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

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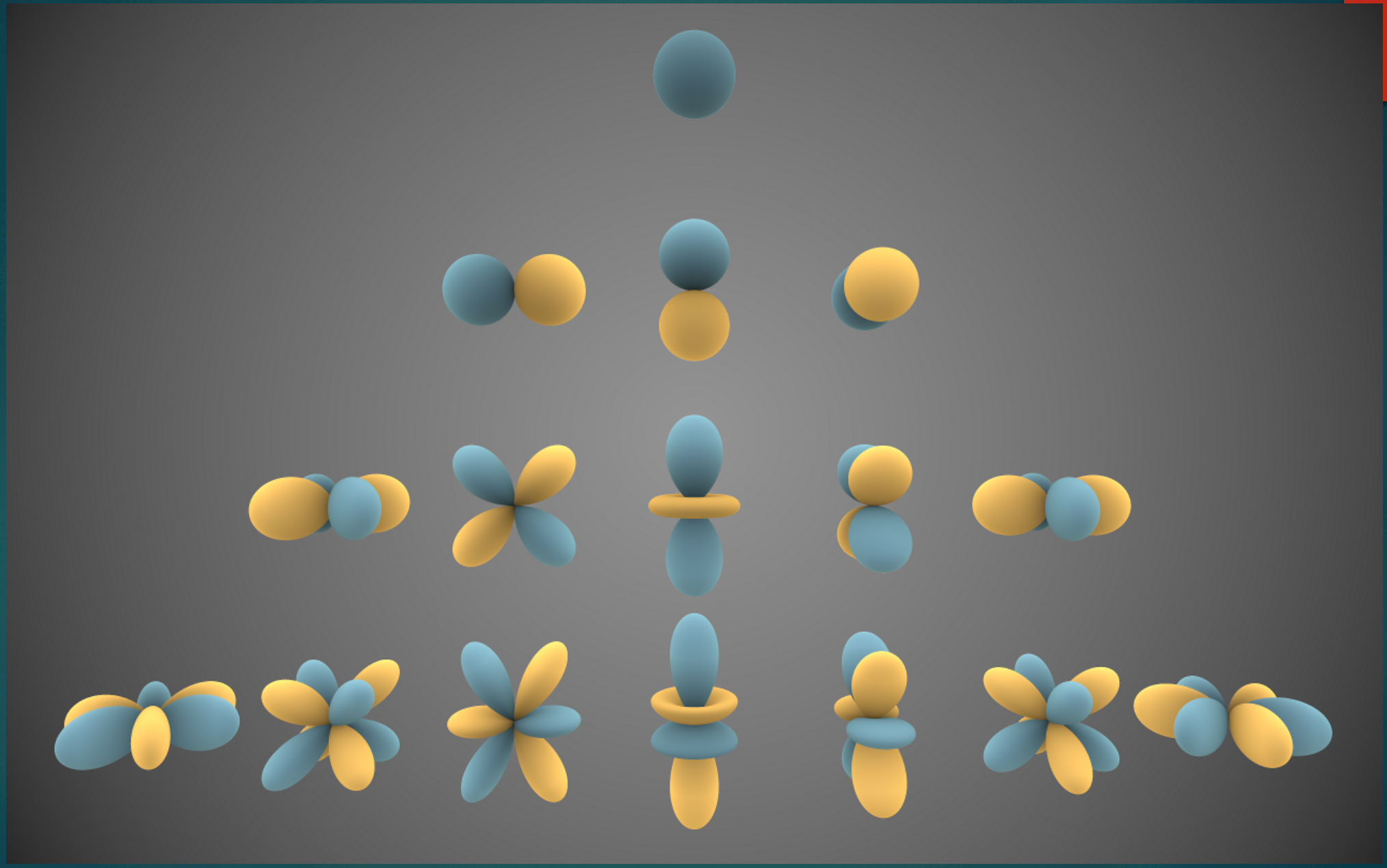
Outline

- Theory
  - DFT-LDA
  - LCGO
  - BZW-EF
- Previous Results
- Our Results
  - Band Structure
  - Equilibrium Lattice Constant
  - Equilibrium Band Structure
  - Density of States
- Conclusion

DFT-LDA and LCGO

- DFT (Density Functional Theory) [1]:
  - $[-\hbar\uparrow 2 /2m \nabla\uparrow 2 + v(\boldsymbol{r}) + 1/2 \int n(\boldsymbol{r}\uparrow\prime)/|\boldsymbol{r}-\boldsymbol{r}\uparrow\prime| d\boldsymbol{r}\uparrow\prime]\Psi + V\downarrow xc\,(n(\boldsymbol{r}))\Psi = E\Psi$
  - $n(\boldsymbol{r}) = \sum i=1\uparrow N \blacksquare |\Psi\downarrow i\uparrow 2|$
- LDA (Local Density Approximation) [2]:
  - Provides form of $V\downarrow xc\,(n(\boldsymbol{r}))$
- LCGO (Linear Combination of Gaussian Orbitals):
  - Numerical simplification that assumes $n(\boldsymbol{r})$ can be written as a sum of atomic orbitals.



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Bagayoko, Zhao, Williams Method, as Enhanced by Ekuma and Franklin (BZW-EF) [3]

- Infinite possible combination of orbitals
- Must select one that represents physical properties
- Selection Rules:
  - Must have minimum total electron energy
  - Must be smallest set of orbitals that has the minimum total energy

Others' Results

Experimental Results:
>6.6 eV [14]
7.0 - 7.5 eV [15]
7.99 eV [16]

Potential for forbidden transitions or Bernstein Moss effect, so experimental measurements may be higher than actual band gap.

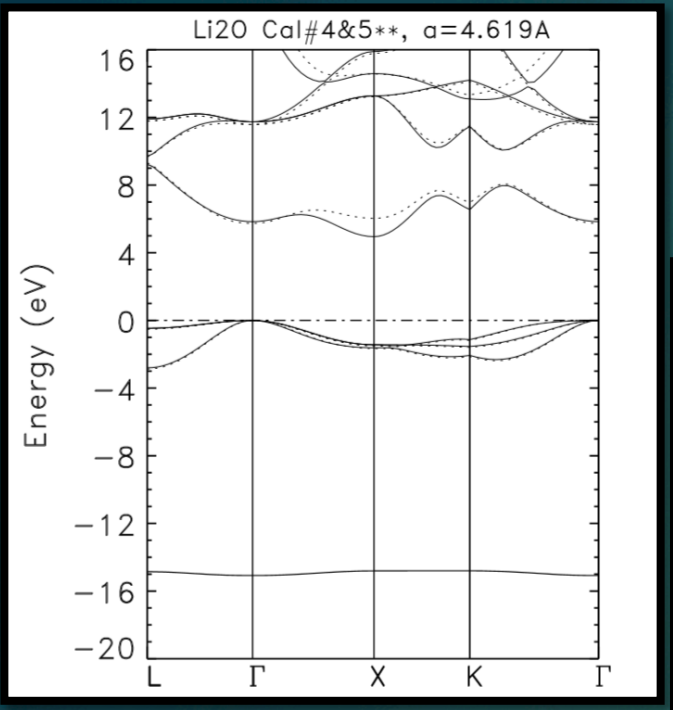
Method	Package	Band Gap (eV)	Reference
DFT-LDA		5.3 [Γ – Γ]	[4]
		5.3 [Γ – X]	[5]
	VASP	5.095 [Γ – X]	[6]
	WIEN2K	4.92 [Γ – X]	[7]
DFT-GGA	WIEN2K	4.96 [Γ – X]	[7]
DFT-WCGGA	WIEN2K	4.96 [Γ – X]	[8]
DFT-EVGGA		6.14 [Γ – X]	[7]
PW91 GGA	VASP	5.39 [Γ – X]	[9]
	VASP	5.00 - 5.02 [Γ – Γ]	[10]
	CRYSTAL03	5.05 [Γ – X] - 8.00 [Γ – Γ]	[10]
PW91PW GGA Hybrid	CRYSTAL03	6.94 [Γ – X] - 10.19 [Γ – Γ]	[10]
B3LYP SemiEmpirical Hybrid	CRYSTAL03	7.19 [Γ – X] - 10.23 [Γ – Γ]	[10]
DFT-SIC		8.3 [Γ – X]	[11]
DFT-LDA+GW		7.4 [Γ – Γ]	[4]
TB-LMTO		5.809 [Γ – X]	[12]
TB-LMTO	WIEN	5.0	[13]

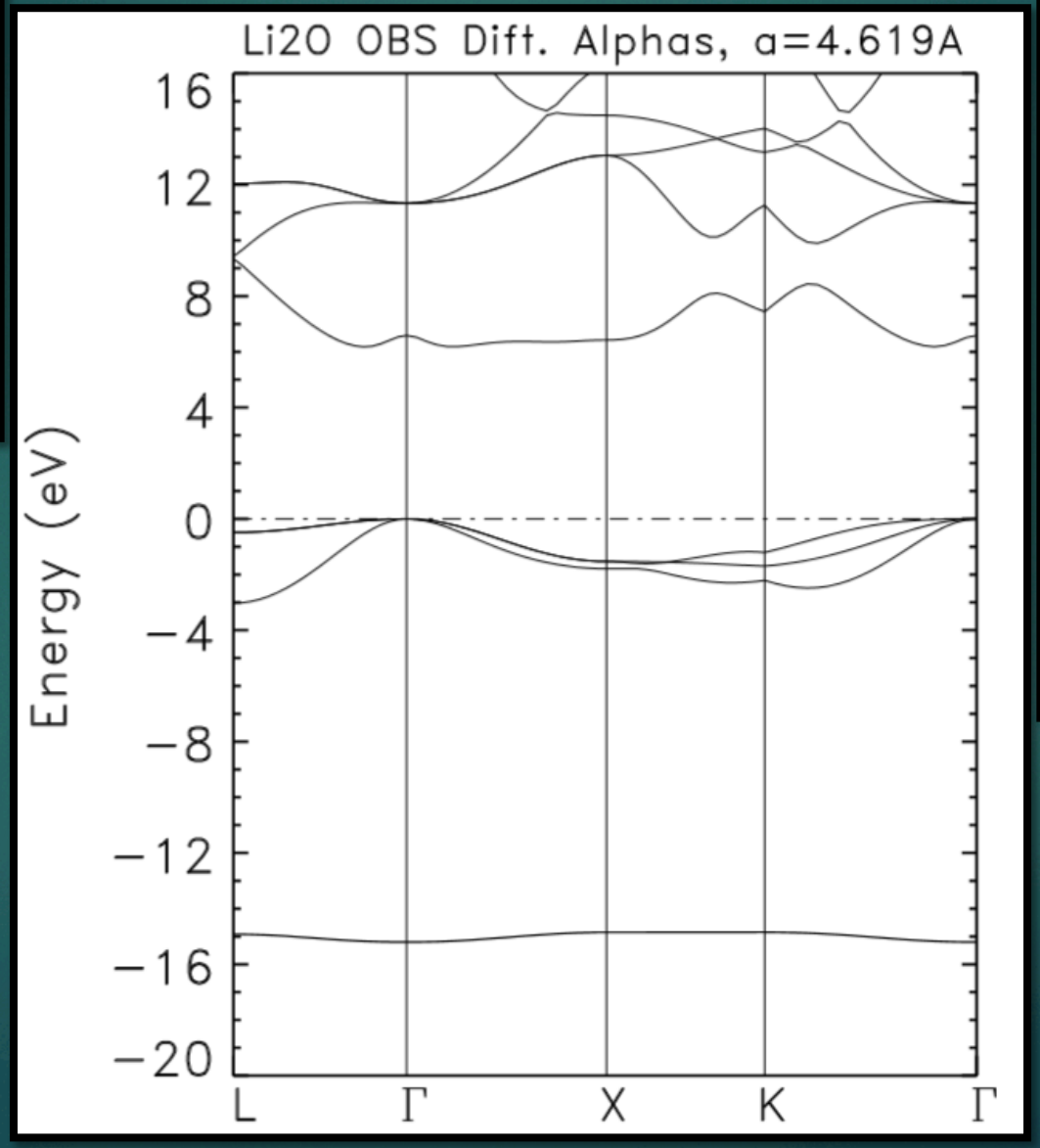
Label	Li^{+} Valence	O^{2-} Valence	Orbitals	Gaps
1	$2s^0 2p^0$	$2s^2 2p^6$	24	5.768 d
2	$2s^0 2p^0 3p^0$	$2s^2 2p^6$	36	5.754 d
3	$2s^0 2p^0 3p^0$	$2s^2 2p^6 3p^0$	42	5.719 d
4	$2s^0 2p^0 3p^0 3d^0$	$2s^2 2p^6 3p^0$	62	4.952 i
5	$2s^0 2p^0 3s^0 3p^0 3d^0$	$2s^2 2p^6 3p^0$	66	4.952 i
6	$2s^0 2p^0 3s^0 3p^0 3d^0$	$2s^2 2p^6 3p^0 3d^0$	76	4.930 i
2*	$2s^0 2p^0 3p^0 4p^0$	$2s^2 2p^6$	48	5.775 d
3*	$2s^0 2p^0 3s^0 3p^0 4s^0 4p^0$	$2s^2 2p^6$	56	5.735 d
3**	$2s^0 2p^0 3s^0 3p^0$	$2s^2 2p^6$	40	5.741 d
4**	$2s^0 2p^0 3s^0 3p^0 4p^0$	$2s^2 2p^6$	52	5.756 d
5**	$2s^0 2p^0 3s^0 3p^0 4p^0$	$2s^2 2p^6 3p^0$	58	5.738 d
4*	$2s^0 2p^0 3s^0 3p^0 4s^0 4p^0$	$2s^2 2p^6 3p^0$	62	5.722 d
5*	$2s^0 2p^0 3s^0 3p^0 4s^0 4p^0$	$2s^2 2p^6 3s^0 3p^0$	74	5.381 d

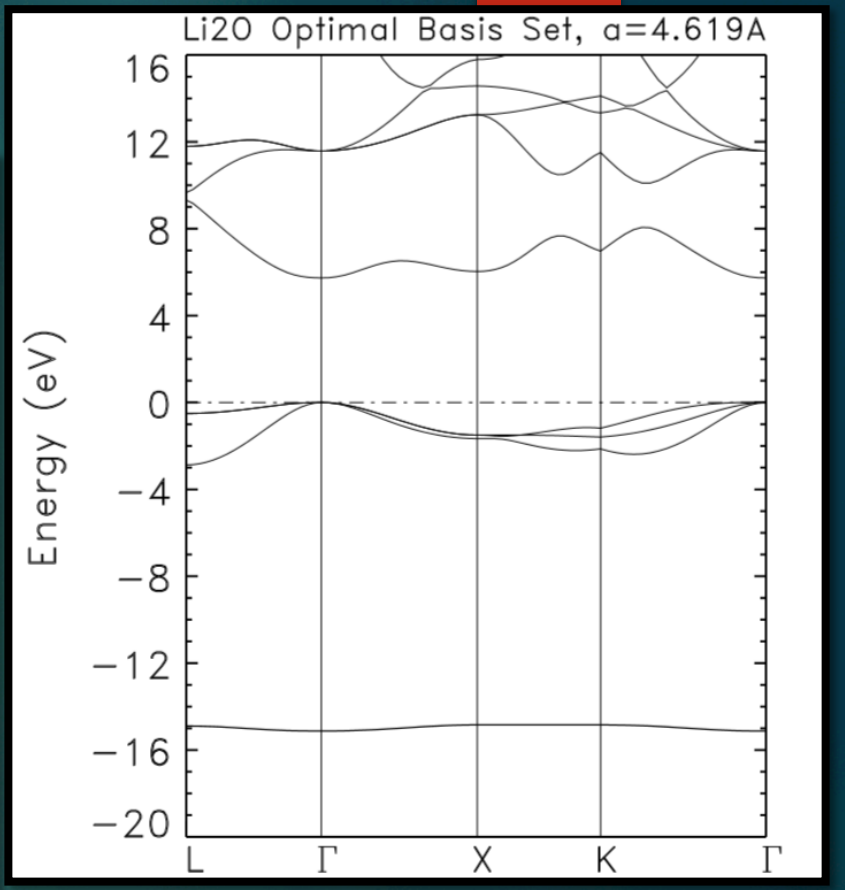
Calculations Performed

Calculations Performed, with band gaps given in eV, and d and i representing direct (Γ) and indirect (Γ - X), respectively

Resulting Band Plots



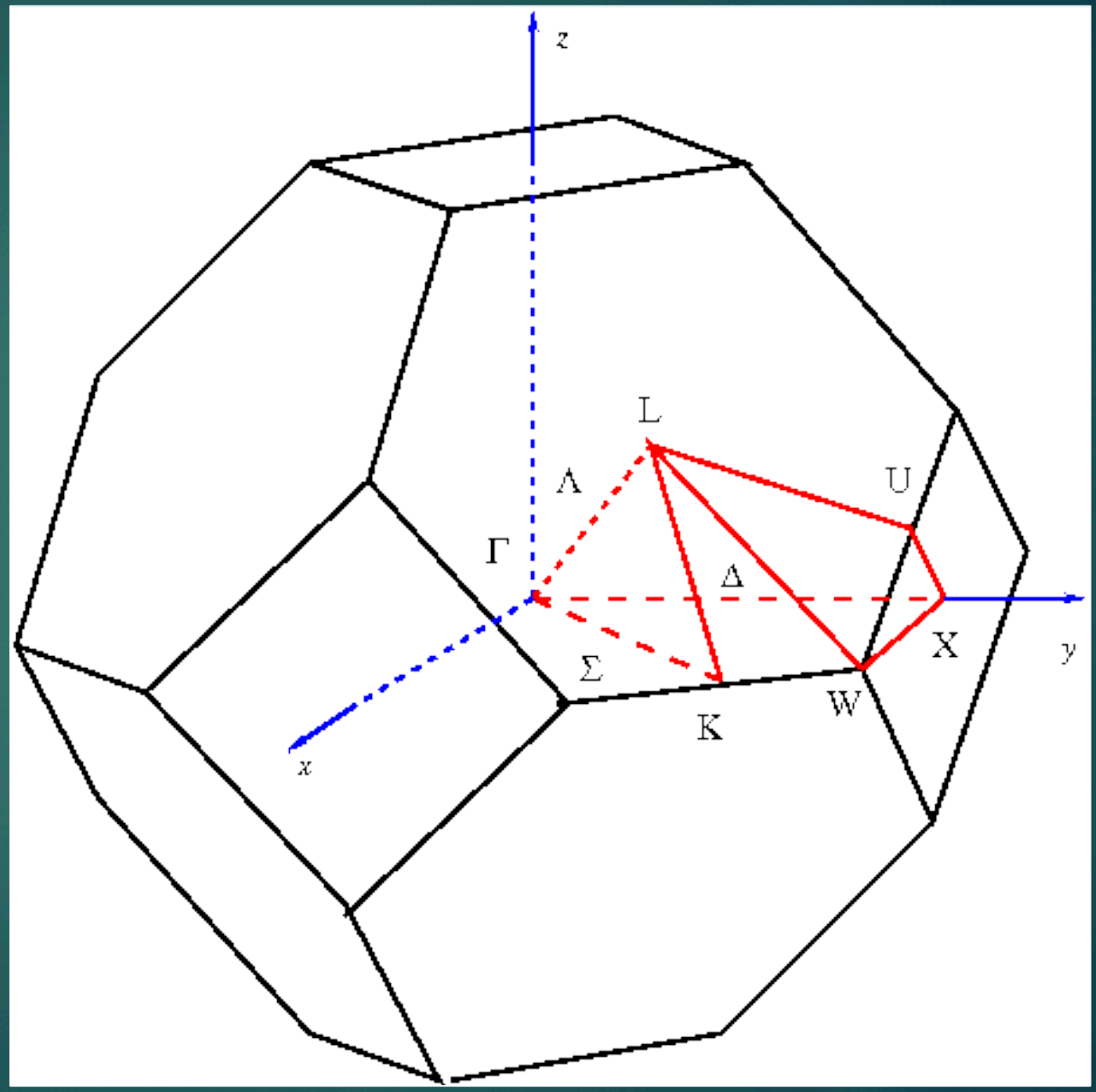




Band Gap for High α:
6.181 eV

Band Gap for Low α:
5.738 eV

Irreducible Brillouin Band



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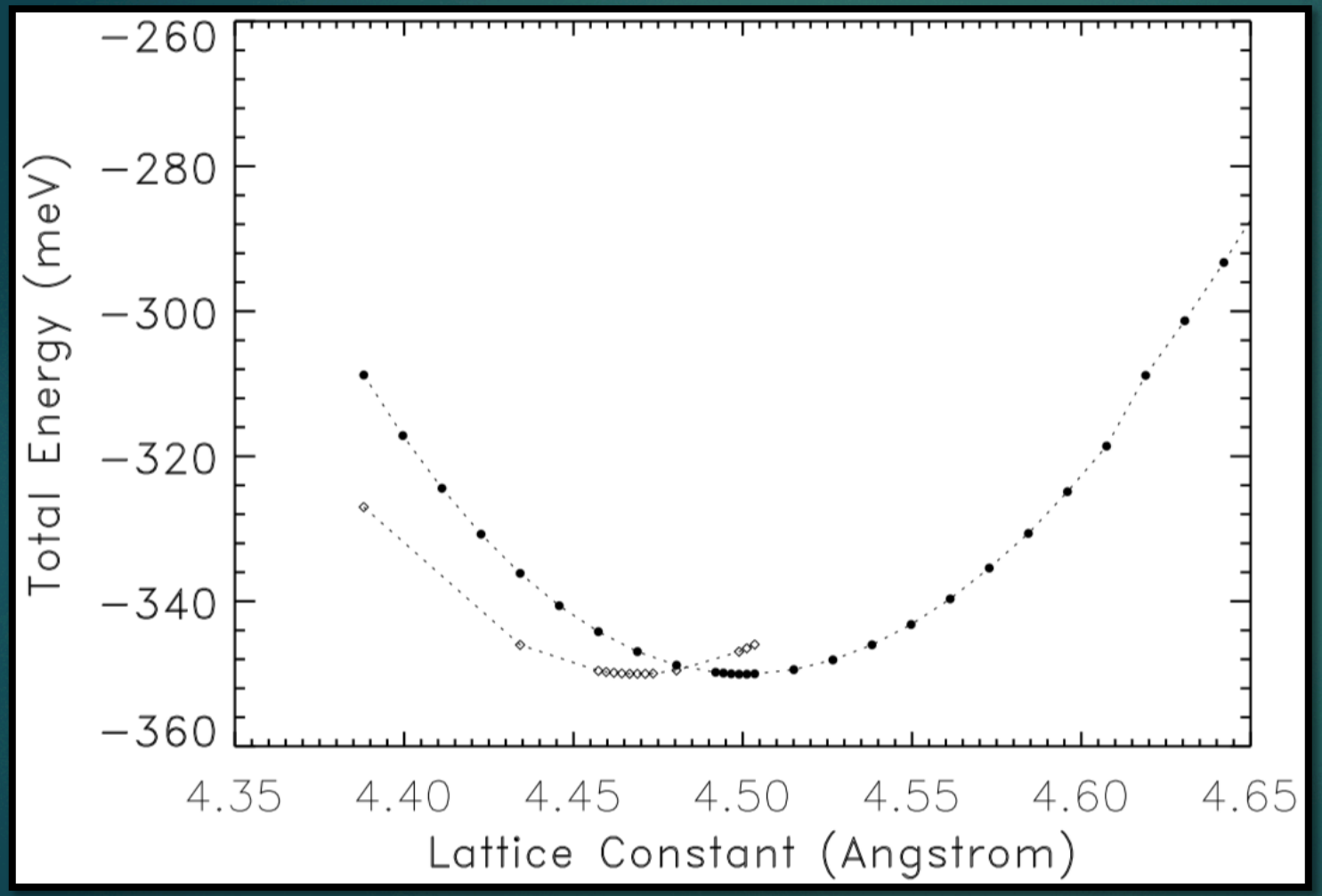
Total Energy vs. Lattice Constant

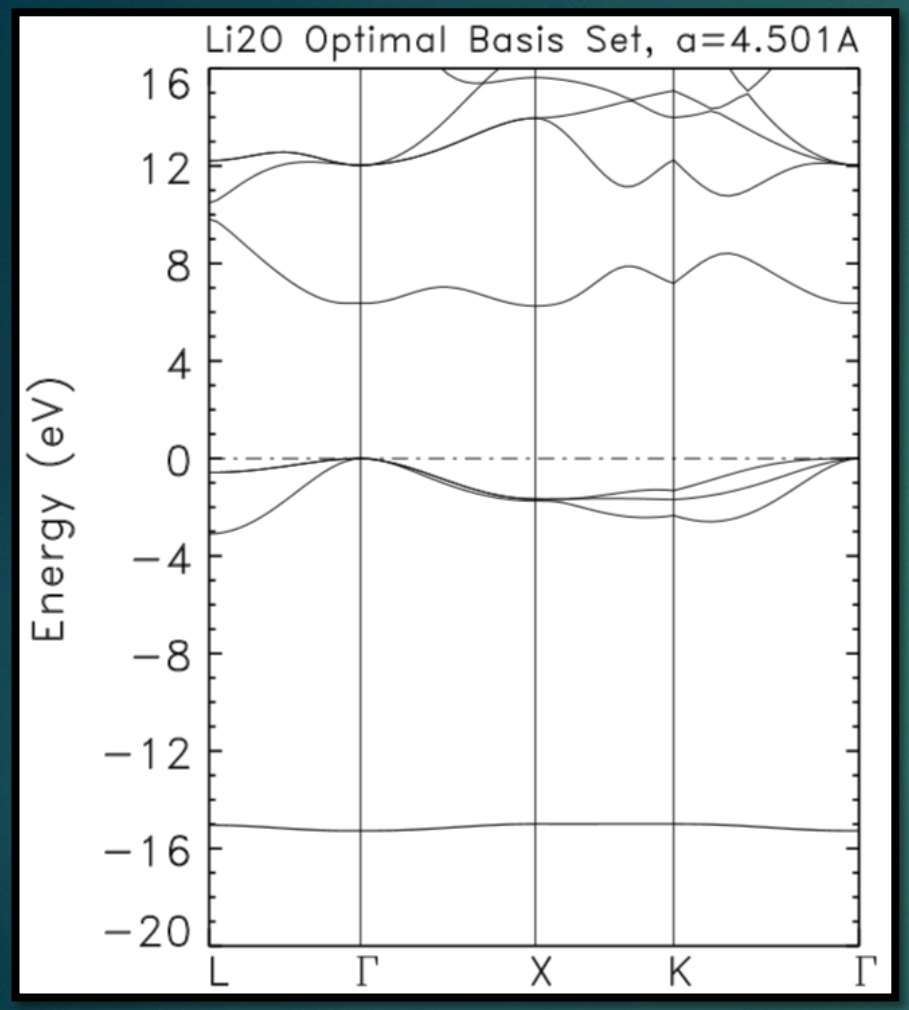


Equilibrium Lattice Constants:

Low α: 4.501 Å
High α: 4.469 Å

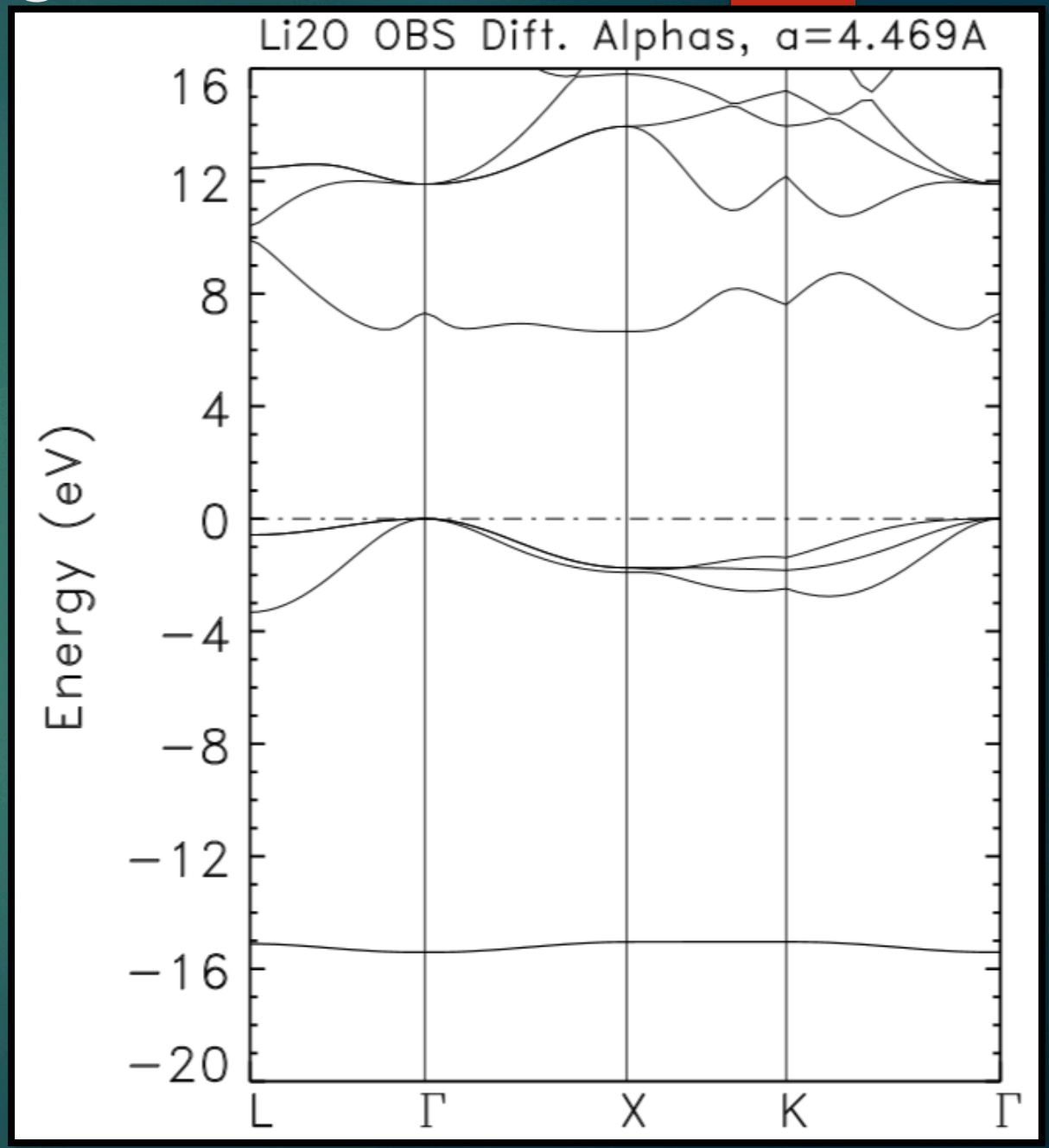
The minimum total energy of both sets of calculations (low and high a) are arbitrarily set to -350 meV so that they can be plotted on the same graph. The high a minimum is **2.00815 eV** lower than the low a minimum.

Equilibrium Band Structure

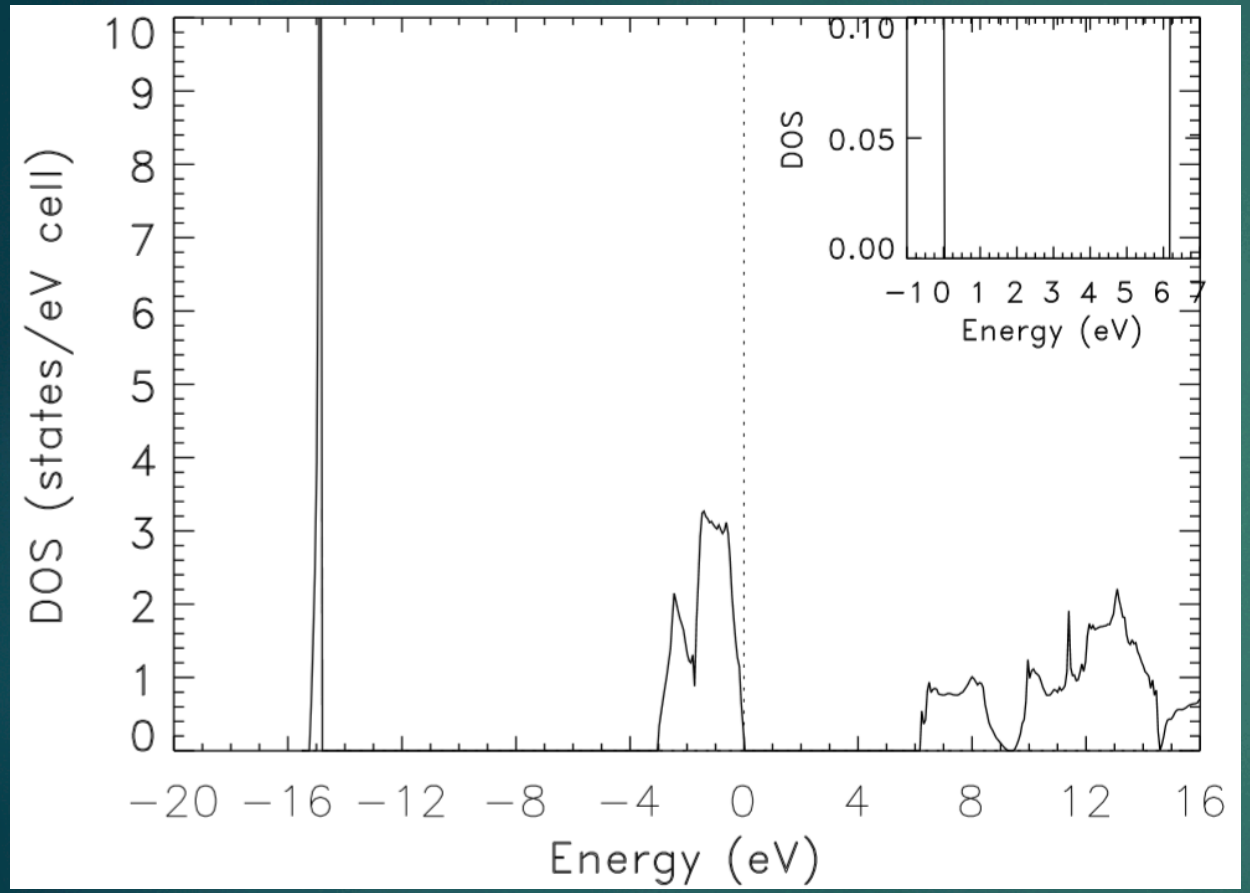


Band Gap for Low α:
6.256 eV

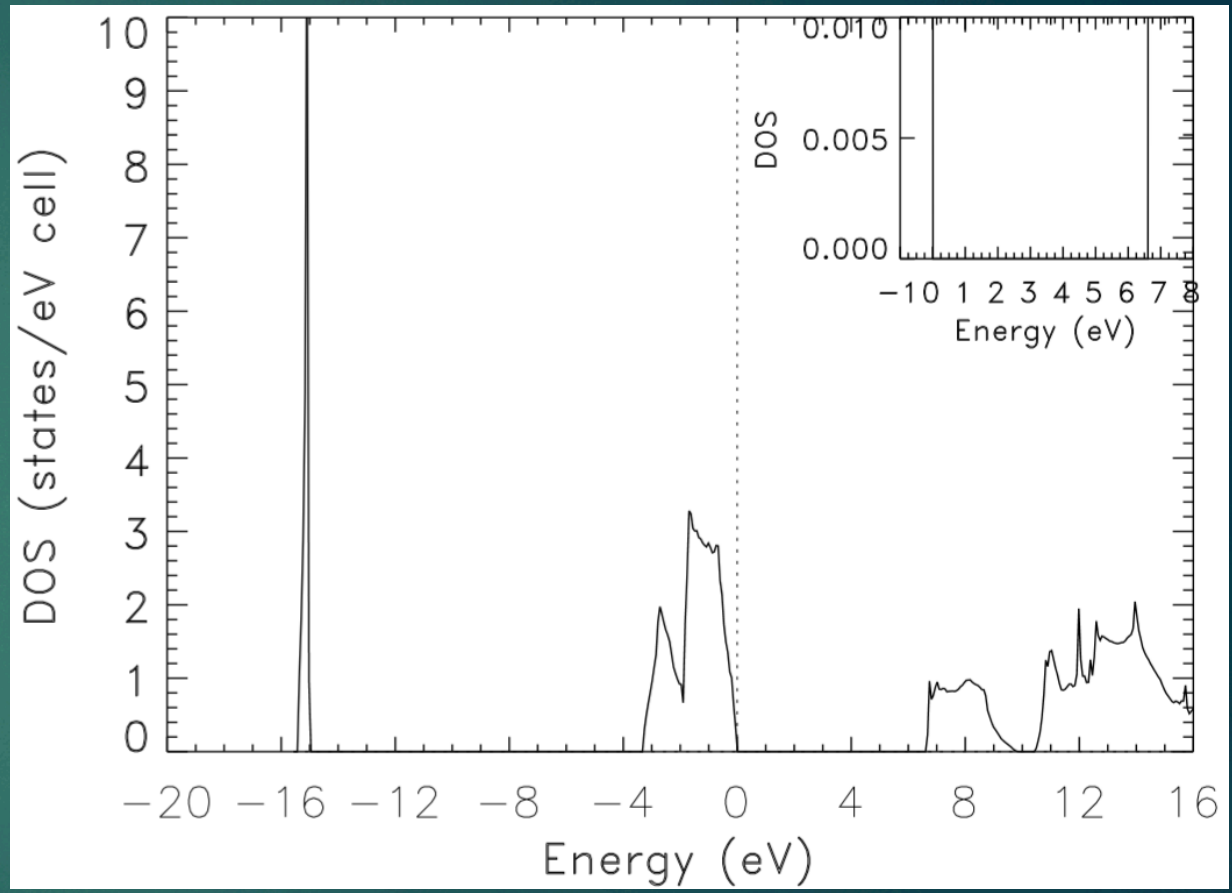
Band Gap for High α:



Densities of States

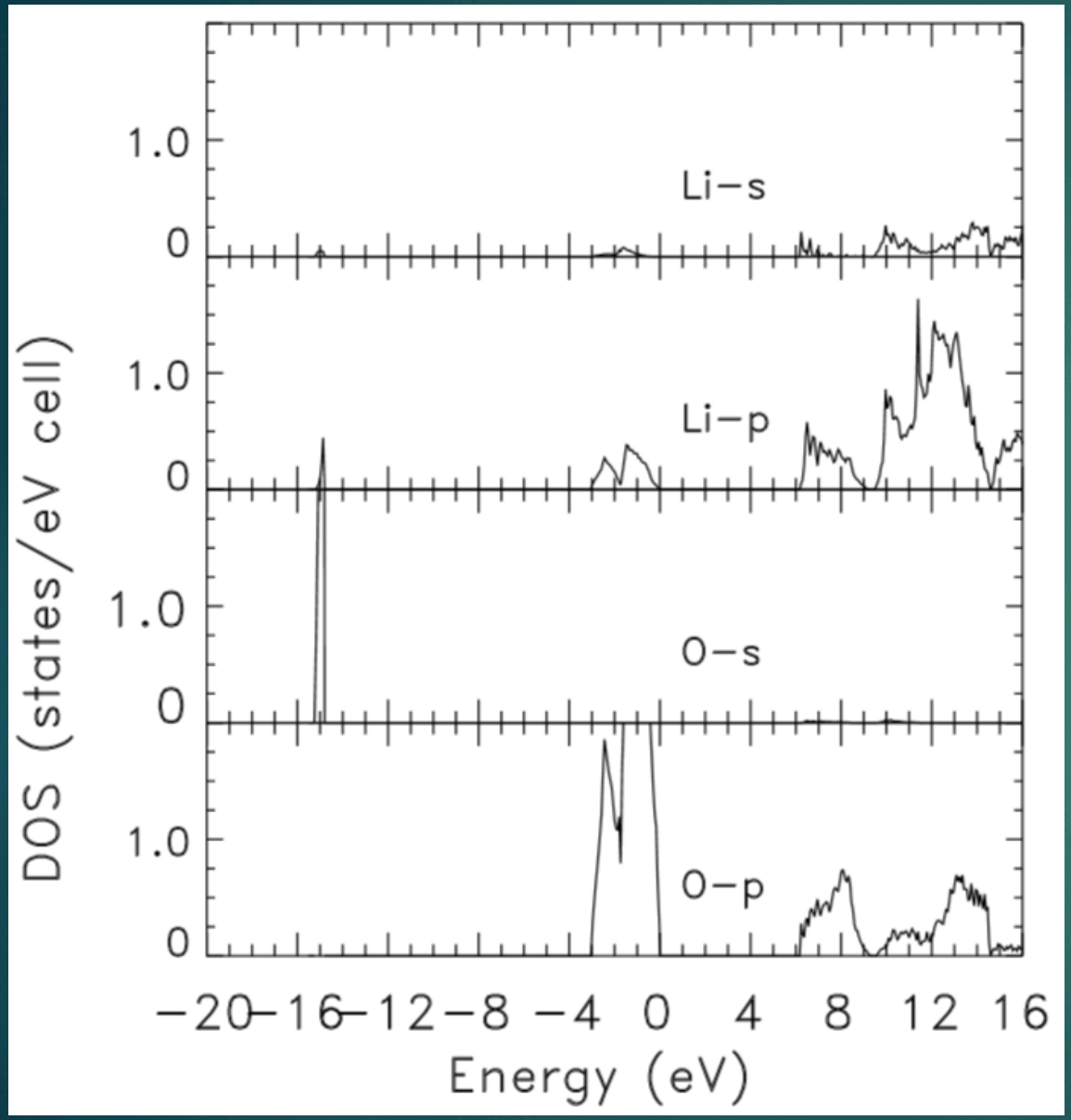


Room Temperature

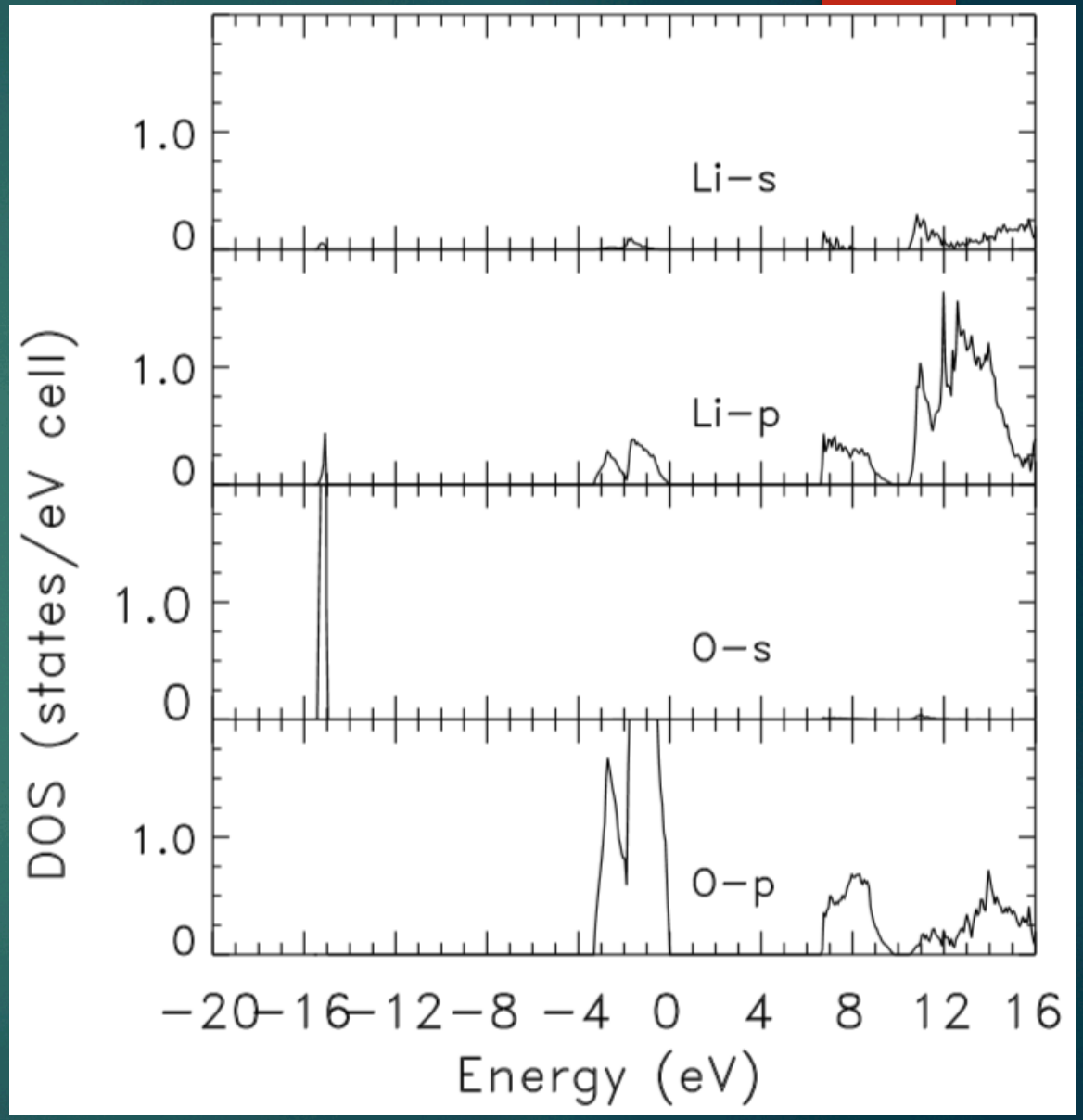


Zero Temperature

Partial Densities of States



Room Temperature



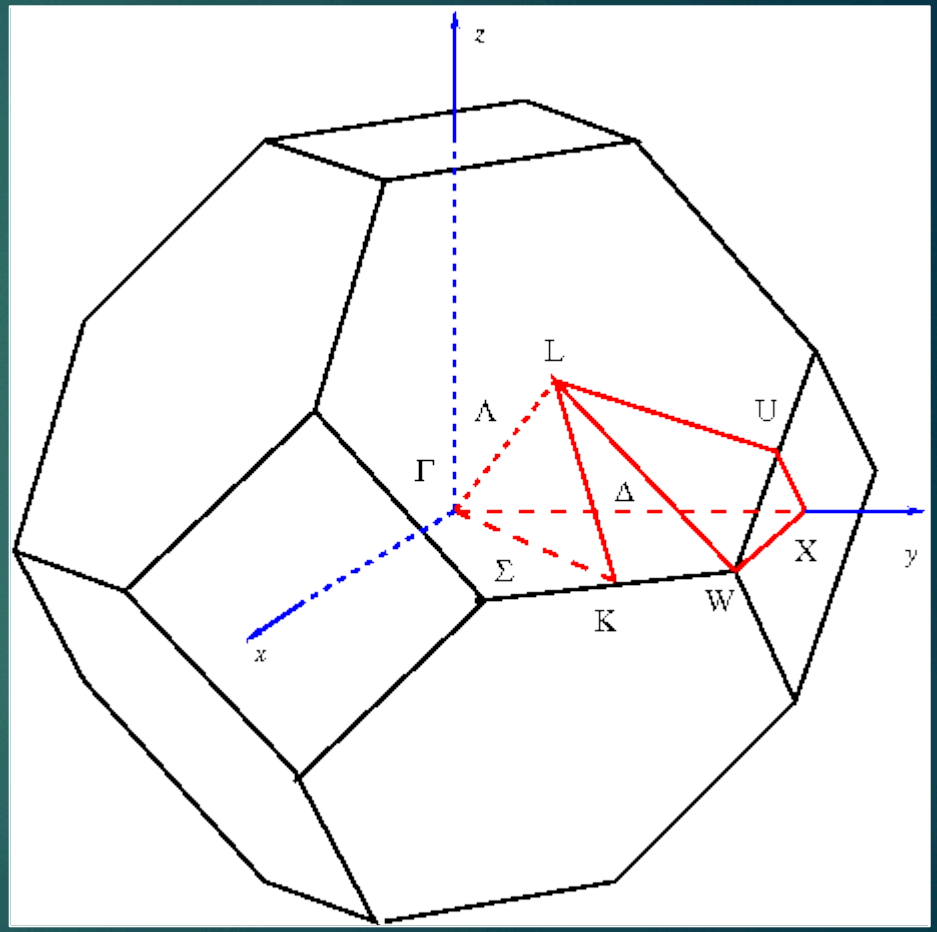
Zero Temperature

Effective Masses

Carrier	Γ -L	Γ -X	Γ -K
Heavy Hole	-4.37	-1.72	-2.88
Heavy Hole	-4.37	-1.72	-1.90
Light Hole	-0.52	-0.80	-0.69

Point	Longitudinal	Transverse	Transverse
Λ Minimum	0.46 (111)	0.69 (110)	0.60 (211)
Δ Minimum	1.02 (010)	2.41 (101)	2.92 (100)
Σ Minimum	0.61 (110)	0.99 (001)	0.85 (111)

All masses are in m_e.



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Conclusion

- Better results than previous ab-initio calculations
- Identified subtle features of Li_2O properties
- More experiments necessary to confirm predictions

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Acknowledgements

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