Initial Investigation:

Started from this article
- Used the code as it was for H_2
- Adjusted symbols, coordinates, number of active electrons and some other stuff like max iterations to find spectral gap for LiH and BH

Molecule	HF / MP2	QMC / VQE	Number of Qubits	Ground State (Ha)	1st Excited State (Ha)	Spectral Gap
H_2	HF	VQE	4	-1.136	-0.4784	0.6577
LiH	HF	VQE	12	-7.7409	-7.0832	0.6576
BH	HF	VQE	12	-24.7558	-23.9854	0.7704

Sometimes the Gradient Descent Method finds the local minimum instead of the global minimum.

So I introduced an Adam optimiser and got:

H_2	HF	VQE	4	-1.1362	-1.1173	0.01883
LiH	HF	VQE	12	-7.7410	-7.7060	0.0351
BH	HF	VQE	12	-24.7873	-24.7433	0.044

I compared with the values using the Root mean squared propagation optimiser and got

H_2	HF	VQE	4	-1.1362	-1.1173	0.01883
LiH	HF	VQE	12	-7.7408	-7.6986	0.0422
BH	HF	VQE	12	-24.7897	-24.7428	0.0469

See Diatomic_Spectral_Gap_with_Spin_.py & Spectral-Gap-With-Adam-and-RMS.ipynb for code.

From what I could find in the literature, it appears these are the expected results:

H2 (Hydrogen Molecule):
Ground State Energy: Approximately -1.17 to -1.18 Hartrees.
First Excited State Energy: Approximately -0.96 to -0.94 Hartrees.

LiH (Lithium Hydride):
Ground State Energy: Approximately -7.50 to -7.45 Hartrees.
First Excited State Energy: Approximately -7.45 to -7.40 Hartrees.

BH (Boron Hydride):
Ground State Energy: Approximately -24.0 to -23.5 Hartrees.
First Excited State Energy: Approximately -23.8 to -23.3 Hartrees.

Now, the bigger the molecule, the more computing power the calculations.
So we go back to H_2 and see how it can be improved.

These were the ideas had for improving the calculation of the spectral gap:

- Use MP2 / CCSD to generate an initial guess for the electronic structure, which provides a reasonably accurate starting point.
- This initial state can serve as a reference for subsequent QMC calculations.

Below is the implementation of MP2 and QMC.

Moller-Plesset Perturbation Theory (MP2):

Investigated the accuracy of Hartree-Fock energy for the H2 molecule generated by pennylane by comparing with the second-order Moller-Plesset perturbation theory energy. The accuracy was found to be 0.85%, showing that for H2, the Hartree-Fock energy is a good measure of energy.

Implementation
Hartree-Fock Accuracy Investigation.ipynb

- Calculated the Second-Order Moller-Plesset Perturbation Theory (MP2) energy of the H2 molecule in the reference state (1100).
- The reference energies and wave functions were obtained using psi4. From this, orbital occupation and energy were obtained.
- The Electron Repulsion Integral (ERI) was obtained using psi4. This was in the Atomic Orbital (AO) basis and needed to be transformed to the Molecular Orbital (MO) basis before it could be used. This was done by obtaining the orbital coefficient matrix, C, from the reference wavefunction.
- ERI in the MO basis along with the energy denominators of the orbitals were used to calculate the total MP2 energy.
- Hartree-Fock energy was found using the hf_energy pennylane function.
- Results were compared

Quantum Monte Carlo (VQMC):

Using QMC for calculating excited states of molecules. Instead of optimising the ground state directly, use QMC to target excited states, such as the first excited state with a specific spin quantum number.

- Implementation:
  VQMC.ipynb
    - The trial Wave Function determinant is generated using qml.chem.excitations(), making use of the HF approach.
    - Jastrow Factor is parameterised RX and RY rotation on each orbital. However, model performed better with just the determinant forming the trial wavefucntion. Likely because the HF approach already provides a reasonable level of accuracy
    - From here, a Variational Quantum Monte Carlo model is implemented, optimising parameters used to generate single and double excitation states and the Jastrow parameters.
    - Cost function minimises the Hamiltonian of the trial wavefunction state
    - Spectral Gap was calculated using ground state energy generated using the HF approach as in the Boson Beach challenge, and the first excited energy was calculated from the optimised cost function.

Then looking past diatomic molecules…

Molecular Geometry Optimisation:

Looking at geometry optimisation to obtain the most stable molecular structure for bigger molecules so that they can be passed through the code.

We use the geometry of a molecule when calculating the qubit Hamiltonian so it is pretty vital to finding the spectral gap. The structure of diatomic molecules is obvious, two atoms a bond length away, but how do they arrange when we increase the number of atoms?

I started off by reading this [article](#) which prepares a HF state and uses a VQE to optimise the shape of H_3. I decided to keep the VQE but compare the results of starting in the HF state to starting in the CISD state. In general, the method using HF should be faster but the method using CISD should provide a more accurate starting point and have better electron correlation considerations. This is more important for more complex molecules.

The code is in optimise-h3.ipynb

For H_3, the code is in the file optimise-h3.ipynb and a plot displaying the accuracy and efficiency of the methods for H_3 can be seen below:

Accuracy and Efficiency for H_3
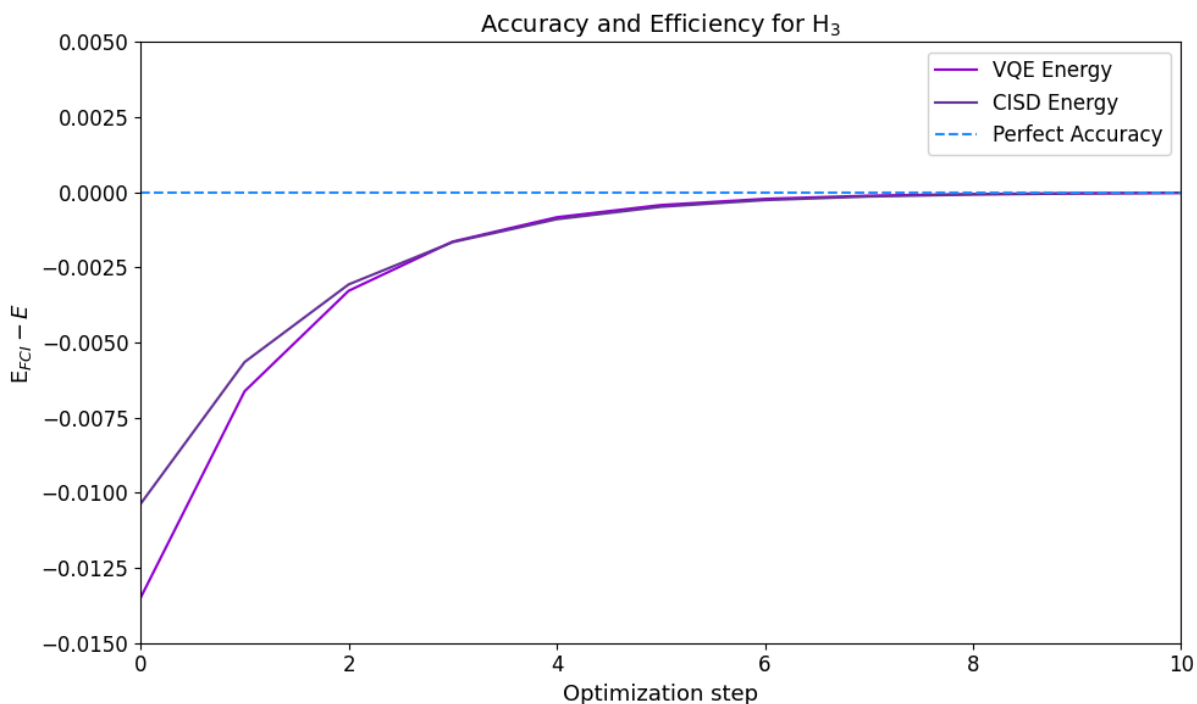
Some of these programs take a very long time to run. That is why we opted for Hydrogen molecules for the most part. For some of the more computationally expensive bits, we used Amazon Braket and connected to their quantum simulators for more power.

Even with Amazon Braket though, the H4 code timed out. By making step size bigger and max_iterations smaller, you can get a less accurate result but to get more correct output, you need a more powerful computer than I had available.

See optimising-h4 .ipynb