The fast and accurate calculation of frequency-dependent response properties using a multiresolution adaptive numerical solver at the basis set limit

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Objectives

We wish to develop a multiresolution numerical solver for the computations of frequency-dependent response properties.

- Linear and non-linear response properties
- User-defined precision in molecular property

Introduction

We have developed a multiresolution analysis solver to compute linear and non-linear response properties. MRA using multiwavelets provides an adaptive and complete basis, guaranteeing precision in the desired property. Compared to other basis-set techniques, MRA also has lower scaling for computing larger molecules. In addition, MRA demonstrated its ability to compute response properties, including CIS excitation energies and static polarizabilities[1, 2]. This work introduces the development of our frequency-dependent solver, which we may use to compute TD-HF/DFT linear and non-linear response properties. We also provide preliminary dynamic polarizabilities calculated in the TDHF formalism compared to standard Gaussian basis sets calculations done in Dalton[3].

Response Properties

We compute the frequency-dependent polarizability via the calculation of the frequency-dependent response density.

$$\alpha_{xy}(-\omega,\omega) = tr(\hat{v}^{(x)}\hat{\rho}^{(y)}(\omega))$$

The objective of our solver is to calculate the response functions of the response density by solving integral form of the response equations.

$$x_p^{(\alpha)}(r) = -2\hat{G}^{(\alpha)}(k_x) * \left[\hat{V}^{(0)}x_p^{(\alpha)}(r) + \Gamma_p^{(\alpha)}(r) + V^{(\alpha)}\right]$$

$$y_p^{(\alpha)}(r) = -2\hat{G}^{(\alpha)}(k_y) * \left[\hat{V}^{(0)}y_p^{(\alpha)}(r) + \Gamma_p^{\dagger(\alpha)}(r) + V^{\dagger(\alpha)}\right]$$

$$k_x = [-2(\epsilon_p+\omega_\alpha)]^{1/2} \quad k_y = [-2(\epsilon_p-\omega_\alpha)]^{1/2}$$

MRA Hartree-Fock Polarizability Results

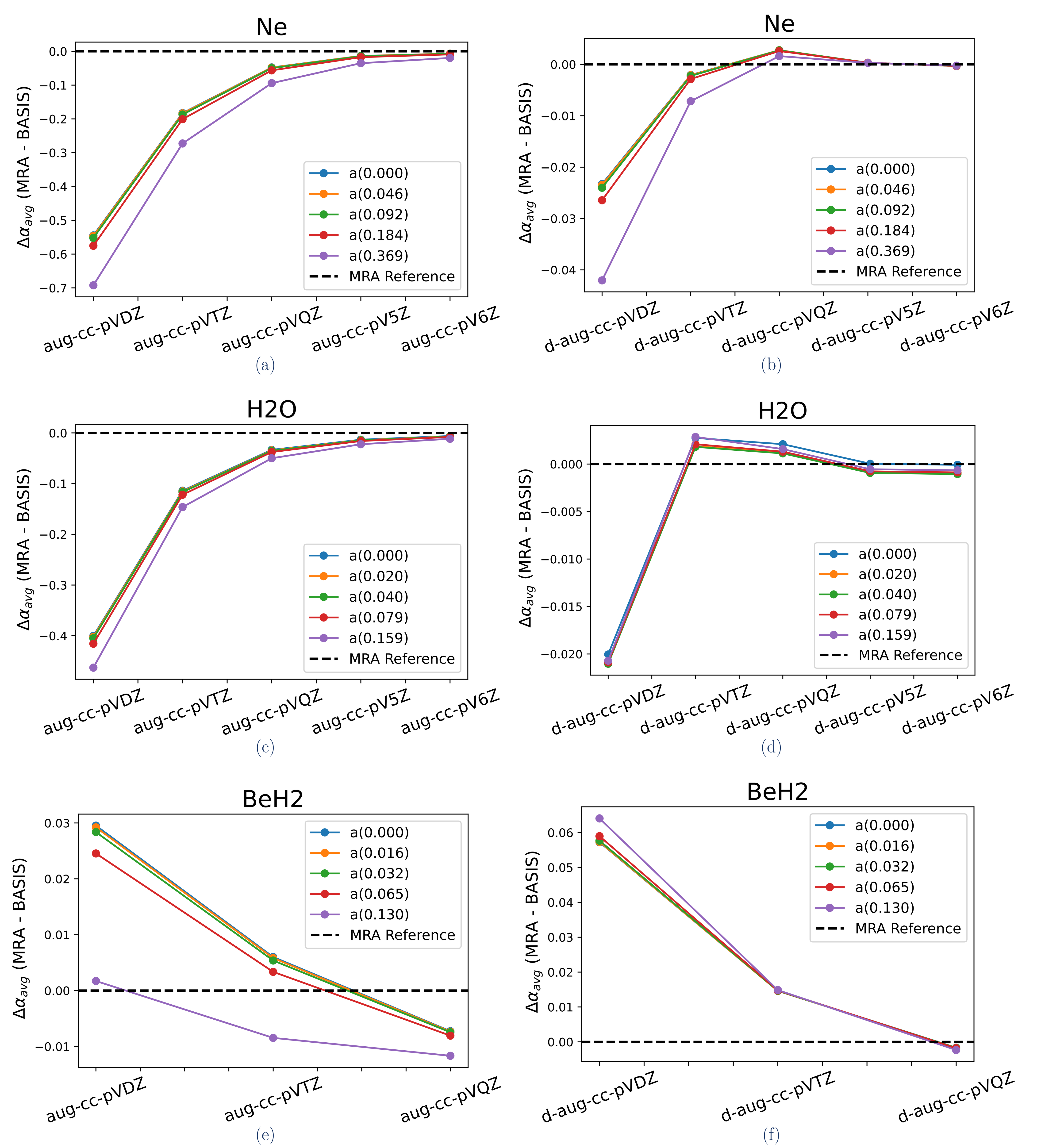

Figure: Average dynamic polarizabilities computed with the MRA multiwavelet basis-set compared to Dunning's correlation-consistent basis sets aug-cc-pVXZ and d-aug-cc-pVXZ. For each polarizability value, the MRA response densities where converged to a 1e-6 difference between iterations. From the data it can be seen that Guassian basis do not all systematically converge to the basis-set limit.

Conclusion

We successfully validated our MRA solver for the computation of frequency-dependent polarizabilities. We illustrated issues when trying to extrapolate response properties using Gaussian basis-sets as they may not always systematically converge. The extension of this work will be to calculate third-order properties such as hyperpolarizabilities and Raman response from first-order frequency-dependent densities.

References

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