1 Introduction to quantum algorithmic approaches

In this section we will attempt to construct quantum algorithms for calculating three of the GFN2-xTB[1] energy terms: E^Γ, E^γ and E^{EHT}. We will showcase three different approaches to doing a calculation as a building block of a larger circuit.

The conceptually simplest approach is to directly translate classical mathematical circuits to the quantum world using ancillary qubits to ensure reversibility. Here most of the computation happens in the state, and the result is readable in the bits of the measurement output. This approach has seen some development beyond this simple translation resulting in some very qubit efficient primitives for multiplication and addition in particular[3, 6]. This approach will be applied to the E^Γ and E^γ terms, and be referred to as Quantum Digital Arithmetic in this report.

Our second approach is Quantum Amplitude Arithmetic[7]. In this approach we try to prepare the desired result not as a easily read measurement result, but as part of the amplitude of a state. We will use this approach for the E^Γ term to prepare a qubit in the state $w|0\rangle + \alpha|0\rangle$ where we can choose α to be proportional to the E^Γ of the molecule. Alternatively we can choose α to be proportional to $E^\Gamma - E^\Gamma_H$ where E^Γ_H is the E^Γ energy for some known high energy isomer. This is not something we imagine being a common thing to want, however it is something which we want for the total energy! The issue that is solved by subtracting a known high energy is the following. Say we know all the energies, and we want to do something with those states that have a low energy. If all the energies lie between 100 and 101 (units not important), which may make a large difference, the relative difference is not large. If we subtract a known high energy of say 100.9 we get much larger relative differences where the low energy isomers will have a much larger α than the high energy isomers.

The final algorithmic approach we will explore uses quantum singular value transformations[4]. In this approach the calculations are being carried out in the singular values of block encoded matrices. We will use this approach to calculate the E^{ETH} term, as it involves a lot of elementwise matrix multiplications. This is well suited for this approach.

For all of these approaches we will assume that we have access to some pretty intricately prepared states. We will not go into how the are prepared other than the fact that classically we can generate the geometries and so for entire isomer spaces without any other information. As any classical computation in theory also can be applied to a quantum computer after modifications it is a possibility to prepare these states.

1.1 Calculating E^Γ using Quantum Digital Arithmetic

The GFN2-xTB E^Γ term has the following form[2]

$$E^\Gamma = \frac{1}{3} \sum_A \sum_{\mu \in A} (q_{A,\mu})^3 \Gamma_{A,\mu}, \tag{1}$$

where $q_{A,\nu} = \sum_B \sum_{\nu \in B} P_{\mu\nu} S_{\mu\nu}$ is the partial charge of shell μ associated with atom A. P, S are the density and overlap matrices. $\Gamma_{A,\mu} = \Gamma_A K_\mu$ is just the product of an element specific constant and a shell specific constant, for our purposes the element is always carbon and the shell is either the first or second in GFN2 thus we have 2 numbers $\Gamma_{\text{Carbon},0(1)}$ henceforth referred to as $\Gamma_{0(1)}$.

Let us first rewrite the inner expression a bit given our new definition and knowledge of the atoms we are working with.

$$\sum_{\mu \in A} (q_{A,\mu})^3 \Gamma_{A,\mu} = \sum_{\mu \in \{0,1\}} (q_{A,\mu})^3 \Gamma_\mu \tag{2}$$

We now need a unitary which computes this function on a given state $|\Gamma_\mu\rangle_\Gamma |q_{A,\mu}\rangle_Q |acc\rangle_E \to |\Gamma_\mu\rangle_\Gamma |q_{A,\mu}\rangle_Q |acc + (q_{A,\mu})^3 \Gamma_\mu\rangle_E$. The subscripts on the kets refer to the quantum register they represent. Consider having access to the following fused multiply add unitary $|A\rangle |B\rangle |acc\rangle \to |A\rangle |B\rangle |acc + A * B\rangle$. Let us to our initial Γ, Q, E registers add two ancillary registers, W_1, W_2. We can now apply the following unitary

$$E_{i\ (\Gamma,Q,W_1,W_2,E)}^{\Gamma} = \text{MADD}_{\Gamma,Q,W_1}^{\dagger} \text{MADD}_{Q,W_1,W_2}^{\dagger} \text{MADD}_{Q,W_2,E} \text{MADD}_{Q,W_1,W_2} \text{MADD}_{\Gamma,Q,W_1} \tag{3}$$

Let us follow the process:

$$E_{i\ (\Gamma,Q,W_1,W_2,E)}^{\Gamma} |\Gamma_\mu\rangle_\Gamma |q_{A,\mu}\rangle_Q |0\rangle_{W_1} |0\rangle_{W_2} |acc\rangle_E \tag{4}$$

$$= \text{MADD}_{\Gamma,Q,W_1}^{\dagger} \text{MADD}_{Q,W_1,W_2}^{\dagger} \text{MADD}_{Q,W_2,E} \text{MADD}_{Q,W_1,W_2} |\Gamma_\mu\rangle_\Gamma |q_{A,\mu}\rangle_Q |\Gamma_\mu q_{A,\mu}\rangle_{W_1} |0\rangle_{W_2} |acc\rangle_E \tag{5}$$
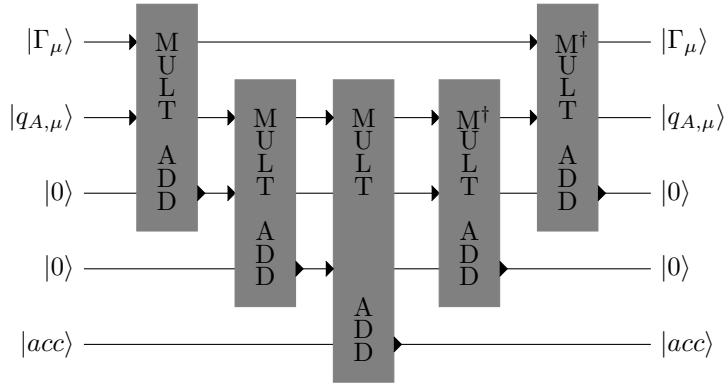
$$= \text{MADD}_{\Gamma,Q,W_1}^{\dagger} \text{MADD}_{Q,W_1,W_2}^{\dagger} \text{MADD}_{Q,W_2,E} |\Gamma_\mu\rangle_\Gamma |q_{A,\mu}\rangle_Q |\Gamma_\mu q_{A,\mu}\rangle_{W_1} |\Gamma_\mu (q_{A,\mu})^2\rangle_{W_2} |acc\rangle_E \tag{6}$$

$$= \text{MADD}_{\Gamma,Q,W_1}^{\dagger} \text{MADD}_{Q,W_1,W_2}^{\dagger} |\Gamma_\mu\rangle_\Gamma |q_{A,\mu}\rangle_Q |\Gamma_\mu q_{A,\mu}\rangle_{W_1} |\Gamma_\mu (q_{A,\mu})^2\rangle_{W_2} |acc + \Gamma_\mu (q_{A,\mu})^3\rangle_E \tag{7}$$

$$= \text{MADD}_{\Gamma,Q,W_1}^{\dagger} |\Gamma_\mu\rangle_\Gamma |q_{A,\mu}\rangle_Q |\Gamma_\mu q_{A,\mu}\rangle_{W_1} |0\rangle_{W_2} |acc + \Gamma_\mu (q_{A,\mu})^3\rangle_E \tag{8}$$

$$= |\Gamma_\mu\rangle_\Gamma |q_{A,\mu}\rangle_Q |0\rangle_{W_1} |0\rangle_{W_2} |acc + \Gamma_\mu (q_{A,\mu})^3\rangle_E \tag{9}$$

$$\tag{10}$$

We see that already in eq. 7 we have the result we want in the accumulation register. We continue with the uncomputation of the W_1, W_2 registers purely to be able to reuse them in the remaining calculations. This saves the qubits required for having a 2 ancillary registers for every calculation. The MADD gates here could be implementing using QFT multipliers[6] in which case we wouldn't need any additional ancillaries. If we decompose our QFT multiplier into its components it is essentially a chain of QFT additions[3, 6] and multiplications by a constant power of two. These additions are built up of two components: (inverse) Fourier transforms and conditional rotations. When we chain them together like this however many of the transforms can be taken out as they are always followed or preceded by their inverse except for in the beginning and end.

Let us say we are given a circuit, SDA, for encoding a molecule from its ID in the following manner, and a circuit DA $= \prod_A \prod_{\mu \in \{0,1\}} E_{i\ (\Gamma_\mu, Q_{A,\mu}, W_1, W_2, E)}^{\Gamma}$. Then

$$
\text{DA SDA} \, |ID\rangle_{ID} \, |0\rangle \rightarrow
$$

$$
\text{DA} \, |ID\rangle_{ID} \left(\bigotimes_{\mu \in \{0,1\}} |\Gamma_\mu\rangle_{\Gamma_\mu} \bigotimes_A |q_{A,\mu}\rangle_{Q_{A,\mu}} \right) |0\rangle_{W_1} |0\rangle_{W_2} |0\rangle_E \rightarrow \tag{11}
$$

$$
|ID\rangle_{ID} \left(\bigotimes_{\mu \in \{0,1\}} |\Gamma_\mu\rangle_{\Gamma_\mu} \bigotimes_A |q_{A,\mu}\rangle_{Q_{A,\mu}} \right) |0\rangle_{W_1} |0\rangle_{W_2} |E^{\Gamma}\rangle_E
$$

will give us the E^{Γ} energy term in the E register corresponding to the ID in the ID register.

1.2 Sampling using Quantum Amplitude Arithmetic

Assume that we are given an equal superposition of all the canonical IDs of the fullerenes in an isomer-space. We can apply SDA to set up the encoding and then apply DA. We now have computed the E^{Γ} energies for every isomer. However we can only sample once! Let us say that we are interested in the isomers with the lowest energies. We then would like the probability of sampling an isomer to be proportional to E^{Γ}. We can achieve this using Quantum Amplitude Arithmetic[7], not to be confused with Quantum Amplitude Amplification, both shortened as QAA but in this writing as QA-Arithmetic and QA-Amplification.

Wang et al. use their introduced addition and multiplication primitives to construct a circuit which transforms the state $|x\rangle_D |0\rangle_C |0\rangle_W \rightarrow \frac{1}{2} \frac{x}{2^n} |x\rangle_D |0\rangle_C |1\rangle_W + \alpha |\omega\rangle_{D \otimes C \otimes W}$ where α is some normalization factor, and $|\omega\rangle$ is some state with no overlap with the state containing all 0's in the control register, C, and 1 in the work register, W.

When using this circuit we can treat the E register containing our resulting E^{Γ} term as the data register, D. We can reuse the W_1, W_2 registers as the

control and work registers. Let us take a look at that.

$$\sum_{ID \in \text{isomers}} |ID\rangle_{ID} \left(\bigotimes_{\mu \in \{0,1\}} |\Gamma_\mu\rangle_{\Gamma_\mu} \bigotimes_A |q_{A,\mu}\rangle_{Q_{A,\mu}} \right) |0\rangle_{W_1} |0\rangle_{W_2} |E^\Gamma\rangle_E \rightarrow$$

$$\sum_{ID \in \text{isomers}} |ID\rangle_{ID} \left(\bigotimes_{\mu \in \{0,1\}} |\Gamma_\mu\rangle_{\Gamma_\mu} \bigotimes_A |q_{A,\mu}\rangle_{Q_{A,\mu}} \right) \left(\frac{1}{2} \frac{E^\Gamma_{ID}}{2^n} |0\rangle_{W_1} |1\rangle_{W_2} |E^\Gamma_{ID}\rangle_E + \alpha_{ID} |\omega_{ID}\rangle \right) \tag{12}$$

If we now sample from this superposition and postselect for $W_1 = 0$ and $W_2 = 1$ we are more likely to sample a low energy fullerene. The likelihood of sampling a given canonical fullerene ID is proportional with E^Γ for that fullerene.

1.3 Calculating E^Γ with Quantum Amplitude Arithmetic.

An alternative strategy would be to go all in on QA-Arithmetic and do all the arithmetic in the amplitudes. Here we would encode a molecule as follows

$$\text{SAA} \, |ID\rangle_{ID} |0\rangle_{E,E_w,C_E,q_{o(1,2,3)},\Gamma_w,\Gamma_{1,\dots,n},q_{1,\dots,n},C_{1,\dots,\lceil log(n+1) \rceil}}$$

$$= |ID\rangle_{ID} |0\rangle_{E,E_w,C_E,q_{o(1,2,3)},\Gamma_w} \bigotimes_{\mu \in \{0,1\}} |\Gamma_\mu\rangle_{\Gamma_{1,\dots,n}} \bigotimes_A |q_{A,\mu}\rangle_{q_{1,\dots,n}} |0\rangle_{C_{1,\dots,\lceil log(n+1) \rceil}} \tag{13}$$

Let us apply the following example circuit to our encoding. Here we focus on one pair of q and Γ.
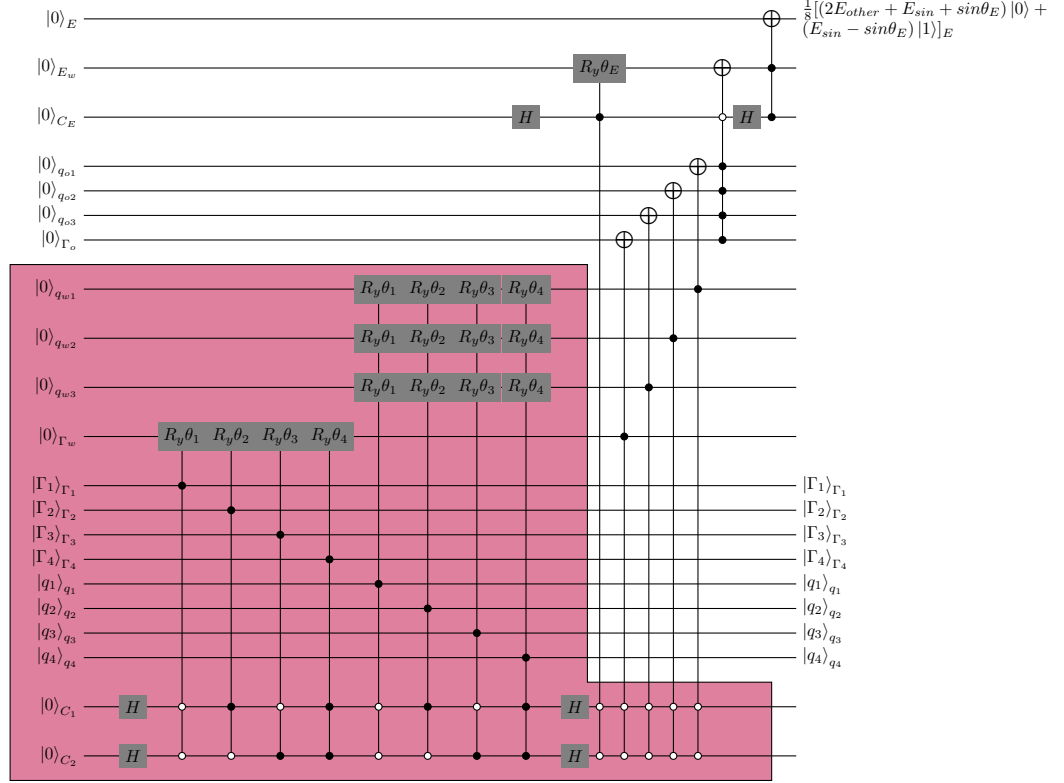
This circuit is built from the addition and multiplication primitives introduced in the QA-Arithmetic paper[7]. We also do a trivial modification to get subtraction. The diagram is for a n=4 bit example i.e. q and Γ are encoded as 4 bit numbers. The crimson region in the diagram is the only part which needs to be scaled up if using larger n.

If using more than one q and Γ the contribution to the final E_w register should include those as well which would just need an extra addition. C_E should be scaled appropriately as the base 2 logarithm of the number of q, Γ pairs plus 1.

Let us go though the mathematics of our 4 bit example.

The controlled gate notation here is the following, t is the target register and $c1, c2, c3, \ldots$ are the control registers. $a, b, c, \ldots$ are all 1 except if there is a bar over the corresponding $c1, c2, c3, \ldots$ in which case it is 0.

$$
\begin{aligned}
CU_t^{c1,c2,c3,\cdots} = (U_t - I_t) \otimes |a\rangle \langle a|_{c1} \otimes |b\rangle \langle b|_{c2} \otimes |c\rangle \langle c|_{c3} \otimes \cdots + \\
\sum_{\alpha,\beta,\zeta,\cdots \in \{0,1\}} I_t \otimes |\alpha\rangle \langle \alpha|_{c1} \otimes |\beta\rangle \langle \beta|_{c2} \otimes |\zeta\rangle \langle \zeta|_{c3} \otimes \ldots .
\end{aligned}
\tag{14}
$$

We neglect writing out the $q_{1,2,3,4}, \Gamma_{1,2,3,4}$ as they never change throughout the calculation, we also neglect the registers outside of the crimson region for now. We begin by applying the Hadamard gates.

$$
\begin{aligned}
H_{C1} H_{C2} |0000\rangle_{q_{w(1,2,3)},\Gamma_w} |00\rangle_{C_{(1,2)}} \rightarrow \\
\frac{1}{2} (|0000\rangle_{q_{w(1,2,3)},\Gamma_w} |00\rangle_{C_{(1,2)}} + \\
|0000\rangle_{q_{w(1,2,3)},\Gamma_w} |01\rangle_{C_{(1,2)}} + \\
|0000\rangle_{q_{w(1,2,3)},\Gamma_w} |10\rangle_{C_{(1,2)}} + \\
|0000\rangle_{q_{w(1,2,3)},\Gamma_w} |11\rangle_{C_{(1,2)}})
\end{aligned}
\tag{15}
$$

when we apply the conditional rotation gates to a register such as Γ_w we do the

following

$$CRy_{\Gamma_w}^{\Gamma_4,C_1,C_2}(2\theta_4)CRy_{\Gamma_w}^{\Gamma_3,\bar{C}_1,C_2}(2\theta_3)CRy_{\Gamma_w}^{\Gamma_2,C_1,\bar{C}_2}(2\theta_2)CRy_{\Gamma_w}^{\Gamma_1,\bar{C}_1,\bar{C}_2}(2\theta_1)$$

$$\frac{1}{2}\sum_{x_1,x_2\in\{0,1\}}|0000\rangle_{q_{w(1,2,3)},\Gamma_w}|x_1x_2\rangle_{C_{(1,2)}} \to$$

$$\frac{1}{2}(CRy_{\Gamma_w}^{\Gamma_1}(2\theta_1)|0000\rangle_{q_{w(1,2,3)},\Gamma_w}|00\rangle_{C_{(1,2)}} +$$

$$CRy_{\Gamma_w}^{\Gamma_2}(2\theta_2)|0000\rangle_{q_{w(1,2,3)},\Gamma_w}|01\rangle_{C_{(1,2)}} +$$

$$CRy_{\Gamma_w}^{\Gamma_3}(2\theta_3)|0000\rangle_{q_{w(1,2,3)},\Gamma_w}|10\rangle_{C_{(1,2)}} + \quad\quad (16)$$

$$CRy_{\Gamma_w}^{\Gamma_4}(2\theta_4)|0000\rangle_{q_{w(1,2,3)},\Gamma_w}|11\rangle_{C_{(1,2)}}) \to$$

$$\frac{1}{2}(|000\rangle\,[\Gamma 1(cos\theta_1|0\rangle+sin\theta_1|1\rangle)+(1-\Gamma_1)|0\rangle]_{q_{w(1,2,3)},\Gamma_w}|00\rangle +$$

$$|000\rangle\,[\Gamma 2(cos\theta_2|0\rangle+sin\theta_2|1\rangle)+(1-\Gamma_2)|0\rangle]_{q_{w(1,2,3)},\Gamma_w}|01\rangle +$$

$$|000\rangle\,[\Gamma 3(cos\theta_3|0\rangle+sin\theta_3|1\rangle)+(1-\Gamma_3)|0\rangle]_{q_{w(1,2,3)},\Gamma_w}|10\rangle +$$

$$|000\rangle\,[\Gamma 4(cos\theta_4|0\rangle+sin\theta_4|1\rangle)+(1-\Gamma_4)|0\rangle]_{q_{w(1,2,3)},\Gamma_w}|11\rangle)$$

Let us adopt the notation $|\Psi_i^t\rangle = t(cos\theta_i|0\rangle+sin\theta_i|1\rangle)+(1-t)|0\rangle$ before redoing the application using our new notation. We also apply the rotation gates for the q_w registers:

$$CRy_{\Gamma_w}^{\Gamma_4,C_1,C_2}(2\theta_4)CRy_{\Gamma_w}^{\Gamma_3,\bar{C}_1,C_2}(2\theta_3)CRy_{\Gamma_w}^{\Gamma_2,C_1,\bar{C}_2}(2\theta_2)CRy_{\Gamma_w}^{\Gamma_1,\bar{C}_1,\bar{C}_2}(2\theta_1)$$

$$CRy_{q_{w1}}^{q_4,C_1,C_2}(2\theta_4)CRy_{q_{w1}}^{q_3,\bar{C}_1,C_2}(2\theta_3)CRy_{q_{w1}}^{q_2,C_1,\bar{C}_2}(2\theta_2)CRy_{q_{w1}}^{q_1,\bar{C}_1,\bar{C}_2}(2\theta_1)$$

$$CRy_{q_{w2}}^{q_4,C_1,C_2}(2\theta_4)CRy_{q_{w2}}^{q_3,\bar{C}_1,C_2}(2\theta_3)CRy_{q_{w2}}^{q_2,C_1,\bar{C}_2}(2\theta_2)CRy_{q_{w2}}^{q_1,\bar{C}_1,\bar{C}_2}(2\theta_1)$$

$$CRy_{q_{w3}}^{q_4,C_1,C_2}(2\theta_4)CRy_{q_{w3}}^{q_3,\bar{C}_1,C_2}(2\theta_3)CRy_{q_{w3}}^{q_2,C_1,\bar{C}_2}(2\theta_2)CRy_{q_{w3}}^{q_1,\bar{C}_1,\bar{C}_2}(2\theta_1)$$

$$\frac{1}{2}\sum_{x_1,x_2\in\{0,1\}}|0000\rangle_{q_{w(1,2,3)},\Gamma_w}|x_1x_2\rangle =$$

$$\frac{1}{2}(CRy_{q_{w1}}^{q_1}(2\theta_1)CRy_{q_{w2}}^{q_1}(2\theta_1)CRy_{q_{w3}}^{q_1}(2\theta_1)CRy_{\Gamma_w}^{\Gamma_1}(2\theta_1)|0000\rangle_{q_{w(1,2,3)},\Gamma_w}|00\rangle +$$

$$CRy_{q_{w1}}^{q_2}(2\theta_2)CRy_{q_{w2}}^{q_2}(2\theta_2)CRy_{q_{w3}}^{q_2}(2\theta_2)CRy_{\Gamma_w}^{\Gamma_2}(2\theta_2)|0000\rangle_{q_{w(1,2,3)},\Gamma_w}|01\rangle + \quad (17)$$

$$CRy_{q_{w1}}^{q_3}(2\theta_3)CRy_{q_{w2}}^{q_3}(2\theta_3)CRy_{q_{w3}}^{q_3}(2\theta_3)CRy_{\Gamma_w}^{\Gamma_3}(2\theta_3)|0000\rangle_{q_{w(1,2,3)},\Gamma_w}|10\rangle +$$

$$CRy_{q_{w1}}^{q_4}(2\theta_4)CRy_{q_{w2}}^{q_4}(2\theta_4)CRy_{q_{w3}}^{q_4}(2\theta_4)CRy_{\Gamma_w}^{\Gamma_4}(2\theta_4)|0000\rangle_{q_{w(1,2,3)},\Gamma_w}|11\rangle) \to$$

$$\frac{1}{2}(|\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{\Gamma_1}\rangle_{q_{w(1,2,3)},\Gamma_w}|00\rangle +$$

$$|\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{\Gamma_2}\rangle_{q_{w(1,2,3)},\Gamma_w}|01\rangle +$$

$$|\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{\Gamma_3}\rangle_{q_{w(1,2,3)},\Gamma_w}|10\rangle +$$

$$|\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{\Gamma_4}\rangle_{q_{w(1,2,3)},\Gamma_w}|11\rangle)$$

Let us now apply the second set of Hadamard gates:

$$
H_{C_1}H_{C_2}\frac{1}{2}(|\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{\Gamma_1}\rangle|00\rangle +
$$

$$
|\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{\Gamma_2}\rangle|01\rangle +
$$

$$
|\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{\Gamma_3}\rangle|10\rangle +
$$

$$
|\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{\Gamma_4}\rangle|11\rangle) \rightarrow
$$

$$
\frac{1}{4}(|\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{\Gamma_1}\rangle [|00\rangle + |01\rangle + |10\rangle + |11\rangle]+
$$

$$
|\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{\Gamma_2}\rangle [|00\rangle - |01\rangle + |10\rangle - |11\rangle]+
$$

$$
|\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{\Gamma_3}\rangle [|00\rangle + |01\rangle - |10\rangle - |11\rangle]+
$$

$$
|\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{\Gamma_4}\rangle [|00\rangle - |01\rangle - |10\rangle + |11\rangle]) =
$$

$$
\frac{1}{4}\left[|\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{\Gamma_1}\rangle + |\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{\Gamma_2}\rangle + |\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{\Gamma_3}\rangle + |\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{\Gamma_4}\rangle\right]|00\rangle +
$$

$$
\frac{1}{4}\left(\left[|\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{\Gamma_1}\rangle - |\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{\Gamma_2}\rangle + |\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{\Gamma_3}\rangle - |\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{\Gamma_4}\rangle\right]|01\rangle +
$$

$$
\left[|\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{\Gamma_1}\rangle + |\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{\Gamma_2}\rangle - |\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{\Gamma_3}\rangle - |\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{\Gamma_4}\rangle\right]|10\rangle +
$$

$$
\left[|\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{\Gamma_1}\rangle - |\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{\Gamma_2}\rangle - |\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{\Gamma_3}\rangle + |\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{\Gamma_4}\rangle\right]|11\rangle\right)
$$

$$
= \frac{1}{4}\left[|\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{q_1}\Psi_1^{\Gamma_1}\rangle + |\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{q_2}\Psi_2^{\Gamma_2}\rangle + |\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{q_3}\Psi_3^{\Gamma_3}\rangle + |\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{q_4}\Psi_4^{\Gamma_4}\rangle\right]|00\rangle + |M\rangle
$$

$$
= |N\rangle + |M\rangle \tag{18}
$$

Before the next step let us define:

$$
q_{sin} = q_1 sin\theta_1 + q_2 sin\theta_2 + q_3 sin\theta_3 + q_4 sin\theta_4 \tag{19}
$$

$$
q_{other} = q_1 cos\theta_1 + q_2 cos\theta_2 + q_3 cos\theta_3 + q_4 cos\theta_4 + 4 - q_1 - q_2 - q_3 - q_4 \tag{20}
$$

$$
\Gamma_{sin} = \Gamma_1 sin\theta_1 + \Gamma_2 sin\theta_2 + \Gamma_3 sin\theta_3 + \Gamma_4 sin\theta_4 \tag{21}
$$

$$
\Gamma_{other} = \Gamma_1 cos\theta_1 + \Gamma_2 cos\theta_2 + \Gamma_3 cos\theta_3 + \Gamma_4 cos\theta_4 + 4 - \Gamma_1 - \Gamma_2 - \Gamma_3 - \Gamma_4 \tag{22}
$$

$$
E_{sin} = \Gamma_{sin}(q_{sin})^3 \tag{23}
$$

$$
E_{other} = \Gamma_{other}(q_{other}^3 + 3q_{other}^2 q_{sin} + 3q_{other}q_{sin}^2 + q_{sin}^3)
$$
$$
+ \Gamma_{sin}(q_{other}^3 + 3q_{other}^2 q_{sin} + 3q_{other}q_{sin}^2) \tag{24}
$$

$$
|\sigma_t\rangle = t_{other}|0\rangle + t_{sin}|1\rangle \tag{25}
$$

$$
\tag{26}
$$

Let us now add in the $_o$ registers and apply the first 4 conditional not gates:

$$
CX^{q_{w1},\bar{C}_1,\bar{C}_2}_{q_{o1}}CX^{q_{w2},\bar{C}_1,\bar{C}_2}_{q_{o2}}CX^{q_{w3},\bar{C}_1,\bar{C}_2}_{q_{o3}}CX^{\Gamma_w,\bar{C}_1,\bar{C}_2}_{\Gamma_o}|0000\rangle_{E,q_{o(1,2,3)},\Gamma_o}(|N\rangle + |M\rangle) \rightarrow
$$

$$
\left(CX^{q_{w1}}_{q_{o1}}CX^{q_{w2}}_{q_{o2}}CX^{q_{w3}}_{q_{o3}}CX^{\Gamma_w}_{\Gamma_o}|0000\rangle|N\rangle\right) + |0000\rangle|M\rangle \rightarrow \tag{27}
$$

$$
|\sigma_q\sigma_q\sigma_q\sigma_\Gamma\rangle_{q_{o(1,2,3)},\Gamma_o}|N\rangle + |0000\rangle|M\rangle
$$

Now let us disregard everything in the crimson region except the C_1, C_2 control

registers and do the final gates involving the $_o$ registers:

$$H_{C_E} CX_{E_w}^{\bar{C}_E, q_{o1}, q_{o2}, q_{o3}, \Gamma_o} CRy_{E_w}^{C_E, \bar{C}_1, \bar{C}_2}(\theta_E) H_{C_E} \ket{000}_{E, E_w, C_E} \frac{1}{4} \Bigg(\ket{\sigma_q \sigma_q \sigma_q \sigma_\Gamma}_{q_{o(1,2,3)}, \Gamma_o} \ket{00}_{C_1, C_2}$$

$$+ \ket{0000}_{q_{o(1,2,3)}, \Gamma_o} [\ket{01} + \ket{10} + \ket{11}]_{C_1, C_2} \Bigg) \rightarrow$$

$$H_{C_E} \frac{1}{4} \Bigg(\ket{0} \frac{1}{\sqrt{2}} \Big[CX_{E_w}^{q_{o1}, q_{o2}, q_{o3}, \Gamma_o} \ket{0}\ket{0} + Ry_{E_w}(\theta_E)\ket{0}\ket{1} \Big] \ket{\sigma_q \sigma_q \sigma_q \sigma_\Gamma}_{q_{o(1,2,3)}, \Gamma_o} \ket{00}_{C_1, C_2}$$

$$+ \ket{00 + 0000}_{E, E_w, C_E, q_{o(1,2,3)}, \Gamma_o} [\ket{01} + \ket{10} + \ket{11}]_{C_1, C_2} \Bigg) \rightarrow$$

$$H_{C_E} \frac{1}{4} \Bigg(\ket{0} \frac{1}{\sqrt{2}} \Big[\ket{\sigma_E}_{E_w} \ket{0}_{C_E} + (cos\theta_E \ket{0} + \sin\theta_E \ket{1})_{E_w} \ket{1}_{C_E} \Big] \ket{\sigma_q \sigma_q \sigma_q \sigma_\Gamma}_{q_{o(1,2,3)}, \Gamma_o} \ket{00}_{C_1, C_2}$$

$$+ \ket{00 + 0000}_{E, E_w, C_E, q_{o(1,2,3)}, \Gamma_o} [\ket{01} + \ket{10} + \ket{11}]_{C_1, C_2} \Bigg) \rightarrow \tag{28}$$

$$\frac{1}{4} \Bigg(\ket{0} \frac{1}{\sqrt{2}} \Big[\ket{\sigma_E}_{E_w} \ket{+}_{C_E} + (cos\theta_E \ket{0} + \sin\theta_E \ket{1})_{E_w} \ket{-}_{C_E} \Big] \ket{\sigma_q \sigma_q \sigma_q \sigma_\Gamma}_{q_{o(1,2,3)}, \Gamma_o} \ket{00}_{C_1, C_2}$$

$$+ \ket{000000}_{E, E_w, C_E, q_{o(1,2,3)}, \Gamma_o} [\ket{01} + \ket{10} + \ket{11}]_{C_1, C_2} \Bigg)$$

Now we can neglect the $q_{o(1,2,3)}, \Gamma_o, C_1, C_2$ registers too and do some preparatory manipulations before applying the final conditional not gate.

$$\frac{1}{4}\left(|0\rangle \frac{1}{\sqrt{2}}\left[|\sigma_E\rangle_{E_w} |+\rangle_{C_E} + (cos\theta_E |0\rangle + \sin\theta_E |1\rangle)_{E_w} |-\rangle_{C_E} \right] + 3|000\rangle \right) =$$

$$\frac{1}{4}\left(|0\rangle \frac{1}{2}\left[|\sigma_E\rangle_{E_w} |0\rangle_{C_E} + |\sigma_E\rangle_{E_w} |1\rangle_{C_E} + (cos\theta_E |0\rangle + \sin\theta_E |1\rangle)_{E_w} |0\rangle_{C_E} \right.\right.$$

$$\left.\left. -(cos\theta_E |0\rangle + \sin\theta_E |1\rangle)_{E_w} |1\rangle_{C_E} \right] + 3|000\rangle \right) =$$

$$\frac{1}{4}\left(|0\rangle \frac{1}{2}\left[(|\sigma_E\rangle + cos\theta_E |0\rangle + \sin\theta_E |1\rangle)_{E_w} |0\rangle_{C_E} \right.\right.$$

$$\left.\left. +(|\sigma_E\rangle - cos\theta_E |0\rangle - \sin\theta_E |1\rangle)_{E_w} |1\rangle_{C_E} \right] + 3|000\rangle \right) =$$

$$\frac{1}{8}\left(|0\rangle[|\sigma_E\rangle + cos\theta_E |0\rangle + \sin\theta_E |1\rangle]_{E_w} |0\rangle_{C_E} \right.$$

$$\left. + |0\rangle[|\sigma_E\rangle - cos\theta_E |0\rangle - \sin\theta_E |1\rangle]_{E_w} |1\rangle_{C_E} + 6|000\rangle \right) = \qquad (29)$$

$$\frac{1}{8}\left(|0\rangle[E_{other} |0\rangle + E_{sin} |1\rangle + cos\theta_E |0\rangle + \sin\theta_E |1\rangle]_{E_w} |0\rangle_{C_E} \right.$$

$$\left. + |0\rangle[E_{other} |0\rangle + E_{sin} |1\rangle - cos\theta_E |0\rangle - \sin\theta_E |1\rangle]_{E_w} |1\rangle_{C_E} + 6|000\rangle \right) =$$

$$\frac{1}{8}\left(|0\rangle[(E_{other} + cos\theta_E) |0\rangle + (E_{sin} + sin\theta_E) |1\rangle]_{E_w} |0\rangle_{C_E} \right.$$

$$\left. + |0\rangle[(E_{other} - cos\theta_E) |0\rangle + (E_{sin} - sin\theta_E) |1\rangle]_{E_w} |1\rangle_{C_E} + 6|000\rangle \right) =$$

$$\frac{1}{8}\left((E_{other} + cos\theta_E) |000\rangle + (E_{sin} + sin\theta_E) |010\rangle \right.$$

$$\left. +(E_{other} - cos\theta_E) |001\rangle + (E_{sin} - sin\theta_E) |011\rangle + 6|000\rangle \right)$$

We now apply the final conditional not gate:

$$CX_E^{E_w,C_E} \frac{1}{8}\left((E_{other} + cos\theta_E) |000\rangle + (E_{sin} + sin\theta_E) |010\rangle \right.$$

$$\left. +(E_{other} - cos\theta_E) |001\rangle + (E_{sin} - sin\theta_E) |011\rangle + 6|000\rangle \right) \rightarrow$$

$$\frac{1}{8}\left((E_{other} + cos\theta_E) |000\rangle + (E_{sin} + sin\theta_E) |010\rangle \right.$$

$$\left. +(E_{other} - cos\theta_E) |001\rangle + X_E(E_{sin} - sin\theta_E) |011\rangle + 6|000\rangle \right) \rightarrow \qquad (30)$$

$$\frac{1}{8}\left((E_{other} + cos\theta_E) |000\rangle + (E_{sin} + sin\theta_E) |010\rangle \right.$$

$$\left. +(E_{other} - cos\theta_E) |001\rangle + (E_{sin} - sin\theta_E) |111\rangle + 6|000\rangle \right)$$

After applying those gates we see that the amplitude on $|1\rangle_E$ across the whole state is

$$\tfrac{1}{8}(E_{sin} - sin\theta_E) = (\Gamma_1 sin\theta_1 + \Gamma_2 sin\theta_2 + \Gamma_3 sin\theta_3 + \Gamma_4 sin\theta_4)(q_1 sin\theta_1 + q_2 sin\theta_2 + q_3 sin\theta_3 + q_4 sin\theta_4)^3 - sin\theta_E.$$

Let us say we know the E^Γ energy of some high energy molecule in the isomer space

$$E_H^\Gamma = (0b0.\Gamma_H)(0b0.q_H)^3$$

If we specify

$$\theta_i = arcsin\frac{1}{2^i}, \quad \theta_E = arcsin[(0b0.\Gamma_H)(0b0.q_H)^3]$$

we get that

$$E_{sin} = (\frac{\Gamma_1}{2} + \frac{\Gamma_2}{2^2} + \frac{\Gamma_3}{2^3} + \frac{\Gamma_4}{2^8})(\frac{q_1}{2} + \frac{q_2}{2^2} + \frac{q_3}{2^3} + \frac{q_4}{2^8})^3 = (0b0.\Gamma_1\Gamma_2\Gamma_3\Gamma_4)(0b0.q_1q_2q_3q_4)^3$$

and that

$$\frac{1}{8}(E_{sin} - sin\theta_E) = \frac{1}{8}[(0b0.\Gamma_1\Gamma_2\Gamma_3\Gamma_4)(0b0.q_1q_2q_3q_4)^3 - (0b0.\Gamma_H)(0b0.q_H)^3]$$

. This is proportional to $E^\Gamma - E_H^\Gamma$!

1.4 Calculating E^γ using Quantum Digital Arithmetic

The E_γ term is formulated as follows:

$$\eta_{AB,ll'} = \frac{1}{2}\left[\eta_A(1 + K_A^l) + \eta_B(1 + K_B^{l'})\right] \tag{31}$$
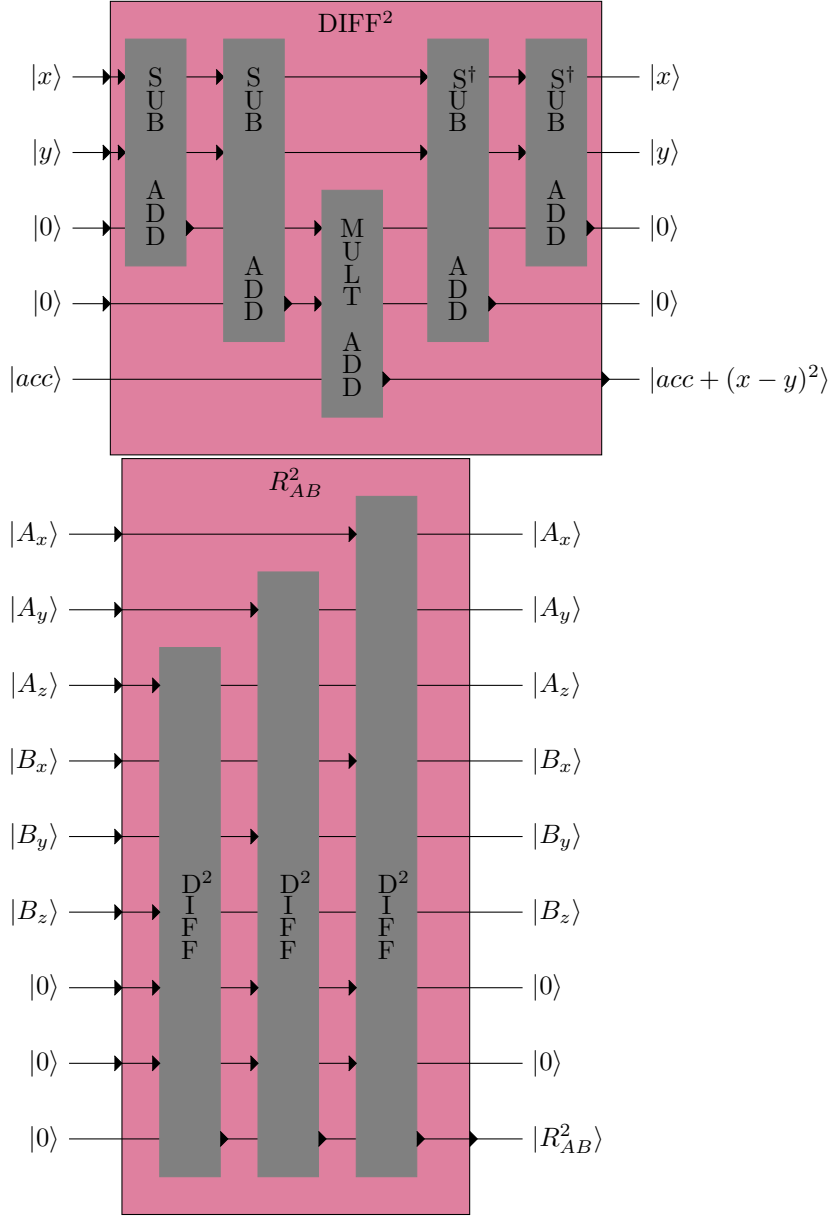
$$R_{AB}^2 = (A_x - B_x)^2 + (A_y - B_y)^2 + (A_z - B_z)^2 \tag{32}$$

$$\gamma_{AB,ll'} = \frac{1}{\sqrt{R_{AB}^2 + \eta_{AB,ll'}^{-2}}} \tag{33}$$

$$E_\gamma = \frac{1}{2}\sum_{A,B}\sum_{l\in A}\sum_{l'\in B} q_l q_{l'} \gamma_{AB,ll'} \tag{34}$$

$$\tag{35}$$

For fullerenes we can view $\eta_{AB,ll'}$ as only dependant on the values of l and l', so there are 4 configurations as there are only 2 shells for carbon in GFN2-xTB. A small circuit for calculating R_{AB}^2 could be made up of the $diff^2$ circuit described bellow:

So using this circuit along with a constant addition of $\eta_{AB,ll'}$ and the use of an inverse square root circuit[5] we get a fixed point approximation of $\gamma_{AB,ll'}$. We can use this with our QFT fused multiply add operation to get the inner sum of the E^γ term. When repeating this over all the pairs it is a good optimisation

to see that saving a little under half the computation.

$$E^{\gamma} = \frac{1}{2} \sum_{A,B} \sum_{l \in A} \sum_{l' \in B} q_l q_{l'} \gamma_{AB,ll'}$$

$$= \sum_{A} \sum_{l \in A} \left[\sum_{l' \in A} q_l q_{l'} \gamma_{AA,ll'} + \sum_{B > A} \sum_{l' \in B} q_l q_{l'} \gamma_{AB,ll'} \right] \qquad (36)$$

1.5 Complexity

The second algorithm has, in terms of big O notation, the same complexity as the state preparation introduced in the QA-Arithmetic paper, as it is simply 4 applications of this circuit. The state preparation can be achieved using $O(\log n)$ extra qubits and $O(n \log n)$ Toffoli gates where n is the number of bits used to represent $\Gamma_\mu, q_{A_n,\mu}$. Thus if we have a m bit canonical fullerene ID we end up using on the order of $m + 2n + 4O(\log n) = O(n + m)$ qubits and $4O(n \log n) = O(n \log n)$ Toffoli gates.

The first circuit on the other hand uses 4 mulitplication circuits, 2 squaring circuits which could just as well be multiplication circuits and an addition circuit. A QFT addition (multiplication) circuit uses $O(n^{2(3)})$ gates and no additional qubits. Thus if we have encoded $\Gamma_\mu, q_{A_n,\mu}, \mu \in \{0,..,l\}, A_n \in \{0,..,o\}$ each using n bits we will need to perform $6lo$ multiplications and lo additions, resulting in $6lo \cdot O(n^3) + lo \cdot O(n^2) = O(lon^3)$ gates, on $m+n+nl+lon = O(m+lon)$ qubits. Additionally we then have to run the state preparation circuit which adds $O(\log n)$ qubits and $O(n \log n)$ gates, however that is not enough to change the asymptotic runtime further.

1.6 Cleaning up ω

We would like to get rid of the $|\omega\rangle$ term in both algorithms to avoid having to post select. We can achieve this with amplitude amplification. To do amplitude amplification we first need to define what a 'good' state is, in our case we know all good states have $|0\rangle_C |1\rangle_W$. Second we need an oracle in terms of a unitary which flips the sign of the good state, i.e. reflecting the state around the bad state, this would be $I - 2|0\rangle_C \langle 0|_C |1\rangle_W \langle 1|_W$, which can be easily implemented with controlled rotations. We also need a circuit which would reflect around the initial state by flipping the sign of it, given that we have a circuit U for preparing the initial state that would be $I - 2U|0\rangle \langle 0| U^\dagger$. In our case the angle between the bad and initial states are $\theta_{DA} = arcsin(\frac{1}{2} \frac{E^\Gamma}{2^n}), \theta_{AA} = arcsin(\frac{1}{2^4} \frac{E^\Gamma}{2^{n4}})$ for the two algorithms. We have to do $\lfloor \frac{\pi}{4\theta} \rfloor$ repetitions to maximize the probability of measuring a good state.

1.7 Concentrating the probabilities on the best candidates

We now have a superposition where the probability of sampling a fullerene is proportional to the energy of that fullerene. But is that ideal? The energies

might be quite close to each other in absolute terms. Therefore we would like to exaggerate the difference between them and then sample according to that difference. If we knew what the highest energy was we could just subtract that from every energy calculation thus getting probabilities proportional to how much lower an energy we are working with. Another option is if we expect the energies to be within $100(1-x)\%$ we could subtract ex from every energy calculation where e is the energy from a random fullerene in the isomer-space. This is of cause not as good but quite achievable. In both algorithms we can encode ex in a register and then use a digital subtraction or do a QAA state preparation addition but with all the R_y gates inverted, resulting in a counter-clockwise rotation, in effect subtracting ex.

1.8 Discussion

From the asymptotic resource use the second algorithm is clearly superior, even if some of the multiplications and additions can be run in parallel in the first one. We do have a factor 8 lower chance of getting a useful state out, but this again does not change the asymptotics, as we can just repeat it. QA-Amplification might be possible since we have a very clear "good" state in both algorithms. This would reduce the need for postselection and repetitions. Preparing the initial encoding of the isomer space seems less straight forwards in the second approach than in the first unfortunately.

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