



Introduction

We present a novel finite temperature, $T > 0$, approach to quantum chemistry and its application to small molecules. Descriptive quantum statistics (molecular Z , S , F) and parameters (E , geometry) are evaluated.

Path Integral Quantum Monte Carlo (PIMC)

An ab initio electronic structure approach with

- FULL ACCOUNT OF CORRELATION
- TEMPERATURE DEPENDENCE
- BEYOND BORN-OPPENHEIMER APPROXIMATION
- INTERPRETATION OF EQUILIBRIUM DISSOCIATION REACTION

Based on the quantum statistics, from the mixed state density matrix (path-integral)

$$\rho(R(0), R(\beta)) = \int_{R(0)}^{R(\beta)} e^{-S(R(\tau))} \mathcal{D}R(\tau)$$

we obtain the partition function

$$Z(\beta) = \text{Tr } \rho,$$

where

$$\beta = 1 / k_B T$$

and $S(R)$ is the action of the path $R(\tau)$ in imaginary time τ .

The path-integral is sampled by Metropolis Monte Carlo algorithm for evaluation of the partition function, distributions and expectation values.

Ps₂ Molecule

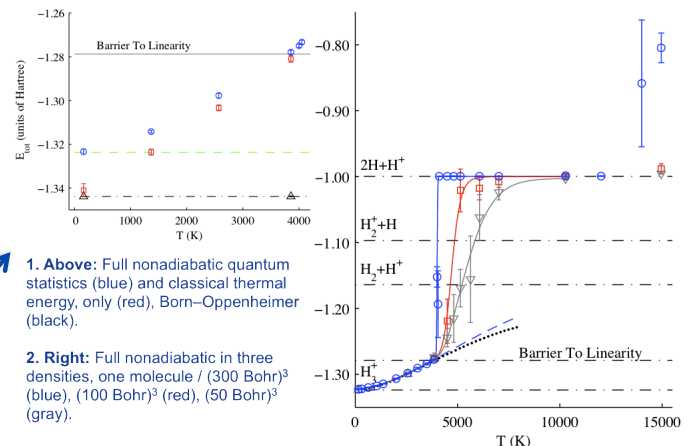
Binding energy of the molecule is about 0.4 eV $\approx$ 5000K. We predict, however, its thermal dissociation at about 1000 K, already, due to exceptionally large entropy factor lowering the free energy at low densities [1].

References

1. Ilkka Kylänpää and Tapio T. Rantala, Physical Review A **80**, 024504 (2009).
2. Ilkka Kylänpää and Tapio T. Rantala, Journal of Chemical Physics **133**, 044312 (2010); and submitted to Journal of Chemical Physics, <http://arxiv.org/abs/1103.3575>

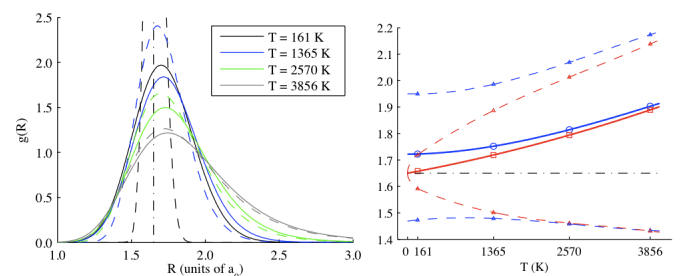
H₃⁺ Molecular Ion

- NVT ensemble energy as function of T [2]



1. Above: Full nonadiabatic quantum statistics (blue) and classical thermal energy, only (red), Born-Oppenheimer (black).
2. Right: Full nonadiabatic in three densities, one molecule / (300 Bohr)³ (blue), (100 Bohr)³ (red), (50 Bohr)³ (gray).

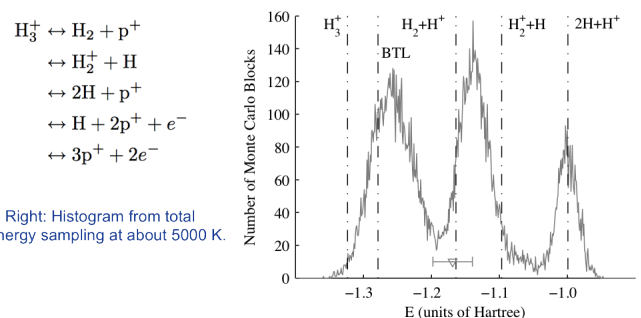
- Zero-point motion and thermal dynamics [2]



3. Left: Nuclear pair correlation functions (bond length distributions) at different temperatures including quantum dynamics (solid curves) and classical thermal dynamics, only (dashed).

4. Right: Expectation values of the internuclear distances from Fig. 3 including quantum dynamics (blue), classical only (red), with the FWHM of distribution (dashed).

- Dissociation-recombination equilibrium [2]



Conclusion

For the first time the first-principles electronic structure approach has been successfully extended to finite temperatures and beyond Born-Oppenheimer approximation, and furthermore, to chemical reactions.