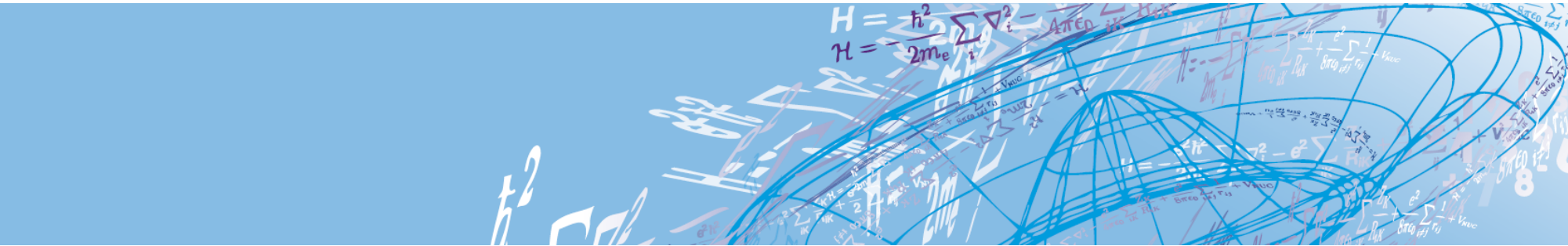
Calculating Excitation Energies Along the Range-Separated Adiabatic Connection

Elisa Rebolini

Center for Computational and Theoretical Chemistry – University of Oslo

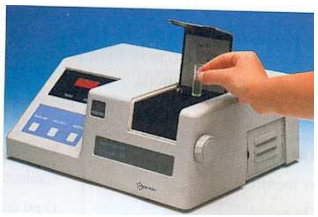
Workshop on "Advances in electronic structure theory", April 29, 2015

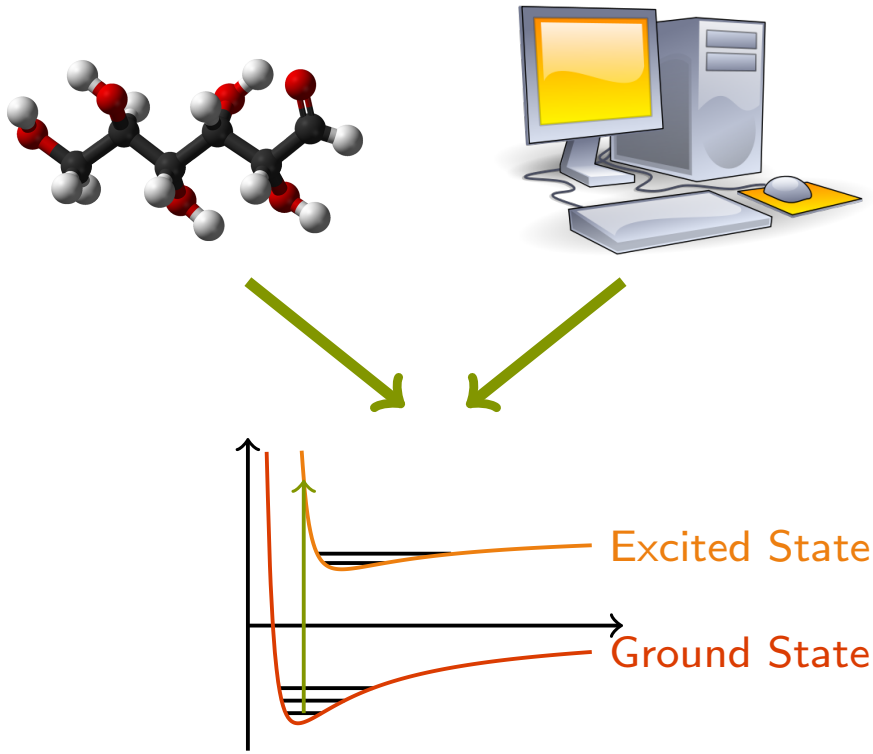


Motivation







Criteria for a "good" method

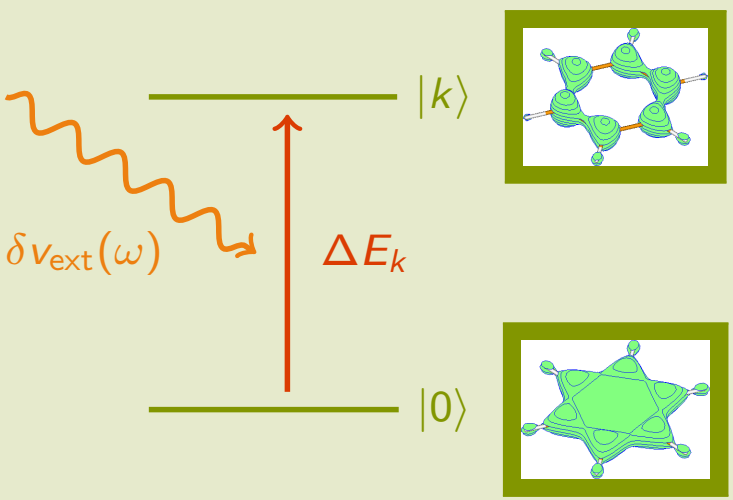
- Computational cost
- Accuracy
- User-friendliness

Frequency-Dependent Density

$$n(\mathbf{r}) \rightsquigarrow n(\mathbf{r}, \omega)$$

Linear Response

External perturbation $\delta v_{\text{ext}}(\omega)$



Linear Response Time-Dependent Density Functional Theory (TDDFT)

Frequency-Dependent Density

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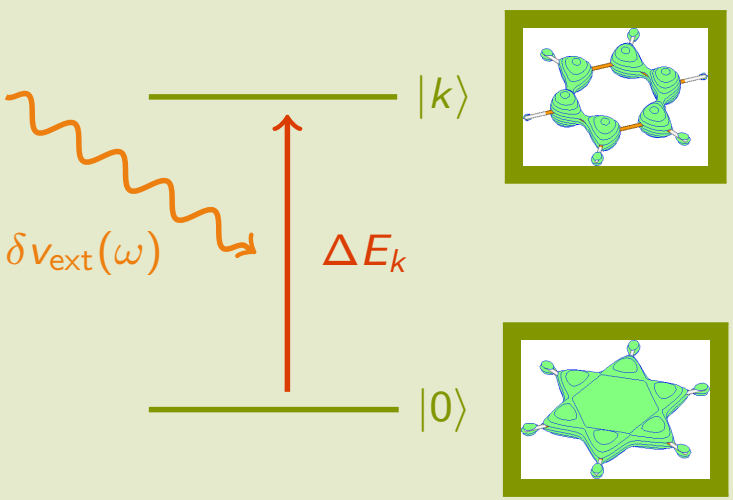

Response Function

$$\delta n(\mathbf{r},\omega) = \int \chi(\mathbf{r},\mathbf{r}',\omega)\delta v_{\text{ext}}(\mathbf{r}',\omega)d\mathbf{r}'$$

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \frac{\delta n(\mathbf{r},\omega)}{\delta v_{\text{ext}}(\mathbf{r}',\omega)}$$

Sum-Over-State Representation

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \sum_{k\neq 0} \frac{\langle 0|\hat{n}(\mathbf{r})|k\rangle\langle k|\hat{n}(\mathbf{r}')|0\rangle}{\omega - \Delta E_k} + \text{c.c.}$$

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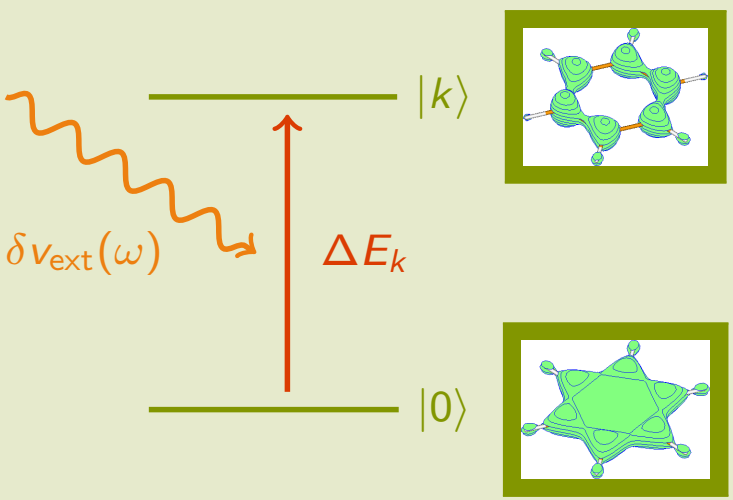

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Inverse Response Function and Excitation Energies

$$\chi(\mathbf{r},\mathbf{r}',\omega)^{-1} = \frac{\delta v_{\text{ext}}(\mathbf{r},\omega)}{\delta n(\mathbf{r}',\omega)} \qquad \text{such that} \qquad \chi(\mathbf{r},\mathbf{r}',\omega = \Delta E_k)^{-1} = 0$$

Usual Approximations

TDDFT Kernel

Within the Kohn-Sham Formalism:

$$\chi(\mathbf{r},\mathbf{r}',\omega)^{-1} = \underbrace{\chi^{\mathrm{KS}}(\mathbf{r},\mathbf{r}',\omega)^{-1}}_{\text{non-interacting}} - \underbrace{f_{\mathrm{Hxc}}(\mathbf{r},\mathbf{r}',\omega)}_{\text{kernel}}$$

$$f_{\mathrm{Hxc}}(\mathbf{r},\mathbf{r}',\omega) \xrightarrow[\text{Approximation}]{\text{Adiabatic}} f_{\mathrm{Hxc}}(\mathbf{r},\mathbf{r}') = \frac{\delta^2 E_{\mathrm{Hxc}}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} \xrightarrow[\text{Approximation}]{\text{(Semi)Local Density}} f_{\mathrm{Hxc}}(\mathbf{r})\delta(\mathbf{r},\mathbf{r}')$$

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Performance of Adiabatic (Semi-)Local Kernels

- ☺ Good description of valence excitation energies
- ☹ Underestimation of Rydberg excitation energies
- ☹ Bad description of charge-transfer excitation energies
- ☹ Absence of multiple excitations

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Performance of Adiabatic (Semi-)Local Kernels

- ☺ Good description of valence excitation energies
- ☹ Underestimation of Rydberg excitation energies
  - ➥ Bad asymptotic behavior of the LDA/GGA potentials at long range
- ☹ Bad description of charge-transfer excitation energies
  - ➥ Locality of the LDA/GGA kernels $\rightsquigarrow$ bad description of the long-range exchange
- ☹ Absence of multiple excitations
  - ➥ Adiabatic approximation $\rightsquigarrow$ frequency-dependent kernel required for multiple excitations (non-linear eigenvalue problem)

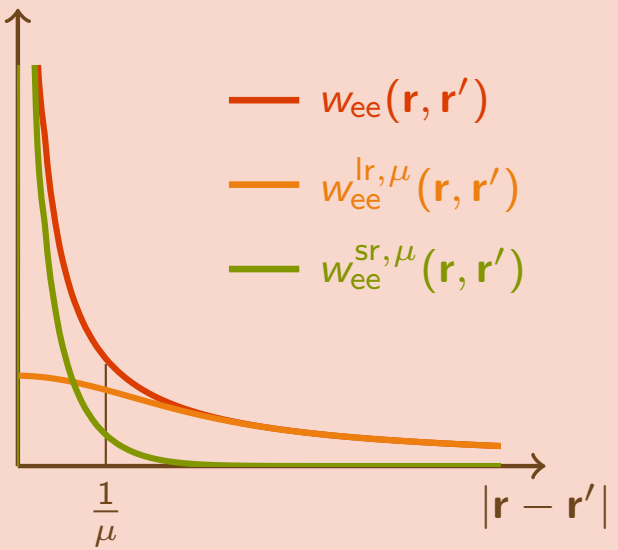
Range Separation

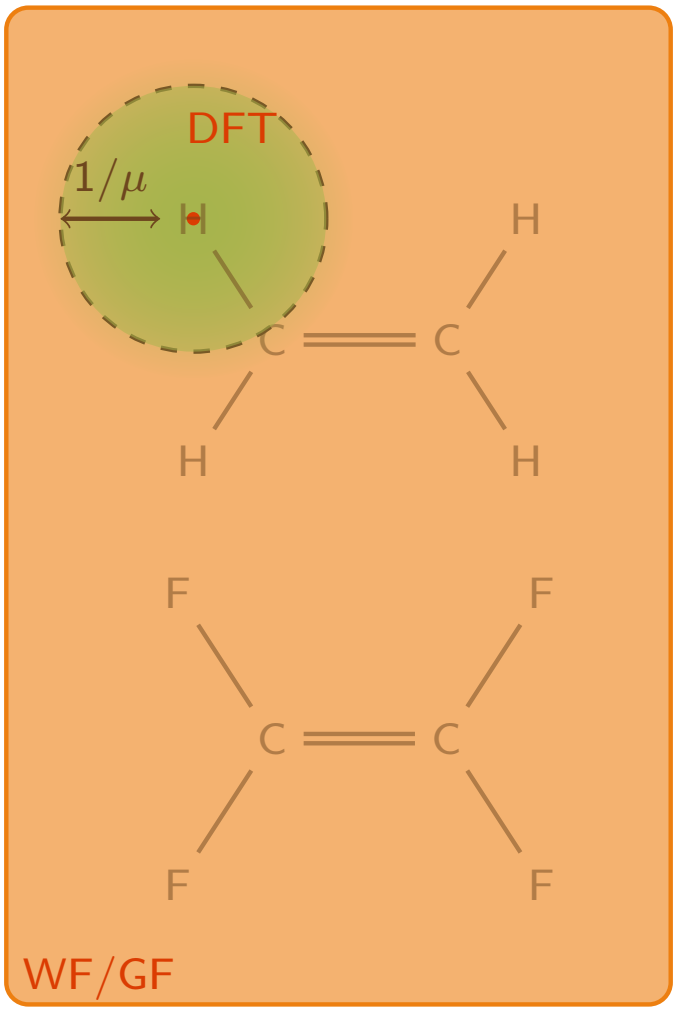
Range Separation

$$\frac{1}{r} = \underbrace{\frac{1-\mathrm{erf}(\mu r)}{r}}_{\text{DFT}} + \underbrace{\frac{\mathrm{erf}(\mu r)}{r}}_{\text{WF/GF}}$$

Savin, in *Recent development and applications of Density Functional Theory*, 1996

Standard Error Function





RSH Approximation for the Response Function

- Single Slater determinant + Adiabatic Approximation

$$\chi(\omega)^{-1} = \chi^{\mathrm{RSH}}(\omega)^{-1} - f_{\mathrm{Hxc}}^{\mathrm{RSH}}$$

$$f_{\mathrm{Hxc}}^{\mathrm{RSH}} = f_{\mathrm{H}} + f_{\mathrm{x,HF}}^{\mathrm{lr},\mu} + f_{\mathrm{xc}}^{\mathrm{sr},\mu}$$

MISSING: ω-dependence, long-range correlation

Range-separated hybrid TDDFT

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Without Range Separation

- ☺ Good description of valence excitation energies
- ☹ Underestimation of Rydberg excitation energies
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- ☹ Bad description of charge-transfer excitation energies
  - Locality of the LDA/GGA kernels $\rightsquigarrow$ bad description of the long-range exchange
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With Range Separation

☺ Good description of valence excitation energies

☺ Correct description of Rydberg excitation energies

➥ Correct asymptotic behavior of the LDA/GGA potentials at long range

☺ Good description of charge-transfer excitation energies

➥ Non-Locality of the Hartree-Fock exchange kernel

☹ Absence of multiple excitations

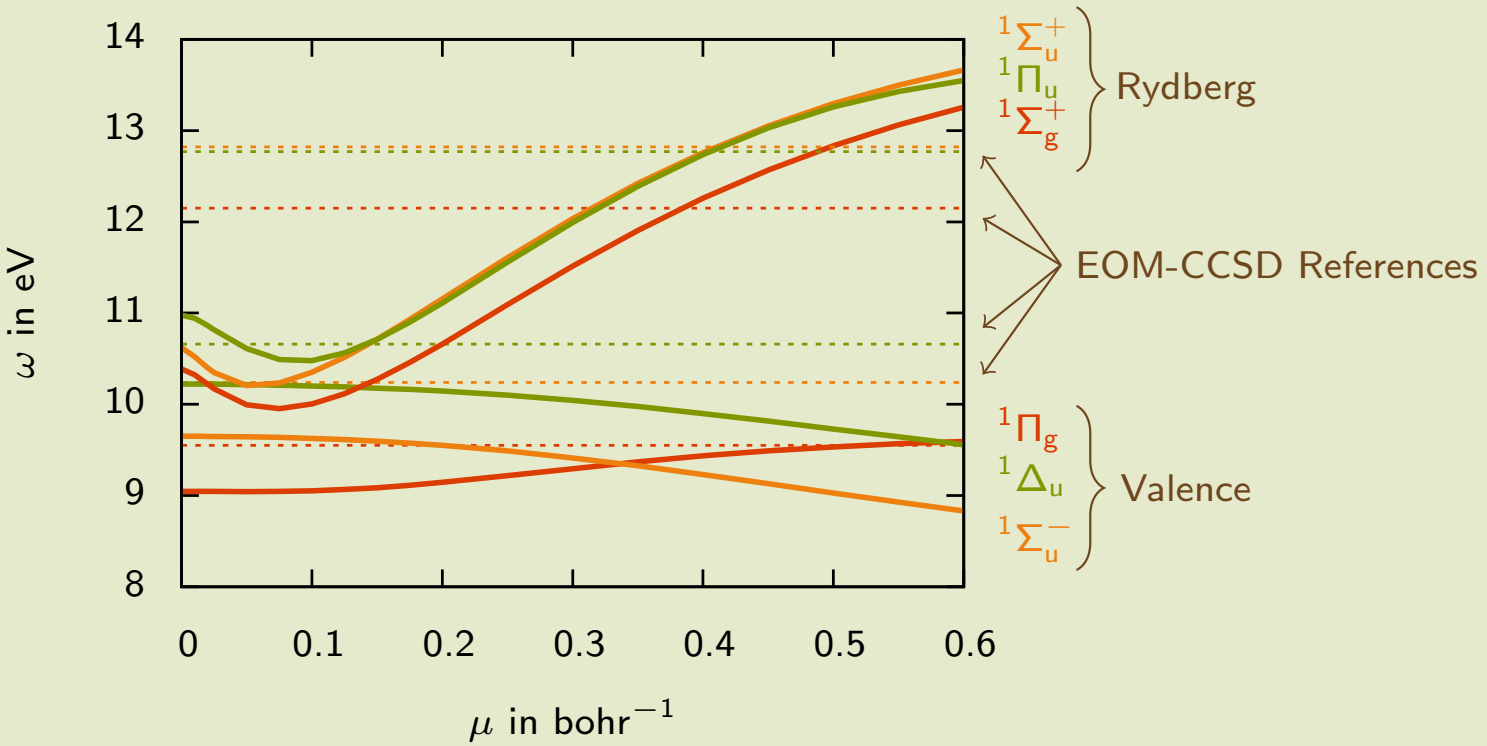
➥ Adiabatic approximation $\rightsquigarrow$ frequency-dependent kernel required for multiple excitations (non-linear eigenvalue problem)

☹ Introduction of triplet instabilities

➥ Introduction of long-range Hartree-Fock exchange

TDRSH: it works but...

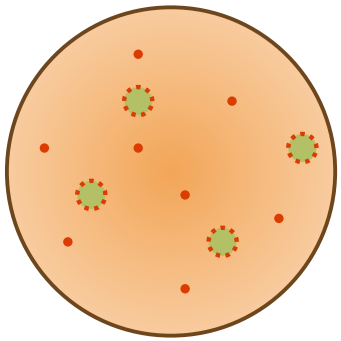
First Singlet Excitations of N_2 Experimental geometry – TD-LDA-RSH – Sadlej+ Basis Set



Can we understand what is really going on? (Way too many electrons !)

- Basis set
- LDA description of the ground state
- Single-Slater determinant wave function
- Adiabatic approximation
- LDA description of the kernel
- Single-Slater determinant wave function

Outline

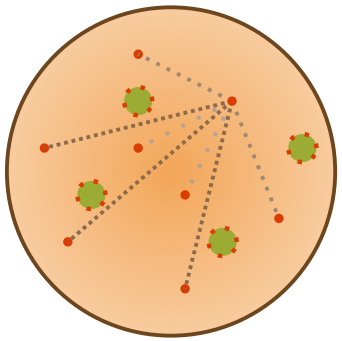


Kohn-Sham System

Kohn-Sham System

Hamiltonian	$\hat{H}^{\mathrm{KS}} = \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{V}_{\mathrm{Hxc}}$
GS Energy	$E_0 = \langle \Phi_0 \vert \hat{T} + \hat{V}_{\mathrm{ne}} \vert \Phi_0 \rangle + E_{\mathrm{Hxc}}[n_0]$
Inverse response function	$\chi(\omega)^{-1} = \chi^{\mathrm{KS}}(\omega)^{-1} - f_{\mathrm{Hxc}}(\omega)$

Outline

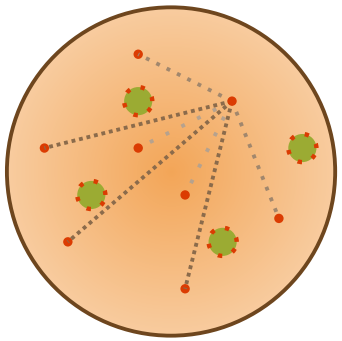


Partially Interacting System

Partially Interacting System

Hamiltonian	$\hat{H}^{\mathrm{lr},\mu} = \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} + \hat{V}_{\mathrm{Hxc}}^{\mathrm{sr},\mu}$
GS Energy	$E_0 = \langle \Psi_0^{\mu} \vert \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} \vert \Psi_0^{\mu} \rangle + E_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n_0]$
Inverse response function	$\chi(\omega)^{-1} = \chi^{\mathrm{lr},\mu}(\omega)^{-1} - f_{\mathrm{Hxc}}^{\mathrm{sr},\mu}(\omega)$

Outline



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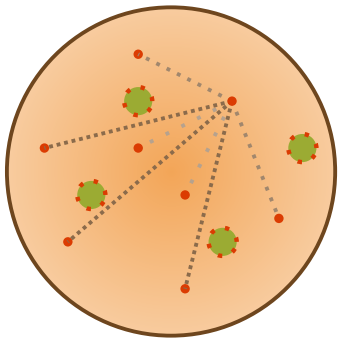
Analysis of the Exact Response Function

- Analytical study of the asymptotic behaviors close to the KS and physical systems
- Multi-configurational treatment without using approximate functionals

Rebolini, Toulouse, Teale, Helgaker, Savin, *J. Chem. Phys.*, 2014

Outline



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Rebolini, Toulouse, Teale, Helgaker, Savin, *J. Chem. Phys.*, 2014

Alternatives to TDDFT

- Perturbation theories: Rayleigh-Schrödinger or Görling-Levy based
- Extrapolation techniques: Use of first- and second-order derivatives around the physical system

Rebolini, Toulouse, Teale, Helgaker, Savin, *Phys. Rev. A*, 2015; Rebolini, Toulouse, Teale, Helgaker, Savin, *Mol. Phys*, 2015

Exact Energies along the Adiabatic Connection

Long-Range Response Function

$$\chi^{\mathrm{lr},\mu}(\mathbf{r},\mathbf{r}',\omega) = \sum_{k\neq 0} \frac{\langle \Psi_0^\mu | \hat{n}(\mathbf{r}) | \Psi_k^\mu \rangle \langle \Psi_k^\mu | \hat{n}(\mathbf{r}') | \Psi_0^\mu \rangle}{\omega - (\mathcal{E}_k^\mu - \mathcal{E}_0^\mu)} + \text{c.c.}$$

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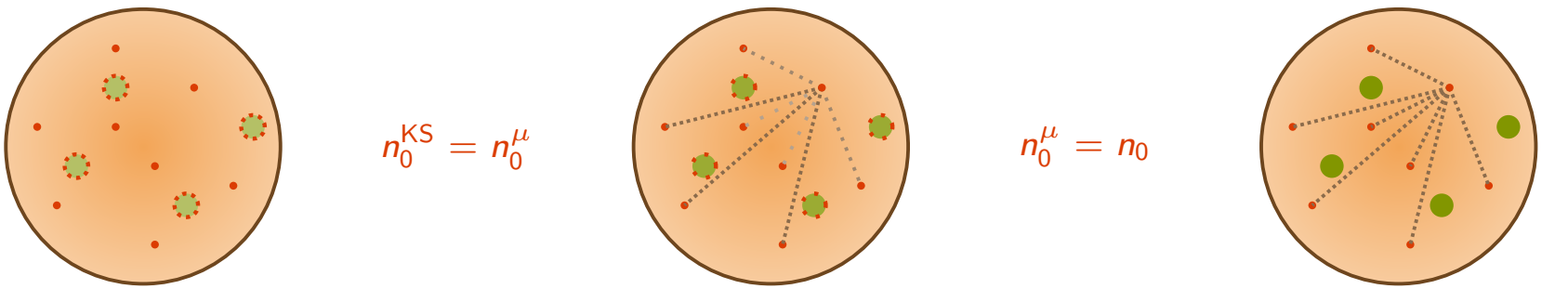


Kohn-Sham

$$\hat{H}^{\mathrm{KS}} = \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{V}_{\mathrm{Hxc}}$$
$$\hat{H}^{\mathrm{KS}}|\Phi_k^{\mathrm{KS}}\rangle = \mathcal{E}_k^{\mathrm{KS}}|\Phi_k^{\mathrm{KS}}\rangle$$

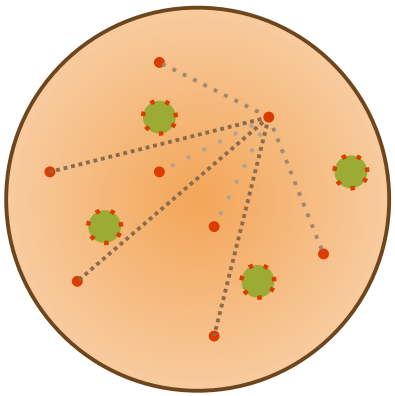
Partially Interacting

$$\hat{H}^{\mathrm{lr},\mu} = \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{V}_{\mathrm{Hxc}}^{\mathrm{sr},\mu} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu}$$
$$\hat{H}^{\mathrm{lr},\mu}|\Psi_k^\mu\rangle = \mathcal{E}_k^\mu|\Psi_k^\mu\rangle$$

Physical

$$\hat{H} = \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}}$$
$$\hat{H}|\Psi_k\rangle = E_k|\Psi_k\rangle$$

Exact Energies along the Adiabatic Connection



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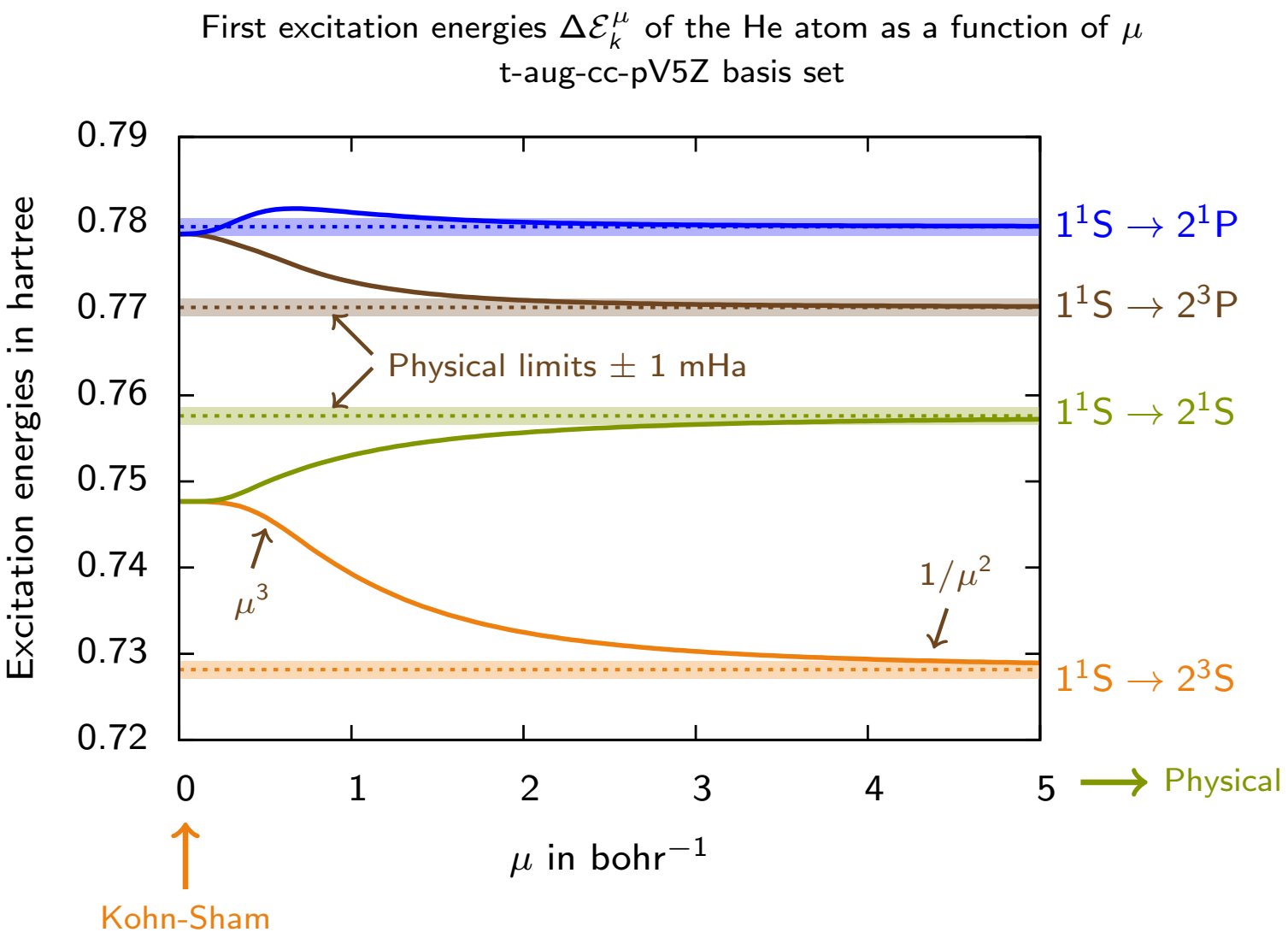
$$\hat{H}^{\mathrm{lr},\mu}|\Psi_k^\mu\rangle = \mathcal{E}_k^\mu|\Psi_k^\mu\rangle$$

Computational Details

Development version of Dalton

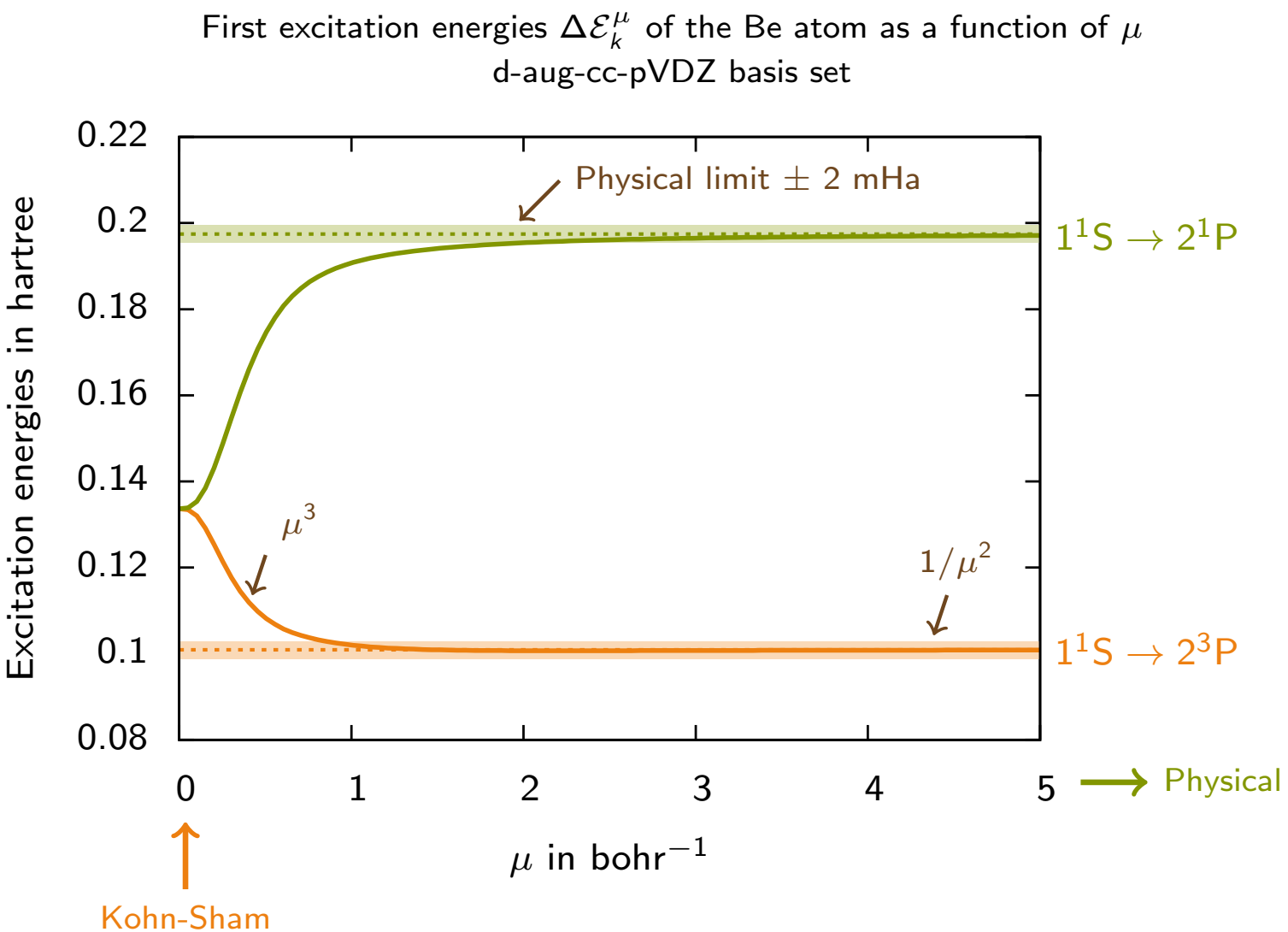
1. Full-CI calculation
   ➟ Exact density n_0^{FCI}
2. Lieb optimization of $\hat{V}_{\mathrm{Hxc}}^{\mathrm{sr},\mu}$ to reproduce n_0^{FCI}
   (No approximate functional)
3. Construction of the long-range Hamiltonian
   $\hat{H}^{\mathrm{lr},\mu} = \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} + \hat{V}_{\mathrm{Hxc}}^{\mathrm{sr},\mu}$
4. Full-CI calculation
   ➟ Exact eigenvalues and eigenvectors
   $\mathcal{E}_k^\mu$ and Ψ_k^μ

Excitation Energies – Helium (Rydberg)



- Kohn-Sham excitation energies: already good approximations
- Introduction of the interaction $\rightsquigarrow$ singlet-triplet splitting

Excitation Energies – Beryllium (Valence)



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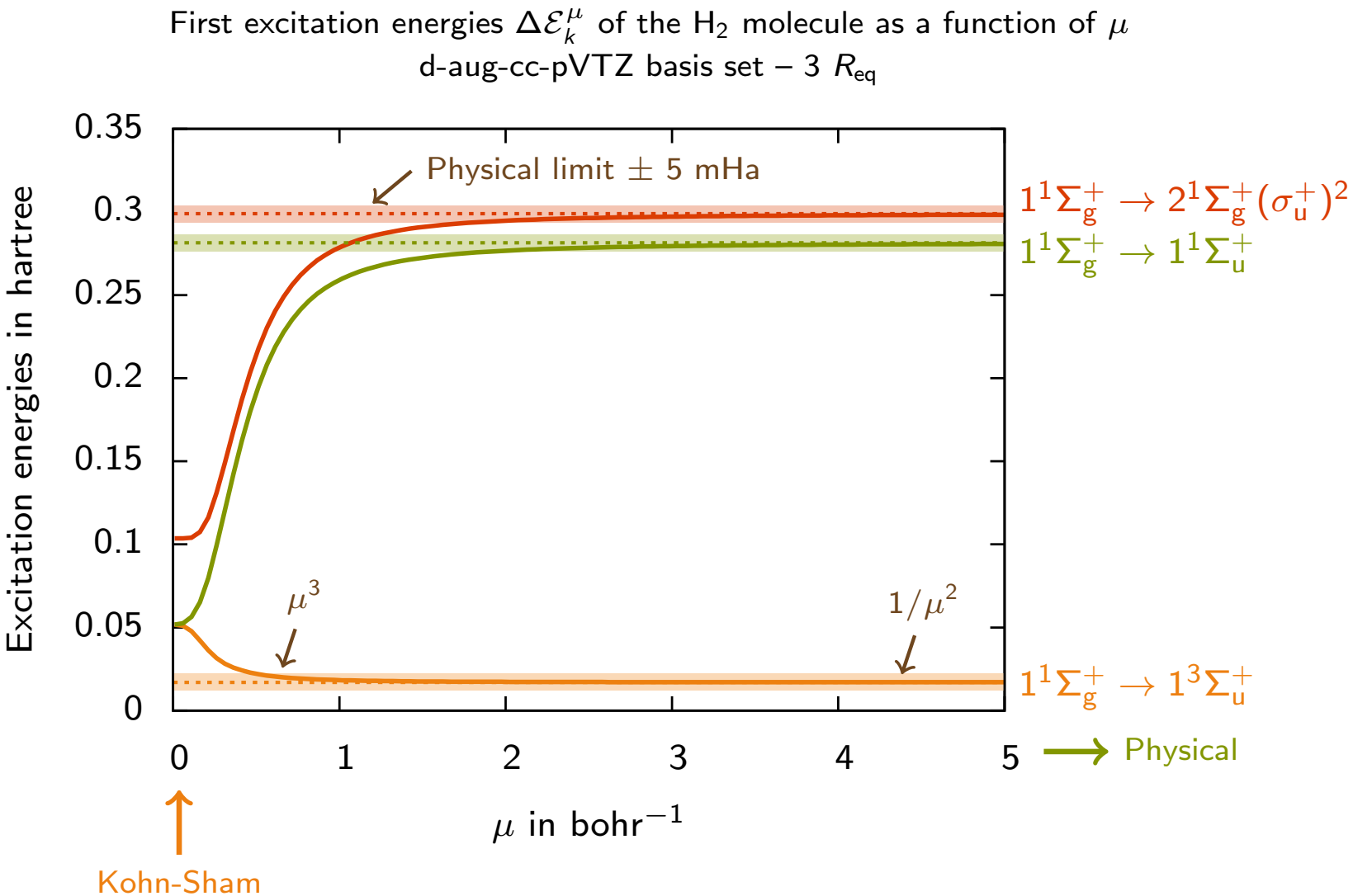
- Introduction of the interaction $\rightsquigarrow$ singlet-triplet splitting

Excitation Energies – Stretched H_2



➠ Static correlation – Double excitation

How to improve on these energies?

Different approaches are possible:

Linear response TDDFT

Addition of a short-range kernel

$$\chi(\omega)^{-1} = \chi^{\mathrm{lr},\mu}(\omega)^{-1} - f_{\mathrm{Hxc}}^{\mathrm{sr},\mu}(\omega)$$

- Adiabatic, (semi-)local approximations

Perturbation theory

- Rayleigh-Schrödinger based

$$\hat{H}^{\mu,\lambda} = \hat{H}^{\mathrm{lr},\mu} + \lambda W^{\mathrm{sr},\mu}$$

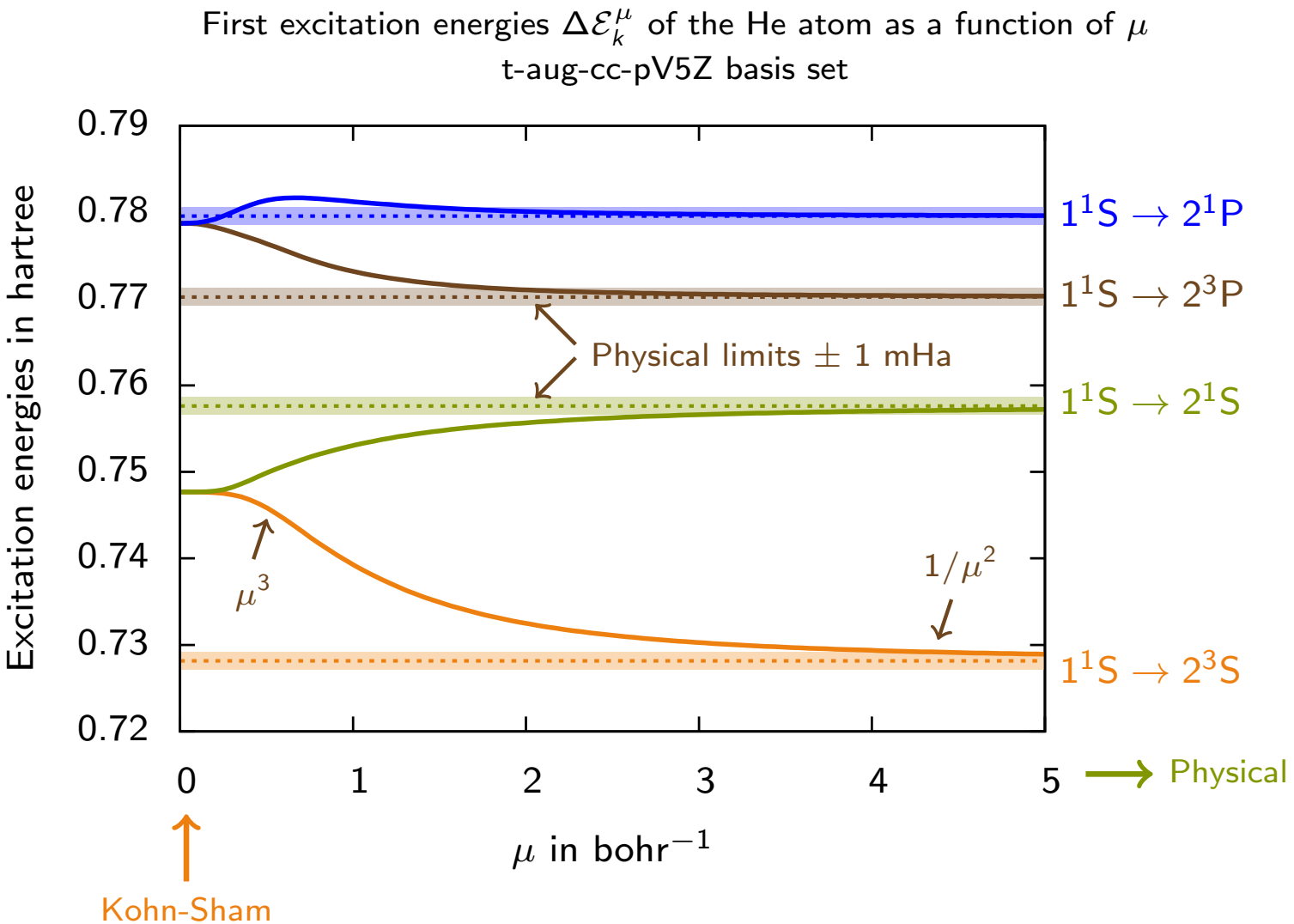
- Görling-Levy based

$$\hat{H}^{\mu,\lambda} = \hat{H}^{\mathrm{lr},\mu} + \lambda W^{\mathrm{sr},\mu} + \hat{V}_{\mathrm{c,md}}^{\mathrm{sr},\mu,\lambda}$$

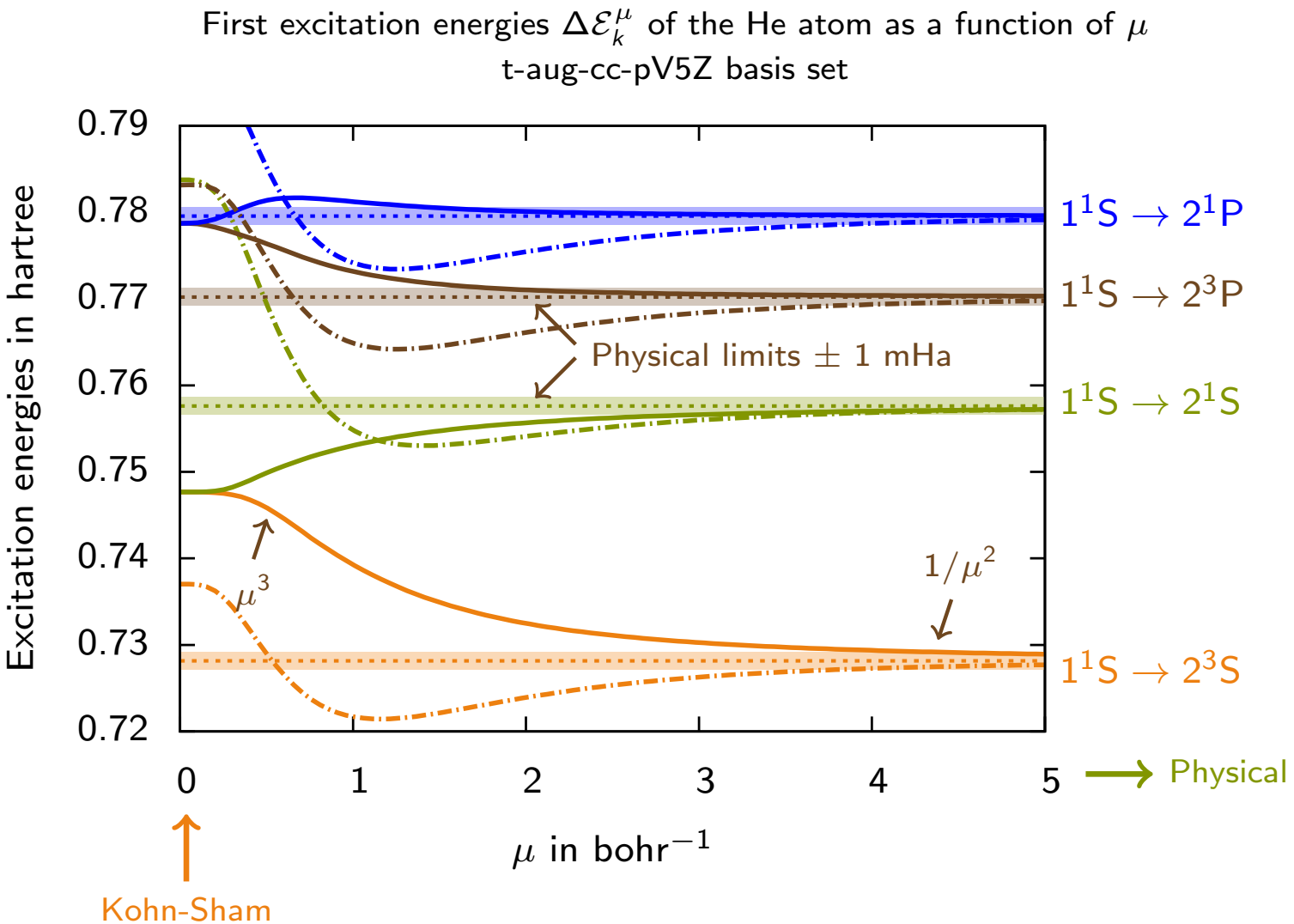
Extrapolation

- Use information on the asymptotic behavior when $\mu \to \infty$
- Energy correction based on low-order derivatives

Perturbation theory – Zeroth order

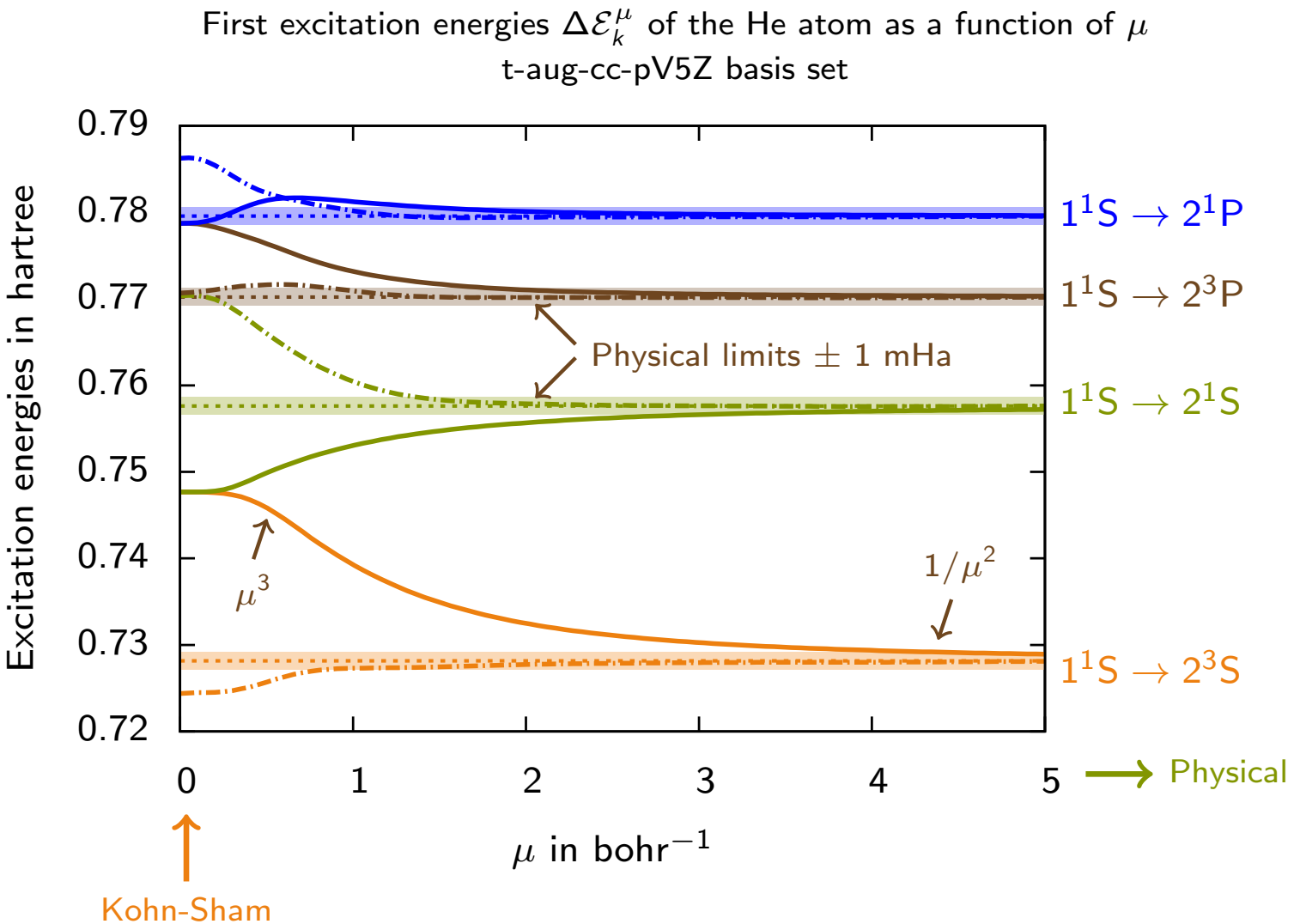


Perturbation theory – Rayleigh-Schrödinger based



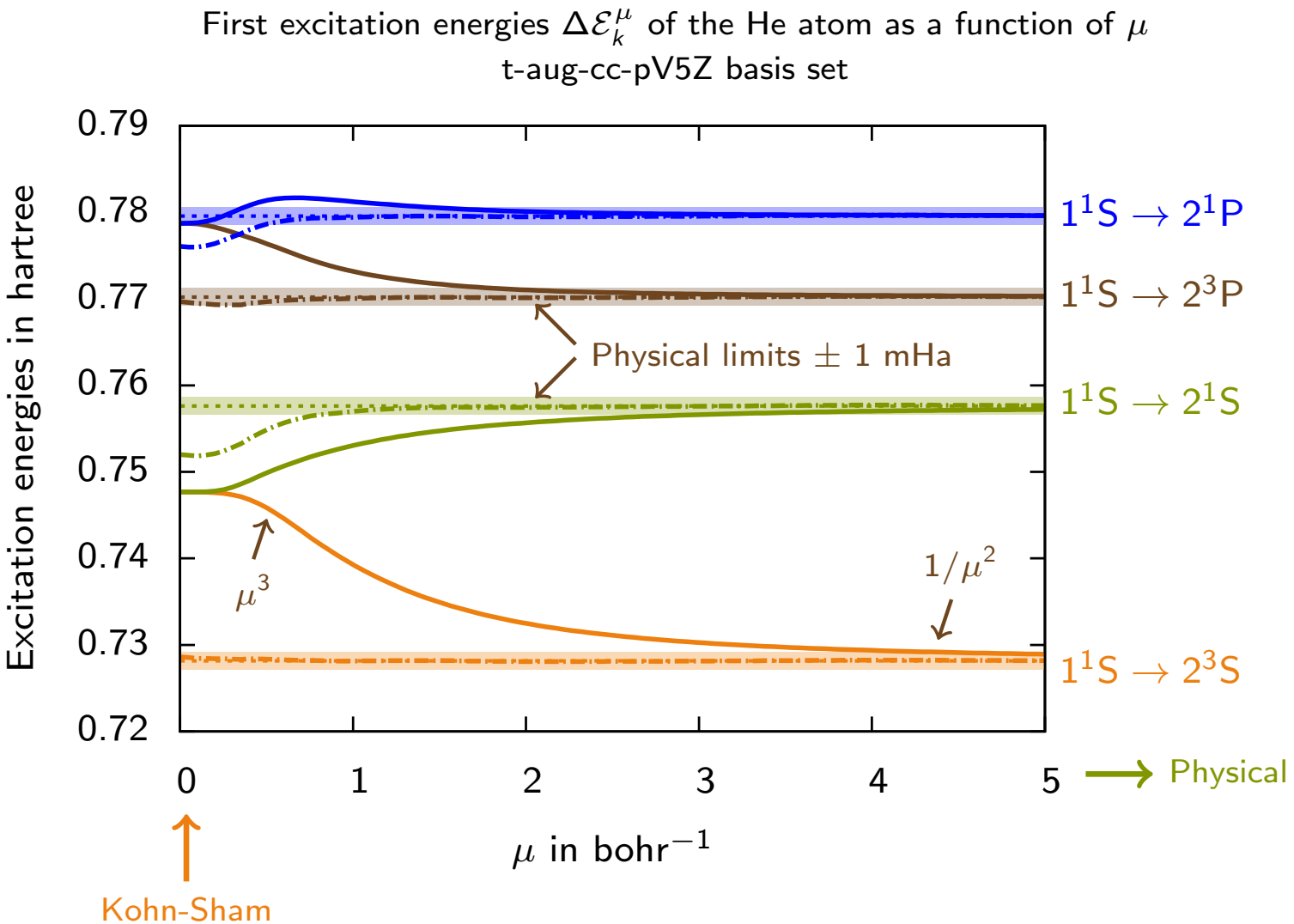
➠ The ionization potential is not kept constant at each order of the perturbation.

Perturbation theory – Görling-Levy based – 1st order



➠ IP constant at each order of the perturbation.

Perturbation theory – Görling-Levy based – 2nd order



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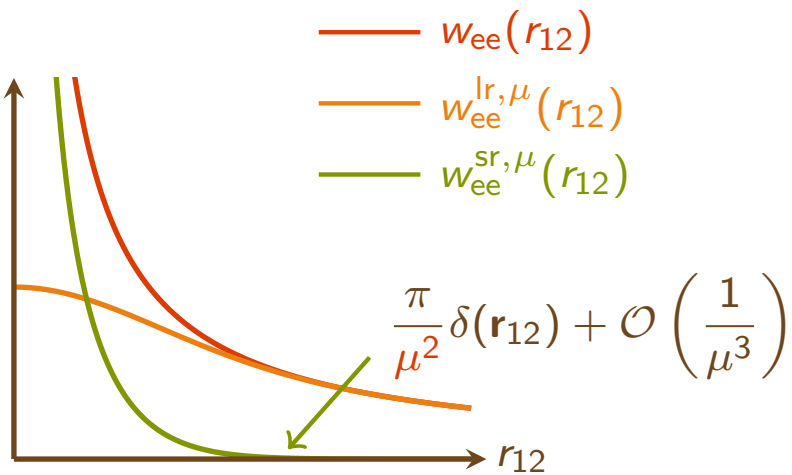
Energy Extrapolation



Taylor expansion

Close to the physical system:

$$\mathcal{E}_k^\mu = E_k + \frac{1}{\mu^2} E_k^{(-2)} + \mathcal{O}\left(\frac{1}{\mu^3}\right)$$

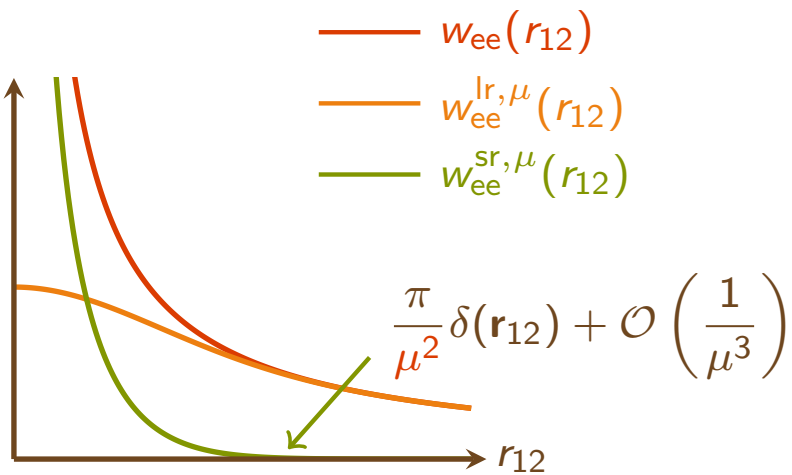
Using only the first-order derivatives

$$\frac{\partial \mathcal{E}_k^\mu}{\partial \mu} = -\frac{2}{\mu^3} E_k^{(-2)} + \mathcal{O}\left(\frac{1}{\mu^4}\right)$$

Extrapolated Energies

$$E_k^{\mathrm{EE},\mu} = \mathcal{E}_k^\mu + \frac{\mu}{2}\frac{\partial \mathcal{E}_k^\mu}{\partial \mu}$$

Energy Extrapolation



Taylor expansion

Close to the physical system:

$$\mathcal{E}_k^\mu = E_k + \frac{1}{\mu^2} E_k^{(-2)} + \frac{1}{\mu^3} E_k^{(-3)} + \mathcal{O}\left(\frac{1}{\mu^4}\right)$$

Using first- and second-order derivatives

$$\frac{\partial \mathcal{E}_k^\mu}{\partial \mu} = -\frac{2}{\mu^3} E_k^{(-2)} - \frac{3}{\mu^4} E_k^{(-3)} + \mathcal{O}\left(\frac{1}{\mu^5}\right)$$

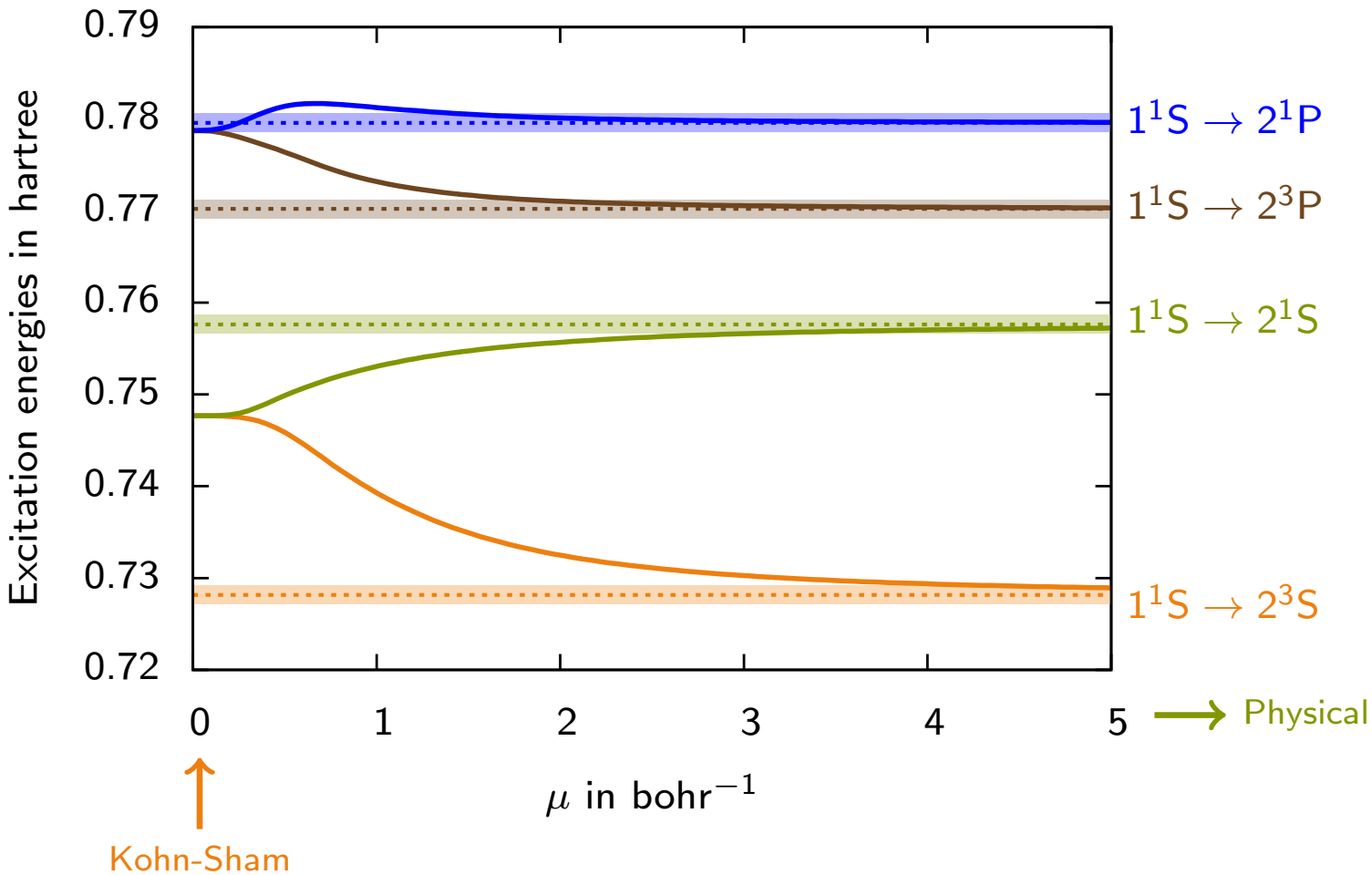
$$\frac{\partial^2 \mathcal{E}_k^\mu}{\partial \mu^2} = \frac{6}{\mu^4} E_k^{(-2)} + \frac{12}{\mu^5} E_k^{(-3)} + \mathcal{O}\left(\frac{1}{\mu^6}\right)$$

Extrapolated Energies

$$E_k^{\mathrm{EE2},\mu} = \mathcal{E}_k^\mu + \mu \frac{\partial \mathcal{E}_k^\mu}{\partial \mu} + \frac{\mu^2}{6} \frac{\partial^2 \mathcal{E}_k^\mu}{\partial \mu^2}$$

Extrapolated Excitation Energies – Helium

First excitation energies $\Delta\mathcal{E}_k^\mu$ of the He atom as a function of μ
t-aug-cc-pV5Z basis set



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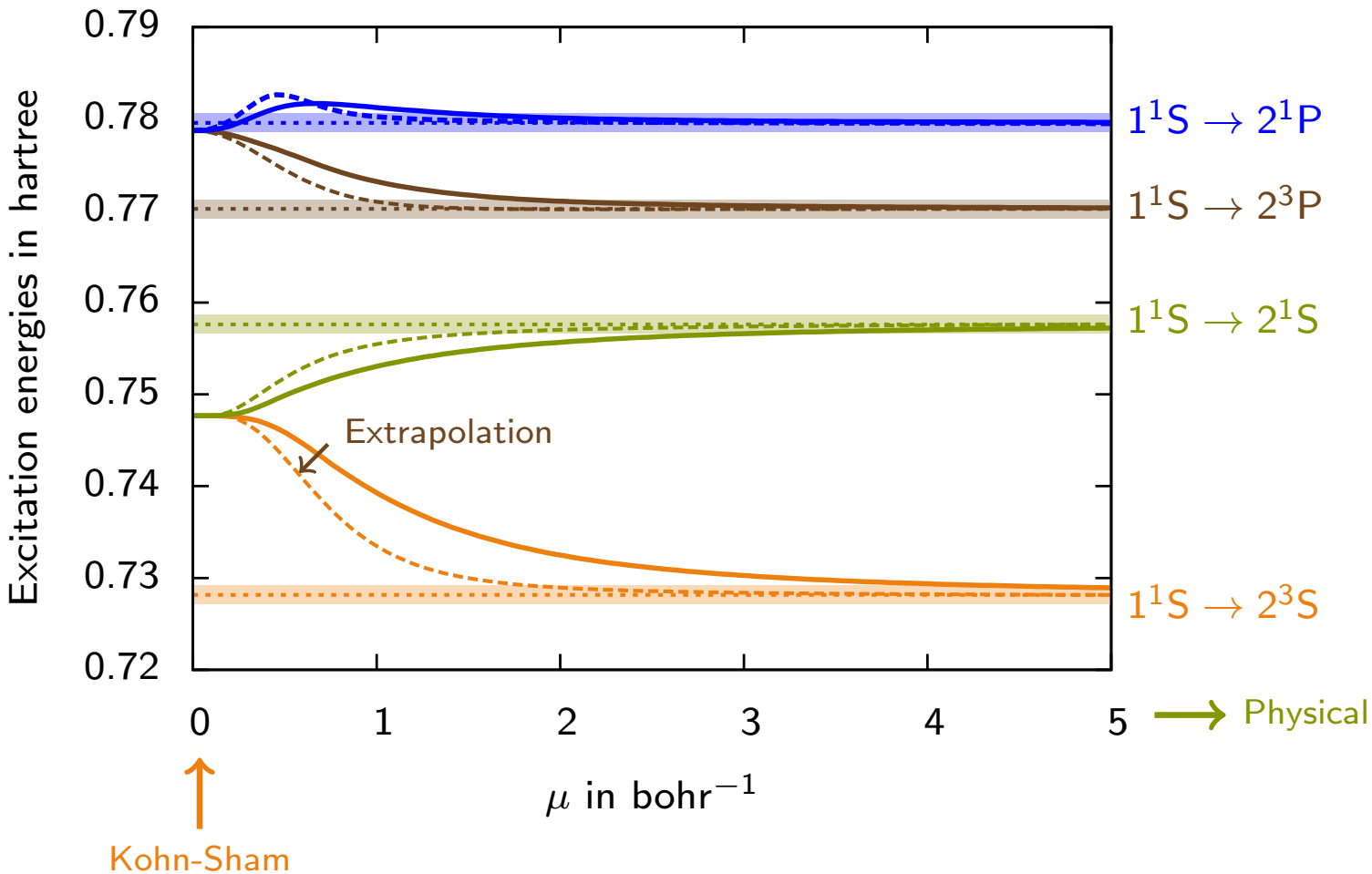

➠ Systematic improvement of the estimation of the physical excitation energies

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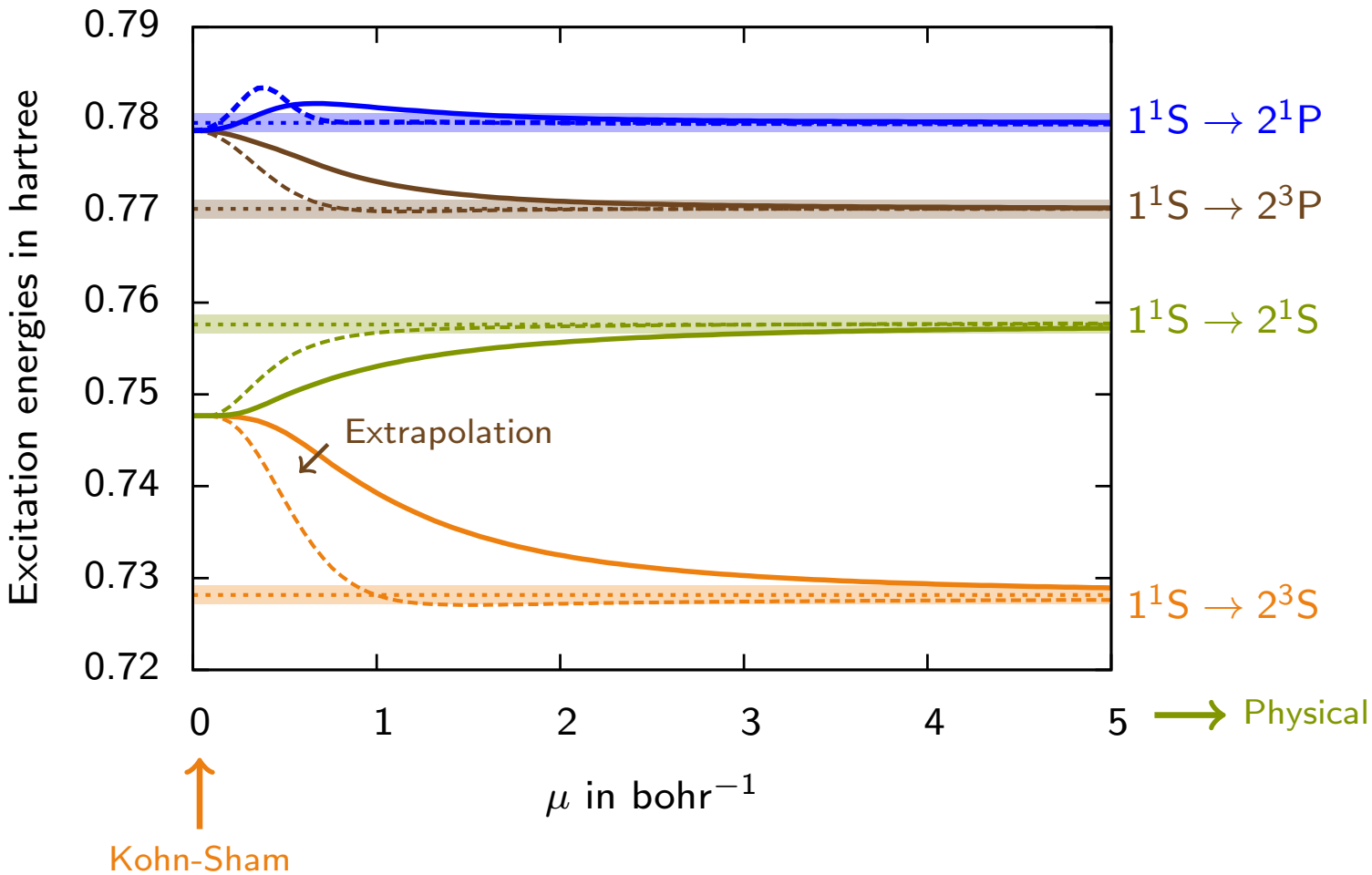
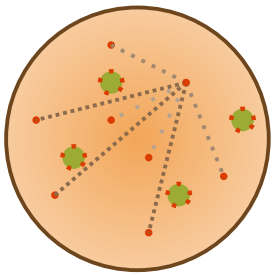


Conclusion and Perspectives



Partially Interacting System

Long-Range Response Function

$$\chi^{\mathrm{lr},\mu}(\mathbf{r},\mathbf{r}',\omega) = \sum_{k\neq 0} \frac{\langle \Psi_0^\mu | \hat{n}(\mathbf{r}) | \Psi_k^\mu \rangle \langle \Psi_k^\mu | \hat{n}(\mathbf{r}') | \Psi_0^\mu \rangle}{\omega - (\mathcal{E}_k^\mu - \mathcal{E}_0^\mu)} + \text{c.c.}$$

Analysis

Multi-determinantal treatment for $\Psi^{\mathrm{lr},\mu}$ and Lieb optimization of $V_{\mathrm{Hxc}}^{\mathrm{sr},\mu}$

- Analysis of the poles along the range-separated adiabatic connection
- Better starting point than the KS energies

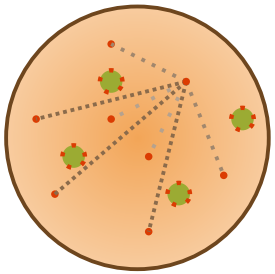
Extrapolation/Perturbation Methods

Use of Taylor expansions around the physical system

Görling-Levy based perturbation theory

- Systematic improvement of the estimation of the energies of the physical system
- Alternative to linear-response TDDFT

Conclusion and Perspectives



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Perspectives

- Effects of a LDA/GGA functional and of a truncated CI
- More advanced extrapolation techniques (two points, extrapolation basis set...)

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