# Electronic Supplementary Information for Phys. Chem. Chem. Phys.

# Occupation Matrix Control of *d*- and *f*-electron Localisations using DFT+*U*

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This electronic supplementary information provides details of the supercell structure and the initial location of localised electronic states for the oxygen-deficient $TiO_2$ and $CeO_2$ cells used in this study. The $TiO_2$ cell with an oxygen vacancy contained 36 Ti ions and 71 O atoms. The initial atomic coordinates of these ions are given in Table S1. While the Ti(III) locations for the 202 symmetry inequivalent structures are detailed in Table S2.

The $CeO_2$ cell with an oxygen vacancy contained 32 Ce ions and 63 O atoms. The initial atomic coordinates of these ions are given in Table S3. While the Ce(III) locations for the 33 symmetry inequivalent structures are detailed in Table S4.

**Table S1**: Initial structural coordinates of the tetragonal anatase-$TiO_2$ cell ($a$=11.7111Å and $c$=9.7333Å) containing an oxygen vacancy at 0.5000, 0.5000, 0.4175. All coordinates are given as fractional.

| Atom | Coordinate | Atom | Coordinate | Atom | Coordinate |
|---|---|---|---|---|---|
| Ti 1 | 0.1667, 0.3333, 0.3750 | O 1 | 0.1667, 0.3333, 0.1675 | O 37 | 0.3333, 0.0000, 0.3325 |
| Ti 2 | 0.8333, 0.6667, 0.3750 | O 2 | 0.8333, 0.6667, 0.1675 | O38 | 0.6667, 0.0000, 0.3325 |
| Ti 3 | 0.1667, 0.6667, 0.3750 | O 3 | 0.1667, 0.6667, 0.1675 | O 39 | 0.1667, 0.0000, 0.5825 |
| Ti 4 | 0.8333, 0.3333, 0.3750 | O 4 | 0.8333, 0.3333, 0.1675 | O 40 | 0.8333, 0.0000, 0.5825 |
| Ti 5 | 0.3333, 0.1667, 0.8750 | O 5 | 0.3333, 0.1667, 0.6675 | O 41 | 0.5000, 0.0000, 0.1675 |
| Ti 6 | 0.6667, 0.8333, 0.8750 | O 6 | 0.6667, 0.8333, 0.6675 | O 42 | 0.5000, 0.0000, 0.5825 |
| Ti 7 | 0.3333, 0.8333, 0.8750 | O 7 | 0.3333, 0.8333, 0.6675 | O 43 | 0.5000, 0.3333, 0.1675 |
| Ti 8 | 0.6667, 0.1667, 0.8750 | O 8 | 0.6667, 0.1667, 0.6675 | O 44 | 0.5000, 0.6667, 0.1675 |
| Ti 9 | 0.1667, 0.1667, 0.6250 | O 9 | 0.1667, 0.1667, 0.4175 | O 45 | 0.5000, 0.1667, 0.4175 |
| Ti 10 | 0.8333, 0.8333, 0.6250 | O 10 | 0.8333, 0.8333, 0.4175 | O 46 | 0.5000, 0.8333, 0.4175 |
| Ti 11 | 0.1667, 0.8333, 0.6250 | O 11 | 0.1667, 0.8333, 0.4175 | O 47 | 0.5000, 0.1667, 0.8325 |
| Ti 12 | 0.8333, 0.1667, 0.6250 | O 12 | 0.8333, 0.1667, 0.4175 | O 48 | 0.5000, 0.8333, 0.8325 |
| Ti 13 | 0.3333, 0.3333, 0.1250 | O 13 | 0.3333, 0.3333, 0.9175 | O 49 | 0.5000, 0.3333, 0.5825 |
| Ti 14 | 0.6667, 0.6667, 0.1250 | O 14 | 0.6667, 0.6667, 0.9175 | O 50 | 0.5000, 0.6667, 0.5825 |
| Ti 15 | 0.3333, 0.6667, 0.1250 | O 15 | 0.3333, 0.6667, 0.9175 | O 51 | 0.0000, 0.1667, 0.6675 |
| Ti 16 | 0.6667, 0.3333, 0.1250 | O 16 | 0.6667, 0.3333, 0.9175 | O 52 | 0.0000, 0.8333, 0.6675 |
| Ti 17 | 0.1667, 0.0000, 0.3750 | O 17 | 0.3333, 0.3333, 0.3325 | O 53 | 0.0000, 0.3333, 0.9175 |
| Ti 18 | 0.8333, 0.0000, 0.3750 | O 18 | 0.6667, 0.6667, 0.3325 | O 54 | 0.0000, 0.6667, 0.9175 |
| Ti 19 | 0.3333, 0.0000, 0.1250 | O 19 | 0.3333, 0.6667, 0.3325 | O 55 | 0.0000, 0.3333, 0.3325 |
| Ti 20 | 0.6667, 0.0000, 0.1250 | O 20 | 0.6667, 0.3333, 0.3325 | O 56 | 0.0000, 0.6667, 0.3325 |
| Ti 21 | 0.5000, 0.0000, 0.3750 | O 21 | 0.1667, 0.1667, 0.8325 | O 57 | 0.0000, 0.1667, 0.0825 |
| Ti 22 | 0.5000, 0.3333, 0.3750 | O 22 | 0.8333, 0.8333, 0.8325 | O 58 | 0.0000, 0.8333, 0.0825 |
| Ti 23 | 0.5000, 0.6667, 0.3750 | O 23 | 0.1667, 0.8333, 0.8325 | O 59 | 0.3333, 0.5000, 0.6675 |
| Ti 24 | 0.5000, 0.1667, 0.6250 | O 24 | 0.8333, 0.1667, 0.8325 | O 60 | 0.6667, 0.5000, 0.6675 |
| Ti 25 | 0.5000, 0.8333, 0.6250 | O 25 | 0.3333, 0.1667, 0.0825 | O 61 | 0.1667, 0.5000, 0.4175 |
| Ti 26 | 0.0000, 0.1667, 0.8750 | O 26 | 0.6667, 0.8333, 0.0825 | O 62 | 0.8333, 0.5000, 0.4175 |
| Ti 27 | 0.0000, 0.8333, 0.8750 | O 27 | 0.3333, 0.8333, 0.0825 | O 63 | 0.1667, 0.5000, 0.8325 |
| Ti 28 | 0.0000, 0.3333, 0.1250 | O 28 | 0.6667, 0.1667, 0.0825 | O 64 | 0.8333, 0.5000, 0.8325 |
| Ti 29 | 0.0000, 0.6667, 0.1250 | O 29 | 0.1667, 0.3333, 0.5825 | O 65 | 0.3333, 0.5000, 0.0825 |
| Ti 30 | 0.3333, 0.5000, 0.8750 | O 30 | 0.8333, 0.6667, 0.5825 | O 66 | 0.6667, 0.5000, 0.0825 |
| Ti 31 | 0.6667, 0.5000, 0.8750 | O 31 | 0.1667, 0.6667, 0.5825 | O 67 | 0.0000, 0.5000, 0.6675 |
| Ti 32 | 0.1667, 0.5000, 0.6250 | O 32 | 0.8333, 0.3333, 0.5825 | O 68 | 0.0000, 0.5000, 0.0825 |
| Ti 33 | 0.8333, 0.5000, 0.6250 | O 33 | 0.1667, 0.0000, 0.1675 | O 69 | 0.5000, 0.5000, 0.8325 |
| Ti 34 | 0.0000, 0.5000, 0.8750 | O 34 | 0.8333, 0.0000, 0.1675 | O 70 | 0.0000, 0.0000, 0.9175 |
| Ti 35 | 0.5000, 0.5000, 0.6250 | O 35 | 0.3333, 0.0000, 0.9175 | O 71 | 0.0000, 0.0000, 0.3325 |
| Ti 36 | 0.0000, 0.0000, 0.1250 | O 36 | 0.6667, 0.0000, 0.9175 | | |

**Table S2**: Positions of the two Ti(III) ions (Ti $\alpha$ and Ti $\beta$) for each configuration within the oxygen-deficient anatase-$TiO_2$ cell. Configuration numbers (Conf#) correspond with those used in the full paper, while Ti site numbers correspond with those given in Table S1.

| Conf# | Ti $\alpha$ | Ti $\beta$ | Conf# | Ti $\alpha$ | Ti $\beta$ | Conf# | Ti $\alpha$ | Ti $\beta$ | Conf# | Ti $\alpha$ | Ti $\beta$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 2 | 52 | 5 | 22 | 103 | 13 | 23 | 154 | 22 | 23 |
| 2 | 1 | 3 | 53 | 5 | 23 | 104 | 13 | 24 | 155 | 22 | 24 |
| 3 | 1 | 4 | 54 | 5 | 24 | 105 | 13 | 25 | 156 | 22 | 25 |
| 4 | 1 | 5 | 55 | 5 | 25 | 106 | 13 | 26 | 157 | 22 | 26 |
| 5 | 1 | 6 | 56 | 5 | 26 | 107 | 13 | 27 | 158 | 22 | 27 |
| 6 | 1 | 7 | 57 | 5 | 27 | 108 | 13 | 28 | 159 | 22 | 28 |
| 7 | 1 | 8 | 58 | 5 | 28 | 109 | 13 | 29 | 160 | 22 | 29 |
| 8 | 1 | 9 | 59 | 5 | 29 | 110 | 13 | 30 | 161 | 22 | 30 |
| 9 | 1 | 10 | 60 | 5 | 30 | 111 | 13 | 31 | 162 | 22 | 32 |
| 10 | 1 | 11 | 61 | 5 | 31 | 112 | 13 | 32 | 163 | 22 | 34 |
| 11 | 1 | 12 | 62 | 5 | 32 | 113 | 13 | 33 | 164 | 22 | 35 |
| 12 | 1 | 13 | 63 | 5 | 33 | 114 | 13 | 34 | 165 | 22 | 36 |
| 13 | 1 | 14 | 64 | 5 | 34 | 115 | 13 | 35 | 166 | 24 | 25 |
| 14 | 1 | 15 | 65 | 5 | 35 | 116 | 13 | 36 | 167 | 24 | 26 |
| 15 | 1 | 16 | 66 | 5 | 36 | 117 | 17 | 18 | 168 | 24 | 27 |
| 16 | 1 | 17 | 67 | 9 | 10 | 118 | 17 | 19 | 169 | 24 | 28 |
| 17 | 1 | 18 | 68 | 9 | 11 | 119 | 17 | 20 | 170 | 24 | 29 |
| 18 | 1 | 19 | 69 | 9 | 12 | 120 | 17 | 21 | 171 | 24 | 30 |
| 19 | 1 | 20 | 70 | 9 | 13 | 121 | 17 | 22 | 172 | 24 | 32 |
| 20 | 1 | 21 | 71 | 9 | 14 | 122 | 17 | 24 | 173 | 24 | 34 |
| 21 | 1 | 22 | 72 | 9 | 15 | 123 | 17 | 26 | 174 | 24 | 35 |
| 22 | 1 | 23 | 73 | 9 | 16 | 124 | 17 | 28 | 175 | 24 | 36 |
| 23 | 1 | 24 | 74 | 9 | 17 | 125 | 17 | 30 | 176 | 26 | 27 |
| 24 | 1 | 25 | 75 | 9 | 18 | 126 | 17 | 31 | 177 | 26 | 28 |
| 25 | 1 | 26 | 76 | 9 | 19 | 127 | 17 | 32 | 178 | 26 | 29 |
| 26 | 1 | 27 | 77 | 9 | 20 | 128 | 17 | 33 | 179 | 26 | 30 |
| 27 | 1 | 28 | 78 | 9 | 21 | 129 | 17 | 34 | 180 | 26 | 32 |
| 28 | 1 | 29 | 79 | 9 | 22 | 130 | 17 | 35 | 181 | 26 | 34 |
| 29 | 1 | 30 | 80 | 9 | 23 | 131 | 17 | 36 | 182 | 26 | 35 |
| 30 | 1 | 31 | 81 | 9 | 24 | 132 | 19 | 20 | 183 | 26 | 36 |
| 31 | 1 | 32 | 82 | 9 | 25 | 133 | 19 | 21 | 184 | 28 | 29 |
| 32 | 1 | 33 | 83 | 9 | 26 | 134 | 19 | 22 | 185 | 28 | 30 |
| 33 | 1 | 34 | 84 | 9 | 27 | 135 | 19 | 24 | 186 | 28 | 32 |
| 34 | 1 | 35 | 85 | 9 | 28 | 136 | 19 | 26 | 187 | 28 | 34 |
| 35 | 1 | 36 | 86 | 9 | 29 | 137 | 19 | 28 | 188 | 28 | 35 |
| 36 | 5 | 6 | 87 | 9 | 30 | 138 | 19 | 30 | 189 | 28 | 36 |
| 37 | 5 | 7 | 88 | 9 | 31 | 139 | 19 | 31 | 190 | 30 | 31 |
| 38 | 5 | 8 | 89 | 9 | 32 | 140 | 19 | 32 | 191 | 30 | 32 |
| 39 | 5 | 9 | 90 | 9 | 33 | 141 | 19 | 33 | 192 | 30 | 33 |
| 40 | 5 | 10 | 91 | 9 | 34 | 142 | 19 | 34 | 193 | 30 | 34 |
| 41 | 5 | 11 | 92 | 9 | 35 | 143 | 19 | 35 | 194 | 30 | 35 |
| 42 | 5 | 12 | 93 | 9 | 36 | 144 | 19 | 36 | 195 | 30 | 36 |
| 43 | 5 | 13 | 94 | 13 | 14 | 145 | 21 | 22 | 196 | 32 | 33 |
| 44 | 5 | 14 | 95 | 13 | 15 | 146 | 21 | 24 | 197 | 32 | 34 |
| 45 | 5 | 15 | 96 | 13 | 16 | 147 | 21 | 26 | 198 | 32 | 35 |
| 46 | 5 | 16 | 97 | 13 | 17 | 148 | 21 | 28 | 199 | 32 | 36 |
| 47 | 5 | 17 | 98 | 13 | 18 | 149 | 21 | 30 | 200 | 34 | 35 |
| 48 | 5 | 18 | 99 | 13 | 19 | 150 | 21 | 32 | 201 | 34 | 36 |
| 49 | 5 | 19 | 100 | 13 | 20 | 151 | 21 | 34 | 202 | 35 | 36 |
| 50 | 5 | 20 | 101 | 13 | 21 | 152 | 21 | 35 | | | |
| 51 | 5 | 21 | 102 | 13 | 22 | 153 | 21 | 36 | | | |

**Table S3**: Initial structural coordinates of the cubic $CeO_2$ cell ($a$=10.9571Å) containing an oxygen vacancy at 0.5000, 0.5000, 0.5000. All coordinates are given as fractional.

| Atom | Coordinate | Atom | Coordinate | Atom | Coordinate |
|---|---|---|---|---|---|
| Ce 1 | 0.3750, 0.3750, 0.6250 | O 1 | 0.2500, 0.2500, 0.7500 | O 33 | 0.0000, 0.5000, 0.5000 |
| Ce 2 | 0.6250, 0.6250, 0.6250 | O 2 | 0.7500, 0.7500, 0.7500 | O 34 | 0.5000, 0.0000, 0.5000 |
| Ce 3 | 0.6250, 0.3750, 0.3750 | O 3 | 0.7500, 0.2500, 0.2500 | O 35 | 0.5000, 0.5000, 0.0000 |
| Ce 4 | 0.3750, 0.6250, 0.3750 | O 4 | 0.2500, 0.7500, 0.2500 | O 36 | 0.2500, 0.0000, 0.5000 |
| Ce 5 | 0.8750, 0.8750, 0.1250 | O 5 | 0.0000, 0.2500, 0.2500 | O 37 | 0.7500, 0.0000, 0.5000 |
| Ce 6 | 0.1250, 0.1250, 0.1250 | O 6 | 0.0000, 0.7500, 0.2500 | O 38 | 0.5000, 0.2500, 0.0000 |
| Ce 7 | 0.1250, 0.8750, 0.8750 | O 7 | 0.0000, 0.2500, 0.7500 | O 39 | 0.5000, 0.7500, 0.0000 |
| Ce 8 | 0.8750, 0.1250, 0.8750 | O 8 | 0.0000, 0.7500, 0.7500 | O 40 | 0.0000, 0.5000, 0.2500 |
| Ce 9 | 0.8750, 0.8750, 0.6250 | O 9 | 0.2500, 0.0000, 0.2500 | O 41 | 0.0000, 0.5000, 0.7500 |
| Ce 10 | 0.1250, 0.1250, 0.6250 | O 10 | 0.2500, 0.0000, 0.7500 | O 42 | 0.0000, 0.2500, 0.5000 |
| Ce 11 | 0.1250, 0.8750, 0.3750 | O 11 | 0.7500, 0.0000, 0.2500 | O 43 | 0.0000, 0.7500, 0.5000 |
| Ce 12 | 0.8750, 0.1250, 0.3750 | O 12 | 0.7500, 0.0000, 0.7500 | O 44 | 0.2500, 0.5000, 0.0000 |
| Ce 13 | 0.6250, 0.8750, 0.8750 | O 13 | 0.2500, 0.2500, 0.0000 | O 45 | 0.7500, 0.5000, 0.0000 |
| Ce 14 | 0.6250, 0.1250, 0.1250 | O 14 | 0.7500, 0.2500, 0.0000 | O 46 | 0.5000, 0.0000, 0.2500 |
| Ce 15 | 0.3750, 0.1250, 0.8750 | O 15 | 0.2500, 0.7500, 0.0000 | O 47 | 0.5000, 0.0000, 0.7500 |
| Ce 16 | 0.3750, 0.8750, 0.1250 | O 16 | 0.7500, 0.7500, 0.0000 | O 48 | 0.2500, 0.0000, 0.0000 |
| Ce 17 | 0.8750, 0.6250, 0.8750 | O 17 | 0.5000, 0.2500, 0.2500 | O 49 | 0.7500, 0.0000, 0.0000 |
| Ce 18 | 0.1250, 0.6250, 0.1250 | O 18 | 0.5000, 0.7500, 0.2500 | O 50 | 0.0000, 0.2500, 0.0000 |
| Ce 19 | 0.8750, 0.3750, 0.1250 | O 19 | 0.5000, 0.2500, 0.7500 | O 51 | 0.0000, 0.7500, 0.0000 |
| Ce 20 | 0.1250, 0.3750, 0.8750 | O 20 | 0.5000, 0.7500, 0.7500 | O 52 | 0.0000, 0.0000, 0.2500 |
| Ce 21 | 0.8750, 0.3750, 0.6250 | O 21 | 0.2500, 0.5000, 0.2500 | O 53 | 0.0000, 0.0000, 0.7500 |
| Ce 22 | 0.1250, 0.6250, 0.6250 | O 22 | 0.2500, 0.5000, 0.7500 | O 54 | 0.2500, 0.5000, 0.5000 |
| Ce 23 | 0.1250, 0.3750, 0.3750 | O 23 | 0.7500, 0.5000, 0.2500 | O 55 | 0.7500, 0.5000, 0.5000 |
| Ce 24 | 0.8750, 0.6250, 0.3750 | O 24 | 0.7500, 0.5000, 0.7500 | O 56 | 0.5000, 0.2500, 0.5000 |
| Ce 25 | 0.6250, 0.8750, 0.3750 | O 25 | 0.2500, 0.2500, 0.5000 | O 57 | 0.5000, 0.7500, 0.5000 |
| Ce 26 | 0.6250, 0.1250, 0.6250 | O 26 | 0.7500, 0.2500, 0.5000 | O 58 | 0.5000, 0.5000, 0.2500 |
| Ce 27 | 0.3750, 0.1250, 0.3750 | O 27 | 0.2500, 0.7500, 0.5000 | O 59 | 0.5000, 0.5000, 0.7500 |
| Ce 28 | 0.3750, 0.8750, 0.6250 | O 28 | 0.7500, 0.7500, 0.5000 | O 60 | 0.2500, 0.2500, 0.2500 |
| Ce 29 | 0.3750, 0.6250, 0.8750 | O 29 | 0.0000, 0.0000, 0.5000 | O 61 | 0.7500, 0.7500, 0.2500 |
| Ce 30 | 0.6250, 0.6250, 0.1250 | O 30 | 0.5000, 0.0000, 0.0000 | O 62 | 0.7500, 0.2500, 0.7500 |
| Ce 31 | 0.3750, 0.3750, 0.1250 | O 31 | 0.0000, 0.5000, 0.0000 | O 63 | 0.2500, 0.7500, 0.7500 |
| Ce 32 | 0.6250, 0.3750, 0.8750 | O 32 | 0.0000, 0.0000, 0.0000 | | |

**Table S4**: Positions of the two Ce(III) ions (Ce $\alpha$ and Ce $\beta$) for each configuration within the oxygen-deficient $CeO_2$ cell. Configuration numbers (Conf#) correspond with those used in the full paper, while Ce site numbers correspond with those given in Table S3.

| Conf# | Ce $\alpha$ | Ce $\beta$ | Conf# | Ce $\alpha$ | Ce $\beta$ | Conf# | Ce $\alpha$ | Ce $\beta$ | Conf# | Ce $\alpha$ | Ce $\beta$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 2 | 10 | 5 | 6 | 19 | 9 | 13 | 28 | 9 | 31 |
| 2 | 1 | 5 | 11 | 5 | 9 | 20 | 9 | 14 | 29 | 21 | 22 |
| 3 | 1 | 6 | 12 | 5 | 10 | 21 | 9 | 16 | 30 | 21 | 24 |
| 4 | 1 | 9 | 13 | 5 | 11 | 22 | 9 | 21 | 31 | 21 | 25 |
| 5 | 1 | 10 | 14 | 5 | 21 | 23 | 9 | 22 | 32 | 21 | 26 |
| 6 | 1 | 11 | 15 | 5 | 22 | 24 | 9 | 23 | 33 | 21 | 28 |
| 7 | 1 | 21 | 16 | 5 | 24 | 25 | 9 | 24 | | | |
| 8 | 1 | 22 | 17 | 9 | 10 | 26 | 9 | 29 | | | |
| 9 | 1 | 24 | 18 | 9 | 11 | 27 | 9 | 30 | | | |