

Electron-nucleus cusp correction for molecular orbitals

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A good presentation always starts like this...

The Schrödinger equation is

$$\forall \mathbf{R} = (\mathbf{r}_1, \dots, \mathbf{r}_n) \in \mathbb{R}^{3n}, \hat{H}\Psi_{\text{exact}}(\mathbf{R}) = E_{\text{exact}}\Psi_{\text{exact}}(\mathbf{R})$$

and can be recast as

$$\frac{\hat{H}\Psi_{\text{exact}}(\mathbf{R})}{\Psi_{\text{exact}}(\mathbf{R})} = \frac{\hat{T}\Psi_{\text{exact}}(\mathbf{R})}{\Psi_{\text{exact}}(\mathbf{R})} + V(\mathbf{R}) = E_{\text{exact}}$$

where

$$T(\mathbf{R}) = -\frac{1}{2} \sum_i \nabla_i^2$$

$$V(\mathbf{R}) = - \sum_A \sum_i \frac{Z_A}{|\mathbf{r}_A - \mathbf{r}_i|} + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

In a “good” wave function, the “explosions” in $V(\mathbf{R})$ must be compensated by $\frac{\hat{T}\Psi_{\text{exact}}(\mathbf{R})}{\Psi_{\text{exact}}(\mathbf{R})}$

Kato coalescence conditions

Kato electron-nucleus (e-n) cusp condition

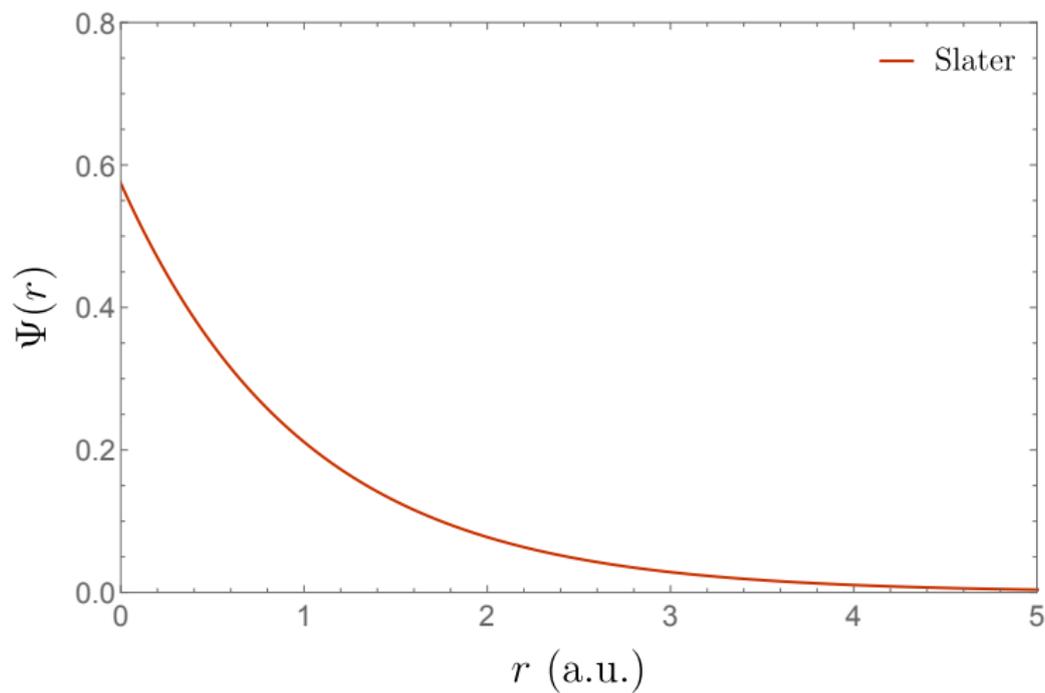
Kato showed that, when an electron meet a nucleus, we must have

$$\forall \text{ nuclei } A \text{ and electrons } i, \left. \frac{\partial \langle \Psi_{\text{exact}}(\mathbf{R}) \rangle}{\partial r_i} \right|_{r_i=r_A} = -Z_A \langle \Psi_{\text{exact}}(\mathbf{R}) \rangle|_{r_i=r_A}$$

This is called the **Kato e-n cusp condition** and it makes the **local energy** finite at each nuclear center

Kato, Com Pure Appl Math 10 (1957) 151

The hydrogen atom



Trial wave functions within quantum Monte Carlo (QMC)

Multideterminant Slater-Jastrow wave function

A typical QMC **trial wave function** has the form

$$\Psi_T(\mathbf{R}) = e^{J(\mathbf{R})} \sum_I c_I D_I^\uparrow(\mathbf{R}^\uparrow) D_I^\downarrow(\mathbf{R}^\downarrow)$$

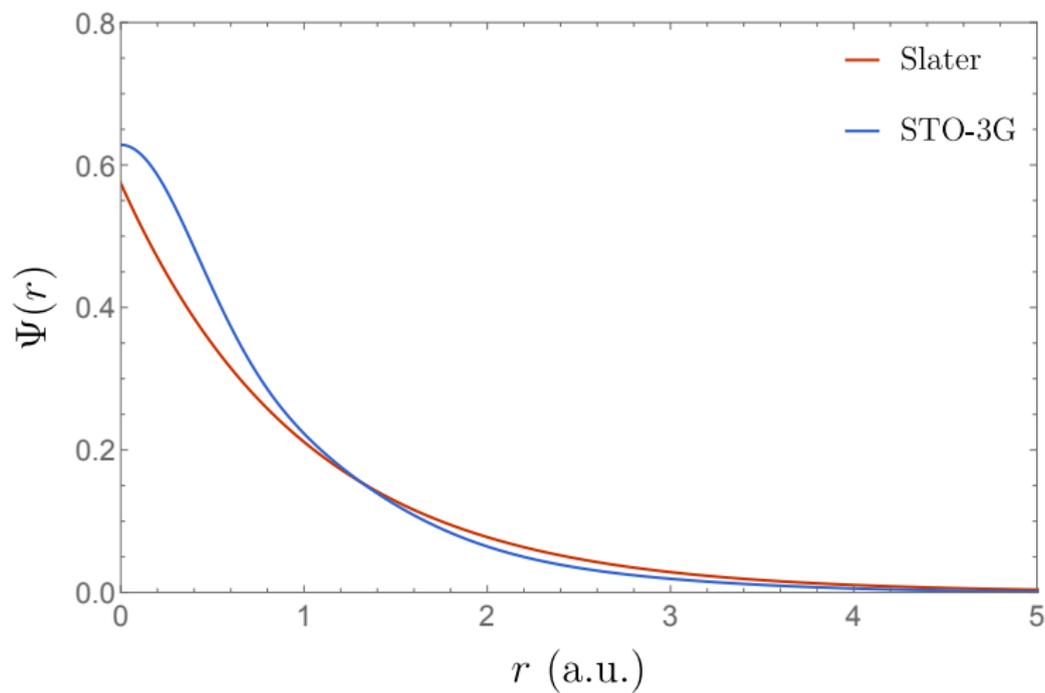
built with **molecular orbitals (MOs)** looking like

$$\phi_i(\mathbf{r}) = \sum_{\mu}^N c_{\mu i} \chi_{\mu}(\mathbf{r}) \quad \text{where } \chi_{\mu}(\mathbf{r}) \text{ is a Gaussian basis function}$$

A Gaussian function centered at $\mathbf{r} = \mathbf{0}$ is **“cusplless”** at $r = 0$, i.e.

$$\left. \frac{\partial \langle \chi_{\mu}(\mathbf{r}) \rangle}{\partial r} \right|_{r=0} = 0$$

The hydrogen atom



Local energy

Trial wave function and local energy

If the trial wave function Ψ_T is approximate,

$$\hat{H}\Psi_T(R) \neq E\Psi_T(R)$$

but one can define

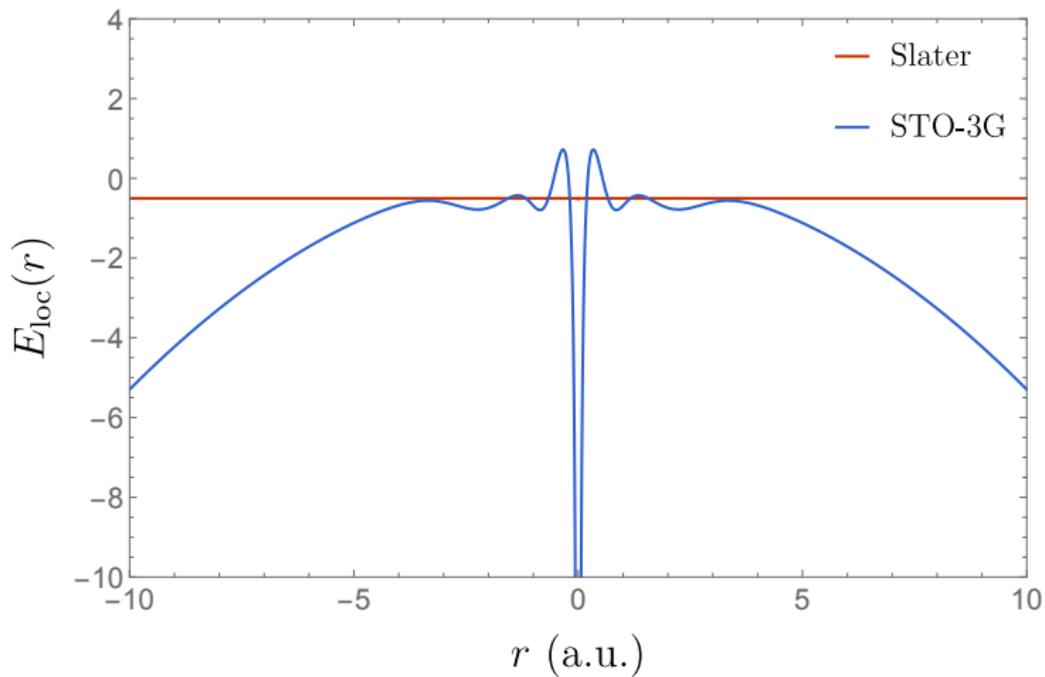
$$\hat{H}\Psi_T(R) = E_{\text{loc}}(R)\Psi_T(R)$$

where the local energy is

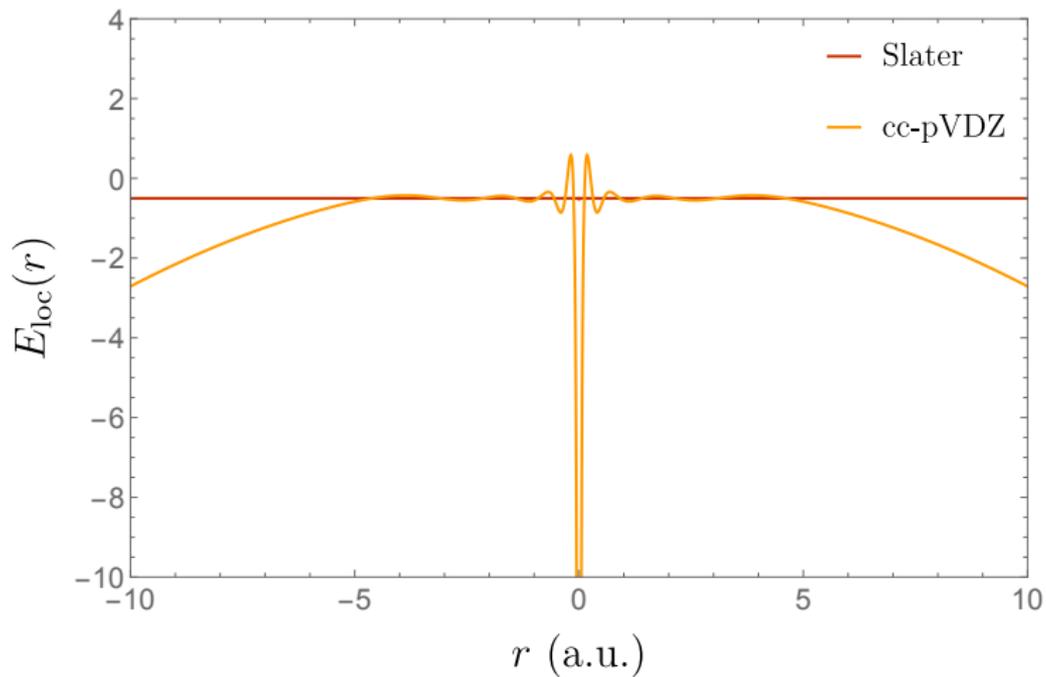
$$E_{\text{loc}}(R) = \frac{\hat{H}\Psi_T(R)}{\Psi_T(R)}$$

The fluctuations of E_{loc} measure the “quality” of Ψ_T

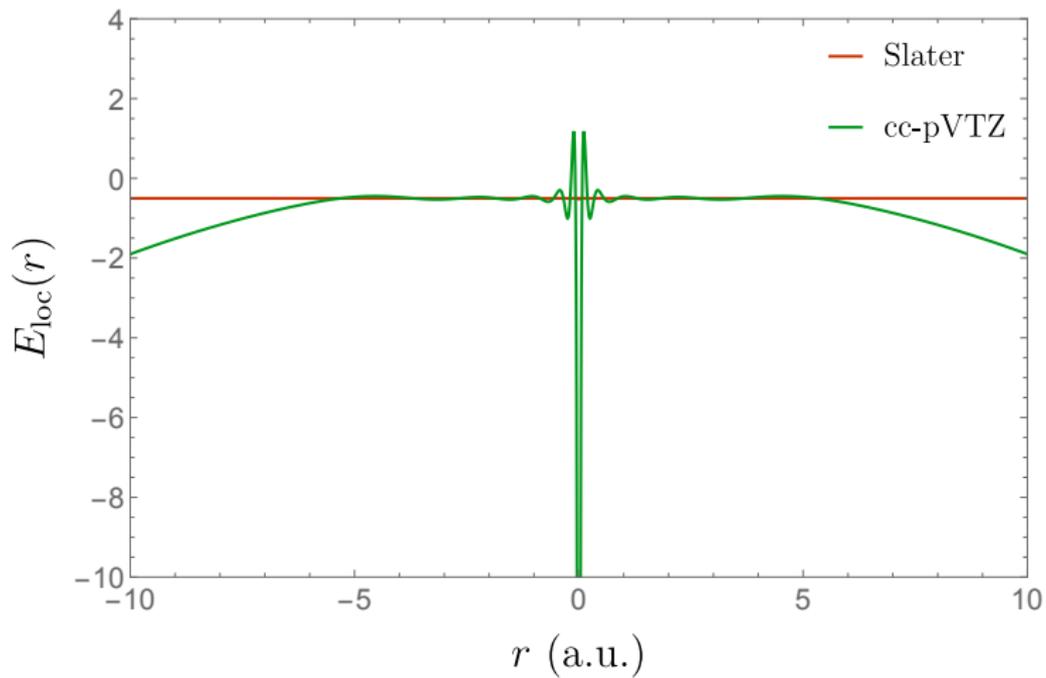
The hydrogen atom



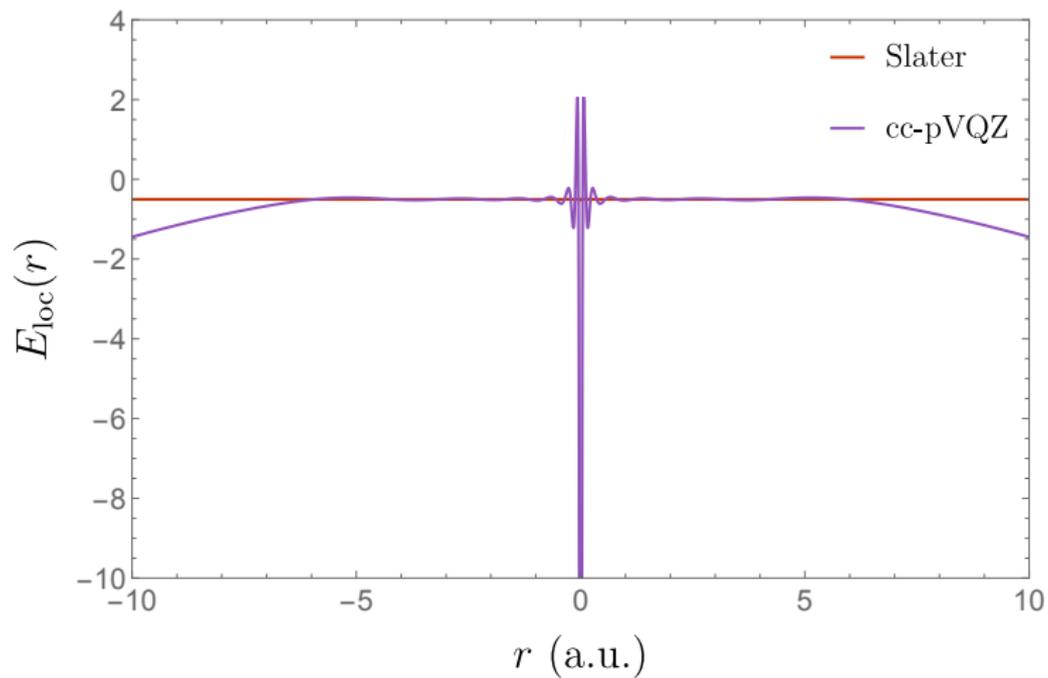
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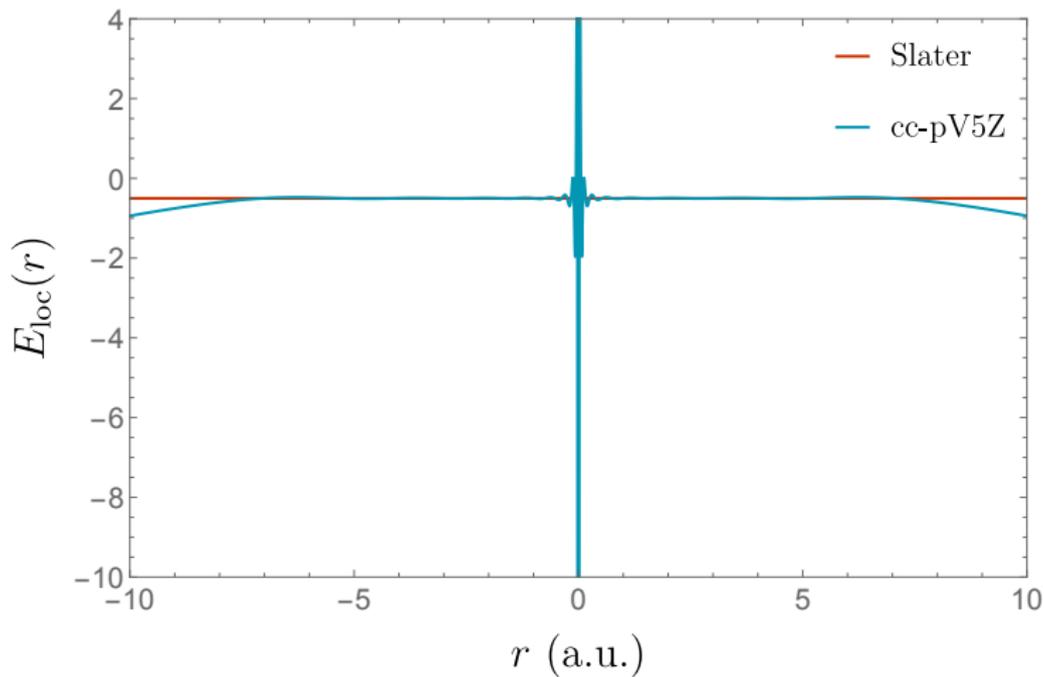
The hydrogen atom



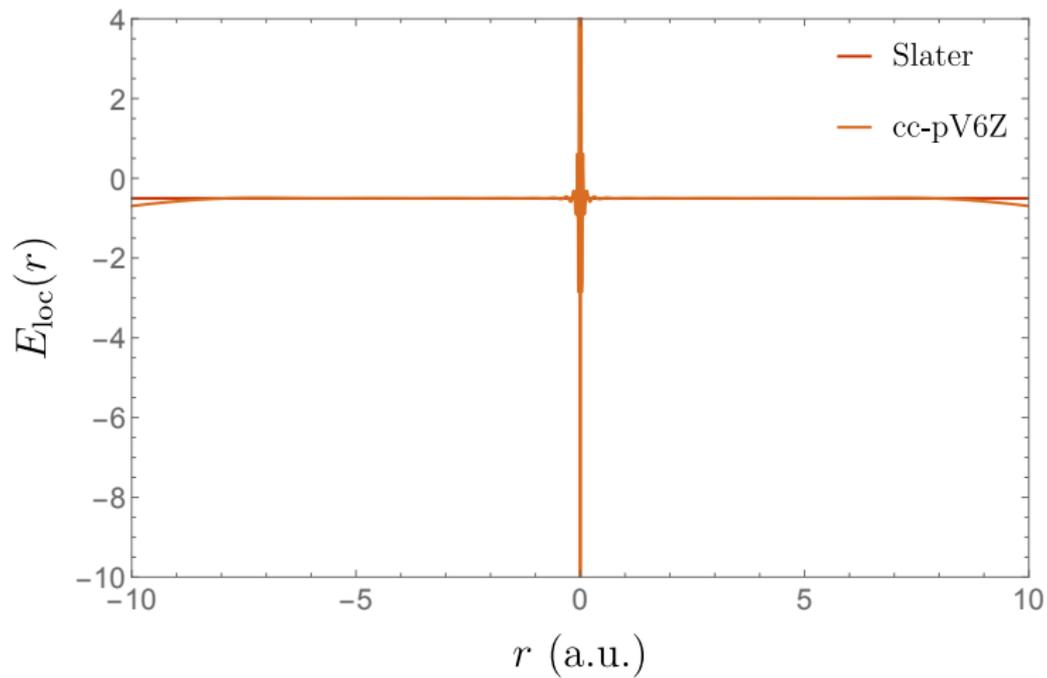
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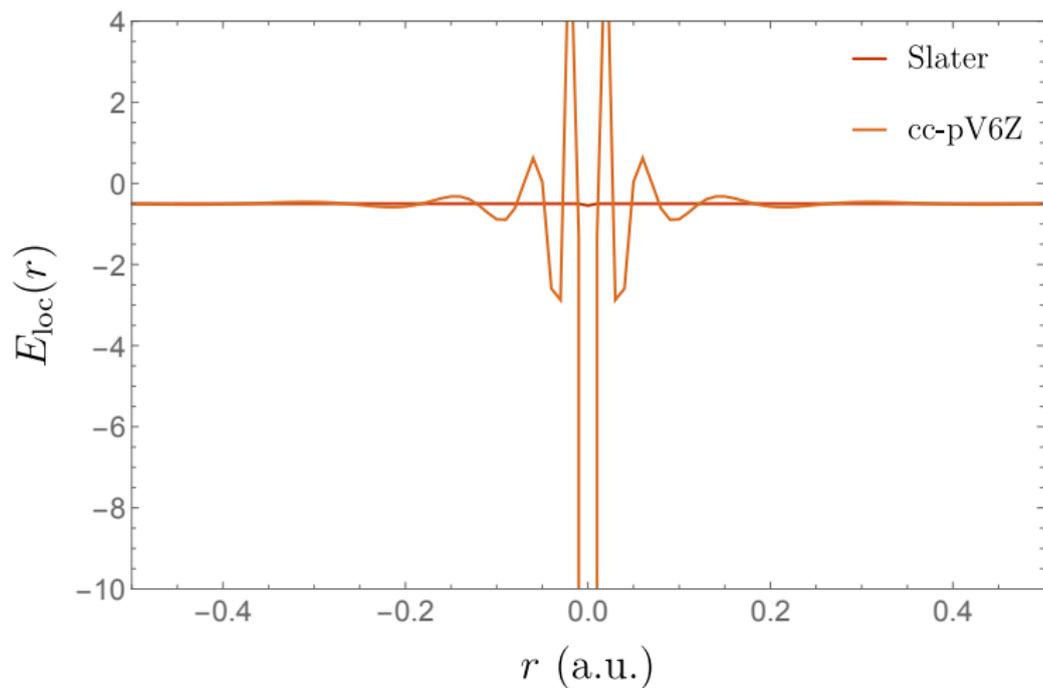
The hydrogen atom



The hydrogen atom



The hydrogen atom



How can we keep E_{loc} finite at the e-n coalescence points?

1. Use a pseudopotential to get rid of the core electrons

- 😊 With Gaussian basis functions, $T(\mathbf{R})$ is **finite** at nuclei.
Therefore, if $V(\mathbf{R})$ is made **finite**, then $E_{\text{loc}}(\mathbf{R})$ will be **finite**
- 😞 One can always blame the pseudopotential...
- 😞 You must use a pseudo for all the atoms!
- 😞😞 (Some) QMC people use a pseudopotential even on the hydrogen atom(!)

How can we keep E_{loc} finite at the e-n coalescence points?

2. Impose e-n cusp via a one-body term within the Jastrow factor

If the Slater determinant $D(\mathbf{R})$ is cusplless, then

$$\Psi_{\text{T}}(\mathbf{R}) = D(\mathbf{R}) \exp\left(\sum_{i,A} \frac{-Z_A r_{iA}}{1 + b_A r_{iA}}\right)$$

has the right e-n cusp

- 😊 **Nodeless function:** doesn't change the nodal structure of Ψ_{T}
- 😞 Not orthogonal to MOs: **redundant work**
- 😞😞 Needs a **(noisy) stochastic optimization** of Jastrow parameters

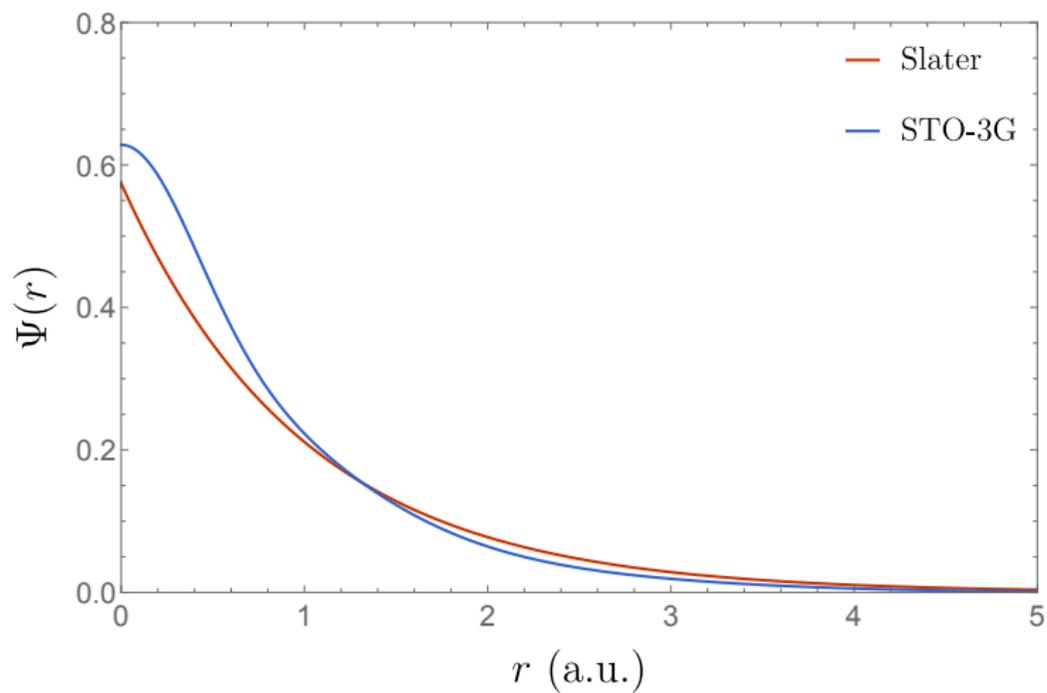
How can we keep E_{loc} finite at the e-n coalescence points?

3. Working on the MOs...

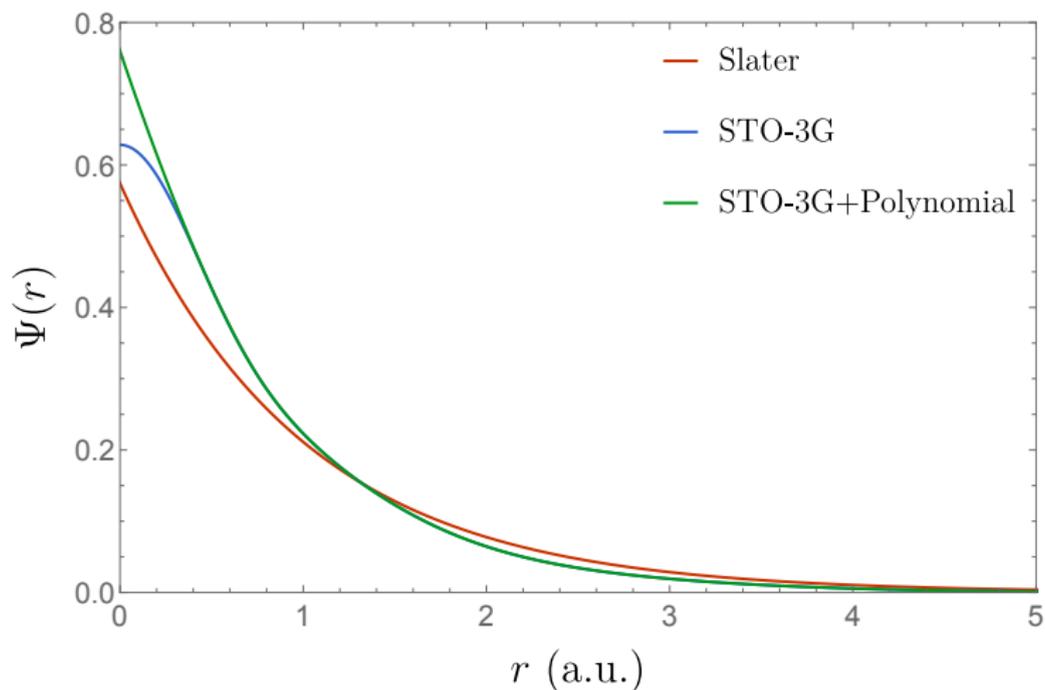
Sufficient condition: if each MO satisfies the Kato cusp condition, then $D(\mathbf{R})$ also satisfies this condition.

- Replace the core MOs with tabulated Slater-based ones
[Scemama et al. JCP 141 \(2014\) 244110](#)
 - ☹ Gaussians basis sets better than Slater ones and yield better nodes
- Create core MOs with STO-NG ($N > 10$), then replace them with STOs
[Petruzielo et al. JCP 136 \(2012\) 124116](#)
 - ☹ Lots of two-electron integrals to calculate
- Use Slater-type basis functions
[Nemec et al. JCP 132 \(2010\) 034111](#)
 - ☹ Expensive for large systems and e-n cusp not guaranteed
- “Circoncision” of the MOs around the nuclei
[Ma et al. JCP 122 \(2005\) 224322](#)
 - ☹ definitely not “ab initio”
 - ☺ widely used

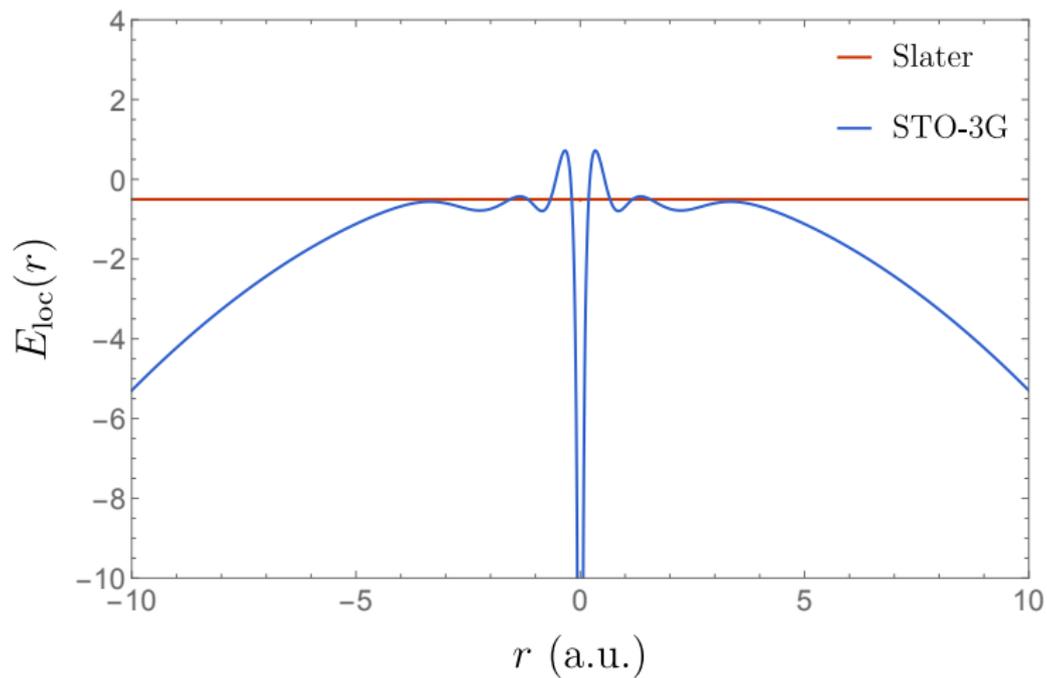
The hydrogen atom (again)



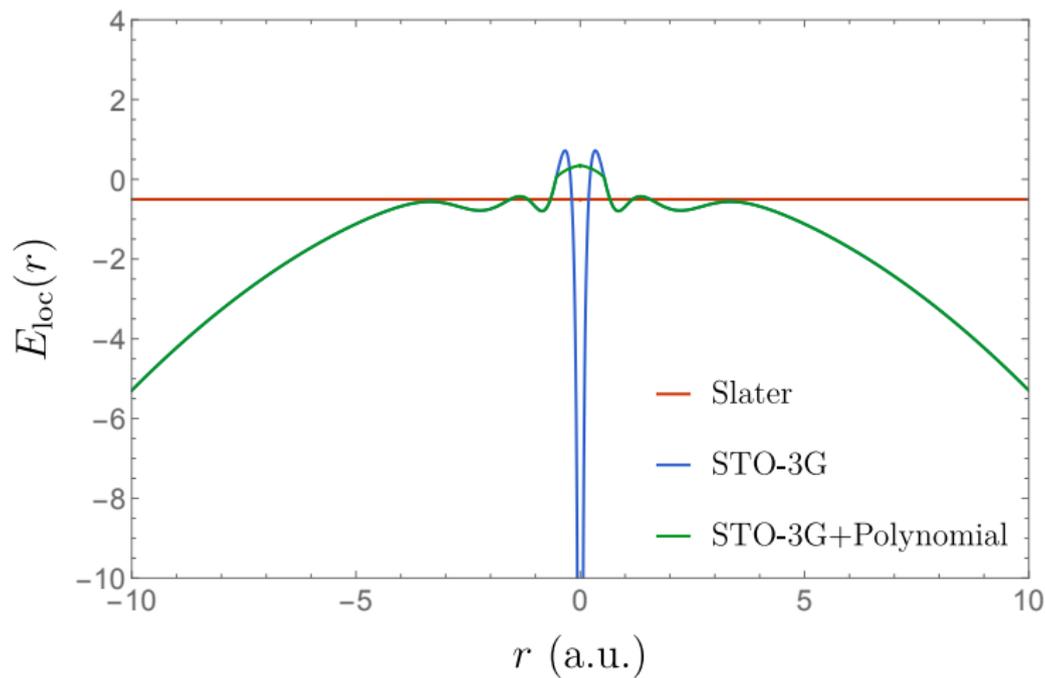
The hydrogen atom (again)



The hydrogen atom (again)



The hydrogen atom (again)



What are we doing?

“We augment the Gaussian basis set with a minimal number of Slater basis functions”

Two procedures

- 1 One-shot (OS)
- 2 Self-consistent dressing (SCD)

Mixed Gaussian-Slater basis: 1. One-shot procedure

- 1 Compute HF or KS **cusplless MOs** $\phi_i(\mathbf{r})$ in your favourite Gaussian basis set
- 2 Add a **cuspl-correcting s-type Slater** on each atom A:

$$\tilde{\chi}_A^i(\mathbf{r}) = \sqrt{\frac{\tilde{\alpha}_i^3}{\pi}} \exp[-\tilde{\alpha}_i |\mathbf{r} - \mathbf{r}_A|] \quad \text{with} \quad \tilde{\alpha}_i = \frac{\phi_i(\mathbf{r}_A)}{\dot{\phi}_i(\mathbf{r}_A)} Z_A$$

to create **cuspl-corrected MOs**

$$\tilde{\phi}_i(\mathbf{r}) = \phi_i(\mathbf{r}) + \hat{P} \phi_i(\mathbf{r}) \quad \text{where} \quad \phi_i(\mathbf{r}) = \sum_A^M \tilde{c}_{Ai} \tilde{\chi}_A^i(\mathbf{r})$$

- 3 Make the **cuspl-correcting MO** $\phi_i(\mathbf{r})$ orthogonal to the space spanned by the Gaussians

$$\hat{P} = \hat{I} - \sum_{\mu} |\chi_{\mu}\rangle \langle \chi_{\mu}|$$

- 4 Adjust \tilde{c}_{Ai} 's to enforce the cuspl conditions for each MO i and each nucleus A

$$\sum_B \left[-\frac{\delta_{AB}}{Z_A} \partial_r \tilde{\chi}_A^i(\mathbf{r}_A) - \tilde{\chi}_B^i(\mathbf{r}_A) + \sum_{\mu} \tilde{S}_{B\mu}^i \chi_{\mu}(\mathbf{r}_A) \right] \tilde{c}_{Bi} = \phi_i(\mathbf{r}_A)$$

Mixed Gaussian-Slater basis: 2. Self-consistent dressing

We want $\tilde{\phi}_i(\mathbf{r})$ to be the **best orbital possible**...

$$\hat{f} |\tilde{\phi}_i\rangle = \tilde{\epsilon}_i |\tilde{\phi}_i\rangle$$

Deng, Gilbert & Gill, JCP 130 (2009) 231101

Projecting out over $\langle \chi_\mu |$ yields

$$\sum_{\nu} F_{\mu\nu} c_{\nu i} + \sum_A \tilde{c}_{Ai} \left(\tilde{F}_{\mu A}^i - \sum_{\lambda} F_{\mu\lambda} \tilde{S}_{\lambda A}^i \right) = \tilde{\epsilon}_i c_{\mu i}$$

where

$$F_{\mu\nu} = \langle \chi_\mu | \hat{f} | \chi_\nu \rangle \quad \tilde{F}_{\mu A}^i = \langle \chi_\mu | \hat{f} | \tilde{\chi}_A^i \rangle \quad \tilde{S}_{\mu A}^i = \langle \chi_\mu | \tilde{\chi}_A^i \rangle$$

To avoid computing $\tilde{F}_{\mu A}^i$, we do the following **approximation**:

$$\tilde{F}_{\mu A}^i - \sum_{\lambda} F_{\mu\lambda} \tilde{S}_{\lambda A}^i \approx \tilde{h}_{\mu A}^i - \sum_{\lambda} h_{\mu\lambda} \tilde{S}_{\lambda A}^i$$

which involves **only** one-electron integrals

Mixed Gaussian-Slater basis: 2. Self-consistent dressing

We obtain the following **eigenvalue problem**:

$$\sum_{\nu} \tilde{F}_{\mu\nu}^i c_{\nu i} = \tilde{\epsilon}_i c_{\mu i},$$

where $\tilde{F}_{\mu\nu}^i$ is an (orbital-dependent) dressed Fock operator

$$\tilde{F}_{\mu\nu}^i = \begin{cases} F_{\mu\mu} + \tilde{D}_{\mu}^i, & \text{if } \mu = \nu, \\ F_{\mu\nu}, & \text{otherwise,} \end{cases}$$

with

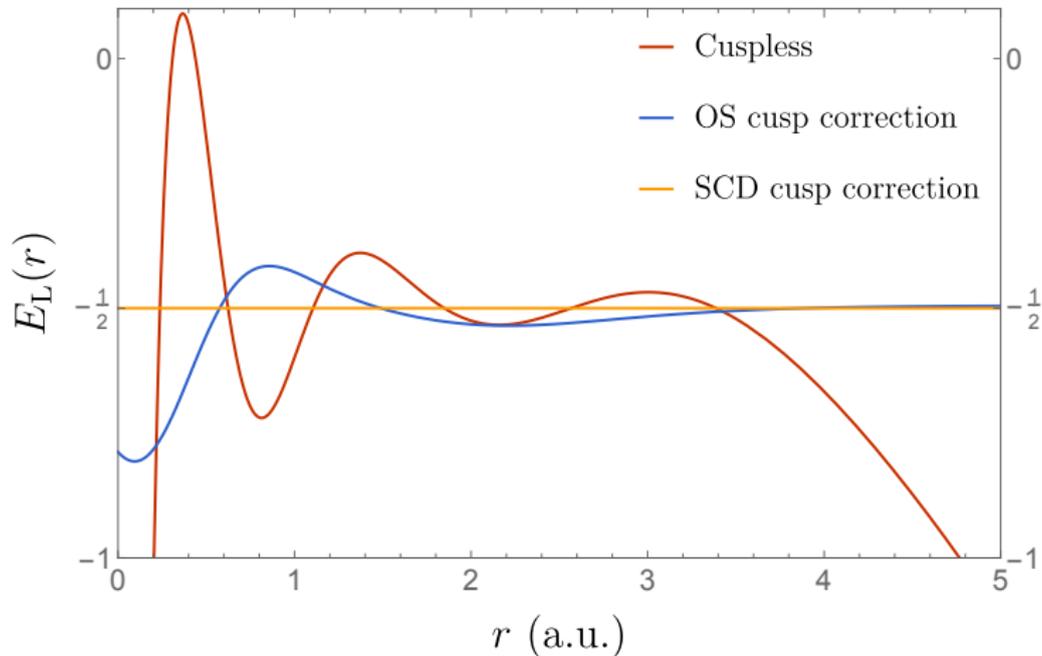
$$\tilde{D}_{\mu}^i = c_{\mu i}^{-1} \sum_A \tilde{c}_{Ai} \left(\tilde{h}_{\mu A}^i - \sum_{\lambda} h_{\mu\lambda} \tilde{S}_{\lambda A}^i \right)$$

The process is repeated until convergence... or not...

NB: somewhat related to the Perdew-Zunger self-interaction correction
Perdew & Zunger, PRB 23 (1981) 5048

The hydrogen atom (again)

Local energy (decontracted STO-3G with $\tilde{\alpha}_H = 1$)

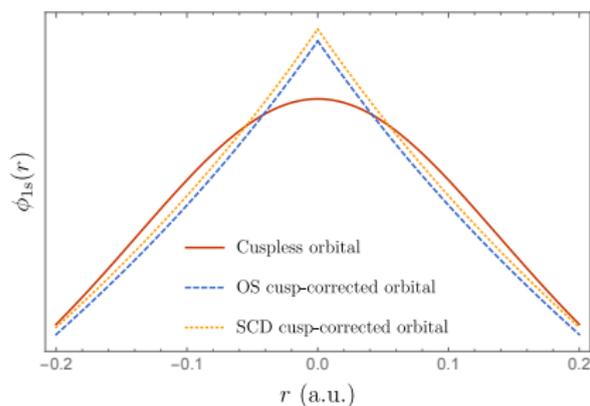
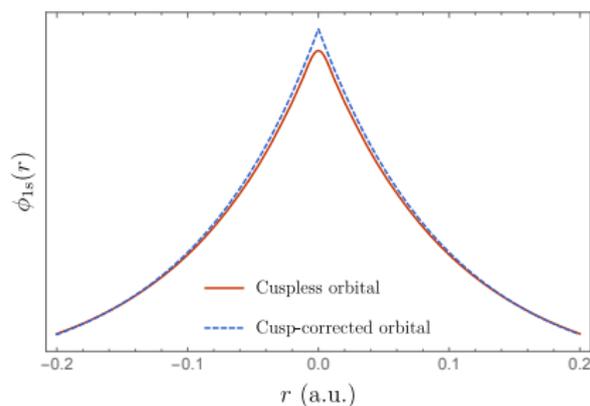


The hydrogen atom (again)

Energy and variance (decontracted STO-3G with $\tilde{\alpha}_H = 1$)

Basis	Cusp correction	Iteration	Energy	Variance
Gaussian			-0.495741	2.23×10^{-1}
Mixed	OS		-0.499270	4.49×10^{-2}
Mixed	SCD	#1	-0.499270	4.49×10^{-2}
		#2	-0.499970	3.07×10^{-6}
		#3	-0.500000	4.88×10^{-9}

Cusp-corrected MOs in atoms

Helium 1s orbital (HF/6-31G) $\tilde{\alpha}_{\text{He}} = 2$ Neon 1s orbital (HF/6-31G) $\tilde{\alpha}_{\text{Ne}} = 10$ 

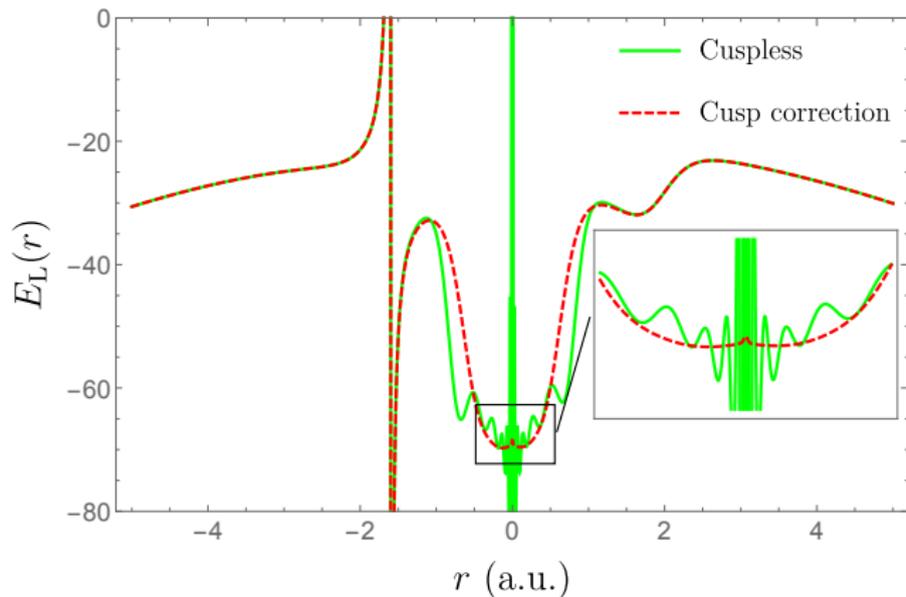
Cusp-corrected schemes for the helium atom

Table: HF and FCI energies of the He atom obtained with the 6-31G basis set. The error bar corresponding to one standard deviation is reported in parenthesis.

System	Method	Cusp correction	Energy (a.u.)			Variance (a.u.)	
			Deterministic	VMC	DMC	VMC	DMC
He	HF		-2.855 160	-2.855 12(6)	-2.903 9(1)	3.99(3)	4.47(18)
		OS		-2.857 89(6)	-2.903 4(3)	0.605(6)	0.498(2)
	SCD		-2.858 17(9)	-2.903 2(2)	0.610(3)	0.498(1)	
	FCI		-2.870 162	-2.870 15(2)	-2.903 8(1)	3.89(3)	4.27(3)
OS			-2.872 06(5)	-2.903 5(3)	0.496(4)	0.428(2)	

Local energy in the neon atom

Local energy for Ne (6-31G basis and $\tilde{\alpha}_{\text{Ne}} = 10$)



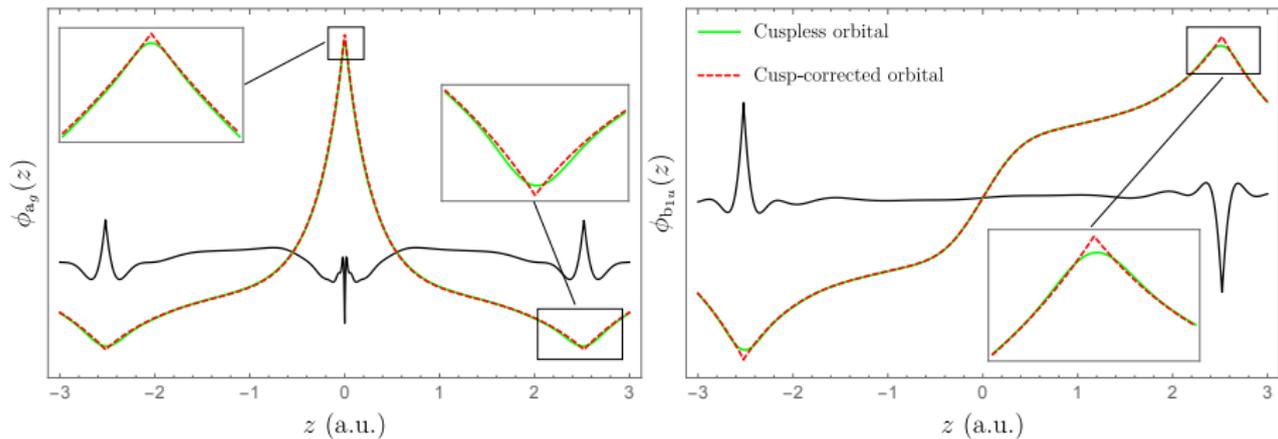
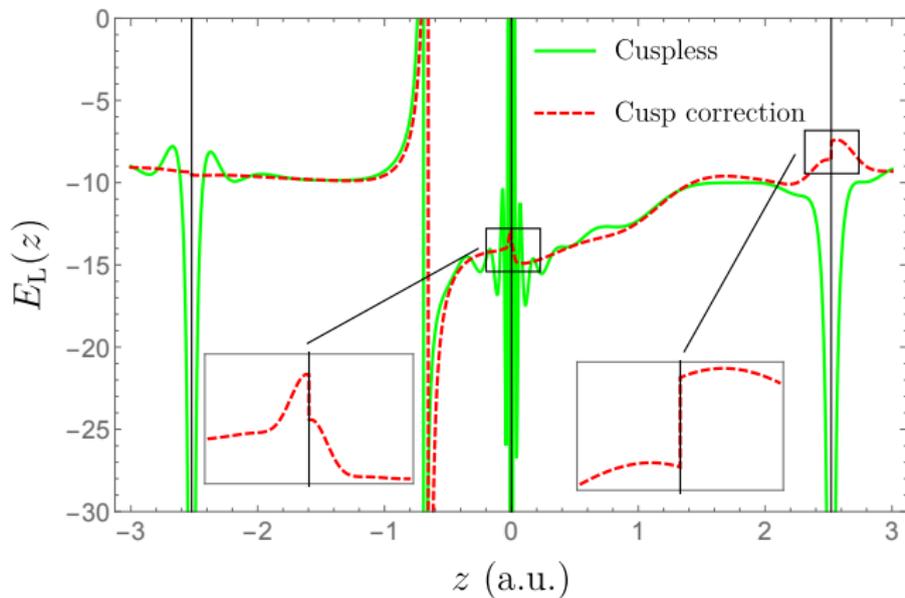
Cusp-corrected MOs in BeH₂

Figure: Cuspless and cusp-corrected HF valence (a_g and b_{1u}) orbitals of the BeH₂ molecule obtained with the 6-31G basis set. For the a_g orbital, we have $\tilde{\alpha}_{Be} = 3.7893$ and $\tilde{\alpha}_H = 1.1199$, while for the b_{1u} orbital, $\tilde{\alpha}_H = 1.2056$. The black line corresponds to the difference between the cuspless and cusp-corrected orbitals magnified by one order of magnitude.

Local energy in BeH_2 

Concluding remarks

Things to explore further...

- Is there a **better strategy** to optimise simultaneously the Gaussian and Slater coefficients (CIS-type, perturbative, other type of dressing, etc)?
- Shall we use **something else** than a Slater function to enforce the cusp (polynomial, erf, ramp, etc)?
- More generally, **how do we get the nodes right?**

Future directions...

- The same procedure could potentially be employed to correct **long-range behaviour** of the electronic density with obvious application in **density-functional theory**
- We are currently working on a similar methodology to enforce **the electron-electron cusp** in **explicitly correlated wave functions**

Collaborators and Funding

- **Collaborators:** Anthony Scemama & Michel Caffarel



- **Job & Money:** Centre National de la Recherche Scientifique (CNRS)

