Electronic Supporting Information

1   **First-principles studies of gas molecules adsorption on LaB$_6$(100) surface**

2   Rui Wang[1], Z. J. Ding[1,2]*

3   [1]*Department of Physics, University of Science and Technology of China, Hefei 230026, Anhui, P.R.*
4   *China*

5   [2]*Hefei National Research Center for Physical Sciences at Microscale, University of Science and*
6   *Technology of China, Hefei 230026, Anhui, P.R. China*

7   *Corresponding Author: zjding@ustc.edu.cn
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9 **1   Convergence test**

10 For the cutoff energy, k-point grid, vacuum layer thickness, and number of atomic layers used in our

11 calculations, we have conducted convergence tests. The following content demonstrates that our

12 choices regarding these parameters are relatively reasonable.

13 **1.1   Cutoff energy**

14 Under the conditions of a fixed k-point grid of 3×3×1, a vacuum layer thickness of 18 Å, and four

15 atomic layers, we conducted convergence tests for the plane-wave basis set cutoff energy. The results

16 of the convergence tests are displayed in Table S1.

17   **Table S1** The relationship between cutoff energy (E_{cut}) and average atomic energy (E/atom).

E_{cut} (eV)	E/atom (eV)
350	-6.9332
400	-6.9332
450	-6.9346
500	-6.9349
550	-6.9355

18 The reason for choosing a cutoff energy of 450 eV is that even if we increase the cutoff energy to 550

19 eV, the change in E/atom is only 0.9 meV. Considering both computational resources and accuracy,

20 selecting a cutoff energy of 450 eV is reasonable.

21 **1.2   K-point grid**

22 Similarly, we fixed the cutoff energy at 450 eV, the vacuum layer thickness at 18 Å, and the number

23 of atomic layers at 4, and conducted a convergence test on the k-point grid. The test results are shown

24 in Table S2. As can be seen, for the 3×3×1 k-point grid that we selected, when compared with the

25 5×5×1 k-point grid, the difference in average atomic energy is only 0.9 meV.

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30   **Table S2** The relationship between k-point grid and average atomic energy (E/atom).

k-point grid	E/atom (eV)
1×1×1	-6.9304
2×2×1	-6.9350
3×3×1	-6.9346
4×4×1	-6.9347
5×5×1	-6.9337

31   **1.3   Vacuum layer thickness**

32   For the convergence test of the vacuum layer thickness, we fixed the cutoff energy at 450 eV, the k-

33   point grid at 3×3×1, and the number of atomic layers at 4. The test results are displayed in Table S3.

34   **Table S3** The relationship vacuum layer thickness (h) and average atomic energy (E/atom).

h/Å	E/atom (eV)
14	-6.9346
16	-6.9346
18	-6.9347
20	-6.9347
22	-6.9337

35   **1.4   Atomic layer**

36   In the testing of atomic layers, continuing to use average atomic energy as a criterion for determining

37   convergence is unreasonable. As the number of atomic layers increases, the atoms exhibiting bulk

38   properties in our simulated system become more prevalent, while those with surface properties be-

39   come fewer. If energy is averaged per atom in this context, there will be a noticeable reduction in

40   atomic energy as the number of layers increases. This reduction occurs because the average atomic

41   energy increasingly approaches that of the bulk atoms. Considering the above perspective, we use

42   surface energy as the convergence criterion for determining the number of atomic layers. The defini-

43   tion of surface energy is as follows:

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$$\gamma_s = \frac{1}{2A}\left(E_s^{\text{unrelax}} - NE_b\right) + \frac{1}{A}\left(E_s^{\text{relax}} - E_s^{\text{unrelax}}\right) \tag{1}$$

45   In equation (1), E_s^{unrelax} represents the energy of the surface without geometric structural optimiza-

46   tion, E_s^{relax} represents the energy of the surface after geometric structural optimization, E_b represents

47   the average energy per atom of the bulk phase LaB_6, N is the number of atoms in the surface model,

48   and A represents the area of the surface. Table S4 displays the relationship between the number of

49   atomic layers obtained and the surface energy. Even with an increase to six atomic layers, the result-

50   ing surface energy error is only 0.0018 eV/$Å^2$.

51   **Table S4** The relationship between the number of atomic layers and surface energy (γ_s).

Atomic layer	$\gamma_s (eV / Å^2)$
2	0.1722
3	0.1729
4	0.1722
5	0.1733
6	0.1740

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53   **2   The most stable adsorption structures**

54   For each molecule, we summarize the detailed geometric data of its most stable molecular adsorption

55   structure and most stable dissociative adsorption structure in table S5, as they have the minimum ad-

56   sorption energy and thus are the focus of our study.

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64   **Table S5** The bond length of the most stable adsorption structure.

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configuration	bond length (Å)	configuration	bond length (Å)
CO_2-M	C-O1=1.33 C-O2=1.33 O1-La3=2.67 O1-La4=2.67 O2-La1=2.66 O2-La2=2.67 C-B1=1.55	CO_2-D	C-O2=1.44 O2-La1=2.46 O2-La4=2.46 C-B1=1.54 O1-B2=1.39
H_2O-M	O-H1=0.97 O-H2=1.11 O-La1=2.66 H2-B1=1.80	H_2O-D	H1-B1=1.22 H2-B2=1.22 O-La1=2.22 O-La2=2.22
O_2-M	O1-La3=2.26 O2-La2=2.21 O1-O2=1.45 O2-La3=2.53	O_2-D	O1-B1=1.47 O2-B1=1.47 O1-La3=2.34 O1-La4=2.34 O2-La1=2.34 O2-La2=2.34
N_2-M	N1-N2=1.56 N1-La1=2.51 N1-La2=2.50 N2-La3=2.50 N2-La4=2.51 N1-B1=1.56 N2-B1=2.56	N_2-D	N1-B1=1.42 N2-B2=1.42

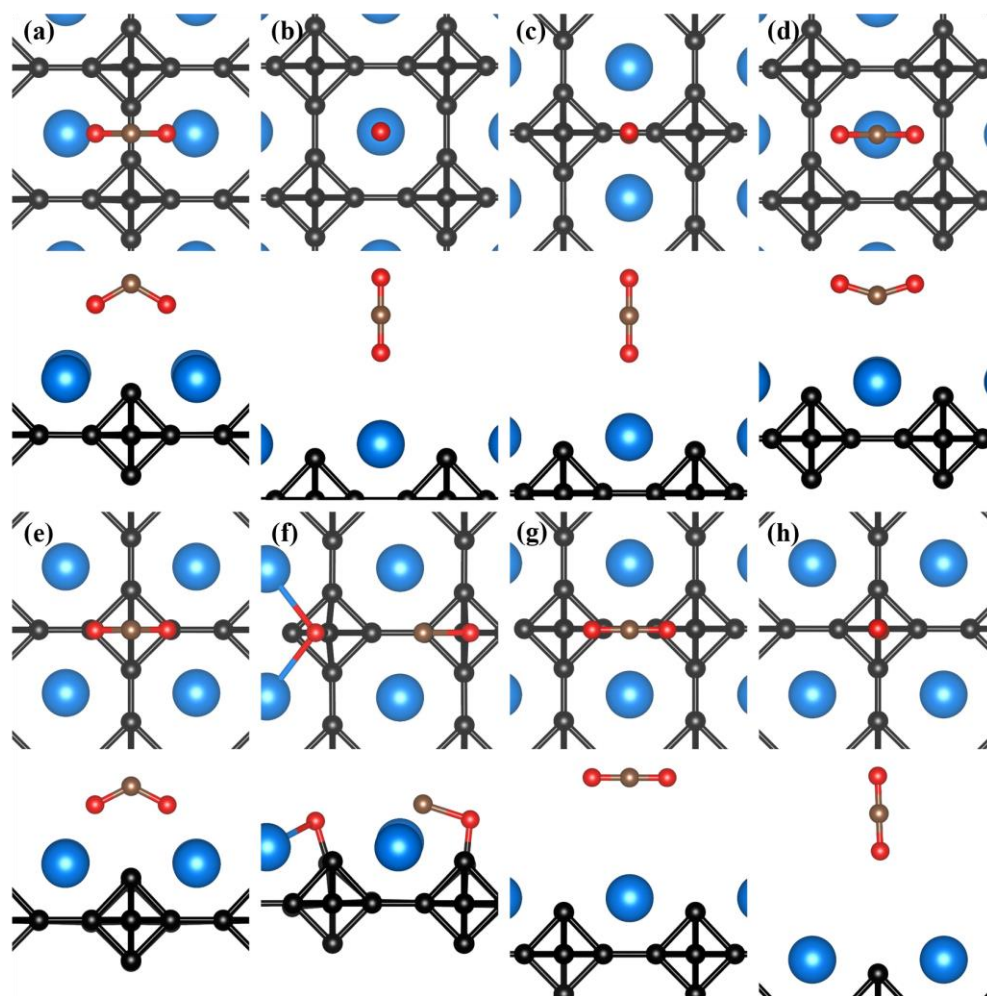66   **3   Other adsorption structure**

67   In this study, we only discuss the most stable molecular adsorption structure and the most stable dis-

68   sociative adsorption structure for each adsorbate. During the geometric optimization process, we ac-

69   tually considered many structures. Therefore, for those structures with negative adsorption energies

70   but not the most stable, we present them collectively in Figures S1 to S4. We will first uniformly

71   name these structures to facilitate the summary of their adsorption energies in Table S6. For the

72 adsorption of O_2 molecules, the adsorption structures are displayed in Figure S1. From left to right,

73 we label them as O_2-1, O_2-2, up to O_2-5, such that the structure in Figure S1 (a) is marked as O_2-1,

74 the structure in Figure S1 (b) as O_2-2, and so forth. For the adsorption of other molecules, we also
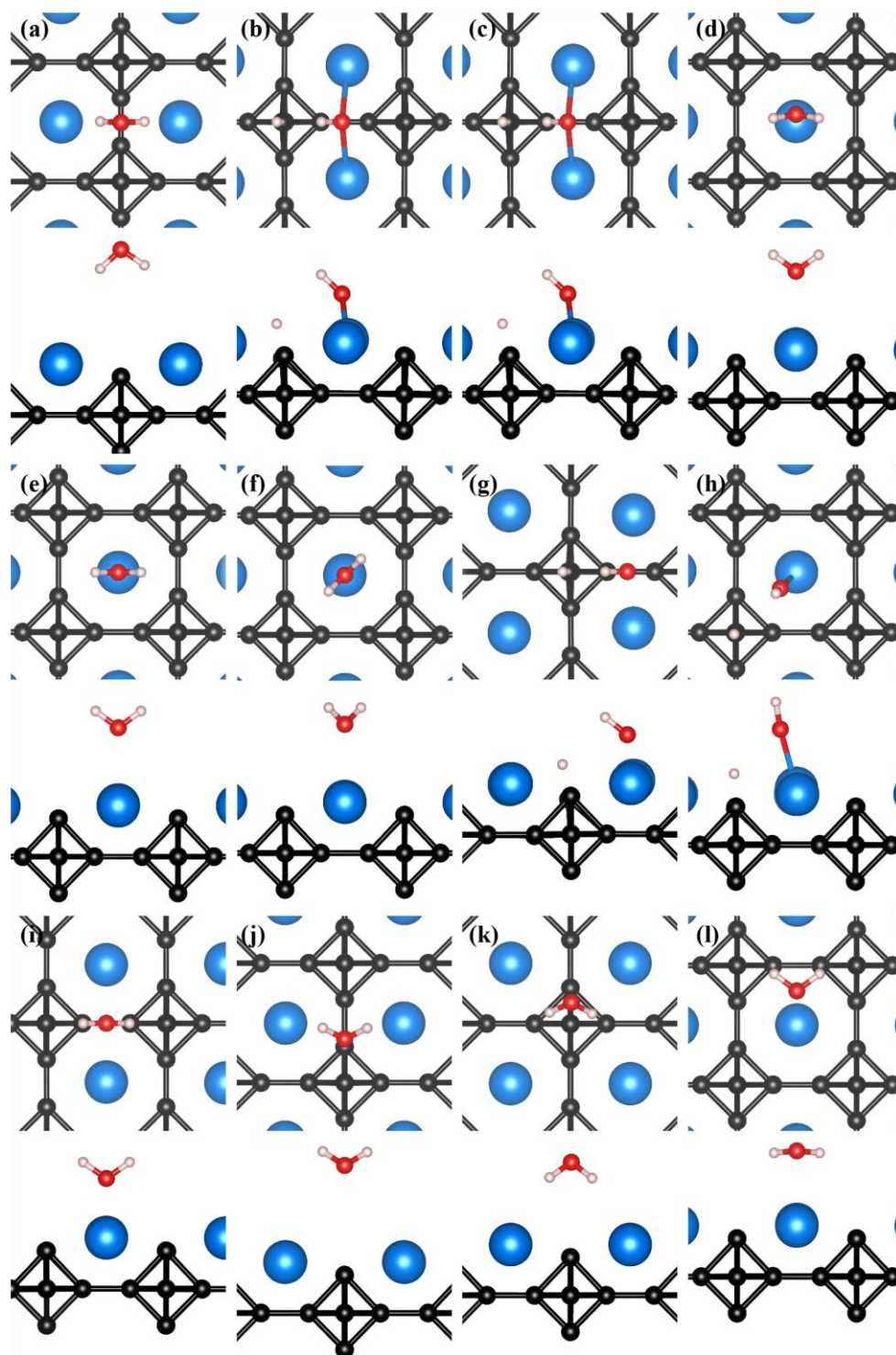
75 adopt a similar labeling scheme.
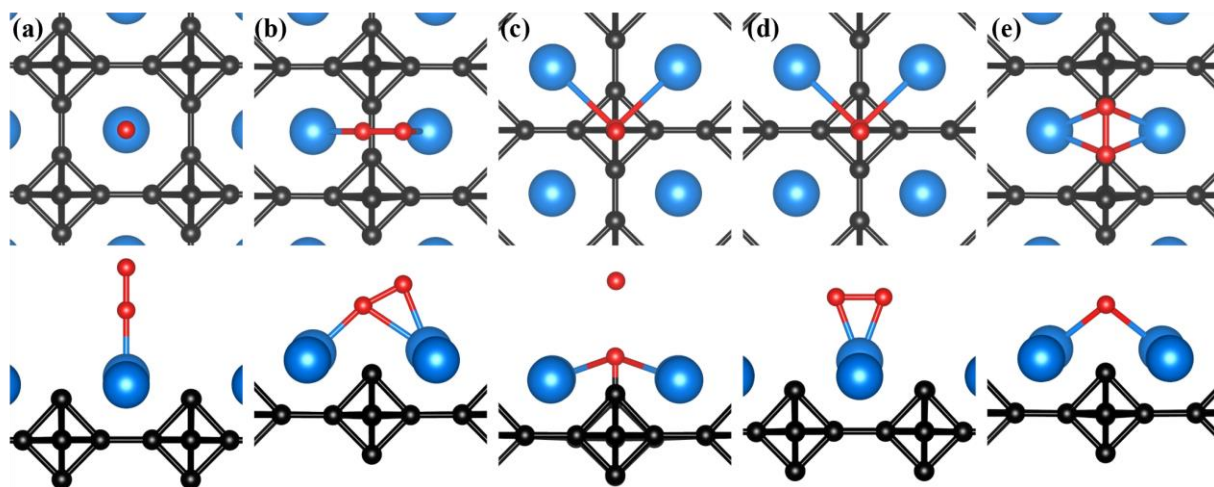
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77 **Figure S1** O_2 on LaB_6(100): Non-most stable molecular adsorption configurations and non-most stable dissociative
78 adsorption configurations. (a)-(e) represent different adsorption structures, with the top half showing top views and
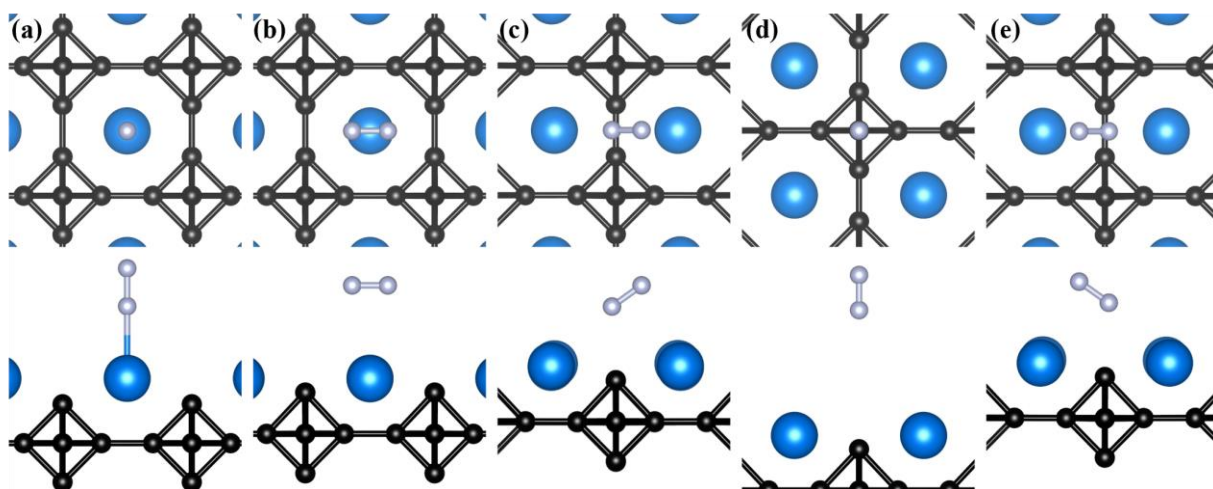79 the bottom half showing side views.

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Figure S2 CO$_2$ on LaB$_6$(100): Non-most stable molecular adsorption configurations and non-most stable dissociative adsorption configurations. (a)-(h) represent different adsorption structures, with the top half showing top views and the bottom half showing side views.

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Figure S3 H_2O on $LaB_6(100)$: Non-most stable molecular adsorption configurations and non-most stable dissociative adsorption configurations. (a)-(l) represent different adsorption structures, with the top half showing top views and the bottom half showing side views.

Figure S4 N_2 on LaB_6(100): Non-most stable molecular adsorption configurations and non-most stable dissociative adsorption configurations. (a)-(e) represent different adsorption structures, with the top half showing top views and the bottom half showing side views.

Table S6 Adsorption energy of non-most stable adsorption structures.

configuration	E_{ads} (eV)	configuration	E_{ads} (eV)	configuration	E_{ads} (eV)
O_2-1	-1.68	CO_2-6	-1.07	H_2O-8	-2.08
O_2-2	-3.55	CO_2-7	-0.10	H_2O-9	-0.51
O_2-3	-3.11	CO_2-8	-0.01	H_2O-10	-0.11
O_2-4	-2.76	H_2O-1	-0.04	H_2O-11	-0.41
O_2-5	-3.43	H_2O-2	-2.15	H_2O-12	-0.61
CO_2-1	-0.74	H_2O-3	-0.48	N_2-1	5.09
CO_2-2	-0.08	H_2O-4	-0.59	N_2-2	-0.17
CO_2-3	-0.06	H_2O-5	-0.53	N_2-3	-0.74
CO_2-4	-0.07	H_2O-6	-0.49	N_2-4	-0.02
CO_2-5	-1.55	H_2O-7	-2.09	N_2-5	-0.71

4 The difference between total energy and free energy

We use E to represent the calculated total energy, F to represent the calculated free energy, and N to represent the number of atoms in the system. Our results show that |E-F|/N less than 1 meV is satisfied for all structures studied. Table S7 shows our calculation results.
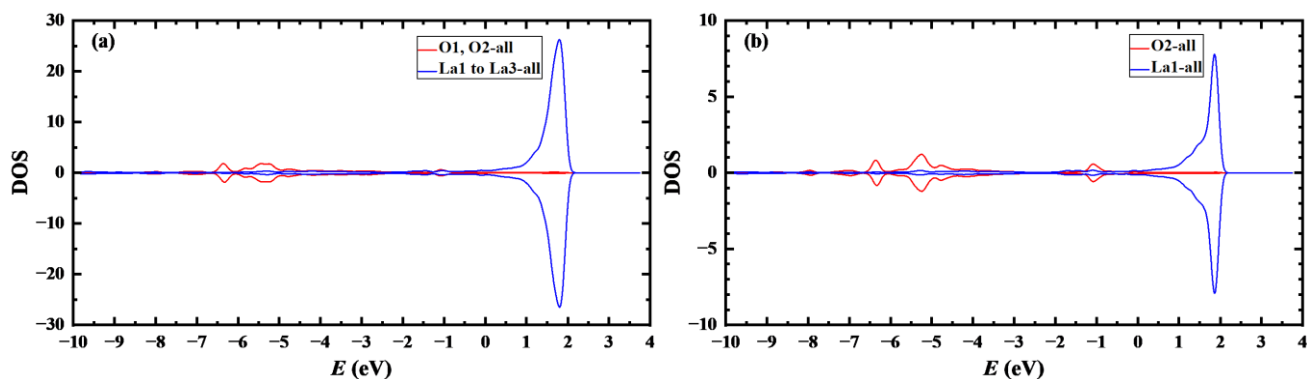
102   **Table S7** Total energy and free energy of the most stable configurations.

| configuration	E (eV)	F (eV)	$|E\text{-}F|/N$ (meV)
CO_2-M	-3133.30	-3133.36	0.13
CO_2-D	-3133.48	-3133.56	0.17
H_2O-M	-3121.85	-3121.92	0.16
H_2O-D	-3123.43	-3123.50	0.16
O_2-M	-3120.17	-3120.26	0.20
O_2-D	-3125.09	-3125.18	0.18
N_2-M	-3124.04	-3124.13	0.20
N_2-D	-3127.13	-3127.21	0.17

103   **5   Density of state**

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105   **Figure S5** The electronic density of states of CO_2M (a) and CO_2-D (b). (a): The sum of the orbitals of O1 and O2
106   (red), the sum of the orbitals of La1 to La3 (blue); (b): The orbitals sum of O2 (red) and the orbitals sum of La1 (blue).
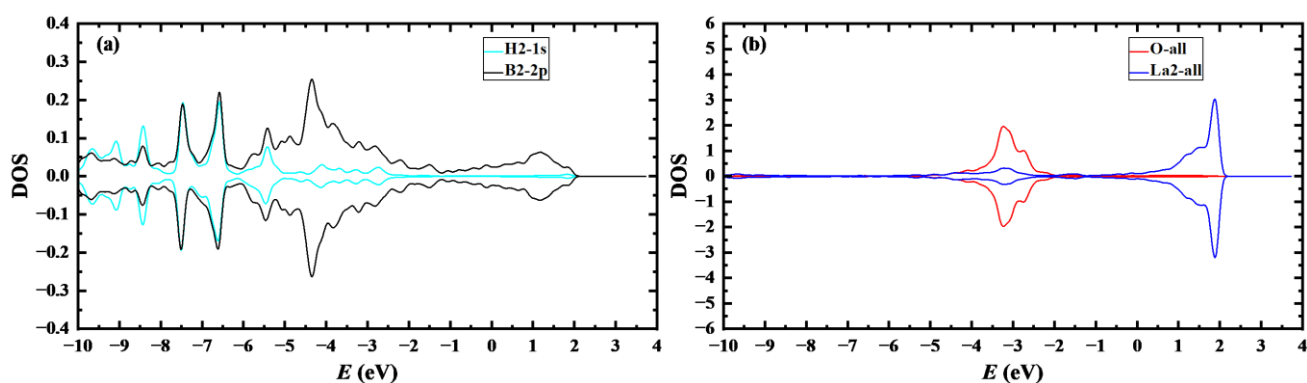
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108   **Figure S6** The electronic density of states of H_2O-D. (a): H2 $1s$ (cyan), B2 $2p$ (black); (b): The orbitals sum of O
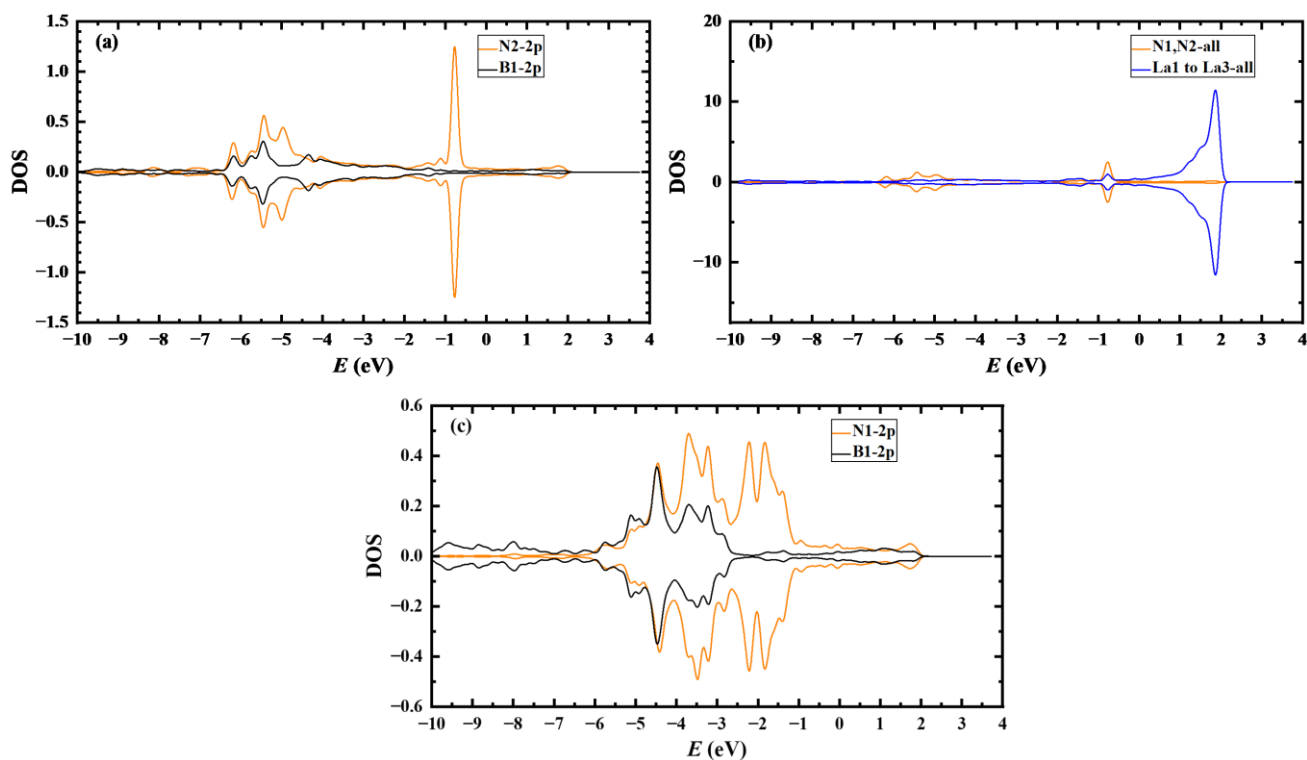109   (red) and the orbitals sum of La2 (blue).
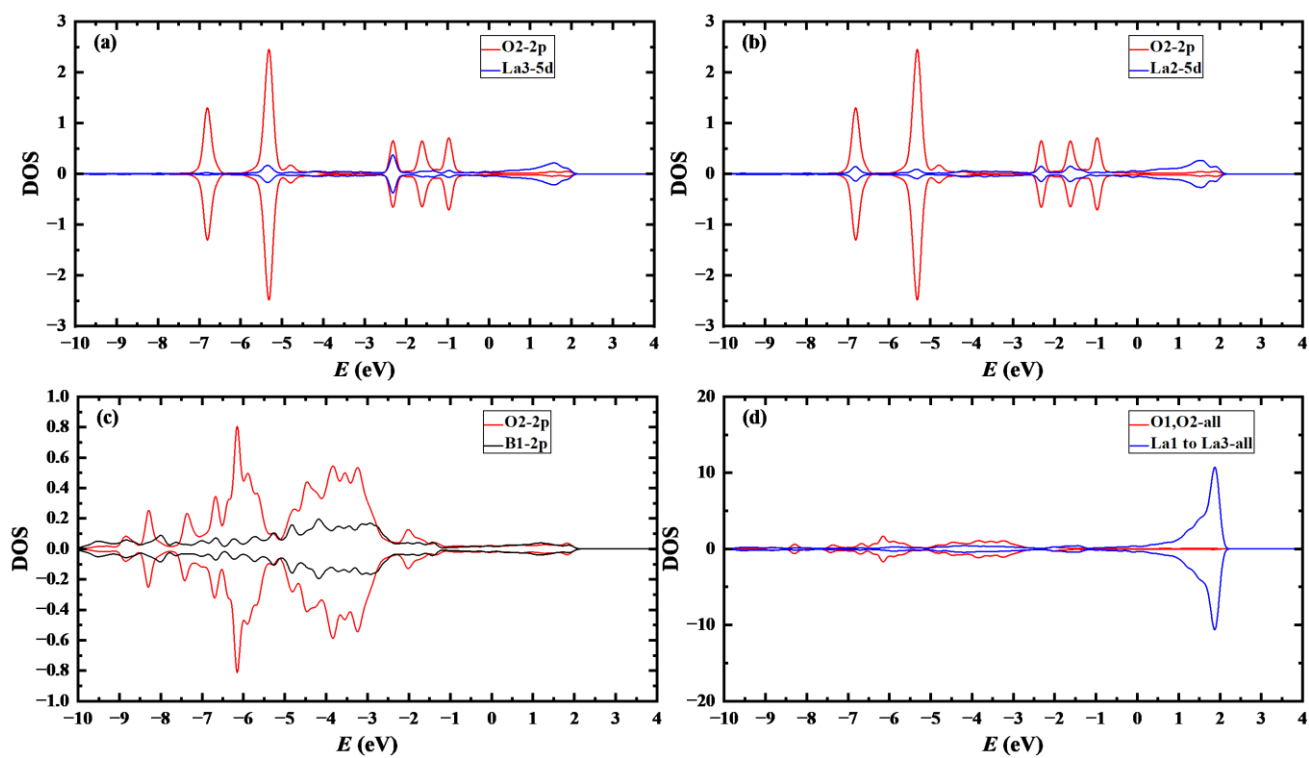
Figure S7 The electronic density of states of O_2-M (a, b) and O_2-D (c, d). (a): O2 $2p$ (red), La3 $5d$ (blue); (b): O2 $2p$ (red), La2 $5d$ (blue); (c): O2 $2p$ (red), B1 $2p$ (black); (d): The total orbitals sum of O1 and O2 (red), as well as the total orbitals sum of La1 to La3 (blue).
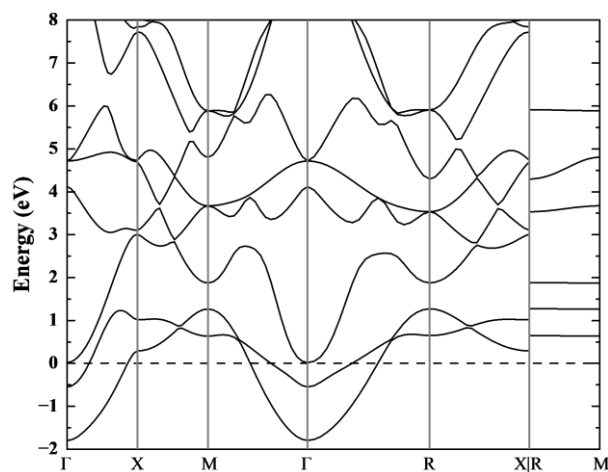
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Figure S8 The electronic density of states of N_2-M (a, b) and N_2-D (c). (a): N2 $2p$ (orange), B1 $2p$ (black); (b): The total orbitals sum of N1 and N2 (orange), as well as the total orbitals sum of La1 to La3 (blue); (c): N1 $2p$ (orange), B1 $2p$ (black).

6   Band structure of bulk LaB$_6$

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Figure S9 The band structure of bulk LaB$_6$, with the dashed line indicating the position of the Fermi level.