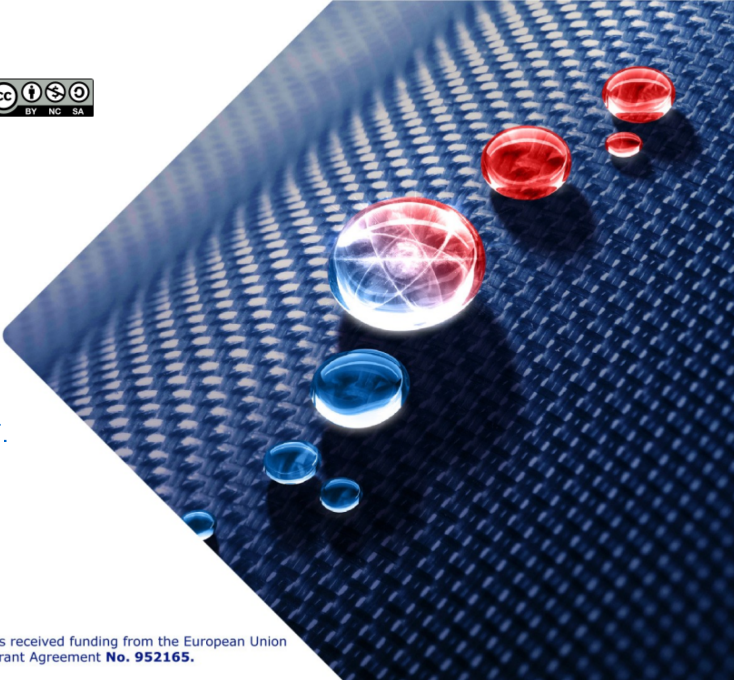
Targeting Real chemical accuracy at the EXascale



Diffusion Monte Carlo with range-separated DFT/CIPSI trial wave functions

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19/12/2021

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First objective

Goal

Estimate the exact non-relativistic energy of a (small) system

How?

1. Full-CI $\Longrightarrow$ The only error is the finite basis set
2. Extrapolate to the Complete Basis Set limit

How to reach the FCI?

Many possibilities

1. CAS-SCF and increase the number of active MOs. Slow convergence.
2. CI S,D,T,Q,. . . : Increase the level of excitation. Slow convergence.
3. CC S,D,T,Q,. . . : Increase the level of excitation. Fast convergence, but wave function as large as FCI.
4. Selected CI methods (CIPSI, SHCI, FCIQMC, . . .)
5. . . .

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5. . . .

Our choice

CIPSI Configuration Interaction using a Perturbative Selection done Iteratively

$\Longrightarrow$ Compact wave functions

CIPSI Algorithm

1. Define a *reference* wave function:

$$|\Psi\rangle = \sum_{I \in \mathcal{D}} c_I |I\rangle \qquad E_{\text{var}} = \frac{\langle\Psi|\mathcal{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

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2. Generate external determinants:

$$\mathcal{A} = \left\{ (\forall I \in \mathcal{D}) \left(\forall \hat{T} \in \mathcal{T}_1 \cup \mathcal{T}_2 \right) : |\alpha\rangle = \hat{T}|I\rangle, (\alpha \notin \mathcal{D}) \right\}$$

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3. Second order perturbative contribution:

$$\delta E_\alpha(\Psi) = \frac{\langle \Psi | \mathcal{H} | \alpha \rangle \langle \alpha | \mathcal{H} | \Psi \rangle}{E_{\text{var}} - \langle \alpha | \mathcal{H} | \alpha \rangle}, \quad E_{\text{PT2}}(\Psi) = \sum_\alpha \delta E_\alpha(\Psi)$$

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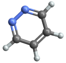
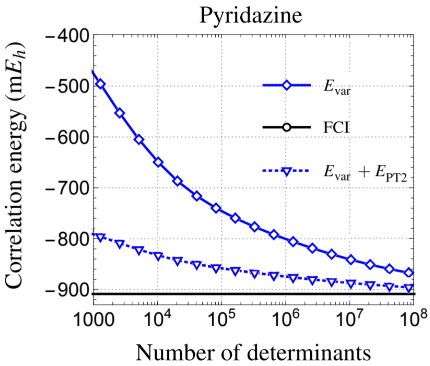
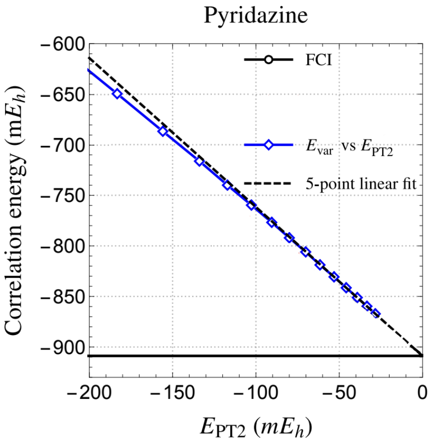
6. Iterate

Convergence of the CIPSI energy

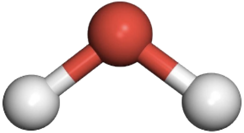




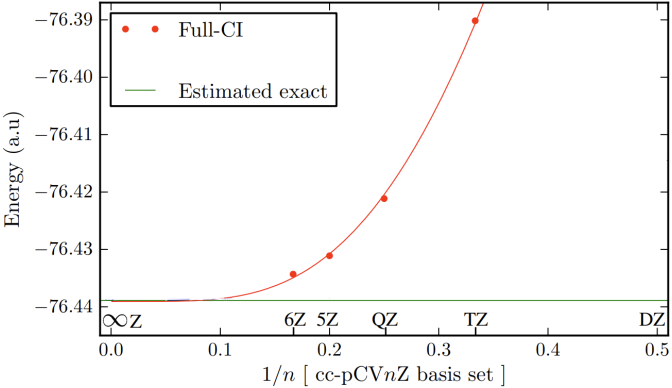


Y. Damour *et al*, 2021, doi:10.1063/5.0065314, arXiv:2108.00321

Extrapolating FCI/DMC to the CBS limit



- FCI/cc-pCVnZ



M. Caffarel *et al*, 2016, doi:10.1063/1.4947093, arXiv:1604.02183

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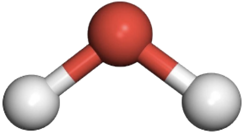
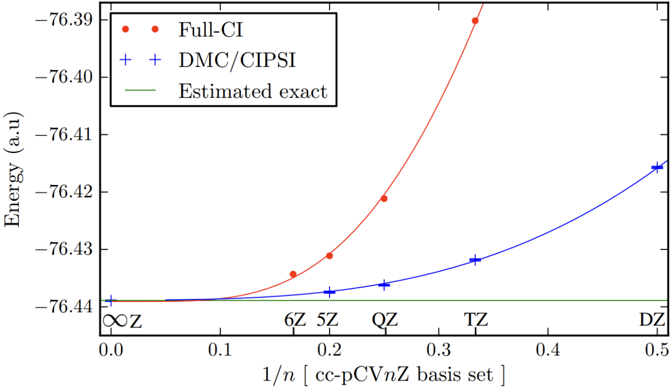


- FCI/cc-pCVnZ
- DMC/CIPSI ($\sim 10^6$ dets)



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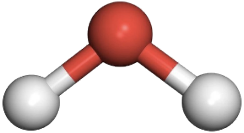

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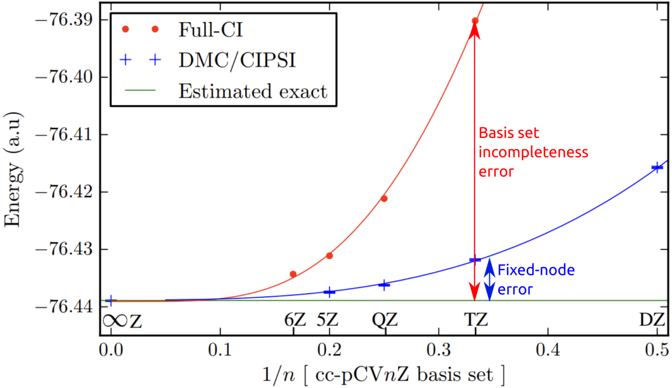

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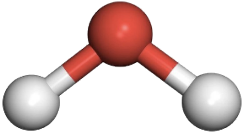
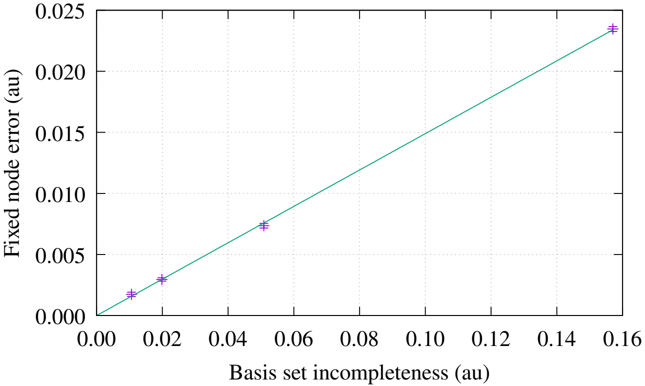
Basis set incompleteness *vs* Fixed node error



$$\delta E_{\mathrm{FN}} \sim \beta\, \delta E_{\mathrm{BSI}}$$



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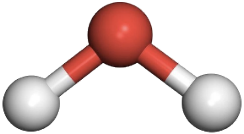
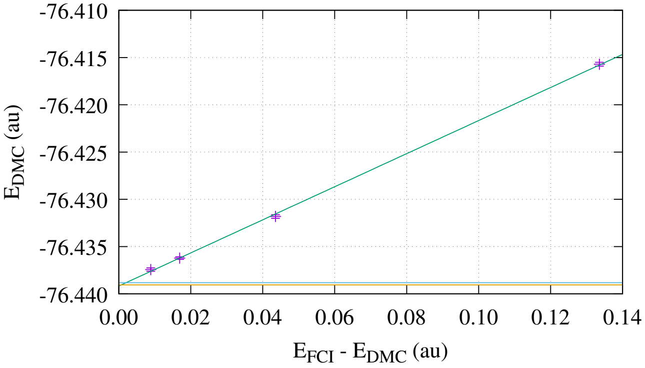


$$E = E_{\text{DMC}} + \alpha(E_{\text{FCI}} - E_{\text{DMC}})$$



Second objective Chemistry

- Total energies are useful for benchmaks, not for chemistry
- Chemistry is all about energy differences
  - Binding energies
  - Reaction barriers
  - Excitation energies
  - ...
- A good compensation of errors is the key:

$$E_{\text{exact}}(A) - E_{\text{exact}}(B) = (E_{\text{approx}}(A) + \delta E(A)) - (E_{\text{approx}}(B) + \delta E(B))$$

- It is OK to increase the total energy of one state if it improves the energy difference

Error cancellations

- Size-consistency is required for a good cancellation of errors
- Selected CI wave functions are not size-consistent
- SCI wave functions with similar $E_{PT2} \Longrightarrow$ good cancellation of errors

$$
\begin{aligned}
\Psi_{\text{FCI}}(\text{A} \cdots \text{B}) &= \Psi_{\text{FCI}}(\text{A}) \times \Psi_{\text{FCI}}(\text{B}) \\
E_{\text{FCI}}(\text{A} \cdots \text{B}) &= E_{\text{FCI}}(\text{A}) + E_{\text{FCI}}(\text{B}) \\
E_{\text{CI}}(\text{A} \cdots \text{B}) + E_{\text{PT2}}(\text{A} \cdots \text{B}) + \dots &= E_{\text{CI}}(\text{A}) + E_{\text{PT2}}(\text{A}) + E_{\text{CI}}(\text{B}) + E_{\text{PT2}}(\text{B}) + \dots
\end{aligned}
$$

If $E_{\text{PT2}}(\text{A}) + E_{\text{PT2}}(\text{B}) = E_{\text{PT2}}(\text{A} \cdots \text{B})$, then $E_{\text{CI}}(\text{A}) + E_{\text{CI}}(\text{B}) \sim E_{\text{CI}}(\text{A} \cdots \text{B})$.

- E. Giner *et al*, 2015, doi:10.1063/1.4905528, arXiv:1408.3672
- M. Dash *et al*, 2020, doi:10.1021/acs.jctc.1c00212, arXiv:2103.01158

For larger systems

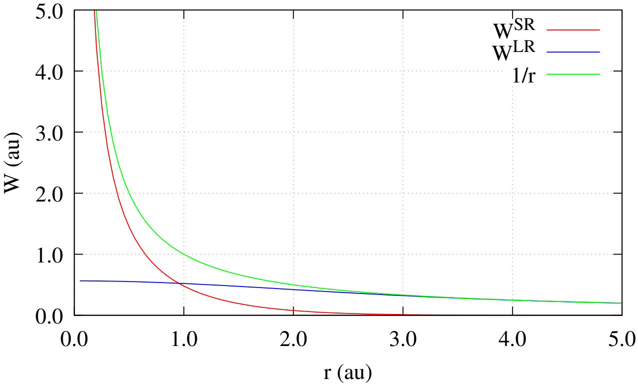
- Convergence to FCI is too hard: E_{PT2} is large and error cancelling is harder
- To reduce the size of the CI expansion
  1. VMC re-optimization with a Jastrow factor: stochastic (noisy) optimization
  2. Trans-correlated FCI + DMC: too expensive for large systems
  3. Range-separated DFT/CIPSI + DMC : deterministic WF optimization

Split the $1/r$ operator into a long-range (LR) and a short range (SR) component:

$$\frac{1}{r} = W^{\text{LR}} + W^{\text{SR}}$$

$$W^{\text{LR}} = \frac{\text{erf}(\mu\, r)}{r}$$

$$W^{\text{SR}} = \frac{1 - \text{erf}(\mu\, r)}{r}$$



A. Savin, Recent Advances in Density Functional Theory, edited by D. P. Chong (World Scientific, 1996) pp. 129–148.

Range-separated DFT

Short range Computed with DFT. LDA works well.

Long range Computed with WFT. Here we use FCI.

$$E = \min_{\Psi} \left(\langle \Psi | \hat{T} + \hat{W}_{\text{ee}}^{\text{LR}} + \hat{V}_{\text{eN}} | \Psi \rangle + E_{\text{Hxc}}^{\text{SR},\mu}[\rho(\Psi)] \right)$$

Range-separation parameter: μ

- $\mu \to 0$: DFT $\implies$ KS Hamiltonian
- $\mu \to \infty$: WFT $\implies$ FCI Hamiltonian

Range-separated DFT

DFT used for short-range correlations

- RS-DFT/CAS, RS-DFT/MP2, *etc*
- Usualy, $\mu = 0.5$ is the optimum

DFT used to correct basis-set incompleteness

- μ depends on r
- Shorter range:
  $\langle \mu \rangle \sim 0.9$ (cc-pVDZ), 1.2 (cc-pVTZ), 1.6 (cc-pVQZ)

- E. Giner *et al*, 2018, doi:10.1063/1.5052714, arxiv:1809.01466
- P.-F. Loos *et al*, 2019, doi:10.1021/acs.jpclett.9b01176 arXiv:1904.10913
- E. Giner *et al*, 2020, doi:10.1063/5.0002892, arxiv:2001.11832

Range-separated DFT

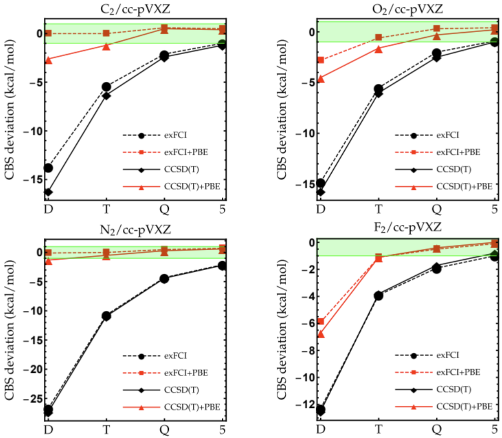
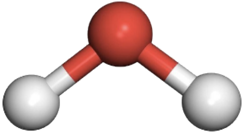
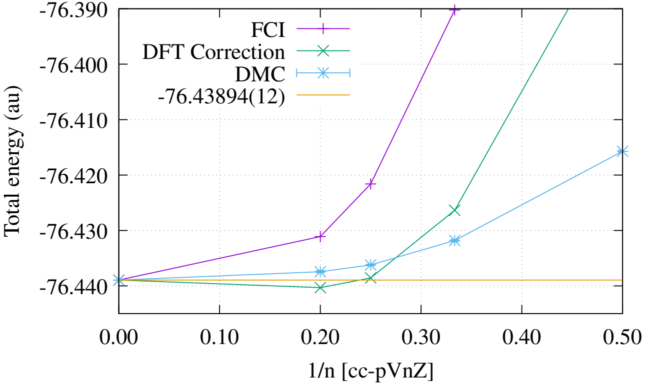


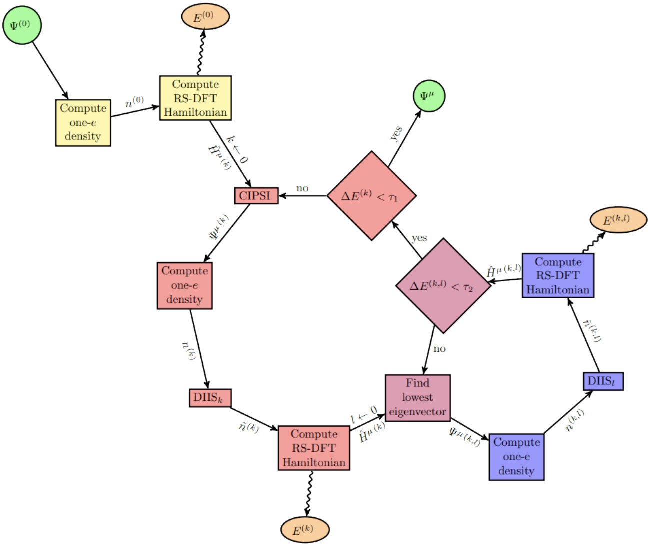
Figure 1: Deviation (in kcal/mol) from CBS atomization energies of C_2 (top left), O_2 (top right), N_2 (bottom left) and F_2 (bottom right) obtained with various methods and basis sets. The green region corresponds to chemical accuracy (i.e. error below 1 kcal/mol). See supporting information for raw data and the corresponding LDA results.

Basis set correction





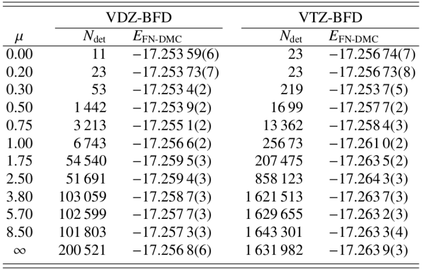
Range-separated DFT/CIPSI



Size-consistent wave functions

1. FCI: adjust the number of determinants by varying μ.
2. DMC with determinant localization approximation → DMC energy independent of the Jastrow

TABLE I. FN-DMC energy $E_{\text{FN-DMC}}$ (in E_h) and number of determinants N_{det} in H_2O for various trial wave functions Ψ^μ obtained with the srPBE density functional.



	VDZ-BFD		VTZ-BFD	
μ	N_{det}	$E_{\text{FN-DMC}}$	N_{det}	$E_{\text{FN-DMC}}$
0.00	11	−17.253 59(6)	23	−17.256 74(7)
0.20	23	−17.253 73(7)	23	−17.256 73(8)
0.30	53	−17.253 4(2)	219	−17.253 7(5)
0.50	1 442	−17.253 9(2)	16 99	−17.257 7(2)
0.75	3 213	−17.255 1(2)	13 362	−17.258 4(3)
1.00	6 743	−17.256 6(2)	256 73	−17.261 0(2)
1.75	54 540	−17.259 5(3)	207 475	−17.263 5(2)
2.50	51 691	−17.259 4(3)	858 123	−17.264 3(3)
3.80	103 059	−17.258 7(3)	1 621 513	−17.263 7(3)
5.70	102 599	−17.257 7(3)	1 629 655	−17.263 2(3)
8.50	101 803	−17.257 3(3)	1 643 301	−17.263 3(4)
∞	200 521	−17.256 8(6)	1 631 982	−17.263 9(3)

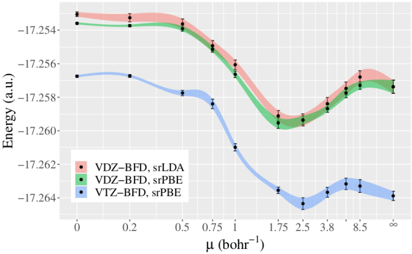


FIG. 2. FN-DMC energy of H_2O as a function of μ for various trial wave functions Ψ^μ generated at different levels of theory. The raw data can be found in the supplementary material.

Comparison with Jastrow + re-optimization

- RSDFT/FCI Hamiltonian is comparable to a transcorrelated FCI Hamiltonian

$$\langle I | H^{\mu} | K \rangle \sim \langle I | e^{-J} H e^{J} | K \rangle$$

- RSDFT/CIPSI: similar to selecting determinants in the presence of a Jastrow and optimizing the WF parameters

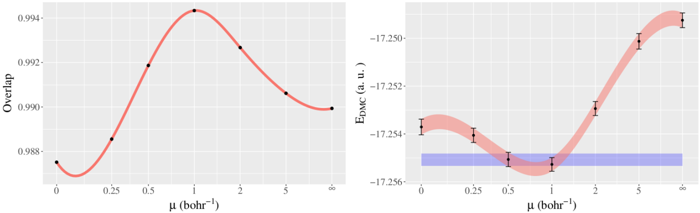


FIG. 3. Left: Overlap between Ψ^{μ} and Ψ^{J} as a function of μ for H_2O. Right: FN-DMC energy of Ψ^{μ} (red curve) as a function of μ, together with the FN-DMC energy of Ψ^{J} (blue line) for H_2O. The width of the lines represent the statistical error bars. For these two trial wave functions, the CI expansion consists of the 200 most important determinants of the FCI expansion obtained with the VDZ-BFD basis (see Sec. IV B for more details). The raw data can be found in the supplementary material.

Atomization energies of the G1 set

Atomization energies are difficult

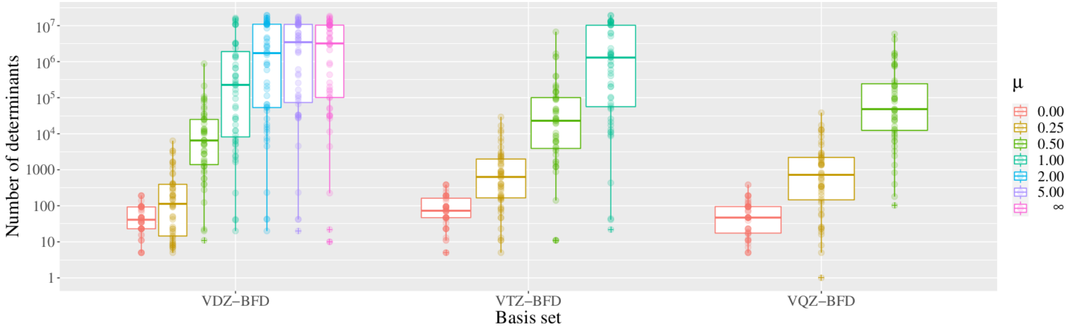
- Basis sets are better suited to atoms than molecules
- Different numbers of interacting pairs in bonded *vs* dissociated molecule

Gaussian-1 set

- 55 molecules
- 12 atoms (Be, C, Cl, F, H, Li, N, Na, O, P, S, Si)

F. R. Petruzielo *et al*, 2012, doi:10.1063/1.3697846, arxiv:1202.0317

Atomization energies of the G1 set



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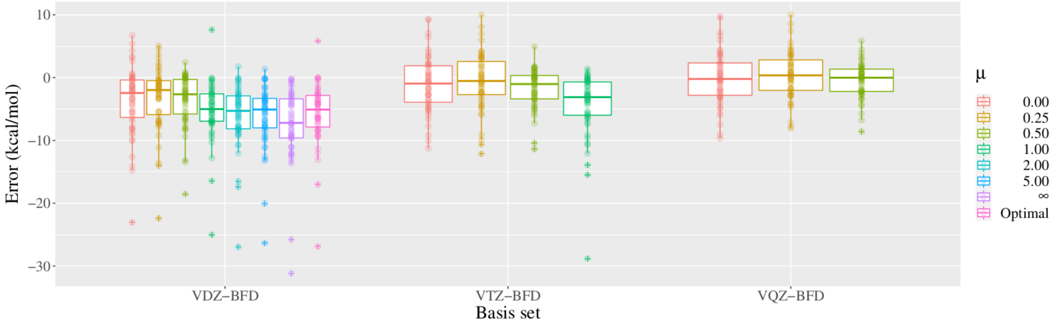

FIG. 5. Errors in the FN-DMC atomization energies (in kcal/mol) for various trial wave functions Ψ^{μ} and basis sets. Each dot corresponds to an atomization energy. The boxes contain the data between first and third quartiles, and the line in the box represents the median. The outliers are shown with a cross. The raw data can be found in the supplementary material.

Atomization energies of the G1 set

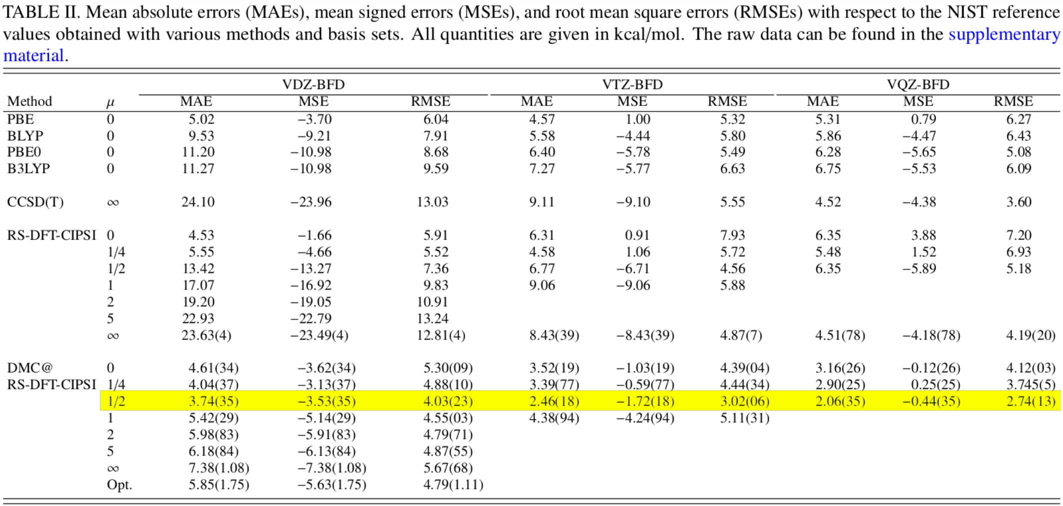

TABLE II. Mean absolute errors (MAEs), mean signed errors (MSEs), and root mean square errors (RMSEs) with respect to the NIST reference values obtained with various methods and basis sets. All quantities are given in kcal/mol. The raw data can be found in the supplementary material.

		VDZ-BFD			VTZ-BFD			VQZ-BFD		
Method	μ	MAE	MSE	RMSE	MAE	MSE	RMSE	MAE	MSE	RMSE
PBE	0	5.02	−3.70	6.04	4.57	1.00	5.32	5.31	0.79	6.27
BLYP	0	9.53	−9.21	7.91	5.58	−4.44	5.80	5.86	−4.47	6.43
PBE0	0	11.20	−10.98	8.68	6.40	−5.78	5.49	6.28	−5.65	5.08
B3LYP	0	11.27	−10.98	9.59	7.27	−5.77	6.63	6.75	−5.53	6.09
CCSD(T)	∞	24.10	−23.96	13.03	9.11	−9.10	5.55	4.52	−4.38	3.60
RS-DFT-CIPSI	0	4.53	−1.66	5.91	6.31	0.91	7.93	6.35	3.88	7.20
	1/4	5.55	−4.66	5.52	4.58	1.06	5.72	5.48	1.52	6.93
	1/2	13.42	−13.27	7.36	6.77	−6.71	4.56	6.35	−5.89	5.18
	1	17.07	−16.92	9.83	9.06	−9.06	5.88			
	2	19.20	−19.05	10.91						
	5	22.93	−22.79	13.24						
	∞	23.63(4)	−23.49(4)	12.81(4)	8.43(39)	−8.43(39)	4.87(7)	4.51(78)	−4.18(78)	4.19(20)
DMC@	0	4.61(34)	−3.62(34)	5.30(09)	3.52(19)	−1.03(19)	4.39(04)	3.16(26)	−0.12(26)	4.12(03)
RS-DFT-CIPSI	1/4	4.04(37)	−3.13(37)	4.88(10)	3.39(77)	−0.59(77)	4.44(34)	2.90(25)	0.25(25)	3.745(5)
	1/2	3.74(35)	−3.53(35)	4.03(23)	2.46(18)	−1.72(18)	3.02(06)	2.06(35)	−0.44(35)	2.74(13)
	1	5.42(29)	−5.14(29)	4.55(03)	4.38(94)	−4.24(94)	5.11(31)			
	2	5.98(83)	−5.91(83)	4.79(71)						
	5	6.18(84)	−6.13(84)	4.87(55)						
	∞	7.38(1.08)	−7.38(1.08)	5.67(68)						
	Opt.	5.85(1.75)	−5.63(1.75)	4.79(1.11)						

Summary

- CIPSI → accurate compact CI wave functions
- To shorten even more the expansion → Jastrow
- Model a Jastrow by short-range DFT → RSDFT/CIPSI
- FCI with a modified Hamiltonian → Size-consistent wave functions
- Excellent atomization energies
- RSDFT/CIPSI/DMC → upper bounds of the exact energy
- Completely automatic and reproducible

A. Scemama *et al*, 2020, doi:10.1063/5.0026324, arxiv:2008.10088