Quantum simulation of parameter-averaged NMR experiments

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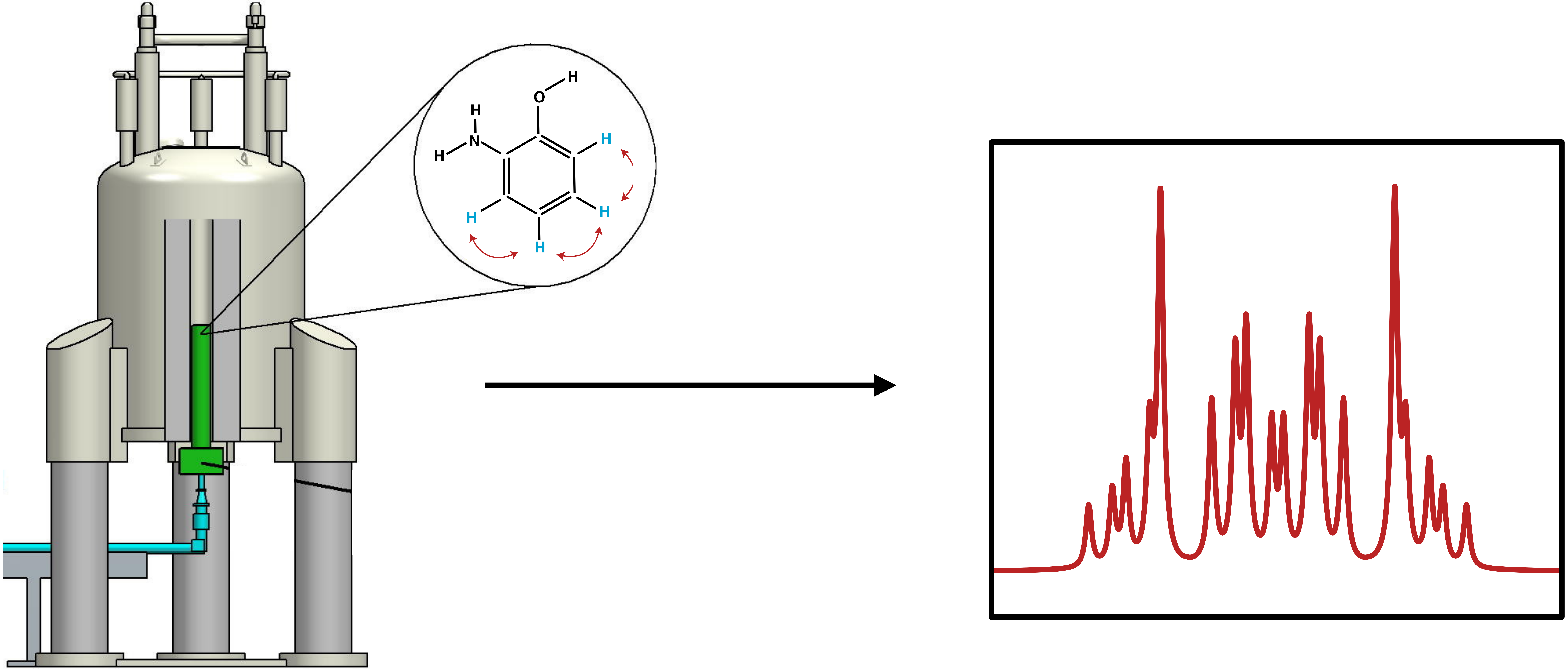
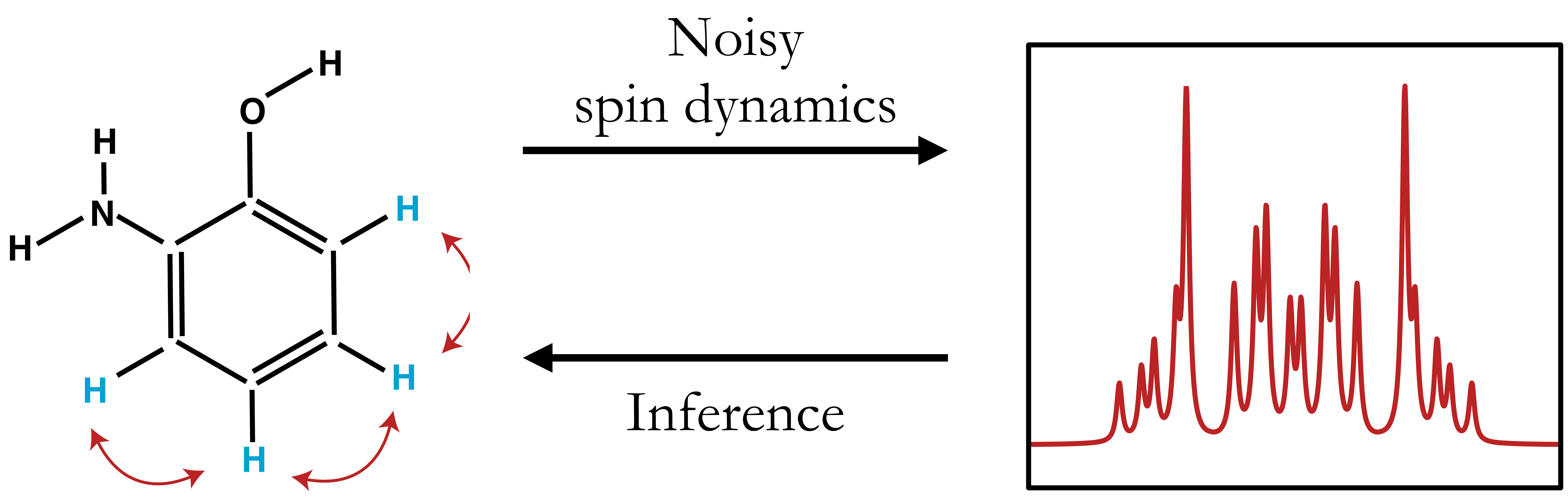
NMR spectroscopy





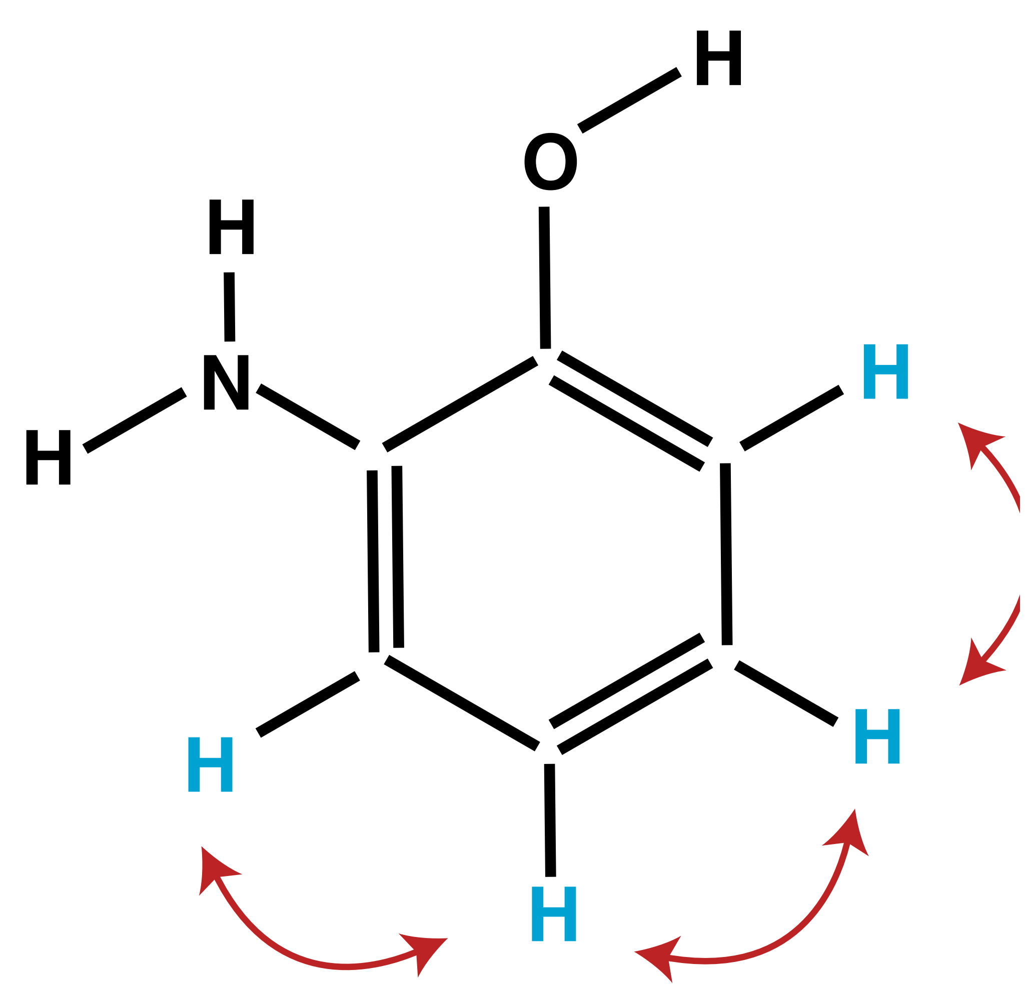
Simulation can be useful

Simulation can be hard

Simulate noisy spin systems with noisy spin systems

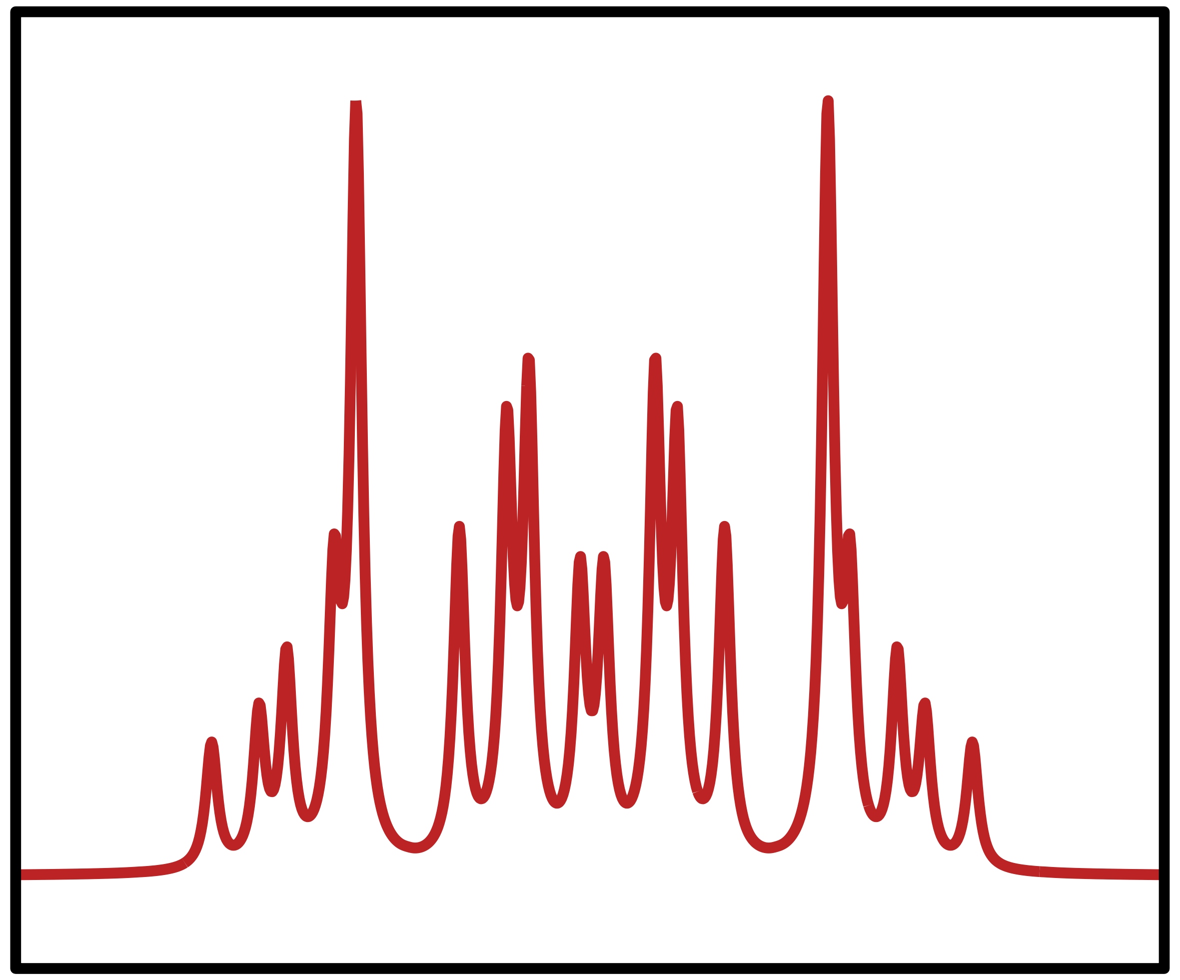
NMR sample

Quantum hardware



Spin dynamics

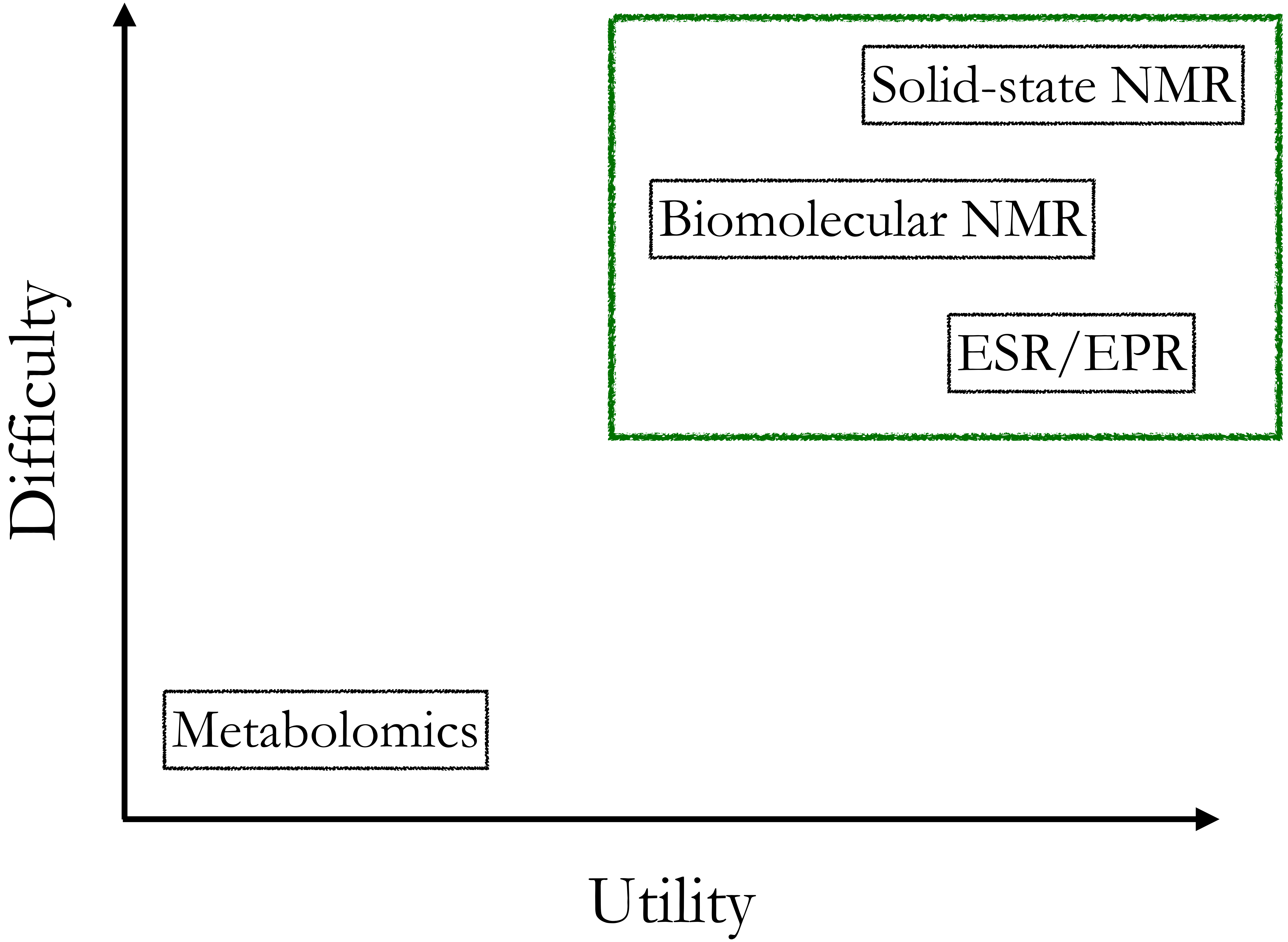
Inference



$$\boxed{S\left(t\right) = \left\langle \hat{S}^{+}_{\text{tot}}\left(t\right)\right\rangle = -\lambda \text{Tr}\left\{ e^{i\hat{H}t}\hat{S}^{+}_{\text{tot}} e^{-i\hat{H}t}\hat{S}^{z}_{\text{tot}}\right\}}$$

$$\hat{H} = \sum_i \underbrace{\left(2\pi h_i\right)}_{\text{Local magnetic response}} \hat{S}^z_i + \sum_{i<j} \underbrace{\left(2\pi J_{i,j}\right)}_{\text{Bond angles}} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + \sum_{i<j} \frac{\left(2\pi \tilde{K}_{i,j}\right)}{\underbrace{r^3_{i,j}}_{\text{Relative positions of nuclei}}} \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j - 3\left(\hat{\mathbf{S}}_i \cdot \mathbf{u}_{i,j}\right)\left(\hat{\mathbf{S}}_j \cdot \mathbf{u}_{i,j}\right)\right)$$

Simulation utility and difficulty



1. Dynamics is hard
(protein NOESY, solid-state NMR)

2. Ensemble averaging
(ESR/EPR, solid-state NMR)

Computing the spectrum

$$A(\omega) = \mathrm{Re}\int_0^\infty dt \cdot e^{i\omega t-\gamma t} S(t)$$

$$S(t) = \left\langle S^+_{\mathrm{tot}}(t)\right\rangle = -\lambda \mathrm{Tr}\left\{\hat{S}^+_{\mathrm{tot}}(t)\,\hat{S}^z_{\mathrm{tot}}\right\}$$

$$|m_j(t)\rangle = \hat{U}(t,0)\,|m_j\rangle$$

Easy to do on a quantum computer given the ability to implement $\hat{U}(t,0)$

$$S(t) = \frac{1}{2^{N_s}}\sum_{j=1}^{2^{N_s}} m_j \langle m_j(t)|\hat{S}^+_{\mathrm{tot}}|m_j(t)\rangle$$

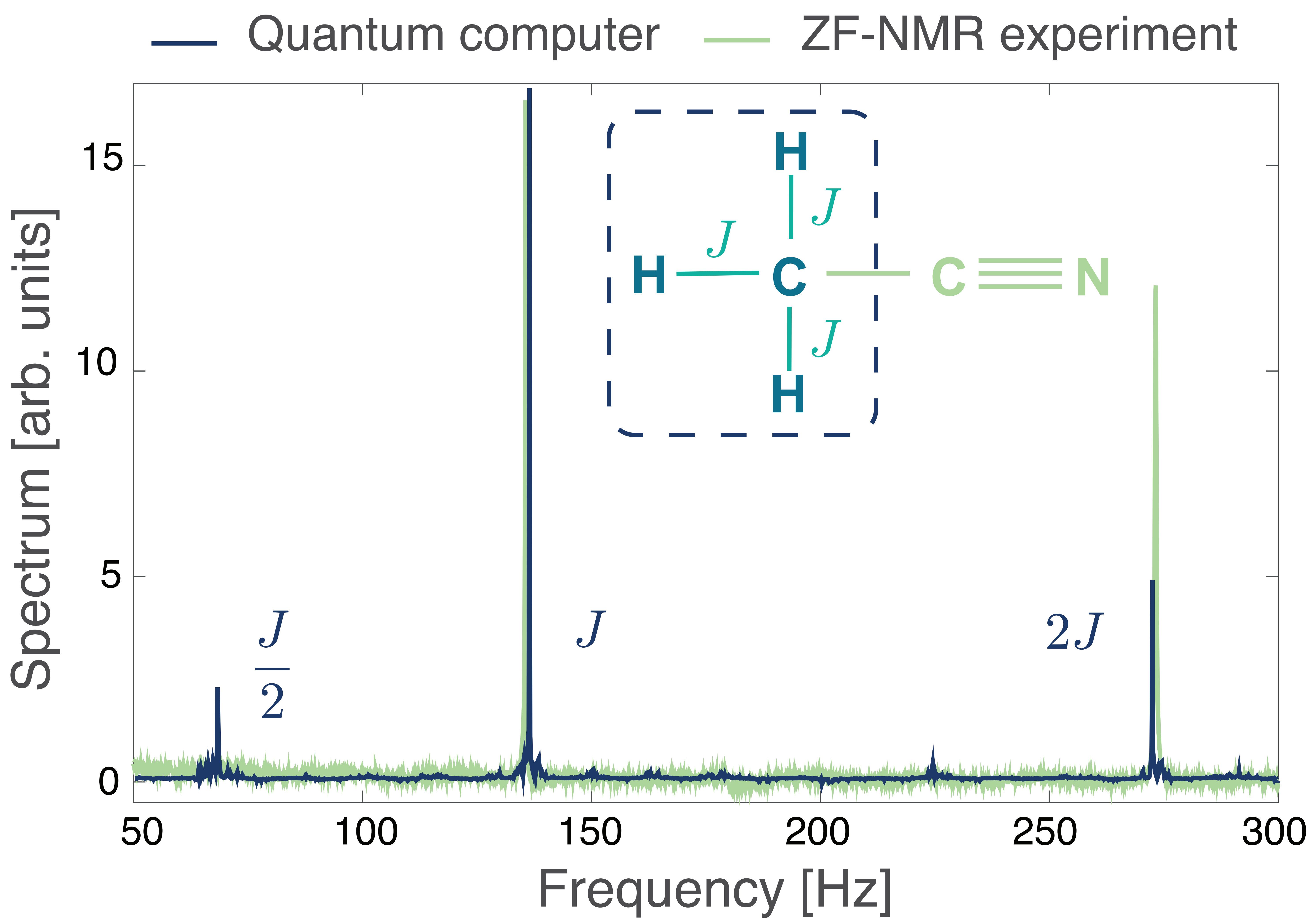
Use importance sampling to reduce cost

Sels - Nature Machine Intelligence (2020)

Experimental demonstration

$$\hat{H} = 2\pi J \left(\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_3 \right) \cdot \hat{\mathbf{S}}_4$$

$$J = 136.2 \text{ Hz}$$



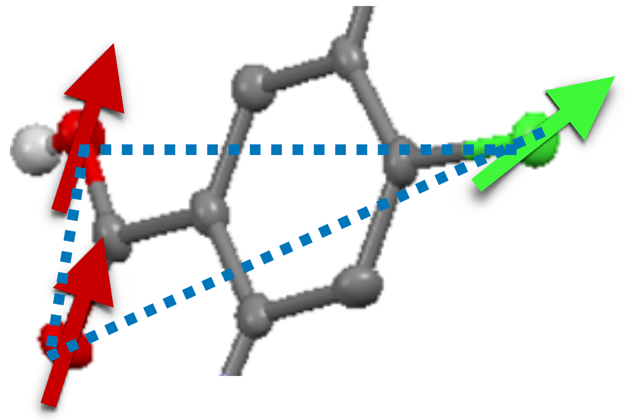
KS - arXiv:2109.13298

Ensemble averaging with discrete ancillas

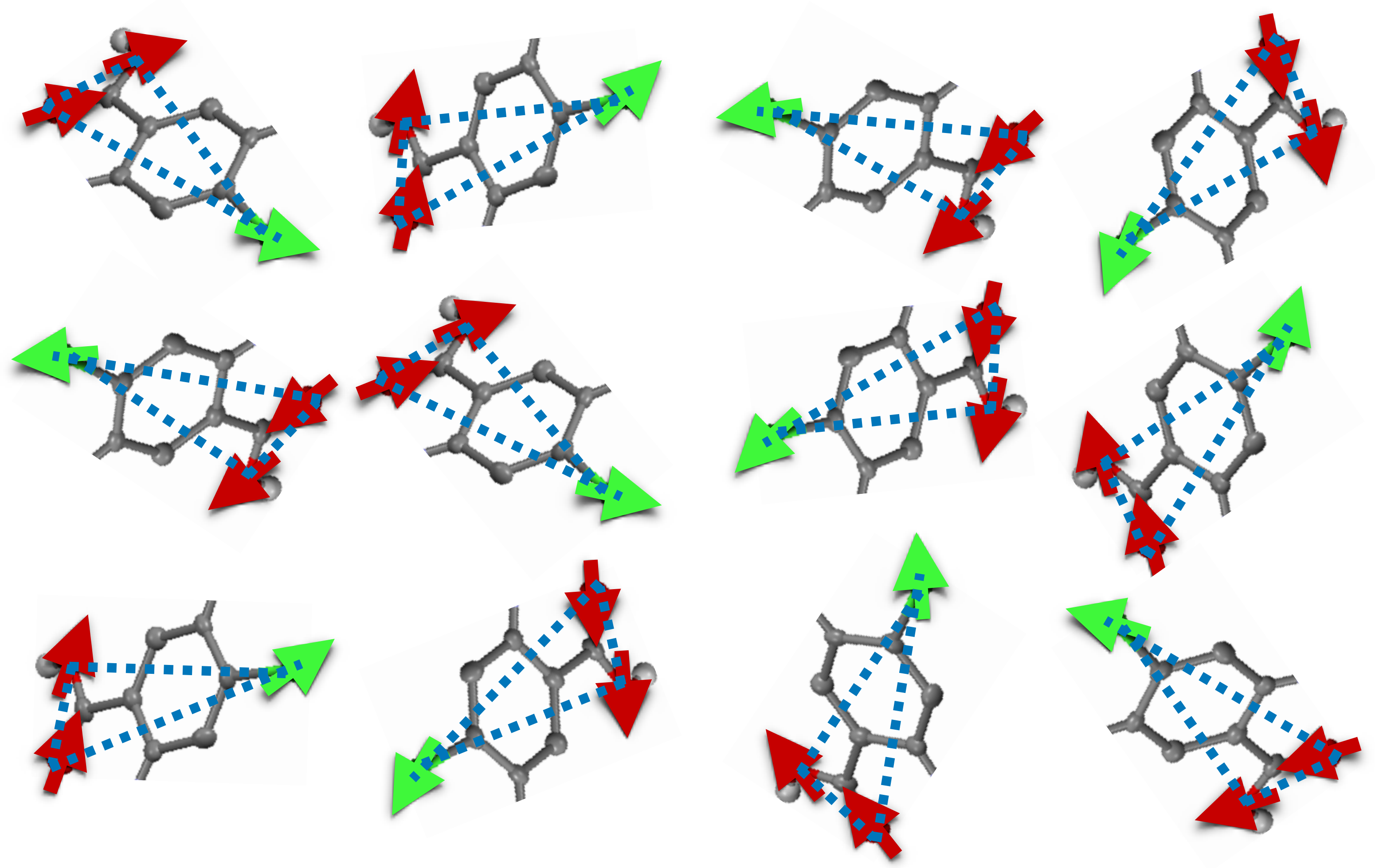
Solid state NMR

Pharma-relevant proteins, Polymers, Industrial catalysts, Battery materials

Simulation often necessary to infer chemical structure



$$d_{ij} \propto \frac{1}{r_{ij}^3}\left(3\cos^2\Theta_{ij} - 1\right)$$



Classical challenges:

(1) long-range dynamics is challenging to classically simulate

↓

Can more naturally encode dynamics on quantum computer/simulator

(2) need to average over 10^3-10^4 angles

↓

Can do in a single pass using 10-15 ancilla qubits

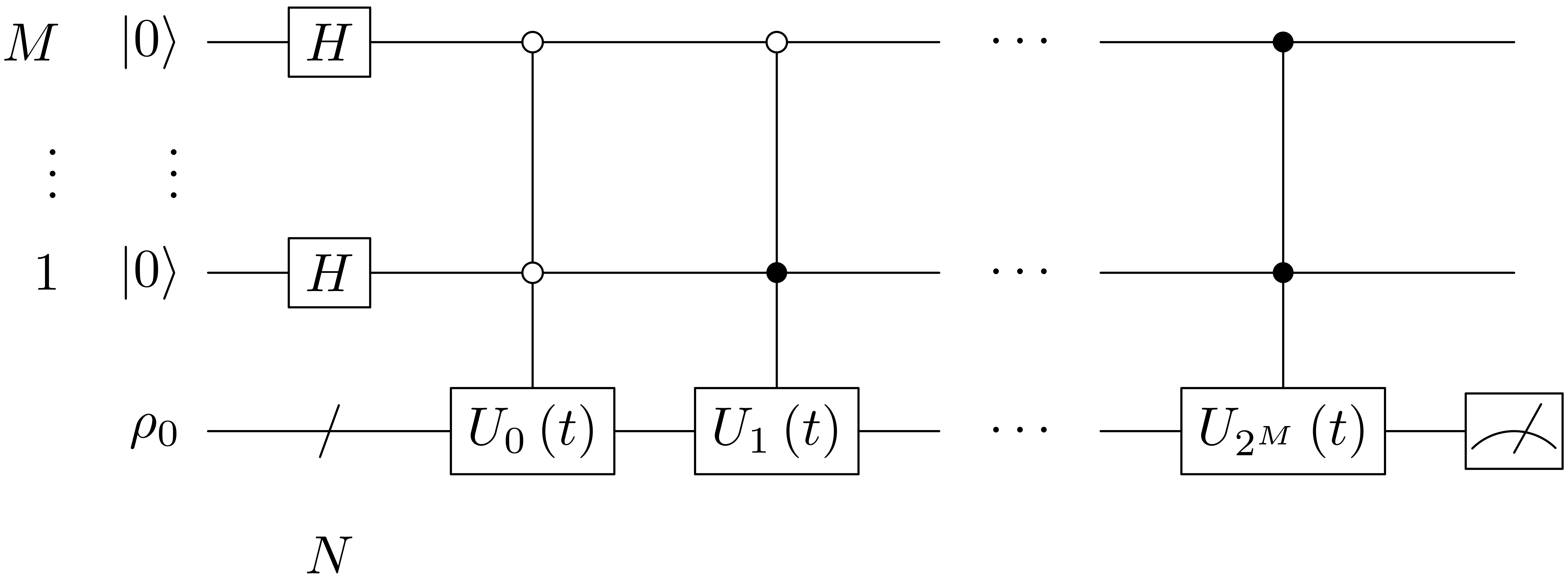
Quantum advantages:

Idea: Use ancilla-controlled operations to parallelize simulation

$$H = \omega_0 S^z_{\mathrm{tot}} + \omega_0 \sum_i \omega_i S_i^z + \sum_{i,j} b_{ij} \left(3(\mathrm{S}_i \cdot \mathrm{e}_{\mathrm{ij}}^{(\Omega)})(\mathrm{S}_j \cdot \mathrm{e}_{\mathrm{ij}}^{(\Omega)}) - \mathrm{S}_i \cdot \mathrm{S}_j \right)$$

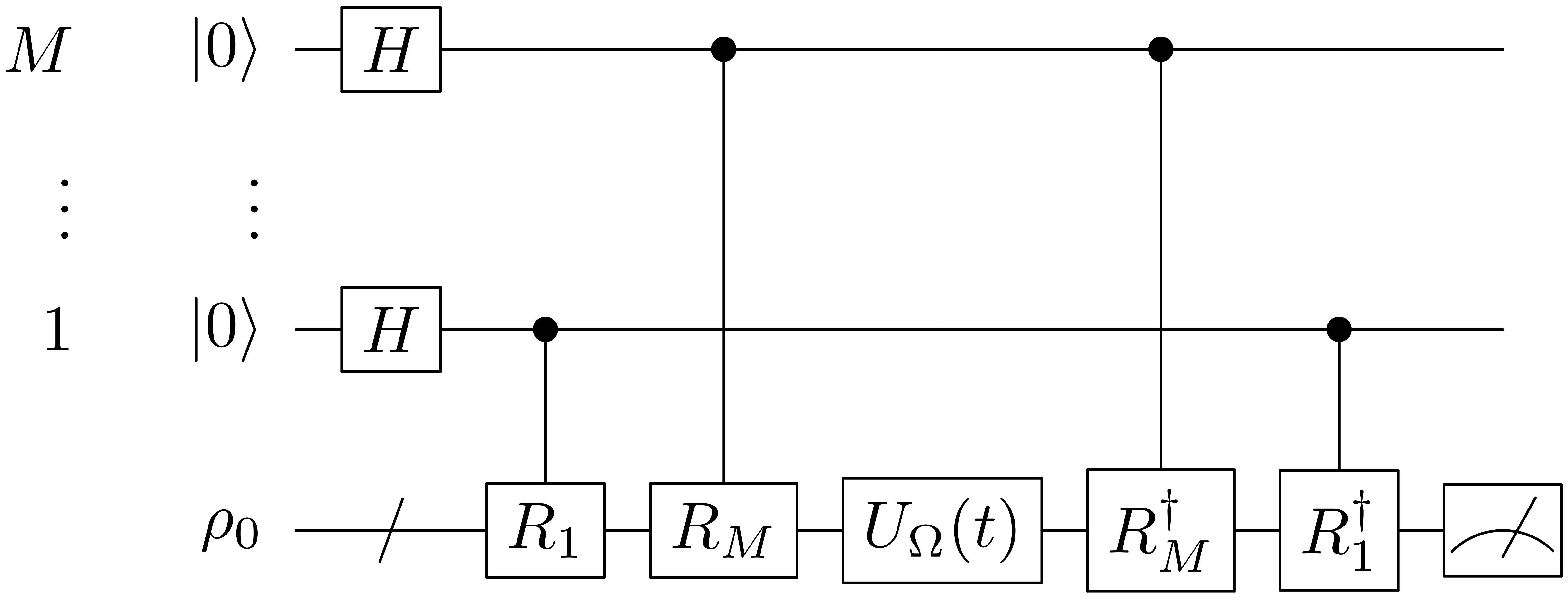
Depends on orientation

$$b_{ij} = -\frac{\mu_0 \gamma^2 \hbar}{4\pi r_{ij}^3}$$



Orientation averaging (simplified)

$$H_\Omega = \sum_{i,j} b_{ij} \left(3(\mathrm{S}_i \cdot \mathrm{e}_{\mathrm{ij}}^{(\Omega)})(\mathrm{S}_j \cdot \mathrm{e}_{\mathrm{ij}}^{(\Omega)}) - \mathrm{S}_i \cdot \mathrm{S}_j \right)$$



$$U_\Omega(t) = e^{-iH_\Omega t}$$

$$R_k = e^{-i\varphi_k \mathbf{n}_k \mathbf{S}_{\text{tot}}}$$

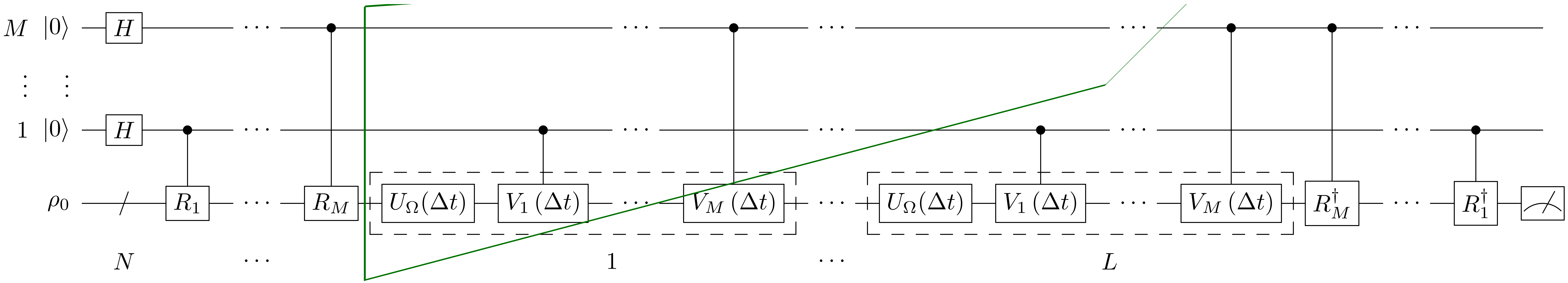
Controlled version

=

Two-qubit gates

Orientation averaging (full)

$$H = \underline{\omega_0 S^z_{\mathrm{tot}} + \omega_0 \sum_i \omega_i S^z_i} + \sum_{i,j} b_{ij} \left(3(\mathrm{S}_i \cdot \mathrm{e}^{(\Omega)}_{\mathrm{ij}})(\mathrm{S}_j \cdot \mathrm{e}^{(\Omega)}_{\mathrm{ij}}) - \mathrm{S}_i \cdot \mathrm{S}_j \right) \qquad b_{ij} = -\frac{\mu_0 \gamma^2 \hbar}{4\pi r_{ij}^3}$$



- Discretize dynamics: $U_\Omega(t) = \left[U_\Omega(\Delta t)\right]^L$

- Fix chemical shift term: $\underline{V_k(\Delta t) = R_k e^{-i\Delta t\ \omega_0 \sum_i (1+\omega_i) S_i^z} R_k^\dagger}$

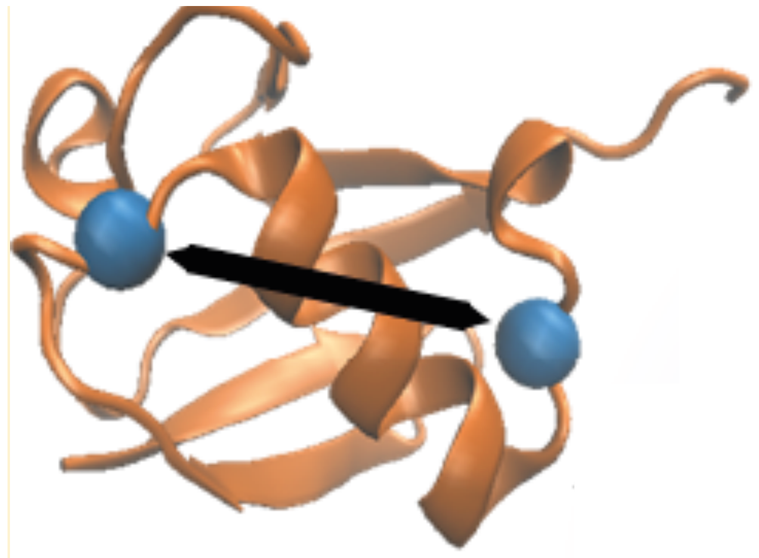
Controlled version = Two-qubit gates

Efficient powder-averaged solid-state NMR simulation!

Ensemble averaging with continuous ancilla

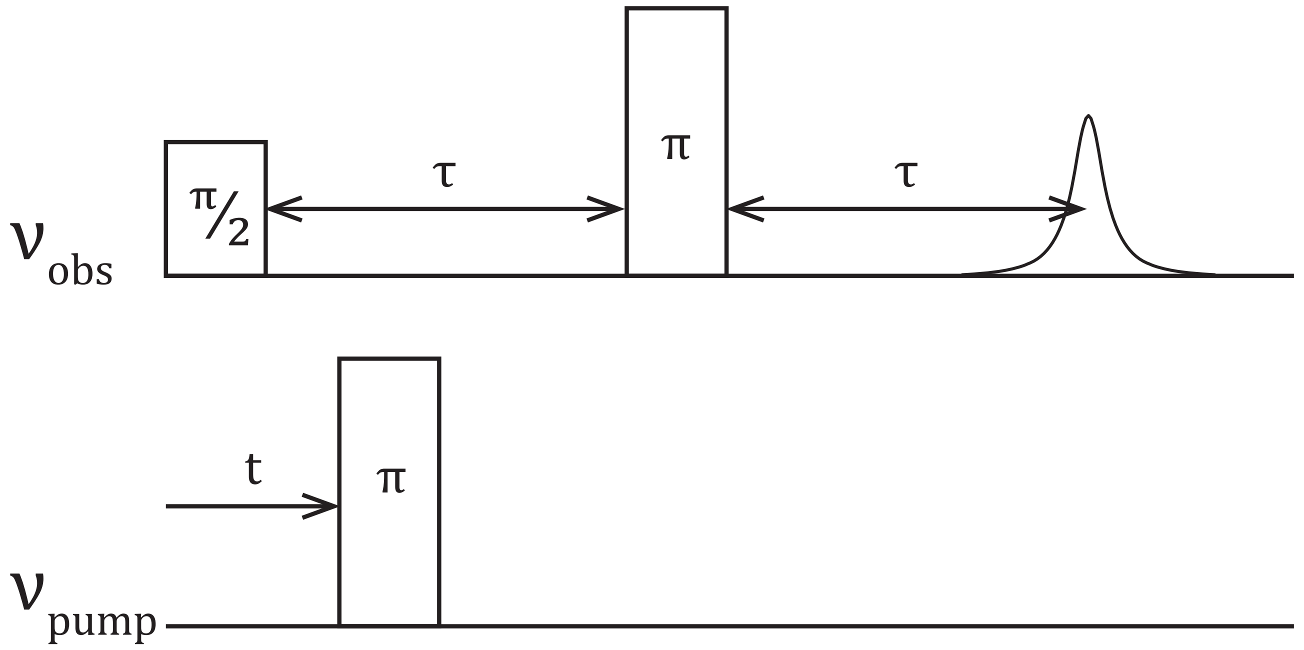
Electron paramagnetic resonance (EPR)

Catalysts, photosystems, molecular conductors, <u>proteins in live cell environment</u>



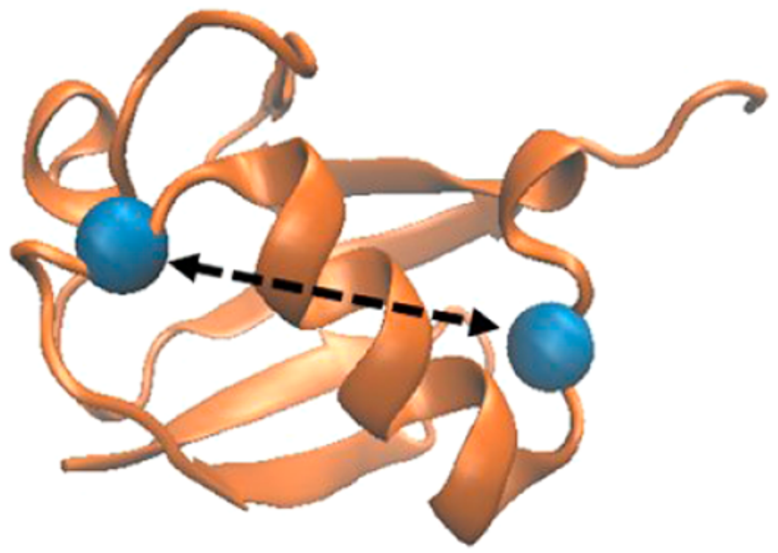
Simulation necessary
to infer structural change

Can be hard due to
ensemble averaging
for spin >1/2



Matorana - JACS (2014)
Manokovsky - J. Chem. Phys. (2017)

High spin EPR



High-field, isotropic g-tensor, pair of electron spins with s>1/2

$$H = \sum_{k=1,2} \left\{ \omega_i S_k^z + \mathbf{S}_k \cdot \overline{\mathbf{D}}_k \cdot \mathbf{S}_k + \mathbf{S}_k \cdot \overline{\mathbf{A}}_k \cdot \mathbf{I}_k \right\} + \frac{\eta}{r_{12}^3} \left(3\cos^2\theta - 1\right) \left\{ S_1^z S_2^z - \frac{1}{2}\left(S_1^+ S_2^- + S_1^- S_2^+\right) \right\}$$

Eigenvalues are distributed
(2 x 2 = 4 parameters)

Distances are distributed
(1 parameter)

Orientations are distributed (1 parameter)

Need to ensemble average simulations over 6 independent parameter distributions!

Prevents use of higher spin labels which have desirable biological properties

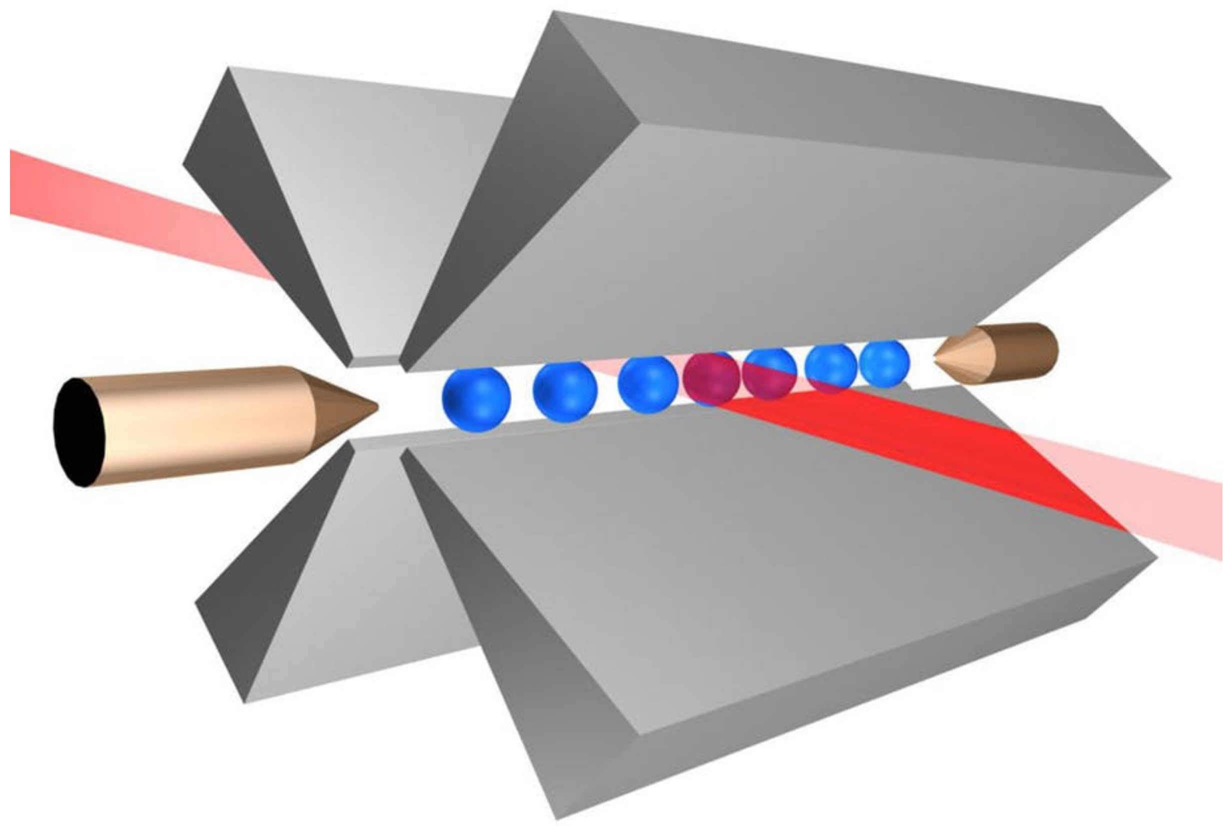
Idea: Use bosonic (continuous variable) ancilla to parallelize simulation

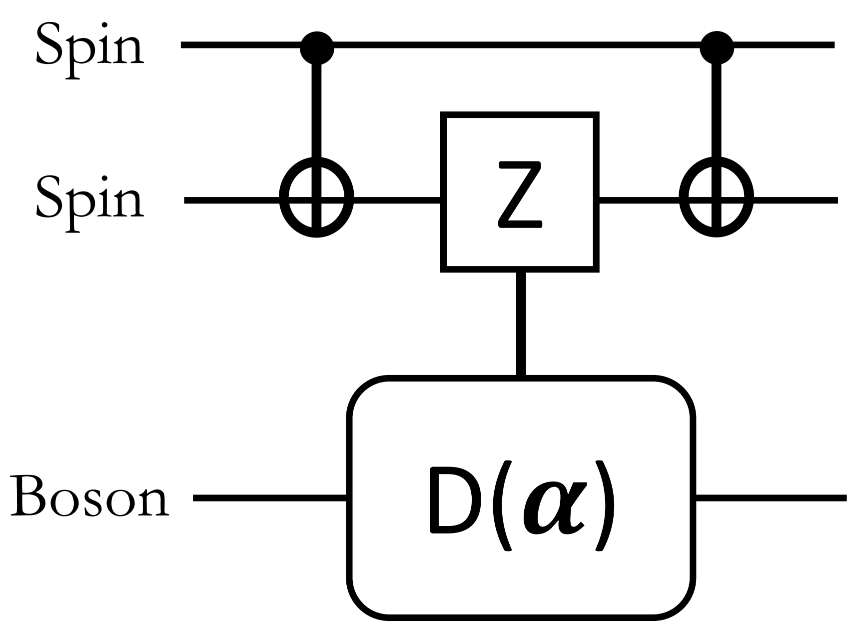
Boson-controlled spin interaction

$$\hat{U}(t) = e^{i\hat{x}\hat{H}_{\text{spin}}t}$$

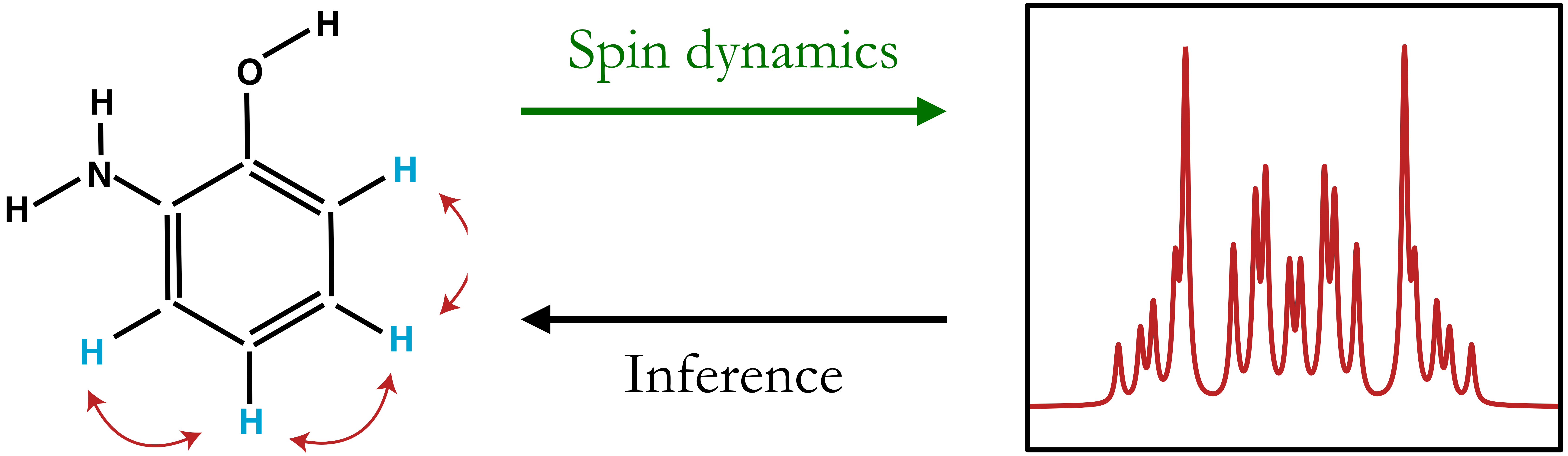
$$|\psi_0\rangle = |\psi_0\rangle_{\text{boson}}|\psi_0\rangle_{\text{spin}} \qquad \boxed{|\psi_0\rangle_{\text{boson}} = \int dx\sqrt{p(x)}\,|x\rangle}$$

$$S(t) = \langle\psi_0|\hat{U}^\dagger(t)\,\hat{S}^+_{\text{tot}}\hat{U}(t)|\psi_0\rangle = \int dx\; p(x)\;\; {}_{\text{spin}}\langle\psi_0|e^{ix\hat{H}_{\text{spin}}t}\hat{S}^+_{\text{tot}}e^{-ix\hat{H}_{\text{spin}}t}|\psi_0\rangle_{\text{spin}}$$





Senko - PRX (2015)



<u>Faithful time-evolution:</u> Decoherence in quantum hardware ≤ Decoherence in NMR system

<u>Efficient ensemble averaging:</u> Use ancillas in a superposition

Acknowledgements

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