UNIVERSITY OF LEEDS

A Path Integral method for quantum accurate atomistic spin dynamics simulations

T. Nussle[1], S. Nicolis[2], J. Barker[1]

[1] *School of Physics and Astronomy, University of Leeds, United Kingdom*

[2] *Institut Denis Poisson, Université de Tours, Université d'Orléans, CNRS (UMR7013) France*

arXiv:2303.00602

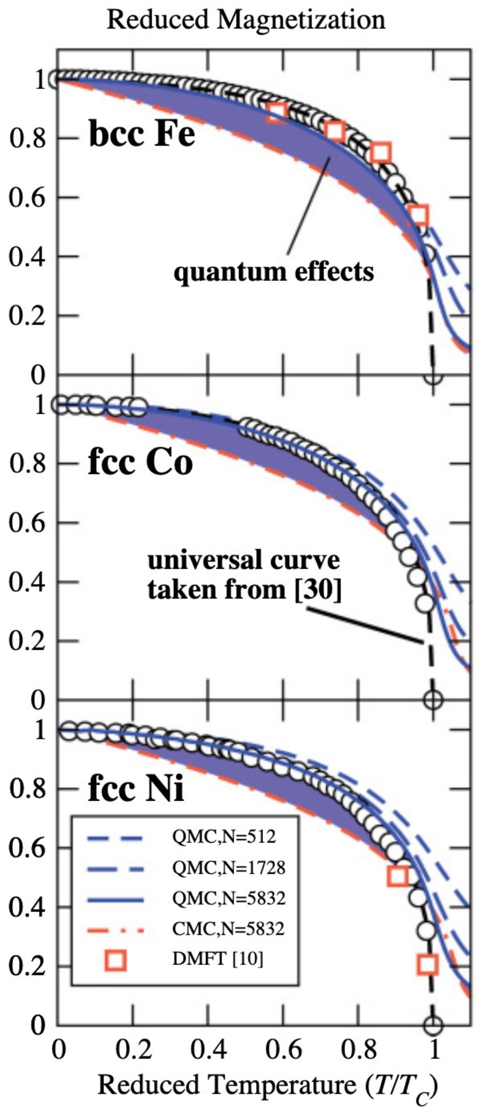
Engineering and Physical Sciences Research Council

Grant Number: EP/V037935/1

INSTITUT DENIS POISSON ORLÉANS • TOURS Mathématiques & Physique Théorique

Quantum effects in magnetism

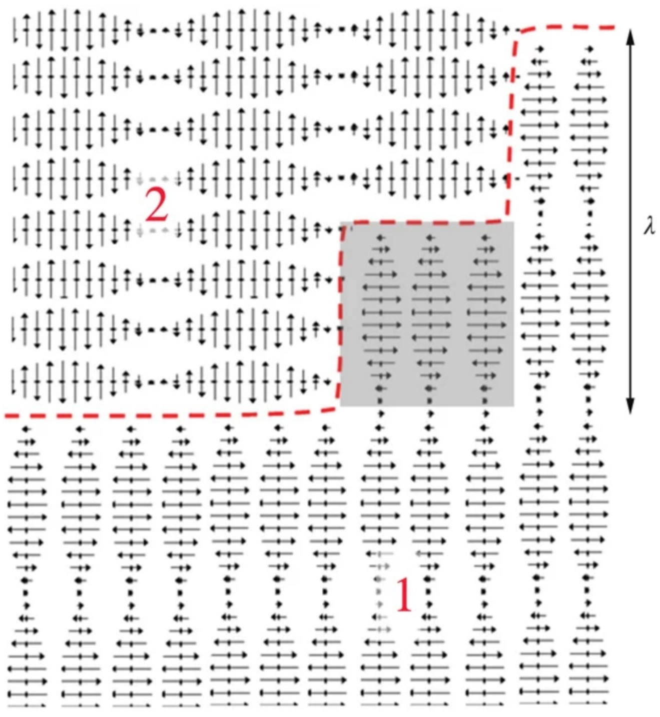
UNIVERSITY OF LEEDS



F. Körmann, *Phys. Rev. B* **83**, 165114 (2011)

- **Quantisation**
- **Quantum tunnelling**

Antiferromagnets



O. Shpyrko, *Nature* **447**, 68–71 (2007)

- **Zero-point motion**

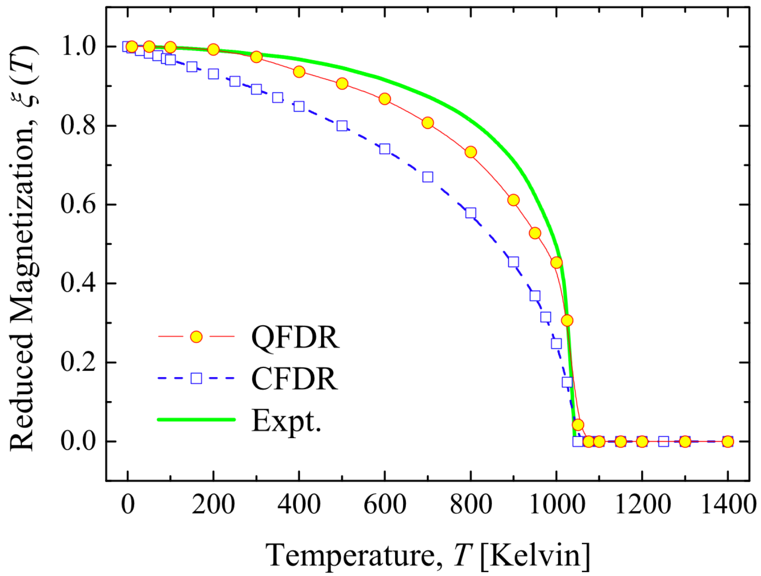
Quantum effects in classical simulations

UNIVERSITY OF LEEDS

Temperature rescaling

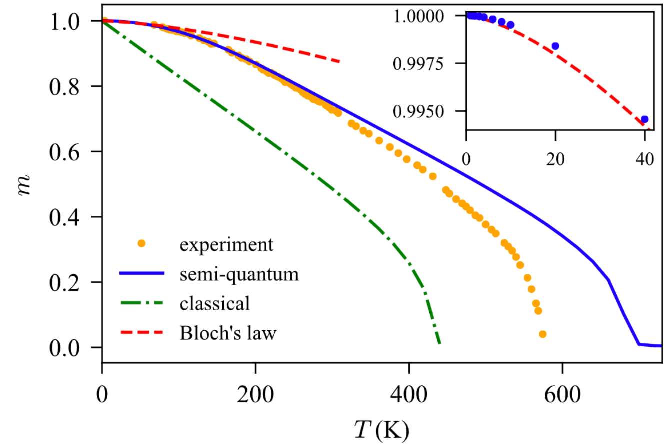
$$\eta_S(T) = \int_0^\infty \frac{\hbar\omega}{\exp(\hbar\omega/k_B T) - 1} g_m(\omega, T) d\omega$$

$$g_m(\omega, T) \equiv \frac{\Omega}{(2\pi)^3} \frac{4\pi k^2}{\nabla_k \omega(T)}$$



C. H. Woo, *Phys. Rev. B* **91**, 104306 (2015)

Semi-quantum thermostats



J. Barker, *Phys. Rev. B* **100**, 140401(R) (2019)

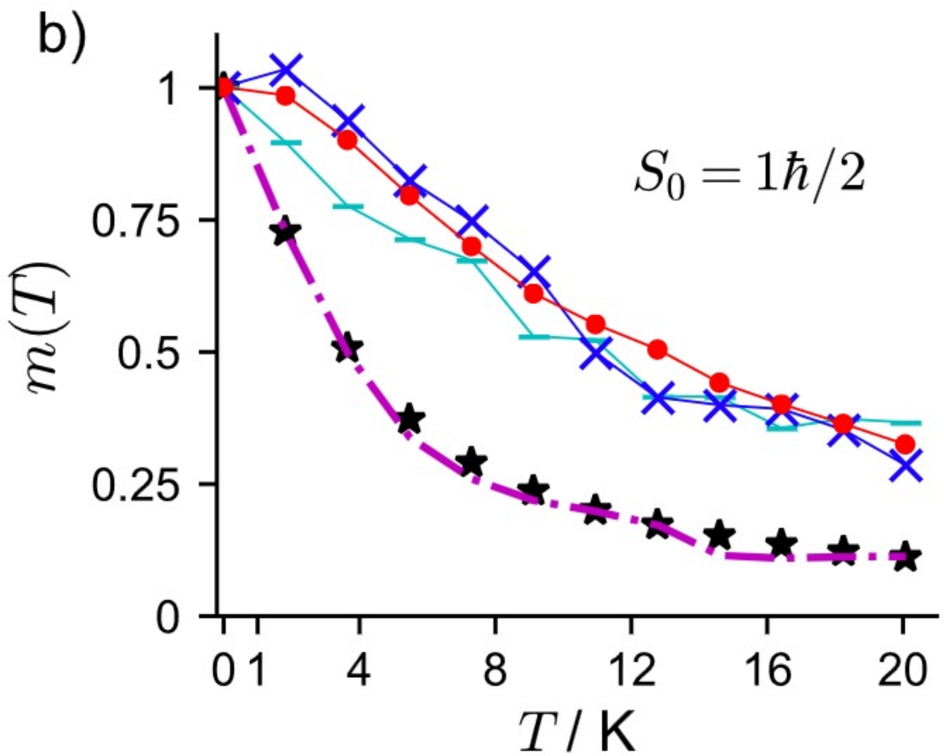
R. F. L. Evans, *Phys. Rev. B* **91**, 144425 (2015)
L. Bergqvist, *Phys. Rev. Materials* **2**, 013802 (2018)
F. Walsh, npj Comput Mater **8**, 186 (2022)
J. Anders, *New J. Phys.* **24** 033020 (2022)

Post-hoc methods

Include quantum effects systematically/rigorously?

Quantum effects in classical simulations

UNIVERSITY OF LEEDS



J. Anders, *New J. Phys.* **24** 033020 (2022)

- More systematically quantum
- **Thermostat** but by inferring **stochastic equations** of motion for **thermostat** and **coupling** to **spin system**

How to include quantum effects systematically?

Simulation techniques

UNIVERSITY OF LEEDS

- Fully quantum simulation
  - very small scale ⃠

→ **Much too expensive**

- Quantum Monte Carlo
  - large scale ✓
  - quantum ✓
  - access to dynamics ⃠

→ **Sign problem for antiferromagnets**

Do not need all the quantum accessible information

Systematic method to include quantum effects in classical model?

Finite temperature atomistic modelling

UNIVERSITY OF LEEDS

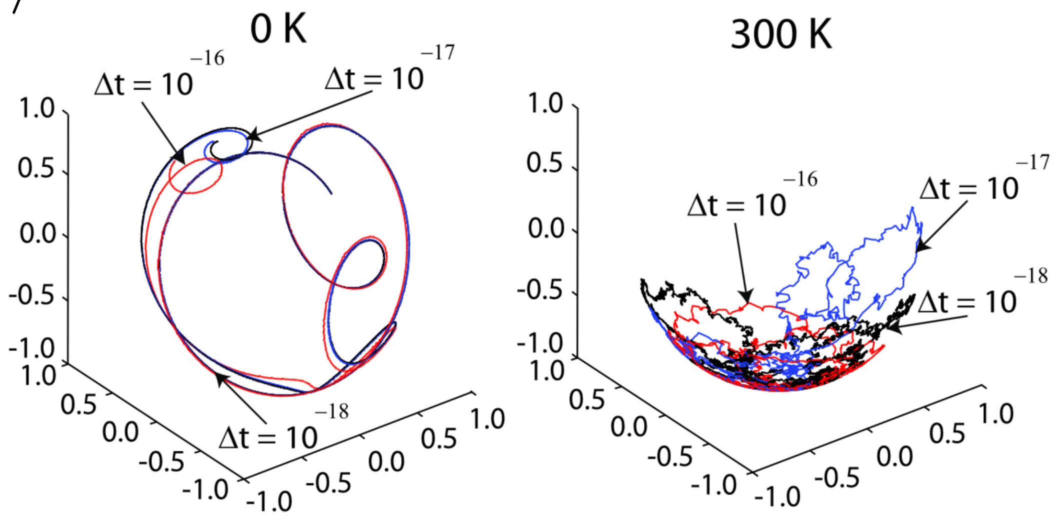
- **Landau-Lifshitz-Gilbert** Equation

$$\dot{\boldsymbol{s}}^{(i)} = -\frac{\gamma}{1+\alpha^2}\left(\boldsymbol{s}^{(i)} \times \boldsymbol{B}_{\text{eff}}^{(i)} + \alpha \boldsymbol{s}^{(i)} \times \left(\boldsymbol{s}^{(i)} \times \boldsymbol{B}_{\text{eff}}^{(i)}\right)\right)$$

- **Stochastic** field with **fluctuation dissipation** theorem

$$\mathcal{H} = -\mu_s \sum_i \boldsymbol{B} \cdot \boldsymbol{s}^{(i)} - J \sum_{\langle ij \rangle} \boldsymbol{s}^{(i)} \cdot \boldsymbol{s}^{(j)} \qquad \boldsymbol{B}_{\text{eff}}^{(i)} = \frac{\partial \mathcal{H}}{\partial \boldsymbol{s}^{(i)}}$$

$$\boldsymbol{B}_{\text{eff}} \rightarrow \boldsymbol{B}_{\text{eff}} + \boldsymbol{\eta}$$



B. Skubic, *J. Phys.: Condens. Matter* **20** 315203 (2008)

Thermodynamical properties

UNIVERSITY OF LEEDS

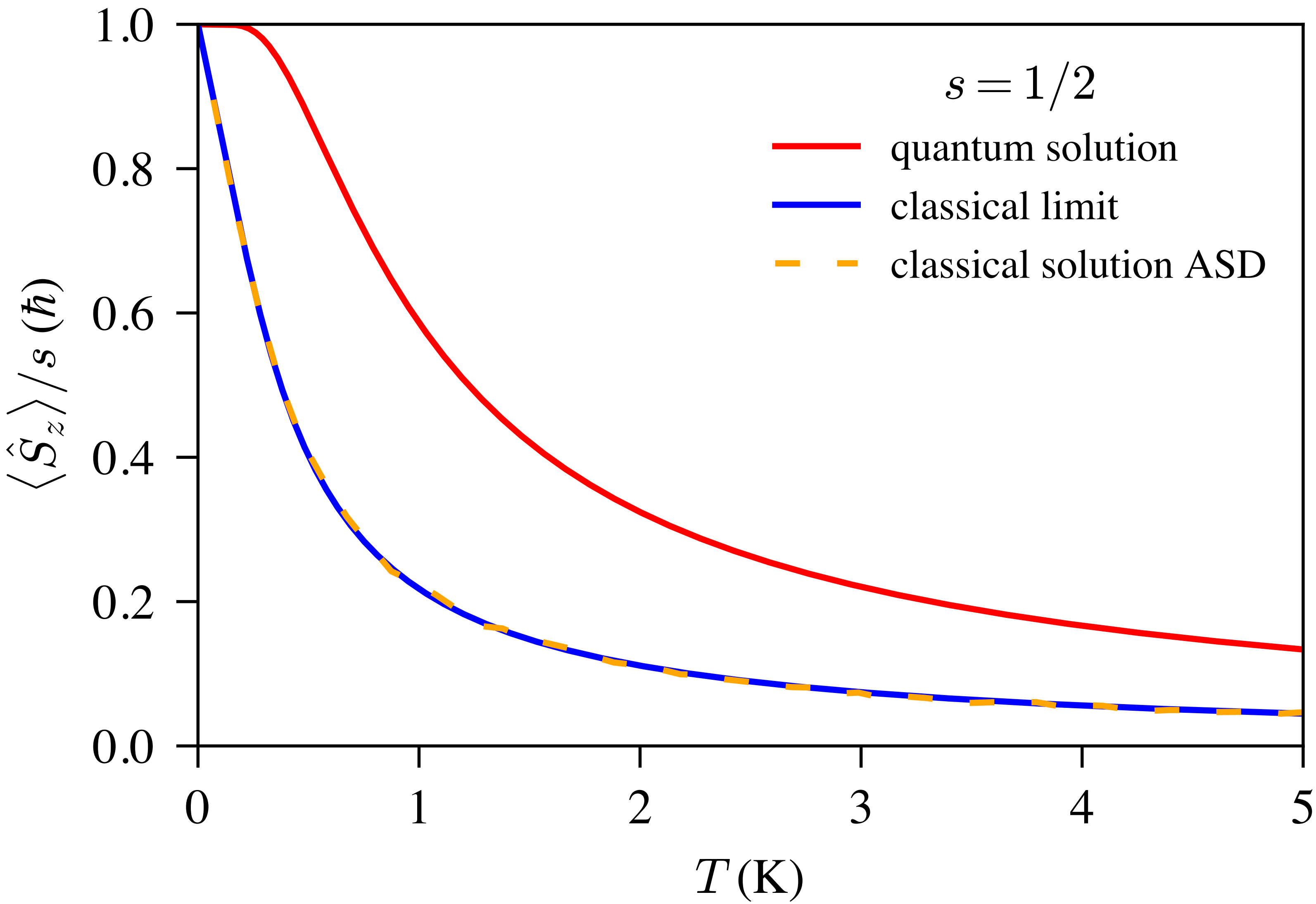
Quantum	Classical
• Hamiltonian **operator** $\hat{\mathcal{H}} = -g\mu_B \boldsymbol{B} \cdot \hat{\boldsymbol{S}}$	• Hamiltonian $\mathcal{H} = \mu_s \boldsymbol{B} \cdot \boldsymbol{s}$
• Partition function $\mathcal{Z} = \sum_{m=-s}^{s} \langle s,m \vert e^{-\beta\hat{\mathcal{H}}} \vert s,m \rangle$	• Partition function $\mathcal{Z} = \oint d\boldsymbol{s} e^{-\beta\mathcal{H}}$
• Expectation value $\langle \hat{S}_z \rangle = \frac{\sum_{m=-s}^{s} \langle s,m \vert \hat{S}_z e^{-\beta\hat{\mathcal{H}}} \vert s,m \rangle}{\mathcal{Z}}$	• Expectation value $\langle s_z \rangle = \frac{\oint d\boldsymbol{s} s_z e^{-\beta\mathcal{H}}}{\mathcal{Z}}$

Continuous vs. discrete basis

How to get classical object without going to classical limit

Magnetisation with temperature

UNIVERSITY OF LEEDS



How to recover quantum expectation values from classical model ?

Quantum effects in molecular dynamics

UNIVERSITY OF LEEDS

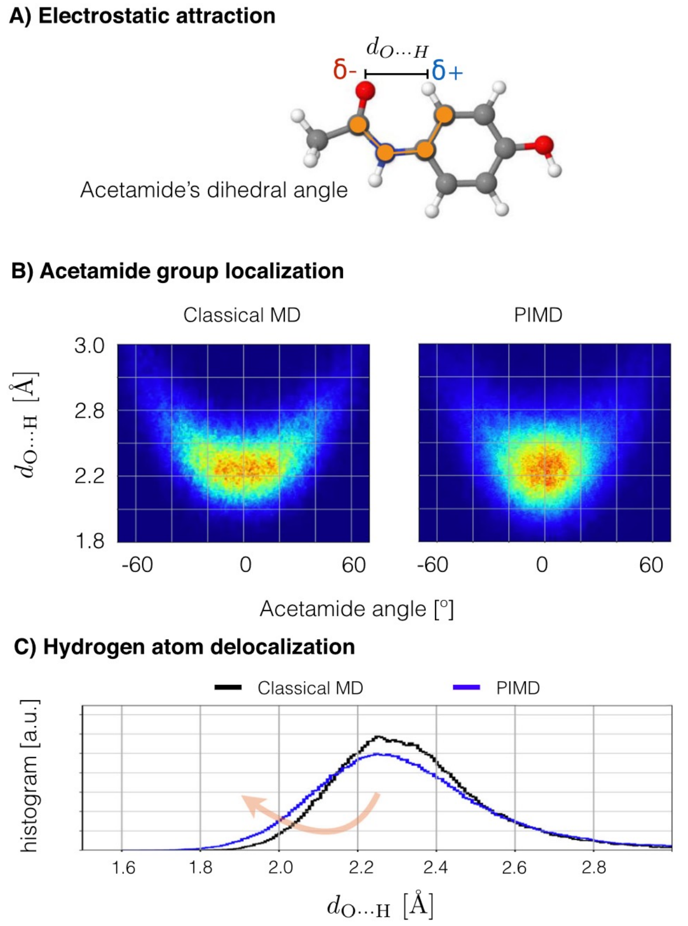


Fig. 4 Strengthening of electrostatic interactions in paracetamol molecule by proton delocalization. A Graphical representation of the paracetamol molecule. **B** Effective free energy surface generated from classical MD and PIMD at room temperature using the sGDML@DFT(PBE0 +MBD) force field. **C** Interatomic distance distribution $d_{O\cdots H}$ generated from classical MD (black) and PIMD (blue).

- Dynamics through **position** and **momenta**
- **Temperature** → stochastic **fluctuations** thereof
- **Low** temperature → **arbitrary precision** for **both**

Breaking Heisenberg uncertainty principle

H.E. Sauceda, *Nat. Com.* **12**, 442 (2021)

Path Integral Molecular Dynamics

UNIVERSITY OF LEEDS

From scalar to operator: $\mathcal{H} \Rightarrow \hat{\mathcal{H}}$

Partition function: $$\mathcal{Z}_{\mathrm{quantum}} = \int dq \langle q | e^{-\beta \hat{\mathcal{H}}} | q \rangle$$

From quantum to classical:

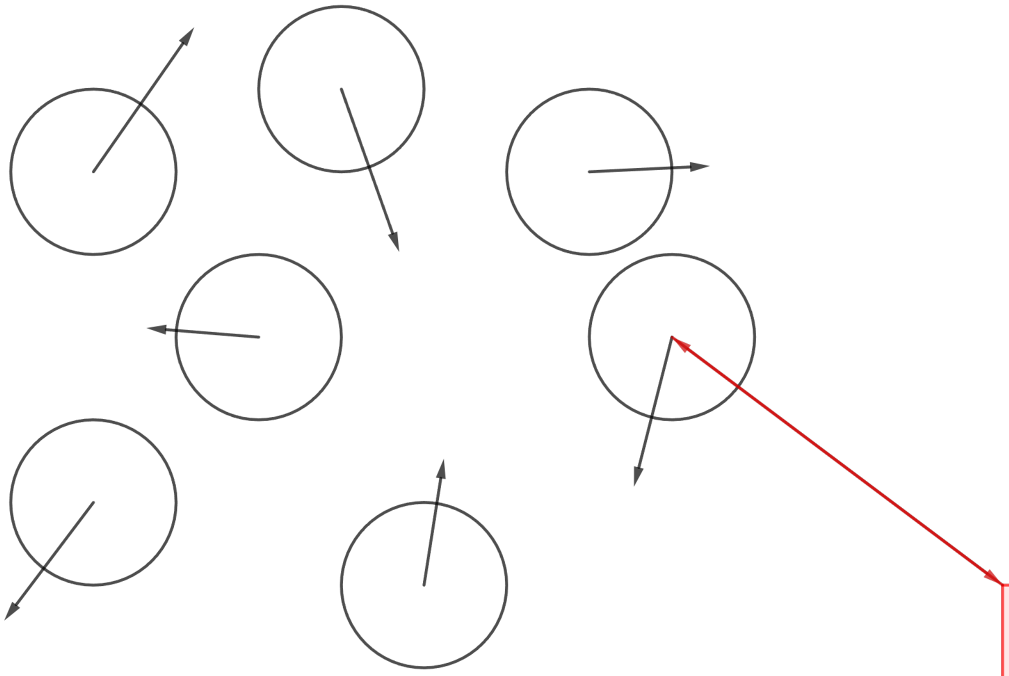
$$\tilde{\mathcal{Z}}_{\mathrm{quantum}} = \int dq \prod_i dp_i e^{-\beta \tilde{\mathcal{H}}_{\mathrm{eff}}}$$

$$\mathcal{H}_{\mathrm{eff}} = \sum_i \frac{\tilde{p}_i^2}{2\tilde{m}} - \phi_{\mathrm{eff}}$$

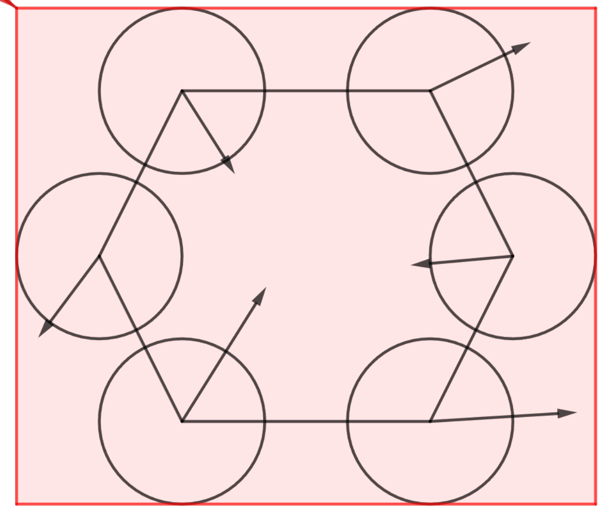
$$\phi_{\mathrm{eff}} = \sum_{i=1}^{P} \left(\frac{1}{2} m \omega_P^2 (q_{i+1} - q_i)^2 + \frac{1}{P} \phi \right)$$

Quantum Molecular Dynamics

Each particle...



... P beads coupled by harmonic springs:



Necklace with P beads

Molecular dynamics vs Spin dynamics

UNIVERSITY OF LEEDS

- Eigenstates of operators

$$\hat{K} \qquad |p\rangle$$

$$\hat{\Phi} \qquad |q\rangle$$

- **Continuous** quantum description

$$\tilde{\mathcal{Z}}_{\text{quantum}} = \int dq \prod_i dp_i e^{-\beta\tilde{\mathcal{H}}_{\text{eff}}}$$

- Eigenstates of **some** operators

$$\hat{\boldsymbol{S}}^2 \qquad \hat{S}_z \qquad |s,m\rangle$$

$$\hat{S}_x \qquad \hat{S}_y$$

- **Discrete** quantum description

$$\langle\hat{S}_z\rangle = \frac{\sum_{m=-s}^{s} \langle s,m|\,\hat{S}_z e^{-\beta\hat{\mathcal{H}}}\,|s,m\rangle}{\mathcal{Z}}$$

Need mapping to classical magnetisation vector
Need to approximate matrix elements

Spin coherent states

- **Continuous** basis $$|z\rangle \equiv (1+|z|^2)^{-s}\, \mathrm{e}^{z\hat{S}_-/\hbar}\, |0\rangle$$
- **Mapping** onto **unit sphere: magnetisation unit vector**

$$|z\rangle \Rightarrow \boldsymbol{n}$$

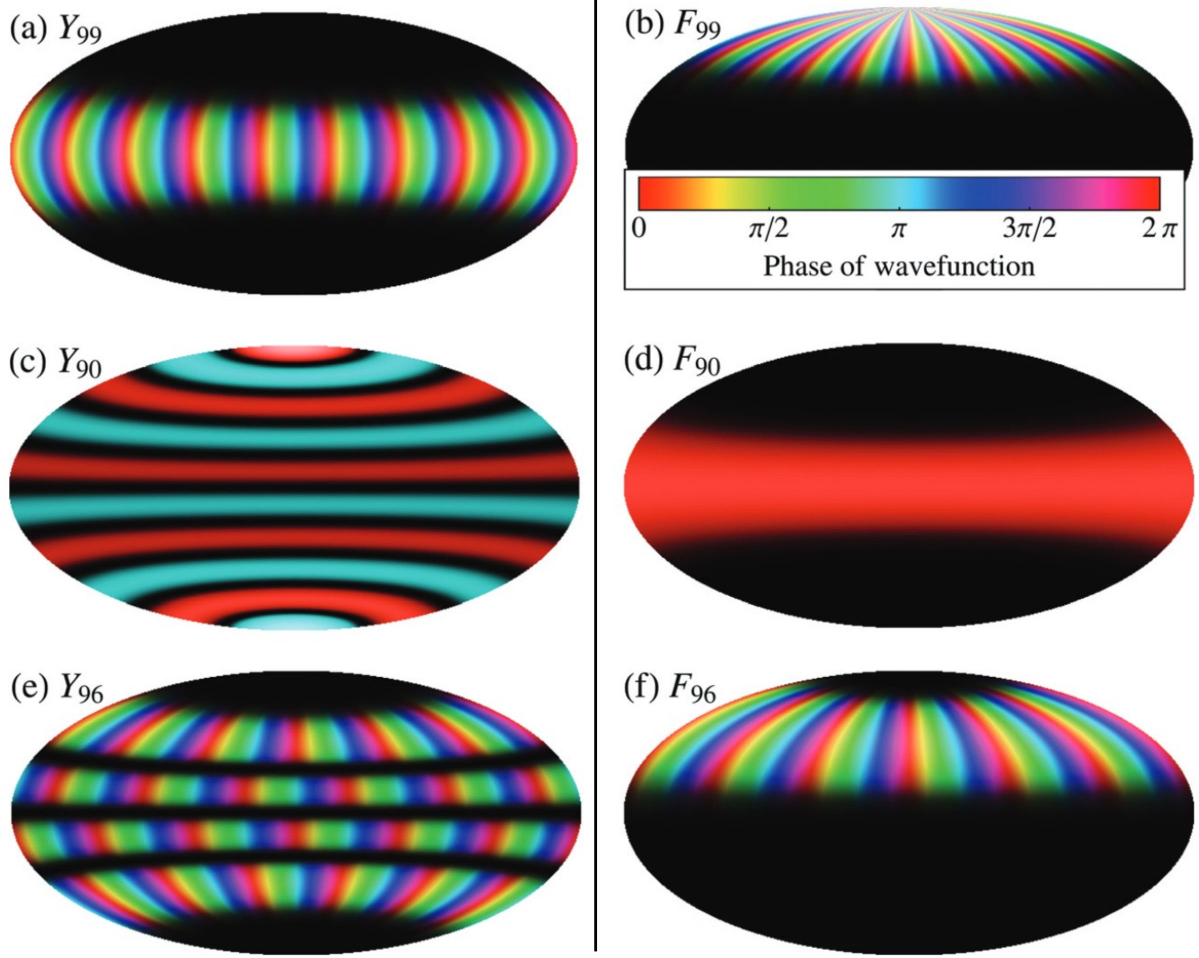
- **Converge** to **classical limit (**but **not only** the classical limit)

$$\mathcal{H}_{\mathrm{eff}} = -g\mu_B s B_z n_z + \cdots \approx -\mu_s \boldsymbol{B} \cdot \boldsymbol{s}$$

Contains information about **non-commutativity** of **operators**

→ **Enables calculating quantum expectation values, classically**

Visualising spin coherent states



Y. Loh, American Journal of Physics **83**, 30 (2015)

Zeeman Hamiltonian

- Single spin in magnetic field

$$\hat{\mathcal{H}} = -g\mu_B \boldsymbol{B} \cdot \hat{\boldsymbol{S}}$$

- Constant field, along **z**-direction

$$\hat{\mathcal{H}} = -g\mu_B B_z \hat{S}_z$$

- Writing spin coherent state as a sum

$$|z\rangle \equiv (1+|z|^2)^{-s} \sum_{p=0}^{2s} \binom{2s}{p}^{1/2} z^p \, |p\rangle$$

A little bit of maths…

UNIVERSITY OF LEEDS

$$\mathcal{Z} = \int \sum_{p=0}^{2s} d\mu(z) \left\langle z \right| e^{\frac{\beta g \mu_B}{\hbar} B_z \hat{S}_z} \left| p \right\rangle \left\langle p | z \right\rangle .$$

$$\mathcal{Z} = \int d\mu(z) \left[e^{-\beta g \mu_B s B_z} \left(\frac{e^{\beta g \mu_B B_z} + |z|^2}{1 + |z|^2} \right)^{2s} \right]$$

$$\ln(F[\beta, z]) \approx \frac{\left(1 - |z|^2\right) \beta g \mu_B s B_z}{1 + |z|^2} + \frac{|z|^2 \beta^2 \left(g \mu_B\right)^2 s B_z^2}{\left(1 + |z|^2\right)^2} - \frac{|z|^2 \left(1 - |z|^2\right) \beta^3 \left(g \mu_B\right)^3 s B_z^3}{3 \left(1 + |z|^2\right)^3} + \mathcal{O}(\beta^4)$$

Mapping from spin state to unit vector

UNIVERSITY OF LEEDS

$$\begin{cases} n_x = \dfrac{z+\bar{z}}{1+|z|^2} \\ n_y = \dfrac{1}{i}\dfrac{z-\bar{z}}{1+|z|^2} \\ n_z = \dfrac{1-|z|^2}{1+|z|^2} \end{cases}$$

$$\begin{cases} |z|^2 = \dfrac{1-n_z}{1+n_z} \\ z = \dfrac{1+n_z}{2}(n_x+in_y) \\ \bar{z} = \dfrac{1+n_z}{2}(n_x-in_y) \end{cases}$$

Clear interpretation of quantum states in terms of classical vector

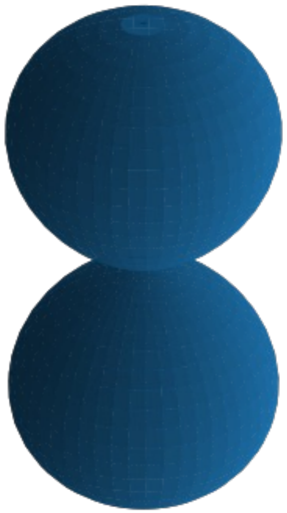
Quantum correction energy surfaces

UNIVERSITY OF LEEDS

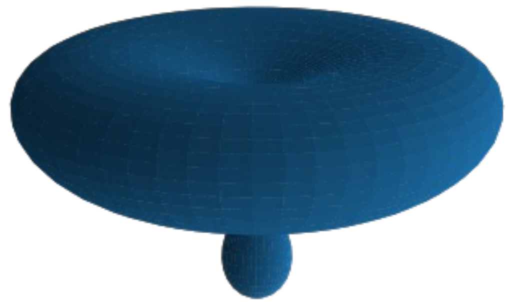
$$\mathcal{H}_{\mathrm{eff}} \approx -g\mu_B s B_z n_z - \frac{1}{4}\beta\,(g\mu_B)^2\, s B_z{}^2(1-n_z{}^2) + \frac{1}{12}\beta^2\,(g\mu_B)^3\, s B_z{}^3 n_z(1-n_z{}^2)$$

First correction

Second correction



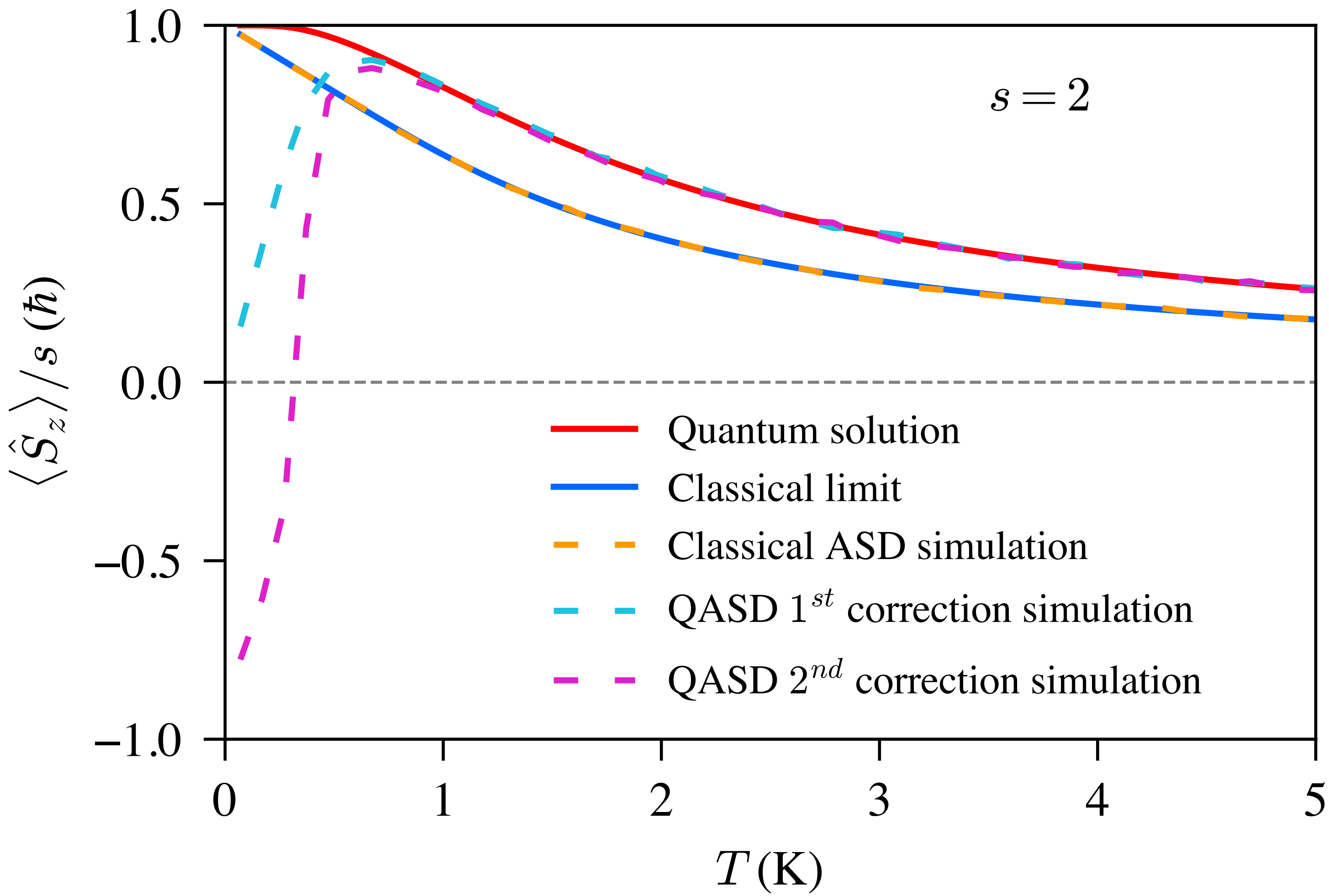
First correction



Second correction

Field and temperature dependent anisotropies

Quantum ASD, spin 2, field along z-axis

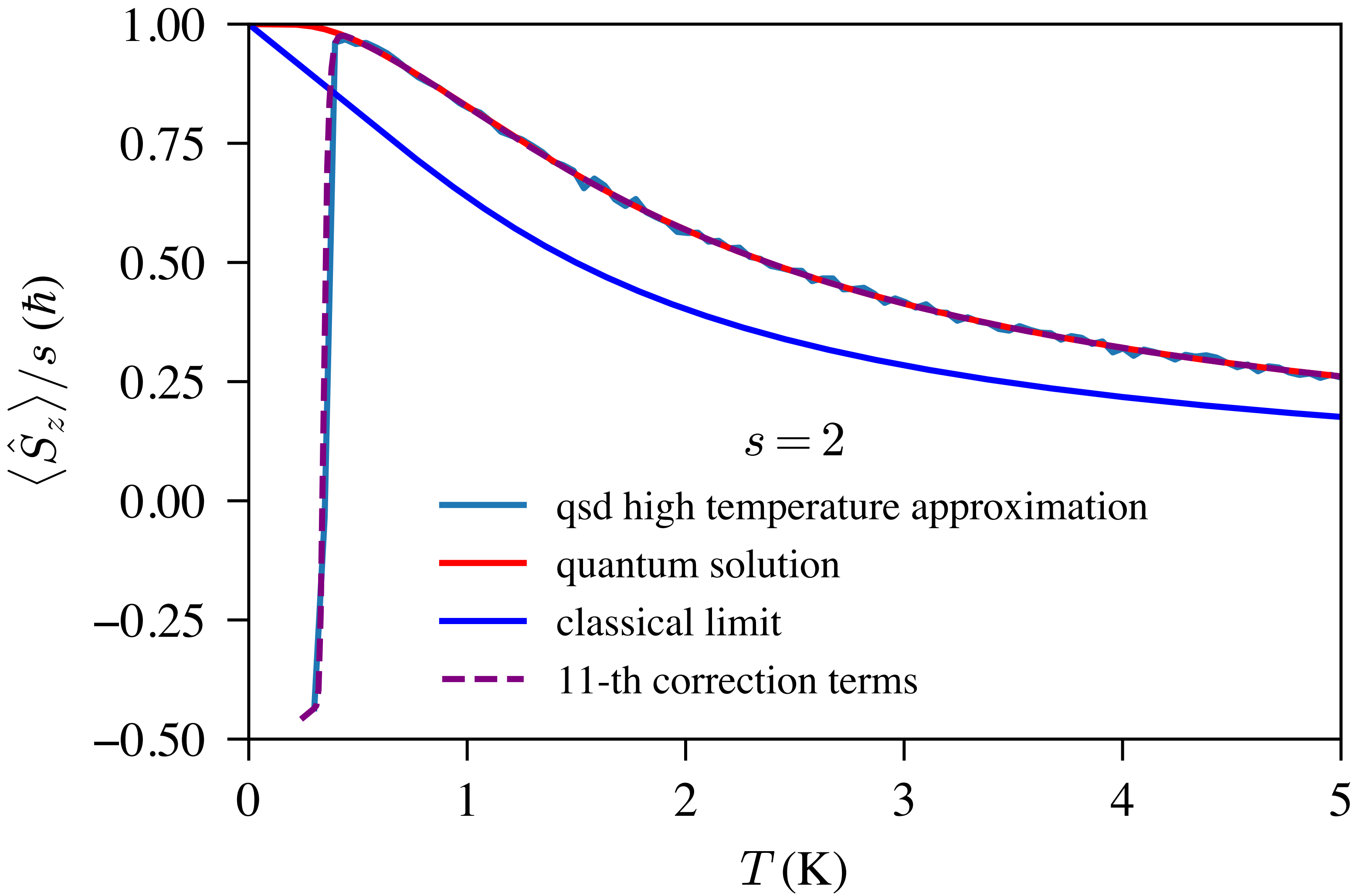


Above 1K, accurate quantum expectation values from enhanced ASD

Extra numerical cost very small

Higher order corrections

UNIVERSITY OF LEEDS



Higher order increase accuracy but not for arbitrary low temperature

Conclusion

UNIVERSITY OF LEEDS

- **Quantum expectation** value **from** effective **classical** model
  - Easy to confront to experiment and computationally cheap
  - Necessary for low temperatures/small scales and complex materials
- Currently **working** on **general field** and **exchange**
  - Exchange dictates the relevant temperature scales in magnets
- Aiming to **include** for **quantum** effects in **antiferromagnets**
  - Including exchange in our formalism should enable describing 0 point fluctuations.

- Python source to **reproduce** all figures from paper

DOI 10.5281/zenodo.7688972

- For now **single spin** in magnetic field along **z**

  Working on **exchange** and **general field**

Thank you for your attention

UNIVERSITY OF LEEDS

END