

# Selective hydrogen production at Pt(111) investigated by Quantum Monte Carlo methods for chemical reactions.

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January 14, 2020

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## Abstract

This rapid communication gives the salient points and results from theoretical investigation of a chemical reaction for efficient selective hydrogen production. The clean fuel produced is a sustainable energy source. Accurate methods based on quantum theory are used because changing electronic structure monitors reactions. The reaction between water and carbon monoxide is used industrially with metal catalysts, usually platinum. There is a considerable economic and environmental challenge underpinning this fundamental investigation where bond dissociation plays an essential role.

A bond dissociation process is often the limiting step of reaction rates for industrial catalysis. Most mainstream quantum approaches fail to greater or lesser degree in the description of this process. The present work advocates a promising alternative: the initial analysis of statistical data generated by the Quantum Monte Carlo (QMC) method to very stringent statistical accuracy for essential information on hydrogen production via the water-gas shift reaction with platinum catalyst.

The transition state structure is obtained from QMC force constants and illustrated here. It corresponds to water OH-stretch concerted with Pt-H bond formation whilst the OH oxygen atom begins to interact with the CO carbon. The present QMC evaluation of the corresponding activation barrier is low:  $17.0 \pm 0.2$  kcal/mol. It is close to the experimental apparent activation energy of 17.05 kcal/mol.

This method is applicable to similar systems.

Keywords: Quantum Monte Carlo calculation, heterogeneous catalysis, metal surface, low activation barrier

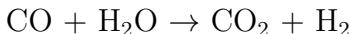
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Over 90 % of all chemical manufacture uses a solid catalyst. Work in this context thus responds to major societal demand.

Due to the size of system and essential role of electron transfer in metal catalysed reactions, even when the metal which is a reducing agent remains in the metallic state (not becoming oxidised), the recent literature only contains Density Functional theory (DFT) studies, which are more or less inaccurate.

This study focusses on the early stages of Water-gas shift (wgs) which follows the overall equation:



The reaction was discovered in 1780 by Fontana. Much of the mechanistic work has postulated a redox mechanism, particularly for metals like copper which are known reducing agents<sup>1</sup>. The alternative family is associative and this work shows no change in the Pt-oxidation state whilst proposing an additive complex between CO and water, prior to CO<sub>2</sub> production from formate-like decomposition. A detailed study of this mechanism on Pt, including experiment, DFT and kinetics is proposed in<sup>2</sup>. This reference also collects previously published activation barriers for the CO oxidation involved. These barriers cover a factor of two: ranging from 11.3 to 23.3 kcal/mol<sup>2</sup>. This is a key step of water-gas shift reaction mechanisms showing mainstream Quantum chemistry gives approximate activation barriers for this system.

The theoretical study of hydrogen production by catalytic addition of water to carbon monoxide adopting the Quantum Monte Carlo (QMC) method represents a breakthrough in reliable information on bond-dissociation limitation of metal catalysed reactions. It was bench-marked for hydrogen dissociation on copper, for which accurate molecular eam measurements are available<sup>3</sup>. Our methodological advances are outlined here and the main results of an enabling 52Mh supercomputer allocation are given here (The full-data can be consulted in the repository FigShare 10.6084/m9.figshare.10293194), pending a full-paper with more detail. This is among the largest heterogeneous systems studied by QMC. The reaction is called water-gas shift and is greatly facilitated on a platinum catalyst.

The reactants are in equilibrium with products and we focussed on theoretical study of the forward reaction in this work, producing hydrogen. We determine the rate-limiting step of the reaction mechanism and the associated activation barrier, on Pt(111).

This paper is organised in a single section, beginning with general methodological description of the Quantum Monte Carlo work on the water gas shift reaction in a molecular addition mechanism with the platinum metal substrate remaining in the (metallic) 0 oxidation state. The molecular active site approach to the high-level (local) portion of the wave-function is described as well as its embedding into a periodic DFT system. Construction of the Jastrow factor at the Variation Monte Carlo level provides explicit correlation before the accurate Diffusion Monte Carlo data-accumulation for 16 offset grids paving the first Brillouin zone allow for twist-averaging and reduction of the standard error. Mechanistic and barrier height results are given here, pending a detailed methodology paper, currently in preparation.

Novel methodology using stochastic approaches to the Schrödinger equation, namely Quantum Monte Carlo (QMC) is used. Motivation for choosing QMC is to obtain reliable description of bond dissociation needed for this reaction to proceed. These phenomena are poorly catered for by main-stream quantum chemistry.

The present work obtains better than chemical accuracy (i.e. energy to within 1 kcal/mol)

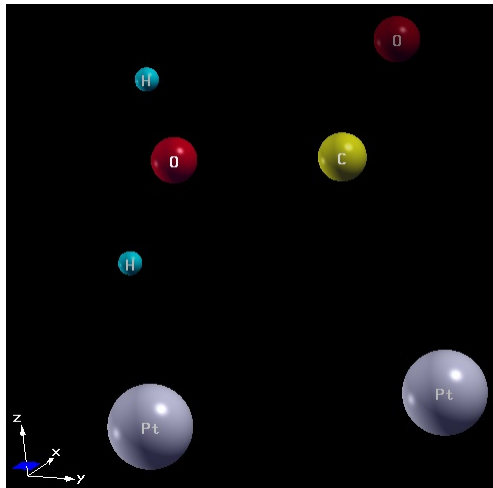


Figure 1: Molecular active site in the plane perpendicular to Pt(111). Pt at origin accepts one water H. CO bondlength 1.43 Å, O (water)–C distance 1.63 Å.

for the rate-limiting step and corresponds well to measured apparent activation energy (17.05 kcal/mol c.f the QMC value we get:  $17.0 \pm 0.2$  kcal/mol). The molecular active site has a Full Configuration Interaction (FCI) wave-function and this is embedded in a periodic Density Functional Theory (DFT)/plane-wave lattice.

Production of hydrogen in this way is found to require a set of conditions. First, note that the polarity of CO must involve a partial positive charge on the carbon for the reaction to proceed (so it is unlikely to occur in the gas-phase, for example). When CO is adsorbed on Pt, the polarity is suitable for attack of the carbon by nucleophiles (water). Second, many studies suggest that O-H bond dissociation in water to give a hydroxide radical is rate-limiting, whilst recent studies<sup>5,6</sup> suggest it is much higher than the DFT barrier given in<sup>2</sup>, which is 16.19 kcal/mol. Our previous QMC value for this pathway is 17.7 kcal/mol<sup>6</sup>. A very complete DFT study<sup>5</sup> gave 17.99 kcal/mol.

We therefore searched for concerted steps, in which the water O-H stretch is accompanied by Pt-H bonding and also the start of interaction between the oxygen atom from water and the CO carbon. The transition-state geometry was obtained for the molecular active sites using QMC force constants.

Other evidence comes from the suggestion in<sup>2</sup> that the OH radical (that is reactive) first binds to a surface Pt-atom and does not diffuse significantly towards the CO that is already adsorbed on another surface Pt-atom. In Figure 2 (below), we give a plan-view with Pt(111) at height 0, as well as the 3-D TS-geometry (Figure 1).

Highly accurate theoretical evaluation of the energy barriers encountered by reacting molecules (activation energy) is the purpose fulfilled by this study. There are numerous possible sources of error that we have minimised and our choices are briefly justified below to back up the reliability of our work. The extremum geometries must be located and justified. These geometries have significant impact on understanding the reaction mechanism.

Activation energy is determined as the difference between two large and similar energies for the same atoms in different geometries. Subtraction of a reference with minimal binding re-arrangements, compatible with our application, leads to cancellation of fixed-node

error arising from maintaining input wave-function antisymmetry (and nodes) for electronic structure in QMC<sup>7</sup>. These nodes are not exact in general and error must be kept small.

The two structures (c.f. corresponding energies) are:

1-The asymptotic geometry (local minimum: adsorbed CO, distant water, as reference).

2-The Transition-state geometry. (Saddle-point, maximum along the reaction co-ordinate).

In such a case, both energies need to be determined very accurately and the second geometry (so-called transition-state, TS) is located using QMC force constants.

Atoms with substantial interaction during the wgs reaction define its molecular and solid active site (see Figure 1, above). This 'active site' system is embedded in a periodic solid, i.e. the metal catalyst.

We refer to CO adsorbed above the centroid of an equilateral triangle with Pt-atoms as apices (defined using translational symmetry from a single unique Pt-atom) in the Pt(111) plane. This gives three C-Pt linkages. The trial wave-function was evaluated for a molecular active site using MOLPRO<sup>8</sup>. This 'molecule' comprises a Pt-atom at the origin and a second Pt to define an apex of the triangle motif in Pt(111). The CO is adsorbed above the centroid. For Pt-atoms, we used the Z=60 effective-core potential (ECP)<sup>9</sup> leaving 18 valence electrons per atom the MOLPRO AVTZ contracted Gaussian basis is used for spd orbitals. First a Multi-Reference CI is carried out for the transition-state (TS) and asymptote geometries. The transition state we obtain using QMC force constants (the Hessian is defined with QMC force constants as matrix elements, then updated using Pulay's Direct Inversion in the Iterative Subspace (DIIS) algorithm adapted by Farkas<sup>10</sup>). The resulting TS is shown in Figure 1. It has a slightly short CO bond, since some electron density involved in beginning the bonding with the water oxygen comes from a CO anti-bonding orbital. The water molecule has a very long OH-bond (1.2 Å), since the hydrogen is bound to Pt at the origin, whereas the other O-H is almost unaffected.

The molecular wave-function is then evaluated to Full-CI, with NECI<sup>11</sup> and the top 20 determinants selected. It is embedded into the 5 unit-cell thick Pt-slab representing the lattice and expanded in plane-waves. This Pt slab comprising 4 atoms in each of 5 layers is defined as face-centred cubic, exposing 2 identical compact 111 faces i.e ABABA.

The top 3 layers are spaced according to experimental measurement. The last two derive from the exact bulk  $a = 3.912$  Å. In plane Pt(111) atom-spacing is always  $\frac{a}{\sqrt{2}}$  and the last layers are  $\frac{a}{\sqrt{3}}$  apart to ensure continuity with the bulk. Periodicity for in plane, x,y directions is physical and on the z-axis the slabs are repeated with a vacuum spacing of 20.8 Å. The super cell used has 1512 electrons, because it is expanded in real space over a 2 by 2 by 1 grid, multiplying the cell and also decreasing finite size effects by spacing the adsorbed molecules by a distance L that is much larger than the overall molecular 'diameter': Here we have L=10.5 au and the molecular diameter is 3.6 au.

The molecular active-site is defined the wave-function obtained from Molpro and NECI, as explained above. This is embedded in the Pt slab using the method of<sup>12</sup> i.e. Green's function for electronic potential additivity and the whole system wave-function is expanded in plane-waves expressed as B-splines<sup>13</sup>.

Quantum Monte Carlo proceeds in two steps. The Variational Monte Carlo (VMC) is initialised using a trial wave-function. In the present work, the trial wave-function is comprised of the Slater determinants obtained with MOLPRO and an adapted ABINIT

code<sup>14</sup>. It is therefore a plane-wave DFT input, using a fully converged control variate k-point grid in the first Brillouin zone which is 16 16 1 in dimension and serves for twist averaging (*videinfra*). At this stage, the ECP must be converted to a norm-conserving pseudo-potential, suitable for input to the CASINO code<sup>15</sup>, which is used for the QMC calculations and possesses utilities for this conversion. VMC is used to optimise a generic Jastrow factor (using Common Algebraic Specification Language (CASL)), with the e-e, e-n and e-e-n polynomials expanded to order 9 with cut off radius of 10 au. The Jastrow factor is fully optimised during the VMC step, first by using the mean-average deviation that reduces variance in the distribution whereby the configurations (instantaneous particle positions in co-ordinate space) represent electronic density. This distribution is updated until the final stages of VMC where fine-tuning of the Jastrow factor is accomplished by energy minimisation over 15 cycles. The resulting Slater-Jastrow wave-function is used to initialise the configurations for Diffusion Monte Carlo (DMC) which is the solution of the diffusion and drift equation arising from transforming the time-dependent Schrodinger equation by replacing the time-variable (t) with it and continuing to advance in small steps of 'imaginary time' as this is the diffusion time-variable that will propagate the ground state solution whilst any excited state contributions fade out in the limit of long DMC runs. The DMC algorithm proceeds using Casula T-moves and a time-step of 0.005 au. These are continued until error in standard error is 0.1, i.e. for 27 500 data points on average for 16 twists (the wave-function is complex since the structure has no inversion center).

On the Irene CEA supercomputer near Paris, 25 DMC steps take 45 mins on 4032 cores.

The data-set supplied for the given k-points in the first Brillouin zone defined for the Transition-State and referred to the asymptote give the tabulated values below: A test on time-step bias yields 30 micro Hartree for the energy difference, or 0.0019 kcal/mol and will be neglected. Tabulated values are for the DMC population target weight.

Summary of data from: 10.6084/m9.figshare.10293194

**Table I: Activation energy evaluation for the online data-sets from this work**

Structure	Transition-state	Asymptote
$E_{tot}$ (Ha)	-549.63218	-549.65924
Variance au/(kcal/mol) <sup>2</sup>	0.604/0.2377	0.528/0.2081

Activation barrier: 0.2706 au or 16.98 (17)  $\pm$  0.67 kcal/mol (this standard error here is obtained from data-analysis of the distribution at the gamma point. It is reduced by almost a factor 4 by twist-averaging i.e. combining independent runs from 16 offset grids in the first Brillouin zone). The final QMC activation barrier is thus 17.0  $\pm$  0.2 kcal/mol.

**Acknowledgements.**

The QMC calculations were made possible by a PRACE allocation of supercomputer resources: PRACE project 2018184349, allocated 51.6 Million core-hours on the Irene supercomputer (CEA, Bruyères-le-Châtel), near Paris, France.

PEH thanks Pablo Lopez-Rios for supplying NECI and for helpful discussions.

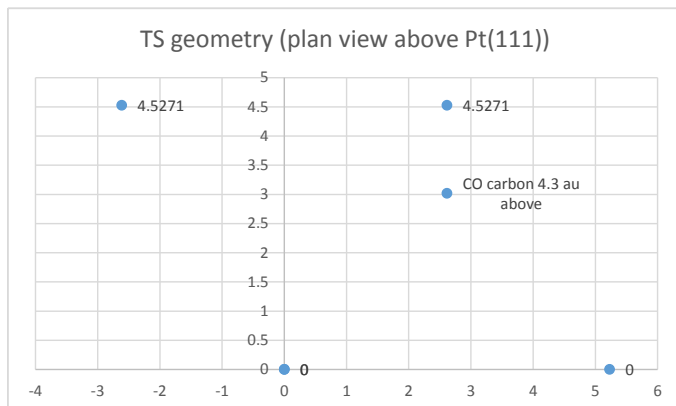


Figure 2: Molecular active site in the plane parallel to Pt(111). Pt at origin accepts one water H. CO carbon highlighted (hollow site).

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Appendix.

Supercell 2 2 1 for Pt lattice parameter 7.3928 Å exposing Pt(111) +CO + H<sub>2</sub>O (TS; asymptote translate water by 12.5 Bohr on z)

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1 78 1 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
2 78 1 0.5000 0.0000 0.0000 5.2275 0.0000 0.0000
3 78 1 0.0000 0.5000 0.0000 -2.6137 4.5271 0.0000
4 78 1 0.5000 0.5000 0.0000 2.6137 4.5271 0.0000
5 78 1 0.3333 0.1667 -0.1073 2.6137 1.5090 -4.2247
6 78 1 0.8333 0.1667 -0.1073 7.8412 1.5090 -4.2247
7 78 1 0.3333 0.6667 -0.1073 0.0000 6.0362 -4.2247
8 78 1 0.8333 0.6667 -0.1073 5.2275 6.0362 -4.2247
9 78 1 0.1667 0.3333 -0.2155 0.0000 3.0181 -8.4843
10 78 1 0.6667 0.3333 -0.2155 5.2275 3.0181 -8.4843
11 78 1 0.1667 0.8333 -0.2155 -2.6137 7.5452 -8.4843
12 78 1 0.6667 0.8333 -0.2155 2.6137 7.5452 -8.4843
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15 78 1 0.0000 0.5000 -0.3239 -2.6137 4.5271 -12.7520
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33 78 1 0.8333 1.6667 -0.1073 -0.0000 15.0905 -4.2247

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