

The Ground State Electronic Energy of Benzene

Janus J. Eriksen,^{*,†} Tyler A. Anderson,[‡] J. Emiliano Deustua,[¶] Khaldoon Ghanem,[§] Diptarka Hait,^{||,⊥}
Mark R. Hoffmann,[#] Seunghoon Lee,[@] [Daniel S. Levine](#),^{||} Ilias Magoulas,[¶] Jun Shen,[¶] [Norman M. Tubman](#),^{||} [K. Birgitta Whaley](#),^{||} Enhua Xu,[△] Yuan Yao,[‡] Ning Zhang,[▽] Ali Alavi,^{*,§,††} Garnet Kin-Lic Chan,^{*,@} Martin Head-Gordon,^{*,||,⊥} Wenjian Liu,^{*,‡‡} Piotr Piecuch,^{*,¶,¶¶} Sandeep Sharma,^{*,§§} Seiichiro L. Ten-no,^{*,△} C. J. Umrigar,^{*,‡} and Jürgen Gauss^{*,|||}

[†]*School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, United Kingdom*

[‡]*Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853, USA*

[¶]*Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA*

[§]*Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany*

^{||}*Kenneth S. Pitzer Center for Theoretical Chemistry, Department of Chemistry, University of California, Berkeley, California 94720, USA*

[⊥]*Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

[#]*Chemistry Department, University of North Dakota, Grand Forks, ND 58202-9024, USA*

[@]*Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA*

[△]*Graduate School of Science, Technology, and Innovation, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan*

[▽]*Beijing National Laboratory for Molecular Sciences, Institute of Theoretical and Computational Chemistry, College of Chemistry and Molecular Engineering, [Peking University](#), Beijing 100871, China*

^{††}*Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom*

^{‡‡}*Qingdao Institute for Theoretical and Computational Sciences, Shandong University, Qingdao, Shandong 266237, China*

^{¶¶}*Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824, USA*

^{§§}*Department of Chemistry, The University of Colorado at Boulder, Boulder, Colorado 80302, USA*

^{|||}*Department Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, 55128 Mainz, Germany*

E-mail: janus.eriksen@bristol.ac.uk; a.alavi@fkf.mpg.de; gkc1000@gmail.com; mhg@ccchem.berkeley.edu; liuwj@sdu.edu.cn;

piecuch@chemistry.msu.edu; sandeep.sharma@colorado.edu; tenno@garnet.kobe-u.ac.jp; cyrusumrigar@gmail.com;

gauss@uni-mainz.de

Abstract

We report on the findings of a blind challenge devoted to computing the frozen-core, full configuration interaction ground state energy of the benzene molecule in a standard correlation-consistent basis set of double- ζ quality. As a broad international endeavour, our suite of wave function-based correlation methods collectively represents a diverse view of the high-accuracy repertoire offered by modern electronic structure theory. In our unbiased assessment, the evaluated high-level methods are all found to qualitatively agree on a final correlation energy. However, we find the accompanying variance across our sample set to be considerable, which in light of the acclaimed performance of each of the methods for smaller molecular systems clearly displays the challenges faced in extending reliable, near-exact correlation methods to larger systems. While the discrepancies exposed by our study thus emphasize the fact that the current state-of-the-art leaves significant room for improvement, we still expect the present assessment to provide a valuable community resource for benchmark and calibration purposes going forward.

At first glance, the electronic structure of the benzene molecule is deceptively simple. Initially proposed by Kekulé in the second half of the 19th century,^{1,2} the depiction of benzene as consisting of an alternating pattern of single and double bonds between degenerate carbon atoms proved radically novel for its time. Popularly ascribed to a vivid dream of a serpent biting its own tail, the original conjugated structure was soon nuanced in favour of a more balanced, D_{6h} -symmetric resonance picture of benzene.^{3,4} However, studies of the finer details of its electronic structure continue to be in vogue to this day,⁵⁻¹¹ and an adequate account of its intra- as well as intermolecular physical effects remains a key constraint on a great number of *ab initio* simulations in the field of computational (bio-)chemistry.¹²⁻²¹ Even more so, benzene may—alongside, for instance, water—easily be named among the members of an exclusive subset of molecules which are identifiable by wider parts of the public. Constituting the smallest aromatic system composed purely of carbon and hydrogen atoms, benzene rings are omnipresent throughout most of organic chemistry as recurring and easily recognizable structural leitmotifs, to the extent that its widespread use as a symbol of the biological and chemical sciences has become commonplace in society nowadays.

That being said, with its total of six carbon atoms, each bonded to a hydrogen atom, benzene has so far been deemed too big to allow for a truly high-level description of its electronic wave function; even in the modest cc-pVDZ basis set,²² which is the smallest meaningful one-electron basis for use in correlated calculations, and disregarding its six inner core molecular orbitals (MOs), the Hilbert space of benzene still exceeds an astonishing 10^{35} Slater determinants. However, given the availability of scalable computational hardware today, and even more importantly the extensive array of emerging new methods for yielding near-exact electronic ground state energies, we believe that the time is now ripe for an ambitious attempt at solving the electronic Schrödinger equation for the ubiquitous benzene molecule.

However trivial a problem it might seem, the quest for a numerically near-exact (i.e., sub- mE_H accuracy) treatment of the electron correlation in benzene quickly turns out to be anything but simple. As an illustrative example, upon traversing up through the standard coupled cluster^{23–25} (CC) hierarchy, satisfactory convergence of the correlation energy cannot be concluded even upon accounting for connected quadruple excitations^{26,27} (CCSDTQ), which is the highest level of sophistication possible today for systems of this size.^{28,29} In general, assuming a reasonably dominant Hartree-Fock (HF) solution, CCSDTQ is expected to recover almost all of the remaining discrepancies against exact full configuration interaction^{30–32} (FCI) present in lower-level (CCSD³³ and CCSDT^{34,35}) CC models.^{36,37} In the case of benzene, CCSDT lowers the energy by a full $-36.45 mE_H$ over CCSD, while the inclusion of quadruple excitations adds an additional $-2.47 mE_H$, yielding a total correlation energy of $\Delta E_{\text{CCSDTQ}} = -862.37 mE_H$. To put these numbers into context, and to probe whether or not convergence fails to be met at the CCSDTQ level of theory, the energy increments from quadruple and higher-level excitations in the N_2 molecule (at the equilibrium geometry) have previously been found to be $-1.61 mE_H$ and $-0.23 mE_H$, respectively.³⁸ Assuming for the sake of argument that higher-level effects are of the same relative order in benzene, the final correlation energy is estimated to be $\Delta E = -863.06 mE_H$ (by multiplying N_2 results by a factor 3), which—with the larger per-electron N_2 quadruples increment in mind—is likely a slight overestimate, taking into account the electronic structure of the nitrogen molecule.

In an attempt to substantiate these projections for what may be expected upon moving towards a higher level of correlation, extended CI wave function expansions have been interpreted for this system by means of cluster decomposition methods,³⁹ cf. the Supporting Information (SI). On the whole, these results appear to indicate that most of the quadruply (and higher) excited determinants in the FCI wave function will stem from disconnected clusters, and the inclusion of connected quintuples, hexuples, etc., in CC theory is thus expected—on this basis—to be relatively insignificant in comparison, as for most generic

systems dominated by dynamic correlation only. The elaborate and accurate determination of the electronic ground state energy of benzene hence becomes more than an exercise of mere academic interest. Not only does the benzene molecule constitute a challenging test application to push the limits of contemporary, near-exact electronic structure theory, but our results will further allow us to scrutinize these preliminary observations, namely to what extent higher-level excitations will contribute to the total FCI correlation energy for archetypal, modest-sized systems with no obvious indications of strong electron correlation.

The present study thus aligns itself with the recent series of meticulous benchmark studies from the *Simons Collaboration on the Many-Electron Problem* concerned with model systems and small transition-metal species.^{40–42} However, as opposed to these earlier assessments, we have conducted the present study as a blind challenge with one of us (J.G.) responsible for compiling all results. This was done in an attempt to conduct an unbiased evaluation of the various methods of the present work, as listed in Table 1. Not only are the results of the present work bound to prove valuable to future benchmarks and for the calibration of future methods across most of electronic structure theory, but their relative distribution further admits a direct assessment of the state-of-the-art nearly a century on from the dawn of modern quantum mechanics,^{43–45} in particular in terms of performance transferability in moving from small- to modest-sized molecular compounds. We will herein refrain from passing judgement on what a tolerable error with respect to our FCI target amounts to, given that all of the results to follow need be weighed up against the amount of computational effort required to obtain them to paint a full picture. As such, we will report our findings below in an intentionally neutral tone, leaving most interpretations of the data to the reader.

For the sake of brevity, technical details on the evaluated methods in Table 1 and the results derived from these are collected in the SI. Here, we will only briefly compare the methods on the basis of their common traits and differences. The adaptive sampling CI^{46–50}

Table 1: Abbreviations used for the method included in the blind challenge.

Acronym	Method	References
ASCI	Adaptive Sampling CI	46–50
SHCI	Semistochastic Heat-Bath CI	51–57
iCI	Iterative CI with Selection	58–61
AS-FCIQMC	Adaptive-Shift FCI Quantum Monte-Carlo	62–66
DMRG	Density Matrix Renormalization Group	67–78
MBE-FCI	Many-Body Expanded FCI	79–82
FCCR	Full CC Reduction	83
CAD-FCIQMC	Cluster-Analysis Driven FCIQMC	84–87

(ASCI), semistochastic heat-bath CI^{51–57} (SHCI), and iterative CI with selection^{58–61} (iCI) methods all belong to a wider class of selected CI (SCI) methods,^{88–100} which approximate the full linear expansion of the FCI wave function by selecting only important determinants in conjunction with perturbative corrections to account for any residual correlation. The FCI quantum Monte-Carlo^{62–65} (FCIQMC) method offers another approach for sampling the wave function, namely via stochastic processes using Monte-Carlo techniques. The FCIQMC method is most often complemented by an initiator approximation (*i*-FCIQMC), but we will here evaluate its most recent version which uses an adaptive shift⁶⁶ (AS-FCIQMC) to mitigate the initiator bias in the wave function sampling. Operating instead using a variational matrix product state Ansatz, density matrix renormalization group^{67–78} (DMRG) methods provide an alternative route towards variationally solving the Schrödinger equation. DMRG methods reduce the exponential scaling of linear CI expansions with volume to an exponential scaling in the cross-section area. In the recently proposed many-body expanded full configuration interaction^{79–82} (MBE-FCI) method, the FCI correlation energy (without recourse to the electronic wave function) is decomposed and solved for. By enforcing a strict partitioning of the complete set of MOs into a reference and an expansion space, the residual correlation in the latter of these two spaces is recovered by means of an MBE in the spatial MOs of a given system. Finally, two methods founded on CC theory have been evaluated. In the full CC reduction⁸³ (FCCR) method, cluster projection manifolds and commutator expressions for higher-level excitations are systematically reduced in order to optimally ex-

exploit the sparsity of the FCI wave function, as recasted using the CC Ansatz. Alternatively, triples and quadruples CC amplitudes may be extracted from Monte-Carlo samplings of the FCI wave function to yield improved, relaxed singles and doubles amplitudes—on par with externally corrected CC^{101–105}—from which a deterministic CC energy may be computed in the recent semistochastic cluster-analysis driven FCIQMC^{84–87} (CAD-FCIQMC) method.

Among the evaluated methods, a number of these make use of extrapolations. In the methods that involve a perturbative correction as an integral component on top of a variational calculation (ASCI, SHCI, and iCI), final results may be extrapolated by systematically reducing the proportion of the total correlation energy accounted for by second-order perturbation theory. In the case of DMRG, extrapolations may be performed towards an infinite bond dimension estimate. In order to isolate the effect of extrapolation from the bare methods themselves, we will present both the unextrapolated and extrapolated results. On the other hand, MBE-FCI and AS-/CAD-FCIQMC make no use of extrapolations of any kind. The FCCR method may also be augmented by either of the Epstein-Nesbet^{106,107} or Møller-Plesset¹⁰⁸ formulations of perturbation theory, and while no extrapolations may be directly drawn from individual FCCR calculations (except for the most recent variant of the theory, cf. the SI), a final result may be derived using the average of these perturbative corrections in combination with adjustments for the internal thresholds.

Besides the methods listed in Table 1, one additional, complementary result has previously been reported in the literature using the same molecular geometry,¹⁰⁹ namely *i*-FCIQMC,¹¹⁰ augmented by perturbation theory.¹¹¹ All of the methods of our study share in common that none are variational, as those that are formulated on top of selected CI and DMRG theory have lost this feature upon being corrected by perturbation theory or extrapolated towards an infinite bond dimension, respectively. In the case of AS- and *i*-FCIQMC, non-variational biases stem from the initiator approximation as well as from perturbation

theory in the latter case.

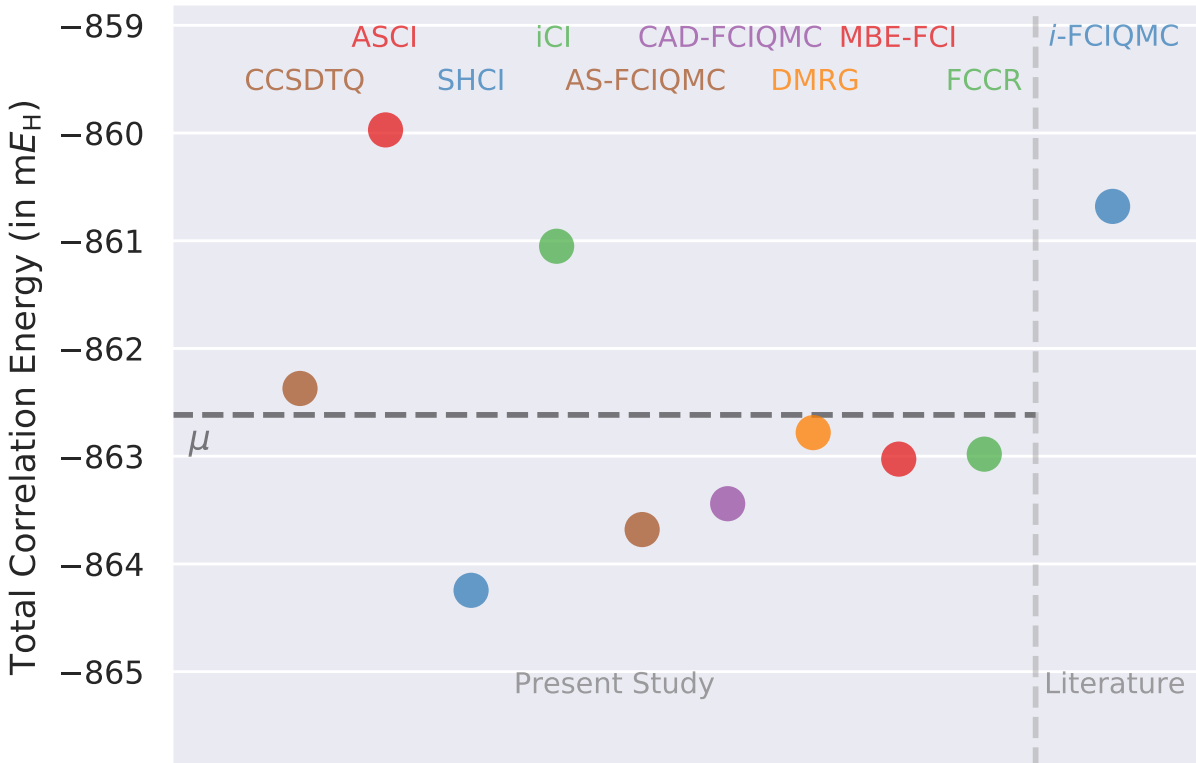


Figure 1: Frozen-core $C_6H_6/cc\text{-pVDZ}$ correlation energies for the methods of Table 1 alongside $i\text{-FCIQMC}$.¹¹⁰ For the results of the present study, the mean value (μ) has been indicated by a dashed horizontal line to ease comparison. See the SI for non-blinded results.

The main results of our study are presented in Figure 1 (with the underlying data tabulated in the SI). No error bars are provided given that these are derived differently in-between the various methods (*vide infra*). While our pool of results is too limited to allow for in-depth statistics to be computed from it (besides a mean value, μ , and a standard deviation, σ), a number of observations may still be made. In the following, we will make use of mE_H as the unit for reporting correlation energies in order to accentuate differences (recalling that $1 mE_H$ corresponds to 2.6 kJ/mol).

- (i) The majority of the evaluated methods of the present work yield a larger correlation

energy (in absolute terms) than that of the CCSDTQ method, in agreement with the general notion that high-level CC methods, although not bounded by the variational theorem,¹¹² often are so in practice. **(ii)** Across the various results, all but those of the three flavours of SCI fall in a bulk within the interval spanned by $-863 \pm 1 \text{ m}E_{\text{H}}$. **(iii)** Taking into account the finer details of the ASCI, iCI, and SHCI calculations (cf. the SI), we expect the result of the latter to be somewhat more accurate than the former two, as evidenced by the smallest extrapolation distance among these three methods, cf. Table 2. Only in the complete absence of any knowledge of the underlying method will this metric reflect the uncertainties in the final results (Fig. 1), but the distances in Table 2 are here meant to serve as an indication as to what degree the individual methods rely on extrapolation procedures. **(iv)** The examples of stochastic CI in Figure 1 (*i*- and AS-FCIQMC) are also observed to disagree with one another, however only by half of that of their deterministic counterparts. AS-FCIQMC, which corrects for the undersampling bias of noninitiator determinants, is expected to be the more accurate of these two. **(v)** The extrapolated DMRG result is observed to lie near the mean of the bulk of results, close to the central value of $-863 \text{ m}E_{\text{H}}$. In addition, it is observed from Table 2 to be far less reliant on an extrapolation of the energy than the tested SCI methods. **(vi)** Likewise, the CAD-FCIQMC and MBE-FCI results, both of which have not been extrapolated, agree with each other to within $0.4 \text{ m}E_{\text{H}}$. **(vii)** Viewing CAD-FCIQMC as a correction to the underlying AS-FCIQMC wave function, calculating the correlation energy by means of the CC rather than the CI Ansatz is observed to increase the final result slightly ($+0.25 \text{ m}E_{\text{H}}$ for the most accurate AS-FCIQMC wave function), albeit generally by less than what results from an increase in the number of walkers in the AS-FCIQMC calculation ($+1.1 \text{ m}E_{\text{H}}$ in moving from 1 to 2 billion walkers). For AS-FCIQMC, the change in energy is a reflection of the initiator bias (or approximation) in addition to the smaller stochastic error, cf. the SI. **(viii)** As further discussed in the SI, the FCCR results exhibit a pronounced dependence on the choice of perturbative treatment, giving rise to an intrinsic variance of $5.3 \text{ m}E_{\text{H}}$. However, the final, perturbatively corrected FCCR correlation energy

is estimated to lie in close proximity of the other results near the mean. **(ix)** To that end, the results of the only four methods, which have not been aided by second-order perturbation theory (DMRG, MBE-FCI, as well as AS- and CAD-FCIQMC), are observed to coincide to a reasonable extent, spanning an interval of only $0.7 \text{ m}E_{\text{H}}$.

Table 2: Extrapolation distances, ΔE_{dist} (in $\text{m}E_{\text{H}}$), involved in computing the final ASCI, iCI, SHCI, and DMRG results in Fig. 1. These are defined by the difference between the final computed energy, ΔE_{final} , and the extrapolated energy, $\Delta E_{\text{extrap.}}$ (final variational energies, that is, in the absence of perturbation theory, are presented as $\Delta E_{\text{var.}}$). For the SCI methods, extrapolations are performed towards the limit of vanishing perturbative correction, while the variational DMRG energy is extrapolated towards an infinite bond dimension. [See the SI for non-blinded results.](#)

Method	$\Delta E_{\text{var.}}$	ΔE_{final}	$\Delta E_{\text{extrap.}}$	ΔE_{dist}
ASCI	-737.1	-835.4	-860.0	-24.6
iCI	-730.0	-833.7	-861.1	-27.4
SHCI	-827.2	-852.8	-864.2	-11.4
DMRG	-859.2	-859.2	-862.8	-3.6

All of the methods evaluated herein are the products of years of intense development, and most of the computed results in Figure 1 have required a non-negligible amount of computational resources to obtain. Due to its high polynomial scaling and memory requirements, the CCSDTQ model is unlikely to enable near-exact results for molecular systems significantly larger than benzene. In addition, its formal target remains different from FCI. Be that as it may, our CCSDTQ result was still obtained over the course of only 5.5k core hours using a single thread on a multicore node equipped with a 120 GB of physical memory, indicating that high-level CC theory represents an affordable, yet robust alternative to many of the other methods of our study for problems of a similar size and a similar nature of the involved electron correlation. In comparison, the FCCR result in Figure 1 required a total of 0.1M core hours (using 640 parallel processes) across all of the involved calculations, while the extrapolated DMRG result required 0.08M core hours in total, distributed across 100 – 200 cores. The DMRG method generally requires a non-negligible amount of memory, on par

or greater than the CC requirements above, while these may be reduced somewhat in the FCCR method. The extrapolated ASCI, SHCI, and iCI results were all obtained in parallel, consuming 0.3k, 2.8k, and 1.5k core hours in the process, respectively, thus all offering relatively inexpensive compromises in comparison with some of the other methods in Figure 1. Again, the memory requirements involved in running the largest possible CI spaces will ultimately hinder their application to significantly larger problem sizes and basis sets. Both the AS-FCIQMC and MBE-FCI results were obtained in a highly parallel manner, but with minimal memory demands. In the case of the former method, a total of 0.06M core hours were consumed, distributed over a group of either 100 or 200 multicore nodes, while for the latter, the calculation was parallelized over 128 nodes for a total of 1.7M core hours, by far the most expensive of all the evaluated methods. Finally, the CAD-FCIQMC correlation energy was computed in just a few hours on a single node, initialized from the converged AS-FCIQMC solution.

In summary, while all of the methods of our assessment yield results in general agreement with one another, the overall low resolution, exemplified by a substantial standard deviation across our sample set (in excess of $1.3 \text{ m}E_{\text{H}}$), ultimately hinders the determination of a final FCI correlation energy too specifically. That being said, this uncertainty is most likely too pessimistic, and our findings do indeed seem to indicate that the most plausible frozen-core correlation energy—for the current geometry in the cc-pVDZ basis set—lies close to a value of $-863 \text{ m}E_{\text{H}}$, in accordance with our preliminary estimate and earlier projections.¹¹³ On this basis, we are led to conclude that the electronic structure of benzene in its equilibrium geometry is **predominantly** described by dynamic correlation alone.

More generally, in particular in view of its format as a blind challenge, our findings collectively represent an unbiased assessment of a diverse set of current state-of-the-art methods. As a consequence of the fact that the sophistication and application range of near-exact

electronic structure continue to be improved, we end by strongly encouraging the continued benchmarking of future correlation methods aimed at FCI against the results presented here. To that effect, we note that updated [ASCI](#), SHCI, iCI, and FCCR results—made possible solely by improvements to the efficacies of their implementations—were submitted following the compilation of the results in Fig. 1. These results are discussed in the SI.

Acknowledgments

The authors thank Dr. Devin A. Matthews of the Southern Methodist University for help with obtaining the CCSDTQ result first reported in Ref. 82. J.J.E. is grateful to the Alexander von Humboldt Foundation and the Independent Research Fund Denmark for financial support. J.J.E. and J.G. gratefully acknowledge access awarded to the Galileo supercomputer at CINECA (Italy) through the 18th PRACE Project Access Call and the Johannes Gutenberg-Universität Mainz for computing time granted on the MogonII supercomputer. D.H. and M.H.G. were supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. N.Z. and W.L. acknowledge support from NSFC (grant no. 21033001 and 21973054). S.L. and G.K.C. were supported by the US National Science Foundation, via grant no. 1665333. E.X. and S.L.T. thank the financial support from JSPS Grant-in-Aids for Scientific Research (A) (Grant No. JP18H03900). [M.H. acknowledges the North Dakota University System.](#) [S.S. was supported by the NSF grant CHE-1800584 and by the Sloan research fellowship.](#) [T.A.A. and C.J.U. were supported in part by the AFOSR under grant FA9550-18-1-0095.](#) [Y.Y. acknowledges support from the Molecular Sciences Software Institute, funded by U.S. National Science Foundation grant ACI-1547580. Some of the SHCI computations were performed at the Bridges cluster at the Pittsburgh Supercomputing Center supported by NSF grant ACI-1445606.](#) [Missing funding information from Ali and Piotr.](#)

Supporting Information

Details on all methods and their results are collected in the Supporting Information.

References

- (1) Kekulé, F. A. Sur la Constitution des Substances Aromatiques. *Bull. Soc. Chim. Paris* **1865**, 3, 98.
- (2) Kekulé, F. A. Untersuchungen über Aromatische Verbindungen. *Liebigs Annalen* **1866**, 137, 129.
- (3) Hückel, E. Quantentheoretische Beiträge zum Benzolproblem. I. Die Elektronenkonfiguration des Benzols und Verwandter Verbindungen. *Z. Phys.* **1931**, 70, 204.
- (4) Pauling, L.; Wheland, G. W. The Nature of the Chemical Bond. V. The Quantum-Mechanical Calculation of the Resonance Energy of Benzene and Naphthalene and the Hydrocarbon Free Radicals. *J. Chem. Phys.* **1933**, 1, 362.
- (5) Cooper, D. L.; Gerratt, J.; Raimondi, M. The Electronic Structure of the Benzene Molecule. *Nature* **1986**, 323, 699.
- (6) Harcourt, R. D. The Electronic Structure of the Benzene Molecule. *Nature* **1987**, 329, 491.
- (7) Messmer, R. P.; Schultz, P. A. The Electronic Structure of the Benzene Molecule. *Nature* **1987**, 329, 492.
- (8) Roos, B. O.; Andersson, K.; Fülcher, M. P. Towards an Accurate Molecular Orbital Theory for Excited States: The Benzene Molecule. *Chem. Phys. Lett.* **1992**, 192, 5.
- (9) Lorentzon, J.; Malmqvist, P.-Å.; Fülcher, M.; Roos, B. O. A CASPT2 Study of the Valence and Lowest Rydberg Electronic States of Benzene and Phenol. *Theor. Chim. Acta* **1995**, 91, 91.
- (10) Bernhardsson, A.; Forsberg, N.; Malmqvist, P.-Å.; Roos, B. O. A Theoretical Study of the $^1B_{2u}$ and $^1B_{au}$ Vibronic Bands in Benzene. *J. Chem. Phys.* **2000**, 112, 2798.

- (11) Liu, Y.; Kilby, P.; Frankcombe, T. J.; Schmidt, T. W. The Electronic Structure of Benzene from a Tiling of the Correlated 126-Dimensional Wavefunction. *Nat. Commun.* **2020**, *11*, 1210.
- (12) Cacelli, I.; Cinacchi, G.; Prampolini, G.; Tani, A. Computer Simulation of Solid and Liquid Benzene with an Atomistic Interaction Potential Derived from ab Initio Calculations. *J. Am. Chem. Soc.* **2004**, *126*, 14278.
- (13) Cockroft, S. L.; Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. Electrostatic Control of Aromatic Stacking Interactions. *J. Am. Chem. Soc.* **2005**, *127*, 8594.
- (14) Tauer, T. P.; Sherrill, C. D. Beyond the Benzene Dimer: An Investigation of the Additivity of π - π Interactions. *J. Phys. Chem. A* **2005**, *109*, 10475.
- (15) Mignon, P.; Loverix, S.; Steyaert, J.; Geerlings, P. Influence of the π - π Interaction on the Hydrogen Bonding Capacity of Stacked DNA/RNA bases. *Nucleic Acids Res.* **2005**, *33*, 1779.
- (16) Matta, C. F.; Castillo, N.; Boyd, R. J. Extended Weak Bonding Interactions in DNA: π -Stacking (Base-Base), Base-Backbone, and Backbone-Backbone Interactions. *J. Phys. Chem. B* **2006**, *110*, 563.
- (17) Amirjalayer, S.; Tafipolsky, M.; Schmid, R. Molecular Dynamics Simulation of Benzene Diffusion in MOF-5: Importance of Lattice Dynamics. *Angew. Chem. Int. Ed.* **2006**, *46*, 463.
- (18) Geng, Y.; Takatani, T.; Hohenstein, E. G.; Sherrill, C. D. Accurately Characterizing the π - π Interaction Energies of Indole-Benzene Complexes. *J. Phys. Chem. A* **2010**, *114*, 3576.
- (19) Villa, A.; Peter, C.; van der Vegt, N. F. A. Transferability of Nonbonded Interac-

- tion Potentials for Coarse-Grained Simulations: Benzene in Water. *J. Chem. Theory Comput.* **2010**, *6*, 2434.
- (20) Tu, C.-F.; Tian, S. X. A Comparative Study for Molecular Dynamics Simulations of Liquid Benzene. *J. Chem. Theory Comput.* **2011**, *7*, 2240.
- (21) Martinez, C. R.; Iverson, B. L. Rethinking the Term “Pi-Stacking”. *Chem. Sci.* **2012**, *3*, 2191.
- (22) Dunning Jr., T. H. Gaussian Basis Sets for use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007.
- (23) Čížek, J. On the Correlation Problem in Atomic and Molecular Systems. Calculation of Wavefunction Components in Ursell-Type Expansion Using Quantum-Field Theoretical Methods. *J. Chem. Phys.* **1966**, *45*, 4256.
- (24) Čížek, J. On the Use of the Cluster Expansion and the Technique of Diagrams in Calculations of Correlation Effects in Atoms and Molecules. *Adv. Chem. Phys.* **1969**, *14*, 35.
- (25) Paldus, J.; Čížek, J.; Shavitt, I. Correlation Problems in Atomic and Molecular Systems. IV. Extended Coupled-Pair Many-Electron Theory and Its Application to the BH_3 Molecule. *Phys. Rev. A* **1972**, *5*, 50.
- (26) Oliphant, N.; Adamowicz, L. Coupled-Cluster Method Truncated at Quadruples. *J. Chem. Phys.* **1991**, *95*, 6645.
- (27) Kucharski, S. A.; Bartlett, R. J. The Coupled-Cluster Single, Double, Triple, and Quadruple Excitation Method. *J. Chem. Phys.* **1992**, *97*, 4282.
- (28) Matthews, D. A.; Stanton, J. F. Accelerating the Convergence of Higher-Order Coupled Cluster Methods. *J. Chem. Phys.* **2015**, *143*, 204103.

- (29) Matthews, D. A.; Stanton, J. F. Non-Orthogonal Spin-Adaptation of Coupled Cluster Methods: A New Implementation of Methods Including Quadruple Excitations. *J. Chem. Phys.* **2015**, 064108.
- (30) Knowles, P. J.; Handy, N. C. A New Determinant-Based Full Configuration Interaction Method. *Chem. Phys. Lett.* **1984**, 111, 315.
- (31) Knowles, P. J.; Handy, N. C. Unlimited Full Configuration Interaction Calculations. *J. Chem. Phys.* **1989**, 91, 2396.
- (32) Olsen, J.; Jørgensen, P.; Simons, J. Passing the One-Billion Limit in Full Configuration-Interaction (FCI) Calculations. *Chem. Phys. Lett.* **1990**, 169, 463.
- (33) Purvis, G. D.; Bartlett, R. J. A Full Coupled-Cluster Singles and Doubles Model: The Inclusion of Disconnected Triples. *J. Chem. Phys.* **1982**, 76, 1910.
- (34) Noga, J.; Bartlett, R. J. The Full CCSDT Model for Molecular Electronic Structure. *J. Chem. Phys.* **1987**, 86, 7041.
- (35) Scuseria, G. E.; Schaefer, H. F. A New Implementation of the Full CCSDT Model for Molecular Electronic Structure. *Chem. Phys. Lett.* **1988**, 152, 382.
- (36) Helgaker, T.; Jørgensen, P.; Olsen, J. *Molecular Electronic-Structure Theory*, 1st ed.; Wiley & Sons, Ltd.: West Sussex, UK, 2000.
- (37) Shavitt, I.; Bartlett, R. J. *Many-Body Methods in Chemistry and Physics: Many-Body Perturbation Theory and Coupled-Cluster Theory*; Cambridge University Press: Cambridge, UK, 2009.
- (38) Chan, G. K.-L.; Kállay, M.; Gauss, J. State-Of-The-Art Density Matrix Renormalization Group and Coupled Cluster Theory Studies of the Nitrogen Binding Curve. *J. Chem. Phys.* **2004**, 121, 6110.

- (39) Lehtola, S.; Tubman, N. M.; Whaley, K. B.; Head-Gordon, M. Cluster Decomposition of Full Configuration Interaction Wave Functions: A Tool for Chemical Interpretation of Systems with Strong Correlation. *J. Chem. Phys.* **2017**, *147*, 154105.
- (40) LeBlanc, J. P. F.; Antipov, A. E.; Becca, F.; Bulik, I. W.; Chan, G. K.-L.; Chung, C.-M.; Deng, Y.; Ferrero, M.; Henderson, T. M.; Jiménez-Hoyos, C. A.; Kozik, E.; Liu, X.-W.; Millis, A. J.; Prokof'ev, N. V.; Qin, M.; Scuseria, G. E.; Shi, H.; Svistunov, B. V.; Tocchio, L. F.; Tupitsyn, I. S.; White, S. R.; Zhang, S.; Zheng, B.-X.; Zhu, Z.; Gull, E. Solutions of the Two-Dimensional Hubbard Model: Benchmarks and Results from a Wide Range of Numerical Algorithms. *Phys. Rev. X* **2015**, *5*, 041041.
- (41) Motta, M.; Ceperley, D. M.; Chan, G. K.-L.; Gomez, J. A.; Gull, E.; Guo, S.; Jiménez-Hoyos, C. A.; Lan, T. N.; Li, J.; Ma, F.; Millis, A. J.; Prokof'ev, N. V.; Ray, U.; Scuseria, G. E.; Sorella, E. M.; Stoudenmire, S.; Sun, Q.; Tupitsyn, I. S.; White, S. R.; Zgid, D.; Zhang, S. Towards the Solution of the Many-Electron Problem in Real Materials: Equation of State of the Hydrogen Chain with State-of-the-Art Many-Body Methods. *Phys. Rev. X* **2017**, *7*, 031059.
- (42) Williams, K. T.; Yao, Y.; Li, J.; Chen, L.; Shi, H.; Motta, M.; Niu, C.; Ray, U.; Guo, S.; Anderson, R. J.; Li, J.; Tran, L. N.; Yeh, C.-N.; Mussard, B.; Sharma, S.; Bruneval, F.; van Schilfgaarde, M.; Booth, G. H.; Chan, G. K.-L.; Zhang, S.; Gull, E.; Zgid, D.; Millis, A.; Umrigar, C. J.; Wagner, L. K. Direct Comparison of Many-Body Methods for Realistic Electronic Hamiltonians. *Phys. Rev. X* **2020**, *10*, 011041.
- (43) Schrödinger, E. Quantisierung als Eigenwertproblem. *Annalen der Physik* **1926**, *384*, 361.
- (44) Born, M.; Oppenheimer, R. Zur Quantentheorie der Molekeln. *Annalen der Physik* **1927**, *389*, 457.

- (45) Dirac, P. A. M. *The Principles of Quantum Mechanics*, 1st ed.; Oxford University Press, 1930.
- (46) Tubman, N. M.; Lee, J.; Takeshita, T. Y.; Head-Gordon, M.; Whaley, K. B. A Deterministic Alternative to the Full Configuration Interaction Quantum Monte Carlo Method. *J. Chem. Phys.* **2016**, *145*, 044112.
- (47) Tubman, N. M.; Freeman, C. D.; Levine, D. S.; Hait, D.; Head-Gordon, M.; Whaley, K. B. Modern Approaches to Exact Diagonalization and Selected Configuration Interaction with the Adaptive Sampling CI Method. *J. Chem. Theory Comput.* **2020**, *16*, 2139.
- (48) Tubman, N. M.; Levine, D. S.; Hait, D.; Head-Gordon, M.; Whaley, K. B. An Efficient Deterministic Perturbation Theory for Selected Configuration Interaction Methods. *arXiv:1808.02049* **2018**,
- (49) Hait, D.; Tubman, N.; Levine, D. S.; Whaley, K. B.; Head-Gordon, M. What Levels of Coupled Cluster Theory Are Appropriate for Transition Metal Systems? A Study Using Near-Exact Quantum Chemical Values for 3d Transition Metal Binary Compounds. *J. Chem. Theory Comput.* **2019**, *15*, 5370.
- (50) Levine, D. S.; Hait, D.; Tubman, N.; Lehtola, S.; Whaley, K. B.; Head-Gordon, M. CASSCF with Extremely Large Active Spaces Using the Adaptive Sampling Configuration Interaction Method. *J. Chem. Theory Comput.* **2020**, *16*, 2340.
- (51) Petruzielo, F. R.; Holmes, A. A.; Changlani, H. J.; Nightingale, M. P.; Umrigar, C. J. Semistochastic Projector Monte Carlo Method. *Phys. Rev. Lett.* **2012**, *109*, 230201.
- (52) Holmes, A. A.; Changlani, H. J.; Umrigar, C. J. Efficient Heat-Bath Sampling in Fock Space. *J. Chem. Theory Comput.* **2016**, *12*, 1561.

- (53) Holmes, A. A.; Tubman, N. M.; Umrigar, C. J. Heat-Bath Configuration Interaction: An Efficient Selected Configuration Interaction Algorithm Inspired by Heat-Bath Sampling. *J. Chem. Theory Comput.* **2016**, *12*, 3674.
- (54) Sharma, S.; Holmes, A. A.; Jeanmairet, G.; Alavi, A.; Umrigar, C. J. Semistochastic Heat-Bath Configuration Interaction Method: Selected Configuration Interaction with Semistochastic Perturbation Theory. *J. Chem. Theory Comput.* **2017**, *13*, 1595.
- (55) Smith, J. E. T.; Mussard, B.; Holmes, A. A.; Sharma, S. Cheap and Near Exact CASSCF with Large Active Spaces. *J. Chem. Theory Comput.* **2017**, *13*, 5468.
- (56) Holmes, A. A.; Umrigar, C. J.; Sharma, S. Excited States Using Semistochastic Heat-Bath Configuration Interaction. *J. Chem. Phys.* **2017**, *147*, 164111.
- (57) Li, J.; Otten, M.; Holmes, A. A.; Sharma, S.; Umrigar, C. J. Fast Semistochastic Heat-Bath Configuration Interaction. *J. Chem. Phys.* **2018**, *149*, 214110.
- (58) Liu, W.; Hoffmann, M. R. SDS: The ‘Static-Dynamic-Static’ Framework for Strongly Correlated Electrons. *Theor. Chem. Acc.* **2014**, *133*, 1481.
- (59) Liu, W.; Hoffmann, M. R. iCI: Iterative CI toward full CI. *J. Chem. Theory Comput.* **2016**, *12*, 1169.
- (60) Lei, Y.; Liu, W.; Hoffmann, M. R. Further Development of SDSPT2 for Strongly Correlated Electrons. *Mol. Phys.* **2017**, *115*, 2696.
- (61) Zhang, N.; Liu, W.; Hoffmann, M. R. Iterative Configuration Interaction with Selection. *J. Chem. Theory Comput.* **2020**, *16*, 2296.
- (62) Booth, G. H.; Thom, A. J. W.; Alavi, A. Fermion Monte Carlo Without Fixed Nodes: A Game of Life, Death, and Annihilation in Slater Determinant Space. *J. Chem. Phys.* **2009**, *131*, 054106.

- (63) Cleland, D.; Booth, G. H.; Alavi, A. Communications: Survival of the Fittest: Accelerating Convergence in Full Configuration-Interaction Quantum Monte Carlo. *J. Chem. Phys.* **2010**, *132*, 041103.
- (64) Booth, G. H.; Grüneis, A.; Kresse, G.; Alavi, A. Towards an Exact Description of Electronic Wavefunctions in Real Solids. *Nature* **2013**, *493*, 365.
- (65) Blunt, N. S.; Booth, G. H.; Alavi, A. Density Matrices in Full Configuration Interaction Quantum Monte Carlo: Excited States, Transition Dipole Moments, and Parallel Distribution. *J. Chem. Phys.* **2017**, *146*, 244105.
- (66) Ghanem, K.; Lozovoi, A. Y.; Alavi, A. Unbiasing the Initiator Approximation in Full Configuration Interaction Quantum Monte Carlo. *J. Chem. Phys.* **2019**, *151*, 224108.
- (67) White, S. R. Density Matrix Formulation for Quantum Renormalization Groups. *Phys. Rev. Lett.* **1992**, *69*, 2863.
- (68) White, S. R. Density-Matrix Algorithms for Quantum Renormalization Groups. *Phys. Rev. B* **1993**, *48*, 10345.
- (69) White, S. R.; Martin, R. L. *Ab Initio* Quantum Chemistry using the Density Matrix Renormalization Group. *J. Chem. Phys.* **1999**, *110*, 4127.
- (70) Mitrushenkov, A. O.; Fano, G.; Ortolani, F.; Linguerri, F.; Palmieri, P. Quantum Chemistry using the Density Matrix Renormalization Group. *J. Chem. Phys.* **2001**, *115*, 6815.
- (71) Legeza, Ö.; Röder, J.; Hess, B. A. Controlling the Accuracy of the Density-Matrix Renormalization-Group Method: The Dynamical Block State Selection Approach. *Phys. Rev. B* **2003**, *67*, 125114.
- (72) Chan, G. K.-L.; Head-Gordon, M. Highly Correlated Calculations with a Polynomial

- Cost Algorithm: A Study of the Density Matrix Renormalization Group. *J. Chem. Phys.* **2002**, *116*, 4462.
- (73) Chan, G. K.-L.; Sharma, S. The Density Matrix Renormalization Group in Quantum Chemistry. *Ann. Rev. Phys. Chem.* **2011**, *62*, 465.
- (74) Sharma, S.; Chan, G. K.-L. Spin-Adapted Density Matrix Renormalization Group Algorithms for Quantum Chemistry. *J. Chem. Phys.* **2012**, *136*, 124121.
- (75) Olivares-Amaya, R.; Hu, W.; Nakatani, N.; Sharma, S.; Yang, J.; Chan, G. K.-L. The *Ab-Initio* Density Matrix Renormalization Group in Practice. *J. Chem. Phys.* **2015**, *142*, 034102.
- (76) Wouters, S.; Van Neck, D. The Density Matrix Renormalization Group for *Ab Initio* Quantum Chemistry. *Eur. Phys. J. D* **2014**, *68*, 272.
- (77) Yanai, T.; Kurashige, Y.; Mizukami, W.; Chalupský, J.; Lan, T. N.; Saitow, M. Density Matrix Renormalization Group for *Ab Initio* Calculations and Associated Dynamic Correlation Methods: A Review of Theory and Applications. *Int. J. Quantum. Chem.* **2015**, *115*, 283.
- (78) Knecht, S.; Hedegård, E. D.; Keller, S.; Kovyrshin, A.; Ma, Y.; Muolo, A.; Stein, C. J.; Reiher, M. New Approaches for *Ab Initio* Calculations of Molecules with Strong Electron Correlation. *Chimia* **2016**, *70*, 244.
- (79) Eriksen, J. J.; Lipparini, F.; Gauss, J. Virtual Orbital Many-Body Expansions: A Possible Route towards the Full Configuration Interaction Limit. *J. Phys. Chem. Lett.* **2017**, *8*, 4633.
- (80) Eriksen, J. J.; Gauss, J. Many-Body Expanded Full Configuration Interaction. I. Weakly Correlated Regime. *J. Chem. Theory Comput.* **2018**, *14*, 5180.

- (81) Eriksen, J. J.; Gauss, J. Many-Body Expanded Full Configuration Interaction. II. Strongly Correlated Regime. *J. Chem. Theory Comput.* **2019**, *15*, 4873.
- (82) Eriksen, J. J.; Gauss, J. Generalized Many-Body Expanded Full Configuration Interaction Theory. *J. Phys. Chem. Lett.* **2019**, *10*, 7910.
- (83) Xu, E.; Uejima, M.; Ten-no, S. L. Full Coupled-Cluster Reduction for Accurate Description of Strong Electron Correlation. *Phys. Rev. Lett.* **2018**, *121*, 113001.
- (84) Deustua, J. E.; Shen, J.; Piecuch, P. Converging High-Level Coupled-Cluster Energetics by Monte Carlo Sampling and Moment Expansions. *Phys. Rev. Lett.* **2017**, *119*, 223003.
- (85) Deustua, J. E.; Magoulas, I.; Shen, J.; Piecuch, P. Communication: Approaching Exact Quantum Chemistry by Cluster Analysis of Full Configuration Interaction Quantum Monte Carlo Wave Functions. *J. Chem. Phys.* **2018**, *149*, 151101.
- (86) Deustua, J. E.; Yuwono, S. H.; Shen, J.; Piecuch, P. Accurate Excited-State Energetics by a Combination of Monte Carlo Sampling and Equation-of-Motion Coupled-Cluster Computations. *J. Chem. Phys.* **2019**, *150*, 111101.
- (87) Yuwono, S. H.; Magoulas, I.; Piecuch, P. Quantum Computation Solves a Half-Century-Old Enigma: Elusive Vibrational States of Magnesium Dimer Found. *Sci. Adv.* **2020**, *6*, eaay4058.
- (88) Huron, B.; Malrieu, J.-P.; Rancurel, P. Iterative Perturbation Calculations of Ground and Excited State Energies from Multiconfigurational Zeroth-Order Wavefunctions. *J. Chem. Phys.* **1973**, *58*, 5745.
- (89) Harrison, R. J. Approximating Full Configuration Interaction with Selected Configuration Interaction and Perturbation Theory. *J. Chem. Phys.* **1991**, *94*, 5021.

- (90) Illas, F.; Rubio, J.; Ricart, J. M.; Bagus, P. S. Selected Versus Complete Configuration Interaction Expansions. *J. Chem. Phys.* **1991**, *95*, 1877.
- (91) Wulfov, A. L. Passing the One-Quadrillion Limit in FCI Extrapolations on a Personal Computer. *Chem. Phys. Lett.* **1996**, *255*, 300.
- (92) Stampfuß, P.; Wenzel, W. Improved Implementation and Application of the Individually Selecting Configuration Interaction Method. *J. Chem. Phys.* **2005**, *122*, 024110.
- (93) Schriber, J. B.; Evangelista, F. A. Communication: An Adaptive Configuration Interaction Approach for Strongly Correlated Electrons with Tunable Accuracy. *J. Chem. Phys.* **2016**, *144*, 161106.
- (94) Schriber, J. B.; Evangelista, F. A. Adaptive Configuration Interaction for Computing Challenging Electronic Excited States with Tunable Accuracy. *J. Chem. Theory Comput.* **2017**, *13*, 5354.
- (95) Garniron, Y.; Scemama, A.; Giner, E.; Caffarel, M.; Loos, P.-F. Selected Configuration Interaction Dressed by Perturbation. *J. Chem. Phys.* **2018**, *149*, 064103.
- (96) Loos, P.-F.; Scemama, A.; Blondel, A.; Garniron, Y.; Caffarel, M.; Jacquemin, D. A Mountaineering Strategy to Excited States: Highly Accurate Reference Energies and Benchmarks. *J. Chem. Theory Comput.* **2018**, *14*, 4360.
- (97) Fales, B. S.; Seritan, S.; Settje, N. F.; Levine, B. G.; Koch, H.; Martínez, T. J. Large Scale Electron Correlation Calculations: Rank-Reduced Full Configuration Interaction. *J. Chem. Theory Comput.* **2018**, *14*, 4139.
- (98) Wang, Z.; Li, Y.; Lu, J. Coordinate Descent Full Configuration Interaction. *J. Chem. Theory Comput.* **2019**, *15*, 3558.

- (99) Greene, S. M.; Webber, R. J.; Weare, J.; Berkelbach, T. C. Beyond Walkers in Stochastic Quantum Chemistry: Reducing Error Using Fast Randomized Iteration. *J. Chem. Theory Comput.* **2019**, *15*, 4834.
- (100) Blunt, N. S. A Hybrid Approach to Extending Selected Configuration Interaction and Full Configuration Interaction Quantum Monte Carlo. *J. Chem. Phys.* **2019**, *151*, 174103.
- (101) Paldus, J.; Planelles, J. Valence Bond Corrected Single Reference Coupled Cluster Approach. I. General Formalism. *Theor. Chim. Acta* **1994**, *89*, 13.
- (102) Planelles, J.; Paldus, J.; Li, X. Valence Bond Corrected Single Reference Coupled Cluster Approach. II. Application to PPP Model Systems. *Theor. Chim. Acta* **1994**, *89*, 33.
- (103) Planelles, J.; Paldus, J.; Li, X. Valence Bond Corrected Single Reference Coupled Cluster Approach. III. Simple Model of Bond Breaking or Formation. *Theor. Chim. Acta* **1994**, *89*, 59.
- (104) Peris, G.; Planelles, J.; Malrieu, J.-P.; Paldus, J. Perturbatively Selected CI as an Optimal Source for Externally Corrected CCSD. *J. Chem. Phys.* **1999**, *110*, 11708.
- (105) Paldus, J. Externally and Internally Corrected Coupled Cluster Approaches: An Overview. *J. Math. Chem.* **2017**, *55*, 477.
- (106) Epstein, P. S. The Stark Effect From the Point of View of Schroedinger's Quantum Theory. *Phys. Rev.* **1926**, *28*, 695.
- (107) Nesbet, R. K. Configuration Interaction in Orbital Theories. *Proc. R. Soc. London, Ser. A* **1955**, *230*, 312.
- (108) Møller, C.; Plesset, M. S. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, *46*, 618.

- (109) Schreiber, M.; Silva-Junior, M. R.; Sauer, S. P. A.; Thiel, W. Benchmarks for Electronically Excited States: CASPT2, CC2, CCSD, and CC3. *J. Chem. Phys.* **2008**, *128*, 134110.
- (110) Blunt, N. S.; Thom, A. J. W.; Scott, C. J. C. Preconditioning and Perturbative Estimators in Full Configuration Interaction Quantum Monte Carlo. *J. Chem. Theory Comput.* **2019**, *15*, 3537.
- (111) Blunt, N. S. An Efficient and Accurate Perturbative Correction to Initiator Full Configuration Interaction Quantum Monte Carlo. *J. Chem. Phys.* **2018**, *148*, 221101.
- (112) Nesbet, R. K. *Variational Principles and Methods in Theoretical Physics and Chemistry*; Cambridge University Press: Cambridge, UK, 2003.
- (113) Yang, J.; Hu, W.; Usvyat, D.; Matthews, D. A.; Schütz, M.; Chan, G. K.-L. *Ab Initio* Determination of the Crystalline Benzene Lattice Energy to Sub-Kilojoule/Mole Accuracy. *Science* **2014**, *345*, 640.