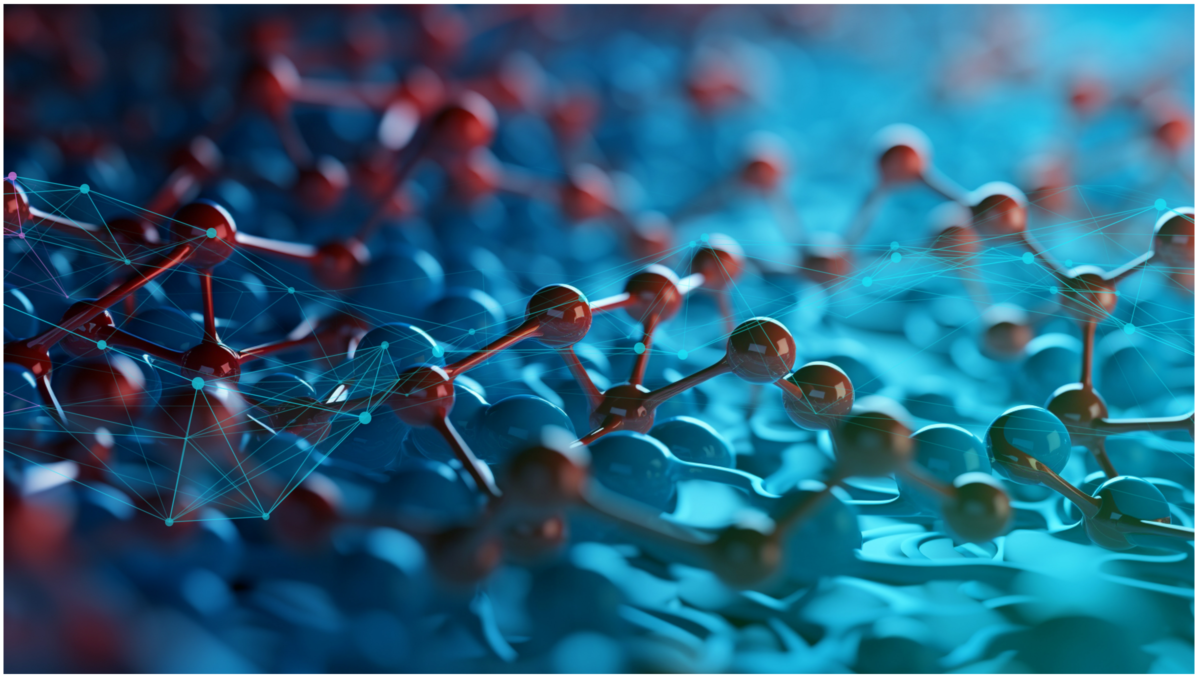

Smart Coating: Investigating Quantum Computing for Corrosion Inhibition

Airbus - BMW Group
Quantum Computing Challenge 2024 | Forward Track
version 1.0

1 Introduction

Preserving the integrity of metal surfaces in the aerospace and automotive industries is of utmost significance to ensure the structural soundness of vehicles, mitigate safety risks, and uphold reliability and performance standards. Consequently, effective management and mitigation of surface degradation are essential in prolonging the lifespan of Airbus and BMW Group products, improving operational efficiency, minimizing downtime, optimizing maintenance plans, and ultimately reducing costs.

Typical surfaces consist of multiple layers, including a topcoat, basic primer, and an aluminium substrate. The degradation of the surface is initiated when mechanical damage in the coating breaches the protective barrier, exposing the underlying aluminium surface to the surrounding atmosphere. Once exposed, the aluminium surface can undergo degradation (*i.e.*, corrosion) due to an oxidation reaction with oxygen, leading to the formation of an amorphous oxide layer on the aluminium surface.[1] The oxide layer prevents further degradation of the aluminium. However, this passive state can be altered by several factors, among which concentration of H^+ ions (pH), temperature and chloride content are the most important.

Certain chemicals, known as inhibitors, can attach to exposed aluminium surfaces and act as protective agents, mitigating the detrimental effects of corrosion and safeguarding the material from degradation. Historically, chromium-based inhibitors held a prominent position due to their exceptional corrosion protection capabilities. Their effectiveness spanned a wide spectrum of pH levels and electrolyte concentrations. Nonetheless, the pronounced toxicity and carcinogenic properties of Cr^{6+} have spurred the search for alternative inhibitors.[2]

Smart coatings have emerged as a possible solution to this conundrum. In a smart coating material, an inhibitor is embedded within a polymer matrix and subsequently released in response to a chemical stimulus. If the surface of aluminium is exposed, the inhibitor adsorbs (*i.e.*, adheres) to it. Numerous inhibitors tested up to now are of inorganic or hybrid organic-inorganic nature. However, purely organic inhibitors are emerging as promising candidates due to their favourable chemical properties, compatibility with the coating substrates, and their environmentally friendly nature. These organic inhibitors originate from amines, mercapto compounds, and aromatic heterocycles. Such functional groups allow the inhibitors to have substantial affinity to the metal surface, resulting in the formation of a protective film that prevents the corrosive agents from reaching the surface and impeding the progression of corrosion.[3, 4, 5] The adsorption of the inhibitors to the metal surface and the protective film can proceed either through physisorption or chemisorption. In physisorption, the molecules adhere to the metal surface through weak interactions, such as Van der Waals forces. Chemisorption involves the establishment of a chemical bond between the molecule and the surface, leading to a stronger binding energy and a notable alteration of the electronic structure of the adsorbate.

The primary goal of this challenge is to understand and model the process of adsorption of inhibitors on the surface of aluminium. The adsorption is paramount to guarantee corrosion inhibition and requires a comprehensive chemical understanding by quantifying the binding energies and identifying the binding sites. Ultimately, the outcome of this research effort will serve as a foundation for the development of smart protective coatings that can provide an environmentally-friendly alternative by replacing the use of chromium-based compounds.

2 Quantum Chemistry using Classical Computation

While experimental techniques like hydrogen gas evolution, linear polarization, galvanostatic discharge, and electrochemical impedance spectroscopy are commonly used to study the passivation of the aluminium surface by an oxide layer, they mainly serve to quantify the degradation kinetics of the surface[6]. Nevertheless, relying solely on these methods offers only a limited comprehension of the passivation process and its underlying molecular mechanisms. In addition, experimental tests incur substantial costs, especially when they need to encompass diverse environmental conditions. Consequently, improved modelling techniques expedite the development process by facilitating more efficient initial design decisions.

To gain the necessary insights into the molecular-level interactions, complementary techniques based on quantum chemistry calculations may be employed. The nature, accuracy, and computational cost of these methods vary drastically. As a general guideline, more accurate techniques tend to be more expensive and are typically applicable to smaller systems only. Fig. 1 and Tab. 1 list a few of the commonly used quantum chemistry techniques, which will be briefly outlined below.

2.1 Density Functional Theory

Density functional theory (DFT) is a widely employed quantum chemistry method[7]. DFT seeks to determine the electron density of a molecular system, $\rho(\mathbf{r})$ where $\mathbf{r}$ are the spatial electronic coordinates in a mean-field fashion. This method offers remarkable computational efficiency and flexibility (see Fig. 1). However, it relies on the knowledge of the exact exchange-correlation function, which needs to

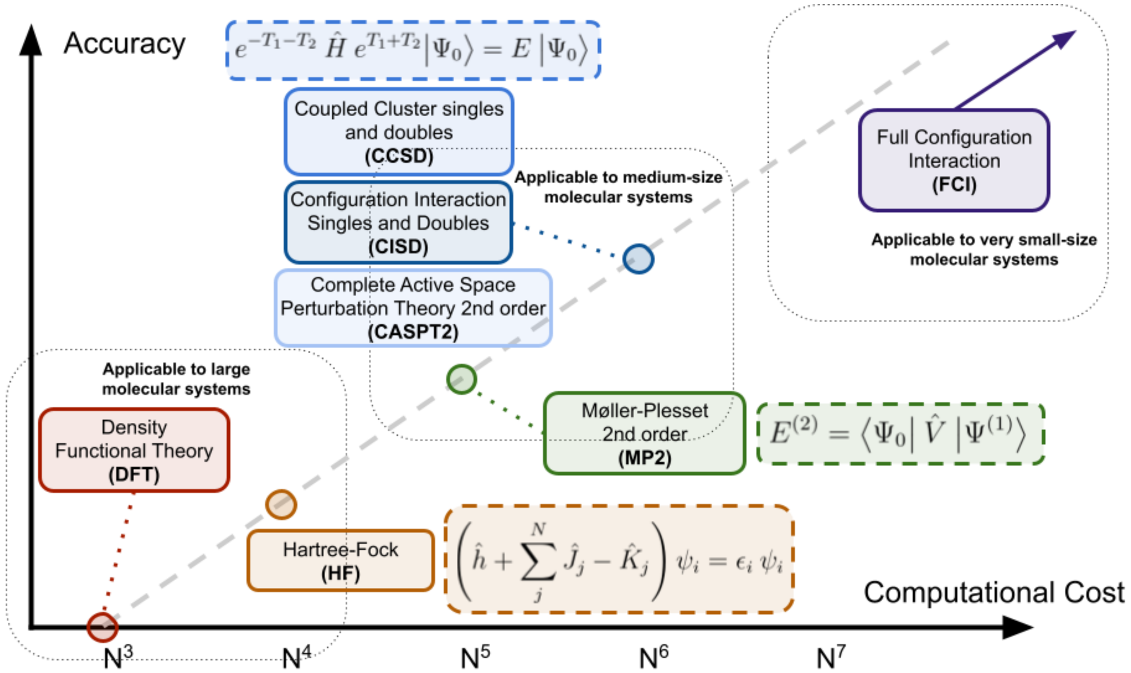

Figure 1: Schematic diagram depicting various widely-used computational chemistry techniques, categorized based on their computational cost (where N roughly represents the system's size) and their precision (measured in arbitrary units).

be approximated. In practice, DFT is always subject to inherent approximations limiting the capability to address specific problems, in particular when correlations play a significant role.

2.2 Wavefunction-Based Methods

Another important class of methods to consider are wavefunction-based methods. A fundamental mean-field theory in this category is Hartree-Fock (HF)[8]. HF calculations are generally computationally more expensive than DFT and, at times, may even be less accurate. However, HF serves as a starting point for developing more accurate methods (called post-HF)[9]. The main objective of post-HF methodologies is to build upon the HF wavefunction to recover the remaining energy, known as correlation energy, which cannot be fully captured within the mean-field framework.

To address the limitations of HF, two complementary approaches can be pursued: the multi-configurational procedure or the perturbation theory (PT) and the coupled cluster (CC) route.

2.2.1 Multi-Configurational Calculations

The multi-configurational approach focuses on recovering *static correlation* energy. To accomplish this, a few crucial electronic wavefunctions, apart from the HF wavefunction, are incorporated into the optimization process. This method has contributed to the advancement of techniques such as complete active space configuration interaction (CASCI) and the more advanced complete active space self-consistent field (CASSCF)[10]. In both techniques, the inclusion of additional electronic wavefunction is achieved by partitioning the orbital space into active and inactive regions, resulting in a more precise depiction of the electronic structure, including strong correlation effects. In the limit of using the whole orbital space, the full configuration interaction (FCI) solution is achieved. It represents the exact solution for the electronic structure problem under consideration, but it comes at a tremendous computational cost (see Fig. 1).

2.2.2 Perturbation Theory and Coupled Cluster

The PT and the CC approaches focus on capturing the *dynamical correlation* energy, which represents instantaneous interactions between electrons that are not accounted for in HF[9, 10]. Utilizing perturbation theory directly with the Hartree-Fock (HF) reference leads to the Møller-Plesset (MP) theory, commonly employing its second-order perturbation, known as MP2. Conversely, when PT is employed with the CASSCI or CASSCF wavefunction, it gives rise to the formulation of NEVPT2[11] and CASPT2[12] theories, respectively. These theories effectively encompass both static and dynamic correlation effects.

Lastly, CC offers an alternative to PT for constructing correlated wavefunctions based on the HF reference[10]. This method provides a systematic and rigorous approach to incorporating dynamic electron correlation (and, to a much lesser extent, static correlation), making it particularly valuable for studying complex molecular systems. Much like PT, CC provides multiple accuracy levels determined by the extent to which we truncate the expansion series. A commonly favoured choice is the coupled cluster singles and doubles (CCSD) method (see Fig. 1).

Method	Wavefunction	Density	Computational efficiency	Static correlation	Dynamical correlation
DFT		○	+	−	(+)
HF	○		(+)	−	−
CASCI	○		(−)	(+)	−
CASSCF	○		(−)	+	−
CCSD	○		−	(−)	+
NEVPT2	○		−	+	+
CASPT2	○		−	+	+
FCI	○		−	+	+

Table 1: General characteristics of commonly used quantum chemistry methods. The first two columns distinguish between wavefunction-based and density-based approaches. The remaining columns highlight the efficiency and ability of each method to recover static or dynamic correlations. Symbols such as +, (+), (−), and − indicate whether the method is suitable, potentially suitable, generally unsuitable, or definitely unsuitable for the indicated properties, respectively.

2.3 Quantum Chemistry in Corrosion Inhibition

In the field of corrosion inhibition, DFT has been extensively employed to identify the chemical descriptors that influence a molecule's corrosion inhibition effectiveness, albeit with limited success[13, 14]. This limitation can be attributed to our limited comprehension of the adsorption process, which encompasses factors such as charge redistribution between the inhibitors and the metal surface, ionization of the inhibitors, and the formation of covalent or ionic bonds with the surface. Observations have highlighted that the presence of sulfur moieties and heteroatoms in inhibitors enhances their effectiveness, likely because of their affinity for binding to metals. Additionally, aromaticity contributes to increased corrosion effectiveness, indicating that self-assembly structures on the metal's surface due to π-π interactions (typical of aromatic compounds) may be an important factor[13].

Exploring the inhibitor adsorption requires highly accurate methods that provide a well-balanced description of electronic correlation. While DFT, with a carefully selected exchange and correlation function, can offer practical compromises in specific situations, it remains crucial to subject these assumptions to rigorous testing against more accurate methods, such as CCSD. Moreover, the interaction between inhibitors and the metal surface may lead to a multiconfigurational scenario where static correlation could become predominant. Unfortunately, the direct application of high-accuracy methods remains unfeasible to date due to the inherent unfavourable scaling required to implement them on classical hardware. (Fig. 1). In this regard, quantum computing has emerged as a promising solution to reduce the burden of solving many-body quantum mechanical problems.

3 Quantum Chemistry Using Quantum Computing

Quantum algorithms – such as quantum phase estimation (QPE) – potentially offer a speedup compared to classical solutions[15, 16]. QPE presents an alternative way to solve the FCI problem, albeit with an acceptable margin of error, while requiring exponentially fewer quantum operations than its classical equivalent[16, 17]. However, it's important to note that the practical implementation of QPE on noisy intermediate-scale quantum computers (NISQ) remains unfeasible to date. This is primarily due to the extensive runtime of the algorithm and the resulting necessity for fault-tolerant quantum computers equipped with a substantial number of qubits. To address these limitations, an alternative approach known as the variational quantum eigensolver (VQE) has been introduced. In the VQE, a portion of the problem's complexity is offloaded to a classical computer, resulting in a significant reduction in the computational load on the quantum computer. Within the VQE framework, a wavefunction ansatz is devised by introducing certain free parameters that can be optimized using classical computational resources, leading to a considerably shorter quantum algorithm. In VQE, the electronic energy takes the form

$$E(\theta) = \langle \Psi(\theta) | \hat{H} | \Psi(\theta) \rangle \,, \tag{1}$$

where $\hat{H}$ is the electronic Hamiltonian of the system and we have assumed the parametrized wavefunction $|\Psi(\theta)\rangle$ to be normalized. Unlike QPE, which provides the exact FCI energy, the accuracy of VQE is determined by the choice of the wavefunction ansatz. This ansatz can take various forms, such as HF [18], CC [19], and CASI [20]. Following the measurement of $E(\theta)$, classical computing resources are employed to optimize the variational parameters and attain the minimum energy.

The VQE algorithm has found applications in a wide range of scenarios, from simple molecules consisting of only a few atoms[18, 21] to more complex cases where a blend of quantum and classical simulations are required to describe the entire system[22, 20]. In the latter approach, the molecular system is divided into two fragments. The first fragment is simulated using a quantum computer, while the surrounding "environment" is handled using classical simulations. To conclude, it's worth noting that VQE doesn't scale efficiently with increasing system size due to the substantial number of measurements needed during the optimization steps [23]. As such, it's advisable to consider VQE primarily for demonstration purposes until fault-tolerant quantum computers become accessible.

4 Case Study

The proposed problem statement consists of modelling the adsorption (physisorption or chemisorption) of a selected corrosion inhibitor molecule onto the surface of aluminium. The corrosion inhibitors can be inorganic or organic; however, a judicious selection is essential, guided by both chemical intuition and considerations of environmental and financial aspects. We recommend starting to look at the comprehensive database provided by CORDATA, which contains detailed information on some of the most popular inhibitors used to date[24].

As an example, we illustrate the case of the 2-mercaptopyrimidine. The 2-mercaptopyrimidine is a potential corrosion inhibitor, proven by its properties such as containing nitrogen and sulfur centres that can chemically bond to aluminium surfaces, as well as its aromatic structure that facilitates surface covering through π-π stacking effects. In terms of corrosion prevention, it demonstrates an efficacy of about 89% with respect Cr^{6+} for AA2024[25], an aluminium-copper alloy recognized for its exceptional mechanical properties but vulnerability to corrosion and deterioration. The 2-mercaptopyrimidine is conveniently available in the market from more than 80 sellers worldwide, priced at a reasonable 120$ for a 50g quantity from Fisher Scientific. However, caution is necessary when handling this compound due to its potential adverse effects, including skin irritation (H315), serious eye irritation (H319), and respiratory irritation (H335). Can you find a better one?

The relationship between the metal surface coverage (φ) and the inhibitor concentration (c) can be modelled in various ways. One possible approach is to use a modified version of the Langmuir isotherm [6]:

$$\frac{c}{\varphi} = \frac{a}{K} + a \cdot c \,, \tag{2}$$

where a is a (empirical) correction coefficient and K denotes the adsorptive equilibrium constant. The equilibrium constant K reflects the thermodynamic driving force associated with adsorption processes and can be expressed as follows:

$$K \propto e^{-\frac{\Delta G}{RT}} \,. \tag{3}$$

Here, ΔG signifies the free energy change related to the adsorption process, R represents the gas constant and T is the temperature. Consequently, the evaluation of the surface passivation process entails examining the energy alteration upon the adsorption of the inhibitor onto the surface. This energy change is expressed by the equation:

$$\Delta G(\mathbf{R}) = G_{ads}(\mathbf{R}) - (G_{surf}(\mathbf{R}) + G_{mol}(\mathbf{R})) \,, \tag{4}$$

where G_{ads} represents the overall free energy of the system after the adsorption of the molecule onto the surface while G_{surf} and G_{mol} denote the individual free energy contributions of the surface and the molecule, respectively, in their non-interacting states. We emphasize the dependence on the nuclear coordinates ($\mathbf{R}$) since there may exist more than one adsorption or chemisorption site.

To calculate the energy components outlined in Equation Eq.(4), it is necessary to establish a workflow that implements at least one quantum chemistry methodology on a quantum computer (some of the most common methods were listed in Tab.1). The choice of methodology remains flexible, but it's important to acknowledge that due to potential instances of strong correlation within the system and dispersion, it is recommended to conduct proper benchmarking. This analysis should encompass various factors, including the level of theory employed, the embedding strategy adopted, the basis set and the active space utilized.

5 Submission Guidelines and Key Performance Metrics

This section outlines the specific guidelines for an ideal submission of this particular problem statement. We also emphasize to follow the general submission guidelines provided on the challenge website. When detailing your solution, which includes explaining your workflow design and the selection of both classical and quantum algorithms, please keep in mind that the assessment process will take into account the following performance metrics:

- The primary objective of the challenge is to devise and implement a systematic workflow to model the adsorption processes of organic or inorganic inhibitors onto a surface. It's essential to ensure that the methods employed are in line with the desired levels of accuracy.

- The workflow must foresee the implementation of at least one quantum chemistry (sub)method on a quantum computer.

- The workflow can rely on data provided by any quantum chemistry software.

- It is required to perform a benchmark encompassing the parameters that influence the calculations, ensuring the reliability and accuracy of the outcomes.
- The feasibility study, scalability potential, and the requirements for the quantum advantage of the approach must be discussed.
- The reaction shall be studied on aluminium with the selection of one inhibitor. While considering additional inhibitor candidates and expanding the calculations to cover the aluminium 2024 alloy is not obligatory, it would be considered a plus.
- Assessing the chemical and physical properties, eco-friendliness, cost, and availability of the chosen inhibitor candidates is encouraged, but it is regarded as an optional extra aspect.
- Incorporating the solvent into the modelling of inhibitor adsorption is a plus.

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