State-averaged multi-determinant density-functional theory based on ensembles and range separation

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Institut de Chimie de Strasbourg - Laboratoire de Chimie Quantique - Université de Strasbourg /CNRS

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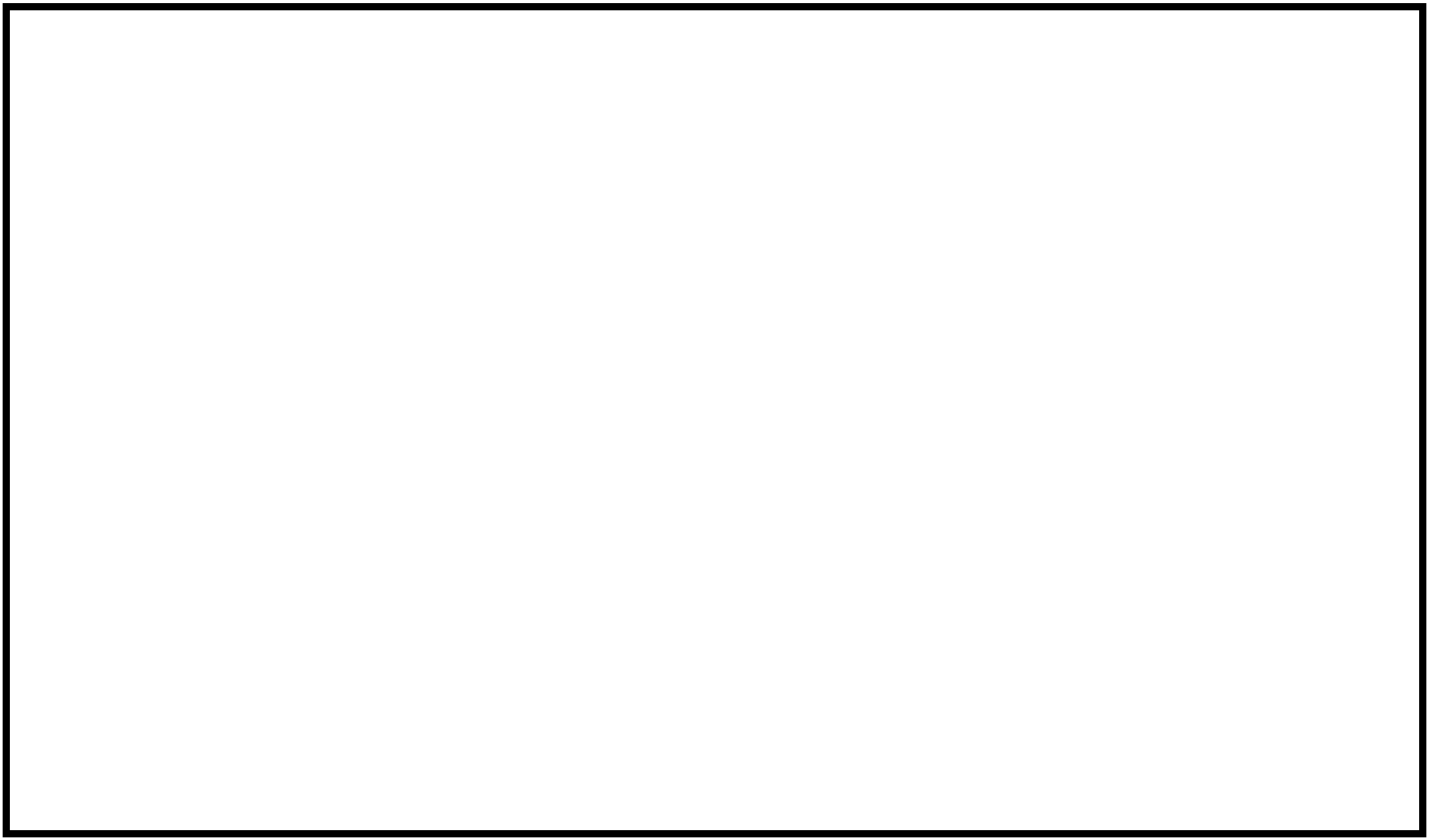


Collaborators

- Hans Jørgen Aa. Jensen *(Odense, Denmark)*
- Stefan Knecht *(ETH, Zürich, Switzerland)*
- Bruno Senjean *(master student, Strasbourg, France)*

- Exact range-separated energy expression (*Savin*):

$$E_0 = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} + \hat{V}_{\mathrm{ne}} | \Psi \rangle + E_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n_\Psi] \right\}$$

- The minimizing wavefunction Ψ_0^μ is the ground state of a long-range interacting system whose density equals the exact ground-state density n_0.
- Ψ_0^μ fulfils the self-consistent equation

$$\left(\hat{T} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} + \hat{V}_{\mathrm{ne}} + \int d\mathbf{r} \, \frac{\delta E_{\mathrm{Hxc}}^{\mathrm{sr},\mu}}{\delta n(\mathbf{r})}[n_{\Psi_0^\mu}] \, \hat{n}(\mathbf{r}) \right) |\Psi_0^\mu\rangle = \mathcal{E}_0^\mu |\Psi_0^\mu\rangle$$

- standard KS-DFT is recovered when $\mu = 0$
- pure WFT is recovered when $\mu \to +\infty$

- Short-range functionals: srLDA, srPBE, ... (*Savin, Toulouse, Gori-Giorgi, Stoll, Goll, Scuseria, ...*)
- Long-range wave function calculation: HF-srDFT, MC-srDFT, FCI-srDFT, ...

- What about the **excited states** ?
- The spectrum $\{\mathcal{E}_i^\mu\}_{i=0,1,\ldots}$ of the long-range interacting Hamiltonian

$$\hat{H}^\mu = \hat{T} + \hat{W}_{\rm ee}^{\rm lr,\mu} + \hat{V}_{\rm ne} + \int d\mathbf{r}\, \frac{\delta E_{\rm Hxc}^{\rm sr,\mu}}{\delta n(\mathbf{r})}[n_0]\, \hat{n}(\mathbf{r})$$

is connected with the true physical spectrum $\{E_i\}_{i=0,1,\ldots}$ since $\mathcal{E}_i^\mu \to E_i$ when $\mu \to +\infty$

- How can we make this connection more explicit ?
- Interpolation techniques [E. Rebolini *et al.*, Phys. Rev. A 91, 032519 (2015)]
- Time-dependent adiabatic **linear response** theory*:

$$\left(\hat{T} + \hat{W}_{\rm ee}^{\rm lr,\mu} + \hat{V}_{\rm ne} + \int d\mathbf{r} \left[\frac{\delta E_{\rm Hxc}^{\rm sr,\mu}}{\delta n(\mathbf{r})}[n_{\Psi^\mu(t)}] + \delta v(\mathbf{r},t)\right] \hat{n}(\mathbf{r})\right) |\Psi^\mu(t)\rangle = \mathrm{i}\frac{\partial}{\partial t}|\Psi^\mu(t)\rangle$$

$$\downarrow$$

time-dependent **perturbation**

*E. Fromager, S. Knecht, and H.J. Aa. Jensen, J. Chem. Phys. 138, 084101 (2013).

- Perturbation expansion of the density and the short-range DFT potential: $n_{\Psi^\mu(t)} = n_0 + \delta n(t)$,

$$\left(\hat{T} + \hat{W}_{\rm ee}^{\rm lr,\mu} + \hat{V}_{\rm ne} + \int d\mathbf{r}\, \frac{\delta E_{\rm Hxc}^{\rm sr,\mu}}{\delta n(\mathbf{r})}[n_0]\, \hat{n}(\mathbf{r}) \quad \longleftarrow \quad \boxed{\hat{H}^\mu} \right.$$

$$\left. + \int d\mathbf{r} \left[\int d\mathbf{r}' \, \underbrace{\frac{\delta^2 E_{\rm Hxc}^{\rm sr,\mu}}{\delta n(\mathbf{r}')\delta n(\mathbf{r})}[n_0]}_{\downarrow} \delta n(\mathbf{r}',t) + \ldots + \delta v(\mathbf{r},t) \right] \hat{n}(\mathbf{r}) \right) |\Psi^\mu(t)\rangle = \mathrm{i}\frac{\partial}{\partial t}|\Psi^\mu(t)\rangle$$

short-range kernel

- Sum over states expression for the first excitation energy (within the Tamm–Dancoff approximation)

$$\omega \approx \mathcal{E}_1^\mu - \mathcal{E}_0^\mu + \int\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\delta^2 E_{\rm Hxc}^{\rm sr,\mu}[n_0]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})} n_{01}^\mu(\mathbf{r}') n_{01}^\mu(\mathbf{r})$$

$$+ \int\int\int\int \mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r}_\mathbf{1}'\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\delta^2 E_{\rm Hxc}^{\rm sr,\mu}[n_0]}{\delta n(\mathbf{r}_\mathbf{1}')\delta n(\mathbf{r_1})} \frac{\delta^2 E_{\rm Hxc}^{\rm sr,\mu}[n_0]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})} n_{01}^\mu(\mathbf{r}) n_{01}^\mu(\mathbf{r}_\mathbf{1}') \sum_{i>1} \frac{n_{0i}^\mu(\mathbf{r_1}) n_{0i}^\mu(\mathbf{r}')}{\mathcal{E}_1^\mu - \mathcal{E}_i^\mu} + \ldots$$

Ensemble DFT

- Variational principle for an equi-ensemble (*Theophilou*): if Ψ and Ψ' are orthonormal then

$$\langle\Psi|\hat{H}|\Psi\rangle + \langle\Psi'|\hat{H}|\Psi'\rangle \geq E_0 + E_1$$

- Generalization: for a given ensemble weight w,

$$(1-w)\langle\Psi|\hat{H}|\Psi\rangle + w\langle\Psi'|\hat{H}|\Psi'\rangle = (1-2w)\underbrace{\langle\Psi|\hat{H}|\Psi\rangle}_{\geq E_0} + w\Big(\underbrace{\langle\Psi|\hat{H}|\Psi\rangle + \langle\Psi'|\hat{H}|\Psi'\rangle}_{\geq E_0 + E_1}\Big)$$

- *Gross-Oliveira-Kohn* variational principle:

$$\boxed{\text{for } 0 \leq w \leq 1/2, \qquad (1-w)\langle\Psi|\hat{H}|\Psi\rangle + w\langle\Psi'|\hat{H}|\Psi'\rangle \geq E^w}$$

where E^w is the exact ensemble energy: $E^w = (1-w)E_0 + wE_1 \quad \rightarrow \quad \omega = \dfrac{\mathrm{d}E^w}{\mathrm{d}w} = E_1 - E_0$

- E^w is a functional of the ensemble density $n^w = (1-w)n_0 + wn_1$

Range-separated ensemble DFT

- **Exact range-separated** expression for the ensemble energy [Pastorczak *et al.* PRA **87**, 062501 (2013)]:

$$E^w = (1-w)\langle\Psi_0^{\mu,w}|\hat{T} + \hat{W}_{\rm ee}^{\rm lr,\mu} + \hat{V}_{\rm ne}|\Psi_0^{\mu,w}\rangle + w\langle\Psi_1^{\mu,w}|\hat{T} + \hat{W}_{\rm ee}^{\rm lr,\mu} + \hat{V}_{\rm ne}|\Psi_1^{\mu,w}\rangle + E_{\rm Hxc}^{\rm sr,\mu,w}[n^w],$$

where the auxiliary ground- and first-excited wavefunctions fulfil the **self-consistent** equation

$$\left(\hat{T} + \hat{W}_{\rm ee}^{\rm lr,\mu} + \hat{V}_{\rm ne} + \int {\rm d}\mathbf{r}\,\frac{\delta E_{\rm Hxc}^{\rm sr,\mu,w}[n^w]}{\delta n(\mathbf{r})}\hat{n}(\mathbf{r})\right)|\Psi_i^{\mu,w}\rangle = \mathcal{E}_i^{\mu,w}|\Psi_i^{\mu,w}\rangle, \qquad i = 0, 1$$

and reproduce the **exact ensemble density** $n^w = (1-w)n_{\Psi_0^{\mu,w}} + w\, n_{\Psi_1^{\mu,w}}$

- Exact range-separated **excitation energy**:

$$\boxed{\omega = \mathcal{E}_1^{\mu,w} - \mathcal{E}_0^{\mu,w} + \left.\frac{\partial E_{\rm xc}^{\rm sr,\mu,w}[n]}{\partial w}\right|_{n=n^w}}$$

O. Franck and E. Fromager, *Mol. Phys.* **112**, 1684 (2014).

Range-separated ensemble DFT

- Connection with time-dependent linear response theory: in the $w \to 0$ limit,

$$\boxed{\omega = \mathcal{E}_1^\mu - \mathcal{E}_0^\mu + \left.\frac{\partial E_{\rm xc}^{{\rm sr},\mu,w}[n_0]}{\partial w}\right|_{w=0}}$$

- Derivative discontinuity* Δ: if the first excitation is a single excitation then, in the $\mu = 0$ limit,

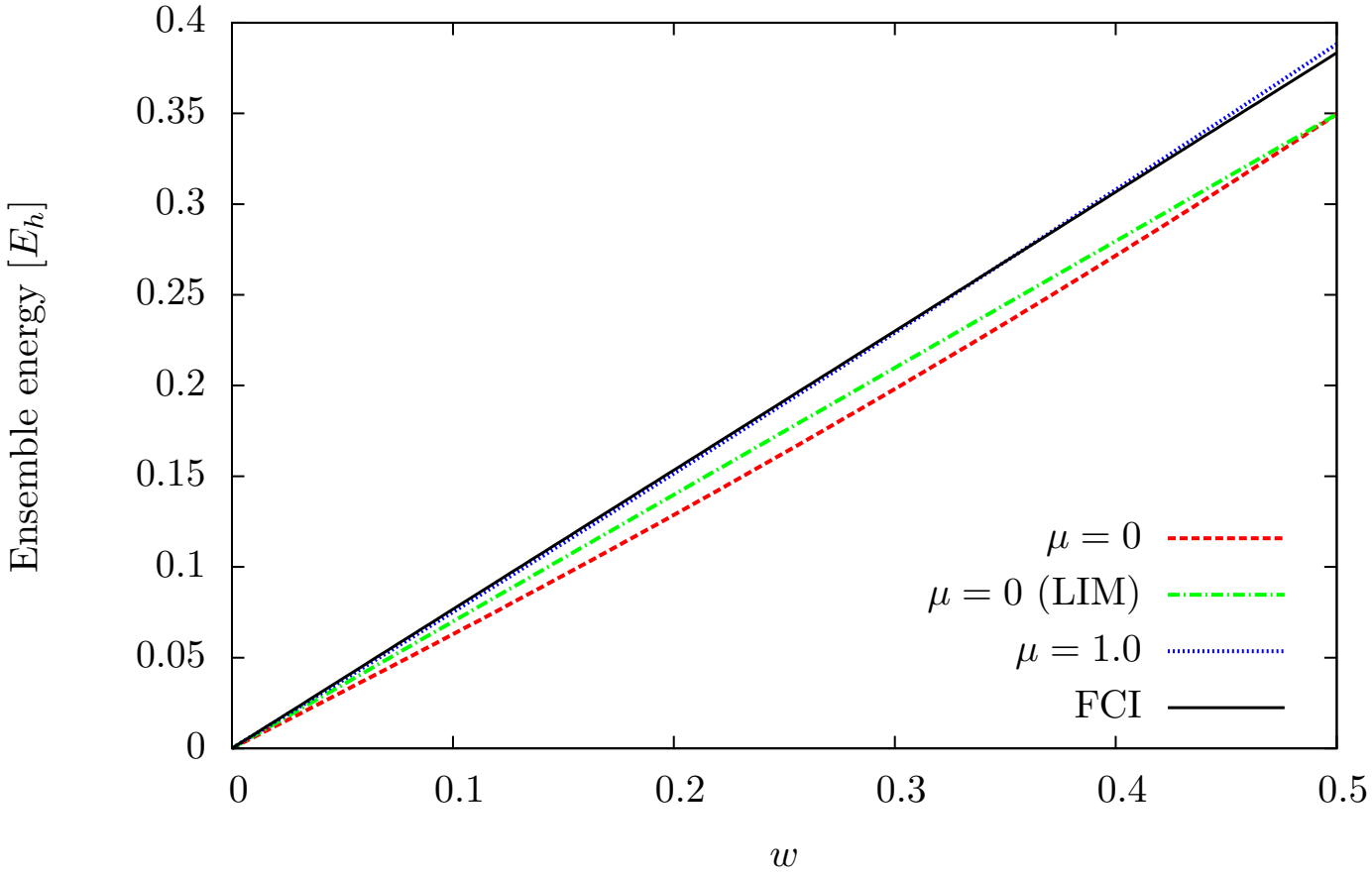
$$\omega = \left(\varepsilon_{\rm L} + \Delta_{\rm xc}\right) - \varepsilon_{\rm H} \qquad \text{where} \qquad \Delta_{\rm xc} = \left.\frac{\partial E_{\rm xc}^{w}[n_0]}{\partial w}\right|_{w=0}$$

- From now on we shall refer to $\Delta_{\rm xc}^{\mu,w} = \left.\frac{\partial E_{\rm xc}^{{\rm sr},\mu,w}[n]}{\partial w}\right|_{n=n^w}$ as the short-range derivative discontinuity (DD).

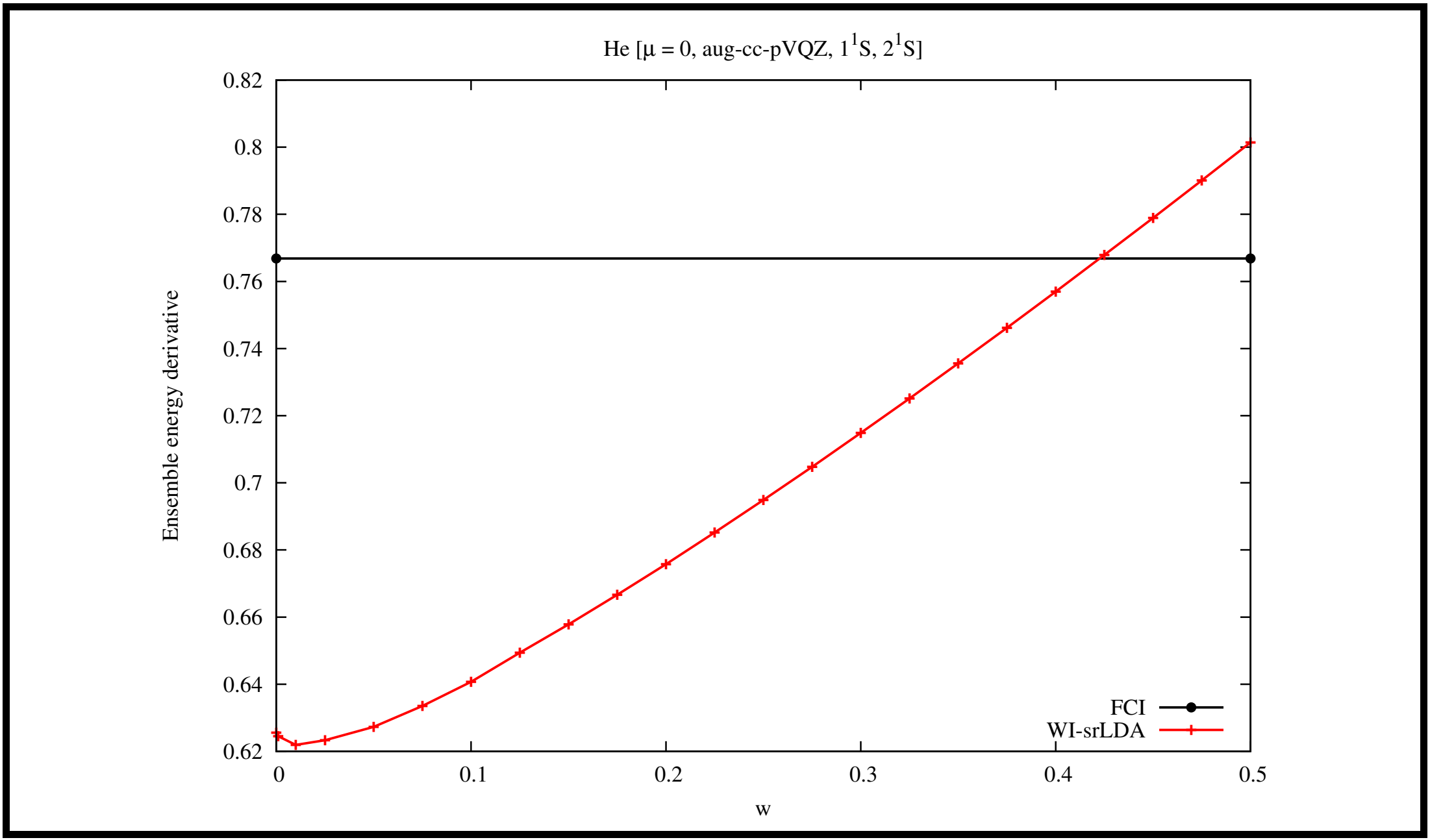
*M.Levy, *Phys. Rev. A* **52**, R4313 (1995).

He[$1^1S, 2^1S$], srLDA, aug-cc-pVQZ

Weight-independent density-functional approximation (WIDFA): $E_{\rm Hxc}^{{\rm sr},\mu,w}[n] \rightarrow E_{\rm Hxc}^{{\rm sr},\mu}[n]$,



B. Senjean, S. Knecht, H. J. Aa. Jensen, and E. Fromager, **arXiv:1504.06477** (2015)


He [μ = 0, aug-cc-pVQZ, 1^1S, 2^1S]
Ensemble energy derivative
0.82
0.8
0.78
0.76
0.74
0.72
0.7
0.68
0.66
0.64
0.62
0
0.1
0.2
0.3
0.4
0.5
w
FCI
WI-srLDA

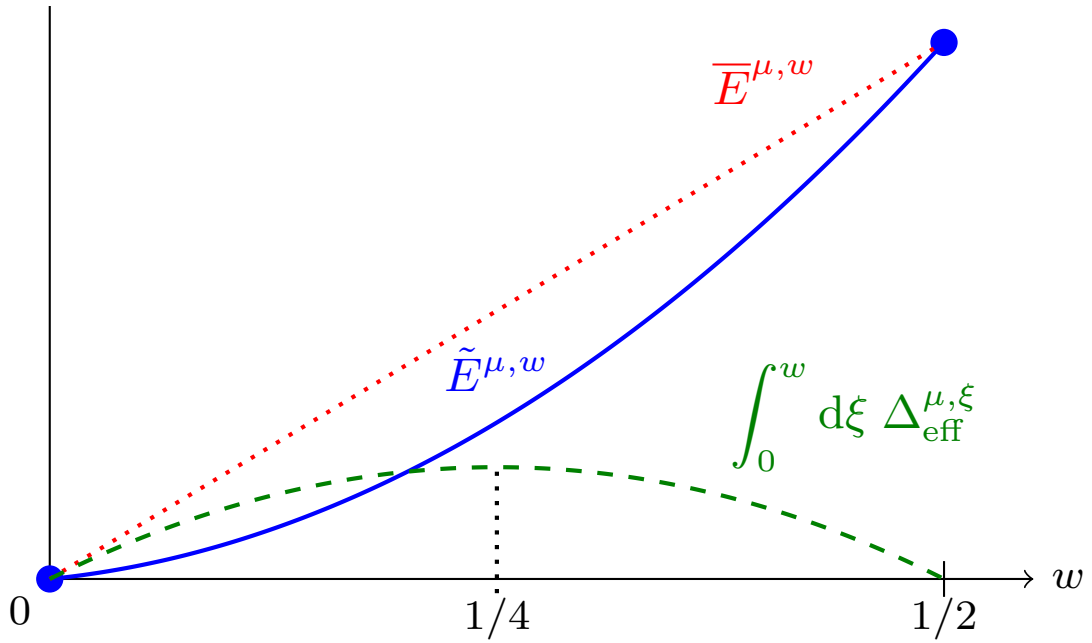
Linear interpolation method (LIM)

- In the exact theory: $2(E^{w=1/2} - E_0) = \omega = \dfrac{\mathrm{d}E^w}{\mathrm{d}w}$
- The WIDFA ensemble energy $\tilde{E}^w$ has curvature
- There is no clear definition for the WIDFA excitation energy from $\boxed{\mathrm{d}\tilde{E}^w/\mathrm{d}w = \tilde{\mathcal{E}}_1^w - \tilde{\mathcal{E}}_0^w = \Delta\tilde{\mathcal{E}}^w}$
- On the other hand we have $\boxed{\omega_{\mathrm{LIM}} = 2(\tilde{E}^{w=1/2} - E_0)}$ that can be chosen as excitation energy,

  by analogy with the fundamental gap problem *

T. Stein, J. Autschbach, N. Govind, L. Kronik, and R. Baer, *J. Phys. Chem. Lett.* **3**, 3740 (2012).

Linear interpolation method (LIM)

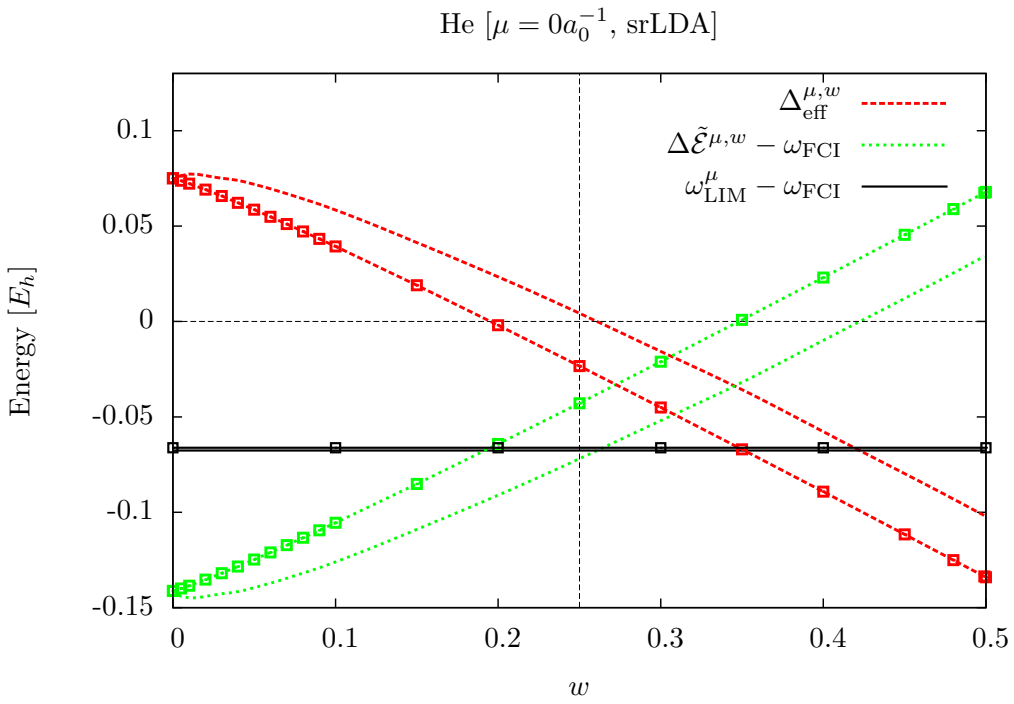


$$\underbrace{E_0 + 2w\left(\tilde{E}^{w=1/2} - E_0\right)}_{\downarrow\ \overline{E}^{w}} = \tilde{E}^{w} + \underbrace{\int_0^w \mathrm{d}\xi\ \Delta_{\mathrm{eff}}^{\xi}}_{\downarrow\ \text{curvature correction}} \quad \Rightarrow \quad \underbrace{2(\tilde{E}^{w=1/2} - E_0)}_{\downarrow\ \text{excitation energy}} = \tilde{\mathcal{E}}_1^{w} - \tilde{\mathcal{E}}_0^{w} + \underbrace{\Delta_{\mathrm{eff}}^{w}}_{\downarrow\ \text{effective DD}}$$

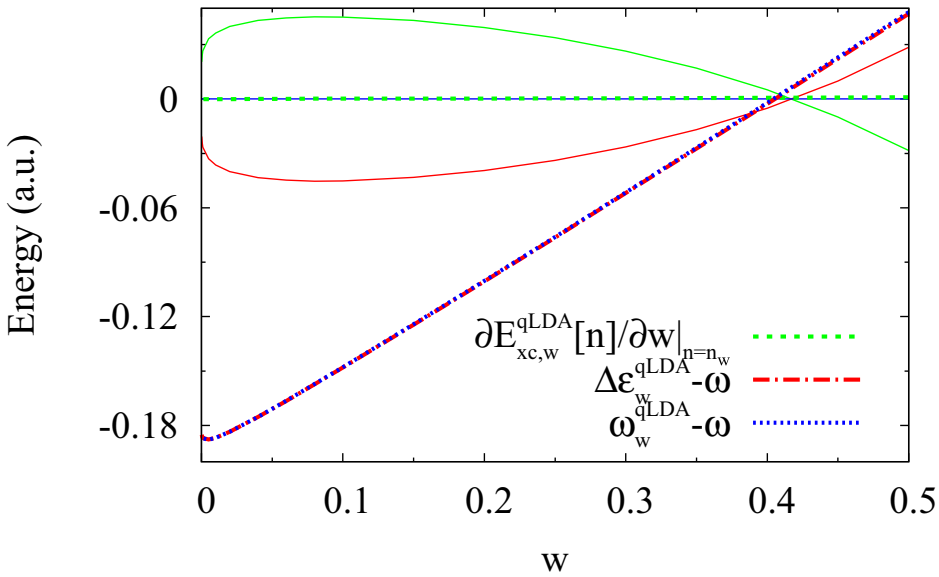
B. Senjean, S. Knecht, H. J. Aa. Jensen, and E. Fromager, **arXiv:1504.06477** (2015)

GOK-LDA ($\mu = 0$) effective DD in He [$1^1S \rightarrow 2^1S$]

□, □ : no self-consistency

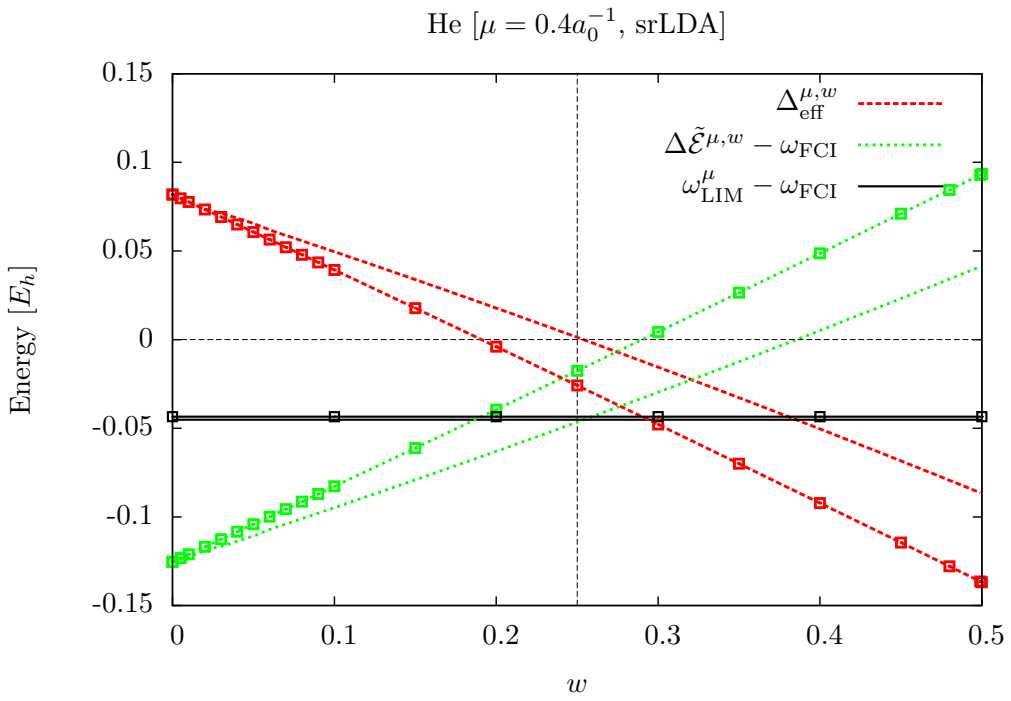


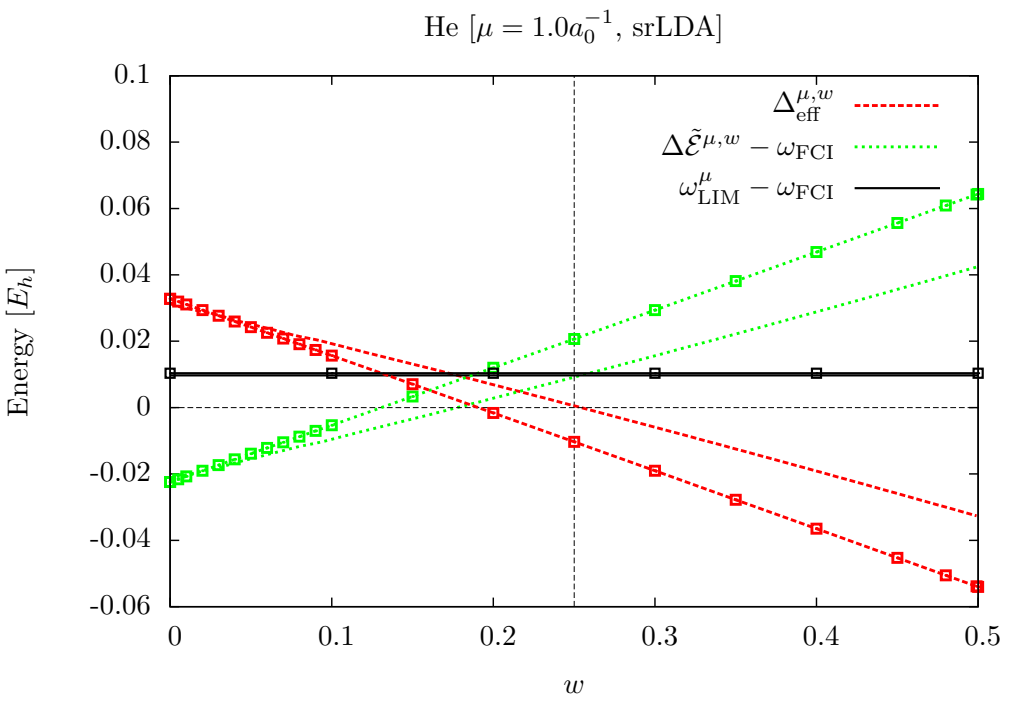
B. Senjean *et al.* **arXiv:1504.06477** (2015).



Z-h. Yang *et al.*, Phys. Rev. A 90, 042501 (2014).

□, □ : no self-consistency





B. Senjean, S. Knecht, H. J. Aa. Jensen, and E. Fromager, **arXiv:1504.06477** (2015)

Comparing LIM with adiabatic linear response theory

- **Taylor expansion** for the LIM excitation energy:

$$\omega_{\text{LIM}} \approx \mathcal{E}_1^\mu - \mathcal{E}_0^\mu + \frac{1}{4}\int\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\delta^2 E_{\text{Hxc}}^{\text{sr},\mu}[n_0]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})} \left(n_{\Psi_1^\mu}(\mathbf{r}') - n_0(\mathbf{r}')\right)\left(n_{\Psi_1^\mu}(\mathbf{r}) - n_0(\mathbf{r})\right)$$

$$+\frac{1}{2}\int\int\int\int \mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r}_\mathbf{1}'\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\delta^2 E_{\text{Hxc}}^{\text{sr},\mu}[n_0]}{\delta n(\mathbf{r}_\mathbf{1}')\delta n(\mathbf{r_1})} \frac{\delta^2 E_{\text{Hxc}}^{\text{sr},\mu}[n_0]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})} \left(n_{\Psi_1^\mu}(\mathbf{r}) - n_0(\mathbf{r})\right)\left(n_{\Psi_1^\mu}(\mathbf{r}_\mathbf{1}') - n_0(\mathbf{r}_\mathbf{1}')\right)$$

$$\times \sum_{i\geq 1} \frac{n_{0i}^\mu(\mathbf{r_1}) n_{0i}^\mu(\mathbf{r}')}{\mathcal{E}_0^\mu - \mathcal{E}_i^\mu} + \dots.$$

- To be compared with the expression from time-dependent adiabatic **linear response** theory ...

$$\omega \approx \mathcal{E}_1^\mu - \mathcal{E}_0^\mu + \int\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\delta^2 E_{\text{Hxc}}^{\text{sr},\mu}[n_0]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})} n_{01}^\mu(\mathbf{r}') n_{01}^\mu(\mathbf{r})$$

$$+\int\int\int\int \mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r}_\mathbf{1}'\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\delta^2 E_{\text{Hxc}}^{\text{sr},\mu}[n_0]}{\delta n(\mathbf{r}_\mathbf{1}')\delta n(\mathbf{r_1})} \frac{\delta^2 E_{\text{Hxc}}^{\text{sr},\mu}[n_0]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})} n_{01}^\mu(\mathbf{r}) n_{01}^\mu(\mathbf{r}_\mathbf{1}') \sum_{i>1} \frac{n_{0i}^\mu(\mathbf{r_1}) n_{0i}^\mu(\mathbf{r}')}{\mathcal{E}_1^\mu - \mathcal{E}_i^\mu} + \dots$$

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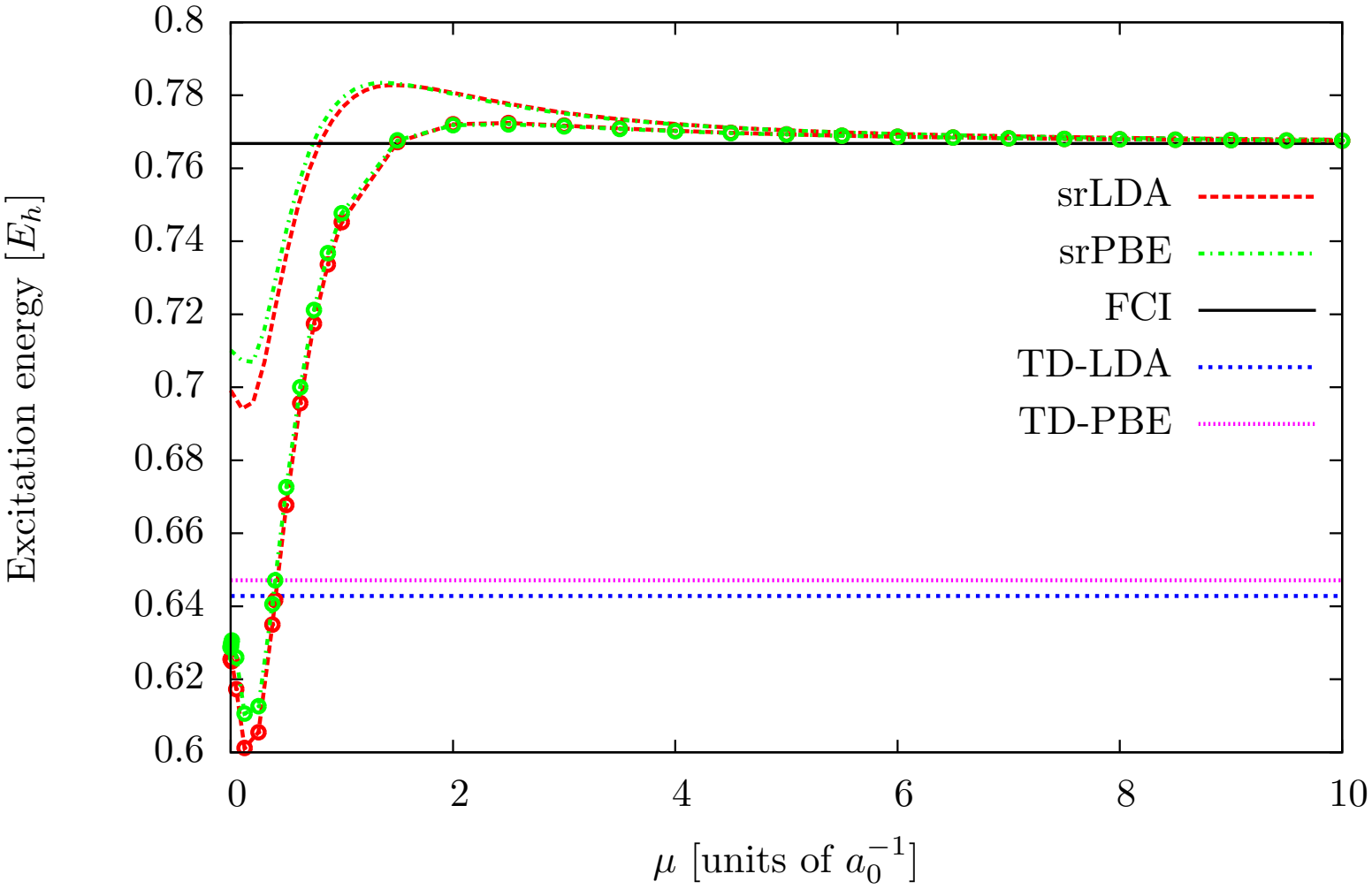
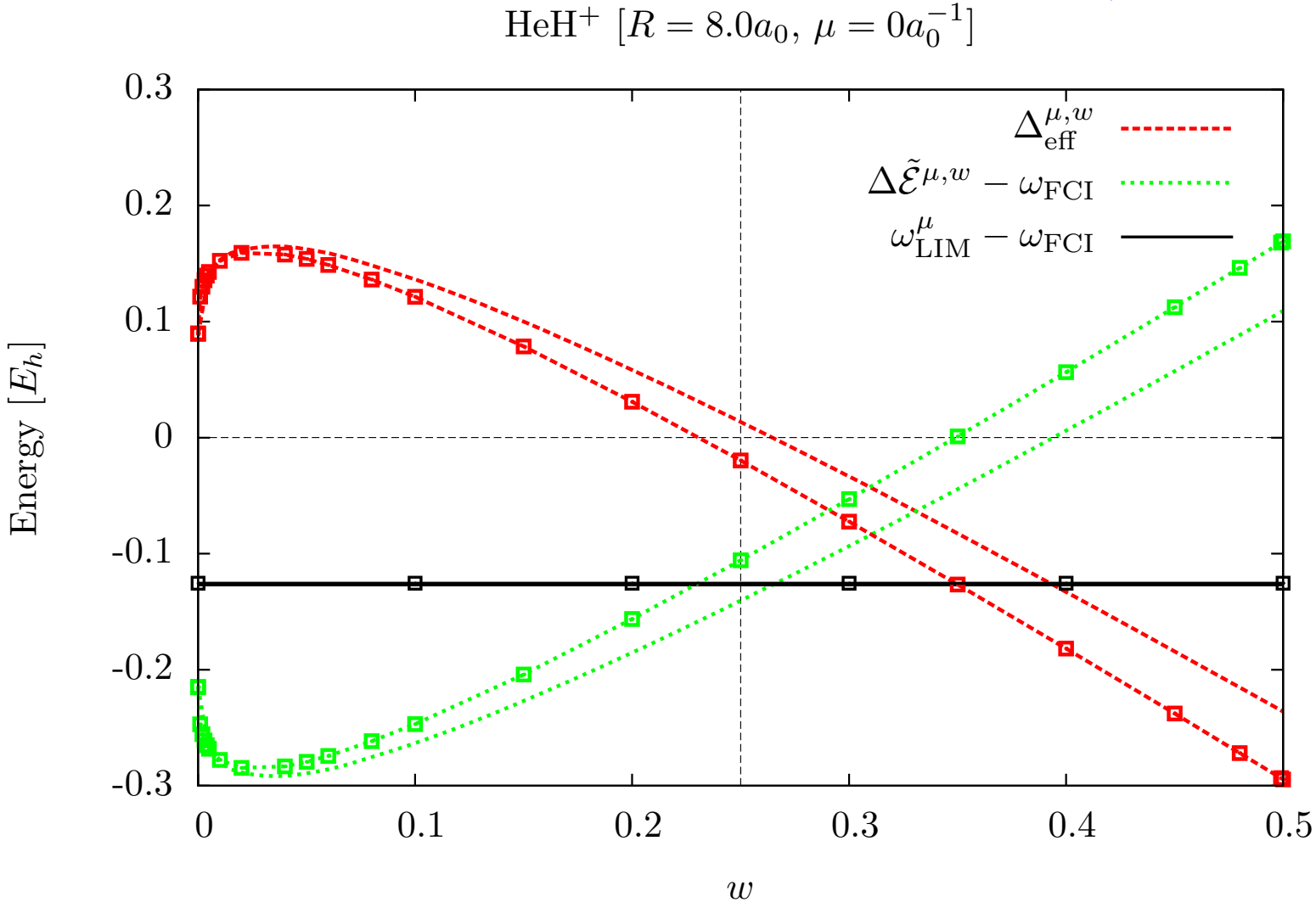
$1^1S \rightarrow 2^1S$



B. Senjean, S. Knecht, H. J. Aa. Jensen, and E. Fromager, **arXiv:1504.06477** (2015).

$1^1\Sigma^+ \rightarrow 2^1\Sigma^+$

□, □ : no self-consistency



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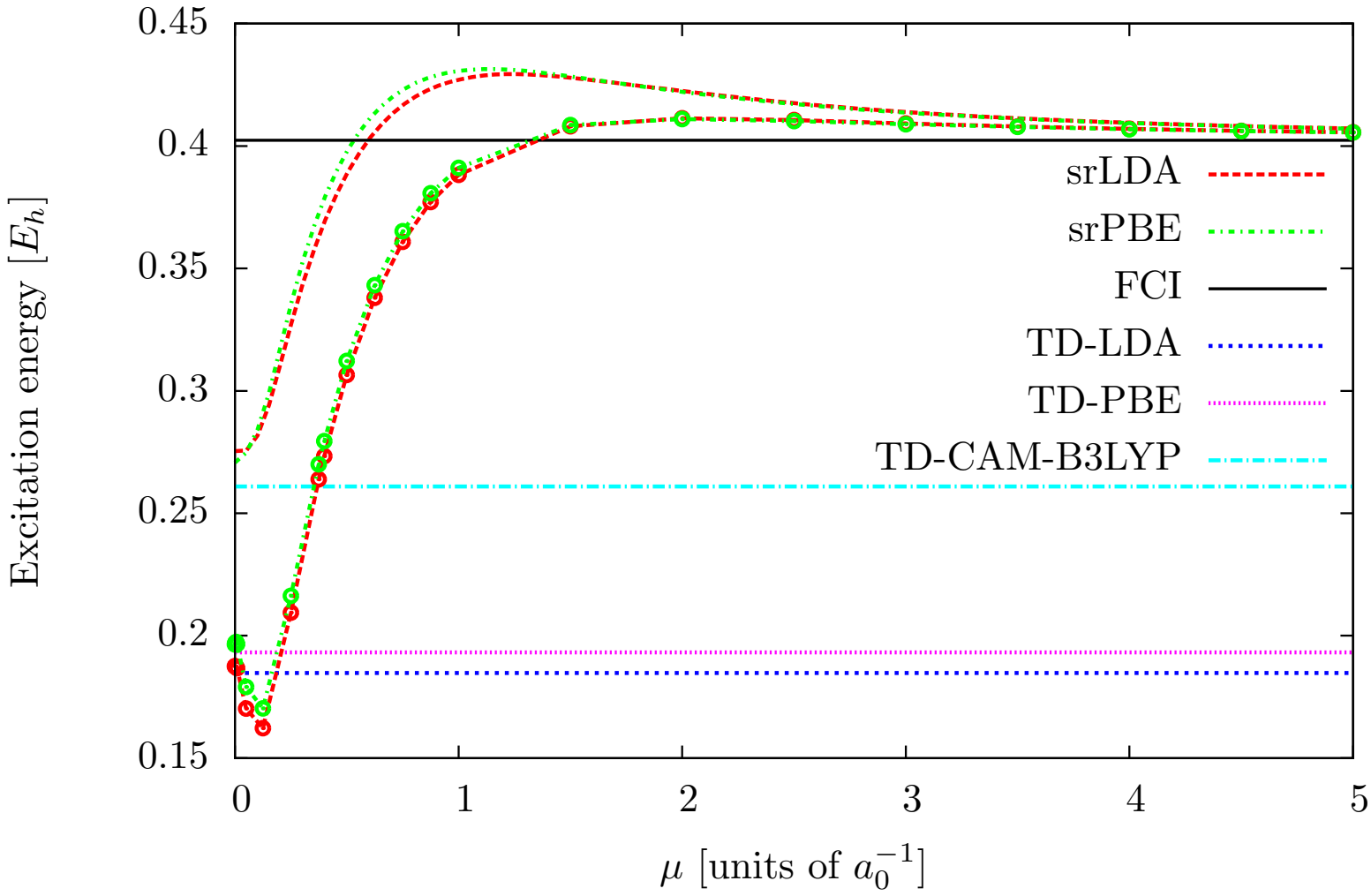
$1^1\Sigma^+ \rightarrow 2^1\Sigma^+$

HeH^+ $[R = 8.0a_0]$

$\circ, \circ$: $\mathcal{E}_1^\mu - \mathcal{E}_0^\mu$

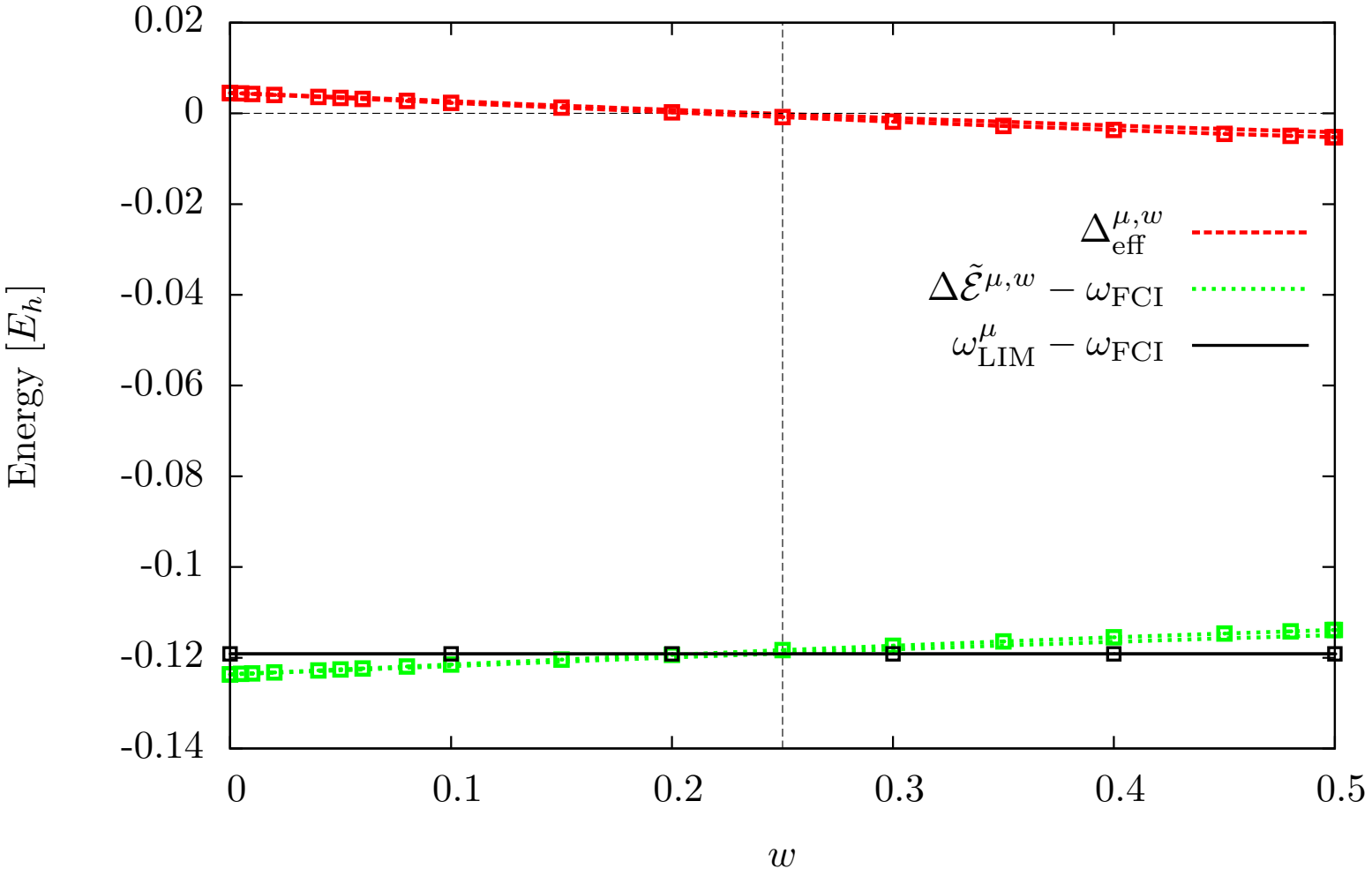


B. Senjean, S. Knecht, H. J. Aa. Jensen, and E. Fromager, **arXiv:1504.06477** (2015).

$1^1\Sigma_g^+ \rightarrow 2^1\Sigma_g^+$

H_2 $[R = 3.7a_0,\ \mu = 0a_0^{-1}]$

□, □ : no self-consistency

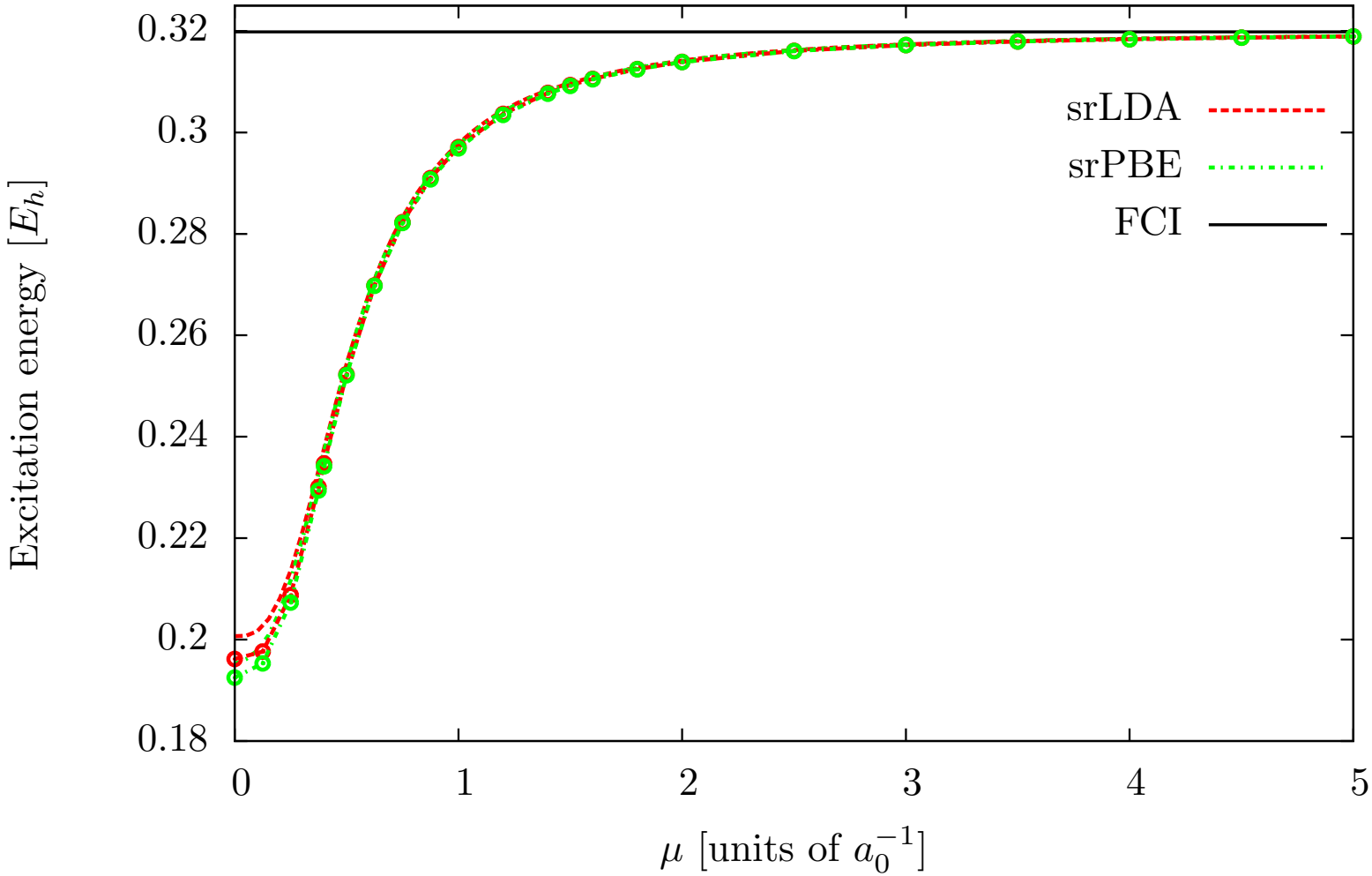


B. Senjean, S. Knecht, H. J. Aa. Jensen, and E. Fromager, **arXiv:1504.06477** (2015).

$1^1\Sigma_g^+ \rightarrow 2^1\Sigma_g^+$

H_2 $[R = 3.7a_0]$

$\circ, \circ$: $\mathcal{E}_1^\mu - \mathcal{E}_0^\mu$



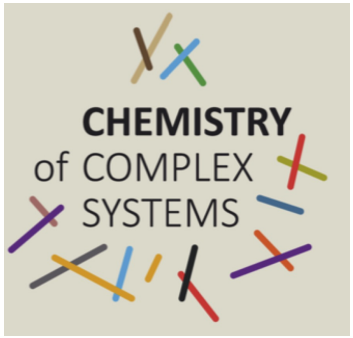
B. Senjean, S. Knecht, H. J. Aa. Jensen, and E. Fromager, **arXiv:1504.06477** (2015).

Reference data: E. Rebolini, J. Toulouse, A. M. Teale, T. Helgaker, and A. Savin, J. Chem. Phys. 141, 044123 (2014).

Conclusions and outlook

- Multi-determinant range-separated DFT can be extended to excited states within the time-independent regime (ensembles).
- Self-consistent implementation at the long-range FCI level in the DALTON program package.
- Long-term project: use state-averaged CASSCF rather than FCI $\rightarrow$ state-averaged CASDFT method !
- The linear interpolation method (LIM) gives very promising results for single excitations (including charge transfer) already at the GOK-DFT level ($\mu = 0$).
- It is worth using LIM rather than the (ground-state density-functional) auxiliary excitation energy when $\mu \leq 1$.
- LIM can be extended to higher excitations (linear interpolations between equiensembles up the multiplet of interest)
- Need for weight-dependent density-functional approximations, especially for modeling double excitations. Model systems like electrons on a ring (*Gill, Loos*) are currently investigated.

Funding



- LabEx "Chimie des Systèmes Complexes"

  project title: "Multi-configuration density-functional theories for excited states"

- ANR jeune chercheur (**MCFUNEX** project)

Opening of a PhD position (application deadline: June 12, 2015)