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## Wave function methods for fractional electrons

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Determining accurate chemical potentials is of considerable interest in various chemical and physical contexts: from small molecular charge-transfer complexes to bandgap in bulk materials such as semi-conductors. Chemical potentials are typically evaluated either by density functional theory, or, alternatively, by computationally more intensive Greens function based GW computations. To calculate chemical potentials, the ground state energy needs to be defined for fractional charges. We thus explore an extension of wave function theories to fractional charges, and investigate the ionization potential and electron affinity as the derivatives of the energy with respect to the electron number. The ultimate aim is to access the chemical potential of correlated wave function methods without the need of explicitly changing the numbers of electrons, making the approach readily applicable to bulk materials. We find that even though second order perturbation theory reduces the fractional charge error considerably compared to Hartree-Fock and standard density functionals, higher order perturbation theory is more accurate and coupled-cluster approaches are even more robust, provided the electrons are bound at the Hartree-Fock level. The success of post-HF approaches to improve over HF relies on two equally important aspects: the integer values are more accurate and the Coulomb correlation between the fractionally occupied orbital and all others improves the straight line behavior significantly as identified by a correction to Hartree-Fock. Our description of fractional electrons is also applicable to fractional spins, illustrating the ability of coupled-cluster singles and doubles to deal with two degenerate fractionally occupied orbitals, but its inadequacy for three and more fractional spins, which occur, for instance, for spherical atoms and when dissociating double bonds. Our approach explores the realm of typical wave function methods that are applied mostly in molecular chemistry, but become available to the solid state community and offer the advantage of an integrated approach: fundamental gap, relative energies, and optimal geometries can be obtained at the same level.  
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### I. INTRODUCTION

Accurate predictions of electron affinities (EAs) and ionization energies (IEs) is of great interest in various fields of physics, chemistry, and materials science. The fundamental (band) gap (IE-EA) is often the target of material design, especially for semi-conductors used in (molecular) electronics. Electron affinity and ionization energy are also important quantities for molecular complexes, e.g., determining the existence of charge-transfer complexes and excitations.

Kohn-Sham density functional theory (KS-DFT)<sup>1</sup> often delivers a good ratio between computational effort and accuracy and is therefore the work horse of electronic structure theory. However, gaps (corresponding to chemical potential differences), estimated from lowest unoccupied, and highest occupied orbital eigenvalues (LUMO-HOMO),<sup>2</sup> are systematically in error with standard density functional approximations<sup>3-5</sup> or even the (nearly) exact functional.<sup>6,7</sup> Mathematically, IE and EA are equivalent to the energy derivatives with respect to the number of electrons, a derivative that is well known to be constant between integers and having a discontinuity at integer numbers of electrons in the exact theory.<sup>8</sup>

The main problem of semi-local density functionals for underestimating energy gaps can be traced back to the delocalization error that is defined as the convex deviation from the exact linear behavior for fractional charges.<sup>9,10</sup> Because the energy derivatives with respect to adding or removing an infinitesimal number of electron are the chemical potentials and their difference gives the fundamental gap, the convex behavior leads to the general underestimation of bandgaps.<sup>11</sup> In addition, approximate functionals tend to over-delocalize the added (fractional) electron or hole. The deviation from the linearity condition was originally termed many-electron self-interaction error<sup>12,13</sup> to link to and differentiate from the one-electron self-interaction error.<sup>14</sup> The concept of delocalization error captures the physical essence of the problem: it highlights the nonphysical delocalization of electrons, or nonphysically low energies for delocalized electrons, an error that has the opposite sign at the Hartree-Fock (HF) level. The consequence of the delocalization error manifests not only in bandgaps, charge transfer excitations,<sup>15</sup> and molecular ions (e.g.,  $\text{Ne}_2^+$ ,  $\text{CO}^-$ , solvated ions, and dissociated alkali halides),<sup>12,13,16-18</sup> but also in thermochemistry and geometries of molecules.<sup>19-21</sup> The extension of fractional electrons to the presence of two or more fractional electrons is called fractional spins.<sup>22</sup> The fractional spin error<sup>23</sup> is highly relevant for strongly correlated systems such as some transition

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metal complexes and stretched covalent bonds (e.g., transition states). Note that fractional electrons are hypothetical entities, occurring (locally) at the dissociation limit of real systems. The prototypical examples for a fractional charge and spin system are  $H^{0.5+}$  and  $H(\frac{1}{2}\alpha, \frac{1}{2}\beta)$ , respectively, corresponding to one half of infinitely stretched  $H_2^+$  and  $H_2$ . Progress has been made in designing functionals with reduced delocalization error.<sup>24–27</sup> Nevertheless, correcting the fractional behavior is very challenging in general: it has been shown that the exact functional cannot be an explicit and differentiable functional of the electron density or density matrix,<sup>11</sup> implying a highly complex structure. Fractional spins are even more challenging and general solutions are still lacking, despite active efforts.<sup>28–31</sup>

While promising approaches for bandgap corrections are actively pursued,<sup>32–34</sup> reliable predictions of fundamental gaps, without performing the explicit computation of the electron attached and detached state, are still typically achieved by approaches beyond DFT. Many-body perturbation theory, such as Hedin’s GW approximation,<sup>35</sup> is especially popular. GW is typically applied to solids, where the charged states are not accessible (some finite differences approaches exist<sup>36,37</sup> but are rarely used). For molecules, the most common approach is to rely on finite differences with integer values.

Cohen, Mori-Sanchez, and Yang have developed analytical derivatives of correlated methods with respect to the electron numbers, starting with second order Møller-Plesset perturbation theory (MP2)<sup>38</sup> and followed by the random-phase approximation.<sup>39</sup> Subsequently, the extension of general many-electron theories expressed in terms of the one-electron Green’s function to systems with fractional charges has been formulated.<sup>40</sup> Higher order terms, that do not occur from the Green’s function perspective<sup>40</sup> and account for the dependence on the occupation number of the orbital energies, but not the orbitals, have been developed by Beste *et al.* for MP2.<sup>41</sup>

Investigating the possible improvement by going beyond MP2 is assessed herein. With the recent implementation of the chemical “gold standard” coupled-cluster singles, doubles, and perturbative triples (CCSD(T)) in a solid state code,<sup>42</sup> we expect applications involving correlated wave function methods to become increasingly popular. Bandgap predictions would nicely complement other attractive features of such robust wave function approaches. Furthermore, in the field of charge-transfer complexes, relevant for charge transport and reactive complexes, MP2 is often applied: higher order methods tend to be too expensive and standard density functional approximations are known to overestimate charge transfer in terms of electron density, while interaction energies can show contrasting trends.<sup>43–45</sup> The assessment of the MP2 chemical potentials thus allows to estimate if more elaborate methods should be applied.

Investigating the fractional charge and spin behavior of wave function methods helps to answer two important questions: which physics allows the common post-HF methods to show a much improved description of fractional charges compared to HF? Which features are required to describe the more challenging fractional spins? Answering these question might inspire novel forms of density functional approximations and

yields insight into the performance of popular post-HF methods such as MP2, MP4, and CCSD(T).

From a practical perspective, our work highlights the reward for analytical derivatives with respect to the number of electrons. Relying only on the system with an integer number of electrons and thus avoiding charged systems, the bandgap of bulk materials could be readily obtained with correlated wave function methods.

## II. THEORETICAL BACKGROUND

The concept of fractional electrons has been introduced in the density functional community in 1982.<sup>8</sup> Nevertheless, the concept of fractional spins<sup>22,23</sup> and the exact conditions for the combination of fractional charges and fractional spins<sup>28</sup> have only been developed recently. The rigorous expression in term of the ensemble average of densities is

$$E \left[ \frac{1}{q} \sum_i^{g_N} c_i \rho_i^N + \frac{1}{q} \sum_j^{g_{N+1}} d_j \rho_j^{N+1} \right] = \frac{q-p}{q} E(N) + \frac{p}{q} E(N+1), \quad (1)$$

where  $\rho_i$  is the  $i$ th density matrix,  $c_i, d_j \in \mathbb{N}_0$ ,  $q = \sum c_i + \sum d_j$ , and  $p = \sum d_j$ , while  $g_N$  and  $g_{N+1}$  are the degeneracies of ground states of the system with  $N$  and  $N+1$  electrons, respectively.<sup>28</sup>

The ensemble average is best described as an averaged energy of pure state density matrices and its computation is trivial. In contrast, an explicitly fractional system corresponds to the energy of an averaged density matrix, which is equivalent to the physical dissociation limits of molecules. Deviations between Eq. (1) and explicitly fractional systems are stringent tests for approximate methods and have come to the attention of several groups.<sup>9,11–13,18,23,28,31,39</sup>

Yang and co-workers have shown that the fractional information affects just the HOMO occupation number<sup>22,23</sup> and therefore theories relying on effective one-electron Hamiltonians, e.g., Hartree-Fock and standard Kohn-Sham density functionals, can be extended straight forwardly to fractional charges and fractional spins. Following the treatment of fractional electrons in effective one-electron theories, methods relying on a non-interacting Green’s function have also been rigorously extended to fractional charge and fractional spin.<sup>40</sup> Yang and co-workers uncovered a promising performance of MP2 for fractional charge,<sup>38</sup> while the particle-hole random-phase approximation (ph-RPA) shows a severe delocalization error<sup>39</sup> akin to semi-local density functionals. Intriguingly, a recently development of RPA variant lead to new functional that is essentially free of the fractional charge error and fractional spins are described well in certain cases.<sup>46</sup>

### A. Wave functions for fractional electrons

MP2 is an ideal starting point to extend the concept of fractional electrons beyond theories relying on a non-interacting Green’s function, most notably to “true” wave

function theories, to which MP2 is commonly counted. Just like for other approximate methods, wave function theories applied to fractional electrons give insight into the behavior of fractional charge (charge-transfer in the broadest sense) and of strong correlation (more than one partially occupied orbital). As it will turn out, our ansatz does not allow us to formulate a rigorous extension that corresponds to a general system at all the dissociation limits. However, the numerical results are qualitatively correct and clearly illustrate the salient features of popular methods such as higher order perturbation theory (MP3-MP4) and CCSD(T).

We start from the exact extension of wave functions to fractional electrons: the wave function can be formulated as a vector in Fock space. Since the second-quantized Hamiltonian is independent on the particle numbers, it can act on all components of the vector, e.g., for a fractional charge. We now define the vector in Fock space for fractional charge as

$$|\Psi^{N+\delta}\rangle = \sqrt{1-\delta}|\Psi^N\rangle + \sqrt{\delta}|\Psi^{N+1}\rangle, \quad (2)$$

and, correspondingly,

$$\hat{H}|\Psi^{N+\delta}\rangle = \sqrt{1-\delta}\hat{H}|\Psi^N\rangle + \sqrt{\delta}\hat{H}|\Psi^{N+1}\rangle. \quad (3)$$

Thus

$$\hat{H}|\Psi^{N+\delta}\rangle = \sqrt{1-\delta}E^N|\Psi^N\rangle + \sqrt{\delta}E^{N+1}|\Psi^{N+1}\rangle, \quad (4)$$

where  $|\Psi^{N+\delta}\rangle$  stands for the wave function with a fractional electron  $0 \leq \delta \leq 1$ ,  $\hat{H}$  is the second quantized Hamiltonian operator, and  $E$  are the eigenvalues. The wave function  $|\Psi^{N+\delta}\rangle$ , written as two independent vectors  $|\Psi^N\rangle$  and  $|\Psi^{N+1}\rangle$ , provides the exact energy of the fractional system as the expectation value

$$\begin{aligned} E^{N+\delta} &= \langle\Psi^{N+\delta}|\hat{H}|\Psi^{N+\delta}\rangle \\ &= (1-\delta)E^N + \delta E^{N+1}. \end{aligned} \quad (5)$$

Similarly, we can write a wave function for fractional spins as a vector of degenerate (and therefore independent) wave functions. For instance, the wave function of the spherically symmetric boron atom can be written as a superposition of the three individual vectors

$$|\Psi^{p_x^{1/3} p_y^{1/3} p_z^{1/3}}\rangle = \sqrt{\frac{1}{3}}|\Psi^{p_x^1}\rangle + \sqrt{\frac{1}{3}}|\Psi^{p_y^1}\rangle + \sqrt{\frac{1}{3}}|\Psi^{p_z^1}\rangle. \quad (6)$$

We assume that  $|\Psi^{N+\delta}\rangle$  corresponds to the projection of a molecular wave function on one fragment of the dissociation limit of a real molecule. Nevertheless, Eq. (2) does not correspond to the wave function of a dissociated system: even in the dissociation limit, the wave function is not separated explicitly into two vectors with independent parametrizations. However, the two descriptions are equivalent, as the physical system is just the direct sum of the vectors, corresponding to the product of wave functions. Furthermore, Eqs. (2) and (4) provide us with starting point to understand the approximation we will introduce.

## B. Wave function in coupled-cluster theory

In single reference coupled-cluster theory, the wave function is parametrized as

$$|\Psi\rangle = e^{\hat{T}}|\Phi_0\rangle, \quad (7)$$

where  $|\Phi_0\rangle$  is a single determinant reference wave function and  $\hat{T}$  is the sum of cluster operators  $\hat{T}_1 + \hat{T}_2 + \dots$ , given in terms of cluster amplitudes  $t_{ij\dots}^{ab\dots}$  and creation  $a_a^\dagger$  and annihilation  $a_i$  operators

$$\hat{T}_m = \frac{1}{(m!)^2} \sum_{\substack{ij\dots \\ ab\dots}} t_{ij\dots}^{ab\dots} \{a_a^\dagger a_i a_b^\dagger a_j\},$$

where the curly brackets indicate normal ordering. Hence, for coupled-cluster, Eq. (2) is reformulated as

$$|\Psi^{N+\delta}\rangle = \sqrt{1-\delta}e^{\hat{T}^N}|\Phi_0^N\rangle + \sqrt{\delta}e^{\hat{T}^{N+1}}|\Phi_0^{N+1}\rangle, \quad (8)$$

where the cluster operator  $\hat{T}^N$  and  $\hat{T}^{N+1}$  are different for the two states with differing number of electrons.

Equation (8) is closely related to an ensemble average, but is it possible to “directly” parametrize the wave function of the ensemble instead?

$$|\Psi^{N+\delta}\rangle = e^{\hat{T}^{N+\delta}}|\Phi_0^{N+\delta}\rangle. \quad (9)$$

Given  $|\Phi_0^{N+\delta}\rangle$  (a vector in the Fock space for a fractional non-interacting system) and  $|\Psi^{N+\delta}\rangle$ ,  $\hat{T}^{N+\delta}$  can be identified and hence we conclude that Eq. (9) represents a valid parametrization of a wave function for fractional electrons. Thereby, the definition of size consistency is extended to open quantum systems, i.e., for practical purposes

$$\Psi^{A+B} = \mathcal{A}\Psi^A\Psi^B = \Psi^A\Psi^B, \quad (10)$$

when system  $A$  and system  $B$  are separated by infinity. Usually, fractional electrons in  $A$  and  $B$  are associated with fluctuating electron numbers, meaning that the two subsystems can be thought of as interacting even at infinite separation.<sup>8</sup> The extension of size consistency to open quantum systems does not, however, imply that size consistent method can physically correctly dissociate covalent bonds: it just ensures that the sum of the (fractionally occupied) fragment energies yields the same energy as the infinitely stretched super system.

The main question is how  $\hat{T}^{N+\delta}$  can be determined, i.e., if the standard techniques are applicable to fractional electrons.

### 1. Connection to Fock space approaches

Valence universal or Fock space coupled-cluster (FS-CC) approaches<sup>47–50</sup> have a very similar wave function as Eq. (9), in the sense that there is a singles excitation operator  $\hat{T}$  that generates wave functions with differing electron numbers. For example, the  $N+1$  wave function in FS-CC theory can be formulated as

$$|\Psi^{N+1}\rangle = \{e^{\hat{T}^N + \hat{T}^{(1,0)}}\}|\Phi_0^{N+1}\rangle, \quad (11)$$

where the curly brackets indicate normal ordering.  $\hat{T}^N$  is obtained from the  $N$ -electron coupled-cluster equations, and

$\hat{T}^{(1,0)}$  covers the elements missing in  $\hat{T}^N$ , corresponding to the effect of adding the additional electron. The  $\hat{T}^{(1,0)}$  amplitudes can be solved by various techniques.<sup>51,52</sup> Our ansatz (Eq. (9)) is different from FS-CC since we desire to smoothly interpolate between  $\hat{T}^N$  and  $\hat{T}^{N+1}$  instead of estimating  $\hat{T}^{N+1}$  based on  $\hat{T}^N$  plus the corrections accounting for the additional electron, i.e., we wish to treat  $\hat{T}^N$  and  $\hat{T}^{N+1}$  on equal footing. Since Eq. (11) reduces to standard coupled-cluster for  $N$ -electrons and the equations for the  $\hat{T}^{(1,0)}$  amplitudes can be formulated as linear equations, the lowest lying solution of Eq. (11) can be seen as the derivative of the coupled-cluster energy  $E_{CC}$  with respect to the number of electrons  $\frac{\partial E_{CC}}{\partial N}$ .

Due to the coupled nature of the equations, the derivative contains contributions from all the orbitals and not only from the frontier orbital in the reference determinant. In fact, the one-electron orbital that corresponds to the electron addition/removal can be constructed as detailed in Ref. 51.

## 2. Intermediate normalization

Intermediate normalization exploits the property of wave functions that the exact energy can be obtained from a wave function that is not normalized to unity, but is composed of components with the correct normalization. The coefficient for the reference determinant in the configuration interaction expansion is set to unity and all other determinants have weights between  $-1$  and  $1$ . This leads to computational simplifications as it relies on the following two identities:

$$\langle \psi_i | \psi_i \rangle = 1 \quad (12)$$

and

$$\langle \psi_0 | \psi_j \rangle = 0. \quad (13)$$

Equation (12) states that each state  $\psi_i$  on its own is normalized to unity and Eq. (13) emphasizes that all the excited states are orthogonal to the reference state  $\psi_0$ . These conditions are easily satisfied in the formulation as a vector in Fock space: states that differ in the number of electrons do not mix and therefore both conditions apply individually to each component of the vector. However, in practice, the computations rely on determinants and there, intermediate normalization can no longer hold in the presence of fractionally occupied and unoccupied orbitals when using the scaled orbital approach (*vide infra*): determinants with differing numbers of electrons are permitted (e.g., exciting one electron from the occupied to a fractionally unoccupied orbital leads to a different normalization). Hence, Eq. (12) is frequently violated. Furthermore, two Slater determinants that only differ by the fractional HOMO/LUMO populations are the same up to a factor and therefore do overlap, violating Eq. (13). These violations might or might not introduce errors depending on the method and algorithm: in standard coupled-cluster methods and for diagrammatic summation rules (applied to perturbation theory beyond MP3, e.g., MP4), intermediate normalization is a numerically exploited concept,<sup>53</sup> i.e., simplifications are introduced that may not be valid if intermediate normalization is violated.

In contrast to Fock space coupled-cluster, at present, we cannot impose intermediate normalization for each particle number separately, since the two states are solved together on equal footing. Therefore, the separation into ‘‘sectors’’ is not possible. However, as the Hamiltonian is independent of the number of electrons and only the wave function can contribute to the derivative with respect to the number of electrons, we expect that the exact derivative  $\frac{\partial E_{CCSD}}{\partial n_f}$  is given by the properly intermediately normalized Fock-space expressions, or, equivalently, by standard EOM-IP(EA)-CCSD.<sup>48,50,51</sup> This view is supported by the analysis of the so-called ‘‘model space,’’ which determines the space of the  $N + 1$  electron wave function: it is only well defined in just such a perturbation theory expansion with respect to the number of electrons.<sup>48</sup>

Even though we do not have an algorithm that allows us to determine the exact  $\hat{T}^{N+\delta}$  for a given method (e.g., CCSD), the leading violation of Eq. (12) (HOMO/LUMO transitions) vanishes for  $n_\alpha + n_\beta = 1$  and it can be hoped that Eq. (13) is of minor importance. If we assume that the reference determinants  $|\Phi^N\rangle$  and  $|\Phi^{N+1}\rangle$  are fairly similar (e.g., the electron is bound in  $|\Phi^{N+1}\rangle$  and spin contamination is not too strong in either of the states), we expect that  $\hat{T}^{N+\delta} \approx \hat{T}^N \oplus \hat{T}^{N+1}$  for the frontier orbital amplitudes and the standard algorithms should provide a good approximation. For perturbation theory, the assumption is irrelevant: given a set of molecular orbitals (MOs) and orbital energies, the excitation amplitudes for an arbitrary number of electrons can be constructed without any artificial coupling between states that differ in electron numbers.

## 3. How to determine the correlated wave function of a fractional electron?

In independent particle theories, the fractional (reference) determinant  $|\Phi_0^{N+\delta}\rangle$  is just the determinant of all the occupied MOs, with the HOMO  $\phi_H$  being scaled

$$\tilde{\phi}_H = \sqrt{n_H} \phi_H, \quad (14)$$

where  $n_H$  is the occupation number of the HOMO orbital.<sup>22,23</sup> Following Refs. 38–40, the degeneracy between HOMO and LUMO is accounted for by introducing an appropriately scaled lowest unoccupied orbital  $\tilde{\phi}_L$  sharing the spatial structure of the HOMO,

$$\tilde{\phi}_L = \sqrt{1 - n_H} \phi_H. \quad (15)$$

Thereby, the density represented by the two fractional orbitals corresponds to the normalized density of one electron:  $\langle \tilde{\phi}_H | \tilde{\phi}_H \rangle + \langle \tilde{\phi}_L | \tilde{\phi}_L \rangle = 1$ . With the scaled frontier orbitals at hand, we may apply any wave function method to fractional electrons – and in the case of MP2, this ansatz gives of course the result of Ref. 38. As we will see, this occupation number scaling approach, when extended to CCSD, works very well, but not exactly for reasons we will discuss in the following.

CCSD is exact for 0, 1, and 2 electrons and therefore is expected to be exact for any number between 0 and 2. However, applying Eqs. (14) and (15) to the hydrogen atom with 0–2 electrons (Figure 1) does not yield the expected exact

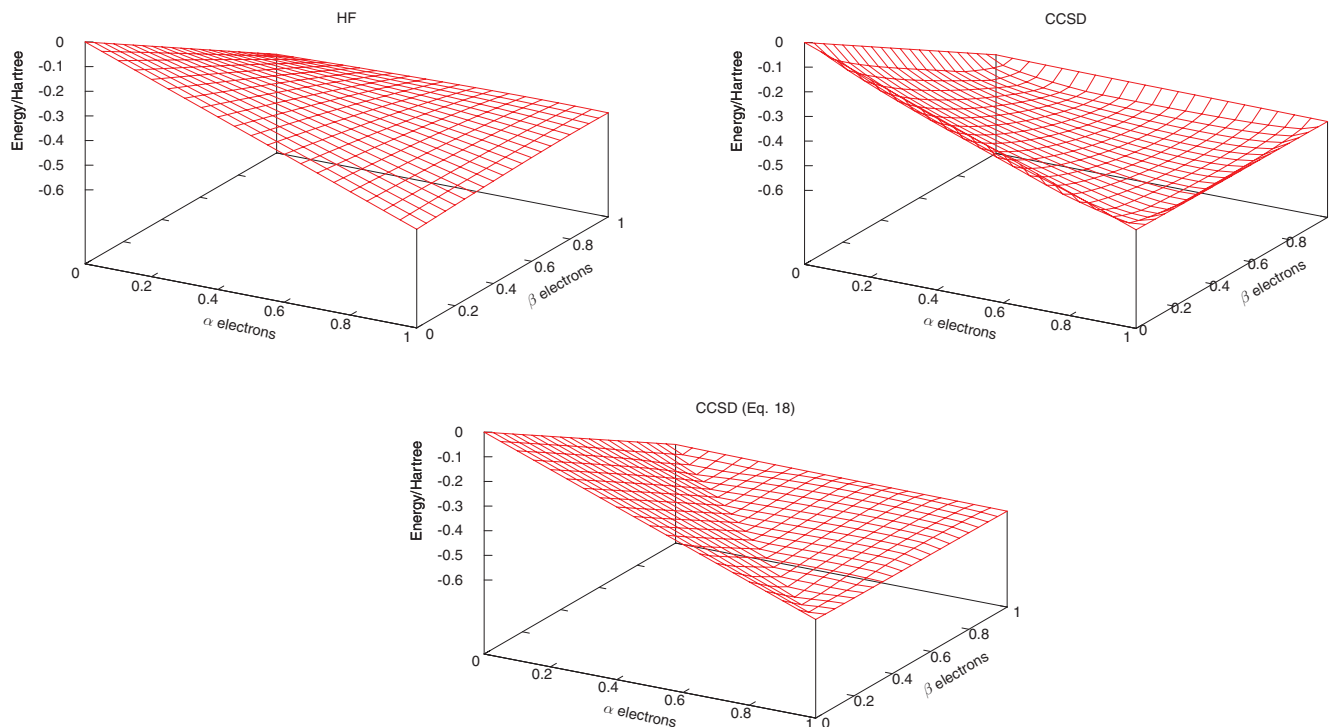


FIG. 1. Total energy of a hydrogen atom as a function of fractional spin and charge. (Top left) Hartree-Fock, (top right) CCSD with virtual orbitals according to Eq. (15), (bottom) CCSD with rescaled virtual orbitals, see Eq. (18). (Basis set) def2-QZVP.

results. We have verified numerically that the CCSD energy of the  $D_{4h}$  solutions of dissociating  $H_4^{2+}$  and  $H_4^{2-}$  (corresponding to four times  $H(\frac{1}{4}\alpha, \frac{1}{4}\beta)$  and  $H(\frac{3}{4}\alpha, \frac{3}{4}\beta)$ , respectively) indeed evaluates to the ensemble averaged energy required by Eq. (1) (for these computations we used the implementation in GAMESS<sup>54</sup> because of its extensive support of molecular symmetry).

The rescaling (Eqs. (14) and (15)) works remarkably well for the edges, i.e., the fractional charge cases (see Table II for a quantitative test of typical examples) and also for the one-electron diagonal  $n_\sigma + n_{\sigma'} = 1$ . However, the “off-diagonal,” i.e.,  $n_\sigma = n_{\sigma'}$  with  $n_\sigma + n_{\sigma'} \notin \mathbb{N}_0$  is convex, just like direct RPA,<sup>39</sup> indicating nonphysically large correlation: apparently, in (some) cases the “simple” virtual orbital rescaling (Eq. (15)) essentially sums up indiscriminately the different components of degenerate solutions (e.g.,  $H(\frac{1}{4}\alpha, \frac{1}{4}\beta)$ , i.e., stretched  $H_4^{2+}$ ). In other words, the “coherence” between degenerate solutions can be lost and, depending on the system and the electronic structure method, this coherence might (CCSD) or might not (RPA) be crucial.

Note that Cohen, Mori-Sanchez, and Yang assumed the ground state energy to be a functional of the one-electron Green’s function, when deriving the occupation number rescaling approach and the fractional energy expressions have been worked out specifically for each method.<sup>40</sup> The reasons for the small deviations in CCSD and MP4 (see Table II) from the simple occupation number rescaling rules are complex and we suspect three possible origins: (i) not all methods are a functional of the one-electron Green’s function, (ii) we did not specifically work out the equations for MP4 and can therefore not guarantee that the standard energy expressions are ap-

propriate for the extension to fractional electrons, and (iii) as stated in Subsection II B 2, we apply standard algorithms that exploit intermediate normalization, potentially incompatible with fractionally (un)occupied orbitals.

In the absence of a rigorous way to generate the exact (and coherent) solutions, we carry out the following analysis.

We discuss the flat plane of a H atom in a minimal basis set, i.e., there is only one  $\alpha$ - and one  $\beta$ -spin orbital. Be reminded that we use the same frontier orbital twice in fractional systems: first as a fractionally occupied orbital (Eq. (14)) and then as a fractionally unoccupied orbital (Eq. (15)). Let us start by considering the Fock space vectors underlying the fractional wave function

$$\begin{aligned} |\Psi^{N+\delta}\rangle &= \sqrt{1-\delta}|\Psi^N\rangle + \sqrt{\delta}|\Psi^{N+1}\rangle \\ |\Psi^{n_\sigma, n_{\sigma'}}\rangle &= \sqrt{n_\sigma}|\Psi^\sigma\rangle + \sqrt{n_{\sigma'}}|\Psi^{\sigma'}\rangle, \end{aligned} \quad (16)$$

where  $\delta$  is a fractional charge,  $n_{\sigma/\sigma'}$  is a fractional spin, and  $|\Psi^{\sigma/\sigma'}\rangle$  stands for the wave function where the  $\sigma/\sigma'$ -spin-orbital is occupied by one electron.

We now can think in the following way about fractional electrons: the two independent vectors can be joined together by looking at the elements in Fock space by which they differ. Since the spatial orbitals are taken to be the same, only the frontier orbital differs, i.e., a fraction  $\sqrt{\delta}$  of the LUMO of  $N$  will be converted into an occupied orbital, leaving  $\sqrt{1-\delta}$  as an unoccupied one (see first line of Figure 2). The same reasoning applies to  $n_\sigma$  and  $n_{\sigma'}$  if  $n_\sigma + n_{\sigma'} = 1$ : we fill  $\sqrt{n_{\sigma'}}$  of the LUMO in the  $n_\sigma$  state, leaving an unoccupied orbital of  $\sqrt{1-n_{\sigma'}}$  – and *vice versa* (see second line of Figure 2).

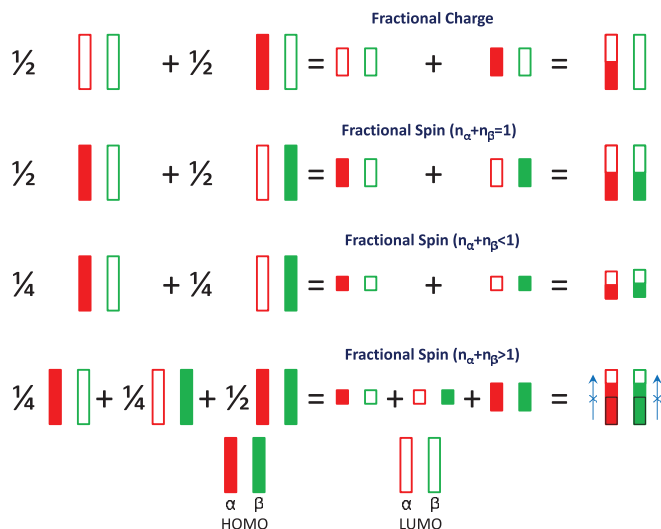


FIG. 2. Illustration of combinations of vectors in Fock space generating fractional electrons. The blue crossed arrows indicate transitions that should be excluded, since they correspond to the part of the electron density would not be correlated in the constituting fragment in a minimal basis set.

However, if  $n_\sigma + n_{\sigma'} < 1$ , then the two virtual spaces are “globally” scaled: by taking  $n_\sigma$  parts of  $|\Psi^\sigma\rangle$  (right part of Eq. (16)), we get only  $n_\sigma$  parts of the unoccupied  $\sigma'$ -orbital and *vice versa*. Hence, the virtual  $\sigma'$ -orbital should be scaled to  $\sqrt{n_\sigma}$  (see third line of Figure 2). For one-electron systems it goes back to  $\sqrt{1 - n_{\sigma'}}$  since  $n_\sigma = 1 - n_{\sigma'}$ .

In the case of  $n_\sigma + n_{\sigma'} > 1$ , a negative fractional charge of  $\delta = n_\sigma + n_{\sigma'} - 1$  is present, meaning that for  $\delta$ -electrons, there is no virtual degenerate orbital to be considered, i.e., the virtual orbital of  $\sigma'$  is of the size  $\sqrt{n_\sigma - \delta} = \sqrt{1 - n_{\sigma'}}$ , just as the scaled orbital ansatz (Eq. (15)) suggests. However, since the  $\delta$ -electron come from components with no virtual orbital available in a minimal basis set, the virtual orbital of  $\sqrt{n_\sigma - \delta}$ , should only be available to excitations of  $n_{\sigma'} - \delta$  electrons (see fourth line of Figure 2). Without derivation, the following *ad hoc* ansatz is proposed:

$$\tilde{\phi}_{L,\sigma} = \sqrt{1 - n_\sigma} \left( 1 - \delta \frac{n_{\sigma'}}{n_\sigma} \right) \phi_H, \quad (17)$$

which has the merits that in the case of  $\delta = 0$ , i.e., for  $1 = n_\sigma + n_{\sigma'}$ , and for fractional charge ( $n_{\sigma'} = 0$ ) the regular  $\sqrt{1 - n_\sigma}$  scaling is recovered, while in between the virtual orbitals are scaled to a smaller value (replacing  $\delta \frac{n_{\sigma'}}{n_\sigma}$  by  $\delta \sqrt{n_{\sigma'}}$  gives similar results) as required to counter the overcorrelation.

To summarize, we arrive at “modified” virtual orbitals which are summarized as

$$\tilde{\phi}_{L,\sigma} = \begin{cases} n_\sigma + n_{\sigma'} \leq 1 & \tilde{\phi}_{L,\sigma} = \sqrt{n_{\sigma'}} \phi_H \\ n_{\sigma'} = 0 & \tilde{\phi}_{L,\sigma} = \sqrt{1 - n_{\sigma'}} \phi_H \\ n_\sigma + n_{\sigma'} \geq 1 & \tilde{\phi}_{L,\sigma} = \sqrt{1 - n_\sigma} \left( 1 - \delta \frac{n_{\sigma'}}{n_\sigma} \right) \phi_H. \end{cases} \quad (18)$$

Figure 1 shows clearly that the flat plane is almost satisfied when Eq. (18) is used instead of the “simple” virtual or-

bit scaling (Eq. (15)), validating our reasoning. Except for the flat plane, we will always deal with systems where there is either just a fractional charge or where  $n_\sigma + n_{\sigma'} \in \mathbb{N}$  and hence for all the results presented later on, Eq. (15) is applied, which gives good accuracy for fractional charges.

Note, that CCSD(T) does not have a wave function and we can therefore expect some more errors when applying our approach when including the perturbative triples.

In order to elucidate the origin of the reduced localization error when going from HF to MP2, a variant termed MP2\* is investigated as a computational experiment. MP2\* retains only terms that correspond to excitations involving one coupled  $\tilde{\phi}_H \rightarrow \tilde{\phi}_L$  transition

$$E_c^{\text{MP2}^*} = \sum_{i < f_H}^{\text{occ}} \sum_{a > f_L}^{\text{virt}} \frac{\langle i f_H || a f_L \rangle^2}{\varepsilon_i + \varepsilon_H - \varepsilon_a - \varepsilon_L}, \quad (19)$$

where the  $f_H$  is the index of the fractionally occupied orbital  $\tilde{\phi}_H$  and  $f_L$  the index of the fractionally unoccupied orbital  $\tilde{\phi}_L$ . In words, MP2\* selects the  $\tilde{\phi}_H \rightarrow \tilde{\phi}_L$  transition “coupled” to all other orbital pairs, thereby correlating exclusively the fractional electron and vanishing for integer numbers of electrons.

### III. COMPUTATIONAL DETAILS

All computations reported herein are performed in a locally modified version of CFOUR.<sup>55</sup> Only the HOMO is scaled, according to Eq. (14), during the SCF procedure.

For the post-HF methods, the implementation consists in adding an extra virtual orbital: after the HF computation, the  $\tilde{\phi}_H$  and its corresponding eigenvalue  $\varepsilon_H$  is available and the degenerate LUMO orbital is introduced:  $\tilde{\phi}_L = \sqrt{\frac{1 - n_H}{n_H}} \tilde{\phi}_H = \sqrt{1 - n_H} \phi_H$  with the eigenvalue  $\varepsilon_L = \varepsilon_H + 10^{-7}$  where the small constant is introduced to ensure that HOMO and LUMO orbitals are easily distinguishable.

For all methods including single excitations (e.g., CCSD, CISD, and MP4) the near singular term corresponding to the  $\tilde{\phi}_H \rightarrow \tilde{\phi}_L$  excitation is set to  $10^{-5}$ , which is numerically equivalent to neglecting it, but gives higher numerical stability in the case of fractional spins. This (near) zero amplitude is an approximation, but at present, it is the only option as this amplitude is not known *a priori*.

Fractional spins lead to at least two HOMO-LUMO excitations with a zero energy denominator. Hence, the MP2 energy diverges and the coupled-cluster equations (initialized with MP2 amplitudes) are virtually impossible to converge. To circumvent this issue, an *ad hoc* fix is applied: for physical reasons, amplitudes should be constrained to  $[-1, 1]$ . Therefore, all amplitudes that exceed these values are scaled back while computing the MP2 energy and storing the corresponding amplitudes, which results in similar behavior as the degenerate corrected perturbation theory (DCPT2) of Assfeld *et al.*<sup>56</sup> Furthermore, the diverging MP2 amplitudes are “frozen” during the CCSD iterations except if they fall within the  $[-1, 1]$  interval.

Correlation consistent basis sets of Dunning<sup>57,58</sup> (aug-cc-pVTZ for molecules and aug-cc-pVQZ for atoms) were applied for the fractional charge computations and, for higher

TABLE I. Ionization energies in eV; the completely uncontracted cc-pVTZ basis set has been used to compare to the results of D- $\Delta$ MBPT(2), taken from Ref. 41. The numerical derivatives are computed with  $\Delta e^- = 0.01$ .

	$\Delta$ HF	$\Delta$ MP2	$\partial E_{\text{HF}}/\partial n_{\text{HOMO}}$	$\partial E_{\text{MP2}}/\partial n_{\text{HOMO}}$	D- $\Delta$ MBPT(2) (Ref. 41)	CCSD(T)/CBS (Ref. 60)
H <sub>2</sub> O	10.91	12.68	13.69	11.11	12.58	12.62
CH <sub>2</sub> O	9.41	11.25	11.97	9.50	10.79	10.89
CH <sub>4</sub>	13.33	14.40	14.82	13.76	14.55	13.6
NH <sub>3</sub>	9.33	10.86	11.58	9.73	10.96	10.82
N <sub>2</sub>	15.63	15.31	17.19	13.98	15.73	15.58

numerical stability, Ahlrichs' def2-QZVPP basis set<sup>59</sup> were used for atoms with fractional spins.

Electron affinities, ionization energies, and fundamental gaps are calculated for a subset of the FG115 database of Chai and co-workers.<sup>60</sup> Only molecules for which we managed to converge all the iterative methods and for which IE and EA correspond at the HF and the CCSD(T) level to a change in the frontier-orbital occupations have been kept, resulting in 81 systems (18 atoms and 63 molecules).

## IV. RESULTS AND DISCUSSION

### A. Fractional charge behavior and gaps

The fractional charge behavior of correlated wave function methods is first illustrated at the example of  $\text{F} \rightarrow \text{F}^-$  (Figure 3), revealing several characteristics. Even though the integer electron is bound at the HF level, a fractional electron ( $<0.6$ ) is (slightly) unbound due to the large curvature. Correlating the fractional electron in MP2\* reduces the HF curvature drastically, leading to only small deviations from the straight line behavior, just as MP2 itself. This demonstrates the correlation of the fractional electron as the origin of the significantly improved description of fractional charges by correlated methods. Although the fractional charge behavior of MP2 is considerably better than for HF, the derivative is significantly less accurate than the integer result. Improving the treatment of electron correlation to CCSD and CCSD(T) not only gives more accurate integer results, but also the deviations from the straight line behavior are reduced considerably, being smallest for the highest level of theory, just as one would hope.

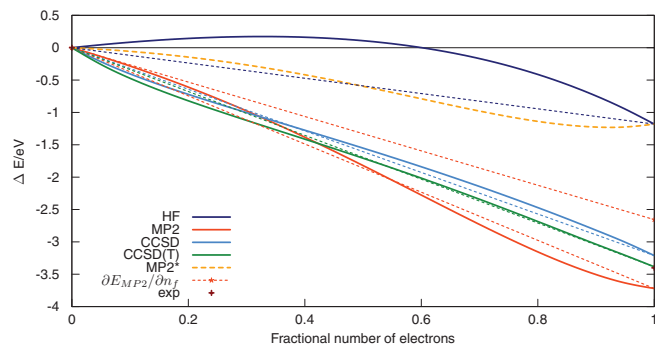


FIG. 3. (Fractional) electron affinity of a fluorine atom. Basis set: aug-cc-pVQZ.

In addition to dissociation limits, the real practical interest in the fractional charge behavior is its effect on the energy derivative with respect to the number of electrons (EA and IE) and the fundamental gap (Figure 4). In analogy to MP2 for the fluorine atom, the derivative can be significantly worse than the overall shape of the connection between the integers might indicate. Note that the method of Beste *et al.*<sup>41</sup> aims at reproducing the integer gap for MP2 through a numerical integration of the energy derivative. Indeed, this approach produces more accurate ionization potentials at the MP2 level (see Table I) (CH<sub>4</sub> is an exception) than our derivative at the integer number of electrons, although at the cost of several energy evaluations of fractionally charged systems.

As is well known, the LUMO energies (equivalent to the analytical derivative) of Hartree-Fock do not well describe the addition of an electron. Climbing to the MP2 level, the EA estimates are significantly more accurate, both from integer differences as well as from derivatives. While the basis set error (CCSD(T) reported herein compared to CCSD(T)/CBS of Ref. 60) is small, some of the CCSD derivatives are significantly off. The largest errors are obtained for atoms where the fractional electron is erroneously unbound at the HF level. However, these systems are outliers and the overall accuracy is much improved over HF.

For the ionization energy, no clear outliers are obtained for the derivatives, most likely because already the HF HOMOs show approximately the right trend, even though the results are biased (the ionization energy is too high). Including electron correlation improves the results. Nevertheless, MP2 overcorrects the HF predictions considerably in numerous cases and higher order methods are more adequate.

Since electron affinities (too low at the HF level) and ionization energies (too high) have the opposite error, their difference (the fundamental gap) has a larger error than either of them. Similarly, error cancellation at the MP2 level does not take place for the fundamental gap. However, for CCSD and CCSD(T), the gaps are in fair agreement, even though the few outliers in EA predictions affect, of course, the overall performance.

To get a statistical view on the performance of different methods for EA, IE, and the fundamental gap, Figure 5 summarizes the mean absolute deviations (MAD) for the estimates from  $\pm 1e^-$  and  $\pm 0.01e^-$ , for integer and derivative gap, respectively.

For the electron affinities (53 out of 81 are negative, indicating that the additional electron is unbound at the benchmark level), the impact of the basis set is almost as large



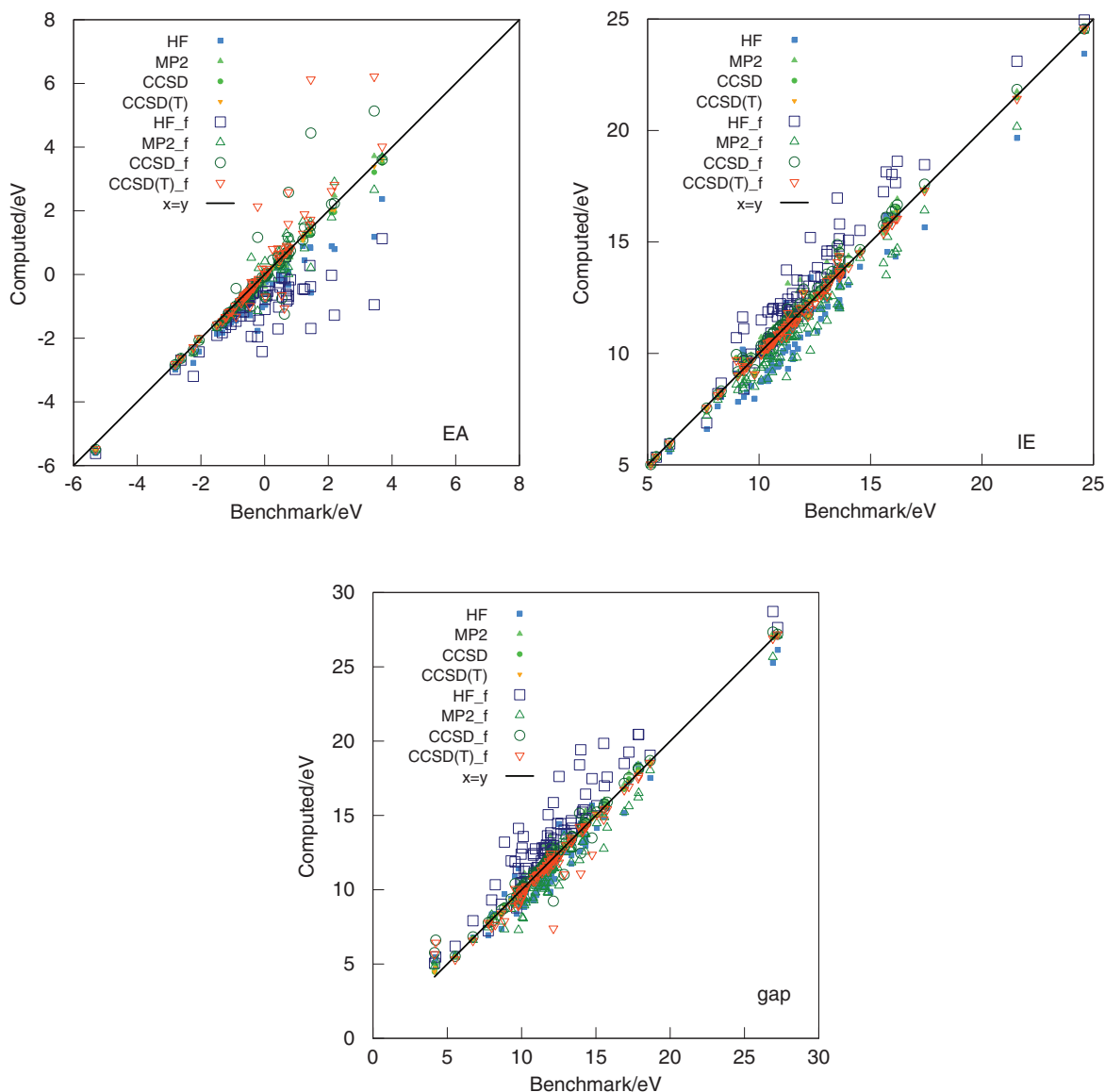


FIG. 4. (Top) electron affinities and ionization energies, bottom fundamental gaps for various methods compared to the CCSD(T)/CBS values of Ref. 60. The suffix “\_f” indicates numerical derivatives with  $\Delta e^- = 0.01$ .

as the difference between correlated methods, e.g., the MAD for MP2 and CCSD(T) is 0.13 and 0.07 eV, respectively, illustrating the good accuracy at integer numbers of electrons. For all methods the errors are larger when the derivative of the energy is considered, revealing some deviation from the straight line behavior.

Ionization potentials tell a somewhat different story, indicating that the electronic structure of the ionized molecules tends to be more challenging than that of the (at best weakly bound) electron attached states. Indeed, the expected hierarchy of methods is nicely reflected (with MP4 being an exception): both at the level of derivative gaps as well as integer gaps MP2 outperforms HF, but MP3 and MP4(SDQ) are progressively more accurate. Similarly, the integer gaps of CC2<sup>61</sup> are more accurate than HF, while CC2 IEs are less accurate than CCSD and CCSD(T). The most surprising observation is that CC2 seems to have a quite severe error for

the derivative gap. This finding is potentially concerning as CC2 has become some kind of a benchmark method for excitation energies of large molecules. One wonders if charge-transfer excitations might be intrinsically problematic for CC2 (see Ref. 62 for one example of a CT transition that is an “outlier”). In order to assess whether the finding that CC2 is especially inaccurate for fractional positive charges is a fluke (due to the approximate treatment of fractional charges) or real, the dissociation limit of a couple of singly charged diatomics is used to check the accuracy at least for the +0.5 points (see Table II). Not only is CC2 of similar (or slightly worse, for  $\text{Ne}_2^+$  even significantly worse) accuracy as MP2 for the stretched  $\text{X}_2^+$  molecules, but the error in the  $\text{X}^{0.5+}$  atom is significantly smaller than the error of the dissociation limit. This is not the case for the more accurate CCSD and CCSD(T) methods, where the two errors are of a similar magnitude. Therefore, CC2 seems to be affected by a non-negligible

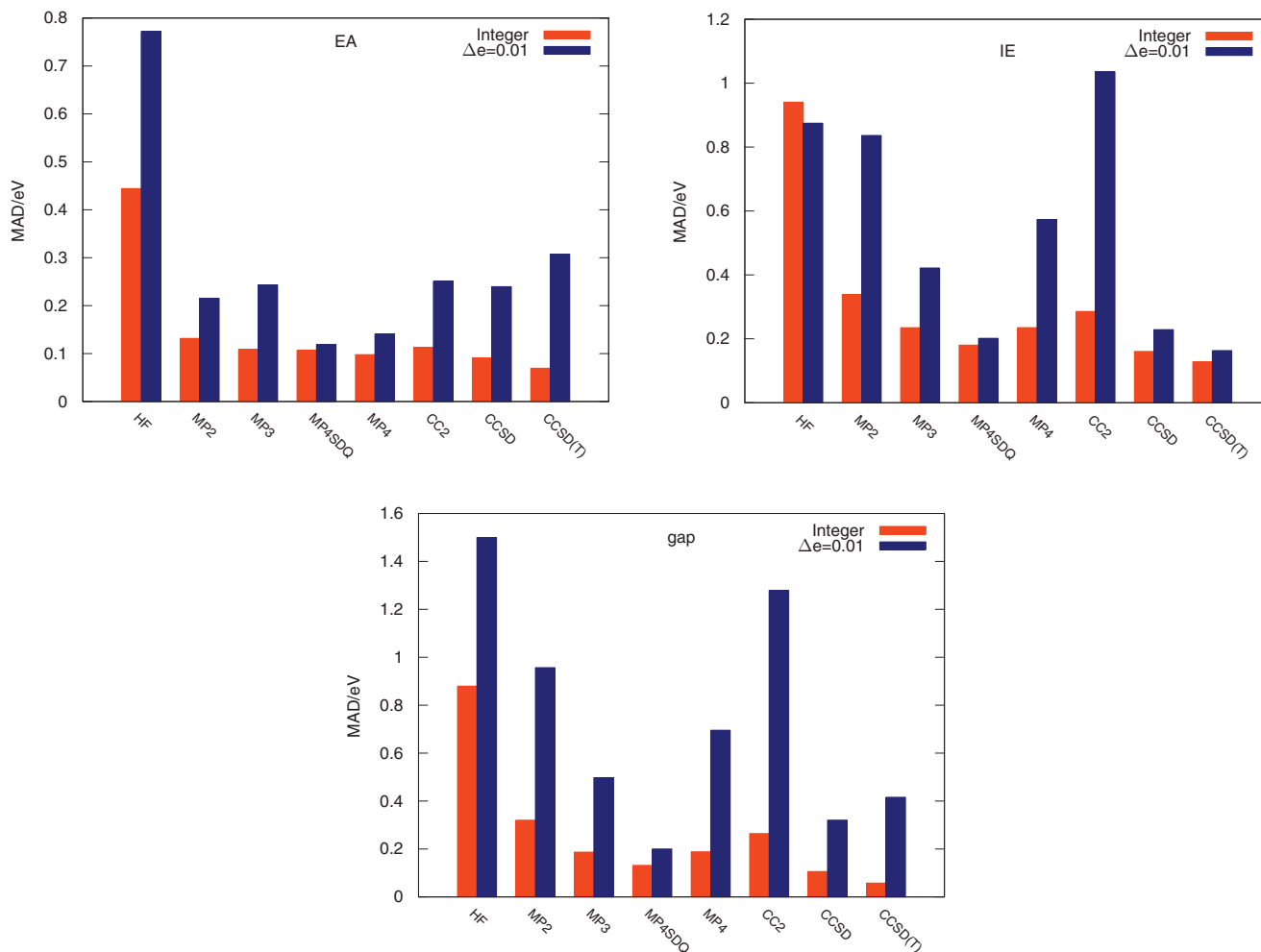


FIG. 5. Mean absolute deviations (MAD) of various methods for electron affinities, ionization energies, and fundamental gaps.

TABLE II. (Top) Reaction energies for  $X_2^+$  ( $R = 999 \text{ \AA}$ )  $\rightarrow X + X^+$  in  $\text{kcal mol}^{-1}$ . Basis set: aug-cc-pVQZ. “Instability” refers to the lowest eigenvalue in the HF molecular orbital stability matrix. (Bottom) Reaction energies for  $X_2^+$  ( $R = 999 \text{ \AA}$ )  $\rightarrow 2 X^{0.5+}$  in  $\text{kcal mol}^{-1}$ . Basis set: aug-cc-pVQZ. The small values of these reaction energies demonstrate the excellent quality of the fractional energy expressions through occupation number scaling.

	Instability	HF	MP2	MP3	MP4(SDQ)	MP4	CC2	CCSD	CCSD(T)
$\text{He}_2^+$	-8.60E-2	14.75	3.92	1.79	0.87	0.75	3.36	0.23	0.03
$\text{Li}_2^+$	-6.13E-5	0.01	-0.02	-0.01	0.00	0.00	-0.02	0.00	0.00
$\text{Be}_2^+$	-2.07E-2	3.55	-1.71	-1.35	-1.03	-1.21	-1.97	0.38	0.10
$\text{B}_2^+$	-3.96E-2	6.65	-0.80	-1.01	0.00	-0.84	-0.74	1.62	0.27
$\text{Ne}_2^+$	-2.06E-1	35.82	-7.04	4.81	3.11	-1.42	-12.16	2.10	-1.17
$\text{Na}_2^+$	-3.65E-4	0.06	-0.01	0.00	0.00	0.00	-0.01	0.00	0.00
$\text{Mg}_2^+$	-1.56E-2	2.68	-1.26	-0.53	-0.29	-0.47	-1.45	0.32	0.07
$\text{Al}_2^+$	-2.20E-2	3.64	-1.23	-0.91	0.05	-0.62	-1.14	0.94	0.13
$\text{Ar}_2^+$	-9.57E-2	16.31	-4.41	0.29	2.69	-0.65	-4.89	2.73	0.16
		HF	MP2	MP3	MP4(SDQ)	MP4	CC2	CCSD	CCSD(T)
$\text{He}_2^+$	0.00	0.00	0.00	0.00	0.18	0.07	0.01	0.40	0.20
$\text{Li}_2^+$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\text{Be}_2^+$	0.00	0.01	0.00	0.00	0.56	0.44	0.04	1.80	1.62
$\text{B}_2^+$	0.00	0.01	0.00	0.00	0.27	0.02	0.01	0.57	0.13
$\text{Ne}_2^+$	0.00	0.01	0.00	0.00	1.62	0.18	-1.40	0.04	-0.99
$\text{Na}_2^+$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\text{Mg}_2^+$	0.00	0.01	0.00	0.00	0.45	0.36	0.04	1.04	0.90
$\text{Al}_2^+$	0.00	0.01	0.00	0.00	0.21	0.05	0.01	0.38	0.14
$\text{Ar}_2^+$	0.00	0.01	0.00	0.00	1.40	0.23	0.04	1.38	0.40

delocalization error, despite being a non-trivial wave function method.

Last but not least, the MADs for the gap show a superposition of the trends found for EA and IE individually: when adding and subtracting an entire electron, the same trend as for the IE alone is obtained, i.e., the successively improved agreement with the reference values as the sophistication of the method increases. Similarly, the gaps derived from the derivative are dominated by the IE trend, except for CCSD and CCSD(T) which suffer from the rather poor performance of EA, or at least some of them: 10 atoms and 3 molecules have errors  $>0.5$  eV (max 4.6 eV for oxygen) when using the numerical derivative of CCSD(T), while only 7 have similarly large errors for IE (max 0.8 eV for methane).

In summary, the fractional charge behavior of standard wave function methods has been investigated and found to improve considerably over Hartree-Fock. In particular, the straight line condition is gradually better obeyed when accounting more and more accurately for electron correlation. Indeed, the energy for fractionally charged systems is closest to a straight line at the CCSD(T) level. Even though the fundamental gaps of correlated wave function methods improve over the HF gaps, the MP2 (and CC2) derivative gaps are, disappointingly, statistically not more accurate than the HF integer gap. According to our findings, the MP4(SDQ) gaps might offer a good accuracy/performance ratio for EA, IE, and the fundamental gap, even though the accuracy might deteriorate in small-gap systems such as semi-conductors.

## B. Fractional spins of many electron atoms

Fractional spins correspond to exact degeneracies of (spin)orbitals and are therefore archetypical systems for

strongly correlated materials. Thereby they shed light on the performance of a method in the strongly correlated limit of physical systems.

Three processes are monitored to assess the fractional spin behavior: (a) spin-polarization, i.e., from  $X(2S\alpha)$  to  $X(2S\beta)$  with  $\delta = 0.5$  being the spin-unpolarized atom  $X(S\alpha, S\beta)$ . (b) Sphericalization of the unpaired electrons in p-orbitals according to  $\rho_{fs}(\delta) = \delta/2[\rho_1(2S\alpha) + \rho_2(2S\alpha)] + (1 - \delta)\rho_3(2S\alpha)$  from  $\delta = 0$  where no fractional spins occur to  $\delta = 1$  with 2 fractional spins; for  $0 < \delta < 1$ , there are three fractional spins. (c) is the combination of (a) and (b), i.e., the sphericalization of the spin-compensated atom: all the occupations in (b) are divided by two to equally occupy the  $\alpha$  and  $\beta$  orbitals. Therefore, during the entire process fractional spins occur. Nevertheless, the number of fractional spins increases from 2 for doublets and 4 for triplets to 6. For oxygen and fluorine,  $\delta = 1$  still corresponds to six fractional spins (e.g.,  $F(p_x^{0.75}, p_y^{0.75}, p_z^{0.5})$  for both spin channels).

Figure 6 presents the HF results: the spin-unpolarized atoms (a) are the most problematic cases and the error increases with the number of unpaired electrons (boron vs. carbon) and with the number of electrons in the same shell (e.g., boron vs. fluorine). The sphericalization (b) is less problematic, most likely because the exchange between the same-spin electrons is conserved. Nevertheless, the increased Coulomb repulsion in the spherical density is not compensated. Sphericalization of a spin-compensated atom (c) has, somewhat surprisingly, the lowest errors. This is most likely the result of strong error compensation: the starting point ( $\delta = 0$ ) corresponds to the maximum error during spin-compensation (a) and the additional increase in Coulomb repulsion by spatial averaging is smaller than in (b) because only half as many electrons (per spin) are involved. Indeed, to a good

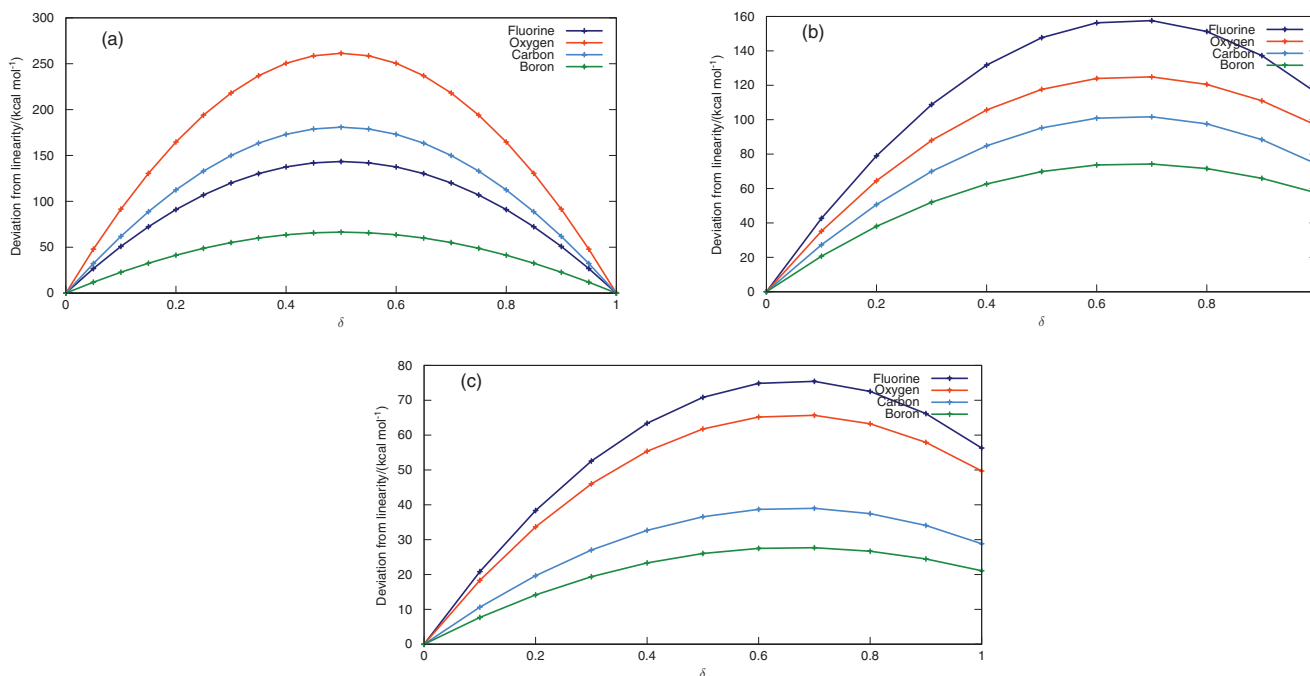


FIG. 6. (Top left) spin-polarization (a), (top right) sphericalization of atomic densities (b), and (bottom) sphericalization of spin-compensated atoms (c) at the HF/def2-QZVP level of theory

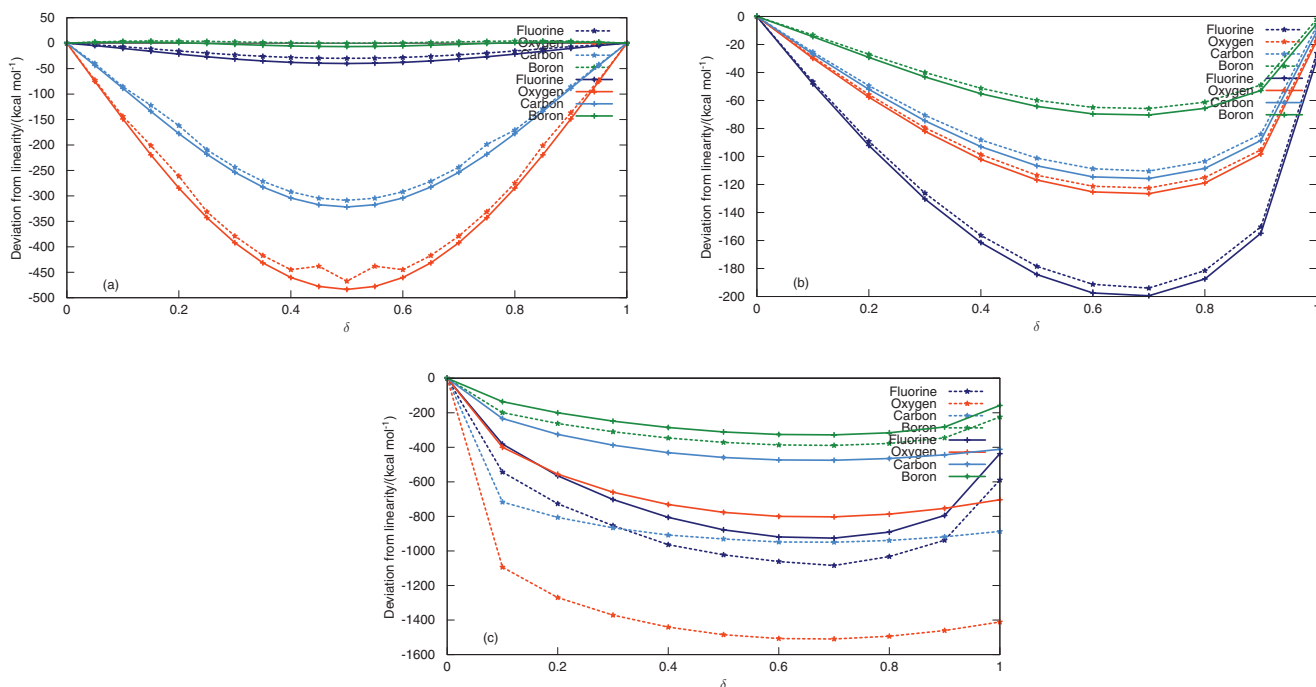


FIG. 7. (Top left) spin-polarization (a), (top right) sphericalization of atomic densities (b), and (bottom) sphericalization of spin compensated atoms (c) at the MP2/def2-QZVP (full lines) and MP2\*/def2-QZVP (broken lines) level of theory

approximation, the sphericalization errors are halved by considering spin-compensated systems (c).

MP2 is not expected to be a good approximation for fractional spins. Nevertheless, due to the amplitude constraint (or the use of DCPT2), results can be obtained (see Figure 7). Interestingly, the amplitude constraint is an excellent approximation as long as only two fractionally occupied orbitals are

involved, i.e., the spin-constancy condition (a) for boron and fluorine is reasonably well met and, similarly, the spatial degeneracy between two orbitals ( $\delta = 1$  in (b)) is described by smaller errors than at the HF level (and opposite sign because of overestimation of the correlation). However, for three and more degenerate orbitals, even when constraining the amplitudes, MP2 is a disaster. Just like for the fractional charge,

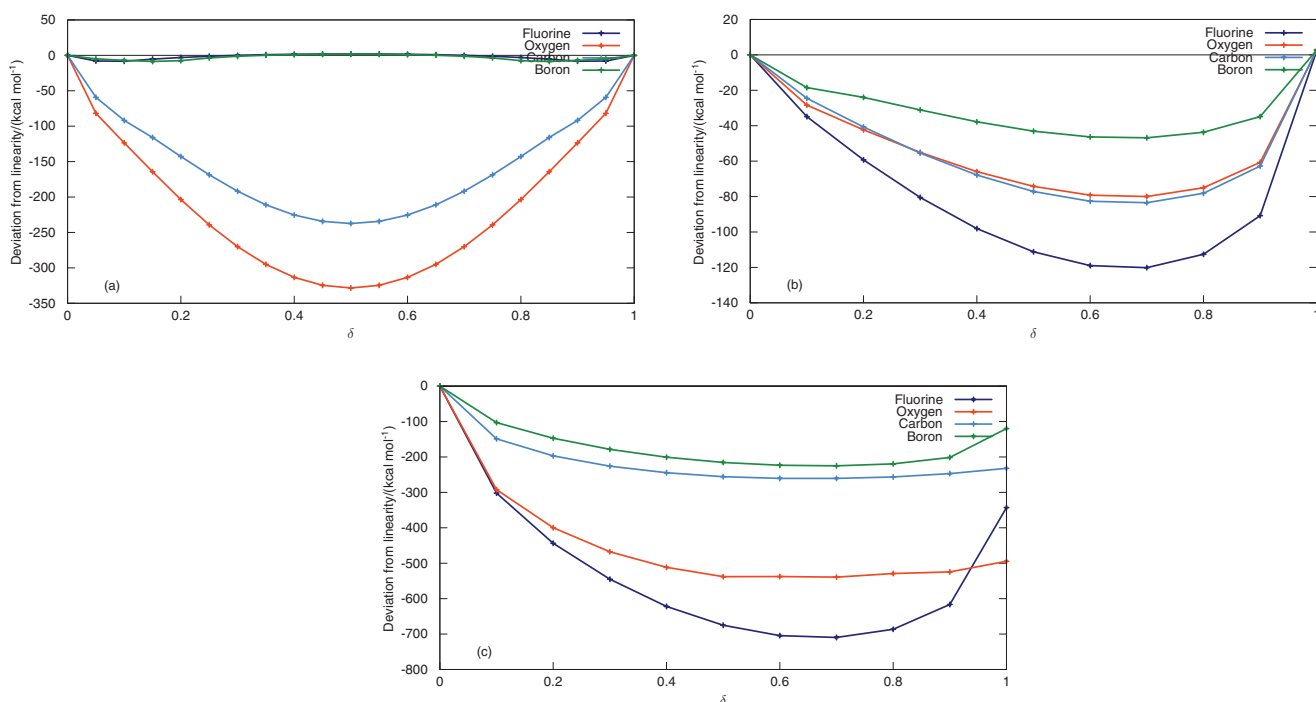


FIG. 8. (Top left) spin-polarization (a), (top right) sphericalization of atomic densities (b), and (bottom) sphericalization of spin compensated atoms (c) at the CCSD/def2-QZVP level of theory.

MP2\* recovers all the improved performance compared to HF. This indicates that the Coulomb repulsion between the fractional electron and all the others is key for improving the concave behavior of Hartree-Fock for fractional electrons.

From molecular computations it is known that CCSD is well able to break single bonds and therefore two degenerate occupied/unoccupied orbital pairs should not constitute a problem. Indeed, fractional computations follow these expectations (Figure 8): the spin-constancy condition for boron and fluorine are much better respected for CCSD than for MP2 and the spatial degeneracy between two orbitals ( $\delta = 1$  in process (b)) is essentially exactly recovered. However, multiple bonds, i.e., three and more degenerate occupied orbitals, are beyond the capabilities of CCSD. The over-correction compared to HF is more severe than the HF error itself and the error of CCSD only marginally smaller than that for MP2. We speculate that a method such as perfect hexuples<sup>63</sup> would be able to deal with this challenging situation.

The over-correction of CCSD can be limited to a certain extent by applying CISD instead of CCSD (Figure 9). Since CISD is not size consistent, fractional numbers of electrons have no strict physical meaning within this methodology. Nevertheless, it can be insightful to analyze the fractional charge behavior compared to CCSD: CISD is a variational method and the large amplitudes obtained with CCSD do not occur, even in systems with more than two degenerate occupied orbitals. However, in some cases multiple solutions seem to lie close to each other, which explains the irregular behavior for fractional spins of up to 0.2 electrons. The Davidson Q-correction<sup>64</sup> (full lines) is supposed to restore size consistency approximately and can be motivated by considering an assembly of non-interacting two-electron systems. The cor-

rection is relatively effective for breaking one bond, single or double (spin unpolarized carbon and oxygen do not have significantly larger errors than spin unpolarized boron and fluorine). Nevertheless, for spatial degeneracies, the Davidson Q-correction is ineffective. The comparably better performance of CISD for the spin-compensated sphericalization process is most likely a coincidence, based on the poor performance for the  $\delta = 0$  point, i.e., the spin unpolarized, maximally asymmetric atom, corresponding to  $\delta = 0.5$  of the spin-polarization process.

As a final example, the energy of the nitrogen atom as a function of the electron number is shown in Figure 10. The fractional charge error (parabolas) for the positively charged nitrogen atom is rather small, diminishing with the number of electrons in the system and excellently reduced by CCSD(T). In contrast, the fractional spin error (due to spatial degeneracy in this case, the atom is kept spin polarized) is significant and leads to qualitative failures: not only is the derivative discontinuity at integers lost, but the error at integers is not even significantly smaller! The spin-unpolarized, equivalent plot (with 6 instead of 3 fractional spins) would be even worse, as the error for the neutral nitrogen atom itself reaches  $\sim 1.2$  hartrees at the CCSD level.

In summary, the description of fractional spins is intriguingly difficult, with the challenge being to go beyond two-fold degeneracies. CCSD treats fractional spins well, as long as there are only two fractionally occupied orbitals, a case which is already well described at the MP2 (or rather DCPT2) level. Dealing with three and more fractionally occupied orbitals requires to go beyond “nominally” pair-correlation methods, i.e., significantly higher order methods, methods based on a multireference wave functions or, possibly, exploiting

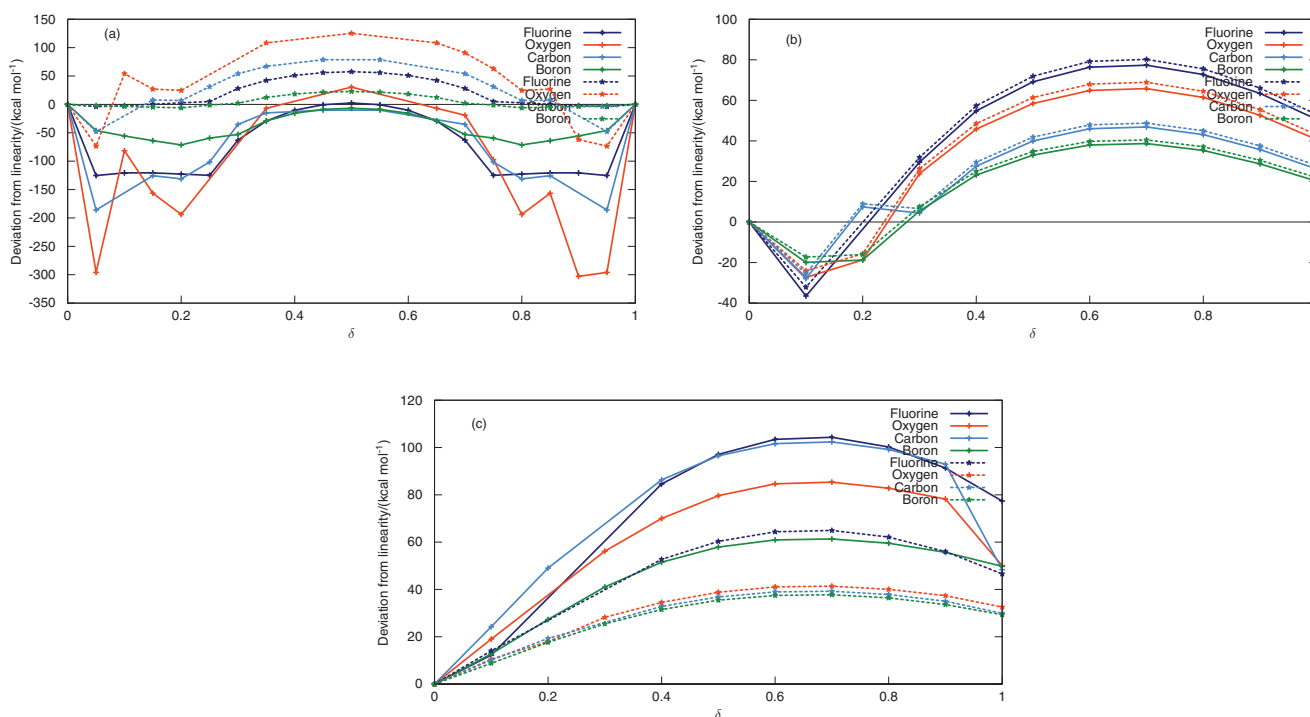


FIG. 9. (Top left) spin-polarization, (top right) sphericalization of atomic densities, and (bottom) sphericalization of spin-compensated atoms at the CISD(+Q)/def2-QZVP (full lines) and CISD/def2-QZVP (broken lines) level of theory.

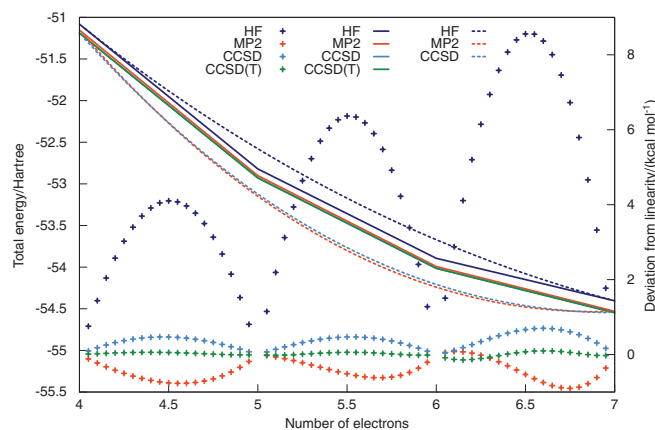


FIG. 10. Nitrogen atom ( $N^{3+} \rightarrow N^0$ ). Full lines: straight lines between integer numbers of electrons and spins, broken lines: energy of the fractional charge and fractional spin, spherical symmetric nitrogen atom; secondary y axis (and points): fractional charge error. Basis set: def2-QZVP.

effective exchange holes, defining local fractional electron numbers.

## V. CONCLUSION

We have extended single reference wave function theories to fractional electrons, probing the fractional charge and fractional spin error of popular techniques such as CCSD. The energy derivatives with respect to the number of electrons (ionization energy and electron affinity) are well behaved and show overall the expected systematic improvement with increasing sophistication of the correlation treatment. The fractional extension of coupled-cluster illustrates that gap predictions of considerably higher accuracy than with MP2 can be obtained at the CCSD level. The improvement through post-HF methods is based on the more accurate description of integer numbers of electrons due to electron correlation and, additionally, on the Coulomb correlation between the fractionally occupied orbital and all others, yielding a near straight line between integer numbers. As expected, we find that CCSD describes two degenerate fractionally occupied orbitals well, but is inadequate for three and more fractional spins. For more than one pair of strongly correlated electrons, variational methods (e.g., CISD) might be more suitable, but are no substitute for genuine multireference methods. Despite the computational expense of the explored popular wave function techniques, these methods become available in solid state codes and promise the advantage of an integrated approach: fundamental gap, relative energies, and optimal geometries can be obtained at the same, highly accurate, level.

## ACKNOWLEDGMENTS

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