Part IV

Appendix

Appendix A

Bulk Pd

Palladium (Pd) is a late $4d$ transition element. Its atomic number is 46 and its atomic configuration is [Kr]$4d^{10}$. In the periodic table of the elements, its nearest neighbors are Rh ([Kr]$5s^1 4d^8$) and Ag ([Kr]$5s^1 4d^{10}$). Bulk palladium crystallizes in the face-centered cubic (fcc) structure and the experimental value for the palladium lattice constant is a_{exp}=3.8903 Å[138]. In order to study the bulk properties of Pd we use the following (L)APW+lo computational parameters: A muffin-tin radius $R_{\text{MT}}^{\text{Pd}}$=2.1 bohr (1 Å=0.529177 bohr) is used throughout[1]. Using basis set parameters as determined in a previous PhD thesis [139], total energies at different lattice constants were calculated using the Wien2k code [33]. The equilibrium unit cell volume V_0 (connected to the equilibrium lattice constant a_0 by $a_0^3 = V_0$ in the cubic structure) is determined by minimization of the total energy function, $E(V)$. The bulk modulus $B(T, V)$ is then related to the curvature of the total energy function $E(V)$ at the equilibrium value.

$$B(T, V) = V \frac{\partial^2 E}{\partial V^2}\Big|_T \tag{A.1}$$

In practice, one evaluates the energy for different unit cell volumes (different lattice constants), and then fits them using an equation of state of the solid. The lattice constant of the Pd cubic unit cell was varied from 3.611 Å to 4.403 Å in 0.1 Å steps, and more points were used near the experimental lattice constant (3.8903 Å). The equilibrium value was then obtained using a Murnaghan equation of state fit [140−142] (Eq. A.2). We additionally varied the number of data points actually used in the Murnaghan fit (Fig. A.1 and Fig. A.2) to ensure that this had no influence on the final equilibrium lattice constant.

$$E(V) = E(V_0) + \frac{B_0 V}{B_0'(B_0' - 1)}[B_0'(1 - \frac{V_0}{V}) + (\frac{V_0}{V})^{B_0'} - 1] \tag{A.2}$$

[1]From the experimental Pd lattice constant, the maximum R_{MT} without overlapping sphere is 2.5 bohr. However at surfaces and in particular in oxygen chemisorption studies the R_{MT} is also limited by the quite short Pd-O bond length (∼3.8 bohr). Accounting also for the expected significant relaxation at vicinal surfaces, we therefore chose the smaller value of 2.1 bohr, which then also allows for a reasonable O muffin-tin radius.

where B_0' is the derivative of the bulk modulus with respect to pressure p=0. In Fig. A.1 and Fig. A.2, the equilibrium lattice constant is determined as 3.95 Å and 3.84 Å using GGA-PBE and LDA as exchange-correlation (xc) functionals, respectively.

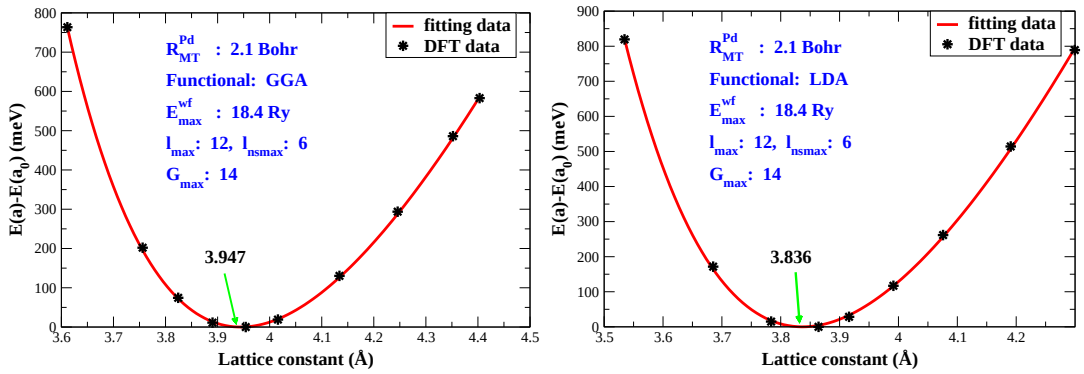

Figure A.1: Determination of the equilibrium lattice constant for the fcc Pd structure for the GGA-PBE and LDA functional by Murnaghan fitting (Eq. A.2): a_0^{GGA}=3.947 Å, a_0^{LDA}=3.836 Å.

The reason why atoms can combine together to construct a solid is that the total energy of the solid is lower than the sum of the energies of the corresponding isolated atoms. In other words the solid is more stable. The process is exothermic, and the released excess energy is called *cohesive energy*. It is defined as,

$$E_{\mathrm{coh}} = -(E_{\mathrm{bulk}}(a_0) - \sum_i E^i_{\mathrm{iso}}) \tag{A.3}$$

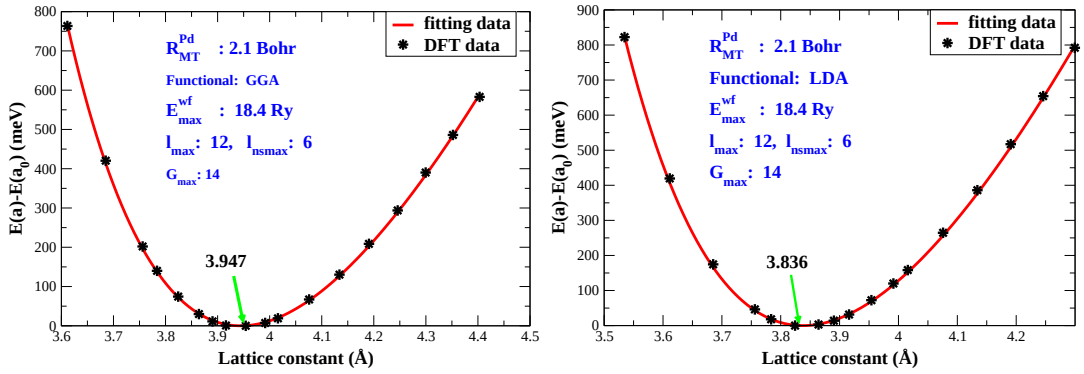

Figure A.2: Determination of the equilibrium lattice constant for the fcc Pd structure for the GGA-PBE and LDA functional with more points than in Fig. A.1. a_0^{GGA}=3.947 Å, a_0^{LDA}=3.836 Å.

Table A.1: Comparison of calculated lattice constant and bulk modulus using the GGA-PBE and LDA functional with experimental data.

	Experiment [20, 138]	GGA-PBE	$\Delta_{\mathrm{GGA-PBE}}$	LDA	Δ_{LDA}
a_0 (Å)	3.89	3.95	1.4%	3.84	-1.4%
B_0 (Mbar)	1.80	1.57	-13.8%	2.16	20%
E_{coh} (eV/atom)	3.94	3.68	-6.6%	5.08	28.9%

where $E_{\mathrm{bulk}}(a_0)$ indicates the total energy of the bulk, i indicates the number of atoms in the bulk, and E^i_{iso} is the total energy of isolated element atom, i. The total energy of an isolated Pd atom is calculated with a supercell geometry *i.e.* a Pd atom is placed in the center of a huge periodically repeating unit cell. The cell size (12 bohr × 13 bohr × 14 bohr) is used to avoid interaction with the periodic images. The non-cubic size of the cell is used to prevent the Wien2K code from symmetry averaging the electron density. In the absence of dispersion in the small Brillouin zone, one k-point at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is enough for this calculation, which in addition is performed spin-polarized to account for the proper Hund occupation of the orbitals. With this procedure, values of $E^{\mathrm{GGA}}_{\mathrm{coh}}$=3.68 eV/atom and $E^{\mathrm{LDA}}_{\mathrm{coh}}$=5.08 eV/atom were computed for the cohesive energy with GGA-PBE and LDA, respectively. The experimental value of the bulk Pd cohesive energy is 3.94 eV/atom [20]. The lattice constant, bulk modulus and cohesive energy from experiment, GGA-PBE and LDA calculations are tabulated in Table A.1, from which the known overbinding of the LDA and overcorrection of the GGA-PBE become apparent [108, 109, 112, 113]. On the other hand, the data in Table A.1 are in excellent agreement with a previous study in the group using the earlier WIEN97 LAPW code, which gave $a = 3.944\,\text{Å}$ and $B = 1.63\,\text{MPa}$, respectively [111].