

FYAP: Computational Studies of Plasmons in Polycyclic Aromatic Hydrocarbons

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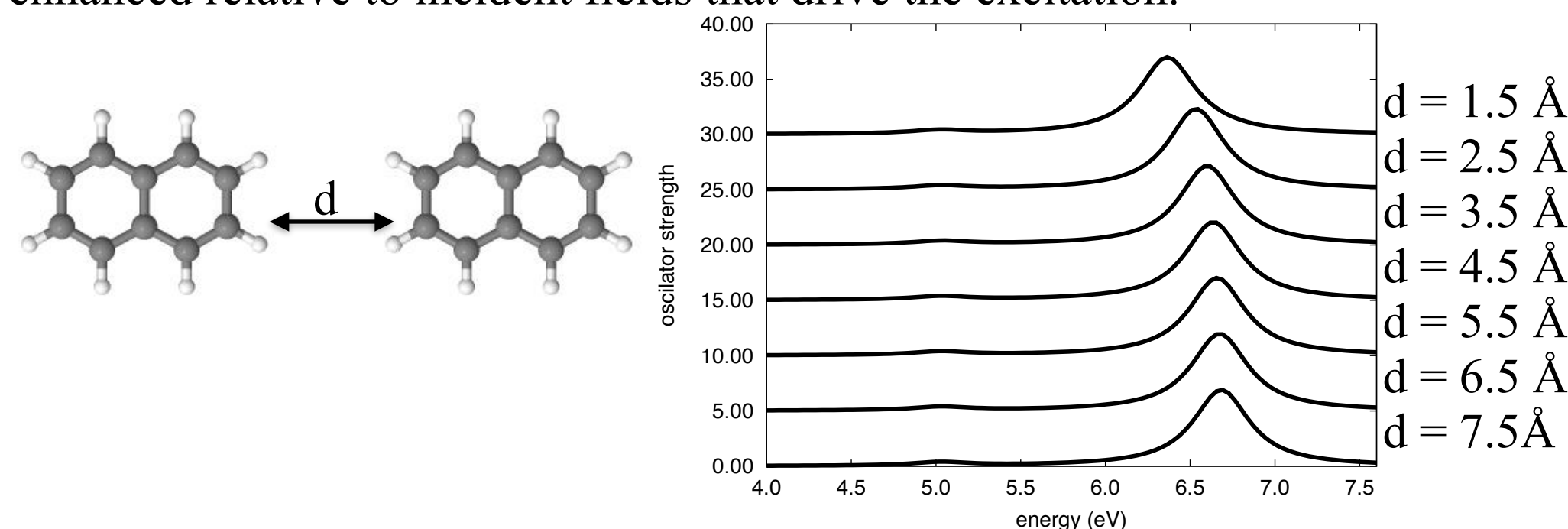
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Abstract:

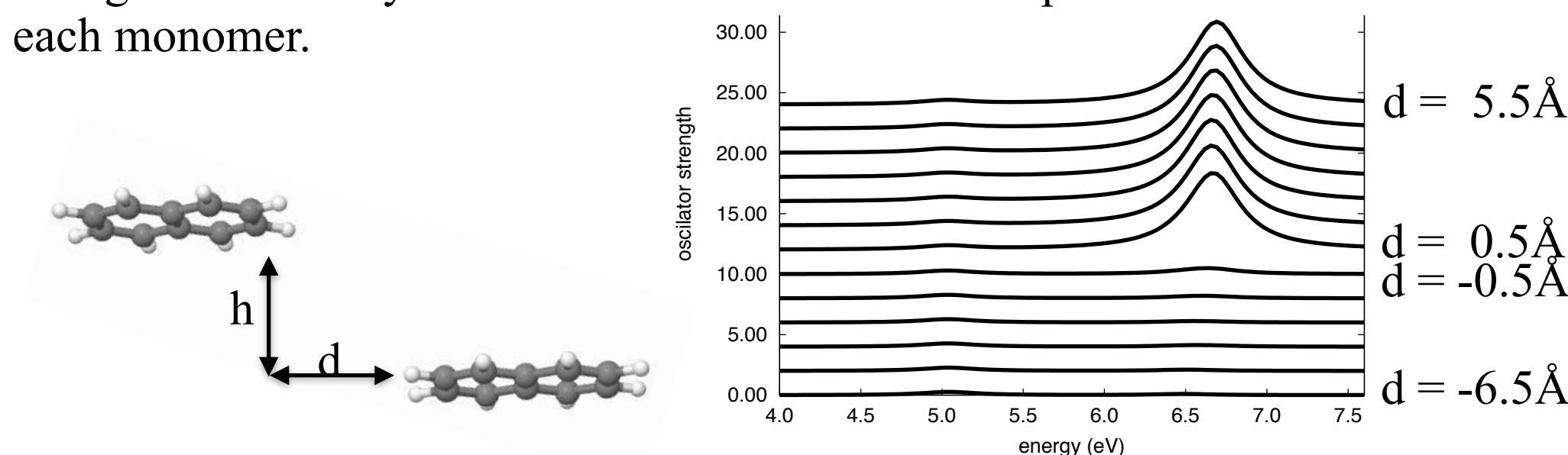
Recent computational studies have suggested that polycyclic aromatic hydrocarbons (PAHs) can serve as components of materials that mimic the properties of conventional plasmonic materials.¹⁻⁴ However, the electronic structure of PAHs is extremely complex and must be treated computationally with care. This work aims to develop theoretical models that can accurately describe the ground- and excited-state electronic structure of these systems, ultimately determining their feasibility as substitutes for conventional plasmonic materials.

Introduction:

As two PAHs are brought in close proximity to one another, two features emerge that are shared with true plasmonic excitations: (i) the electronic excitation energies redshift¹ and (ii) the electric field between the molecules is enhanced relative to incident fields that drive the excitation.⁴



When PAHs such as naphthalene adopt a stacked configuration, the brightest excitation in the spectra is quenched. The optical properties of the dimer change dramatically when there is conductive overlap between the π -clouds on each monomer.



Clearly, the optical properties of PAHs are sensitive to intermolecular interactions. One should take extreme care when modeling these systems, as many popular quantum-chemical methods inadequately describe noncovalent interactions. Further, the ground-state electronic structure of isolated PAHs is also challenging to describe. With these considerations in mind, we have developed a new electronic structure method to describe low-lying excited states in complex systems.

Ground electronic states:

The ground-state energy for a many-electron system is expressed as

$$E = \langle \Psi | \hat{H} | \Psi \rangle$$

or, without approximation, as the trace of the two-electron reduced-density matrix (2D) with the reduced Hamiltonian (2K):

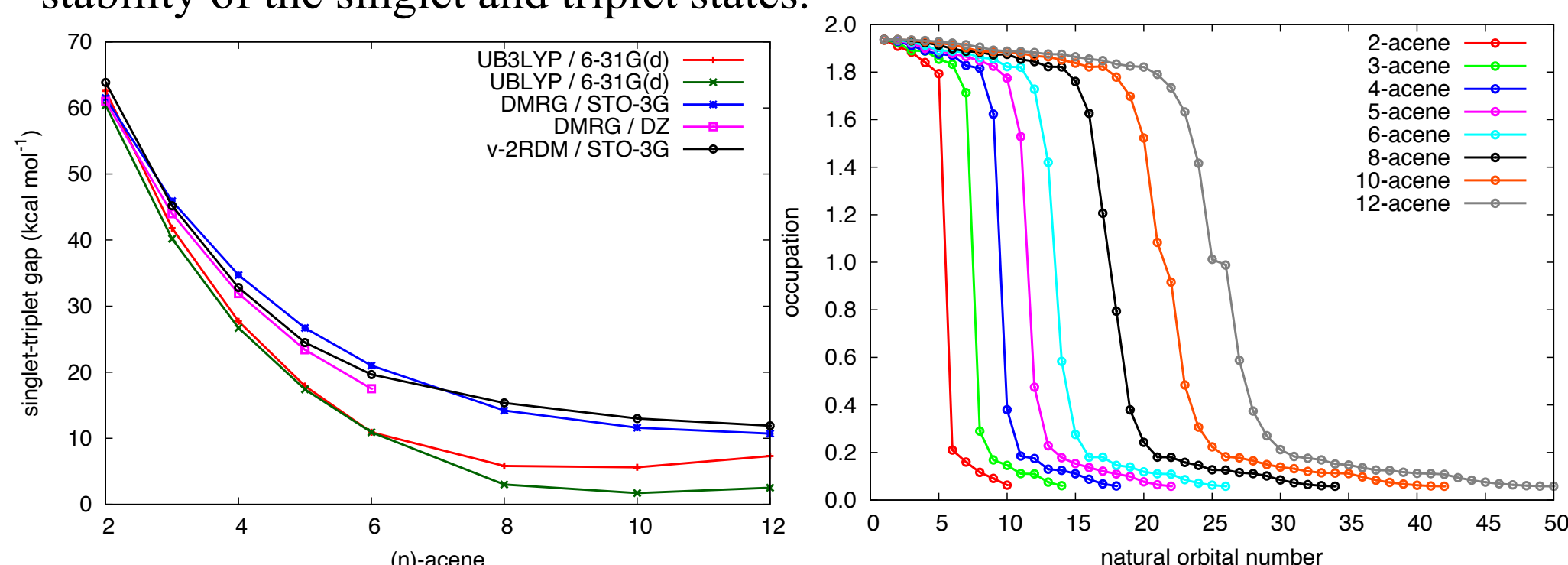
$$E = \text{Tr}({}^2K {}^2D)$$

Since 2D is a much more compact mathematical object than the many-electron wave function, it is tempting to try to optimize the energy with respect to the elements of the 2-RDM. However, this process is complicated by the fact that not all 2-RDMs correspond to realistic N -electron wave functions. This N -representability problem leads to the requirement that the 2-RDM (and other probability density matrices) have nonnegative eigenvalues:

$${}^2D, {}^2Q, {}^2G \geq 0$$

This type of optimization is known as a semidefinite optimization, which can be found in other unrelated fields like financial mathematics. We have implemented a semidefinite solver for the 2-RDM problem in the Psi4 electronic structure package.

Here, we apply the 2-RDM method to the lowest-energy singlet and triplet states of the linear acene series. Few methods correctly describe the relative stability of the singlet and triplet states.



Density matrix renormalization group (DMRG) and DFT results are taken from Ref. 5.

The 2-RDM method predicts qualitatively correct trends in the singlet/triplet gap, whereas popular density functional theory (DFT) methods do not. The natural orbital occupations for the singlet states reveal the onset of polyradical character for larger members of the series.⁶

Excited electronic states:

Information about excited electronic states is embedded in the response of a quantum system to an external oscillating electric field. The time-dependence of the 1-electron reduced-density matrix (1-RDM, 1D) depends on the 2-RDM

$$\frac{\partial}{\partial t} {}^1D_j^i = \frac{1}{i\hbar} \sum_{qrs} \left({}^2K_{rs}^{jq} {}^2D_{rs}^{iq} - {}^2K_{iq}^{rs} {}^2D_{jq}^{rs} \right)$$

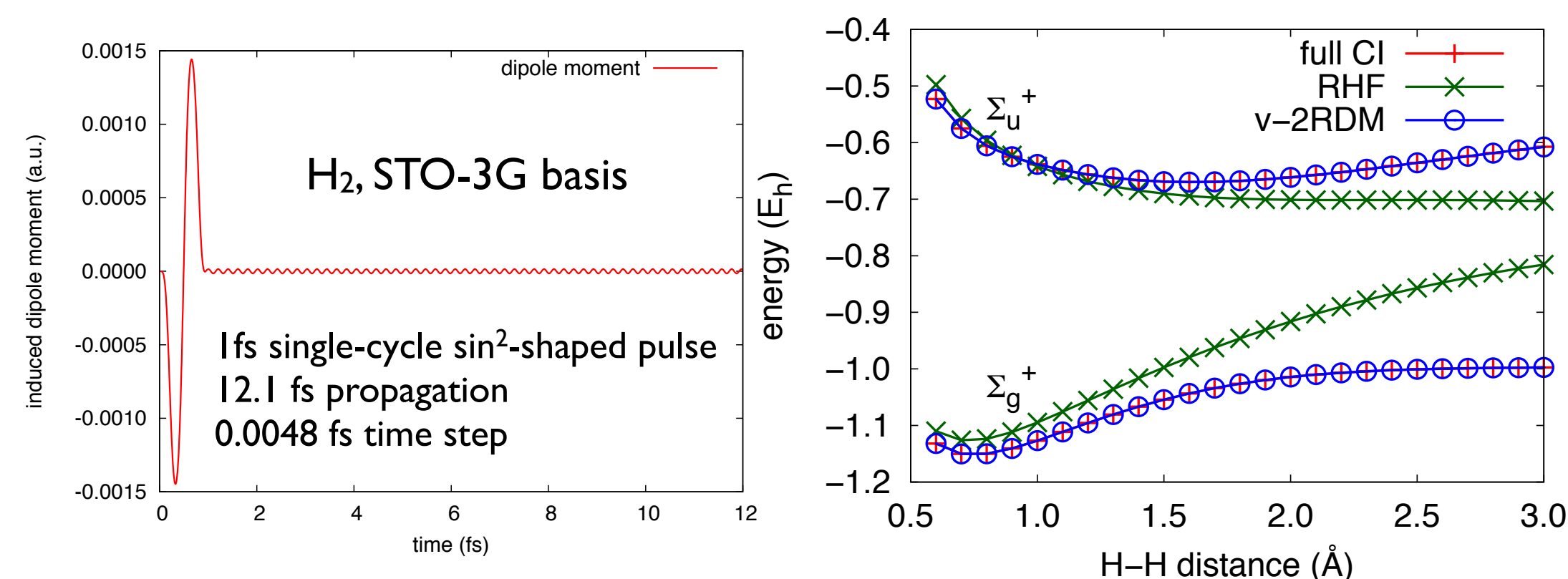
and the 1-RDM and 2-RDM are related through a contraction relation

$$(N-1) {}^1D_j^i = \sum_k {}^2D_{jk}^{ik}$$

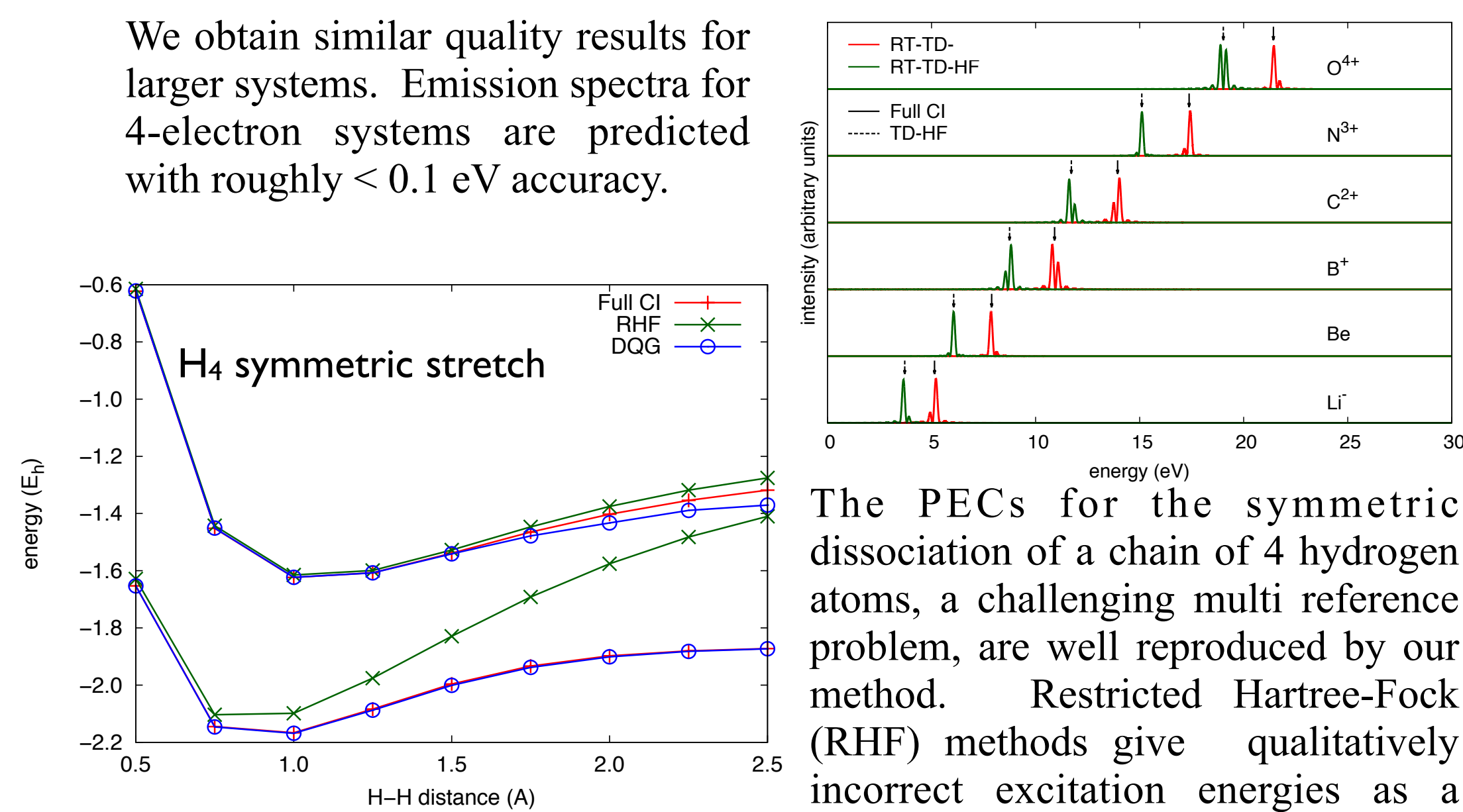
In order to propagate 1D in time, we need to know 2D . We can reconstruct a possible 2D from 1D from this contraction relation, but we have no guarantee that this 2D corresponds to a realistic N -electron system. Hence, the time-dependent 1-RDM problem is similar to the ground-state energy problem. We use ideas from ground-state variational 2-RDM theory to remove the indeterminacy of this expression to model the time dependence of quantum systems without the use of the N -electron wave function.⁷

Results:

As a proof of concept, we consider the time evolution of the 1-RDM for the simplest neutral molecule: H₂. The system is exposed to a short oscillating external electric field, and the time evolution of the dipole moment gives us information about excited energies. For this system, our method yields a PEC for the ground and excited states that are indistinguishable from the exact full configuration interaction (CI) results.



We obtain similar quality results for larger systems. Emission spectra for 4-electron systems are predicted with roughly < 0.1 eV accuracy.



The PECs for the symmetric dissociation of a chain of 4 hydrogen atoms, a challenging multi reference problem, are well reproduced by our method. Restricted Hartree-Fock (RHF) methods give qualitatively incorrect excitation energies as a function of H-H separation.

Future directions:

We have developed a semidefinite solver that is several orders of magnitude more efficient than that used in the present time-dependent studies. We will extend this solver for the treatment of complex density matrices and explore the ability of our time-dependent 2-RDM method to describe excited states in larger systems, including PAHs and other strongly-correlated materials.

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