There is considerable interest in the pH-dependent switchable biocatalytic properties of cerium oxide nanoparticles (CeNPs) in biomedicine, where these materials exhibit beneficial antioxidant activity against reactive oxygen species at neutral and basic physiological pH but cytotoxic prooxidant activity at acidic pathological pH. Oxygen vacancies play a key role in such biocatalytic activities. While the general characteristics of the role of oxygen vacancies are known, the mechanism of their action at the atomic scale under different pH conditions has yet to be elucidated. The present work applies density functional theory (DFT) calculations to interpret the pH-induced behavior of the stable {111} surface of CeO_2 at the atomic scale. For detailed information please refer to the paper[1].

Input:

```
CERIA BULK ---------------------------------------------------------- Title
EXTERNAL   ---------------------------------------------------------- Geometry read from the external .gui file
OPTGEOM    ---------------------------------------------------------- Geometry optimization
FULLOPTG   ---------------------------------------------------------- Both atomic positions and lattice parameters are optimized
FRAGMENT   ---------------------------------------------------------- Partial optimization; the following atoms are free to move
82
1   2       3       4       5   6   7   8       9       10
     23      24      25      26      27      28      29
     45      46      47      48      49      50      51
     91      92      93      94      95      96      97
END
END
258 9
INPUT
30. 0 1 1 1 1 1                                                       Basis set section
20.137829 580.083457 0
15.998482 310.302833 0
14.974187 167.813944 0
```

```
99 0    ------------------------------------------------------------- End of Basis set
CHEMOD  ------------------------------------------------------------- Modification of electronic configuration
1
93
2 7 0 0 0
CHARGED------------------------------------------------------------- Charged system
ENDBS
DFT
BLYP-D3------------------------------------------------------------- Use BLYP functional with Grimme D3 correction
HYBRID  ------------------------------------------------------------- Use hybrid functional
12      ------------------------------------------------------------- Mix 12 % Hartree Fock in the exchange energy
NONLOCAL------------------------------------------------------------- Local term parameterization
0.9 0.81
SPIN    ------------------------------------------------------------- Spin polarized calculation
ENDM
MPP     ------------------------------------------------------------- Massive parallel (MPP) extension
GUESSP  ------------------------------------------------------------- Restart from a previous run density matrix
TOLINTEG
7 7 7 7 14
NODIIS
LEVSHIFT
20 1
TOLDEE  ------------------------------------------------------------- Convergence on total energy
5
SHRINK  ------------------------------------------------------------- Pack-Monkhorst/Gilat shrinking factors
2 2
MAXCYCLE------------------------------------------------------------- Maximum number of SCF cycles
1024
FMIXING------------------------------------------------------------- Percent of Fock/KS matrices mixing
65
PPAN    ------------------------------------------------------------- Mulliken Population Analysis
SAVEWF  ------------------------------------------------------------- Write wave function
ENDSCF
```

Output:

```
MAX GRADIENT       0.000214  THRESHOLD              0.000450 CONVERGED YES
RMS GRADIENT       0.000027  THRESHOLD              0.000300 CONVERGED YES
MAX DISPLAC.       0.000865  THRESHOLD              0.001800 CONVERGED YES
RMS DISPLAC.       0.000220  THRESHOLD              0.001200 CONVERGED YES
```

Geometry optimization converging criteria

```
CONVERGENCE TESTS SATISFIED AFTER  55 ENERGY AND GRADIENT CALCULATIONS

*****************************************************************
* OPT END - CONVERGED * E(AU):  -1.758444501740E+04  POINTS   55 *
*****************************************************************

ENERGY CONTRIBUTIONS OF SEMICLASSICAL CORRECTIONS
 D3 DISPERSION ENERGY (AU)      -1.470017895128E+00
```

Converged total energy

```
  ALPHA BAND GAP:                0.3402  eV
  BETA BAND GAP:                 3.0421  eV
```

Band gap

```
CHARGE NORMALIZATION FACTOR   1.00000000
TOTAL ATOMIC CHARGES:
  9.1948841   9.3144570   9.2693357   9.2659110   9.3272587   9.2027513
  9.3385839   9.4284884  27.4175772  27.4240843  27.4132421  27.4365928
 27.4496394  27.6798339  27.4337185  27.4186776  27.6553188   9.3129207
  9.2982522   9.3637794   9.3197586   9.3558272   9.3572487   9.3023331
  9.3475153   9.4031584   9.3011337   9.3209620   9.3078683   9.3235100
  9.3221859   9.3339348   9.3216051   9.3331111   9.3322963  27.3951248
 27.3950470  27.3931713  27.4029665  27.3991881  27.4045522  27.3931199
 27.3925672  27.3877054   9.3376817   9.3342727   9.3322626   9.3331170
  9.3370757   9.3341715   9.3310810   9.3299895   9.3346779   9.3081648
  9.3048413   9.3108329   9.3118923   9.3139638   9.3123244   9.3086768
  9.3072140   9.3090599  27.4235623  27.4234520  27.4228079  27.4235731
 27.4233917  27.4237238  27.4232693  27.4236241  27.4229624   9.2384708
  9.2382890   9.2381775   9.2386285   9.2384635   9.2385134   9.2388404
  9.2387240   9.2388561   8.8412805   0.5224998   0.6567045   8.8802370
  0.6189496   0.5966147   0.7065368   8.7438488   0.5669845   0.5875759
  8.7092969   0.7169499   8.6683804   0.6549230   0.6441037   8.7395441
  0.5613005   0.7069849   0.6152033   8.6582425   0.7138511   8.6792636
  0.6300091   0.6812700   8.7378423   0.5634018   0.6747776   8.6680244
  0.6247998   0.6907717
```

Mulliken charge of each atom

```
SUMMED SPIN DENSITY            2.00000000
TOTAL ATOMIC SPINS  :
 -0.0022869  -0.0063002  -0.0029883  -0.0019517  -0.0033895  -0.0014703
 -0.0014882  -0.0022942   0.0145989   0.0105647   0.0435001   0.0120985
  0.0206494   0.8617259   0.0100976   0.0561895   0.8860451  -0.0006614
 -0.0019513  -0.0047466  -0.0007096  -0.0028425  -0.0051616  -0.0020750
 -0.0043084  -0.0045520  -0.0004224  -0.0005850  -0.0014812  -0.0010110
 -0.0007332  -0.0057632  -0.0005563  -0.0008424  -0.0024436   0.0007850
  0.0028324   0.0141762   0.0013155   0.0304549   0.0672563   0.0023114
  0.0060350   0.0236214  -0.0001665  -0.0003559  -0.0007507  -0.0004186
  0.0010225  -0.0013670  -0.0001669  -0.0006621  -0.0011056  -0.0000400
 -0.0001009  -0.0002405  -0.0000838  -0.0006781  -0.0014428  -0.0000951
 -0.0001086  -0.0004559   0.0000364   0.0001117   0.0002283   0.0003890
  0.0009661   0.0009880   0.0000595   0.0008526   0.0010544  -0.0000820
 -0.0000529  -0.0001015  -0.0000981  -0.0000575  -0.0000749  -0.0000470
 -0.0000186  -0.0000477   0.0005058   0.0006182  -0.0002691   0.0018228
  0.0001608   0.0001421   0.0000192  -0.0001985   0.0000949  -0.0001414
  0.0004837   0.0004927  -0.0000540  -0.0000644  -0.0000103  -0.0001598
  0.0005034   0.0000884   0.0000265  -0.0000641   0.0000245  -0.0001179
  0.0000119   0.0001545  -0.0000745  -0.0000111   0.0000096  -0.0000765
 -0.0000099   0.0000063
```

Sum of electron spin in the system

Electron spin of each atom

References

1. Ma, H.; Ren, H.; Liu, Z.; Koshy, P.; Sorrell, C. C.; Hart, J. N., DFT Investigation of pH-Driven Oxygen Vacancy Formation-Annihilation in CeO_2. *arXiv preprint arXiv: 2104.10992* **2021**.