Diatomic potential energy surfaces and the effect of temperature

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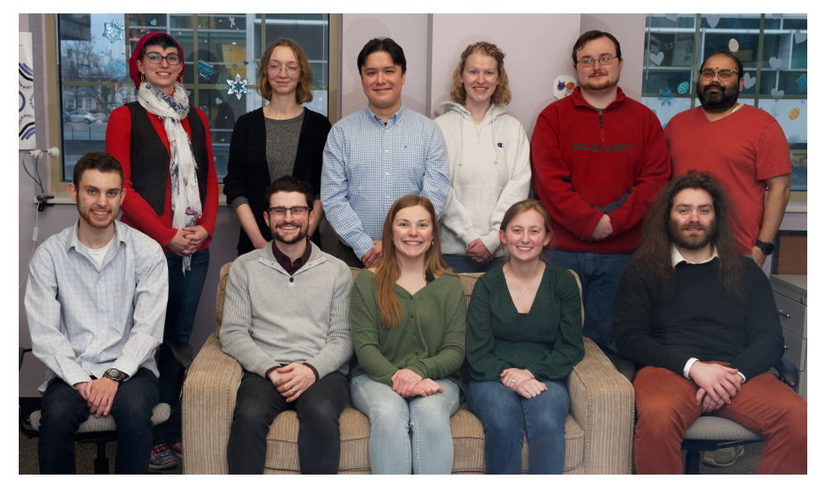
Hayley Petras, graduate student since 2018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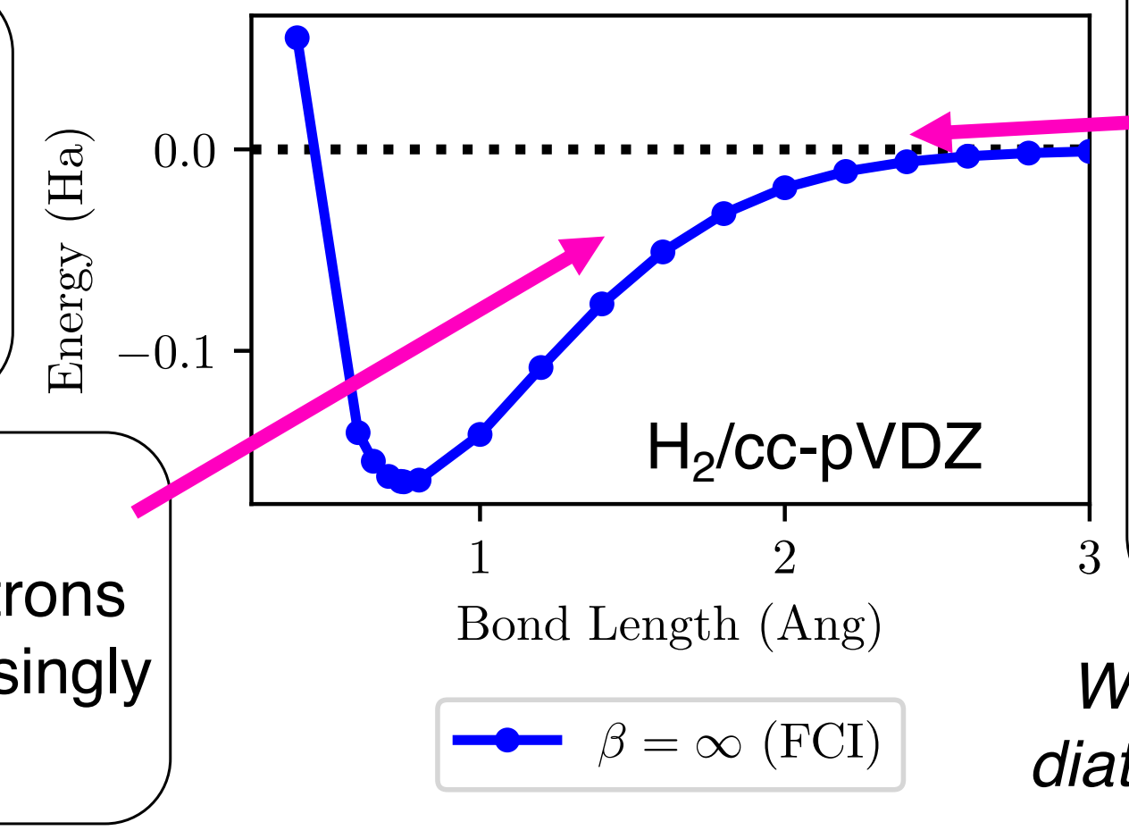
Potential energy surfaces are a model for studying strong correlation and diatomic molecules represent a variety of chemical environments

Research Question: How does the electronic structure of diatomics differ at equilibrium and stretched bond lengths at finite temperature?

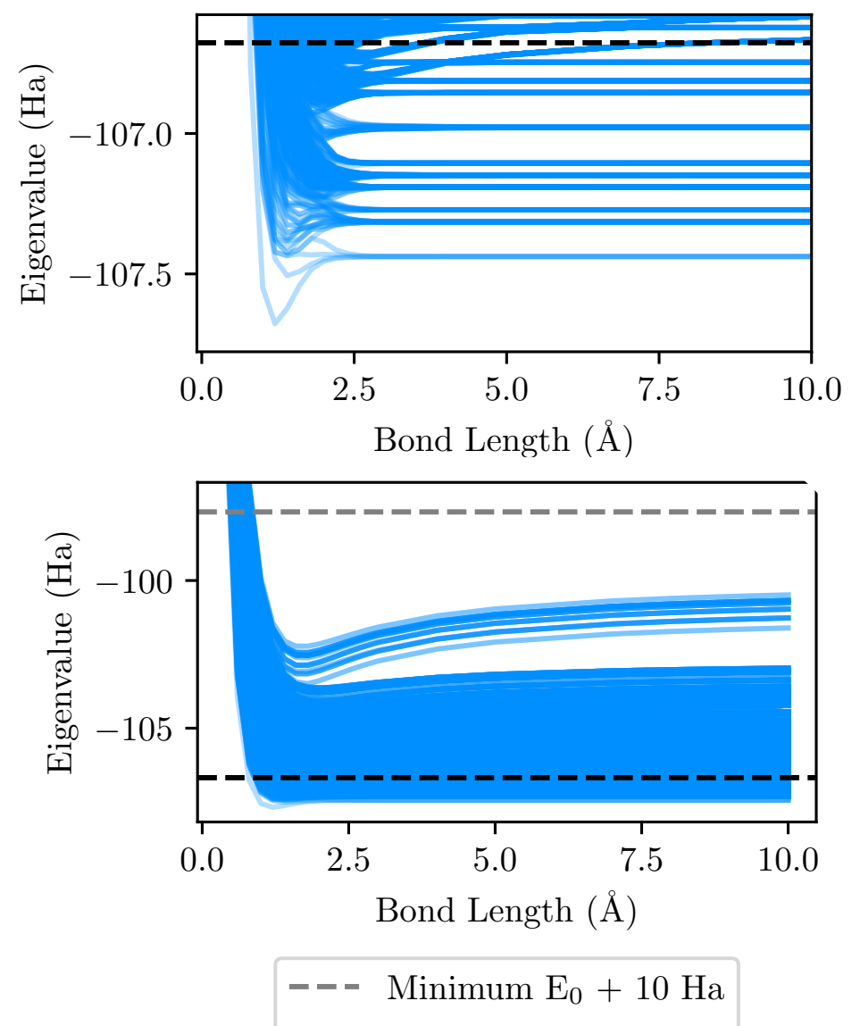


Energies near equilibrium are generally "easier" to solve for

As the bond is stretched, electrons become increasingly correlated

Higher excitations begin to mix in, and too much HF character can give too low of an energy

We know a lot about diatomics in the ground state!



(Left) The FCI eigenvalues from N$_2$/STO-3G at two different energy scales. The top shows a molecular like distribution with clear quantized levels, but at the bottom the diatomic appears more "solid" like with many near degenerate energy levels.

We use full configuration interaction and density matrix quantum Monte Carlo to calculate temperature dependent energies and properties

Finite temperature FCI (ft-FCI)

$$\langle E(\beta)\rangle = \frac{\sum_i \epsilon_i \exp(-\beta\epsilon_i)}{\sum_i \exp(-\beta\epsilon_i)}$$

$\beta = (k_B T)^{-1}$ ϵ_i : i$^{\text{th}}$ FCI eigenvalue

We use HANDE-QMC for both FCI and DMQMC calculations.

https://github.com/hande-qmc/hande/

Density matrix quantum Monte Carlo (DMQMC)

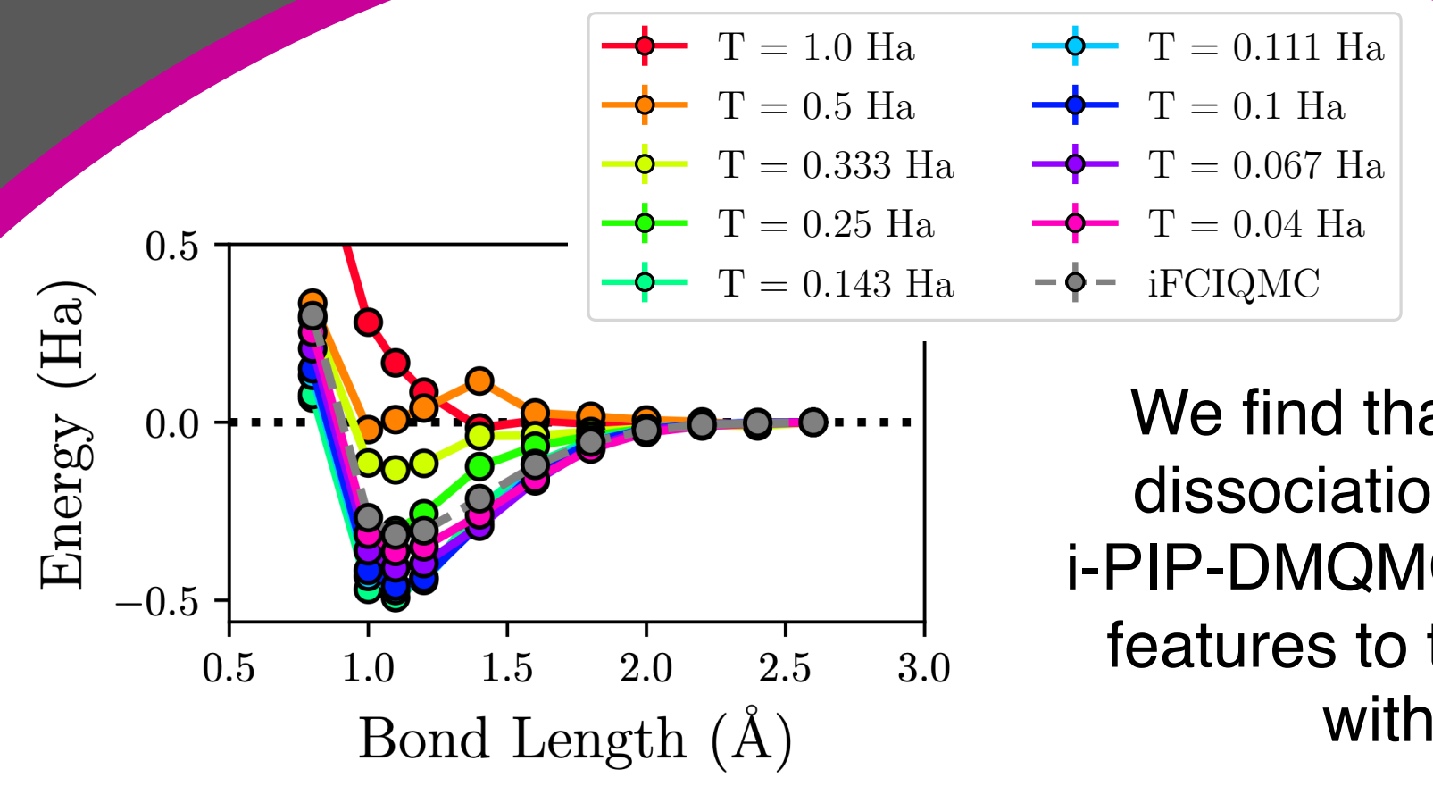
Uses the *N*-body thermal density matrix:
$\hat{\rho} = \exp(-\beta\hat{H})$, which satisfies
$d\hat{\rho}/d\beta = -1/2\,(\hat{H}\hat{\rho} + \hat{\rho}\hat{H})$.
The Hamiltonian is expressed in a finite basis of Slater determinants, $|D_i\rangle$ and the energy is calculated as:
$\langle\hat{H}\rangle = \mathrm{Tr}(\hat{\rho}\hat{H})/\mathrm{Tr}(\hat{\rho})$.
The following equation is evolved through inverse temperature following "rules" defined at the right:

$$\rho_{\mathbf{ij}}(\beta+\Delta\beta) = \rho_{\mathbf{ij}} + \frac{\Delta\beta}{2}\sum_{\mathbf{k}}(T_{\mathbf{ik}}\rho_{\mathbf{kj}} + \rho_{\mathbf{ik}}T_{\mathbf{kj}})$$

where $T_{\mathbf{ij}} = -(H_{\mathbf{ij}} - S\delta_{\mathbf{ij}})$.
The data from many simulations is gathered and averaged to obtain the final energy as a function of inverse temperature.

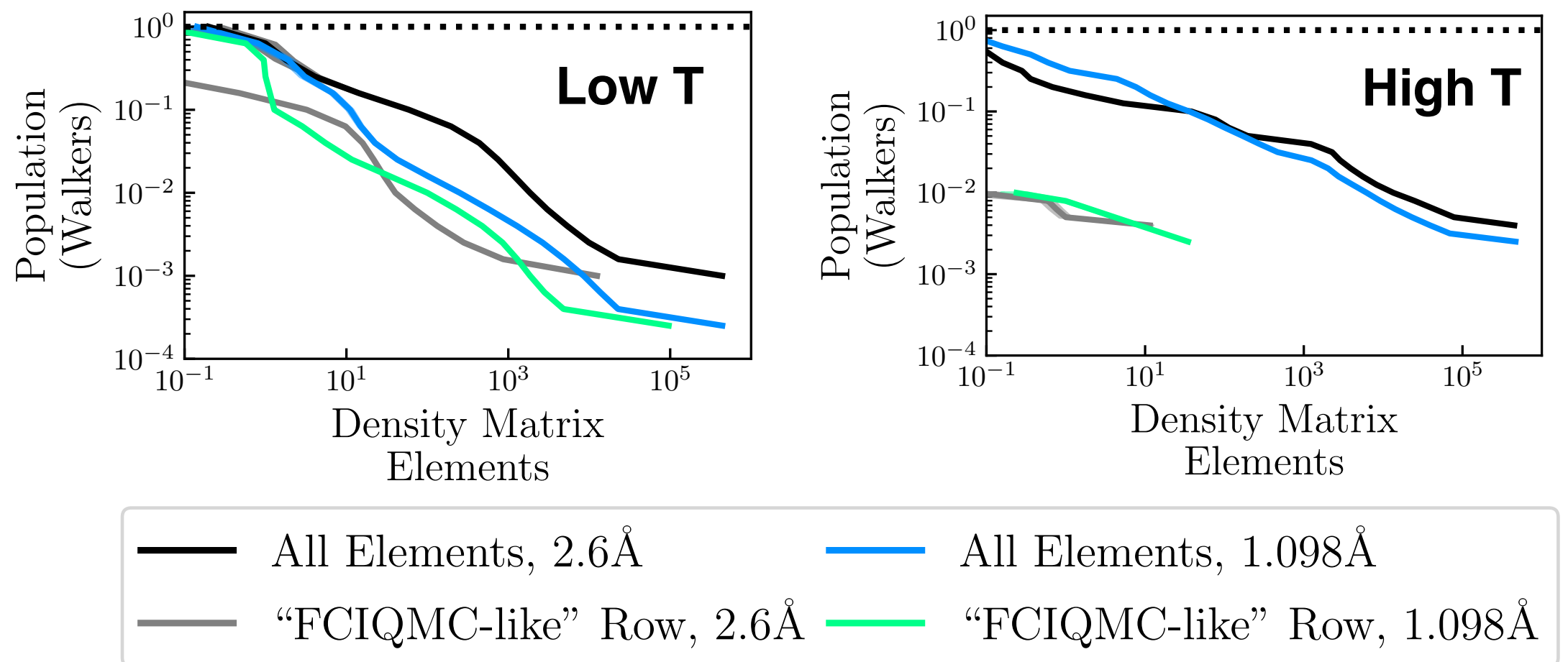
Particle "rules":
1. Spawning: Occurs along both rows and columns, and happens with the probability $p_s(\mathbf{ik}\rightarrow\mathbf{ij}) = \frac{\Delta\beta|T_{\mathbf{kj}}|}{2}$.
2. Death/cloning: Occurs on single elements, according to a probability $p_d(\mathbf{ij}) = \frac{\Delta\beta}{2}|T_{\mathbf{ii}} + T_{\mathbf{jj}}|$; the particle clones if $\mathrm{sign}(T_{\mathbf{ii}} + T_{\mathbf{jj}})\times\mathrm{sign}(\rho_{\mathbf{ij}}) > 0$ and dies otherwise.
3. Annihilation: Particles of the opposite sign on matrix elements are removed from the simulation.

DMQMC: Blunt *et al. Phys. Rev. B* **89**, 245124 *(2014);* i-DMQMC: Malone *et al. Phys. Rev. Lett.* **2016** 117, 115701; IP-DMQMC: Malone *et al. J. Chem. Phys.* **143,** 044116 (2015). PIP-DMQMC: Van Benschoten *et al. J. Chem. Phys.* **156**, 184107 (2022).



We find that N$_2$/cc-pVDZ dissociation curves from i-PIP-DMQMC shares similar features to those obtained with ft-FCI.

Beyond FCI: N$_2$/cc-pVDZ with i-PIP-DMQMC

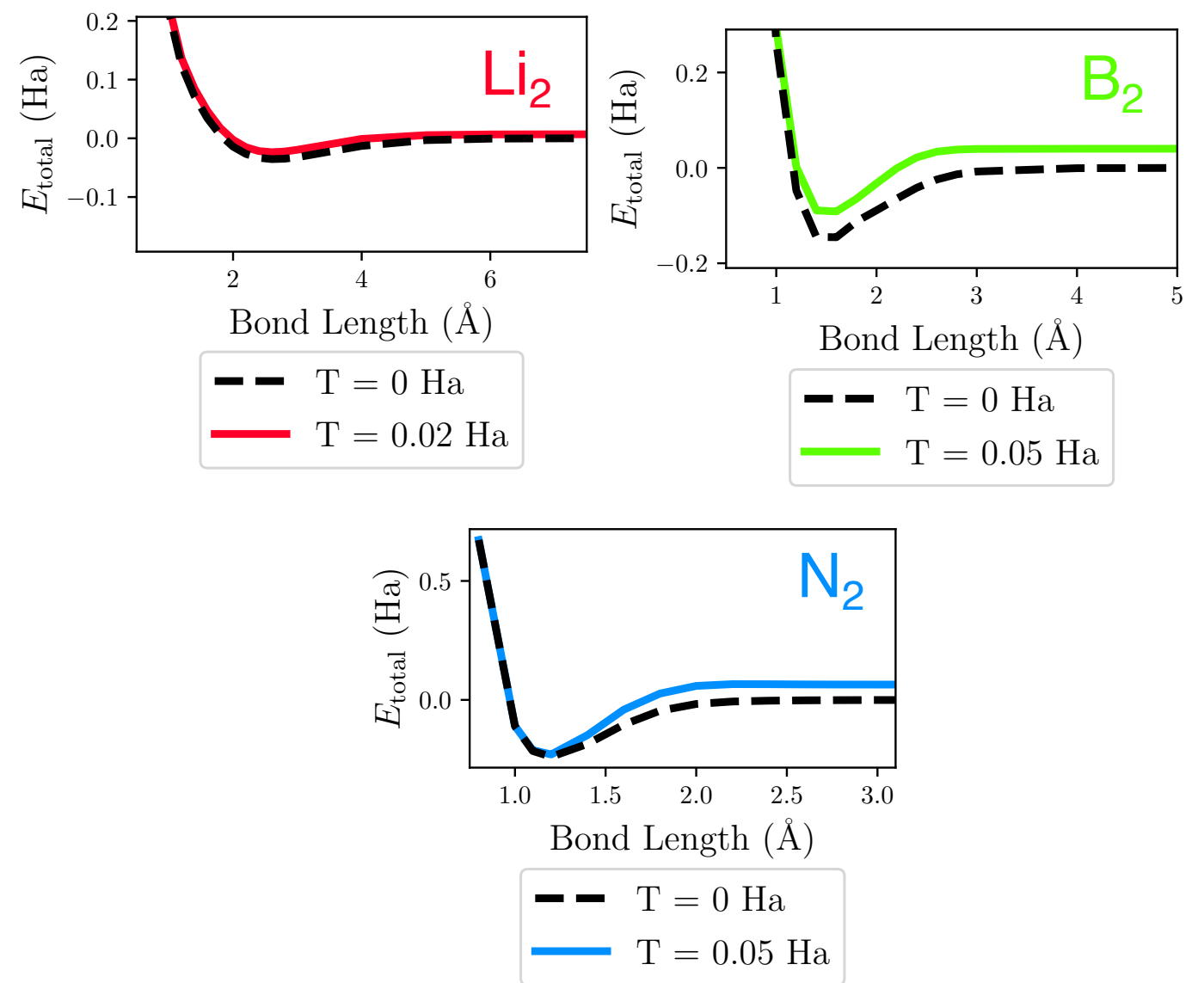


Relative populations of the density matrix elements of N$_2$/cc-pVDZ from i-PIP-DMQMC. The more evenly distributed the weights of the elements are, the more difficult the system is to simulate.

Potential energy surfaces of STO-3G diatomics share qualitative features across finite temperatures

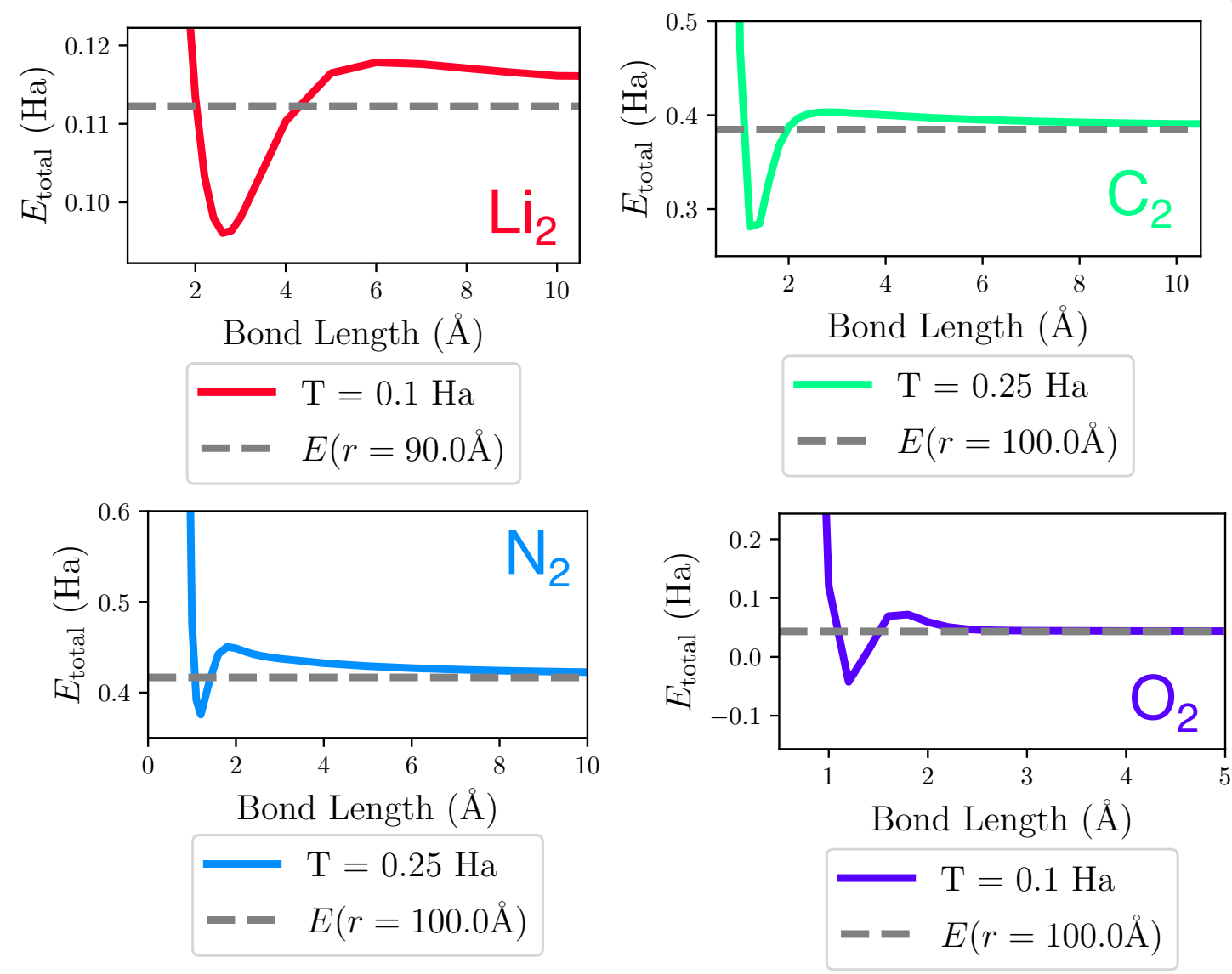
Energies are relative to twice the atom's energy

Comparisons with FCI



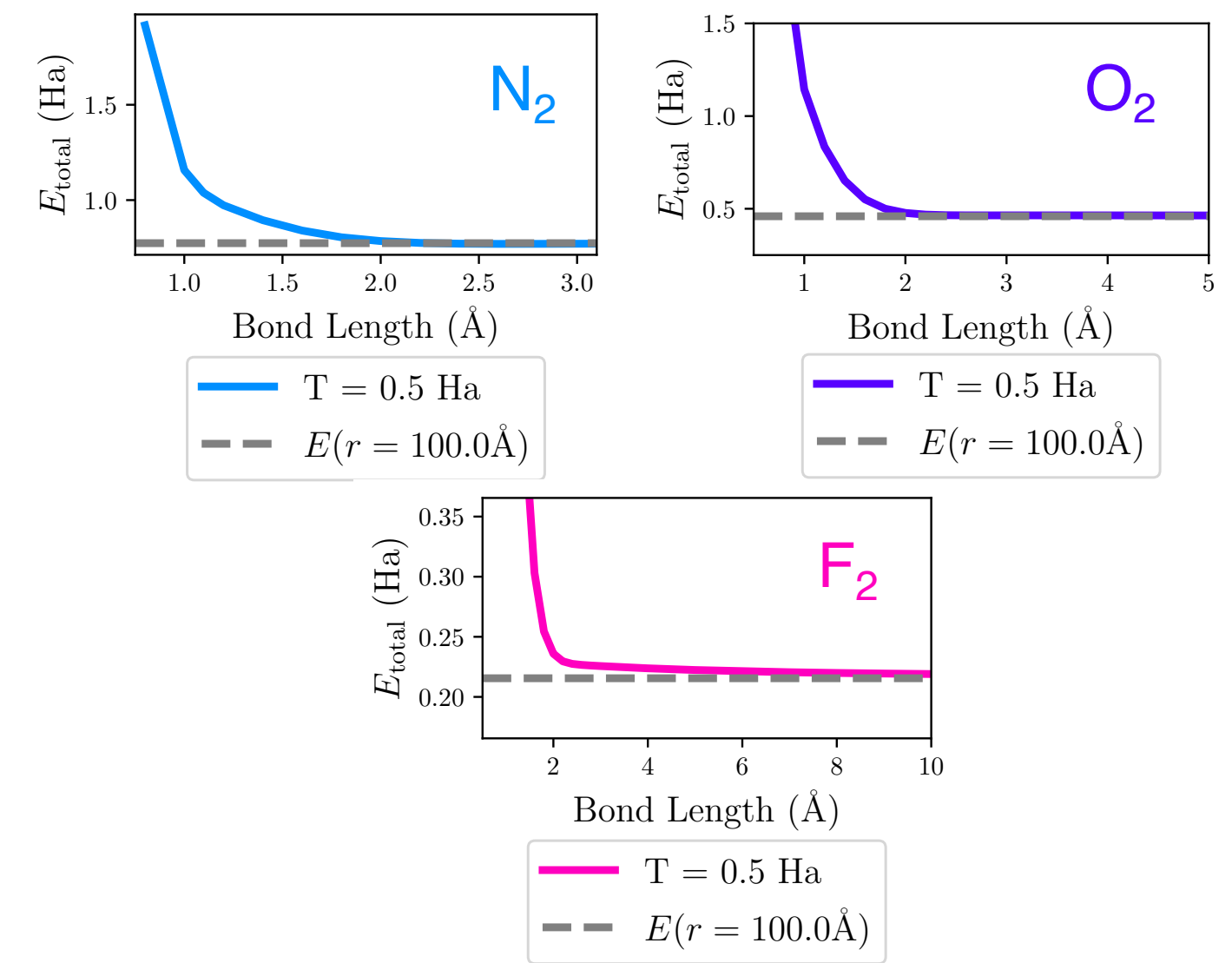
At low temperatures, we can compare to FCI ($T = 0$ Ha), and we find evidence that for some diatomics the depth of the bonding well increases with a small increase in temperature.

Energy Barrier



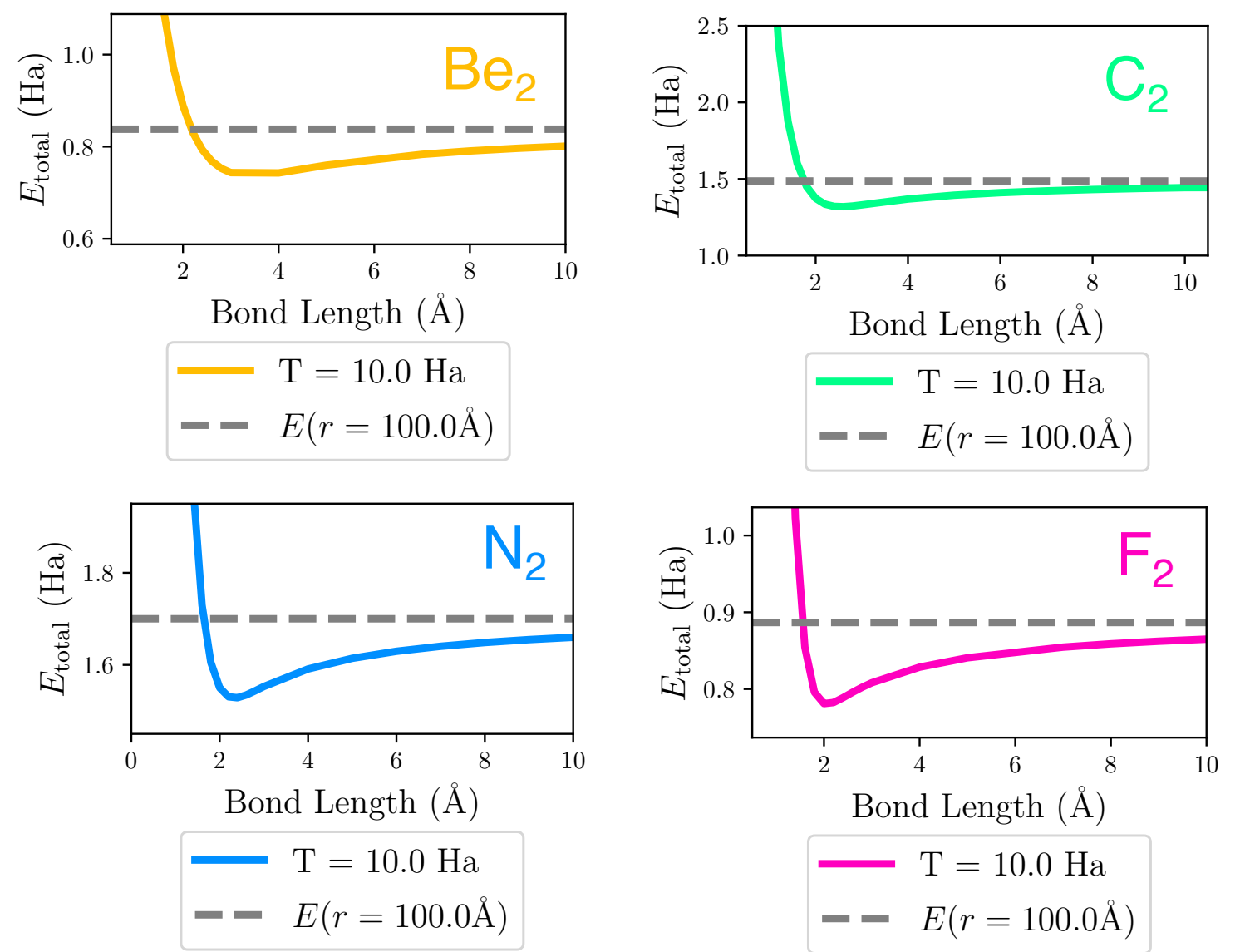
At intermediate temperatures, we find that for all the diatomics there is a small energy barrier to association relative to the $r = 100$ Å molecule.

Completely Repulsive



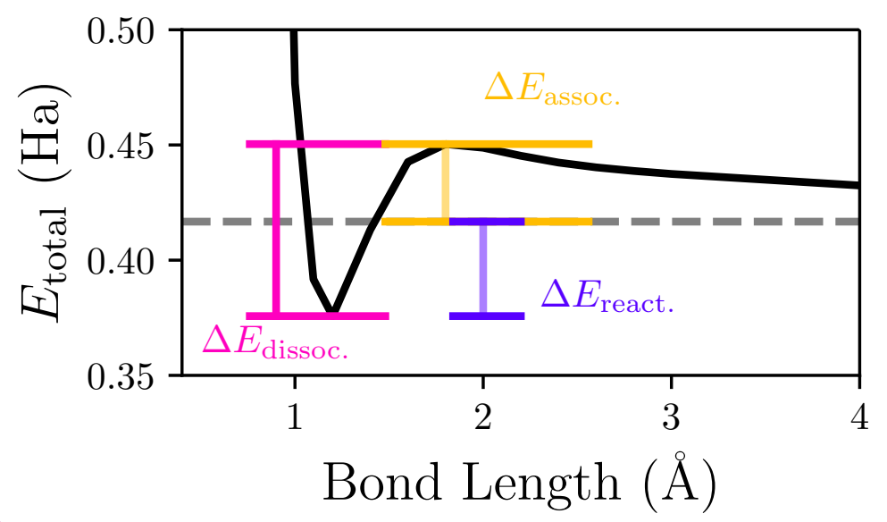
For N$_2$, O$_2$ and F$_2$ we found that there are temperatures where the potential energy curve is completely repulsive.

High T bonding well

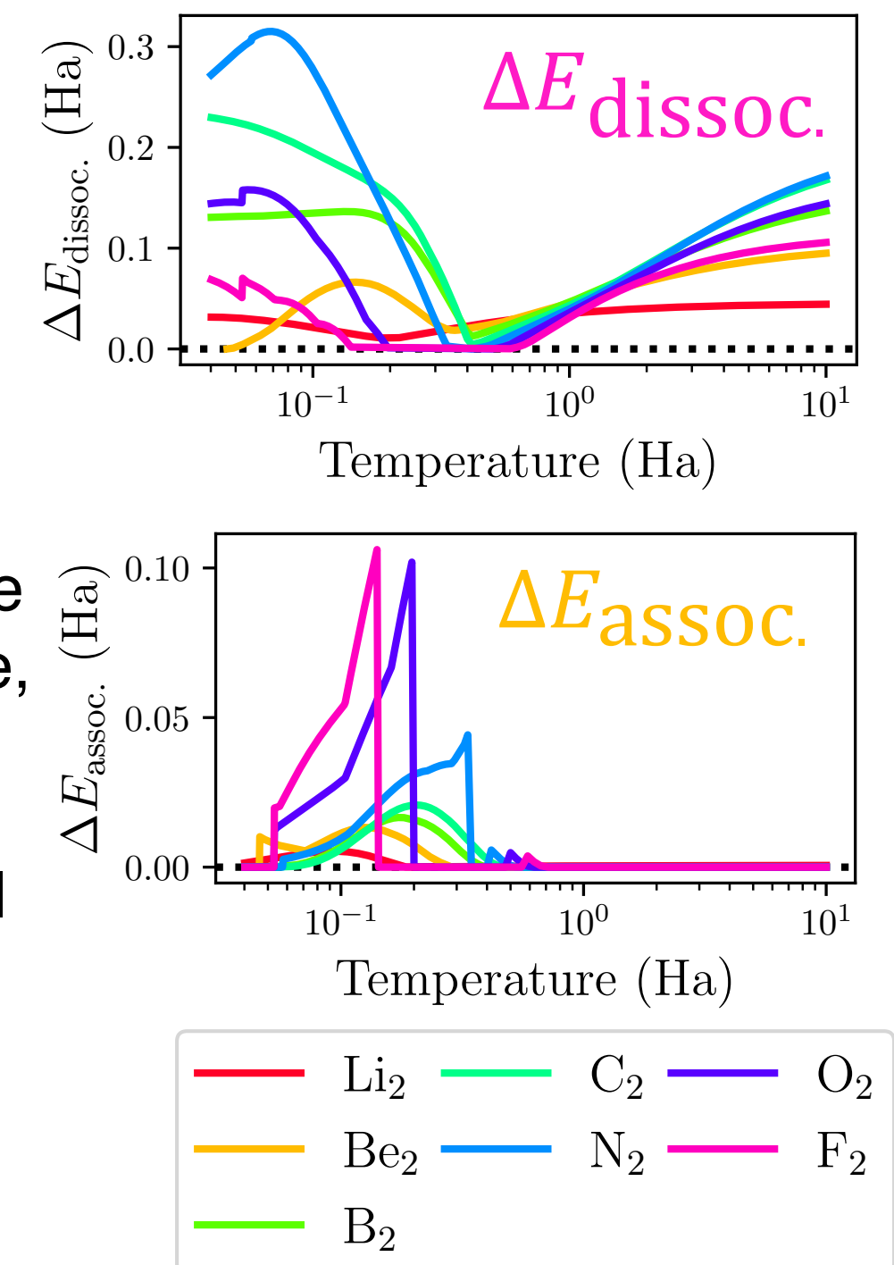


At extremely high temperatures, we found evidence of a second bonding well, further out in bond length.

The reaction energies for association and dissociation can be estimated across a large temperature range



In the intermediate temperature range, there are energy barriers to association for all the diatomics.



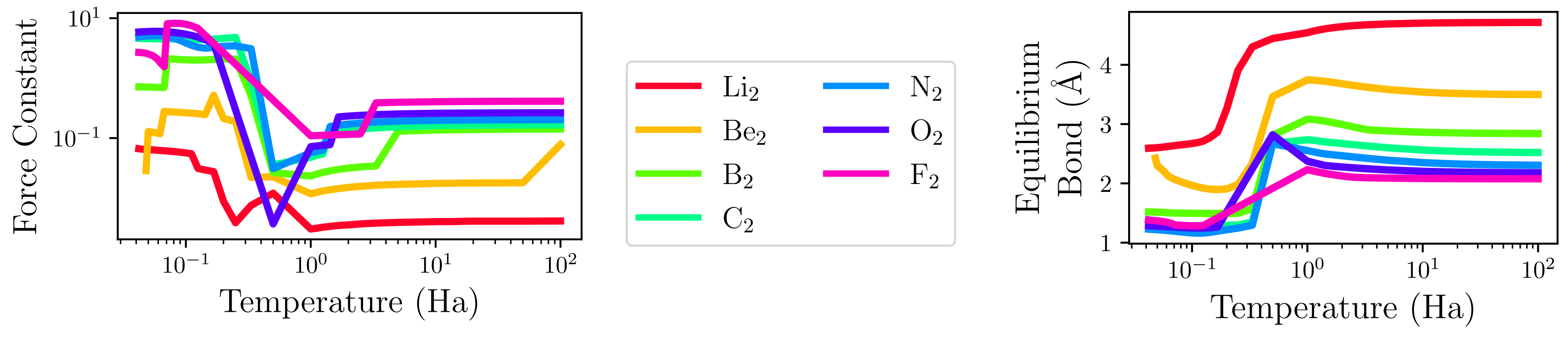
At low temperatures, all of the dissociation energies of the diatomics are nonzero, indicating the presence of a bonding well.

There is a small region in the intermediate temperature range where the dissociation energy is equal to zero for some diatomics.

At high temperatures, we find that there is a second bonding minimum with a slightly lower dissociation energy.

Temperature effects the stiffness of the bond; measured by the force constant and modeled with a Harmonic Oscillator approximation

(Left) We find that as temperature is increased the force constant first generally decreases, and then increases for the p-block diatomics. For Li$_2$ and Be$_2$, the force constant generally decreases with increasing temperature. In general, the force constant increases as we go from left to right across the first row.



(Right) FCI data is collected in 0.2 Å steps for $r < 3.0$ Å; we used our quadratic interpolations to estimate the "true" equilibrium bond length in STO-3G for a range of temperatures. Similar to the force constant, we see that there are two "phases": a low temperature shorter bond length region, and a high temperature longer bond length region.

Acknowledgements

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