but also the densities or states and the bulk modulus.

Acknowledgments

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