

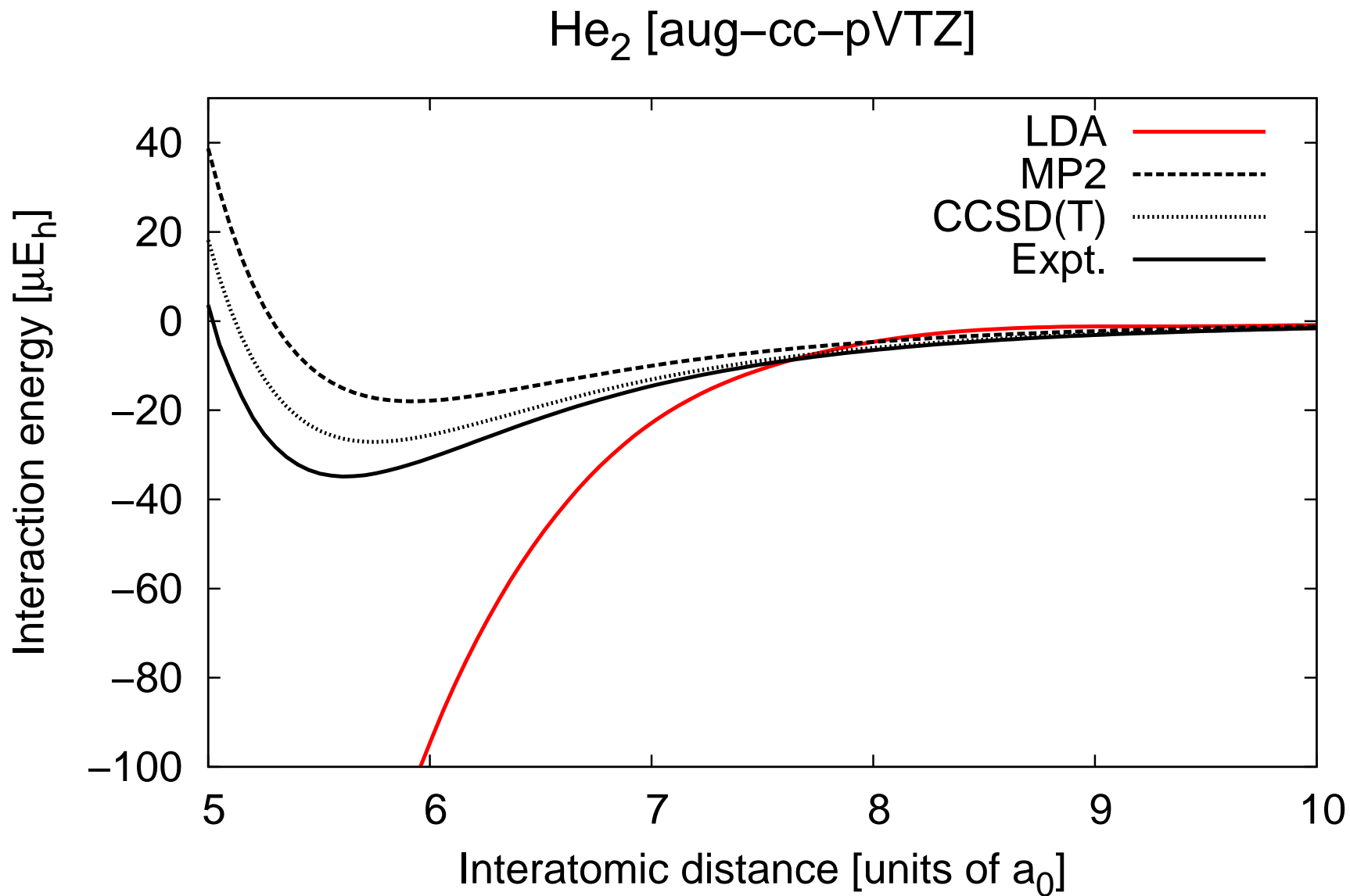
# Multideterminant density-functional theory based on the linear adiabatic connection

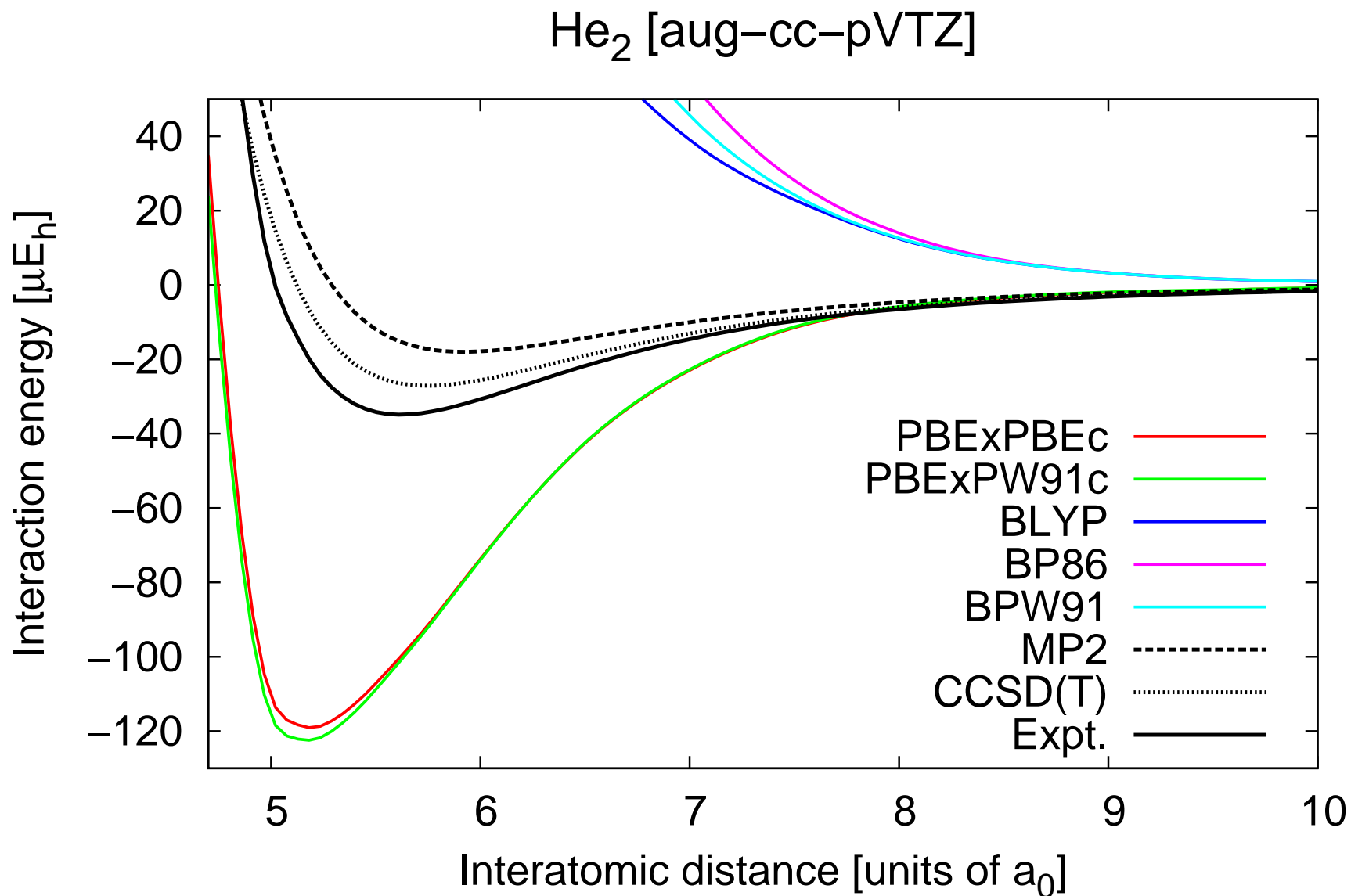
*Emmanuel Fromager*

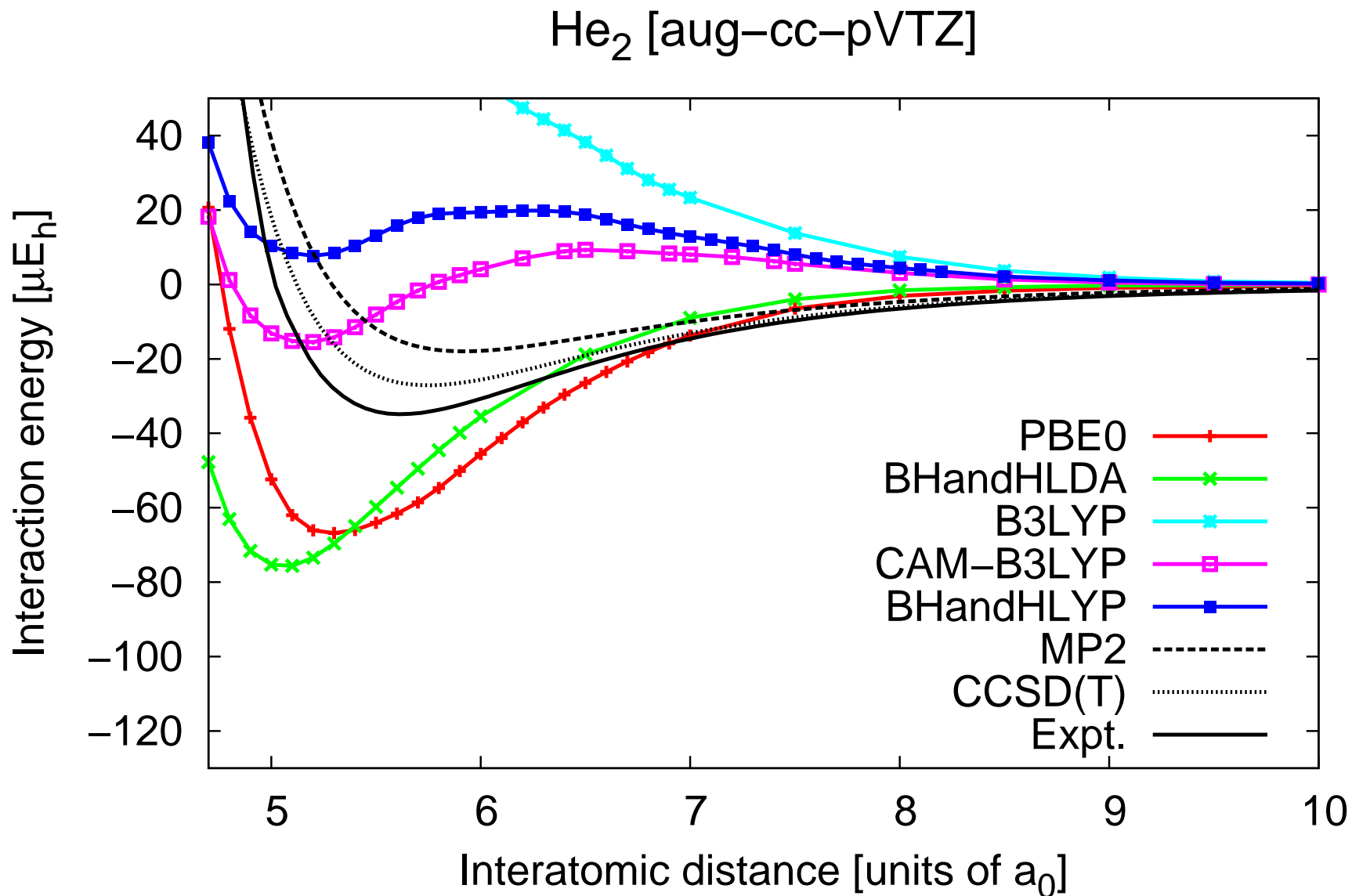


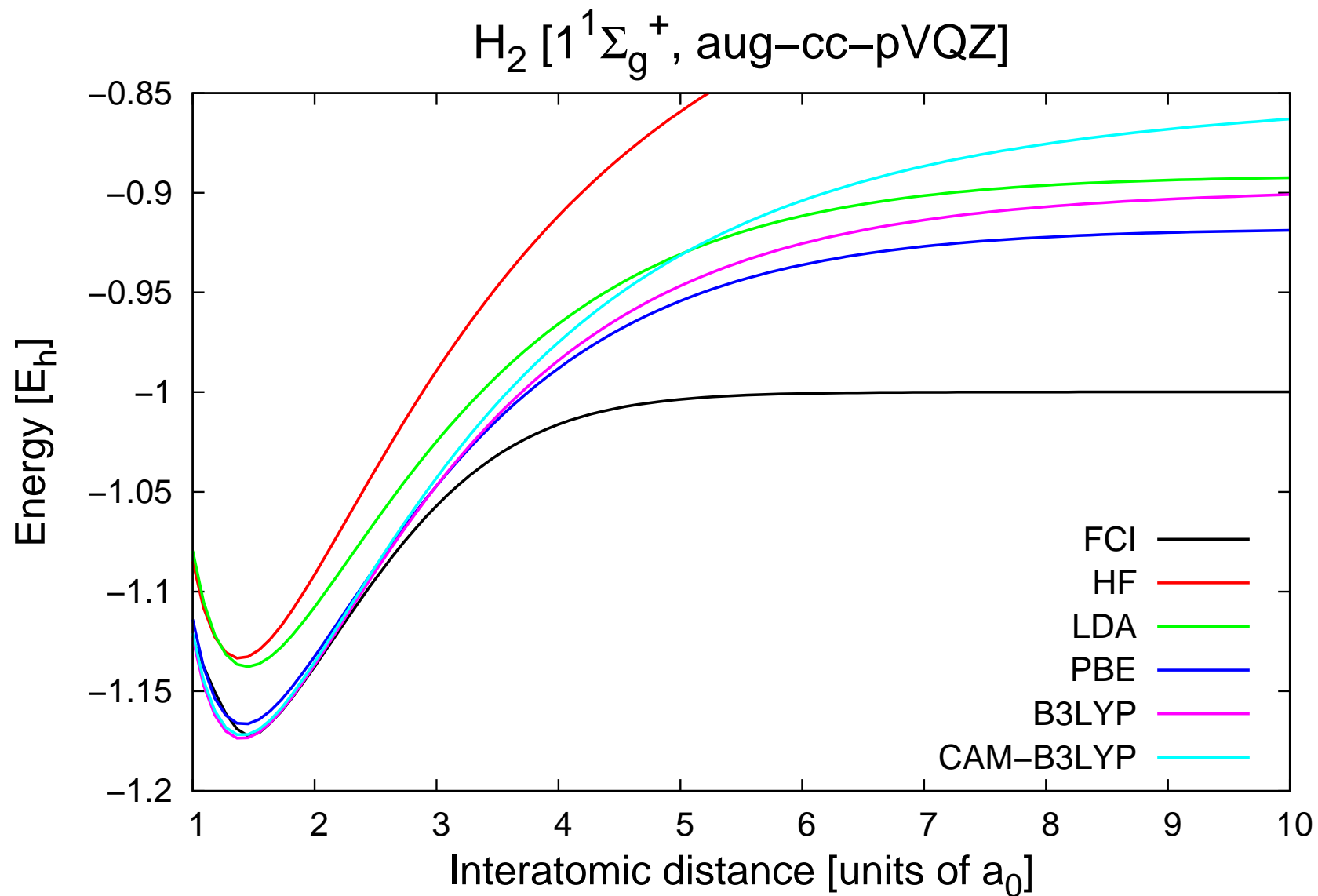
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## Linear adiabatic connection

$$\left( \hat{T} + \hat{W}_{ee} + \sum_{i=1}^N v^1(\mathbf{r}_i) \times \right) \Psi = E\Psi \quad \boxed{\lambda = 1}$$



$$\left( \hat{T} + \lambda \hat{W}_{ee} + \sum_{i=1}^N v^\lambda(\mathbf{r}_i) \times \right) \Psi^\lambda = \mathcal{E}^\lambda \Psi^\lambda \quad \boxed{0 < \lambda < 1}$$



$$\left( \hat{T} + \sum_{i=1}^N v^0(\mathbf{r}_i) \times \right) \Phi^{\text{KS}} = \mathcal{E}^0 \Phi^{\text{KS}} \quad \boxed{\lambda = 0}$$

$$\boxed{\forall \lambda \in [0, 1] \quad n_\Psi = n_{\Psi^\lambda} = n_{\Phi^{\text{KS}}} = n} \quad \leftarrow \text{density constraint !}$$

- Partially-interacting Levy–Lieb functional:  $F^\lambda[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \lambda \hat{W}_{ee} | \Psi \rangle = \langle \Psi^\lambda | \hat{T} + \lambda \hat{W}_{ee} | \Psi^\lambda \rangle$
- **Exact expression** for the correlation energy density functional:

$$E_{\text{Hxc}}[n] = \int_0^1 d\lambda \frac{dF^\lambda[n]}{d\lambda} = \int_0^1 d\lambda \langle \Psi^\lambda | \hat{W}_{ee} | \Psi^\lambda \rangle$$

$$\longrightarrow E_c[n] = \int_0^1 d\lambda \underbrace{\left( \langle \Psi^\lambda | \hat{W}_{ee} | \Psi^\lambda \rangle - \langle \Phi^{\text{KS}} | \hat{W}_{ee} | \Phi^{\text{KS}} \rangle \right)}_{\text{correlation integrand } \mathcal{W}_c^\lambda[n]}$$

- **Scaling** relation\*:

$$E_c^\lambda[n] = \int_0^\lambda d\nu \left( \langle \Psi^\nu | \hat{W}_{ee} | \Psi^\nu \rangle - \langle \Phi^{\text{KS}} | \hat{W}_{ee} | \Phi^{\text{KS}} \rangle \right) = \lambda^2 E_c[n_{1/\lambda}]$$

where  $n_{1/\lambda}$  is the density obtained by **uniform coordinate scaling**:  $n_{1/\lambda}(\mathbf{r}) = (1/\lambda)^3 n(\mathbf{r}/\lambda)$

- Correlation integrand written as a density functional:  $\mathcal{W}_c^\lambda[n] = \frac{\partial E_c^\lambda[n]}{\partial \lambda}$

\*M. Levy and J. P. Perdew, Phys. Rev. B **48**, 11638 (1993).

## Legendre–Fenchel transform

- According to the variational principle, for **any trial potential**  $v(\mathbf{r})$ , the following inequality is fulfilled,

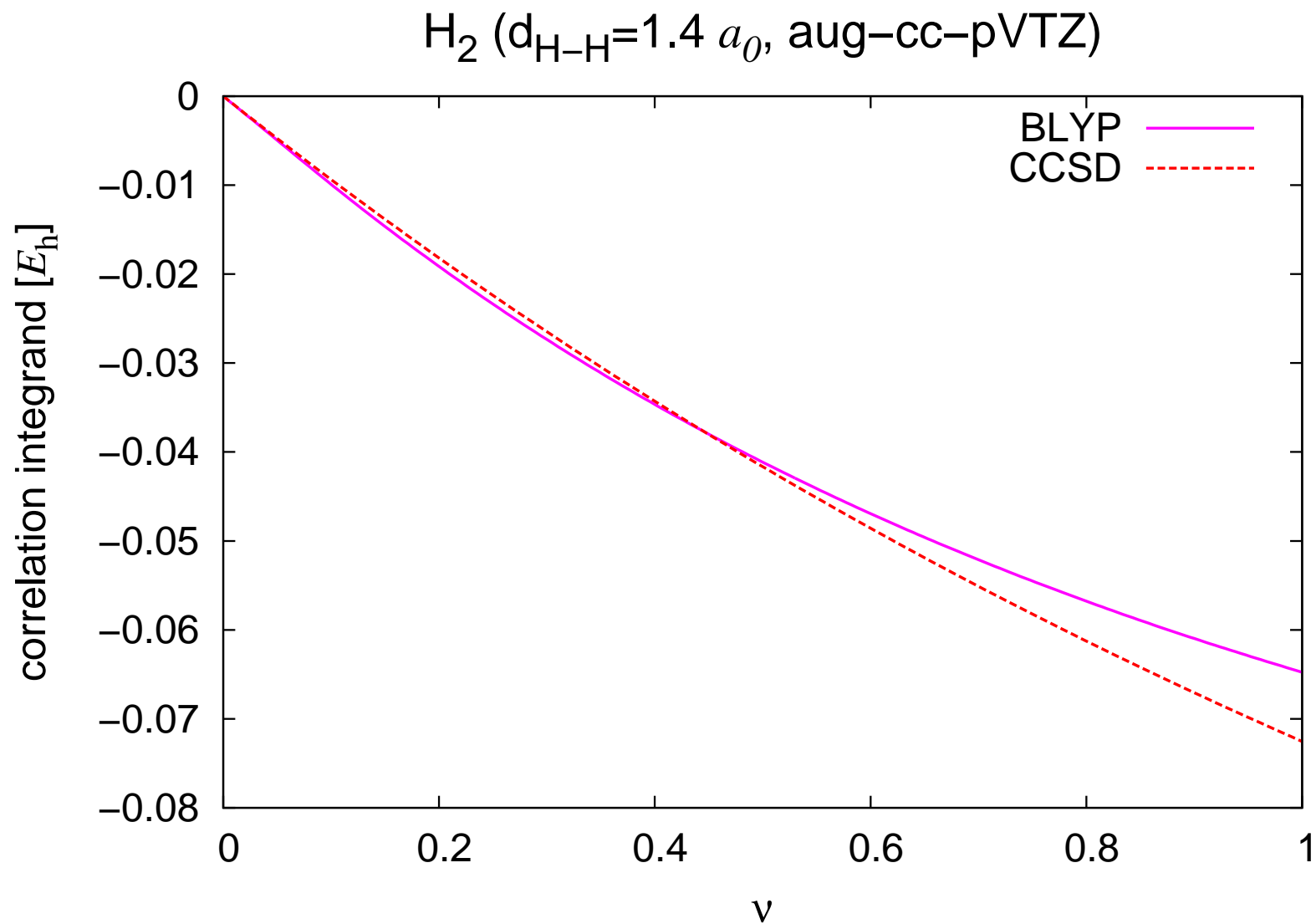
$$\left\langle \Psi^\lambda \left| \hat{T} + \lambda \hat{W}_{ee} + \sum_{i=1}^N v(\mathbf{r}_i) \times \right| \Psi^\lambda \right\rangle \geq \mathcal{E}^\lambda[v]$$

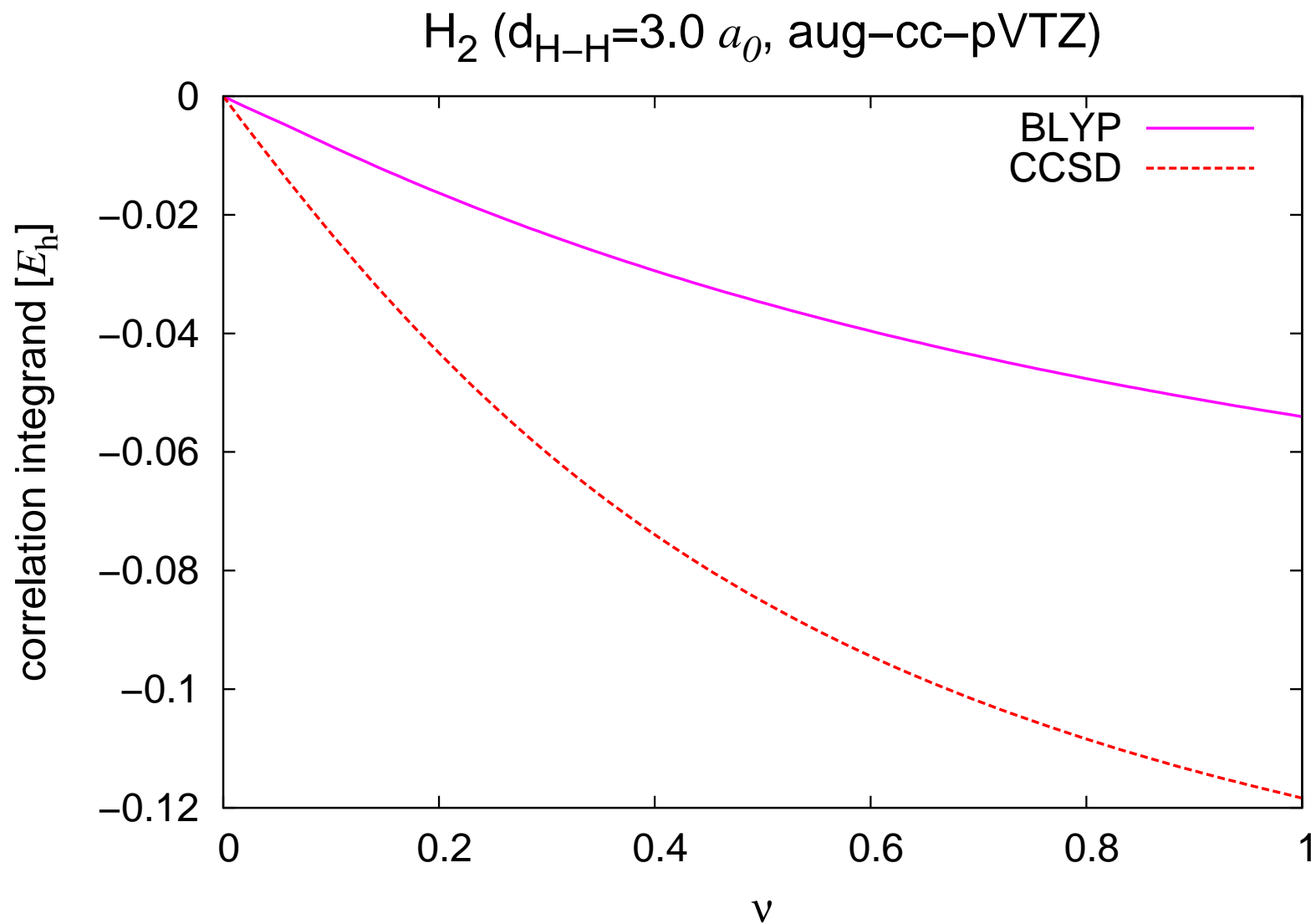
where  $\mathcal{E}^\lambda[v]$  is the ground-state energy of  $\hat{T} + \lambda \hat{W}_{ee} + \sum_{i=1}^N v(\mathbf{r}_i) \times$ , thus leading to

$$F^\lambda[n] = \sup_v \left\{ \mathcal{E}^\lambda[v] - \int d\mathbf{r} v(\mathbf{r})n(\mathbf{r}) \right\}$$

- Note that the **maximizing potential** is  $v^\lambda$ .
- In the particular case  $\lambda = 0$ , the Legendre–Fenchel transform enables to calculate the **exact KS potential**.
- By varying  $\lambda$  in the range  $0 \leq \lambda \leq 1$  we can fully construct the adiabatic connection.







For the *ab initio* calculation (CCSD) of the adiabatic connection see

A.M. Teale, S. Coriani and T. Helgaker, J. Chem. Phys. 130, 104111 (2009).

A.M. Teale, S. Coriani and T. Helgaker, J. Chem. Phys. 132, 164115 (2010).

A.M. Teale, S. Coriani and T. Helgaker, J. Chem. Phys. 133, 164112 (2010).

## Multideterminant density-functional theory

- What about a density-functional theory based on  $\Psi^\lambda$  rather than  $\Phi^{\text{KS}}$  \*?

$$F[n] = F^\lambda[n] + \underbrace{\left( F[n] - F^\lambda[n] \right)}_{\bar{E}_{\text{Hxc}}^\lambda[n]}$$

where 
$$\bar{E}_{\text{Hxc}}^\lambda[n] = \int_\lambda^1 d\nu \frac{dF^\nu[n]}{d\nu} = (1 - \lambda)(E_{\text{H}}[n] + E_{\text{x}}[n]) + E_{\text{c}}[n] - E_{\text{c}}^\lambda[n]$$

- KS-DFT is recovered when  $\lambda = 0$
- For **any normalized wavefunction**  $\Psi$ ,

$$\langle \Psi | \hat{T} + \lambda \hat{W}_{\text{ee}} + \hat{V}_{\text{ne}} | \Psi \rangle + \bar{E}_{\text{Hxc}}^\lambda[n_\Psi] \geq F^\lambda[n_\Psi] + \bar{E}_{\text{Hxc}}^\lambda[n_\Psi] + \int_{\mathbb{R}^3} d\mathbf{r} v_{\text{ne}}(\mathbf{r}) n_\Psi(\mathbf{r}) \geq E_0$$

\*K. Sharkas, J. Toulouse, and A. Savin, J. Chem. Phys. 134, 064113 (2011)

## Comparing wavefunction theory with multideterminant DFT

$$\bullet E_0 = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \Psi \rangle \right\} = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \lambda \hat{W}_{\text{ee}} + \hat{V}_{\text{ne}} | \Psi \rangle + \bar{E}_{\text{Hxc}}^{\lambda}[n_{\Psi}] \right\}$$

↓

$$\Psi = \underbrace{\Phi_{\text{HF}} + \sum_k C_k \text{det}_k}_{\text{multideterminantal wave function}}$$

multideterminantal wave function

↓

$$\Psi = \underbrace{\Phi_{\text{HF}}^{\lambda} + \sum_k C_k^{\lambda} \text{det}_k^{\lambda}}_{\text{multideterminantal character induced by } \lambda \hat{W}_{\text{ee}}}$$

multideterminantal character induced by  $\lambda \hat{W}_{\text{ee}}$

- Applying **MP2** in this context<sup>1,2,3</sup> leads to the rationalization of semi-empirical **double hybrid DFT** methods as initially proposed by Grimme<sup>4</sup>.

<sup>1</sup>K. Sharkas, J. Toulouse, and A. Savin, J. Chem. Phys. 134, 064113 (2011)

<sup>2</sup>E. Fromager, J. Chem. Phys. 135, 244106 (2011).

<sup>3</sup>Y. Cornaton, O. Franck, A. M. Teale, and E. Fromager, Mol. Phys. 111, 1275 (2013)

<sup>4</sup>S. Grimme, J. Chem. Phys. 124, 034108 (2006)