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ABSTRACT

High-accuracy noncovalent interaction energies are indispensable as data points for potential energy surfaces and as benchmark values for improving and testing more approximate approaches. The preferred algorithm (the *gold standard*) for computing these energies has been the coupled-cluster method with singles, doubles, and perturbative triples [CCSD(T)] converged to the complete basis set (CBS) limit. However, gold-standard calculations are expensive as correlated interaction energies converge slowly with the basis set size, and establishing the CBS limit to better than 0.05 kcal/mol typically requires a CCSD(T) calculation in a basis set of at least triple-zeta quality. If an even higher accuracy is required (for example, for the assignment of complicated high-resolution spectra), establishing a superior *platinum standard* requires both a precisely converged CCSD(T)/CBS limit and the corrections for the core correlation, relativistic effects, and higher-order coupled-cluster terms at least through the perturbative quadruple excitations. On the other hand, if a triple-zeta CCSD(T) calculation is not feasible but a double-zeta one is, it is worthwhile to look for a *silver standard* that provides the most accurate and consistent approximation to the gold standard at a reduced computational cost. We review the recent developments aimed at (i) increasing the breadth and diversity of the available collection of gold-standard benchmark interaction energies, (ii) evaluating the best computational strategies for platinum-standard calculations and producing beyond-CCSD(T) potential energy surfaces for spectroscopic and scattering applications of the highest precision, and (iii) improving the accuracy of the silver-standard, double-zeta-level CCSD(T)/CBS estimates through the use of explicit correlation and midbond basis functions. We also outline the remaining challenges in the accurate *ab initio* calculations of noncovalent interaction energies.

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I. INTRODUCTION

A reliable description of intermolecular interactions is essential for a large variety of problems in chemistry, physics, biology, and materials science. Weak interactions between gas molecules give rise to deviations from ideal gas law, which can be quantified, e.g., via second and higher virial coefficients. The latter coefficients can be used, for example, to establish a connection between pressure, temperature, and the speed of sound in a gas that can be employed to construct a new temperature standard.¹ Weak interactions with a background gas result in broadening and shifting of spectral lines, and a combination of accurate measurements and calculations is required to advance the description of spectral line shapes beyond the conventional convolution of Lorentzian and Gaussian pictures.² The intermolecular rovibrational bound states give rise to rich (and

hard to assign) infrared and microwave spectra,³ while the unbound states determine cross sections for elastic and inelastic scattering processes essential for astrophysical modeling.⁴ A delicate balance of two-, three-, and higher-body interactions determines the stability of molecular clusters,⁵ the structure and polymorphism of molecular crystals,⁶ and the thermodynamical properties of liquids.⁷ Noncovalent interactions are an important factor in catalysis as they can preferentially stabilize the transition state for a desired reaction.⁸ Interactions within layered materials⁹ and between adsorbate molecules and surfaces or porous media¹⁰ are crucial for the performance of modern materials in a variety of applications ranging from semiconductors to carbon capture. Last but not least, weak interactions stabilize the structures of proteins and nucleic acids and bind substrates (as well as inhibitors) to the active sites of enzymes.¹¹ Thus, it is not a surprise that the field of intermolecular interactions has

continually attracted widespread interest from experimentalists and theorists alike.

From the computational perspective, the necessary prerequisite to determining spectra, scattering cross sections, and many other quantities of experimental interest is the generation (in whole or in part) of the *potential energy surface* (PES), that is, a function that expresses the energy of the complex in terms of the internal and relative geometries of its constituent molecules. This energy is a sum of the energies of individual molecules (monomers), including the energetic penalty incurred when the monomers adapt their geometric configurations in the complex instead of their individually optimized structures, and the actual interaction energy. The construction of a PES involves three steps: establishing a grid of configurations that span the surface, interaction energy calculations for each grid point, and a fitting or interpolation of an analytical function that provides a reasonable PES approximation in between the computed grid points as well as at larger intermolecular separations. Recently, significant advances have been made on optimizing the selection of grid points,¹² making the fitting more robust,¹³ and automating the whole process of PES construction;^{14,15} however, the vast majority of computer time still needs to be spent on the middle step, that is, electronic structure calculations on each configuration from the grid. While the individual interaction energies can be computed directly via symmetry-adapted perturbation theory (SAPT),¹⁶ it is more common to obtain these values via subtraction of monomer energies from the total energy of the complex, within the so-called supermolecular framework. In such a case, the accuracy of interaction energy hinges on a cancellation of errors (which arise due to the use of an approximate electronic structure theory and an incomplete basis set) between the quantities that are subtracted. Obviously, this cancellation is much easier if the individual errors are small to begin with: this is one of the reasons why intermolecular interaction energies place particularly high demands on the accuracy of the underlying electronic structure theory. The other reason is the van der Waals dispersion forces which arise entirely out of electron correlation and thus require a high-level account of the correlation energy.

Except for few-electron complexes where full configuration interaction (FCI) calculations are possible, the most successful strategy for computing accurate correlated interaction energies has been the coupled-cluster (CC) approach.¹⁷ In particular, the coupled-cluster variant with single, double, and perturbative triple excitations [CCSD(T)]¹⁸ has been termed the *gold standard* of electronic structure theory as it provides consistently accurate interaction energies for closed-shell complexes. In fact, due to favorable error cancellation, CCSD(T) typically performs in this context just as well as the variant with full iterative triples, CCSDT.¹⁹ It should be noted that, when the interacting molecules cannot be qualitatively described by individual determinants, single-reference CC methods in general, and perturbative variants such as CCSD(T) in particular, are unable to provide reliable interaction energies. In such a case, computing a high-accuracy PES is a much more difficult task, and multireference electronic structure methods of benchmark quality are still under active development—see, e.g., a recent perspective for a review.²⁰ It might be noted in passing that the CC methods have the attractive property that the extent of multireference character for a problematic system can be inferred from examining the cluster amplitudes. In this perspective, we will be concerned with single-reference

complexes so that CCSD(T) is indeed a reliable gold standard *as long as the results are converged to the complete basis set limit* (CBS).

Computing a gold standard CCSD(T)/CBS interaction energy is an expensive task due to both an unfavorable N^7 computational scaling of CCSD(T) with the system size and a slow basis set convergence of correlated interaction energies. The scaling can be reduced by exploiting spatial locality of electron correlation; however, the errors of the local approximation sometimes exceed the accuracy one would expect from the gold standard interaction energies.²¹ Nevertheless, local CCSD(T) variants are undergoing constant improvement^{22–25} and are on the verge of becoming a reliable source of benchmark-quality gold standard estimates. The basis set convergence of CCSD(T) interaction energies can be improved by a number of techniques—see Ref. 26 for a recent review. These techniques can be used separately or in combination and include the composite MP2/CBS+ δ [CCSD(T)] treatment {where the easier-to-compute CBS limit of the second-order Møller-Plesset perturbation theory (MP2) is augmented with a δ [CCSD(T)] = CCSD(T)–MP2 correction computed in a moderate basis set}, CBS extrapolations, midbond functions, and various variants of the explicitly correlated CCSD(T)-F12 approach.^{27,28} Even with these enhancements, one typically cannot avoid performing a CCSD(T) calculation in at least a partially augmented triple-zeta basis set: otherwise, the basis set truncation errors overwhelm the intrinsic errors of the CCSD(T) approach.

The gold standard CCSD(T)/CBS estimates are a centerpiece of the field of accurate *ab initio* studies of weakly interacting complexes and a centerpiece of this perspective. In addition to numerous investigations of PESs for individual systems of experimental interest, the gold standard calculations have led to the establishment of benchmark noncovalent databases that compile accurate interaction energy values for a diverse selection of complexes and configurations. The available noncovalent databases have been recently reviewed in Refs. 26 and 29: the most widely employed sets include the S22³⁰ and S66³¹ databases of the Hobza group. In the last couple of years, benchmark databases have grown larger and more diverse in order to meet the growing demands of the community as various more approximate (but much less computationally demanding) approaches are formulated and tested against high-accuracy *ab initio* data. Such approximate but efficient techniques may be based on density functional theory (DFT),³² semiempirical methods,³³ or machine learning (ML).³⁴ At the same time, one frequently needs to go either above or slightly below the gold standard. For example, using PESs to reproduce and interpret high-resolution spectroscopic data might call for interaction energies beyond the CCSD(T)/CBS level. Thus, it has been worthwhile to establish a *platinum standard* of interaction energy calculations of subspectroscopic accuracy. On the other hand, for larger complexes, a CCSD(T) calculation in a triple-zeta basis set, required by the gold standard, might be unaffordable and one needs to resort to CCSD(T)/CBS estimates that only require a CCSD(T) calculation in a double-zeta basis set or even estimates that do not require a CCSD(T) calculation at all. For this purpose, *silver*, *bronze*, and even *pewter standards* of interaction energy calculations have been designated,³⁵ with the goal of providing the most accurate approximations to the gold standard at a given (significantly reduced) level of computational complexity.

The aim of this perspective is to describe the current state of the art for the entire family of “precious metals” standards of intermolecular interaction energies. Therefore, after a brief introduction to the methodology of interaction energy calculations in Sec. II, we continue by reviewing recent progress in gold-standard calculations, with emphasis on the development of diverse and balanced benchmark databases and accurate PESs for systems of experimental interest, in Sec. III. We then move on to calculations of even higher accuracy, illustrating some important applications of platinum-standard interaction energies in Sec. IV. Finally, in Sec. V, we review the establishment and refinement of the silver-standard level of theory as a cost-effective alternative to the gold standard. In all cases, we try to focus on the current directions of research as well as the remaining challenges that will likely be addressed in the near future. As the accuracy of more approximate approaches (for example, those based on DFT) has been steadily improving,^{36,37} the bronze and pewter standards do not provide benchmark interaction energies with sufficient precision to evaluate the best performers. Therefore, the primary focus of this perspective is the levels of accuracy from the silver standard onward.

II. METHODOLOGY

For a given complex A–B, the interaction energy calculation at the silver, gold, or platinum level requires three CCSD(T) runs¹⁸ combined within the supermolecular framework³⁸

$$E_{\text{int}}^{\text{CCSD(T)}} = E_{\text{A-B}}^{\text{CCSD(T)}} - E_{\text{A}}^{\text{CCSD(T)}} - E_{\text{B}}^{\text{CCSD(T)}}. \quad (1)$$

The energies for the individual subsystems A and B are evaluated at their geometries adopted in the complex, which might not be the same as the optimal geometries for isolated monomers. The energetic penalty of distorting A and B to their geometries in the complex, called the *deformation energy*,³⁹ can (and often should) be included separately; however, in this perspective, we will focus on the computation of the interaction energy proper, that is, Eq. (1) [which can be used with CCSD(T) or with any other electronic structure method, for example, MP2]. The typical choice of basis sets used to perform the CCSD(T) computations is the correlation-consistent cc-pVXZ family of Dunning and coworkers,⁴⁰ enhanced with diffuse functions to form the completely augmented aug-cc-pVXZ \equiv aXZ sets⁴¹ or the partially augmented “calendar” bases such as jun-cc-pVXZ.⁴² In order to achieve a cancellation of most of the electronic structure and basis set errors between the quantities subtracted in Eq. (1) and obtain an interaction energy that goes to zero at large A–B separations, the basis functions centered on molecule A have to be the same in the calculations of $E_{\text{A-B}}^{\text{CCSD(T)}}$ and $E_{\text{A}}^{\text{CCSD(T)}}$, and those centered on B have to be the same in the calculations of $E_{\text{A-B}}^{\text{CCSD(T)}}$ and $E_{\text{B}}^{\text{CCSD(T)}}$ [note that another possible issue that would break the correct long-range limit could be the use of a size-inconsistent approach, such as a truncated configuration interaction method, in place of CCSD(T)]. However, if the $E_{\text{A}}^{\text{CCSD(T)}}$ and $E_{\text{B}}^{\text{CCSD(T)}}$ calculations contain only the subsystem’s own basis functions, another problem appears: the description of, say, A is more complete in $E_{\text{A-B}}^{\text{CCSD(T)}}$ than in $E_{\text{A}}^{\text{CCSD(T)}}$, thanks to the additional flexibility afforded by the basis functions centered on the other subsystem. This inconsistency is called the *basis set*

superposition error (BSSE), and the most popular remedy for it is the counterpoise (CP) correction of Boys and Bernardi.⁴³ In the CP-corrected supermolecular framework, all three quantities in Eq. (1) are computed in the full basis set of the complex, that is, the calculation of $E_{\text{A}}^{\text{CCSD(T)}}$ includes *ghost basis functions* centered at the locations of B’s nuclei in the complex and vice versa. As the basis set is enlarged, the CP-corrected and uncorrected interaction energies [the latter obtained from Eq. (1) with the calculations of $E_{\text{A}}^{\text{CCSD(T)}}$ and $E_{\text{B}}^{\text{CCSD(T)}}$ utilizing only the basis set of the subsystem] typically bracket the CBS value of $E_{\text{int}}^{\text{CCSD(T)}}$, converging there from below (CP-uncorrected) and above (CP-corrected). This behavior has two consequences. First, some authors have argued that the CP scheme overcorrects the true BSSE⁴⁴ and the merits of the counterpoise correction were a hot topic in the literature some time ago. Second, a “half-corrected” scheme, that is, the arithmetic mean of the CP-corrected and uncorrected interaction energies,^{45,46} might sometimes be more accurate than either variant alone. On the practical side, an extensive comparison of CCSD(T)/CBS estimates obtained from CP-corrected, uncorrected, and half-corrected calculations was performed by Burns *et al.*,⁴⁷ concluding that the averaged scheme avoids the worst errors incurred by either variant alone; however, in most cases, the fully corrected and half-corrected approaches perform similarly well and either one can be recommended. As the fully CP-corrected interaction energy calculations are currently the most prevalent, throughout the rest of this perspective, all computations will be assumed CP-corrected unless explicitly stated otherwise. Another point that, in our opinion, tips the scales toward the fully CP-corrected approach is that it is the only one compatible with the addition of extra basis functions centered on the intermolecular bond.⁴⁸

For the gold and silver standard accuracy, an approximation to CCSD(T)/CBS is all that is needed, and it is normally sufficient to perform the CCSD(T) calculations of Eq. (1) within the frozen core approximation, where only the valence electrons are correlated. However, going beyond the gold-standard level of theory requires a concerted effort as several neglected contributions might be of comparable size: the core-core and core-valence correlation, the coupled-cluster excitations beyond CCSD(T), the relativistic effects, and sometimes even the quantum electrodynamics (QED) term. At the same time, residual errors of the leading, frozen-core CCSD(T)/CBS term tend to be comparable to the corrections mentioned above, and the generation of a PES beyond the gold standard of accuracy requires *both a further refinement of the CCSD(T)/CBS estimate and the inclusion of terms beyond the frozen-core CCSD(T) level*.

If one sets out to compute, say, a double zeta-level CCSD(T) interaction energy, there are many variants to choose from, and all of them are of comparable computational complexity. One can opt for conventional CCSD(T) or for any variant of explicitly correlated CCSD(T), such as the CCSD(T)-F12a, CCSD(T)-F12b,^{49,50} or CCSD(F12*) (T) \equiv CCSD(T)-F12c⁵¹ approximations. The triples contribution in an F12 calculation can be included as-is or scaled to approximately account for the lack of explicit correlation in (T). The scaling factor is commonly taken as the ratio of MP2-F12 and MP2 correlation energies,⁵⁰ and when the ratio obtained for the dimer is also used in monomer calculations to maintain size consistency,⁵² such an approach is denoted (T**).⁵³ Alternatively,

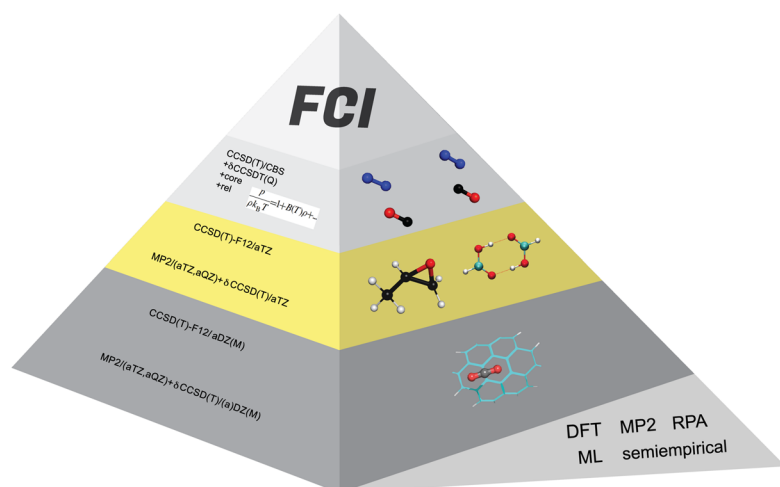


FIG. 1. Summary of the silver, gold, and platinum standards described in this perspective, providing successive approximations to the FCI/CBS interaction energy.

the triples scaling factor can be chosen as the ratio of the correlation energies from CCSD-F12b (or CCSD-F12c) and conventional CCSD.⁵⁴ Instead of the standard aDZ basis set, one might opt for the cc-pVDZ-F12 set specifically developed for F12 calculations⁵⁵ or even its aug-cc-pVDZ-F12 counterpart with additional diffuse functions added.⁵⁶ The atom-centered basis set might be supplemented by midbond functions. Basis set superposition error might be alleviated by the CP correction, but uncorrected or half-corrected calculations are also possible. Finally, for any choice described above, one might perform a simple CCSD(T) calculation or a composite MP2/CBS+ δ [CCSD(T)] one, with the MP2/CBS limit established with either conventional MP2 or MP2-F12, with or without a complete basis set extrapolation. Thus, a “double zeta-level CCSD(T) interaction energy” might mean many different things, and we need to be precise when defining the actual theory and basis set level designated by the precious-metal standard. This issue becomes even more pronounced in the case of the gold standard which is colloquially known as simply CCSD(T)/CBS. Sections III–V of this perspective will review the research that established what it means to converge the CCSD(T) interaction energy to the CBS limit sufficiently well to be accepted as the gold (or silver) standard, and what precise combinations of CCSD(T)/CCSD(T)-F12 variants, basis sets, and other details mentioned above are the most effective in achieving the required accuracy at an optimal computational cost. Here, we just summarize the recommendations that have been established and give the most important examples of precise theory and basis set levels that have been deemed worthy of a platinum/gold/silver standard designation. These examples as well as representative applications of precious-metal standards described in this work are summarized in Fig. 1.

The most common precise designation of the gold standard CCSD(T)/CBS approximation³⁵ is MP2/(aTZ,aQZ)+ δ [CCSD(T)]/aTZ, where the notation (aXZ, aYZ) signifies that the two sets have been employed in the standard X^{-3} extrapolation of the correlation energy contribution.^{57,58} The Hartree-Fock part of the MP2 interaction energy is usually quite well converged in the aQZ basis and no extrapolation is performed for this part. A platinum-standard

calculation needs to extend the coupled-cluster level at least to CCSDT(Q),⁵⁹ that is, include full triple and perturbative quadruple excitations on top of CCSD(T). In addition, the leading frozen-core CCSD(T) term has to be converged to CBS even tighter than for the gold standard, and corrections for the core-core and core-valence correlation, relativistic effects, and possibly even terms neglected in the Born-Oppenheimer approximation⁶⁰ need to be included. Such a composite designation of the platinum standard is inspired by the high-accuracy composite approaches to thermochemistry, such as HEAT (high accuracy extrapolated *ab initio* thermochemistry),⁶¹ the Weizmann-n (Wn) family of methods,⁶² the Feller-Peterson-Dixon algorithm,⁶³ and the correlation consistent composite approach (ccCA).⁶⁴ The silver standard has been designated in Ref. 35 as the DW-CCSD(T^{**})-F12/aDZ level, employing the dispersion-weighted combination of CCSD(T^{**})-F12a and CCSD(T^{**})-F12b proposed in Ref. 53. Several other possible silver standards using double-zeta basis sets with midbond functions will be introduced in Sec. V.

III. THE GOLD STANDARD—CCSD(T) AT THE COMPLETE BASIS SET LIMIT

A. Designation of the gold standard

We envision the gold standard of interaction energy calculations to be suitable for *all benchmarking applications*, where the quality of, e.g., DFT or ML approaches is assessed, and *most PES applications*, where the experimental spectroscopic, scattering, or thermophysical data are to be recovered from the *ab initio* PES. At present, the strictest challenge to the former requirement arises from the recent combinatorially optimized density functionals such as ω B97M-V,⁶⁵ which attains a root mean standard deviation of 0.18 kcal/mol on an extensive set of (comparatively) “easy” dimers.³⁷ The severity of the latter requirement obviously varies, and many latest high-resolution spectroscopic and scattering experiments necessitate going beyond the gold standard of theory, as will be illustrated

in detail in Sec. IV. Overall, it is clear that the successful gold standard needs to be accurate, on the average, to well below 0.1 kcal/mol: one would actually prefer the errors to stay within 0.05 kcal/mol even for (most) outliers. At this level of precision, it is quite nontrivial to even assess the performance of a gold standard candidate—we need something better than gold standard for reference! It would be highly desirable to obtain such a reference from experiment, but it is immensely difficult.⁶⁶ Interaction energies are not directly measurable, and other experimental quantities such as spectra or cross sections require further calculations (such as solving the nuclear Schrödinger equation) beyond the PES construction (which brings about other sources of uncertainty besides the interaction energy itself) and always probe more than a single geometry on the PES. Thus, our best option to assess potential gold-standard candidates is by comparison to even higher-level *ab initio* interaction energies and, as of right now, there is exactly one benchmark database that has sufficient accuracy to serve as a reference: A24.^{67,68}

The current best-estimate A24 interaction energies contain the frozen-core CCSD(T)/CBS term extrapolated from the aQZ and a5Z bases (a5Z and a6Z for selected systems)⁴⁷ enhanced by the corrections for core correlation, relativistic effects, and an estimate of the higher-order coupled-cluster terms from the CCSDT(Q)⁵⁹ calculations. Thus, these energies are sufficiently accurate to both judge the performance of the CCSD(T)/CBS treatment and evaluate various approximations to this CBS limit. Note that while the gold standard level is often referred to simply as CCSD(T)/CBS, its practical realization requires a particular, sufficiently precise, way to estimate the CBS limit using finite-basis calculations. In fact, the screening of potential gold-standard candidates should be performed in reference to a precise CCSD(T)/CBS estimate (such as the one computed in Ref. 47 and adopted in Ref. 68) with the higher-level corrections omitted to keep the candidate and the reference on an equal footing. For the A24 database, such a screening was performed in Ref. 69 for conventional CCSD(T) and CCSD(T)-F12, and Ref. 70 extended this screening to bases with midbond functions. The results of Ref. 69 show that the CCSD(T) estimates that require only aDZ-level coupled-cluster calculations are quite accurate on the average {with the mean unsigned error (MUE) of only 0.03 kcal/mol for MP2/(aTZ,aQZ)+ δ [CCSD(T)]/aDZ}; however, individual errors extend all the way from -0.1 to 0.1 kcal/mol, so this level of theory cannot be recommended as an unambiguous gold standard. In contrast, in the aTZ basis sets, both straight-up F12 calculations [e.g., CCSD(T^{**})-F12b/aTZ^{49,50}] and composite conventional ones [e.g., MP2/(aTZ,aQZ)+ δ [CCSD(T)]/aTZ, the originally designated gold standard from Ref. 35] are capable of bringing the MUE down to 0.01 kcal/mol, with all results within 0.05 kcal/mol of the CBS reference. Therefore, any of these variants can be adopted as the gold standard.

We will review the strategies for improving gold-standard interaction energies, and the applications for which such improvement is crucial, in Sec. IV, and the most accurate double-zeta-level approximations to the gold standard in Sec. V. For now, we go back to the two primary areas of gold-standard applications stated at the beginning of this section: the construction of benchmark noncovalent databases and the generation of accurate PESs for individual complexes. Both areas have witnessed an enormous progress in recent years, and it is worthwhile to summarize the most significant new developments.

B. Benchmark noncovalent databases

We have established how to calculate a gold-standard interaction energy for an individual structure of an intermolecular complex. Now, we have to consider how to select the structures and complexes that make up a noncovalent database suitable for benchmarking applications, that is, sufficiently *diverse* and *balanced*. While the early benchmark databases such as the widely popular S22 set³⁰ were composed of a handful of (mostly organic) dimers in their respective van der Waals minimum geometries, it was realized soon afterward that the off-minimum radial and angular configurations, including long-range (nearly asymptotic) and short-range (repulsive) ones, are just as important as the minimum structures. In fact, when constructing a dataset, it is not even crucial to precisely pin down the optimal geometry of the complex (unless the geometry itself serves as a reference^{71–73}), as an adequate coverage of different PES regions is much more important than having a single point at the actual minimum configuration. As a result, most of the newer databases contain also off-minimum configurations (radially displaced, angularly displaced, or both). A way to achieve the ultimate configurational diversity is to pick the entire set of grid points used to construct an *ab initio* PES for a given system, or the full set of configurations that are attained in actual systems (such as the entire set of amino acid sidechain-sidechain contacts found in the Protein Data Bank⁷⁴). Beyond the geometries of a single system, it is imperative to build a database out of complexes with different interaction types. One particularly useful way of elucidating the physical origins of interaction and classifying systems into interaction types is symmetry-adapted perturbation theory (SAPT).^{16,75,76} The relative importance of three possible attractive SAPT components, electrostatics, induction, and dispersion, can be displayed and analyzed by means of ternary diagrams^{35,77} so that the relative coverage of the diagram is a measure of the database diversity. It might be noted in passing that the presence of very different interaction strengths (both between different complexes and between different radial configurations of the same system) makes it nontrivial to select a suitable statistical measure to quantify the agreement of an approximate approach with the benchmark values. The commonly used mean unsigned error (MUE), also termed mean absolute deviation (MAD), is not a good description of structures with very different interaction energies, and the mean unsigned relative error (MURE) runs into a problem around the points where the PES crosses zero as small absolute errors can lead to very large relative errors in this case. Several improved metrics have been proposed,^{78–81} and the reader is referred to Ref. 26 for a more detailed discussion of the database diversity and performance assessment. Overall, several highly diverse benchmark databases have been constructed in recent years^{37,81,82} by combining (and sometimes extending) smaller sets available in the literature: each of these composite datasets contains more than 1000 accurate interaction energies. An even larger dataset, with 247 560 interaction energies, has been created in order to improve the MP2 theory with neural network-optimized spin component scaling;⁸³ however, this set can hardly be called balanced as nearly half of the structures involve a water molecule as one of the subsystems.

In parallel to the improvements in the database scope and diversity, the accuracy of some older benchmark interaction energies has undergone improvement as well. At the beginning of this decade, quite a bit of effort was directed into refining the original S22

benchmark data³⁰ as some of them were obtained at the MP2/(cc-pVTZ,cc-pVQZ)+ δ [CCSD(T)]/cc-pVDZ level that, as we will see in Sec. V, is not even up to the silver standard of accuracy. The currently established benchmark values compiled in Ref. 84, termed S22B, have been computed^{184–87} at several different levels of basis set saturation: importantly, the δ [CCSD(T)] term has been obtained in at least the aTZ basis set for all 22 systems. The differences between the refined S22B values and the original benchmark range up to nearly 0.7 kcal/mol, confirming that the original data of Ref. 30 were not up to current benchmark standards. Besides the S22 set, several other popular databases such as S66x8³¹ and WATER27⁸⁸ have been recently refined using explicitly correlated coupled-cluster calculations;^{54,89–91} see Sec. V for more details. It should be stressed that, according to our theory level classification, the existing benchmark databases are split into gold-standard and silver-standard data. In fact, complete gold-standard calculations would be too costly for some of the largest databases such as the amino acid sidechain-sidechain interactions (SSI) set of Ref. 74. The bare minimum that can be considered as silver-standard benchmark accuracy is the inclusion of the CCSD(T) interaction energy in at least a partially augmented double-zeta basis, in either stand-alone CCSD(T)-F12 calculation or the composite MP2/CBS+ δ [CCSD(T)] one (Sec. V will examine the optimal strategies for computing silver-standard interaction energies). While the silver-standard accuracy is sufficient for current applications of the benchmark datasets, some potential upgrades to gold-standard accuracy might be pursued in the future. Overall, in our opinion, the existing collection of benchmark noncovalent databases is sufficiently accurate and sufficiently broad for the assessment and development of new DFT, wavefunction, semiempirical, and machine-learning approaches for *ground-state closed-shell complexes involving small and medium-sized molecules composed of light atoms*; however, the extensions to open-shell systems, excited states, heavy atoms, and large systems still require significant progress. The most notable applications of benchmark noncovalent databases have been reviewed, e.g., in Refs. 26, 29, and 36; see also Refs. 37 and 92.

C. Accurate potential energy surfaces

The other key application of gold-standard interaction energies is the development of spectroscopically accurate PESs for individual systems of interest. While going beyond CCSD(T)/CBS is sometimes necessary for the highest accuracy (some relevant examples will be discussed in Sec. IV), there exists a large class of complexes (roughly speaking, those containing 2–6 nonhydrogen atoms) for which post-CCSD(T) calculations on the entire set of PES grid points are not feasible; however, the CCSD(T)/aTZ or even CCSD(T)/aQZ calculations (with or without F12 and/or midbond functions) can be carried out with relative ease and used to generate all data points. With the recent progress in the automated PES generation^{14,15} and the improved understanding of the CBS convergence of finite-basis CCSD(T) interaction energies (brought about by many developments reviewed in this perspective), the construction of gold-standard PESs is nowadays close to a routine task. Thus, *ab initio* electronic structure theory has happily delivered on the numerous requests for accurate intermolecular PESs, with applications to spectroscopy, scattering, virial coefficients, viscosities, and condensed phase properties. In the rest of this

section, we will review a few of these PESs. Their selection is motivated only by their subjective appeal to us, and the list is far from complete.

The particular significance of interaction potentials for water stems from both its special role in sustaining life and its unusual physical properties in the liquid (such as the density maximum at 4 °C). While an accurate description of any condensed phase requires at least the three-body potential (that is, the account of nonadditive interactions in molecular trimers) in addition to the two-body one,⁶ water is a particularly demanding case where the three-body interactions are unusually significant and even the four-body ones are not entirely negligible.⁹³ Therefore, both two-body and three-body potentials for water have attracted widespread attention. While reaching this point required many years of development by multiple research groups, *ab initio* potentials for (H₂O)₂⁹⁴ and (H₂O)₃⁹⁵ are now available at the gold-standard level of theory including all internal degrees of freedom for the water molecules. The two-body potential⁹⁴ was built from 42 508 interaction energies computed at the CCSD(T)/(aTZ+(3s3p2d1f),aQZ+(3s3p2d1f)) level, where the additional (3s3p2d1f) basis functions are centered on the midbond. The three-body potential⁹⁵ employed 12 347 trimer interaction energies obtained with CCSD(T)/aTZ+(3s3p2d1f). These potentials have been successful at reproducing a range of experimental quantities, from strictly dimer data such as the vibration-rotation-tunneling spectrum⁹⁶ and the second virial coefficient⁹⁷ to the structure and energetics of small water clusters^{5,98,99} to properties of liquid water such as density and radial distribution functions.¹⁰⁰ Several other CCSD(T)-level PESs for water have been introduced^{101–103}—see Ref. 104 for a review.

At the beginning of this century, a strong driving force for the generation of *ab initio* PESs was the spectroscopy of molecules embedded in superfluid helium nanodroplets.¹⁰⁵ Many molecules were investigated in this way, and carbonyl sulfide (OCS) has been one of the most popular as it is quite rigid, linear (so the spectra are simple), and polar (so it is a strong chromophore in both microwave and infrared regions). One of the first experiments compared the infrared spectrum of OCS in ⁴He and ³He nanodroplets, with the sharp rotational lines in the former environment confirming its superfluid nature.¹⁰⁶ Early on, it seemed that the gold-standard level of theory is not absolutely necessary for the He-OCS interaction since the fourth-order Møller-Plesset perturbation theory MP4/aTZ+(3s3p2d) potential has proven quite successful at reproducing experimental vibrational shifts in He_n-OCS clusters with $n = 1, \dots, 8$.¹⁰⁷ Later, a gold-standard four-dimensional He-OCS PES has been constructed by Li and Ma¹⁰⁸ employing the CCSD(T)/aQZ+(3s3p2d1f1g) theory and basis set combination, resulting in substantially improved agreement with experimental microwave and infrared transitions relative to the potential of Ref. 107. Helium is not the only important interacting partner for OCS: the availability of high-resolution infrared¹⁰⁹ and microwave¹¹⁰ spectra of OCS in *para*- and *ortho*-hydrogen clusters prompted the development of a six-dimensional H₂-OCS PES at the gold-standard CCSD(T)-F12a/aTZ level.¹¹¹ The (OCS)₂ homodimer is also of significant interest to spectroscopy, and the interplay of its polar and nonpolar minima has been elucidated with the help of a CCSD(T)-F12b/cc-pVTZ-F12 potential energy surface.¹¹²

Another source of demand for high-level PESs is the astrophysical community, where accurate scattering cross sections are required to understand and model the rates of collisional processes occurring in various interstellar objects.¹¹³ One of the collisional partners is usually helium or H₂, but the other partner can be selected from the long and ever-growing list of molecules detected in interstellar media. An important and unusual (from the perspective of Earth) class of such systems are linear carbon chains, both unsubstituted and capped at one end by hydrogen or another atom. The astrophysical applications have prompted the creation of several high-accuracy PESs involving such chains. The linear tricarbon (C₃) molecule is an important member of this class, and in the past, our group has contributed to the development of a new He–C₃ potential that was employed to compute rate coefficients for the rotational excitation and deexcitation of C₃ by helium¹¹⁴ [the underlying PES actually went beyond the gold standard and contained contributions from coupled-cluster excitations beyond CCSD(T)]. More recently, Walker *et al.* have constructed rigid C₆H[−]–H₂ and C₆H[−]–He potential surfaces at the gold-standard CCSD(T*)-F12b/cc-pVTZ-F12 level.¹¹⁵ Interestingly, the long and highly anisotropic C₆H[−] anion interacts very differently with helium and hydrogen, leading to strongly different rotationally inelastic cross sections. We mention in passing another interesting astrophysically motivated PES, the very recent CCSD(T)-F12b/(cc-pVTZ-F12,cc-pVQZ-F12) potential for a helium atom interacting with a propylene oxide molecule.¹¹⁶ Propylene oxide is the first chiral organic molecule detected in the interstellar space,¹¹⁷ and the measurement and modeling of its spectral and collisional properties might shed some light onto the (likely extraterrestrial) origins of the homochirality of life.^{118,119}

We conclude this section by mentioning a few of the largest systems for which gold-standard (or close) PESs have been constructed. The sizes of these complexes illustrate the current computational capabilities for running a large number of triple-zeta CCSD(T) calculations and manipulating the resulting data (for example, fitting an analytical PES expression). For CCSD(T) calculations with the full aTZ basis set on all atoms, the largest system with a PES is probably the ethane dimer, for which the MP2/(aQZ,a5Z)+ δ [CCSD(T)]/(aDZ,aTZ) potential has been developed by Hellmann¹²⁰ and used to compute the second virial coefficient and some transport properties of dilute ethane gas. In the partially augmented haTZ basis (with diffuse basis functions on nonhydrogen atoms only), one should mention the CCSD(T)-F12a PES for the formic acid dimer by Qu and Bowman.¹²¹ While this surface does not extend to all possible geometries, it is sufficiently broad to cover not only all normal modes of the complex but also the entire pathway for the concerted double proton tunneling between the HCOOH molecules. Quite surprisingly, the largest atom-molecule system with a gold-standard PES comes from a 10-year old paper on the benzene-argon complex,¹²² with the *ab initio* data obtained at the CCSD(T)/aTZ+(3s3p2d1f1g) level. The interaction energies turned out to be very similar to those obtained in an earlier CCSD(T)/aDZ+(3s3p2d1f1g) study;¹²³ therefore, subsequent PES calculations on complexes between a rare gas atom and an aromatic molecule tend to use the aDZ basis supplemented by bond functions.^{124,125} To our knowledge, no gold-standard PESs for interactions between two aromatic molecules exist; however, all symmetry-nonequivalent close dimers

in the benzene crystal have been studied at the CCSD(T)-F12a/aTZ level.¹²⁶

IV. THE PLATINUM STANDARD—WHEN CCSD(T) IS NOT ENOUGH

A. What is a good platinum standard?

Even the gold-standard CCSD(T)/CBS interaction energies are not always accurate enough to interpret high-resolution spectra or scattering cross sections. However, as already mentioned, going beyond the gold standard requires a simultaneous further refinement of the CCSD(T)/CBS leading term and the inclusion of corrections beyond the frozen-core CCSD(T) level. As far as the former improvement is concerned, one needs to go to basis sets of augmented quintuple-zeta (or even sextuple-zeta) quality, combined with CBS extrapolation, the F12 approach, and/or midbond functions. The best strategy for pinpointing an ultra-precise CBS estimate is actually an interesting question. While explicit correlation is so effective in improving small- and medium-basis estimates, conventional CCSD(T) calculations in the largest possible bases are sometimes superior to the CCSD(T)-F12 calculations in the largest basis sets available at that level.^{127,128} The primary reason for this somewhat unexpected observation is the residual inaccuracies of the a/b/c approximations to full CCSD(T)-F12. Overall, the accuracy of both CCSD(T) and CCSD(T)-F12 is strongly enhanced by the presence of bond functions, and ultra-precise CBS estimates might need ultra-large midbond sets. Below, we focus on the additional contributions past the CBS limit of the frozen-core CCSD(T) interaction energy.

The interaction energy contribution arising from the correlation of core electrons is easy to compute as the difference between the all-electron and frozen-core CCSD(T) values, obtained in a basis set that includes compact functions optimized for core correlation, such as the aug-cc-pCVXZ and aug-cc-pwCVXZ sequences of Dunning and co-workers.¹²⁹ The relativistic correction can be approximated at the scalar one-electron level using the second-order Douglas-Kroll-Hess Hamiltonian¹³⁰ or, more recently, the spin-free exact two-component theory in the one-electron approximation (SFX2C-1e or X2C for short).¹³¹ However, the two-electron relativistic interaction energy corrections, such as the spin(own)-orbit term, might also be nonnegligible.¹³² The effects of higher-order coupled-cluster excitations might be the most difficult to compute due to the steep computational scaling increase with every excitation level included. Overall, there are two strategies for computing post-CCSD(T) interaction energy terms: full-configuration-interaction (FCI) calculations for few-electron systems and coupled-cluster calculations with full triples (CCSDT), perturbative quadruples [CCSDT(Q)], or even full quadruples (CCSDTQ) for systems where FCI is not feasible. For the latter strategy, it is important to identify the theory level that provides consistent improvement over the gold-standard CCSD(T) calculation—a level that can be recommended as the “platinum standard” for computing interaction energies of subspectroscopic accuracy.

The importance of the CCSDT, CCSDT(Q), and CCSDTQ interaction energy corrections was first studied on individual systems, mainly rare gas dimers.^{133,134} The first systematic study of these

corrections over a range of systems (including the newly established A24 database of 24 small complexes⁶⁷) was performed by Hobza and co-workers.^{19,135} By comparison with interaction energies computed with the full inclusion of pentuple excitations (CCSDTQP) or with FCI for the smallest systems, Šimová *et al.* showed¹⁹ that the inclusion of full noniterative triples does not provide a systematic improvement over CCSD(T). In order to reach a “platinum standard” level of electron correlation, one needs to include connected quadruple excitations. Fortunately, the perturbative treatment of quadruples via the CCSDT(Q) approach⁵⁹ provides an excellent approximation to full iterative CCSDTQ results. Thus, CCSDT(Q) [more precisely, the composite CCSD(T)/CBS+ $\delta_{T+(Q)}$ treatment] is a good candidate for the platinum standard level of theory, but what basis sets are appropriate for computing the very expensive $\delta_{T+(Q)}$ = CCSDT(Q)–CCSD(T) correction?

In the benchmark studies of the Hobza group,^{19,67,135} the post-CCSD(T) corrections were computed using very small bases 6-31G*(0.25) and 6-31G**(0.25,0.15) (with the numbers in parentheses indicating the altered exponents of the polarization functions relative to 6-31G**)—only a limited subset of complexes employed the somewhat larger aDZ basis. However, the $\delta_{T+(Q)}$ correction, just like the δ [CCSD(T)] one,^{84,136} strongly varies with the basis set and requires at least the aTZ basis to obtain a reasonably saturated value. This behavior of $\delta_{T+(Q)}$ was established by one of us and co-workers¹³⁷ on a set of 21 small weakly bound complexes. Relative to the benchmark $\delta_{T+(Q)}$ values computed in basis sets aTZ and larger, the 6-31G**(0.25,0.15) estimates were off by 80% on average, showing that it is almost as bad to neglect the post-CCSD(T) contribution altogether as to calculate it in such a small basis set! The aDZ results were better but still far from converged, deviating by an average 35% from the $\delta_{T+(Q)}$ benchmark. In view of this observation, the earlier CCSDT(Q) benchmarks of the Hobza group were subsequently refined⁶⁸ by including the $\delta_{T+(Q)}$ /aDZ estimate. The resulting improved A24 database remains the only set of benchmark interaction energies for diverse systems computed at the platinum standard level of theory, and this database has become a keystone for high-accuracy studies of intermolecular interactions including the further refinement of the gold standard.⁶⁹

B. Ultra-accurate calculations for four-electron complexes

Having made recommendations on how to compute platinum-standard interaction energies for small complexes, we now turn to several important examples where attaining accuracy beyond the gold standard is critical for experimental or fundamental reasons. We first examine the simplest systems which have four electrons total, namely, the He–He, He–H₂, and H₂–H₂ complexes. In this case, CCSDTQ is equivalent to FCI and is feasible in at least a moderate basis set.

The helium dimer poses the most stringent demands for the accuracy of the pair potential as its second virial coefficients (density, acoustic, and dielectric) are necessary for the most accurate measurements of the thermodynamic temperature and, consequently, for the development of an improved temperature (and pressure) standard.¹ These measurements utilize constant-volume, acoustic, and dielectric-constant gas thermometers filled with helium, and

the nonideality effects of the gas need to be known to extrapolate to zero pressure (note that these effects are particularly minor for helium as the virial coefficients are small in the first place). Indeed, the current best available pair potential for helium,¹³⁸ the culmination of a long-term series of ever-improving descriptions of this interaction,^{139–145} exhibits millikelvin (nanohartree) accuracy, with the total interaction energy at the near-minimum separation of 5.6 bohrs amounting to $-10.995\,57 \pm 0.000\,20$ K. Attaining this accuracy has only been possible by going beyond one-electron basis sets and computing the nonrelativistic potential variationally (that is, at the FCI level) in a four-electron explicitly correlated Gaussian basis. Moreover, the relativistic, quantum electrodynamic, and adiabatic corrections were carefully determined and included in the potential.

The accuracy of the best available He–He interaction energies is truly remarkable, and it cannot at present be matched for any other weakly interacting system, including the seemingly similar four-electron complexes He–H₂ and H₂–H₂. There are three reasons why the latter systems, especially the hydrogen dimer, are much more difficult than He–He: the dimensionality of the problem (the fully flexible He–He, He–H₂, and H₂–H₂ PESs are 1D, 3D, and 6D, respectively), the number of required centers for basis functions, and the point-group symmetry of the problem (which simplifies the He–He calculations significantly while a general H₂–H₂ configuration may have no symmetry elements at all). Consequently, the uncertainties for the best available He–H₂ and H₂–H₂ potentials, while still impressively low, cannot match the He–He potential uncertainty. Specifically, the interaction energies at the van der Waals minima amount to -15.870 ± 0.065 K for He–H₂¹⁴⁶ and -56.96 ± 0.16 K for H₂–H₂.¹⁴⁷ The potentials of Refs. 146 and 147 were obtained using large one-electron Gaussian basis sets with all excitation levels up to FCI taken into account. At the respective minimum configurations, these higher-level excitations contribute about -0.57 and -1.8 K [beyond gold standard, FCI–CCSD(T)] or -0.005 and -0.044 K [beyond platinum standard, FCI–CCSDT(Q)] for He–H₂ and H₂–H₂, respectively. The two potentials have been employed in fully quantum calculations of the second virial coefficient including the effects of monomer flexibility.^{148,149} While the flexibility effects are not entirely negligible and the quantum treatment is the only one appropriate below about 50 K, overall, the second virial coefficients are only moderately sensitive to the interaction potential. Some more demanding applications of these PESs include scattering cross sections,¹⁵⁰ bound state properties, and the pressure broadening and shifting effects on the line shapes of Raman transitions in H₂. The quest for a precise description of the spectral line shapes has already prompted an extension of the original He–H₂ potential¹⁴⁶ to a substantially larger range of H–H vibrations, which has a noticeable effect on the computed pressure broadening and shifting coefficients.¹⁵¹ In conjunction with the ongoing improvement in the spectral resolution of the experimental H₂ transitions, the “platinum-standard” theoretical PES of Refs. 146 and 151 is expected to enable a fundamentally new description of spectral line shapes beyond the commonly used Voigt profile (the convolution of Lorentzian and Gaussian shapes).^{2,152}

The same He–H₂ complex poses a significant and exciting challenge to *ab initio* quantum chemistry also in the excited state, where experimental rate coefficients^{153,154} for the Penning ionization $\text{He}(2^3S) + \text{H}_2 \rightarrow \text{He} + \text{H}_2^+ + e^-$ are precise enough to pinpoint

inaccuracies even in the platinum-standard calculation. While the inclusion of a post-CCSD(T) correction from FCI/aQZ clearly improved the CCSD(T)/CBS description of rate coefficients, some discrepancies remain at low collision energies. In Ref. 154, these discrepancies were resolved by an *ad hoc* scaling of the correlation energy by a factor of 1.004; however, a purely *ab initio* description of the experimentally observed low-energy resonances has not yet been achieved.

C. Applications of the CCSDT(Q)-level platinum standard

We now move on to somewhat larger complexes where a FCI calculation is not feasible, but the interaction energy accuracy beyond the gold-standard level can be achieved by including higher-order coupled-cluster corrections. In many cases, the existing spectroscopic data are sufficiently precise to confirm the advantage of a post-CCSD(T) treatment over the CCSD(T) one or at least to pinpoint the residual inaccuracies in the CCSD(T)/CBS estimates. Our first example of this kind is the H₂-CO complex which has been thoroughly studied with both theory and experiment. The high-resolution infrared spectrum of this system is rich in features and strongly depends on the nuclear spin coupling in the H₂ monomer. While the infrared spectrum of *para*-H₂-CO has been measured and assigned a long time ago,¹⁵⁵ the assignment of the more complex *ortho*-H₂-CO spectrum, also recorded in Ref. 155, provided a challenge that took more than a decade to overcome. Importantly, an older H₂-CO potential computed at the CCSD(T)/CBS level of theory¹⁵⁶ had insufficient accuracy to explain the congested spectrum, so a platinum-standard PES was necessary. In fact, H₂-CO was one of the first complexes for which the importance of post-CCSD(T) corrections was demonstrated as the CCSDT(Q) calculations at the two minimum geometries gave substantial (and unequal) corrections beyond CCSD(T).¹⁵⁷ Accordingly, a new PES was constructed in Ref. 3 using the CCSD(T)/CBS+ $\delta_{T+(Q)}/aDZ$ level of theory, with an estimated accuracy within 0.5 cm⁻¹ around the van der Waals minimum. This platinum-standard PES led to an impressive agreement with the experimental high-resolution *ortho*-H₂-CO spectrum, with the discrepancies in infrared transition energies not exceeding 0.06 cm⁻¹, so that a complete assignment of the spectral lines was finally possible. The same PES was also highly successful in the reproduction of experimental microwave spectra,¹⁵⁸ scattering cross sections,¹⁵⁹ and second virial coefficients.¹⁶⁰ More recently, a similar inclusion of the $\delta_{T+(Q)}/aDZ$ interaction energy term significantly improved the He-HCN potential,¹⁶¹ reducing the deviations of rovibrational energy levels from experimental values¹⁶² by a factor of five.

In some cases, the calculation of a PES at a level of theory higher than CCSD(T) is not feasible, but high-resolution experimental data indicate that the accuracy of the CCSD(T)/CBS treatment might not be sufficient. A prime example is the combined experimental-theoretical study of low-energy resonances in the H₂-NO interaction.¹⁶³ Two CCSD(T)-level NO-H₂ potentials are available,^{164,165} differing in the details of how the CBS limit has been established. The experimental integral cross sections at near-resonance collision energies¹⁶³ were sufficiently precise to favor the CCSD(T)-F12a/aTZ+(3s3p2d2f1g1h) potential of Ref. 165 over the conventional CCSD(T) potential extrapolated from the (aTZ,aQZ) bases.¹⁶⁴

However, as stated in Ref. 163, this does not mean that the former CCSD(T)/CBS estimate is more accurate than the latter: quite likely, the opposite is true. However, the slight deviation of the Ref. 165 potential from the CBS values of Ref. 164 might be compensating for the lack of interaction energy terms beyond CCSD(T). Thus, it would be worthwhile to construct a CCSDT(Q)-level H₂-NO PES to resolve the remaining differences. This is, however, a very formidable task, due in no small part to the open-shell, orbitally degenerate character of NO and the necessity to compute two PESs for the two diabatic states of the complex.

A careful reader has noticed by now that all many-electron examples presented so far involve a molecule with a triple bond (CO, HCN, NO). This is not a coincidence. Interactions of triply bonded molecules are notoriously difficult to describe with low levels of electron correlation. A simple (and crude) justification of this behavior is the importance of $\pi \rightarrow \pi^*$ excitations for the electronic structure of the interacting molecule: for a triple bond, a full description of the $\pi \rightarrow \pi^*$ states requires a method with quadruple excitations such as CCSDT(Q) or, preferably, full CCSDTQ. Therefore, complexes involving triply bonded monomers typically come out as the worst offenders in database-level benchmarks of coupled-cluster interaction energies: notable examples are the HF-HCN and H₂O-CN⁻ systems among 16 hydrogen-bonded complexes investigated by Boese¹⁶⁶ and the two N₂-N₂ structures among the 21 complexes examined in Ref. 137. Interactions involving triply bonded molecules require extra care at all stages of the calculation: not only the $\delta_T = \text{CCSDT} - \text{CCSD(T)}$ and $\delta_{(Q)} = \text{CCSDT(Q)} - \text{CCSDT}$ differences constitute up to several percent of interaction energy each but even the $\delta_Q = \text{CCSDTQ} - \text{CCSDT(Q)}$ contribution might alter the final result by another percent or so.¹³⁷ Moreover, the pioneering CCSDT(Q) investigations on the P₂-P₂ and PCCP-PCCP complexes¹⁶⁷ suggest that the importance of post-CCSD(T) corrections does not diminish as heavier atoms are present.

The complexes of two triply bonded molecules present quite a range of different behaviors of the post-CCSD(T) corrections. For the N₂-N₂ system, the CCSDT-CCSD(T) and CCSDT(Q)-CCSDT effects are substantial but cancel each other to a large extent. At the near van der Waals minimum geometry, the CCSD(T)/CBS interaction energy amounts to -108.2 cm⁻¹, while the δ_T/aQZ , $\delta_{(Q)}/aTZ$, and δ_Q/aDZ corrections are 3.7, -5.3, and 1.3 cm⁻¹, respectively. This cancellation of higher-order effects appears to hold throughout the entire N₂-N₂ PES: a highly accurate, CCSD(T)/CBS+ $\delta_{T+(Q)}/aDZ$ potential (including also core correlation and relativistic effects) was constructed by Hellmann¹⁶⁸ and it successfully reproduced the best experimental data for virial coefficients, viscosity, and thermal conductivity of a dilute nitrogen gas. Hellmann observed that his $\delta_{T+(Q)}$ correction for different angular configurations was similar in magnitude, but opposite in sign, to the correction for full triples only, illustrating the (partial but consistent) cancellation. Hellmann also found that his recovery of experimental second virial coefficient data was improved when the $\delta_{T+(Q)}$ contribution was scaled by a factor of 0.5. This scaling likely implicitly accounts for both the basis set incompleteness effects of the $\delta_{T+(Q)}/aDZ$ value and the contribution from full quadruple excitations.

For a long time, the isoelectronic CO-N₂ complex was computationally investigated only at lower levels of accuracy. However, in 2018, three CCSD(T)/CBS level surfaces for this system were

published.^{169–171} The precise theory level for the *ab initio* grid points ranged from CCSD(T)-F12b/aQZ¹⁶⁹ to CCSD(T)/aQZ+(3s2p1d)¹⁷⁰ to CCSD(T)/aQZ+(3s3p2d1f1g).¹⁷¹ These small differences in the CCSD(T)/CBS estimates resulted in differences of below 0.01 bohr for the minimum intermolecular separation, up to 7° in the angles of CO and N₂ with respect to the center-of-mass axis and up to 0.8 cm⁻¹ (out of about 118 cm⁻¹) in the minimum interaction energies. The potential of Ref. 171, a tiny bit deeper than the other two, was observed to provide the best agreement with the experimental rovibrational level data, suggesting that a properly selected “gold-standard” estimate might be adequate for CO–N₂. However, our calculations at the van der Waals minimum geometry indicate that δ_T/aQZ , $\delta_{(Q)}/aTZ$, and $\delta_Q/cc-pVDZ$ contribute 2.2, -3.9, and 0.6 cm⁻¹, respectively, to the interaction energy. Thus, CCSD(T) calculations require some error cancellation between basis set incompleteness effects and the higher-order terms to produce a spectroscopically accurate representation of the CO–N₂ surface.

The CO–CO complex happens to be especially difficult for low-level electronic structure methods. It was observed already in 1999 that CCSD(T) is not accurate for this system as it misses important fifth-order interaction terms.¹⁷² Nevertheless, the CCSD(T)-level potential developed by Dawes *et al.*¹⁷³ was successful at accurately reproducing experimental rovibrational levels¹⁷³ as well as rotationally inelastic cross sections.¹⁷⁴ However, the success of this potential is a consequence of picking a specific, reasonably accurate but not converged, CCSD(T)/CBS estimate so that the basis set incompleteness errors partially cancel the post-CCSD(T) effects. Dawes *et al.* chose the all-electron CCSD(T)-F12b approach without the counterpoise correction extrapolated from the cc-pCVXZ-F12 \equiv CVXZ-F12¹⁷⁵ basis set family with $X = D, T, Q$. The different CO–CO minima are connected by a pathway with very minimal barriers so that even the lowest rovibrational states of this complex extend over all of them. Thus, the precise landscape of the minimum-energy pathway, in particular, the difference between the minimum depths, has a large influence on the computed spectroscopic data.

The dependence of the CO–CO interaction energy along the minimum-energy pathway on the theory level is presented in Fig. 2 [the calculations in this figure used a slightly different C–O bond length (2.137 bohrs) than Ref. 173 (2.132 bohrs)]. In addition to the CCSD(T)-F12b/CVXZ-F12 levels employed in Ref. 173, $X = D, T, Q$, we present our best estimate of the all-electron CCSD(T)/CBS limit, computed by combining the frozen-core CCSD(T^{**})-F12b/(aQZ,a5Z) value with the CCSD(T)/aug-cc-pCV5Z correction for the core-core and core-valence correlation. Note that the standard X^{-3} extrapolation used above, while not exactly optimal for explicitly correlated calculations,¹⁷⁶ is certainly better than no extrapolation at all (and it was employed for some variants of the PES in Ref. 173). Furthermore, we add the corrections for full triples (from CCSDT/aQZ) and perturbative quadruples [from CCSDT(Q)/aTZ]. The large discrepancies between different theory and basis set levels in Fig. 2 indicate the inherent difficulty of this complex: the lowest level shown, CCSD(T)-F12b/CVDZ-F12, predicts a saddle point in the global minimum location! One can see that the post-CCSD(T) effects are large and drastically alter the landscape of the minimum-energy pathway. While the $\delta_{(Q)}$ term is fairly constant, deepening the surface by 2.1–3.4 cm⁻¹, the δ_T

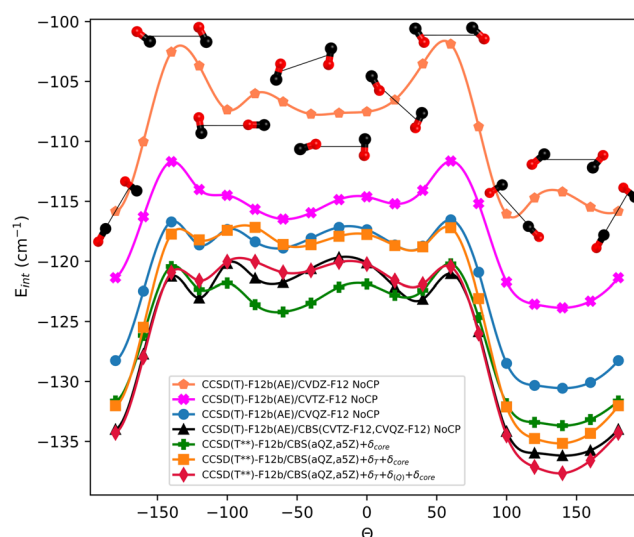


FIG. 2. CO–CO interaction energies along the pathway passing through the global and local minima of the complex, computed at various levels of theory. The angle Θ is the angle of one of the CO molecules with respect to the line joining the centers of masses; all other intermolecular degrees of freedom are optimized [at the counterpoise-corrected CCSD(T)-F12b/aTZ level] for each Θ to stay on the minimum energy pathway. All results have been computed in the present work. The results marked in black are similar (but not identical) to the data points of the best-performing PES of Ref. 173—our calculations use a slightly different C–O bond length and a different CBS extrapolation scheme.

contribution is quite erratic, ranging all the way from -1.9 to 6.4 cm⁻¹. Thus, the two leading post-CCSD(T) effects can both amplify each other (like in the global minimum) or partially cancel out (like in the local minima). This behavior is illustrated in Fig. 3 which presents the differences between lower levels of theory and our benchmark CCSDT(Q)-level interaction energies. The (very computationally demanding) full CCSDTQ/aDZ calculations were performed for two high-symmetry minima, and even the δ_Q correction turned out to be nonnegligible, amounting to -0.7 cm⁻¹ for the global minimum and 0.6 cm⁻¹ for the local one [thus, even the platinum standard CCSDT(Q)/CBS approach underestimates the difference between the two minima by more than 1 cm⁻¹]. Figure 3 shows that the CCSD(T)/CBS gold standard description of the CO–CO potential valley, enhanced only by the core correlation, is highly inaccurate. However, the level of theory selected in Ref. 173 is consistently close to our CCSDT(Q)-level results thanks to an error cancellation between the basis set incompleteness effects at the CCSD(T) level and the contribution from higher-order coupled-cluster excitations. Thus, the potential of Ref. 173 owes its very good performance to a clever selection of a CCSD(T)/CBS estimate that facilitates this error cancellation. The large discrepancies shown in Figs. 2 and 3 are clearly not typical and result from a particularly unfortunate combination of a large magnitude of the post-CCSD(T) terms and their variations in sign. We present this worst-case scenario to serve as a cautionary tale against automatically neglecting the interaction energy contributions beyond the gold standard.

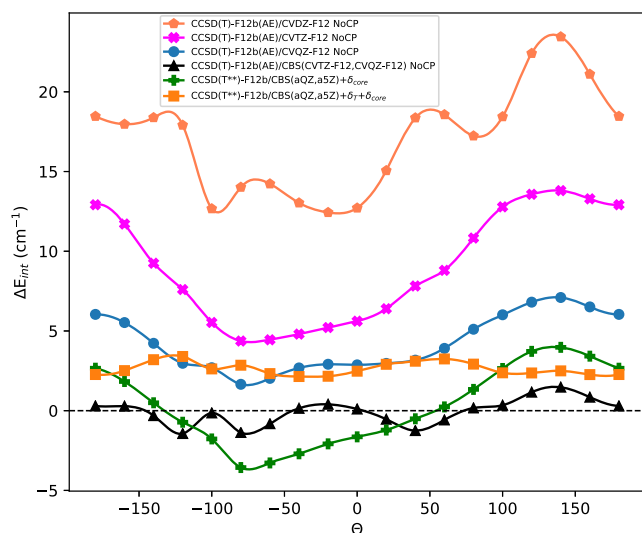


FIG. 3. Differences between lower levels of theory and our best platinum-standard CCSD(T)/CBS-level estimate (the red diamonds in Fig. 2) for the CO–CO minimum interaction energy pathway depicted in Fig. 2.

V. THE SILVER STANDARD—WHEN CCSD(T)/ATZ IS NOT AN OPTION

A. Approximations to the gold standard

We have postulated in Sec. III that the gold-standard precision in the determination of the CCSD(T)/CBS limit requires, one way or another, a CCSD(T) calculation in a basis set of triple-zeta quality and size. When such a calculation is available, a suitable CCSD(T)/CBS estimate can be generated in several ways including the explicitly correlated approach [for example, CCSD(T^{**})-F12b/aTZ], the composite treatment [for example, MP2/(aQZ,a5Z)+ δ [CCSD(T)]/aTZ], or a combination of both. It should be noted, however, that a CBS extrapolation involving a double- and triple-zeta basis set {for example, CCSD(T)/(aDZ,aTZ) or MP2/(aQZ,a5Z)+ δ [CCSD(T)]/(aDZ,aTZ)} is typically inferior to plain aTZ as the information from the small aDZ basis set does more harm than good.⁸⁴

Unfortunately, for a large class of medium-sized systems, CCSD(T)/aDZ is feasible but CCSD(T)/aTZ is not. In such a case, the precision attained by a CBS limit estimate involving only aDZ-level CCSD(T) [or CCSD(T)-F12] calculations might not be up to the gold-standard requirements. Nevertheless, it is highly useful to establish a level of theory and basis set that can be termed “silver standard,” that is, it is feasible when CCSD(T)/aDZ is feasible, reasonably accurate, and free from particularly bad outliers as long as the underlying complexes are entirely single reference. A silver-standard benchmark calculation is accurate enough for many practical purposes, including the refinement of more approximate methods based on DFT, semiempirical approaches, or machine learning. Therefore, there is a large market for accurate silver-standard benchmark interaction energies and it is worthwhile to examine the best options to utilize CCSD(T)/aDZ-level results in the determination of benchmark values.

The selection of approximate electronic structure methods that do the best job at recovering gold-standard interaction energy benchmarks was thoroughly studied by Burns *et al.*³⁵ In this work, which should be credited for coining the terms “silver standard” and “bronze standard,” the benchmark level of theory was chosen as MP2/(aTZ,aQZ)+ δ [CCSD(T)]/aTZ. Relative to this realization of the gold standard, 394 different combinations of theory level and basis set were tested on a dataset of 345 weak interaction energies. Among the methods that require some aDZ-level CCSD(T) calculation, the best performer (the “silver standard”) was found to be the DW-CCSD(T^{**})-F12/aDZ dispersion-weighted approach.⁵³ The silver-standard interaction energies deviated by an average of 0.05 kcal/mol from the gold-standard values, indicating a very acceptable and consistent accuracy. Burns *et al.*³⁵ went on to propose also a “bronze standard” MP2C-F12/aDZ model chemistry, based on the “coupled MP2” (MP2C) approach of Hesselmann,¹⁷⁷ that leads to an average error of 0.16 kcal/mol and is significantly cheaper than even a double-zeta CCSD(T) calculation. One should note, however, that the 0.16 kcal/mol accuracy is only marginally better than the one afforded (on similar weakly interacting systems) by the most modern variants of density functional theory.³⁷ Therefore, the bronze standard may not be accurate enough for an important class of applications, the benchmarking and refinement of DFT-based approaches to weak interactions, and we will focus exclusively on the silver standard from now on.

B. Double-zeta CCSD(T) interaction energies

As we have already stated in Sec. II, a “double zeta-level CCSD(T) interaction energy” might mean many different things. Therefore, a thorough assessment of the performance of different possible variants is worthwhile. A careful study of the influence of the F12 variant and basis set on the quality of the CCSD(T)-F12 interaction energies was published by Sirianni *et al.*⁶⁹ The authors examined in detail the A24⁶⁷ and S22³⁰ noncovalent databases and compared the performance of different CCSD(T)-F12 approximations as well as of the aXZ and cc-pVXZ-F12 basis set families. Probably the most interesting finding of Ref. 69 was the clearly inferior performance of the cc-pVXZ-F12 sequence compared to the standard aXZ one (the same phenomenon was observed earlier for a much smaller class of systems^{127,128}). The underperformance of CCSD(T)-F12/cc-pVXZ-F12 interaction energies might be somewhat surprising—contrary to what the basis set name suggests, for atoms other than H and He, the cc-pVXZ-F12 set has more functions than the aXZ one at the same X. It has been argued⁶⁹ that the high-angular-momentum exponents of the cc-pVXZ-F12 sets, optimized for molecular correlation energies, are not diffuse enough for noncovalent interaction energy computations. Our criticism of the cc-pVXZ-F12 basis sets in the context of interaction energy calculations is not meant to discredit a series of recent benchmark interaction energy reevaluations^{54,89–91} for the S66x8,³¹ WATER27,⁸⁸ and X40x10¹⁷⁸ databases using a combination of MP2-F12/CBS and the CCSD–MP2 and CCSD(T)–CCSD corrections calculated using either the F12 approach with cc-pVXZ-F12 basis sets or the conventional approach with heavy-augmented cc-pVXZ bases. The benchmark interaction energies computed in this way are clearly superior to the original estimates due to the sheer power of the F12 approach and a careful selection of the CCSD-F12 variant, the (T) estimate,

and the treatment of the counterpoise correction. However, it is quite likely that similarly accurate (or better) CCSD(T)/CBS estimates could have been obtained at a reduced computational cost should the authors of Refs. 54 and 89–91 have chosen the standard aXZ basis set family instead of the cc-pVXZ-F12 one.

As far as the aXZ basis sets are concerned, Sirianni *et al.*⁶⁹ found that the CCSD(T^{**})-F12b and CCSD(F12^{*})(T^{**}) variants exhibited very similar (and impressive) performance on both the A24 and S22 databases. The performance of CCSD(T^{**})-F12a is more erratic—it happens to be the best aDZ-level variant for A24 but the worst one for S22. For the latter dataset, the highest aDZ-level accuracy was attained by the DW-CCSD(T^{**})-F12 combination.⁵³ As DW-CCSD(T^{**})-F12/aDZ performed also respectably well on the A24 dataset, its designation as the silver standard³⁵ was confirmed in Ref. 69. Overall, the combination of the F12 approach, aXZ basis sets, and the counterpoise correction emerged as the best strategy to converge to the CBS limit, especially at the silver-standard level requiring only double-zeta coupled-cluster calculations.

C. The role of midbond functions

The authors of Ref. 69 did not consider one more technique that has proven successful in accurately recovering weak interaction energies—the addition of midbond functions. Such functions increase the basis set size only slightly as one additional basis function center is added to all the atomic centers in the complex (one may note in passing that the placement of more than one midbond center, or even the determination whether more than one center is needed, has not been investigated so far, but some initial tests have been carried out for a “cloud” of off-center Gaussians surrounding the complex^{179,180}). As a result, for molecules of the size targeted by the silver standard, an aDZ+(bond) calculation is significantly cheaper than an aTZ one. The use of midbond functions has initially been popularized by Tao,^{181,182} who designed standard midbond sets such as (3s3p2d) and established, through tests on very simple complexes, that neither the precise location of the midbond center nor the precise midbond exponents have a significant influence on the accuracy of the resulting interaction energies. Thus, present-day calculations involving midbond functions typically use either one of the standard midbond sets (independent of the atom-centered basis set) or a hydrogenic aXZ basis with the cardinal number X that varies together with the cardinal number of the atom-centered set. The latter choice somewhat simplifies calculations that require density-fitting and/or resolution-of-identity basis sets [such as MP2-F12 and CCSD(T)-F12] as the required auxiliary bases are readily available for aXZ. In contrast, for standard midbond sets, only one auxiliary basis has been constructed and tested.¹⁸³ While the use of bond functions requires a dimer basis set in all calculations (in other words, the counterpoise correction must be included), there is nothing wrong with combining midbond functions with CBS extrapolation¹⁸⁴ and/or the F12 approach.¹²⁷ Thus, it is worthwhile to check if the inclusion of bond functions in aDZ-level CCSD(T) and/or CCSD(T)-F12 calculations can lead to an improved silver standard of interaction energy. A recent study from our group⁷⁰ has shown that the answer is yes.

In order to build directly on the findings of Ref. 69, Ref. 70 examined the same A24⁶⁷ and S22³⁰ databases. The performance of CCSD(T), CCSD(T)-F12a, and CCSD(T)-F12b (with or without the scaling of triples) has been compared between midbond-less aXZ bases and the same atom-centered aXZ sets augmented by a constant [(3s3p2d) and (3s3p2d2f)] or variable (hydrogenic aXZ) set of functions centered on the intermolecular bond. The one-step CCSD(T) approaches were compared to the composite MP2/CBS+ δ [CCSD(T)] ones, and the partially augmented basis sets (from the “calendar” family: jul-cc-pVXZ, jun-cc-pVXZ, ...⁴²) were investigated together with the fully augmented aXZ ones. As far as the F12 variant is concerned, an interesting observation was made that confirmed earlier findings for a more limited class of systems:^{80,185} the CCSD-F12a variant, which is more approximate (contains fewer diagrams) than CCSD-F12b,^{49,50} performs best when combined with unscaled triples (which can be viewed as more approximate than scaled triples—even if the scaling is imperfect, it is almost certainly better than no scaling at all). An exception to this observation are the data in the smallest aDZ basis when CCSD(T^{**})-F12a accidentally happens to be the best one. The CCSD-F12b variant, in turn, performs best when a scaled (T^{**}) contribution is added to it. This suggests that while the CCSD(T^{**})-F12b [or CCSD(F12^{*})(T^{**})] combination provides “the right answer for the right reason,” the CCSD(T)-F12a approach benefits from an (accidental but quite systematic) error cancellation between the CCSD part and the triples part. By comparing against separate CCSD/CBS and (T)/CBS benchmarks for the A24 database, the authors of Ref. 70 showed that this is indeed the case, especially for larger basis sets and when the milder, CCSD-based scaling⁵⁴ is used for the triples contribution instead of the MP2-based one.

The addition of midbond functions improved the accuracy of all variants considered in Ref. 70 except for CCSD(T^{**})-F12a. In the case of conventional CCSD(T) and of CCSD(T)-F12b with unscaled and CCSD-scaled triples, the improvement increased systematically as the midbond basis set was enlarged, while for CCSD(T)-F12a and CCSD(T^{**})-F12b, the ordering of results with different midbonds was more erratic. It was observed that the combination of midbond functions and CCSD(T)-F12b with CCSD-scaled triples was the least reliant on error cancellation between the CCSD part and the triples part and thus likely to provide the most consistent performance for systems outside of the investigated databases. Moreover, the combination of midbond functions and the composite MP2/CBS+ δ [CCSD(T)] treatment is still capable of providing accurate results when some or all diffuse functions are removed from the atom-centered part of the basis set. In fact, the cheapest variant that delivered an average accuracy within 0.1 kcal/mol for both databases was MP2/CBS+ δ [CCSD(T)]/cc-pVDZ+(3s3p2d2f), where the only diffuse functions present were those centered on the midbond. The switch from δ [CCSD(T)] to a suitably chosen variant of δ [CCSD(T)-F12] decreased the errors further, and considering both the accuracy and the computational cost, the authors of Ref. 70 went ahead to propose three new silver standards. The aforementioned MP2/CBS+ δ [CCSD(T)]/cc-pVDZ+(3s3p2d2f) level was designated the “silver-minus” one as it is significantly cheaper than the established DW-CCSD(T^{**})-F12/aDZ silver standard³⁵ but only slightly less accurate. The newly designated “silver” level, MP2/CBS+ δ [CCSD(T)-F12a]/jun-cc-pVDZ+(3s3p2d2f), is both a

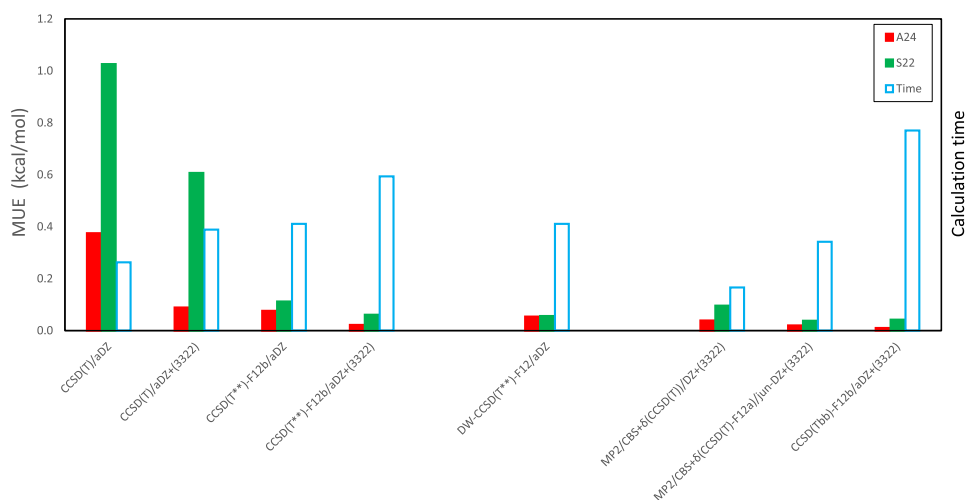


FIG. 4. The accuracy (MUE values on the A24 and S22 databases) and computational efficiency (relative timings for the parallel-displaced benzene dimer) of different CCSD(T)/CBS approximations that require only double-zeta coupled-cluster calculations. The original silver standard of Ref. 35 and the new “silver-minus,” “silver,” and “silver-plus” standards introduced in Ref. 70 are included. (3322) is a shorthand notation for the (3s3p2d2f) set of midbond functions. Reprinted with permission from Dutta and Patkowski, *J. Chem. Theory Comput.* **14**, 3053–3070 (2018). Copyright 2018 American Chemical Society.

little more accurate and a little more efficient than the silver standard of Ref. 35. Finally, the “silver-plus” level, CCSD(Tbb)-F12b/aDZ + (3s3p2d2f), where (Tbb) denotes the CCSD-F12b-based scaling of triples,⁵⁴ is somewhat more expensive than the original silver standard but provides much higher accuracy. The performance of different silver-standard variants considered in Ref. 70 is summarized in Fig. 4.

In Ref. 70, substantial improvement to the double-zeta-level CCSD(T)/CBS estimates was achieved with standard, off-the-shelf sets of midbond functions. It remains to be seen whether additional gains in the accuracy can be attained by optimizing the exponents of midbond functions and/or their precise placement in the interaction region. As the original work of Tao¹⁸² suggested this is not the case, little effort has been made in the literature to design improved midbond sets. However, a recent work by Shaw and Hill¹⁸⁶ has challenged this paradigm. These authors optimized compact sets of bond functions at the MP2 and CCSD(T) levels for several noble gas dimers, alkali metal dimers, and small molecular complexes investigated in Ref. 128. Shaw and Hill concluded that while the commonly used intermolecular midpoints were close to the optimal location for the midbond center, the dependence of the interaction energy on the midbond exponents was quite considerable, and the optimization made their compact midbond sets highly competitive with larger unoptimized sets (on the negative side, the optimized exponents did not appear to be transferable between different systems). The findings of Ref. 186 suggest that there is still room for improvement of the silver standard by choosing carefully optimized midbond sets instead of the unoptimized ones. We expect this direction of research to be pursued in the near future, together with an extension of the silver-standard performance studies to larger and more diverse databases including off-minimum intermolecular separations.

VI. CONCLUDING REMARKS

We have presented the current state of the art in the calculations of accurate interaction energies in small- and medium-sized

complexes. This state of the art is quite impressive—there exists an established gold standard that is typically accurate to several hundredths of a kcal/mol and capable of producing PESs that reproduce experimental observables for all but the highest-resolution spectroscopic and scattering measurements. Moreover, this gold standard can be either further improved if even higher accuracy is required or relaxed to provide interaction energies of near-gold-standard accuracy at a significantly reduced computational cost. Thus, the gold standard, realized in practice by MP2/(aTZ,aQZ)+ δ [CCSD(T)]/aTZ or a similar calculation, is supported by the higher-accuracy platinum standard, composed of an accurate frozen-core CCSD(T)/CBS estimate plus corrections for higher-level coupled-cluster excitations through CCSDT(Q), the correlation of core electrons, and relativistic effects. On the other side, the gold standard is accompanied by the silver one, with average interaction energy errors still well below 0.1 kcal/mol attained using only a double-zeta CCSD(T) calculation. The accuracy of CCSD(T)/aDZ is strongly improved by the explicitly correlated CCSD(T)-F12 approach, the composite MP2/CBS+ δ [CCSD(T)] treatment, the addition of midbond functions, or, preferably, by a combination of at least two of these enhancements.^{69,70} Thus, at this point, we have a very clear understanding of how to attain a given level of accuracy for a small closed-shell complex, and given the recent advances in the automatic generation of the entire PES,^{14,15} the development of new gold-standard-level potentials for complexes of experimental interest is now close to routine. Moreover, with significant computational effort required to compute CCSDT(Q) interaction energies, one can produce an even more accurate platinum-standard PES that is capable of resolving the intricacies of complicated spectra and locating resonances in elastic and inelastic cross sections.

Impressive progress has also been made in the construction of gold- and silver-standard benchmark noncovalent databases, both in terms of the accuracy of the individual data points and the breadth and diversity of the entire dataset. As a result, the newest composite databases involve at least 10^3 CCSD(T) interaction energies: in one case,⁸⁵ the number of data points is over 10^5 ! This increase in

the amount of available high-accuracy data is particularly helpful for developing machine-learning approaches which are notoriously data-intensive. Interestingly, while nearly all gold-standard PESs for individual complexes have been obtained in bases with midbond functions (cf. Sec. III), very few numbers included in noncovalent databases have been computed with midbonds. There is no good algorithmic reason for this: it is likely that the awareness of the benefits of midbonds in the benchmarking community is lower than in the PES community. One relatively unexplored issue of adding midbond functions is the dependence of the accuracy improvement on the size of the complex: it is quite intuitive that the addition of a single midbond center will provide more benefit for an atom-atom complex, where the midbond constitutes 1/3 of the basis function centers, than, say, for a coronene dimer where the midbond is just 1 out of 73 centers. For a stacked structure of the latter system, it is likely that more than one midbond center is required for a good coverage of the large contact area between the molecules. However, the best practices of placing multiple midbond centers, or even deciding whether more than one center is needed, are yet to be explored.

Contrary to the situation for closed-shell systems, the existing benchmark data for open-shell noncovalent complexes are quite scarce. A few small datasets for interactions involving radicals have been constructed using high-level calculations,^{187–189} but each set is composed of fairly similar systems and none of them contain off-minimum configurations. Thus, substantial progress is required to assess the accuracy of approximate approaches for open-shell interactions on an equal footing with the closed-shell ones, and we expect new extended open-shell databases to appear in the near future. Another direction of current and future progress is the extension of benchmark datasets beyond just interaction energies. Indeed, there already exist pilot benchmark studies of noncovalent geometries,^{72,73} and a recent database of CCSD(T)-level dipole moments¹⁹⁰ includes some noncovalent complexes in addition to single molecules. However, more variety in the benchmark data for each of these kinds would be desirable as would a benchmark dataset of harmonic vibrational frequencies in some noncovalent complexes. Actually, there is some evidence that these frequencies are even more sensitive to the theory level than interaction energies: some MP2 normal modes for water clusters are very far off the benchmark CCSD(T) values.¹⁹¹ Finally, several current applications including the construction of first-principles-based force fields^{192,193} and physics-based machine learning of noncovalent interaction energies¹⁹⁴ strongly benefit from an accurate physical energy decomposition, that is, a partitioning of the overall interaction energy into well-defined terms of different physical origins. Such a partitioning can be provided by SAPT,¹⁶ and in recent years, the accuracy of different-level SAPT decompositions has been thoroughly tested,¹⁹⁵ including the generation of a small set of benchmark SAPT data for the highest-accuracy, coupled-cluster treatment of intramolecular electron correlation.¹⁹⁶

Perhaps the most pressing issue in the accurate calculations of noncovalent interaction energies is an extension of the benchmark methodology to larger systems. This specific issue has been the subject of a recent perspective by Al-Hamdani and Tkatchenko;¹⁹⁷ here, we will just mention a few obstacles that lie ahead. There currently exist two small benchmark datasets of large intermolecular complexes: L7¹⁹⁸ and S12L.^{199,200} The reference energies for the S12L

set were obtained by (approximately) back-correcting experimental association free energies for effects such as harmonic zero-point energy, entropy, and solvent influence. The L7 reference interaction energies were computed *ab initio*, using MP2/CBS plus a correction for higher-level correlation obtained from the quadratic configuration interaction method with singles, doubles, and perturbative triples [QCISD(T)] in a very small 6-31G*(0.25) basis set. Thus, both reference data are not fully up to even the silver standard discussed in Sec. V. Several other high-level calculations have been performed for partial or whole L7 and S12L datasets,^{21,201,202} including domain-based local pair natural orbital CCSD(T) [DLPNO-CCSD(T)]²⁰³ and diffusion Monte Carlo (DMC).²⁰⁴ However, those high-level results differ from the original reference energies and from each other by several kcal/mol,¹⁹⁷ indicating that the accuracy with which the L7 and S12L interaction energies are known is significantly inferior to the precious metals standards discussed in this perspective. The challenges facing such accurate calculations are not limited to the computational cost: one has to also minimize the residual errors of the local CCSD(T) approximation (or, alternatively, the fixed-node errors in DMC), and for some important classes of complexes (for example, those involving large polycyclic aromatic hydrocarbons), even full CCSD(T) might be inaccurate due to the emerging multireference character. Thus, the accurate *ab initio* treatment of larger complexes still leaves a lot to be desired, and we expect continuous improvement of large benchmarks in the near future.

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