Quantum Algorithm for Simulating Single-Molecule Electron Transport

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Electric current

The current flowing through a molecular junction, in the limit of weak coupling between the junction and the conducting electrodes, is a result of electron transfers between the molecule and the electrodes. This leads to consequent changes in the charge state of the molecule when an electron is transferred to the molecule and when the molecule loses the electron. The probability of the molecule being at these electronic states is denoted respectively by P_{ox} and P_{red} . The current is computed from these occupation probabilities as ^{1,2}

$$I = e(P_{ox}k_{red}^S - P_{red}k_{ox}^S), \tag{S1}$$

where k_a^b is the electron transfer rate as defined below in Fig. S1 and e is the electron charge. The occupation probabilities are time dependent and can be estimated from master equations of the form

$$\frac{dP_{ox}}{dt} = -(k_{red}^S + k_{red}^D)P_{ox} + (k_{ox}^S + k_{ox}^D)P_{red}.$$
(S2)

The current is computed in the steady-state limit where $dP_{ox}/dt = 0$ and by recalling that $P_{ox} + P_{red} = 1$, the current is then obtained as ^{1,3–7}

$$I = e \frac{k_{red}^S k_{ox}^D - k_{ox}^S k_{red}^D}{k_{red}^S + k_{ox}^D + k_{ox}^S + k_{red}^D}.$$
 (S3)

For the magnesium porphine (MgP) molecule considered in the main text, we plot the values of the electron transfer rates as a function of the bias voltage in Fig. (S2). The current computed from the electron transfer rates, for different bias and gate voltages, is plotted in Fig. (S3). If we neglect oxidation at the source electrode and reduction at the drain electrode, Eq. (S3) can be written as

$$I = e \frac{k_S k_D}{k_S + k_D}.$$
 (S4)



Figure S1: Schematic representation of a single-molecule junction bridging a source (S) and a drain (D) electrode. The electron transfer rates in Eq. (S3) are also defined.



Figure S2: Electron transfer rates for magnesium porphine computed as a function of the bias voltage at gate voltages of (a) -200.0 mV, (b) 0.0 mV and (c) 200.0 mV. The gate voltage is shifted by -1252.6 mV.



Figure S3: Electric current in magnesium porphine computed as a function of bias and gate voltages. The gate voltage is shifted by -1252.6 mV.

Photonic gates

In photonic quantum computing, the fundamental physical systems of interest are optical modes of the quantized electromagnetic field. They are mathematically represented by a Hilbert space of infinite dimension, where a general state can be expressed as $|\psi\rangle =$ $\sum_{n=0}^{\infty} c_n |n\rangle$, with $\sum_{n=0}^{\infty} |c_n|^2 = 1$. The basis states $|n\rangle$ are known as *Fock states*, and they have the physical interpretation of a mode with *n* photons.

The state of a multi-system can also be uniquely specified by its Wigner function. Gaussian states have a Wigner function which is a Gaussian distribution. Similarly, Gaussian gates are unitary transformations that map Gaussian states into Gaussian states. In terms of the creation and annihilation operators a_i and a_i^{\dagger} on mode i, a squeezing gate is given by

$$\hat{S}(r_i) = \exp[r_i(a_i^{\dagger 2} - a_i^2)/2],$$
(S5)

a displacement gate by

$$\hat{D}(\alpha_i) = \exp(\alpha_i a_i^{\dagger} - \alpha_i^* a_i), \tag{S6}$$

and the linear interferometer $\hat{R}(U)$ characterized by a unitary matrix U transforms the mode operators as

$$\begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_m \end{pmatrix} \longrightarrow \begin{pmatrix} a'_1 \\ a'_2 \\ \vdots \\ a'_m \end{pmatrix} = U \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_m \end{pmatrix}.$$
 (S7)

All of these gates are Gaussian, which means that the quantum algorithm can be implemented using Gaussian boson sampling devices. In the main text, we use the shorthand $\hat{D}(\boldsymbol{\alpha}), \hat{S}(\boldsymbol{r})$ with $\boldsymbol{\alpha} = (\alpha_1, \ldots, \alpha_m), \, \boldsymbol{r} = (r_1, \ldots, r_m)$ to respectively denote displacement and squeezing gates acting individually on each mode, with α_i, r_i the displacement and squeezing parameters in mode *i*.

Molecular parameters

We apply the Franck-Condon approximation^{8–10} and assume that the change in the electronic state leads to a vertical transition between the vibrational energy levels of the two different electronic states of the molecule. The relation between the vibrational normal coordinates of these different electronic states, \boldsymbol{q} and $\boldsymbol{q'}$, is described by the Duschinsky transformation¹¹

$$\boldsymbol{q}' = U_D \boldsymbol{q} + \boldsymbol{d},\tag{S8}$$

where U_D is the Duschinsky matrix, which is related to the overlap between the normal modes, and d is a real vector that describes the change in the molecular geometries of the electronic states. The Duschinsky matrix is obtained from the eigenvectors of the Hessian matrices of the initial and final electronic states, L and L', respectively¹²

$$U_D = (\boldsymbol{L}')^T \boldsymbol{L}.$$
 (S9)

The displacement vector d is obtained from the the Cartesian geometry vectors of the initial and final electronic states, x and x', as¹²

$$\boldsymbol{d} = (\boldsymbol{L}')^T m^{1/2} (\boldsymbol{x} - \boldsymbol{x}'), \tag{S10}$$

where m is a diagonal matrix of atomic masses. The quantities L, L', and x were obtained from density functional theory (DFT) calculations performed on both electronic states of MgP. The Duschinsky matrix for MgP is plotted in Fig. (S4). The off-diagonal non-zero terms in this matrix are due to the mixing of the vibrational modes of the initial and final electronic states.

The Duschinsky matrix and displacement vector are used to program the quantum computer with parameters that determine the unitary operator \hat{U}_{Dok} . This operator is defined in terms of displacement $\hat{D}(\boldsymbol{\alpha})$, squeezing $\hat{S}(\boldsymbol{r})$, and rotation $\hat{R}(U_L)$, $\hat{R}(U_R)$ operations^{13,14}

$$\hat{U}_{\text{Dok}} = \hat{D}(\boldsymbol{\alpha})\hat{R}(U_L)\hat{S}(\boldsymbol{r})\hat{R}(U_R), \qquad (S11)$$

where U_L and U_R are unitary matrices. The matrices U_L , U_R , and the vector \boldsymbol{r} are obtained from the singular value decomposition $J = U_L \operatorname{diag}(\boldsymbol{r}) U_R$ of the matrix $J := \Omega' U_D \Omega^{-1}$ where¹³

$$\Omega = \operatorname{diag}(\sqrt{\omega_1}, \dots, \sqrt{\omega_M}), \tag{S12}$$

$$\Omega' = \operatorname{diag}(\sqrt{\omega'_1}, ..., \sqrt{\omega'_M}). \tag{S13}$$

The terms ω and ω' in Eq. (S12) are the vibrational frequencies of the two electronic states which are also obtained from DFT calculations. The displacement vector $\boldsymbol{\alpha}$ in Eq. (S11) is obtained from the Duschinsky displacement vector as $\boldsymbol{\alpha} = \hbar^{-1/2} \Omega' \boldsymbol{d} / \sqrt{2}$ where \hbar is the reduced Planck constant.



Figure S4: Duschinsky matrix for magnesium porphine computed from Eq. (S9). The molecule has 37 atoms and 105 vibrational modes.

Complexity

The number of optical modes in the quantum computer is equal to the number of vibrational modes, so the algorithm has linear space complexity. The squeezing and displacement gates act individually on each mode, leading to a constant depth circuit. The largest set of operations occur in the interferometer, where it is known that arbitrary interferometers can be decomposed into circuits of linear depth.¹⁵ Therefore, the complexity of generating a single sample scales linearly with problem size.

Now consider the number of samples needed. The averages of the Fermi function

$$\bar{f}(i,V) = \int_{\epsilon_i - \Delta}^{\epsilon_i + \Delta} d\epsilon \ f(\epsilon, V), \tag{S14}$$

are one-dimensional integrals that can be computed efficiently. In fact, since they are independent of the molecule, they can be pre-computed and loaded from memory. To compute transfer rates, we need to estimate M probabilities q(i). Each such estimation can be viewed as a Bernoulli trial where success corresponds to observing a sample inside of the energy subinterval $[\epsilon_i - \Delta, \epsilon_i + \Delta]$. In the limit of a large number of samples N, the unbiased estimator $\hat{q}(i) = \frac{N_i}{N}$ follows a normal distribution with standard deviation $\sigma = \sqrt{\frac{q(i)[1-q(i)]}{N}}$, which can be used to quantify the error in the estimation as

$$\varepsilon := \frac{\sigma}{q(i)} \approx \sqrt{\frac{1}{Nq(i)}},$$
(S15)

where the approximation holds when q(i) is small. Since there are only M probabilities q(i), the average probability is exactly 1/M. Probabilities that are much smaller than 1/M don't contribute significantly to the transfer rates. Therefore, in terms of the target error ε and the algorithm parameter M, the number of samples needed scales polynomially as

$$N = O\left(\frac{M}{\varepsilon^2}\right). \tag{S16}$$

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