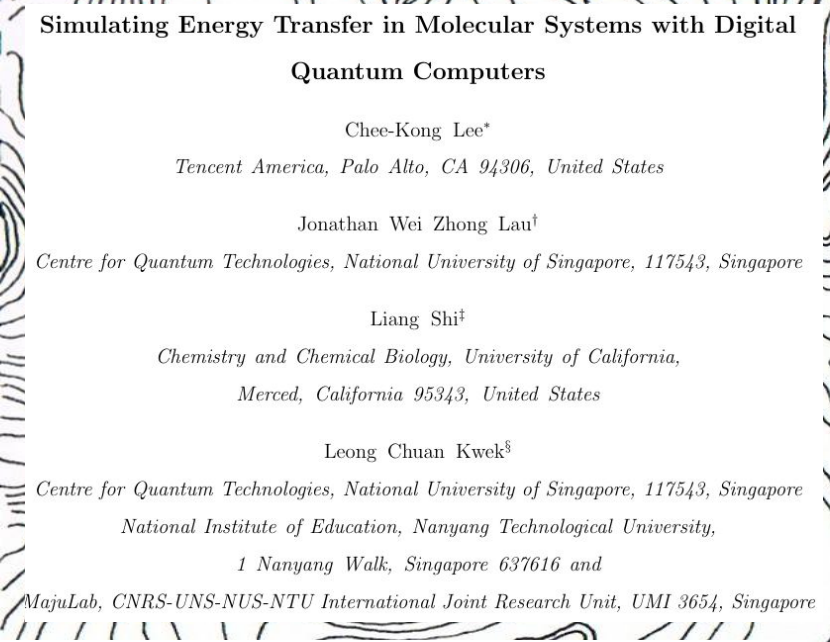
02/07/21

Martin Larocca[1,2] @ **Fenomenos Colectivos en Solidos**

Prof. **Pablo Tamborenea,** Dept. Fisica, Universidad de Buenos Aires



Simulating Energy Transfer in Molecular Systems with Digital Quantum Computers

Chee-Kong Lee*

Tencent America, Palo Alto, CA 94306, United States

Jonathan Wei Zhong Lau†

Centre for Quantum Technologies, National University of Singapore, 117543, Singapore

Liang Shi‡

Chemistry and Chemical Biology, University of California, Merced, California 95343, United States

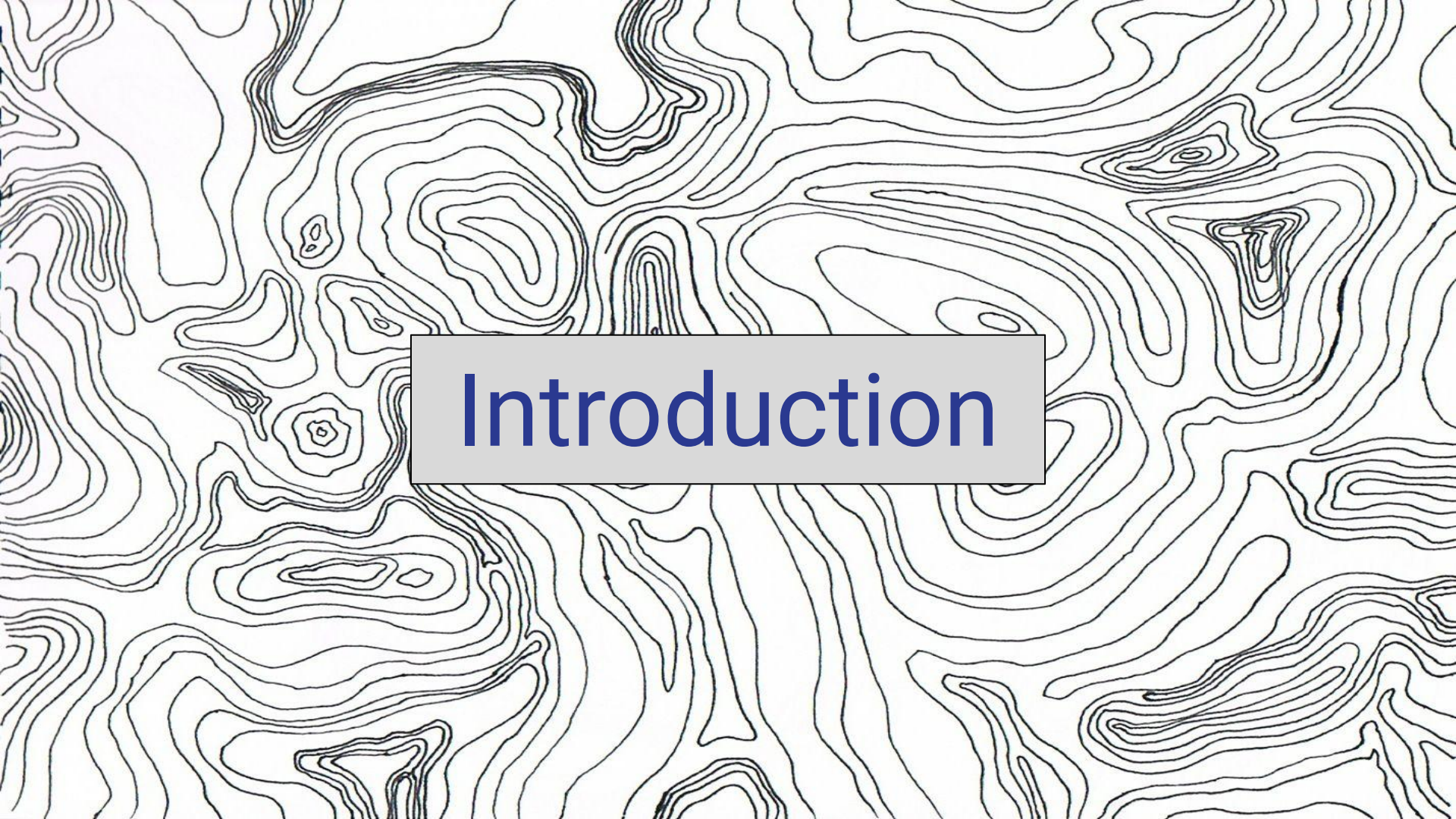
Leong Chuan Kwek§

Centre for Quantum Technologies, National University of Singapore, 117543, Singapore

National Institute of Education, Nanyang Technological University, 1 Nanyang Walk, Singapore 637616 and

MajuLab, CNRS-UNS-NUS-NTU International Joint Research Unit, UMI 3654, Singapore

1. **PhD** @ Universidad de Buenos Aires. **Mentor**: Diego Wisniacki
2. **GRA** @ Los Alamos National Laboratory. **Mentors:** Patrick J. Coles & Marco Cerezo


Introduction

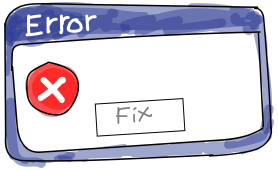
Introduction

Fault-tolerant quantum computation

Quantum Computers promise speed-ups.

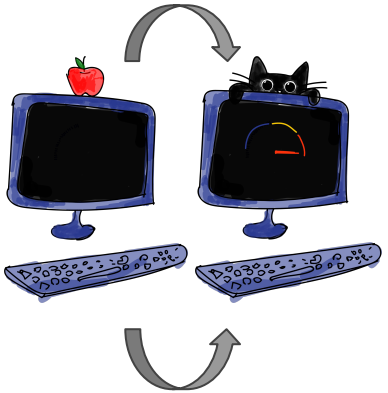
...but need error-correction schemes, that in turn need many “extra” qubits

NISQ era



Present Day devices are noisy and error prone.

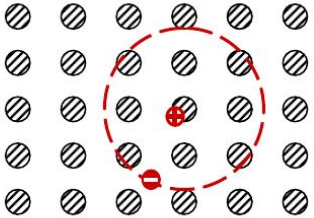
Variational Algorithms



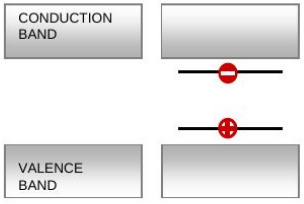
Hybrid Quantum-Classical Algorithms are believed to constitute a way around this problem.

Excitones

Wannier exciton
(typical of inorganic semiconductors)



SEMICONDUCTOR PICTURE



GROUND STATE WANNIER EXCITON

binding energy ~10meV
radius ~100Å

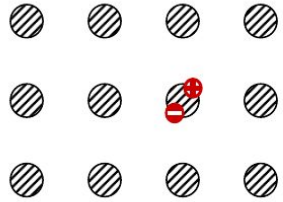
Excitons
(bound electron-hole pairs)

treat excitons as chargeless particles capable of diffusion,

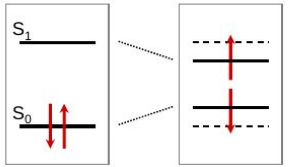
also view them as excited states of the molecule

Charge Transfer (CT) Exciton
(typical of organic materials)

Frenkel exciton
(typical of organic materials)



MOLECULAR PICTURE



GROUND STATE FRENKEL EXCITON

binding energy ~1eV
radius ~10Å

Electronic Processes in Organic Crystals and Polymers by M. Pope and C.E. Swenberg

Modelo de excitones localizados

Los excitones que vamos a considerar son **“de Frenkel”**: a diferencia de los de **Mott**, estan localizados!

Consideremos un sistema de N sitios “excitables” (cromoforos). El estado con un exciton en el sitio “m” se notara $|m\rangle = e_m^\dagger |0\rangle$

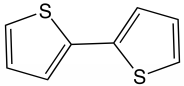
$$\hat{H}_{\text{exciton}} = \sum_m E_m(t)\,|m\rangle\langle m| + \sum_{m\neq n} V_{mn}(t)\,|m\rangle\langle n|\,,$$

excitation energy of molecule m

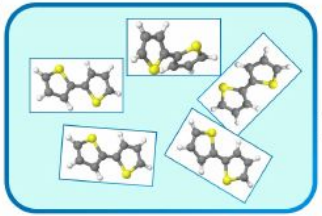
Coupling between local excitations on molecules m and n

La dependencia temporal tiene que ver con el movimiento nuclear, en particular con el acoplamiento “exciton-phonon”. Para E y V, usan MD y TDDFT.

Esquema del approach

bi-thiophene (T2) $(C_4H_3S)_2$ 

(a)



Molecular configurations from molecular dynamics simulations

Quantum chemistry calculations

$$\hat{H} = \begin{pmatrix} E_1 & \cdots & V_{1,N} \\ & \ddots & V_{nm} \\ \vdots & E_n & \vdots \\ V_{mn} & & \\ V_{N,1} & \cdots & E_N \end{pmatrix}$$

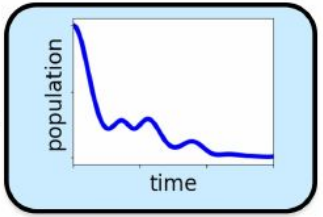
Exciton Hamiltonian

Qubit encoding

$$\hat{H} = \sum_{i,j=1}^{\log_2(N)} c_{ij}\hat{\sigma}^i\hat{\sigma}^j$$

Hamiltonian in Pauli matrices

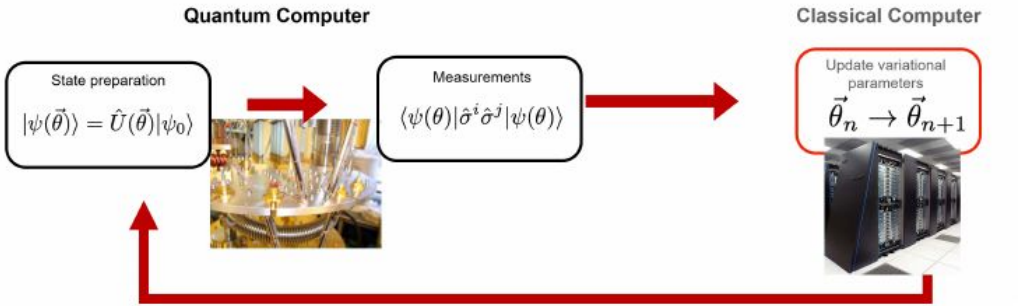
Quantum computer



Exciton dynamics

Mediante mediciones en la computadora cuantica calculo la evolucion de mi theta(t) → psi(theta(t)) approx psi(t)

(b) Variational implementation of $e^{-i\hat{H}\delta t}$



Digital quantum simulation, step 0: **qubit encoding**

$$
\begin{aligned}
|1\rangle &\mapsto |\bar{1}\rangle = |0\rangle|0\rangle\cdots|0\rangle|0\rangle|0\rangle \\
|2\rangle &\mapsto |\bar{2}\rangle = |0\rangle|0\rangle\cdots|0\rangle|0\rangle|1\rangle \\
|3\rangle &\mapsto |\bar{3}\rangle = |0\rangle|0\rangle\cdots|0\rangle|1\rangle|0\rangle \\
|4\rangle &\mapsto |\bar{4}\rangle = |0\rangle|0\rangle\cdots|0\rangle|1\rangle|1\rangle \\
|5\rangle &\mapsto |\bar{5}\rangle = |0\rangle|0\rangle\cdots|1\rangle|0\rangle|0\rangle, \text{ etc.},
\end{aligned}
$$

$$
|m\rangle = |\boldsymbol{x}\rangle = |x_1\rangle \otimes |x_2\rangle \otimes \ldots |x_L\rangle\,, \tag{2}
$$

where where the subscript denotes the qubit number, $m = x_1 2^0 + x_2 2^1 \ldots + x_L 2^{L-1}$ and x_i can be 0 or 1.

$$
|m\rangle\langle n| = |\boldsymbol{x}\rangle\langle \boldsymbol{x'}| = |x_1\rangle\langle x_1'| \otimes |x_2\rangle\langle x_2'| \otimes \ldots \otimes |x_L\rangle\langle x_L'|\,.
$$

Ejemplo: 4-site exciton Hamiltonian in two qubits

$$
\begin{aligned}
H \;=\; & \frac{1}{4}(E_1 + E_2 - E_3 - E_4)\hat{\sigma}_z^1 + \frac{1}{4}(E_1 - E_2 + E_3 - E_4)\hat{\sigma}_z^2 \\
& + \frac{1}{4}(E_1 - E_2 - E_3 + E_4)\hat{\sigma}_z^1\hat{\sigma}_z^2 + \frac{1}{2}(V_{13} + V_{24})\hat{\sigma}_x^1 \\
& + \frac{1}{2}(V_{12} + V_{24})\hat{\sigma}_x^2 + \frac{1}{2}(V_{12} - V_{34})\hat{\sigma}_z^1\hat{\sigma}_x^2 \\
& + \frac{1}{2}(V_{13} - V_{24})\hat{\sigma}_x^1\hat{\sigma}_z^2 + \frac{1}{2}(V_{23} + V_{14})\hat{\sigma}_x^1\hat{\sigma}_x^2 + \frac{1}{2}(V_{23} - V_{14})\hat{\sigma}_y^1\hat{\sigma}_y^2,
\end{aligned}
$$

An exciton Hamiltonian of N sites can be encoded in log2 (N) qubits !

→ In other words, three dimensional molecular systems consisting of millions of sub-units can be encoded in as few as tens of qubits. This opens the possibility of studying exciton transport in systems of experimentally relevant sizes fully quantum mechanically.

Digital quantum simulation

Aproximo la dinamica con un estado parametrizado

$$|\Psi(t)\rangle = \hat{T}\mathrm{e}^{-i\int_0^t \hat{H}(t')dt'}|\Psi_0\rangle \approx \left|\psi(\vec{\theta}(t))\right\rangle$$

Producto de una secuencia de compuertas parametrizadas

$$|\psi(\theta)\rangle = \hat{U}(\vec{\theta})|\psi_0\rangle = \prod_k \hat{U}_k(\theta_k)|\psi_0\rangle = \prod_k \mathrm{e}^{i\theta_k\hat{R}_k}|\psi_0\rangle\,.$$

Evoluciono mi vector de parámetros: McLachlan's principle $\|\left(i\frac{\partial}{\partial t} - \hat{H}(t)\right)|\psi(\theta\rangle\|$

$$\vec{\theta}(t+\delta t) = \vec{\theta}(t) + \dot{\vec{\theta}}(t)\delta t;\;\; \dot{\vec{\theta}}(t) = \hat{M}^{-1}\vec{V},$$

where the matrix elements of $\hat{M}$ and $\vec{V}$ are

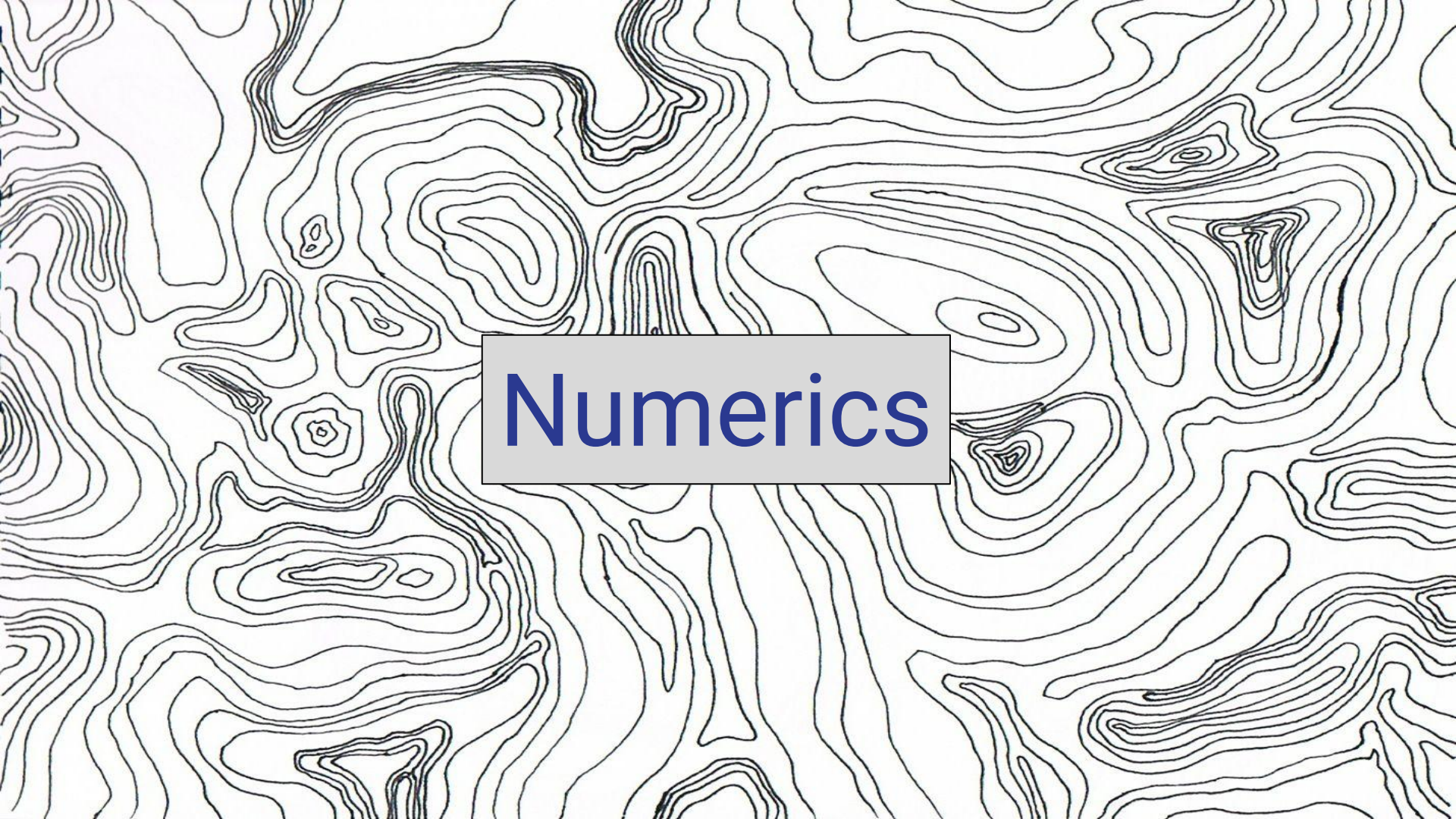
$$\hat{M}_{kl} = \mathrm{Re}\left\langle \frac{\partial\psi(\vec{\theta})}{\partial\theta_k}\middle|\frac{\partial\psi(\vec{\theta})}{\partial\theta_l}\right\rangle; \vec{V}_k = \mathrm{Im}\left\langle\psi(\vec{\theta})\middle|\hat{H}\middle|\frac{\partial\psi(\vec{\theta})}{\partial\theta_k}\right\rangle.$$

Voy "midiendo" las matrices M y V en la computa

$$\begin{aligned}
\hat{M}_{kl} &= \mathrm{Re}\big(\langle\psi_0|\hat{U}_1^\dagger...\hat{U}_k^\dagger\hat{R}_k^\dagger...\hat{U}_L^\dagger\hat{U}_L..\hat{R}_l\hat{U}_l...\hat{U}_1|\psi_0\rangle\big)\\
&= \mathrm{Re}\big(\langle\psi_0|\hat{U}_1^\dagger...\hat{U}_k^\dagger\hat{R}_k^\dagger\hat{U}_{k+1}^\dagger...\hat{U}_l^\dagger\hat{R}_l\hat{U}_l...\hat{U}_1|\psi_0\rangle\big),\\
\vec{V}_k &= \mathrm{Im}\big(i\sum_j c_j\langle\psi_0|\hat{U}_1^\dagger...\hat{U}_L^\dagger\hat{h}_j\hat{U}_L..\hat{R}_k\hat{U}_k...\hat{U}_1|\psi_0\rangle\big),
\end{aligned}$$

$$\frac{\partial\hat{U}_k(\theta_k)}{\partial\theta_k} = i\hat{R}_k\hat{U}_k(\theta_k),$$

where we have expressed the Hamiltonian as $\hat{H} = \sum_j c_j\hat{h}_j$.


Numerics

Numerics

- crystal of 64 T2 molecules, arranged in a 4 × 4 × 2 super cell (each unit cell contains 2 molecules)

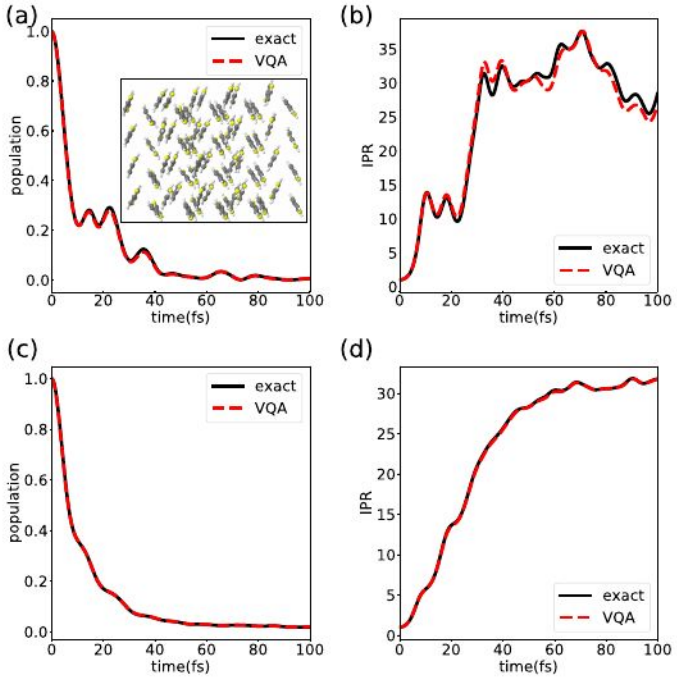


FIG. 3: Exciton dynamics in a molecular crystal of 64 bi-thiophene molecules obtained from exact calculations (black solid lines) and variational quantum algorithm (red dashed lines). (a) Exciton population dynamics in molecule where the exciton is initially located. (b) Time evolution of inverse participation ratio (IPR) defined in Eq. 10. (c) and (d) Dissipative exciton and IPR dynamics obtained by averaging over an ensemble of 100 pure state trajectories.

a)

- The exciton Hamiltonian is encoded in 6 qubits, and a VQA simulation time-step of 0.04fs is used
- a molecule at the center of the molecular crystal is initially excited and we study the time evolution of the exciton population in this molecule
- Despite the fast delocalization, clear oscillatory behavior due to quantum coherence is also seen within the first 40 fs

(b)

- We next investigate the inverse participation ratio (IPR) of the exciton wavefunction, a global quantity that measures the extent of wavefunction delocalization.

$$\mathrm{IPR} = \frac{1}{\sum_m p_m^2},$$

pm is the probability of locating the exciton at molecule m.

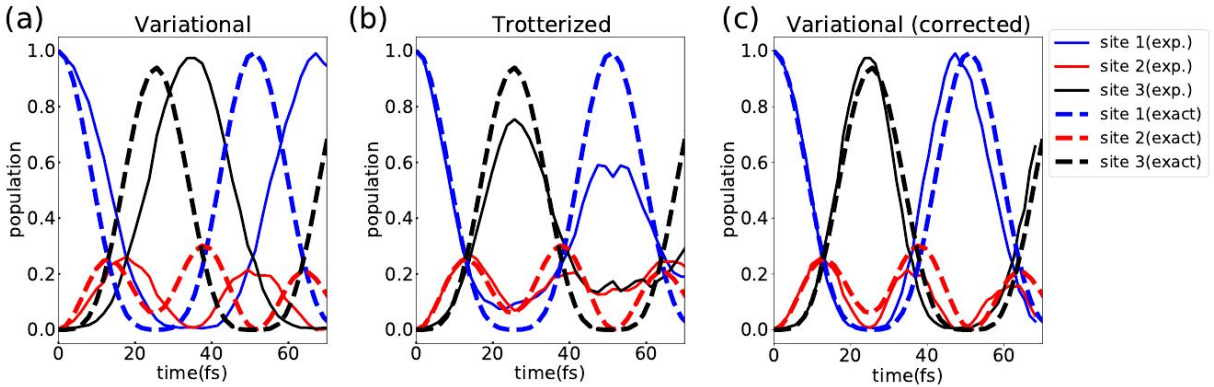
- Limites: **delocalized** IPR=N, **localized** IPR=1.

On an actual Quantum Computer: 5-qubit ***ibmq_rome***

linear chain (PBC) of 4 T2 molecules. **“Static”** setting: nearest neighbor coupling **V(t)=V= 40meV**
Energies: E1 = E2, E3 = E4 and E1 − E3 = ΔE = **20meV**

→ **encode** in 2 qubits: $H = \frac{\Delta E}{2}\sigma_z^1 + V\sigma_x^2 + V\sigma_x^1\sigma_x^2.$

→ **Hamiltonian Variational ansatz*** $\left|\psi(\vec{\theta})\right\rangle = \mathrm{e}^{i\theta_3\sigma_x^1\sigma_x^2}\mathrm{e}^{i\theta_2\sigma_x^2}\mathrm{e}^{i\theta_1\sigma_z^1}\left|\psi_0\right\rangle$ a time step of $\delta t = 1.97\mathrm{fs}$ is used (i.e. $3\hbar\mathrm{eV}^{-1}$)



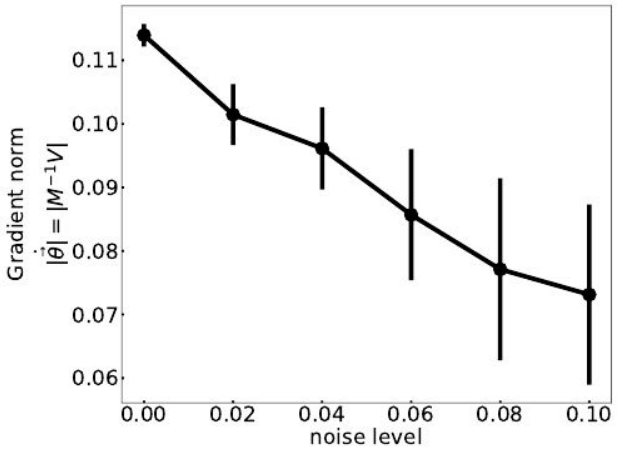
Pega las amplitudes pero no las frecuencias! → shift! **porque?**

* Wecker, D., Hastings, M. B. & Troyer, M. Progress towards practical quantum variational algorithms. Physical Review A 92, 042303 (2015).

Source of shift and mitigation/correction scheme

The accuracy of the VQA dynamics is principally determined by three factors:

1. the **expressive** power of the ansatz
2. error due to finite number of measurements (**sampling**)
3. imperfections of quantum devices (**decoherence / noise**)

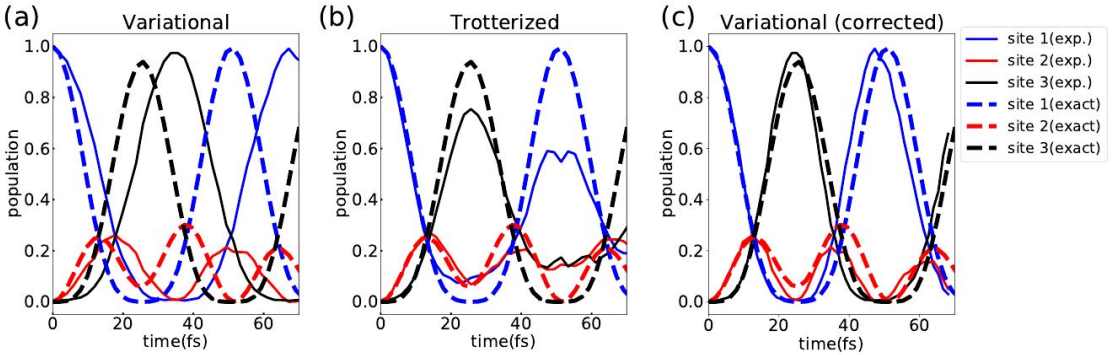


simulations. It can be seen that the norm $|\vec{\theta}|$ decreases monotonically as a function of λ, an observation consistent with the experimental observations that noise in quantum devices leads to an under-estimation of gradient norm. The under-estimation of the gradient seen in Fig. 5 therefore leads to an effective update time-step that is smaller than the actual time-step, i.e. $\delta t_{\text{eff}} < \delta t$, leading to the right-shift of the VQA dynamics compared to the exact results.

Trotter approach

$$|\Psi(t)\rangle = \prod_n \mathrm{e}^{-iH\delta t} |\Psi(0)\rangle$$

$$\mathrm{e}^{-iH\delta t} \approx \mathrm{e}^{-iV\sigma_x^1\sigma_x^2\delta t}\mathrm{e}^{-iV\sigma_x^1\delta t}\mathrm{e}^{-i\Delta E\sigma_z^1\delta t}$$



Fail to capture the amplitudes of the oscillations, but capture frequency !

→ **proposal:** use VQA with corrected $\delta t_{\mathrm{eff}} = \delta t/\alpha$

Obtain alfa from $$\min_{\alpha} \int_0^{t_c} \left(p_1^{\mathrm{VAQ}}(t) - p_1^{\mathrm{Trotter}}(t)\right)^2 dt$$

Transverse Field Ising Model