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Article

Accurate Prediction of Vertical Ionization Potentials and Electron Affinities from Spin-Component Scaled CC2 and ADC(2) Models

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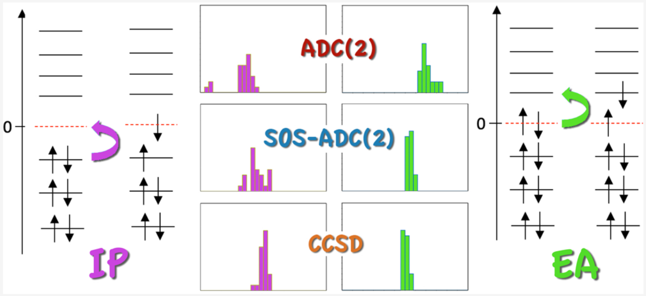
ABSTRACT: The CC2 and ADC(2) wave function models and their spin-component scaled modifications are adopted for predicting vertical ionization potentials (VIPs) and electron affinities (VEAs). The ionic solutions are obtained as electronic excitations in the continuum orbital formalism, making possible the use of existing, widespread quantum chemistry codes with minimal modifications, in full consistency with the treatment of charge transfer excitations. The performance of different variants is evaluated via benchmark calculations on various sets from previous works, containing small- and medium-sized systems, including the nucleobases. It is shown that with the spin-scaled approximate methods, in particular the scaled opposite-spin variant of the ADC(2) method, the accuracy of EOM-CCSD is achievable at a fraction of the computational cost, also outperforming many common electron propagator approaches.



■ INTRODUCTION

Ionized and electron attached states of molecular systems play a key role in many different areas of chemistry. The difficulties associated with the distinctive electronic structure of these states make their reliable modeling a real challenge for many theoretical methods. There is a very large variety of techniques available for the prediction of energy changes associated with electron attachment or detachment processes, with different accuracy and computational costs. Most of these methods have dedicated implementations for ionization potentials (IPs) and electron affinities (EAs) in the most popular quantum chemistry program suites, but many either lack a corresponding theory for electronically excited states or their reliability considerably differs for ionic and neutral systems. There is a high demand for universally applicable models with good accuracy and favorable computational scaling, but these criteria are often contradictory.

Over the past few years, we identified[1−3] that the rather large errors of the CC2 and ADC(2) models observed in many situations related to electronically excited states are considerably reduced if their spin-component scaled modifications are used. The consistency of this improvement over the wide range of problems (Rydberg states, potential energy surfaces, charge transfer (CT) states, etc.) is an indication that these methods may offer a general reliability, while their low computational cost makes them applicable to larger systems. This is especially important for CT states which, due to the fact that the source and destination domains are separate spacial regions, normally show up in large molecules where the high-level treatment of electron correlation is no longer possible. As the accurate treatment of CT states is critical for modeling electron transport phenomena, effective approximate models are warranted. Since these states are formed by a simultaneous local ionization and electron attachment, such methods should provide a consistent, high accuracy for ionized and electron attached states, in particular, predict accurate vertical ionization potentials (VIPs) and electron affinities (VEAs). Moreover, a method appropriate for CT states should either possess a rigorous charge transfer separability (CTS) property[4−7] or have a satisfyingly low CTS error.[3,8] In this study, we use the CC2 and ADC(2) methods and the spin-component scaled variants of the latter for the calculation of VIPs and VEAs. By measuring their accuracy on several benchmark sets available in the literature, we discuss the accuracy of consistency of these models in the handling of ionic states. We achieve this by invoking the very effective *continuum orbital formalism*[9−11] which allows the direct application of these excited state models to ionized and electron attached ones.

A popular family of methods to calculate VIPs and VEAs are the cost-effective electron propagator approaches[12−15] that are based on some approximation of the self-energy matrix.[12,15,16] The inclusion or negligence of the off-diagonal elements, combined with various perturbational considerations, results in

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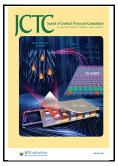

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a wide range of computational models,[15,16] among which the partial third-order quasiparticle approximations P3[17] and P3+,[18,19] as well as their off-diagonal, renormalized extension NR2[19,20] by Ortiz and co-workers, were found to offer outstanding performance in previous studies,[15,16,21,22] reportedly being the best compromises of accuracy and efficiency among these electron propagator approaches. We use these variants in the present work as a comparison for evaluating the accuracy of CC2 and ADC(2)-based models.

Problems with electron propagator approaches can arise from their sometimes complicated concept and limited availability, as well as the possible lack of an excited state wave function model directly corresponding to their formulation of VIPs and VEAs. From the viewpoint of a method's general applicability, the widely adopted excited state theories modified to predict ionic states, such as the popular EOMIP[23−26] and EOMEA[27,28] formalisms of Coupled-Cluster (CC) theory, are more appealing. Although several efficient implementations of the EOMIP-CC theory have been made available recently[29−31] that can handle large systems and higher ionizations using special algorithms, the adoption of common approximate excited state CC models in this area offers various advantages. These alterations, as it will be evident from the following section, do not necessarily require a separate formalism and program code for the ionic systems.

■ METHODS

Spin-Component Scaled Models for Ionic States. The concept of spin-component scaling (SCS) was originally proposed by Grimme[32,33] as the introduction of different scaling factors C_{SS} and C_{OS} for the same-spin and opposite-spin integrals, respectively, in the MP2 energy expression. This rather pragmatic adjustment was later justified by the arguments of Szabados,[34] relating the recommended and most commonly adopted parameters ($C_{SS} = 1/3$ and $C_{OS} = 6/5$) to Feenberg's minimal condition. We refer to this choice of the parameters with the SCS notation hereafter. The so-called scaled opposite-spin (SOS) parametrization[35] corresponds to a complete abandonment of the same-spin components, compensated by the upscaling of the opposite-spin part by a factor of $C_{OS} = 1.3$. Hättig and co-workers[36,37] created effective implementations for spin-component scaled modifications of the CC2 and the closely related Algebraic Diagrammatic Construction Second Order ADC(2)[38,39] models, today available in the Turbomole[40] program system, but several other packages[41−43] offer the functionality of spin-component scaling as an easily activatable feature, as well. From the practical standpoint, the SOS methods are especially important since implementations with a computational scaling of no more than the fourth power of the system size are possible,[44−47] making them powerful competitors of the commonly used DFT-based approaches in calculations on larger systems.

Invoking spin-component scaling to improve the accuracy of calculated ionization potentials has been proposed by several studies.[48−53] Romero and co-workers[48] evaluated the scaled modifications of the EP2 electron propagator method for ionization potentials, showing that the average error of the IPs, as compared to experiment and higher level methods, can be reduced by up to 51% with this adjustment. Later, Lim et al.[49] engaged in optimizing the C_{SS} and C_{OS} scaling factors specifically for ionized states by fitting to a set of experimental vertical IPs of a set of small molecules. With the values 0.5 and 0.7, respectively, the mean absolute error (MAE) of the original EP2 model was reduced by 53%, approaching that of the higher level P3 method to 0.011 eV.

The study of Śmiga and Grabowski[52] revealed the outstanding achievable accuracy with the spin-component scaled modifications of the ΔMP2 method, a cost-effective frequency-independent diagonal electron propagator approach offering an accuracy similar to EP2 in its original form. With the standard parameters, the MAE relative to high-level Δ-CCSD(T) data could be reduced from 0.63 eV of the parent method to 0.37 and 0.27 eV for the SCS and SOS variants, respectively. By specifically optimizing the parameters to reduce these errors in a training set, an MAE around 0.1 eV could be achieved, with a Mean Signed Error (MSE) in the 0.01 eV range. Recently, the authors reported a more extensive benchmark[53] using this latter set of scaling parameters for VIPs of various larger systems, using either experimental or EOMIP-CCSD data as reference, confirming that a mean accuracy around 0.1 eV can be expected for VIPs in the complete basis set (CBS) limit.

To our knowledge, no study investigated the benefits of spin-component scaling in the prediction of electron affinities with electron propagator techniques so far. Nevertheless, knowing the conceptual differences of the two quantities originating from the fact that the latter is associated with the energy of virtual orbitals, not occupied ones, it is doubtful that the scaling parameters tuned for accurate VIPs could be equally optimal for electron affinities. Our principal objective being the identification of universal methods, i.e., those offering a similar performance for both VIPs and VEAs as well as, for example, CT excited states, we prefer to refrain from the optimization or fitting of the SCS parameters, sticking to the use of the commonly adopted "standard" values in our investigation. This standpoint is also supported by our previous study[1] where no pair of constants could be identified that provide a significantly better accuracy for all types of excited states than the standard ones.

Continuum Orbital Approach. The idea of formulating ionized and electron attached states as electronic excitations was first proposed by Nooijen and Bartlett,[9] followed by the work of Stanton and Gauss.[10] Despite still not being widely adopted, it was used later by others[25,55] and us[3,8,11,54] with great success. This technique adds an empty continuum orbital to the system, and the ionized states are obtained as excitations to this orbital from the occupied ones. Alternatively, the orbital can be occupied by two excess electrons, and the excited states of this artificial dianion, dominated by excitations from the continuum orbital to one of the virtual MOs, provide the electron attached states of the neutral system. The continuum orbital can be realized by adding a single, Gaussian type basis function of very low (around 10^{-18}) exponent at one of the atomic centers. This basis function will, without any overlap with others, produce a molecular orbital with a precisely zero orbital energy. Since this modification is a trivial task in most quantum chemistry codes, basically any excited state program can be adopted. It should be noted though, that the use of the continuum orbital can result in some computational overhead due to the handling of zero-sized quantities that are omitted in a regular VIP or VEA calculation. Thus, the performance of the wave function model needs to compensate for the suboptimal nature of this approach for real applications. The automatic inclusion of a continuum orbital is available as a feature in the CFOUR[56,57] and Q-Chem[58] program suites.

Table 1. Statistics on the Error (in eV) of First Vertical Ionization Potentials (VIPs) and Electron Affinities (VEAs) of 24 Acceptor Molecules, Relative to CCSD(T) References

	CCSD	CC2	ADC(2)	SCS-ADC(2)	SOS-ADC(2)	P3[a]	P3+[a]	NR2[a]	ADC(3)[a]
					Ionization Potentials				
MSE	0.008	−0.572	−0.504	−0.281	−0.168	0.168	0.059	−0.051	0.055
MAE	0.070	0.572	0.504	0.287	0.222	0.170	0.112	0.119	0.132
SD[b]	0.090	0.284	0.315	0.222	0.197	0.129	0.127	0.135	0.190
Min.[c]	0.000	0.328	0.194	0.006	0.030	0.001	0.004	0.014	0.004
Max.[c]	0.220	1.314	1.314	0.759	0.513	0.389	0.289	0.260	0.514
					Electron Affinities				
MSE	0.019	0.472	0.524	0.152	−0.036	−0.125	−0.052	0.046	−0.098
MAE	0.046	0.472	0.524	0.157	0.112	0.138	0.104	0.093	0.099
SD[b]	0.060	0.112	0.142	0.127	0.128	0.109	0.109	0.113	0.069
Min.[c]	0.003	0.312	0.371	0.003	0.007	0.001	0.017	0.003	0.002
Max.[c]	0.150	0.715	0.848	0.420	0.277	0.317	0.237	0.282	0.206

[a] Data are from ref 21. [b] Standard deviation of the signed errors. [c] Absolute values are shown.

This approach has several advantages. One is its simplicity, eliminating the need of an open-shell formalism for handling ionic states. Second, all ionized or electron attached states are described on an equal footing with respect to a common reference state, i.e., not as excited states of a singly charged ground state. In this respect, it is analogous to the EOMIP and EOMEA formalisms of coupled-cluster theory[23,27] or the self-energy methods mentioned above. If applied to a coupled-cluster reference state, the wave functions and electronic energies provided by the continuum orbital strategy are, obviously, precisely identical to the respective EOMIP-CC or EOMEA-CC solutions.[10] (For this reason, this explicit notation of the method used for obtaining a certain result will be omitted in this work, e.g., EOMIP-CCSD, EOMEA-CCSD, and EOM-CCSD are all referred to as *CCSD* hereafter.) This also illustrates the appealing nature of this formalism that the distinction between excited state, ionization energy, or electron affinity methods can be lifted, providing a formally universal wave function model.

To take practical advantage of the continuum orbital strategy, it might also be necessary to specifically target the requested ionic solutions during the calculation. This is particularly important for VIPs where the energetically favored states which are normally first obtained in the calculation will correspond to actual excitations of the system, only followed by the ionized states in a high-energy region. For implementations based on the iterative search for eigenvectors of a Jacobian, such as those of most coupled-cluster and ADC methods, this is achievable using algorithms specifically modified for this purpose, such as shifted[59] or energy-bracketing[60] eigensolvers. Alternatively, the program can be fed with custom guess vectors targeting the requested ionic solutions, and by selecting and following the roots during the iterative process by their maximum overlap with these vectors, the procedure converges to the desired states. This feature can usually be implemented with a relatively low effort in programs that do not officially support it. For the benchmark calculations presented below, this functionality was created in a development version of Turbomole for the CC2 and ADC(2) excited state models.

For certain high-level reference calculations (see below), we also used the continuum orbital approach to calculate VIPs and VEAs with the CCSD(T)(a)* method of Matthews and Stanton,[61] using the CFOUR[56] program system.

Benchmark Calculations. Benchmark calculations on several sets were executed to evaluate the accuracy of VIPs and VEAs in a statistical manner. The set of Sherrill and co-workers,[62−65] denoted *acceptor set* hereafter, consists of 24 medium-sized organic acceptor molecules, for which accurate CCSD(T) reference values were presented in ref 62 for the first vertical VIPs and VEAs. The use of large basis sets (up to aug-cc-pV5Z at the MP2 level and aug-cc-pVQZ for the additional CCSD(T) correction) allowed the estimation of complete basis set (CBS) extrapolated values and, thus, a direct comparison to experiment. The Δ-CCSD(T) computational approach limited the number of ionic states to one state in each symmetry. Using these states as the benchmark set, we calculated VIPs and VEAs with the approximate methods using the aug-cc-pVDZ basis set.

To obtain a picture of the accuracy of VIPs associated with lower lying valence orbitals, we evaluated the set studied recently by Opoku et al.[16] This benchmark is a subset of that from Bartlett and co-workers,[66] referred hereafter as the *Bartlett (Ortiz) CCSDT set*. The selection contained 170 valence ionized states of 33 closed-shell systems built from H, C, N, O, and F atoms, for which EOMIP-CCSDT reference data with the cc-pVTZ basis set was available. For a smaller set of 11 molecules, the very accurate EOMIP-CCSDTQ/cc-pVTZ results were also reported in the original study.[66] Since the differences of CCSDT and CCSDTQ data were found to be negligible in practice (a mean absolute error of 0.03 eV with a 0.02 eV standard deviation),[66] the use of EOMIP-CCSDT as reference is a reliable choice for our purposes. The inclusion of many high-energy states in this benchmark raises concerns about the quality of the EOMIP-CCSD wave function itself. It is known[66] that if the single-excitation (singly ionized) character of the EOMIP-CCSD solution is low, the method fails to provide a balanced description of the ionic state, which results in large errors compared to higher-level CC models such as EOMIP-CCSDT. Since both CC2 and ADC(2), as well as their scaled versions should be regarded as approximations to CCSD,[39] no acceptable performance can be expected by these models for such problematic states. To filter out these situations from the set, we calculated the Approximate Excitation Level (AEL)[67] measure of the CCSD wave function and dropped all AEL > 1.15 states from the benchmark. The ozone molecule was also removed from the set as the ground state CC2 solution is well-known to suffer from serious flaws[68] for this system.

Nucleobases are in the focus of scientific interest for many reasons. Their electron attachment and detachment properties are relevant for the appropriate description of CT states in polynucleotide chains and, thus, the characterization of long-range electron transport properties. Śmiga and co-workers[53] have recently evaluated the first two VIPs of these five important molecules, extrapolated to the CBS limit from cc-pVDZ and cc-pVTZ data. Besides reporting ZPE-corrected experimental references, results from EOMIP-CCSD and several electron propagator methods, as well as spin-component scaled ΔMP2 variants were presented.

We calculated both VIPs and VEAs of six ionic states of the nucleobase molecules, three of each symmetry, using the structures from ref 53. The core electrons were ignored in the correlation treatment in all cases. Results obtained in the cc-pVDZ and cc-pVTZ basis sets were extrapolated to the complete basis set (CBS) limit using the commonly adopted cubic formula also employed in ref 53. Because of the known general overestimation of non-HOMO VIPs by CCSD (see also below), we use a composite reference defined as

$$\begin{aligned}\Delta E^{IP}_{ref} &= \Delta E^{IP}_{\mathrm{CCSD,CBS}} + \delta_{\mathrm{CCSD(T)(a)*}}\\ &= \Delta E^{IP}_{\mathrm{CCSD,CBS}} + (\Delta E^{IP}_{\mathrm{CCSD(T)(a)*,cc\text{-}pVDZ}} - \Delta E^{IP}_{\mathrm{CCSD,cc\text{-}pVDZ}})\end{aligned} \tag{1}$$

i.e., the CCSD ionization potential extrapolated to the complete basis set limit, augmented by a correction accounting for the effect of connected triple excitations. This latter term is evaluated in the cc-pVDZ basis set using the CCSD(T)(a)* method of Matthews and Stanton,[61] which we found many times[69−71] to approximate the respective CCSDT excitation energy results to a very good accuracy.

■ RESULTS AND DISCUSSION

Table 1 shows statistics on the error of the first VIPs and VEAs of the molecules of the *acceptor set*, relative to the aug-cc-pVDZ/CCSD(T) reference of ref 62. The mean absolute error (MAE), mean signed error (MSE), standard deviation (SD), and minimum and maximum values of the MSE are presented. (The full data sample is available in the Supporting Information.) The distribution of errors is shown in Figure 1. The use of the same basis set as that of the high level reference allows a direct comparison of the methods' performance, regardless of further basis set effects. Note that this choice is different from the one of ref 21 where the finite-basis results were compared to the CCSD(T)/CBS limit.

In our benchmark, CCSD shows, for both the VIPs and VEAs, a very small error with a low standard deviation, indicating the consistency of this theory. This practically suggests, at least as long as only the first ionizations are considered, its safe use as a reference for calibrating lower level methods. CC2 and ADC(2) show a severe under- and overestimation of the VIPs and VEAs, respectively, with a mean absolute error of around 0.5 eV in all cases. Also remarkable is the large standard deviation of these errors for the VIPs, picturing a generally quite inconsistent description of ionic states by these native methods.

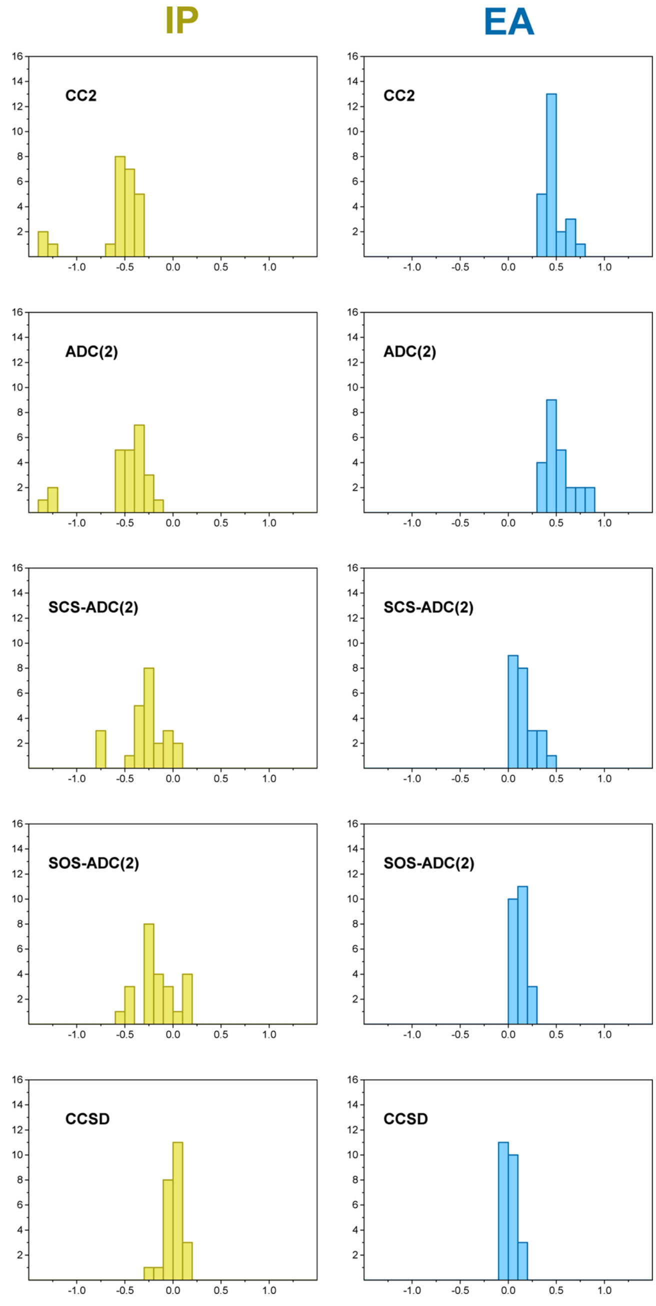

Figure 1. Distribution of the errors (in eV) for first vertical ionization potentials (VIPs) and electron affinities (VEAs) of the *acceptor set*, relative to CCSD(T) references.

The spin-component-scaled variants, on the other hand, show a much better accuracy. The mean error of VIPs is reduced by at least 44% (in the case SCS-ADC(2) versus the parent ADC(2)), but for SOS-ADC(2), a 67% improvement is observed, pushing the mean signed error to near −0.15 eV. An even better improvement is seen for the VEA values, with SOS-ADC(2) approaching the mean accuracy of CCSD. However, the reduction in the standard deviation of the errors, as compared to CC2 and ADC(2), is less significant in this set, practically negligible for the electron affinities. Also the maximum errors remain remarkably large and, although lower than for the parent methods, nowhere near the performance of CCSD.

From the two scaled versions, the SOS parametrization produces much more accurate results by all statistical measures. This method, as shown in the respective columns of Table 1, outperforms the P3 and P3+ electron propagator methods that neglect off-diagonal elements of the self-energy matrix for electron affinities, while for VIPs, it produces slightly larger, yet still similar errors. It is also comparable to the much

Table 2. Statistics on the Error (in eV) of Vertical Valence Ionization Potentials (VIPs) for 33 Small Molecules[b] of the Bartlett (Ortiz) CCSDT Set, Relative to EOMIP-CCSDT/cc-pVTZ References[66]

	CCSD[a]	CC2	ADC(2)	SCS-ADC(2)	SOS-ADC(2)	P3[a]	P3+[a]	NR2[a]	ADC(3)[a]
MSE	0.184	−0.696	−0.610	−0.276	−0.101	0.314	0.144	0.008	0.388
MAE	0.168	0.628	0.560	0.301	0.214	0.292	0.173	0.112	0.361
SD[c]	0.138	0.384	0.406	0.310	0.272	0.265	0.196	0.184	0.286
Max.[d]	0.689	1.888	1.686	1.062	0.754	1.303	0.983	0.888	1.199

[a] Data are from ref 16. [b] 152 VIPs with $\text{AEL}_{\text{CCSD}} < 1.15$ are considered. [c] Standard deviation of the signed errors. [d] Absolute values are shown.

Table 3. Statistics on the Error (in eV) of CBS-Extrapolated Vertical Ionization Potentials (VIP) and Electron Affinities (VEAs) of the Nucleobase Molecules[d]

	CCSD	CC2	ADC(2)	SCS-ADC(2)	SOS-ADC(2)	ΔMP2-SCS(IP)[a]	ΔMP2-SOS(IP)[a]
				Ionization Potentials			
MSE	0.147 (0.108)	−0.806 (−0.414)	−0.716 (−0.319)	−0.353 (−0.099)	−0.168 (0.012)	(0.01)	(0.09)
MAE	0.147 (0.108)	0.806 (0.414)	0.716 (0.319)	0.353 (0.099)	0.189 (0.082)	(0.08)	(0.10)
SD[b]	0.059 (0.039)	0.328 (0.037)	0.342 (0.068)	0.210 (0.086)	0.150 (0.098)	(0.10)	(0.10)
Min.[c]	0.032 (0.063)	0.381 (0.381)	0.242 (0.242)	0.007 (0.007)	0.015 (0.036)	(0.02)	(0.01)
Max.[c]	0.286 (0.156)	1.204 (0.478)	1.168 (0.415)	0.670 (0.191)	0.413 (0.126)	(0.12)	(0.20)
				Electron Affinities			
MSE	−0.036 (0.042)	0.322 (0.537)	0.379 (0.676)	0.068 (0.283)	−0.086 (0.084)		
MAE	0.054 (0.047)	0.322 (0.537)	0.379 (0.676)	0.162 (0.283)	0.135 (0.084)		
SD[b]	0.062 (0.037)	0.201 (0.036)	0.257 (0.064)	0.177 (0.047)	0.137 (0.043)		
Min.[c]	0.000 (−0.013)	0.062 (0.494)	0.028 (0.597)	0.005 (0.221)	0.008 (0.030)		
Max.[c]	0.224 (0.076)	0.629 (0.576)	0.749 (0.733)	0.344 (0.344)	0.317 (0.146)		

[a] Data are from ref 53. [b] Standard deviation of the signed errors. [c] Absolute values are shown. [d] Relative to composite reference values defined by eq 1. The sample includes 30 ionized and 30 electron attached states. In parentheses: data for only the first VIPs and VEAs of each system.

more sophisticated NR2 and ADC(3) models, predicting VIPs lower by 0.117 and 0.110 eV on average, respectively. For electron affinities, SOS-ADC(2) shows a very similar accuracy to NR2 and P3+ (a mean error of −0.036 eV compared to 0.046 eV of NR2 and −0.052 eV for P3+, with a 13 and 17% larger standard deviation, respectively). Both NR2 and P3+ were found in ref 65 to offer the best overall performance among the electron propagator methods that consider the full self-energy matrix or just its diagonal part, respectively.

In Table 2, the statistics on valence VIPs of the Bartlett (Ortiz) benchmark set[16,66] is presented. (The native VIP values are shown in the Supporting Information.) As mentioned above, only the 152 VIPs with a CCSD AEL value below 1.15 were considered. It has to be emphasized that in ref 16 the set was also reduced for the statistical analysis based on the satisfaction of single-excitation contribution and convergence criteria for certain self-energy methods. Here, however, we apply nothing but the universal AEL restriction above, showing the statistical data for the P3, P3+, and NR2 electron propagator techniques, as well as for ADC(3) in Table 2 for comparison. (This analysis uses the values presented in the Supplement of ref 16.)

The general underestimation of VIPs by CC2 and ADC(2), observed for the *acceptor set* above, is also clearly visible here, with ADC(2) showing a slightly better accuracy. With the scaled methods, the error is reduced considerably, to near 0.1 eV for SOS-ADC(2) which again appears as the better of the two variants, both in terms of the mean error and its standard deviation. The improvement is similar to what was found for the *acceptor set*, indicating the effectiveness of spin-component scaling for the higher valence VIPs as well. One should note that even CCSD shows an overestimation of the reference CCSDT VIPs by more than 0.18 eV on average, outperformed by SOS-ADC(2) in this measure. On the other hand, the nearly two times larger standard deviation of the latter model's error is an indication of a lower consistency. Nevertheless, the data demonstrate the overall performance of SOS-ADC(2) quite similar to that of CCSD, slightly better than the P3 and P3+ electron propagator methods, and clearly more accurate than ADC(3) which only shows a moderate improvement compared to the original ADC(2) model. Only the NR2 method shows an accuracy clearly better than SOS-ADC(2), its 0.11 eV mean absolute error being the lowest of any method evaluated in this benchmark.

Table 3 presents the statistics for error of VIPs and VEAs for the nucleobases. (The entire data set can be found in the Supporting Information.) With the inclusion of three ionic states per symmetry for both VIPs and VEAs, the sample consists of 30 states for both quantities. The values shown in parentheses correspond to the five-membered subset of the first VIPs and VEAs (associated with the HOMO and LUMO, respectively) of each molecule only. The CC2 and ADC(2) results are in line with those of the other sets seen above, with the significant over- and underestimation of the VIPs and VEAs, respectively. This effect is intensified for VIPs, showing a mean absolute error close to 0.8 eV. The respective data on the first (HOMO) VIPs is, however, closer to those observed for the *acceptor set*, indicating that the error increases for ionizations from lower lying orbitals. An opposite, yet much less significant effect is seen for VEAs, where the error of first VEAs is larger than for the entire set. Nevertheless, the introduction of spin-component scaling reduces the mean errors and their standard deviations on this set as well, pushing the accuracy well below 0.1 eV for electron affinities. For the VIPs, despite the improvement, the underestimation remains significant, no less than 0.17 eV for SOS-ADC(2). This is clearly the consequence of the huge error of higher IPs by the parent methods, not compensated by the scaling modifications to a satisfactory extent.

At the same time, for the HOMO VIPs, the SOS-ADC(2) results are again very close, about 0.01 eV off from the reference, picturing this method as a reliable choice for predicting first VIPs of the nucleobases, while for higher valence VIPs, a somewhat larger uncertainty should be assumed.

Table 3 also lists the respective statistics of the first (HOMO) VIPs predicted by the extremely effective ΔMP2-SCS(IP) and ΔMP2-SOS(IP) methods of Śmiga et al.[53] which share with SCS-ADC(2) and SOS-ADC(2) the spirit of relying on spin-component scaling. It is seen that—taking into consideration the very small sample size and thus the lack of robustness of the precise statistical values—that these methods offer very similar performances for this quantity as both SCS-ADC(2) and SOS-ADC(2). We should note here that the variants from ref 53 use a pair of scaling factors tuned to reproduce Δ-CCSD(T) VIPs, while in our SCS and SOS calculations, the standard parameters were adopted.

CONCLUSIONS

In this study, popular excited state wave function methods were evaluated for the prediction of ionization potentials and electron affinities. Obtaining these quantities from excited state calculations using the continuum orbital technique allows the adoption of existing program codes with little to no modification, without the need of an explicit formulation of the ionization or attachment energy and its elaborated implementation. The spin-component scaled versions of CC2 and ADC(2), as discussed by many earlier studies, are successful excited state methods, and their favorable computational scaling makes them important tools in applications from medium- to large-sized systems, especially using the remarkably effective CC2 and ADC(2) code in the Turbomole[40,72] program system. We evaluated the accuracy of the VIPs and VEAs predicted by the above methods on several benchmark sets, also considering their unmodified counterparts.

The native CC2 and ADC(2) formulations were found, in line with what was observed for Rydberg[69,73] and charge transfer[8,71] type electronic states, to have a large error for VIPs and VEAs as well. This is the consequence of the inconsistent treatment of electron correlation in these models which results in an overstabilization of ionized and electron attached states. Spin-component scaling, similarly to the cases of challenging excited states mentioned above,[1−3] is able to correct this artifact in a pragmatic, yet very effective manner. In particular, the SOS-ADC(2) modification based on the complete abandoning of same-spin contributions to the correlation energy was found to provide a consistently high accuracy for both VIPs and VEAs. This holds not only for the first ionization or electron affinity (electron detachment from the HOMO or attachment to the LUMO, respectively) but also for that from lower/higher lying orbitals. Nevertheless, the errors seen for higher VIPs are clearly larger than the HOMO ones, although not more so than those of CCSD. One should also be aware that spin-component scaling should not be expected to remedy situations where the results provided by the parent method are qualitatively incorrect.

For ionization potentials, the overall accuracy of SOS-ADC(2) competes with the best-performing diagonal electron propagator techniques and even most nondiagonal ones whose computational cost scales with at least the fifth power of the system size. This finding agrees with that of Śmiga and coworkers[53] who achieved a similar performance with the ΔMP2 method using spin-component scaling parameters tuned for VIPs. Electron affinities are predicted even more accurately by SOS-ADC(2), in line with the most popular $O(N^6)$ methods including CCSD.

Also considering its favorable, fourth-power computational scaling, our results depict SOS-ADC(2) as a very efficient method for the calculation of ionized states of larger systems. Besides the outstanding accuracy, we regard the consistent treatment of ionized and electron attached states in the generalized excited state framework, provided by the continuum orbital formalism, as an important benefit. The description of ionic states being in full theoretical harmony with the corresponding excited state method is of utmost importance in the treatment of charge transfer states that can, especially in large systems, approximately be interpreted as a local ionization and an electron attachment process taking place simultaneously. Our present results regarding the performance of spin-component-scaled models are in agreement with those of previous studies on CT type excited states, further supporting them as the recommended tools of choice in the modeling of electron transport in larger molecular systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.2c00624.

Calculated vertical ionization potentials and electron affinities of systems benchmarked in this study (PDF)

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Notes

The authors declare no competing financial interest.

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