

# CNDO Studies of Electronic Structure of PdH<sub>x</sub>

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The highest stability of  $^1[\text{Pd}_{14}]^q$  cluster for  $q = -2$  is found by nonempirical quasi-relativistic CNDO method. The quantum-chemical calculations of  $^1[\text{Pd}_{14}\text{H}_2]^q$  clusters ( $q = 0, -2$ ) for different H—H distances indicate significant shifts of positions of energy minima for Pd—H and H—H subsystems. The dependence on  $q$  is not important.

During the electrolysis of deuterated water on Pd electrodes the anomalous heat evolution with neutron and  $\gamma$  radiation has been observed. This experiment has been misinterpreted as the nuclear fusion of deuterium atoms dissolved in the palladium [1].

The best theoretical treatment in the electronic structure investigations is provided by the MO—LCAO—SCF methods at nonempirical level. The results for Pd—H and Pd—D systems are the same because the total energy is independent of the isotope mass for frozen atomic positions. The quantum chemistry studies have been concentrated on the problem of the H—H interatomic distance with the conclusion that this distance is even longer than in the isolated dihydrogen molecule. Consequently, the forces sufficient to get two hydrogen (deuterium) atoms significantly closer than in diatomic H<sub>2</sub> (D<sub>2</sub>) molecule appear unlikely and the nuclear fusion is very improbable [2, 3]. Due to such unidirectional orientation, the electronic structure of the model system has not been studied in detail and alternative mechanisms have not been investigated.

## METHOD

Palladium crystallizes in  $\text{O}_h^5\text{-Fm}3\text{m}$  space group with lattice parameter  $a_0 = 0.38808$  nm. It possesses the special ability to dissolve the hydrogen. During this absorption the lattice extension (up to  $a_0 = 0.407$  nm for  $\beta\text{-PdH}_x$ ) is observed [4, 5].

Our model systems are based on Pd<sub>14</sub> cluster in the experimental geometry of the face-centred cubic unit cell. The atomic coordinates may be described as follows

$$\begin{array}{ccc} \pm 0.5 a_0, & \pm 0.5 a_0, & \pm 0.5 a_0 \\ \pm 0.5 a_0, & 0, & 0 \\ 0, & \pm 0.5 a_0, & 0 \\ 0, & 0, & \pm 0.5 a_0 \end{array} \quad (1)$$

Additional two hydrogen atoms of  $[\text{Pd}_{14}\text{H}_2]$  cluster are arranged in (0, 0, 1) axis with H coordinates  $x = y = 0$  and  $z = \pm(a_0 - r)$ , where  $r$  is the distance from H to the nearest face-centred Pd atom,  $r(\text{Pd—H})$ . This is related to the H—H interatomic distance by the relation

$$r(\text{H—H}) = a_0 - 2 r(\text{Pd—H}) \quad (2)$$

Nonempirical quasi-relativistic CNDO/1 method with  $\beta$  parameters scaled by the factor  $K = 1.4$  [6, 7] has been used for MO—LCAO—SCF calculations of  $^1[\text{Pd}_{14}\text{H}_n]^q$  clusters with various total cluster charges  $q$  and  $n = 0$  or 2. All model systems are in singlet electron states as no paramagnetism is supposed in real PdH<sub>x</sub> systems [2—5].

## RESULTS AND DISCUSSION

The dependence of the total energy  $E$  of the  $^1[\text{Pd}_{14}]^q$  on the total cluster charge  $q$  for  $a_0 = 0.38808$  nm is studied in the first step. Our results indicate (Fig. 1) that the most stable system corresponds to  $q = -2$  (the absolute minimum for

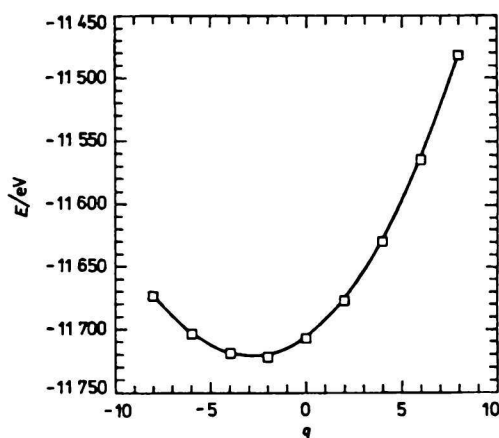


Fig. 1. The dependence of the total energy  $E$  of  $^1[\text{Pd}_{14}]^q$  clusters on its total charge  $q$ .

$q = -3$  demands an unpaired electron in our cluster) and not to  $q = 0$ . This is in accordance with the experimental condition of Pd cathode for hydrogen evolution.

In the next step the model systems of  $^1[\text{Pd}_{14}\text{H}_n]^q$  with  $a_0 = 0.407$  nm were studied for  $q = 0$  and  $-2$ .

The total energy of the whole system  $E$  exhibits the minimum for  $r(\text{Pd}-\text{H})$  between 0.14 and 0.15

nm, i.e.  $r(\text{H}-\text{H}) = 0.12$  nm, for both the systems (Fig. 2). This is in agreement with literature data for *ab initio* calculations of  $[\text{Pd}_6\text{H}_2]$  systems [2, 3]. The negatively charged systems are more stable than the neutral systems. The energy barrier for  $r(\text{Pd}-\text{H}) \rightarrow 0$  is much higher than for  $r(\text{H}-\text{H}) \rightarrow 0$ .

The situation is changed if restricting to the bi-centric part of the total energy  $E(\text{Pd}-\text{H})$  related

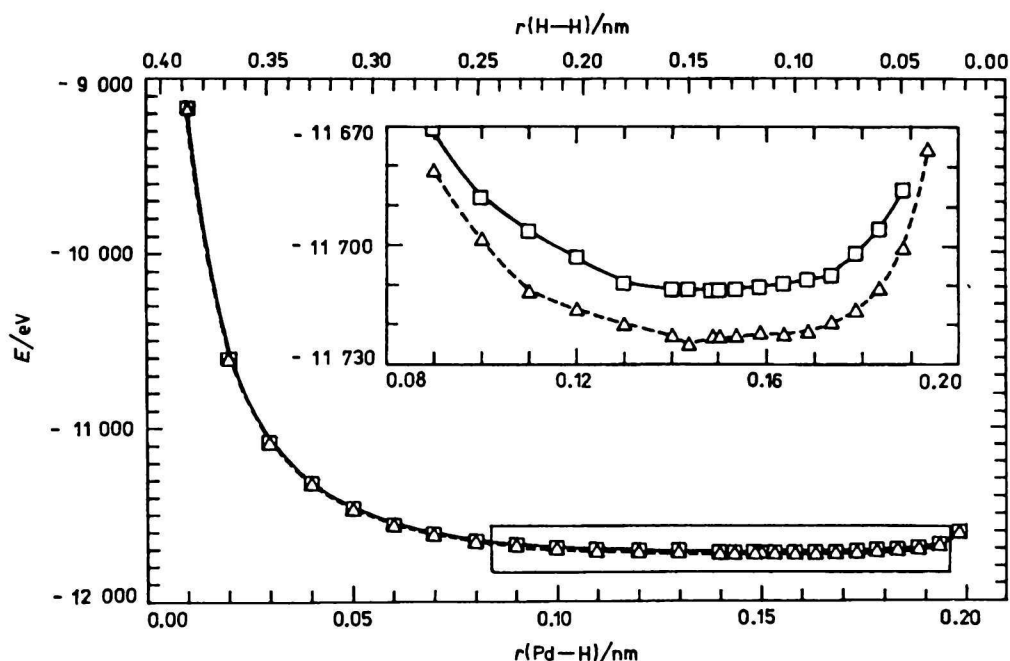


Fig. 2. The dependence of the total energy  $E$  of  $^1[\text{Pd}_{14}\text{H}_2]^q$  clusters on the interatomic distance  $r(\text{Pd}-\text{H})$ . Squares and triangles denote the systems with  $q = 0$  and  $q = -2$  total charges, respectively.

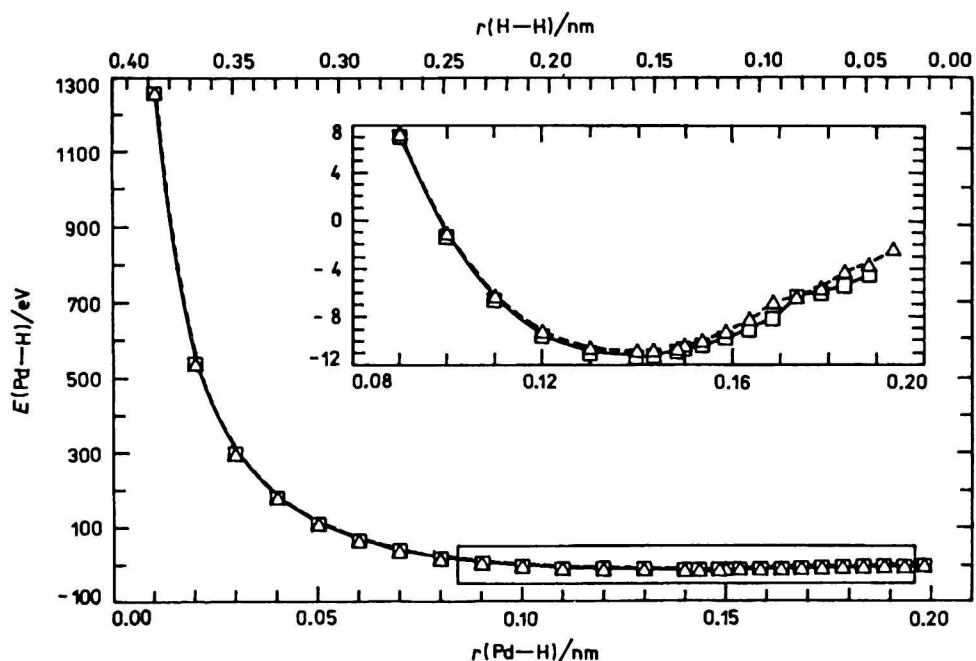


Fig. 3. The dependence of the bicentric part of the total energy related to the Pd-H subsystem  $E(\text{Pd}-\text{H})$  of  $^1[\text{Pd}_{14}\text{H}_2]^q$  clusters on the interatomic distance  $r(\text{Pd}-\text{H})$  (symbols as in Fig. 2).

to the interaction of H with the nearest (face-centred) Pd atom only (Fig. 3). The energy minima for both the systems occur at  $r(\text{Pd}-\text{H}) = 0.14$  nm, but  $E(\text{Pd}-\text{H})$  for the neutral system ( $q = 0$ ) is a little bit lower.

If restricting to the bicentric part of the total energy  $E(\text{H}-\text{H})$  related to the mutual interactions of both H atoms only (Fig. 4), the energy minimum

is at  $r(\text{Pd}-\text{H}) = 0.17$  nm corresponding to  $r(\text{H}-\text{H}) = 0.07$  nm. Another very shallow minima at higher  $r(\text{H}-\text{H})$  distances are out of interest.

The total dihydrogen charges  $Q(\text{H}-\text{H})$  (Fig. 5) are positive with maximal values of ca. +0.8, which corresponds to  $\text{H}_2^+$ . Minimal  $Q(\text{H}-\text{H})$  values of ca. +0.2 are at  $r(\text{H}-\text{H}) = 0.33$  nm or  $r(\text{Pd}-\text{H}) = 0.04$  nm.

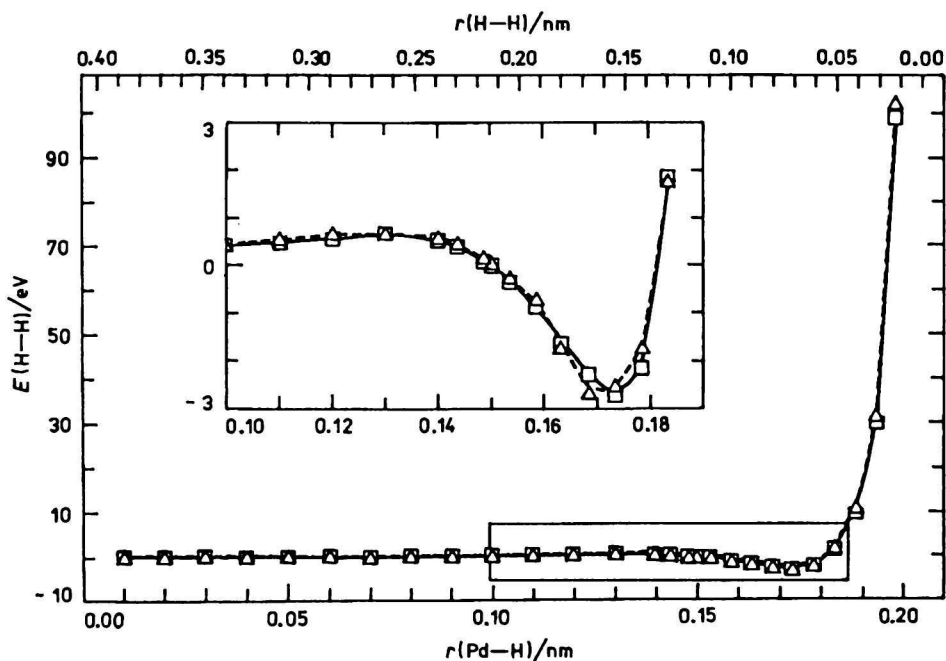


Fig. 4. The dependence of the bicentric part of the total energy related to the H—H subsystem  $E(\text{H}-\text{H})$  of  $^1[\text{Pd}_{14}\text{H}_2]^q$  clusters on the interatomic distance  $r(\text{Pd}-\text{H})$  (symbols as in Fig. 2).

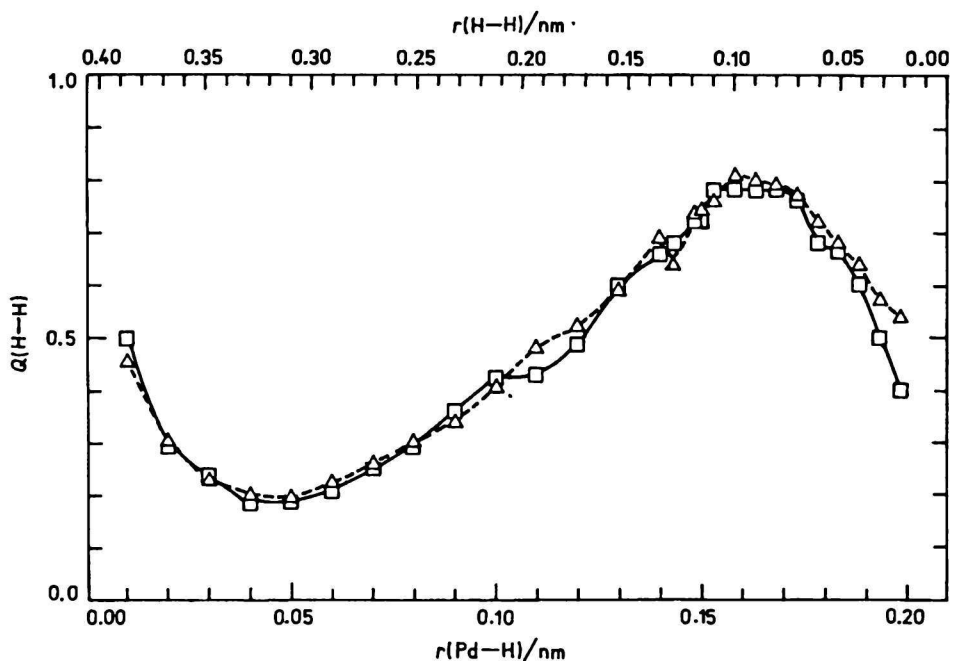


Fig. 5. The dependence of the total dihydrogen charges  $Q(\text{H}-\text{H})$  of  $^1[\text{Pd}_{14}\text{H}_2]^q$  clusters on the interatomic distance  $r(\text{Pd}-\text{H})$  (symbols as in Fig. 2).

Wiberg (bond strength) indices of Pd—H bond  $W(\text{Pd—H})$  (Fig. 6) exhibit maximal values of ca. 0.85 at  $r(\text{Pd—H}) = 0.06$  nm, *i.e.* nearly single bond ( $W = 1.0$ ).

Wiberg indices of H—H bond  $W(\text{H—H})$  exhibit maximal values of ca. 0.6 at  $r(\text{H—H}) = 0.01$  nm (Fig. 7) that is much weaker than the single bond. The bond strength for  $r(\text{H—H}) > 0.1$  nm is vanishing.

## CONCLUSION

Our results indicate that the energy profile is not significantly influenced by the total system charge. The negative charge is more advantageous. However, this does not hold for energies of Pd—H and H—H subsystems. This fact may be of a great importance for real systems exhibiting a large pos-

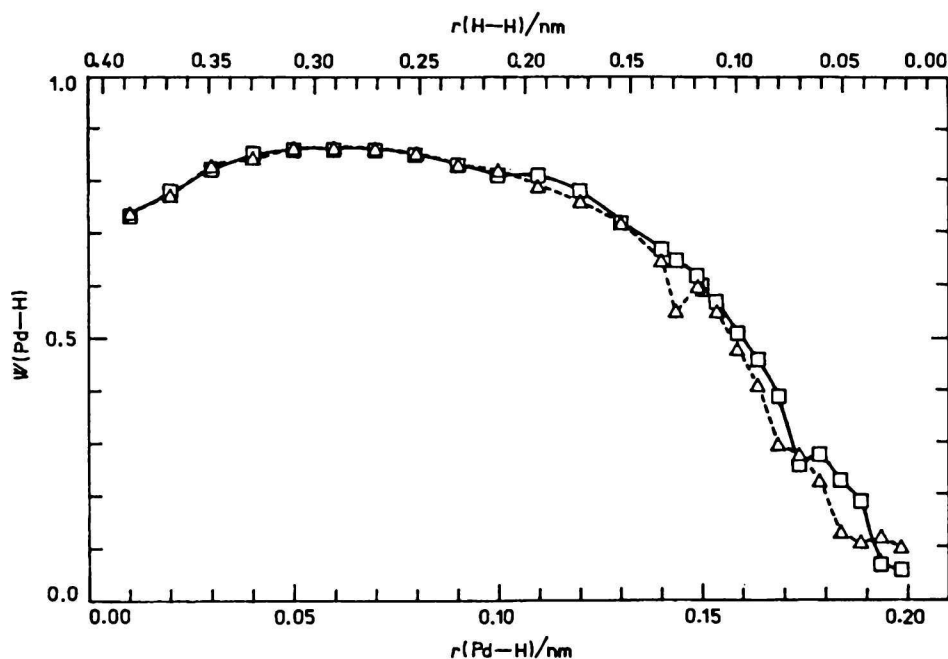


Fig. 6. The dependence of Wiberg indices of the Pd—H bond  $W(\text{Pd—H})$  of  $^1[\text{Pd}_{14}\text{H}_2]^q$  clusters on the interatomic distance  $r(\text{Pd—H})$  (symbols as in Fig. 2).

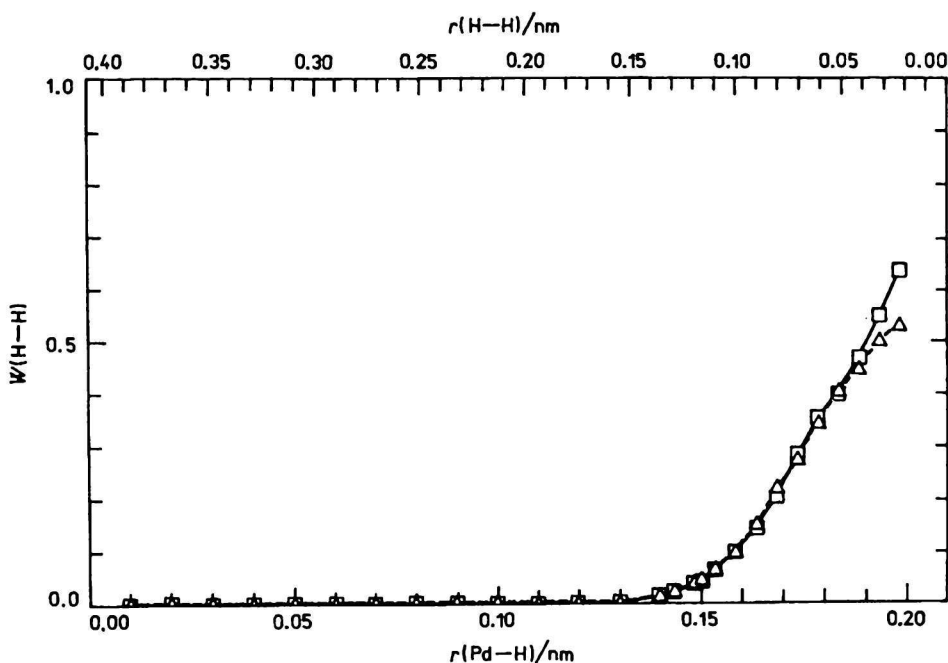


Fig. 7. The dependence of Wiberg indices of the H—H bond  $W(\text{H—H})$  of  $^1[\text{Pd}_{14}\text{H}_2]^q$  clusters on the interatomic distance  $r(\text{Pd—H})$  (symbols as in Fig. 2).

sibility of local fluctuations. The positions of energy minima of the whole system and its subsystems are significantly changed, too.

Finally it must be mentioned that the obtained results must be taken carefully because of the restrictions of the CNDO method and the cluster model used. Nevertheless, the calculated trends seem to be correct.

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# The Photocatalytic Degradation of Cyclic Acetals in Aqueous Titanium Dioxide Suspension

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The photocatalytic oxidation of 2-ethoxytetrahydropyran in aqueous titanium dioxide suspension in the presence of oxygen was studied. On the basis of quantum-chemical calculations, IR, FTIR, and UV—VIS spectroscopy and GC—MS analysis the reaction mechanism was proposed.

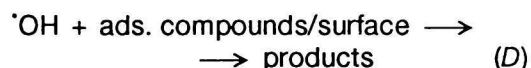
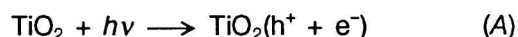
New photocatalytic processes for conversion of carbohydrates, starch and cellulose into hydrogen and carbon dioxide in the irradiated TiO<sub>2</sub> suspensions were investigated by Kawai and Sakata [1—3]. St. John *et al.* studied the photocatalytic degradation of glucose in aqueous suspension of titanium dioxide. Hydrogen and carbon dioxide were determined under inert atmosphere and CO<sub>2</sub> alone under oxygen atmosphere [4].

The mechanism of photocatalytic degradation of saccharidic structures was not yet published in detail.

During irradiation in the Pt/TiO<sub>2</sub> aqueous suspension the significant changes in the polymerization degree of hydroxyethylcellulose (HEC) and carbon dioxide evolution were observed [5]. The proposed mechanism of HEC polymer chain cleavage includes the attack of the photogenerated hydroxyl radical onto the C-1 atom of the hexopyranose unit [5]. EPR studies confirmed high concentra-

tions of hydroxyl radicals in the irradiated TiO<sub>2</sub> aqueous suspensions in the presence of oxygen [6].

The formation of the basic reactive intermediates on the irradiated titanium dioxide surface in aqueous suspension is described by the following equations [7]



where h<sup>+</sup>, e<sup>-</sup> are photogenerated hole and electron.

Information on electronic structure (charges) in the molecule implying the possible reaction centra