

# 29<sup>th</sup> Symposium on Chemistry Postgraduate Research in Hong Kong

## Nucleus Electron Coupled Self Consistent field Approach for Correlated Electron

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## Abstract

- Conventional nucleus electron coupled self-consistent field (NECSCF) is based on the exact factorization of the total wavefunction into conditional electronic wavefunction and marginal nuclear wavefunction. [1]
- The original electronic wavefunction is in mean-field. A novel NECSCF-based method is exploited in presence of correlation.
- An Entropic functional is applied to correlate the electrons within mean-field computational cost.
- Nonadiabatic effect on the molecular bonding character in the correlated many-electron system is demonstrated.

## Natural Orbital &amp; Density Matrix functional theory

Molecular orbitals are fixed to natural orbitals (NO), which associate with the corresponding occupation number (ON). One-body reduced density matrix (1RDM) is applied as the variable to NECSCF.

$$\gamma_{\mathbf{R}}(\mathbf{r}, \mathbf{r}') = \sum_p n_p(\mathbf{R}) \psi_p(\mathbf{r}|\mathbf{R}) \bar{\psi}_p^*(\mathbf{r}'|\mathbf{R}) \quad (1)$$

The electronic energy is exact to be approximated by 1RDM, where the cumulant energy of the system is unknown in exact form. J. Wang proposed an i-DMFT functional to the cumulant energy in form of the entropy of electrons with some empirical constants. [2]

$$E_{cum}(\mathbf{R}) = -\kappa S - b \quad (2)$$

## Electronic and nuclear solution

## Vibrational frequency calculation

By considering equation (2) as a part of energy, a new Lagrangian is built under the partial normalization condition of the electronic and nuclear wavefunction and N-representability issue. By differentiating the Lagrangian, the solutions to the electronic, nuclear and ON problems can be rewritten as follows.

$$\left[ \hat{F}_{BO} - \sum_v \frac{1}{M_v} \left( \frac{\nabla_v \chi}{\chi} \nabla_v + \frac{\nabla_v^2}{2} + \sum_q n_q \left( \langle \bar{\psi}_q | \nabla_v \psi_q \rangle \nabla_v - |\nabla_v \psi_q\rangle \langle \bar{\psi}_q | \nabla_v \right) + \frac{\chi \nabla_v^2 \chi}{2|\chi|^2} \right) \right] \psi_p(\mathbf{r}|\mathbf{R}) = \frac{\epsilon_p}{|\chi|^2} \psi_p(\mathbf{r}|\mathbf{R}) \quad (3)$$

$$\left[ -\sum_v \frac{1}{2M_v} \nabla_v^2 + E_{el}(R) \right] \chi(R) = E_{\chi}(R) \quad (4)$$

Due to  $\frac{\nabla_v \chi}{\chi} \nabla_v$  in the operator in equation (3), the operator is non-Hermitian but symmetric. Bi-orthogonal pairs of orbitals are applied to induce non-Hermitian character.

$$n_p = \frac{1}{1 + \exp\left(\frac{\epsilon_p - \mu}{\kappa}\right)} \quad (5)$$

Note that equation (5) is exactly Fermi-Dirac distribution but none of the temperature effect is considered. Since the equation (5) is cheap to compute in the whole self-consistent field procedure, the computational cost is similar to the original NECSCF calculation.

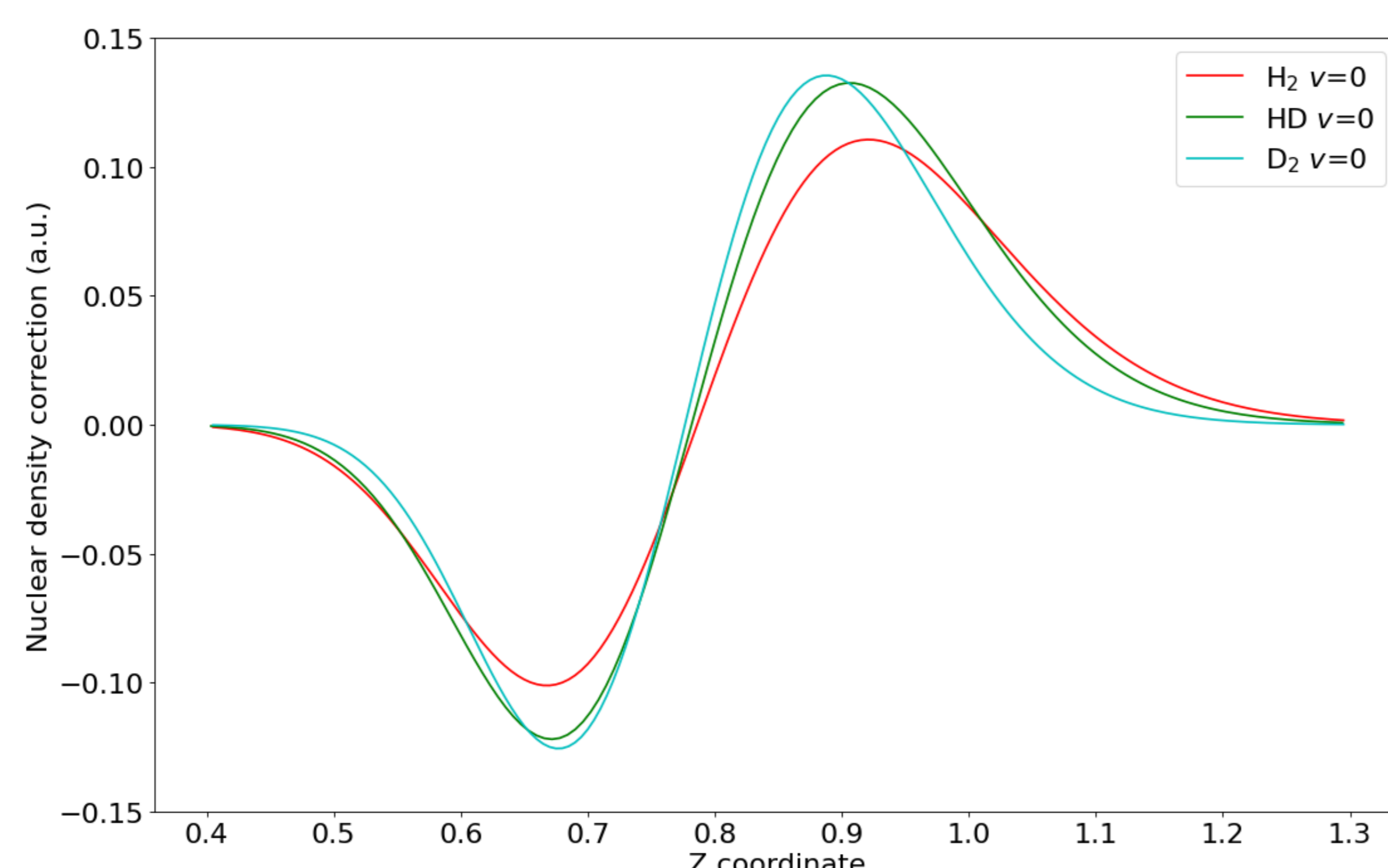
Molecule	H <sub>2</sub>	HD	D <sub>2</sub>
NECSCF	4374.334	3812.997	3137.430
NECSCF-iDMFT	4110.142	3589.276	2959.536
Experiment[3]	4161.130	3632.055	2993.548

Table1. Vibrational frequencies (cm<sup>-1</sup>) from v=0 to v=1 under cc-pVDZ basis set

## Nuclear density correction in presence of correlation

## Further work

$$P_v^{NECSCF} = \chi_{v,NECSCF}^\dagger(\mathbf{R}) \chi_{v,NECSCF}(\mathbf{R}) \quad \Delta P_v = P_v^{NECSCF-iDMFT} - P_v^{NECSCF}$$



We are currently trying to improve algorithm by including non-adiabatic adjustment to the empirical constants in equation (2). The best way is to solve a new set of parameters in iteration. Baldsiefen and Gross proposed a different point of view to induce Fermi-Dirac distribution and solve the parameters iteratively, which will be a direction for our model. [4] On the other hand, other DMFT functionals are applied to compare the non-adiabatic effects in order to select the best functional.

## Reference

- [1] Chen, Z.; Yang, J., *J. Chem. Phys.*, **2021**, *155*, 104111-104119
- [2] Wang, J.; Baerends, E. J., *Phys. Rev. Lett.*, **2016**, *128*, 013001-013006
- [3] R. D. I. Johnson, NIST Computational Chemistry Comparison and Benchmark Database, <http://cccbdb.nist.gov/>; accessed January 2022.
- [4] Baldsiefen, T.; Gross, E.K.U., *Comput. Theor. Chem.*, **2013**, *1003*, 114-122