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Fractional charge and spin errors in self-consistent Green's function theory

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We examine fractional charge and spin errors in self-consistent Green's function theory within a second-order approximation (GF2). For GF2, it is known that the summation of diagrams resulting from the self-consistent solution of the Dyson equation removes the divergences pathological to second-order Møller-Plesset (MP2) theory for strong correlations. In the language often used in density functional theory contexts, this means GF2 has a greatly reduced *fractional spin error* relative to MP2. The natural question then is what effect, if any, does the Dyson summation have on the *fractional charge error* in GF2? To this end, we generalize our previous implementation of GF2 to open-shell systems and analyze its fractional spin and charge errors. We find that like MP2, GF2 possesses only a very small fractional charge error, and consequently minimal many electron self-interaction error. This shows that GF2 improves on the critical failings of MP2, but without altering the positive features that make it desirable. Furthermore, we find that GF2 has *both* less fractional charge and fractional spin errors than typical hybrid density functionals as well as random phase approximation with exchange. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4921259]

I. INTRODUCTION

Self-consistent single-particle electronic structure methods are of great interest because they combine conceptual and computational simplicity while being free of a starting reference bias. Probably, the most well known example of this is density functional theory (DFT).[1] Often these methods are designed to satisfy known constraints that an exact electronic structure theory should obey. For example, the total electronic energy should vary linearly in the fractional electron occupancy between integer electron numbers,[2–5] while for a simple one-electron system like the hydrogen atom, the energy should be degenerate with respect to variations in the fractional spin.[6] To the extent that a method disobeys these two exact constraints, such a method will display many electron self-interaction error (SIE) and static correlation error, respectively. To understand how these errors are connected to fractional electron behavior, let us consider the H_2 molecule in the infinite dissociation limit in two different scenarios.

First, let us focus on a *fractional charge error*. If an extra electron were placed on this system with fractional occupancies on each H atom given by n_a, n_b, $n_a + n_b = 1$, then the net energy change of the system would be $E_\Delta = -(n_a A + n_b A) = -A$, where A is the electron affinity of the hydrogen atom. The energy of each subsystem would vary linearly in the occupation, and the total energy of the entire $[H_2]^-$ system would be the same regardless if the extra electron were delocalized across both atoms, or localized only on one. If the energy of the subsystem varied nonlinearly, then either the delocalized or localized solution would become unphysically lower in energy depending on whether the curve was convex or concave. This unphysical behavior would be a simple manifestation of many electron self-interaction error.

Let us examine now a *fractional spin error*. For neutral singlet H_2 in the infinite dissociation limit, each H atom should have half a spin up and down electron, and the energy of the singlet should be identical to that of broken-symmetry solutions where spin up and spin down electrons have localized on different atoms; therefore, a method's failure to yield equivalent energies for one-electron H with fractional or integer spin is equivalent to the failure to describe multireference static correlation energy.

From this simple example, it is clear that fractional charge and fractional spin errors are deeply connected to many electron self-interaction and static correlation errors. For this reason, these errors have been studied extensively and are known to have severe negative consequences for a given method's description of properties that depend on electron delocalization and static correlation effects.[6–11] This language of fractional charge and spin has traditionally been used mainly within the DFT community to analyze approximate density functionals; however, these concepts have begun to make inroads into other areas such as wavefunction[12] and many-body theory,[13–17] and density matrix theory as well.[18] For example, it has been shown that MP2 (second order Møller-Plesset[19]) possesses relatively little fractional charge error but displays a massive diverging fractional spin error (which is an alternative way of stating that MP2 diverges for strong correlations).[13] Double-hybrid density functionals that include some MP2 correlation are expected to have a similar fractional electron behavior.[20,21] The Random Phase Approximation (RPA)[22] on the other hand has minimal fractional spin error, but a severe fractional charge error.[14] The closely related GW approximation[23] displays a fractional charge error similar to RPA, but a larger fractional spin error.[17]

Motivated by these works, we find it interesting to extend this analysis to self-consistent Green's function theory in a second order approximation (GF2).[24,25] Similar to MP2, GF2 includes all diagrams to second order in the bare

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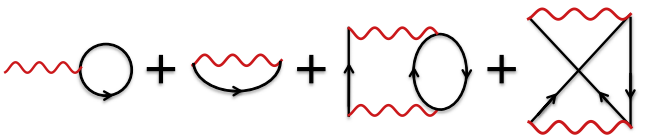

FIG. 1. Feynman diagrams for the second order self-energy in GF2. Here a red wavy line represents a two electron integral, while a black arrow line represents a Green's function. From left to right the diagrams shown are the first order Hartree and exchange diagrams, and the second order pair bubble and second order exchange.

electron-electron interaction, as shown in Figure 1, and is therefore exact for one electron systems; however, in contrast to MP2, these diagrams are evaluated with self-consistent Green's functions, obtained by iterative solution of the Dyson equation,

$$\begin{aligned} G(\omega) &= G_0(\omega) + G_0(\omega)\Sigma(\omega)G_0(\omega) \\ &\quad + G_0(\omega)\Sigma(\omega)G_0(\omega)\Sigma(\omega)G_0(\omega) + \cdots \\ &= G_0(\omega)\Big(\sum_n \big(\Sigma(\omega)G_0(\omega)\big)^n\Big) \\ &= \big[G_0(\omega)^{-1} - \Sigma(\omega)\big]^{-1}. \end{aligned} \tag{1}$$

Here, $G_0(\omega)$ is the Green's function of a non-interacting system, while $\Sigma(\omega)$ is the proper self-energy, which in GF2 is truncated at second order and written as an approximate functional of the Green's function, $\Sigma[G(\omega)]$. Because of the structure of the Dyson equation, the self-consistent $G(\omega)$ will contain an infinite order summation of the second order proper self-energy parts, $\Sigma(\omega)$. As we recently showed, this summation of diagrams allows GF2 to give reasonably fine results for strongly correlated systems such as stretched hydrogen lattices[24] when MP2 would diverge. In the language of fractional electron errors, this suggests that GF2 improves tremendously over MP2 for fractional spins as a result of the self-consistent infinite order summation. An interesting question that arises then is what effect does this Dyson summation have on the more general fractional electron behavior? Relative to other methods such as RPA, GW, approximate DFT, and Hartree-Fock (HF), MP2 has only a very small fractional charge error,[13] and consequently little many electron SIE. Ideally, one would hope that GF2 improves on the disastrous fractional spin error of MP2 without deteriorating MP2's impressively small fractional charge error. To investigate this question, here, we will generalize our previous GF2 implementation[24] to open-shell systems and then investigate its fractional charge and spin behavior.

Before closing this section, it should be emphasized that what is challenging about the fractional charge and fractional spin errors is that any attempt to reduce one error tends to exacerbate the other.[14,26,27] For example, a semilocal DFT functional (such as BLYP[28,29] or PBE[30]) will tend to have a large fractional charge error but a relatively smaller fractional spin error. On the other end of the extreme Hartree-Fock will have significantly less fractional charge error but a much greater fractional spin error. Any hybrid of these two (B3LYP[29,31] or PBEh,[30,32] for example) will essentially trade one error for the other to the extent that the HF-type exchange is admixed in place of DFT exchange. What is worth noting is that, in the language of hybrid DFT, the Fock matrix in GF2 contains full HF-type exchange (which in Green's function theory is usually referred to as first order exchange); yet, we will show GF2 yields *both* less fractional charge and fractional spin errors than HF, B3LYP, and PBEh. This unique result comes about from a combination of the Dyson summation with including all diagrams to second order.

II. SPIN UNRESTRICTED GF2 THEORY

To study open-shell systems, we generalize $\mathbf{G}(\omega)$ to have two spin blocks,

$$\mathbf{G} = \begin{bmatrix} \mathbf{G}_\alpha & \mathbf{0} \\ \mathbf{0} & \mathbf{G}_\beta \end{bmatrix}, \tag{2}$$

where the spin-up and spin-down blocks are given by

$$\mathbf{G}_\sigma(\omega) = \big[(\mu_\sigma + \omega)\mathbf{S} - \mathbf{F}_\sigma - \mathbf{\Sigma}_\sigma(\omega)\big]^{-1}, \quad \sigma = \alpha, \beta. \tag{3}$$

The off-diagonal spin-blocks of $\mathbf{G}(\omega)$ here are identically $\mathbf{0}$, meaning we do not allow for the possibility of spin-flips, and our solutions are constrained to be eigenstates of $\hat{S}_z$. In Eq. (3), $\mathbf{S}$ and $\mathbf{F}_\sigma$ are the overlap and Fock matrices, $\mathbf{\Sigma}_\sigma(\omega)$ is the self-energy, μ_σ is the chemical potential, and ω is an imaginary frequency. By introducing μ_α, μ_β as separate chemical potentials, we can allow for different numbers of electrons in the respective correlated density matrices, $\mathbf{P}_\alpha$, $\mathbf{P}_\beta$, which are given by $\mathbf{P}_\sigma = -\mathbf{G}_\sigma(\tau = 1/k_B T)$, $\sigma = \alpha, \beta$, where $\mathbf{G}_\sigma(\tau)$ is the Green's function fast Fourier transformed (FFT)[33] to the imaginary time domain, and $1/k_B T$ is the inverse-temperature. The expression for $\mathbf{F}_\sigma$ is the standard result from spin-unrestricted HF theory,

$$\begin{aligned} F^\alpha_{ij} &= h_{ij} + \sum_{kl}(P^\alpha_{kl} + P^\beta_{kl})\mathrm{v}_{ijkl} - P^\alpha_{kl}\mathrm{v}_{iklj}, \\ F^\beta_{ij} &= h_{ij} + \sum_{kl}(P^\alpha_{kl} + P^\beta_{kl})\mathrm{v}_{ijkl} - P^\beta_{kl}\mathrm{v}_{iklj}. \end{aligned} \tag{4}$$

However, unlike HF theory, the density-matrices that enter this expression are those obtained from the Green's function and thus include electron correlation effects from solving the Dyson equation. This covers the electron-electron interaction from zeroth through first order (the first order diagrams in Figure 1 are described by the HF mean-field). At second order in GF2, the electron-electron interaction is described by the frequency dependent self-energy, which is given in the imaginary time domain as

$$\begin{aligned} \Sigma^\alpha_{ij}(\tau) &= \sum_{klmnpq} -G^\alpha_{mn}(\tau)G^\alpha_{kl}(\tau)G^\alpha_{pq}(-\tau)\mathrm{v}_{imqk}\big(\mathrm{v}_{lpnj} - \mathrm{v}_{nplj}\big) - G^\alpha_{mn}(\tau)G^\beta_{kl}(\tau)G^\beta_{pq}(-\tau)\mathrm{v}_{imqk}\mathrm{v}_{lpnj}, \\ \Sigma^\beta_{ij}(\tau) &= \sum_{klmnpq} -G^\beta_{mn}(\tau)G^\beta_{kl}(\tau)G^\beta_{pq}(-\tau)\mathrm{v}_{imqk}\big(\mathrm{v}_{lpnj} - \mathrm{v}_{nplj}\big) - G^\beta_{mn}(\tau)G^\alpha_{kl}(\tau)G^\alpha_{pq}(-\tau)\mathrm{v}_{imqk}\mathrm{v}_{lpnj}. \end{aligned} \tag{5}$$

The reasoning for this expression is that at second order, a spin-up (down) electron can have a pair-bubble interaction with both spin-up and down electrons; yet, the second-order exchange (SOX) can only proceed between like-spin electrons because we do not allow for the possibility of spin-flips. Once $\mathbf{\Sigma}_\sigma(\tau)$ has been built, it can be FFT to the frequency domain, and then we can rebuild $\mathbf{G}_\sigma(\omega)$ with Eq. (3). Looking at Eqs. (3)–(5), the spin-up and spin-down Green's functions are coupled by the fact that $\mathbf{G}_\beta$ appears in the expression for $\mathbf{\Sigma}_\alpha$ (likewise with $\mathbf{G}_\alpha$ for $\mathbf{\Sigma}_\beta$), and that $\mathbf{G}_\beta$ contributes to $\mathbf{F}_\alpha$ through $\mathbf{P}_\beta = -\mathbf{G}_\beta(\tau = 1/k_BT)$ (likewise with $\mathbf{G}_\alpha$, $\mathbf{P}_\alpha$, and $\mathbf{F}_\beta$); therefore, (3)–(5) will need to be solved self-consistently, and at every iteration, μ_α and μ_β will need to be adjusted to give the desired number of α and β electrons. To start this self-consistent procedure, we use a HF Green's function generated by output from the Dalton program.[34] Note when $\mathbf{G}_\alpha = \mathbf{G}_\beta$, then $\mathbf{\Sigma}_\alpha = \mathbf{\Sigma}_\beta$ and Eq. (5) reduces to the familiar expression for spin-restricted GF2.[24,25]

Overall in the large system limit, the most CPU time intensive step in this procedure will be the self-energy formation in Eq. (5). With appropriate programming, this step scales as $N_\tau N_b^5$, where N_τ and N_b are the number of imaginary time grid points and basis functions, respectively. For the practical numerical evaluation of $\mathbf{\Sigma}(\tau)$ in Eq. (5), we use a power mesh imaginary time grid[35] that spans the interval $0 \leq \tau \leq 1/k_BT$. It is important to understand that for each time grid point τ_n, the building of $\mathbf{\Sigma}(\tau_n)$ is completely independent, and thus as a whole the self-energy formation is embarrassingly parallel; therefore, in practical calculations, the N_τ prefactor will be reduced to N_τ/N_{proc}, where N_{proc} is the number of available processors. Furthermore, it should be emphasized that the second order diagrams in Eq. (5), along with the entirety of the GF2 procedure, are written and can be implemented in the local atomic-orbital (AO) basis; therefore, this means that first, the sparsity of the integrals can be exploited to reduce the computational cost, and second, that GF2 is a natural formalism for Green's function-based embedding approaches.[36,37]

The energy is evaluated as

$$E = \frac{1}{2}\mathrm{Tr}\big[(\mathbf{h} + \mathbf{F}_\alpha)\mathbf{P}_\alpha + (\mathbf{h} + \mathbf{F}_\beta)\mathbf{P}_\beta\big] + k_BT \sum_n \mathrm{Re}\Big[\mathrm{Tr}\big[\mathbf{G}_\alpha(\omega_n)\mathbf{\Sigma}_\alpha(\omega_n) + \mathbf{G}_\beta(\omega_n)\mathbf{\Sigma}_\beta(\omega_n)\big]\Big], \tag{6}$$

where ω_n is a Matsubara frequency, $\omega_n = (2n+1)\pi k_BT$. This can be understood as essentially a spin-unrestricted HF-like energy expression supplemented with a frequency dependent correlation contribution from GF2, where the density matrix dependent terms are evaluated using the correlated $\mathbf{P}_\sigma$ as obtained from $\mathbf{G}_\sigma$. It should be noted that Eq. (6) is actually the Galitskii-Migdal expression,[38] but recast into a simpler form.[39,40] While there exist many non-unique expressions defining the total electronic energy in terms of $\mathbf{G}(\omega)$ (*e.g.*, the Luttinger-Ward[41] and Klein[42] functionals, in addition to Eq. (6)), at self-consistency, these different expressions all yield the same energy.[39] This is in fact an added benefit of performing Green's function calculations fully self-consistently. Furthermore, Green's functions obtained from the self-consistent solution of the Dyson equation will satisfy the conservation laws of the reference Hamiltonian,[43] meaning that for example particle number will be conserved[44] and the calculated energy will agree with the virial theorem.[25]

Because the GF2 approximation includes in the proper self-energy all exchange and Coulomb type diagrams to second order, it is by construction exact for one-electron systems, *i.e.*, it is one-electron self-interaction and self-correlation free. Less clear, however, is its many electron SIE for general systems. To this end, in the following, we investigate the fractional electron behavior of GF2 for several archetypical cases, and compare to standard density functional theory calculations ran with Gaussian 09.[45]

III. RESULTS

First, we consider a single hydrogen atom with fractional spin up and down electron occupations, n_α, n_β, that are varied in the interval $0 \leq n_\alpha \leq 1.0$ and $0 \leq n_\beta \leq 1.0$. For this case with an exact method, the energy should change linearly in the fractional electron number $n = n_\alpha + n_\beta$, while for constant n, it should be invariant with respect to changes in the fractional spin $m = n_\alpha - n_\beta$. Furthermore, there should be a discontinuity in the slope $dE(n)/dn$ across the line $n_\alpha + n_\beta = 1.0$. Hence, the resulting energy surface should be two flat planes that intersect along a seam.[10] In Figure 2, we show the exact result, compared against that obtained with spin-unrestricted GF2. If first we focus only on the edge of the plane where one occupation is held fixed at integer values of 0 or 1.0, this corresponds to the fractional charge behavior of a method and thus SIE. It is clear that GF2 reproduces the exact linear behavior almost perfectly, similar to the result for MP2 in Ref. 13. Now if we focus on the more interesting region towards the interior, discrepancies between GF2 and the

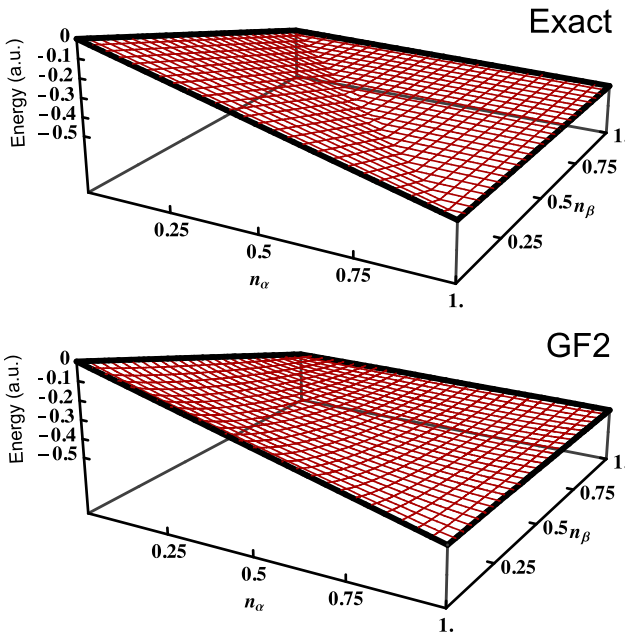

FIG. 2. The total energy for hydrogen with fractional spin up and down occupations n_α, n_β evaluated with aug-cc-pVDZ. Top: the exact result. Bottom: GF2.

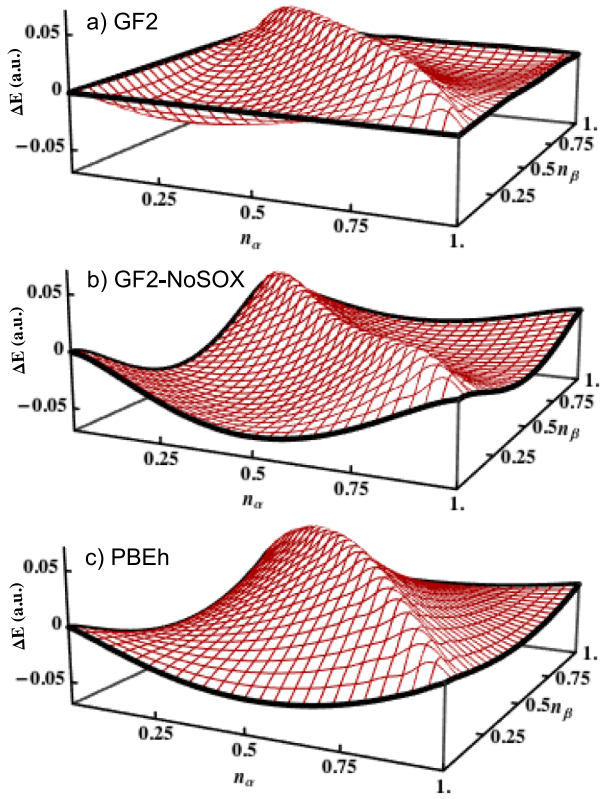

FIG. 3. The energy difference $\Delta E = E - E_{\text{lin}}$ for the hydrogen atom with fractional spin up and down occupations n_α, n_β, where E is the energy evaluated with fractional electron number, and E_{lin} is the flat-plane linear interpolation for (a) GF2, (b) GF2-NoSOX, and (c) hybrid PBEh. All calculations are with aug-cc-pVDZ.

exact flat-plane behavior become apparent. To see this more clearly, in Figure 3, we plot the difference between GF2 and its interpolated flat-plane surface. Looking at the diagonal region connecting the coordinates $\{n_\alpha = 1.0,\ n_\beta = 0.0\}$ and $\{n_\alpha = 0.0,\ n_\beta = 1.0\}$, we find a hill of fractional spin error, where GF2 is not able to fully recover the static correlation energy. On either side of the hill ($n_\alpha + n_\beta < 1.0$ and $n_\alpha + n_\beta > 1.0$), we find shallow valleys where GF2 moderately overestimates the correlation energy. The GF2 results here for fractional spin are in severe contrast to the MP2 result from Figure 4 of Ref. 13, which rapidly diverges to $-\infty$ correlation energy as one moves towards the center at $\{n_\alpha = 0.5,\ n_\beta = 0.5\}$.

For purpose of comparison, we also show in Figure 3 the surface obtained with PBEh, as well as the GF2 result obtained when the SOX diagram is neglected in the self-energy (we call this GF2-NoSOX for short). Neglect of the SOX diagram introduces an unphysical one electron self-correlation error at second order. Because many electron SIE and static correlation are known to be connected,[14,27,46–48] GF2-NoSOX should provide an interesting contrast to standard GF2. First, let us compare the energy landscapes for GF2 and PBEh. Despite being a hybrid functional, PBEh still yields a significant fractional charge error along the outer rim of the surface, along with a pronounced hill of fractional spin error running through the center. The GF2 energy landscape in contrast is appreciably flatter, with less fractional spin and fractional charge error. This is notable, because it has been stressed that simultaneously reducing the fractional charge and spin errors in a single-particle method is very difficult.[14] For example, RPA+X (RPA with HF-type exchange) greatly improves over the fractional charge error of RPA, but at the price of gaining a considerably larger fractional spin error that is comparable to Hartree-Fock.[14] Now let us examine the GF2-NoSOX result. As mentioned, neglect of the SOX diagram introduces a self-correlation error at second order, and as a result, GF2-NoSOX gives significant fractional charge errors comparable to PBEh. At the same time, the hill of fractional spin error is appreciably reduced relative to both PBEh and GF2.

To see the static correlation error more clearly, in Figure 4, we plot the energy with respect to fractional spin $m = n_\alpha - n_\beta$ for hydrogen with GF2, GF2-NoSOX, PBEh, B3LYP, and HF. This corresponds to the line running along the energy surface from the coordinates $\{n_\alpha = 1.0,\ n_\beta = 0.0\}$ to $\{n_\alpha = 0.0,\ n_\beta = 1.0\}$. As stated previously, an exact method should give a flat energy curve from $m = -1$ to $m = 1$. For example, HF has a massive hill at $m = 0$, which reflects the complete absence of static correlation energy in this method. Hybrid DFT yields much smaller fractional spin errors, with B3LYP being slightly lower than PBEh, likely because it includes less HF-type exchange than PBEh. In comparison, the fractional spin error is relatively lower for GF2, as a result of the infinite order summation from the Dyson equation recovering some static correlation. GF2-NoSOX has a much reduced fractional spin error relative to all four methods, with its energy at $m = 0$ being not much different from that at $m = \pm 1$. It has been understood for some time that SIE can mimic static correlation.[14,27,46–48] Usually, this is considered in the context of SIE resulting from incomplete cancellation of Coulomb and exchange terms at first order. GF2-NoSOX's small fractional spin error in contrast is purely arising from incomplete cancellation of Coulomb and exchange terms at second order, resulting in an unphysical one-electron self-correlation that mimics static

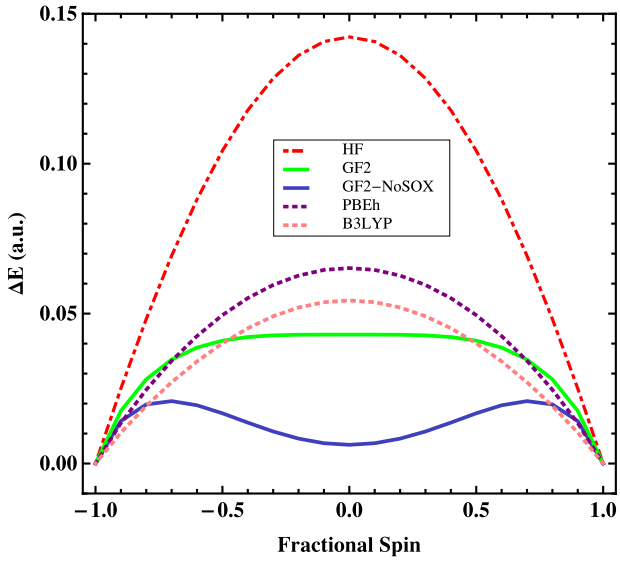

FIG. 4. The energy difference $\Delta E = E^X - E^X_{\text{int}}$ for the fractional spin hydrogen atom, where E^X is the energy from method X evaluated with the fractional spin population $m = n_\alpha - n_\beta$, $n_\alpha + n_\beta = 1$, and E^X_{int} is the energy from X with integer $m = \pm 1$. All calculations are with aug-cc-pVDZ.

correlation energy, analogous to the situation that occurs with RPA vs. RPA+SOSEX[27] (second order screened exchange). We think this is an example of getting the right result for the wrong reason. Furthermore, GF2-NoSOX must obtain this slightly reduced fractional spin error at the price of gaining a tremendous fractional charge error, which is not a desirable trade. In contrast, from comparing Figures 4 and 3, it is clear that GF2 has less static-correlation error than typical hybrid density functionals, and importantly achieves this while being essentially one and two electron self-interaction free. This means GF2 genuinely recovers some static correlation energy, rather than fortuitously exploiting spurious self-interaction or self-correlation. It is worth mentioning that a similar analysis has been performed for RPA and RPA+X.[14] Comparing our GF2 result in Figure 4 to Figure 1 in Ref. 14, GF2 yields an appreciably smaller fractional spin error than RPA+X, but is still larger than RPA.

Finally, to analyze the fractional charge error in closer detail, we consider the energy of helium with respect to fractional electron number. In Figure 5, we plot $E^X(n) - E^X_{\text{lin}}$, where $E^X(n)$ is the energy from method X for electron number $1.0 \le n \le 2.0$, while E^X_{lin} is the linear-interpolation between integer points with the same method. A method is said to be M-electron SIE free if $E^X(n) - E^X_{\text{lin}} = 0$ for $M - 1 \le n \le M$.[4] We find that GF2 has a very small concave curvature. In contrast, HF is moderately concave, while PBEh, B3LYP, and GF2-NoSOX are significantly convex. This clearly establishes that GF2 is one and almost perfectly two electron SIE free. Interestingly, comparing Figure 5 to Figure 4 in Ref. 14, it is reasonable to conclude that GF2 should have less SIE than both RPA and RPA+X.

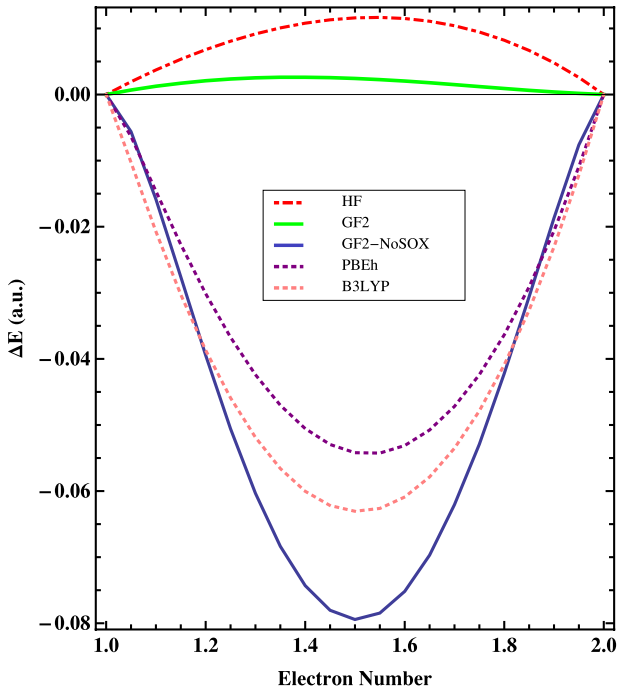

FIG. 5. The energy difference $\Delta E = E^X - E^X_{\text{lin}}$ for the helium atom, where E^X is the energy from method X evaluated with fractional electron number, and E^X_{lin} is the linear interpolation from method X. All calculations are with cc-pVTZ.

IV. CONCLUSIONS

We have analyzed fractional electron errors in self-consistent Green's function theory by generalizing our previous GF2 implementation[24] to open-shell systems. Overall, we find that GF2 has a very small fractional charge error and a moderate fractional spin error. In comparison to other well known methods, we find that GF2 has both less static correlation and self-interaction error than hybrid density functionals such as B3LYP and PBEh, as well as RPA+X and HF. Because the GW approximation is diagrammatically identical to RPA, GF2 will very likely have significantly less self-interaction error than GW as well. Furthermore, it has been shown that CCSD (coupled cluster singles doubles) has a roughly similar fractional charge error to MP2.[12] From this, it stands to reason that GF2 and CCSD will have comparable fractional charge errors.

Essentially, by virtue of the self-consistent Dyson summation, GF2 greatly improves on the tremendous fractional spin error of MP2, but without deteriorating MP2's relatively excellent fractional charge behavior. GF2 includes the second order exchange diagram, and such a diagram is important for the description of localized densities. Moreover, the iterative procedure includes a series of diagrams containing second order exchange, and due to the recalculation of the Fock matrix allows us to establish a new reference on which the perturbation is done, thus resulting in a much better scheme having a small perturbation at every step. These results could suggest a way towards removing the fractional spin error from double hybrid density functionals.[20,21]

As a further salient point, GF2 is fully self-consistent and thus the converged density should reflect the relative lack of many-electron self-interaction error in a second order approximation. MP2 in contrast does not revise the underlying mean-field reference and thus inherits the Hartree-Fock density with its bias towards localization. This suggests that GF2 could find good application for properties that sensitively depend on electron delocalization. For example, much of the interesting physics in transition metal complexes depends on the slight delocalization of unpaired d electrons onto ligands, which is determined by the interplay of dynamic correlation and self-interaction error effects.[49]

Conceptually, GF2 is essentially a self-consistent single-particle theory where the energy is expressed as a functional of the single-particle Green's function $E[G]$, in obvious analogy to DFT with density functionals $E[\rho]$. In terms of the energy, it is fair to say GF2 is a "Green's function functional" with desirable fundamental properties compared to standard hybrid density functionals.

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[1]P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[2]J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Jr., Phys. Rev. Lett. **49**, 1691 (1982).

[3]P. Mori-Sánchez, A. J. Cohen, and W. Yang, J. Chem. Phys. **125**, 201102 (2006).
[4]A. Ruzsinszky, J. P. Perdew, G. I. Csonka, O. A. Vydrov, and G. E. Scuseria, J. Chem. Phys. **126**, 104102 (2007).
[5]J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, V. N. Staroverov, and J. Tao, Phys. Rev. A **76**, 040501 (2007).
[6]A. J. Cohen, P. Mori-Sánchez, and W. Yang, J. Chem. Phys. **129**, 121104 (2008).
[7]O. A. Vydrov, G. E. Scuseria, and J. P. Perdew, J. Chem. Phys. **126**, 154109 (2007).
[8]A. J. Cohen, P. Mori-Sánchez, and W. Yang, Phys. Rev. B **77**, 115123 (2008); P. Mori-Sánchez, A. J. Cohen, and W. Yang, Phys. Rev. Lett. **100**, 146401 (2008).
[9]E. R. Johnson, P. M. Sánchez, A. J. Cohen, and W. Yang, J. Chem. Phys. **129**, 204112 (2008).
[10]P. Mori-Sánchez, A. J. Cohen, and W. Yang, Phys. Rev. Lett. **102**, 066403 (2009).
[11]E. R. Johnson and J. Contreras-García, J. Chem. Phys. **135**, 081103 (2011).
[12]S. N. Steinmann and W. Yang, J. Chem. Phys. **139**, 074107 (2013).
[13]A. J. Cohen, P. Mori-Sánchez, and W. Yang, J. Chem. Theory Comput. **5**, 786 (2009).
[14]P. Mori-Sánchez, A. J. Cohen, and W. Yang, Phys. Rev. A **85**, 042507 (2012).
[15]H. van Aggelen, Y. Yang, and W. Yang, Phys. Rev. A **88**, 030501 (2013).
[16]W. Yang, P. Mori-Snchez, and A. J. Cohen, J. Chem. Phys. **139**, 104114 (2013).
[17]M. Hellgren, F. Caruso, D. R. Rohr, X. Ren, A. Rubio, M. Scheffler, and P. Rinke, Phys. Rev. B **91**, 165110 (2015).
[18]H. Van Aggelen, P. Bultinck, B. Verstichel, D. Van Neck, and P. W. Ayers, Phys. Chem. Chem. Phys. **11**, 5558 (2009).
[19]C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
[20]N. Q. Su and X. Xu, Int. J. Quantum Chem. **115**, 589 (2015).
[21]N. Q. Su, W. Yang, P. Mori-Snchez, and X. Xu, J. Phys. Chem. A **118**, 9201 (2014).
[22]D. Bohm and D. Pines, Phys. Rev. **82**, 625 (1951); D. Pines and D. Bohm, *ibid.* **85**, 338 (1952); D. Bohm and D. Pines, *ibid.* **92**, 609 (1953); M. Gell-Mann and K. A. Brueckner, *ibid.* **106**, 364 (1957).
[23]L. Hedin, Phys. Rev. **139**, A796 (1965).
[24]J. J. Phillips and D. Zgid, J. Chem. Phys. **140**, 241101 (2014).
[25]N. E. Dahlen and R. van Leeuwen, J. Chem. Phys. **122**, 164102 (2005).
[26]R. Haunschild, T. M. Henderson, C. A. Jiménez-Hoyos, and G. E. Scuseria, J. Chem. Phys. **133**, 134116 (2010).
[27]T. M. Henderson and G. E. Scuseria, Mol. Phys. **108**, 2511 (2010).
[28]A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[29]C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[30]J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); M. Ernzerhof and J. P. Perdew, J. Chem. Phys. **109**, 3313 (1998).
[31]A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
[32]C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).
[33]J. Keiner, S. Kunis, and D. Potts, ACM Trans. Math. Software **36**, Article No. 19:1 (2009).
[34]K. Aidas, C. Angeli, K. L. Bak, V. Bakken, R. Bast, L. Boman, O. Christiansen, R. Cimiraglia, S. Coriani, P. Dahle, E. K. Dalskov, U. Ekström, T. Enevoldsen, J. J. Eriksen, P. Ettenhuber, B. Fernández, L. Ferrighi, H. Fliegl, L. Frediani, K. Hald, A. Halkier, C. Hättig, H. Heiberg, T. Helgaker, A. C. Hennum, H. Hettema, E. Hjertenæs, S. Høst, I.-M. Høyvik, M. F. Iozzi, B. Jansík, H. J. A. Jensen, D. Jonsson, P. Jørgensen, J. Kauczor, S. Kirpekar, T. Kjærgaard, W. Klopper, S. Knecht, R. Kobayashi, H. Koch, J. Kongsted, A. Krapp, K. Kristensen, A. Ligabue, O. B. Lutnæs, J. I. Melo, K. V. Mikkelsen, R. H. Myhre, C. Neiss, C. B. Nielsen, P. Norman, J. Olsen, J. M. H. Olsen, A. Osted, M. J. Packer, F. Pawlowski, T. B. Pedersen, P. F. Provasi, S. Reine, Z. Rinkevicius, T. A. Ruden, K. Ruud, V. V. Rybkin, P. Sałek, C. C. M. Samson, A. S. de Merás, T. Saue, S. P. A. Sauer, B. Schimmelpfennig, K. Sneskov, A. H. Steindal, K. O. Sylvester-Hvid, P. R. Taylor, A. M. Teale, E. I. Tellgren, D. P. Tew, A. J. Thorvaldsen, L. Thøgersen, O. Vahtras, M. A. Watson, D. J. D. Wilson, M. Ziolkowski, and H. Ågren, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **4**, 269 (2014).
[35]A. Albuquerque, F. Alet, P. Corboz, P. Dayal, A. Feiguin, S. Fuchs, L. Gamper, E. Gull, S. Gürtler, A. Honecker, R. Igarashi, M. Körner, A. Kozhevnikov, A. Läuchli, S. Manmana, M. Matsumoto, I. McCulloch, F. Michel, R. Noack, G. Pawłowski, L. Pollet, T. Pruschke, U. Schollwöck, S. Todo, S. Trebst, M. Troyer, P. Werner, and S. Wessel, J. Magn. Magn. Mater. **310**, 1187 (2007).
[36]A. A. Rusakov, J. J. Phillips, and D. Zgid, J. Chem. Phys. **141**, 194105 (2014).
[37]A. A. Kananenka, E. Gull, and D. Zgid, Phys. Rev. B **91**, 121111 (2015).
[38]V. Galitskii and A. Migdal, Sov. Phys. JETP **7**, 96 (1958).
[39]N. E. Dahlen, R. van Leeuwen, and U. von Barth, Phys. Rev. A **73**, 012511 (2006).
[40]F. Caruso, P. Rinke, X. Ren, A. Rubio, and M. Scheffler, Phys. Rev. B **88**, 075105 (2013).
[41]J. M. Luttinger and J. C. Ward, Phys. Rev. **118**, 1417 (1960).
[42]A. Klein, Phys. Rev. **121**, 950 (1961).
[43]G. Baym, Phys. Rev. **127**, 1391 (1962).
[44]A. Stan, N. E. Dahlen, and R. van Leeuwen, J. Chem. Phys. **130**, 114105 (2009).
[45]M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, GAUSSIAN 09, Revision A.1, Gaussian, Inc., Wallingford, CT, 2009.
[46]V. Polo, E. Kraka, and D. Cremer, Mol. Phys. **100**, 1771 (2002).
[47]J. E. Bates and F. Furche, J. Chem. Phys. **139**, 171103 (2013).
[48]F. Caruso, D. R. Rohr, M. Hellgren, X. Ren, P. Rinke, A. Rubio, and M. Scheffler, Phys. Rev. Lett. **110**, 146403 (2013).
[49]J. Cabrero, C. J. Calzado, D. Maynau, R. Caballol, and J. P. Malrieu, J. Phys. Chem. A **106**, 8146 (2002).