A piecewise propagator for stochastic simulations of electrons with finite temperature

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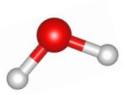
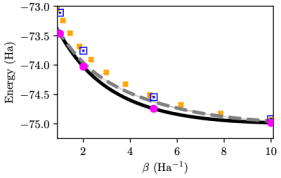
1 Density matrix quantum Monte Carlo calculates the energy and properties of *ab initio* Hamiltonians using the *N*-body thermal density matrix

$$\hat{\rho} = \exp(-\beta \hat{H})$$
$$\beta = (k_B T)^{-1}$$



$$\hat{H}\text{AN}|\text{D}\rangle E$$



FT-FCI/GCE — i-DMQMC Sym/Spin
FT-FCI/CE — FT-AFQMC
i-DMQMC

Data from: Petras, *et al. J. Chem. Theory Comput.* **2020***16*(2), 1029. AFQMC from the Rubenstein group.

2 There are two flavors of DMQMC

DMQMC (1)

Samples:
- $\hat{f}(\tau) = e^{-\tau \hat{H}}$

Uniform initialization:
- $\hat{f}(\tau = 0) = \mathbb{I}$

Propagation:
- $\frac{\mathrm{d}\hat{f}}{\mathrm{d}\tau} = -\frac{1}{2}\left[\hat{H}\hat{f} + \hat{f}\hat{H}\right]$

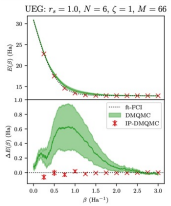
IP-DMQMC (2)

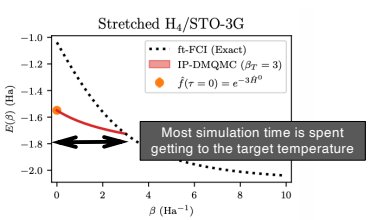
Samples:
- $\hat{f}(\tau) = e^{-(\beta_T - \tau)\hat{H}^0} e^{-\tau \hat{H}}$

Thermal initialization:
- $\hat{f}(\tau = 0) = e^{-\beta_T \hat{H}^0}$

Propagation:
- $\frac{\mathrm{d}\hat{f}}{\mathrm{d}\tau} = -\left[-\hat{H}^0\hat{f} + \hat{f}\hat{H}\right]$

3 IP-DMQMC only samples one temperature point in a calculation

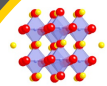




Can we make IP-DMQMC sample more than one temperature point?

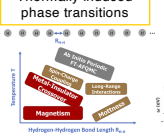
Electronic temperature is important in molecular and solid-state applications

Thermally induced phase transitions

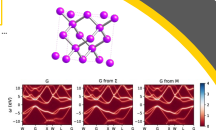


González-Cataldo, Soubiran, Peterson and Militzer. Phys. Rev. B. (2020) 101, 024107

Planetary Interiors

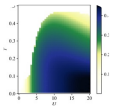


Liu, Shen, Zhang, Rubenstein. J. Chem. Theory Comput. (2020) 16, 7, 4298.



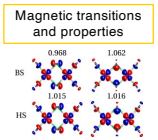
Fei, Yeh, Zgid and Gull. Phys. Rev. B (2021) 104, 165111.

Temperature dependence in excited states

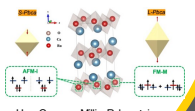


Sun, Ray, Cui, Stoudenmire, Ferrero, Chan. Phys. Rev. B. (2020) 101, 075131.

Magnetic transitions and properties



Pokhilko and Zgid. J. Chem. Phys. (2021) 155, 024101.



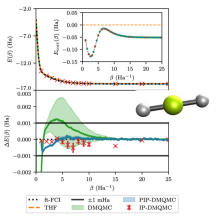
Hao, Georges, Millis, Rubenstein, Han and Shi. Phys. Rev. B. (2020) 101, 235110

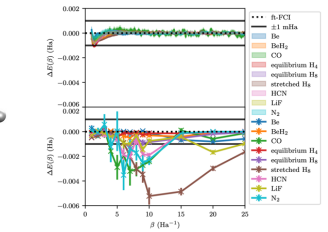
4 The piecewise adaptation of interaction picture DMQMC decreases compute time while improving the accuracy

Propagate to target β with IP-DMQMC and then beyond with DMQMC

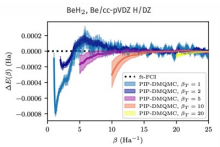
$$f_{ij}(\tau + \Delta\tau) = \begin{cases} f_{ij}(\tau)[1 + \Delta\tau S] - \Delta\tau \sum_k \left[-H^{(0)}_{ik} f_{kj}(\tau) + f_{ik}(\tau) H_{kj}\right] & \tau < \beta_T \\ f_{ij}(\tau)[1 + \Delta\tau S] - \frac{\Delta\tau}{2} \sum_k \left[H_{ik} f_{kj}(\tau) + f_{ik}(\tau) H_{kj}\right] & \tau \geq \beta_T \end{cases};$$

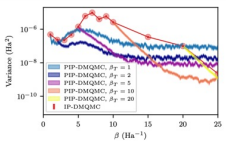
… works at least as well as IP-DMQMC for a variety of systems





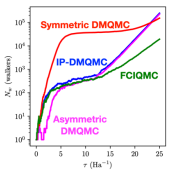
5 Performance is insensitive to crossover point



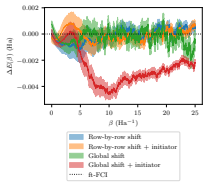


6 Future work will focus on exploiting the structure of the density matrix to improve sampling

Asymmetric DMQMC splits up quantum and classical degrees of freedom



…and we have been able to develop an improvement on the initiator approximation



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