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Ab-initio calculation of optoelectronic and structural properties of lithium oxide (Li_2O)

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Abstract

Using the inherently ab-initio method of density functional theory (DFT), we calculated material properties of the ionic solid lithium oxide (Li_2O). To counteract problems observed in other DFT calculations, we utilized a DFT calculation procedure known as BZW-EF. This method allowed us to obtain results much closer to experimental observation than other DFT calculations. In particular, we found a room temperature band gap of 5.738 eV, compared against experimental values ranging from 5 to 7.99 eV. We also calculated total and partial density of states (DOS and PDOS), effective masses of charge carriers, the optimal lattice constant, and the bulk modulus. All of these agree with limited experimental data, within the error inherent in the extrapolation process used to obtain experimental values.

Introduction and Method

Lithium oxide has attracted much attention for its potential applications, including as a blanket breeder material for fusion reactors and solid state batteries. As such, multiple experiments and several theoretical studies have explored structural properties of Li_2O and reported room temperature lattice constants around 4.619 Å[1]. Further experiments report the bulk modulus of Li_2O to be around 89.0 eV[2], and dozens of theoretical computations have reproduced this result. However, experimental studies have reported band gaps ranging from 5.0[3] to 7.99[5] eV. In order to explore more fully this wide range, we employed density functional theory (DFT) with the local density approximation (LDA) and linear combination of Gaussian orbitals (LCGO) using the BZW-EF method[6] described below.

The Bagayoko, Zhao, and Williams method, as enhanced by Ekuma and Franklin (BZW-EF) employs the commonly used techniques of DFT, LDA, and LCGO, but extends conventional calculations in order to better align with the motivational principles behind these techniques. In particular, BZW-EF explicitly considers only systems in which the number of particles stays constant, a feature implied by general DFT. In addition, BZW-EF requires the successive self-consistent solution of the Kohn-Sham equation (underlying DFT) using bases that are augmented iteratively by the addition of atomic orbitals. This iteration is completed when the optimal basis set (OBS) is found. The OBS is distinguished as the smallest set of atomic orbitals which gives the minimal total electron energy. This is determined by comparison of the valence energy bands in successive calculations until convergence is reached.

Results

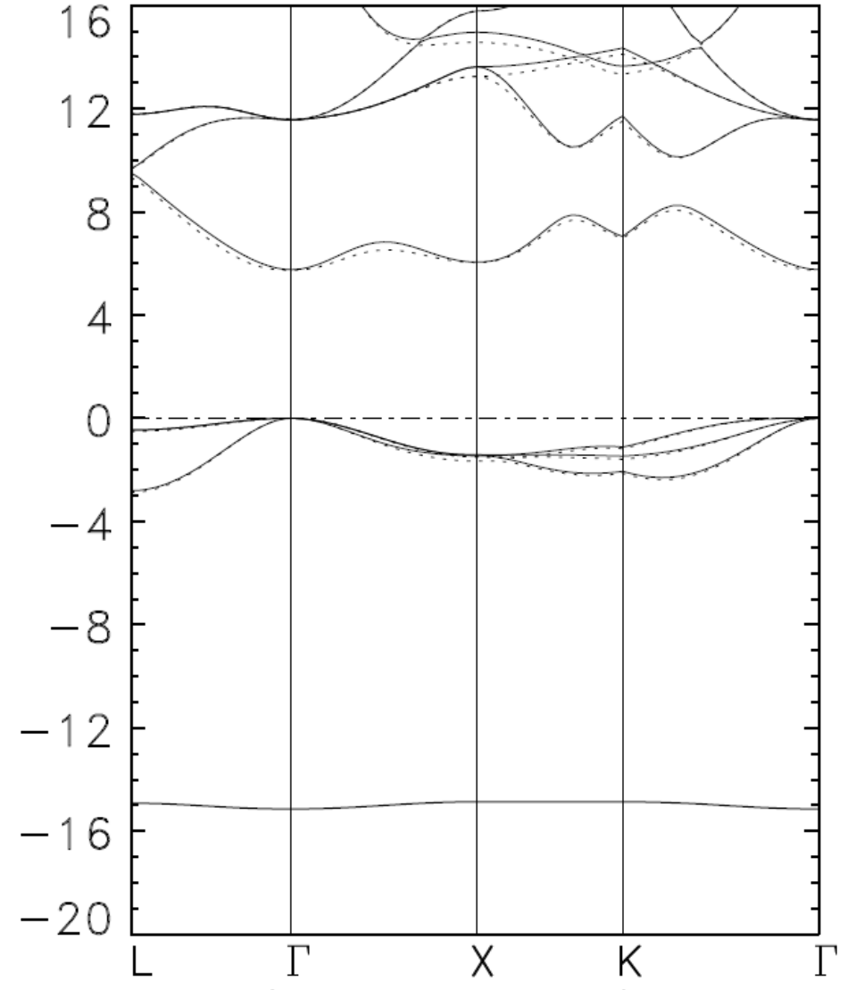

Figure 1: Comparison of calculations IV and V show that the electron energy of V is lower.

No.	Li^+ Valence	O^{2-} Valence
I	$2s^02p^0$	$2s^22p^6$
II	$2s^02p^03p^0$	$2s^22p^6$
III	$2s^02p^03s^03p^0$	$2s^22p^6$
IV	$2s^02p^03s^03p^04p^0$	$2s^22p^6$
V	$2s^02p^03s^03p^04p^0$	$2s^22p^63p^0$
VI	$2s^02p^03s^03p^04s^04p^0$	$2s^22p^63p^0$
VII	$2s^02p^03s^03p^04s^04p^0$	$2s^22p^63s^03p^0$

Table 1: Combinations of atomic orbitals that define iteratively augmented basis sets. The OBS is defined by Calculation V.

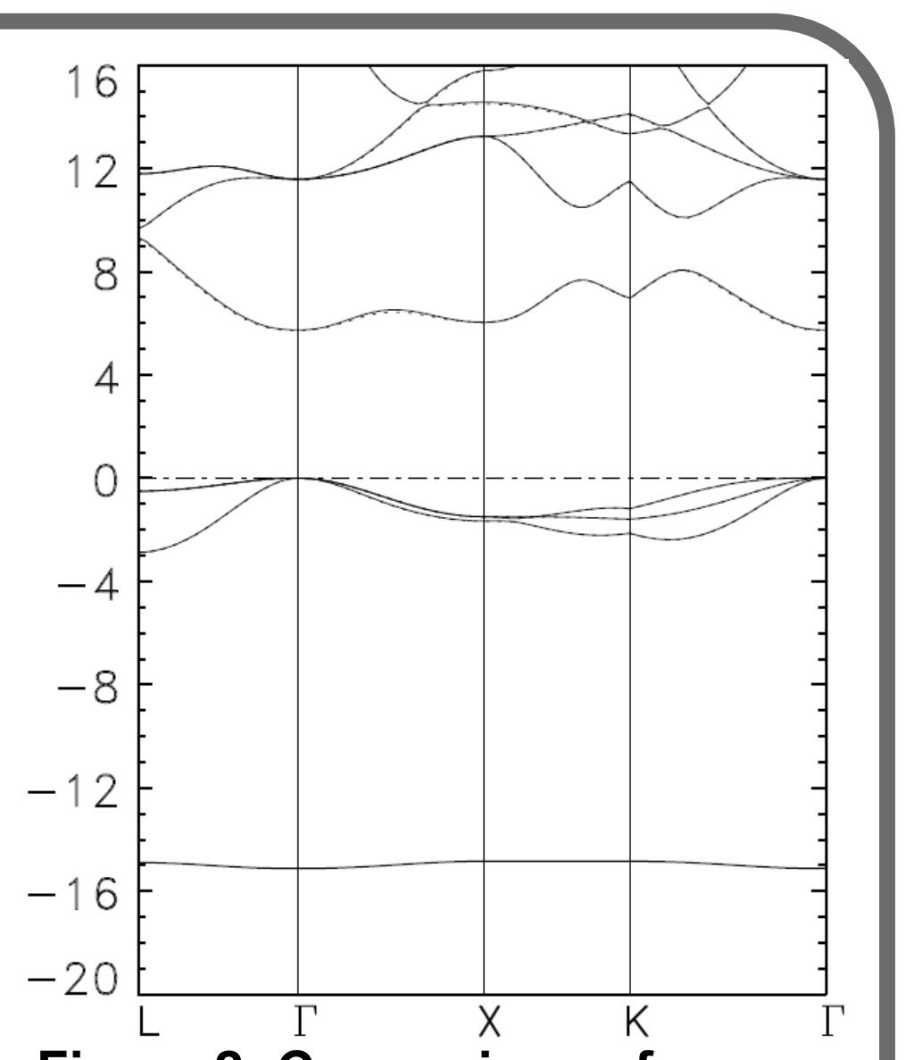

Figure 2: Comparison of calculations V and VI show that the electron energies are the same.

Results

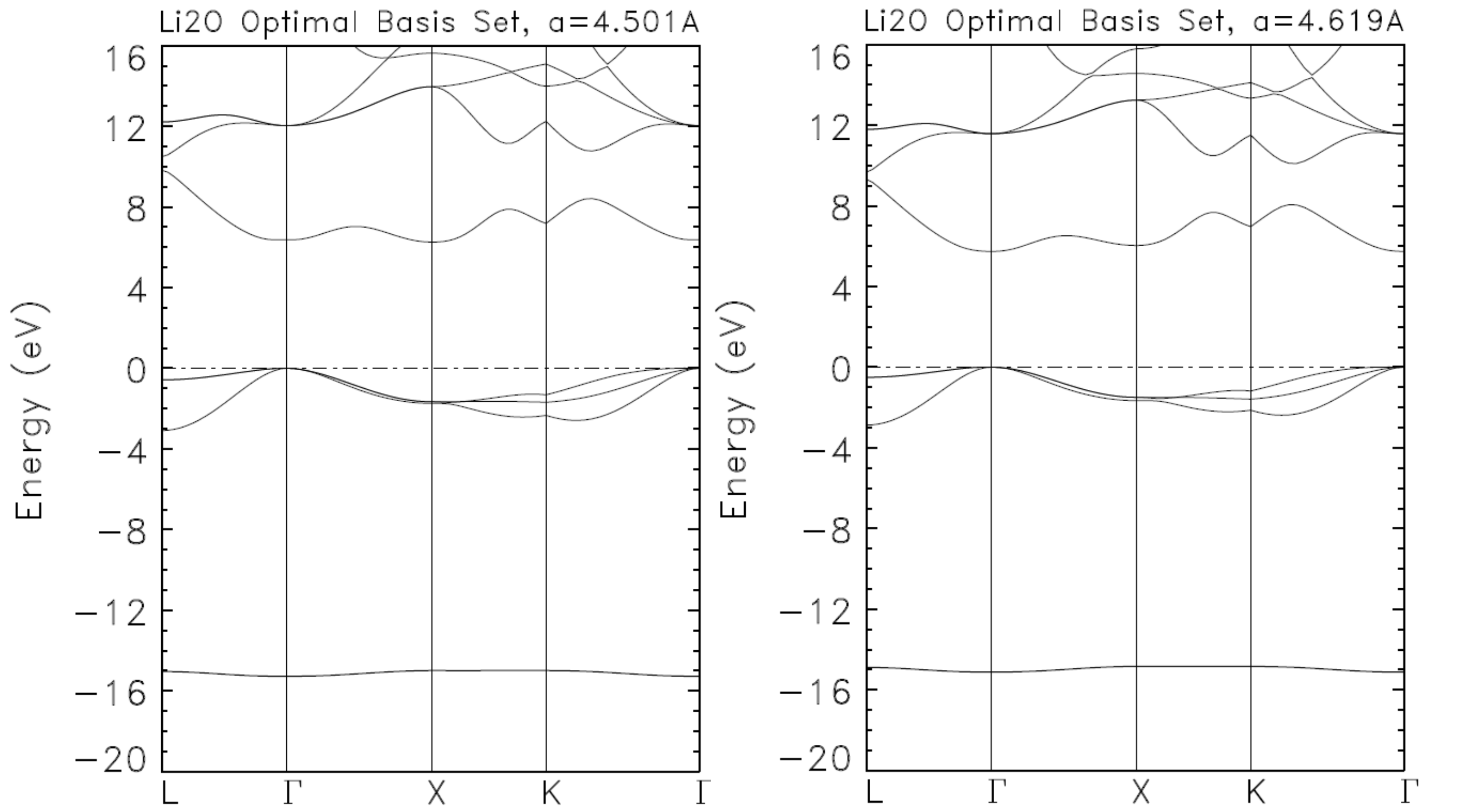

Figure 1: Band structure plots using the equilibrium lattice constant (left) and an experimentally determined room-temperature lattice constant (right) show both direct and indirect band gaps.

Using the optimal basis set described at the bottom of the left panel (Calculation V), we calculated self-consistent solutions to the Kohn-Sham equation using matrix methods. Performing these calculations using different lattice constants determined the equilibrium lattice constant, having the lowest total electron energy. The eigenvalues obtained from this method form the band structures shown above. From these eigenvalues, we calculated density of states and effective masses, shown below, and band gaps, shown at right.

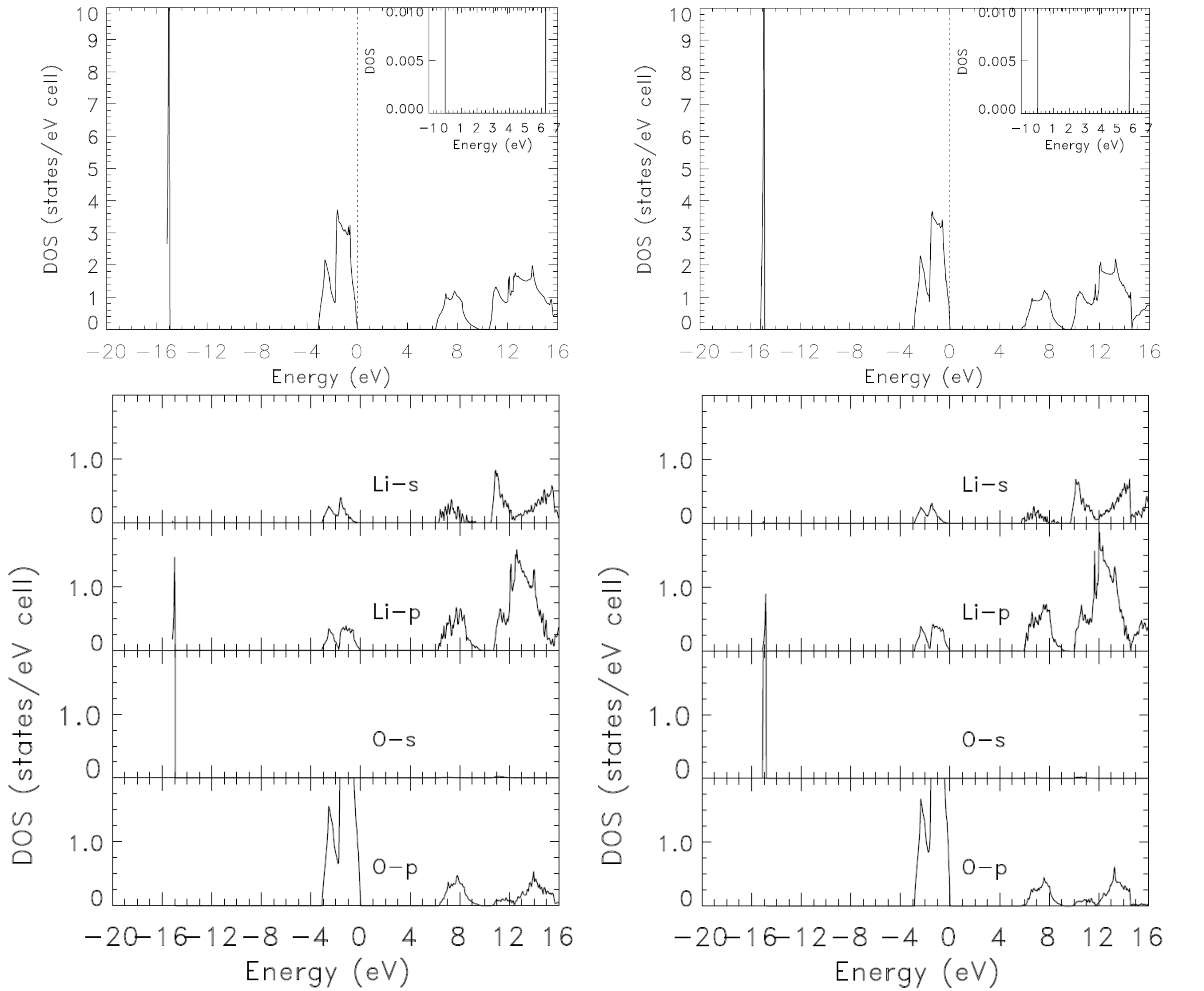

Figure 2: From the eigenvalues obtained via self-consistent calculations, plots of the density of states for the equilibrium (left) and room temperature (right) lattice constants were generated.

	Γ-X	Γ-L	Γ-K	X-U	X-W
Electron	2.05	1.94	1.91	1.08	0.99
Heavy Hole	-1.54	-5.34	-2.99	--	--
Heavy Hole	-1.56	-5.34	-1.75	--	--
Light Hole	-1.48	-0.56	-0.78	--	--

Table 2: Using eigenvalues generated from the room temperature lattice constant, the effective masses of the electron and three types of holes were calculated. Values are given in units of m_e.

Results

Band Gaps	Γ-Γ	Γ-X	Γ-K
Equilibrium Lattice Constant	6.371	6.256	7.182
Room Temp Lattice Constant	5.738	6.034	6.969
Experiment	5.0[3], 7-7.5[4], 7.99[5]		

Table 3: Band gaps were calculated using eigenvalues from the equilibrium and room temperature lattice constants. All values in the table are presented in eV with the zero point set at the Fermi Energy.

We also calculated the bulk modulus from the total energy data obtained in finding the equilibrium lattice constant. Our calculated bulk modulus is 92.03 GPa, compared against the experimental bulk modulus, extrapolated to 0 K, of 89.0 GPa[2].

Discussion

- **Using the BZW-EF approach to DFT, we have calculated the electronic properties of lithium oxide more accurately than other ab-initio calculations.**
- **Our calculated band gaps agree with one experiment but are lower than most experimental values. This difference may correspond to a bizarre spectroscopic peak in the range of 4-6 eV that changes intensity with different experimental setups. As such, it is commonly attributed to a defect, rather than bulk, property of Li_2O. If this were found not to be the case, the experimental value for the band gap would drop significantly.**
- **Our calculated bulk modulus is within experimental error of the experimentally determined bulk modulus.**

- **The band structure of Li_2O is often described as primarily composed of oxygen bands in the occupied states and lithium bands in the unoccupied states. Based on our calculated PDOS, this is an oversimplification of significantly hybridized upper valence and lower conduction bands.**
- **Li_2O is often characterized as an indirect band gap insulator, particularly by other ab-initio calculations. We argue that at most temperatures, Li_2O is a direct band gap insulator.**
- **At low temperatures (lattice constant near equilibrium), the indirect band gap is very slightly (0.12 eV) lower than the direct band gap.**
- **When determining the optimal basis set, we noticed that including a lithium d-orbital in a basis set significantly decreased the indirect band gap, *while raising the energy of the valence bands at several points*. This may be the source of our disagreement with other ab-initio studies.**

- **To further determine the agreement of our calculations with experimental results, there must be greater study of Li_2O experimentally. In particular, greater attention must be given to determining the properties of the strange spectroscopic peak between 4 and 6 eV.**
- **In addition, future studies could explore properties of the recently discovered anti-cotunnite phase of lithium oxide (as opposed to our anti-fluorite phase). In particular, comparison of the pressure at which phase transition occurs should be possible.**

References

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