Enabling Quantum Chemistry using Quantum Computers

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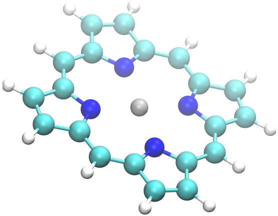
Schrödinger Equation

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \tag{1}$$

Molecular Electronic Hamiltonian

$$\hat{H} = -\sum_i \frac{1}{2}\nabla_i^2 + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,A} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \tag{2}$$



Finite basis expansion

$$\{\phi_0, \phi_1, ..\phi_N\}, \quad \langle \phi_i | \phi_j \rangle = \delta_{ij} \tag{3}$$

State vector

$$|\psi\rangle = c_0 |1100\rangle + c_1 |0110\rangle + \ldots \tag{4}$$

Eigenvalue problem

$$\boldsymbol{H}\boldsymbol{C}_0 = E_0 \boldsymbol{C}_0 \tag{5}$$

$$\boldsymbol{H}_{0011,0110} = \left\langle 0011 \middle| \hat{H} \middle| 0110 \right\rangle \tag{6}$$

Exponential scaling

For $N_{\text{electrons}}$ in M_{orbitals},

$$N_{\text{determinants}} = \binom{N_{\text{orbitals},\alpha}}{N_{\text{electrons},\alpha}}\binom{N_{\text{orbitals},\beta}}{N_{\text{electrons},\beta}} \tag{7}$$

Size	Memory (GB)
(10,10)	5.1e-4
(12,12)	6.8e-3
(14,14)	9.4e-2
(16,16)	1.3
(18,18)	19
(20,20)	270
(22,22)	4000

Ansatz

$$\hat{H}\left|\psi\right\rangle \rightarrow \hat{H}\boldsymbol{U}(\boldsymbol{\theta})\left|\mathrm{HF}\right\rangle \tag{8}$$

Unitary Product State

$$\boldsymbol{U}(\boldsymbol{\theta}) = \prod_I \boldsymbol{U}_I(\theta_I) \tag{9}$$

Product of single parameter unitaries.

Expectation values

$$\hat{H} = \sum_i c_i \hat{P}_i \tag{10}$$

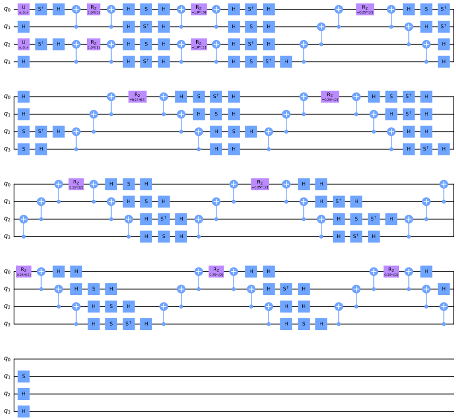
$\hat{P}_i$ being a Pauli-string, i.e. product of I, X, Y, Z.

$$E = \left\langle \mathrm{HF} \middle| \boldsymbol{U}^\dagger(\boldsymbol{\theta})\hat{H}\boldsymbol{U}(\boldsymbol{\theta}) \middle| \mathrm{HF} \right\rangle = \sum_i c_i \left\langle \mathrm{HF} \middle| \boldsymbol{U}^\dagger(\boldsymbol{\theta})\hat{P}_i\boldsymbol{U}(\boldsymbol{\theta}) \middle| \mathrm{HF} \right\rangle \tag{11}$$

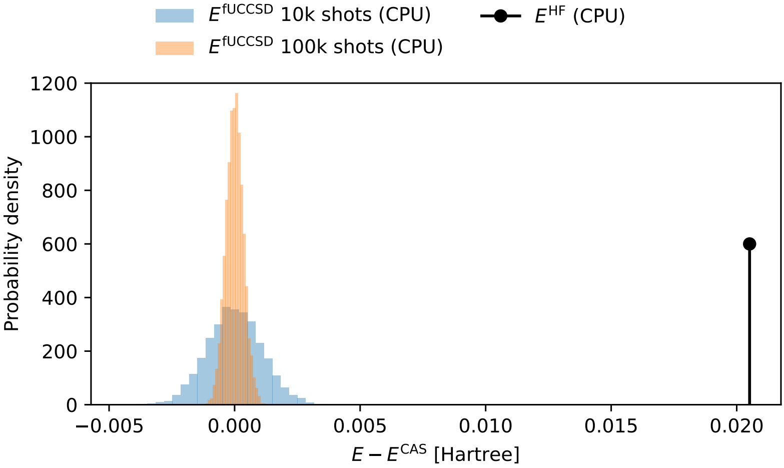
Running on QPU

System

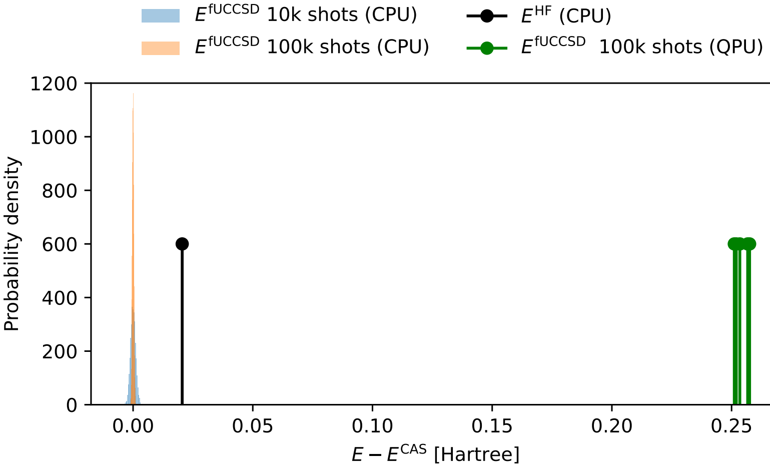
- LiH
- (2,2) space
- STO-3G
- fUCCSD: 'cx': 56, 'rz': 50, 'sx': 31 (transpiled).
- IBM Mumbai (retired device)

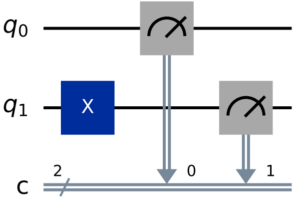


Running on ideal simulated QPU



Running on real QPU





Prepared	Measured	Notation
$\|01\rangle$	$\|00\rangle$	$P(00\|01)$
$\|01\rangle$	$\|10\rangle$	$P(10\|01)$
$\|01\rangle$	$\|01\rangle$	$P(01\|01)$
$\|01\rangle$	$\|11\rangle$	$P(11\|01)$

M standard - 2 qubit example

$$\boldsymbol{M} = \begin{pmatrix} P(00|00) & P(00|10) & P(00|01) & P(00|11) \\ P(10|00) & P(10|10) & P(10|01) & P(10|11) \\ P(01|00) & P(01|10) & P(01|01) & P(01|11) \\ P(11|00) & P(11|10) & P(11|01) & P(11|11) \end{pmatrix} \tag{12}$$

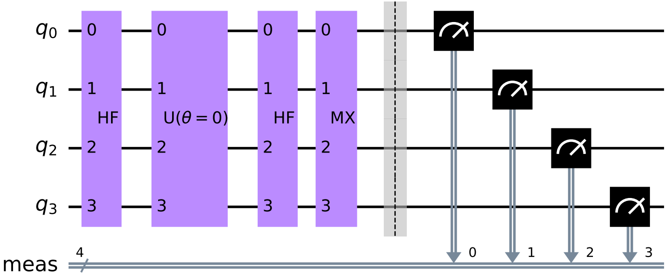
$$\boldsymbol{C} = \begin{pmatrix} P(00) \\ P(10) \\ P(01) \\ P(11) \end{pmatrix} \tag{13}$$

Read-out mitigation

$$\boldsymbol{C}_{\text{mitigated}} = \boldsymbol{M}^{-1}\boldsymbol{C}_{\text{measured}} \tag{14}$$

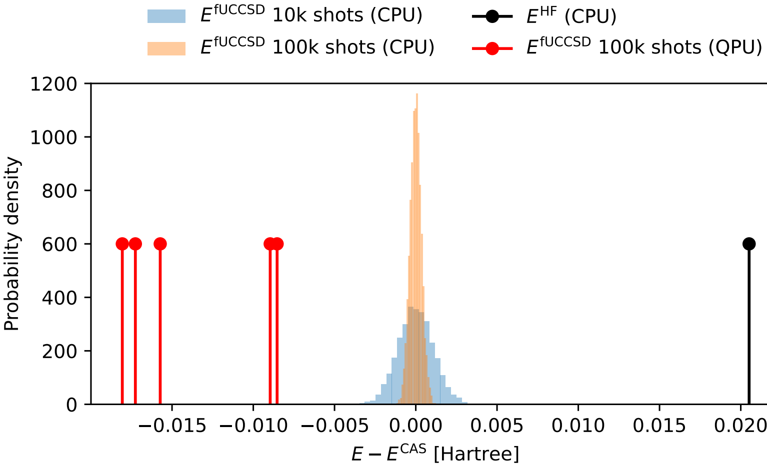
Read-out and gate-error mitigation

$$\boldsymbol{C}_{\text{mitigated}} = \boldsymbol{M}_{\theta=0}^{-1} \boldsymbol{C}_{\text{measured}} \tag{15}$$



Ziems, Karl Michael, et al. "Understanding and mitigating noise in molecular quantum linear response for spectroscopic properties on quantum computers." Chemical Science (2025).

20 min QPU per red line



Post-selection

For Pauli strings in the computational basis, only Z and I.

$$\sum_i b_i = N_e \tag{16}$$

F.x.:

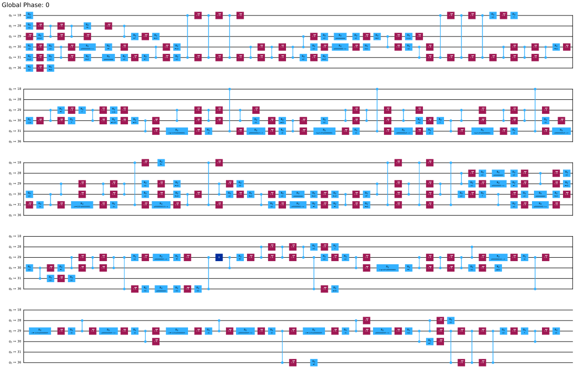
$$1100 \rightarrow 2 \text{ electrons}$$

Waiting

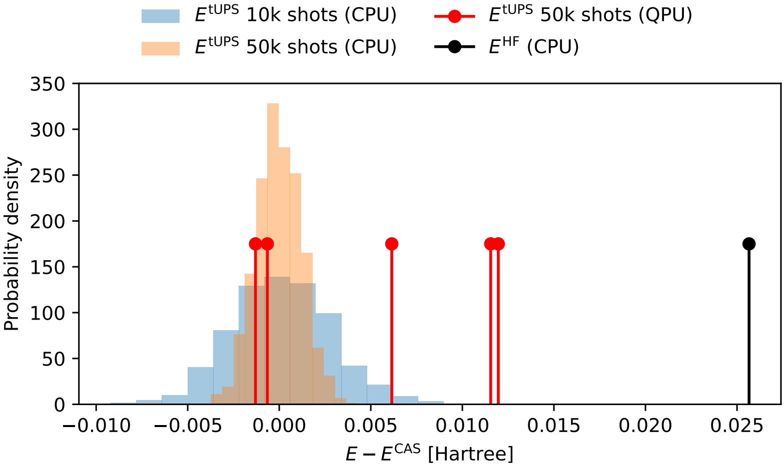
- Hardware becomes better
- Hardware vendors become more experienced in calibration

System

- H_2
- (2,3) space
- aug-cc-pVTZ
- tUPS: 'sx': 178, 'rz': 137, 'cz': 84, 'x': 1 (transpiled).
- IBM Torino (still active device)



21 min QPU per red line



Isotripic hyperfine coupling constant

$$\left[\alpha_{\text{iso}}^{(K)}\right]_A = \frac{f_K}{2\pi M}\text{tr}\left[\left[\boldsymbol{A}_\alpha^{(K)}\right]_A\left[\boldsymbol{D}_\alpha\right]_A - \left[\boldsymbol{A}_\beta^{(K)}\right]_A\left[\boldsymbol{D}_\beta\right]_A\right] \tag{17}$$

$$D_{v\sigma,w\sigma} = \langle \text{HF}| \boldsymbol{U}^\dagger(\boldsymbol{\theta})\hat{E}_{vw}^\sigma \boldsymbol{U}(\boldsymbol{\theta})|\text{HF}\rangle = \sum_i c_i \langle \text{HF}| \boldsymbol{U}^\dagger(\boldsymbol{\theta})\hat{P}_i \boldsymbol{U}(\boldsymbol{\theta})|\text{HF}\rangle \tag{18}$$

RDM purification

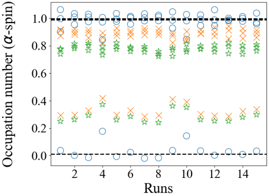
$$\text{Tr}(\boldsymbol{D}_\sigma) = N_\sigma \tag{19}$$

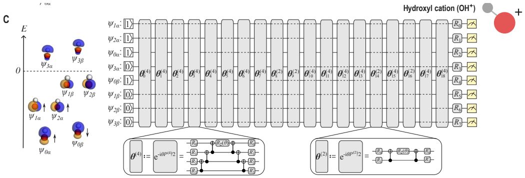
$$\overline{\boldsymbol{\lambda}}_\sigma = \left(N_\sigma / \sum_i \lambda_i\right)\boldsymbol{\lambda}_\sigma \tag{20}$$

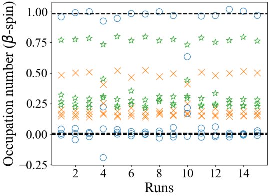
$$\overline{\boldsymbol{D}}_\sigma = \boldsymbol{V}_\sigma \overline{\boldsymbol{\lambda}}_\sigma \boldsymbol{V}_\sigma^\mathsf{T} \tag{21}$$

Beyond Energy Calculations

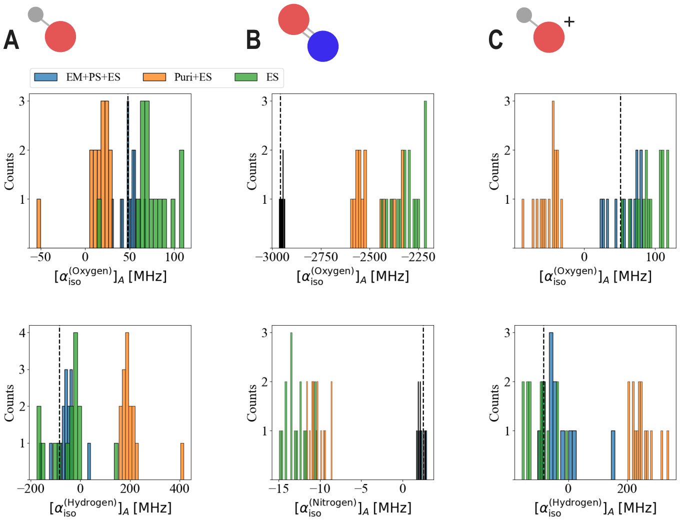
- Error Mitigation, Error Suppression and Post Selection
- Error Suppression and RDM purification
- Error Suppression
- IBM Torino
- Error Suppression = Pauli Twirling + Dynamical Decoupling







Jensen, Phillip WK, et al. "Hyperfine Coupling Constants on Quantum Computers: Performance, Errors, and Future Prospects." arXiv preprint arXiv:2503.09214 (2025).



Jensen, Phillip WK, et al. "Hyperfine Coupling Constants on Quantum Computers: Performance, Errors, and Future Prospects." arXiv preprint arXiv:2503.09214 (2025).

Website: https://hqc2.github.io/

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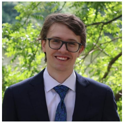
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