Ch 2 Band Gap of OLED

QC to study electronic structure & dynamic properties of molecules and materials

Goal: predict the excited state energies of TADF materials

2a/2b : Atomic & Molecular Orbits
→ reduce the number of orbitals using "active space transformations"

2c/2d : compute ground state of $PSPC_2$

2e : calculate excited state energy of $PSPC_2$ using Quantum Equation of Motion algorithm

2f : Run VQE on cloud

Review of Qiskit Nature Notebook:

Molecular Orbits → 2 e^- per (of course, Pauli exclusion)

α electrons → spin ↑
β electrons → spin ↓

1. Born-Oppenheimer approx (stationary nucleus)

Hamiltonian

$$H = \sum_p \left(-\frac{1}{2}\nabla_p^2 - \sum_k \frac{Z_k}{r_{pk}} \right) + \sum_{q>p} \frac{1}{r_{pq}}$$

2. Transform to 2nd quantization representation

(need to remember how this is done.)

$$H \rightarrow \hat{H}_{qubit} = \sum_i c_i \hat{P}_i$$

Use Variational Quantum Eigensolver

Start with a pre-trial state $\psi(\vec{\theta})$

Measure expectation values $\langle \psi(\theta) | \hat{P}_i | \psi(\theta) \rangle$

Calculate energy

$$E = \sum_i c_i \langle \psi | \hat{P}_i | \psi \rangle \geq E_{exact}$$

Adjust $\vec{\theta} \rightarrow \vec{\theta}'$ and recompute.

Optimize terms θ to minimize E

Qiskit implements a GroundStateEigensolver which can be constructed with a VQEUCCFactory class

So, how do you represent $\psi(\theta)$ in a QC & how do you map the Fermionic Hamiltonian to a qubit Hamiltonian?

$$\sum_{pq} h_{pq} a_p^\dagger a_q + \sum_{pqrs} g_{pqrs} a_p^\dagger a_q^\dagger a_r a_s \rightarrow \sum_i c_i P_i$$

We reduce the problem size with Active Space Transformer

t = ActiveSpaceTransformer ($n_{e^-} = 2$, $n_{mo} = 3$)

p' = ElectronicStructureProblem (d, [t])

p'.second_q_ops() → a simplified 2nd quantization

↓ Reduces the electron structure energy ~~level~~ levels being to calculated by the QC by doing those computations classically

Molecular Orbitals are obtained from the Atomic orbitals by a unitary transformation. Each MO is a linear comb of the AO (& thus there should be equal numbers of them)

Next the 2nd quant H is mapped to a qubit operator

Most straight-forward mapping is the Jordan-Wigner which stores the occupation information of one spin orbital in one qubit.

Further reductions of the problem space ~~are~~ can be accomplished by exploiting symmetries of the problem

ParityMapper object

Ultimately, we have reduced the problem to ~~floating~~ be represented by a Qubit Operator; next goal is to find the eigenvalue of the ground state of the system.

$$\hat{H} = \sum_{pq} h_{pq} a_p^+ a_q + \frac{1}{2} \sum_{pqrs} g_{pqrs} a_p^+ a_q^+ a_r a_s$$

$a^+ \rightarrow$ creation

$a \rightarrow$ annihilation operator

$h_{pq} + g_{pqrs}$ are integrals

To generate the 2nd quant representation of the system.
first define the molecule

m = Molecule (geometry, multiplicity, ...)

Then define a Driver object

d = Electronic Structure Molecule Driver (molecule = m, other ...)

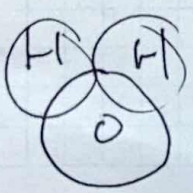
Then define a Problem object

p = Electronic Structure Problem (d)

p.second_q_ops() → generates the second quantization structure (computes h_{pq} & g_{pqrs})

which can be viewed in various ways

H_2O



8 electrons in O
2 electrons from H_2

10 electrons total
in g.s. 5 ↑, 5 ↓

An ansatz is a quantum circuit that represents a trial state

In the demo calculated the g.s. of H_2O, an EfficientSU2 object is instantiated to build the circuit

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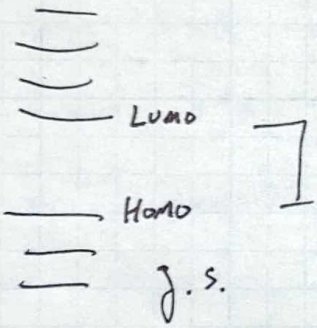
Challenge: Calculate the Bandgap of OLED molecules



$\Delta E = E_{lumo} - E_{homo}$

L=0, L=1 states
(singlet, triplet)
$m = \pm 1, 0$

Trying to understand the diagrams

→ Three different PSPCz molecules w/ differen F atoms

→ 0F, 2F & 4F result in different shapes

If the colored blobs represent the electron ψ, at the g.s. & @ 1st excited state, then these are pretty amazing different ψ

In this example, the driver has already been transformed, reduced to just the active space of interest

Qubit converter utilizes Jordan-Wigner mapping

spin orbit α occupation $\longleftrightarrow$ 1 qubit

In VQE, we begin with a trial state for the G.S. wave function for which we are trying to find its g.s. energy.

We aren't computing an analog form of Ψ, but rather defining a general wave function that is approximately correct and parameterized by various rotations. (Will be super interesting to see how this works.)

Ansatz $\rightarrow$ $\psi(\vec{\theta})$

Set of operators P_i as defined by $\hat{H}_{qubit}$

On the Q.C. measure

$$\langle \psi(\vec{\theta}) | P_i | \psi(\vec{\theta}) \rangle$$

On Classical, measure

$$E = \sum_i c_i \langle P_i \rangle \geq E_{exact}.$$

Adjust $\vec{\theta}$ and re-compute to minimize E.

But... we don't know E_{exact}... so, we + adjust $\vec{\theta}$ must the algorithm be interesting

Excited State Calculation using QEOM

Quantum Equation of Motion

$$\begin{pmatrix} M & Q \\ Q^* & M^* \end{pmatrix} \begin{pmatrix} X_n \\ Y_n \end{pmatrix} = E_{0n} \begin{pmatrix} V & W \\ -W^* & -V^* \end{pmatrix} \begin{pmatrix} X_n \\ Y_n \end{pmatrix}$$

eigenvalue problem

(why does it call it a pseudo-eigenvalue problem? → bc its not a scalar. or real?)

$$W_{\nu_\alpha \nu_\beta} = -\langle 0 | \left[\hat{E}^{(\alpha)\dagger}_{\nu_\alpha}, \hat{E}^{(\beta)\dagger}_{\nu_\beta} \right] | 0 \rangle$$

~~[the subscript indexing here isn't super clear. maybe it's just a $\nu_\alpha \nu_\beta$ subscript...?]~~

↳ W = the negative of the ~~expectation value~~ amplitude of this commutator $\left[\hat{E}^{(\alpha)\dagger}_{\nu_\alpha}, \hat{E}^{(\beta)\dagger}_{\nu_\beta} \right]$ → W is a complex scalar

Of course, Q, M, V, X_n, Y_n, & E_{0n} are not specified in the doc! ☺ It doesn't mean a whole lot to me yet.

→ These are found in Qiskit Nature Excited State Solvers tutorial

$M_{\nu_\alpha \nu_\beta}$, $Q_{\nu_\alpha \nu_\beta}$, V & W are all defined.

← a double commutator!

$$M_{\mu\nu} = \langle 0 | \left[\hat{E}^+_\mu , \hat{H}, \hat{E}^+_\nu \right] | 0 \rangle$$

$$Q = -\langle 0 | \left[\hat{E}^+_\mu , \hat{H}, \hat{E}^+_\nu \right] | 0 \rangle$$

$$V = \langle 0 | \left[E^+_\mu , E_\nu \right] | 0 \rangle$$

$$W = -\langle 0 | \left[E^+_\mu , E^+_\nu \right] | 0 \rangle$$

$$E_{0n} \rightarrow \Delta E = E_n - E_0$$

$$[A,B,C] = [A,B]C - C[A,B]$$

The QEOM interface is the same as VQE