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?

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. 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.

For $N_2$, $O_2$, and $F_2$, we found that there are temperatures where the potential energy curve is completely repulsive. At extremely high temperatures, we found evidence of a second bonding well, further out in bond length.

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

**Comparisons with FCI**

**Energy Barrier**

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**Beyond FCI: $N_2$-cc-pVDZ with i-PIP-DMQMC**

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

**Finite temperature FCI (t-FCI)**

$$\langle \langle \beta \rangle \rangle = \sum_i \beta_i \exp(-\beta \varepsilon_i)$$

**Density matrix quantum Monte Carlo (DMQMC)**

Use the N-body thermal density matrix:

$$\delta = \exp(-\beta \mathcal{H})$$

**We use HANDE/QMC for both FCI and DMQMC calculations.**

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

**Potential energy surface of $N_2$-cc-pVDZ with i-PIP-DMQMC.**

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

**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.

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