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## The main origin of basis-set error

- ▶ We know since Kato's work[4] that **all exact wave functions** exhibit a **cusp** at the electron **coalescence point**:

$$\Psi(\mathbf{r}_1, r_{12}) = \Psi(\mathbf{r}_1, 0) \left( 1 + \underbrace{\frac{1}{2}r_{12}}_{\text{Cusp}} + \dots \right)$$

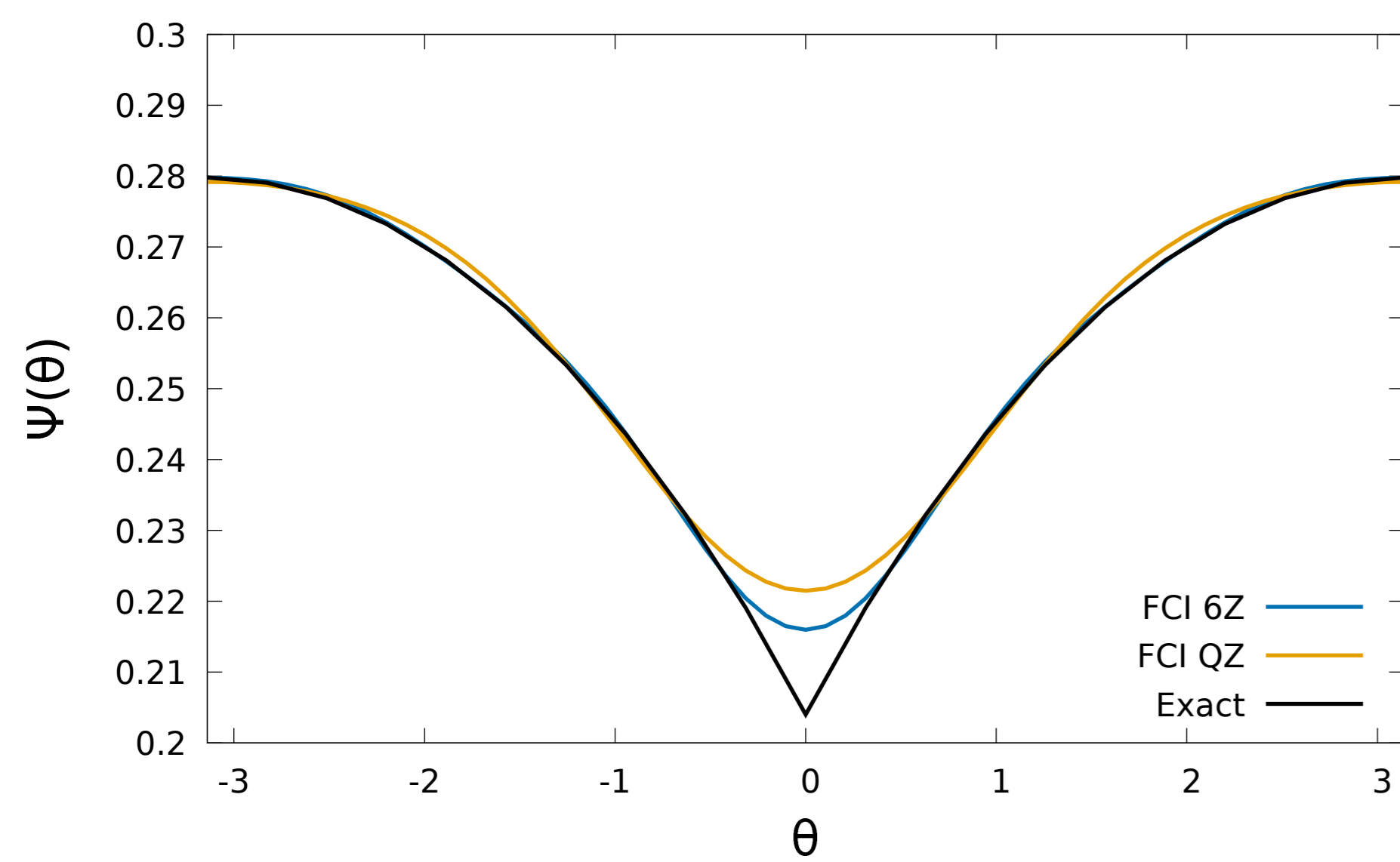


FIGURE 1 – Exact and approximated wave functions for the Helium atom.

Origin: the **divergence of the coulomb operator**

- ▶ Use an **incomplete** basis set  $\mathcal{B}$ :

- **no cusp** in the wave function  $\Psi^{\mathcal{B}}$

$$\Psi^{\mathcal{B}}(\mathbf{r}_1, r_{12}) = \Psi^{\mathcal{B}}(\mathbf{r}_1, 0) \left( 1 + \underbrace{0 \times r_{12}}_{\text{no cusp!}} + \dots \right)$$

- Bad description of **short-range correlation** ( $r_{12} \approx 0$ ).

- Impact the total energies and energy differences.

## An alternative point of view

- ▶ **DFT main features**:

- Energy only **need one- and two-body objects**
- **DFT**: approximate the two-body density with one-body objects

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = \underbrace{n(\mathbf{r}_1)n(\mathbf{r}_2)}_{\text{System dependant}} + \underbrace{n_{xc}(\mathbf{r}_1, \mathbf{r}_2, n, \nabla n, \dots)}_{\text{quite universal}}$$

- **LDA**:  $n_{xc}(\mathbf{r}_1, \mathbf{r}_2)$  is taken from the electron gas
- $r_{12} \approx 0 \Leftrightarrow$  Cusp region  $\Leftrightarrow$  **universal!**
- **Large  $r_{12}$**   $\Leftrightarrow$  **very system dependent ...**

- ▶ **Range-separated DFT**[3]: (RS-DFT)

A rigorous framework for **mixing WFT/DFT**

- **WFT**: deals with a **non-divergent** interaction

$$w^{\text{lr},\mu}(r_{12}) = \frac{\text{erf}(\mu r_{12})}{r_{12}}$$

- **non-divergent** interaction: **no cusp**  
 $\Rightarrow$  **Faster convergence** with the basis set[5]
- **Tunable parameter  $\mu$**

$$\lim_{\mu \rightarrow \infty} w^{\text{lr},\mu}(r_{12}) = \frac{1}{r_{12}}$$

- **DFT**: deals with the **divergent part**  
 $\Rightarrow$  captures the **universal correlation effects**
- Looks-like complementary with WFT

- ▶ **Using RS-DFT for basis set error**

1. Formalism to **mix basis-set and DFT**
2. Finite basis set  $\Leftrightarrow$  non-divergent interaction  
 $\Rightarrow$  define an **effective interaction** in  $\mathcal{B}$
3. Fit the effective interaction with  $\mu(\mathbf{r})$   
 $\Rightarrow$  Use RS-DFT for the basis set error !!

## DFT formalism for basis-set incompleteness [1]

- Rewrite Levy-Lieb functional with  $\Psi^{\mathcal{B}}$ :  
 wave function in a basis set  $\mathcal{B}$

$$E = \min_{n(\mathbf{r})} \left\{ (v_{\text{ne}}|n) + \min_{\Psi^{\mathcal{B}} \rightarrow n(\mathbf{r})} \langle \Psi^{\mathcal{B}} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle + \underbrace{\bar{E}^{\mathcal{B}}[n(\mathbf{r})]}_{\text{what is missing in } \mathcal{B}} \right\} \quad (1)$$

$$\lim_{\mathcal{B} \text{ is complete}} \bar{E}^{\mathcal{B}}[n(\mathbf{r})] = 0$$

- $\bar{E}^{\mathcal{B}}[n(\mathbf{r})]$  is a functional of the **density**

- Non self consistent approximation:

Estimating (1) at the **FCI density within  $\mathcal{B}$**   $n_{\text{FCI}}^{\mathcal{B}}(\mathbf{r})$

$$E \approx E_{\text{FCI}}^{\mathcal{B}} + \bar{E}^{\mathcal{B}}[n_{\text{FCI}}^{\mathcal{B}}(\mathbf{r})] \quad (2)$$

## Definition of an effective interaction within $\mathcal{B}$ [1]

- Write with  $W_{ee}^{\mathcal{B}} = \sum_{mnpq} a_m^\dagger a_n^\dagger a_p a_q V_{mn}^{pq}$  in **real space**
- Write  $\langle \Psi^{\mathcal{B}} | W_{ee} | \Psi^{\mathcal{B}} \rangle$ , do **quite some math** and get to

$$\langle \Psi^{\mathcal{B}} | W_{ee} | \Psi^{\mathcal{B}} \rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 W^{\mathcal{B}}(\mathbf{r}_1, \mathbf{r}_2) n_2^{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_2)$$

$$W^{\mathcal{B}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\sum \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) V_{ij}^{kl} \Gamma_{kl}^{mn} \phi_m(\mathbf{r}_1) \phi_n(\mathbf{r}_2)}{n_2^{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_2)}$$

- $W^{\mathcal{B}}(\mathbf{r}_1, \mathbf{r}_2)$ : **effective interaction within  $\mathcal{B}$**

- is **non-divergent** and **not isotropic**
- **tends to  $1/r_{12}$**  when  $\mathcal{B}$  is **complete**

- Link with SR-DFT:

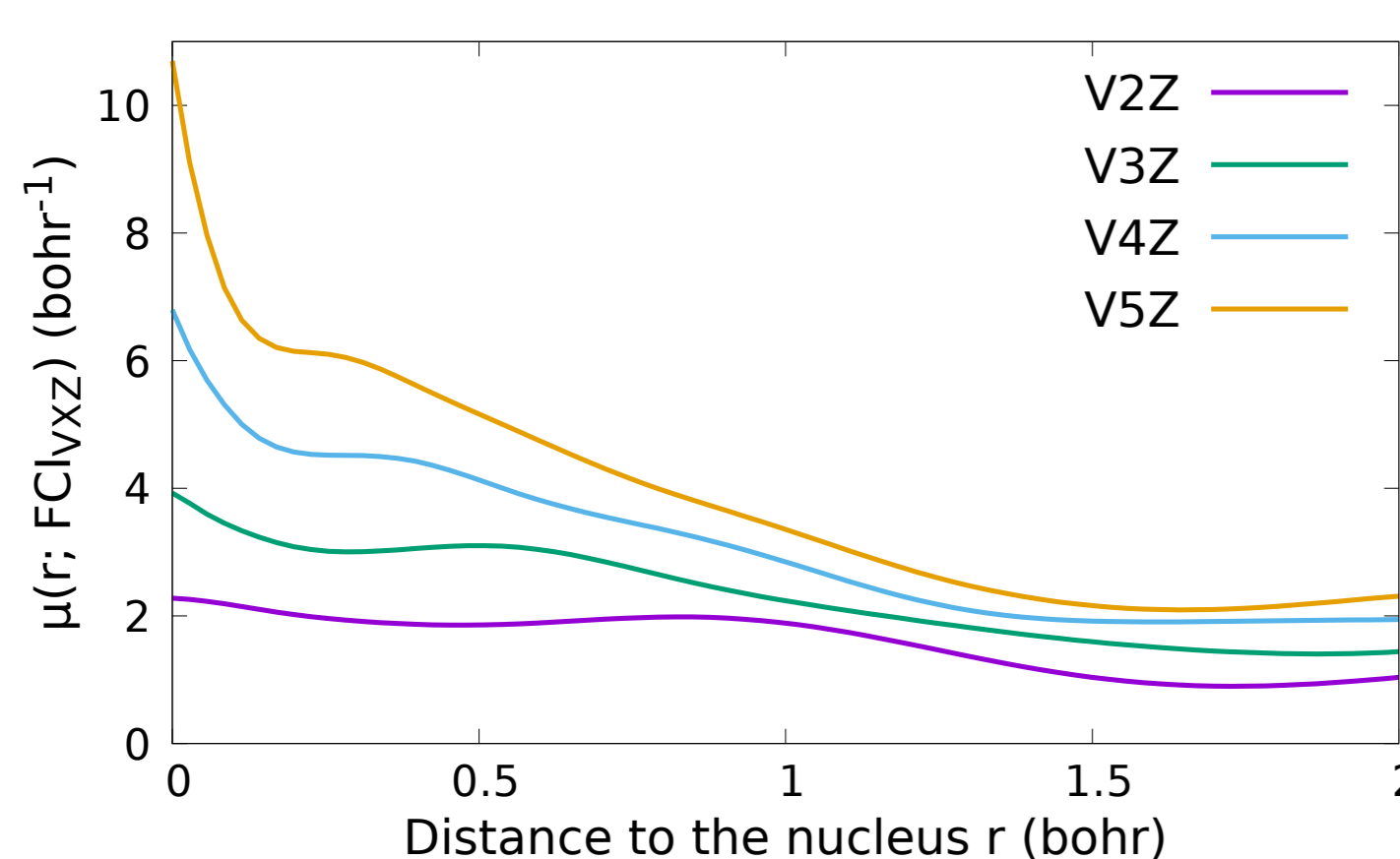
- **Fit**  $W^{\mathcal{B}}(\mathbf{r}_1, \mathbf{r}_2)$  with  $\text{erf}(\mu_{\mathcal{B}}(\mathbf{r})r_{12})/r_{12}$
- Use RS-DFT correlation functionals with  $\mu_{\mathcal{B}}(\mathbf{r})$

$$\bar{E}^{\mathcal{B}}[n(\mathbf{r})] \approx \bar{E}_{\text{c,md}}^{\text{RS-DFT}}[n(\mathbf{r}), \mu_{\mathcal{B}}(\mathbf{r})]$$

- Good asymptotic limits:

$$\lim_{\mathcal{B} \rightarrow \text{CBS}} \mu_{\mathcal{B}}(\mathbf{r}) = \infty \Leftrightarrow \lim_{\mathcal{B} \rightarrow \text{CBS}} \bar{E}^{\mathcal{B}}[n(\mathbf{r})] = 0$$

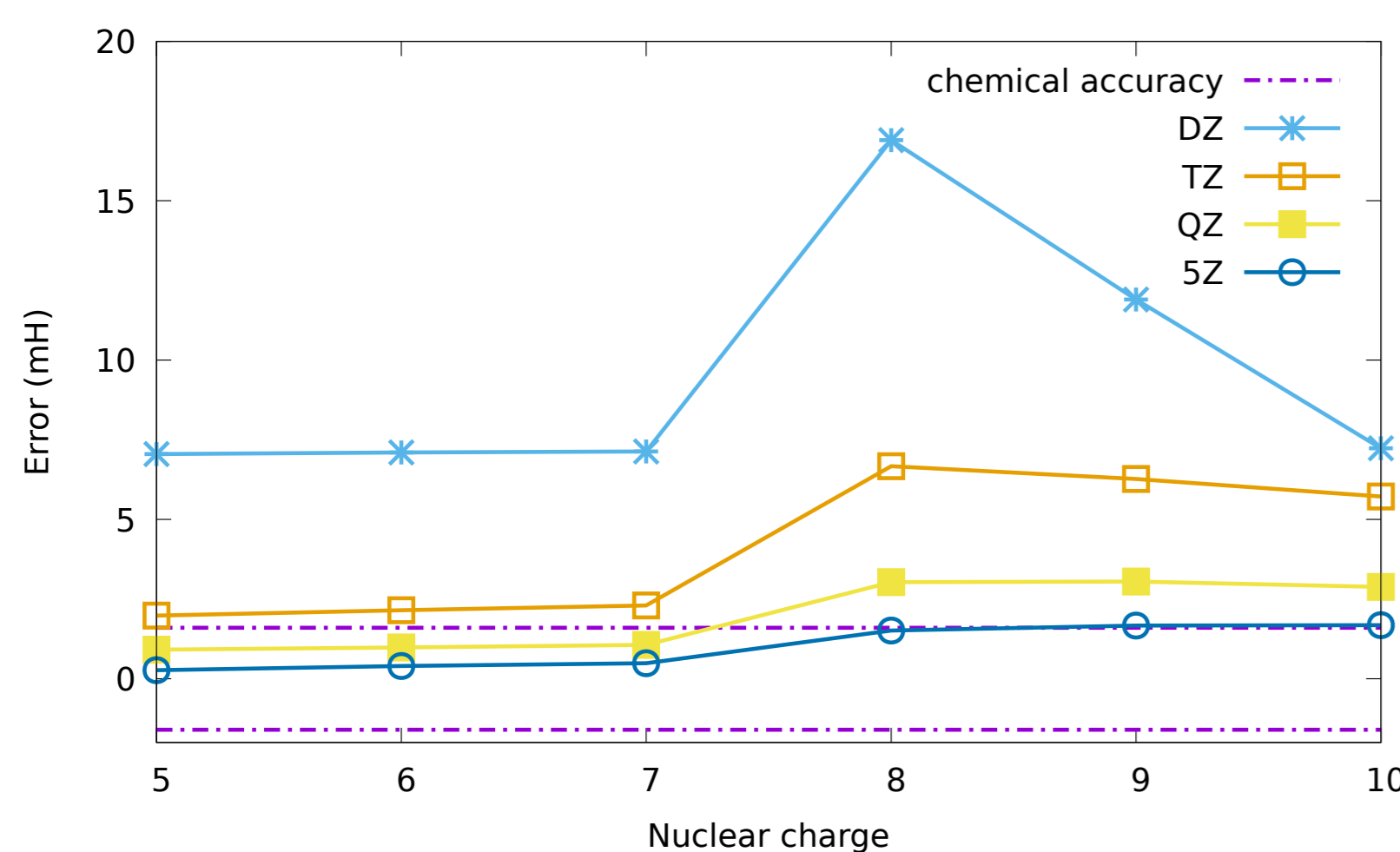
- ▶ Example:  $\mu_{\mathcal{B}}(\mathbf{r})$  for He [1]



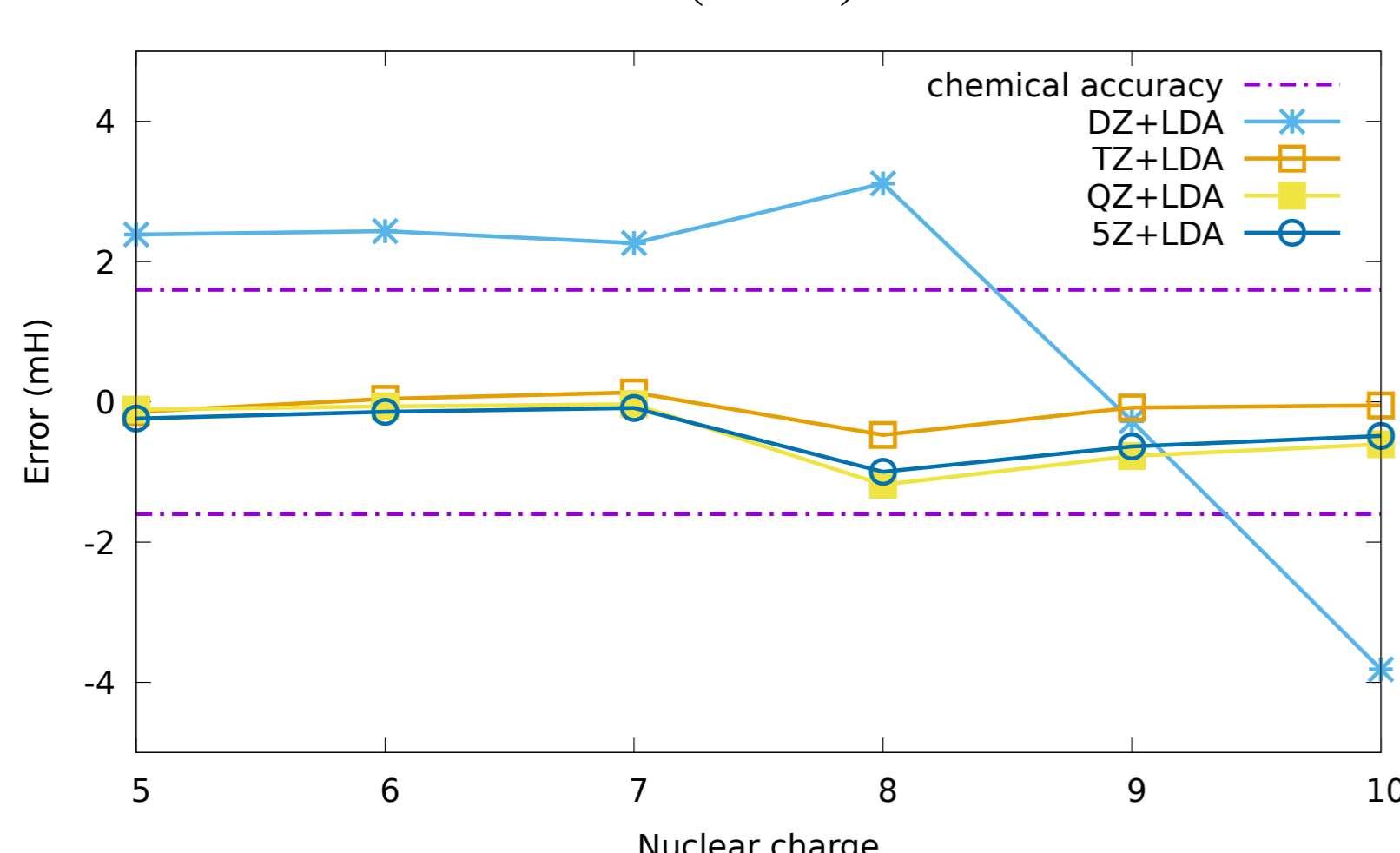
- $\mu_{\mathcal{B}}(\mathbf{r})$  increases with  $\mathcal{B}$
- $\mu_{\mathcal{B}}(\mathbf{r})$  is larger where  $\mathcal{B}$  is centered
- Energy correction diminishes with  $\mathcal{B}$

- ▶ **Convergence of the IP for the B-Ne series** [1]

- FCI



- FCI + DFT correction (LDA)



## Numerical tests on the G2 test with CCSD(T) [2]

For weakly correlated systems:

- CCSD(T) energy is a **good approximation of  $E_{\text{FCI}}^{\mathcal{B}}$**
- HF density is a good approximation of  $n_{\text{FCI}}^{\mathcal{B}}(\mathbf{r})$
- Basis set correction using only **HF one-body density**
- Using a kind of **PBE** approximation for DFT
- Very cheap compared to CC calculation

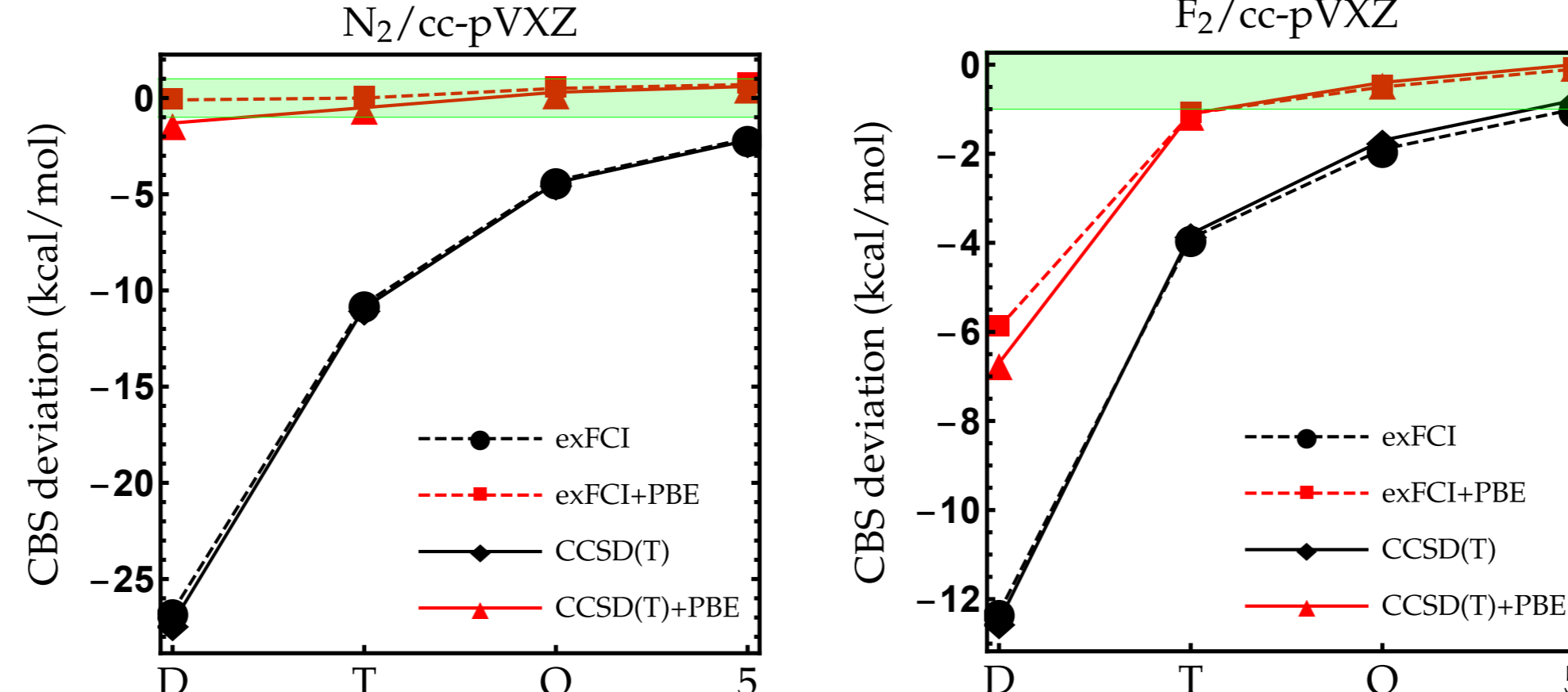


TABLE 1 – Errors in **kcal/mol** of the G2 atomization energies.

Method	MAD	MAX	CA
CCSD(T)/cc-pVDZ	14.29	36.95	2
CCSD(T)/cc-pVTZ	6.06	14.25	2
CCSD(T)/cc-pVQZ	2.50	6.75	9
CCSD(T)/cc-pV5Z	1.28	3.46	21
CCSD(T)+PBE/cc-pVDZ	1.96	2.59	7.33
CCSD(T)+PBE/cc-pVTZ	0.85	1.11	2.64
CCSD(T)+PBE/cc-pVQZ	0.31	0.42	1.16

- **Systematically improves** the energy difference
- **Extremely cheap** compared to CCSD(T) calculations
- It is **cheap** compared to other basis-set corrections  
 $\Rightarrow$  Relies on DFT not on F12
- Sub **kcal/mol** accuracy with cc-pVTZ basis set

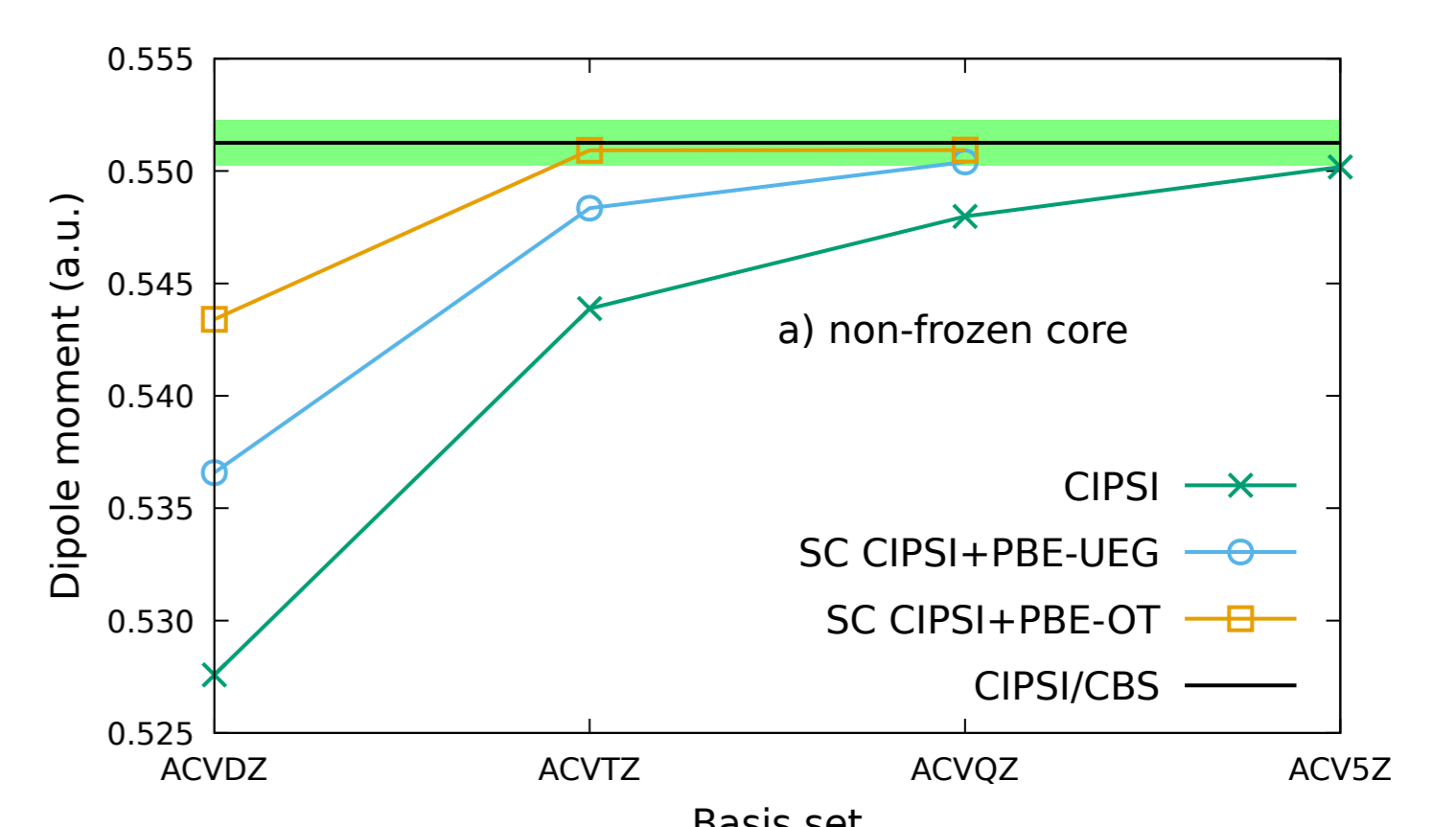
[2] Loos, P.F.; Pradines, B.; Scemama, A.; Toulouse, J.; Giner, E.; *J. Phys. Chem. Lett.* 2019.

## Recent developments of the formalism

- Correct some basis effects of **GW methods** [3]
- First attempts on **excited states** [4]
- Treatment of **strongly correlated systems** [5]
  - Functional depending on the **on top pair density**,
  - Allows to properly **break multiple bonds** (ex:  $\text{N}_2$ ).
  - Size consistent and  $S_z$  invariant functional
  - First tests on **transition metals oxides** [6]

- **Fully variational formalism**: change  $\psi^{\mathcal{B}}$  [7]

- Functional derivative  $\frac{\delta \bar{E}^{\mathcal{B}}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \Leftrightarrow$  effective potential
- Obtain self-consistent Schrodinger-like equations
- Change  $\psi^{\mathcal{B}}$  and therefore the properties
- Improves convergence of dipole moments



- Compute **energy derivatives** (Diata's talk :)

- Applicable to a wide spectrum of WFT models
- Illustration for dipole moments

- Alternative and **rigorous** derivation for a 1 D model [8]

- Proper definition of an LDA basis set functional

- Julien's poster

[3] P.F. Loos, B. Pradines, A. Scemama, E. Giner, *JCTC* 2020.

[4] E. Giner, A. Scemama, J. Toulouse, P.F. Loos, *J. Chem. Phys.* 2020.

[5] Giner, E.; Scemama, A.; Toulouse, J.; Loos, P-F., *J. Chem. Phys.* 2020.

[6] Y. Yao, E. Giner, T. A. Anderson, J. Toulouse, C. J. Umrigar, *J. Chem. Phys.* 2021.

[7] E. Giner, D. Traore, B. Pradines, J. Toulouse., *J. Chem. Phys.* 2021.

[8] D. Traore, E. Giner, J. Toulouse, *J. Chem. Phys.* 2021.

[1] Giner, E.; Pradines, B.; Ferté, A.; Assaraf, R.; Savin, A.; Toulouse, J.; *J. Chem. Phys.* 2018.