COMPUTING THERMAL EFFECTS ON NONLINEAR OPTICAL PROPERTIES OF SMALL ATOMS

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The significance of nonlinear optical properties (NOP) is pronounced in many physical scales starting from microscopic interactions, such as van der Waals, to macroscopic properties, like dielectric constant and refractive index. Obtaining NOP, that is, dipole and multipole moments and (hyper)polarizabilities of matter, by computational simulation is particularly important in systems beyond experimental reach, such as exotic light-nucleus molecules in warm dense matter present in stars and gas planets, or short life-time particles such as positron. Most first-principles approaches are straightforward in 0 K but become tedious in thermal ensembles and beyond the adiabatic approximation.

The path-integral Monte Carlo method (PIMC) provides a tangible interface between the tensorial and the thermally averaged character of molecular (hyper)polarizabilities. In a recent study [1], we have derived field-free estimators that make the computation even more straightforward than our previous finite-field approach [2]. With the adiabatic, i.e. Born–Oppenheimer, approximation we obtain accurate tensorial ground state (hyper)polarizabilities, while the non-adiabatic simulation adds in considerable rovibrational effects and thermal coupling. In case of several two-electron systems, our results at the 0 K limit are either novel or in excellent agreement with the literature (e.g., see Fig. 1). Besides these results, we are presenting the derivation and demonstration of yet unpublished estimators for dipole-quadrupole polarizabilities of small molecules.

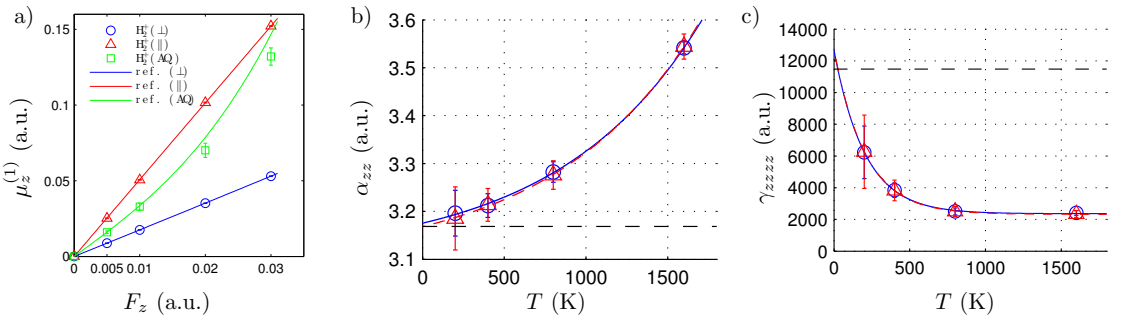

Figure 1. H_2^+ molecular ion. (a) Finite electric field F_z induces dipole moments $\mu_z^{(1)}$ with different total (hyper)polarizabilities depending on fixed-nuclei orientation (red, blue) or thermal rovibrational averaging of free quantum nuclei (green) [2]. (b, c) In non-adiabatic simulations, static dipole polarizability α_{ZZ} and second hyperpolarizability γ_{ZZZZ} change by the temperature but meet the literature references (dashed) at 0 K [1].

[1] J. Tiihonen, I. Kylänpää, and T. T. Rantala. *Phys. Rev. A*, 94, 032515, Sep 2016
[2] J. Tiihonen, I. Kylänpää, and T. T. Rantala. *Phys. Rev. A*, 91, 062503, Jun 2015