Parameterization and validation of Pd and Pd nanoclusters using SCC-DFTB

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Abstract. The self-consistent-charge density functional tight binding (SCC-DFTB) approach has been used to describe large scale Pd systems with accuracy and precision than the density functional theory method [1]. DFTB+ has been used to develop a set of SCC-DFTB parameters for Pd-Pd atomic pairs of elements. The SCC-DFTB parameterization has been performed to describe bulk Pd structure and nanoclusters. It was found that the predicted equilibrium lattice parameters using the recently developed set of SCC-DFTB parameters are in good agreement with the experimental data. The Pd-Pd interaction in the Pd_n (n = 2 – 6 atoms) nanoclusters gives better prediction of bond length with DFTB+ than the conventional DFT [2, 3]. Furthermore, their calculated bond lengths lie within 0.1% with the available literature data [4].

1. Introduction

Noble metals such as silver and gold, together with the platinum group metals (PGMs) namely: platinum, palladium, ruthenium, rhodium, iridium and osmium have been extensively studied recently, and are regarded as good catalysts for chemical and electrochemical reactions [5, 6]. These metals are mostly used as catalysts in fuel cells and emissions control technology. Unfortunately, due to their excessive production cost and poor durability, fuel cells including direct methanol (DM) and proton exchange membrane (PEM) fuel cells are finding it difficult to reach the desired markets [5].

In recent years, metal nanoparticles have been of interest in several areas including physics and material sciences for application in heterogeneous catalysis, fuel cells and chemosensors. The properties of these nanoparticles were found to differ from those of bulk materials [7]. It has also been reported that metal atoms in small clusters exhibit particular electronic, structural and chemical properties that relate to their catalytic activities [8, 9].

The catalyst that is commonly used in proton exchange membrane fuel cells (PEMFC) is the platinum-based catalyst, however, because of the high cost [10] and limited resources of platinum, further developments become more challenging and costly, thus other materials are now being taken into consideration. For example, palladium nanoclusters because of their similar electronic

configurations, lattice constants and cheaper than platinum [4], and ability of high methanol-tolerant, are considered a promising future catalyst.

In the current paper, we use DFTB+ code to develop a set of SCC-DFTB parameters for Pd-Pd atomic pairs of elements. The set of parameters has been developed to describe Pd structure and Pd_n (n = 2 – 6 atoms) nanoclusters. The optimised parameters were validated by performing a geometry optimization on bulk Pd structure and the dependence on bond length of the Pd_n nanoclusters are also evaluated.

2. Computational methodology

2.1. SCC-DFTB method

The self-consistent density functional tight-binding (SCC-DFTB) method is used to improve the description of the Pd-Pd bonds for Pd bulk and nanoclusters, when the balance of charges between pairs of atoms is small. It is an approximate method derived from DFT and is based on the second order expansion of the Khohn-Sham total energy with respect to charge density fluctuations [11-14], given by

$$E_{tot} = E_{BS} + E_{rep} + E_2(n, \Delta n), \tag{1}$$

where the total energy E_{tot} includes the electrostatic-interaction term $E_2(n, \Delta n)$ to the standard tight-binding E_{BS} and the short range repulsive E_{rep} term. The electrostatic-interaction accounting for the charge fluctuations is written as

$$E_2(n, \Delta n) = \frac{1}{2}\sum_{x,y}^{M} \gamma_{xy} \Delta q_x \Delta q_y. \tag{2}$$

This term is represented by the Mulliken charges based atomic charge fluctuation Δq_x and Δq_y together with the analytical interpolating function, γ_{xy}.

2.2. SCC-DFTB calculations

The SCC-DFTB parameterization of bulk Pd and nanoclusters was carried out using DFTB+ code [15], and geometry optimizations calculations were performed with all parameters allowed to relax. Thus the major properties such as bond length and electronic aspects of the Pd system are produced with agreement to the experimental results. The GGA-PBE and LDA-PWC exchange-correlation function coupled with DND basis set was used. Mankhorst-Pack grids [16] for k-points sampling of 6x6x6 was used for the bulk palladium structure. The smart algorithm was applied with a maximum force of 0.5 Kcal/mol/Å. During geometry optimization, thermal smearing was varied from 0.005 to 0.3 Ha.

3. Results and discussion

The developed SCC-DFTB set of parameters for Pd-Pd pair of elements for describing Pd system was validated by performing a geometry optimization on the bulk Pd structure. Two sets of parameters were developed using different exchange-correlation fuctionals namely GGA and LDA. The obtained structural properties were compared with the experimental results to validate the developed set of parameter as shown in Table 1. We notice that, as the thermal smearing was increased, the lattice parameters of bulk Pd structure for both set of parameters decreases. More importantly, a thermal smearing of 0.2 and 0.3 Ha for the set of parameters using LDA and GGA, respectively, was sufficient to adjust the lattice parameters to 3.891 Å, in good agreement with the experimental results. It was also observed that LDA gives better structural lattice, than the set of parameters using GGA exchange-

correlation functional. Moreover, the GGA is found to overestimate the lattice constants while LDA underestimates, as expected. We also note that the smearing of 0.2 Ha correspond to the energy of -48.735 eV/atom using LDA, which is in reasonable energy change as the smearing is increased from 0.005 Ha compared to GGA.

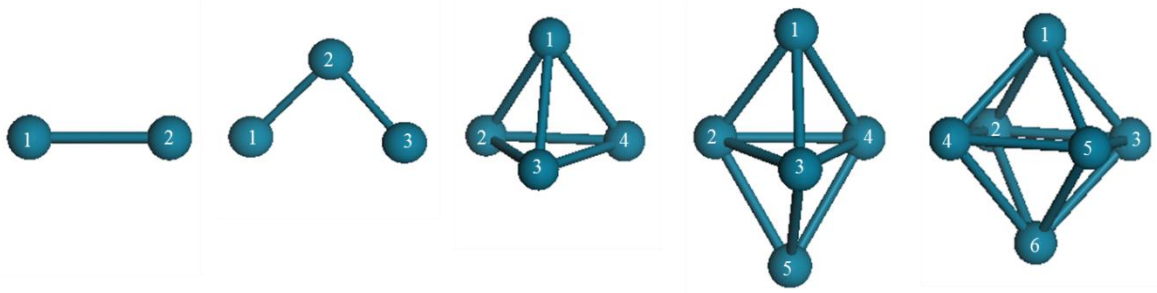
Table 1. Comparison of the structural properties of bulk Pd with experimental data.

Properties	SCC-DFTB						Experimental[a]
	GGA			LDA			
Smearing (Ha)	0.005	0.200	0.300	0.005	0.200	0.300	-
a (Å)	4.075	3.991	3.891	3.896	3.891	3.683	3.891
Volume (Å^3)	67.692	63.555	58.896	59.144	58.896	49.975	58.896
Energy (eV/atom)	-45.795	-44.708	-40.133	-48.922	-48.735	-45.187	-

[a] The lattice and volume were taken from ref [4]

The various palladium nanoclusters were constructed starting from the optimized bulk Pd. The structures (a) and (b) represent the planar structures while (c), (d) and (e) represent the three dimensional structures namely, triangular pyramid, triangular bipyramid and tetragonal bipyramid, respectively, as shown in Fig. 1.

The planar structure in (a) is a Pd_2 and (b) representing Pd_3 nanocluster, is a line style structure with 90˚ angle between atoms 1 and 3. The triangular pyramid is made up of an isosceles triangle as a base with three scalene triangles above. The triangular bipyramid is made up of an isosceles triangle in the middle with three unequal sided taper on both sides. The tetragonal bipyramid used for these calculations has a square in the middle and four isosceles sides both below and above.



(a) (b) (c) (d) (e)

Figure 1. The structures of Pd_n nanoclusters (a) Pd_2, (b) Pd_3, (c) Pd_4, (d) Pd_5 and (e) Pd_6.

The Pd_n nanoclusters were optimized using the developed set of parameters with LDA exchange correlation functional and applied a thermal smearing of 0.2 Ha. The possible Pd-Pd bonds in Pd_n (n = 2 – 6 atoms) were calculated and are shown in Table 2. The average Pd_n bond length increased with an increase in the size of the nanoclusters. The calculated bond lengths and the values obtained from the literature have a difference of 0.1 Å.

Table 2.comparism of Pd-Pd average bond lengths with literature and total energies per atom (E_T) of Pd_2 to Pd_6 nanoclusters.

Nanocluster	Bond Length (Å)		E_T (eV/atom)
	SCC-DFTB	Literature	
Pd_2	2,679	2.480[a]	-39,0645
Pd_3	2,684	-	-39,941
Pd_4	2,686	2.580[b]	-42,039
	2,686	2.840[b]	
	2,686	2.580[b]	
	2,686	2.580[b]	
	2,686	-	
Pd_5	2,692	-	-42,774
Pd_6	2,694	-	-43,425

[a] The literature bond length was found from ref. [2] and the similar value was also obtained in ref. [3].
[b] The experimental values were obtained from ref [17].

4. Conclusions

The SCC-DFTB sets of parameters for Pd-Pd atomic pair of elements were successfully developed. The lattice parameters for bulk Pd structure obtained using LDA are in better agreement with the experimental results compare to GGA. In addition, less smearing was required to adjust the lattice parameters to the experimental value of 3.891 Å when using LDA. For Pd_n nanocluster, the Pd – Pd bond lengths were found to be within 0.1% with the available literature. The total energy per atom trend suggests that the Pd_6 is more favourable since it has the lowerst energy value, thus the energy is lowered with size of the nanocluster.

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