Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Can we enhance diradical character using interaction with stoichiometric surfaces of ionic oxides? A theoretical investigation using chemical indices

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Details of computational conditions for DFT

The DFT/plane-wave calculations were performed using a generic programme for ab initio band calculations, VASP [S1-S4]. The exchange-correlation functional for DFT was GGA-PBE [S5]. The core electrons were treated using the projector augmented plane-wave (PAW) scheme [S6], and the numbers of valence electrons were 11 (Au), 10 (Mg), 10 (Ba), and 6 (O). The cut-off energy for the wavefunction was 500 eV. We investigated the dependence of the estimated diradical characters on the cut-off energy in our previous study [S7]. We assumed that the electron density by the self-consistent field approach converged when the energy difference was below the threshold of 1.0×10^{-7} eV.

The surface sizes of the MgO (001) and BaO (001) models were 3 × 3 (here, the size of the unit cell was 1 × 1), and the Γ-centred 3 × 3 × 1 meshes were used for k-point sampling. The surfaces were slab-vacuum models, the layer thickness of the slabs was four atomic layers, and the vacuum region was 2.0 nm. The optimised lattice constant in our previous work [S8] was used for slab models. The geometry optimisation of the atoms in the slabs was performed except for the atoms in the bottom layer; the atoms were fixed to mimic the bulk structure. For Au atoms, movement in the horizontal direction of the surface was restricted, and geometry optimisation was performed only in the vertical direction of the surface.

In this study, the diradical character and other chemical indices were approximately calculated from the charge density. Hence, the approximation accuracy was examined using non-adsorbed models whose exact values of chemical indices can be obtained from the results of the ab initio molecular orbital (AI-MO) calculations, which uses atom-centred basis. The AI-MO calculations were performed using the DFT procedure and the same functional (GGA-PBE) as that used in the band calculation (DFT/plane-wave). The used atom-centred basis set for Au atoms was SDD [S9] and the corresponding core potential was used. The calculations were performed by the Gaussian16 programme [S10].

The values estimated using the electron densities from the DFT/plane-wave and AI-MO calculations, whose results are summarised in Table S1, are compared. Although the chemical indices were estimated using the same equations, there were some differences. These differences originate from the difference in the basis set and core potentials. DFT is a method with a relatively small basis set dependence; however, the calculated electron density and orbitals are not completely the same. Because chemical indices are calculated from orbitals or electron density, the basis set selection should affect the estimated values [S11, S12]. It is difficult to obtain the basis set limit of electron density when using the AI-MO scheme (atom-centred basis sets). While using a plane-wave basis set, it is possible to systematically confirm the convergence to the basis set limit value by increasing the cut-off energy [S7]. However, pseudo-potentials are often used for the core region. In this study, although the wavefunctions for the electrons in the core region are projected to the results of all-electron calculations via the PAW scheme, the electron density is affected by the core region potentials, similar to the dependence of J values on the core potential of the PAW scheme [S13]. Nevertheless, the results of the DFT/plane-wave and AI-MO were qualitatively the same.

Table S1. Chemical indices of Au_2 model diradicals without the surface interaction estimated using electron densities obtained from DFT calculations with plane-wave and atom-centred (SDD) basis sets.

	Basis sets	d = 2.954 Å * (Au_2/MgO@O^1) **	d = 4.177 Å * (Au_2/MgO@O^2) **	d = 3.929 Å * (Au_2/BaO @O^1) **	d = 5.562 Å * (Au_2/BaO @O^2) **
$y = 1 - B$	Plane wave	0.0000	0.0964	0.0002	0.7428
	SDD	0.0000	0.4309	0.3022	0.8298
$T = b$	Plane wave	1.0000	0.6326	0.9821	0.1308
	SDD	1.0000	0.3123	0.4066	0.0857
$n_b = 2 - n_a$	Plane wave	2.0000	1.6326	1.9821	1.1308
	SDD	2.0000	1.3123	1.4066	1.0857
I	Plane wave	-1.3863	-0.4324	-1.2841	-0.0172
	SDD	-1.3863	-0.0992	-0.1702	-0.0074

* Distance between Au atoms. ** Corresponding adsorbed models.

Details of electronic structures of Au_2/MgO and Au_2/BaO

Au is weakly chemisorbed by oxide ions on the stoichiometric oxide surface [S8, S14-S16]. The interactions include hybridisation with O 2p orbitals while the Au/O orbitals hybridisation is generally small. In the Au/MgO (001) and Au/BaO (001) systems, the O $2p_z$ orbital and the Au $5d_{z^2}$ orbital interact (Fig. S1). Since the $5d_{z^2}$ orbital is hybridized with the 6s orbital, polarisation is induced in the 6s orbital. The sd hybrid orbital becomes the singly occupied molecular orbital (SOMO), which is the magnetic orbital of Au/MgO and Au/BaO systems. The SOMO contributes to the formation of the Au–Au bond. As polarisation is induced on Au although the orbital correlation between Au/O is small, the charge–dipole interaction occurs because of the charge of the oxide ion and the Au adsorption is stabilised. This Au/O interaction becomes stronger when the surface basicity is higher (i.e., the oxide ion is more electron rich). Therefore, when comparing Au/MgO and Au/BaO, the SOMO energy of Au is higher in Au/BaO, while BaO adsorbs Au with more stability [S8]. The Au/O interaction is detrimental to the formation of Au–Au bonds by SOMO coupling. Therefore, in the adsorption systems, the electron spin remains on Au even in the region where the Au–Au covalent bond occurs in the gas phase and the diradical state becomes stable [S8, S14]. Fig. S2 shows the spin density distributions of three calculated models [Au_2/MgO@O^2 (a), Au_2/BaO@O^1 (b), and Au_2/BaO@O^2 (c)] whose ground states are diradical. From these distributions, it can be confirmed that the hybridised orbital Au sd and O p orbitals are the magnetic orbitals. In addition, the Au–O interaction affects the magnetic coupling between Au atoms. This was confirmed by the estimated J values and J-y plots shown in Figs. S3–S5. These variations for the Au–Au interaction can be shown using chemical indices and the calculated results and discussions are described in the main text of the presented paper.

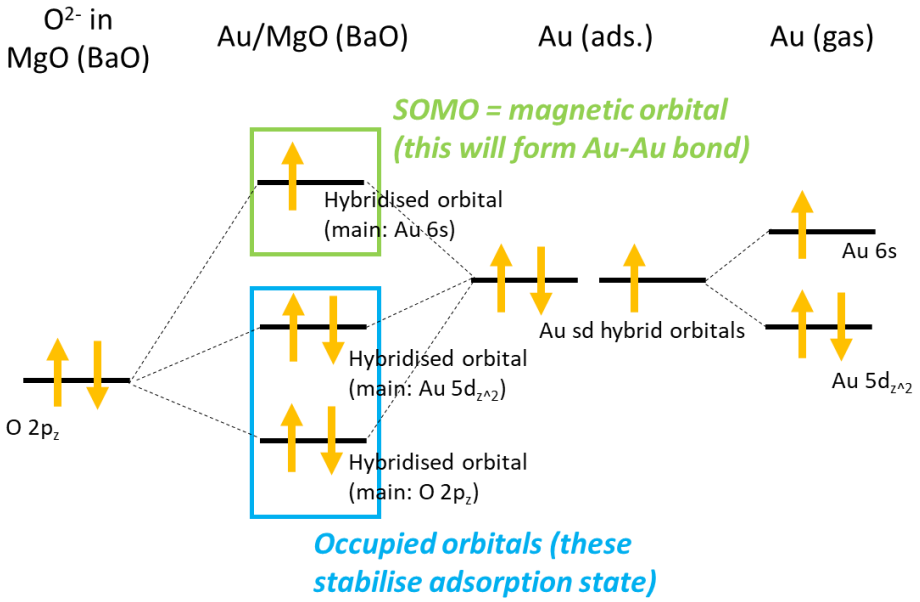


Figure S1. Schematic view of the interactions between Au and MgO (BaO).

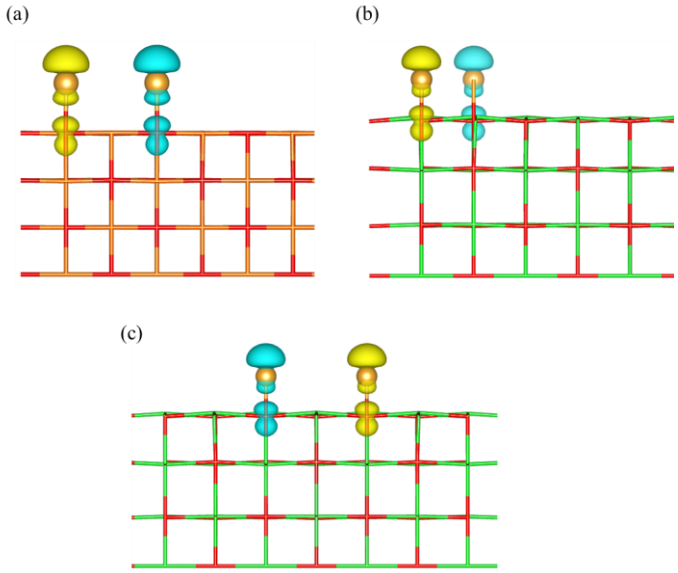


Figure S2. Spin distributions of $Au_2/MgO@O^2$ (a), $Au_2/BaO@O^1$ (b), and $Au_2/BaO@O^2$ (c). Yellow and blue represent the distributions of majority and minority spins, respectively. The threshold is 0.005 e^- $Bohr^{-3}$.

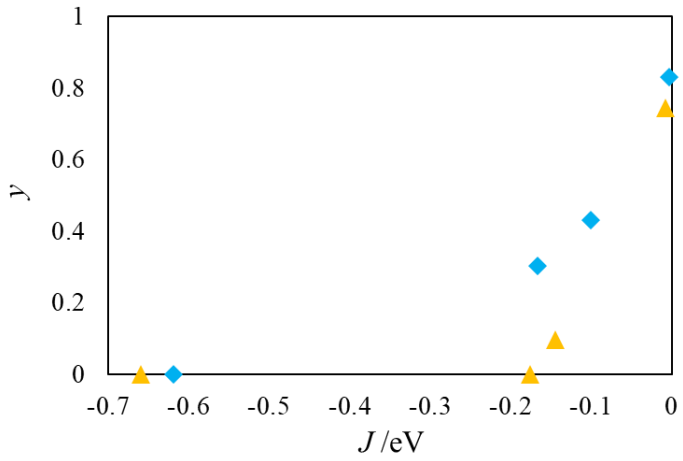


Figure S3. Relationship between *y* and *J* values. The yellow triangle and blue diamond represent the values calculated using plane-wave basis and atom-centred basis (SDD), respectively.

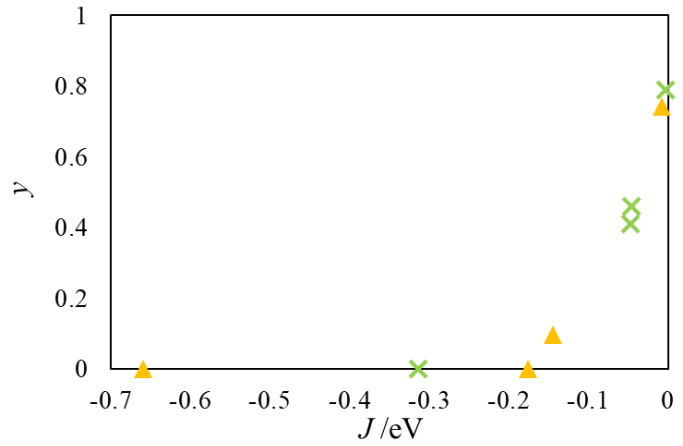


Figure S4. Relationship between *y* and *J* values. The yellow triangle and green cross represent the values of the models without and with the surface interactions, respectively.

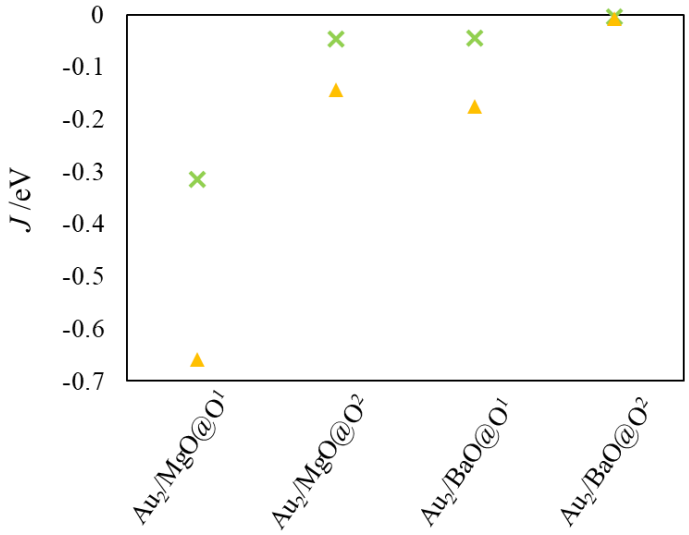


Figure S5. Calculated *J* values estimated by the AP scheme. The yellow triangle and green cross represent the values of the models without and with the surface interactions, respectively.

Investigation of difference in catalytic activity of TiO_2/Ag and ZrO_2/Cu toward NO reduction

The reduction of NO_x in the exhaust gas is an indispensable catalytic reaction for gas purification. Heterogeneous catalysts with noble metals such as Rh, Pt, and Pd are used for the catalytic reaction. Therefore, the development of technology that uses alternatives to noble metals is important. Moreover, the catalysts based on non-noble metals must be durable. To this end, we have developed a core–shell catalyst wherein Ag and Cu are covered with stable oxides [S17-S19]. The NO reduction over this core–shell catalyst consists of the following three reactions [S18-S20].

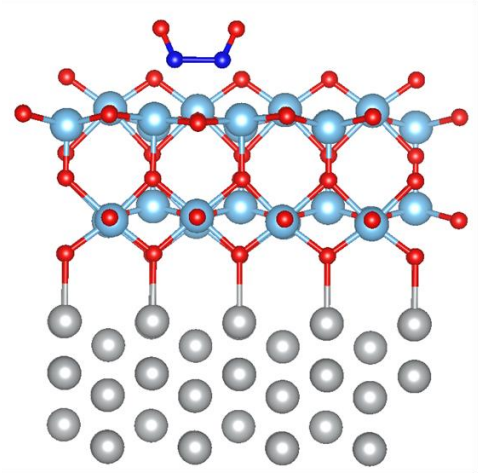
$$2NO(ad) \rightarrow N_2O + O(ad) \quad (s1)$$

$$N_2O(ad) \rightarrow N_2 + O\,(ad) \quad (s2)$$

$$O(ad) + CO \rightarrow CO_2 \quad (s3)$$

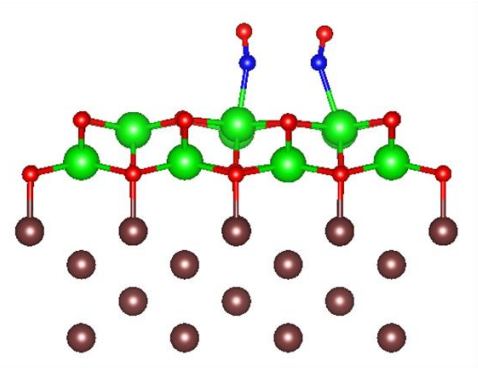
Reaction s1 proceeds through the dimerisation of NO, which is a stable radical; hence, the analysis of the diradical state is important. Fig. S6 shows the transition state structures of the first step of reaction s2 (NO dimerisation) and corresponding activation energies estimated by DFT calculation. The computational procedures of the DFT calculation and full path of reaction (s1) were described in our previous work [S20]. TiO_2/Ag has a lower barrier than ZrO_2/Cu, but the reason has not been clear. Then, we estimated the chemical indices using the developed scheme and we show *y* and *b* (= *T*) values for the NO–NO interactions in Fig. S6. Since the adsorbed NO has two SOMOs, the *T* values were estimated as the average value ($T = \sqrt{(N + \int \rho_{BS}^{-}(r)dr - \int \rho_{HS}^{-}(r)dr)/N}$; here, *N* indicates the number of SOMO), and the *y* values were estimated using the average *T* values. As is clear from the chemical indices (*y*, *T*, and *b*), the NO dimer in the TiO_2/Ag system allows a stronger covalent interaction between NO molecules than the NO dimer in the ZrO_2/Cu. The increase in covalency results the decrease in activation energy. The difference between ZrO_2/Ag and TiO_2/Ag is due to the difference in distance between cations on the surface. Because the distance between the cations of TiO_2 is shorter than that of ZrO_2, the distance between N and N in the transition state becomes small; therefore, the bond order and activation barrier were decreased. Thus, based on the chemical indices, the variation in covalent interaction during the reaction process can be analysed with the numerical values; hence, it is concluded that the proposed scheme can be used for the theoretical design and investigation of heterogeneous catalysts.

(a)



$d_{N\text{-}N} = 1.63$ Å
$d_{Ti\text{-}Ti} = 3.00$ Å
$E_a = 0.169$ eV
$y = 0.011$
$b = T = 0.864$

(b)



$d_{N\text{-}N} = 2.51$ Å
$d_{Zr\text{-}Zr} = 3.64$ Å
$E_a = 0.349$ eV
$y = 0.246$
$b = T = 0.455$

Figure S6. Optimised structures (left panels), atomic distances ($d_{X\text{-}X}$ indicates the X–X distance), activation energies (E_a), diradical character (y), and effective bond order between NO molecules ($b = T$) of the transition states of NO dimerisation by TiO_2/Ag (a) and ZrO_2/Cu (b) core–shell catalyst models. Red, blue, light blue, green, silver, and brown balls represent O, N, Ti, Zr, Ag, and Cu atoms, respectively.

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Optimised geometry of Au_2/MgO@O[1]

The lattice constant vectors are in the Å unit. The atomic coordinates are shown as the coordinates relative to the lattice constant.

Lattice constants

a = (12.5317125300000001, 0.0000000000000000, 0.0000000000000000)

b = (0.0000000000000000, 12.5317125300000001, 0.0000000000000000)

c = (0.0000000000000000, 0.0000000000000000, 26.2658557891999997)

Atomic coordinates

Au	0.000000000	0.000000000	0.341410461
Au	0.166666667	0.166666667	0.342281316
Mg	0.000000000	0.000000000	0.000000000
Mg	0.166666667	0.166666667	0.000000000
Mg	-0.000199267	0.166796405	0.082124074
Mg	0.166796404	-0.000199269	0.082124074
Mg	3.19365E-05	3.19329E-05	0.163851828
Mg	0.166547672	0.166547672	0.16390225
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Mg	0.499893821	-4.04312E-05	0.082068468
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Mg	0.833374491	0.833374492	0.164658431
Mg	0.666201388	0.833120292	0.245973864

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O	0.000000000	0.166666667	0.000000000
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O	0.166330802	0.000254357	0.165062478
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O	0.166895307	0.832692804	0.247374704
O	0.500000000	0.333333333	0.000000000

O	0.333333333	0.500000000	0.000000000
O	0.333300939	0.333300954	0.082358699
O	0.500007232	0.500007244	0.082228718
O	0.499908109	0.333386565	0.164434447
O	0.333386556	0.499908116	0.164434465
O	0.333472781	0.333472768	0.247732015
O	0.500029143	0.500029127	0.247507338
O	0.500000000	0.666666667	0.000000000
O	0.333333333	0.833333334	0.000000000
O	0.333315833	0.666622337	0.082317837
O	0.499967547	0.833646144	0.082104052
O	0.500004157	0.666562129	0.164402551
O	0.33348098	0.833441590	0.164374972
O	0.333509182	0.666553194	0.247661322
O	0.500088622	0.833278318	0.247691975
O	0.833333334	0.333333333	0.000000000
O	0.666666667	0.500000000	0.000000000
O	0.66662234	0.333315842	0.082317828
O	0.833646152	0.499967553	0.082104054
O	0.833441603	0.333480977	0.164374965
O	0.666562127	0.500004163	0.164402540
O	0.666553196	0.333509167	0.247661286
O	0.833278303	0.500088611	0.247691964
O	0.833333334	0.666666667	0.000000000
O	0.666666667	0.833333334	0.000000000
O	0.666659553	0.666659557	0.082310601
O	0.833441652	0.833441648	0.082359867
O	0.833459901	0.666576122	0.164343804
O	0.666576116	0.833459899	0.164343800
O	0.666612440	0.666612439	0.247640301
O	0.833274897	0.833274912	0.247611812

Optimised geometry of Au_2/MgO@O^2

The lattice constant vectors are in the Å unit. The atomic coordinates are shown as the coordinates relative to the lattice constant.

Lattice constants

a = (12.5317125300000001, 0.0000000000000000, 0.0000000000000000)

b = (0.0000000000000000, 12.5317125300000001, 0.0000000000000000)

c = (0.0000000000000000, 0.0000000000000000, 26.2658557891999997)

Atomic coordinates

Au	0.000000000	0.000000000	0.334763807
Au	0.000000000	0.333333333	0.335203693
Mg	0.000000000	0.000000000	0.000000000
Mg	0.166666667	0.166666667	0.000000000
Mg	2.96698E-06	0.166643109	0.081942337
Mg	0.166990779	1.057E-05	0.082097428
Mg	1.10271E-05	0.999913654	0.163028999
Mg	0.166505555	0.166597824	0.165171620
Mg	-1.13478E-05	0.166557995	0.248062148
Mg	0.170275777	0.999644653	0.247025803
Mg	0.333333333	0.000000000	0.000000000
Mg	0.500000000	0.166666667	0.000000000
Mg	0.333384604	0.166586685	0.082178059
Mg	0.499997764	5.44792E-07	0.082046715
Mg	0.333510274	0.999979522	0.164518749
Mg	0.499997526	0.166561746	0.164545946
Mg	0.334236778	0.166469114	0.246026048
Mg	0.499985419	0.999833608	0.245927124
Mg	0.666666667	0.000000000	0.000000000
Mg	0.833333334	0.166666667	0.000000000
Mg	0.6666083	0.166587936	0.082171906
Mg	0.833025263	1.9209E-05	0.082087159
Mg	0.666492628	-1.70457E-05	0.16450899
Mg	0.833489644	0.166593014	0.165167992
Mg	0.665747018	0.166457573	0.246027471
Mg	0.829707324	0.999639255	0.247020067
Mg	0.000000000	0.333333333	0.000000000
Mg	0.166666667	0.500000000	0.000000000
Mg	7.28413E-06	0.500225642	0.081965524
Mg	0.16690071	0.333349075	0.082042728
Mg	-2.44038E-06	0.333488472	0.16304304

Mg	0.166531242	0.499852901	0.164811528
Mg	-8.52795E-06	0.502867876	0.246987178
Mg	0.170294513	0.333727279	0.247073699
Mg	0.000000000	0.666666667	0.000000000
Mg	0.166666667	0.833333334	0.000000000
Mg	8.38733E-06	0.833034678	0.082053313
Mg	0.166685464	0.666549541	0.082185114
Mg	1.34803E-06	0.666546699	0.164559928
Mg	0.166574796	0.833432856	0.164888047
Mg	2.92372E-06	0.830053761	0.246988487
Mg	0.167478386	0.666453545	0.245963365
Mg	0.333333333	0.333333333	0.000000000
Mg	0.500000000	0.500000000	0.000000000
Mg	0.333359785	0.500003156	0.082169719
Mg	0.49999561	0.333325678	0.082148647
Mg	0.333468032	0.333322997	0.164624014
Mg	0.500000762	0.499961506	0.164497309
Mg	0.334019494	0.500299556	0.245926034
Mg	0.49999861	0.333456427	0.245948369
Mg	0.333333333	0.666666667	0.000000000
Mg	0.500000000	0.833333334	0.000000000
Mg	0.333385658	0.833343613	0.082125256
Mg	0.500001053	0.666612776	0.082122384
Mg	0.333405047	0.66658487	0.16457022
Mg	0.500000518	0.833398972	0.164503063
Mg	0.334003581	0.832990975	0.245930633
Mg	0.499997048	0.666530536	0.245879117
Mg	0.666666667	0.333333333	0.000000000
Mg	0.833333334	0.500000000	0.000000000
Mg	0.666641738	0.499996748	0.082169274
Mg	0.833097302	0.333340876	0.082040847
Mg	0.666526749	0.333314116	0.164623942
Mg	0.833462744	0.499835189	0.164814434
Mg	0.665980394	0.500293316	0.245932941
Mg	0.829698003	0.333707582	0.247074237
Mg	0.666666667	0.666666667	0.000000000
Mg	0.833333334	0.833333334	0.000000000
Mg	0.666620840	0.833341199	0.082114814
Mg	0.833320489	0.666540552	0.082180423
Mg	0.666593624	0.666569828	0.164568937
Mg	0.833432026	0.833434604	0.164876547
Mg	0.665988973	0.832982924	0.245926816

Mg	0.832517432	0.666459813	0.245965707
O	0.166666667	0.000000000	0.000000000
O	0.000000000	0.166666667	0.000000000
O	8.639E-06	0.000111121	0.082106963
O	0.166410088	0.166651108	0.082446541
O	0.166104379	-1.05346E-05	0.16473985
O	-2.32508E-06	0.166547069	0.165139194
O	-1.85721E-05	0.998848696	0.247159253
O	0.167048209	0.166732114	0.247058321
O	0.500000000	0.000000000	0.000000000
O	0.333333333	0.166666667	0.000000000
O	0.333397517	8.7042E-06	0.082195475
O	0.49999812	0.166356013	0.082086916
O	0.500011156	-7.15268E-06	0.16417615
O	0.333453177	0.166546312	0.164347967
O	0.334304150	-7.00994E-05	0.24762193
O	0.499983471	0.166532787	0.247585569
O	0.833333334	0.000000000	0.000000000
O	0.666666667	0.166666667	0.000000000
O	0.666585678	1.07683E-05	0.082175747
O	0.833600350	0.166662368	0.082441636
O	0.833892991	-1.85451E-05	0.164732911
O	0.666539661	0.166533569	0.164354013
O	0.665676028	-6.04194E-05	0.24761462
O	0.832945783	0.166705279	0.247062402
O	0.166666667	0.333333333	0.000000000
O	0.000000000	0.500000000	0.000000000
O	-1.31638E-06	0.33344636	0.082104803
O	0.166273691	0.499736383	0.082184761
O	0.16588401	0.333209469	0.164864643
O	3.46011E-06	0.499562736	0.164456787
O	-1.33283E-05	0.334310543	0.247645131
O	0.166987398	0.500040690	0.247222649
O	0.166666667	0.666666667	0.000000000
O	0.000000000	0.833333334	0.000000000
O	5.09662E-06	0.666374562	0.082207482
O	0.166501535	0.833417293	0.082381518
O	0.166512476	0.666552266	0.164345841
O	-1.75804E-05	0.833884452	0.164711601
O	1.34245E-05	0.666368195	0.247575904
O	0.167151977	0.833067122	0.247234523
O	0.500000000	0.333333333	0.000000000

O	0.333333333	0.500000000	0.000000000
O	0.333274000	0.333332709	0.082371955
O	0.499998604	0.499903108	0.082129270
O	0.500009173	0.333428067	0.164292504
O	0.333424494	0.499903222	0.164376019
O	0.334302661	0.333299843	0.247596115
O	0.499986639	0.500013532	0.247455603
O	0.500000000	0.666666667	0.000000000
O	0.333333333	0.833333334	0.000000000
O	0.333302875	0.666582863	0.082299291
O	0.499998465	0.833623218	0.082085352
O	0.499992456	0.666562795	0.164285238
O	0.33346407	0.833462953	0.164347176
O	0.333553386	0.666587423	0.247563181
O	0.500005605	0.833225133	0.247583687
O	0.833333334	0.333333333	0.000000000
O	0.666666667	0.500000000	0.000000000
O	0.666730939	0.333330194	0.082363499
O	0.833722251	0.499727907	0.082183538
O	0.834099068	0.333204222	0.164864581
O	0.666578345	0.499897444	0.164388415
O	0.665675789	0.333301663	0.247601734
O	0.832986086	0.500029433	0.247220237
O	0.833333334	0.666666667	0.000000000
O	0.666666667	0.833333334	0.000000000
O	0.666698270	0.666567029	0.082292818
O	0.833532927	0.833440137	0.082366945
O	0.833479202	0.666535455	0.164340850
O	0.666541015	0.833443004	0.164331109
O	0.666434477	0.666595884	0.247551930
O	0.83283722	0.833044166	0.247230851

Optimised geometry of Au_2/BaO@O^1

The lattice constant vectors are in the Å unit. The atomic coordinates are shown as the coordinates relative to the lattice constant.

Lattice constants

a = (16.6846246700000016, 0.0000000000000000, 0.0000000000000000)

b = (0.0000000000000000, 16.6846246700000016, 0.0000000000000000)

c = (0.0000000000000000, 0.0000000000000000, 28.3423118591000005)

Atomic coordinates

Au	0.000117496	0.000204716	0.368910239
Au	0.166666667	0.166666667	0.368961998
Ba	0.000000000	0.000000000	0.000000000
Ba	0.166666667	0.166666667	0.000000000
Ba	0.333502927	0.166589515	0.096289988
Ba	0.166994525	0.999648916	0.096507321
Ba	0.000177292	0.333404659	0.198296871
Ba	0.166283893	0.166252194	0.198255975
Ba	0.338576435	0.167646364	0.297630799
Ba	0.167650752	0.338531578	0.297644322
Ba	0.333333333	0.000000000	0.000000000
Ba	0.500000000	0.166666667	0.000000000
Ba	0.666842459	0.166691642	0.096059296
Ba	0.499984813	0.99985673	0.096099365
Ba	0.332787906	0.332758263	0.198135768
Ba	0.500170959	0.166580663	0.197787894
Ba	0.665966361	0.167766289	0.296118377
Ba	0.500415991	0.334803545	0.295809264
Ba	0.666666666	0.000000000	0.000000000
Ba	0.833333333	0.166666667	0.000000000
Ba	0.999640493	0.166996713	0.096534506
Ba	0.833323612	1.35922E-05	0.096324552
Ba	0.666439279	0.333465891	0.197475612
Ba	0.833245679	0.166495025	0.198318406
Ba	0.994046551	0.172687226	0.298773611
Ba	0.831069883	0.335634966	0.295855514
Ba	0.000000000	0.333333333	0.000000000
Ba	0.166666667	0.500000000	0.000000000
Ba	0.333193367	0.499709091	0.096104823
Ba	0.166582943	0.333414799	0.096304432
Ba	0.000130019	0.666689762	0.197865722

Ba	0.166607079	0.500066275	0.197773114
Ba	0.334686733	0.500341966	0.295818166
Ba	0.167792239	0.665984005	0.296110157
Ba	0.000000000	0.666666666	0.000000000
Ba	0.166666667	0.833333333	0.000000000
Ba	0.333320725	0.833327462	0.096036806
Ba	0.166731347	0.666808534	0.096073344
Ba	0.000473413	0.000482077	0.19832599
Ba	0.166564126	0.833299749	0.198242777
Ba	0.335626510	0.831077713	0.295822013
Ba	0.172719700	0.994115560	0.298740002
Ba	0.333333333	0.333333333	0.000000000
Ba	0.500000000	0.500000000	0.000000000
Ba	0.666800871	0.499926183	0.095959841
Ba	0.499770916	0.333175916	0.096046985
Ba	0.333385165	0.666318953	0.197421838
Ba	0.499815848	0.499811742	0.197232419
Ba	0.666116631	0.500563864	0.295576108
Ba	0.500490560	0.665941162	0.295528428
Ba	0.333333333	0.666666666	0.000000000
Ba	0.500000000	0.833333333	0.000000000
Ba	0.666976243	0.833393362	0.096045124
Ba	0.499938121	0.666678295	0.095883168
Ba	0.333482431	0.000156287	0.198190361
Ba	0.500286221	0.833166514	0.197437539
Ba	0.666228936	0.831836887	0.29577804
Ba	0.500765179	0.998941874	0.296022346
Ba	0.666666666	0.333333333	0.000000000
Ba	0.833333333	0.500000000	0.000000000
Ba	0.99994453	0.499919943	0.096116351
Ba	0.833356451	0.333259682	0.096087532
Ba	0.666854281	0.666693217	0.197258760
Ba	0.833295748	0.500305727	0.197436746
Ba	0.999055968	0.500657972	0.296123211
Ba	0.831977431	0.666152214	0.295814856
Ba	0.666666666	0.666666666	0.000000000
Ba	0.833333333	0.833333333	0.000000000
Ba	0.000111974	0.833247610	0.096252748
Ba	0.833494033	0.666977521	0.096068201
Ba	0.666792784	5.0175E-05	0.197814612
Ba	0.833967716	0.833942049	0.198196205
Ba	0.999111836	0.828148279	0.297675044

Ba	0.828103371	0.999122490	0.297762724
O	0.166666667	0.000000000	0.000000000
O	0.000000000	0.166666667	0.000000000
O	0.000287871	8.77777E-05	0.095768670
O	0.166478471	0.166577120	0.095703298
O	0.166774762	0.000125034	0.202023761
O	8.56728E-05	0.166753725	0.202033138
O	0.998814144	0.334032735	0.290076769
O	0.166829494	0.167138300	0.290915877
O	0.500000000	0.000000000	0.000000000
O	0.333333333	0.166666667	0.000000000
O	0.333694122	-0.000148999	0.093497574
O	0.499854378	0.166335821	0.094037492
O	0.500569657	-0.00025281	0.201880204
O	0.332962327	0.166593927	0.202057666
O	0.334032925	0.334046631	0.289838509
O	0.499921952	0.166556132	0.290527585
O	0.833333333	0.000000000	0.000000000
O	0.666666666	0.166666667	0.000000000
O	0.667158421	-1.74041E-06	0.094395532
O	0.833076408	0.166672567	0.093360527
O	0.833934979	0.000425572	0.202212415
O	0.666195451	0.166896767	0.201979268
O	0.666181417	0.333936675	0.290069024
O	0.832512958	0.167886530	0.290146042
O	0.166666667	0.333333333	0.000000000
O	0.000000000	0.500000000	0.000000000
O	1.81544E-05	0.333306715	0.093022964
O	0.166654185	0.500011147	0.094478233
O	0.166512417	0.332868842	0.202030907
O	-2.91702E-05	0.500322786	0.201979621
O	-6.42545E-06	0.666664648	0.290607971
O	0.166648116	0.499979075	0.290607592
O	0.166666667	0.666666666	0.000000000
O	0.000000000	0.833333333	0.000000000
O	0.000507285	0.667039878	0.094147474
O	0.166653729	0.833334382	0.093057691
O	0.166700724	0.666390212	0.201982254
O	0.000305830	0.833807953	0.202206929
O	0.999479914	-8.57751E-05	0.290961542
O	0.167844412	0.832758138	0.290012552
O	0.500000000	0.333333333	0.000000000

O	0.333333333	0.500000000	0.000000000
O	0.333317657	0.333308594	0.093022007
O	0.499994966	0.499992940	0.094455373
O	0.500108854	0.333298029	0.201613592
O	0.333366025	0.500006063	0.201618790
O	0.333795047	0.666019439	0.290085807
O	0.499708533	0.499799437	0.290282779
O	0.500000000	0.666666666	0.000000000
O	0.333333333	0.833333333	0.000000000
O	0.333381323	0.666157813	0.093393000
O	0.499995070	0.833349257	0.093049448
O	0.500072882	0.666546014	0.201602333
O	0.334223489	0.832416109	0.201598415
O	0.334007300	0.998781357	0.290062111
O	0.500389512	0.832567081	0.290077975
O	0.833333333	0.333333333	0.000000000
O	0.666666666	0.500000000	0.000000000
O	0.666673284	0.333335317	0.093053016
O	0.833383040	0.500367899	0.093626524
O	0.832444248	0.334258493	0.201605051
O	0.666590747	0.500068032	0.201607464
O	0.666610563	0.666072369	0.290184585
O	0.832737833	0.500511254	0.290082838
O	0.833333333	0.666666666	0.000000000
O	0.666666666	0.833333333	0.000000000
O	0.666902454	0.666622867	0.094136491
O	0.833344575	0.833357771	0.093014469
O	0.83329647	0.666732992	0.201646847
O	0.666639639	0.833343611	0.201694604
O	0.666666158	-7.86439E-06	0.290615118
O	0.832573446	0.832576002	0.289816633

Optimised geometry of Au_2/BaO@O^2

The lattice constant vectors are in the Å unit. The atomic coordinates are shown as coordinates relative to the lattice constant.

Lattice constants

a = (16.6846246700000016, 0.0000000000000000, 0.0000000000000000)

b = (0.0000000000000000, 16.6846246700000016, 0.0000000000000000)

c = (0.0000000000000000, 0.0000000000000000, 28.3423118591000005)

Atomic coordinates

Au	6.75322E-06	0.666526358	0.368506928
Au	6.75322E-06	0.333193024	0.368459654
Ba	0.000000000	0.000000000	0.000000000
Ba	0.166666667	0.166666667	0.000000000
Ba	0.333117755	0.166550772	0.09606647
Ba	0.166760248	-5.74336E-05	0.096192267
Ba	-9.95368E-05	0.332932324	0.197175599
Ba	0.166342977	0.166928871	0.198199023
Ba	0.334186932	0.165642047	0.295732589
Ba	0.172338098	0.332813777	0.297354085
Ba	0.333333333	0.000000000	0.000000000
Ba	0.500000000	0.166666667	0.000000000
Ba	0.666853388	0.166548984	0.095965125
Ba	0.499985480	-4.75754E-05	0.095748864
Ba	0.333429112	0.333330376	0.197557951
Ba	0.499933500	0.166464509	0.197483372
Ba	0.665658880	0.165590029	0.295747578
Ba	0.499984684	0.332941529	0.295824734
Ba	0.666666666	0.000000000	0.000000000
Ba	0.833333333	0.166666667	0.000000000
Ba	-3.45057E-05	0.166277917	0.096114987
Ba	0.833184347	-6.70332E-05	0.096196538
Ba	0.666481618	0.333251527	0.197532343
Ba	0.833554207	0.166947889	0.198252901
Ba	-5.59004E-05	0.161515315	0.297396659
Ba	0.827550377	0.332771911	0.297410206
Ba	0.000000000	0.333333333	0.000000000
Ba	0.166666667	0.500000000	0.000000000
Ba	0.333185195	0.499999970	0.096191174
Ba	0.167060700	0.333404551	0.096291825
Ba	-5.26802E-05	0.667053427	0.197237850

Ba	0.166299902	0.499989941	0.198553772
Ba	0.334420234	0.499910893	0.296001589
Ba	0.172417611	0.667029301	0.297430197
Ba	0.000000000	0.666666666	0.000000000
Ba	0.166666667	0.833333333	0.000000000
Ba	0.333137917	0.833369332	0.096078093
Ba	0.167065971	0.666602916	0.096273889
Ba	-2.03046E-05	-6.32429E-05	0.197600707
Ba	0.166360650	0.832910862	0.198294716
Ba	0.334205101	0.834170295	0.295795300
Ba	0.168727288	-2.83079E-05	0.295942153
Ba	0.333333333	0.333333333	0.000000000
Ba	0.500000000	0.500000000	0.000000000
Ba	0.666860028	0.499965105	0.096131699
Ba	0.499974111	0.333313496	0.095841956
Ba	0.333492074	0.666560243	0.197573161
Ba	0.500041196	0.499834513	0.197675714
Ba	0.665546295	0.499875355	0.295987174
Ba	0.500024721	0.667002179	0.295852399
Ba	0.333333333	0.666666666	0.000000000
Ba	0.500000000	0.833333333	0.000000000
Ba	0.666868848	0.833355945	0.096064969
Ba	0.500005015	0.666603940	0.095949460
Ba	0.333222591	-0.000152882	0.197337867
Ba	0.500015974	0.833280981	0.197512991
Ba	0.665715776	0.834291615	0.295811029
Ba	0.499952869	-6.70655E-05	0.295621117
Ba	0.666666666	0.333333333	0.000000000
Ba	0.833333333	0.500000000	0.000000000
Ba	-4.10705E-06	0.500022090	0.096335533
Ba	0.832919252	0.333384886	0.096198189
Ba	0.666506274	0.666599895	0.197589688
Ba	0.833652418	0.499934477	0.19856688
Ba	-0.00014713	0.499964067	0.297988644
Ba	0.827553565	0.667129076	0.297454266
Ba	0.666666666	0.666666666	0.000000000
Ba	0.833333333	0.833333333	0.000000000
Ba	-4.01148E-05	0.833690837	0.096133147
Ba	0.832920349	0.666609333	0.096283907
Ba	0.666643600	-9.38906E-05	0.197306256
Ba	0.833578318	0.832970889	0.198292745
Ba	-3.81213E-05	0.838460784	0.29747375

Ba	0.831261025	-4.51557E-06	0.295943498
O	0.166666667	0.000000000	0.000000000
O	0.000000000	0.166666667	0.000000000
O	3.23792E-05	5.69443E-05	0.094509069
O	0.166603589	0.166673312	0.092981219
O	0.166718660	-8.8327E-05	0.201619375
O	-5.98909E-05	0.167053501	0.202052367
O	-8.77053E-06	0.333323361	0.290641346
O	0.167666070	0.165938302	0.289795505
O	0.500000000	0.000000000	0.000000000
O	0.333333333	0.166666667	0.000000000
O	0.333683386	0.000104053	0.093883740
O	0.500026662	0.166671143	0.093052378
O	0.499973008	-0.000102689	0.201623098
O	0.333561469	0.166656444	0.201611847
O	0.333490164	0.333173424	0.290482694
O	0.500009730	0.165848252	0.290034236
O	0.833333333	0.000000000	0.000000000
O	0.666666666	0.166666667	0.000000000
O	0.666665336	-0.000403865	0.093837328
O	0.833371225	0.166660583	0.092995757
O	0.833330555	-6.71863E-05	0.201683433
O	0.666398087	0.166562854	0.201609692
O	0.666267411	0.333182586	0.290387121
O	0.832664072	0.165789616	0.289868052
O	0.166666667	0.333333333	0.000000000
O	0.000000000	0.500000000	0.000000000
O	-0.00010837	0.333534055	0.095868673
O	0.16664337	0.500023796	0.09275072
O	0.165913514	0.332945384	0.201805548
O	-0.00014347	0.500135256	0.201998504
O	-1.71572E-05	0.666799406	0.290715408
O	0.168356964	0.499736618	0.289448462
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O	0.166635694	0.833316246	0.093006125
O	0.166234895	0.666738950	0.202067242
O	-1.06311E-05	0.832983997	0.202078789
O	1.05436E-05	-2.15244E-05	0.290603576
O	0.167675647	0.833963633	0.289895644
O	0.500000000	0.333333333	0.000000000

O	0.333333333	0.500000000	0.000000000
O	0.333335078	0.333330388	0.094468643
O	0.500024529	0.499987847	0.093052749
O	0.499969557	0.333234745	0.20163941
O	0.333938494	0.500014602	0.201631704
O	0.333506231	0.666691178	0.290514663
O	0.500187093	0.499226258	0.290080534
O	0.500000000	0.666666666	0.000000000
O	0.333333333	0.833333333	0.000000000
O	0.333309562	0.666678591	0.094457275
O	0.499999105	0.833297544	0.093045739
O	0.499986718	0.666685354	0.201738751
O	0.333519007	0.83333569	0.201565709
O	0.333888713	-0.00050308	0.290090954
O	0.500307824	0.832633988	0.290061401
O	0.833333333	0.333333333	0.000000000
O	0.666666666	0.500000000	0.000000000
O	0.666837611	0.333077919	0.094051492
O	0.833442254	0.499998393	0.092752720
O	0.833604746	0.333043367	0.202006634
O	0.666266006	0.499880452	0.201606036
O	0.666523287	0.666603461	0.290525141
O	0.832228717	0.499595484	0.289596302
O	0.833333333	0.666666666	0.000000000
O	0.666666666	0.833333333	0.000000000
O	0.666672926	0.666669615	0.094464297
O	0.833343584	0.833307118	0.092994785
O	0.833718502	0.666759917	0.202057767
O	0.666463969	0.833333508	0.201606033
O	0.665923988	-9.74066E-05	0.290077817
O	0.832465096	0.833960792	0.289886444