# Supplementary material for: Modelling Carbon Capture on Metal-Organic Frameworks with Quantum Computing

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## DISSOCIATION CURVES USING DIFFERENT FRAGMENTATION STRATEGIES

The fragmentation strategies displayed in Fig. S1 were also used to determine the Al-fumarate+CO<sub>2</sub> dissociation energy. Fig. S1a shows a fragmentation in which the stretched Al-O<sub>CO<sub>2</sub></sub> bond is contained in one fragment. When a correlated wavefunction solver CCSD (or AS-UCCSD with large enough active space) is used for a fragment containing the Al atom and the oxygen of CO<sub>2</sub> (the "AlO" fragment), with RHF or MP2 applied to the remaining parts of the system, the Al-fumarate+CO<sub>2</sub> complex is found to be unbound, with a monotonic decrease of the energy spanning all adsorbate-adsorbent distances r, (Fig. S1b,c). Such a behavior is inconsistent with brute force classical calculations, and with expected adsorption properties in MOFs [1, 2]. Fig. S1d also shows a fragmentation consisting of the AlO fragment, but the rest of the fumarate is considered as one large fragment. The corresponding results in Fig. S1e show a similar conclusion - Al-fumarate+CO<sub>2</sub> complex is unbound for large enough active spaces of the AlO fragment. Hence, for these particular fragmentations, DMET is found to fail in describing the CO<sub>2</sub> binding to the Al site of the fumarate.

In Fig. S1c, we also show that the unphysical behaviour is manifested when a sufficiently large amount of correlation is included by sufficiently large active spaces. Indeed, the 4 qubit AS-UCCSD simulation (with RHF applied to the non-active fragments, *i.e.* those fragments not directly involved in the Al-O<sub>CO2</sub> bond) shows a bound state (purple squares), while the 16 qubit counterpart (black squares and black triangles) shows an unbounded state. Spurious dissociation behaviour can also be obtained when MP2 is used as a fragment solver, and the inset of Fig. S1c shows this is not exclusively due to the known weaknesses [3] of MP2 for dissociation in some systems.

Fig. S1f shows the same fragmentation as Fig. 2a. Hence the results shown in Fig. S1g are the classical counterparts to Fig. 2c. For this case, physical bound state dissociation curves without artifacts are observed, yet only when a mixture of solvers are used. When all fragments are solved with the same post-Hartree-Fock solver (MP2 or CCSD), discontinuities and/or non-monotonic behaviour is observed. Hence, the use of different solvers (maintaining democratic mixing), along with a careful choice of fragmentation appears to ameliorate the unphysical dissociation behaviour.

To summarise these results, no combination of DMET solver methods was found that resulted in qualitatively correct dissociation curves for larger active spaces when the high level fragment contains the stretched AlO bond, while in Fig. S1g it is shown that physical dissociation curves are not possible when the same solvers are used on all fragments (where the stretched bond lies between fragments). By comparing Fig. 2 to Fig. S1, our results show that small changes in fragmentation lead to large qualitative differences in dissociation behaviour - this is observed for small changes in fragmentation geometry and solver methods.

# ORBITAL CONTRIBUTION TO DMET CORRELATION ENERGY

In this section, the correlation contribution to the total DMET energy is plotted as a function of active space (AS) size, for all the fragmentations strategies discussed in this work. CCSD and UCCSD are shown for comparison in Figs.

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FIG. S1: **a.** Fragmentation strategy consisting of the fumarate Al and the O of CO<sub>2</sub> (O<sub>CO<sub>2</sub></sub>) as one fragment (AlO), the CO of CO<sub>2</sub> as a separate fragment, and the rest of the fumarate divided into fragments. **b.** and **c.** show  $\Delta E$ curves for fragmentation in **a** obtained using classical and quantum solvers, respectively. In **c** quantum AS-UCCSD is applied to the AlO fragment, while RHF or MP2 is used for all other fragments. The inset of **c** shows RHF and MP2 calculations (brute force, no DMET) compared to 4-qubit AS-UCCSD. **d.** Same as **a** but the fumarate (not including the Al bonding to CO<sub>2</sub>) is one large fragment. **e.** shows  $\Delta E$  curves for fragmentation in **d** obtained using classical and quantum solvers. **f.** Same fragmentation strategy as shown in Fig. 2a, with  $\Delta E$  curves shown in **g** for classical solvers. RHF and MP2 solvers for the AlO (**b**) and Al (**g**) fragments are also shown for comparison.

S2 - S5. Note that the contribution of correlation for full active spaces is much larger in Figs. S2 and S3 compared to Figs. S4 and S5, due to the larger number of orbitals contributed by the  $O_{CO_2}$  atom in the AlO fragment.

In Fig. S3 it can be seen that for 6 active spatial orbitals, the UCCSD correlation energy is approximately 20 mHa



FIG. S2: Correlation energy versus active space size for CCSD and UCCSD fragment solvers, using the fragmentation depicted in Fig.S1a.  $N_{\text{act-orb}}$  refers to the number of active molecular spatial orbitals.



FIG. S3: Correlation energy versus active space size for CCSD and UCCSD fragment solvers, using the fragmentation depicted in Fig.S1d.  $N_{\text{act-orb}}$  refers to the number of active molecular spatial orbitals.

smaller than CCSD for a comparable AS. This is consistent with the difference in total energies between UCCSD (N<sub>q</sub> = 12) and CCSD with 3 HOMO and 3 LUMO spatial orbitals at Al-O<sub>CO2</sub> distance r = 2 Å. The agreement between UCCSD and CCSD correlation energies does not improve for a larger AS using the fragmentations from Fig. S1a,d. At variance, the agreement in correlation energy between UCCSD and CCSD is much better in Figs. S4 and S5. This translates to better agreement in dissociation curves for a given AS size (the AS-CCSD dissociation curves are not shown in the main text for brevity). Hence the fragmentations from Fig. 2a and Fig. 2b exhibit better agreement between UCCSD and CCSD and CCSD for feasible active space sizes in addition to physical dissociation curves.

#### CLASSICAL CALCULATIONS OF AL-FUMARATE+CO<sub>2</sub>

In order to determine the optimal position of the  $CO_2$  molecule interacting with the fumarate molecule, a series of classical calculations at various levels of theory (including mean-field and wavefunction techniques) were carried out in which a  $CO_2$  molecule was placed at varying distances and orientations relative to the fumarate. In these calculations, the internal geometries of the constituents are kept frozen to their isolated configurations. The lack of inversion symmetry with respect to the horizontal molecular plane prompts the investigation of the lowest energy incidence angle of  $CO_2$  as it approaches the Al center. To this end, we calculate the energy as a function of Al-



FIG. S4: Correlation energy versus active space size for CCSD and UCCSD fragment solvers, using the fragmentation depicted in Fig.2a.  $N_{\rm act-orb}$  refers to the number of active molecular spatial orbitals.



FIG. S5: Correlation energy versus active space size for CCSD and UCCSD fragment solvers, using the fragmentation depicted in Fig.2b.  $N_{\text{act-orb}}$  refers to the number of active molecular spatial orbitals. For  $N_{\text{act-orb}} = 9$ , 4 occupied and 5 virtual orbitals are used.



FIG. S6: Perpendicular orientation of  $CO_2$  molecule relative to the Al-fumarate molecule, corresponding to  $CO_2$  angle = 90°.

 $O_{CO_2}$  distance at perpendicular orientation (relative to the horizontal plane), for the CO<sub>2</sub> molecule approaching the fumarate from "above" and "below" the horizontal plane (where "above" corresponds to Figs. S6 and S7). Results



FIG. S7: Flat orientation of  $CO_2$  molecule relative to the Al-fumarate,  $CO_2$  angle =  $0^{\circ}$ .



FIG. S8: Total energy of the Al-fumarate+ $CO_2$  complex as a function of Al-O distance, for the  $CO_2$  molecule incident from "above" (as in Fig. S6), or from the opposite direction "below". The latter corresponds to increased interaction between  $CO_2$  and the fumarate oxygens. No dispersion correction has been added.

are plotted in Fig. S8. Following this, Fig. S9 shows the energy as a function of  $CO_2$  angle relative to the fumarate plane (keeping the Al- $C_{CO_2}$  distance fixed), in which the  $CO_2$  is placed "above" the fumarate plane.

The dependence of fumarate+ $CO_2$  energy on  $CO_2$  incidence angle was also evaluated for the purpose of determining the optimal geometry. Solid angle parameters are defined as in Fig. S10, while in Fig. S11 the energy as a function of solid angle coordinates for the  $CO_2$  molecule is reported at the mean-field Hartree-Fock level. This further indicates



FIG. S9: Total energy of the Al-fumarate+ $CO_2$  complex as a function of  $CO_2$  orientation. Distance between Al and C (of  $CO_2$ ) corresponds to 3.197Å.

that the minimum energy geometry for the minimal STO-3G basis set corresponds to the  $CO_2$  at perpendicular incidence from "above" the fumarate plane (see Fig. S6) with the Al-O<sub>CO<sub>2</sub></sub> distance at approximately 2 Å.

## QUANTUM COMPUTATIONAL DMET IN DETAIL

If the exact ground state wavefunction of the full system is known one can construct a projector  $\hat{P}^x$  for fragment x such that the projected reduced size Hamiltonian (embedding Hamiltonian)  $\hat{H}^x = \hat{P}^x \hat{H} \hat{P}^x$  results in the same exact ground state[4, 5]. As the exact wavefunction is in general unknown, the embedding Hamiltonian is constructed with a wavefunction approximated by a low level theory such as HF.

The DMET algorithm starts by constructing the Hamiltonian  $(\hat{H})$  with a localised and orthogonal basis, in which the domain of each fragment can be specified. Then the algorithm solves the full problem with the HF theory and calculates the one-electron reduced density matrix (1-RDM) in the localised basis. More precisely, a modified total Hamiltonian  $\hat{H}'$  is solved with HF theory,

$$\hat{H'} = \hat{H} + \sum_{x} \sum_{ij \in A^x} u^x_{ij} a^{\dagger}_i a_j \tag{S1}$$



FIG. S10: Solid angles of  $CO_2$  incident on the Al center of the fumarate.



FIG. S11: Total energy of the Al-fumarate+ $CO_2$  complex as a function of  $CO_2$  solid incidence angle. For all geometries considered, the  $CO_2$  molecule at perpendicular incidence from "above" the fumarate plane, with the fumarate Al facing the  $CO_2$  O atom, corresponds to the minimum energy.

where  $A^x$  refers to the subspace spanned by fragment x, and  $a_i^{\dagger}$  is a fermionic creation operator in the localised basis. The extra one-body term in Eq. S1 is the correlation potential that accounts for the effects of correlations on the 1-RDM. The values of  $u_{ij}^x$  are to be determined such that the 1-RDM on each fragment block matches the 1-RDM calculated with the high level methods, and they are improved self-consistently as described by Wouters et al.[5]. In this paper we perform only the one-shot DMET method, which is equivalent with the first iteration of DMET when the initial correlation potential is zero, thus  $\hat{H}' = \hat{H}$ .

Following the calculation of the one-electron reduced density matrix of the full system, a fragment projector  $\hat{P}^x$ can be constructed based on the HF solution and the embedding Hamiltonian  $\dot{H}^x$  can be expressed [5]. In practice, the Schmidt decomposition of the HF wavefunction allows one to partition the 1-RDM into a fragment and its complementary subsystems, and by diagonalising the complementary sub-block of the 1-RDM one can construct a useful basis (Schmidt basis) in which the fractionally occupied orbitals are kept as bath orbitals and the occupied and empty orbitals are designated as the environment. The embedding Hamiltonian in the Schmidt basis is

$$\hat{H}^{x}(\mu_{\text{global}}) = \sum_{ij \in A^{x} \cup B^{x}} \left( h_{ij}^{x} + \sum_{kl \in N} (V_{ijkl}^{x} - V_{ilkj}^{x}) \boldsymbol{D}_{kl}^{\text{env},x} \right) \hat{c}_{i}^{\dagger} \hat{c}_{j} + \frac{1}{2} \sum_{ijkl \in A^{x} \cup B^{x}} V_{ijkl}^{x} \hat{c}_{i}^{\dagger} \hat{c}_{k}^{\dagger} \hat{c}_{l} \hat{c}_{j} - \mu_{\text{global}} \hat{N}_{x}$$
(S2)

where  $h_{ij}^x$  and  $V_{ijkl}^x$  are the one and two-electron integrals in the Schmidt basis, respectively,  $c_i^{\dagger}$  is the corresponding fermionic creation operator, and  $B^x$  refers to the subspace of the bath orbitals. The  $D_{kl}^{\text{env},x}$  is the one-electron reduced density matrix of the fully occupied orbitals in the environment. The last term is not the result of the projection, but it is added to control the charge distribution between the fragment and the bath.  $\hat{N}_x = \sum_{i \in A^x} \hat{c}_i^{\dagger} \hat{c}_i$  is the particle number operator for fragment x and  $\mu_{global}$  is the global chemical potential, independent of the fragment, and is determined from the constraint

$$\sum_{x} \langle \Psi_x(\mu_{\text{global}}) | \hat{N}_x | \Psi_x(\mu_{\text{global}}) \rangle = N_e \tag{S3}$$

where  $\Psi_x(\mu_{\text{global}})$  is the ground state of the  $\hat{H}^x(\mu_{\text{global}})$  obtained with a high level method, such as VQE, and  $N_e$  is the total number of electrons in the molecule. In practice, this constraint is satisfied iteratively, with initial value  $\mu_{\text{global}} = 0$ . Once the final value of  $\mu_{\text{global}}$  and  $\Psi_x(\mu_{\text{global}})$  are found the energy of each fragment is obtained (assuming "democratic" mixing of local RDMs [5]) from

$$E^{x} = \sum_{i \in A^{x}} \left[ \sum_{j \in A^{x} \cup B^{x}} \left( h_{ij}^{x} + \frac{1}{2} \sum_{kl \in N} (V_{ijkl}^{x} - V_{ilkj}^{x}) \boldsymbol{D}_{kl}^{\text{env}, x} \right) \boldsymbol{P}_{ij}^{x} + \frac{1}{2} \left( \sum_{jkl \in A^{x} \cup B^{x}} V_{ijkl}^{x} \Gamma_{ijkl}^{x} \right) \right]$$
(S4)

where  $\boldsymbol{P}_{ij}^x = \langle \Psi_x(\mu_{\text{global}}) | \hat{c}_i^{\dagger} \hat{c}_j | \Psi_x(\mu_{\text{global}}) \rangle$  and  $\boldsymbol{\Gamma}_{ijkl}^x = \langle \Psi_x(\mu_{\text{global}}) | \hat{c}_i^{\dagger} \hat{c}_k^{\dagger} \hat{c}_l \hat{c}_j | \Psi_x(\mu_{\text{global}}) \rangle$ . In Quantinuum's computational chemistry platform, one may choose to calculate the density matrix for each fragment either classically or with one of the available quantum algorithms. This enables a mixing of algorithms for different fragments: less important regions of the molecule can be solved with a cheap classical method, while the important fragments where the interesting chemistry occurs (in this case the Al-CO<sub>2</sub> interaction) may be treated with high accuracy wavefunction methods. The latter can include a quantum computational solver for the fragment of interest, which allows for the combination of classical and quantum calculation methods for different parts of the molecule. In addition, we can choose active orbital spaces for different fragments, which allows for more efficient simulations in terms of the number of qubits and number of interaction terms. Once all these quantities have been calculated, the total energy of the molecule will consist of a sum of fragment energies  $E^x$  plus the nuclear repulsion contribution

$$E = \sum_{x} E^x + E_{nuc}.$$
 (S5)

While many embedding approaches are available [6], DMET is an approach that has been shown to accurately describe the dissociation of strongly correlated systems whose dissociated state is in general difficult to capture, even when the system is fragmented to individual atoms [4]. In this work, the energetics of  $CO_2$  dissociation from the fumarate will be investigated as a means to study the  $Al-CO_2$  interaction, and for this reason an embedding approach which is expected to capture the strong coupling between the embedded fragment and its environment, as well as the static correlation resulting from the dissociation of the fragmented system, is desired. Hence, we select the DMET approach for this purpose. However, despite these previous works [4], our results show that the predicted dissociation behavior is highly dependent on the adopted fragmentation strategy. While quantitative differences between different DMET fragmentations of the same system have been reported recently [5, 7], our work shows that

different fragmentations can result in *qualitative* differences in the predicted behavior of the total system, even leading to differing predictions as to whether a chemical complex is bound or unbound.

The variational quantum eigensolver (VQE) [8] is a hybrid quantum/classical algorithm that can variationally solve for the ground state (or other eigenstates, given appropriate constraints) of a given Hamiltonian. We use VQE as the parameter optimiser of the UCCSD wavefunction ansatz. The latter has been implemented to support active orbital spaces, which is useful for controlling the number of qubits in the simulation. This comprises our quantum computational fragment solver. Note that the UCCSD wavefunction can be written as

$$|\Psi_{\rm UCCSD}\rangle = \mathcal{U}|\psi_0\rangle \tag{S6}$$

where  $\psi_0$  labels the reference state, typically the HF wavefunction, and  $\mathcal{U}$  is the unitary operator constructed from anti-hermitian excitation generators

$$\mathcal{U} = e^{\sum_{i} \theta_i (\hat{T}_i - \hat{T}_i^{\dagger})} \tag{S7}$$

where the fermionic excitations  $\hat{T}_i$  are restricted to single and double excitations, and  $\theta_i$  are variational parameters. Due to the difficulty of implementing  $\mathcal{U}$  directly in the NISQ era, it is typically decomposed into an ordered product of tractable operations, which is known as Trotter decomposition [9]

$$e^{\sum_{i}\theta_{i}(\hat{T}_{i}-\hat{T}_{i}^{\dagger})} \approx \left[\prod_{i} e^{\frac{\theta_{i}(\hat{T}_{i}-\hat{T}_{i}^{\dagger})}{t}}\right]^{t}.$$
(S8)

This is an approximate relation since the generators in the exponent do not commute in general. The first-order Trotter approximation, utilised in Quantinuum's computational chemistry platform, is obtained when t = 1. In our implementation, we order the terms such that single excitations are applied first, followed by double excitations. Within the singles and doubles, orbital indexes are ordered such that lowest occupied and virtual orbitals are applied first. We use the same basis sets as the classical calculations to generate the integrals for the UCCSD calculations.

In order to run 16 or more qubit simulations using a classically simulated quantum hardware, high performance computational resources are required. We utilise Microsoft's Azure for idealised noise-free simulations. This allows for the benchmarking of this method without the interference of hardware noise. Hence, results from idealised calculations are used to study the intrinsic accuracy of this approach. The IBMQ emulator for *ibm\_lagos* is used for simulations with a noise model (the calibration data for this noise model is available from the authors on request). This allows for the effect of noise on calculations of a dissociation barrier, and the impact of the choice of error mitigation scheme. Thus our work sheds light on the theoretical accuracy of this approach, as well as the effect of hardware error and its mitigation, for systems relevant to carbon capturing MOFs which will serve as a guide to future simulations on fault-tolerant quantum devices.

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