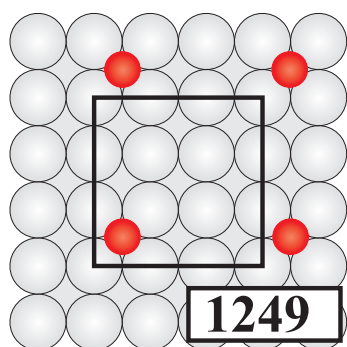


Appendix E

Computed Ordered Configurations for O-Pd(100)

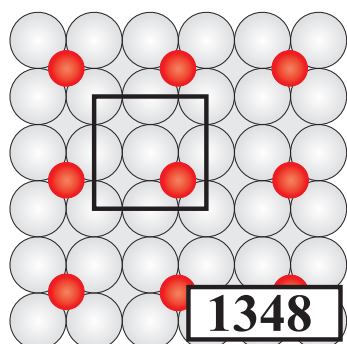
Listed are all ordered configurations of O at Pd(100) that were computed by (L)APW+lo DFT. Shown is a schematic top view indicating the surface unit-cell. The computed DFT average binding energy is given in meV, and the LGH expansion using all cluster figures in the considered pool is stated. Configurations (hol-hol)-1 to (hol-hol)-27 correspond to configurations with O in hollow sites; configurations (br-br)-1 to (br-br)-18 to configurations with O in bridge sites; and configurations (hol-br)-1 to (hol-br)-6 to configurations with O in hollow and bridge sites. Light grey spheres represent Pd atoms, and dark (red) spheres represent O atoms.



(hol-hol)-1

$$E_b^{(\text{hol-hol})-1} = E^{\text{on-site}}$$

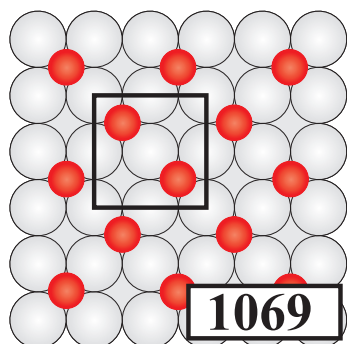
1249



(hol-hol)-2

$$E_b^{(\text{hol-hol})-2} = E^{\text{on-site}} + 2V_{3p} + 2V_{5p}$$

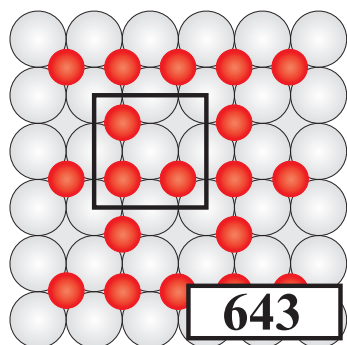
1348



(hol-hol)-3

$$E_b^{(\text{hol-hol})-3} = E^{\text{on-site}} + 2V_{2p} + 2V_{3p} + 2V_{5p} \\ + 4V_{4t} + 2V_{6t} + 8V_{7t} \\ + V_{3q}$$

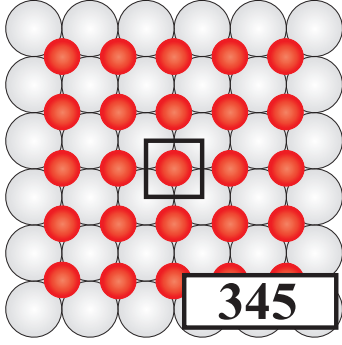
1069



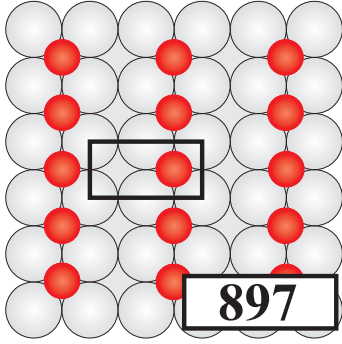
(hol-hol)-4

$$E_b^{(\text{hol-hol})-4} = E^{\text{on-site}} + 4/3V_{1p} + 4/3V_{2p} + 2V_{3p} + 8/3V_{4p} \\ + 2V_{5p} + 4/3V_{1t} + 4/3V_{2t} + 8/3V_{3t} + 8/3V_{4t} \\ + 16/3V_{5t} + 4/3V_{6t} + 16/3V_{7t} + 8/3V_{8t} \\ + 4/3V_{2q} + 2/3V_{3q} + 1/3V_{1qu}$$

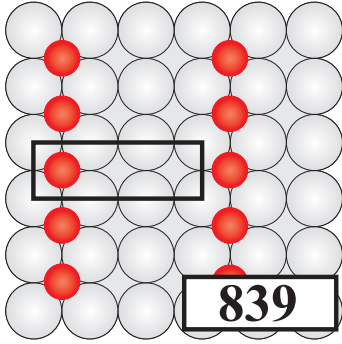
643


(hol-hol)-5

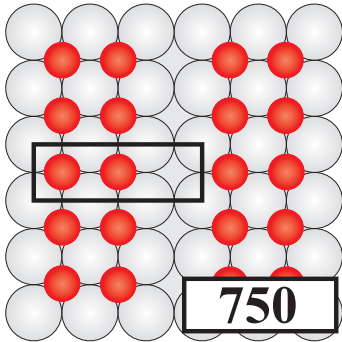
$$\begin{aligned}
 E_b^{(\text{hol-hol})-5} = & E^{\text{on-site}} + 2V_{1p} + 2V_{2p} + 2V_{3p} + 4V_{4p} + 2V_{5p} \\
 & + 2V_{1t} + 4V_{2t} + 8V_{3t} + 4V_{4t} + 8V_{5t} + 2V_{6t} \\
 & + 8V_{7t} + 4V_{8t} + V_{1q} + 4V_{2q} + V_{3q} \\
 & + V_{1qu}
 \end{aligned}$$


(hol-hol)-6

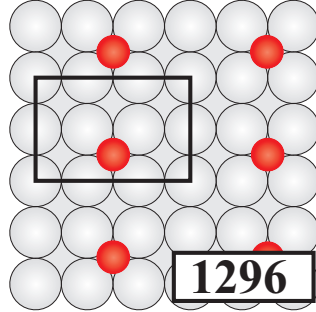
$$\begin{aligned}
 E_b^{(\text{hol-hol})-6} = & E^{\text{on-site}} + V_{1p} + 2V_{3p} + 2V_{4p} + 2V_{5p} \\
 & + V_{1t} + 4V_{5t} + 2V_{8t}
 \end{aligned}$$


(hol-hol)-7

$$\begin{aligned}
 E_b^{(\text{hol-hol})-7} = & E^{\text{on-site}} + V_{1p} + V_{3p} \\
 & + V_{1t} + 2V_{8t}
 \end{aligned}$$

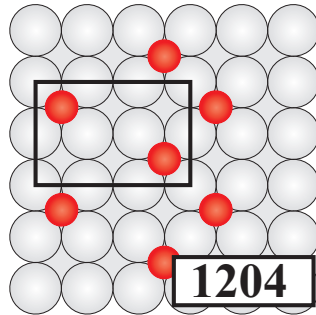

(hol-hol)-8

$$\begin{aligned}
 E_b^{(\text{hol-hol})-8} = & E^{\text{on-site}} + 3/2V_{1p} + V_{2p} + 3/2V_{3p} + 2V_{4p} + V_{5p} \\
 & + V_{1t} + 3V_{2t} + 2V_{3t} + V_{4t} + 4V_{5t} \\
 & + 4V_{7t} + 3V_{8t} + 1/2V_{1q} + V_{2q}
 \end{aligned}$$



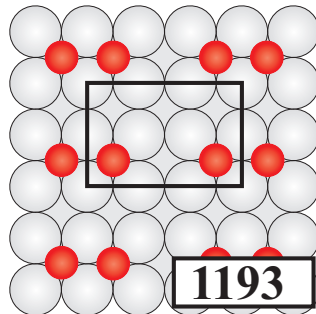
(hol-hol)-9

$$E_b^{(\text{hol-hol})-9} = E^{\text{on-site}} + V_{3p}$$



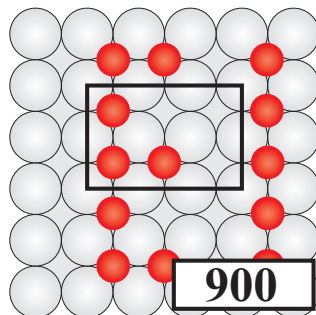
(hol-hol)-10

$$E_b^{(\text{hol-hol})-10} = E^{\text{on-site}} + V_{2p} + V_{3p} + V_{4p} \\ + V_{4t} + 2V_{7t}$$



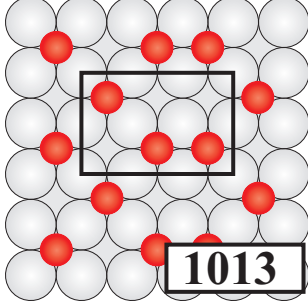
(hol-hol)-11

$$E_b^{(\text{hol-hol})-11} = E^{\text{on-site}} + 1/2V_{1p} + 3/2V_{3p} + V_{4p} + V_{5p} \\ + 2V_{5t} + V_{8t}$$

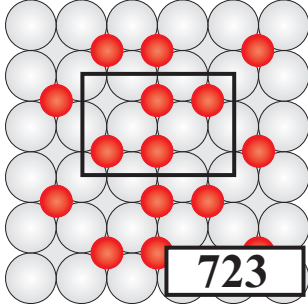


(hol-hol)-12

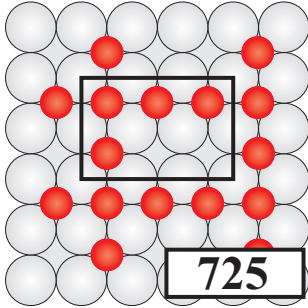
$$E_b^{(\text{hol-hol})-12} = E^{\text{on-site}} + V_{1p} + 2/3V_{2p} + 4/3V_{3p} + 4/3V_{4p} + 2/3V_{5p} \\ + 2/3V_{1t} + 2/3V_{2t} + 2/3V_{3t} + 2/3V_{4t} + 2V_{5t} + 2V_{7t} \\ + 2V_{8t} + 1/3V_{2q}$$


(hol-hol)-13

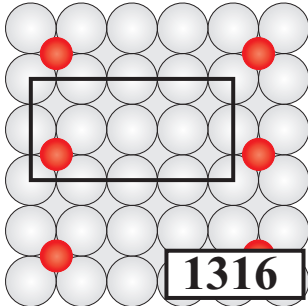
$$E_b^{(\text{hol-hol})-13} = E^{\text{on-site}} + 1/3V_{1p} + 4/3V_{2p} + 4/3V_{3p} + 2V_{4p} + 2/3V_{5p} \\ + 4/3V_{3t} + 2V_{4t} + 4/3V_{5t} + 2/3V_{6t} + 8/3V_{7t} + 2/3V_{8t} \\ + 1/3V_{3q}$$


(hol-hol)-14

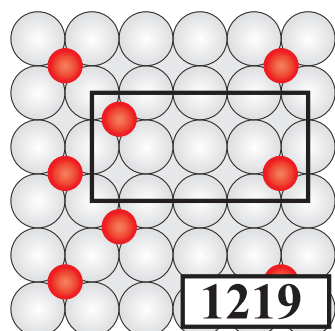
$$E_b^{(\text{hol-hol})-14} = E^{\text{on-site}} + V_{1p} + 3/2V_{2p} + 3/2V_{3p} + 5/2V_{4p} + V_{5p} \\ + 1/2V_{1t} + V_{2t} + 3V_{3t} + 5/2V_{4t} + 3V_{5t} \\ + V_{6t} + 4V_{7t} + 2V_{8t} + 1/2V_{2q} + 1/2V_{3q}$$


(hol-hol)-15

$$E_b^{(\text{hol-hol})-15} = E^{\text{on-site}} + 5/4V_{1p} + V_{2p} + 7/4V_{3p} + 5/2V_{4p} + 3/2V_{5p} \\ + 5/4V_{1t} + V_{2t} + 2V_{3t} + 3/2V_{4t} + 4V_{5t} \\ + 1/2V_{6t} + 3V_{7t} + 5/2V_{8t} + V_{2q} + 1/4V_{3q} \\ + 1/4V_{1qu}$$

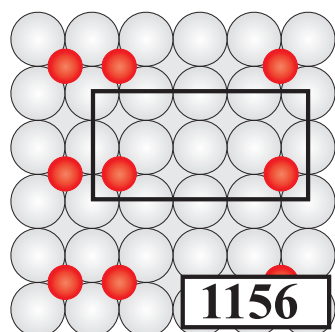

(hol-hol)-16

$$E_b^{(\text{hol-hol})-16} = E^{\text{on-site}} + V_{3p}$$



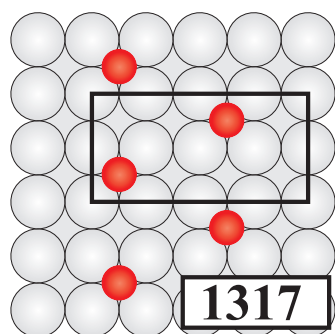
(hol-hol)-17

$$E_b^{(\text{hol-hol})-17} = E^{\text{on-site}} + V_{2p} + V_{3p}$$



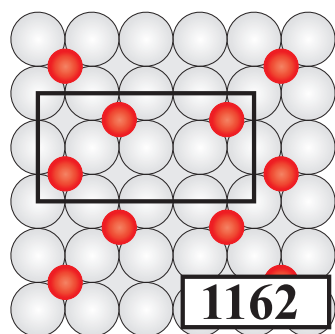
(hol-hol)-18

$$E_b^{(\text{hol-hol})-18} = E^{\text{on-site}} + 1/2V_{1p} + V_{3p} + V_{4p} + 2V_{5t}$$



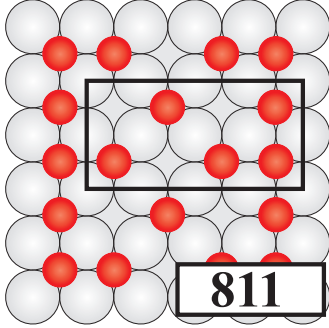
(hol-hol)-19

$$E_b^{(\text{hol-hol})-19} = E^{\text{on-site}} + V_{3p} + 2V_{4p}$$

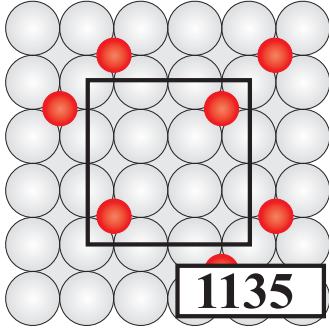


(hol-hol)-20

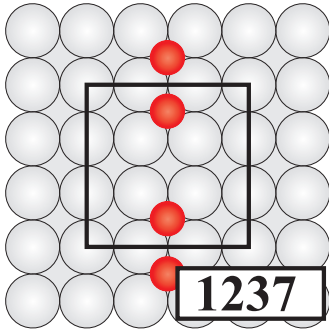
$$E_b^{(\text{hol-hol})-20} = E^{\text{on-site}} + 4/3V_{2p} + 5/3V_{3p} + 4/3V_{5p} + 2V_{4t} + 2/3V_{6t} + 4V_{7t} + 1/3V_{3q}$$


(hol-hol)-21

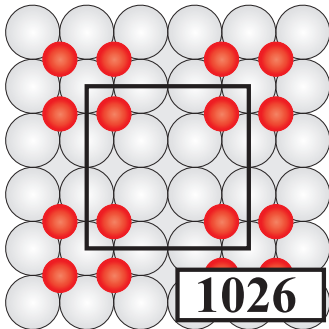
$$\begin{aligned}
 E_b^{(\text{hol-hol})-21} = & E^{\text{on-site}} + 4/5V_{1p} + 8/5V_{2p} + 9/5V_{3p} + 8/5V_{4p} \\
 & + 8/5V_{5p} + 3/5V_{1t} + 4/5V_{2t} + 8/5V_{3t} + 16/5V_{4t} \\
 & + 12/5V_{5t} + 8/5V_{6t} + 32/5V_{7t} + 6/5V_{8t} \\
 & + 4V_{2q} + 4V_{3q} + 1/5V_{1qu}
 \end{aligned}$$


(hol-hol)-22

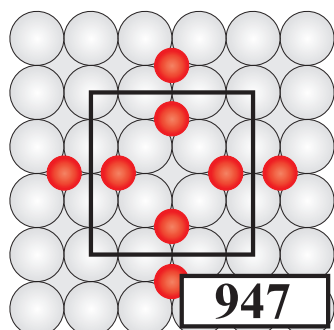
$$E_b^{(\text{hol-hol})-22} = E^{\text{on-site}} + 1/2V_{2p} + V_{4p} + 1/2V_{5p}$$


(hol-hol)-23

$$\begin{aligned}
 E_b^{(\text{hol-hol})-23} = & E^{\text{on-site}} + 1/2V_{1p} + 1/2V_{3p} \\
 & + V_{8t}
 \end{aligned}$$

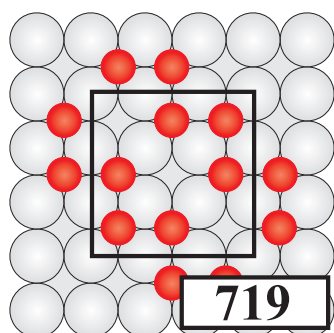

(hol-hol)-24

$$\begin{aligned}
 E_b^{(\text{hol-hol})-24} = & E^{\text{on-site}} + V_{1p} + 1/2V_{2p} + V_{3p} + V_{4p} + 1/2V_{5p} \\
 & + V_{2t} + 2V_{5t} + 2V_{7t} + 2V_{8t}
 \end{aligned}$$



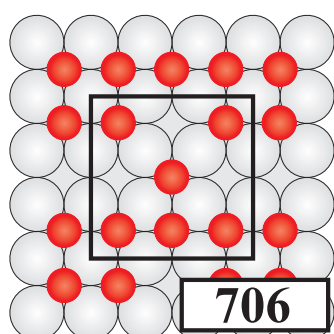
(hol-hol)-25

$$E_b^{(\text{hol-hol})-25} = E^{\text{on-site}} + 1/2V_{1p} + V_{2p} + 1/2V_{3p} + 2V_{4p} + 2/3V_{5p} \\ + 2V_{3t} + V_{4t} + V_{8t} \\ + 1/4V_{3q}$$



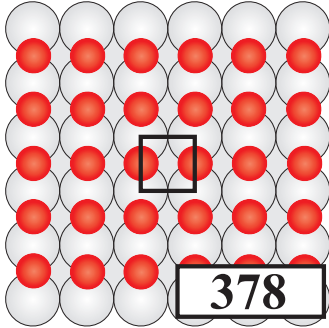
(hol-hol)-26

$$E_b^{(\text{hol-hol})-26} = E^{\text{on-site}} + V_{1p} + 3/2V_{2p} + V_{3p} + 3V_{4p} + 3/2V_{5p} \\ + V_{2t} + 4V_{3t} + 2V_{4t} + 2V_{5t} + V_{6t} + 2V_{7t} \\ + 2V_{8t} + 1/2V_{3q}$$

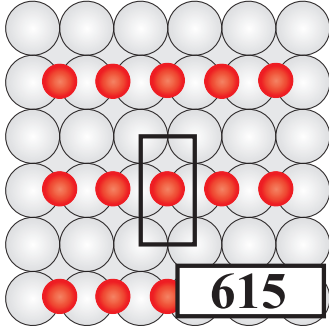


(hol-hol)-27

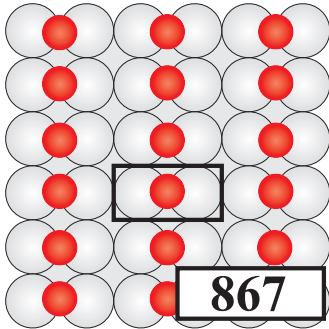
$$E_b^{(\text{hol-hol})-27} = E^{\text{on-site}} + 7/6V_{1p} + 4/3V_{2p} + 7/6V_{3p} + 8/3V_{4p} \\ + 4/3V_{5p} + 1/2V_{1t} + 4/3V_{2t} + 3V_{3t} + 3/2V_{4t} \\ + 8/3V_{5t} + V_{6t} + 8/3V_{7t} + 7/3V_{8t} \\ + 1/3V_{1q} + 1/2V_{2q} + 1/3V_{3q}$$


(br-br)-1

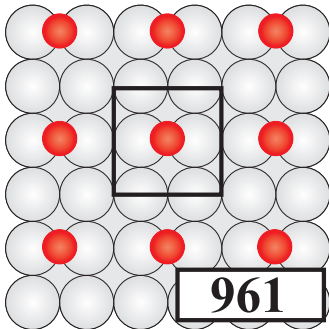
$$\begin{aligned}
 E_b^{(\text{br-br})-1} &= E_{\text{bridge}}^{\text{on-site}} + V_{1p} + V_{1p}' + 2V_{2p} + V_{4p} + V_{4p}' \\
 &\quad + V_{1t} + V_{1t}' + 4V_{2t} + 4V_{3t} + 4V_{3t}' \\
 &\quad + 2V_{6t} + 2V_{6t}' + 4V_{7t} + 4V_{7t}' + 2V_{8t}
 \end{aligned}$$


(br-br)-2

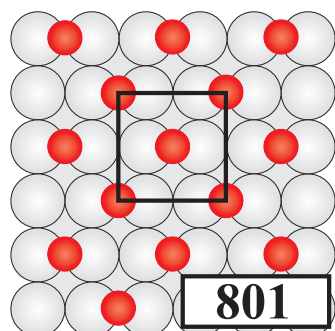
$$\begin{aligned}
 E_b^{(\text{br-br})-2} &= E_{\text{bridge}}^{\text{on-site}} + V_{1p} + V_{4p} + V_{4p}' \\
 &\quad + V_{1t} + 4V_{7t}'
 \end{aligned}$$


(br-br)-3

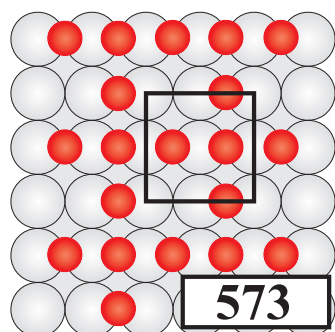
$$\begin{aligned}
 E_b^{(\text{br-br})-3} &= E_{\text{bridge}}^{\text{on-site}} + V_{1p}' + V_{4p} + V_{4p}' \\
 &\quad + V_{1t}' + 4V_{7t}
 \end{aligned}$$


(br-br)-4

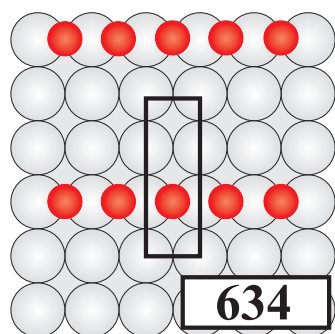
$$E_b^{(\text{br-br})-4} = E_{\text{bridge}}^{\text{on-site}} + V_{4p} + V_{4p}'$$


(br-br)-5

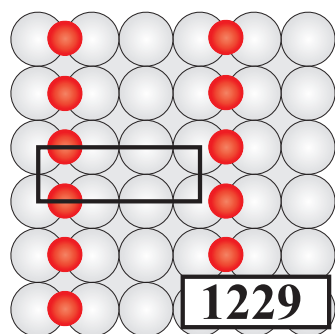
$$E_b^{(\text{br-br})-5} = E_{\text{bridge}}^{\text{on-site}} + V_{2p} + V_{4p} + V_{4p}' + 2V_{6t} + 2V_{6t}' + 2V_{8t}$$


(br-br)-6

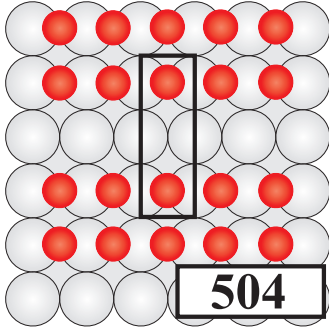
$$E_b^{(\text{br-br})-6} = E_{\text{bridge}}^{\text{on-site}} + 2/3V_{1p} + 2/3V_{1p}' + 4/3V_{2p} + V_{4p} + V_{4p}' + 2/3V_{1t} + 2/3V_{1t}' + 4/3V_{2t} + 4/3V_{3t} + 4/3V_{3t}' + 4/3V_{6t} + 4/3V_{6t}' + 8/3V_{7t} + 8/3V_{7t}' + 4/3V_{8t}$$


(br-br)-7

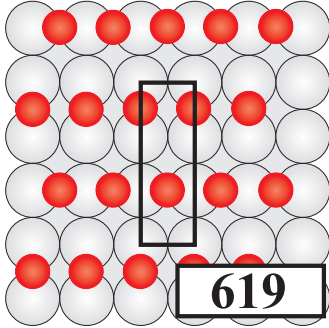
$$E_b^{(\text{br-br})-7} = E_{\text{bridge}}^{\text{on-site}} + V_{1p} + V_{4p} + V_{1t}$$


(br-br)-8

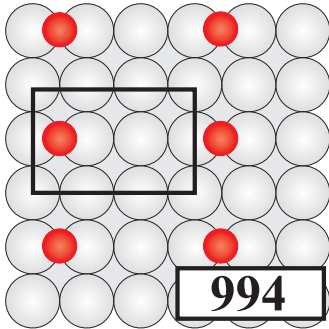
$$E_b^{(\text{br-br})-8} = E_{\text{bridge}}^{\text{on-site}} + V_{1p}' + V_{4p}' + V_{1t}'$$


(br-br)-9

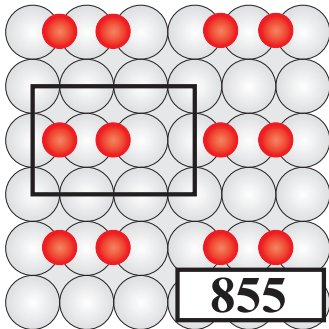
$$E_b^{(\text{br-br})-9} = E_{\text{bridge}}^{\text{on-site}} + V_{1p} + 1/2V_{1p}' + V_{2p} + V_{4p} + 1/2V_{4p}' + V_{1t} + 2V_{2t} + 2V_{3t}$$


(br-br)-10

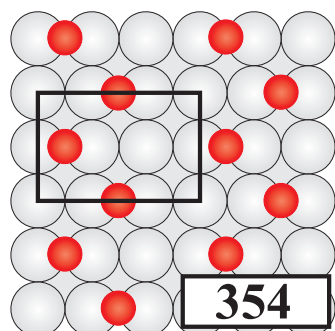
$$E_b^{(\text{br-br})-10} = E_{\text{bridge}}^{\text{on-site}} + 1/2V_{1p} + 1/2V_{1p}' + 2V_{3p} + 1/2V_{4p} + 1/2V_{4p}' + 2V_{5p} + 1/2V_{1t} + 1/2V_{1t}' + 2V_{4t} + 2V_{4t}' + V_{5t} + V_{5t}'$$


(br-br)-11

$$E_b^{(\text{br-br})-11} = E_{\text{bridge}}^{\text{on-site}} + 1/2V_{4p}'$$

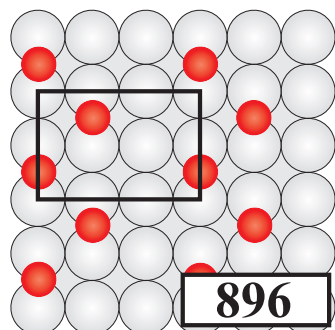

(br-br)-12

$$E_b^{(\text{br-br})-12} = E_{\text{bridge}}^{\text{on-site}} + 1/2V_{1p} + 1/2V_{4p} + V_{4p}' + 2V_{7t}'$$



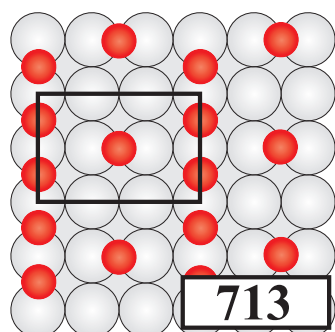
(br-br)-13

$$E_b^{(\text{br-br})-13} = E_{\text{bridge}}^{\text{on-site}} + V_{2p} + V_{4p} + V_{6t}'$$



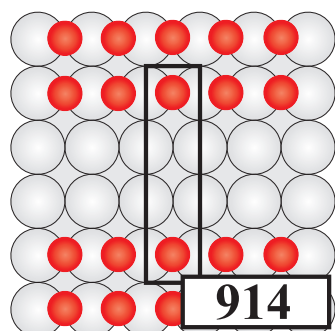
(br-br)-14

$$E_b^{(\text{br-br})-14} = E_{\text{bridge}}^{\text{on-site}} + V_{2p} + V_{4p} + V_{6t}'$$



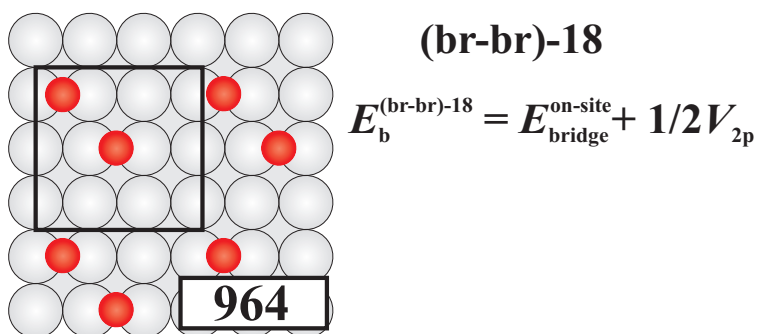
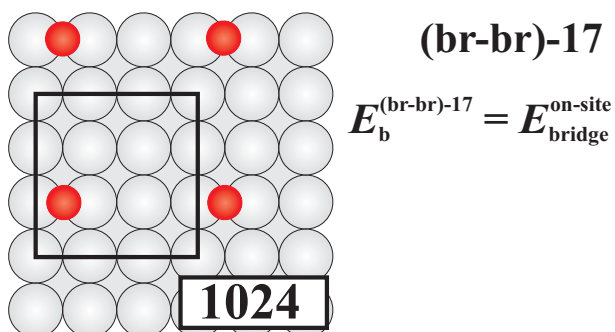
(br-br)-15

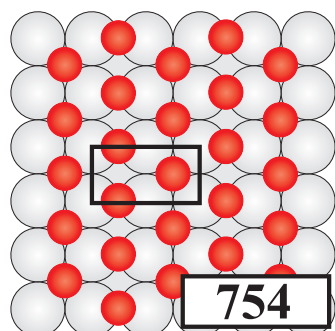
$$E_b^{(\text{br-br})-15} = E_{\text{bridge}}^{\text{on-site}} + \frac{2}{3}V_{1p} + \frac{4}{3}V_{3p} + \frac{2}{3}V_{4p} + \frac{1}{3}V_{4p}' + \frac{4}{3}V_{5p} + \frac{2}{3}V_{1t} + \frac{4}{3}V_{4t} + \frac{2}{3}V_{5t}$$



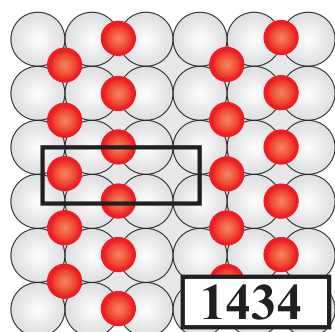
(br-br)-16

$$E_b^{(\text{br-br})-16} = E_{\text{bridge}}^{\text{on-site}} + V_{1p}' + V_{4p} + V_{1t}'$$

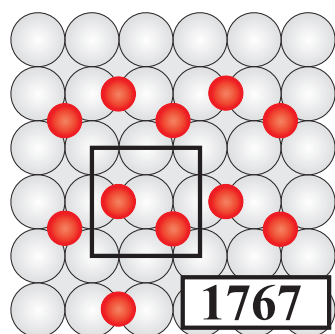



(hol-br)-1

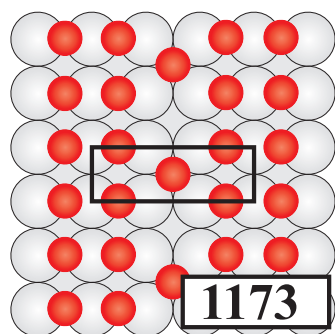
$$E_b^{(\text{hol-br})-1} = E_{\text{bridge}}^{\text{on-site}} + E_{\text{hollow}}^{\text{on-site}} + 4V_{1p} + 4V_{3p} + 2V_{1t} + 2V_{1t}' + 2V_{3t} + 2V_{3t}' + 2V_{4t} + 2V_{4t}'$$


(hol-br)-2

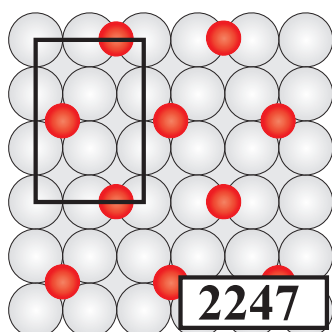
$$E_b^{(\text{hol-br})-2} = E_{\text{bridge}}^{\text{on-site}} + E_{\text{hollow}}^{\text{on-site}} + 2V_{2p} + 4V_{3p}$$


(hol-br)-3

$$E_b^{(\text{hol-br})-3} = E_{\text{bridge}}^{\text{on-site}} + E_{\text{hollow}}^{\text{on-site}} + 2V_{1p} + 2V_{3p} + V_{3t} + V_{3t}'$$

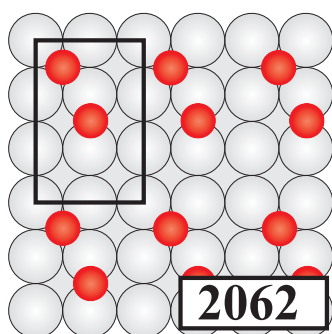

(hol-br)-4

$$E_b^{(\text{hol-br})-4} = 2E_{\text{bridge}}^{\text{on-site}} + E_{\text{hollow}}^{\text{on-site}} + 4V_{1p} + 4V_{3p} + 4V_{4p} + 3V_{1t} + 3V_{1t}' + 3V_{3t} + 3V_{4t}'$$



(hol-br)-5

$$E_b^{(\text{hol-br})-1} = E_{\text{bridge}}^{\text{on-site}} + E_{\text{hollow}}^{\text{on-site}} + 4V_{3p}$$



(hol-br)-6

$$E_b^{(\text{hol-br})-2} = E_{\text{bridge}}^{\text{on-site}} + E_{\text{hollow}}^{\text{on-site}} + V_{1p} + V_{3p} + V_{4p}$$

