Bridge bond between potential energy surfaces and fuel cells on Pt-H$_2$ interaction

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Reaction mechanisms between catalyst (Pt) and one of the fuels (H$_2$) are found by means of DFT-B3LYP calculation, which represents a bridge bond between the theoretical calculations and the processes of fuel transformation in the fuel cells. All the closed shell energies involved in the process are obtained, starting when the platinum and the hydrogen are completely separated and ending until the hydrogen atoms separate and stay bound to the platinum, forming a new product. The equilibrium geometry of the latter system is reached with a broken H-H bond at an HPtH angle of about $90°$. The latter was obtained using the DFT-B3LYP method. The confidence in all of these results is based on the fact that the potential energy well of the Pt-H$_2$ interaction calculated using the DFT-B3LYP method is located between those calculated using Moller-Plesset and PSHONDO-IJKL-FOCK-CIPSI ab initio methods.

Keywords: Potential energy surfaces; fuel cells; platinum hydrgen interaction.

Se encontraron los mecanismos de reacción entre el catalizador Pt y uno de los combustibles (H$_2$) por medio de cálculos DFT-B3LYP, lo cual representa un vínculo entre los cálculos teóricos y el proceso de transformación del combustible en las celdas de combustible. Se obtuvieron todas las energías de capa cerrada en el proceso, empezando cuando el platino y el hidrógeno están completamente separados y terminando hasta que los átomos de hidrógeno se separan y quedan ligados al platino, formando un nuevo producto. La geometría de equilibrio de este sistema se alcanza con el enlace H-H roto en un ángulo HPtH de cerca de $90°$. Esto se obtuvo usando el método DFT-B3LYP. La confianza en todos estos resultados está basada en el hecho de que el pozo de energía potencial de la interacción Pt-H$_2$ calculado con el método DFT-B3LYP está localizado entre aquellos calculados con los métodos Moller-Plesset y PSHONDO-IJKL-FOCK-CIPSI.

Descriptores: Superficies de energía potencial; celdas de combustible; átomo de platino; molécula de hidrógeno.

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1. Introduction

The fuel cells (FC) depend on the interaction of one metal atom (Pt, Ru, Re, Cu,...) with a gas (H$_2$, O, CO, CH$_4$, CH$_3$-OH, C$_2$H$_5$-OH,...). The fuel cells are electrochemical devices that directly convert the chemical energy of a fuel to electrical energy. The energy that is required in the electrochemical transformation of the fuel can be established by means of the reaction mechanisms involved in the combustion. These mechanisms are associated with changes in energy, which is determined theoretically by means of quantum calculations. This permits the quantification of the energy required through the use of molecular simulation.

Mavrikakis *et al.*[i] clearly show the effect caused by the interaction between Pt(111) and methanol in an animated graphic of the potential energy of deprotonation of methanol in the platinum surface Pt(111). In the animated graphic we observe how methanol reacts at the surface of the catalyst as a function of the energy required to complete each step of deprotonation. Mavrikakis *et al.* [1-4] found the one-dimensional potential energy surface along the reaction co-ordinate for partial oxidation of methanol on a model of the Pt(111) surface, in whose animated graphic there appear only the two steps of the reaction, which illustrate one stage of the transition state.

First, the methanol molecule loses its hydroxyl hydrogen to yield a methoxy intermediate. Another atom H is expelled subsequently from methoxy to yield a formaldehyde molecule at the surface of the Pt. In addition, the abstraction of H will lead to CO formation, which poisons the Pt catalyst. It is also important to mention that they use a fully parallelized and efficient planewave total energy density functional theory (DFT)-based code for modeling elementary reaction steps on transition metal surfaces.

A similar effect occurs when using other reactants such as Pt and H$_2$ in our case, so that the theoretical prediction of the interaction energy surfaces is of fundamental interest. From the latter information, both the adsorption energy and the activation energy for one H$_2$ molecule of gas on a surface of a Pt metal atom is obtained. The adsorption energy is equivalent to the equilibrium energy in among oxide-reductive reactions,

whereas the activation energy corresponds to the energy of hydrogen oxidation. This represents a bridge bond of information that helps in the design of fuel cells. Some theoretical studies about the capture of the hydrogen molecule by platinum atoms were carried out by different investigators [5-10].

As additional information, it is important to mention, however, that the metal-gas reactions can be altered when some other type of energy acts on the system. If this new energy excites the metal to a certain excited state, then the trajectory in the graph of the reaction is different. We may excite via temperature, or pressure, although it is most efficient to use light (or electromagnetic radiation), etc. Light, in fact, causes efficient photoexcitation of the metal (a phenomenon that is well-known), as long as we know the frequency of the light that causes the metal atom to be photoexcited. These frequencies can be predicted by carrying out molecular quantum calculations for the first excited states of the metal.

The basic physical structure of a FC consists of a solid electrolyte layer in contact with a porous anode and a cathode to each side, respectively. The fuel and oxidant gases [11] pass through the surfaces of the anode and cathode opposite the electrolyte, respectively, and they generate electrical energy by oxidation of the fuel (hydrogen), and reduction of the oxidant (oxygen of the air). The hydrogen flows towards the anode of the cell, where a catalytic platinum agent helps to oxidize. An electrolytic membrane allows the passage through it only of the resulting ions. Because the electrons cannot pass through the membrane, they are forced to leave the anode by an external circuit, thus generating the electrical current. This electrochemical transformation is isothermal, since it directly uses the energy available in the fuel at the temperature of operation. The production of water and heat is carried out in different parts, depending on the electrolyte used; heat is generally produced in the anode. The reactions involved in the processes within a FC are induced to study the interaction between the surface of the catalyst and the fuel.

Here, all the closed shell energies involved in the process are obtained starting when the platinum and the hydrogen are completely separated until the hydrogen moieties of H₂ split and are bound to platinum, forming a new product. The adsorption and the activation energies were obtained using the DFT-B3LYP method. Adsorption was also corroborated using an *ab initio* method.

2. Methodology

DFT and MP2 calculations via software NWChem were implemented [12]. The functional B3LYP was used in all these DFT calculations [13]. The non-local correlation in the functional B3LYP is given by expression LYP, and VWN is a functional III. Both in DFT calculations and in MP2 (Moller-Plesset second-order) calculations, the set of bases 6-311G** was used. This computational level has shown good results for interaction between hydrogen and platinum [10]. Platinum data employed in this work were taken from a previous report [11]. Our potential energy surface takes into account

a Pt atom and a hydrogen molecule. On the basis of the criterion of minimum energy, the preferential orientation of the hydrogen molecule used in the interaction with platinum was determined. Before running a single point energy calculation, the hydrogen molecule was optimized using the corresponding methodology, either MP2/6-311G** or DFT-B3LYP. In addition, pseudopotential LANL2DZ was used [13] to carry out both calculations of points and the calculation of the optimization of the Pt atom.

Calculations at the *ab initio* level were also carried out in which the core electrons were taken into account by means of the use of an effective core potential [14]. The energy surface is determined by means of *ab initio* Hartree Fock of self-consistent field (HF-SCF) calculations[ii]. These were obtained using the program PSHF [15] in a more recent PSHONDO-IJKL-FOCK-CIPSI coupled programs structure. This means that the contribution of the energy of dynamic electronic correlation was obtained by means of interaction calculations of multireferential configurations at variational and perturbative levels of second order in Moller-Plesset (MP2) through an iterative algorithm CIPSI in its second version [16]. Basis functions s, p and d were employed.

3. Pt-H₂ interaction

When optimizing the platinum atom, it is placed at the origin of the geometry, and when applying the optimization to the hydrogen molecule, the two hydrogen atoms end up with one as a reflection of the other with a separation of 0.747 Å, which indicates that one perpendicular plane of symmetry passes through the middle of the line that joins both hydrogen atoms, and also passes through the center of the platinum atom. The geometry (in Å) of the optimized molecules is given in Table I.

Using the DFT-B3LYP method, the curve of the potential energy of interaction between platinum and hydrogen in its fundamental state is obtained. To obtain the potential energy curve, the platinum was placed at distances of separation between 1 and 10 Å along the r axis. The results obtained are shown in Fig. 1, in which a potential well was found. The coordinates of the minimum in the potential curve are the relative energy E_{rel} = -31.87 kcal/mol, and the distance r = 3.00 (au). Making use of the DFT B3LYP hybrid, with double-zed base functions, Cui *et al.* [10] find that the binding energy of H₂ to the Pt atoms is 47.4 kcal/mol, which is far from the size of the binding energy (absolute value) found by us. An

TABLE I. Initial geometry positions (Å) of the Pt atom and the H hydrogens in Cartesian coordinates.

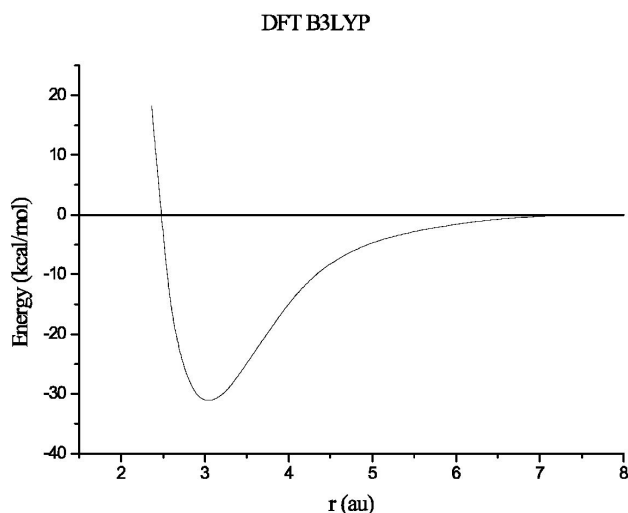|	X	Y	Z
Pt	0.0	0.0	0.0
H	0.01834556	0.37319624	-0.00039635
H	-0.01834556	-0.37319624	0.00039635

DFT B3LYP

FIGURE 1. Potential energy surface of Pt interacting with H_2 by means of DFT-B3LYP. Minimum at (3.0 au, -31.87Kcal/mol).
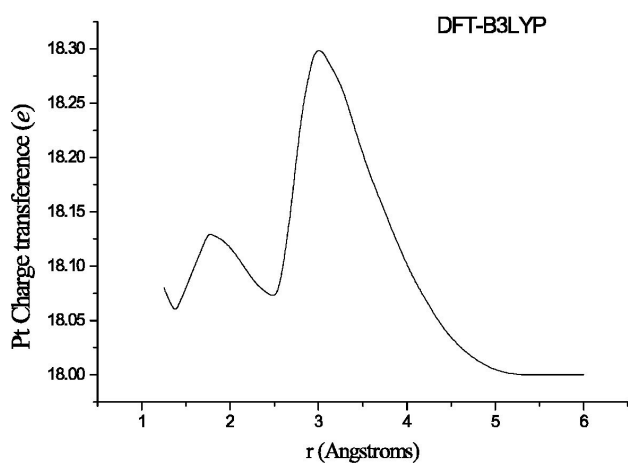
DFT-B3LYP

FIGURE 2. Mulliken population analysis of the interaction Pt-H_2. The highest maximum of the charge transference is located at (3.0 Å, 18.3 e)

DFT-B3LYP

FIGURE 3. Analysis HOMO-LUMO.

FIGURE 4. Calculation of the transition state value.

essential step in order to be able to trust the results was to optimize, independently, the atom and the molecule.

In the same procedure of energy calculation, the Mulliken population analysis indicates that the platinum, initially with a charge of 18 e, gains 0.02 of charge, which is transferred from the hydrogen atoms of H_2 at the rate of 0.01 e. Figure 2 exhibits a graph of Pt charge transference as a function of the distance obtained from the Mulliken Population Analysis. The lowest maximum is placed at 1.77 Å and 18.13 e, while the highest maximum is located at 3 Å and 18.3 e. The highest maximum indicates that platinum gains the maximum charge transference from the hydrogen molecule, causing an adsorption phenomenon of the hydrogen molecule on the platinum atom.

The frontier orbital analyses of the highest occupied molecular orbital and the lowest occupied molecular orbital (HOMO-LUMO) gap energy are obtained by means of the DFT-B3LYP method. The following figure shows the HOMO LUMO energy difference. The greatest reactivity gap energy is observed at the region 2-3 Å in Fig. 3.
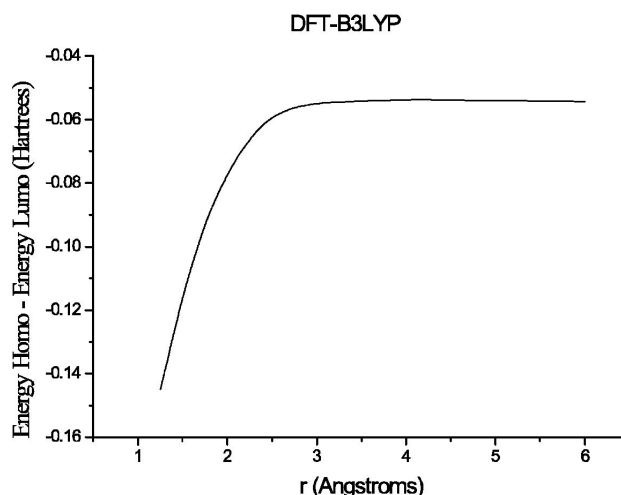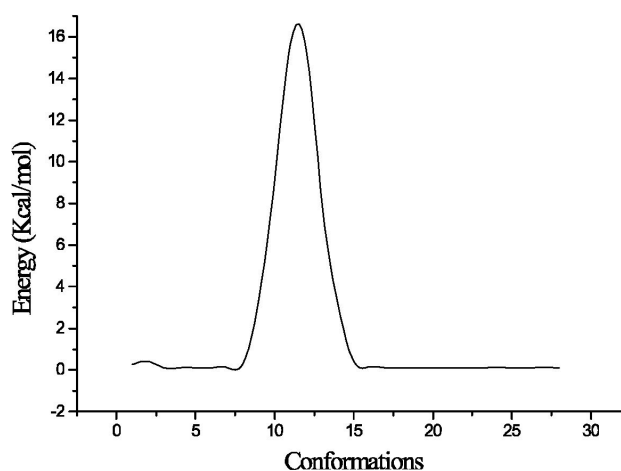
Knowing that the minimum of the potential curve was located at a distance of 3.00 au, the transition state optimization was also calculated using DFT-B3LYP by taking the geometry at r = 4.5 au of Pt-H_2 interaction, which is the approximate point where the reaction is considered to occur. Then, at the separation distance of 4.5 au, the calculation of the geometry optimization was initiated in which the transition state point was sought for this system. The results can be observed in the graph of Fig. 4, where the maximum 16.61 Kcal/mol of energy at a conformation 12 is associated with the transition state point. This energy value agrees with the experimental value of 17.5 Kcal/mol [17] for the transition state from the excited state $^1S(d^{10})$ to the ground state $^3D(d^9s^1)$.

For effects of comparison, the potential curve was obtained again, this time employing the method of self-consistent field implemented by Moller-Plesset (MP2) via NWChem calculation. Proceeding in a similar way to that used previously with DFT-B3LYP, the graph shown in Fig. 5 was obtained. The energies calculated for different separations between the platinum and the hydrogen shown in this graph indicate a region in which they are attracted when the

distance between them is not so large; nevertheless, when the distance is very large, the electric field generates an effect of repulsion among the particles.

Calculations with the atom and the rigid molecule were made, and to move them by either approaching them or moving them away along the same line, the adsorption of the hydrogen in the platinum is found. The curve in the previous graph indicates to us that the hydrogen itself physically adsorbs in the platinum when the separation between them is 3.0 au, and the relative energy is -32.55 (kcal/mol). That is to say, the hydrogen molecule is joined to the platinum as that molecule. If an optimization of the platinum-hydrogen system using the self-consistent field method implemented by Moller-Plesset (MP2), with platinum separated at a distance of 3.0 Å (5.67 au) from the hydrogen, is now carried out on the region of adsorption, then there is a reaction which breaks up the hydrogen and the product PtH₂ is obtained, with a separation between H-H of 1.97 Å (3.72 au) and a distance Pt-H of 1.49 Å (2.82 au). The angles of the triangle formed are 82.764, 48.618 and 48.618°.

Taking the geometry already mentioned and using *ab initio* calculations with the coupled programs PSHONDO-IJKL-FOK-CIPSI in symmetry C_{nv}, a relative binding energy of -29.36 kcal/mol was obtained to a distance at 3 (au) for $5d^{10}$ (closed shell) state as seen in the Fig. 6.

The same binding distance 3.00 (au) is obtained using each methodology, while binding energies -31.87 kcal/mol (DFT-B3LYP), -32.55 (MP2) kcal/mol and -29.36 kcal/mol (PSHONDO-IJKL-FOK-CIPSI), agree[iii]. It should be mentioned that the equilibrium potential among oxide-reductive reactions is 1.23 V[18]. Then, considering that the electrons are accelerated to this potential, the latter value corresponds to the energy of 28.37 Kcal/mol of the well-potential energy surface. Furthermore, Mîšek [19] found 1.31 eV (30.21 Kcal/mol) as the formation energy of single vacancy in platinum, a value which was improved to 1.15 eV (26.523 Kcal/mol) by high pressure quenching experiments [20]. Jackson [21] found a value of 1.2 eV (27.68 Kcal/mol) for water quenches on single crystals of platinum. The source of disagreement between values of the formation energy for vacancies in platinum was also discussed by Emrick [20].

The *ab initio* calculations (PSHONDO-IJKL-FOK-CIPSI) offer the best result (in absolute value) for this value. Nakatsuji *et al.* [7] calculated 32.0 kcal/mol for the heat adsorption on the interaction Pt-H₂ from the Pt(^{1}S) + H₂ state of $^1A_1$ symmetry relative to the dissociation limit of Pt(^{3}D) + H₂ state of the Pt atom using the *ab initio* CASSCF method, including the spin-orbit coupling based on the SAC/SAC-CI method in comparison with the 40 kcal/mol obtained, without including the spin-orbit coupling. They also comment that the experimental value for the extended surface is 26 kcal/mol [22]. They state that the spin-orbit coupling effect on this value is mainly due to the large splitting of the ^{3}D state of the Pt atom in the infinite separation of Pt and H₂. They also say that, as the reaction proceeds, the electronic
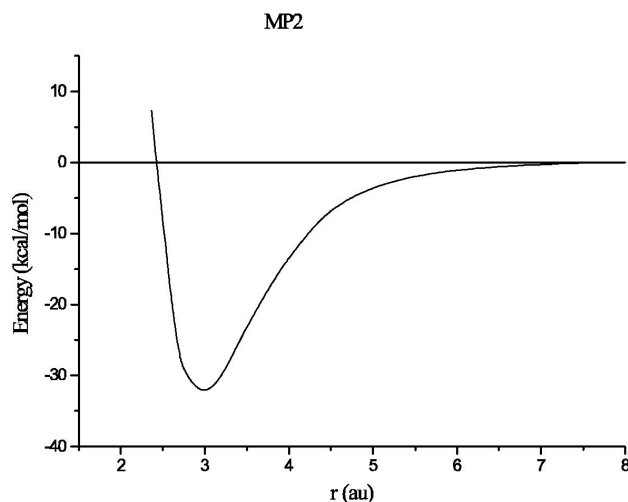

FIGURE 5. Potential energy surface of Pt interacting with H₂ by means of MP2. Minimum al (3.0 au, -32.55 Kcal/mol).
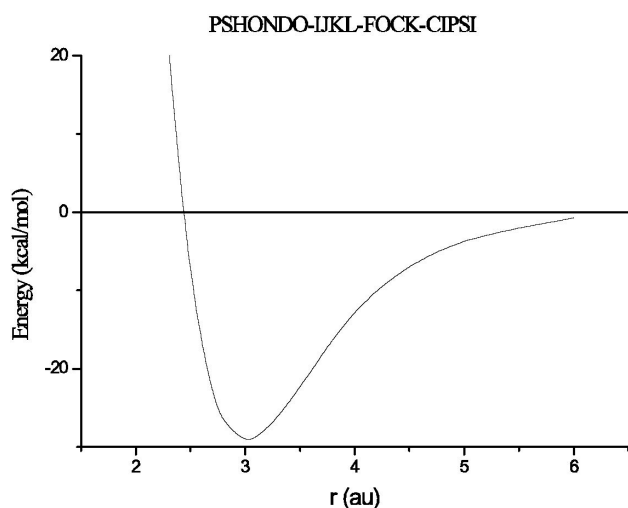

FIGURE 6. Potential energy surface of Pt interacting with H₂ by means of PSHONDO-IJKL-FOCK-CIPSI. Minimum at (3.0 au, -29.36 Kcal/mol).

configuration of the Pt atom changes from d^{10} to a mixture of d^9s^1 and d^8s^2. As the Pt atoms prefers the d^9s^1 and d^8s^2 configurations by 17.5 and 15.2 Kcal/mol, respectively, to the d^{10} configuration, this reaction proceeds very smoothly to dissociate the H₂ molecule completely.

The interaction energy was obtained by using the relation

$$E_{int} = E_{Pt+H_2} - \left(E_{Pt} + E_{H_2} \right),$$

where E_{Pt+H_2} is the energy of each point of the potential curve, E_{Pt} is the energy of the base state of platinum, and E_{H_2} is the energy of the base state of hydrogen. The following results were obtained by means of the DFT-B3LYP method. The interaction energy of platinum plus the interaction energy of hydrogen $E_{Pt}+E_{H_2}$ turned out to be equal to -120.303 Hartrees, which is equal to cero kcal/mol in the diagram of the energy positions of Fig. 7. The interaction energy of the hydrogen molecule physically adsorbed on the

platinum is -31.87 kcal/mol, and it is also observed in the schematic diagram of Fig. 7. We proceeded to obtain the activation energy for breaking up the hydrogen molecule. The energy necessary for breaking up the molecule H_2 in the interaction between the H_2 molecule and the Pt atom is, as a result, $E_{TS}PtH_2$=16.61 kcal/mol, as seen in Fig. 7, this energy corresponds to the bond H-H activation of the hydrogen molecule, and consequently to its breaking up. Finally, in that same sketch, shown in Fig. 7, the energy with which each one of the atoms of hydrogen is adsorbed on the platinum to form a new product (PtH_2) is observed; the value of this energy in the optimized conformation is $E_{OPT}PtH_2 = 3.21$ kcal/mol.
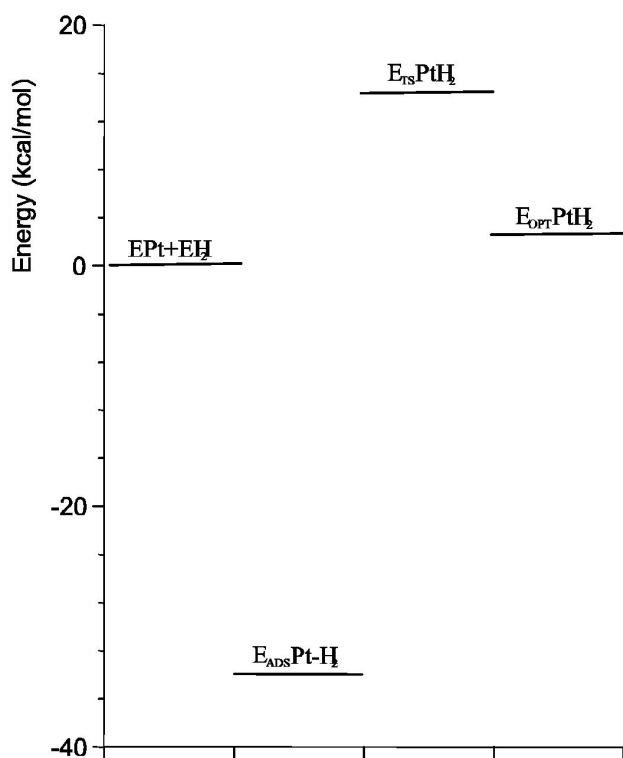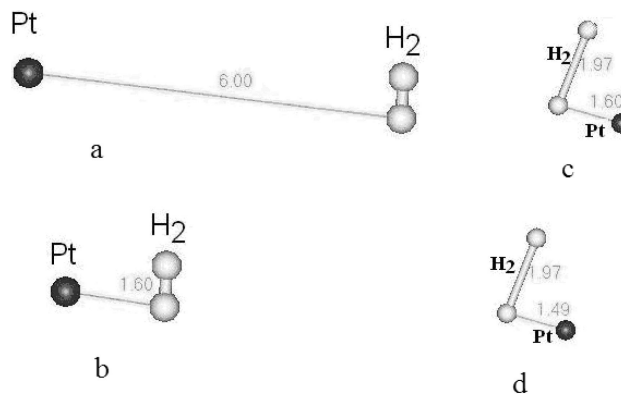

FIGURE 8. The sequence of distances is seen in this figure, where: a) there is no interaction in Pt-H_2; b) the hydrogen molecule is adsorbed on the platinum atom; c) a exists reaction and the molecule PtH_2 is formed; d) the atoms of hydrogen remain in the surface of platinum.

The sequence of energies shown in Fig. 8 has been found, since the platinum and the hydrogen are separated, passing for the adsorption energy of the hydrogen as it is by itself on the surface of the platinum, and also by the activation energy with which the hydrogen molecule breaks up, until the adsorption of each of the hydrogen atoms at the surface of the platinum is completed.

4. Conclusion

The wells of potential of the interaction Pt-H_2 were obtained with three different methodologies (DFT-B3LYP, Moller-Plesset, and PSHONDO-IJKL-FOCK-CIPSI), and the distances and the energies of adsorption were respectively found. The equilibrium energy of the interaction Pt-H_2 was found between oxide and reductive reactions, which represents a bridge bond between the theoretical calculations and the processes of transformation of the fuel in the FCs. Utilizing the method DFT-B3LYP, all the closed shell energies involved in the process were obtained, since the platinum and the hydrogen are completely separated until the atoms of hydrogen are separated, then activated, and finally remain bonded to the platinum, forming a new product.

FIGURE 7. Energetic position diagram referred to the reactants Pt and H_2, and the product PtH_2.

∗∗. Member of El Colegio Nacional.

i. Mavrikakis *et al.* http://www.nersc.gov/news/annual_reports/ annrep01/sh_BES_10.html, Joshua Lynn Ratts Homepage http://atom.ecn.purdue.edu/∼jratts/che697m/

ii. Hartree-Fock self consistent field consists in proposing initial wave functions to solve the representative equation of the physical system, and from an eigenvalue equation (Roothaan equations) to calculate an average potential for each electron of the physical system under initial approximations. Once this potential is found out, a new set of wave functions is calculated, then using these new sets as initial approximations, new fields can be found. This procedure is repeated until reaching self consistency.

iii. Moller-Plesset (MP2) and PSHONDO-IJKL-FOCK-CIPSI (PIFC) do not produce the same result because these methodologies actually are different. On one hand, polarization functions 6-31G** were used as basis functions of MP2, while s-p-d type basis functions were used for the PIFC method. On the other hand, MP2 is based on the perturbation theory which normally takes the deepest well of potential energy that we found, while PIFC uses both variational and perturbative calculations, producing a better approximation to the experiment.

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