

Appendix B

Low-index Pd Surfaces

B.1 Clean Surfaces

Using the calculated equilibrium bulk Pd fcc lattice constant, we construct Pd(111) and Pd(100) slabs using each time 5 layers (Fig. B.1). The surface unit area is 6.75 \AA^2 (GGA-PBE) and 6.37 \AA^2 (LDA) for Pd(111), while it is 7.79 \AA^2 (GGA-PBE) and 7.36 \AA^2 (LDA) for Pd(100).

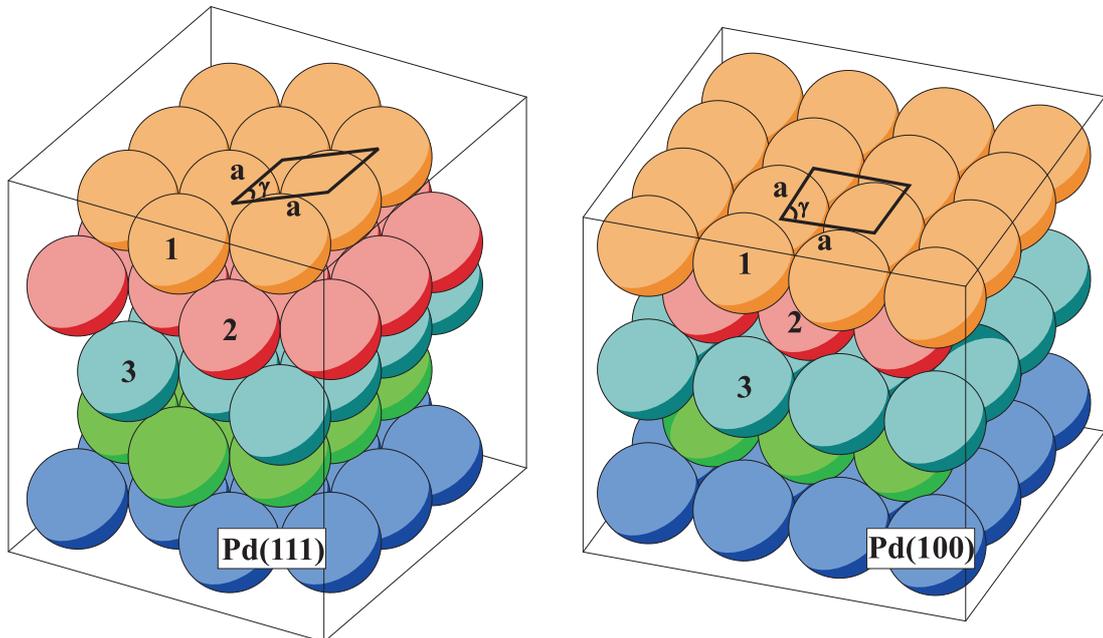


Figure B.1: Schematic figures of the Pd(111) [left] and Pd(100) [right] slab structures. For the GGA-PBE functional the in-plane surface unit-cell parameters are: Pd(111), $a=2.79 \text{ \AA}$, $\gamma = 60^\circ$; Pd(100), $a=2.79 \text{ \AA}$, $\gamma = 90^\circ$.

The surface energy is obtained via Eq. 4.8 for different energy cutoffs ($E_{\text{max}}^{\text{wf}}$) and

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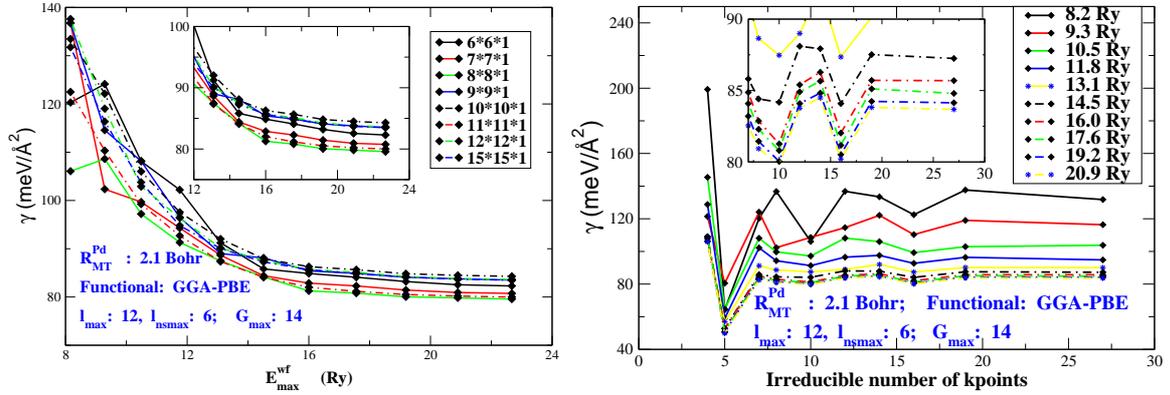


Figure B.2: Convergence test for the optimal energy cutoff and \mathbf{k} -points on a 5 layer Pd(111) slab using the GGA-PBE functional.

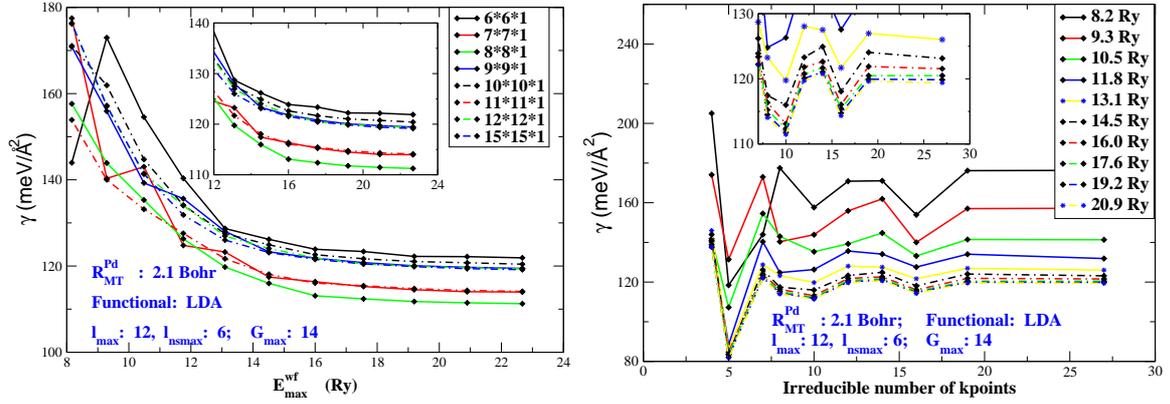


Figure B.3: Convergence test for the optimal energy cutoff and \mathbf{k} -points on a 5 layer Pd(111) slab using the LDA functional.

\mathbf{k} -points to find out the convergence behavior with respect to these basis set parameters. Fig. B.2 shows corresponding curves of the surface energy versus E_{\max}^{wf} (\mathbf{k} -points) for different \mathbf{k} -points (E_{\max}^{wf}) and the GGA-PBE functional. In the left figure (energy cutoff test), the surface energy is rapidly decreasing with increasing E_{\max}^{wf} , but converges to within $\pm 5 \text{ meV}/\text{\AA}^2$ when E_{\max}^{wf} reaches 16.0 Ry. In the right figure of Fig. B.2 (\mathbf{k} -points test), the curve oscillates very fast with increasing irreducible number of \mathbf{k} -points when E_{\max}^{wf} is small. For larger energy cutoff (≥ 16.0 Ry), all curves are, however, converged very well for meshes containing more than 12 irreducible \mathbf{k} -points [k-mesh: $(9 \times 9 \times 1)$]. Similar tests, but using the LDA functional are shown in Fig B.3, arriving at a similar conclusion. With basis sets exceeding $E_{\max}^{\text{wf}} = 16.0$ Ry and 12 irreducible \mathbf{k} -points the surface energy of Pd(111) can therefore be converged to within $\pm 5 \text{ meV}/\text{\AA}^2$.

In the same way, we tested the energy cutoff and \mathbf{k} -points convergence for Pd(100)

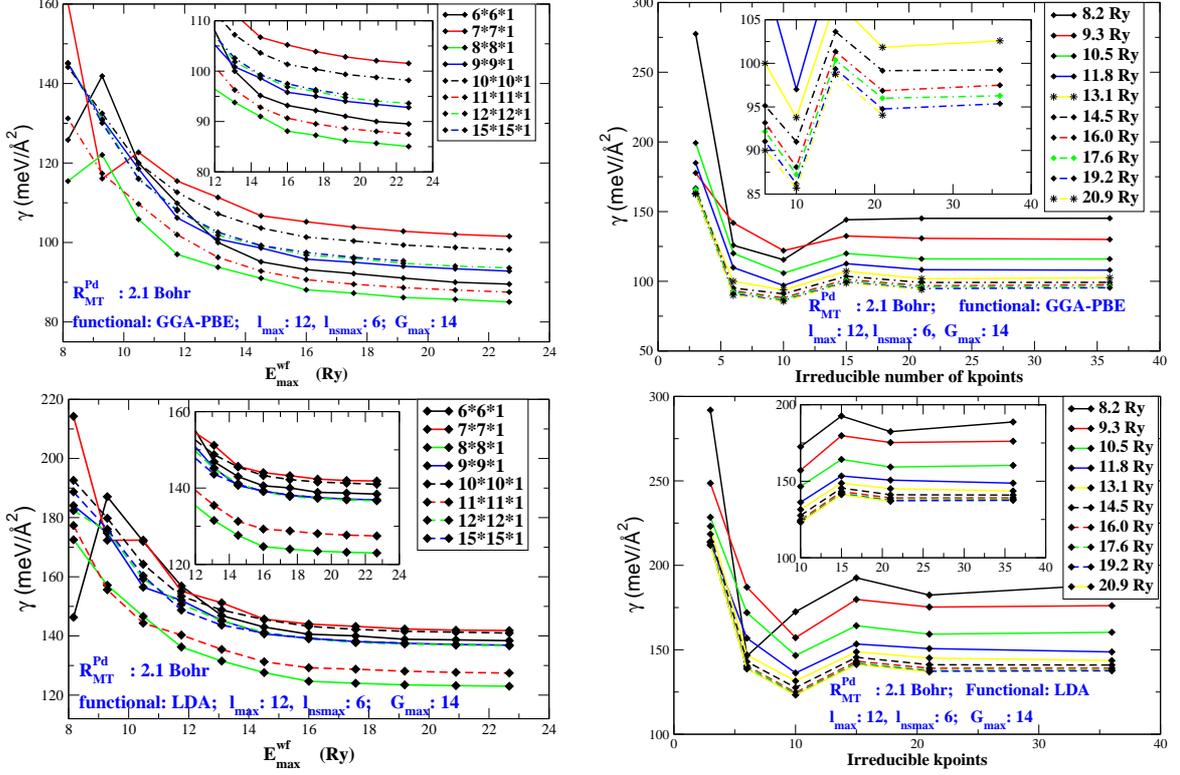


Figure B.4: Convergence test for the optimal energy cutoff and \mathbf{k} -points on a 5 layer Pd(100) slab using the GGA-PBE (upper two panels) and the LDA (lower two panels) functional.

using again the GGA-PBE and LDA functional. From Fig. B.4, it can be discerned that again a convergence to within $\pm 5 \text{ meV}/\text{\AA}^2$ can be reached for $E_{\text{max}}^{\text{wf}} = 16.0 \text{ Ry}$ and more than 15 irreducible \mathbf{k} -points (k -mesh: $(9 \times 9 \times 1)$).

As mentioned before, the number of layers in the slab is another important parameter in the surface simulation. In our slab model, we therefore increased the number of layers to construct different slabs (3, 5, 7, 9 and 11 layers of Pd(111) and Pd(100) slabs), while keeping the total thickness of the supercell (slab+vacuum) fixed. The vacua in all cases are large enough ($>13 \text{ \AA}$ in the Pd(111) supercell and $>11 \text{ \AA}$ in the Pd(100) supercell) to avoid the interaction between surfaces of consecutive slabs (see vacuum tests below). The optimal basis set parameters from the above tests were used to calculate the Pd(111) and Pd(100) surface energies of the different slabs, both with the GGA-PBE and LDA functional. As apparent from Fig. B.5, the curves show a small oscillation with the number of layers, but the differences are very small ($\pm 2 \text{ meV}/\text{\AA}^2$ for GGA-PBE and $\pm 5 \text{ meV}/\text{\AA}^2$ for LDA). 5 layers is therefore good enough for the clean surface calculation. Addressing finally the finite vacuum thickness, we used 7 layer slabs and halved and doubled the standard vacuum thickness. As apparent from Table B.2, the surface energy of each kind of low-Miller-index surface is hardly changed (within $\pm 1 \text{ meV}/\text{\AA}^2$) when the vacuum thickness is larger than 10 \AA .

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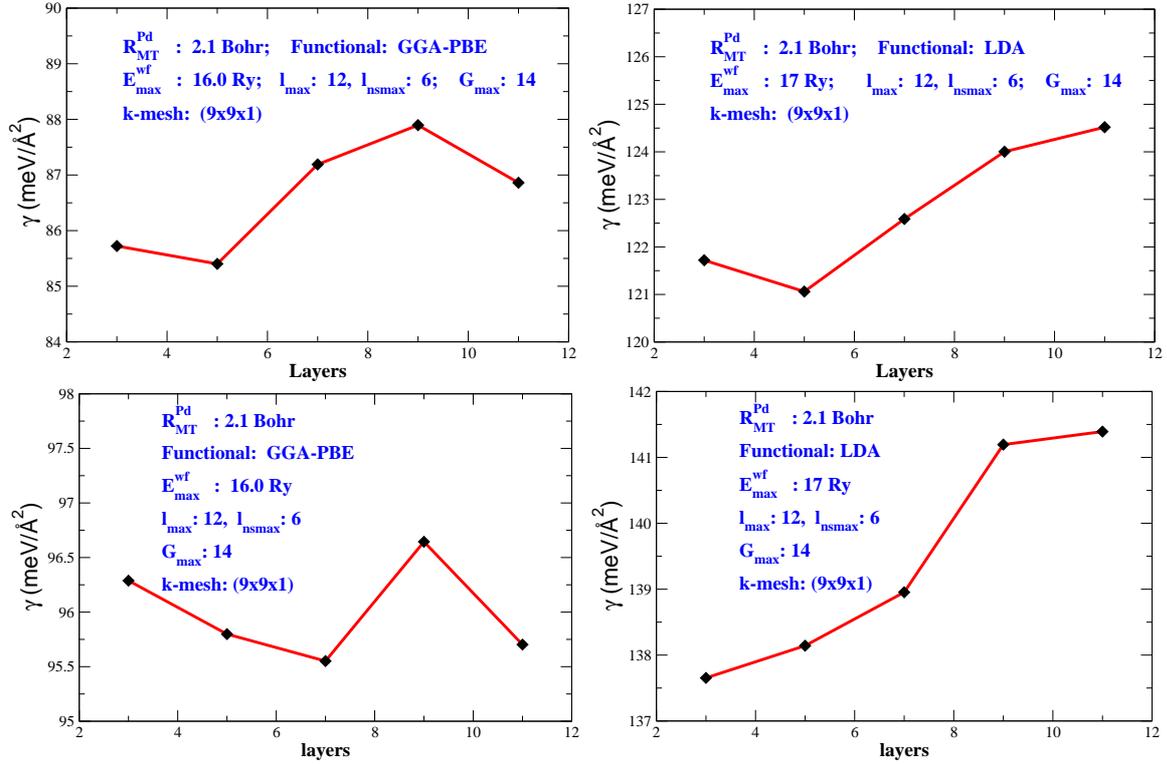


Figure B.5: Convergence test for the optimal layer number for Pd(111) (upper two panels for the GGA-PBE and LDA functional, respectively) and Pd(100) (lower two panels for the GGA-PBE and LDA functional, respectively). Note the scale on the y-axis.

Table B.1: Optimized basis set parameters for the clean Pd(111) and Pd(100) surface.

		E_{\max}^{wf} (Ry)	k-mesh	K_{irre}	layers
Pd(111)	GGA	16.0	$(9 \times 9 \times 1)$	12	5
	LDA	16.0	$(9 \times 9 \times 1)$	12	5
Pd(100)	GGA	16.0	$(9 \times 9 \times 1)$	15	5
	LDA	16.0	$(9 \times 9 \times 1)$	15	5

The determined basis set and supercell parameters are finally collected in Table B.1. With these parameters the computed values for the surface energy are $87 \text{ meV}/\text{\AA}^2$ and $96 \text{ meV}/\text{\AA}^2$ for Pd(111) and Pd(100) within the GGA-PBE, respectively. They are much smaller than the corresponding values in the LDA calculation, $122 \text{ meV}/\text{\AA}^2$ and $139 \text{ meV}/\text{\AA}^2$ in our work or corresponding LDA results from ref. [114, 123] for Pd(111) and Pd(100), respectively. As expected the surface energy of Pd(100) is larger than the one of Pd(111), as the Pd(100) surface is more open than the Pd(111) surface (see definition of *open* surfaces in Chapter 4).

Table B.2: Surface energies for various vacuum thicknesses (7 layer Pd(111) and Pd(100) slabs in supercells using the GGA-PBE functional).

	Pd(111)			Pd(100)		
Vacuum (\AA)	11	23	46	10	20	41
γ (meV/ \AA^2)	86.8	87.2	87.3	96.5	96.4	96.7

B.2 Oxygen at Pd(100)

The basis set parameter tests for the calculations with adsorbed oxygen at the Pd(100) surface use the binding energy (E_b) as the central quantity. In these calculations, the clean surface calculation for each configuration has the corresponding same basis set parameters as its adsorption configuration. We choose 3 representative configurations, 1O-Pd(100)(1 \times 1), p (2 \times 2) and c (2 \times 2), to carry out energy cutoff tests (left panel of Fig. B.6). From the figure, the absolute binding energies of each configuration show a slow convergence. The relative binding energies of each configuration compared to the 1O-Pd(100)(1 \times 1) configuration, however, are converged very well to within 10 meV/O atom above 20 Ry. For the determination of lateral interactions, it is primarily those energy differences that matter and we correspondingly use 20 Ry as the optimum energy cutoff for all DFT calculations. At this cutoff, Fig. B.6 shows that the absolute binding energy is converged to within 150 meV/O atom. A similar test for the k-mesh summarized in the right panel of Fig. B.6 reveals a (12 \times 12 \times 1) mesh as the optimum k-mesh. One reason for that is that the binding energies are converged to within 5 meV/O atom, and another one is \mathbf{k} -points compatibility for various O-Pd(100) cells. In these cells, the k-meshes of configurations are different due to the different Brillouin zone sizes. Our target is to get consistent lateral parameters from the binding energies of configurations. In these cells to cancel the error from different BZ sampling one uses compatible k-meshes and the (12 \times 12 \times 1) mesh can be suitably divided by all our calculated surface unit cells. For example, the compatible k-mesh of O-Pd(100)(3 \times 3) is (4 \times 4 \times 1), and so on.

Fig. B.7 shows the layer and vacuum thickness tests for the 1O-Pd(100)(1 \times 1) configuration with full surface relaxation. The binding energies are converged to within 15 meV/O atom for slabs with more than 5 layers. When the vacuum thickness is larger than 10 \AA , the binding energies are also fully converged. The thereby determined computational setup for O-Pd(100) is the following: 20 Ry energy cutoff, compatible k-meshes to a (12 \times 12 \times 1) grid in (1 \times 1) cells, 5 layer slabs, and 12 \AA vacuum thickness.

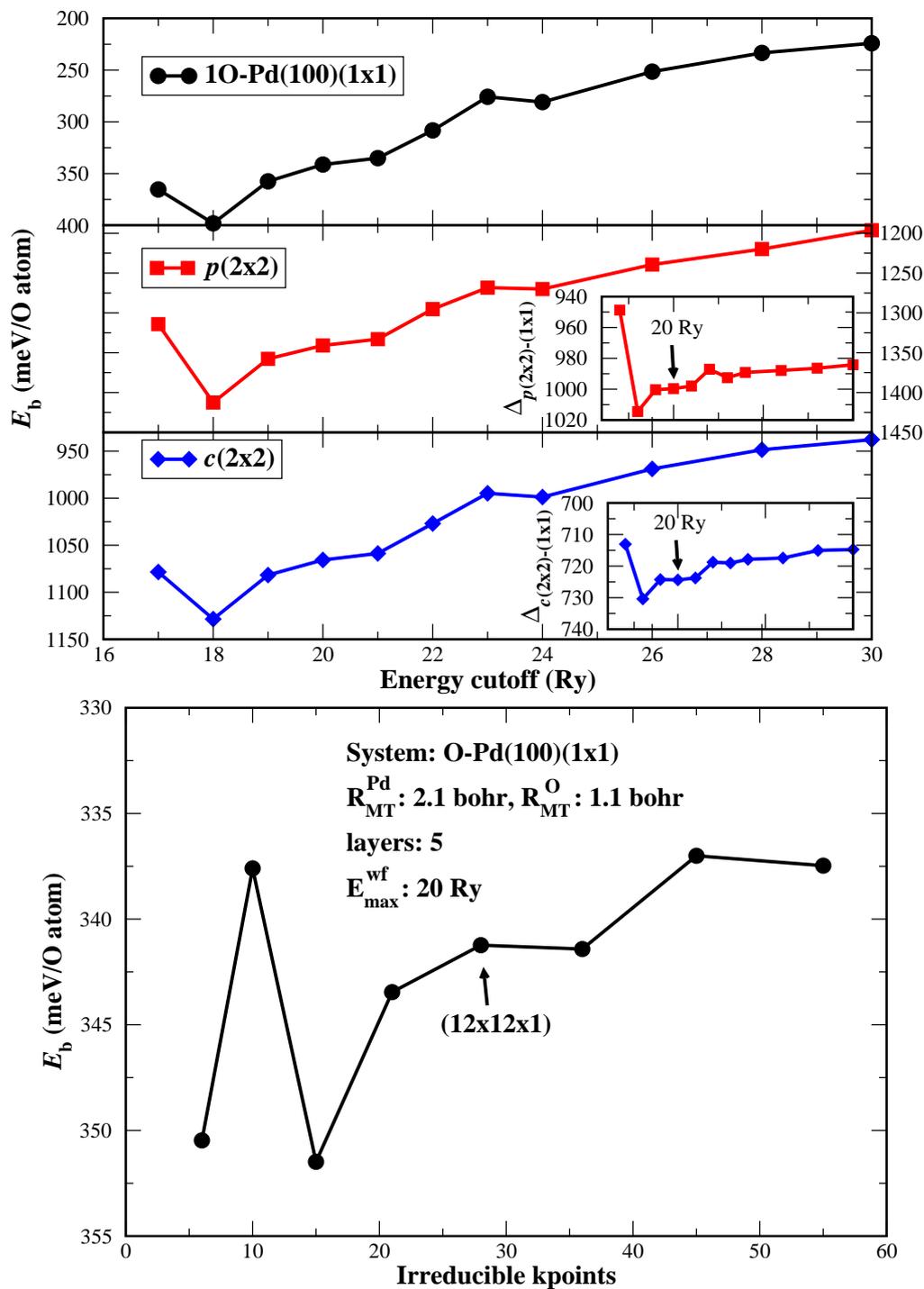


Figure B.6: Top panel: Cutoff convergence test for the 1O-Pd(100)(1x1), p(2x2), and c(2x2) oxygen adsorption configurations. Above 20 Ry, the relative binding energies (insert panels) compared to the binding energy of 1O-Pd(100)(1x1) are converged to within 10 meV/O atom. Bottom panel: k-mesh test for 1O-Pd(100)(1x1). (12x12x1) is selected as the optimum k-mesh.

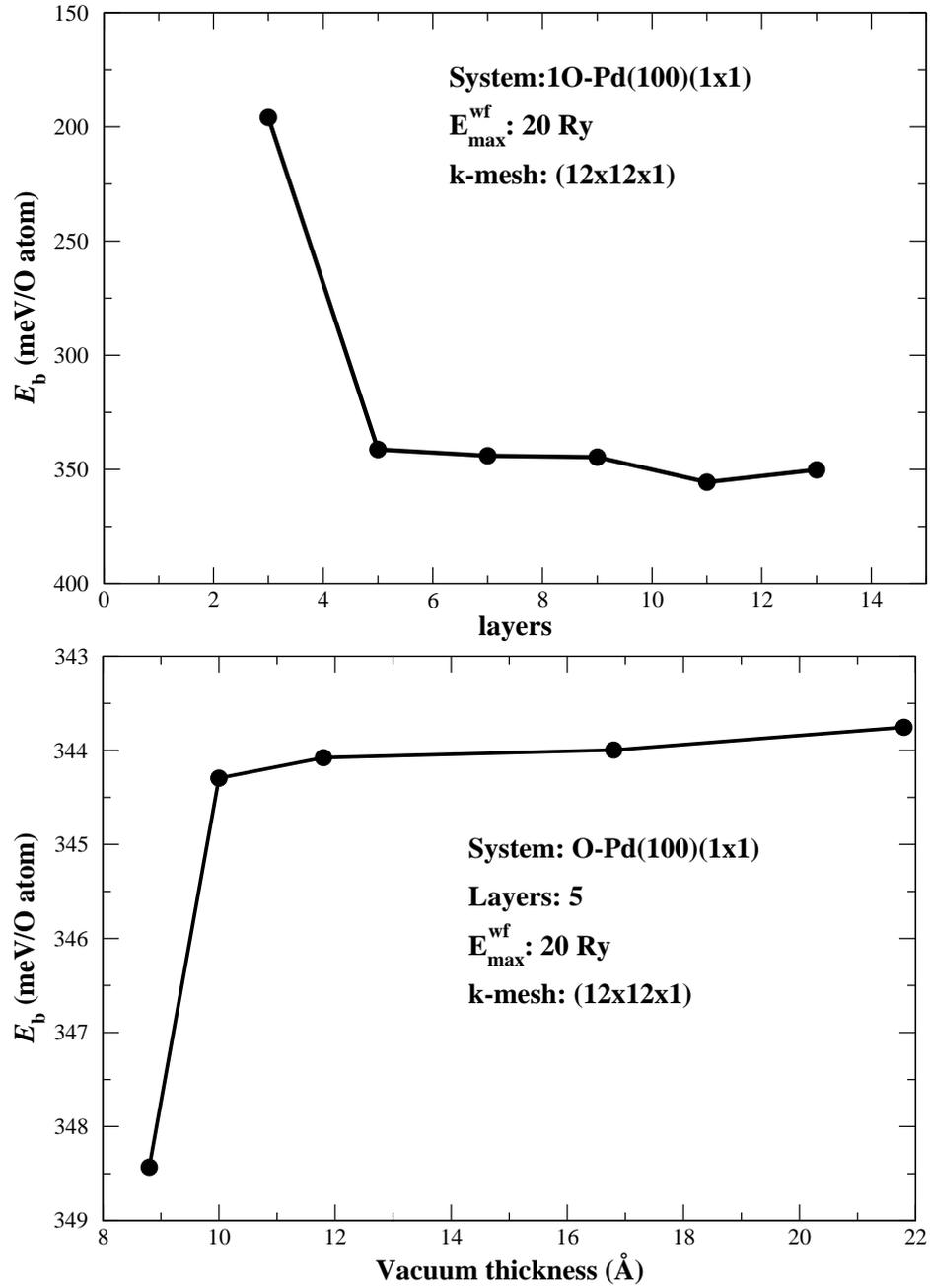


Figure B.7: Top panel: Convergence test for the optimum number of layers for 1O-Pd(100)(1x1) configuration. Bottom panel: Vacuum thickness test.

