

# Quantum Monte Carlo approach for determining the activation barrier of water addition to carbon-monoxide adsorbed on Pt(111) within 1 kJ/mol.

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## Abstract

Quantum Monte Carlo methods offer *ab initio* calculations of remarkable accuracy for reaction activation barriers (to 1 kJ/mol or 0.01 eV), even at solid surfaces.

Chemical reactions generally involve bond-dissociation that is poorly described by Hartree-Fock and Density Functional (DFT) methods. However, such processes are often the key to rate-limiting reaction steps at solid surfaces. In this work, novel Quantum Monte Carlo (QMC) methodology is demonstrated as a solution.

Carbon-monoxide (CO) on platinum reacts with water, first giving the addition products. QMC methods are used here to investigate addition at close-packed Pt(111).

The CO is pre-adsorbed on Pt(111). An approaching water molecule is first only partially dissociated. At the same time, its oxygen atom binds to CO giving an adsorbed formate moiety (COOH) and Pt-H. This concerted addition is rate-limiting.

The QMC activation barrier (in kJ/mol) is  $71.0 \pm 0.7$  and its apparent measured value is 71.4. This showcases QMC as a method to investigate related catalytic systems.

## Introduction

Quantum Monte Carlo (QMC) methods allow small energy differences to be resolved (i.e. determined) very accurately. Effective strategy compares the same atoms in two geometries. Precise access to energy and other physical observables of importance to chemistry results. QMC for periodic systems (like metals) and their surfaces is developing, even when they are interacting with reacting molecules. Reactions involve bond breaking and formation, only accessible to Hartree-Fock approaches when followed by a large configuration interaction in a multi-reference context (MRCI). This multi-reference procedure is required to describe dissociation with observed products. The CI could, ideally be full CI (FCI). At present the FCI procedure is limited to modest active space sizes (around 20-40 electrons depending on computational resources). Size restrictions are partly circumvented with a small molecular active site that describes the reaction and is embedded into a periodic wave-function. The number of active electrons (and bonds) for FCI or MRCI calculation is limited by including few solid (e.g. metal) atoms. This MRCI is then re-expanded in a suitable basis, to smoothly combine it with the solid periodic basis. Such trial wave-functions initialise our QMC work.

The QMC approach used here thus includes an active site, aiming to eventually provide an accurate and feasible *ab initio* approach to heterogeneous catalysis. The first step in the water-gas shift reaction on platinum is water addition to pre-adsorbed carbon-monoxide. This takes place at the Pt(111) face<sup>1</sup> ultimately producing H<sub>2</sub> as a clean, sustainable fuel. In the present work, we evaluate the activation barrier for this water addition, to showcase the accuracy of QMC. Platinum is represented by a five-layer slab, with planar Pt(111) faces. The active site structure has one surface Pt-atom co-ordinating a water H-atom at the origin and another Pt-atom defining the apex of an equilateral triangle.

Carbon-monoxide adsorbs by its carbon-atom in a hollow site above these 3 Pt atoms.

Topologically this (local, active) molecular site is Pt-H and H-O-(Pt)-C=O.

This so-called 'transition state' (TS) structure, between Pt-H-O-H (from adsorbed water) with vicinal Pt-CO (pre-adsorbed CO) initially and Pt-H with vicinal Pt-CO-OH (formate) as addition product formed after the TS. The formate is a reaction intermediate that is relatively stable. The TS corresponds to the maximum energy on the reaction path between the initial reference and the first intermediate structure (i.e. formate: Pt-CO-OH). Obviously, all-electron calculations at the FCI level are inaccessible for this system, therefore we use an effective core potential (ECP) to generate the MRCI wave-function and the corresponding pseudo-potential for QMC. That chosen has  $Z=60$  for Pt (instead of the full  $Z=78$ ) leaving 18 valence electrons per platinum atom. Including two Pt-atoms in the active site brings it close to the current active-space size limit for FCI and the trial wave-function has selected MRCI determinants with weights above a threshold which restricts the number of determinants retained to one in four. Nevertheless, QMC recovers well from trial wave-functions of moderate accuracy, provided that its nodal structure resembles that of the exact wave-function.

An approximation in our model stems from evidence of rough and non-planar '111' faces in real systems after relaxation to reduce surface formation energy.<sup>2</sup> Even so, the present QMC and measured apparent activation energy values differ by less than our statistical error.

Nowadays, stochastic methods are increasingly useful innovative electronic structure approaches to work on those challenging systems which require electron correlation accurately. Molecule-solid interactions, for heterogeneous catalysis is a growth area of these applications, e.g. for adsorbed reactions on metals. The water-gas shift reaction (wgs) which follows the overall equation:  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$  is an industrially important example.<sup>3</sup>

On a Pt(111) surface, step-by-step water dissociation followed by OH. radical attack of CO was rejected in favor of a **concerted**, partial water-dissociation whilst the water oxygen is already beginning to bind to the CO carbon, on the basis of our previous evaluation of the water dissociation barrier as significantly higher.<sup>4</sup>

A full study of this mechanism on Pt, including experiment, Density Functional Theory (DFT) and kinetics is proposed in the review.<sup>5</sup> The electron correlation energy contribution varies dramatically during adsorption and reaction, hence it must be determined exactly. DFT benchmarks<sup>6</sup> of this energy contribution are imprecise for 11 much used functionals.

Recently, however, several new DFT functionals have emerged that improve performance compared to calorimetric measurements of adsorption energies. Hence, DFT is very informative e.g. on nano-structured substrates and kinetics (combined with kinetic Monte Carlo).<sup>7-9</sup>

QMC benchmarks by one of us for hydrogen dissociation on Cu(111) and other metals compared to molecular beam results are available with accuracy of 1-5 kJ/mol (with progress in controlling statistical or standard error [se] and systematic error), see.<sup>10</sup>

Hence, this theoretical study develops novel QMC methodology for water addition to pre-adsorbed carbon monoxide in a hollow site in the Pt(111) plane of the catalyst. The results below give the relevant transition-state geometry obtained with QMC force constants. The corresponding activation barrier is the energy difference for this TS (at the energy maximum for water addition) compared to that of adsorbed CO at Pt(111) with water at 8Å. Subtracting ground-state energy from the QMC results for these two geometries enables us to achieve remarkable accuracy for this activation barrier. The QMC activation energy that results has error bars below 1 kJ/mol. Therefore, it is close to measured apparent activation energy values and well within 95% confidence limits.

## Computational Method:

The method of choice must scale well with system size, be able to efficiently use modern supercomputer facilities that are massively parallel and, above all, produce quantitative, accurate physical properties that are difficult to obtain otherwise. QMC benchmarks of activation barriers for reactions adsorbed on solid catalyst surfaces fit this description well. Developing and applying QMC calculations on this scale require access to a super computer.

## The stages of our approach are as follows:

1-An active site is defined with 2 Pt-atoms. Pt<sub>1</sub> receives H and Pt<sub>2</sub> defines an equilateral triangle motif (with translation symmetry) in the (111) face and a hollow site at this triangle's center of mass where CO is adsorbed: The atoms involved are Pt<sub>1</sub>, Pt<sub>2</sub>, CO and H<sub>2</sub>O.

Active site co-ordinates in a.u. for TS input geometry from QMC force constants (below).

Atom	x	y	z
Pt <sub>1</sub>	0.0000	0.0000	0.0000
Pt <sub>2</sub>	2.6137	4.5271	0.0000
C	2.6137	3.0179	4.3000
O	2.6137	4.4344	6.5864
O	1.9000	0.0000	4.3000
H	0.0000	0.0000	3.0500
H	1.3155	0.0000	6.0126

2-Molpro<sup>11</sup> uses this input to evaluate a Multi Reference Configuration Interaction (MRCI) wave-function, which is embedded in the Pt-lattice with a 2x2 atom face and 5 (ABABA) layers. This defines a periodic slab. The 'active site' embedded in Pt-slab (without Pt-atom duplication) is expanded in plane waves, with periodic boundary conditions in k-space.

Embedding simply uses standard Green matrix addition for the electronic potential.<sup>12</sup>

3-The Slater determinants obtained from this wave-function are expressed as products with a generic Jastrow factor i.e. in Slater-Jastrow form, giving a Trial wave-function (TWF). QMC proceeds in two steps: Variational and Diffusion Monte Carlo or VMC and DMC.

4-The TWF with arbitrary parameters (polynomial coefficients of inter-particle distances in the Jastrow factor and Slater determinant weights) are optimised using VMC.

5-Then Diffusion Monte Carlo (DMC) uses a population of 'walkers' (instantaneous particle positions) generated from the optimal TWF, propagated in imaginary time.

DMC and DFT-MRCI methods, when compared, give percentage errors of 3 % for DFT-MRCI and only 0.4 % for DMC in total excitation energies for systems of similar size.<sup>13</sup>

A simple model of the catalyst surface (planar, no steps, terraces or defects) is retained. This shows that even the nano-structuring of the real surface and an excellent agreement between the apparent activation energy and the value calculated using QMC (for a planar surface) are compatible. The energy is referenced to that of adsorbed CO, in its optimised geometry. It is based on a transition state for water addition without complete dissociation. This work treats among the largest heterogeneous systems studied by QMC with a metal surface and adsorbed interacting molecules. The forward water-gas shift reaction is greatly facilitated on Pt(111) catalyst giving hydrogen. The first step is water and pre-adsorbed CO addition, studied here at Pt(111).

CASINO software<sup>14</sup> is used. It cannot be treated as a 'black box' for these applications.

The electrophilic CO carbon is in a hollow site near 3 equivalent Pt-atoms (see above). One Pt atom thus accounts for all 3, as the key to embedding a high-level wave function for a relatively small active site containing only the two 'distinct' Pt-atoms. One begins binding to the H-atom of the stretched water bond and defines our origin and the other defines the triangle within which the hollow site adsorbing CO is situated.

A QMC saddle point or energy maximum on this reaction path step gives us TS geometry.

The TS is shown in Figure 1 (TS1). The water oxygen is binding to the (CO) carbon whilst the hydrogen from the stretched O-H binds to a vicinal Pt-atom. The activation energy obtained from TS1 is significantly lower than that for water dissociation. TS1 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), its hydrogen binding to Pt at (0,0,0). The other OH is almost unchanged.

For water dissociation on Pt(111), our previous QMC calculation gave (in kJ/mol) 74.27 (with standard error [se] 1.3) compared to a DFT value of 75.32.

The present TS gives a significantly lower barrier of 71.0 (se 0.7). Any OH-radicals first bind to a surface platinum atom. Hence, diffusion of these 'bound' hydroxides is difficult.<sup>5</sup>

Standard error (se) is evaluated from the raw QMC data, after the equilibration phase.

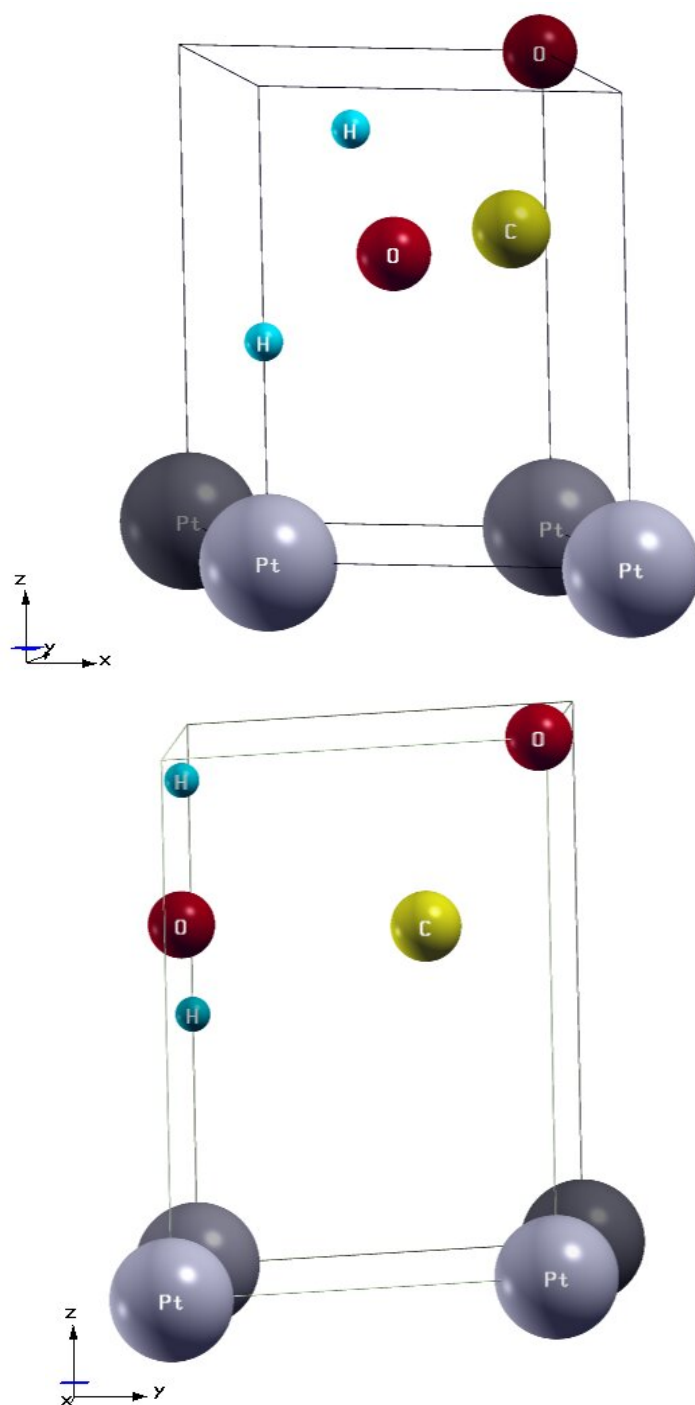


Figure 1: Molecular active site (TS) TS1: the  $z=0$  plane is the Pt(111) surface (bottom face). Pt at the origin accepts one water H-atom. CO carbon in a hollow site (Pt-C bond-length 1.43 Å), The oxygen is above a vicinal Pt. Water (oxygen) O-C distance is 1.63 Å.  
 Top pane: from negative y.  
 Bottom pane: from positive x

Twist-averaging is used to markedly lower standard error. It requires a new run for each offset grid and removal of equilibration data-points, then extrapolating to the small time-step limit.<sup>14</sup> This gives error-bars of these activation barriers that are much lower than in our QMC benchmarks for Cu(111).<sup>10</sup> Due to the 3d electrons, hydrogen dissociation barriers at Cu(111) had statistical-error slightly above chemical accuracy (i.e. 1 kcal/mol or 4kJ/mol).

Water dissociation before attack of CO can be eliminated in favor of a concerted (partial) dissociation accompanied by attack of CO by barrier differences and low error, as seen on Pt(111) but this would not have been possible for error bars obtained with copper catalyst, using the QMC calculations of.<sup>10</sup> Some indications on possible improvements were discussed in.<sup>10</sup> These studies provided useful indications on the tendencies. Extrapolation to the basis set limit in plane-waves indicates that the QMC barrier is an upper bound on the actual value and, generally it was rather lower than accurate molecular beam measurements. This trend explains why the measured value (which may be lower due to defect sites for reaction) agrees with the QMC value well (that has been seen to give values below those measured).

In fact, 95% confidence limits are within 1.4 kJ/mol and this shows a modest effect of statistical error and the significantly higher water dissociation barrier (3.2 kJ/mol greater).

Hence, QMC methods described here represent a breakthrough in reliable information on bond-dissociation limitation of metal catalysed reactions.

Methodological advances needed built on benchmark work are given here.

For details of computational results see Supporting Information (SI) and also the

[/figshare.com/articles/dataset](https://figshare.com/articles/dataset).<sup>15 1</sup>

Platinum has a  $5d^9 6s^1$  ground state. Since all-electron calculations are inaccessible, a Pt-atom is represented by 18 valence electrons with a suitable pseudo-potential (PP). Core-valence occupation is low in any given region of space: related densities are well-separated. This confers low variance on the metal wave-function, only about 10 % of that for problematic copper metal wave-functions. The platinum PPs used gives reliable excitation energies.<sup>16</sup>

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<sup>1</sup>using the PRACE PROMISE 52 Mh allocation



Basis and PP will influence accuracy for adsorption by metals. Plane waves with complex exponent allow basis sets to include Slater type orbitals, which facilitates embedding.<sup>17,18</sup>

In the present work the CASINO QMC code is used. The force constant algorithm therein,<sup>19</sup> gave a molecular active site in a Slater type orbital basis for the TS, expanded in plane-waves like the periodic solid (extending our previous work<sup>18,20</sup>).

Transferrable atomic core electrons must be replaced by effective-core potentials, or PPs. For QMC, norm-conserving PPs are needed. Core-electrons account for nearly all the total correlation energy.<sup>21</sup> With suitable PPs (see SI), electron correlation contributions approach the all-electron limit. PP non-locality can cause havoc, if the core is too large or a poor choice of local channel (l-value) is made, especially for elements with valence 3d shells: see.<sup>22</sup>

The 4d and 5d are 10 times lower in variance, ascribed to the lower dispersion of the electron distributions, for increasing effective atomic charge.

## The Quantum Monte Carlo Method: specifications.

The present study underpins heterogeneous catalysis that enhances bond dissociation. This step is frequently the initial (and often limiting) step of an industrial reaction (see, for example<sup>23,24</sup>). Bond dissociation is difficult to describe using Hartree-Fock (HF) approaches.

HF methods incorrectly describe bond dissociation. This is so, even for homo-nuclear diatomics. However, extensive CI caters for electron correlation adequately (but limits the size of accessible systems). DFT methods are a rapid computational alternative.

DFT includes some electron correlation and performs better than HF in the dissociation limit for certain functionals. The Perdew, Burke, Ernzerhof (PBE) functional (reproducing experimental lattice parameters accurately) gives a reasonable gas phase barrier for ammonia synthesis.<sup>25</sup> The initial QMC trial wave-function should have precise nodes if possible, in particular close to dissociation. A high-level wave-function<sup>26</sup> embedded in periodic Kohn-Sham PBE plane-waves is a suitable starting point for QMC work on transition metal systems.

This work uses the Quantum Monte Carlo (QMC) method, that proceeds in a Variational (VMC) then Diffusion (DMC) stage. DMC includes almost all the correlation energy and is suited to bond dissociation.

The QMC approach uses statistical physics over a large population, comprising sets of instantaneous particle positions in co-ordinate space (or configurations). They are often called 'walkers' (c.f. the one-dimensional random-walk). 'Walkers' are chosen randomly giving initial electron density of the trial wave-function.

After equilibration, many data-points  $N$  give error decreasing as  $1/\sqrt{N}$ . Trial wave-function quality is carefully optimised. Finite size effects are catered for. Solid-state QMC scales slowly with system size ( $n$  electrons scale as  $n^3$ ), using a cubic spline (blips)<sup>27</sup> basis.

The purpose of the work reported here is to study the stability of two possible catalytic reaction paths for water addition to pre-adsorbed CO, distinguished via their specific TS.

The statistical error (0.7 kJ/mol) on the mean calculated reaction barrier heights does not include specific systematic contributions (due to non-locality of the pseudo-potential and poor nodes of the trial wave-function). We strive to limit them here.

We found water addition to CO pre-adsorbed on Pt (111) can occur in two ways:<sup>4</sup>

I-a step by step process, with rate limiting water dissociation on Pt.<sup>28</sup>

II-a concerted step, with CO and water co-ordinated to the metal.

We have excluded pathway I above. Hence, we consider pathway II: QMC energies of asymptotic physisorbed geometries for CO and H<sub>2</sub>O are subtracted from that of the stringently optimised QMC geometry for the adsorbed Transition State (TS).

The TS geometry results from the Hessian with QMC force constants as matrix elements. (The matrix is updated using Pulay's Direct Inversion in the Iterative Subspace (DIIS) algorithm adapted by Farkas<sup>29</sup>). Hence, the TS geometry uses optimisation guided by QMC force constants and permits precise evaluation of the activation barrier height.

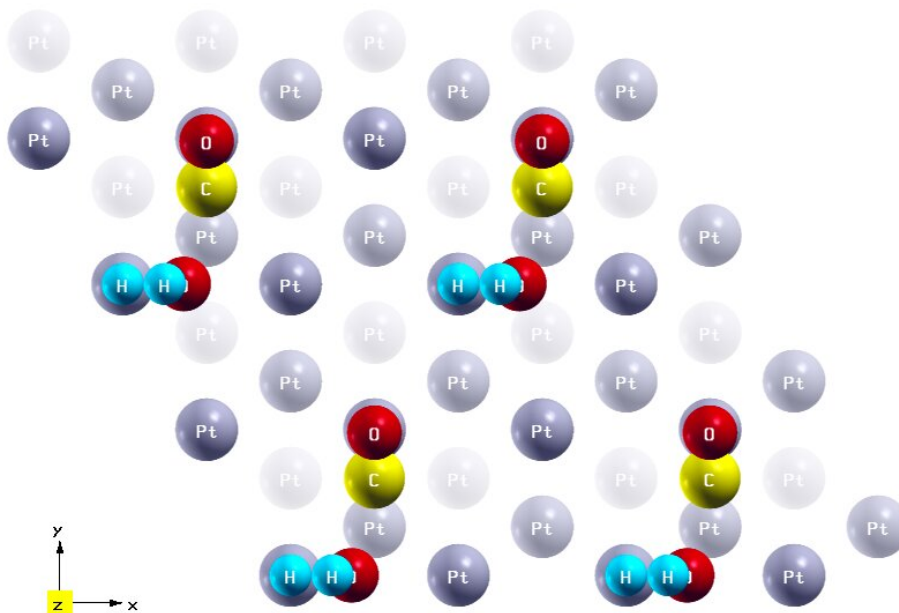


Figure 2: Molecular active site (TS): the  $z=0$  plane is the Pt(111) surface (bottom face). Top view of all four cells corresponding to Figure 1 in the  $2 \times 2 \times 1$  co-ordinate-space expansion.

## Setting up the model system.

Figure 2: is a view from above the periodic cell used in this work, with adsorbed molecules and using translational symmetry. The dark grey Pt-atoms define unique positions in a planar (111) surface at  $z=0$ . A 5-layer Pt-slab is defined (80 atoms) and a Generic Jastrow factor is used for all distinct atoms, i.e. each atom of water, carbon-monoxide and surface and bulk Pt-atoms (surface Pt atom types may also be distinguished by adsorbate interactions). The geometry (Figure 1, co-ordinates in SI) serves as QMC transition-state input.

Finite-size effects are reduced on a large grid: a  $3 \times 3 \times 1$  grid defines the largest accessible real-space super-cell, much smaller than that converged in DFT/plane waves (RAM limit).

The DFT calculations converge only at  $16 \times 16 \times 1$  or higher.

They are useful as control variate in twist-averaging. This corrects for finite size error which cancels between asymptotic and Transition State geometries leaving below  $1/10$  of the error. Runs on a  $2 \times 2 \times 1$  grid reduced finite size-error by a factor 25 (127 for  $3 \times 3 \times 1$ ) compared to a gamma-point calculation.

Semi-core electrons are required but have much less influence on metallic systems conserving the number of metal atoms in very similar geometries (bulk metal atoms are almost bystanders). Comparing asymptote and QMC optimised TS geometries for reaction barriers is such a case. Co-ordination of the TS to the metal surface occurs but the distance between atoms is at most 40 % more than the equilibrium bond-length and referring to un-stretched bonds little affects semi-core electrons. A Z=60 core for Pt is validated below.<sup>30</sup>

## Results.

### Validating pseudo-potentials for a simple test reaction of platinum:

Previous work used Troullier Martins norm conserving pseudo-potentials (TMPP). The core-size (68) was too large to accurately monitor the reaction:  $\text{Pt}_2 + \text{H}_2 \rightarrow 2\text{PtH}$ .

This work converts the ECP used in Molpro for the active site molecular wave-function to a norm conserving form which has the same local channel as ECP60MDF.<sup>30</sup>

The above PtH formation reaction tests both the PP and performance of DMC options used in these QMC calculations.

Numerical integrals over these choices of PP (with Casula T-moves to correct for non-locality<sup>31</sup>) use finite expansion order, limiting accuracy. The TMPP is relatively hard, conferring low variance on the wave-function. Variance is further reduced using the ECP60MDF.

Test calculations refer to:  $\text{Pt} + \text{H}_2$  (giving  $\text{PtH}_2$  (a) and  $\text{Pt}_2 + \text{H}_2$  giving 2 Pt-H (b).

Activation for (b) that has been shown to proceed via a squarish/rectangular TS with the TMPP, gave a QMC value 21 kJ/mol above that from reference Multi-Reference Singles and Doubles CI (MRSDCI) calculations of 61 kJ/mol.<sup>32</sup>

For  $\text{Pt}_2 + \text{H}_2$  a binding energy of 147.4 kJ/mol is obtained with a TMPP by QMC. The value 128.5 kJ/mol is obtained from MRSDCI benchmarks.<sup>32</sup> This major discrepancy shows residual local approximation errors in the TMPP prohibiting its use in the Pt(111) work.

Hence, we designed a hard pseudo-potential (with 18 electrons treated explicitly).

Based on Dolg’s MDF60PP<sup>30</sup> (8 of the 4f electrons are included, as valence, with the electronic ground-state (5d<sup>9</sup> 6s<sup>1</sup>) see SI) it was found to permit accurate evaluation the test reaction energies. The QMC binding energy was 130.2 (c.f. MRSDCI 128.5) kJ/mol<sup>32</sup> with a standard error of 2.1 kJ/mol. The activation barrier was 62 within 2.5 kJ/mol.

These results confirm the accuracy of our approach, using a trial wave-function from Molpro for molecular systems. These reacting systems are embedded in a periodic cell.

### Use of QMC to describe CO+H<sub>2</sub>O adsorbed on a Pt(111) surface.

Molecules interact with both the surface, of 2-D periodicity and each other. A slab construct, limited by relaxed Pt(111) (reaching the experimental bulk geometry in 4 layers) is used.

Carbon monoxide (CO) adsorption is at a hollow site of Pt(111), denoted CO<sub>ads</sub>. Carbon monoxide gas is rather inert. The carbon atom has a small partial negative charge.

The strong bonding of gaseous CO-molecules is weakened during adsorption and its polarity reversed by Pt-C interactions at Pt(111), facilitating its attack by water.

Structure	Clean Pt(111)	Pt(111) CO <sub>ads</sub>	CO	H <sub>2</sub> O
E <sub>tot</sub> (Ha)	-511.792	-533.448	-21.517	-16.210

Reference QMC calculations (in Hartree cf Table I below)

It was found to be more accurate to refer the CO<sub>ads</sub> geometry with a physisorbed incoming water molecule (asymptote of Table I ) to evaluate activation barriers.

Investigation of this phenomenon has been carried out using infrared reactor cells (*in situ* FTIR,<sup>33</sup>) at a number of solid surfaces. Here, we give QMC results for its reaction with water. Removal of toxic carbon monoxide molecules is a typical de-pollution reaction, of interest FOR catalytic exhausts. Furthermore, the reaction with water is of industrial importance in producing clean fuels (hydrogen gas) in a sustainable process. In earlier work,<sup>20,33</sup> it was shown that the stretch frequency of carbon monoxide makes it a highly sensitive probe to surface interactions. This frequency is a measure of adsorption. The carbon monoxide bond-length is just below 120 pm. It is now a **carbonyl** group i.e. site of nucleophilic attack.

### CO and water addition on Pt(111) investigated here:

Water reacts with pre-adsorbed CO, as shown by preliminary DFT (PBE) investigations.

Final reaction products are CO<sub>2</sub> and gaseous hydrogen (fuel restoring water as combustion product). CO adsorbed on Pt (111) was optimized using QMC force constants.

The C-O bond-length was found to be 118 pm, only slightly longer than the gas-phase value of 113 pm, with water interaction depleting CO anti-bonding electron density.

From FTIR work on CO (above): the dipole implies a partial positive charge on carbon (evaluated by QMC at +0.098e), ready for water attack. The Pt-C distance is 2.28 Å.

Water dissociation concerted with oxygen binding to the CO carbon is rate limiting.

In Figure 1, (see the above **model** section) we show the present QMC geometry of the TS. Water with the leaving H<sup>δ+</sup> binds with a surface Pt-atom, whilst the remaining O-H forms a V-shaped H-O<sup>δ-</sup>-C<sup>δ+</sup>=O intermediate. The CO carbon atom and H<sub>2</sub>O oxygen are 2.27 Å above the Pt(111) face. QMC optimized geometry yields three Pt-C bonds: 2.28 Å.

The O-C linkage forming is still 1.63 Å long (in this TS). The four-Pt atom **skin** lozenge, are at the apices of a trigonal (i.e. hexagonal) close-packed cell with Pt-Pt distance 2.783 Å.

DMC energy calculations for the TS and asymptote geometries, after averaging 16 stochastically generated twists for each geometry using the CASINO/pwscf interface for I or II:

I-water dissociation at Pt(111): QMC barrier of 74.27 (standard error is 1.3 kJ/mol). This is in good agreement with PW91 Ultra-soft (USPP) values: 75.32 kJ/mol.<sup>28</sup> N.B. gas-phase water dissociation has a barrier above 492 kJ/mol.

II-water dissociation concerted with the start of nucleophilic attack of CO at Pt(111): QMC Study based on the TS of Figure 1 above, in the Model section (with the carbonyl polarization of adsorbed CO, i.e. partial positive charge on carbon unlike CO (gas)). Some mechanistic studies of the water gas-shift reaction<sup>28,34</sup> have suggested water dissociation is rate limiting and followed by attack of CO (I). This scenario was studied and found to be less favorable in.<sup>4</sup> A concerted TS (II) illustrated in Figure 1 was determined here.

Concerted addition II is validated in this work. It has also previously been postulated.<sup>5</sup>

The repository data-set<sup>15</sup> 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:

Tabulated values are for the DMC population target weight.

Structure	Transition-state	Asymptote
$E_{tot}$ (Ha)	-549.63223	-549.65924
Variance au/(kJ/mol) <sup>2</sup> : se kJ/mol	0.507/3.5: 1.87*	0.528/3.64: 1.91*

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

[Summary of data from: /figshare.com/articles/dataset.](https://figshare.com/articles/dataset)<sup>15</sup> Activation barrier: 0.02701 au or 70.96 (5)  $\pm$  2.7 kJ/mol (i.e. using \*, the standard error value in kJ/mol from analysis of the gamma point distribution). The se is reduced by a factor 4 by twist-averaging (combining runs from 16 offset grids in the first Brillouin zone) to under 0.7 kJ/mol (see SI).

The final QMC barrier is 71.0 with a standard error of 0.7 kJ/mol. This QMC value could be taken as a lower bound for the activation barrier, limited by the activated complex. The actual system will depend on temperature, surface re-arrangement and possible defects. Agreement is perfect with this model: apparent activation energy measured is 71.4 kJ/mol.

## Perspectives and conclusions.

This Quantum Monte Carlo determination of the transition state structure and reaction barrier height for water addition to CO pre-adsorbed on Pt(111) is accurate to 1 kJ/mol. The so-called chemical accuracy is over 4 times less stringent. A concerted water-stretch and addition step is favored (see Figure 1). Water dissociation giving OH-radicals is excluded by their adsorbed and activation of bond-breaking before addition to CO is 3 kJ/mol higher.

Platinum metal is studied, acting via its close-packed surface. A small molecular structure, described by an MRCI Slater determinant that is optimized using QMC forces and the CASINO software is embedded in plane-waves. A DFT calculation of the Pt-slab structure yields Kohn-Sham PBE orbitals. They define the trial QMC wave-function, combined with a

generic Jastrow factor. This embedding procedure is validated for hydrogen dissociation on platinum<sup>35</sup> (testing the Pt(111) slab used here). The trial wave-function thus shows accurate nodes, limiting barrier height systematic errors. Statistical (standard) error of 0.7 kJ/mol reflects total error, close to that of measured apparent activation energy.

A truncated CI was used here (20-100 determinants), however many configurations of small but similar weight may have an influence and have so-far been neglected. Perspectives for extending this strategy use compact molecular full-CI input available from NECI.<sup>26</sup>

The present work obtains the activation barrier to less than 1 k J/mol, better than chemical accuracy (i.e. energy to within 4 kJ/mol) for water addition to adsorbed CO in a close-packed platinum plane and corresponds well to measured apparent activation energy.

Pt-atoms form an equilateral triangle in the Pt(111) plane. A unique Pt-atom defined using translational symmetry represents all 3. We refer to CO adsorbed above the centroid.

This gives three C-Pt linkages. The data giving the TS structure uses CASINO QMC forces code and a contact molecule, comprising CO+H<sub>2</sub>O and a monolayer of Pt(111) optimized using QMC and placed on the slab at the experimental spacing. The size and complexity of this system require considerable supercomputer resources.

## Supporting Information Available

The following Supporting Information file and content is available.

- Supporting Information:
- Trial wave-function and Pseudo-potential. S2
- Periodic super-cell (definition and atom co-ordinates). S4
- Limiting possible systematic error in QMC. CASINO software version. S9
- Generic Jastrow factor structure and definition rules. S11



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Asymptote: [https://figshare.com/articles/dataset/Raw\\_QMC\\_dataset\\_for\\_water\\_at\\_13\\_4\\_au\\_from\\_Pt\\_111\\_with\\_pre-adsorbed\\_CO\\_/10293194](https://figshare.com/articles/dataset/Raw_QMC_dataset_for_water_at_13_4_au_from_Pt_111_with_pre-adsorbed_CO_/10293194)  
Text summary: [https://figshare.com/articles/presentation/out\\_mds\\_pdf/10293065](https://figshare.com/articles/presentation/out_mds_pdf/10293065)  
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# Appendix: Variation and Diffusion Quantum Monte Carlo

## Variation Monte Carlo:

A preliminary Variational Monte Carlo (VMC) calculation is carried out generating several thousand configurations ('walkers': instantaneous points in electron co-ordinates), to sample electron density. VMC is driven by energy minimisation. The *local energy*:  $\frac{H\psi}{\psi}$  is minimised.

The kinetic energy terms involved are smoother and have lower variance in exponentially decaying bases, as shown in our work on wave-function quality.<sup>36,37</sup> A Jastrow factor including electron pair, electron-nucleus and three-body (two-electron and nucleus) is defined. This Jastrow factor<sup>38,39</sup> is carefully optimised (essential work, taking up to 5 % of the total time). This factor uses a polynomial expansion in the variables of explicit correlation.

The product of a Jastrow factor with a Slater determinant gives the trial wave-function.

## Generic Jastrow factor

Defining a Slater-Jastrow wave-function as the product of  $\Psi_S$ , a Slater determinant and the exponential with, as argument, an explicit correlation Jastrow factor  $J(\mathbf{R})$ :

$$\Psi(\mathbf{R}) = e^{J(\mathbf{R})}\Psi_S(\mathbf{R}) = \mathbf{e}^{J(\mathbf{R})}\mathbf{D}_u(\mathbf{R}_u)\mathbf{D}_d(\mathbf{R}_d) \quad (1)$$

The determinants  $D_u(R_u)$  and  $D_d(R_d)$  treat 'up' and 'down' spin separately if necessary. This new approach<sup>39</sup> which generates a huge parameter set was tested for our platinum slab model, presented above. The set can be reduced somewhat by translational using symmetry, otherwise subsequent (diffusion) DMC steps become extremely time-consuming.

The generic Jastrow factor used had e-e, e-n and e-e-n polynomials expanded to 9<sup>th</sup> order, truncated to a finite range (around 10 au) with the factor:  $t(R) = (r - L)^C \Theta_H(r - L)$  Usually C=3, since the wave-function and at least the first two derivatives are continuous.

$\Theta_H$  is the Heaviside function,  $L$  the range, e.g. Wigner–Seitz cell diameter.

$$J(\mathbf{R}) = \sum_{i<j}^N u_{P_{ij}}(r_{ij}) + \sum_i^N \sum_I^{N_n} \chi_{S_{iI}}(r_{iI}) + \sum_{i<j}^N \sum_I^{N_n} f_{T_{ijI}}(r_{iI}, r_{jI}, r_{ij}) \quad (2)$$

$u, \chi$  and  $f$  are parameterised (polynomial) functions in the inter-particle distances. The symbols P, S, T denote the pair, single and three-particle channel indices.

The  $u$  term caters for inter-electron contributions over  $r_{ij}$  and the  $\chi$  term for electron-nuclear terms over  $r_{iI}$ . They are both constructed to obey Kato’s cusp conditions.

The  $f$  term is the three-particle electron pair and nucleus contribution that cannot be neglected. It is expanded over  $r_{ij}$  and two  $r_{iI}$  variables.

This Jastrow factor (in Common Algebraic Specification Language (CASL)) is fully optimised during the VMC step. It contains many polynomial coefficients, as variational parameters, offering flexibility. The parameter set structure used for optimisation in TS and asymptotic geometry generic Jastrow factors are given in Supporting Information.

The electron distribution is updated until the final stages of VMC where fine-tuning of the Jastrow factor is accomplished by energy minimisation over 15 cycles. Our fully-optimised generic Jastrow factor is given in the online repository.<sup>15</sup>

The resulting Slater-Jastrow wave-function is used to initialise the configurations for Diffusion Monte Carlo (DMC). This gives prohibitively long DMC cycles.

Three parameter-sets are obtained for each of the 25 atoms in the super-cell, treated individually. It is seen to approach the variational energy minimum for the system defined: (-448.32 Ha, with the PP from the Effective Core Potential (ECP) ECP60MDF with  $l=1$  as local channel).<sup>30</sup>

DMC cycle duration is cut down by maintaining individual parameter-sets only for atoms in molecular species (CO and water). The platinum atoms are grouped according to rules for surface and bulk atoms (using translation symmetry). These rules allow us to use a single parameter set for each of the inter-particle terms for each group.

Therefore, a Jastrow will be optimal for a given parameter-set for these rules, reaching a minimum energy known to be somewhat above the variational limit. It is therefore of paramount importance to conserve the same rules for definition of the generic Jastrow-factor in each of the limiting geometries (TS and asymptote). Because the same atoms are involved, with some 'bonding' surface interaction for the TS and very little interaction for the asymptote. The correlation space spanned by the parameter-sets used is conserved in the present work. When generic Jastrow optimisation has reached a stable minimum, a final VMC calculation generates the initial configurations required for the Diffusion Monte Carlo step (DMC); 10-20 per core. The previous VMC steps must generate at least as many configurations.

### Diffusion Monte Carlo:

In the DMC method the ground-state component of the trial wave function is projected out by solving the Schrödinger equation (SWE) in imaginary time. DMC is carried out in the fixed-phase approximation, which uses the nodes from the input trial wave-function.

An updated overview of the VMC and DMC methods is given in.<sup>14</sup> These trial wave-functions can be optimised with a complex Jastrow factor,<sup>40</sup> because they potentially provide the input with exact nodes. This improves the single Slater determinant describing a ground-state from the DFT orbitals for heterogeneous systems. DFT nodes may well be poor. The nodes are improved by embedding the MRCI active site.

The The time-dependent Schrödinger equation (TDSWE) is transformed into a Diffusion equation in the 3N-dimensional space of electron coordinates (with the potential energy acting as a source/sink term) by replacing  $t$  by the pure-imaginary time  $it$ , in the TDSWE:

$$i \frac{d}{dt} \Psi(\mathbf{r}, t) = -\frac{1}{2} \nabla^2 \Psi(\mathbf{r}, t) + V(\mathbf{r}) \Psi(\mathbf{r}, t) \tag{3}$$

where  $\nabla^2$  is the scalar Laplacian of an instantaneous electron-position vector:  $\mathbf{r}$ .



Defining the Hamiltonian (for stationary states):

$$\mathcal{H} = -\frac{1}{2}\nabla^2 + V(\mathbf{r}) \quad (4)$$

As outlined above in eqn 2, the time-dependent SWE (replacing  $it$  with  $\tau$ ), becomes the diffusion eqn 4 below. Excited state density contributions contain exponentially decreasing factors, fading out as the 'time' variable  $\tau = it$  is increased in many small steps.

The best-estimate of the ground-state energy eigenvalue ( $E_0$ ) is adjusted. Note that the exact value gives a zero derivative. This is solved combining diffusion and branching or dying processes.

$$-\frac{d}{d\tau}\Psi(\mathbf{r}, \tau) = (\mathcal{H} - E_0)\Psi(\mathbf{r}, \tau) \quad (5)$$

Introducing importance sampling, using the trial wave function transforms the problem into one involving drift as well as diffusion but greatly reduces the population fluctuations due to the branching/dying process. The Fermionic wave function antisymmetry is maintained by constraining the nodal surface to equal that of the trial wave function.

To resolve energy values, QMC statistical error in total values must be relatively small.

When the cost of the equilibration phase of a QMC calculation is negligible,  $\sigma = k/\sqrt{T}$ . Accuracy for a given time hence also depends on the quality (nodes) of the trial wave-function. Lower fixed-phase error reduces the equilibration time.

The DMC algorithm proceeds using Casula T-moves<sup>31</sup> 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 (requiring complex wave-functions as for our structure with no inversion center).