Vibrational frequencies with Quantum Monte Carlo

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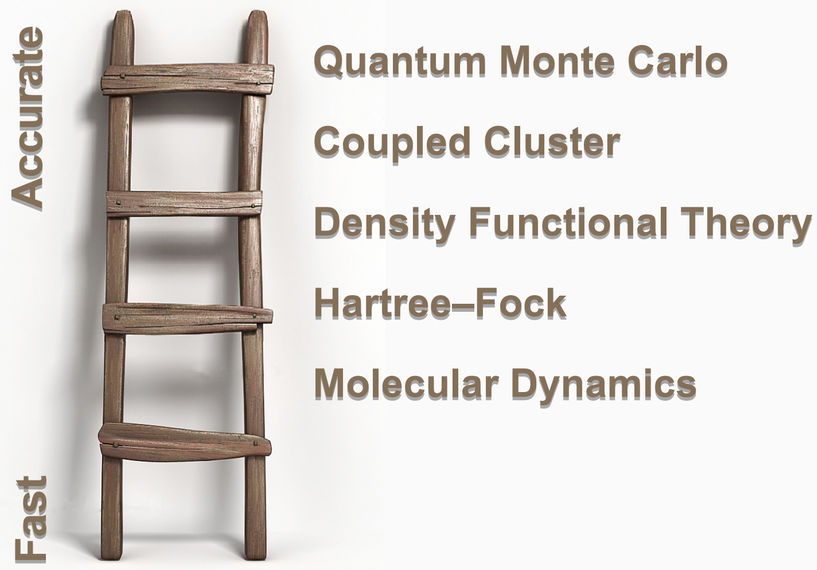
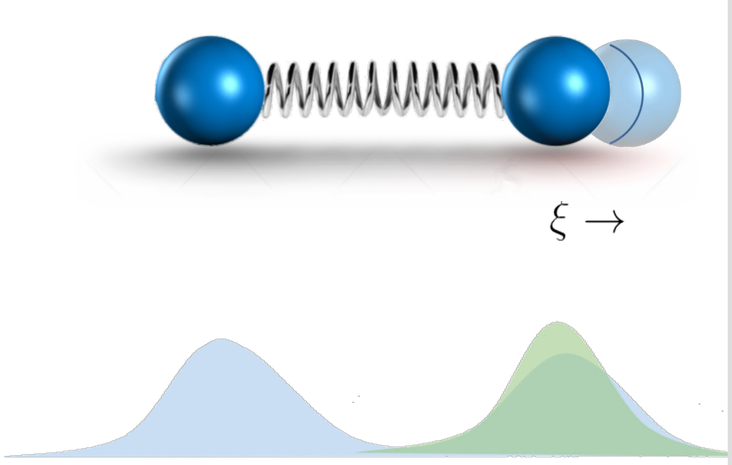
There is a hierarchy of electronic structure methods to calculate ground state properties.

Quantum Monte Carlo is the method to fully capture all quantum physics, here we develop the formalism to calculate vibrational frequencies. This will allow electronic structure calculations to study vibrational modes of molecules and phonon dispersion of solids with a full account of strong correlations.





Quantum Monte Carlo

A stochastic approach to sample states. It solves the variational ground state wavefunction Ψ .

The expectation value for an operator is the average over the probability distribution Ψ^2, found using the Monte Carlo integration.

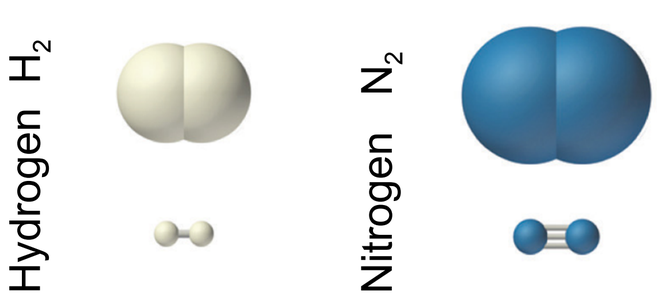
Energy: $$E = \frac{\int \Psi\Psi \frac{H\Psi}{\Psi} \mathrm{d}V}{\int \Psi\Psi \mathrm{d}V} = \left\langle \frac{H\Psi}{\Psi} \right\rangle$$

By evaluating the interatomic force constants, we can derive important physical properties such as vibrational frequencies.

$$\frac{\partial^2 E}{\partial \xi_i \xi_j} = \left\langle \frac{H''\Psi}{\Psi} \right\rangle + 2 \left\langle \frac{\Psi'}{\Psi} \left(\frac{H'\Psi}{\Psi} - \left\langle \frac{H'\Psi}{\Psi} \right\rangle \right) \right\rangle$$

Case study: diatomic molecules

We performed Quantum Monte Carlo simulations on the diatomic molecules H_2 and N_2, and achieved good agreement between the predicted vibrational frequency and experiment.



	Bond length (pm)	Quantum Monte Carlo frequency (THz)	Experimental frequency (THZ)
Hydrogen H_2	74.13	132.49	131.95
Nitrogen N_2	109.76	69.86	70.71

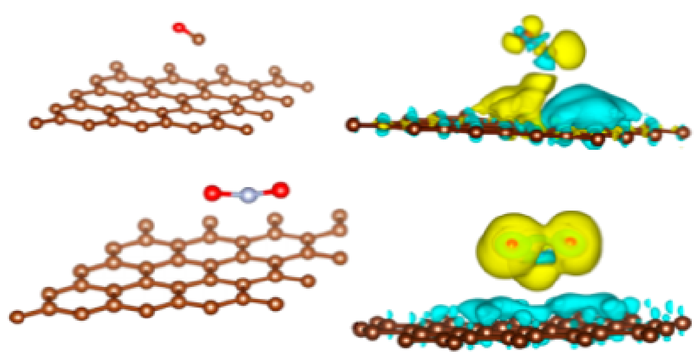
Conclusions

Vibrational frequencies can now be calculated with Quantum Monte Carlo.

Results for the diatomic molecules hydrogen and nitrogen are in good agreement with experiment.

Future applications: Graphene

adsorption of molecules on surface.



Electrocaloric materials

candidates for solid-state refrigeration. However, the underlying mechanism is undetermined.