# Electronic Properties of Realistic Anatase $TiO_2$ Nanoparticles from $G_0W_0$ Calculations on a Gaussian and Plane Waves Scheme

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**Table S1.** $O_{gap}$, $E_{gap}$ and $\Delta E_{ex}$ (in eV) calculated by using primary DZ-MOLOPT (labeled as DZ) and cc-TZ (labeled as TZ) basis set with PBE (0% Fock) exchange correlation functional for $(TiO_2)_n$ NPs.

| | **DZ** | | | **TZ** | | | **\|Δ\| = \|TZ – DZ\|** | | |
|---|---|---|---|---|---|---|---|---|---|
| $n$ | $O_{gap}$ | $E_{gap}$ | $\Delta E_{ex}$ | $O_{gap}$ | $E_{gap}$ | $\Delta E_{ex}$ | $O_{gap}$ | $E_{gap}$ | $\Delta E_{ex}$ |
| 29 | 2.644 | 5.770 | 3.126 | 2.679 | 5.495 | 2.816 | 0.035 | 0.275 | 0.310 |
| 35 | 2.472 | 5.907 | 3.435 | 2.507 | 5.649 | 3.142 | 0.035 | 0.280 | 0.293 |
| 78 | 2.086 | 4.723 | 2.637 | 2.131 | 4.530 | 2.399 | 0.045 | 0.193 | 0.238 |
| 84 | 1.910 | 4.681 | 2.771 | 1.980 | 4.509 | 2.529 | 0.070 | 0.172 | 0.242 |
| 97 | 1.369 | 4.196 | 2.827 | 1.428 | 4.031 | 2.603 | 0.059 | 0.165 | 0.224 |
| 151 | 1.331 | 3.714 | 2.383 | 1.363 | 3.559 | 2.196 | 0.032 | 0.155 | 0.187 |
| 165 | 1.206 | 3.881 | 2.675 | 1.291 | 3.733 | 2.442 | 0.085 | 0.148 | 0.233 |
| | | | | | | **MAE** | 0.052 | 0.195 | 0.247 |

**Table S2.** $O_{gap}$, $E_{gap}$ and exciton energy calculated by using primary DZ-MOLOPT (labeled as DZ) and cc-TZ (labeled as TZ) basis set with hybrid PBEx (12.5% Fock) exchange correlation functional.

| | **DZ** | | | **TZ** | | | **\|Δ\| = \|TZ – DZ\|** | | |
|---|---|---|---|---|---|---|---|---|---|
| $n$ | $O_{gap}$ | $E_{gap}$ | $\Delta E_{ex}$ | $O_{gap}$ | $E_{gap}$ | $\Delta E_{ex}$ | $O_{gap}$ | $E_{gap}$ | $\Delta E_{ex}$ |
| 29 | 3.862 | 6.323 | 2.461 | 3.913 | 6.056 | 2.143 | 0.051 | 0.267 | 0.318 |
| 35 | 3.501 | 5.814 | 2.313 | 3.575 | 5.567 | 1.992 | 0.074 | 0.247 | 0.321 |
| 78 | 3.185 | 5.224 | 2.039 | 3.251 | 5.013 | 1.762 | 0.066 | 0.211 | 0.277 |
| 84 | 2.954 | 5.167 | 2.213 | 3.035 | 4.946 | 1.911 | 0.081 | 0.221 | 0.302 |
| 97 | 2.479 | 4.803 | 2.324 | 2.557 | 4.627 | 2.070 | 0.078 | 0.176 | 0.254 |
| 151 | 2.317 | 4.132 | 1.815 | 2.371 | 3.971 | 1.600 | 0.054 | 0.161 | 0.215 |
| 165 | 2.148 | 4.256 | 2.108 | 2.258 | 4.081 | 1.823 | 0.110 | 0.175 | 0.285 |
| | | | | | | **MAE** | 0.073 | 0.208 | 0.282 |

**Table S3.** $QP_{HOMO}$, $QP_{LUMO}$, and $E_{gap}$ of $(TiO_2)_{29}$ and $(TiO_2)_{35}$ NPs by using PBE functional with Ti-cc-TZ and with Ti-RI basis sets. Units are in eV. Calculations based on numerical basis set as implemented in FHI-aims are also included for comparison.

| | CP2K | | | FHI-AIMS |
|---|---|---|---|---|
| | $QP_{HOMO}$ | $QP_{LUMO}$ | $E_{gap}$ | $E_{gap}$ |
| | | Ti-cc-TZ | | |
| $(TiO_2)_{29}$ | -7.728 | -2.203 | 5.50 | |
| $(TiO_2)_{35}$ | -8.184 | -2.535 | 5.65 | |
| | | Ti-RI | | light tier 1 |
| $(TiO_2)_{29}$ | -7.942 | -2.019 | 5.92 | 5.95 |
| $(TiO_2)_{35}$ | -8.386 | -2.333 | 6.05 | 6.15 |
| |Δ|[(Ti-cc-TZ)-(Ti-RI)] | | | | |
| $(TiO_2)_{29}$ | 0.214 | 0.184 | 0.420 | |
| $(TiO_2)_{35}$ | 0.202 | 0.202 | 0.400 | |

**Table S4.** $QP_{HOMO}$, $QP_{LUMO}$, and $E_{gap}$ of $(TiO_2)_{29}$ and $(TiO_2)_{35}$ NPs by using PBEx functional with Ti-cc-TZ and Ti-RI basis sets. Units are in eV.

| | CP2K | | | FHI-AIMS |
|---|---|---|---|---|
| | $QP_{HOMO}$ | $QP_{LUMO}$ | $E_{gap}$ | |
| | | Ti-cc-TZ | | |
| $(TiO_2)_{29}$ | -8.141 | -2.085 | 6.06 | |
| $(TiO_2)_{35}$ | -7.999 | -2.432 | 5.57 | |
| | | Ti-RI | | light tier 1 |
| $(TiO_2)_{29}$ | -8.374 | -1.849 | 6.52 | 6.53 |
| $(TiO_2)_{35}$ | -8.225 | -2.211 | 6.01 | 6.07 |
| |Δ|[(Ti-cc-TZ)-(Ti-RI)] | | | | |
| $(TiO_2)_{29}$ | 0.233 | 0.236 | 0.460 | |
| $(TiO_2)_{35}$ | 0.226 | 0.221 | 0.440 | |

## Basis set employed in the present study: Primary, RI, and ADMM basis sets

### Primary basis sets

```
 O  DZVP-MOLOPT-GTH DZVP-MOLOPT-GTH-q6
 1
 2 0 2 7 2 2 1
    12.015954705512 -0.060190841200  0.065738617900  0.036543638800 -0.034210557400  0.014807054400
     5.108150287385 -0.129597923300  0.110885902200  0.120927648700 -0.120619770900  0.068186159300
     2.048398039874  0.118175889400 -0.053732406400  0.251093670300 -0.213719464600  0.290576499200
     0.832381575582  0.462964485000 -0.572670666200  0.352639910300 -0.473674858400  1.063344189500
     0.352316246455  0.450353782600  0.186760006700  0.294708645200  0.484848376400  0.307656114200
     0.142977330880  0.092715833600  0.387201458600  0.173039869300  0.717465919700  0.318346834400
     0.046760918300 -0.000255945800  0.003825849600  0.009726110600  0.032498979400 -0.005771736600
#
 Ti DZVP-MOLOPT-SR-GTH DZVP-MOLOPT-SR-GTH-q12
 1
 2 0 3 6 3 2 2 1
     7.884569925997  0.004750577412 -0.002690702837  0.075105591562 -0.108736525246  0.023185061556
0.052842407451 -0.038307431199 -0.002442658125
     3.894698463070  0.499503858222  0.103956524568  0.048602853477  0.100912855636 -0.027189036213
0.195986532018 -0.076880250937  0.013119020987
     1.513588828959 -0.664995883766 -0.256641947580  0.079732563787  0.527328996047 -0.230044390357
0.330343722079 -0.242486488988 -0.206817889885
     0.596768079836 -0.726044574739 -0.451591547817  1.660896378972  0.468197803110 -0.126795185046
0.396808432313 -0.118369379707 -0.546596492823
     0.222222125842 -0.029011079755  0.165167622946 -2.748651632733  0.077640626075  0.343517279356
0.347092399871  0.038099375809 -0.279145975103
     0.077078461321  0.075171747143  0.993127316430  1.368227638651 -0.007523238420  0.946960702315
0.132320900948  1.046553050597  0.934394052863
#
O cc-TZ
6
2 0 1 3 1 1
10.2674419938 0.0989598460 -0.0595856940
3.7480495696 0.1041178339 -0.1875649045
1.3308337704 -0.3808255700 -0.3700707718
2 0 1 1 1 1
0.4556802254 1.0000000000 1.0000000000
2 0 1 1 1 1
0.1462920596 1.0000000000 1.0000000000
3 2 2 1 1
2.3140000000 1.0000000000
3 2 2 1 1
0.6450000000 1.0000000000
4 3 3 1 1
1.4280000000 1.0000000000
#
Tl cc-TZ
10
2 0 0 3 2
3.7986698150634766E+00 -1.0531476885080338E-01 -6.8273013830184937E-01
1.9114010334014893E+00 2.1265093982219696E-01 6.9480454921722412E-01
7.5023883581161499E-01 -9.7143632173538208E-01 2.2611095011234283E-01
2 0 1 1 1 1
0.3 1.0 1.0
2 0 1 1 1 1
```

```
0.2 1.0 1.0
2 0 2 1 1 1 1
0.13 1.0 1.0 1.0
2 1 1 3 1
9.4607772827148438E+00 -9.9228985607624054E-02
1.8190858364105225E+00 6.7078214883804321E-01
7.1252536773681641E-01 7.3498630523681641E-01
2 2 2 3 1
5.8364233970642090E+00 2.9940614104270935E-01
2.2766182422637939E+00 5.6059896945953369E-01
9.0494173765182495E-01 7.7206534147262573E-01
2 2 2 1 1
3.6325827240943909E-01 1.0
2 3 3 1 1
1.2482999563217163E+00 1.0
2 3 3 1 1
2.8360000252723694E-01 1.0
2 4 4 1 1
7.2509998083114624E-01 1.0
#
```

## Resolution of the Identity (RI) basis sets

```
 O    RI_TZ
  20
   1   0   0   1   1
    0.3001921181    1.0000000000
   2   0   0   1   1
    0.7130597908    1.0000000000
   3   0   0   1   1
    1.4016729558    1.0000000000
   4   0   0   1   1
    3.1081574153    1.0000000000
   5   0   0   1   1
    7.1960320376    1.0000000000
   6   0   0   1   1
   16.3153012804    1.0000000000
   7   1   1   1   1
    0.4010742879    1.0000000000
   8   1   1   1   1
    1.0344215872    1.0000000000
   9   1   1   1   1
    2.2421928067    1.0000000000
  10   1   1   1   1
    5.5721697450    1.0000000000
  11   1   1   1   1
   15.5109987721    1.0000000000
  12   2   2   1   1
    0.3420404074    1.0000000000
  13   2   2   1   1
    1.1851070865    1.0000000000
  14   2   2   1   1
    1.7809528984    1.0000000000
  15   2   2   1   1
    4.3991091556    1.0000000000
  16   2   2   1   1
   10.8808436795    1.0000000000
  17   3   3   1   1
```

```
    1.1441005868    1.0000000000
   18   3   3   1   1
    2.7045067621    1.0000000000
   19   3   3   1   1
    5.5454963053    1.0000000000
   20   4   4   1   1
    2.3581227526    1.0000000000
#
Ti RI
34
1 0 0 1 1
9.8703935249 1.0000000000
2 0 0 1 1
5.3949794100 1.0000000000
3 0 0 1 1
2.7086611925 1.0000000000
4 0 0 1 1
1.8082742275 1.0000000000
5 0 0 1 1
1.0801564940 1.0000000000
6 0 0 1 1
0.7584164945 1.0000000000
7 0 0 1 1
0.4045769082 1.0000000000
8 0 0 1 1
0.1330852528 1.0000000000
9 1 1 1 1
8.1808558939 1.0000000000
10 1 1 1 1
4.5538321857 1.0000000000
11 1 1 1 1
2.7521196163 1.0000000000
12 1 1 1 1
1.6446789196 1.0000000000
13 1 1 1 1
0.9542861525 1.0000000000
14 1 1 1 1
0.6028776093 1.0000000000
15 1 1 1 1
0.3343917702 1.0000000000
16 1 1 1 1
0.1787815275 1.0000000000
17 2 2 1 1
7.9133457786 1.0000000000
18 2 2 1 1
3.4989438788 1.0000000000
19 2 2 1 1
1.6217483065 1.0000000000
20 2 2 1 1
0.7728081912 1.0000000000
21 2 2 1 1
0.4387679132 1.0000000000
22 2 2 1 1
0.2146775819 1.0000000000
23 3 3 1 1
4.4157045752 1.0000000000
24 3 3 1 1
1.8006904504 1.0000000000
```

```
25 3 3 1 1
1.1570683357 1.0000000000
26 3 3 1 1
0.6099266869 1.0000000000
27 3 3 1 1
0.3727449239 1.0000000000
28 4 4 1 1
4.2120733320 1.0000000000
29 4 4 1 1
1.9995398809 1.0000000000
30 4 4 1 1
0.9095934373 1.0000000000
31 4 4 1 1
0.4436121782 1.0000000000
32 5 5 1 1
1.9719657313 1.0000000000
33 5 5 1 1
0.8502189480 1.0000000000
34 6 6 1 1
1.1815873138 1.0000000000
#
```

## Auxiliary density matrix method (ADMM) basis sets

```
O FIT9
 9
 1 0 0 1 1
   0.10973395   1.0
 1 0 0 1 1
   0.30997753   1.0
 1 0 0 1 1
   0.90701568   1.0
 1 0 0 1 1
   8.36590290   1.0
 1 1 1 1 1
   0.15487182   1.0
 1 1 1 1 1
   0.51904315   1.0
 1 1 1 1 1
   1.68161321   1.0
 1 1 1 1 1
   6.51644897   1.0
 1 2 2 1 1
   0.87492263   1.0
#
Ti cFIT11
 7
 1 0 0 1 1
      0.10001738     1.00000000
 1 0 0 3 2
      0.51778507     0.66923159     0.10374122
      1.22453356     0.63752925     0.42847815
      4.22013330     0.38168794    -0.89757681
 1 1 1 1 1
      0.53247041     1.00000000
 1 1 1 2 1
      1.57742596     1.00000000
```

```
     11.78131390    -0.09732223
 1 2 2 1 1
      0.24966492     1.00000000
 1 2 2 2 1
      1.01468694     0.88730943
      4.19817352     0.46117452
 1 3 3 1 1
      0.32508090     1.00000000
```

**CP2K input file for PBEx (HFX = 12.5%) calculations and MOLOPT-type double-zeta primary basis sets for oxygen and titanium.**

```
&FORCE_EVAL
 METHOD Quickstep
 &DFT
  BASIS_SET_FILE_NAME ./BASIS_TIO2
  BASIS_SET_FILE_NAME BASIS_ADMM_MOLOPT
  POTENTIAL_FILE_NAME POTENTIAL
  &MGRID
   CUTOFF 400
   REL_CUTOFF 50
  &END MGRID
  &QS
   METHOD GPW
   EPS_DEFAULT 1.0E-15
   EPS_PGF_ORB 1.0E-30
   EPS_FILTER_MATRIX 1.0E-32
  &END QS
  &POISSON
   PERIODIC NONE
   PSOLVER MT
  &END
  &SCF
   SCF_GUESS RESTART
   EPS_SCF 1.0E-6
   MAX_SCF 2000
   &OT
    PRECONDITIONER FULL_ALL
    ENERGY_GAP 0.01
   &END OT
```

```
&END SCF
&AUXILIARY_DENSITY_MATRIX_METHOD
   METHOD BASIS_PROJECTION
   ADMM_PURIFICATION_METHOD MO_DIAG
&END AUXILIARY_DENSITY_MATRIX_METHOD
&XC
  &XC_FUNCTIONAL
   &PBE
    SCALE_X 0.875
    SCALE_C 1.0
   &END PBE
  &END XC_FUNCTIONAL
  &HF
   FRACTION 0.125
   &SCREENING
     EPS_SCHWARZ 1.0E-11
     SCREEN_ON_INITIAL_P FALSE
   &END
   &MEMORY
     MAX_MEMORY 1000
     EPS_STORAGE_SCALING 0.1
   &END
  &END
  &WF_CORRELATION
   METHOD RI_RPA_GPW
   ERI_METHOD OS
   RI OVERLAP
   &WFC_GPW
     EPS_FILTER 1.0E-12
     EPS_GRID   1.0E-12
   &END WFC_GPW
   &RI_RPA
     MINIMAX
     RPA_NUM_QUAD_POINTS  50
     IM_TIME
     &IM_TIME
       EPS_FILTER_IM_TIME 1.0E-11
       GROUP_SIZE_3C 8
       GROUP_SIZE_P 1
```

```
        MEMORY_CUT  12
        GW
       &END IM_TIME
       &RI_G0W0
        CORR_OCC   15
        CORR_VIRT  15
        OMEGA_MAX_FIT 10.0
        ANALYTIC_CONTINUATION PADE
        CROSSING_SEARCH NEWTON
        NPARAM_PADE 16
        RI_SIGMA_X
       &END RI_G0W0
      &END RI_RPA
        MEMORY 8.19200000E+003
    &END
  &END XC
 &END DFT
 &SUBSYS
  &CELL
    ABC 19.393693  18.893521  22.382111
    PERIODIC NONE
  &END CELL
  &COORD
……................
  &END COORD
  &TOPOLOGY
    &CENTER_COORDINATES
    &END
  &END TOPOLOGY
  &KIND O
    BASIS_SET DZVP-MOLOPT-GTH
    RI_AUX_BASIS RI_TZ
    BASIS_SET AUX_FIT FIT9
    POTENTIAL GTH-PBE-q6
  &END KIND
  &KIND Ti
    BASIS_SET DZVP-MOLOPT-SR-GTH
    RI_AUX_BASIS RI
    BASIS_SET AUX_FIT cFIT11
```

```
    POTENTIAL GTH-PBE-q12
   &END KIND
  &END SUBSYS
&END FORCE_EVAL
&GLOBAL
  RUN_TYPE     ENERGY
  PROJECT      ALL_ELEC
  PRINT_LEVEL  MEDIUM
&END GLOBAL
```

In the CP2K code, Gaussian functions are used as the primary basis set, whereas plane-waves are rather an auxiliary basis, primarily to construct the Hartree potential. CP2K uses a multi-grid system (i.e., multiple grids with differing cutoff/spacing) for mapping the product of Gaussian basis functions onto real-space grids, so that wide and smooth Gaussian functions are mapped onto a coarser grid than narrow and sharp Gaussians.

**CUTOFF 400 Ry** The plane-wave cutoff of the finest level of the multigrid.

**REL_CUTOFF 50 Ry** Determines the grid at which a Gaussian basis function is mapped, giving the cutoff used for a Gaussian with unit exponent.

**RPA_NUM_QUAD_POINTS 50** Number of quadrature points for the numerical integration in the RI-RPA (Resolution of the Identity-Random Phase Approximation) method.

**MINIMAX** The Minimax quadrature scheme is used for performing the numerical integration.

**OMEGA_MAX_FIT 10 eV** Determines fitting range for the self-energy on the imaginary axis: [0, **OMEGA_MAX_FIT]** for virtual orbitals, **[-OMEGA_MAX_FIT,0]** for occupied orbitals.

**ANALYTIC_CONTINUATION PADE** Padé approximation is used for the analytic continuation of the self energy.

**NPARAM_PADE 16** Number of parameters for the Padé approximation when using the latter for the analytic continuation of the self energy. 16 parameters (corresponding to 8 poles) are defined.

Numbers of occupied and virtual orbitals:

n = 29 DZ: 348, 1160 TZ: 348, 2929

n = 35 DZ: 420, 1400 TZ: 420, 3535

n = 78 DZ: 936, 3120 TZ: 936, 7878

n = 84 DZ: 1008, 3360 TZ: 1008, 8484

n = 97 DZ: 1164, 3880 TZ: 1164, 9797

n = 151 DZ: 1812, 6040 TZ: 1812, 15251

n = 165 DZ: 1980, 6600 TZ: 1980, 16665