The Ground State Electronic Energy of Benzene

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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 assessment, the evaluated high-level methods are all found to qualitatively agree on a final correlation energy. However, we find the root-mean-square deviation of the energies from the studied methods to be considerable (1.3 mE_{H}), 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 was 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,[5–12] and an 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.[13–22] Even more so, benzene—alongside, for instance, water—may 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,[23] 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 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 is complicated by the sheer scale of the combinatorial problem associated with distributing 30 electrons among 108 orbitals. As an illustrative example, upon traversing up through the standard coupled cluster[24–26] (CC) hierarchy, satisfactory convergence of the correlation energy cannot be concluded even upon accounting for connected quadruple excitations[27,28] (CCSDTQ), which is the highest level of sophistication possible today for systems of this size.[29,30] 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[31–33] (FCI) present in lower-level (CCSD[34] and CCSDT[35,36]) CC models.[37,38] 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.[39] 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,[40] 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, hextuples, 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 (post-quadruple) connected excitations will contribute to the magnitude of 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.[41–43] 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,[44–46] 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 accuracy generally 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

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

Acronym	Method	References
ASCI	Adaptive Sampling CI	47–51
SHCI	Semistochastic Heat-Bath CI	52–58
iCI	Iterative CI with Selection	59–62
AS-FCIQMC	Adaptive-Shift FCI Quantum Monte-Carlo	63–67
DMRG	Density Matrix Renormalization Group	68–79
MBE-FCI	Many-Body Expanded FCI	80–83
FCCR	Full CC Reduction	84
CAD-FCIQMC	Cluster-Analysis Driven FCIQMC	85–88

methods on the basis of their common traits and differences. The adaptive sampling CI[47–51] (ASCI), semistochastic heat-bath CI[52–58] (SHCI), and iterative CI with selection[59–62] (iCI) methods all belong to a wider class of selected CI (SCI) methods,[89–101] 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[63–66] (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 shift[67] (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[68–79] (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[80–83] (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 reduction[84] (FCCR) method, cluster projection manifolds and commutator

expressions for higher-level excitations are systematically reduced in order to optimally exploit the sparsity of the FCI wave function, as recast 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[102–106]—from which a deterministic CC energy may be computed in the recent semistochastic cluster-analysis driven FCIQMC[85–88] (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 portion 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[107,108] or Møller-Plesset[109] 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,[110] namely i-FCIQMC,[111] augmented by perturbation theory.[112] 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,

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non-variational biases stem from the initiator approximation as well as from perturbation theory in the latter case.
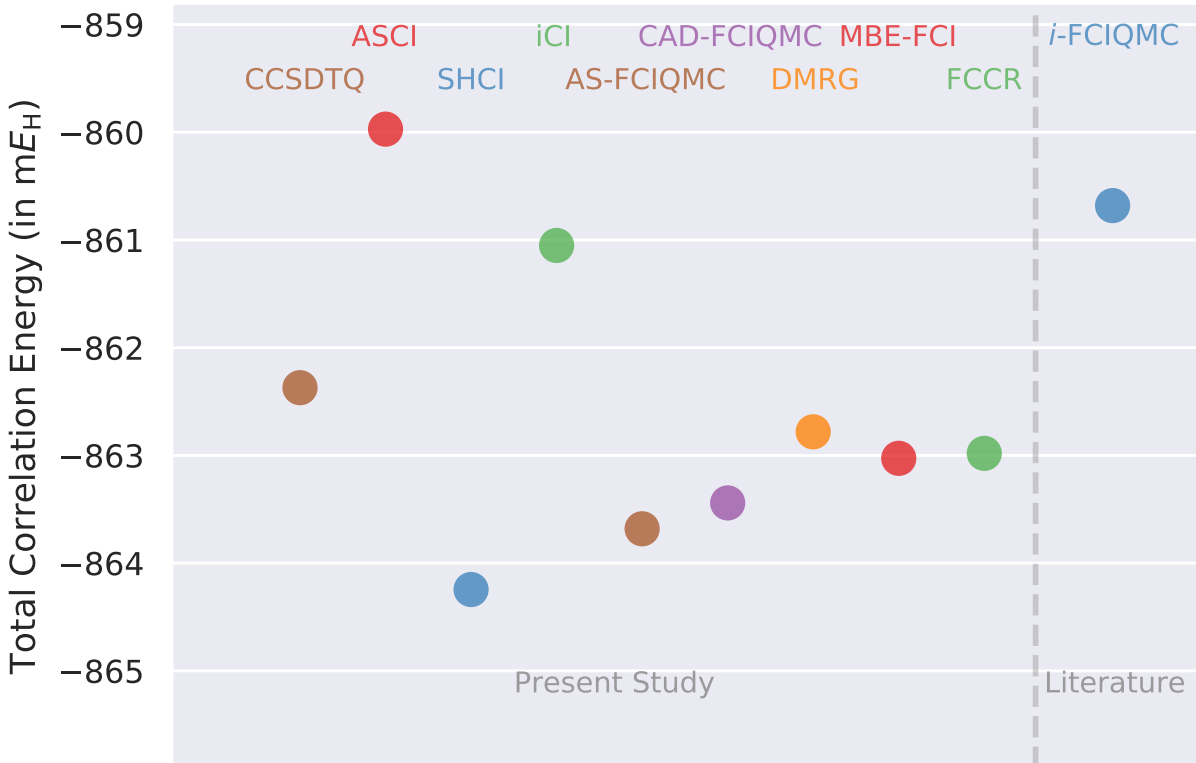

Figure 1: Frozen-core C_6H_6/cc-pVDZ correlation energies for the methods of Table 1 alongside i-FCIQMC.[111] See the SI for results obtained after the blind test was completed.

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 the various methods. 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,[113] 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 ± 1 mE_{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 mE_{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 mE_{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 ($+0.25$ mE_{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 ($+1.1$ mE_{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 mE_{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 mE_H.

Table 2: Extrapolation distances, ΔE_dist (in mE_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, $\Delta E_\mathrm{extrap.}$ (final variational energies, that is, in the absence of perturbation theory, are presented as $\Delta E_\mathrm{var.}$). 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 results obtained after the blind test was completed.

Method	$\Delta E_\mathrm{var.}$	ΔE_final	$\Delta E_\mathrm{extrap.}$	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 considerable 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. Be that as it may, our CCSDTQ result was still obtained using only 5.5k core hours using a single thread on a multicore node equipped with 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 with 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 latter method. In the case of AS-FCIQMC, a total of 0.06M core hours were consumed, distributed over a group of either 100 or 200 multicore nodes, while the MBE-FCI 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 mE_{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, taking into account also the post blind-test energies of some of the methods, 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 mE_{H}, in accordance with our preliminary estimate in the introduction and earlier projections.[114] On this basis, we are led to conclude that the electronic structure of benzene in its equilibrium geometry is predominantly dynamic in character.

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 efficiencies of their implementations or the use of optimized MOs in combination with larger correlation spaces—were submitted following the compilation of the results in Fig. 1. These results are discussed in the SI.

Acknowledgments

Supporting Information

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

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