Application of first-principle electronic free energy calculations to bond breaking in the nitrogen dimer

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Using the free-energy Born—Oppenheimer (FEBO) approximation we calculate the free energy (F) surface for the nitrogen dimer, a benchmark system. We use exact finite temperature full configuration interaction (ft-FCI) method in a minimal basis, and density matrix quantum Monte Carlo calculations for larger basis sets. Considering only the internal energy (U) surface one finds a counterintuitive bond strengthening at temperatures T>0. However, when considering the free-energy surface, we see only a gradual bond weakening with increasing T. This gradual bond weakening is caused by the thermally scaled entropic (-TS) component for F which counteracts the behavior in U. Using the free-energy surface, we can calculate a dissociation temperature, and find this temperature is below the experimentally measured dissociation energy. We explore the impact that the determinant space has on our calculated dissociation temperature and determine that including more symmetries for the determinant space lowers the calculated dissociation temperature. We also investigate the basis set dependence for the dissociation temperature and find that using a larger basis set increases the dissociation temperature.
We explore the origins for the free-energy surface behaviors using histograms for the density matrix and find that the longer bond length density matrix is more sensitive to changes in temperature.

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