Recent Developments with Transcorrelated Methodologies:
combining real-space concepts with orbital-based quantum chemistry

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Quantum Chemistry

Transcorrelation

Quantum Monte Carlo

HF
MP2
CCSD
CCSD(T)
…
CASSCF
SCI
DMRG
FCIQMC

TC-MP2
TC-CCSD
TC-CCSD(T)
…

TC-SCI
TC-DMRG
TC-FCIQMC

VMC
DMC
BF-DMC
MD+BF-DMC

Good energy differences
Total energies not great:
Good error cancellation

Basis set convergence slow
(F12 methods)

Total energies much closer to
exact limit
Energy differences not great:
Error cancellation not so good

Many-Electron Schrödinger Hamiltonian

$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i<j}\frac{1}{r_{ij}} + \sum_{i}v(\mathbf{r}_i)$$

Coulomb interaction is problematic both at **short-range** and at **long-range**

Short-range singularity leads to cusp conditions, and slow convergence of correlation energy with basis set. This has brought about **explicitly correlated** methods where r12 terms enter the wavefunction ansatz.

Long-range behaviour leads to slow convergence of the energy to the thermodynamic limit, and in metals is the cause of term-by-term divergence of the (per electron) correlation energy in perturbation theory. Random-phase-approximation is required to save the day.

Transcorrelation: a brief history

- Method to **analytically** transform known physics of the wave function into the Hamiltonian

- Introduced in the 1960s by Boys and Handy (following earlier work by Hirschfelder)

- Leads to an non-Hermitian effective Hamiltonian

- Abandoned in the mid-1970s due to serious non-variational difficulties, especially in Slater-Jastrow forms

- Resurrected in the 1990's by Nooijen and Bartlett, and Ten-no, in the context of quantum chemistry

- Development of R12/F12 methods once again lead to declining interest

- Non-hermiticity has been repeatedly cited as the main problem of the TC method, and many "hermitianized" forms of the the TC method have been proposed instead.

- Tsuneyuki and group has pursued TC within a single SD form for

Since 2018

- The Stuttgart group showed that non-hermiticity is not a problem as long an appropriate solver for the TC Hamiltonian is used (initially FCIQMC) [Luo, Alavi, JCTC, **14**, 1403, (2018)]

- Transcorrelation was also found to be highly effective in the 2D Hubbard model, rendering a tough strongly-correlated problem into an eigenvalue problem dominated by one SD [Dobrautz, Luo, Alavi, PRB **99**, 075119 (2019)]

- Implementation of **TCHint library** for efficient evaluation of TC integrals with very flexible Jastrow factors

- TC-FCIQMC implemented in NECI

- TC-CC implemented in elemco.jl (Daniel Kats)

- TC-DMRG in BLOCK2 (Ke Liao, Huanchen Zhai)

Outline

- Transcorrelation: theory, and problems with it.

- FCIQMC and near-exact TC calculations on small molecules

- Optimisation of Jastrow factors

- xTC: eliminating explicit three-body interactions via a mean-field approximation

- TC-Coupled Cluster theory: molecules and UEG

- TC-Perturbation Theory on UEG at high density

Transcorrelation: Non-unitary similarity transformations

$$\Psi = e^{\hat{\tau}}\Phi \qquad\qquad \hat{\tau} = \hat{\tau}^{\dagger}$$

$$\hat{H}\Psi = E\Psi$$

Only if $\hat{\tau}^{\dagger} = -\hat{\tau}$ is the transformation unitary

$$\Rightarrow (e^{-\hat{\tau}}\hat{H}e^{\hat{\tau}})\Phi = E\Phi$$

Baker-Campbell-Hausdorff expansion of the similarity-transformed Hamiltonian:

$$e^{-\hat{\tau}}\hat{H}e^{\hat{\tau}} \equiv \tilde{H} = \hat{H} + [\hat{H}, \hat{\tau}] + \frac{1}{2!}[[\hat{H}, \hat{\tau}], \hat{\tau}] + \ldots$$

Two forms of the correlators lead to analytically exact Hamiltonians

(1) **Jastrow** correlator, useful for ab initio Hamiltonians, starts in 1st quantisation,

$$\tau(\mathbf{R}) = \sum_{i<j} u(\mathbf{r}_i, \mathbf{r}_j), \qquad \mathbf{R} = \{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$$

u is symmetric, but not necessarily merely a function of $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$
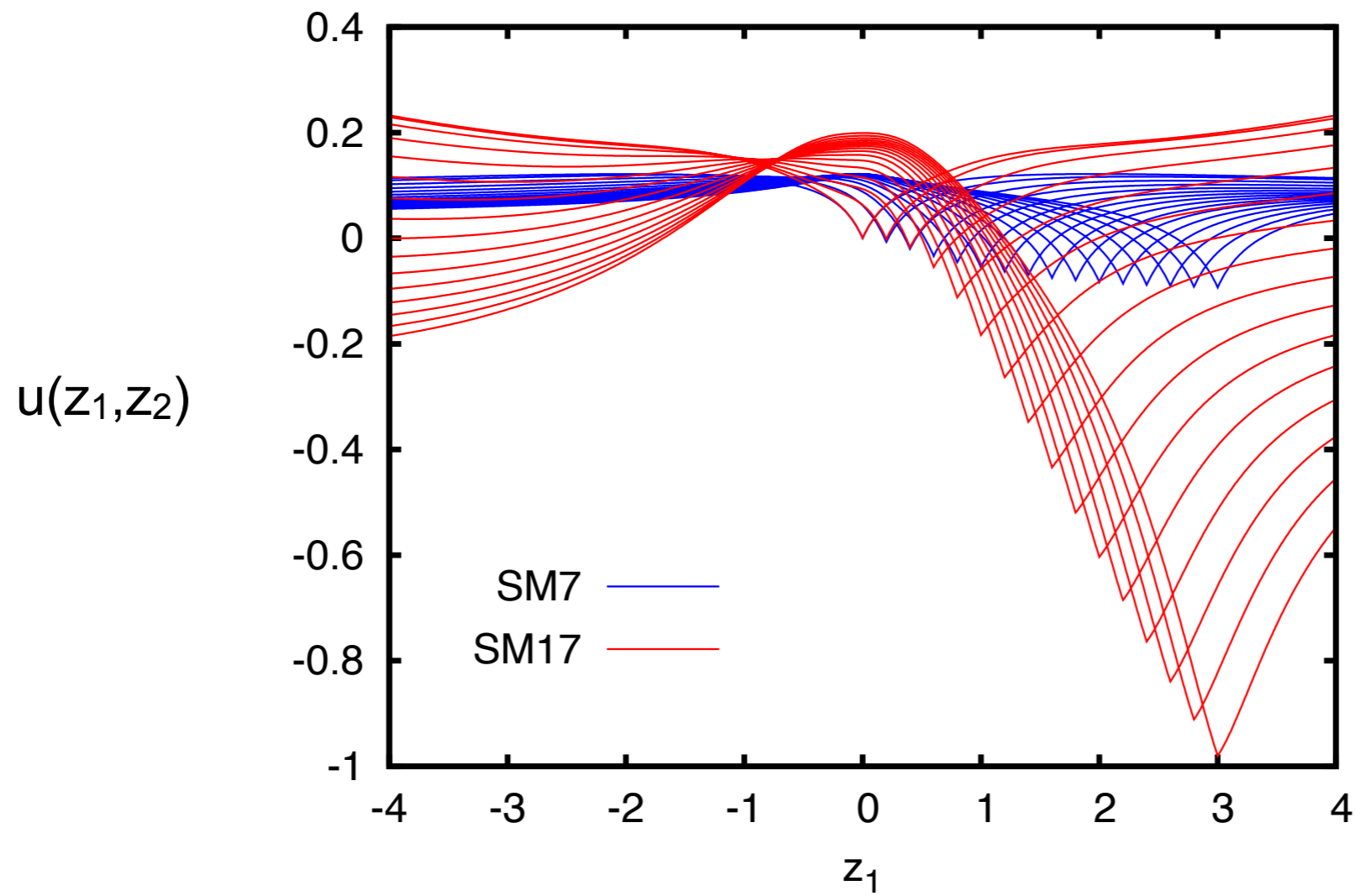
$$u(\mathbf{r}_i, \mathbf{r}_j) = u(\mathbf{r}_j, \mathbf{r}_i)$$

(2) **Gutzwiller** correlator, useful in the Hubbard model, starts in 2nd quantisation
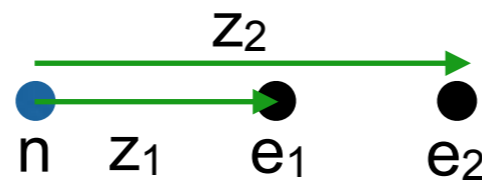
$$\hat{\tau} = J \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

Hubbard model is a good `toy' model to study strong correlation
Dobrautz, Luo, Alavi, PRB **99**, 075119 (2019)

Correlation factor (Ne) with and without e-e-n term

The cusps locate the position of e_2

Jastrow Factorised Similarity Transformation of the S.E.
(Hirschfelder 1963, Boys and Handy 1969)

$$\tau(\mathbf{R}) = \sum_{i<j} u(\mathbf{r}_i, \mathbf{r}_j), \qquad \mathbf{R} = \{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$$

BCH expansion terminates at second order (kinetic energy is 2nd order one-body differential operator):

$$\tilde{H} = \hat{H} - \sum_i \left(\frac{1}{2} \nabla_i^2 \tau + (\nabla_i \tau) \nabla_i + \frac{1}{2}(\nabla_i \tau)^2 \right)$$

What do these terms do: a simple exercise

Consider a simple correlation factor of Coulomb-Yukawa form and apply to the UEG

$$u(r_{ij}) = -\frac{1}{\omega_p r_{ij}}(1 - e^{-\sqrt{\omega_p} r_{ij}}), \quad \omega_p = \sqrt{4\pi\rho}$$

The first term of the TC hamiltonian:

$$-\frac{1}{2}\sum_i \nabla_i^2 \tau = \frac{1}{2}\sum_{i \neq j} \nabla_i^2 u(r_{ij}) = -\frac{1}{2}\sum_{i \neq j} \frac{e^{-\sqrt{\omega_p} r_{ij}}}{r_{ij}}$$

At small r_{ij} this cancels the Coulomb singularity

The second term contains gradient terms and is non-hermitian. It leads to a modified correlated electron drift term which we return to shortly.

The third term:

$$-\frac{1}{2}\sum_i (\nabla_i \tau)^2 = -\frac{1}{2}\sum_{i \neq j} (\nabla_i u(r_{ij}))^2 - \frac{1}{2}\sum_{i \neq j \neq k} \nabla_i u(r_{ij}) \cdot \nabla_i u(r_{ik})$$

A simple exercise continued

$$-\frac{1}{2}\sum_{i\neq j\neq k}\nabla_i u(r_{ij}) \cdot \nabla_i u(r_{ik}) = -\frac{1}{2}\sum_{j\neq k}\frac{1}{r_{jk}} - \frac{(\sqrt{\omega_p}\,r_{jk}+2)e^{-\sqrt{\omega_p}\,r_{jk}}}{2r_{jk}}$$

$$\sim -\frac{1}{2}\sum_{j\neq k}\frac{1}{r_{jk}} \quad \text{for large } r_{jk}$$

The three-body terms account for **long-range screening** of the Coulomb interaction between pairs of distant electrons
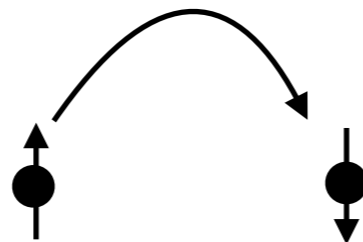
And finally

$$(\nabla_i u(r_{ij}))^2 = \left(-\frac{1}{\omega_p r_{ij}^2} + \left(\frac{1}{\omega_p r_{ij}^2} + \frac{1}{\sqrt{\omega_p} r_{ij}}\right)e^{-\sqrt{\omega_p} r_{ij}}\right)^2$$

$$\sim \frac{1}{\omega_p^2 r_{ij}^4} \text{ for large } r_{ij}$$

$$\frac{1}{2} \text{ for } r_{ij} \to 0$$

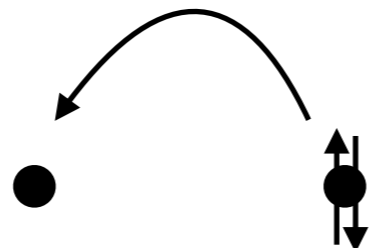Therefore the effective interaction in the TC hamiltonian has a much faster decay than Coulomb (but is still algebraic)

For the Hubbard model, BCH expansion does not terminate but can be resummed

$$\tilde{H} = -t \sum_{<ij>,\sigma} a_{i\sigma}^{\dagger} a_{j\sigma} e^{J(n_{j,\bar{\sigma}} - n_{i,\bar{\sigma}})} + U \sum_{l} n_{l\uparrow} n_{l\downarrow}$$

t is reduced if two electrons are coming together (for J<0)

t is enhanced if two electrons are going to be separated

The non-hermiticity of the TC hamiltonian plays a critically important role

- It modifies the KE operator, turning it from a one-body operator which propagates electrons irrespective of the location of the other electrons, into a two-body operator which reduces the probability amplitude that two distant electrons move towards each other, whilst enhancing the probability amplitude that two near-by electrons move apart

$\tilde{H}$ is a "pseudo-Hermitian" operator

- The non-Hermitian nature of $\tilde{H}$ has been considered a great source of difficulty in the past, which has prevented the wide-spread adoption of the TC method

- As a non-unitary similarity transformation,

$\tilde{H}$ is **iso-spectral** with $\hat{H}$

- The eigenvalues of $\tilde{H}$ are real

- However $\tilde{H}$ has distinct **left** and **right**-eigenvectors

$$\tilde{H}|\Phi^{(R)}\rangle = E|\Phi^{(R)}\rangle$$
$$\langle\Phi^{(L)}|\tilde{H} = \langle\Phi^{(L)}|E$$

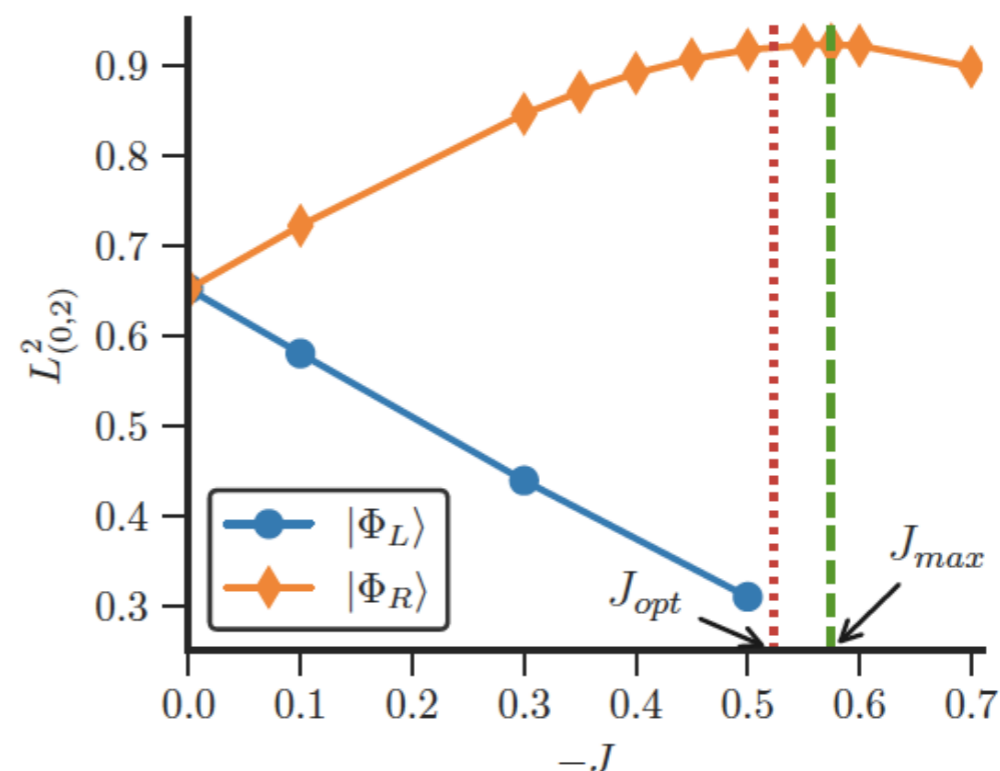- Note that in $\tilde{H}^\dagger$, τ acts in the **wrong** way

$$\tilde{H}^\dagger |\Phi^{(L)}\rangle = E |\Phi^{(L)}\rangle$$

$$\tilde{H}^\dagger = e^\tau \hat{H} e^{-\tau}, \text{i.e.} \quad \tau \to -\tau$$

- The left-eigenvector is less compact.

- Therefore approaches which must compute $\langle \Phi^{(L)} |$ are not ideal (eg bi-variational)

- Need methods which need **only** compute the **right-eigenvector** of $\tilde{H}$

Dobrautz, Luo, Alavi, PRB **99**, 075119 (2019)

18-site 2D Hubbard model, U/t=4

Strategies and approximations to compute $\Phi^{(R)}$

- Transcorrelated FCIQMC

- Transcorrelated DMRG

[Baiardi and Reiher, JCP 153, 164115 (2020)

Time-independent form Liao et al, JCTC 2023]

Main use of these methods is in **multi-reference problems**

- Transcorrelated CC $\Phi^{(R)} = e^{\hat{T}} | D_0 \rangle, \quad \hat{T} \approx \hat{T}_1 + \hat{T}_2$

    Main use is for **weak/medium correlation**

Schraivogel et al, JCP 155, 191101 (2021); 158, 214106 (2023)

Jastrow Factorised Similarity Transformation of the S.E.

$$\tilde{H} = \hat{H} - \sum_{i<j} \hat{K}(\mathbf{r}_i, \mathbf{r}_j) - \sum_{i<j<k} L(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$$

$$\hat{K}(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{2} \left(\underbrace{\nabla_i^2 u + \nabla_j^2 u + (\nabla_i u)^2 + (\nabla_j u)^2} \right)$$
$$+ \left(\nabla_i u \cdot \nabla_i + \nabla_j u \cdot \nabla_j \right)$$

$$L(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = \nabla_i u_{ij} \cdot \nabla_i u_{ik} + \nabla_j u_{ji} \cdot \nabla_j u_{jk} + \nabla_k u_{ki} \cdot \nabla_k u_{kj}$$

The Hamiltonian in 2nd quantised form
(eg in an MO basis)

$$\tilde{H} = \sum_{pq\sigma} h_q^p a_{p\sigma}^\dagger a_{q\sigma} + \frac{1}{2} \sum_{pqrs} (V_{rs}^{pq} - K_{rs}^{pq}) \sum_{\sigma\tau} a_{p\sigma}^\dagger a_{q\tau}^\dagger a_{s\tau} a_{r\sigma}$$

$$- \frac{1}{6} \sum_{pqrstu} L_{stu}^{pqr} \sum_{\sigma\tau\lambda} a_{p\sigma}^\dagger a_{q\tau}^\dagger a_{r\lambda}^\dagger a_{u\lambda} a_{t\tau} a_{s\sigma}$$

$$K_{rs}^{pq} = \langle \phi_p \phi_q | \hat{K} | \phi_r \phi_s \rangle$$

$$L_{stu}^{pqr} = \langle \phi_p \phi_q \phi_r | L | \phi_s \phi_t \phi_u \rangle$$

48-fold symmetry in *L* for real orbitals

K and *L* integrals are computed numerically using standard DFT grids over gaussian orbitals. Main problem is the storage of *L*. Current code can handle ~150 orbitals with sparse storage

Boys-Handy form for *u*

$$u(\mathbf{r}_i, \mathbf{r}_j) = \sum_{\substack{mno \\ m+n+o \le 6}} c_{nml}(\bar{r}_i^m \bar{r}_j^n + \bar{r}_j^m \bar{r}_i^n)\bar{r}_{ij}^o$$

Includes e-e, e-n, and e-e-n terms

$$\bar{r} = \frac{r}{1+r}$$

$$\bar{r} \approx r - r^2 \text{ for small } r$$

$$\bar{r} \approx 1 - 1/r \to 1 \text{ for large } r$$

For the first-row atoms, the 17 parameters have been obtained by a **Variance minimisation** VMC by Schmidt and Moskowitz, JCP, **93**, 4172 (1990)

First application of TC-FCIQMC: First row atoms

Cohen, Luo, Guther, Dobrautz, Tew, Alavi, JCP **151**, 0161101 (2019)

TABLE I. Total atomic energies (hartrees), for CCSD(T), CCSD(T)-F12, and the ST Hamiltonian, using the SM7 and SM17 correlation factors. MAE for each method across the series is also shown.

| Method	Basis	Li	Be	B	C	N	O	F	Ne	MAE
CCSD(T)	cc-pVDZ	−7.432 64	−14.617 41	−24.590 26	−37.761 56	−54.479 94	−74.911 155	−99.529 32	−128.680 69	0.121
	cc-pVTZ	−7.446 06	−14.623 79	−24.605 38	−37.789 53	−54.524 87	−74.984 94	−99.632 19	−128.815 13	0.069
	cc-pVQZ	−7.449 83	−14.640 08	−24.623 50	−37.812 09	−54.553 09	−75.023 19	−99.681 58	−128.876 76	0.039
F12	cc-pVDZ	−7.474 58	−14.654 00	−24.631 21	−37.809 01	−54.537 07	−74.992 08	−99.636 23	−128.811 25	0.053
	cc-pVTZ	−7.472 67	−14.656 53	−24.636 26	−37.818 83	−54.552 93	−75.017 52	−99.669 94	−128.858 90	0.036
	cc-pVQZ	−7.473 70	−14.659 33	−24.641 87	−37.828 84	−54.569 16	−75.040 56	−99.700 70	−128.898 16	0.020
SM7	cc-pVDZ	−7.467 26	−14.655 17	−24.632 79	−37.814 69	−54.534 48	−74.977 85	−99.606 02	−128.783 85	0.063
	cc-pVTZ	−7.476 27	−14.659 43	−24.644 58	−37.837 03	−54.572 36	−75.040 55	−99.694 21	−128.893 89	0.019
	cc-pVQZ	−7.477 85	−14.667 91	−24.654 17	−37.847 91	−54.587 78	−75.062 96	−99.725 07	−128.929 67	0.003
SM17	cc-pVDZ	−7.477 07	−14.667 93	−24.645 21	−37.827 72	−54.557 19	−75.016 39	−99.658 34	−128.836 82	0.036
	cc-pVTZ	−7.478 04	−14.667 89	−24.650 03	−37.839 28	−54.579 89	−75.053 03	−99.713 77	−128.909 44	0.010
	cc-pVQZ	−7.478 45	−14.667 49	−24.652 87	−37.844 61	−54.588 44	−75.066 09	−99.732 83	−128.935 42	0.001
Expt.		−7.478 06	−14.667 36	−24.653 91	−37.845 00	−54.589 20	−75.067 30	−99.733 90	−128.937 60	

Errors in the Total Energies of the first-row atoms
(SM7 i.e. without any e-e-n terms, SM17, and F12)
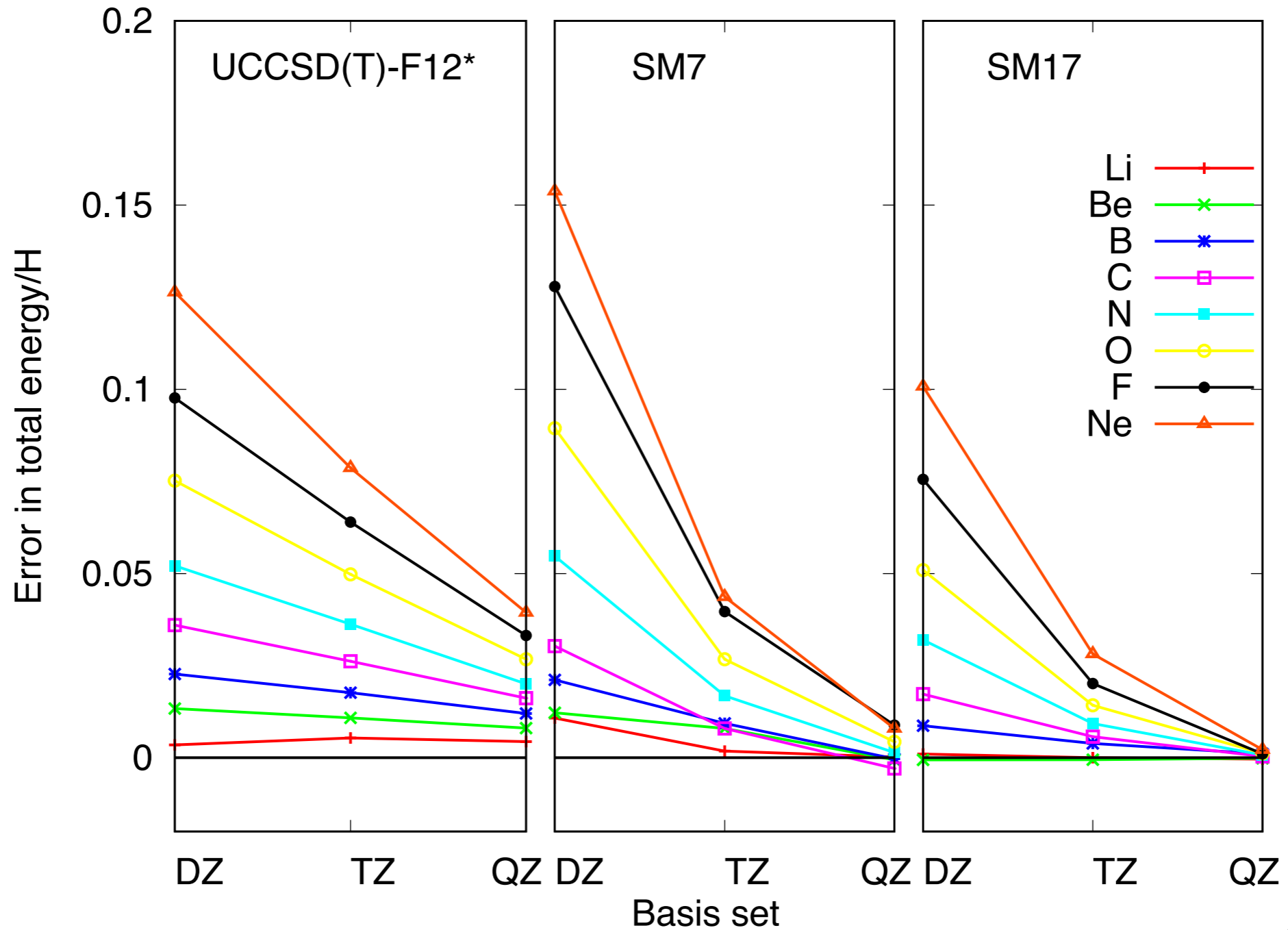
Comparison of TC-CC methods with CC-F12 methods

Schraivogel et al, JCP, **155**, 191101 (2021)

Ionization potentials of the first-row atoms (Li-Ne) in cc-pVTZ basis set
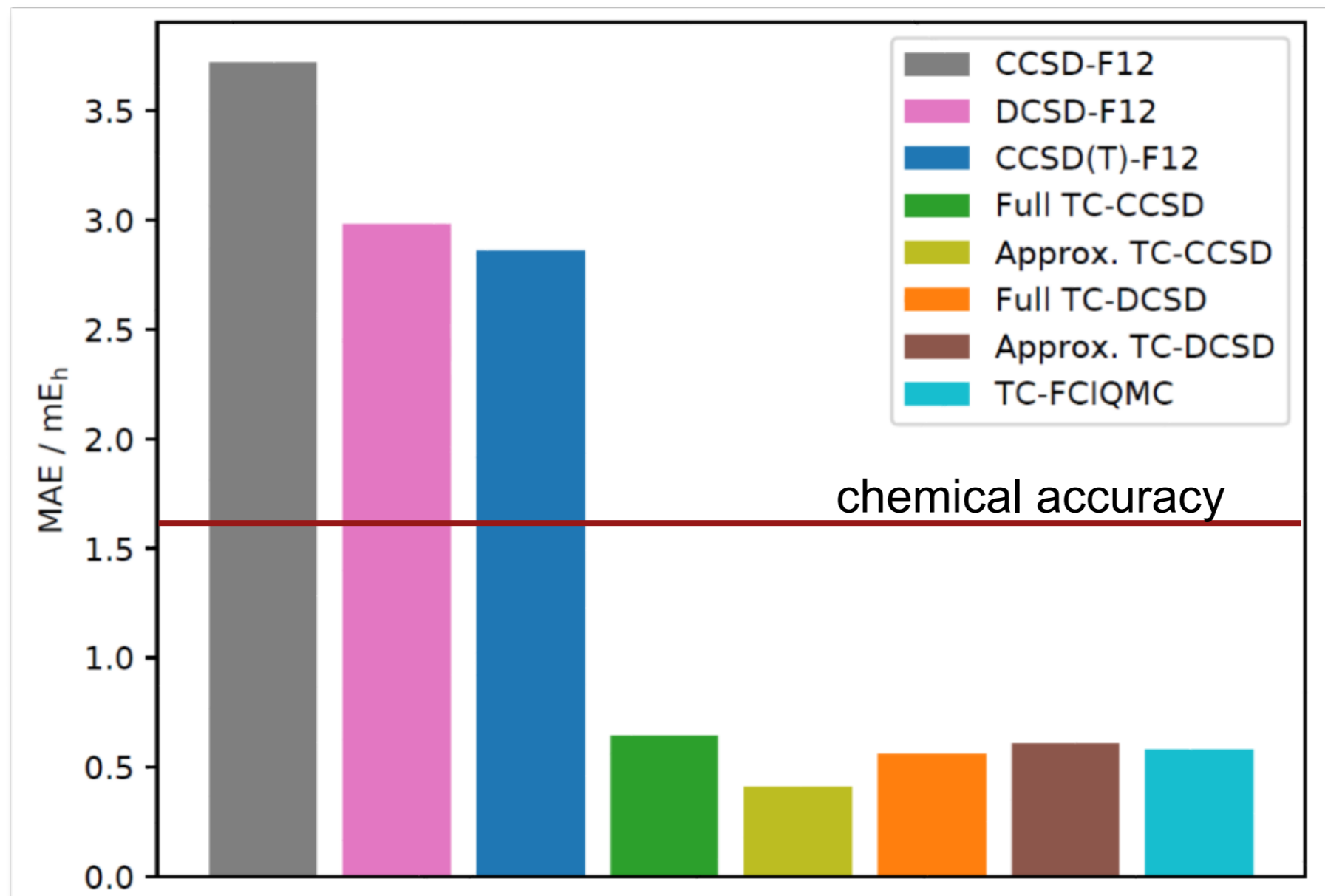
The role of the *K* and *L* terms

Ne atom cc-pVQZ with SM17 correlation factor

$$\langle D_{HF} | \hat{K} | D_{HF} \rangle = -382 \text{ mH}$$

$$\langle D_{HF} | L | D_{HF} \rangle = +108 \text{ mH}$$

The effect of the three-body (*L*) terms is to raise the energy, countering the large negative (non-Hermitian) contributions coming from the two-body (*K*) terms.

It is necessary to have an accurate treatment of the 3-body terms

Form of the Jastrow (CASINO)
Drummond Towler Needs form

$$\tau = \sum_{i<j}^{N_e} u(r_{ij}) + \sum_{i}^{N_e} \sum_{I}^{N_n} \chi(r_{iI}) + \sum_{i<j}^{N_e} \sum_{I}^{N_n} f(r_{ij}, r_{iI}, r_{jI}) \ .$$

$$u(r_{ij}) = t(r_{ij}, L_u) \sum_{k} a_k r_{ij}^k \ ,$$

$$\chi(r_{iI}) = t(r_{iI}, L_\chi) \sum_{k} b_k r_{iI}^k \ ,$$

$$f(r_{ij}, r_i, r_j) = t(r_{iI}, L_f) t(r_{jI}, L_f) \sum_{k,l,m} c_{klm} r_{ij}^k r_{iI}^l r_{jI}^m \ ,$$
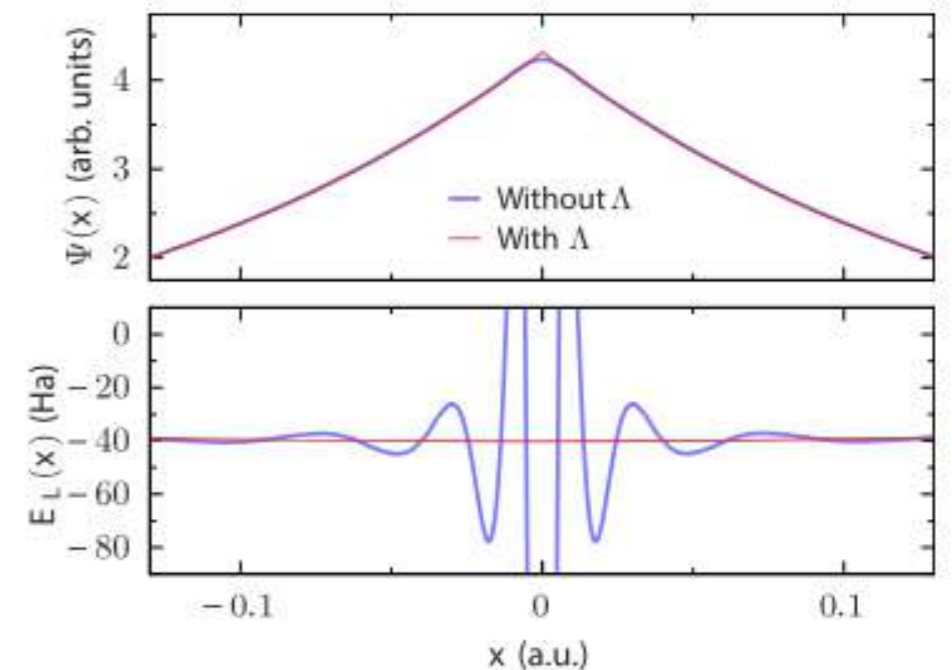
FIG. 1. Wave function value and local energy as a function of the x coordinate of an electron in a carbon atom as it crosses the nucleus at x = 0, both without and with a cusp-correcting Λ Jastrow factor term applied to a HF wave function using the cc-pVDZ basis.

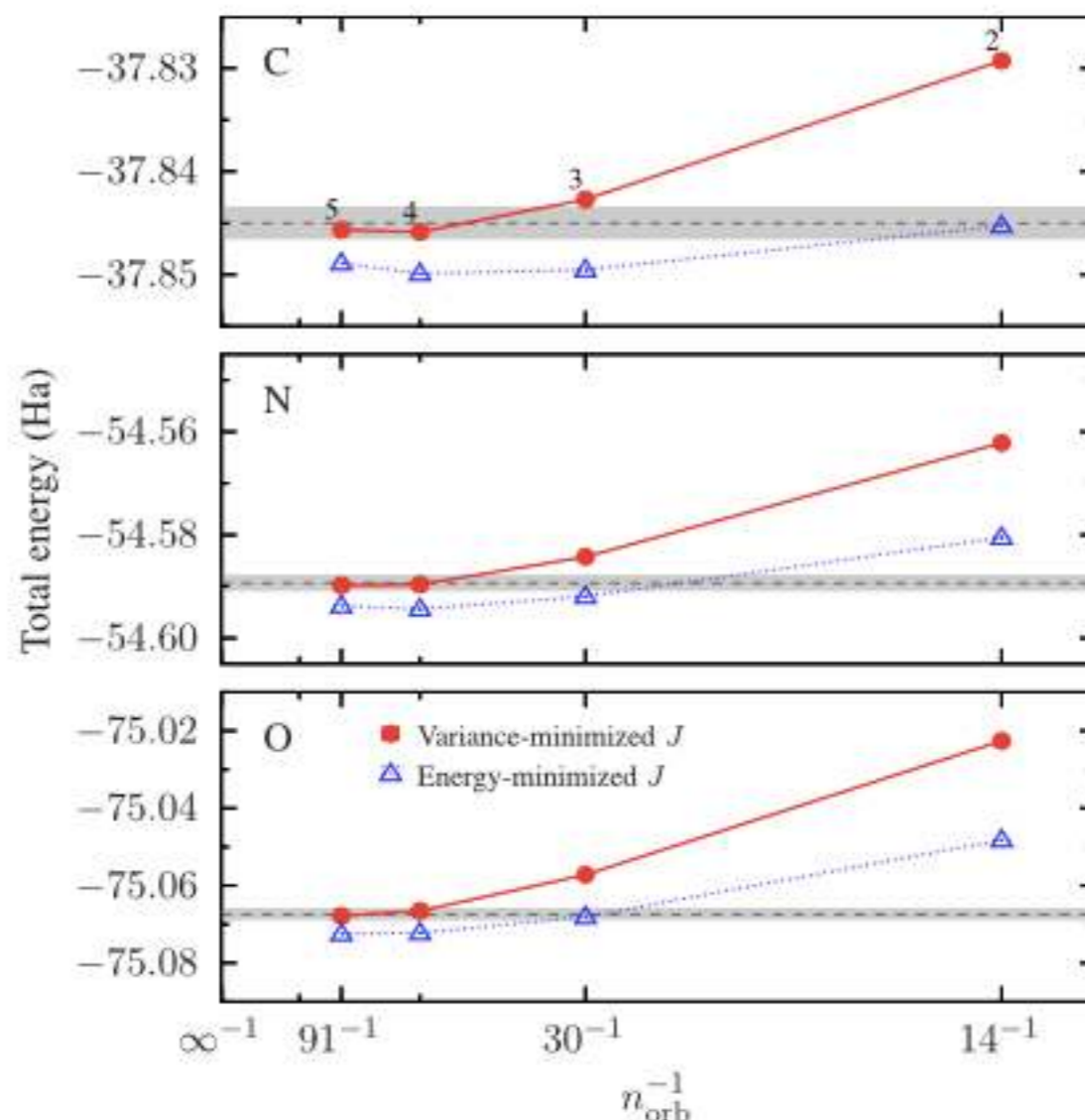# Energy vs variance-minimised Jastrow factors

FIG. 4. Total energy of the C, N, and O atoms as a function of the reciprocal of the number of molecular orbitals in the cc-pVxZ basis set. The non-variational behavior of up to about 5 mHa is evident for the energy-minimized Jastrow factors, for which convergence to the exact energy as a function of basis-set size is rather slow. The shaded areas represent ±1 kcal/mol around the exact non-relativistic total energy from Ref. 50. The points in the top panel are annotated with the basis set cardinal number x.

Energy minimised Jastrow factors tend to lead to non-variational TC energies: convergence to the basis-set limit atomisation energies is from above (wrong!)

Variance-minmized Jastrows show the correct convergence to the exact atomisation energies in the basis-set limit

Optimising Jastrow via a TC Variance Minimisation VMC
## Haupt, Lopez-Rios, et al, JCP 158, 224105 (2023)

Variance minimisation in VMC is a problematic procedure which we found does not lead to stable Jastrow factors useful for the TC method.

Instead we found that minimising the variance of the TC reference energy produces good Jastrow factors

$$\sigma^2_{TC} = \frac{\langle \Psi_{HF} | e^{-\tau}(\hat{H} - E)^2 e^{\tau} | \Psi_{HF} \rangle}{\langle \Psi_{HF} | \Psi_{HF} \rangle}$$

28
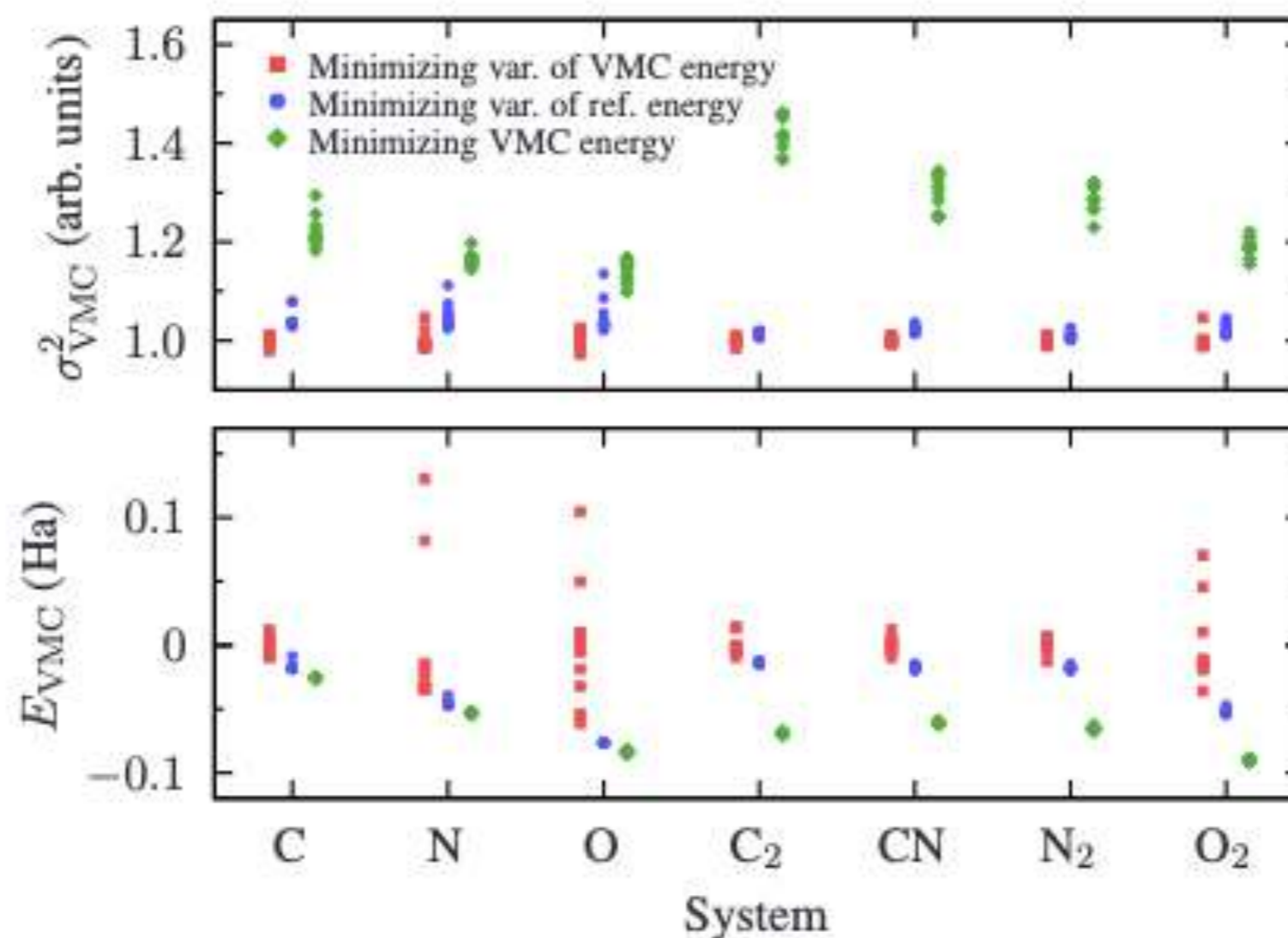
TC-FCIQMC atomisation energies:
basis set convergence towards exact all-electron NR limit
$2E(A)-E(A_2)$
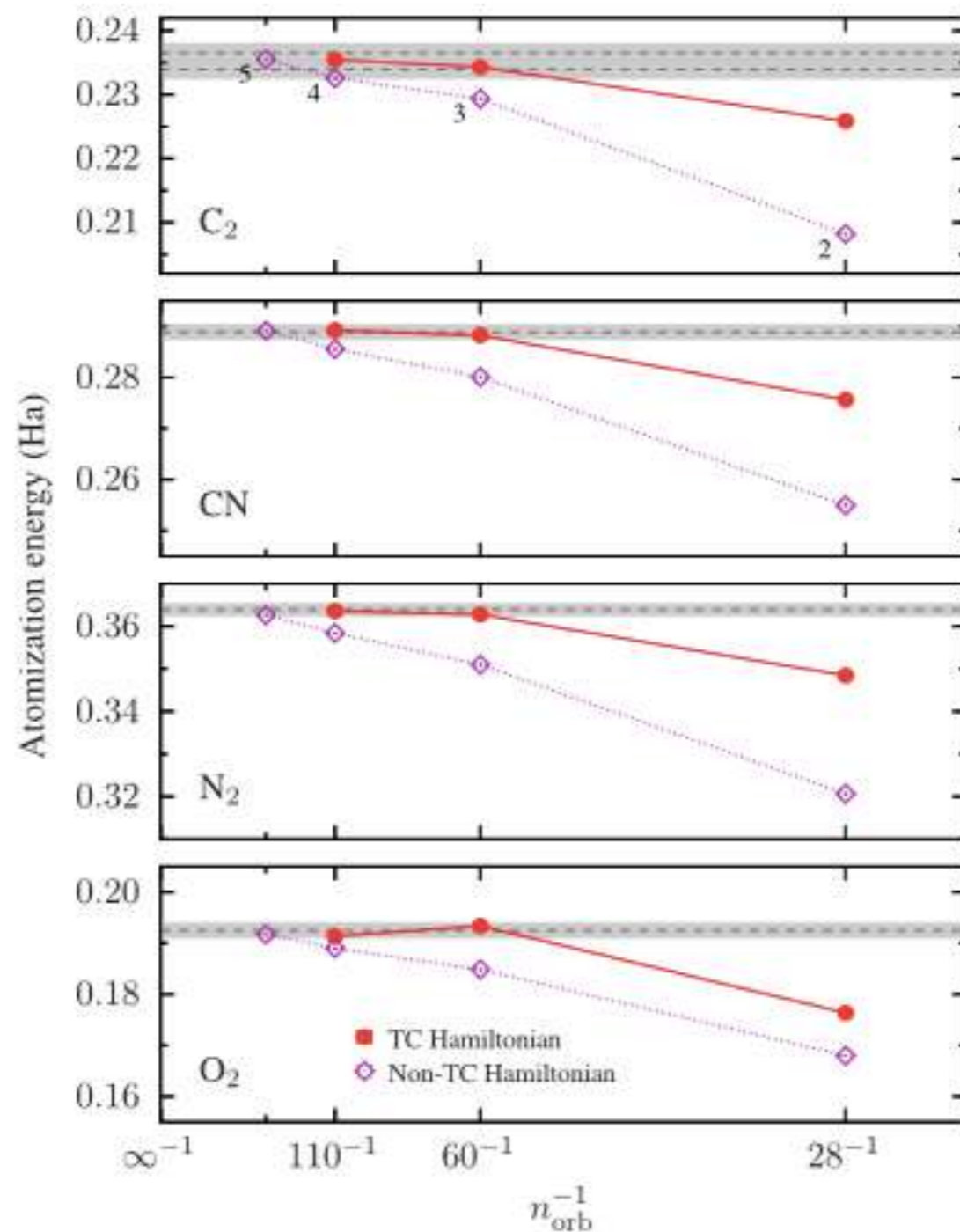
Chemical accuracy is achieved with standard cc-pVTZ basis
(30 basis functions per atom).
Use of larger basis sets is unnecessary.

With the standard (non-TC) approach cc-pV5Z (100 functions per atom) is necessary

3-body mean-field approximation: xTC normal-order wrt HF reference

In spin-orbital notation

$$L_N = \frac{1}{6} \sum_{PRT,QSU} (PQ|RS|TU)\{a_P^\dagger a_R^\dagger a_T^\dagger a_U a_S a_Q\}$$

Setting T=U=I (an HF occupied orbital) and summing over the occupied orbitals

$$\Delta(PQ|RS) = \sum_{I \in HF} [(PQ|RS|II) - (PQ|RI|IS) - (RS|PI|IQ)]$$

$$V_N = \frac{1}{2} \sum_{PQ,RS} [(PQ|RS) + \Delta(PQ|RS)]\{a_P^\dagger a_R^\dagger a_S a_Q\}$$

Dressed 2-particle interactions.

Subsequent CCSD calculation remains $O(N^6)$

Computation of $\Delta(PQ|RS)$: $O(M^4 N_g)$

$$\Delta(PQ|RS) = - \mathscr{P}^{(PQ)}_{(RS)} \left(\sum_g \rho^Q_P(g) A^S_R(g) + \vec{V}^Q_P(g) \cdot \vec{B}^S_R(g) \right)$$

$$\rho^Q_P(g) = w_g \phi^*_P(g) \phi^Q(g)$$

$$\vec{B}^S_R(g) = \frac{1}{2} \tilde{W}(g) \vec{V}^S_R(g) - \vec{Z}^S_R(g)$$

$$A^S_R(g) = \tilde{V}^S_R(g) - \tilde{Z}^S_R(g)$$

$$\tilde{W}(g) = \rho^U_T(g) \gamma^T_U$$

$$\tilde{V}^S_R(g) = \vec{W}(g) \cdot \vec{V}^S_R(g)$$

$$\vec{Z}^S_R(g) = \rho^U_R(g) \vec{X}^S_U(g) + \vec{Y}^T_R(g) \rho^S_T(g)$$

$$\vec{W}(g) = \vec{V}^U_T(g) \gamma^T_U$$

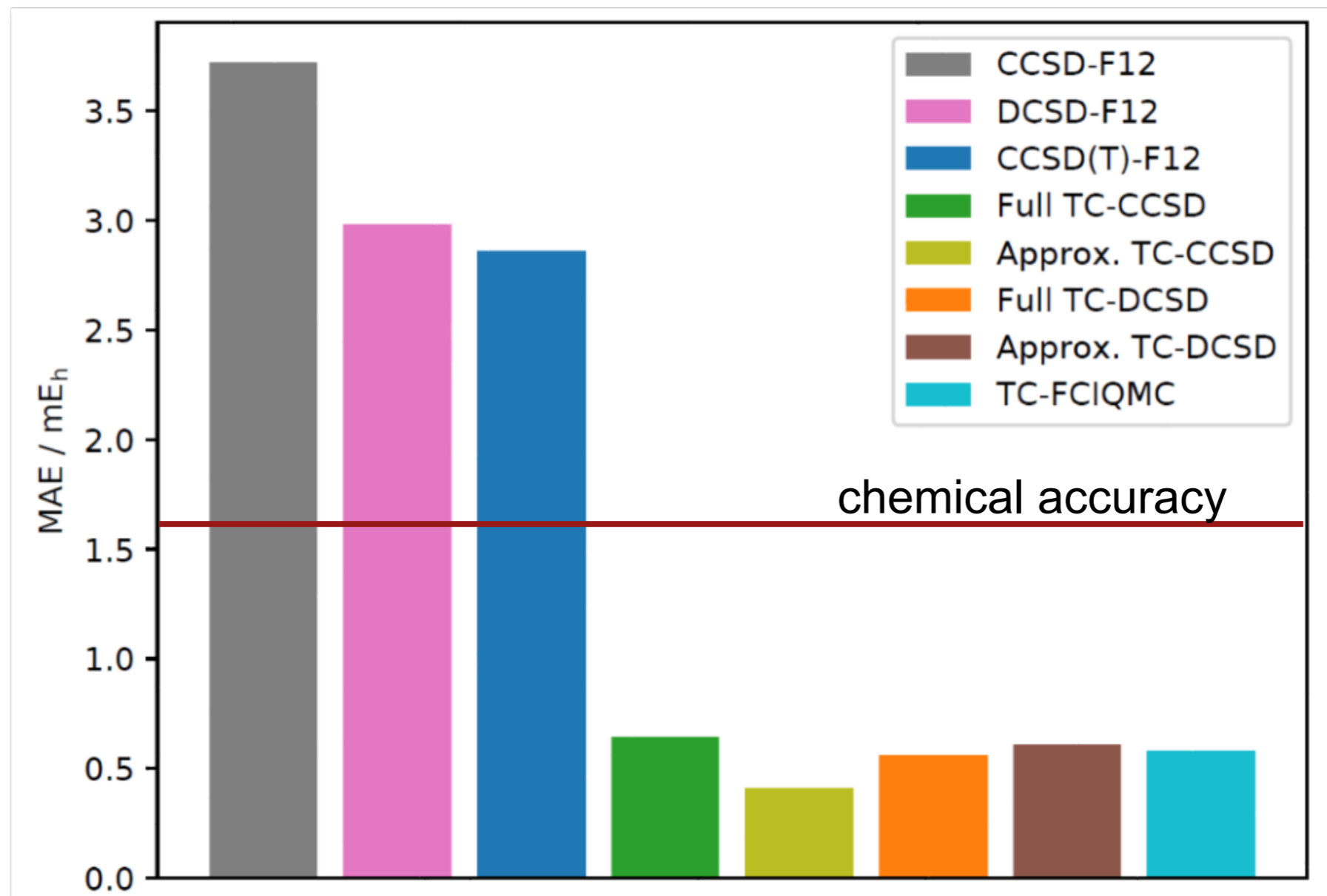$$\vec{Y}^T_R(g) = \vec{V}^U_R(g) \gamma^T_U$$

$$\tilde{Z}^S_R(g) = \vec{V}^U_R(g) \cdot \vec{X}^S_U(g)$$

$$\vec{X}^S_U(g) = \vec{V}^S_T(g) \gamma^T_U$$

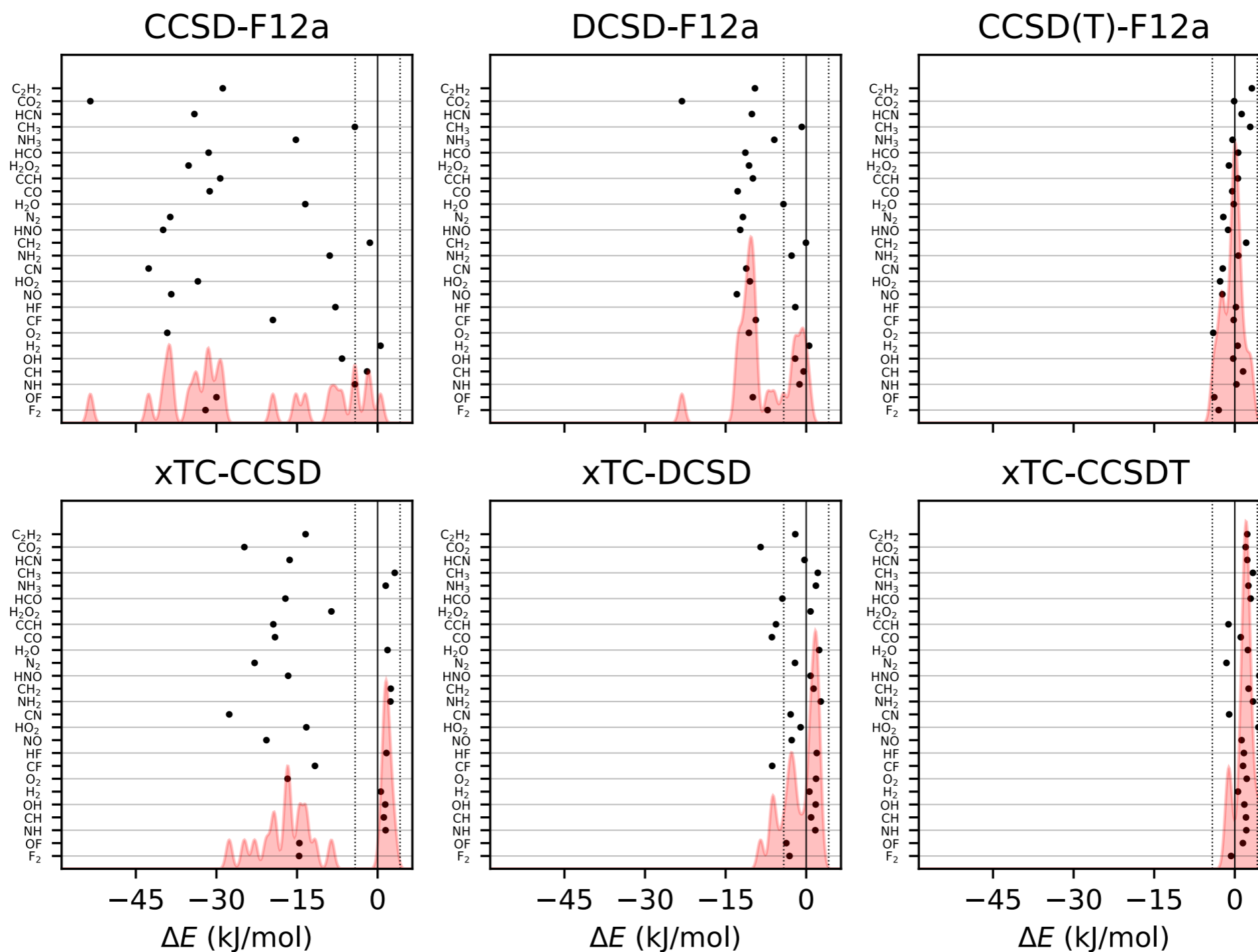# Comparison of TC-CC methods with CC-F12 methods

Schraivogel et al, JCP, **155**, 191101 (2021)

Ionization potentials of the first-row atoms (Li-Ne) in cc-pVTZ basis set
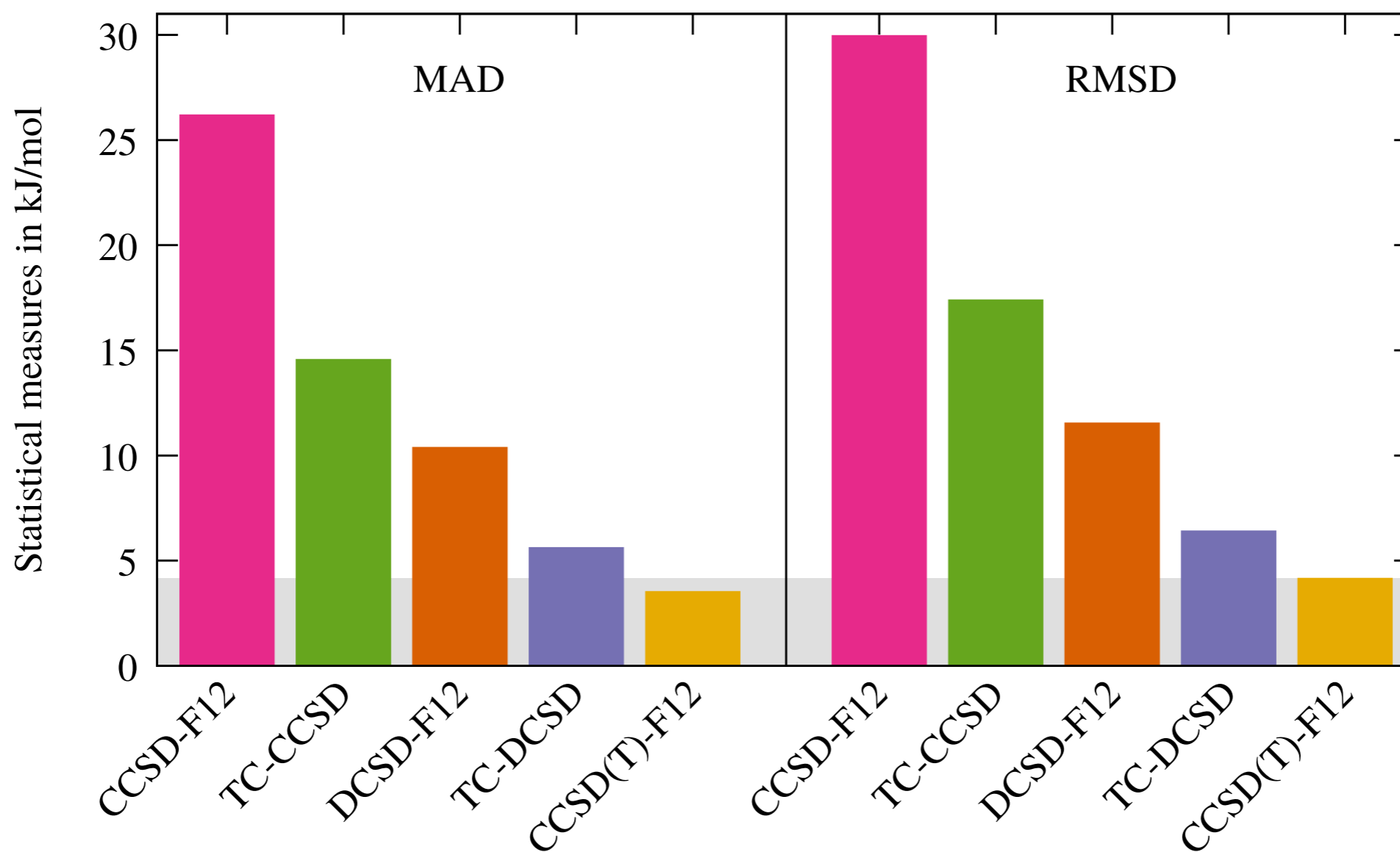
TC-CC Atomisation energies
(errors compared to HEAT benchmark of 26 molecules)
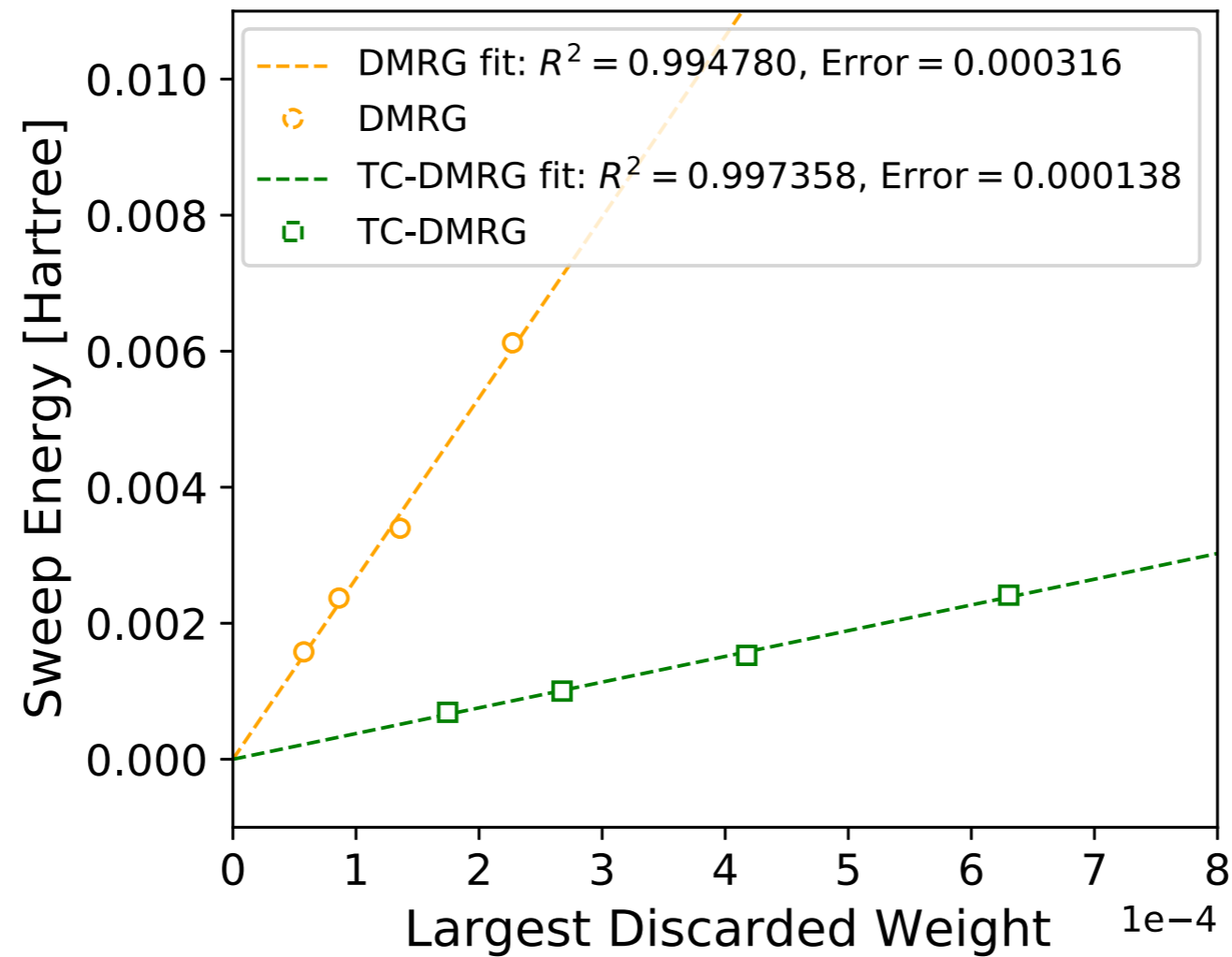Christlmaier et al, JCP **159**, 014113 (2023)

Statistical measures of the errors in atomisation energies for various methodologies compared to the HEAT dataset (cc-pVTZ basis)

TC-DMRG

Liao et al, JCTC 19, 1734 (2023)

replace the original Davidson solver of effective Hamiltonian with a general Davidson solver

Transcorrelated Perturbation Theory
Luo and Alavi, JCP, 157, 074105 (2022)

- For metals, PT theory starting from the HF approximation is divergent at all orders, and requires RPA type approach to obtain convergent energies

- The root cause of this divergence is the long-range tail of the Coulomb potential, which in reciprocal space is given by $4\pi/k^2$ where k is the momentum transfer

- The RPA result is found to be:

$$\frac{E_c}{N} = \frac{1 - \ln 2}{\pi^2} \ln r_s - 0.047 + \cdots . \qquad r_s \sim \rho^{-1/3}$$

- 2nd order PT theory on the uniform electron gas using the TC Hamiltonian

- Obtain a Jastrow factor (optimised with a Hartree-Fock reference determinant) with the correct asymptotic properties

- PT2 calculation can be analytically performed

Asymptotic properties of the Jastrow factor for the UEG

For the uniform electron gas (uniform positively charged background)

$$u(\mathbf{r}_1, \mathbf{r}_2) = u(\,|\,\mathbf{r}_1 - \mathbf{r}_2\,|\,)$$

At short and large distances the behaviour of the correlation function in reciprocal space mcc have the following asymptotic properties:

$$\tilde{u}(k) \sim -\frac{w(k)}{k^2} \qquad \text{when } k \sim \infty$$

$$\tilde{u}(k) \sim -\frac{\sqrt{w(k)}}{\sqrt{\rho}k} \qquad \text{when } k \sim 0$$

$$w(k) = \frac{4\pi}{k^2}$$

A Jastrow factor can be analytically obtained by minimizing the variational energy of the Slater-Jastrow wave function in the TDL

$$\tilde{u}(k) = \frac{k^2 - \sqrt{k^4 + 4\rho w(k)k^2 T_2^2(k)}}{2\rho k^2 T_2(k)} \, .$$

$$T_2(k) = \begin{cases} 1, & k > 2, \\ \frac{3}{4}k - \frac{1}{16}k^3, & k \leq 2. \end{cases}$$

T Gaskell, Proc Phys Soc, **77**, 1182 (1961)

TC Perturbation theory in the TDL

$$\hat{H}_{TC} = \hat{H}_0 + \hat{W}_1, \qquad \hat{W}_1 = \hat{W} + \hat{K} + \hat{L}$$

$$\hat{H}_0 = \sum_{p\sigma} \frac{1}{2} p^2 \hat{n}_{\mathbf{p},\sigma}$$

$$\hat{W} = \frac{1}{2\Omega} \sum_{\sigma\sigma'} \sum_{kpq} w(k)\, a^{\dagger}_{\mathbf{p}-\mathbf{k},\sigma} a^{\dagger}_{\mathbf{q}+\mathbf{k},\sigma'} a_{\mathbf{q},\sigma'} a_{\mathbf{p},\sigma}.$$

$$E_0 = \langle \Phi_0 | \hat{H}_0 | \Phi_0 \rangle$$

$$E_1 = \langle \Phi_0 | \hat{W}_1 | \Phi_0 \rangle$$

$$E_2 = -\langle \Phi_0 | (\hat{W}_1 - E_1) \frac{1}{\hat{H}_0 - E_0} (\hat{W}_1 - E_1) | \Phi_0 \rangle$$

Transcorrelated Perturbation Theory for UEG

- The correlation energy per electron in high density limit can be obtained:

$$\frac{E_c}{N} = \left[\frac{1 - \ln 2}{\pi^2} \ln(r_s) - 0.05075 \right] + o(r_s^2) .$$

- The logarithmic term is exact (same as in RPA)

- Constant term is ~7% larger than RPA result

- This result indicates TC method with 2nd-order PT may be useful for metallic systems

Transcorrelated CC applied to the uniform electron gas

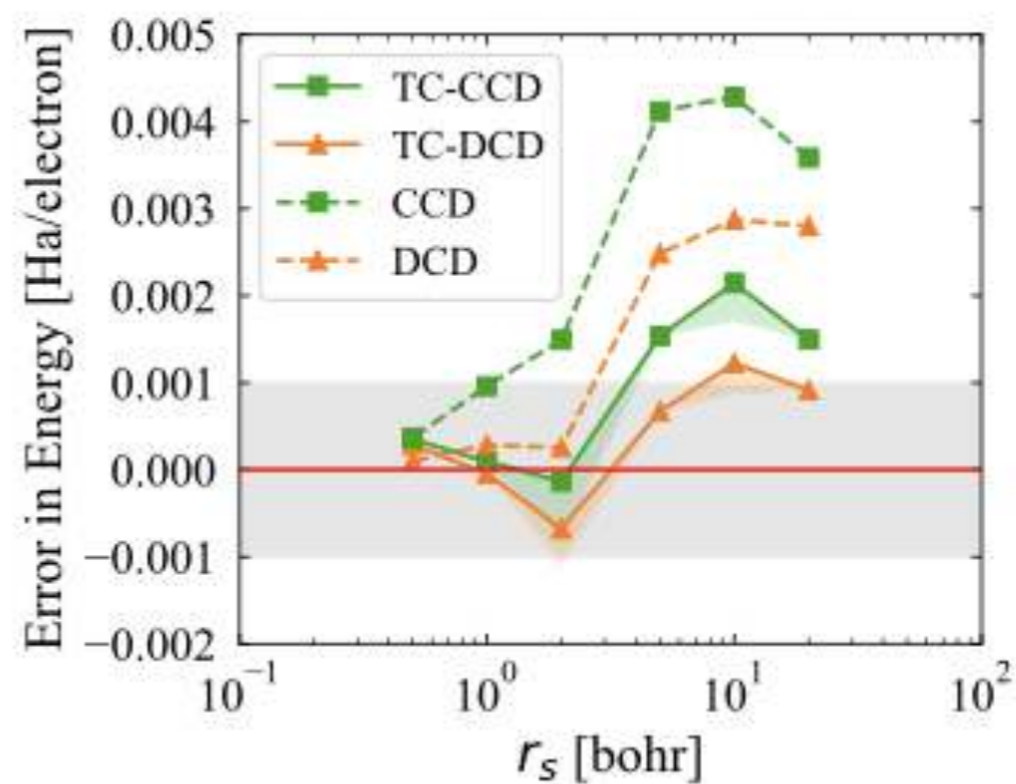Liao, Schraivogel, Luo, Kats and Alavi, PRR 3, 033072 (2021)

Errors in the total energies of the UEG across a wide range densities for canonical CC/DC methods and the corresponding transcorrelated methods

14 electrons
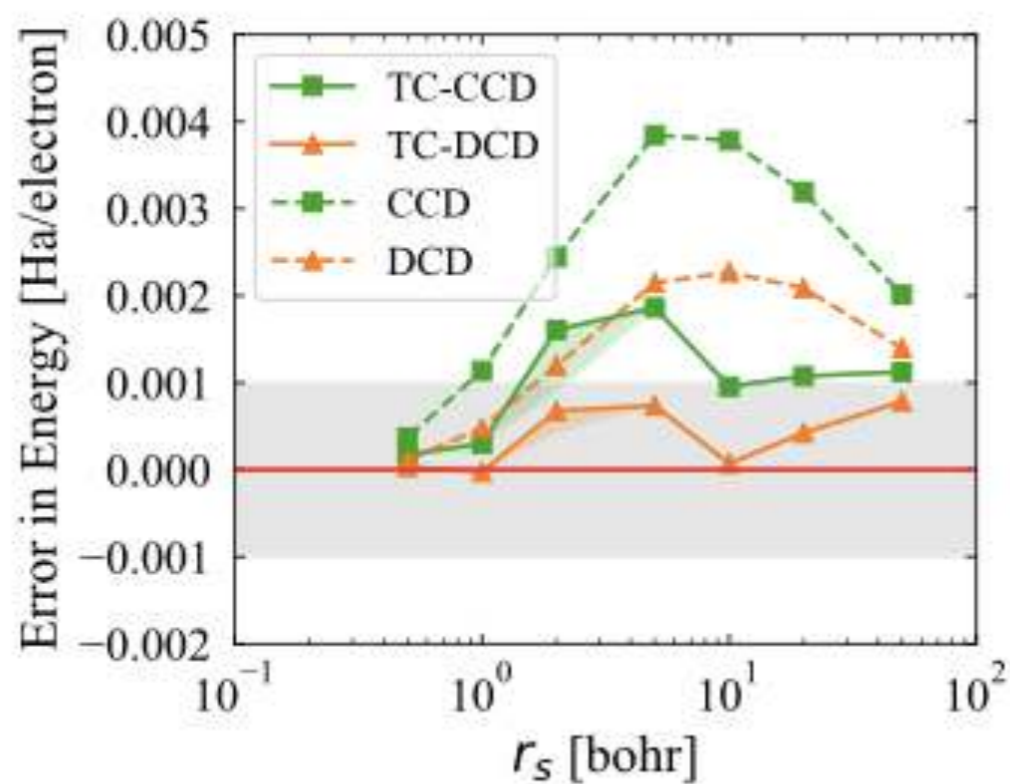
54 electrons

Conclusions

- Transcorrelation is a promising methodology. We have successfully overcome the difficulties associated with the non-Hermitian nature of the TC Hamiltonian.

- It allows explicit correlation in the form of sophisticated Jastrow factors obtained from Variational Monte Carlo to be incorporated into the Hamiltonian.

- Improved basis set convergence as well as convergence with respect to correlation method

- In solids, it leads to much shorter range interactions, and trivially captures RPA physics in a one-shot PT2 calculation

- The xTC-DCSD method is chemically accurate whilst remaining a $O(N^6)$ method

- Methodology can be extended to higher orders of CC theory

- The TC-CC methods may provide a viable method to treat solids with a wave function theory with fast convergence to the TDL

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