Variations of the Hartree–Fock fractional-spin error for one electron

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Fractional-spin errors are inherent in all current approximate density functionals, including Hartree–Fock theory, and their origin has been related to strong static correlation effects. The conventional way to encode fractional-spin calculations is to construct an ensemble density that scales between the high-spin and low-spin densities. In this article, we explore the variation of the Hartree–Fock fractional-spin (or ghost-interaction) error in one-electron systems using restricted and unrestricted ensemble densities, and the exact generalized Hartree–Fock representation. By considering the hydrogen atom and H2+ cation, we analyze how the unrestricted and generalized Hartree–Fock schemes minimize this error by localizing the electrons or rotating the spin coordinates. We also reveal a clear similarity between the Coulomb hole of He-like ions and the density depletion near the nucleus induced by the fractional-spin error in the unpolarized hydrogen atom. Finally, we analyze the effect of the fractional-spin error on the Møller–Plesset adiabatic connection, excited states, and functional- and density-driven errors.

I. INTRODUCTION

When is Hartree–Fock (HF) theory exact for a one-electron system? It is certainly exact for the ground-state of a single occupied orbital containing a spin-up or spin-down electron (i.e., \( m_s = \pm \frac{1}{2} \)). It must also be exact for any single non-collinear spin orbital, corresponding to a one-electron generalized HF wave function. 1–14 But what about a one-electron problem with fractionally-occupied spin orbitals? In this case, HF theory fails. In fact, the resulting “fractional-spin error” is asymptotically equivalent to the static correlation error in stretched diatomic molecules 15–18 and occurs in all standard density functional approximations. 16,19 Removing these errors requires more sophisticated functionals such as those based on the exact-exchange random-phase approximation 20,21 or on the strictly-correlated-electrons (SCE) limit of density-functional theory (DFT). 22–24 This connection with static correlation has made the fractional-spin error a popular metric for assessing and improving the quality of approximate density functionals 15,17,19,25–27 many-body perturbation theory, 28 and wave function methods. 29,30 Variants of fractional-spin DFT have also been successfully applied to various chemical problems, particularly for predicting the energetics of open-shell diradical systems. 31–37

The physical origins of the fractional-spin error have been extensively studied by Cohen, Mori-Sanchez and Yang. 15–17,26 In particular, they have shown that the energy of the exact functional with fractional spins should be constant. 15 When an approximate functional fails to conserve this constancy condition, the resulting error can be associated with static correlation. This condition is analogous to the piecewise linearity of the energy for fractional charges, which leads to delocalization errors when not satisfied. 16,17

Through fractional spins and fractional charges, many of the failures of electronic structure theory can be studied as properties of the functional rather than the structure of an approximate density or wave function. 16 This analysis relies on the idea that a well separated fragment of a pure-state system might be locally described as an ensemble, and that it should be correctly described in this way by an energy functional (for an in-depth critical analysis, see Refs. 38 and 39). Furthermore, these errors can be directly connected to the ghost interaction between different states in an ensemble density calculation. 40

While the relationship between fractional-spin errors and static correlation are now well established, the corresponding short-comings of the exchange-correlation functional remain elusive. Hartree–Fock theory does not satisfy the fractional-spin condition, suggesting that artificial Coulomb interactions play a significant role. 15 However, HF theory exists in many different forms depending on the symmetry restrictions applied to the electronic state, and each of these approximations may yield different fractional-spin errors. Restricted HF (RHF), uses the same spatial orbitals for both spin-up and spin-down electrons, conserving both \( S^+ \) and \( S \) spin symmetry. The unrestricted HF (UHF) approach uses different orbitals for different spins, allowing broken \( S^2 \) symmetry but enforcing \( S \) symmetry. While UHF theory often correctly describes the dissociation of closed-shell molecules into open-shell fragments, it yields qualitatively incorrect binding curves in systems such as \( \text{H}_2^+ \) (square and chain), \( \text{F}_2 \), \( \text{O}_2^+ \) and \( \text{O}_2^2+(+) \) and fails for processes where the total \( m_s \) value is not conserved as the nuclear coordinates change. 8 Finally, generalized HF (GHF) allows each orbital to have high- and low-spin components and is not guaranteed to conserve either \( S^2 \) or \( S \) symmetry. Fukutome classified these three formalisms as time-reversal invariant closed-shell, axial spin density waves, and torsional spin density waves respectively, 1 while extensions with complex orbitals also exist. 5,11,44–48 and point group symmetry can always be independently imposed.

In this contribution, we systematically investigate the fractional spin error of the HF potential using different symmetry-restricted formalisms. By considering the optimized HF energy and densities for a series of hydrogen-based one-electron models, we show that the fractional-spin error arises from an artificial Coulomb interaction between the high-spin and low-
spin densities that leads to artificially spin-polarized densities and additional mean-field solutions. The magnitude of this error therefore depends on the form of HF approximation applied. We also discover a density depletion zone created by this fractional-spin error in the H atom that is remarkably similar to the Coulomb hole (i.e., the difference between the exact and HF system-averaged pair densities) induced by electron correlation effects in helium-like ions. 49,50 Finally, we demonstrate how the fractional-spin error decreases as the electron density becomes increasingly delocalized.

Unless otherwise stated, all results are computed using Mathematica 12.0 and are provided in an accompanying notebook available for download from https://doi.org/10.5281/zenodo.4765100. Atomic units are used throughout.

II. FORMULATING FRACTIONAL SPINS

In the high- or low-spin \( m_s = \pm \frac{1}{2} \) configurations, the exact (ground state) wave function of a one-electron system is represented by a single occupied orbital \( \psi_0(r) \), where \( r \) is the electronic position vector. The corresponding spatial electron density is then

\[
n_0(r) = |\psi_0(r)|^2, \tag{1}
\]

with the normalization constraint \( \int n_0(r) \, dr = 1 \). The corresponding exact energy is given by the kinetic \( T[n_0] \) and external potential energy \( v_{\text{ext}}[n_0] \) terms as

\[
E_0 = T[n_0] + v_{\text{ext}}[n_0] = \hbar n_0. \tag{2}
\]

where we introduce the combined one-body component of the energy as \( \hbar n_0 \).

At fractional-spin values \( -\frac{1}{2} < m_s < \frac{1}{2} \), the electron density can be represented by a two-state weighted ensemble of a high-spin and low-spin density as

\[
n^w(r) = (1 - w) n^\sigma(r) + w n^\beta(r), \tag{3}
\]

with \( 0 \leq w \leq 1 \). In the spin-unrestricted framework, the high-spin and low-spin densities are built from different orbitals \( \psi^\sigma(r) \) and \( \psi^\beta(r) \) as \( n^\sigma(r) = |\psi^\sigma(r)|^2 \) (with \( \sigma = \alpha \) or \( \beta \)), providing individually normalized densities, i.e., \( \int n^\sigma(r) \, dr = 1 \). The ensemble density is therefore normalized, i.e., \( \int n^w(r) \, dr = 1 \), and spin-pure states are recovered at \( w = 0 \) and \( w = 1 \), with \( m_s = \pm \frac{1}{2} \). The equiweight ensemble (i.e., \( w = \frac{1}{2} \)) is of particular interest as it corresponds to a closed-shell system containing half a spin-up and half a spin-down electron. For any other weight, there is no spin symmetry. The fractional-spin error is maximum in the case of the equiweight ensemble,15,16,26 as we shall illustrate below.

The simplest way to build the high-spin and low-spin spatial densities is to introduce the constraint \( n^\sigma(r) = n^\beta(r) \equiv n(r) \) and build the spatial density from a single occupied orbital \( \psi(r) \). This approximation leads to a spin-restricted framework with the corresponding RHF ensemble energy

\[
E^w_{\text{RHF}} = \hbar[n] + (1 - w) w (\psi \psi^\ast \psi \psi^\ast) = \int \psi^\ast(r_1) \psi^\ast(r_1) \psi^\ast(r_2) \psi^\ast(r_2) \, dr_1 dr_2, \tag{4}
\]

with the inter-electronic distance \( r_{12} = |r_1 - r_2| \). Equation (4) shows that the exact energy is only recovered for \( w = 0 \) or \( 1 \), while an artificial Coulomb interaction arises for all other \( w \) values. This fractional-spin error occurs because the exchange interaction between the high- and low-spin components of the electron density (which in this case represent the same electron) is missing from the restricted ensemble energy. As a result, the artificial Coulomb repulsion is not completely cancelled.

Alternatively, allowing the high-spin and low-spin densities to differ leads to the UHF ensemble energy

\[
E^w_{\text{UHF}} = (1 - w) \hbar[n^\sigma] + w \hbar[n^\beta] + (1 - w) w (\psi^\sigma \psi^\ast \psi^\beta \psi^\ast). \tag{5}
\]

In Fukutome’s classification, the real UHF solution is described as an “axial spin density wave”. From Eq. (6), we see that the fractional-spin error for \( 0 < w < 1 \) corresponds to an artificial Coulomb repulsion between the high-spin and low-spin components of the density. In contrast to the restricted ensemble, the unrestricted orbitals allow this error to be reduced through independent spatial relaxation of the high- and low-spin electron densities. As we shall see later, the extent to which this relaxation can eradicate the fractional-spin error at a fixed value of \( w \) is greatly increased when spatial separation of the high- and low-spin densities becomes possible. Finally, using a GHF-based approach for the fractional-spin leads to the correct energy for all \( w \) (see Appendix A).

The artificial interaction term in Eqs. (4) and (6) is reminiscent of the ghost-interaction in ensemble DFT that causes the non-linearity of the ensemble energy for approximate density functionals.40,52–57 Under the exact exchange-correlation functional, the fractional-spin ensemble density must yield the exact energy for all \( w \).15,58 As in Gross–Oliveira–Kohn DFT (GOK-DFT)59–61 and N-centered ensemble DFT52,63 [and unlike in the original Perdew–Parr–Levy–Balduz (PPLB) theory58], the exact exchange-correlation functional is therefore weight-dependent as the total density (which integrates to the same number of electrons for all weights) does not contain enough information to unambiguously describe all the states belonging to the ensemble. However, this constancy condition of the ensemble energy (which is a particular case of the piecewise-linearity of the ensemble energy58,64–66) is not fulfilled for any currently available approximate functionals.67–69 Including HF theory. The resulting energy deviation is usually equated with a static correlation error.15,16

III. HYDROGEN ATOM

A. Ground State Energy

To illustrate the fractional-spin error for different HF formalisms, we first consider the hydrogen atom in a minimal spatial basis set comprising the lowest-energy 1s and 2s atomic
Alternatively, the high-spin and low-spin orbitals in an unrestricted ensemble leads to some energetic relaxation at the spin-pure states at \( w = 0 \) and 1 (\( m_z = \pm \frac{1}{2} \)) and the spin-unpolarized state at \( w = \frac{1}{2} \) (\( m_z = 0 \)). However, the greater flexibility of the unrestricted ensemble leads to some energetic relaxation for intermediate \( w \) values, although this effect is marginal in comparison to the total fractional-spin error.

Under the exact functional, or within the GHF formalism (see Appendix A), the spatial density \( n_0(r) \) remains the same for all \( w \). Fixing the spatial density at its exact value \( n(r) = n_0(r) \) and computing the energy via the (incorrect) HF energy functional allows the functional-driven error (FDE) to be defined, with the remaining part of the error being the density-driven error (DDE).\(^{73,74}\) In Ref. 72 the relation between DDE and static correlation has been analyzed for RHF using the Hubbard dimer, where the DDE has been shown to be very small and becomes zero for the symmetric dimer. In Fig. 1, we find that the fractional-spin DDE is also very small in the H atom, and thus this system is dominated by the FDE. However, in contrast to the symmetric Hubbard dimer, the DDE in RHF for the H atom is not zero and becomes maximally large at \( w = \frac{1}{2} \). Furthermore, the DDE in UHF is always larger (in magnitude) than RHF, reaching maximum magnitude when the UHF energetic stabilization is most significant. In other words, the energetic stabilization provided by the unrestricted approach has a detrimental effect on the quality of the electron density,\(^{75}\) while the restricted ensemble has a greater energy error but a more accurate density. This result is consistent with the broader symmetry-dilemma in HF theory, where lower electronic energies are achieved at the expense of less accurate electronic densities and the loss of well-defined quantum numbers.\(^{74}\)

### B. Unrestricted Density Relaxation

In Fig. 2, we explore the UHF density relaxation by computing the change in the radial probability density for different \( w \) values, defined as

\[
\Delta P^w(r) = 4\pi r^2 \left[ n^w(r) - n_0(r) \right].
\]

As \( w \) increases from 0 to \( \frac{1}{2} \), the fractional-spin electrons shift away from the nucleus to become less dense and reduce the strength of the artificial Coulomb repulsion. While this relaxation decreases the fractional-spin error, it also reduces the strength of the electron-nuclear attraction. If the nuclear charge \( Z \) is increased continuously to non-integer values, it becomes

\[
\psi(r) = \cos \theta \chi_{1s}(r) + \sin \theta \chi_{2s}(r), \quad (8)
\]

where \( \theta \) represents an orbital rotation angle to be optimized. Alternatively, the high-spin and low-spin orbitals in an unrestricted ensemble may be built using different rotation angles for each spin, \( \theta^0 \) and \( \theta^1 \), to give

\[
\psi^0(r) = \cos \theta^0 \chi_{1s}(r) + \sin \theta^0 \chi_{2s}(r), \quad (9a)
\]

\[
\psi^1(r) = \cos \theta^1 \chi_{1s}(r) + \sin \theta^1 \chi_{2s}(r). \quad (9b)
\]

In Fig. 1, we compare the optimized energies for the restricted (solid red) and unrestricted (solid blue) fractional-spin ensembles. At the spin-pure values \( w = 0 \) or 1, both representations are equivalent and yield the exact hydrogen ground-state energy \( E_0 = -1/2 \ E_h \). However, at fractional-spin values with \( 0 < w < 1 \), we find the previously observed fractional-spin error,\(^{15}\) reaching a maximum at \( w = \frac{1}{2} \). The restricted and unrestricted ensembles yield equivalent results for the spin-pure states at \( w = 0 \) and 1 (\( m_z = \pm \frac{1}{2} \)) and the spin-unpolarized state at \( w = \frac{1}{2} \) (\( m_z = 0 \)). However, the greater flexibility of the unrestricted ensemble leads to some energetic relaxation for intermediate \( w \) values, although this effect is marginal in comparison to the total fractional-spin error.
increasingly less favorable for the electrons to relax away from
the nucleus and optimizing the density does not reduce the frac-
tional-spin error as much. On the contrary, if the nuclear
charge is reduced to \( Z < 1 \), it becomes more energetically
favorable for the electron density to relax away from the nu-
cleus. Eventually, relaxation becomes so favorable that the
fractional-spin electrons are ionized from the nucleus. This
analysis explains the existence of an artificial critical nuclear
charge for the bound-state stability of the one-electron atom
that has recently been observed using numerical fractional-spin
RHF calculations at \( w = \frac{1}{2} \).

Figure 2 also illustrates a close similarity between the dif-
ference of density probabilities in the unpolarized H atom and
the system-averaged Coulomb hole in the He-like ions, defined
as the difference between the exact intracule \( I(r_{12}) \) and either
the HF or the Kohn–Sham intracule \( I_0(r_{12}) \) as

\[
\Delta I(r_{12}) = I(r_{12}) - I_0(r_{12}).
\]

The intracule gives the probability of finding two electrons at a
distance \( r_{12} \) and has been extensively used to study the physics
of electronic correlation. In He-like ions, the Coulomb
hole results from the electrons being too close together at
the mean-field HF or Kohn–Sham level. Electron correlation
pushes the electrons apart, creating a depletion of probability
density at short inter-electronic distances. The same physics
are clearly involved in the fractional-spin H atom: the ensemble
HF approximation pushes the electrons away from each other
to lower their artifical Coulomb interaction. In this sense, the
fractional-spin one-electron atom behaves as a two-electron
system with electron correlation.

In Fig. 3, we consider the radial spin-density probability for
different \( w \) values, defined as

\[
\Delta S^w(r) = 4\pi r^2 \left[ (1 - w) n^\alpha(r) - w n^\beta(r) \right].
\]

Although it is not explicitly specified, both \( n^\alpha(r) \) and \( n^\beta(r) \) de-
pend implicitly on \( w \) as the underlying orbitals \( \psi^\alpha(r) \) and \( \psi^\beta(r) \)
are obtained with a weight-dependent energy functional. For
\( w < \frac{1}{2} \), the majority high-spin density preferentially occupies
the region closest to the nucleus with the minority low-spin
density at larger radial distances. This spatial separation of the high-
and low-spin density minimizes the (artificial) Coulomb
repulsion between the two spin components while maximizing
the overall electron-nuclear attraction. The magnitude of this
spin-polarization decreases as \( w \) increases until eventual-
ly yielding a spin-unpolarized (restricted) density at \( w = \frac{1}{2} \).
Spatial separation of the different spin components is therefore
essential for providing the additional relaxation of the
unrestricted ensemble relative to the restricted ensemble.

The additional relaxation of the unrestricted ensemble
appears analogous to symmetry-broken wave functions in
strongly correlated molecules, such as the dissociation limit
of \( \text{H}_2 \). In \( \text{H}_2 \), a lower-energy UHF solution emerges at
the Coulson–Fischer point to become the global HF ground-
state, with the high-spin and low-spin electrons localized
on opposite atoms, while the delocalized RHF solution be-
comes a saddle point of the UHF energy. However, in the
fractional-spin H atom, the restricted ensemble is only a sta-
tionary point of the UHF energy at \( w = 0, \frac{1}{2} \) and 1. This can
be seen by considering the electronic energy landscape with
the restricted ensemble as a function of \( \theta^\alpha \) and \( \theta^\beta \), as shown
in Fig. 4. For all other values of \( w \), the stationary points on
the unrestricted energy surface do not correspond to restricted
ensembles with \( \theta^\alpha = \theta^\beta \) (black line). Consequently, the optimal
restricted ensemble is only a constrained minimum along the
line \( \theta^\alpha = \theta^\beta \), rather than a saddle point of the UHF energy.
This unusual type of instability in HF is reminiscent of open-
shell systems where the restricted open-shell HF (ROHF) is
not a stationary point of the UHF energy, and is likely to be
the case in many open-shell systems. Alongside the ground-
state ensemble, there are additional stationary points on the
unrestricted ensemble energy that we will address in Sec. III D.
C. Spin Components

With different densities for different spins, the restricted and unrestricted ensembles both have the potential for introducing spin-contamination. Analytic formulae for the expectation values of the square of the spin operator \( \langle S^2 \rangle = \langle S_x^2 + S_y^2 + S_z^2 \rangle \) can be derived (see Appendix B) for the RHF and UHF ensembles as

\[
\langle S^2 \rangle_{\text{UHF}} = \langle S^2 \rangle_{\text{exact}} - \frac{1}{2} w(1-w)|S_{\alpha\beta}|^2,
\]

(13a)

\[
\langle S^2 \rangle_{\text{RHF}} = \langle S^2 \rangle_{\text{exact}} - \frac{3}{2} w(1-w),
\]

(13b)

where \( S_{\alpha\beta} = \langle \psi_{\alpha}|\psi_{\beta} \rangle \) is the spatial overlap between the spin-up and spin-down orbitals, and \( \langle S^2 \rangle_{\text{exact}} = \frac{3}{4} \). The corresponding GHF expectation value \( \langle S^2 \rangle_{\text{GHF}} \) is exact and independent of \( w \), with the individual components

\[
\langle S_{\tau}^2 \rangle_{\text{exact}} = \langle S_{\tau}^2 \rangle_{\text{exact}} = \langle S_{\tau}^2 \rangle_{\text{exact}} = \frac{1}{4},
\]

(14)

In contrast, the individual components in the restricted and unrestricted approximations are given by

\[
\langle S_{\tau}^2 \rangle_{\text{UHF}} = \langle S_{\tau}^2 \rangle_{\text{exact}} - \frac{1}{2} w(1-w)|S_{\alpha\beta}|^2,
\]

(15a)

\[
\langle S_{\tau}^2 \rangle_{\text{UHF}} = \langle S_{\tau}^2 \rangle_{\text{exact}} - \frac{1}{2} w(1-w)|S_{\alpha\beta}|^2,
\]

(15b)

\[
\langle S_{\tau}^2 \rangle_{\text{UHF}} = \langle S_{\tau}^2 \rangle_{\text{exact}} - \frac{1}{2} w(1-w),
\]

(15c)

and

\[
\langle S_{\tau}^2 \rangle_{\text{RHF}} = \langle S_{\tau}^2 \rangle_{\text{exact}} - \frac{1}{2} w(1-w),
\]

(16)

where \( \tau \in \{x, y, z\} \).

For the restricted ensemble, the spin contamination adopts a quadratic form that reaches \( \langle S^2 \rangle = \frac{1}{8} \) at \( w = \frac{1}{2} \), which is exactly half the physically correct value (see Fig. 5). We believe that the \( w = \frac{1}{2} \) ensemble can be interpreted as an equally-weighted sum of the exact singlet states corresponding to the \( \text{H}^+ \) nucleus with no electrons \( n^- \) and the two-electron \( \text{H}^- \) ground state \( n^1 \), and the one-electron doublet states corresponding to either a spin-up electron \( n^+ \) or spin-down electron \( n^1 \), giving

\[
n^w = \frac{1}{4} \left( n^- + n^+ + n^1 + n^1 \right). \tag{17}
\]

Taking the weighted sum of expectation values then yields

\[
\langle S^2 \rangle = \frac{1}{4} \left( 0 + \frac{3}{4} + \frac{3}{4} + 0 \right) = \frac{3}{8}. \tag{18}
\]

This result can be compared with the symmetry-broken UHF wave function in the dissociation limit of \( \text{H}_2 \) where the value \( \langle S^2 \rangle = 1 \) indicates that the wave function is an equal combination of a singlet and triplet state.\(^82\) However, when fractional numbers of electrons are allowed, it appears that the ensemble can become a combination of exact densities with different numbers of particles. A detailed study of this intriguing feature of fractional spins is left for future work.

FIG. 4. Unrestricted ensemble energy surface for the fractional-spin H atom as a function of the orbital rotation angles \( \theta^x \) and \( \theta^y \). The restricted ensembles are indicated by the black line \( \theta^x = \theta^y \). At \( w = 0 \) and 1, the energy is invariant to \( \theta^x \) and \( \theta^y \) respectively, and stationary points occur as continuous “ridge” (red dashed) lines. For intermediate values, four discrete stationary points occur (colored dots) with additional periodic repeats. Here, the different colors of stationary points correspond to the multiple solutions shown in Fig. 7.

FIG. 5. Spin expectation values in the H atom as functions of the weight \( w \). Both the restricted and unrestricted ensemble approximations result in spin contamination.
With the unrestricted orbitals, spatial separation generally gives $|S_{\text{eff}}^2| < 1$, hence reducing the spin-contamination in the $\langle S_z^2 \rangle$ and $\langle S_z^2 \rangle$ components. This result is surprising and counter-intuitive as, elsewhere, spin-contamination is generally found to increase in an unrestricted representation.\cite{Fur86,Fur87,Fur88} Furthermore, using $\langle S_z \rangle_{\text{UHF}} = \langle S_z \rangle_{\text{RHF}} = \frac{1}{2} - w$, the variance of $S_z$ is given in both the restricted and unrestricted approximations as

$$\langle S_z^2 \rangle - \langle S_z \rangle^2 = \frac{1}{2} w(1 - w),$$

confirming that the ensemble densities are only eigenstates of $S_z$ at $w = 0$ or 1.

The spin-contamination in the RHF and UHF approximations has exactly the same origin as the fractional-spin error in the energy: an “exchange” contribution to $\langle S_z^2 \rangle$ that corresponds to the spin coupling of the spin-up and spin-down components of the density is missing. The spin expectation values can therefore be used to understand how GHF is able to provide the correct exchange energy to fully cancel the fractional-spin error. For this, we turn to the individual spin components. Figure 6 shows $\langle S_x \rangle$ and $\langle S_y \rangle$ as functions of $w$ for the RHF/UHF and GHF approximations. In the RHF/UHF case (red curve in Fig. 6), the (fractionally-occupied) orbitals are constrained to be eigenfunctions of the $S_z$ operator and we find $\langle S_z \rangle = \langle S_z \rangle = 0$ and $\langle S_x \rangle = \frac{1}{2} - w$. The overall spin-vector therefore remains (anti-)parallel to the $z$-axis throughout the transformation from $\langle S_z \rangle = \frac{1}{2}$ to $-\frac{1}{2}$. In contrast, the additional flexibility of the GHF approximation (blue curve in Fig. 6) allows the electron spin vector to rotate in the $xz$-plane with components $\langle S_x \rangle_{\text{GHF}} = \sqrt{(1 - w)} w$ and $\langle S_y \rangle_{\text{GHF}} = \frac{1}{2} - w$ (blue curve in Fig. 6). This rotation conserves the overall norm of the spin vector and results in an exchange interaction that cancels out the Coulomb interaction. The curves in Fig. 6 further illustrate Fukutome’s classification of the UHF and GHF approximations as axial and torsional spin density waves, respectively.\cite{Fuk00}

D. Excited States

In Fig. 4, we see that the lowest energy solutions are not the only stationary points of the unrestricted ensemble energy surface. For $w = 0$ and 1, there is another solution with energy $-1/8 E_0$ that corresponds to the physical 2s excited state. At these limits, the energy becomes invariant to the orbital rotation angle representing the vacant spin orbital ($\theta^\alpha$ for $w = 0$ and $\theta^a$ for $w = 1$) and the 1s and 2s states occur as one-dimensional stationary “ridges” in the ensemble energy. In contrast, for $0 < w < 1$, we find that the 1s and 2s solutions become isolated stationary points on the energy surface, alongside a further two stationary points with intermediate energies, as shown in Fig. 7. Between $0 < w < 1$, these additional solutions evolve smoothly from the 1s ground state to the 2s excited state (and vice versa) and can be qualitatively assigned to (fractional) open-shell $(1s)^{\frac{1}{2}}(2s)^{\frac{1}{2}}$ states at $w = \frac{1}{2}$.

The existence of these additional solutions is directly linked to the breakdown of the ensemble UHF equations for fractional spins. While the optimized ground $1s$ and excited $2s$ solutions can be considered as an approximation to the corresponding exact states, the $(1s)^{\frac{1}{2}}(2s)^{\frac{1}{2}}$-like solutions have no physical interpretation for a single electron. We can therefore consider them as transient states that occur in regions where the unrestricted ensemble is not exact. The similarities between these configurations and the excited states of a two-electron atom further indicates that the fractional-spin HF ensemble behaves as a two-body problem. Furthermore, these transient states create an interesting new connection between the physical ground and excited states. Similar connecting pathways of stationary points can also be identified using non-Hermitian operators in the complex plane.\cite{Lee09,Lee05} In both contexts, these connections arise from an approximate description of electronic structure, and we predict that such phenomena will be present across a broad range of theoretical techniques.
Beyond the HF approximation, fractional-spin errors also play an important role in driving the physics of the restricted Möller–Plesset (MP) adiabatic connection, as discussed in Ref. 18. In the MP adiabatic connection, a parametrized $\lambda$-dependent Hamiltonian is constructed to connect the zeroth-order MP reference states to the exact wave function at $\lambda = 1$. The small-$\lambda$ series expansion for the eigenvalues of this Hamiltonian corresponds to the conventional MP perturbation series, with the $n$th-order MP correction directly proportional to the $n$th derivative of the $\lambda$-parametrized energy at $\lambda = 0$.

In Ref. 18, the MP adiabatic connection for the stretched H$_2$ molecule is compared with twice the energy of the H atom at $w = \frac{1}{2}$ (Fig. 10 of Ref. 18), giving a perfect agreement as $R$ increases, except at $\lambda = 0$ where the energy is discontinuous for $R \to \infty$. The conventional $n$th-order MP corrections are therefore not well-defined for $R \to \infty$, as expected because the restricted MP2 correlation energy diverges to $-\infty$ in the H$_2$ dissociation limit. In the current context, one particularly interesting result from Ref. 18 is the suggestion that the spin of the $\lambda$-parametrized wave function in the fractional-spin H atom will flip discontinuously as $\lambda$ passes through 1, except for the special case $w = \frac{1}{2}$.

While previously only the H atom with $w = 0$, $\frac{1}{2}$, and 1 were considered, here we extend this analysis to general $w$ values. After finding the weight-dependent RHF spatial orbital $\psi$ (which is held fixed in the following equations), we consider the $\lambda$-dependent Hamiltonian

$$H_\lambda = \hat{T} + \hat{V}_{\text{ext}} + (1 - \lambda)(\hat{J}^\mu - \hat{K}^\nu),$$

(20)

where the exact energy is recovered as the eigenvalue at $\lambda = 1$. Here, the multiplicative Hartree operator is defined as

$$J^\mu = \int \frac{|\psi(r')|^2}{|r' - r|} \, dr',$$

(21)

and the non-local exchange operator $\hat{K}^\nu$ is defined by its action on a generalized orbital $\tilde{\psi}$ as

$$\hat{K}^\nu \tilde{\psi} = (1 - w) \psi(r) \langle \alpha | \int \frac{\psi^*(r') \tilde{\psi}^\nu(r')}{|r' - r|} \, dr' + w \psi(r) \langle \beta | \int \frac{\psi^*(r') \tilde{\psi}^\nu(r')}{|r' - r|} \, dr'.

(22)

The generalized orbital $\tilde{\psi}$ can have both a high-spin ($\alpha$) and low-spin ($\beta$) component with different spatial orbitals $\tilde{\psi}^\alpha$ and $\tilde{\psi}^\beta$, giving

$$\tilde{\psi}(x) = \tilde{\psi}^\alpha(r) |\alpha\rangle + \tilde{\psi}^\beta(r) |\beta\rangle,$$

(23)

where $x$ represents the combined spin and spatial coordinates (see also Appendix A).

In Ref. 18, the ground-state wave function $\psi_\lambda$ and energy $E_\lambda$ were computed and analyzed in the range $\lambda \in [0, \infty)$ for $w = 0$, 1, and $\frac{1}{2}$, while the spin of $\psi_\lambda$ was constrained to be the same as the RHF orbital, essentially forbidding any spin flip. In this work, we release this constraint and give $\psi_\lambda$ full variational freedom by defining

$$\psi_\lambda(x) = \psi_\lambda(r) \left( \sqrt{1-q}|\alpha\rangle + \sqrt{q}|\beta\rangle \right)$$

(24)

where $0 \leq q \leq 1$. We can then analyze how the spin of $\psi_\lambda$ changes with $w$ and $\lambda$. Note that, in the general many-electron case, the exact $\psi_\lambda$ is a correlated wave function and Eq. (24) cannot be interpreted as a GHF state. However, in this case, the two are equivalent because GHF is exact for one-electron systems.

Within the $w$- and $\lambda$-dependent Hamiltonian (20), only the expectation value of $\hat{K}^\nu$ depends on $q$

$$\langle \psi_\lambda | \hat{K}^\nu | \psi_\lambda \rangle = [(1-q)(1-w) + q w] \langle \psi_\lambda | \tilde{\psi}_\lambda | \psi_\lambda \rangle.$$

(25)

Since $\hat{K}^\nu$ is a positive-definite operator, we therefore find that the optimal value of $q$ depends on both $\lambda$ and $w$ as

$$q = \begin{cases} 1 & w > \frac{1}{2} \\ 0 & w < \frac{1}{2} \end{cases}$$

(26a)

and

$$q = \begin{cases} 0 & w > \frac{1}{2} \\ 1 & w < \frac{1}{2} \end{cases}$$

(26b)

In other words, the optimal $\psi_\lambda$ is always in either a pure high-spin or low-spin configuration, and the spin will flip relative to the reference RHF orbital if $\lambda$ crosses 1 at fixed $w$ or if $w$ crosses $\frac{1}{2}$ at fixed $\lambda$. At $\lambda = 1$ and/or at $w = \frac{1}{2}$, the energy is independent of $q$. At $w = 0$ or 1, the spin-flip that occurs when $\lambda$ crosses 1 is analogous to a similar phenomenon in the MP adiabatic connection for the stretched H$_2$ molecule with a UHF reference, in which the two spins are exchanged between the two nuclei. This feature is also responsible for the slow convergence of the unrestricted MP series in stretched H$_2$, as discussed for the Hubbard dimer in Ref. 90, and is intimately related to a critical point singularity in MP theory 91–94.

Finally, we note that forbidding spin-flip as $\lambda$ changes is equivalent to setting $q = w$. Under this constraint, the prefactor for the expectation value of $\hat{K}^\nu$ becomes $s = 1 - 2w + 2w^2$, recovering the form used in Ref. 18.

IV. HYDROGEN MOLECULE CATION

We now turn to the one-electron homonuclear diatomic H$_2^+$, restricting our discussion to the ground state and its behavior in the dissociation limit. In particular, we are interested in the possibility of spatially symmetry-broken UHF solutions for bond lengths greater than a (potentially) weight-dependent critical value, forming an analogy to the Coulson–Fischer point in H$_2$. We employ the minimal basis set STO-3G containing two contracted $s$-type gaussian functions $\chi_\alpha(r)$ and $\chi_\beta(r)$ centered on the left and right H atoms respectively, with bond length $R$. Again, the use of a minimal basis allows analytic expressions to be derived, but the physics is similar in larger basis sets (see Supplementary Material for additional results).
FIG. 8. Left: UHF (solid) and RHF (dashed) energies of H$_2^+$ as functions of the internuclear distance $R$ for various weights $w$. Right: RHF energies of H$_2^+$ in the dissociation limit as a function of the weight $w$. Both graphs are computed with the STO-3G basis set.

The occupied and vacant (symmetry-pure) RHF orbitals form a delocalized orthogonal basis set

$$\psi_1(r) = \frac{\chi_L(r) + \chi_R(r)}{\sqrt{2(1 + S_{LR})}}$$

$$\psi_2(r) = \frac{\chi_L(r) - \chi_R(r)}{\sqrt{2(1 - S_{LR})}},$$

where $S_{LR} = \langle \chi_L | \chi_R \rangle$ defines the overlap of the atomic orbitals at a given bond length. The ground-state UHF orbitals can then be parametrized in terms of these orthogonal orbitals using a single rotation angle $\phi$ as $^{82}$

$$\psi_1^\phi(r) = \cos \phi \psi_1(r) + \sin \phi \psi_2(r),$$

$$\psi_2^\phi(r) = \cos \phi \psi_1(r) - \sin \phi \psi_2(r),$$

while the corresponding virtual orbitals are

$$\psi_1^\phi(r) = -\sin \phi \psi_1(r) + \cos \phi \psi_2(r),$$

$$\psi_2^\phi(r) = +\sin \phi \psi_1(r) + \cos \phi \psi_2(r).$$

The symmetric RHF orbitals are recovered for $\phi = 0$, while $\phi = \pm \pi/4$ recovers spin-up and spin-down orbitals localized on opposite H atoms. The UHF ensemble energy is then given as

$$E_{UHF}^w(\phi) = \cos^2 \phi h_{11} + \sin^2 \phi h_{22} + (1 - w)w [\cos^4 \phi J_{11} + \sin^4 \phi J_{22} + 2 \cos^2 \phi \sin^2 \phi (J_{12} - 2K_{12})],$$

where the one-electron, Coulomb, and exchange matrix elements in the orthogonal RHF basis are denoted

$$h_{ij} = \langle \psi_i | h | \psi_j \rangle, \quad J_{ij} = \langle \psi_i \psi_i | h | \psi_j \psi_j \rangle, \quad K_{ij} = \langle \psi_i \psi_j | h | \psi_j \psi_i \rangle.$$

Differentiating Eq. (30) with respect to $\phi$ yields the ground-state RHF and UHF solutions as

$$\phi_{RHF} = 0$$

$$\cos^2 \phi_{UHF} = \frac{h_{11} - h_{22} + 2w(1 - w)(J_{12} - J_{22} - 2K_{12})}{-2w(1 - w)(J_{11} - 2J_{12} + J_{22} + 4K_{22})}.\quad (32a)$$

Analogously to H$_2$, the UHF solutions are spatially symmetry-broken, with the spin-up and spin-down electron densities localizing on opposite atoms, and do not necessarily exist for all ensemble weights or bond lengths. The location of the (weight-dependent) Coulson–Fischer point can be identified by solving $\phi_{RHF} = \phi_{UHF}$, or equivalently

$$h_{11} - h_{22} + 2w(1 - w)(J_{12} - J_{22} - 2K_{12})$$

$$-2w(1 - w)(J_{11} - 2J_{12} + J_{22} + 4K_{22}) = 1.\quad (33)$$

Therefore, in complete analogy with H$_2$, $^{82}$ there exists a (weight-dependent) critical bond-length $R_c^w$, where, for $R > R_c^w$, it becomes energetically favorable for the spatial symmetry to be broken by localizing the high-spin and low-spin orbitals on opposite centers. This symmetry breaking only occurs for $w \neq 0$ or 1; at other ensemble weights, the UHF solution is symmetric and equivalent to the RHF solution. Like the H atom, spatial separation of the high- and low-spin densities minimizes the fractional-spin error, leading to more accurate UHF energies, as illustrated in Fig. 8. However, the energetic relaxation is more significant in H$_2^+$ than the H atom as the two atomic centers increase the possible extent of spatial separation. Since the UHF energy is variational and the fractional spin error is positive, the energy and associated error are lowered by increasing the DDE (which is always negative). For example, in Fig. 9, we show the minimal basis FDE and DDE at $R = 4a_0$. We find no DDE in RHF, while the DDE in UHF has maximum amplitude at $w = \frac{1}{2}$. Figure 8 also reveals that the critical bond-length $R_c^w$ decreases as $w$ increases between 0 and $\frac{1}{2}$, reaching a minimum at $w = \frac{1}{2}$. The shortest bond length for UHF symmetry breaking therefore occurs for $w = \frac{1}{2}$, which can be understood because the fractional-spin error is largest at this ensemble weight.
where the dissociation error is equal to the difference between the RHF and UHF energy of a dissociated H₂⁺ cation. This similarity can be understood by considering the H₂⁺ cation as a two-electron problem, and that electron correlation effects between the high- and low-spin components of the electron density suggest that generalized HF formalisms. Our results show that the fractional-spin error arises from an artificial Coulomb depletion that mirrors the Coulomb hole in He-like ions. These results further demonstrate that a fractional-spin electron behaves as a two-electron problem, and that electron correlation concepts fundamentally underpin the physics of fractional-spin errors. Finally, delocalization of the electron density reduces the fractional-spin error, and this effect is enhanced when the high- and low-spin electron densities can become spatially separated under an unrestricted approximation.

Overall, we have shown that the physics of one-electron systems is much more subtle that it may first appear. Our results demonstrate several new insights into the unusual properties of a fractional-spin electron within HF theory, and we also expect these properties to occur in density-functional approximations as well. Looking forwards, we anticipate that these insights will inspire new directions for improving the performance of density functional approximations under the effects of strong static correlation. In particular, the importance of capturing exchange-correlation effects between the high- and low-spin components of the electron density suggest that generalized extensions of DFT may provide a fruitful direction for future research.

V. CONCLUDING REMARKS

In this work, we have investigated the physical origins and consequences of the fractional-spin error in one-electron systems using the HF potential. Building on the work of Cohen, Mori-Sanchez and Yang, we have explored the variations in the fractional-spin error for the restricted, unrestricted, or the exact generalized HF formalisms. Our results show that the fractional-spin error arises from an artificial Coulomb interaction between the high- and low-spin components of the one-electron density and, for all weights \( w \neq 0, \frac{1}{2}, \) and 1, there exists an unrestricted solution in the H atom that is lower in energy than the restricted one. In the H atom, this fractional-spin can also create additional solutions representing unphysical open-shell excited states, and a region of density depletion that mirrors the Coulomb hole in He-like ions. These results further demonstrate that a fractional-spin electron behaves as a two-electron problem, and that electron correlation concepts fundamentally underpin the physics of fractional-spin errors. Finally, delocalization of the electron density reduces the fractional-spin error, and this effect is enhanced when the high- and low-spin electron densities can become spatially separated under an unrestricted approximation.

Overall, we have shown that the physics of one-electron systems is much more subtle that it may first appear. Our results demonstrate several new insights into the unusual properties of a fractional-spin electron within HF theory, and we also expect these properties to occur in density-functional approximations as well. Looking forwards, we anticipate that these insights will inspire new directions for improving the performance of density functional approximations under the effects of strong static correlation. In particular, the importance of capturing exchange-correlation effects between the high- and low-spin components of the electron density suggest that generalized extensions of DFT may provide a fruitful direction for future research.

SUPPLEMENTARY MATERIAL

Included in the Supplementary Material are high-accuracy numerical data for the H atom and H₂⁺ cation that mirror the minimal basis results presented in the main text.

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**Appendix A: Generalized Hartree–Fock ensemble**

The aim of this Appendix is to demonstrate that a one-electron fractional-spin ensemble built from GHF densities must be independent of the ensemble weight, and thus always exact. To achieve this, we attempt to build a two-state generalized ensemble density in the same form of the UHF-based ensemble in Eq. (3). We find that any generalized ensemble of this form will give the exact energy for any ensemble weighting.

A GHF-based two-state ensemble can be seen as an extension of the UHF-based ensemble defined in Eq. (3). The additional flexibility of the GHF formalism means that every orbital can include both a high-spin and low-spin component, giving

\[
\psi_f(x) = \psi_f^\sigma(r)|\alpha\rangle + \psi_f^\prime(r)|\beta\rangle, \quad (A1)
\]

where \(x = (\sigma, r)\) is a composite coordinate gathering spin and spatial coordinates, and the index \(I = 1, 2\) labels the states belonging to the two-state ensemble. In what follows, we will exploit the two-component spinor basis

\[
|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad (A2)
\]

such that

\[
\psi_f = \begin{pmatrix} \psi_f^\sigma \\ \psi_f^\prime \end{pmatrix}. \quad (A3)
\]

The corresponding GHF ensemble density is then

\[
n_{\text{GHF}}^w(r) = (1 - w)n_1(r) + wn_2(r), \quad (A4)
\]

where the two-component density is defined as

\[
n_f(r) = \begin{pmatrix} n_f^{\alpha\alpha}(r) & n_f^{\alpha\beta}(r) \\ n_f^{\beta\alpha}(r) & n_f^{\beta\beta}(r) \end{pmatrix}, \quad (A5)
\]

and \(n_f^{\sigma\sigma}(r) = \psi_f^\sigma(r)|\psi_f^\sigma(r)\rangle\). Similarly to the unrestricted ensemble, the only two-electron contributions to the ensemble energy arise from interactions between the two densities. The corresponding GHF energy expression can then be derived as

\[
E_{\text{GHF}}^w = (1 - w)h[n_1] + wh[n_2] + w(1 - w)\sum_{\sigma\tau\sigma'} \left[ (\psi_f^\sigma^\dagger|\psi_f^\tau\rangle|\psi_f^{\tau'}\rangle - (\psi_f^\sigma^\dagger|\psi_f^\prime\rangle|\psi_f^{\prime'}\rangle) \right].
\]

(A6)

From this expression, we see that the exact energy is recovered when the two individual densities, and their corresponding orbitals, are equivalent. For any ensemble weight \(w\), variational optimization of the ensemble density will therefore recover the exact energy \(E_{\text{GHF}}^w = E_0\) with \(\psi_1 = \psi_2 = \psi_0\). In other words, the two-state generalized ensemble introduces a redundant parametrization and, since the GHF representation of a one-electron system must always be exact, only a single GHF state is required.

Comparing Eq. (A6) with the UHF energy function Eq. (6), we see that the fractional-spin error arises from the missing exchange interaction between high- and low-spin densities in the ensemble. This missing term in the restricted and unrestricted ensembles leads to a fractional-spin error where the Coulomb interaction between the high- and low-spin components is not sufficiently cancelled, leading to the static correlation error for fractional spins.

**Appendix B: Spin Expectation Values**

To derive the spin-expectation values \(\langle S_x^2 \rangle, \langle S_y^2 \rangle, \text{ and } \langle S_z^2 \rangle\) for the fractional-spin ensemble densities, we start with the second-quantized spin operators\(^{95}\)

\[
S_x = \frac{1}{2} \sum_p \left( a_p^\dagger a_p - a_p a_p^\dagger \right), \quad (B1a)
\]

\[
S_y = \frac{1}{2i} \sum_p \left( a_p^\dagger a_p - a_p a_p^\dagger \right), \quad (B1b)
\]

\[
S_z = \frac{1}{2} \sum_p \left( a_p^\dagger a_p - a_p a_p^\dagger \right). \quad (B1c)
\]

Here, and in what follows, the indices \(p\) and \(q\) are used to denote an orthogonal spatial orbital basis used to construct the molecular orbitals. Expanding the squared operators and considering the non-zero contractions\(^{96}\) allows the corresponding expectation values to be expressed using the two-component
density matrices as

\[
\langle S^z_x \rangle = \frac{1}{4} \sum_p \left[ (n^{\alpha\alpha})_{pp} + [n^{\beta\beta}]_{pp} \right]
\]

\[
+ \frac{1}{4} \sum_p \left[ (n^{\alpha\beta})_{pp} + [n^{\beta\alpha}]_{pp} \right]^2
\]

\[
- \frac{1}{2} \sum_{pq} \left[ (n^{\alpha\alpha})_{pq}[n^{\beta\beta}]_{qp} + [n^{\beta\alpha}]_{pq}[n^{\alpha\beta}]_{qp} \right].
\]

\[
\langle S^z_y \rangle = \frac{1}{4} \sum_p \left[ (n^{\alpha\alpha})_{pp} + [n^{\beta\beta}]_{pp} \right]
\]

\[
- \frac{1}{4} \sum_p \left[ (n^{\alpha\beta})_{pp} - [n^{\beta\alpha}]_{pp} \right]^2
\]

\[
- \frac{1}{2} \sum_{pq} \left[ (n^{\alpha\alpha})_{pq}[n^{\beta\beta}]_{qp} - [n^{\beta\alpha}]_{pq}[n^{\alpha\beta}]_{qp} \right].
\]

\[
\langle S^z_z \rangle = \frac{1}{4} \sum_p \left[ (n^{\alpha\alpha})_{pp} + [n^{\beta\beta}]_{pp} \right]
\]

\[
+ \frac{1}{4} \sum_p \left[ (n^{\alpha\beta})_{pp} - [n^{\beta\alpha}]_{pp} \right]^2
\]

\[
- \frac{1}{2} \sum_{pq} \left[ (n^{\alpha\alpha})_{pq}[n^{\beta\beta}]_{qp} + [n^{\beta\alpha}]_{pq}[n^{\alpha\beta}]_{qp} \right].
\]

These formula are entirely generalized for any two-component electronic density matrix.

For the unrestricted ensemble density, where \( n^{\alpha\beta} = n^{\beta\alpha} = 0 \), these spin expectation values reduce to

\[
\langle S^z_x \rangle = \frac{1}{4} \left[ (1 - w) \text{Tr} [n^{\alpha\alpha}] + w \text{Tr} [n^{\beta\beta}] \right]
\]

\[
- \frac{(1 - w)w}{2} \text{Tr} [n^{\alpha\beta} n^{\beta\alpha}].
\]  

\[
\langle S^z_y \rangle = \frac{1}{4} \left[ (1 - w) \text{Tr} [n^{\alpha\alpha}] + w \text{Tr} [n^{\beta\beta}] \right]
\]

\[
- \frac{(1 - w)w}{2} \text{Tr} [n^{\alpha\beta} n^{\beta\alpha}].
\]  

\[
\langle S^z_z \rangle = \frac{1}{4} \left[ (1 - w) \text{Tr} [n^{\alpha\alpha}] + w \text{Tr} [n^{\beta\beta}] \right]
\]

\[
+ \frac{1}{4} \left[ (1 - w) \text{Tr} [n^{\alpha\beta}] - w \text{Tr} [n^{\beta\alpha}] \right]^2
\]

\[
- \frac{1}{4} \left[ (1 - w)^2 \text{Tr} [n^{\alpha\alpha} n^{\alpha\alpha}] + w^2 \text{Tr} [n^{\beta\beta} n^{\beta\beta}] \right].
\]

Further simplification can be achieved by noting that individual state densities in the ensemble are normalized such that \( \text{Tr} [n^{\alpha\alpha}] = \text{Tr} [n^{\beta\beta}] = 1 \), and idempotent such that \( n^{\alpha\alpha} n^{\alpha\alpha} = n^{\alpha\alpha} \) and \( n^{\beta\beta} n^{\beta\beta} = n^{\beta\beta} \). Furthermore, exploiting the invariance of the matrix trace with respect to cyclic permutations allows \( \text{Tr} [n^{\alpha\alpha} n^{\beta\beta}] \) to be expressed in terms of the spatial orbital between the occupied orbitals as

\[
\text{Tr} [n^{\alpha\alpha} n^{\beta\beta}] = \text{Tr} [S^{\alpha\beta} S^{\beta\alpha}],
\]

where the overlap elements are defined as \( [S^{\alpha\beta}]_{ij} = \langle \psi^\alpha_i | \psi^\beta_j \rangle \).

Through these relationships, we recover the spin expectation values for the one-electron unrestricted fractional-spin ensemble as

\[
\langle S^z_x \rangle = \frac{1}{4} - \frac{1}{2} w(1 - w)[S^{\alpha\beta}]^2,
\]  

\[
\langle S^z_y \rangle = \frac{1}{4} - \frac{1}{2} w(1 - w)[S^{\alpha\beta}]^2,
\]  

\[
\langle S^z_z \rangle = \frac{1}{4} - \frac{1}{2} w(1 - w).
\]

**DATA AVAILABILITY**

The data that support the findings of this study are openly available in zenodo at https://doi.org/10.5281/zenodo.4765100.

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